ORGANIC GEOCHEMISTRY: CHALLENGES FOR THE 21^{st} CENTURY

VOL. 1

Book of Abstracts of the Communications presented to the
22^{nd} International Meeting on Organic Geochemistry
Seville – Spain. September 12 -16, 2005

Editors:
F.J. González-Vila, J.A. González-Pérez and G. Almendros

Equipo de trabajo:
Rocío González Vázquez
Antonio Terán Rodíguez
José Mª de la Rosa Arranz

Maquetación:
Rocío González Vázquez

Fotomecánica e impresión:
Akron Gráfica, Sevilla

Depósito legal: SE-61181-2005
I.S.B.N.: 84-689-3661-8

FOREWORDS

The IMOG is the official conference of the European Association of Organic Geochemists (EAOG) and one of the most important events on this subject in the world. After the previous IMOG meetings in Madrid (7th IMOG; 1975) and San Sebastian (17th IMOG; 1995), Seville is proud to host the third IMOG edition in Spain during September 12-16, 2005. The Conference is organized under the auspices of the Spanish Ministry of Education and Science (MEC), Spanish Council for Scientific Research (CSIC), Geological and Mining Institute of Spain (IGME), University of Seville and Andalusian Regional Government.

This book, divided in two volumes, encomprises all communications to the 22 IMOG. For this IMOG edition a grand total of 625 abstracts were submitted by authors from 43 countries from all around the world. During the last weekend of February 2005 the 22 IMOG Scientific Committee (SC) meet in Seville to review and discuss the distribution and form of presentation of the communications, and the Conference's general chart of the events was produced.

For this IMOG edition, the SC identified the following main scientific themes:

- Biogeochemistry
- Biomarkers
- Black carbon
- Carbon sequestration
- Coal geochemistry
- Environmental biogeochemistry
- Gas geochemistry
- Geochemistry of Precambrian rocks and oils
- Microbial processes
- New methods in organic geochemistry
- Paleoclimate
- Regional and basin studies
- Petroleum systems
- Reservoir predictions
- Soil biogeochemistry
- Understanding petroleum mixing

Finally 575 papers were accepted for presentation at the Conference, of which 92 were orals and 483 posters. Oral presentations were divided into 7 morning plenary sessions (Monday to Thursday) and 22 parallel thematic sessions on Thursday and Friday morning and in the afternoon from Monday to Thursday. Posters were divided in two sessions and presented each afternoon for two consecutive days (Mon/Tue and Wed/Thu) so presenters had the opportunity to appropriately present and discuss their work.

The number, diversity and quality of the submitted abstracts guaranteed an interesting and well-balanced scientific programme. The 22 IMOG addressed recent developments in emerging fields, and continued the tradition of IMOG as a unique opportunity to meet top scientists, to have stimulating discussions and to watch the latest developments in Organic Geochemistry. This 22nd edition was also honoured in hosting the Geochemical Society's Alfred Treibs Award Ceremony.

We would like to thank the 22 IMOG Organizing Committee and our collegues from IRNAS-CSIC for the facilities given and their constant work in the hard tasks needed for a succesfull meeting, the Scientific Committee for valuable advice and the production of our solid and outstanding Scientific Program, the EAOG for their confidence in Seville as the venue for their meeting and all donors, sponsorsing companies and expositors for their support without which the Seville 22 IMOG would not have been possible.

The editors:

Francisco J. González-Vila	*José Antonio González-Pérez*	*Gonzalo Almendros*
Chairman	Vice-Chairman	SC. Member

COMMITTEES INVOLVED IN THE ORGANIZATION OF THE 22 IMOG 2005

Chairman: Francisco J. GONZÁLEZ-VILA
Vice-Chairman: José A. GONZÁLEZ-PÉREZ
Consejo Superior de Investigaciones Científicas (CSIC)
Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS)

Scientific Committee

Francisco J. GONZÁLEZ-VILA (Chairman)
IRNAS-CSIC, Spain

Gonzalo ALMENDROS
CCMA-CSIC, Spain
Pim van BERGEN
SHELL Global Solutions, The Netherlands
Jørgen A. BOJESEN-KOEFOED
GEUS, Denmark
Chris CORNFORD
IGI, UK
Gary ISAKSEN
EXXONMOBIL, USA

Claude LARGEAU
ENSC, France
José C. del RÍO
IRNAS-CSIC, Spain
Jürgen RULLKÖTTER
ICBM, Germany
Stefan SCHOUTEN
NIOZ, The Netherlands
Eugenio VAZ dos SANTOS NETO
PETROBRAS RD, Brazil

Local Committee

José Ramón de ANDRÉS
IGME, Spain
Mª Enriqueta ARIAS
Universidad de Alcalá
Tomasz BOSKI
Universidad do Algarve, Faro, Portugal
Ignacio BRISSON
Repsol YPF
Juan COTA
Universidad de Sevilla

Mª Carmen DORRONSORO
Universidad del País Vasco
Antonio GUERRERO
Universidad de Sevilla
Juan LLAMAS
ETSI Minas de Madrid
Albert PERMANYER
Universidad de Barcelona

EAOG Board

Richard L. PATIENCE (Chairman)
Sylvie DERENNE (Secretary)
Ger W. van GRAAS (Treasurer)
Walter MICHAELIS (Awards)
Francisco J. GONZALEZ-VILA (Newsletter)
C. Anthony LEWIS (Membership and Website)
James MAXWELL – Co-opted (Editor-in-Chief of Organic Geochemistry)

22 IMOG SPONSORS

Ministerio de Educación y Ciencia (MEC)
Consejo Superior de Investigaciones Científicas (CSIC)
Instituto Geológico y Minero de España (IGME)
Universidad de Sevilla
Junta de Andalucía
Consejería de Innovación, Ciencia y Empresa
Instituto Andaluz de Investigación y Formación Agraria, Pesquera, Alimentaria y de la Producción Ecológica (IFAPA)
Consejería de Turismo, Comercio y Deporte. Delegación Provincial de Cádiz
Consorcio de Turismo de la Provincia de Sevilla. Turismo de Sevilla
Patronato del Real Alcázar de Sevilla

Repsol YPF
Chevron Texaco
Unocal 76
British Petroleum
Shell
Exxon Mobil
Statoil
Hydro

Integrated Geochemical Interpretation Ltd.
Humble Instruments & Services Inc.
Baseline Resolution Inc.
Vinci Technologies S.A.
Thermo Electron Corp.

Iberia
Renfe
Viajes el Corte Inglés
Anorsur S.L.
Cruzcampo

CONTENT

VOL-1

ORAL PRESENTATIONS

OPG-2. *H. Camacho and J. Boles.* Evidence for generation and migration of hydrocarbons along thermally anomalous faults in the Los Angeles basin, California, USA

OPG-3. *A.E. Borgund, S. Høiland, K. Askvik, T. Barth and P. Fotland.* Characterisation of crude oil components with affinity for gas-hydrate surfaces

UNDERSTANDING MIXED OILS (UM) 105
Chairman: Michael ERDMANN

OUM-1. *M. Li, L.R. Snowdon and D. Issler.* Unraveling the source/maturity signature of crude oils in the Beaufort Mackenzie Basin using geochemical parameters within the context of petroleum mass fractions

OUM-2. *K. Manzano-Kareah and S. Ramos.* Unravelling mixed oils using multivariate statistical analysis

OUM-3. *W. Meredith, C.E. Snape, C.Ugama, A.D. Carr, I. C. Scotchman and G. D. Love.* The use of the hydropyrolysis of oil asphaltenes to characterise mixed oils from the Clair field

GAS/COAL GEOCHEMISTRY (GC) 110
Chairman: Françoise BEHAR

OGC-1. *Y. Sun, S. Xu, J. Chen, S. Zhang, D. Liu and P. Chai.* A reassessment of the source for a large, ultra-high pressured gas reservoir of China: clues from the associated condensates

OGC-2. *D. Strapoc, M. Mastalerz, A. Schimmelmann, C. Eble.* Biogenic and thermogenic coalbed gas in the Illinois Basin: insight from compound-specific carbon isotopic ratios

OGC-3. *R. di Primio, B. Horsfield and A. Fuhrmann.* Predicting gas composition and its effect on petroleum phase behaviour during secondary migration

OGC-4. *R. Patience, C. Schile, E. Graven and K.K. Bissada.* Using gas geochemistry to determine commingling in East Breaks 160 (Cerveza) Field, offshore Gulf of Mexico

GEOCHEMISTRY OF PRECAMBRIAN ROCKS AND OILS (GPR) 119
Chairman: *Lloyd R. SNOWDON*

OGPR-1. *S. Dubant, P. Adam and P. Albrecht.* Metal sulfide catalyzed geosynthesis of lipids from carbon oxides and hydrogen sulfide: implications for prebiotic chemistry and organic geochemistry

OGPR-2. *M.B. Vogel, D.J. Des Marais, J., D. Zinniker and J.M. Moldowan.* Branched alkanes in Precambrian manganese carbonates and modern hypersaline environments

OGPR-3. *G.D. Love, E. Grosjean, D.A. Fike, J.P. Grotzinger, S.A. Bowring, D.Condon, A.N. Lewis, C. Stalvies, C.E. Snape and R.E. Summons.* A >90 million year molecular record of neoproteroic sponges (Porifera) in the South Oman Salt Basin

RESERVOIR PREDICTIONS (RP) 125
Chairman: Ignacio BRISSON

ORP-1. *P.J. Hicks, Jr.* A fill, spill and leak approach to pre-drill fluid property prediction

ORP-2. *D.M. Jarvie, R.J. Hill, K.F.M. Thompson, F.D. Mango, and C. Jiang.* Source facies identification from light hydrocarbon analysis – Implications for petroleum system analysis

PALEOENVIRONMENT I (PE1) **178**
Chairman: Richard D. PANCOST

OPE1-1. *G. Mollenhauer and T. Eglinton.* Selective degradation of organic compounds in sediments from the California Borderland Basins: evidence from compound specific $\Delta^{14}C$ and $\delta^{13}C$ analyses

OPE1-2. *P.F. Poussart, N.J. Drenzek, A.L. Lima, T.I. Eglinton, C.M. Reddy and K.A. Hughen.* The Continental residence time of terrestrial biomarkers as determined by molecular level radiocarbon analysis. A case study from the Pettaquamscutt River Basin (USA)

OPE1-3. *T. Boski, L. Albardeiro, D. Moura, C. Veiga-Pires and H. Martins.* Transgression/regression cycles on Continental shelves – A modulator of varying atmospheric CO_2 levels?

PALEONVIRONMENT II (PE2) **185**
Chairman: Antoni ROSELL-MELÉ

OPE2-1. *J. Toporski, C. Ostertag-Henning, J. Eigenbrode, G. Cody and A. Steele.* Biomarkers in bacterial fossils: observations from the 25 million years old Enspel formation

OPE2-2. *Y. Huang, S. Clemens, W. Liu, Y. Wang and W. Prell.* A 10 million year, high-resolution record of carbon and hydrogen isotope ratios of leaf waxes from Arabian Sea ODP Site 722: implications for the late Miocene C_4 plant expansion

OPE2-3. *R.E. Summons, C. Cao, G.D. Love, K. Grice, E. Grosjean and Y. Jin.* Molecular records of Euxinia and protracted environmental disturbance from Permian to early Triassic sediments at Meishan, South China

BIODEGRADATION I (BD1) **191**
Chairman: Eugenio vaz dos Santos NETO

OBD1-1. *A. Vieth and H. Wilkes.* Quantifying the mass loss of light hydrocarbons during in-reservoir biodegradation using their stable isotopic compositions

OBD1-2. *H.L.B. Penteado, J.P. Lopes and S.M. Barbanti.* Some unexpected biodegradation features in oils from a Brazilian marginal Basin

OBD1-3. *A.G. Holba, L.I. Dzou, R. Tharp, D. Stansbury, P. Walker and S.R. Palmer.* Low temperature pyrolysis. The UCM and biomarker regeneration from biodegraded oils

BIODEGRADATION II (BD2) **196**
Chairman: Lorenz SCHWARK

OBD2-1. *C. McIntyre, P. Harvey, I. Snape and S.C. George.* Diamondoids as bioremediation indicators for diesel spills

OBD2-2. *I. Deniau, F. Behar, C. Largeau, C. Beaucaire and H. Pitsch.* Early production of polar **OBD2-2.**products from the Boom Clay Kerogen (Mol underground laboratory) upon thermal stress in relation with nuclear waste disposal

OBD2-3. *A. Chabbi, C. Rumpel, J.A. González-Pérez and F.J. González-Vila.* Lignite mineralization in lignite-containing mine sediment with contrasting redox conditions

Chairman: Ingrid KÖGEL-KNABNER

OSB1-1. *H.R. Mottram and R.P. Evershed.* The fate of rubisco in soils

OSB1-2. *K. Quénéa, S. Derenne, C. Largeau, A. Mariotti.* Influence of change in land use on the abundance and composition of the refractory organic macromolecular fraction of a sandy spodosol (Landes de Gascogne, France)

OSB1-3. *H. Knicker, A. Hilscher, G. Almendros and F.J. González-Vila.* Cluster-size of aromatic domains in charred humic material and its impact on the stability of pyromorphic soil organic matter

Chairman: Gonzalo ALMENDROS

OSB2-1. *M.-F. Dignac, H. Bahri, C. Rumpel, D.P. Rasse, G. Bardoux, A. Mariotti and C. Chenu.* Lignin monomers display contrasted and specific turnover rates in a cultivated soil

OSB2-2. *S. Spielvogel, J. Prietzel and I.Kögel-Knabner.* Chemical composition and age of organic carbon pools in topsoil and subsoil horizons of acid forest soils with different pedogenesis

OSB2-3. *A. Miltner, R. Kindler, C. Hoffmann-Jähniche, H-H. Richnow, F-D. Kopinke and M. Kästner.* Incorporation of CO_2 into soil microbial biomass and its conversion to soil organic matter

Chairman: Patrick HATCHER

OMN-1. *T.B.P. Oldenburg, S.R. Larter, H. Huang, K. Kaster, G. Voordouw, A. Rowan, I.M. Head, J. Lipp, K-U. Hinrichs, and T. Thielemann.* Scanning for indigenous biomass contributions in petroleum and coals using LC-MS techniques

OMN-2. *W.T. Cooper, L.B. Tremblay, J. Chanton, T. Dittmar, and T.R. Filley.* Recurring molecular themes in the Ultrahigh Resolution Mass Spectra of aquatic humic substances from a variety of sources

OMN-3. *M. Elvert, V. Heuer, X. Prieto Mollar, L. R. Hmelo, M. Krummen, J. M. Hayes, and K-U. Hinrichs.* Carbon isotopic compositions of volatile fatty acids in sediment/pore-water systems measured by Isotope-Ratio-Monitoring Liquid Chromatography/Mass Spectrometry

POSTER COMMUNICATIONS

POS1-3. ***The $\delta^{34}S$ values of the early-cleaved sulfur upon thermal alterations as determined by closed and open systems pyrolyses.*** A. Amrani, S. A. Ward, M. Lewan, Z. Aizenshtat

POS1-4. ***Stable hydrogen isotope ratios of petroleum hydrocarbons to evaluate the thermal history of highly-mature and pre-Devonian sedimentary organic matter.*** D. Dawson, K. Grice, R. Alexander

POS1-5. ***Kinetic simulating experiment on carbonate source rocks and the isolated kerogens.*** X. Geng, A. Geng, Y. Xiong, J. Liu, H. Zhang, Q. Zhao

POS1-6. ***Thermal effects of basaltic sill emplacement into source rocks on maturity & hydrocarbon generation.*** J.H. Hubred, D.A. Karlsen, S. Dahlgren

POS1-7. ***Relationship between TOC contents and palynofacies distribution of a paleogene section from Jequitinhonha basin, Brazil.*** T.R. Menezes, C.V. Araujo, O. Strohschoen Jr., J.R. Maizatto, C.C.Lana

POS1-8. ***Hydrocarbon generation in high thermal maturity samples.*** Ll. R. Snowdon, L.D. Stasiuk

POS1-9. ***Comparative characteristic of nitrogen compounds in oils and dispersed organic matter of Upper Jurassic rocks in the Southeast of West Siberia.*** S.S. Yanovskaya, T.A. Sagachenko, O.V. Serebrennikova

POS1-10. ***Detailed geochemical evaluation Green River Shale core: implications for an unconventional source of hydrocarbons.*** B.M. Jarvie, D.M. Jarvie, H. Alimi, C. Jiang, J.D. Burgess, R.J. Drozd, R.J. Hill

POS1-11. ***Formation of organic matter from the Upper Jurassic oil shales of Sysola shale-bearing basin (Russia).*** N.S. Burdelnaya, D.A. Boushnev

POS1-12. ***Organic geochemical study of sediment from Sangkarewang formation, West Sumatra, Indonesia.*** R.Y.P. Burhan, S.R. Putra, Y. Zetra, F. Riandra

POS1-13. ***Organic matter maturation and the acquisition of chemical remanent magnetizations in the Sawtooth Mountains, Montana.*** M.H. Engel, R.D. Elmore, V.J. O'Brien, L.A. Totten, K. Imbus, J.E. Zumberge

POS1-14. ***Experimental generation and transport of petroleum in oil shales***. E. Eseme, R. Littke, B.M. Krooss, J. Schwarzbauer

POS1-15. ***Hydrocarbon generation and expulsion using hydrous pyrolysis experiments – two examples from Brazilian source rocks.*** N. Franco, G. Machado, H. Penteado, W. Kalkreuth

POS1-16. ***Fractionation of stable isotopes in strong redox gradients – basic principles for petroleum geochemistry applications.*** H. Johansen

OIL SOURCE ROCKS-2 (OS2) 319

POS2-1. ***Molecular comparison of pyrolysate compositions from adjacent lacustrine oil shales and coals (NW Anatolia, Turkey).*** A. Jurisch, F. Leistner, U. Mann, R.G. Schaefer, N. Volkmann, M.N. Yalçin

POS2-2. ***Alternative mode of naphthenic oil formation in the depths.*** V.F. Kamyanov, A.K.Golovko

POS2-3. ***Geochemical and petrographical study of Irati and Ponta Grossa formations, Paraná basin, Brazil.*** M. Kern, R. Pacheco, N. Franco, W. Kalkreuth

POS2-4. ***Optical characterization of hydrogenized dispersed organic matter applied to source rocks of Mexico.*** J.A. Perez-Ortiz, E. Gutierrez-Mejia, L. Lopez-Lopez.

POS2-5. ***Environmental control on the gas potential of Cretaceous and Tertiary source rocks in the Mackenzie Delta, Northwest Territories Delta (Canada).*** A. Saison, V. Dieckmann, B. Horsfield

POS2-6. ***Organic geochemical study on Hungarian oil shales.*** C. Sajgó, A. Brukner-Wein, M. Hetényi

POS2-7. ***Organic petrology of Mesozoic marine source rocks in the Qiangtang basin,Tibet, SW China.*** J. Tu, S. Zhang, D. Liu, L. Bian

POS2-8. ***Source rocks of the Sarawak basin, Malaysia: variation in hydrocarbon composition in relation to depositional setting.*** P. Abolins, W.H. Abdullah

POS2-9. ***Kumsk suite - high-potential source rock in the Caucasian-Scythian region.*** L. Distanova, O. Bazhenova

POS2-10. ***Petroleum generating potential of marine-influenced organic-rich sediments from the Middle Miocene Belait formation of Brunei Darussalam, NW Borneo***. W.H. Abdullah

POS2-11. ***Stable carbon isotope fractionation and organic sulphur content in hydrous pyrolysis (24 to 108 hours and 300 to 365 ºC) immiscible oils, bitumens and kerogens from the Oligocene Menilite shales of the Polish Flysch Carpathians.*** M.J. Kotarba, M.D. Lewan, D. Wieclaw, J.B. Curtis

POS2-12. ***Potential hydrocarbon generation in the Lake Baikal Rift, Eastern Siberia.*** A.G. Polozov, D.K. Martikhaeva, V.A. Makrygina, A.P. Gize, P.A. Hall, K. Hall

POS2-13. ***Geochemical preconditions of oil-bearing strata on the Western Geenland margin.*** E. Poludetkina, J. Boesen-Koefoed

POS2-14. ***Biological markers distribution in Bahloul source rock extracts from Central-Northern Tunisia.*** H. Affouri, M. Montacer

POS2-15. ***Importance of the paleothermometers that can be used for the study of the organic matter content in the potential generating rocks with low level of maturity.*** J.A. Pérez-Ortiz, L.F. Fuentes-Pacheco, E. Gutiérrez-Mejía, L. López-López

PRG1-1. ***Simulated maturation of sulfur-rich asphaltite by hydrothermal conversion***. V.R. Antipenko, O.A. Golubina, I.V. Goncharov, S.V. Nosova, J.V. Rokosov

PRG1-2. ***Geochemical characterisation of crude oils from the Mittelplate oil field, Germany: implications for oil quality distribution and field development.*** C. Brinzer, E. Mueller

PRG1-3. ***Effects on geochemical parameters caused by mixing of lacustrine and marine oils.*** J.R. Cerqueira, E.V. dos Santos Neto, J.V.P. Guzzo

PRG1-4. *Compositional alteration of crude oils from different petroleum systems during initia biodegradation.* R. Elias, A. Müller, A. Vieth, A. Riva, H. Wilkes

PRG1-5. *High-molecular weight hydrocarbons distribution in marine oils, Volga-Ural basin, Russia.* J. Golovko, R.P. Philp, G.S. Pevneva

PRG1-6. *Low- and high-molecular weight hydrocarbons in heavy oils.* J. Golovko, G. Pevneva, A. Golovko

PRG1-7. *Using asphaltene-bonded biomarkers released by RICO reaction to identify source and filling direction of biodegraded oil reservoir—The application to the PL19-3 oilfield.* G. Xu

PRG1-8. *Sulfur fingerprinting of cude oils for reservoir characterization.* R.J. Hwang

PRG1-9. *Mixing of crude oils and deposition of solid hydrocarbons in the Hitch sandstone reservoir, Southwest Kansas.* D. Kim, P.R. Philp

PRG1-10. *Structural alteration of native soil hydrocarbons by thermolysis.* O.V. Kovaleva

PRG1-11. *Geochemical factors controlling H_2S production in petroleum reservoirs during steam injection process: TSR experimental simulation.* I. Kowalewski, V. Lamoureux-Var, F. Lorant

PRG1-12. *Different occlusion characteristics of asphaltenes: some implication concerning asphaltene structural features and its secondary evolution processes in the oil reservoir.* Z. Liao, A. Geng, A. Graciaa, H. Zhou, A. Laporte-chrostowska, P. Creux.

PRG1-13. *Compound-specific stable carbon and hydrogen isotope ratios as a diagnostic oil-source correlation tool in the Canadian Beaufort-Mackenzie basin.* M. Li, Y. Xiong, L. Snowdon, D. Issler

PRG1-14. *Evidence of mature oils with low-maturity biomarkers in Brazilian marginal basins*. J.P. Lopes, H.L.B. Penteado, M.D. Rangel, J.V.P. Guzzo, H.G.M. Aguiar

PRG1-15. *Evaluation of reservoir compartmentalization in the deep-water Gulf of Mexico oil fields through the integration of seismic, pressure, PVT and geochemical data.* A.V. Milkov, L. Dzou

PRG1-16. *Relationship between oils in granite basement and in Miocene and Oligocene reservoirs at White Tiger oil field.* Y.V. Savinykh, D.H. Luong, V.K. Utoplennikov

PRG1-17. *Microbial alteration of crude oils: chain length dependency of n-alkane degradation.* A.-K. Scherf, H. Wilkes, J. Rullkötter

PRG1-18. *Reservoir geochemistry of Cendere, Kuzey Karakus, Karakus and Guney Karakus oil fields, SE Turkey.* O. Soyhan, C. Soylu, S. Sayili

PRG1-19. *Reservoir geochemistry of Silivanka oil field, SE Turkey.* O. Soyhan, S. Sayili, A. Akalin

PRG1-20. *Stable C and H isotopic fractionations of individual n-alkanes accompanying biodegradation:evidence from a group of progressively biodegraded oils*. Y. Sun, Z. Chen, S. Xu, P. Cai

PRG1-21. *Hydrogen isotope systematics of individual hydrocarbons in gasoline fraction of Western Canada sedimentary basin oils.* M.J. Whiticar, P. Eby

RESERVOIR GEOCHEMISTRY-2 (RG2) 387

PRG2-1. ***Depositional and diagenetic history of the Mauddud formation in the Great Burgan field in Kuwait.*** F.H. Abdullah

PRG2-2. ***Detection of acidic metabolites of anaerobic hydrocarbon degradation using negative-ion chemical ionisation mass spectrometry.*** C. Aitken, M. Jones, S. Larter

PRG2-3. ***Influence of Production activities on the field crude oil composition.*** N. Cañipa-Morales, A. Pérez-Ortiz, L. López-López, E. Gutierrez-Mejía, J. Mandujano-Velazquez, N. Pintado-Moscoso

PRG2-4. ***Bitumens in North Sea Jurassic sandstone reservoirs: evidence for low temperature degradation rather than oil cracking.*** A.D. Carr, I.C. Scotchman, W. Meredith, C.E. Snape

PRG2-5. ***Are aulphur-rich oils more susceptible to biodegradation than other oils?*** M. Fowler, M. Obermajer, S. Larter

PRG2-6. ***Factors controlling the quality of oils from the Oriente Basin, Ecuador.*** M. Fowler, M. Obermajer, M. Dashwood, J. Cody

PRG2-7. ***Integrated geochemical methods for recognition of oil-condensate mixtures: implications for basin scale petroleum processes.*** R. Hill, D. Jarvie, Z. Wei, J. Dahl, M. Moldowan

PRG2-8. ***Use of organic geochemistry in allocation of production: application in the Chihuido de la Sierra Negra-Lomitas field, Neuquina basin, Argentina.*** I. Labayén, M. Fasola, A. del Monte, R. Castelo, E. Lovrincevich

PRG2-9. ***The use of alkylbenzene ratios for the determination of reservoir fluid communication.*** S.R. Palmer, P. Walker, R. Tharp, D. Rocher

PRG2-10. ***Does dissolved oxygen in the water of Açu formation (Potiguar Basin, Brazil) affects biodegradation of its petroleum?*** P.F. Parente, F.F. Lima Neto, L. Landau

PRG2-11. ***Biodegradation of crude oil on the Norwegian Continental Shelf.*** B.S. Pedersen, N. Mills, H. Wilkes, T. Barth

PRG2-12. ***Origin and alteration of oils and oil seeps from the Sinú San Jacinto basin, Colombia.*** C. Sánchez, A. Permanyer

PRG2-13. ***Comparative study and optimization of asphaltenes and maltenes quantification for diffferent API petroleums.*** C. Zúñiga-Santillán, N. Cañipa-Morales, Y. Contreras-Santiago, K. Magos-Carmona,

PRG2-14. ***TAN and TBN determination of acids and bases in crude oils compared with extraction and molecular analysis.*** T. Barth, K. Erstad, T. Negash

PRG2-15. ***Charge histories of Ness and Tarbert sands, Northern Oseberg area, using reservoir geochemistry.*** B. Dahl, W. Mathiassen, I. Meisingset

PRG2-16. ***A tale of two Eromanga oil fields: a comparison of the hydrocarbon charge histories of sandstone reservoirs at Strzelecki and Acrasia.*** L. Kramer, D.M. McKirdy, K.R. Arouri, L. Schwark, D. Leythaeuser, P.J. Boult

PRG2-17. ***Biodegradation, mixing and lithological controls in the Heidrun field.*** T.L. Leith, D.A. Leith

PRG2-18. ***Formation and thermal evolution of insoluble reservoir bitumen in Angolan carbonate reservoirs.*** A. Mort, F. Laggoun-Défarge, I. Kowalewski, A.Y. Huc, J.N. Rouzaud, F. Muller

PRG2-19. ***Genetic mechanisms of the heavy oils in the North Steep Slope of Dongying Depression, Bohai Bay Basin, East China.*** S. Li, X. Pang, G. Qiu, Y. Gao

PRG2-20. ***Variability of molecular maturity parameters in isothermal source rocks - Implications for assessing the thermal maturity of oils.*** H. Volk, S.C. George, M. Ahmed, R. Sykes

PRG2-21. ***Reservoir petroleum inclusion GOR characteristics and geological significance from the Lunnan Low Uplift of the Tarim Basin.*** X. Xianming, H. Yunxia, X. Zhongyao, S. Zhiguang

BASIN STUDIES (CASE STUDIES) (BS) 423

PBS-1. ***Tertiary saline lacustrine petroleum geochemistry in Qaidam basin, NW China.*** A. Su, D. Liang, S. Zhang, Y. Zhu, D. Peng, H. Huang

PBS-2. ***Hydrocarbon content of organic matter and oils of the Anadyr basin.*** O.K. Bazhnova, T.A. Kirjukhina, E.N. Poludetkina, N.P. Fadeeva

PBS-3. ***A Mesozoic Davis Strait? – an example of the use of molecular markers in paleogeographic reconstructions.*** J.A. Bojesen-Koefoed, H.P. Nytoft, F.G. Christiansen

PBS-4. ***Organic geochemical study of the organic-rich facies in the lacustrine sequences of the Crato formation (Aptian-Albian, Araripe basin, NE Brazil).*** A.G. Borrego, V.H. Neumann, L. Cabrera, C.G. Blanco

PBS-5. ***Geochemical characteristics of the hydrocarbons in the Ulleung Basin, offshore Korea.*** T.-J. Cheong, Y.-J. Lee, S.-J. Park, S. Yi

PBS-6. ***Petroleum geochemistry of the Wessex basin (Dorset, UK).*** P. Farrimond, M. England, R. Paterson, M. Erhuma, A. Hindle

PBS-7 ***Petroleum characterisation of Salambo formation by organic petrography & organic geochemistry (Gulf of Gabes - Tunisia).*** H. Inoubli

PBS-8. ***Organic geochemistry and organic petrography of petroleum systems in the Western Kamchatka coastal margin, Russian Far East.*** M. Li, L. Stasiuk, R. Maxwell, F. Monier, O. Bazhenova

PBS-9. ***Organic geochemistry of the petroleum systems in the Zhanhua depression, Bohai Bay basin (China).*** M. Li, X. Pang, D. Chen, S. Zhang, Y. Wang, D. Shi

PBS-10. ***Saturated hydrocarbons of oil-producing rocks of the Cambrian Kuonamka formation (Eastern Siberian platform).*** T.M. Parfenova, E.N. Ivanova, E.A. Zubova

PBS-11. ***The hydrocarbon occurrences of Mrah area in the Hayan Block-Syria.*** I. Stanković, L. Rumenjak, D. Španić, T. Troskot- Ćorbić, M. Maričić, V. Čuljak

PBS-12. ***Two contrasting scenarios for thermochemical sulfate reduction and sour gas accumulation: case studies in the Chinese sedimentary basins.*** S. Zhang, M. Li, G. Zhu, J. Li, J. Dai

PBS-13. *Geochemical characterization of lacustrine oils in Recôncavo basin, Brazil.* H.G.M. Aguiar, L.B. Penteado

PBS-14. *Hydrocarbon charge modelling in deepwater NW Sabah, Malaysia.* A. Anuar, P. Abolins

PBS-15. *A geochemical overview of oils and condensates of the Barents Sea region.* P.B. Hall, M. Bjoroy, I. Ferriday

PBS-16. *Temporal resolution of an oil-charging history – A case study from the Gidgealpa field.* C. Hallmann, K. Arouri, D. McKirdy, L. Schwark

PBS-17. *Can we correlate liquid hydrocarbons accumulations with Miocene source rocks in Eastern part of the Carpathian Foredeep, Poland?* I. Matyasik, A. Steczko

PBS-18. *An organic geochemical study of Palaeozoic sediments and petroleums from the Scandinavian on- and offshore areas.* J.H. Pedersen, D.A. Karlsen, R. di Primio, J.E. Lie, B. Harald

PBS-19. *Source rock - oil correlation in the Eastern flank of the Upper Magdalena Valley basin, Colombia.* M. Torres, A. Permanyer, C. Mora

PBS-20. *Oil-source rock correlation of oils from Northern part of Pechora basin.* O.V. Valyaeva

PBS-21. *Characterizing the oil source of the Lower Paleozoic Tarim basin by oil geochemistry of the Tahe oilfield.* C.-J. Wang, F.-Q. He, C.-G. Wang, T.-G. Wang

PBS-22. *Oil and gas potential mapping of the Upper Jurassic source rocks using accumulation rates, Danish Central Graben.* B. Dahl, C. Andersen, E. Thomsen

PBS-23. *Potential petroleum systems in the Labrador and Baffin Shelf areas, offshore North Eastern Canada.* M. Fowler, L. Stasiuk, M. Avery

PBS-24. *Integrated approach to characterize non-marine "dual petroleum systems" in Southeast Asia*. A. Okui

PBS-25. *Carbon isotope and Cambrian oil families in the Baltic sedimentary basin.* O. Zdanaviciute

PBS-26. *Paleostructural evolution and geochemical characterization of the Silurian bed source basin of Sbaa. Algerian Sahara.* M. Sadaoui

PETROLEUM MIGRATION (PM) 469

PPM-1. *Blender: a surface geochemistry tool to sample interstitial hydrocarbons in soils and piston core sediments.* C.S. Bandeira de Mello, R.C.S. Gonçalves, D.J. Miller, J.B.L. Francolin

PPM-2. *An integrated multi-component model for petroleum generation, expulsion, and cracking.* D.J. Curry, A.E. Bence, C.C. Walters, S.R. Kelemen, H. Freund

PPM-3. *Geochemical study of natural shows of gas and surface OM in the regions of hypothetical oil-and-gas accumulations, West Siberia, Russia.* A. Golovko, G. Pevneva, E. Ivanova, J. Golovko, N. Savinikh

PPM-4. ***3D petroleum secondary migration modeling of the Jurassic petroleum system in part of the West Siberia basin.*** I.V. Goncharov, A.G. Romanov, A.N. Gagarin, D.J. Carruthers, P.W.M. Corbett, A.P. Afanasenkov

PPM-5. ***Isotopic fractionation effect of primary migration in simulation experiment of selected terrestrial source rocks***. Y. Liao, A. Geng

PPM-6. ***Investigation on hydrocarbon migration direction of the Silurian paleo-pools in Tarim basin, Northwest China.*** L. Luofu, H. Hoiland, H. Hong C. Lixin, C. Yuanzhuang, Z. Suping, L. Chao, L. Shuangwen

PPM-7. ***Change of geochemical parameters during phase.*** D.H. Luong, V.S. Yuri, P.D. Hai, I.U. Vyacheslav, T.L. Dong

PPM-8. ***Understanding synchronisation and migration processes associated to the Caribbean Tectonic during the Oligocene to Miocene in Eastern Venezuelan basin.*** C. Olivares, W. Rodriguez, L. Duerto, I. Rojas, J. Noya

PPM-9. ***Estimating hydrocarbon expulsion from the Shahejie formation in the Niuzhuang South slope of Bohai Bay basin, E China.*** X. Pang, M. Li, S. Li, Z. Jin

PPM-10. ***Petroleum migration and accumulation in Gaoyou depression, East China.*** Y. Zheng, H. Huang, Y. Wang

PPM-11. ***Surface geochemistry from deep water offshore Brunei.*** M. Bjorøy, I.L. Ferriday

PPM-12. ***The origin of hydrocarbons in the Gorleben salt dome, a 3D basin modelling study.*** B. Cramer, P. Gerling, O. Bornemann

PPM-13. ***Competing mechanisms of geochromatography***. C. Hallmann, K. Arouri, D. McKirdy, L. Trindade, L. Schwark

PPM-14. ***Identifying diagnostic compositional features in gasoline range hydrocarbons using genetic algorithm optimisation with procrustes criterion.*** N. Pasadakis, K.G. Osadetz, M. Obermajer, A. kardamakis

PPM-15. ***Crude oil predictions of source rock depositional environments help constrain paleoclimatic models.*** J.E. Zumberge, C.R. Scotese, S.W. Brown, H.A. Illich

GAS (G) **496**

PG-1. ***Genetic characterization of natural gases by stable carbon and hydrogen isotope composition in the Southern part of the Pannonian basin, Croatia.*** V. Culjak, I. Stankovic, D. Spanic, S. Cadez

PG-2. ***The origin of hydrocarbon gases in the South-East of Western Siberia (Russia).*** I.V. Goncharov, V.G. Korobochkina, N.V. Oblasov, S.V. Nosova, V.V. Samoilenko

PG-3. ***Unusual natural gas resources of Hamitabat -(Eocene-Oligocene) (!) gas system of the Thrace basin: implication to future exploration activity.*** K. Gürgey, P. Philp, C. Clayton

PG-4. ***The geochemical characteristics of natural gas and its charging history in the Eastern part of Tarim basin in China.*** H. Guoyi, L. Zhisheng, L. Xia, X. Zengye, M. Chenghua, Z. Ying

PG-5. ***The index optimization and application of the biomaker of nature gas in the gas source correlation.*** L. Jian, L. Xia, Z. Ying, L. Zhisheng, W. Xiaojuan

PG-6. ***Paleo-pressure calculation of P1s2 and the relationship study between the paleo-pressure and the gas accumulation of Ordos basin.*** Luoxia, Shanxiuqing, Lijian, C. Honghan, Huguoyi, Machenghua, W. Xiaojuan

PG-7. ***Correlation of gases with source rocks in Sonliao basin, China.*** Luoxia, Lijian, Liurenhe, Lizhisheng, Huguoyi, Liuchenglin, Machenghua, W. Xiaojuan

PG-8. ***Compound specific carbon and hydrogen isotopic composition of Rotliegend gases in the Voelkersen gas field, NW Germany: applications in field characterization and drilling operations.*** E. Mueller, T. Scholz

PG-9. ***Unusual hydrogen content and its isotopic composition in biogenic gases of the Qaidam basin, Western China.*** Y. Shuai, S. Zhang, A. Su, H. Huang

PG-10. ***Gas alteration and maturation trends in the Western Canada sedimentary basin from three mud gas depth profiles.*** B.J. Tilley, K. Muehlenbachs

PG-11. ***Methane generation from Miocene lacustrine sedimentary rocks containing different types of organic matter.*** M.N. Yalsin, R.G. Schaefer, U. Mann

PG-12. ***Simulation experiments of TSR process and the investigation on thermodynamics and kinetics.*** C. Yue, S. Li, K. Ding, N. Zhong

PG-13. ***The origin of natural gases in Kuqa depression, Tarim basin, NW China.*** Y.-R. Zou, P. Peng, Y. Shuai

PG-14. ***Gases of the kerogen pyrolysis products.*** D. Bouchnev, S. Shanina

PG-15. ***A new approach for geochemical correlation of gases and condensates from the Burgos basin, Mexico.*** T. Carrillo Hernández, M. Guzmán Vega, A. Prinzhofer, A.Y. Huc, M. Escudero

PG-16. ***Methane generation during dry open-system pyrolysis, insights from isotope specific reaction kinetic modelling.*** B. Cramer, Y. Sun

PG-17. ***Origin of carbon dioxide and hydrocarbon gases in Dodan and Silivanka fields (SE-Turkey).*** H. Hosgörmez, M.N. Yalçin, C. Soylu

PG-18. ***Geochemical characterization of gas system associated to oil biodegradation in the Liaohe basin, NE China.*** H. Huang, T.B.P. Oldenburg, B. Bennett, J. Adams, K. Noke, S. Lartera

PG-19. ***Geochemical indicators for formation of natural gas hydrates in the Southeastern Ulleung basin, East Sea off the East coast of Korea.*** B.J. Ryu, J.H. Kim, Y.J. Lee, T.J. Cheong

PG-20. ***Gas expulsion from coals (Brent and Åre Fm NOCS); new proofs and understanding.*** D.A. Karlsen, S.E. Ohm

PG-21. ***Early versus late generation of gas from coals and marine source rocks.*** F. Lorant, F. Behar, M.D. Lewan

PG-22. ***A new genetic scheme for natural gas formation and isotopic evidence for oil cracking as a potentially significant source of natural gas in sedimentary basins.*** Y. Tang, M. Schoell

PG-23. ***Methane formation in the Nile Delta (Egypt): thermogenic versus microbial mechanisms.*** C. Vandré, B. Cramer, P. Gerling, J. Winsemann

PG-24. ***Nous andIndige imported gases in the Pannonian basin system.*** I. Veto

PG-25. ***Experimental study of n-octadecane thermal cracking.*** H. Zhang, A. Geng, Y. Xiong, J. Liu

PG-26. ***Sorption of methane and carbon dioxide in hard coalsand its consequences for the gas storage.*** P. Baran, G.S. Jodłowski, A. Nodzenski, M. Wójcik

PG-27. ***Sorption of the small molecule organic substances in the hard coals.*** G.S. Jodłowski, J. Milewska-Duda, M. Wójcik

PG-28. ***Origin and accumulation model of the AK-1 natural gas pool from the Tarim basin, China.*** X.M. Xiao, Q.H. Zheng, Y.C. Tang, R.W.T. Wilkins

COAL (C) **548**

PC-1. ***Quantitative organic sulphur functionality study of a Bulgarian low rank coal lithotypes by reductive pyrolysis off-line coupled with GC/MS.*** S. Marinov, M. Stefanova, V. Stamenova, L. Gonsalvesh, R. Carleer, J. Yperman

PC-2. ***Lignite carboxylic acid moieties view by CuO oxidation and thermochemolysis.*** M. Stefanova

PC-3. ***Aliphatic chains in coals of different age: controls on the ability to generate liquid hydrocarbons.*** H.I. Petersen, H.P. Nytoft

PC-4. ***Fractionation of petroleum during expulsion from coal: how much is due to molecular retention processes?*** U. Ritter, A. Grøver

PC-5. ***Effects of marine influence on the paraffinic oil potential of humic coals: Eocene Mangahewa formation, Taranaki basin, New Zealand.*** R. Sykes, P.E. Johansen, L.R. Snowdon

PC-6. ***The New Zealand coal band – Molecular compositional changes of a complete maturity series and their potential for feeding the deep biosphere.*** T.T.A. Vu, K.G. Zink, V. Dieckmann, F. Gaidies, K. Mangelsdorf, B. Horsfield

PC-7. ***Hydrocarbons generation by applying artificial confined pyrolysis to coals from the Asturian Central basin (Spain), Sabinas-Piedras Negras (Mexico) and Donets (Ukraine) basins.*** D. Alsaab, L. Martinez, A. Izart, M. Elie, I. Suarez-Ruiz, N. Piedad-Sanchez, F. Lannuzel, C. Menetrier

PC-8. ***Variability of coalification parameters and CH groups content of thermally metamorphosed Tertiary coal from Tanjung Enim area, South Sumatra Basin, Indonesia.*** H. Amijaya, J. Schwarzbauer, R. Littke

PC-9. ***Compound specific carbon stable isotope analysis on biomarker of Late Palaeozoic coals.*** R. Meier, J. Schwarzbauer, P. Weniger, H. Strauß, R. Littke

PC-10. ***Cretaceous and Paleogene coals in Japan as source rocks of natural gas and petroleum.*** H. Oda

PC-11. ***Origin and distribution of biomarkers in the Utrillas coal basin.*** M.A. Olivella, R. Gorchs, F.X.C. de las Heras

PC-12. ***Organic geochemistry and coal petrology of Tertiary brown coal in the Soko mine, Soko Banja basin, Serbia and Montenegro.*** D. Životić, H. Wehner, O. Cvetković, B. Jovančićević, I. Gržetić, W. Hiltmann, G. Scheeder, A. Vidal, A. Šajnović

PBG1-1. ***Organic Geochemistry - A retrospective.*** K.A. Kvenvolden

PBG1-2. ***Source and diagenesis of organic matter from the Middle Jurrassic epicontinental basin of Poland.*** L. Marynowski, M. Zaton, M.O. Jedrysek, C. Grelowski.

PBG1-3. ***Effect of UVB irradiation on Cu^{2+}-binding organic ligands and Cu^{2+} speciation in alpine lake waters of New Zealand.*** S.G. Sander, J.P. Kim, B. Anderson, K.A. Hunter

PBG1-4. ***Discovery of strong copper-binding organic matter in the mixing zone of hydrothermal fluids and sea water.*** S.G. Sander, K.A. Hunter, A. Koschinsky

PBG1-5. ***Effects of adsorbed humic acids on iron oxide and alumina surface properties: iInvestigation ofi interparticle forces in natural waters.*** S.G. Sander, L. Mosely, K.A. Hunter

PBG1-6. ***Abiotic carbon in areas of thermal systems discharge in mid-Atlantic ridge.*** V.N. Sharapov, K.G. Ione, V.M. Mysov, M.P. Mazurov

PBG1-7. ***The geochemistry of the organic matter (OM) of the Upper Quaternary glacial sediments of the peri-Polar Urals***. L.A. Anischenko, S.S. Klimenko, D.A. Bouchnev

PBG1-8. ***Carbon isotopic composition of extracted and bound OM in sediments of hypersaline lake Karachi, West Siberia.*** V.N. Burkova, E.A. Kurakolova

PBG1-9. ***The fate of organic matter in mangrove sediments under variable environmental conditions (French Guiana).*** E. Lallier-Vergès, C.l. Marchand, P. Albéric, J. Disnar

PBG1-10. ***Positioning of the Silurian-Devonian boundary at the North Rim of the Arabian plate (Hazro Area, SE Anatolia, Turkey): an organic-geochemical assignment.*** U. Mann, R. Brocke, U. Herten, O. Kranendonck

PBG1-11. ***Terrestrial organic matter transport: a comparison between tropical and temperate rivers.*** P.M. Medeiros, B.R.T. Simoneit

PBG1-12. *Use of* ***biomarker isomerisation ratios in estimating paleo thermicity and erosion: limitations and applications to the Paris basin.*** C. Ménétrier, M. Elie, A.Le Solleuz, L. Martinez, P. Faure, C. Rigollet.

PBG1-13. ***Compound-specific radiocarbon dating of organic compounds in the oceanic sediments: tools for assessing chronology, transport processes, and biogeochemical cycles.*** N. Ohkouchi, D. Montlucon, T.I. Eglinton

PBG1-14. ***Organic matter of the Cenozoic bottom sediments (sedimentary cover) within the Mendeleev Rise (Arctic Ocean).*** V. Petrova, G. Batova, M. Galishev, A. Kursheva, E. Kostyreva

PBG1-15. ***Geochemical modelling of the hydrothermal alteration of komatiites and the abiogenic production of organic carbon in the Archean.*** L. Richard, M. van Zuilen, C. Biache, M. Crovisier, T. Filhine-Tresarrieu, M. Franiatte, N. Kammer

PBG1-16. ***Prebiotic reactions and synthesis of organic compounds under hydrothermal conditions.*** A.I. Rushdi, B.R.T. Simoneit

BIOGEOCHEMISTRY GENERAL-2 (BG2) 603

PBG2-1. ***Stable hydrogen isotopic fractionation patterns of long chain alkenones.*** S. Schouten, J. Ossebaar, M. Kienhuis, J. Bijma

PBG2-2. ***Organic matter of East Siberian metal-bearing formations.*** O.V. Serebrennikova, V.K. Nemerov, V.V. Evseev, D.I. Vekulenkova

PBG2-3. ***Free and bound carboxylic acids in carbonaceous chondrites.*** J.S. Watson, Z. Martins, O. Botta, P. Ehrenfreund, I. Gilmour, M.A. Sephton

PBG2-4. ***Composition of organic matter in Cretaceous sediments of the ICDP-Chicxulub drill core YAX-1.*** H. Wilkes, A. Fuhrmann, V. Lüders, V. Dieckmann, B. Horsfield

PBG2-5. ***Terrestrial-plant derived leaf waxes in boundary layer aerosols: estimators of carbon isotopic discrimination of terrestrial photosynthesis on large regional scales.*** M.H. Conte, J.C. Weber

PBG2-6. ***Wildfire contribution to long-range transport of terrestrial plant biomarkers.*** M.H. Conte, J.C. Weber, P. Medeiros, B.R.T. Simoneit

PBG2-7. ***Nature, genesis and sources of the carbonaceous polymorphs tracing the 4-kyr BP impact.*** M.A. Courty, M. Fedoroff, K. Grice, P.l Greenwood, M. Mermoux, G. Sagon, D. Smith, M. Thiemens, M. Walls

PBG2-8. ***The carbon isotopic composition of organic matter from Miocene lacustrine sediments (Göynük, NW-Turkey): a function of quality and/or preservation?*** H. Hosgörmez, U. Herten, U. Mann, R. G. Schaefer, M. N. Yalçin, Ö.B. Yesiladali

PBG2-9. ***Inferring ancient food-chain dynamics from the fluctuating isotopic compositions of specific organic compounds.*** D.H. Rothman, R. Summons, J.M. Hayes

PBG2-10. ***Preliminary organic geochemical analysis of surficial marine sediments from the Makassar Strait, Indonesia.*** J. Sáenz, D. Montluçon, D. Oppo, Y. Rosenthal, B. Linsley, Y.S. Djajadihardja, A. Ridlo, F. Syamsudin, T. Eglinton

PBG2-11. ***Application of optical, chemical and thermal methods to the analysis of inorganic and organic constituents in phosphatic pellets (Tunisia).*** A. Ben hassen, J. Trichet

PBG2-12. ***Radiocarbon ages and biomarker compositions of organic matter in size-fractionated sediments from the Washington Margin.*** M. Uchida, T.I. Eglinton, J.M. Hayes, L. Coppola, Ö. Gustafsson, P. Andersson

PBG2-13. ***Relationships between the radiocarbon age and modes of association of natural organic matter in coastal sediments.*** H.K. White, C.M. Reddy, T.I. Eglinton

PBG2-14. ***Organics temporal changes in the Têt prodelta upper deposit (Gulf of Lions – NW Mediterranean sea): relation between the sediment dynamic events and the biogeochemical properties.*** R. Buscail, F. Bourrin, J. Guillen, G. Jeanty, G. Sarragoni

ORAL PRESENTATIONS

PLENARY SESSIONS

OP1-1: Geochemical study of fuel spilled by Prestige and its evolution in affected shorelines

J.L.R. Gallego[1], M.J. García-Martínez[2], J.E. Ortiz[2], T. de Torres[2], J.F. Llamas[2]

1) Campus de Mieres, Universidad de Oviedo. C/Gonzalo Gutiérrez Q., S/N- 33600 Mieres (Asturias- Spain). 0034985458064 (e-mail: jgallego@uniovi.es)
2) LEB, ETSMinas, U. Politécnica de Madrid. C/Ríos Rosas, 21- 28003 Madrid (Spain). 0034913364175 (e-mail: jfllamas@qyc.upm.es)

After Prestige oil spill (November 2002), a great number of environmental studies have been developed to get as much information as possible about the consequences of the massive presence of hydrocarbons in the coastal areas affected. In this work, authors have focused on the quantification and qualification of hydrocarbons in rocky beaches in order to control weathering, biodegradation and toxicity of the residues.

One of the first problems to face hydrocarbon pollution in shoreline environments is related with the local quantitation of remaining pollutants after spillages. To this scope we selected the "Coido de Cuño", granite rocky area of 5.000 m^2 located on the Atlantic coast of Galicia, 80 km far from La Coruña. This site belongs to one of the more affected areas by Prestige fuel. To quantify the total amount of fuel remaining on the rocks, after several months of the spillage, special techniques of image analysis were applied to determine total area covered by fuel; then it was necessary a statistical measurement of the thickness of fuel layers. The results of this calculation showed that approximately 4 kg/m^2 of fuel were covering the rocks.

Geochemical characterization of the oily residues was carried out with habitual GC/MS techniques. Sampling design was made up by dividing the area in five zones where three replicates were taken. Each one of them consisted on a complex sample of ten randomly distributed sub samples of surfaces of 4 cm^2 where the fuel laying on the rock was retired. With this methodology, a total number of fifteen samples were initially taken and analysed from Cuño's site. Results showed an important heterogeneity that suggested differential weathering and biodegradation processes in an apparently homogeneous scenario. These questions were studied in a second sampling at "hot" points were natural attenuation was being evident and effective in the degradation of toxic compounds.

After this study, environmental characterization of the site (nutrients concentration, pH, dissolved oxygen, rock and sand analysis, etc.), some bioremediation techniques were suggested. In fact, the benefits of bioremediation to reduce environmental impacts in oil spills are clear and well-known. In this sense, the remediation of Exxon Valdez oil spill in Alaska is an essential reference to understand how definitive clean up works in coasts affected by Prestige residues should have been considered. So, additionally in this article, we will show some of our experiences with bioremediation not only in Cuño site but in other points in Atlantic and Cantabric coasts. Everything referred to the discussion about the application of chemical biomarkers to determine biodegradation indexes, will be pointed out.

An example of a biodegradation index, as usually defined, consist on a relationship between asphaltenes fraction and total hydrocarbons, being supposed that asphaltene fraction is basically non-biodegradable. As an approximation, this ratio might be useful but there are at least two problems to consider; the most important refers to the evidences of asphaltene biodegradation, which have been reported recently, a secondary obstacle is the abscense of uniform SARA (saturate, aromatic, resins and asphaltenes determination) protocols for analysis. Isoprenoids, such as pristane and phytane, are the second feasible option but they are only useful in the first stages of biodegradation process, because their degradation starts before than it is usually believed, as we will show in this work.

Hopane normalization has been reported as the best method to quantify hydrocarbon degradation, specifically the use of 17α (H), 21β (H) hopane as an internal conserved standard. Further, it is one of the most abundant terpene in oil products and its extremely low solubility, biodegradability and volatility strongly suggests that remains in the residual fuel on shoreline sediments. As a consequence, this compound was selected to measure advances in bioremediation treatments in Alaska during the works in Exxon Valdez oil spill and, since then, it has been used to control biodegradation in many other studies. In this work different biodegradation indexes made up with PAH/hopane ratios, alkane/hopane ratios, etc. have been obtained. Finally, the application of hopanes, and also steranes, was considered to distinct between Prestige wastes and other sources of oil products affecting shorelines.

OP1-2: From the Equator to the Arctic – The occurrence of norlupanes and bisnorlupanes in Tertiary deltaic basins. Are oil-source rock correlations compromised?

J. Curiale[1], J. Decker[2], R. Lin[3]

1) Unocal Corporation, Sugar Land, Texas, USA (e-mail: jcuriale@unocal.com)
2) Unocal Indonesia, Jakarta, Indonesia
3) Unocal Bangkok, Bangkok, Thailand

The occurrence of angiosperm-derived hydrocarbons in Tertiary deltaic sediments and crude oils sourced from those sediments has been reported extensively. Hydrocarbons of the lupanoid family, including lupane, norlupanes, bisnorlupanes and des-A-lupanes, have been reported less commonly in rocks and oils, whereas bisnorlupanes in particular have been observed only rarely, usually in sediments or oils which are currently in Arctic environments. Here, we (a) report, for the first time, the presence of norlupanes and bisnorlupanes in oils of an equatorial basin, the Kutei Basin of Indonesia, (b) compare this observation with reported observations of these compounds in Arctic basins, and (c) review the occurrence and potential origin(s) of these components in Tertiary deltaic basins worldwide.

Several oils of the Kutei Basin, located along the east coast of the island of Borneo in Indonesia, contain 24-norlupane and 24,28-bisnorlupanes, as part of a large suite of angiosperm-derived hydrocarbons including oleananes and ursanes and their olefinic and ring-A-degraded analogs (Curiale et al., in press). Although several of these components are likely to be source-contributed and occur in oils which are confined to deep water regions of the basin, others – including several olefinic hydrocarbons – may have been contributed to the oil during migration or after entrapment. Regardless of how they were specifically contributed, their presence in the Kutei oils strongly supports a Tertiary origin from sediments rich in angiosperm debris, deposited originally by the Mahakam River of Borneo.

Previous identifications of 24-norlupane and (especially) bisnorlupanes, have been limited primarily to samples from specific areas along the west coast of Greenland, offshore northwest Canada, coastal Oregon (USA), and the Gulf of Suez [see Christiansen et al. (1996) for a summary and references to published work]. Most efforts to examine these hydrocarbons have focussed on their Arctic occurrences -- the Beaufort-Mackenzie Basin of northwestern Canada (see Snowdon et al., 2004) and on Nuussuaq Peninsula of western Greenland (Christiansen et al., 1996).

Although the occurrence of norlupanes and bisnorlupanes in oils of the Kutei Basin is unique from the standpoint of latitude, their presence is interpretted in a similar fashion to other worldwide occurrences – a Tertiary source rock containing predominantly angiosperm-derived debris has contributed a molecular signature during generation, and expelled this component into a migration pathway. However, in the case of the Kutei oils, and possibly in the case of the Canadian oils, angiosperm-derived molecular debris has been added to the oil during migration or after entrapment (Curiale et al., in press). It is clear that olefinic oleanoids, ursanoids and bicadinoids are involved in this migration-contamination process, and it is possible that lupanoid hydrocarbons are also involved. If so, all of these angiosperm-derived molecular markers could seriously compromise efforts to correlate oil to source rock at the molecular level, both in terms of molecular distributions and molecular isotopic ratios. Until the effects of migration are deconvoluted from the molecular contribution derived directly from the source rock, such correlations should not be considered accurate. In this paper, in addition to presenting and discussing data on the lupanoid hydrocarbons at extreme latitudes, we document the migration-contamination problem in the Kutei Basin, and introduce conceptual approaches to resolving the question of source-*vs*-migration input in sedimentary basins.

References

Christiansen, F.G., Bojesen-Koefoed, J., Dam, G., Nytoft, H.P., Larsen, L.M., Pedersen, A.K., Pulvertaft, T.C.R., 1996. The Marraat oil discovery on Nuussuaq, West Greenland: Evidence for a Latest Cretaceous-Earliest Tertiary Oil Prone Source Rock in the Labrador Sea-Melville Bay Region. Bulletin of Canadian Petroleum Geology 1996, pp 39-54.

Curiale, J., Lin, R., Decker, J., in press. Isotopic and molecular characteristics of Miocene-Reservoired oils of the Kutei Basin, Indonesia. Accepted in Organic Geochemistry.

Snowdon, L.R., Stasiuk, L.D., Robinson, R., Dixon, J., Dietrich, J., McNeil, D.H., 2004. Organic geochemistry and organic petrology of a potential source rock of early Eocene age in the Beaufort-Mackenzie Basin. Organic Geochemistry 35, 1039-1052.

OP2-1: Fossil DNA as a recorder of ancient microbial communities and palaeoenvironments

M.J.L. Coolen[1], B. Abbas[1], S. Schouten[1], G.M. Muyzer[2], J.K. Volkman[3], J. Overmann[4], J.S. Sinninghe-Damsté[1]

1) Royal Netherlands Institute for Sea Research, PO Box 59, 1790 AB, Den Burg Texel, The Netherlands
2) Delft University of Technology, The Netherlands
3) CSIRO Marine Research, Australia
4) Ludwig-Maxilians-University, Germany

Fossilized organic components provide an archive of ancient aquatic microbial communities and, hence, can be used to reconstruct climate-induced environmental changes and their impacts on biodiversity. However, the interpretation of these data is complicated by the limited source specificity of some traditional biomarkers, such as lipids and pigments. The ultimate biomarkers are genes coding for ribosomal RNA (rDNA), which sequences provide information at the species level by phylogenetic comparison. It was generally believed, however, that DNA becomes rapidly degraded within sediments. However, we have recently shown that under excellent preservation conditions such as low temperatures and in the presence of H_2S, DNA can survive in the Holocene and Pleistocene fossil record[1,2]. In this presentation we will show how fossil DNA can be used as a new organic geochemical tool in the reconstruction of ancient palaeodepositional environments and evolution of past microbial communities.

From Holocene anoxic sediments of the Antarctic Ace Lake (Vestfold Hills), we found that the lakes climate-induced postglacial development from freshwater lake to fjord system and the present-day sulfate-depleted, methane saturated stratified lake with a brackish photic zone, caused changes in the species composition of prokaryotes (cyanobacteria, anoxygenic photolithotrophic green sulfur bacteria (GSB), archaea and methanotrophic bacteria) as well as the phytoplankton such as diatoms and haptophytes. Quantitative stratigraphic analysis of lipid biomarkers and group-specific rDNA, revealed information on the survival of fossil DNA in comparison to lipid biomarkers. It was shown that most of the DNA was degraded before dead cells reach the bottom but the remaining part was found to be well protected and became fossilized. For example, fossil DNA of GSB was found to be less prone to diagenetic processes compared to their specific carotenoids. On the other hand, sedimentary alkenones showed a good correlation with fossil 18S rDNA of their biological source; haptophyte algae of the order Isochrysidales, demonstrating that fossil rDNA can be used as a quantitative biomarker to identify unknown biological precursors of lipids at the species-level.

A $C_{25:2}$ highly branched isoprenoid (HBI) alkene was found in Holocene sediments of Ellis Fjord (Vestfold Hills). Recently, the combined lipid and phylogenetic analysis from a large set of diatom cultures revealed that four different genera of diatoms (*Navicula*, *Haslea*, *Pleurosigma* and *Rhizosolenia*) biosynthesize HBI alkenes[3]. Partial 18S rDNA sequences related to extant C_{25} HBI alkene producing *Navicula*-species revealed the identity of the HBI producer. Although the HBI in the sediments of Ellis Fjord was completely sulfurized after 500 years of deposition, significant amounts of the fossil DNA survived degradation for at least 3,000 years.

Fossil DNA of ancient water column derived micro organisms was not only recovered from stratified, sulfidic lakes and fjords with a relative shallow water column but also from Quaternary deep-sea sediments. Here, decaying cells travelled through a water column of at least 2,000 m before their cellular remains, including nucleic acids became sequestered within the sediments. For example, within Unit I sediments of the Black Sea, we identified fossil DNA of the coccolithophorid alkenone biosynthesizing haptophyte *Emiliania huxleyi*. Within Holocene to Pleistocene eastern Mediterranean sapropels, we identified the carotenoid isorenieratene and 18S rDNA sequences closely related to the isorenieratene biosynthesizing *Chlorobium phaeovibrioides*. The presence of molecular remains of GSB showed that sulfidic bottom waters penetrated into the photic zone and that different species of GSB colonized the ancient chemocline during Holocene and Pleistocene sapropel formation.

In conclusion, these examples show that fossil DNA of various types of ancient water column derived micro organisms survived degradation under sulfidic conditions in lakes as well as deep-sea environments. Furthermore the fossil DNA seems to be less prone to diagenetic processes compared to lipid biomarkers such as carotenoids and HBIs. Therefore, fossil DNA can be used as a new biomarker in the reconstruction of ancient palaeodepositional environments and evolution of past microbial communities at an unprecedented species-level.

References

1. Coolen, M.J.L., Overmann, J., 1998. Appl. Environm. Microbiol. 64, 4513-4521.
2. Coolen, M.J.L., Muyzer, G., Rijpstra, W.I.C., Schouten, S., Volkman, J.K., Sinninghe Damsté, J.S., 2004. Earth Planet. Sci. Lett. 223, 225-239.
3. Sinninghe Damsté, J.S. et al., 2004. Science 304, 584-587.

OP2-2: Characterising the major terrestrial methane sink via ^{13}C-labelling of lipid biomarkers of ambient methanotrophic biomass in soils

R.P. Evershed[1], Z.M. Crossman[1], P. Maxfield[1], E. Brennand[1], E. Hornibrook[2], P. Ineson[3], D. Powlson[4]

1) Organic Geochemistry Unit, Bristol Biogeochemistry Research Centre, School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS UK
2) Bristol Biogeochemistry Research Centre, Department of Earth Sciences, University of Bristol, Wills Memorial Building, Queens Road, Bristol BS8 1RJ UK
3) Department of Biology, University of York, PO Box 373, York YO10 5YW UK
4) Rothamsted Reseach, Harpenden, Herts AL5 2QJ UK

Ambient methane concentrations have been increasing to reach a current global mean of ~ 1.8 ppm from their previous levels of ~0.7 ppm since the industrial revolution. A mole of methane has a global warming potential of 23 times that of a mole of CO_2 and, hence, methane is one of the greenhouse gases that comes under the terms of the Kyoto Protocol to lower emissions (IPCC, 2001). Biological oxidation by methane oxidising bacteria residing in soils, account for between 15-45 Tg CH_4 yr^{-1} and is significant in terms of the overall methane cycle, most importantly, because it is potentially influenced or managed by man. For this reason there has been considerable recent interest in the characterisation of and treatment effects on the ambient methane oxidising bacteria present in soils.

The majority of investigations have focussed on methanotrophic bacteria capable of oxidising high concentrations of methane, termed low affinity methanotrophs, as these are amenable to current methods of culturing. However, the most important group of soil methane oxidising bacteria, termed high affinity methanotrophs, are more difficult to investigate, since they cannot be cultured in the laboratory using conventional techniques. Thus, culture independent methods of analysis have been employed. While, methane flux measurements give an indirect indication of methanotrophic activity, if there is significant methanogenesis it becomes impossible to relate measured fluxes to actual biomass and this approach provides no information of the nature of the organisms involved. A major advance has been to use stable isotope probing (Radajewski *et al.* 2000, *Nature* 403, 646). This method uses density gradient fractionation to isolate ^{13}C-labelled DNA produced by microoganisms cultured on ^{13}C-labelled carbon sources, such as $^{13}CH_4$. While the technique has great potential problems arise where the microbial group under investigation is only a small fraction of the total microbial biomass, exactly as is the case for high affinity methanotrophs in soil.

Using this approach we have studied high affinity methanotrophs in a wide range of natural and managed soils, including grasslands, forests, long-term agricultural experiments and landfill sites (Crossman *et al.* 2004, *Environ. Sci. Technol.*, **38**, 1359).

The method we have developed (Bull *et al*., 2000, *Nature* **405**, 175) for investigating the high affinity methanotrophic biomass involves laboratory exposure of soils to $^{13}CH_4$ for various time periods. Following incubations membrane lipids are extracted and characterised by gas chromatogragraphy/mass spectrometry (GC/MS) and their $\delta^{13}C$ values determined by GC-combustion-isotope ratio MS. As can be seen from Figure 1a the compound-specific stable isotope analysis of phospholipid fatty acids (PLFAs) readily reveals those compounds produced by methanotrophic bacteria. Conversion of $\delta^{13}C$ values to quantities of ^{13}C-labelled PLFA allow 'fingerprint' distributions (Fig. 1b) to be generated for taxonomic classifications. The ^{13}C-labelled methanotrophic PLFA analyses have been complemented by compound-specific analyses of bacteriohopanoids as shown in Figure 1c (Crossman *et al*. 2001, *Organic Geochem*., **32**, 359, in press). This ^{13}C-labelled lipid biomarker-based approache has significant advantages due its high sensitivity and selectivity and, hence, capability to detect and classify chemo-taxonomically microbes present as a minute proportion of the overall microbial biomass.

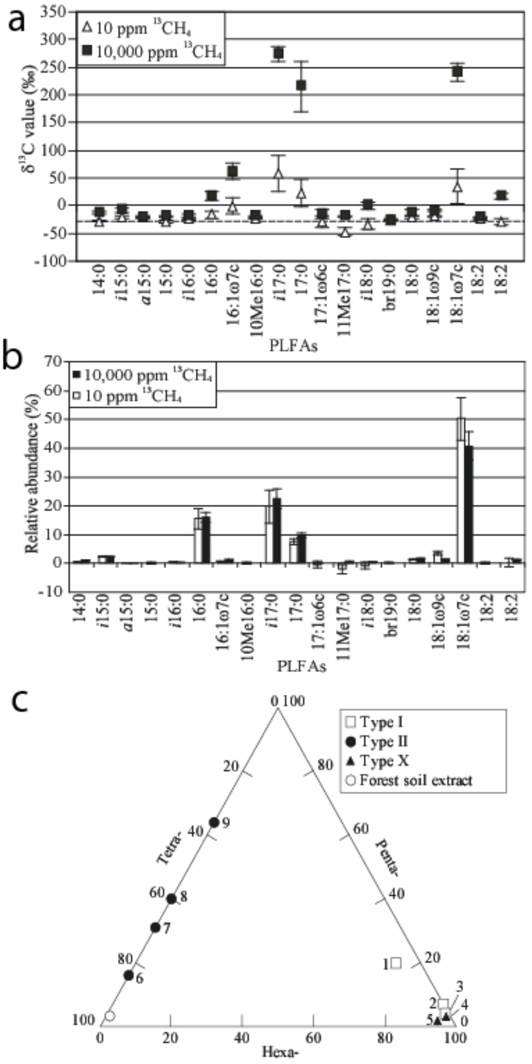


Fig.1. (a) $\delta^{13}C$ values of PLFAs from incubation of soil with different concentrations of atmospheric methane; (b) ^{13}C-labelled PLFA distribution derived from (a), and (c) triangular plot showing that hopanoid biomarkers and PLFAs confirm the major high affinity methantrophs present are Type II.

A more recent development has been the use of a flow through system, which allows long-term exposures of soils to $^{13}CH_4$ in order to determine growth kinetics *in vitro* and the size of the high affinity methanotrophic population. Typical times to achieve full ^{13}C-labelling (from lag to stationary phase) of the methanotroph population is >10 weeks, with cell number estimates, based on a ^{13}C-labelled PLFA conversion factor, indicating that this key group of bacteria constitute less than 0.1% of the total soil microbial biomass.

OP2-3: Enhanced gas formation from deep terrestrial source rocks: new insights from laboratory experiments and natural case studies

V. Dieckmann, B. Horsfield

GeoForschungsZentrum Potsdam, Telegrafenberg, 14473 Potsdam, Germany (e-mail: dieckm@gfz-potsdam.de)

Predicting rates of gas formation from coals is not a straightforward matter. This is because processes others than laboratory simulated cracking reactions are taking place in nature. These processes result in a shift of the natural petroleum formation window to maturities which are beyond those predicted by conventional approaches (Schenk & Horsfield, 1998). We will focus on structural rearrangements occurring in laboratory coalification processes and in nature, and relate these findings to deep basin gas formation.

One of our major study areas is located in the Mackenzie Delta. Upper Cretaceous to Tertiary Delta are buried to 12km and more, and should have therefore experienced high levels of thermal maturity (e.g. >3.0%Ro). Laboratory simulation experiments on one of the major source rocks in this area, the Taglu Sequence (Snowdon *et al.*, 2004), imply that gas formation is still ongoing at such extreme levels of thermal stress. This gas, formed only under closed system conditions, occurs at, and even beyond, the temperature of oil to gas cracking. The residues from closed system experiments (TR~0.2, 0.5 and 0.8) display pyrolytic features consistent with the formation of petroleum beyond the temperatures originally predicted using conventional devices (Fig. 1). Several unusual petroleum characteristics are observed at those extreme maturities. Carbon isotopes of e.g. methane and hexane are marked by a sudden drop of around Δ5‰ (Fig. 1), a high temperature gas formation pulse is identified and a significant drop of the frequency factors in the Ea/A distributed kinetics (Dieckmann, 2005) are observed. Isotopic balancing on coal residues the C6+ fraction and the gas indicate, that these features must account for the neoformation and recombination processes between previously formed hydrocarbons with residual coal/kerogen, through aromatisation/polycondesation processes.

Using a natural coalification series from the Westphalian of Germany, of high volatile to anthracite rank range, similar processes have been ascertained using coupled open and closed system pyrolysis (to 550°C), and IR-spectroscopy. In the early part of the high volatile rank range aliphatic carbon is highest, protonated aromatic carbon is lowest, average alkyl chains are at their longest and phenolic species in open system pyrolysates are very abundant. As rank increases to the medium volatile range, protonated aromatic carbon increases dramatically because of the aromatisation of alicyclic ring components. Chain shortening is very pronounced between Ro = 0.92 and 1.26%. We have used the ratio of (closed minus open)/(closed) system gas yields as a pointer towards whether aliphatic coal substituents at a given rank generate primary or secondary gas. In this regard, values are highest in the high volatile bituminous range and fall smoothly with increasing rank relative to open system yields. In the rank range Ro = 1.5 – 4.0% a big change occurs: Open system yields actually exceed closed system, a feature paralleled by decreasing aromatic proton concentrations. It is clear that over the latter range, structural moieties which under open systems appear as gas-generating moieties are instead retained within polyaromatic systems. Above 4.0% Ro, open and closed system yields are identical, and gas probably originate from the alpha-cleavage of methyl groups from both original and neoformed precursor. .

These results show that neoformation of a high maturity macromolecular structure, as observed in nature, can be broadly simulated using analytical open and closed system pyrolysis associated with extended kinetic modelling. Only the combination of kinetics from immature samples and those from neoformed organic matter can account for the structural reorganisations and gas generation processes as they occur in coals.

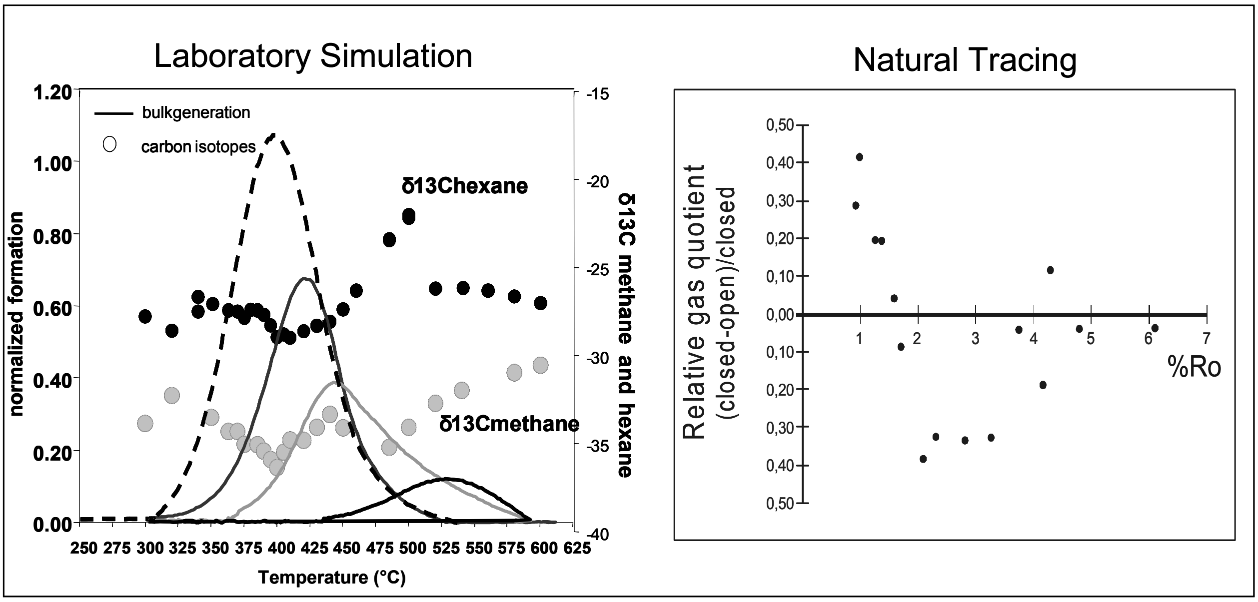


Fig.1. Simulation and detection of the formation of deep gas precursors along laboratory experiments (a) and in a natural maturity sequence (b)

References

Dieckmann, V. (2005): Predicting petroleum formation from heterogeneous source rocks: The influence of frequency factors on activation energies and geological predictions, Marine and Petroleum Geology. (in press)

Schenk, H.J., Horsfield, B., (1998) Using natural maturation series to evaluate the utility of parallel reaction kinetics models: an investigation of Toarcian Shales and Carboniferous coals, Germany. *Organic Geochemistry*, 29(1-3), 137-154.

Snowdon, L.R., Stasiuk, L.D., Robinson, R., Dixon, J., Dietrich, J., McNeil, D.H., (2004) Organic geochemistry and organic petrology of a potential source rock of early Eocene age in the Beaufort-Mackenzie Basin. *Organic Geochemistry*, 35(9), 1039-1052.

OP2-4: Separation of complex mixtures of hydrocarbon for paleobiological reconstruction: comprehensive two dimensional gas chromatography (GC×GC) and GC×GC-mass spectrometry of ~2.7 Ga argillites from Timmins (Ontario, Canada)

F. Kenig[1], G.T. Ventura[1], C.M. Reddy[2], R.K. Nelson[2],
G.S. Frysinger[3], R.B.Gaines[3]

1) Department of Earth and Environmental Sciences, University of Illinois at Chicago, M/C 186, 845 West Taylor Street, Chicago IL 60607-7059, USA (e-mail: fkenig@uic.edu)
2) Department of Marine Chemistry and Geochemistry, MS#4, Woods Hole Oceanographic Institution, Woods Hole, MA 02543-1543, USA
3) Department of Science, U.S. Coast Guard Academy, New London, CT 06320-8101, USA

The presence of Archaea on Earth ~2.7 billion years (Ga) ago is inferred from the ^{13}C depleted composition of kerogen (-60 to -40‰), which may be due to carbon cycling between methanogens and methanotrophs [1]. The existence of Archaea in the Late Archaean is not disputed, even though biomarker evidence is lacking. Biomarker analyses of Archaean sediments are limited by the need to demonstrate that the organic matter observed is syngenetic. Also, the occurrence of unresolved complex mixtures (UCM) sometimes interferes with observing potential biomarkers (see Fig. 1A). Here we use the increased resolution and compound-class separation provided by comprehensive two-dimensional gas chromatography (GC×GC) and GC×GC-time of flight mass spectrometry to resolve the UCM of hydrocarbons in Archaean samples. This novel technology (along with specialized software) allows for chromatographic data to be visualized and navigated in 3D space (e.g. Fig. 1B and C). Overall, GC×GC provides an unprecedented means to observe chromatographic and mass spectrometric data from Archaean samples.

Extracts from three argillitic samples of the Viapond Fm. (2.707-2.705 Ga) and three argillitic Hoyle Fm. (Porcupine Assemblage; 2.685-2673 Ga; Figure 1) from Timmins (Ontario, Canada) were analyzed. The syngenetic origin of the organic matter and hydrocarbon extracts of these samples is demonstrated by Ventura *et al.* (this volume). The outstanding power of GC×GC allowed us to identify biomarkers of Archaea, such as biphytane, monocyclic, bicyclic and tricyclic biphytane as well as 10 other structural isomers of C_{37}, C_{38} and C_{39} mono, bi and tricyclic isoprenoids; the latter form the bulk of the UCM in the Hoyle Fm. samples (see UCM 2, Fig. 1). These Archaeal biomarkers are also present in GC×GC images from Viapond and Gold Center Fm. but in lesser amounts. To the best of our knowledge, these biomarkers constitute the oldest direct evidence for the presence of Archaea on Earth and confirm that branching between Archaea and Eukaryote domains must have occurred prior to 2.7 Ga.

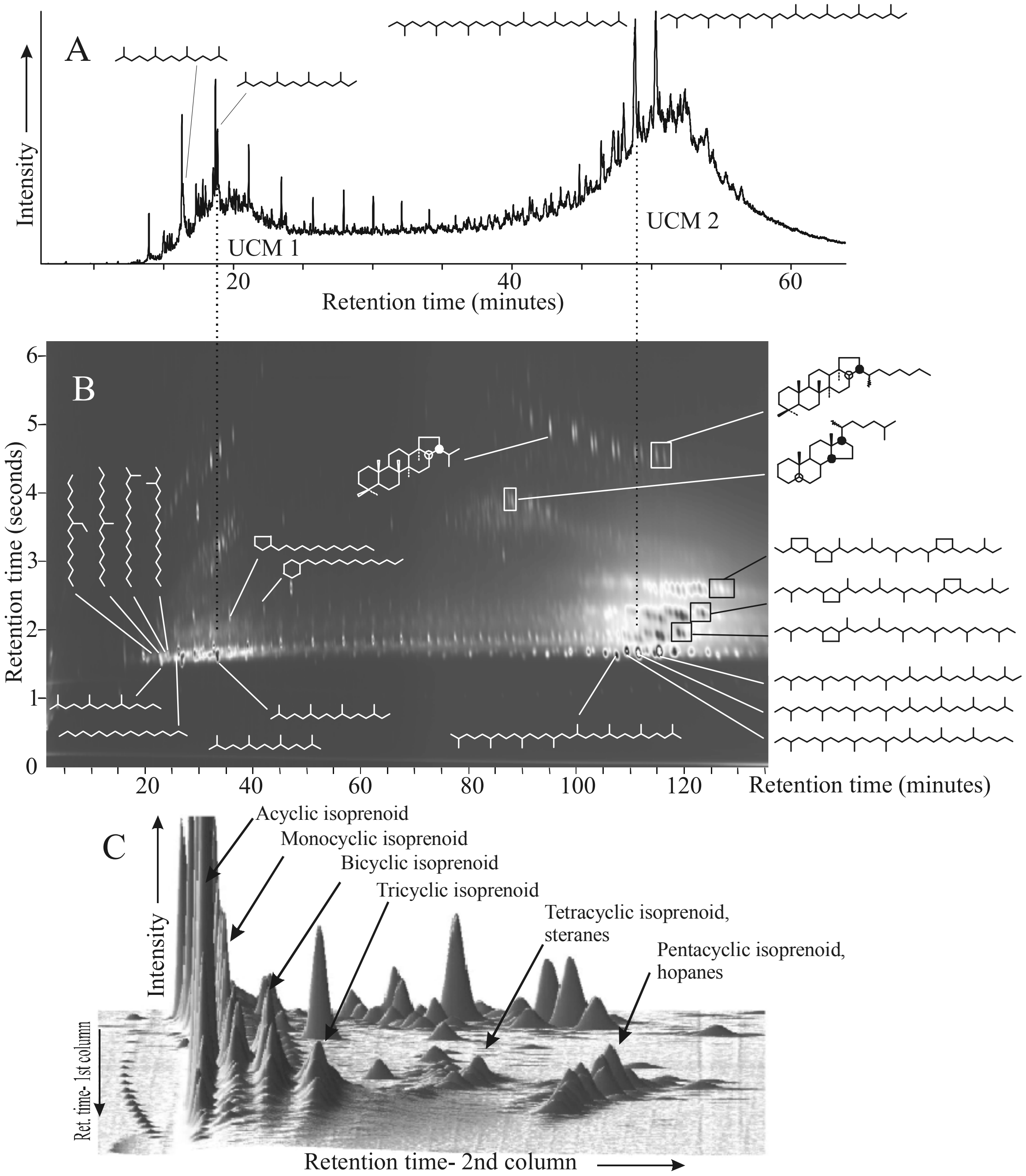


Fig.1. Chromatographic data for the saturated/unsaturated hydrocarbon fraction of sample Owl Creek 113m (Hoyle Fm., Timmins, Ontario, Canada.). (A) GC-MS Total ion current. (B) color contour plot of the GC×GC FID chromatogram. (C) Matlab© 3D rendering of the GC×GC FID data.

References

[1] Hayes J. M. (1994) Global methanotrophy at the Archean-Proterozoic transition. In Bengston, S. (ed.) Early Life on Earth. Nobel Symposium 84. Columbia University Press, New York. pp 220-236

OP3-1: Resistant bio- and geomacromolecules in fossil spores, pollen and wood

J.W. de Leeuw[1,2,3], I. Poole[1], P. Blokker[3,4], P.F. van Bergen[1,5]

1) Geochemistry, Fac. Earth Sciences, Utrecht University, Utrecht, The Netherlands
2) Palaeoecology, Fac. Biology, Utrecht University, Utrecht, The Netherlands
3) Royal NIOZ, Texel, The Netherlands
4) Current address: Systems Ecology, Free University Amsterdam, Amsterdam, The Netherlands
5) Current address: Flow Assurance, Shell Global Solutions, Amsterdam, The Netherlands

Morphologically recognizable micro- and macrofossils, such as pollen, spores and wood have a long history of use, ranging from stratigraphic markers to entities that provide palaeoenvironmental and palaeoecological information.

In most cases, the main underlying reason for their preservation in the fossil record is thought to be the resistance of their chemical constituents against acid and base treatments. In particular poly-ether constituents of biopolymers such as lignin, cutan and algaenan in resp. wood, some plant cuticles and some algal cell walls are thought to be responsible for the preservation of biological tissues, whereas tissues made up of hydrolysable biopolymers such as polysacharides, proteins, DNA and polyesters are not preserved under common diagenetic conditions. This phenomenon may significantly affect the fossil record as these differences in the chemical composition of the biological tissues and fossils may bias against those that contain less or no resistant organic constituents. In order to understand and, possibly, correct for such biases, detailed insights into the chemical composition of both modern and fossil spores, pollen and wood is needed. This study presents an overview of the currently available literature information in combination with new molecular and atomic data from sporopollenin and lignin in extant tissues, sub-fossil and fossil entities and new insights into the diagenetic production of stable aliphatic geopolymers.

The new data clearly reveal that:

a) The chemical composition of the fossil materials is in most cases not representative of the original biomacromolecules present in the modern counterparts and that significant chemical changes occur during fossilisation.

b) The structure of sporopollenin is probably fully aromatic and not a partly aliphatic, partly aromatic one as recently suggested.

c) The structures of sporopollenin and lignin are very similar, strongly suggesting that they are biosynthesised by very similar biosynthetic pathways implying a highly interesting evolutionary relationship highlighting the evolution of land plants.

d) Resistant aliphatic geopolymers comparable to the biopolymers cutan and algaenan can be produced diagenetically by oxidative cross-polymerisation of unsaturated membrane or other lipids.

e) The stable carbon isotope composition of lignin can be studied on the intramolecular atomic level revealing highly unexpected and very large differences in the stable carbon isotope signature of the individual side chain carbon atoms of the monolignols.

OP3-2: Experimental evidence for lipids as a source for aliphatic component of fossils and sedimentary organic matter

N.S. Gupta[1], R. Michels[2], D.E.G. Briggs[3], M.E. Collinson[4], R.P. Evershed[1], R.D. Pancost[1]

1) Organic Geochemistry Unit, Bristol Biogeochemistry Research Center, School of Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1RJ, UK
2) CNRS, UMR7566-CNRS, Faculté des Sciences, BP236, 54501Vandoeuvre les Nancy, France
3) Department of Geology and Geophysics, Yale University, PO Box 208109, CT 06520, USA
4) Department of Geology, Royal Holloway University of London, Egham, Surrey, TW20 0RB, UK

Pre-Tertiary arthropod and leaf fossils are comprised of recalcitrant aliphatic macromolecules, similar in composition to Type I/II kerogen. Typically, their extant counterparts lack analogous resistant precursor compounds, precluding selective preservation of such compounds as a source for the fossil aliphatic character. Instead, recent research reveals that fossil aliphatic macromolecules could be a product of lipid polymerisation. To understand this process, confined pyrolysis gold tube experiments were carried out on pure and chemically treated modern arthropod and plant tissues and model compounds. The experiments were conducted at 350°C, 700 Bars, for 24 hours and were subsequently analysed using pyrolysis-gas chromatography-mass spectrometry (Stankiewicz et al., 2000).

Modern arthropod cuticles consist of chitin fibres in a protein matrix; chitin is selectively preserved during controlled decay of arthropods and hence encountered in fossils as old as 25 Ma. However, fossils older than these invariably yield an aliphatic composition upon pyrolysis (although occasionally associated with aromatic components). In the absence of a recalcitrant aliphatic precursor, it has been speculated that these could be a product of polymerisation of cuticular waxes/internal lipids (Briggs 1999). Our confined pyrolysis experiment provides direct evidence for this argument. The artificially matured untreated cuticle yields pyrolysis products related to phenols, pyridines, pyrroles and possibly indenes (derived from matured chitin). Amides, C_{16} and C_{18} fatty acids and *n*-alkane/*n*-alkene homologues ranging from C_{10} to C_{20} are also present, the latter indicating the presence of a macromolecular component containing *n*-alkyl moieties. In contrast, cuticles matured after lipid extraction and saponification do not release any detectable *n*-alkyl compounds during pyrolysis, indicating that n-alkyl moieties cannot arise from thermal alteration of pure chitin. Similarly, purchased, purified and artificially matured lignin and cellulose also failed to yield an aliphatic composition during pyrolysis. Instead, lipids derived from the cuticle/internal tissue appear to be responsible for the aliphatic polymer encountered in fossil arthropods.

We observe analogous results from artificial maturation of modern leaves. Pyrolysis of untreated and artificially matured *Castanea*, *Quercus*, *Ginkgo*, *Acer* and *Pinus* leaves (all of which lack detectable cutan) yielded *n*-alkane/*n*-alkene homologues ranging from *n*-C_{10} to *n*-C_{33} and phenols. *n*-C_{16} and *n*-C_{18} fatty acids derived from cutin and/or internal lipids were also detected. However, leaves matured *after* lipid extraction yielded a predominance of short-chain *n*-alkane/*n*-alkene homologues upon pyrolysis but a marked decrease in the relative abundances of long-chain homologues. The leaves matured after both lipid extraction and hydrolysis did not yield any detectable alkyl components during pyrolysis. In contrast, artificially matured *Agave* leaves, which do contain cutan, always released a wide range of *n*-alkane/*n*-alkene homologues during pyrolysis, regardless of chemical pre-treatment.

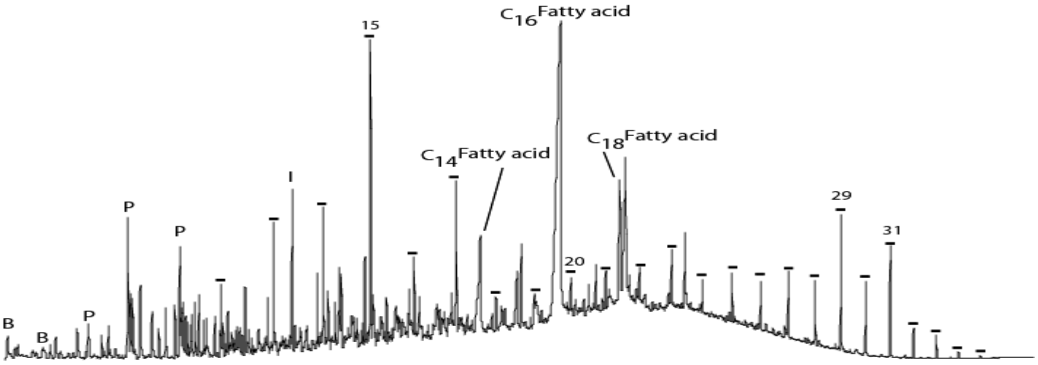


Fig.1. Partial ion chromatogram of modern *Castanea* leaf matured without prior chemical treatment. P: Phenols, B: Benzene derivatives, I: Indole.— *n*-alkane/alkene homologues released during pyrolysis, number indicating the carbon chain length.

To understand further the behaviour of cutin during artificial maturation, chemically treated tomato peel was investigated. Pyrolysis of matured tomato peel yielded short chain *n*-alkane/*n*-alkene homologues similar to the distribution observed in lipid-extracted plants, suggesting that the long chain *n*-alkanes in the pyrolysate of untreated leaves likely derive from waxes, etc. Additionally, the internal tissue of tomato was matured, yielding an aliphatic component during pyrolysis comprising *n*-C_{10} to *n*-C_{27} *n*-alkane/*n*-alkene homologues. This suggests that internal plant tissue components could also contribute to the formation of fossil aliphatic macromolecules. Thus, cutin, waxes and internal lipids all appear to be probable contributors to the aliphatic composition of fossil organic matter.

References

Stankiewicz, B. A., Briggs D.E.G., Michels R., Collinson M. E. and Evershed R. P., 2000. Alternative origin of aliphatic polymer in kerogen. Geology 28, 559-562

Briggs, D.E.G., 1999. Molecular taphonomy of animal and plant cuticles: selective preservation and diagenesis. Philosophical Transactions of the Royal Society of London series B- Biological Sciences 354, 7-16

OP3-3: Circum-Arctic petroleum systems identified using biomarkers, isotopes, and a new chemometric approach

K.E. Peters[1], L.S. Ramos[2], J.E. Zumberge[3], D.L. Gautier[1]

1) U.S. Geological Survey, 345 Middlefield Road, MS 969, Menlo Park, CA 94025 (e-mail: kpeters@usgs.gov)
2) Infometrix, Inc., 10634 E. Riverside Drive, Suite 250, Bothell, WA 98011
3) GeoMark Research, Ltd., 9748 Whithorn Drive, Houston TX 77095

The Circum-Arctic is one of the last major frontiers in petroleum exploration. As part of the World Energy Consortium organized by the U.S. Geological Survey, source- and age-related biomarker and isotopic data were measured for more than 1000 crude oil and seep samples collected above 55°N latitude. A unique, multi-tiered decision tree consisting of multiple KNN (K-Nearest Neighbor) and SIMCA (soft independent modeling of class analogy) models created using Pirouette® allowed statistical classification of genetically related groups. A similar approach was used to classify mycobacteria (Ramos, 1994) and crude oils from other locations (Zumberge and Ramos, 1996). Our Circum-Arctic results show that the new chemometric approach is far more reliable than conventional methods for oil-oil and oil-source rock correlation. Using 986 'training set' samples, an automated protocol was created using InStep™ to classify newly acquired samples of crude oils, seeps, and source-rock extracts, and assign corresponding confidence limits.

Multivariate analysis of the geochemical data was also used to infer the age, lithology, organic matter input, and depositional environment of the source rock for each oil group in the training set using parameters described in Peters et al. (2005). Thirty oil groups were identified, mapped, and linked to source rocks; examples include Paleocene distal marine shale (Mackenzie Delta), Upper Jurassic distal marine shale (West Siberia), Lower-Middle Jurassic paralic-deltaic marine shale (West Siberia), Triassic marine marl (North Slope), Devonian fluvial lacustrine shale (Scotland), Devonian marine carbonate (Western Canada Basin), Ordovician-Silurian distal-deltaic marine shale (Sweden), Precambrian marine marl (East Siberia). To better assess the original and present-day distributions of each petroleum system, paleo-latitudes and paleo-longitudes of the samples were reconstructed using PointTracker© and located on paleogeographic maps using Earth System History-GIS© (PaleoMap Project, C. Scotese).

References

Peters, K.E., Walters, C.C., and Moldowan, J.M. (2005) The Biomarker Guide – 2nd Edition. Cambridge University Press, Cambridge, U.K., 1155 p.

Ramos, S.L. (1994) Characterization of mycobacteria species by HPLC and pattern recognition. *Journal of Chromatographic Science,* 32, p. 219-227.

Zumberge, J. and Ramos, S. (1996) Classification of crude oils based on genetic origin using multivariate modeling techniques. Abstract, 13th Australian Geological Convention, Canberra, 19-25 February.

OP3-4: Unravelling multiple processes determining petroleum bulk properties: use of aromatic hydrocarbons to deconvolute source, maturity, biodegradation and mixing

B. van Aarssen[1], A. Murray[2], C. Barber[1], A. Bishop[2], R. Elsinger[2], H. Ganz[2], P. Taylor[2], E. Idiz[2]

1) Centre for Applied Organic Geochemistry, Curtin University of Technology, GPO Box U1987,
Perth, Western Australia, 6845 (e-mail: B.vanAarssen@curtin.edu.au)
2) Shell International Exploration and Production B.V., Postbus 60, 2280 AB Rijswijk, The Netherlands

The bulk properties of any petroleum accumulation (GOR, API, viscosity etc) are determined by a complex interplay of source, maturity and various secondary alteration processes. While these processes can often be elucidated by established saturate biomarker and isotope methods, uncertainties will always remain as to how well compounds present in trace quantities reflect the origin and history of the bulk fluid. Aromatic hydrocarbons are an order of magnitude more abundant in crude oils than the saturate biomarkers and are a major determinant of their density and viscosity. The utility of aromatic molecular data has been limited in the past by the seemingly uniform composition of the aromatic fraction of many crude oils and a lack of understanding of the processes determining the detailed composition. This deficiency arises partly from studies in which samples sets were insufficiently diverse to allow unravelling of the multiple influences.

For this study, we analysed a large set of crude oils (> 110) from Oman, Nigeria, Italy South East Asia and the Gulf of Mexico. The oils represent various source rock types, maturities and degrees of alteration/mixing. Their origins are constrained by good geological context and by a comprehensive set of other bulk property and geochemistry data including compound specific isotopes. The analyses for aromatic hydrocarbons provide data for over 90 alkylbenzene, alkylnaphthalene and alkylphenanthrene isomers including semi-volatile species. Several case studies will be used to show how the results reflect the origin and accumulation history of the oils. For example, in the Gulf of Mexico (GOM), mixing of oil and a second charge of gas condensate can give rise to a simple relationship between GOR and aromatic maturity indicators derived from the alkyl benzenes. Regionally in the GOM, the carbonate and clastic lithology sources, well known from studies of saturate biomarker fractions, are equally apparent in the alkylnaphthalene distribution, strengthening the link to bulk property variation.

Mixing histories of crude oils were unravelled where the maturities of the end member oils were different, by comparing the distributions and concentrations of tri- tetra and pentamethylnaphthalenes, which all display the same maturity in an unaltered oil. Mixing oils of different maturities resulted in mixed maturity signals in these compound classes. A similar approach, using xylenes, tri- and tetramethylbenzenes was applied in cases where one end member oil was very light and contributed mainly methylbenzenes to the mixture.

In general, biodegradation affects benzenes at a higher rate than naphthalenes which degrade faster than phenanthrenes. Within each group, compounds with more methyl substituents are more resistant, within each class of methyl aromatic hydrocarbons different isomers degrade at different rates. Some are very resistant and remnants of these isomers can be found in cases where an earlier charge has been degraded and later mixed with a fresh charge. This knowledge has been applied to unravel accumulation histories involving several episodes of charging and biodegradation.

Physical processes such as in-reservoir fractionation affects each group of aromatic hydrocarbons in different ways since there is a large difference in volatility between benzenes, naphthalenes and phenanthrenes. This principle was applied to detect fractionation processes where the fluids were either depleted in benzenes, reflecting the residual oil, or in phenanthrenes, reflecting the removed light fraction.

OP4-1: Molecular-isotopic approaches to continental climate reconstructions from marine sediments: African aridity, vegetation and terrestrial carbon export

E. Schefuß[1,2], T.I. Eglinton[1], S. Schouten[3], P.M. Grootes[4], J. Rullkötter[5], R.R. Schneider[6], J.M. Hayes[1]

1) Woods Hole Oceanographic Institution, USA (e-mail: eschefuss@whoi.edu)
2) DFG-Research Center Ocean Margins at the University of Bremen, Germany
3) Royal Netherlands Institute for Sea Research, Texel, The Netherlands
4) Leibniz-Labor for Radiometric Dating and Isotope Research, Kiel, Germany
5) Institute of Chemistry and Biology of the Marine Environment, Carl von Ossietzky University Oldenburg, Germany
6) Institute of Geosciences, Christian-Albrechts University Kiel, Germany

Molecular isotopic methods supply a wealth of valuable information for continental paleoclimate reconstruction. Compound-specific stable carbon isotope analyses of higher-plant derived lipid biomarkers reveal the photosynthetic pathway of terrestrial vascular plants and enable discrimination of C_3 (e.g. trees) and C_4 plants (e.g. tropical grasses). In addition, compound-specific hydrogen isotopic signatures of plant waxes yield information on the balance of precipitation and evapo-transpiration in soils and plants, while lipid-specific radiocarbon analyses allow the assessment of eolian or fluvial transport times of terrigenous lipids prior to final deposition in aquatic sediments.

Here, we present results of molecular isotopic investigations of higher-plant derived lipids to improve our understanding of continental climatic and environmental changes. Analyses were carried out on sediment samples from an accurately-dated, high-accumulation marine core recovered off the Congo River, draining a large central African area mainly covered by rainforest. Generally light stable carbon isotope values (ca. -33.5 ‰) of the sedimentary leaf waxes confirm that rainforest (C_3 plant) sources predominate. A slight increase of C_3 plant contributions from the Last Glacial to the Holocene was detected, whereas during the Holocene several short-term excursions towards heavier, i.e. C_4 type, values occurred. The latter may be due to extensions of grassland in the Congo Basin or to changes in the source area of the lipids. Hydrogen isotope signatures of plant waxes record changes in the isotopic composition of precipitation combined with the fractionation effects during evaporation from soils and transpiration from plants. In tropical regions, all these effects are strongly coupled, i.e. increased precipitation leads to lighter isotope ratios of rain and to less fractionation by evapo-transpiration, and vice versa. Thus, hydrogen isotope compositions of plant lipids in tropical regions are a direct measure of continental moisture availability. Hydrogen isotope ratios of leaf waxes were relatively heavy (ca. –130 ‰) in the Last Glacial and became lighter during deglaciation, indicating a general increase in precipitation. Around 12,000 years ago, the hydrogen isotope ratios drop abruptly to heavier values, reflecting a rapid aridification. Afterwards, hydrogen isotope values decreased again, until lightest values (ca. –165 ‰) indicate the most humid conditions in central Africa at around 9,000 years ago. Subsequently, a gradual trend to a drier climate was observed towards the present. To determine the climatic control of the large-scale hydrological changes, we compare the reconstructed humidity changes with various sea-surface temperature records from the Atlantic Ocean. We find that central African rainfall changes were mainly driven by the tropical-subtropical sea-surface temperature gradient in the South Atlantic, which controls the trade-wind strength, counter-acting the inflow of moist air onto the African continent. The sudden increases in the stable carbon isotope compositions of the plant lipids during the Holocene, however, coincided with high humidity estimates. Therefore, the short-term increases in the abundance of C_4-plant-derived lipids were not caused by grassland extensions in the Congo catchment, but, more likely, by changes of the source area of the plant lipids, indicating shifts in the position of the main rainfall belt. The Congo catchment contains C_4 dominated grasslands at its northern fringe, which could temporarily contribute C_4 plant-derived lipids, when the main rainfall belt moved northward. As plants take up the rainwater via soils, they would adjust their hydrogen isotopic composition rapidly, whereas they would retain their stable carbon isotope signature. A spread of forest into grassland, in contrast, would require much longer time.

Radiocarbon analyses of the terrestrial plant waxes, as well as of the total sedimentary organic matter, show variable, and in some cases, substantial age differences relative to marine carbonate microfossils. Comparison with compound-specific radiocarbon dates of marine lipids suggests, however, that sedimentary redistribution is an insignificant process in this depositional setting. Since transfer times associated with fluvial transport are assumed to be minor, the main factor determining the age of the terrigenous lipids must be the balance between contributions from contemporaneous vegetation sources and from eroded soils or weathered ancient sediments. Indeed, the relative ages of the plant waxes correspond well with the humidity estimates derived from the hydrogen isotope compositions of the wax lipids. Under more arid conditions, more soil is exposed, leading to a greater contribution of pre-aged terrigenous lipids. Multi-isotopic molecular analyses thus supply an integrated perspective of climatic and environmental changes and terrestrial carbon export in continental paleoclimate reconstructions.

OP4-2: Hopanoids as soil markers

H.M. Talbot, M.A. Sugden, C.I. Yurdokök, M.P. Cooke, P. Farrimond

NRG, School of Civil Engineering and Geosciences, Devonshire Building, University of Newcastle, Newcastle upon Tyne, NE1 7RU, UK (e-mail: h.m.talbot@ncl.ac.uk)

Here we present new data demonstrating the occurrence of a suite of unusual bacteriohopanepolyols (BHPs) in diverse soils (e.g. urban garden, arable, grassland, wooded), and their use as novel markers of soil input to aquatic depositional settings where they are preserved up to at least 8000 years old.

Hopanoids are the most abundant group of biomarker molecules in the geosphere (Ourisson *et al.*, 1984), yet their potential as markers for specific bacterial populations, depositional environments, and environmental/climate change, has been largely unrealised. Despite the ubiquity of hopanoids in the geosphere limited data is available about their composition in modern environments, particularly soils and peats.

Early work on hopanoids in soils concentrated on the detection of degraded compounds such as hopanols and hopanoic acids (e.g. Ries-Kautt and Albrecht, 1989) or used the periodic acid cleavage method which converts polyfunctionalised BHPs into GC-MS amenable primary alcohol products thus loosing the more source-specific information present in the structure of the intact side chain (e.g. Crossman et al., 2001). To date only one intact BHP has been reported in a soil (bacteriohopanetetrol, **I**; Ries-Kautt and Albrecht, 1989). However, using our recently developed LC-ion trap-MS based method for the analysis of intact BHPs (Talbot et al., 2003a, b) we are now able to detect a wide range of BHP structures indicative of a variety of organisms such as cyanobacteria, methanotrophic and methylotrophic bacteria in total lipid extracts from soils.

Here we report a wide range of BHP structures in a suite of urban and agricultural soils including a group of 5 compounds common to all of the soils studied to date (Fig. 1). This group includes the commonly reported bacteriohopanetetrol, a highly specific cyanobacterial marker 2-methylbacteriohopanetetrol (**II**) and three compounds with an unusual cyclised side chain structure. Adenosylhopane (**III**) was originally identified in a purple non-sulphur bacterium (Neunlist and Rohmer, 1985) and has subsequently been observed in an ammonia-oxidiser and a nitrogen fixing bacterium. The side chain structures for compounds **IV** and **V** (guanosylhopane and 2-methylguanosylhopane) are tentative based on comparison of their APCI MS^2 spectra with that of adenosylhopane.

We have also found these novel marker compounds in sediments of lakes (e.g. Windermere [Fig. 1] and Loch Ness) with known significant soil input, whilst they are not detected in offshore marine sediments. We thus propose their use as markers of soil input to aquatic sediments, and present a lake sediment record extending back at least 8,000 years. We also show results from a study of soils from different climatic regimes and from pasture subjected to different fertilization procedures that better constrains their specific bacterial origin.

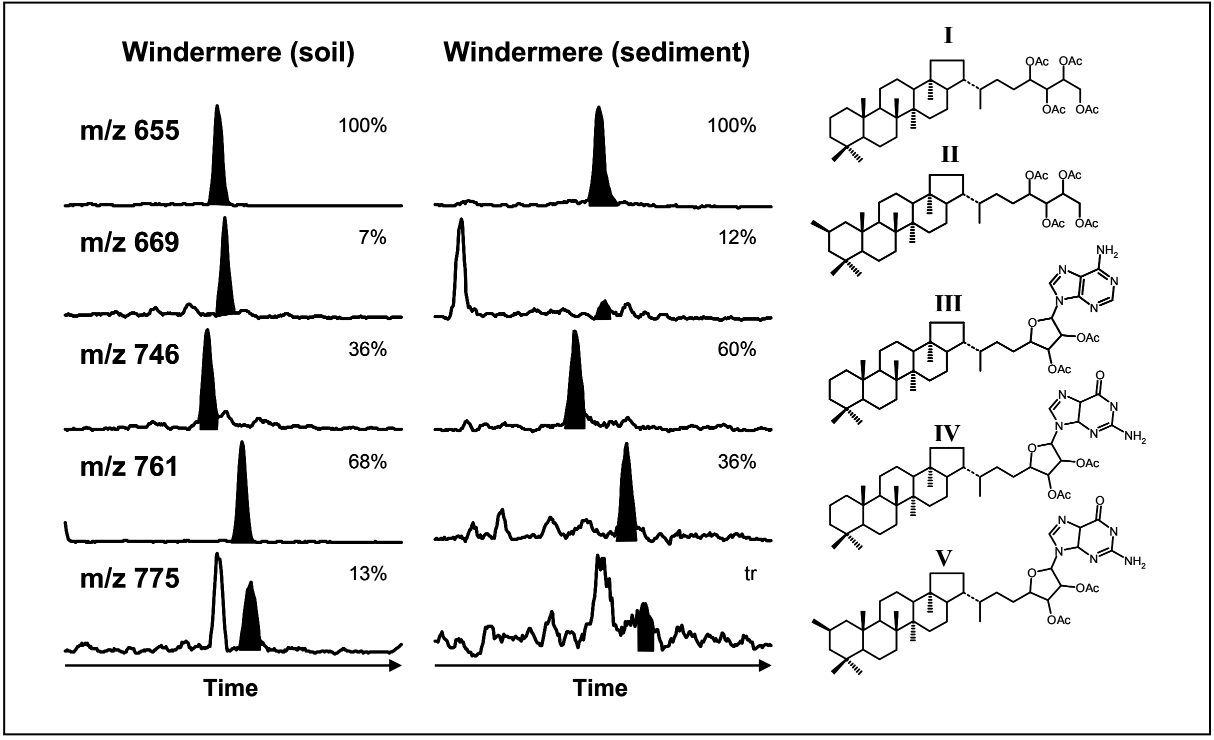


Fig.1. Partial APCI mass chromatograms and structures of BHPs present in soil from Lake Windermere catchment and sediment from a water depth of 15 m. (Ac=COCH$_3$; tr= trace)

References

Crossman, Z.M., Mc Namara, N., Parekh, N., Ineson, P., Evershed, R.P., 2001. A new method for identifying the origins of simple and complex hopanoids in sedimentary materials using stable isotope labelling with $^{13}CH_4$ and compound specific stable isotope analyses. Organic Geochemistry 32, 359-364.

Neunlist, S., Rohmer, M., 1985. A novel hopanoid, 30-(5'-adenosyl)hopane, from the purple non-sulphur bacterium Rhodopseudomonas acidophila, with possible DNA interactions. Biochemical Journal 228, 769 - 771.

Ries-Kautt, M., Albrecht, P., 1989. Hopane-derived triterpenoids in soils. Chemical Geology 76, 143-151.

Talbot, H.M., Squier, A.H., Keely, B.J., Farrimond, P., 2003a. Atmospheric pressure chemical ionisation reversed-phase liquid chromatography/ion trap mass spectrometry of intact bacteriohopanepolyols. Rapid Communications in Mass Spectrometry 17, 728-737.

Talbot, H.M., Summons, R., Jahnke, L., Farrimond, P., 2003b. Characteristic fragmentation of bacteriohopanepolyols during atmospheric pressure chemical ionisation liquid chromatography/ion trap mass spectrometry. Rapid Communications in Mass Spectrometry 17, 2788-2796.

OP4-3: Integrated hydrocarbon system analyis in the Niger delta

H. Ganz[1], S. Obilaja[1], K. Ladipo[1], C. Otoghile[1], U. Aneke[2], C. Anowai[3],
J. Ejedawe[3], B. Lehner[3]

1) Shell Petroleum Development Company of Nigeria Ltd., Port Harcourt, Nigeria
(e-mail: Herwig.Ganz@shell.com)
2) Shell International E&P, Houston, USA
3) Shell International E&P B.V, Rijswijk, The Netherlands

Shell's oil and gas reserves in the onshore of the Niger Delta are distributed over more than 4000 reservoirs. Although some areas have been classified as predominantly oil or gas prone, occurrence of oil and gas reservoirs often seems random and unpredictable. Particularly the occurrence of high CGR (condensate-gas-ratio) gas is very poorly understood since historically they were not considered valuable commodities. However, with the rapidly developing Nigerian gas market and ambitious plans to ever increasing LNG (liquefied natural gas) capacity with strong and very specific gas quality criteria, hydrocarbon type/phase and quality is one of the major risks and uncertainties of most exploration and development targets in Nigeria. Thus, understanding and predicting hydrocarbon type and distribution and particularly CGR are of prime economic importance. The following processes are most critical to understand oil and gas distribution in the Niger Delta:

1. The hydrocarbon system
2. Primary processes that control CGR and GOR variations
3. Secondary processes that control biodegradation and occurrence of biogenic gas
4. Migration mechanisms and other transformation processes

Compared to other petroleum provinces with well-defined source rock and reservoir horizons such as the North Sea Kimmeridge Clay/Fulmar Sand system, the hydrocarbon system in the Niger Delta is much more complicated due to:

- the presence of numerous reservoir seal pairs,
- thousands of feet of potential source rock intervals of Miocene to Lower Cretaceous age well below the main reservoir sands,
- a complicated dynamic filling and spilling history and
- associated transformation processes.

Although the presence of Pre-Miocene source rocks in the Niger Delta is undisputed, 3D charge modelling clearly indicates that timing of charge relative to availability of reservoirs and traps does not favour significant preservation and trapping of hydrocarbons from Pre-Miocene source rocks in most onshore areas. Wide spread occurrence of over-pressure at greater depth in the Niger Delta also suggests very good sealing potential of the deep shale sections, actively preventing the older source rocks expelling significant amounts of hydrocarbons into the main hydrocarbon system.

Conventional geochemical tools such as maturity parameters in the light, medium and heavy fraction of oils, asphaltene kinetics etc. seem to be almost invariable and do not show for instance any correlation with API gravity, reservoir depth or modelled source rock maturity. This is due to the complicated filling and spilling history of the fields, which favoured extensive mixing and the formation of hybrid oils and equilibration of most geochemical parameters. Due to the poor control on the total thickness and quality of source rocks in prospect locations (the Top Marine Shale is usually very deep, not penetrated in most wells and the base is not visible on seismic) deterministic 3D charge modelling in the Niger Delta is facing huge uncertainties, which is also severed by the inability to use geochemical maturity parameters for calibration purposes. However, while hydrocarbon type, amount and quality of hydrocarbons expelled are difficult to model deterministically in the Niger Delta, source rock maturity at the Top Marine Shale level (Akata Shale) from 3D maturity modeling correlates very well with hydrocarbon distribution on a field scale. In order to understand hydrocarbon distribution on a reservoir scale additional tools such as geochemical fingerprinting are applied. Fingerprints as generated by Shell's exclusive Multi Dimensional Gas Chromatography (MDGC), do not suffer from homogenization defects to the same degree as most other geochemical parameters. Very subtle but consistent differences between various aromatic components in the C8-C10 range can not only be used to identify connectivity between reservoirs in the classical sense of 'reservoir' geochemistry, but also allow to distinguish oil families/fields belonging to the same hydrocarbon system/pressure cell. Together with newly developed parameters of the C7-fraction this not only enables to distinguish between the various elements of the hydrocarbon system within a field (biodegraded oils/biogenic gas, black oil, volatile oil and dry gas systems) but it is also possible to distinguish important transformation processes such as gas washing. Identification of gas washing is particularly important because it indicates access to a deep gas kitchen, which at intermediate maturity ranges causes the formation of volatile oils, or - at higher maturity – dry gas. The identification of volatile oil systems in a field and prospect is of paramount importance, because wet gases of high CGR's can only be found in volatile oil systems. Gases associated with low mature black oil systems or high mature dry gas systems do not yield high CGR's.

Biodegradation in the Niger Delta is understood to be controlled by 'open' and 'closed' system processes where the combined effect of percolating fresh water and nutrients in the sand-rich Continental clastics at relatively low reservoir temperatures (<60 ºC) causes most severe biodegradation and lowest API gravities/highest viscosities. If at reservoir temperatures between 60-80 ºC fresh water does not have access to the reservoirs, biogenic activity in these zones is reduced to closed system processes, where nutrient supply is very limited and biodegradation much reduced, and thus API gravities are usually somewhat higher compared to reservoirs, which had access to fresh water. If reservoir temperatures are higher than about 80ºC oils are usually fresh and not transformed by biodegradation. These empirical correlations can effectively be used to predict API gravity on a reservoir scale in the Niger Delta. It is also observed that a strong link exists between the onset-depth of biodegradation within a field and the occurrence of isotopically light biogenic gas. Fluid Inclusion Screening data show wide spread occurrence of for instance CO_2 and Acetic Acid within the same shallow sequences where biodegraded oils and biogenic gas are encountered. It is believed that a genetic relationship between the two processes exists, where products of biodegradation processes such as CO_2 are transformed by methanogenic bacteria to generate 'secondary biogenic gas'.

OP4-4: Molecular fossils and the rarity of eukaryotes in mid-Proterozoic seas

J.J. Brocks

Research School of Earth Sciences, The Australian National University, Canberra, Australia

Large microfossils of possible eukaryotic origin occur in sedimentary rocks as old as 2 billion years (Ga). However, the oldest fossil remains with signs of a cytoskeletal architecture, one of the defining characteristics of the eukaryotic cell, were collected from the ~1.5 Ga Roper Group in the McArthur Basin of northern Australia (JAVAUX et al., 2001). The most enigmatic characteristic of the Roper fossils, however, is their ecological distribution which is different from most younger ecosystems. The number of eukaryotic species is highest in agitated shoreline facies, but diversity as well as abundance declines rapidly towards the inner and outer shelf. Roper sediments deposited below deep basinal waters only rarely yielded one simple and small species (JAVAUX et al., 2001). Javaux and co-authors suggest that this unusual ecological pattern reflects an environmental chemical onshore-offshore gradient and is not preservational artifact.

To test this hypothesis, and to assess the occurrence and abundance of eukaryotes in Proterozoic basins, we analyzed steroids in deep water sediments of the McArthur Basin. As biomarkers of the Roper Group are poorly preserved, we chose exceptionally well preserved bitumens from the 1.64 Ga Barney Creek Formation as the first sample set. The samples were collected from 12 drill holes along the north-south axis of the basin and analyzed by GC-MS-MS. In extreme contrast to most Neoproterozoic (1.0-0.54 Ga) and Phanerozoic (<0.54 Ga) successions, and despite the excellent thermal preservation of the host-rocks, C_{26} to C_{30} steranes, biomarkers indicative of eukaryotes, were close to, or below, the detection limit of 0.1 ppm (1 ppm = 1 ng/mg bitumen). In some thermally well preserved samples, individual steranes were more than 1000 times less abundant than C_{30} $\alpha\beta$-hopane. In contrast, triaromatic steroids were commonly present at levels of 60 to 130 ppm. However, their distribution is highly unusual (Fig. 1B). The triaromatic steroids entirely lack side-chain alkylation and are predominantly methylated at C-4 (> 90%), a pattern suggesting a bacterial source. A plausible biological source of the dominant C-4 methylated steroids is Type I methanotrophic bacteria (BIRD et al., 1971; VOLKMAN, 2003) that, along with abundant 3β-methylhopanoids, offer support for the presence of these organisms in the Barney Creek Formation. The detected low levels of aromatic steroids lacking methylation at C-4 (<10%) have no distinct source and might be derived from bacteria or eukaryotes (BROCKS and SUMMONS, 2004). The scarcity of diagnostic eukaryotic steroids in the analyzed sample range, despite the abundance of steroids with a typical bacterial distribution, is a phenomenon that has never been observed before in any sedimentary sequence of any age. It might reflect a strongly restricted activity of eukaryotic algae in the deep water environment of the Barney Creek Formation.

In extreme contrast to most younger marine environments, the biomarker abundances suggest that eukaryotic organisms did not play a significant role in the offshore environment of the McArthur Group during deposition of the Barney Creek Formation. The scarcity of diagnostic eukaryotic steroids might be analogous to the rarity of eukaryotic body fossils in basinal facies of the superjacent Roper Group and suggests that the unusual microfossil distribution indeed might reflect ecological reality and is not simply preservational artifact.

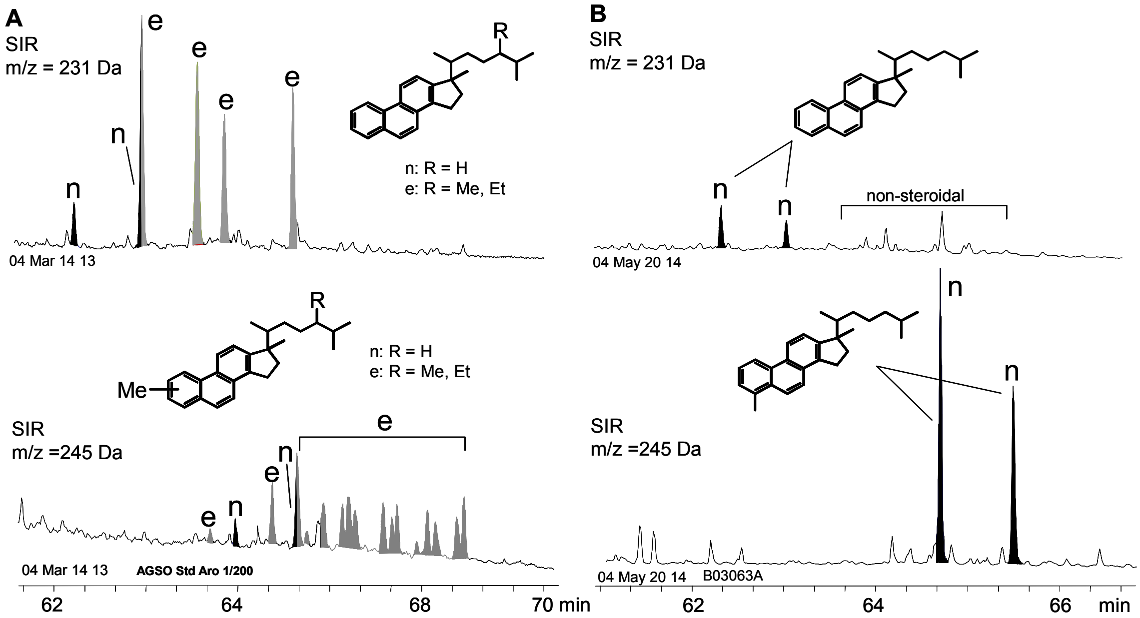


Fig.1. **(A)** Typical distribution of triaromatic steroids (TA) in Phanerozoic bitumens (AGSO Standard) and **(B)** in a representative sample of the Barney Creek Formation. Unmarked signals are non-steroidal. e = diagnostic eukaryotic TA with alkylation at C-24, n = TA without eukaryotic side chain alkylation.

References

Bird C. W., Lynch J. M., Pirt F. J., Reid W. W., Brooks C. J. W., and Middleditch B. S. (1971) Steroids and squalene in *Methylococcus capsulatus* grown on methane. *Nature* **230**, 473-474.

Brocks J. J. and Summons R. E. (2004) Sedimentary hydrocarbons, biomarkers for early life. In *Treatise on Geochemistry*, Vol. 8 - Biogeochemistry (ed. H. D. Holland and K. K. Turekian), pp. 63-115. Elsevier.

Javaux E., Knoll A. H., and Walter M. R. (2001) Morphological and ecological complexity in early eukaryotic ecosystems. *Nature* **412**, 66-69.

Volkman J. K. (2003) Sterols in microorganisms. *Applied Microbiology and Biotechnology* **60**, 496-506.

OP5-1: Compound-specific isotope analysis of hydroxyarchaeols at the Lost City hydrothermal field and in cultured methanogenic Archaea

A.S. Bradley[1], H. Grover[2], S. Sylva[3], K. Londry[2], J.M. Hayes[3], R.E. Summons[1]

1) Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology,
77 Massachusetts Ave, Cambridge, MA 02139 USA
2) Department of Microbiology, University of Manitoba, Winnipeg, Manitoba, R3T 2N2 CANADA
3) Department of Geology & Geophysics, Woods Hole Oceanographic Institution, Woods Hole, MA 02543 USA

The Lost City Hydrothermal Field (LCHF; Kelley et al., 2001) is 15 km off the axis of the Mid-Atlantic Ridge. The composition of the fluids is shaped by exothermic serpentinization reactions which produce abundant H_2 and OH^-. At the Lost City vents, temperatures range up to 90˚C, the pH is 9-11, and concentrations of H_2 range up to 15 millimolar (Proskurowski et al., 2003). Production of methane is strongly favored. Phylogenetic data confirm the presence of a single group of methanogens related to the *Methanosarcinales* (Schrenk et al., 2004).

Active and inactive carbonate vent structures contain up to 0.6% organic carbon including diverse lipids. Values of $\delta^{13}C$ for total organic carbon (TOC) range from -18.7‰ vs. VPDB at the active, high-temperature vent known as “The Beehive” (90˚C) to -3.1‰ at Marker 7 (active, 70˚C). Samples with relatively high levels of ^{13}C also contained high amounts of isoprenoidal and nonisoprenoidal glycerol diethers. Samples more depleted in ^{13}C lacked or contained low amounts of these diethers.

The correlation between high ^{13}C and abundant glycerol diethers is supported by compound-specific isotopic analyses. Archaeal and bacterial diethers are enriched in ^{13}C relative to photosynthetically derived marine carbon. The biomarkers *sn*-2 hydroxyarchaeol, *sn*-3 hydroxyarchaeol, and dihydroxyarchaeol – considered diagnostic for methane-cycling Archaea – had δ values ranging from -8.5 to +4.8‰. Diethers with non-isoprenoidal alkyl chains are also present, are of presumed bacterial origin, and may indicated the presence of sulfate-reducing bacteria. Values of δ for these compounds range from -7.3 to +1.0‰. At the Beehive vent, diether lipids are absent and the TOC is depleted in ^{13}C.

The distribution of lipid diethers at many of Lost City’s active vents is remarkably similar to that at marine, cold-seep environments at which concentrations of H_2 are low and methane is oxidized anaerobically. However, the microbial consortia at such seeps typically produce lipids that are extremely depleted in ^{13}C relative to photosynthetically derived marine carbon. To explain the dramatically different isotopic compositions at Lost City, we propose that the millimolar concentrations of H_2 allow the simultaneous growth of carbon-fixing autotrophic methanogens and sulfate-reducing bacteria and that, due both to the high pH and to the H_2/DIC ratio, carbon is the limiting substrate.

Ongoing parallel laboratory studies on cultures of *Methanosarcina barkeri* are consistent with earlier reports (House et al., 2003) that, under high partial pressures of H_2, fractionation of ^{13}C between CO_2 and *Methanosarcina* biomass is approximately 20‰. Hydroxyarchaeol is more strongly depleted, by approximately 35‰ relative to source CO_2. The contrast with observations at Lost City suggests that isotopic fractionations imposed by autotrophic Archaea can vary at least as strongly as those imposed by algae and other photoautotrophs.

References

House, C.H., Schopf, J.W., Stetter, K. O. (2003) Carbon isotopic fractionation by Archaeans and other thermophilic prokaryotes. Organic Geochemistry **34**: 345-356.

Kelley D. S., Karson J. A., Blackman D. K., Fruh-Green G. L., Butterfield D. A., Lilley M. D., Olson E. J., Schrenk M. O., Roe K. K., Lebon G. T., and Rivizzigno P. (2001) An off-axis hydrothermal vent field near the Mid-Atlantic Ridge at 30 degrees N. *Nature* **412**(6843), 145-149.

Proskurowski, G., Lilley, M.D., Olsen, E.J., and Larson, B. (2003) Preliminary geochemistry of volatile species from active vents at the Lost City Hydrothermal Field. Eos, Trans. American Geophysical Union 84(46): Fall Meeting Suppl. Abstract #B12A-0770.

Shrenk, M.O., Kelley, D.S., Bolton, S.A., and Baross, J.A. (2004) Low archaeal diversity linked to sub-seafloor geochemical processes at the Lost City Hydrothermal Field, Mid-Atlantic Ridge. Environmental Microbiology 6(10) 1086-95.

House, C.H., Schopf, J.W., Stetter, K. O. (2003) Carbon isotopic fractionation by Archaeans and other thermophilic prokaryotes. Organic Geochemistry **34**: 345-356.

OP5-2: Recognising oil mixing using maturity parameters from different molecular weight fractions of oils

S.C. George, H. Volk, M. Ahmed

CSIRO Petroleum, PO Box 136, North Ryde, NSW 1670, Australia (e-mail: Simon.George@csiro.au)

Commonly-observed phenomena in petroleum geochemistry are inconsistent thermal maturity parameters for oils, and to a lesser extent for source rocks. Commonly this is ascribed to source influences on various parameters. For example, it is well known that the methylphenanthrene index is affected by organic matter type. Similarly, biomarkers ratios such as Ts/Tm, diahopanes/hopanes and diasteranes/steranes are influenced by both source and thermal maturity. Different levels of biodegradation can also affect some maturity parameters (e.g. isoprenoids/*n*-alkanes and the heptane value). A third factor that commonly contributes to apparent anomalies is that maturity ratios have variable sensitivity ranges. Many but not all biomarker parameters equilibrate within the oil window (e.g. van Grass, 1990), and some aromatic ratios do likewise (e.g. some trimethylnaphthalene and tetramethylnaphthalene ratios; George and Ahmed, 2002). Other aromatic ratios may be relatively insensitive in the main part of the oil window, but may respond more rapidly at greater levels of thermal stress (e.g. alkylbiphenyl ratios; George and Ahmed, 2002). Although some maturity parameters respond remarkably evenly in certain circumstances, these variable sensitivity ranges are not surprising given the wide range of chemical controls on the relative abundance of the constituents of each ratio. There is no known maturity parameter that is not at all influenced by source or biodegradation, and which is sensitive from the pre-oil window to the gas window.

Instead of searching for a universal thermal maturity parameter, it is more useful to consider what mixing information about oils is contained in apparently inconsistent parameters. The figure shows the molecular weight ranges of commonly applied maturity parameters for a typical crude oil. Oils are commonly mixtures or “incrementers” of oil charge over a long period of time, minus possible partial or complete losses from the trap, and perhaps overprinted by biodegradation. Therefore it is not surprising to find that maturity parameters calculated from different molecular weight ranges can indicate differing maturities. For example, crude and fluid inclusion oils from the Laminaria High (Timor Sea) have peak oil window maturities based on C_5-C_{11} parameters, but parameters based on trimethylnaphthalenes (C_{13}), higher molecular weight aromatic hydrocarbons and aliphatic biomarkers indicate early oil window maturities (George *et al.*, 2004). This is due to early mixing of a low maturity oil from the Elang-Plover depositional system (Jurassic) with a high maturity oil, perhaps with some migration contamination. Similar mixed signatures have been noted in crude oils from Barrow Island (Carnarvon Basin) and from fluid inclusion oils in the Proterozoic Roper Superbasin in northern Australia. Use of a large suite of maturity markers covering a wide molecular weight range is advocated to understand these influences.

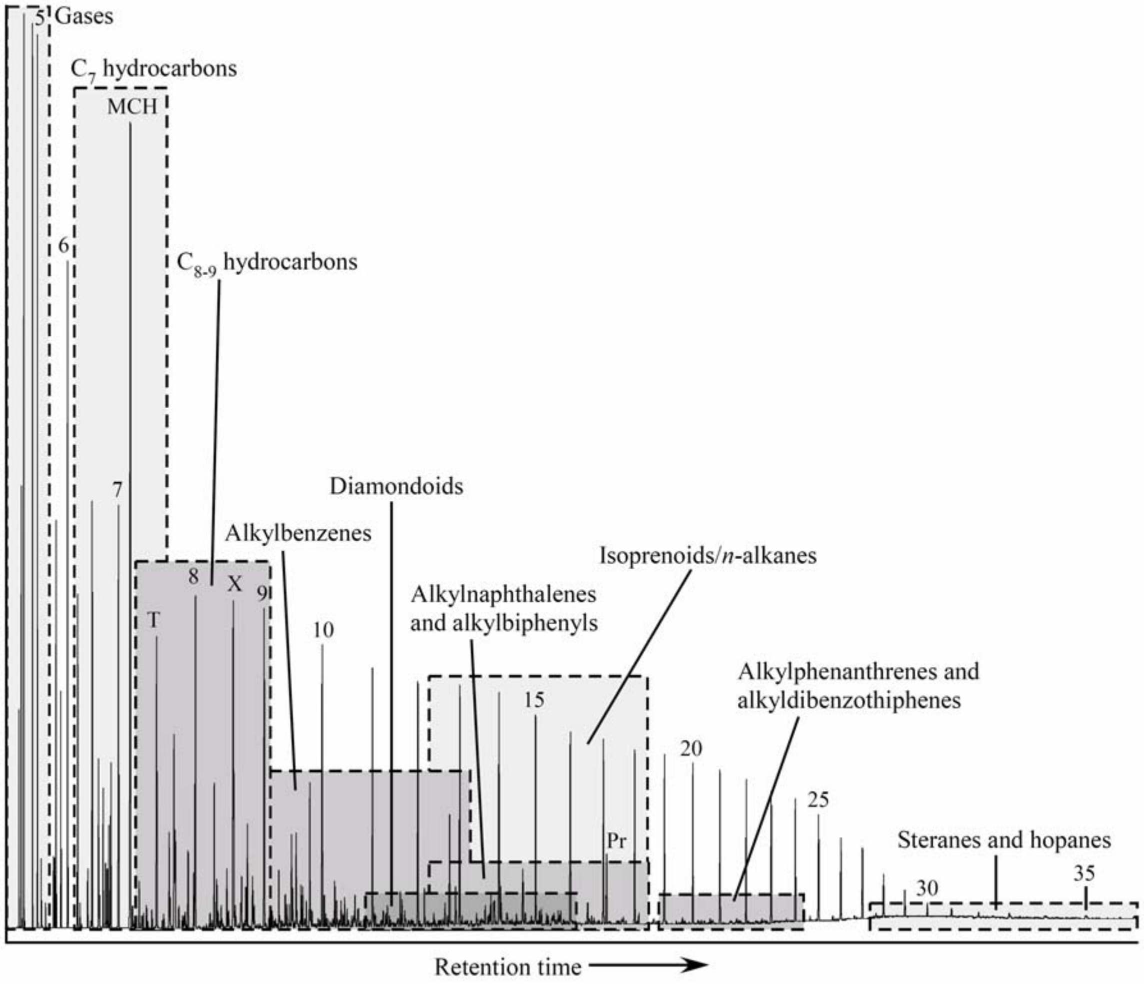


Fig.1. Whole oil gas chromatogram of Blackback-2 MDT oil (Gippsland Basin, Australia). Numbered peaks are *n*-alkanes, MCH = methylcyclohexane, T = toluene, X = *m*-+*p*-xylene, Pr = pristane. Shaded panels show the molecular weight distribution of different classes of thermal maturity ratios.

References

George, S. C. and Ahmed, M. (2002) Use of aromatic compound distributions to evaluate organic maturity of the Proterozoic middle Velkerri Formation, McArthur Basin, Australia. In *The Sedimentary Basins of Western Australia 3*, eds Keep, M. and Moss, S. J., pp. 253-270. Proceedings of the Petroleum Exploration Society of Australia Symposium, Perth, WA, 2002.

George, S. C., Ruble, T. E., Volk, H., Lisk, M., Brincat, M. P., Dutkiewicz, A. and Ahmed, M. (2004) Comparing the geochemical composition of fluid inclusion and crude oils from wells on the Laminaria High, Timor Sea. In: *Timor Sea Petroleum Geoscience, Proceedings Of The Timor Sea Symposium, Darwin, Northern Territory, 19-20 June 2003* (eds G. K. Ellis, P. W. Baillie and T. J. Munson), Northern Territory Geological Survey, Special Publication 1, pp. 203-230.

van Graas, G. W. (1990) Biomarker maturity parameters for high maturities: Calibration of the working range up to the oil/condensate threshold. *Organic Geochemistry* **16**, 1025-1032.

OP5-3: The methane cycle in peat bogs revisited: methanotrophic symbionts provide carbon for photosynthesis

J.S. Sinninghe-Damsté[1,2], A.A. Raghoebarsing[3], A.J.P. Smolders[3], M.C. Schmid[3], W.I.C. Rijpstra[1], M. Wolters-Arts[3], J. Derksen[3], M.S.M. Jetten[3], S. Schouten[3], L.P.M. Lamers[3], J.G.M. Roelofs[3], H.J.M. Op den Camp[3], M. Strous[3]

1) Royal Netherlands Institute for Sea Research (NIOZ), PO Box 59, 1797 AB Den Burg – Texel, the Netherlands (e-mail: damste@nioz.nl)
2) University of Utrecht, the Netherlands, [3]University of Nijmegen, the Netherlands

Wetlands are the largest natural source for atmospheric methane, the second most important greenhouse gas, and the fluxes to the atmosphere depend strongly on climate conditions. However, by far the largest part of the methane formed in these ecosystems is recycled and does not reach the atmosphere. The biogeochemical controls on the efficient oxidation of methane are still poorly understood.

We investigated the methane oxidizing activity of submerged *Spaghnum cuspidatum* from bog pools at different field locations in the Mariapeel bog (the Netherlands) and compared it to the activity of *S. magellanicum* and *S. papillosum* growing in hummocks. The potential methane oxidizing activity was substantially higher in the submerged mosses. In control experiments with bog water without *Sphagnum*, methane was not oxidized, indicating that the methanotrophic bacteria were mainly present on or in the living *Sphagnum* tissue. The identity and location of these methanotrophs was determined with molecular biology methods. Total genomic DNA from washed *Sphagnum* plants was isolated and bacterial 16S ribosomal RNA genes were amplified, cloned, sequenced and analyzed phylogenetically. One of the 16S rRNA gene sequences of the clone library was affiliated to a cluster of type II methanotrophs that contained acidophilic methanotrophs isolated from *Sphagnum* bogs. FISH probes developed to specifically detect these bacteria revealed their presence in the hyaline cells of the plant and on stem leaves.

The predominance of type II methanotrophs was further substantiated by the presence of bishomohopanoic acid, after periodic acid treatment of the lipid extract of *Sphagnum* plants. This compound was previously shown to be formed after periodic acid treatment from the C_{35} hopanetetrol derivatives, membrane rigidifiers produced by methanotropic bacteria. The natural ^{13}C-contents of this compound ($\delta^{13}C$= -40‰) was substantially depleted relative to *Sphagnum* cell material and enriched compared to that of methane ($\delta^{13}C$= -56‰), in accordance with its origin from type II methanotropic bacteria. Using this methanotrophic biomarker it was determined whether the methanotrophs associated with *Sphagnum* were actively growing. After incubating *Sphagnum* with ^{13}C-labelled methane for 5 days, isotopic analysis showed that $^{13}CH_4$ was incorporated into this lipid in substantial amounts; nearly 50% of the lipid was biosynthesized from the labelled methane, indicating that the methanotrophic population had doubled over the course of the experiment. The observed tight association of methanotrophs with *S. cuspidatum* suggests the efficient recycling of methane derived from decaying plants into living mosses according to the following set of equations:

CH_4 oxidation:	$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$	(1)
CO_2 fixation:	$2\,CO_2 + 2\,H_2O \rightarrow 2\,CH_2O + 2\,O_2$	(2)
balance:	$CH_4 + CO_2 \rightarrow 2\,CH_2O$	(3)

To provide experimental evidence for this scenario, the potential contribution of methane to carbon fixation by *S. cuspidatum* was investigated by incubation with $^{13}CH_4$ in the presence of unlabeled CO_2. As a control experiment, only $^{13}CO_2$ was supplied. During 5 days, incorporation of the label by *S. cuspidatum* was determined via the ^{13}C incorporation into sitosterol, a *Sphagnum*-derived sterol (Fig. 1). Methane was assimilated into the sitosterol pool at a rate of 0.20±0.03 µg C/g dry weight/day, compared to 1.4±0.1 µg C/g dry weight/day for CO_2. Thus, in the presence of CO_2, at near *in situ* concentrations, the capacity of methane incorporation by *S. cuspidatum* was ~15% of the CO_2 assimilation capacity.

Our results show that methane is a significant and as yet overlooked supplement to the carbon intake of submerged *S. cuspidatum* in peat bogs. Peat bogs in the Northern hemisphere store up to one third of the carbon sequestered in soils globally. This is surprising considering that the primary production is limited by the nutrient delivery through rain water and the limited delivery of CO_2 to the acidic waters of these ecosystems. The efficient recycling of peat decomposition products (such as methane) as demonstrated here may mechanistically explain the paradox of peatlands as ecosystems with low primary productivity combined with high carbon burial.

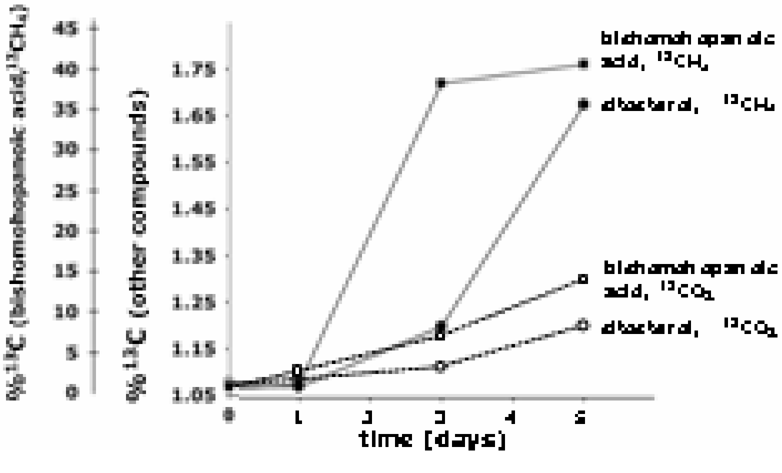


Fig.1. Incorporation of ^{13}C label in biomarkers for Sphagnum (circles) and methanotrophic bacteria (squares). Closed circles/solid lines and open symbols/dashed lines show the results for labeled methane in the presence of unlabeled/ labeled CO_2, respectively.

OP5-4: Predicting oil and gas compositional yields via chemical structure-chemical yield modeling (CS-CYM)

H. Freund[1], C.C. Walters[1], S.R. Kelemen[1], M. Siskin[1], D.J. Curry[2], Y. Xiao[3], W.N. Olmstead[1], M.L. Gorbaty[1], A.E. Bence[3]

1) ExxonMobil Research & Engineering Co., 1545 Route 22 East, Annandale, NJ, 08801-0998
(e-mail: howard freund@exxonomobil.com)
2) ExxonMobil Exploration Co., 233 Benmar. Houston TX, 77060-2501
3) ExxonMobil Upstream Research Co., PO Box 2189, Houston, TX 77252-2189

The ability to accurately predict the thermal conversion of complex carbonaceous materials under a wide range of heating rates and temperatures is of value to both exploration and refining petroleum operations. Modeling the thermal cracking of kerogens and coals under basinal heating conditions improves the pre-drill prediction of oil and gas yields and quality, ultimately lowering exploration risk. Modeling the chemical structure and reactivity of asphaltenes from petroleum residua enables the prediction of coke formation and properties in refinery processes, lowering operating cost. Previous compositional yield models based on laboratory yield measurements have been developed for specific materials, such as isolated coals and kerogens, but extrapolation to predict oil and gas generation during geologic burial is problematic. Furthermore, models based on a few reference carbonaceous materials may not simulate varying compositions of kerogen and residua seen in nature.

We have developed a method to calculate from first principles the amounts and composition of products resulting from the thermal decomposition of a solid complex carbonaceous material [1]. This procedure provides a means of using laboratory measurements of complex carbonaceous solids to construct a representative model of its chemical structure (CS) that is then coupled with elementary reaction pathways to predict the chemical yield (CY) upon thermal decomposition. Data from elemental analysis (CHSNO), solid state ^{13}C NMR, X-ray Photoelectron Spectroscopy (XPS), Sulfur XANES, and pyrolysis-GC are used to constrain the construction of core molecular structures that are representative of the complex carbonaceous material. These core structures are expanded stochastically to describe large macromolecules ($>10^4$ cores with $\sim10^6$ atoms) with bulk properties that match the experimental results. Gas, liquid and solid product yields, resulting from thermal decomposition, are calculated by identifying reactive functional groups within the CS stochastic ensemble and imposing a reaction network constrained by fundamental thermodynamics and kinetics. An expulsion model is coupled to calculate the chemical products in open systems. Product yields may then be predicted under a wide-range of time-temperature conditions used in rapid laboratory pyrolysis (open or closed systems), refinery processes, or slow geologic heating rates.

We have developed numerous CS-kerogen models for different organic matter types and levels of thermal maturity and have shown that the yields calculated by CS-CYM are consistent with laboratory and geologic observations. For example, open-system, rapid heating simulations accurately model all Rock-Eval parameters and the composition of the pyrolyzate products (Fig 1a). Similarly, the product yields and compositions of free and retained bitumen produced in hydrous pyrolysis experiments (close system) and by the CS-CYM are comparable (Fig 1b). The model is extremely robust and allows us to test numerous assumptions associated with kerogen structure, generation, and expulsion. Thermodynamic parameters needed to describe chemical fractionation during expulsion [2] may be derived from CS-models and calculated as a function thermal maturation.

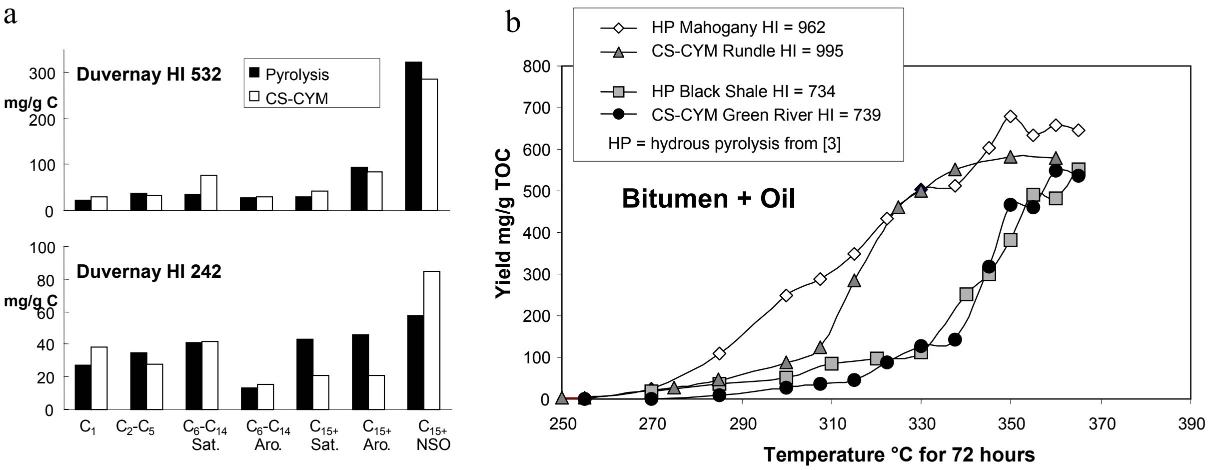


Fig.1. (1.a) Measured [3] and CS-CYM predicted yields in open-system pyrolysis (25°C/min) for two samples of kerogen isolated from Duvernay Fm. shale at different levels of thermal stress. (1b). Comparison of hydrous pyrolysis product (bitumen + free oil) yields (72 hr at varying temperatures) for two facies of Green River Shale [4] to CS-CYM product yields for Type I kerogen from Green River (Mahogany) and Rundle formations.

References

[1]Kelemen, S.R., Freund, H., Siskin, M., Curry, D.J., Xiao, Y., Olmstead, W.N., Gorbaty, M.L., Bence A.E., 2004. Chemical structural and compositional yields model for predicting hydrocarbon thermolysis products. US Patent Publication No, 2004/0019437 ExxonMobil Upstream Research Co., Houston TX (assignee), 21 claims, 10 p.

[2] Kelemen, S.R., Freund, H., Ertas, D. Walters, C.C., Kwiatek, L.M., Curry, D.J., Bence, A.E. (2005). Chemical Fractionation During Expulsion Explained by Selectivity Solubility, 22st International Meeting Organic Geochemistry, Seville, Spain.

[3]Vandenbroucke, M., Bence, A.C., Behar, F, Kelemen, S.K., Curry, D.J.., Xiao, Y., Leblond, C. 2003. Assessment of changes in kerogen structure and generated products upon geochemical burial by pyrolyis of a maturity series of Type II kerogen (Duvernay, Canada). 21st International Meeting Organic Geochemistry, Krakow, Poland.

[4]Ruble, T. E., Lewan, M.D., Philp, R.P., 2001. New insights on the Green River petroleum system in the Uinta basin from hydrous pyrolysis experiments. *AAPG Bulletin* **85**(8), 1333-1372.

OP6-1: Biodegradation of petroleum compounds by complex microbial communities: kinetics, community change, and metabolites

J. Köster, Th. Brinkhoff, N.M.D. Safi, J. Rullkötter

Institute of Chemistry and Biology of the Marine Environment (ICBM), Carl von Ossietzky University of Oldenburg, P.O. Box 2503, D-26111 Oldenburg, Germany (e-mail: juergen.koester@icbm.de)

Natural microbial communities are capable to degrade pollutants effectively. We studied the kinetics, community change, and metabolism of degradation under different levels of oxygen by a complex bacterial consortium present in surface sediments of Wadi Gaza (Palestine).

The fine-grained sediment was suspended in autoclaved sea water. Four selected petroleum compounds (*n*-octadecane, pristane, phenanthrene, and dibenzothiophene) were adsorbed on a hydrophobic clay mineral (benzyl trimethyl ammonium montmorillonite) and added simultaneously as pollutants (day 0, Fig. 1). Biodegradation started immediately when an oxygen level of 4-6 mg l^{-1} was established by aeration and stirring (day 8). Degradation of *n*-octadecane occurred at a high rate within one day (39 mg ml^{-1} d^{-1}). Ca. 20% of this compound was not available for degradation. Pristane disappeared slowly following an exponential decrease with a half-life period of 14 days. In the case of the aromatic compounds degradation accelerated until both compounds were completely removed (day 14). After the suspension was polluted a second time (day 21), the degradation of all four compounds followed first-order kinetics (exponential decrease in concentration), but with different half-life periods (Fig. 1). Now, the highest degradation rates were found for the aromatic compounds. In a parallel experiment under low oxygen concentrations (<1 mg l^{-1}) degradation followed the same kinetics but with lower rates and longer half-life periods. The observed kinetics can be explained by comparison with degradation models in terms of growth (aromatic compounds during first contamination) and non-growth conditions (rates depending on the concentration of the pollutant, e.g. all compounds during the second pollution).

Community changes and growth of certain bacteria was indicated by simultaneous increase of concentrations of bacterial fatty acids (e.g. *iso*-pentadecanoic acid) and disappearance of contaminants during the first contamination phase. The initial bacterial community of the Wadi Gaza sediment is complex comprising *Proteobacteria* (50%), *Bacteriodetes* (25%), *Cyanobacteria* (13%), *Clostridia* (4%), *Verrucomicrobia* (2%), and other unidentified bacteria (7%; see [2]). However, at the end of the experiment all prominent bacteria identified by molecular microbiological tools belonged to the group of *Bacteriodetes*. Their closest relatives in the database are mainly uncultivated *Bacteroidetes* from environmental samples. This provides circumstantial evidence that these heterotrophic bacteria are responsible for the observed biodegradation [1].

The metabolites identified in the suspensions indicate simultaneous degradation of the hydrocarbons following different known pathways (aromatic compounds via mono- and dioxygenase-initiated pathways; terminal, sub-terminal, and mid-chain oxidation of alkanes). Metabolites did not accumulate and were mostly found during the second exposure to pollutants.

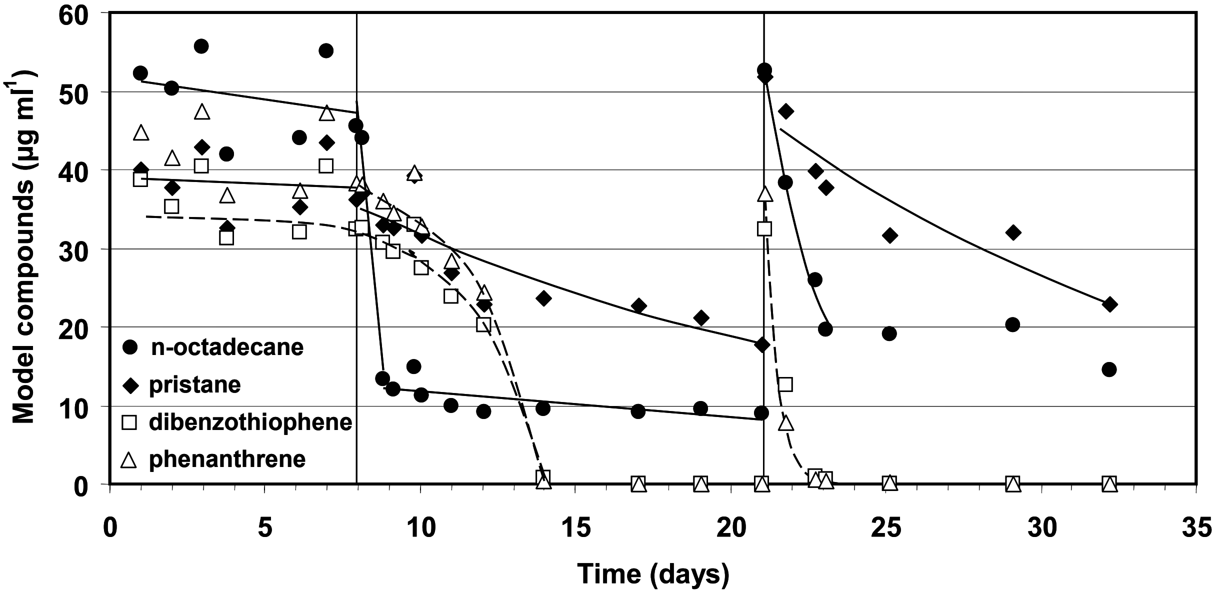


Fig.1. Degradation of petroleum model compounds and kinetics observed in an experiment with an aerated suspension of a microbial community from Wadi Gaza.

In similar experiments performed with intact microbial mats that developed from Wadi Gaza sediments the degradation followed first-order kinetics (non-growth conditions) already during a first contamination [2]. This demonstrates, that suspensions allow strong community changes and an enrichment of bacteria responsible for biodegradation. In contrast, microbial communities in mats are obviously stabilized by the mat structure with its sharp, diurnally fluctuating gradients of electron acceptors. Community changes may occur, but seem to be confined to the different compartments in the mat system.

References

[1] Abed, R.M.M., Köster, J., 2005. The direct role of aerobic heterotrophic bacteria associated with cyanobacteria in the degradation of oil components. International Biodeterioration & Biodegradation 55, 29-37.

[2] Safi, N.M.D., 2004. Environmental organic geochemistry of sediments from Wadi Gaza and investigation of bioremediation of petroleum derivatives and herbizides by cyanobacterial mats under different experimental conditions. Doctoral Thesis, Carl von Ossietzky University Oldenburg.

OP6-2: Triterpenoids and their possible source organisms in methane fuelled anoxic environments

M. Blumenberg[1], M. Krüger[2], H.M. Talbot[3], R. Seifert[1], W. Michaelis[1]

1) Institute of Biogeochemistry and Marine Chemistry, University of Hamburg, Bundesstrasse 55, 20146 Hamburg, Germany (e-mail: michaelis@geowiss.uni-hamburg.de)
2) Bundesanstalt für Geowissenschaften und Rohstoffe, Stilleweg 5, 30655 Hannover, Germany
3) NRG, School of Civil Engineering and Geosciences, Devonshire Building, University of Newcastle upon Tyne NE1 7RU, UK

Triterpenoids of the hopane series are widely distributed in the biosphere and their diagenetic products are the oldest biomarkers described up to now, dating back to early Precambrian times. Biohopanoids occur in several higher plants, ferns, mosses, fungi, protozoans, and in about half of the isolated eubacteria analysed so far. Within the domain eubacteria they were nearly exclusively found in aerobes or facultative anaerobes although it is a common view that hopanoid biosynthesis requires no oxygen ([1]).

Recently it was reported that strictly anaerobic bacteria, belonging to the planctomycetes and *Geobacter* species, are capable to synthesize a variety of hopanoids ([2], [3]). However, several anoxic environments exhibit large amounts of structurally different extended and non-extended hopanoids for which both microbial groups as sources are unlikely, suggesting so far unknown microorganisms as additional hopanoid sources.

Hopanoid containing environments of specific interest are sites dominated by the process of the anaerobic oxidation of methane (AOM), such as microbial mats growing in methane rich anoxic waters of the Black Sea with yet unknown anaerobic bacteria as possible hopanoid sources ([4]). These mats are unique for studies of anaerobic microbial processes, populations, and their lipid biomarkers because of a lack of influences from overlying oxic processes. High amounts of extended and non-extended triterpenoids were found and partly identified at this and other AOM-environments. For instance, ^{13}C-depleted tetrahymanol is often present at AOM-sites and is suggested to derive from ciliated protozoans adopted to anaerobic conditions ([5]). These anaerobic eukaryotes host endosymbiotic methanogenic Archaea or ectosymbiotic sulphate reducing bacteria (SRB) and are, like their aerobic relatives, capable of biosynthesising tetrahymanol. However, other hopanoids (e.g. diploptene, diplopterol, and bacteriohopanepolyols) are also present to a large content at sites of AOM, and their sources are still obscure.

In the line of our previous work on methane fuelled microbial mats, we show here for the first time that specific sulphate reducing bacteria synthesize extended and non-extended hopanoids under strictly anoxic conditions. These hopanoid producing bacteria were isolated from a Black Sea microbial mat and belong to the genus *Desulfovibrio*, whereas others, such as members of the *Desulfobacter* and *Desulfobacterium* lack these components. The SRB were cultivated with lactate and CO_2 as sole carbon sources and contain large amounts of several common (diploptene, diplopterol, bacteriohopanetetrol) and uncommon bacteriohopanepolyols. Moreover, ^{13}C enrichments of isoprenoids (e.g. diplopterol) compared to *n*-alkyl lipids suggest the new so-called non-mevalonate pathway ([6], [7]) being responsible for the biosynthesis of triterpenoids in these SRB.

Members of the genus *Desulfovibrio* are widely distributed in marine and freshwater environments. Our results show that sulphate reducing bacteria now have to be taken into account while interpreting the presence of hopanoids in recent and fossil aquatic environments.

References

[1] Ourisson, G., Rohmer, M., 1992. Hopanoids. 2. Biohopanoids: a novel class of bacterial lipids. Accounts of Chemical Research 25, 403-408.

[2] Sinninghe Damsté, J.S., Rijpstra, I.C., Schouten, S., Fuerst, J.A., Jetten, M.S.M., Strous, M., 2004. The occurrence of hopanoids in planctomycetes: implications for the sedimentary biomarker record. Organic Geochemistry 35, 561-566.

[3] Härtner, T., Straub, K.L., Kannenberg, E., 2005. Occurrence of hopanoid lipids in anaerobic *Geobacter* species. FEMS Microbiology. Letters 243, 59-64.

[4] Thiel, V., Blumenberg, M., Pape, T., Seifert, R., Michaelis, W., 2003. Unexpected occurrence of hopanoids at gas seeps in the Black Sea. Organic Geochemistry 34, 81-87.

[5] Embley, T.M., Finlay, B.J., Dyal, P.L., Hirt, R.P., Wilkinson, M., Williams, A.G., 1995. Multiple origins of anaerobic ciliates with hydrogenosomes within the radiation of aerobic ciliates. Proceedings of the Royal Society, London B, Biological Sciences 262, 87-93.

[6] Rohmer, M., Knani, M., Simonin, P., Sutter, B., Sahm, H., 1993. Isoprenoid biosynthesis in bacteria: a novel pathway for the early steps leading to isopentenyl diphosphate. Biochemical Journal 295, 517-524.

[7] Schouten, S., Klein Breteler, W.C.M., Blokker, P., Schogt, N., Rijpstra, I.C., Grice, K., Baas, M., Sinninghe Damsté, J.S., 1998. Biosynthetic effects on the stable carbon isotopic compositions of algal lipids: Implications for deciphering the carbon isotopic biomarker record. Geochimica et Cosmochimica Acta 62, 1397-1406.

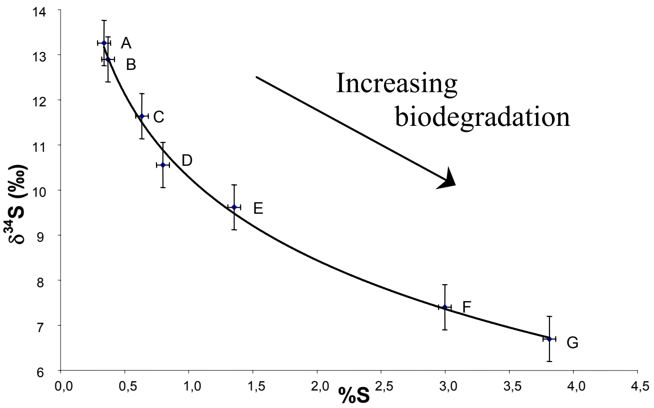
OP6-3: Role of anaerobic biodegradation on secondary incorporation of sulfur in the organic matter of petroleum reservoirs

S. Méhay[1], I. Kowalewski[2], A. Fafet[2], P. Adam[1], H. de Penteado[3], P. Albrecht[1]

1) Laboratoire de Géochimie Bioorganique ECPM, Université L. Pasteur, 25 rue Becquerel, 67087 Strasbourg, France (e-mail: mehays@chimie.u-strasbg.fr)
2) Institut Français du Pétrole, Division Géologie-Géochimie, 1 et 4 avenue de Bois Préau, 92852 Rueil Malmaison, France
3) Petrobras Research and Development Center (CENPES), Cidade Universitaria, Quadra 7, Ilha de Fundão, Rio de Janeiro, Brazil

Alteration phenomena observed in shallow reservoirs of many petroliferous basins modify the original properties of crude oil in place with major economic impact. Microbial degradation is one of the most important of these alteration processes. It occurs at any oil-water interface as soon as the conditions in the reservoir enable bacterial activity (e.g. T<90°C, salinity<100g/l) (Connan, 1984). It has been thought for decades to happen only in oxic conditions but recent works suggest that anaerobic degradation is a common process in biodegraded oil reservoirs (Aitken *et al.*, 2004). The influence of the latter and, in particular, the role of sulfate reducing bacteria in the process of degradation was investigated by molecular and isotopic (S-IRMS) analyses. Two different series (Alberta basin, Canada; Potiguar basin, Brazil) of genetically related oils and covering different levels of biodegradation were studied. Focus was also put on the analysis of organic sulfur compounds (abundance, structure, isotopic composition) in order to better understand their origin and their geochemical significance in biodegraded oils.

One of the most significant results of this study is the variation of the sulfur isotopic composition as a function of biodegradation extent in the series of crude oils from Alberta.



Thus, a decrease of the $^{34}S/^{32}S$ ratio, expressed in terms of $\delta^{34}S$ was observed as well as an increase of the organic sulfur content of the oil with increasing biodegradation, as can be evaluated from molecular parameters and, in particular, from the distribution of the saturated hydrocarbons (Peters and Moldowan, 1993).

Part of the increase of the sulfur content of the biodegraded oils is certainly due to a concentration effect related to the progressive degradation of saturated hydrocarbons.

However this cannot account for the variation of the sulfur isotopic composition. Hence, the enrichment in light sulfur isotope ^{32}S (reflected by the decrease of the $\delta^{34}S$ value) might be the result of an external contribution of sulfur to organic matter. Reduced sulfur species derived from anaerobic processes like bacterial reduction of dissolved sulfates in reservoir waters which may have a different isotopic composition from that of organically bound sulfur in the unaltered oils might be this external sulfur sources (Rueter *et al.*, 1994). As a consequence, the isotopic shift observed for the most altered oil might be explained by a secondary incorporation of reduced species resulting from bacterial sulfate reduction into the organic matter from reservoir.

Aromatics and polar fractions (resins and asphaltenes) of selected crude oils were also studied. The same trend was observed for both the sulfur content and the $\delta^{34}S$ with progress of biodegradation extent, especially in the case of resins and asphaltenes. Indeed, in the latter fractions, between the less biodegraded and the more biodegraded oils, the variation in sulfur content is almost twice higher while the enrichment in ^{32}S shows a more significant increase than in the aromatic fractions. In addition, contrary to the case of the complete oil samples, the variation of the sulfur content of macromolecular material can certainly not be explained by concentration effects. Hence, this favours the hypothesis of an external contribution of sulfur into the organic matter of biodegraded oils. Furthermore, this led us to envisage that a secondary incorporation of reduced sulfur species formed by bacterial sulfate reduction during anaerobic biodegradation would have occurred mainly on macromolecular structures which are dominating compounds in highly biodegraded oils. The investigation of the type of organic sulfur compounds (functionality) formed by such a process as well as the mechanism of the sulfurization process itself is underway.

References

Aitken C. M., Jones D. M., Larter S. R., *Nature* **431**, 291-294, 2004.

Connan J. in *Advances in Petroleum Geochemistry* (eds Brooks J. & Welte D. H.) Vol. **1**, 299-335, London, 1984.

Peters K. E. & Moldowan J. M., *The Biomarker Guide*, Prentice Hall, New York, 1993.

Rueter P., Rabus R., Wilkes H., Aeckersberg F., Rainey F. A., Jannash H. W., Widdel F., *Nature* **372**, 455-458, 1994.

OP6-4: Hydrogen, carbon and nitrogen isotopic fractionations during chlorophyll biosynthesis in C3 higher plants

Y. Chikaraishi, K. Matsumoto, N.O. Ogawa, H. Suga, H. Kitazato, N. Ohkouchi

Institute for Research on Earth Evolution, Japan Agency for Marine-Earth Science and Technology (JAMSTEC),
2-15 Natsushima-cho, Yokosuka, Kanagawa 237-0061, JAPAN (e-mail: ychikaraishi@jamstec.go.jp)

Biomolecules have large variations of stable isotopic compositions, particularly for hydrogen (Sessions et al., 1999; Chikaraishi et al., 2004), due to the isotopic fractionations associated with the biochemical processes involved in their biosynthetic pathways. Chlorophylls are useful biomarkers for molecular isotopic studies, since they will provide multiple isotope information (i.e. H, C and N) directly related to photoautotrophs. Although the isotopic fractionations of carbon and nitrogen associated with chlorophyll biosynthesis have been reported and discussed for various photoautotrophs (e.g. Bidigare et al., 1991; Sachs et al., 1999), that of hydrogen has never been reported. This study aims to determine hydrogen isotopic fractionations of chlorophylls *a* and *b* relative to ambient water in C3 higher plants as well as carbon and nitrogen isotopic fractionations relative to bulk carbon and nitrogen, respectively.

Fresh leaves from natural five C3 higher plants (*Benthamidia japonica, Prunus japonica, Acer carpinifolium, Acer argutum and Querus mongloica*) were examined in this study. Chlorophylls in these plants are depleted in D relative to ambient water by ~189‰ and enriched in ^{13}C relative to bulk tissue by ~1.6‰ (Fig. 1). Such isotopic depletions can be explained by the integration of isotopic fractionations during the biosyntheses of phytol side chain and chlorophyllide nucleus. The phytol in the chlorophylls is more depleted in both D (by ~308‰) and ^{13}C (by ~4.3‰), while chlorophyllide is less depleted in D (by ~44‰) and enriched in ^{13}C (by ~4.8‰). Such inhomogeneous distribution of isotopes in chlorophylls suggests that 1) the phytol reflects strong D- and ^{13}C-depletions due to the isotopic fractionations during methylerythritol phosphate (MEP) pathway followed by hydrogenation, and 2) the chlorophyllides reflect D- and ^{13}C-enrichments in tricarboxylic acid (TCA) cycle before C5 pathway. On the other hand, chlorophylls are slightly (~1.2‰) depleted in ^{15}N relative to the bulk tissue, indicating that net isotopic fractionation of nitrogen during chlorophyll biosynthesis is small compared with those of hydrogen and carbon.

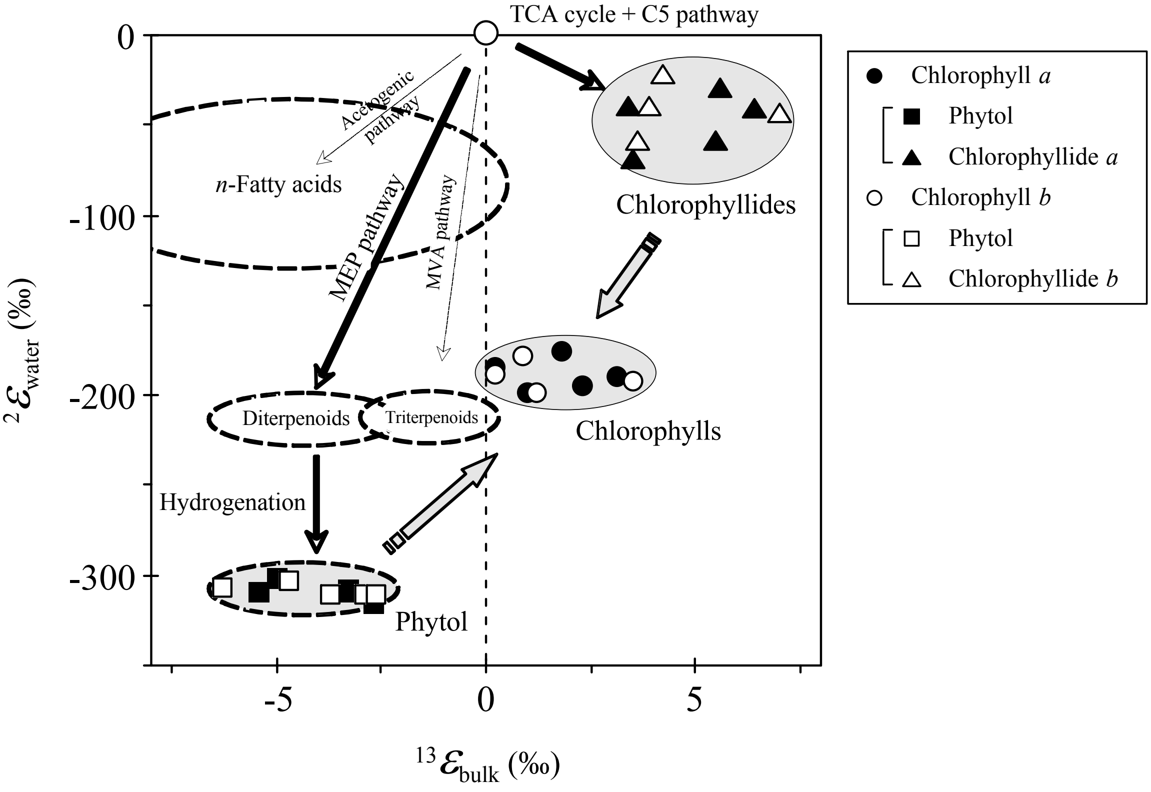


Fig.1. The $^{2}\varepsilon_{water}$ and $^{13}\varepsilon_{bulk}$ of chlorophylls (chl) isolated from five higher plants, and those of phytol (phy) and chlorophyllides (chlide) in the chlorophylls. Elliptic area with dashed line indicates isotopic fractionations associated with the biosyntheses of *n*-fatty acids, diterpenoids, teriterpenoids and phytol (Chikaraishi et al., 2004).

$$^{2}\varepsilon_{water} = 1000\ [(^{2}\delta_{chl,\ phy\ or\ chlide}+1000)/(^{2}\delta_{water}+1000)-1]$$
$$^{13}\varepsilon_{bulk} = 1000\ [(^{13}\delta_{chl,\ phy\ or\ chlide}+1000)/(^{13}\delta_{bulk}+1000)-1]$$

References

Bidigare, R.R., Kennicutt II, M.C., Keeny-Kennicutt, W.L., 1991. Isolation and Purification of chlorophylls *a* and *b* for the determination of stable carbon and nitrogen isotope compositions. Analytical Chemistry 63, 130-133.

Chikaraishi, Y., Naraoka, H., Poulson, S.R., 2004. Hydrogen and carbon isotopic fractionations of lipid biosynthesis among terrestrial (C3, C4 and CAM) and aquatic plants. Phytochemistry 65, 1369-1381.

Sachs, J., Pepeta, D.J., Goericke, R., 1999. Nitrogen and carbon isotopic ratios of chlorophyll from marine phytoplankton. Geochimica et Cosmochimica Acta 65, 1431-1441.

Sessions, A.L., Burgoyne, T.W., Schimmelman, A., 1999. Fractionation of hydrogen isotope in lipid biosynthesis. Organic Geochemistry 30, 1193-1200.

OP7-1: A revised global dataset of molecular and isotopic composition of natural gas hydrates and basic interpretations in the context of geological settings

A.V. Milkov

BP America, 501 Westlake Park Blvd, Houston, TX 77079, USA (e-mail: alexei.milkov@bp.com)

A global dataset of molecular and isotopic composition of gases released from 209 different specimens of natural gas hydrate has been compiled and investigated. 26 studied hydrate-bearing areas from 21 geographic regions are grouped into high gas flux (HGF) settings, low gas flux (LGF) settings, and hydrated gas accumulations (HGA). Methane (C_1) composes, on average, >99.9% of hydrocarbon gases in 19 of the studied 26 areas. Such a predominance of C_1 is more common in LGF settings than in HGF settings. CO_2 is present in most gas hydrates and often is the second most abundant component after C_1. The other non-hydrocarbon gases commonly are absent or present in trace amounts. Isotopic properties of hydrate-bound gases vary significantly (e.g., $\delta^{13}C$ of C_1 ranges from –74.7 to –39.6‰) and suggest that gases of both microbial and thermogenic origin form gas hydrates. Hydrate-bound gases are derived from autochthonous (located predominantly within the gas hydrate stability zone (GHSZ)) and allochthonous (located in deep sediments) sources. The occurrences and concentrations of gas hydrates in sediments are controlled not by the origin of gases, but rather by their sources, which in turn strongly depend on geological settings.

Hydrate-bound gases in localized HGF and HGA settings may have various origins. Although thermogenic gases prevail in some areas, microbial gases dominate in the others. Most gases are certainly allochthonous, and they are focused into the shallow GHSZ along faults, within mud volcanoes, permeable carrier beds and other geological features from underlying petroleum systems. The dominance of allochthonous gas source(s) results in commonly high concentrations of gas hydrate in pore space, which perhaps average around 5-15% in the GHSZ and locally reach up to 100%. The contribution of autochthonous gases in HGF areas is minor.

Exclusively or predominantly microbial gases (the "global average" $\delta^{13}C$ of C_1 is around –67‰) are trapped in gas hydrates in areally extensive LGF settings. Gas hydrates form from both autochthonous and allochthonous gases. The exact contribution of these two sources is often unknown and cannot be generalized for the global scale yet. However, it appears that a significant portion of microbial gases is generated well below the GHSZ thus limiting the supply of autochthonous gases. Allochthonous gases may predominate where locally concentrated gas hydrates (e.g., nodules and lenses) are observed. Sediments in the

LGF settings contain much smaller average concentration of gas hydrate (~2% of pores) than in HGF settings, even where some allochthonous gases migrate into the GHSZ.

A major implication of this study is that a successful prediction of resource and geohazard potential of gas hydrates is possible only if regional petroleum systems extending well below the GHSZ are properly evaluated. In addition to the diagnosis of origins and sources of hydrate-bound gases, molecular and isotopic data help to better identify hydrate-bearing intervals and provide valuable insights into the dynamics of hydrate-bearing sites.

OP7-2: Reassessment of the distributions and double bond locations of C_{37}-C_{40} unsaturated alkenones in open and coastal marine environments

J.F. Lopez, J.O. Grimalt

Institute of Chemical and Environmental Research (CSIC) 08034-Barcelona (e-mail: jgoqam@cid.csic.es)

Di-, tri- or tetraunsaturated linear methyl and ethyl C_{37}-C_{40} ketones, also known as alkenones, have been found in both recent and ancient sediments throughout the world oceans. These compounds are synthesized by few species of haptophyte algae (Marlowe et al., 1984; Volkman et al., 1980). Cultures of these species showed a linear change in the relative proportion of di- and tri-unsaturated alkenones with water temperature (Prahl and Wakeham, 1987; Brassell et al., 1986). This finding and the ubiquity of these compounds has led to the widespread use of the C_{37} homologues for the estimation of sea surface temperatures (SST) in climate change studies (Brassell et al., 1986; Cacho et al., 1999; Zhao et al., 1995) becoming, at present, a reference standard for the measurement of paleotemperatures in paleoceanography.

However, these compounds may also be found in other sedimentary environments, e.g. coastal areas. In these cases, the sedimentary alkenone distributions and unsaturation ratios provide unreliable paleotemperature estimates which is likely due to contributions from species different than those currently found in open marine environments.

Insight into the origin of these alkenones in open and coastal marine systems may be obtained from a detailed study of their distributions, including the characterization of the position of the unsaturations. In this respect, a method has been recently reported allowing the identification of double bond position in polyunsaturated low volatile lipids such as the C_{37}-C_{40} ketones (Lopez and Grimalt, 2004). This method is used in the present study for a comprehensive reassessment of the composition of the alkenone mixtures found in open and coastal marine environments, including recent and ancient samples. The areas included in the study involve the Mediterranean Sea and the North Atlantic between 30 and 70ºN.

The observed locations of double bond positions are found at $\Delta^{8,15,22,29}$ and $\Delta^{9,16,23,30}$ in the methyl and ethyl ketones, respectively, (Fig. 1) indicating that the number of carbon atoms between the carbonyl group and the first double bond remains constant. These positions are different from C_{37}-C_{40} alkenone mixtures previously described in open sea waters or freshwater environments in which the patterns of double bond location were reported to be defined with respect to the terminal methyl.

The present results suggest that C_{37}-C_{40} alkenones in marine systems have a different structural composition than that currently assumed. This composition may provide interesting clues for the bio-synthetic pathways of these compounds in Hapthophyceae algae.

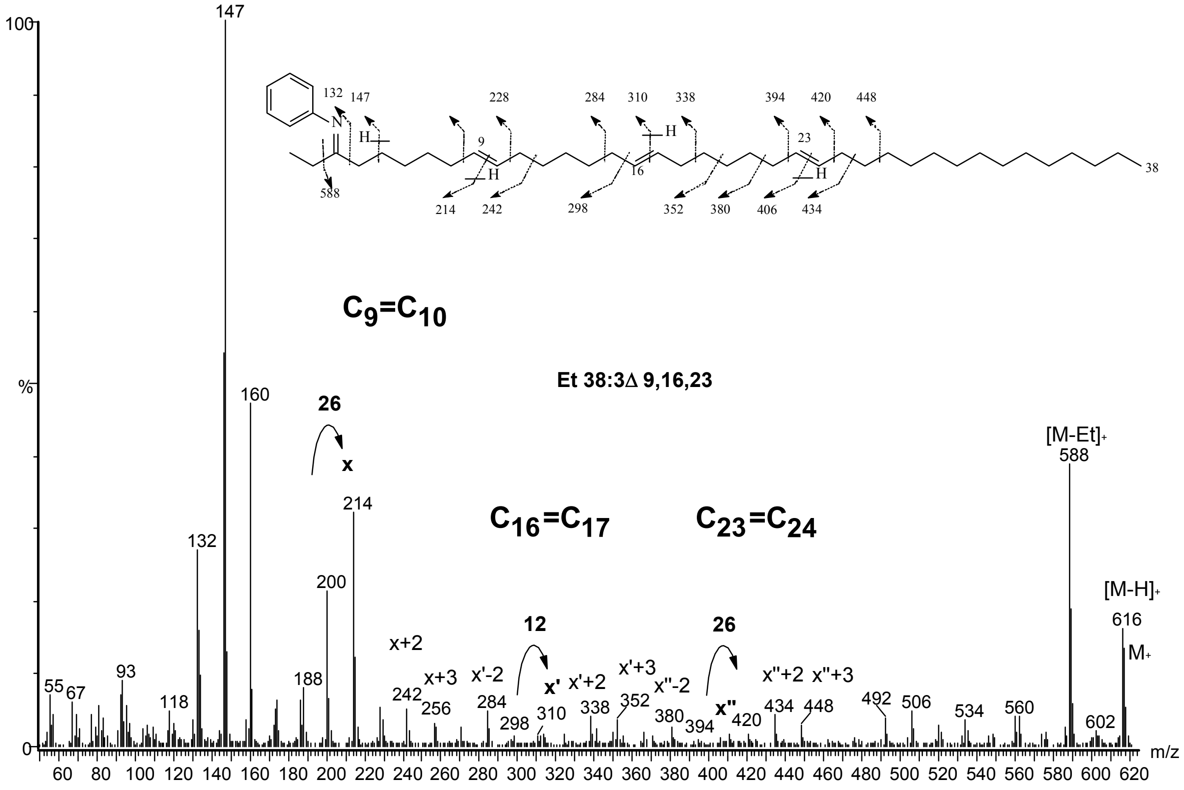


Fig.1. Mass spectra of octatriaconta-9*E*,16*E*,23*E*-trien-3-one as phenylamine derivative

References

Brassell, S.C., Eglinton, G., Marlowe, I.T., Pflaumann, U., Sarnthein, M., 1986. Molecular stratigraphy: a new tool for climatic assessment. Nature 320, 129-133.

Cacho, I., Grimalt, J.O., Pelejero, C., Canals, M., Sierro, F.J., Flores, J.A., Shackleton, N., 1999. Dansgaard-Oeschger and Heinrich event imprints in Alboran Sea paleotemperatures. Paleoceanography 14**,** 698-705.

Lopez, J.F. and Grimalt, J.O., 2004. Phenyl- and cyclopentylimino derivatization for double bond location in unsaturated C_{37}-C_{40} alkenones by GC-MS. Journal of the American Society for Mass Spectrometry, 15, 1161-1172.

Marlowe, I.T., Green, J.C., Neal, A.C., Brassell, S.C., Eglinton, G., Course, P.A., 1984. Long chain (*n*-C_{37}-C_{39}) alkenones in the Prymnesiophyceae. Distribution of alkenones and other lipids and their taxonomic significance. British Journal of Phycology 19, 203-216.

Prahl, F.G., Wakeham, S.G., 1987. Calibration of unsaturation patterns in long-chain ketone compositions for palaeotemperature assessment. Nature 330, 367-376.

Volkman, J.K., Eglinton, G., Corner, E.D.S., Forsberg, T.E.V., 1980. Long-chain alkenes and alkenones in the marine coccolithophorid *Emiliania huxleyi.* Phytochemistry 19, 2619-2622.

Zhao, M., Beveridge, N.A.S., Shackleton, N.J., Sarnthein, M., Eglinton, G., 1995. Molecular stratigraphy of cores off northwest Africa: Sea surface temperature history over the last 80 ka. Paleoceanography 10, 661-675.

OP7-3: "In-situ" coupling of abiotic feedstock generation and microbial utilization

B. Horsfield[1], K. Zink[1], R. Ondrak[1], V. Dieckmann[1], J. Kallmeyer[1], K. Mangelsdorf[1],
R. di Primio[1], H. Wilkes[1], R.J. Parkes[2], J. Fry[2], B. Cragg[2]

1) GeoForschungsZentrum Potsdam, Telegrafenberg, 14473 Potsdam, Germany
2) Cardiff School of Biosciences, Cardiff University, Cardiff CF10 3TL, U.K.

While migrated or migrating thermogenic fluids help sustain microbial consortia at gas hydrates and petroleum reservoirs, an *in-situ* coupling of abiotic generation and microbial utilization has not been found. In this communication we show that deep microbial ecosystems and active hydrocarbon generation occur together at a convergent continental margin, and argue that thermal degradation reactions can provide substrates for microbial activity. We go on to consider the same phenomenon at passive margins.

Southeast of Shikoku Island (Japan) the Philippine Sea plate is being subducted to the northwest under the Eurasian plate at a rate of 2-4 cm/a, and active sediment accretion is presently taking place in the Nankai Trough. The Nankai Trough is characterised by variable but generally high heat flow (160-200 mW/m^2), and contains Cenozoic hemipelagic muds and turbidites whose organic matter is in low concentration and of Type III. Temperature histories for several ODP Leg 190 sites have been reconstructed from subsidence profiles, compaction modelling, present-day heat flow, down-hole temperature measurements and organic maturity parameters. The bulk kinetic parameters for total hydrocarbon generation were determined on three samples richest in organic carbon (1.2 – 2.6 %) using laboratory pyrolysis experiments, and values were found to be closely similar to one another. The kinetic parameters were utilized by the model to predict generation in time and space. The model predicts that the onset of present day generation lies between 300 and 500m below sea floor (5100 – 5300m below mean sea level), 5-10% conversion of precursor structures into products having taken place by a present day temperature of ca. 85°C. Predictions were largely validated by on-site hydrocarbon gas measurements; gases became richer in C_2-C_4 components and the carbon isotopic composition of methane became heavier over the same depth interval. The potential rate of methanogenesis, determined microbiologically, decreased away from the sediment-water interface, but increased again where the abiotic generation reactions began. Intact phospholipids were also detected, demonstrating unequivocally the presence of living microbial ecosystems within the zone of early generation.

Two lines of evidence indicate that the generation products might be being utilised by the microbes. Firstly, the organic matter preserved in Nankai Trough sediments is of a type that generates potential feedstocks for microbial activity, namely oxygenated compounds and hydrocarbons. Secondly, the rates of thermal degradation calculated from the kinetic model closely resemble rates of respiration and electron donor consumption independently measured in other deep biosphere environments. We can assume that substrate utilisation in the range of 10^{-5} to 10^{-8} mg substrate g^{-1} y^{-1} is a good approximation of deep bacterial consumption rates based on the literature. The putative feedstock reaction for a sediment with 1% TOC and a Hydrogen Index of 100 mg/g TOC yields $1*10^{-7}$ mg g^{-1} sediment y^{-1} using the measured kinetics over the last one million years i.e. the rate falls within the same range as for utilisation. Even taking into account that only proven substrates such as acetate make up but a few percent of the total generated products, and that adsorption immobilises higher molecular weight generated compounds preferentially, the rates of supply are still within the assumed range of deep biosphere utilisation rates, but now at the lower end. We deduce that a steady state system can apply, with the carbon-related metabolic needs of deep micro-organisms being quantitatively met by the extremely slow thermal degradation of a recalcitrant carbon pool which is immense when compared to that of the microbial community (10^3-10^7 times greater, even for organic-poor sediments).

At passive margins, such as along the Atlantic coast, where prolific petroleum source rocks with e.g. 10% TOC and a Hydrogen Index of 600mg/g TOC have been deposited, rates of generation turn out to be about the same as for the Nankai Trough because increased richness and quality is compensated by heating rates that are up to 25 times lower.

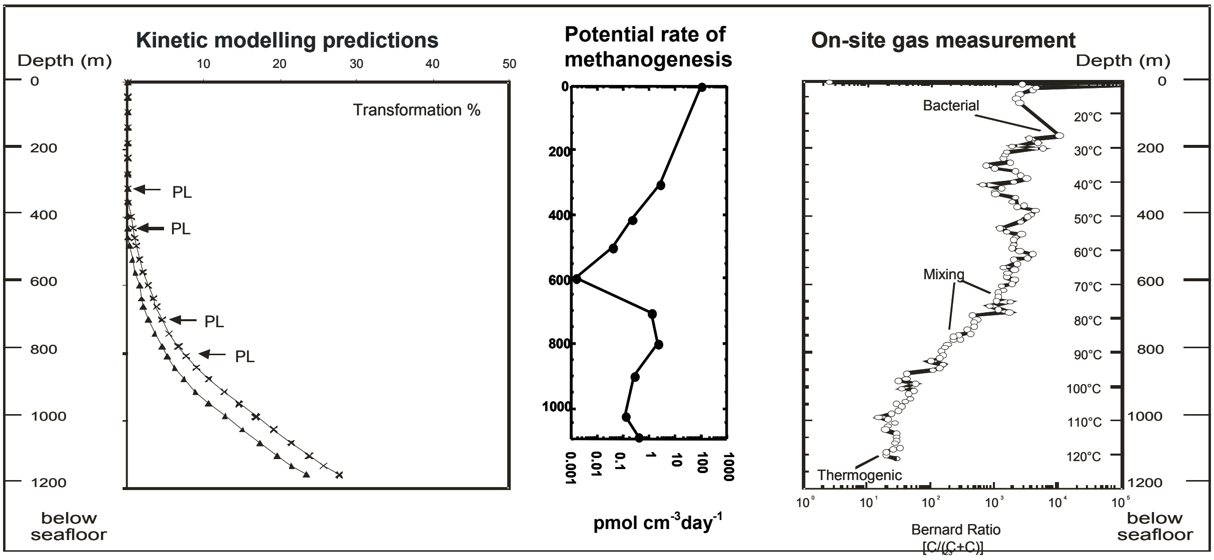


Fig.1. Kinetic predictions, microbiologically determined rate measurements and gas composition, ODP Leg 190, Site 1174. PL = depth at which intact phospholipids found.

OP7-4: Cumulative reservoir maturity – A mass balance approach to petroleum system efficiencies and reservoir filling history

C. Burgess, T. Gliddon, C. Cornford

IGI Ltd, Hallsannery, Bideford, Devon EX39 5HE UK (e-mail: chris@igiltd.com)

Petroleum geochemists commonly use molecular ratios to infer the maturity of reservoired hydrocarbons. Variations in maturity across a reservoir, between separate reservoir compartments or across a series of fill-spill accumulations have been used to infer fill points, filling history and reservoir connectivity. The theory is simple: as a source rock is progressively buried so the hydrocarbon generated in and expelled from the source rock becomes more mature. Over time the reservoir will be filled with a stream of progressively more mature oil.

With the numerous published case studies, this model of ascribing a source rock 'expulsion maturity' to an oil is widely accepted but poorly understood: an oil with a 'single maturity' is in fact the exception (Figure 1). Based on molecular data, we model and test reservoir filling in terms of a cumulative maturity model in the context of basin geometry and evolution, placing limits on efficiencies, timing and the "openness" of the Petroleum System.

In addition to the absolute volumes of hydrocarbons generated, the relative abundance of different hydrocarbon species varies as generation progresses through the oil window (Figure 2).

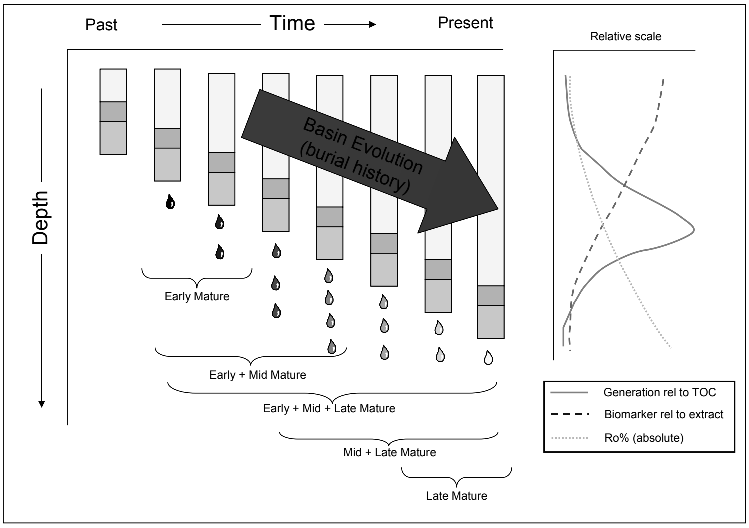


Fig.1. Schematic of the concept of cumulative expulsion maturity

The results obtained from a simple 1-D burial history model (Platte River's BasinMod™) are summarised in Table 1. The model considers the generation and maturity history of a source rock that has passed through the main oil window and has exhausted its generative potential. The kerogen Transformation Ratio allows calculation of the extract or pyrolysis S1 in ppm. Our scant evidence suggests that in the North Sea the biomarkers decrease from ~100ppm to ~10ppm of the source rock extract over the oil window.

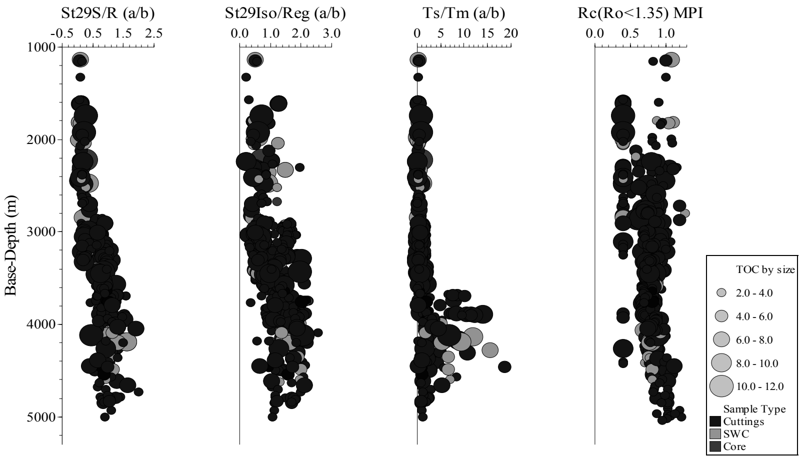


Fig.2. Molecular maturity depth trends for 488 selected Kimmeridge Clay source rock extracts from Central, Witch Ground and Viking Grabens (TOC = 2-12%).

The mass balance approach (Table 1) shows that if all the hydrocarbons that have been generated and expelled are trapped, then the cumulative maturity based on a theoretical biomarker ratio cannot exceed 0.75%R_{equiv}. An alternative calculation based on separating cumulative ppm values for denominator and numerator (St20S and St20R in the illustrated case) indicates a maximum cumulative ratio of 0.90. Using both calculations applied to the North Sea data set, the cumulative oil maturity simplistically points to a source rock at 3,600m or 0.73%Ro, though the actual charge was from source rocks expelling oil from 3,200-5,200m (0.65-1.14%Ro). In short the late mature source rock expulsion products are under-represented in the reservoir.

Table 1. Generation calculation for 36kg/t source rock modelling sterane 20R➔20S isomerisation resulting in cumulative maturity of 0.75% Re & apparent generation from 3,600m

Depth	Time	Kerogen TR	Extract or S1	St20S	St20S	St20S/R ratio	St20R	St20R	Cum. ratio	Appar-ent	Meas-ured
(m)	(my)	(0-1)	(ppm rock)	(ppm extract)	(Cum ppm)	(a/b, Fig 2)	(Cum ppm)	(ppm extract)	(a/b)	%Re	%Ro
2000	100	0	0	100	0.00	0.00	1000	0.00		0.00	0.46
2200	95	0.001	36	94	0.00	0.12	767	0.03	0.12	0.00	0.50
2400	90	0.003	108	89	0.01	0.12	716	0.10	0.12	0.00	0.53
2600	85	0.009	324	83	0.04	0.24	347	0.22	0.18	0.01	0.56
2800	80	0.021	756	78	0.10	0.36	216	0.38	0.26	0.03	0.61
3000	75	0.046	1656	72	0.22	0.42	171	0.66	0.33	0.06	0.64
3200	70	0.096	3456	66	0.45	0.60	111	1.05	0.43	0.12	0.66
3400	65	0.178	6408	61	0.84	0.72	84	1.59	0.53	0.21	0.70
3600	60	0.3	10800	55	1.43	0.89	62	2.26	0.63	0.33	0.73
3800	55	0.464	16704	50	2.26	0.95	52	3.13	0.72	0.47	0.76
4000	50	0.639	23004	44	3.27	0.98	45	4.16	0.79	0.58	0.79
4200	45	0.8	28800	38	4.38	0.99	39	5.29	0.83	0.67	0.84
4400	40	0.901	32436	33	5.44	0.87	38	6.51	0.84	0.72	0.88
4600	35	0.957	34452	27	6.38	1.04	26	7.41	0.86	0.74	0.93
4800	30	0.985	35460	22	7.15	1.04	21	8.15	0.88	0.75	1.00
5000	25	0.996	35856	16	7.72	1.04	15	8.70	0.89	0.75	1.08
5200	20	1	36000	10	8.09	1.10	9	9.04	0.90	0.75	1.14

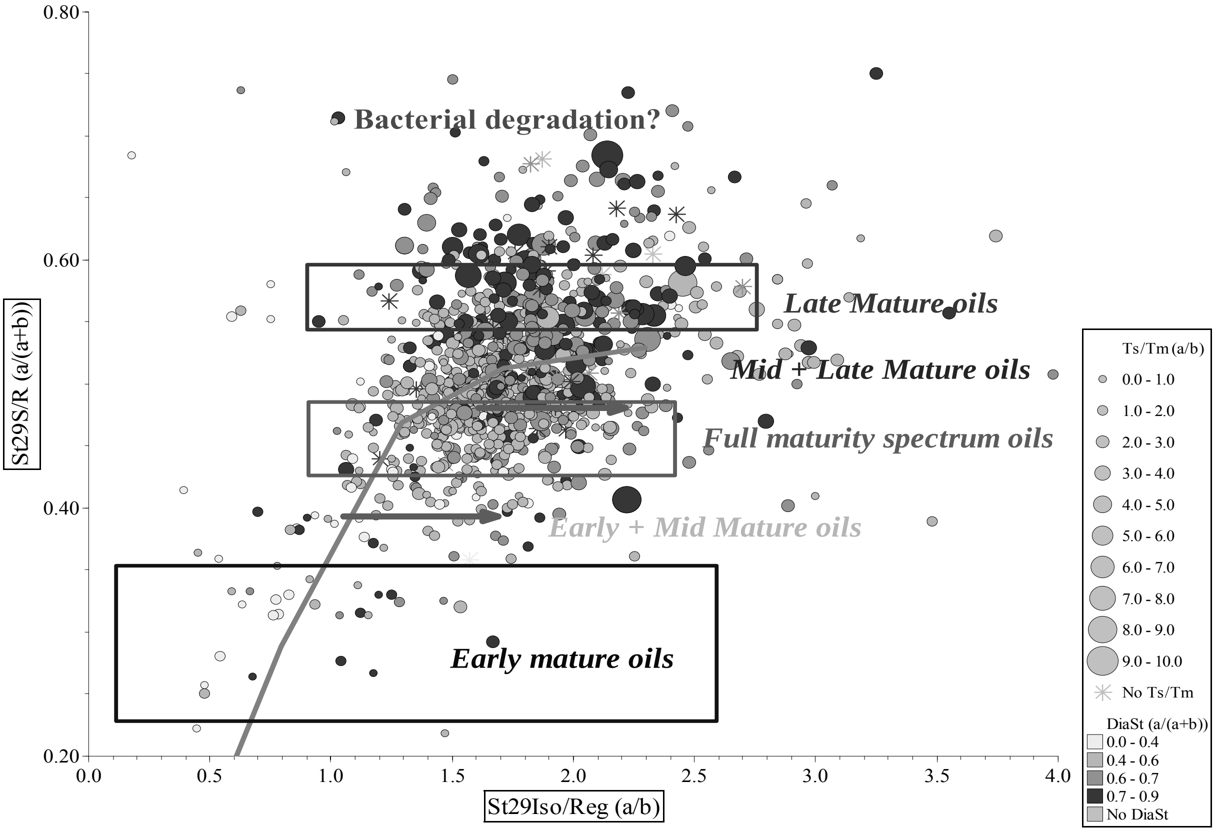


Fig.3. Data for 1,059 Kimmeridge Clay sourced North Sea oils illustrating cumulative maturity groups from steranes (axes), Ts/Tm (symbols) and C_{27} dia-sterane (colour). Source rock trend is shown in grey and arrows show sterane fractionation.

Figure 3 illustrates the sub-division of a large database of North Sea oils sourced from the Kimmeridge Clay Fm. This approach will be illustrated by generation within, and expulsion from specific drainage areas for the various cumulative maturity groups. A closed Petroleum System will tend to generate a full maturity spectrum, while an open system will produce accumulations with various combinations of maturity sub-fractions. With low expulsion efficiencies expulsion is deferred and the early mature oil fraction is missing. Since low oil expulsion efficiencies lead to high gas/oil ratios, this approach can be used to predict bulk oil properties.

ORAL PRESENTATIONS

TOPIC SESSIONS

OIL, GAS & COAL GEOCHEMISTRY

OPS1-1: Origin and biodegradation patterns impacting on oil quality and distribution in the Manantiales Behr area, North flank of the Golfo San Jorge Basin, Argentina

H.J. Villar[1], G.A. Jalfin[2]

1) FCEyN – Geol. Sc. Department., UBA-Conicet, Buenos Aires, Argentina (e-mail: lqvillar@fibertel.com.ar)
2) Repsol YPF, Geol. Department, Geosciences Direction, Madrid, Spain (e-mail: gajalfins@repsolypf.com)

The Manantiales Behr Area, located in the North Flank of the Golfo San Jorge Basin, encompasses circa fifteen productive blocks, which, according to their geologic patterns, diversity of hydrocarbon types and production complexities, should be considered as independent oil fields. During the late nineties, the acquisition and integration of structural, sedimentary and geochemical data allowed the development of a conceptual model of reservoir filling that conducted to the prognosis of sweet spots locations. The successful exploration of remote zones and deeper reservoirs has triggered an aggressive development plan which resulted in a significant increment of the daily oil production.

This paper focuses on the assessment of the petroleum systems and hydrocarbon habitat of the Manantiales Behr Area, regarding development of hydrocarbon kitchens through time, availability of migration pathways and traps, processes of reservoir charge, and conditions for hydrocarbon preservation.

Particular attention is paid to the alteration effects experienced by the oil pools in the area. Biodegradation has been a widespread process in the Golfo San Jorge Basin, and the Manantiales Behr Area is not an exception. In fact, the effects of null-slight to severe biodegradation combined with full spectrum maturity ranges originated oils of diverse qualities and producibilities (API gravities ~10-45°), with the consequent impact on the economics of the area. The source of the oils was determined to be the characteristic D-129 shale, deposited in an anoxic fresh-water to brackish lacustrine environment with variable carbonate influence, displaying quite different thermal maturity across the evaluated area. Contribution of the deeply buried, more suboxic and terrestrial-influenced, fresh-water lacustrine shales of the "Neocomiano" source (the outstanding generative unit in the West Flank of the Basin) cannot be ruled out in the lighter oils, as proved in close areas northwards of the Manantiales Behr fields.

OPS1-2: MDBT ratio as an instrument for estimation of transformation ratio organic matter of Bazhenov formation of Western Siberia (Russia)

I.V. Goncharov, V.V. Samoilenko, N.V. Oblasov, S.V. Nosova

TomskNIPIneft, 72 Av. Mira, Tomsk, 634027, Russia (e-mail: GoncharovIV@nipineft.tomsk.ru)

Evaluation of organic matter (OM) maturity level of source rocks is one of the key questions in oil geology because it has a direct influence on many practical decisions. Investigations of source rocks using Rock-Eval method allows to determine a present-day (residual) generative potential of source rocks (HI, mg HC/g TOC). Determination of OM maturity needs to be done to determine initial generative potential and amount of generated hydrocarbons. The parameter generally used for evaluation of OM catagenesis is vitrinite reflectance (Ro). However, as applied to classic source rocks of marine genesis, its direct determination is impossible because vitrinite constituent is absent in OM composition. As a result, a number of articles appeared in which calibration of molecular parameters of rocks extracts catagenesis and Ro was performed [1].

Detailed investigation of extracts from rocks using gas chromatography-mass spectrometry method has revealed that for Bazhenov formation in Western Siberia, the ratio 4MDBT/1MDBT is the most informative parameter for OM maturity evaluation. This ratio has the least variability of values in section of source formation and MDBT content in extracts is always high in a wide range of OM maturity. Fig. 1a shows that this parameter varies in accordance with Ro values. However, this interrelation is uncertain and at low 4MDBT/1MDBT values there is a wide spread of Ro values (from 0.50 to 0.75%). This fact was also noted earlier by Radke and Willsch on the example of source rocks in Germany and North Sea [2]. At the same time, there is a much closer interrelation between 4MDBT/1MDBT and HI of Bazhenov formation rocks than with Ro (fig. 1b). This is caused by the fact that 4MDBT/1MDBT is determined with greater accuracy and characterizes directly OM of a source rock itself.

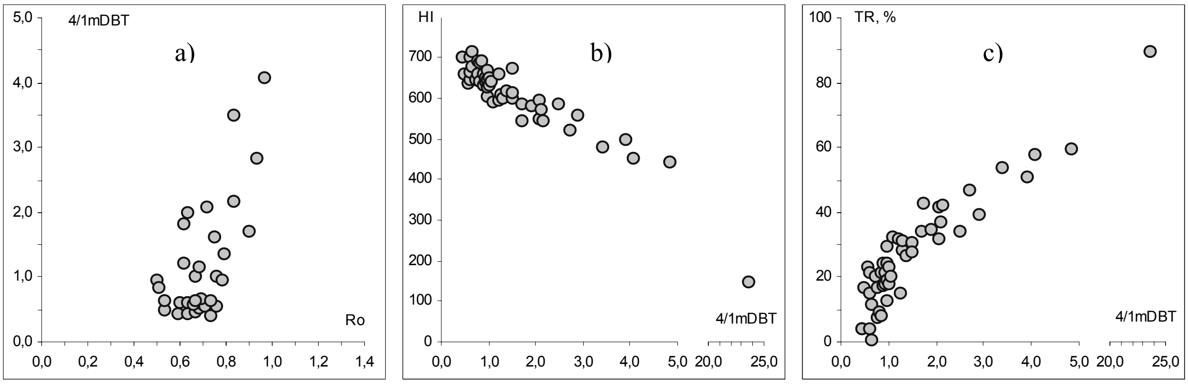


Fig.1. Relations of some geochemical parameters

A good correlation between HI and 4MDBT/1MDBT allows to proceed to direct determination of realized generation potential (TR) using not Ro but 4MDBT/1MDBT ratio. On the other hand, it became possible because investigations of Bazhenov formation in South-East of Western Siberia revealed that there are areas when OM of Bazhenov formation has anomalously high hydrogen index values. Based on analysis results of 24 samples from three wells, the average initial HI value is 710 mg HC/g TOC. This value differs significantly from the recommended values for II-type organic matter (627 mg HC/g TOC) [3]. Rock-Eval parameters and all the molecular parameters (4MDBT/1MDBT, TA(I)/TA(I+II), Ts/(Ts+Tm), 20S/(20S+20R)-Sterane (C_{29}) indicate a very low maturity of OM. Besides, in these areas oil fields related to Bazhenov formation were not struck. All these findings allow to consider that OM doesn't reach the "oil window" there and HI values may be accepted as initial value-HIo. Fig. 1c shows TR– 4MDBT/1MDBT dependence obtained by us for samples of Bazhenov formation. It can be seen from the figure that in the range of TR 0 – 60%, 4MDBT/1MDBT values increase from 0.50 to 5.00, while Ro value varies only from 0.50 to 1.00 (fig. 1a, c).

It is absolutely evident that such high sensitivity of this parameter (fig. 1b, c) towards change in catagenic maturity of source rocks allows to evaluate the territories for oil-and-gas prospect with much greater minuteness and accuracy. Analysis of more then 300 oil samples in Western Siberia genetically related to Bazhenov formation shows that 4MDBT/1MDBT varies in them from 0.80 to 25; and this corresponds to realization of source rock potential of Bazhenov formation at 10 – 90%. However, extensions of oilfields with 4MDBT/1MDBT value of 0.80 – 0.90 are very small. This points to the fact that the amount of generated hydrocarbons within the bound of oil gathering area was insufficient for large oilfields formation. Perhaps, as applied to specific geological conditions of Western Siberia, the values of 4MDBT/1MDBT equal to 0.80 – 0.90 in extracts of Bazhenov formation should be considered as minimal values of OM maturity at which formation of commercial oilfields is possible. Oils of main giant oilfields in Western Siberia have value of 4MDBT/1MDBT in the range of 1.3 – 2.5.

References

[1] Andrew S. Mackenzie, Detlev Leythaeuser, Franz-Josef Altebäumer, Ulrich Disko, Jürgen Rullkötter, 1988. Molecular measurements of maturity for δ Lias shales in N.W. Germany. Ceochimica et Cosmochimica Acta. V.52. pp.1145-1154

[2] Radke M., Willsch H., 1994. Extractable alkyldibenzothiophenes in Posidonia shale (Toar-sain) source rock: Relationship of yields to petroleum formation and expulsion. Geochim. et Cosmochim. Acta. V. 58. pp. 5223-5244

[3] Lopatin, N.V., Zubairaev, S.L., Kos, I.M., Emets, T.P., Romanov, E.A., Malchikina, O.V., 2003. Unconventional oil accumulations in the Upper Jurassic Bazhenov black shale formation, West Siberian basin: a self-sourced reservoir system. Journal of Petroleum Geology. V.26 (2). pp. 225-224.

OPS1-3: Thermal cracking history by laboratory kinetic simulation of Paleozoic oil in Eastern Tarim Basin, NW China, implications for the occurrence of residual oil reservoirs

Y. Wang[1], S. Zhang[2], F. Wang[3], Z. Wang[2], C. Zhao[2]
H. Wang[2], J. Liu[1], J. Lu[1], A. Geng[1], D. Liu[1]

1) State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640,China (e-mail:wangyp@gig.ac.cn)
2) RIPED of PetroChina, Beijing 100083, China
3) Department of Geosciences, Petroleum University of China, Beijing 102200, China

The Paleozoic strata in eastern Tarim Basin, NW China are very good petroleum source rocks due to their good biogenetic origins (type I/II kerogen), big thickness and high TOC concentration (2.84% averagely by Sun et al, 2003). The exploration to the Paleozoic strata is focusing on the cracking gases due to the high maturity-levels (>2.0%). The discovery of residual oil in well TD-2 in 2001 arouses the exploration expects of oils in this area. Because the oil-bearing strata (Є-O_1) experienced very high temperature alteration (>200°C), it is dominantly regarded that oil reservoirs have been destroyed. The key is the study of oil stability and the recovery of oil cracking history. This paper derived the kinetic parameters of cracking gases (C_{1}-$_{5}$) generation from selected oil sample through laboratory closed pyrolysis system, recovered the oil-cracking history using the geothermal history of TD-2, calculated the threshold temperature in geologic condition and cracking rate-Ro(%) pattern, and probed the possible geological controls for the occurrence of residual oil reservoirs in this area.

The oil sample selected for the experiment was a drill stem test oil from the Ordovician reservoir at the depth of 4010m of well LG-1 in Tarim Basin, which was proved originated from the Cambrian source rock (Zhao, 2001). The pyrolysis apparatus used is a closed, temperature programmed, gold-tube system similar to those described by Burnham (1988), Behar (2002), Tang et al. (1995) and Lorant (2002). The laboratory pyrolysis results indicated the oil required higher temperature for cracking. For example, oil began to crack at 390-400 °C in laboratory heating rates (2-20°C/h), the oil-cracking rate could reach 75% at 550°C, and the laboratory temperature was about 650°C for the complete cracking. The kinetic parameters of oil cracking exhibited a relatively high active energy (Ea) (Fig.1 A), which was ranging from 59 to 72 kcal (with $A = 1.0\times10^{14}\ s^{-1}$). From the Ea distribution, it was found that there were two types of gas precursors. Type 1 has lower Ea, which is less than 63 kcal/mol and accounts for 65.9% of the total cracking potential, and type 2 has higher Ea, which is bigger than 65 kcal/mol and accounts for 34.1% of the total cracking potential (Fig.1

A). A series of geologic heating rate including 0.5, 1, 2, 3, 5 and 10°C/My were used for the kinetic calculating for the required geologic temperature of oil cracking. The threshold temperature for cracking start is about 148-162°C and the temperature for complete cracking is about 245-276°C in geological conditions (Fig. 1 B). These results demonstrated a relatively high stability of the Earlier Paleozoic oil in Tarim Basin.

The thickness of O_{2-3} is over 5000m in TD-2, which made the strata of Є-O_1 quickly buried to depth of over 6000m, the temperature increased from 30°C to 210°C and the Ro% increased from 0.5 to 2.6-3.0% (Fig. C). The fast maturation of the source rocks was accompanied with the process of oil generating and cracking. It was computed kinetically that the oil-cracking rate in the strata of Є-O_1 reached 60-70% at the end of Silurian (Fig. 1 D). The oil cracking stopped as the strata uplifted. The relation between oil-cracking rate and maturity (EasyRo% by Sweeney, 1990) and the threshold temperature for the oil cracking in TD-2 were also computed (Fig. 1, E and F). It could be found that the oil cracking started at temperature of 165°C (Ro=1.45%) in TD-2 site. Obviously, the high cracking temperature reflects the fast heating rate in this site. In summary, the key geological controls for occurrence of residual oil in TD-2 include: (1) The higher stability of the Paleozoic oil in Tarim Basin, especially the type of precursor with higher cracking Ea makes it difficult for oil cracking; (2) The fast heating rate (>5 °C/My) and maturation rate requires higher geological temperature for oil cracking; (3) The later uplift did not cause serious biodegradation; and (4) The good preservation of the palaeo-reservoirs and the moderate structural adjustment.

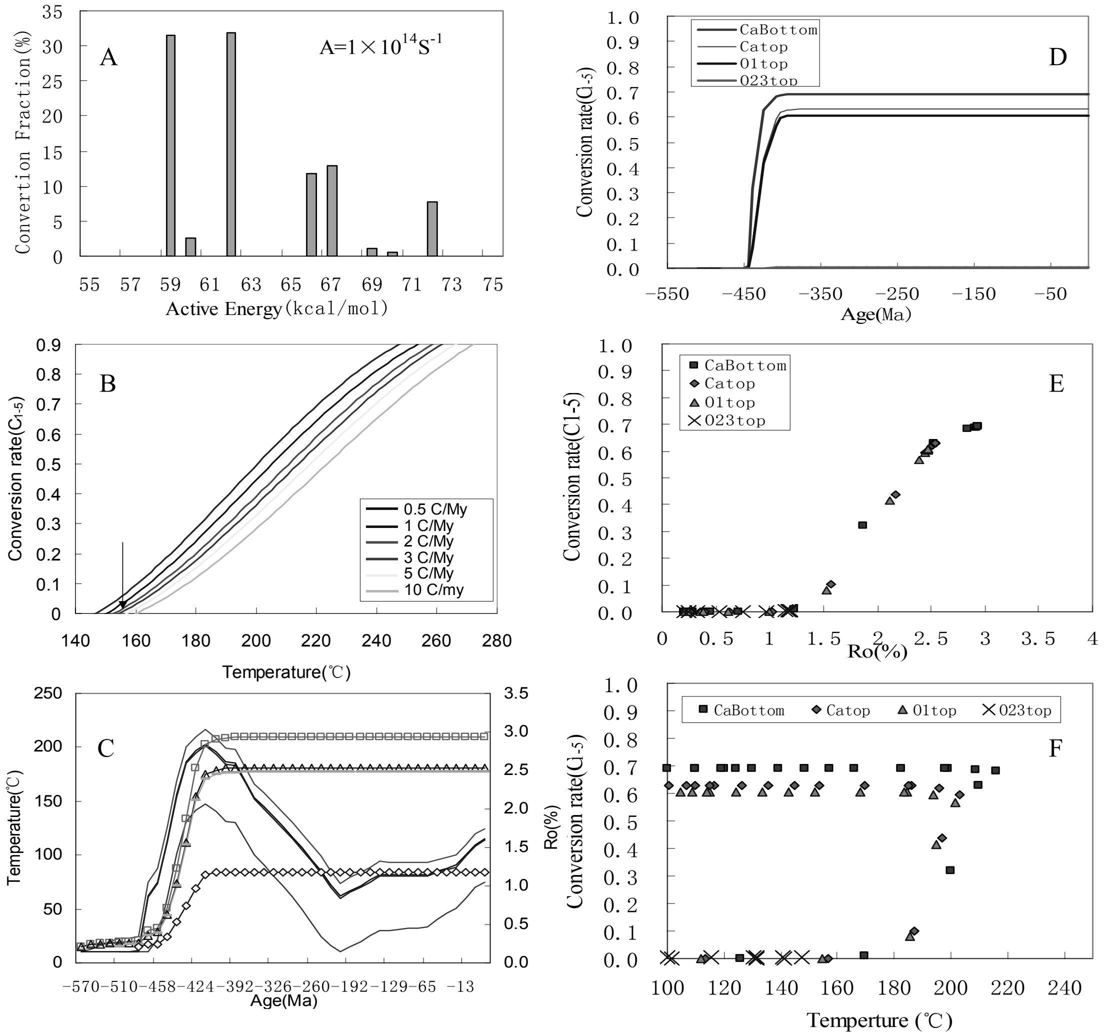


Fig.1. Thermal cracking history by laboratory-based kinetic simulation of oil in Paleozoic strata of Eastern Tarim Basin, NW China. A: Discrete activation energy distribution and frequency factor of oil cracking; B: Conversion rate of cracked gas from oil in geologic temperature and heating rate; C: Temperature and maturity history of Well TD-2; D: Conversion rate of cracking gas from oil of TD-2 in geologic history; E: Conversion rate of cracking gas from oil in site of TD-2 versus maturity (Ro%) and geologic temperature (F);

OPS2-1: Chemical fractionation during expulsion explained by selectivity solubility

S.R. Kelemen[1], D. Ertas[1], C.C. Walters[1], L.M. Kwiatek[1], H. Freund[1], D.J. Curry[2], A.E. Bence[3]

1) ExxonMobil Research & Engineering, 1545 Route 22 East, Annandale, NJ 08801-0998
(e-mail: clifford.c.walters@exxonmobil.com)
2) ExxonMobil Exploration Co., PO Box 2189, Houston, TX 77252-2189
3) ExxonMobil Upstream Research Co., PO Box 2189, Houston, TX 77252-2189

The expulsion of hydrocarbon fluids from kerogen is the first and poorly understood stage in the migration of hydrocarbons from source organic material to reservoir accumulations. Most expulsion models explain the large compositional differences seen between retained bitumen (polar-rich) and related expelled oil (saturated hydrocarbon-rich) by evoking rate-limiting processes involving either the selective release of generated hydrocarbons from the kerogen, or movement of hydrocarbons within the source rock matrix. Expulsion controlled primarily by the amount and composition of the kerogen and its thermal products is particularly attractive for inclusion in basin simulators, as expulsion is then modeled as a process coupled with generation and does not require the additional complexity imposed by lithological controls. In the latest publication to examine this concept, Ritter (2003) concluded that polymer solution theory based on the relative solubility of petroleum compounds in kerogen, suggests the nature, but not the magnitude, of observed hydrocarbon fractionation. He surmised that selective solubility is only one contributing factor to chemical fractionation during expulsion, though it may be the dominant process in specific circumstances.

We have constructed a theoretical framework and conducted laboratory experiments to test the extent that selective solubility influences chemical fractionation during expulsion. The model postulates that: 1. the kerogen/bitumen/oil system remains in thermodynamic equilibrium, 2. kerogen swells as an elastomer network, and 3. solvent-solvent and solvent-kerogen interactions are largely non-specific. From these assumptions, a theoretical framework is constructed that incorporates concepts from the Flory-Rehner [1] Theory of Rubber Elasticity and the Regular Solution Theory of Hildebrand *et al.* [2] to explain the swelling behavior of kerogen by different solvents and solvent mixtures.

A series of experiments was conducted whereby 14 different isolated kerogens, representing organic matter types II and IIIC at varying levels of thermal maturity, were swelled in a series of different organic solvents and solvents in 50:50 mixtures of hexadecane (reference solvent). The solvents were distinguished by their solubility parameter (δ) and molar volume. The change in kerogen volume is expressed by the mean volumetric swelling ratio Q_v, and by a compositionally based swelling ratio, Q_c , that was calculated from the compositional changes in solvent mixture as determined by gas chromatography and mass balances for the kerogen/solvent system. Directional agreement between the Q_v and Q_c confirmed the preferential absorption of the solvent over the reference solvent. Statistically significant mean swelling differences were found among different solvents and among different kerogens. The level of swelling drops significantly only for overmature samples within the Type II and Type IIIC maturation series.

All kerogen swelling data could be interpreted within this theoretical framework. Thermodynamic parameters needed to model chemical fractionation during expulsion (solubility parameter, cross-link density and native swelling) were determined for average kerogen types by optimizing the match between the sets of experimental data and theoretical predictions. With the thermodynamic parameters defined, fractionation effects are calculated for model compounds that are used as surrogates for describing the composition of expelled petroleum fluids and retained bitumen. Chemical fractionation is very sensitive to the kerogen organic richness and cross-link density, which is a function of organic matter type and thermal maturity. The composition of the generated fluids exerts a lesser influence. The interplay between these factors determines the nature and extent of chemical fractionation during expulsion. The calculated composition of expelled oils from a variety of Type II and IIIC kerogens (Fig. 1A) compare favorably with the measured composition of produced oils (Fig. 1B).

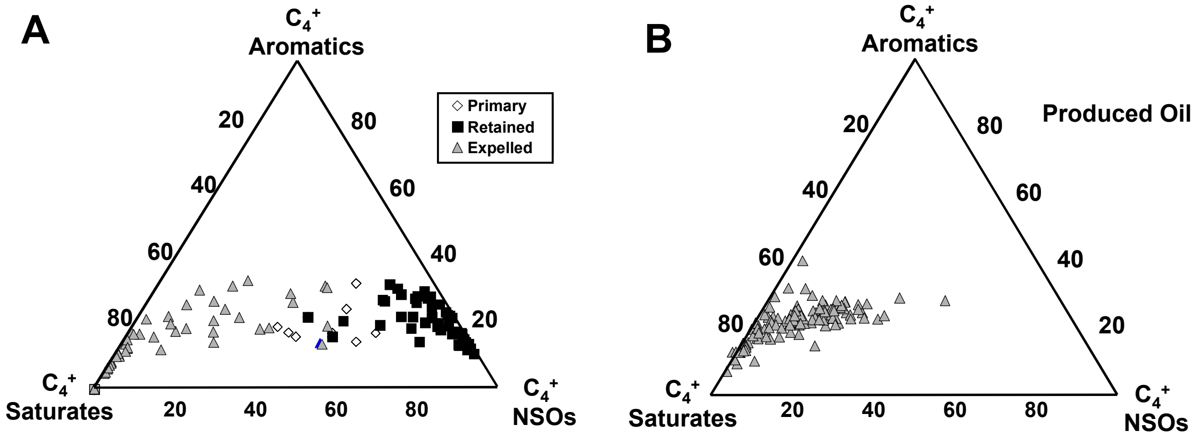


Fig.1. A) Modeled compositions of chemical fractionation during expulsion at 50% kerogen conversion and B) Produced oil composition

References

[1]Ritter U., 2003. Solubility of petroleum compounds in kerogen: implications for petroleum expulsion. *Organic Geochemistry* **34**(3), 319-326.

[2]Flory, P.J., Rehner Jr., J., 1943. Statistical mechanics of cross-linked polymer networks. II. Swelling. *Journal of Chemical Physics* **11**, 521-526.

[3]Hilderbrand, J.H., Praudnitz, J.M., Scott, D.L., **19**70. *Regular and Related Solutions*, Van Nostrand Reihold, Princeton, NJ.

OPS2-2: Investigation of the petroleum systems of the South Viking Graben, Norway by pseudo-3D basin modeling and geochemical characterization of hydrocarbons and source rocks

H. Justwan[1], B. Dahl[1], G.H. Isaksen[2], I. Meisingset[3]

1) Department of Earth Science, University of Bergen, Allegaten 41, 5007 Bergen, Norway
(e-mail: holger.justwan@geo.uib.no)
2) ExxonMobil Exploration Company Co., 233 Benmar, Houston, Texas 77210, USA
3) Aker Kvaerner Geo AS, P.O. Box 242, Lilleaker, 0216 Oslo, Norway

Although considered to be in a mature phase of exploration, discoveries are still being made in the Norwegian South Viking Graben. Recoverable reserves in this well explored hydrocarbon province include 329.8 x 10^6 Sm^3 oil and 456.8 x 10^9 Sm^3 gas, most of which are reservoired in sandstones of Paleogene age (83% and 48% respectively). The remaining reserves are stored in Upper and Middle Jurassic as well as Triassic reservoirs. Although numerous studies covering different aspects of the petroleum systems and various sub-areas have been undertaken previously, a comprehensive study of the area using the large amount of available data remains unpublished. This study aims at investigating the active petroleum systems of the South Viking Graben in order to facilitate exploration efforts in the area. It comprises a detailed study of source rocks and hydrocarbons in the area, as well as pseudo-3D basin modeling.

Major source rocks in the area are the shales of the Upper Jurassic Heather and Draupne Formations, and the Middle Jurassic Vestland Group. Based on Rock-Eval analysis, the oil- and gas potential is determined for the Upper Jurassic source rocks using the method described by Dahl et al. [1]. Mapping reveals significant facies and potential variations, which are shown to be related to dilution effects and varying degrees of anoxia using results from Rock-Eval pyrolysis, gas chromatography, biomarker and stable carbon isotope analysis. Based on the mapping results, the up to 1500 m thick Lower Draupne Formation is classified as mostly gas-prone source, while the up to 360 m thick upper, post-rift section of the Draupne Formation is a rich oil-prone source. The Heather Formation is a lean gas-prone source.

Interpretation of molecular and isotopic characteristics and multivariate analysis of biomarker data allows identification of seven hydrocarbon families, which can be related to the three active source horizons based on carbon isotopic and biomarker data. Three families are sourced from the Draupne Formation, the Heather Formation and the Middle Jurassic strata each source one family, while the remaining families represent mixtures of Upper and Middle Jurassic sources. The available data in this study allows characterization of 87% of the recoverable oil reserves and indicates that the main source rock in the area is the Upper Jurassic Draupne Formation with 278.1 x 10^6 Sm^3 of recoverable oil, equaling over 96% of the total characterized oil reserves (Figure 1).

Pseudo-3D basin modeling, based on the source rock potential maps generated, allows the investigation of timing of oil and gas generation in the area, calculation of generated and expelled hydrocarbon mass and timing for in-reservoir alteration. Based on the identification of hydrocarbon families and calculated mass generated, the efficiency of the hydrocarbon systems is evaluated.

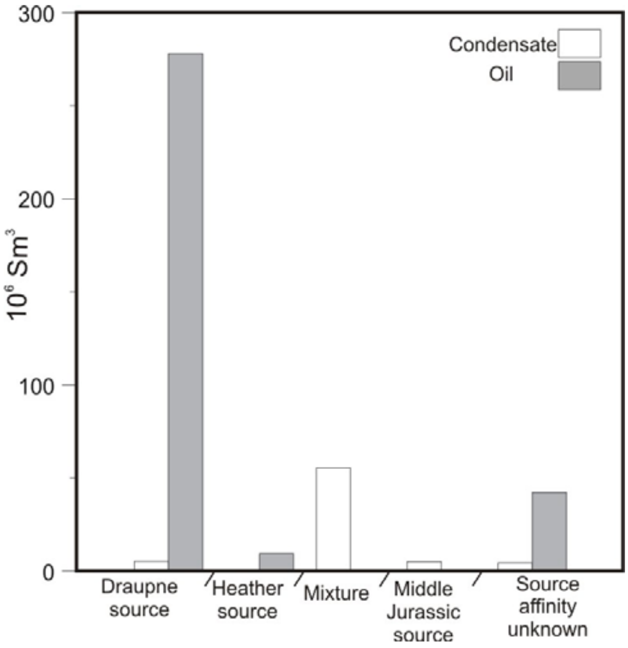


Fig.1. Contribution of the identified source horizons to the total recoverable oil and condensate reserves based on oil-source rock correlations.

References

[1] Dahl, B., Bojesen-Koefoed, J., Holm, A., Justwan, H., Rasmussen, E., Thomsen, E., 2004. A new approach to interpreting Rock-Eval S2 and TOC data for kerogen quality assessment. Organic Geochemistry 35 (11-12), 1461-1477.

OPS2-3: The search for pre-Cretaceous hydrocarbons in Venezuela

J.M. Moldowan[1], D. Zinniker[1], J. Dahl[1], T. Hara[2], P. Pestman[3]

1) Department of Geological and Environmental Sciences, Stanford University, Stanford, CA 94305-2115, USA
2) Teikoku Oil Company, Ltd., 31-10 Hatagaya 1-Chome, Shibuya-Ku, Tokyo 151-8565, Japan
3) Teikoku Oil Company de Venezuela, C.A., Caracas, Venezuela

Discovery of pre-Cretaceous hydrocarbons in Venezuela would substantially change the focus and exploration potential of some areas. Geochemical correlation for the producing oil and gas fields of Venezuela has so far only shown Cretaceous and younger sources. However, some hypotheses, especially regarding the sources of thermal gas, include pre-Cretaceous possibilities. Our search for pre-Cretaceous hydrocarbons focused on the Guarico Sub-basin of Eastern Venezuela, which overlies a portion of the Espino Graben. Jurassic and older sediments imaged on seismic in the Espino Graben may contain potential oil and gas source rocks.

A battery of molecular geochemical parameters were applied to address questions and develop scenarios concerning the origins of oil and especially gas accumulations in the sub-basin, all of which found so far are in Tertiary reservoirs. Of primary concern is (*i*) whether hydrocarbons can be related to pre-Cretaceous source rocks presumed to be deeply buried in the Espino Graben, and (*ii*) to define the effective hydrocarbon source systems and oil and gas maturities in the basin.

Three principal oil families are described in these results, (1) a Tertiary-terrestrial oil family (proximal), (2) a marine-algal oil family (Cretaceous or younger, but possibly Upper Cretaceous), and (3) a Tertiary-terrestrial/marine oil family (distal). All oil samples contain the Cretaceous or younger age-related biomarkers, oleanane and the C_{25} highly branched isoprenoid. Therefore, there cannot be any wholly pre-Cretaceous sourced oil among those samples. However, it may not be possible to detect pre-Cretaceous biomarkers in mixtures with younger oil due to relatively much higher biomarker concentrations in less mature, younger sourced oil that would obscure any older sourced biomarkers.

Another approach was taken by the analysis of diamondoid hydrocarbons, which can be the most abundant components in highly mature hydrocarbon liquids. By the diamondoid-biomarker cracking analysis it was determined that several oils in the Guarico Sub-basin show substantial cracking to gas and pyrobitumen (Figure 1). Most are mixed oils with both cracked and non-cracked components. The high levels of oil cracking point to deeply buried (hot) source kitchens with the cracked hydrocarbons arriving in the Tertiary reservoirs by complex migration routes. Access to deep faults that could tap deep pre-Cretaceous source rocks is one indication of the origin for these cracked fluids from the deep graben. An alternative scenario suggests that long range lateral migration brought in the fluids from deeply buried Cretaceous and younger source rocks, elsewhere in the basin.

In order to distinguish geochemically between these two possibilities for sources of the cracked oil a method that can correlate the isotopic (source) signature of diamondoids was applied. This compound specific isotope analysis of diamondoids (CSIAD) suggests that the cracked components of several oils analyzed by CSIAD were derived from a common source or mixture of sources. Efforts to narrow the possibilities for that source(s) will be discussed.

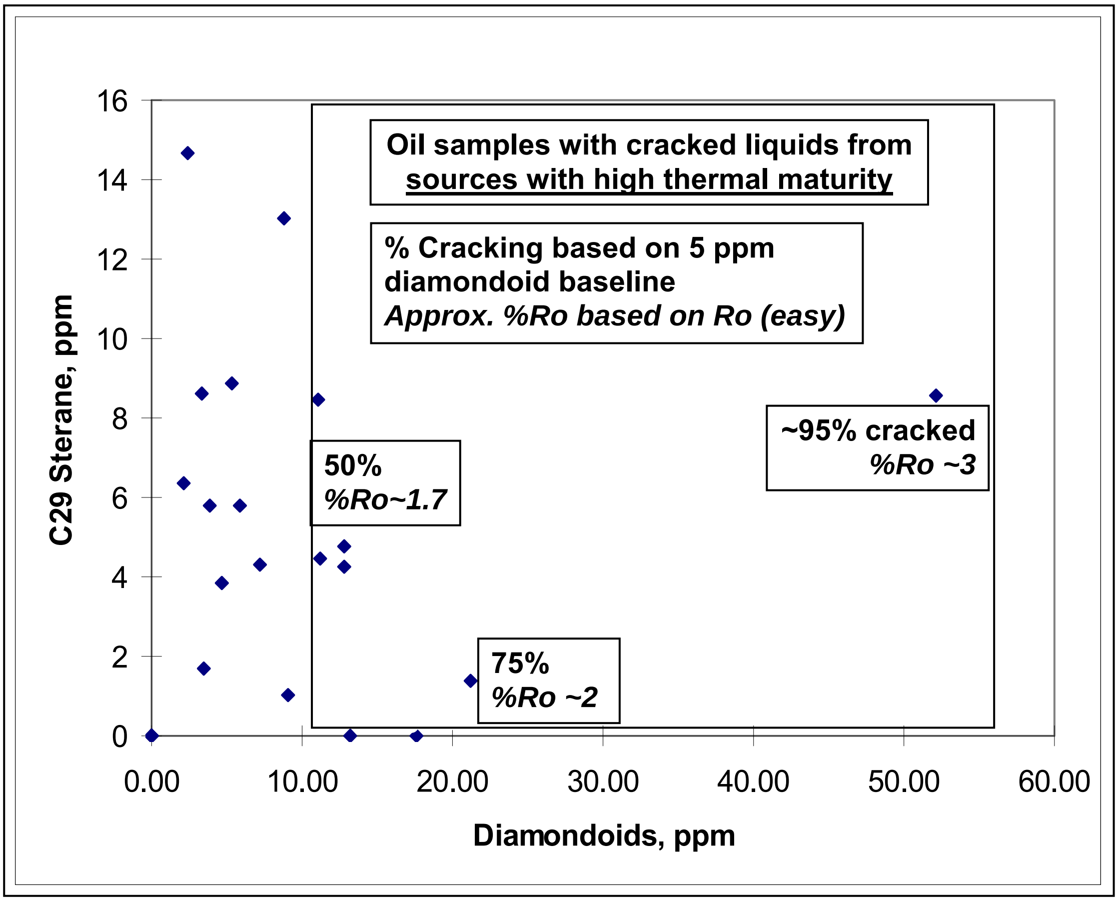


Fig.1. Occurrence of highly cracked oil in Guarico Sub-basin suggests generation from great depth. Pre-Cretaceous sources in the Espino Graben could account for these results

OPG-1: Thermal cracking of crude oil light aromatic fraction in closed system – temperature and pressure effect in high pressure-high temperature reservoirs

T. Al Darouich[1,2], F. Behar[1], C. Largeau[2]

1) Geochemistry Department, Institut Français du Pétrole (IFP), 1-4 Avenue de Bois Préau, 92852 Rueil-Malmaison France (e-mail: francoise.behar@ifp.fr).
2) Laboratoire de Chimie Bioorganique et Organique Physique, UMR CNRS 7573, ENSCP, 11, rue Pierre et Marie Curie, 75231 Paris Cedex 05

The aim of this work is to study the thermal stability of the light aromatic fraction (C_6-C_{14}) of crude oil through laboratory pyrolysis in order to predict its behaviour under geological conditions (T>150°C and P>400 bars). Such a prediction is of prime importance in petroleum exploration as it allows to estimate the composition of reservoired oils. The light cut <250 °C of a conventional non-biodegraded type II crude oil, Safaniya, was selected for this study. This cut contains a complex mixture of saturated and aromatic hydrocarbons. We developed a method for obtaining a clear-cut separation of these two families: liquid phase chromatography was thus optimised for separating a complete and pure aromatic fraction, in large enough amounts for characterisation and all subsequent kinetic studies. Thereafter, Preparative High Performance Liquid Chromatography (PHPLC) of an aliquot was used to separate the aromatic compounds according to aromatic ring number into monoaromatics, indenes, diaromatics and biphenyls. Detailed molecular characterisation of the aromatic sub-fractions thus obtained was achieved by Gas Chromatography coupled to Mass Spectrometry (GC/MS). Then, individual aromatic compounds were quantified by GC-FID and lumped into five global classes according to their estimated thermal stability: stable compounds (BTXN), methylaromatics (methylnaphthalenes and dimethylnaphthalenes), alkylaromatics (C_2-C_7 alkylbenzenes and ethylnaphthalenes), naphtenoaromatics (indane, C_1-C_4 indanes, indene, C_1-C_2 indenes and C_1-C_3 tetralins) and sulphur-containing aromatics (methyl- and ethylbenzothiophenes). The detailed knowledge thus derived on the composition of each class and its relative abundance in the total C_{15}- aromatics allows following its temporal evolution during subsequent pyrolysis experiments.

Closed pyrolysis of the C_{15}- aromatic fraction was performed in gold tubes, under an inert atmosphere (Nitrogen). Temperature and pressure were kept constant during each experiment. The first set of pyrolysis was carried out under 100 bars and a wide set of temperature/time conditions (325-500°C/2-504 h). All the pyrolysis effluents (Gas, liquid and solid) were recovered, fractionated and analysed. The individual compounds generated under each condition were quantified then lumped into classes. These pyrolysis data were used to elaborate a semi-empirical kinetic scheme of stoichiometric reactions accounting for mass balances between the reactants and the pyrolysis products and allowing to predict the thermal stability of C_{15}- aromatics in oil and their behaviour under geological conditions.

Aromatic compound effect on the thermal cracking of saturated hydrocarbons was studied by performing another set of pyrolysis. Gold tubes were loaded in this case with a mixture of *n*-hexadecane (*n*-C_{16}) with the light aromatic fraction of Safaniya crude oil. Results are compared to those of pure *n*-hexadecane pyrolysis available in the literature.

In order to simulate conditions in deep prospects and to evaluate pressure effect on the thermal cracking of the aromatic fraction, a third set of pyrolysis experiments was performed under high pressures: 400 to 1200 bars. Continuous relative slowing down in conversion rate with increasing pressure was thus observed whatever the pression (- 30 % between 100 bars and 400 bars). This is in contrast to pressure effect on saturated hydrocarbons (Fabuss et al. 1964, Behar and Vandenbroucke 1996), where pressure increased the thermal cracking up to 400 bars, then decreased it between 400 and 800 bars down to its value at 100 bars. Aromatic hydrocarbons undergo thermal cracking in geological conditions at 150-180°C corresponding to a pressure of 350-450 bars. Pressure delays this cracking and that explains that some aromatic compounds are still present in HP/HT reservoirs. No selective effect on the charge aromatic classes was observed. However cracking production of pyrobitumen precursors is enhanced with increasing pressure.

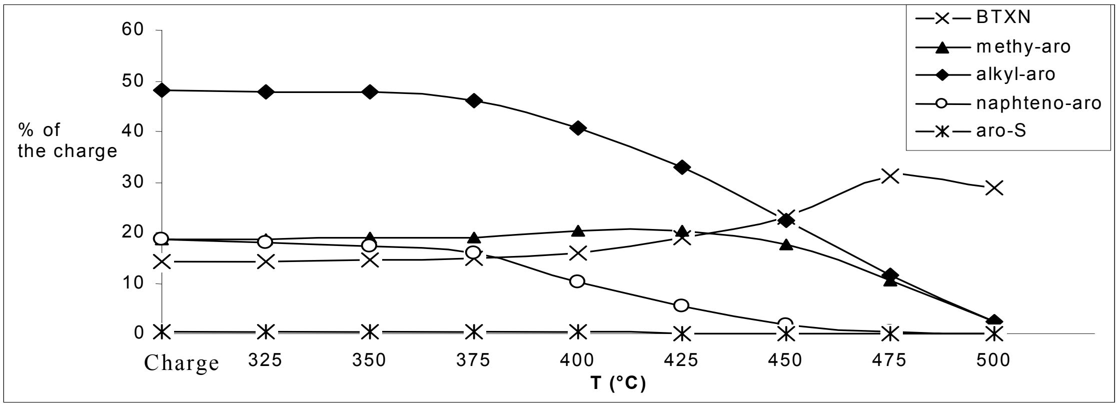


Fig.1. Example of evolution of the aromatic classes of Safaniya crude oil during temperature screening pyrolyses (heating time: 24 h)

References

Behar, F. and Vandenbroucke, M. (1996) Experimental Determination of rate constants of the *n*-C_{25} Thermal cracking at 120, 140, and 800 bar: Implication for high-pressure/high-temperature prospects. *Energy and fuel*, 10, 4, 932-940.

Fabuss, B. M., Smith, J. O. and Satterfield, C. N. (1964) Thermal Cracking of Pure Saturated Hydrocarbons. *Adv. Pet. Chem. Refin.*, **9**, 157-201.

OPG-2: Evidence for generation and migration of hydrocarbons along thermally anomalous faults in the Los Angeles basin, California, USA

H. Camacho[1], J. Boles[2]

1) Signal Hill Petroleum, Inc. Long Beach CA 90806 (e-mail: camachoh@shpi.net)
2) University of California, Santa Barbara, CA 93106

The Los Angeles basin in Southern California (USA), with over 8.4 billion barrels produced to date, is one of the most prolific oil basins in the world. The basin formed in late Miocene time and has experienced accelerated periods of subsidence that have resulted in the accumulation of more than 9000 meters of sediments. The Los Angeles basin is also of particular interest because of the presence of complex, active fault zones to which most of the oil fields are associated. The Los Angeles basin is in general normally pressured and has a complex thermal regime associated with faulting, due to fluid movement along fault zones.

Petroleum generation and migration models confront special difficulties when applied to basins with high subsidence rates and complex thermal histories. Oil exploration and production in the Los Angeles basin have provided a wealth of subsurface data, which combined with the complex thermal and structural history of the basin, provide a unique setting on which to evaluate the effects of faulting on the geothermal gradient and hydrocarbon generation and migration.

Previous studies of organic matter maturation in the Los Angeles basin have assumed that oil generation takes place mainly on the deepest part of the central syncline, or structural lows, from Miocene age rocks, laterally migrating to fill the structural highs associated with complex fault zones. These previous studies, however, assume a simple thermal history and do not account for the complex thermal regime of the basin. The fact that most of the oil fields in the basin have very thick production intervals (over 2000 meters in some fields) with multiple stacked reservoirs, the association of oil accumulation with fault zones, and the compositional differences both vertically and horizontally of the oils, cannot be fully explained by existing oil generation/migration models.

In this study, the role of faults on heat distribution and the generation and migration of hydrocarbons have been assessed from temperature, oil geochemistry and C isotope data. Temperature data suggest that the fault zones are responsible for bringing deeper, hotter fluids to shallower depths causing the observed variations in geothermal gradient and the thermal anomalies associated with faulting. Results suggest that structural highs associated with complex fault zones and high geothermal gradient in the Los Angeles basin may act as secondary petroleum generation areas for overlying structures. Time-temperature modeling suggest that the onset of oil generation in anomalously high geothermal gradient areas can occur hundreds of thousand years earlier than in the cooler structural lows. Light hydrocarbon correlation plots of oils from similar production intervals throughout the basin, and formation water chemistry suggest that the fault zones may act as preferential vertical and lateral migration pathways. Biomarker data suggest that the vertical compositional differences of oils found in the Los Angeles basin fields may be the result of mixing of different groups of oils generated not only from Miocene age source rocks, but also from Pliocene age rocks. This study provides a new framework for the exploration of potentially productive areas not previously recognized in the Los Angeles basin, as well as other structurally complex basins.

OPG-3: Characterisation of crude oil components with affinity for gas-hydrate surfaces

A.E. Borgund[1], S. Høiland[1], K. Askvik[2], T. Barth[1], P. Fotland[2]

1) University of Bergen, Department of Chemistry, Allegaten 41, 5007 Bergen, Norway
(e-mail: anna.borgund@cipr.uib.no)
2) Norsk Hydro, Research Centre, Sandslivn. 90, 5254 Sandsli, Norway

Gas hydrates consist of gas molecules trapped in a framework of water molecules making a crystalline material. Formation of hydrates is temperature and pressure dependent, and natural gas hydrates can be a severe problem during petroleum production. The hydrates can either agglomerate into large hydrate clusters that may plug pipelines and platform equipment, or they may be unproblematic because they are present in the oil as a dispersion [1]. Some oils contain organic components that adsorb to the hydrate surface and prevent them from agglomerating, and the hydrate plugging tendency is thus correlated to crude oil composition [2, 3]. We are interested in identifying these active components for the purpose of utilizing this knowledge in the planning of better hydrate strategies. Such knowledge will be of help in understanding the morphological features of hydrate formation and also reveal information on the details of the kinetic and anti-agglomerant action. Ultimately, one may predict the plugging tendency of a given fluid system and develop differentiated hydrate strategies. Furthermore, the identification of the molecular structures is important for the development of new low-concentration hydrate inhibitors.

Due to the complexity of crude oil, fractionation must be performed in order to perform good molecular analysis. In this work, surface active components have been isolated by a variety of extraction methods: Ion exchange chromatography, column chromatography, and extraction by adsorption on freon hydrates [4], natural gas hydrates and ice. The extracts from hydrate plugging oils and non-plugging oils are then compared, and compositional differences are investigated in the search for natural hydrate inhibitors.

A sample set of 15 crude oils, spanning from heavy biodegraded oils enriched in asphaltenes to light non-biodegraded oils and condensates, has been analysed. Most of the oils originate from the Norwegian continental shelf. FTIR is used to get an indication of the functional groups in the molecules, and Gel Permeation Chromatography (GPC) is used to obtain information on the molecular weights. Liquid chromatography, gas chromatography and mass spectrometry are used for further molecular identification of the components. The results from GPC analysis show that the molecular weights are intermediate (around 500 g/mol). Standard geochemical analysing methods are therefore not well suited for molecular identification. The samples must be hydrolysed and derivatized for the GC-MS analysis to be possible. Hence, it has been necessary to introduce other analysing techniques, such as liquid chromatography, in order to handle samples of higher molecular weights.

Previous results have shown that non-plugging oils are biodegraded, but not all biodegraded oils are non-plugging. This indicates that the active components are products from microbial activity. Hence, biosurfactants are of particular interest. In fact, one particular biosurfactant structure has been found able to alter the plugging tendency of a crude oil from plugging to non-plugging when tested at realistic conditions in our laboratories.

The present results show that the extraction procedures on model hydrates and ice enrich the amount of polar components compared to the crude oil as a whole. This confirms the assumption that the components adsorbing to hydrate surfaces contain polar functional groups. Furthermore, the results generally show that biodegraded oils have more organic material associated with the hydrates than non-biodegraded oils, indicating that products from microbial activity may have a special affinity for these surfaces. No standard procedures are available as of today for identification of biosurfactants in crude oil. Hence, the analytical results are consistently compared to results for available biosurfactants which have been treated by corresponding procedures as the crude oil fractions. The relationship to bulk properties is modelled using multivariate statistical data analysis.

Results comparing the different types of extracts will be presented, emphasizing the molecular structural differences between biodegraded and non-biodegraded oils. The results will be related to the a priori knowledge on the plugging tendencies of the oils in the data set, and suggestions for natural hydrate inhibiting structures will be given.

References

[1] Sloan, E.D. Clathrate Hydrates of Natural Gases, 1990, Marcel Dekker, Inc, New York and Basel

[2] Fadnes, F.H. Natural hydrate inhibiting components in crude oils. *Fluid Phase Equilibria*, 117:186-192, 1996

[3] Gaillard, C., Monfort, J.P. and Peytavy, J.L. Investigation of methane hydrate formation in a recirculating flow loop: Modeling of the kinetics and tests of efficiency of chemical additives on hydrate inhibition. *Oil and Gas Technology*, 54(3):365-374, 1999

[4] Borgund, A.E., Høiland, S., Alagic, E., Askvik, K.M., Barth, T. and Fotland, P., Organic molecular analysis of hydrate adsorbing components. Presented at the 9th NMOG, Sept. 2004, Trondheim, Norway

OUM-1: Unraveling the source/maturity signature of crude oils in the Beaufort Mackenzie Basin using geochemical parameters within the context of petroleum mass fractions

M. Li, L.R. Snowdon, D. Issler

Geological Survey of Canada, 3303-33 Street NW Calgary, Alberta T2L 2A7, Canada
(e-mail: mali@nrcan.gc.ca)

Petroleum geochemistry contributes to exploration successes by providing key constraints for geological models and critical input to exploration scenarios. One of the most important tasks in a typical exploration program is to identify the most effective source intervals or kitchens in a basin, through oil-source correlation. The results of correlation are valid only if the geochemical parameters used address adequately the genetic characteristics of the source rocks as well as the mass transport and mixing processes of hydrocarbon fluids occurring in the carrier beds and reservoirs. This paper discusses the fundamental assumptions and potential flaws of the molecular geochemical parameters used with conventional oil-source correlation approaches. Several case studies in the Beaufort Mackenzie Basin (Canada) are presented to suggest the need of considering molecular geochemical parameters within the context of petroleum mass fractions in order to unravel the oil source/maturity signatures.

Beaufort-Mackenzie Basin contains significant petroleum resources. The discovery of large quantities of oil and gas in this Tertiary deltaic complex in the 1970s and 1980s resulted from, and promoted, extensive geological and geochemical studies in the region. Earlier correlation work suggests a significant contribution of terrestrial source rocks to the discovered oils in the Tertiary deltaic reservoirs, but many uncertainties remain unresolved. For example, the occurrence of bisnorlupanes in the oils from the Tertiary reservoirs was cited as evidence for the contribution of the Eocene Richards Formation to most of the oils, but the recent detection of these compounds in the older Taglu Formation suggests that they are not unique to the Richards Formation. In an attempt to define more source-specific molecular markers, we recently identified a number of partially aromatized triterpenoid hydrocarbons in the source rock extracts and crude oils of the Beaufort Mackenzie Basin. These compounds are present in much higher abundance and wider structural diversity than the conventional biomarkers, thus potentially adding new dimensions to biomarker analysis and reducing the uncertainty in oil-source correlation studies.

Another question that has yet to be answered is if there is any contribution of liquid hydrocarbons in the Tertiary reservoirs from the underlying but not confirmed Mesozoic source rocks. Whereas the resinite-rich Tertiary humic coals show variable hydrocarbon potential and are gas or gas condensate prone, Upper Cretaceous marine source rocks in the

Smoking Hills-Boundary Creek formations appear to have made significant contribution to the oils in the Tuktoyaktuk Peninsula-South Delta. Crude oils in the Kamik, Parsons and Siku discoveries also correlate well with Mesozoic nonmarine source rocks such as those in the Jurassic McGuire formations. The generally high gas/oil ratios for major Tertiary petroleum discoveries and the large variation observed in the absolute concentrations of many biomarker molecules in various source rocks suggest a highly possible scenario for fluid mixing and migration contamination when hydrocarbons generated in deeper source rocks migrate upward through highly fractured coal seams. Thus, the possible presence of Mesozoic source rocks beyond the Tuktoyaktuk Peninsula-South Delta cannot be ruled out based on available data.

Immature oils have been reported from many Cenozoic basins. Because of the large resource potential of such oils, several hydrocarbon generation models have been proposed. The low maturity levels of some of the oils in the offshore parts of the Beaufort Mackenzie Basin, as indicated by sterane isomerization ratios, were supported by a zigzag pattern in the hydrogen isotope distributions of *n*-alkanes. However, the many other oils appear to show internally inconsistent maturity signatures from parameters in different oil fractions. Variation in the aliphatic and aromatic biomarker concentrations observed from potential source rocks with different maturity levels suggests that the oil maturity signatures may be potentially compromised by migration contamination. Variation in the level of oil biodegradation could also create uncertainties in the use of gross oil compositions as an indicator of oil maturity. Although the recent rapid subsidence of the basins along the southern Arctic Ocean favor oil generation at relatively low maturity levels, most of the economic oils discovered in the Beaufort Mackenzie Basin appear to have derived from conventionally mature source rocks but contain lower maturity fluids admixed with them.

This study suggests caution with the use of conventional biomarker data in oil/oil and oil/source correlation when the concerned source rocks contain biomarkers in drastically different concentrations. Because many of the commonly used C_{15+} molecular tracers for source facies and maturity show several orders of magnitude variation in petroleum systems, they do not reliably track facies or maturity signals in mixed oils. Light hydrocarbon and aromatic hydrocarbon parameters are valuable in this situation. As mixtures are the norm, the concept of the source/maturity of oils needs revision. An alternative approach for oil-source correlation is needed to track the relationships of source/maturity indices and petroleum mass fraction for accumulated oils.

OUM-2: Unravelling mixed oils using multivariate statistical analysis

K. Manzano-Kareah[1], S. Ramos[2]

1) Institute of Geological and Nuclear Sciences Limited, 69 Gracefield Road, Lower Hutt, New Zealand (e-mail: k.manzano-kareah@gns.cri.nz)
2) Infometrix, Inc., 10634 E. Riverside Dr., Suite 250, Bothell, WA, USA, 98011

The Taranaki Basin, located on the west coast of the North Island, is currently New Zealand's only economic petroleum producing basin. This basin is approximately 100,000km^2 and in comparison to other basins of similar size, is considered to be relatively under-explored, with about 270 wells drilled since 1955. The total original reserves are estimated to be 465 MMBBL oil/condensate and 6470 BCF gas [1]. Previous studies have shown that most of the hydrocarbons discovered in the Taranaki Basin are derived from primarily terrestrial source rocks ranging from Late Cretaceous to Eocene in age [2]. Biomarker distributions and basin modelling studies have indicated that the hydrocarbons in some reservoirs may have been derived from multiple source rocks; however, quantifying the different contributions from potentially different sources using conventional geochemical techniques can be difficult.

This study uses a multivariate statistical approach to predict the relative proportions of end members in oil mixtures. In order to evaluate the use of the Alternating Least Squares method (ALS) [3] to unravel mixtures, four oils from the Taranaki Basin, (Maui-B, Kora-1, Kupe South-4 and Tariki-1A) were used to make twenty-two oil mixtures. Three of these oils, Maui-B, Kupe South-4 and Tariki-1A, are understood to be sourced from three different coaly source rocks, while the Kora-1 oil is derived primarily from a marine shale. The 22 oil mixtures include ten mixtures of two oils, six mixtures of three oils and six mixtures of all four oils. Whole oil GC-FID analysis was then carried out on the four end member oils and the 22 oil mixtures. GC-FID normal alkane peak areas and concentrations were analysed using ALS to unravel the mixtures. This presentation will demonstrate that ALS can be used to predict the number and the concentrations of end members in oil mixtures containing two, three or four different oils using GC-FID whole oil peak concentrations. Less accurate results were obtained using GC-FID whole oil peak areas.

References

[1] Ministry of Economic Development, 2004. New Zealand Oil Statistics. http://crownminerals.med.govt.nz/petroleum/facts/oil-stats.html.

[2] Killops, S.D., Woolhouse, A.D., Weston, R.J., Cook, R.A., 1994. A geochemical appraisal of oil generation in the Taranaki Basin, New Zealand. American Association of Petroleum Geologist Bulletin, 78, 1560-1585.

[3] Tauler, R., Kowalski, B., Fleming, S., 1993. Multivariate curve resolution applied to spectral data from multiple runs of an industrial process. Analytical Chemistry 65, 2040-2047.

OUM-3: The use of the hydropyrolysis of oil asphaltenes to characterise mixed oils from the Clair field

W. Meredith[1], C.E. Snape[1], C. Ugama[1], A.D. Carr[2], I.C. Scotchman[3], G.D. Love[4]

1) Nottingham Fuel and Energy Centre, School of Chemical, Environmental and Mining Engineering, University of Nottingham, NG7 2RD, UK (e-mail: William.Meredith@nottingham.ac.uk)
2) Advanced Geochemical Systems, Burton-on-the-Wolds, UK
3) Statoil, 11A Regent Street, London, UK
4) Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, USA

Catalytic hydropyrolysis (hypy), which refers to pyrolysis assisted by high hydrogen gas pressures (15 MPa) in the presence of a dispersed sulphided Mo catalyst, has been developed as a method for liberating covalently bound biomarkers from macromolecular organic fractions in coals, source rocks and crude oils. It possesses the unique ability to produce very high yields of aliphatic biomarkers compared to mild catalytic hydrogenation or traditional pyrolysis methods, whilst minimising alteration to their isomeric distributions (1). The bound biomarkers offer solutions to many problems in oil exploration, especially where the conventional geochemical approach using free biomarkers fails. A recent study has suggested that that bound biomarkers released from asphaltenes adsorbed to petroleum cores reveal the maturity and source characteristics of the oil that first came into contact with the carrier substrate, so allowing for the elucidation of migration pathways and reservoir filling events (2).

This study will describe the use of the hypy of oil asphaltenes to try and understand more about the source and filling history of oils from the Clair field in the West of Shetland area, which is one of the largest oil discoveries on the UK continental shelf. It is known to contain oils formed from the mixture of two distinct pulses, which vary both in terms of their source characteristics, and the degree of biodegradation to which they have been subjected (3).

In an attempt to identify the sources of the two components, the saturated hydrocarbon fraction isolated from a number of free oil samples, which are assumed to represent the non-biodegraded second charge of oil will be compared to that recovered from the hypy of the oil asphaltenes which are assumed to reflect the source characteristics of the first charge of oil (4). Preliminary results in Fig. 1 show that the distribution of *n*-alkanes in the free oils varies from the fairly waxy characteristics of a Type I source such as the lacustrine Middle Jurassic shales (e.g. oil A), to the more typical type II Kimmeridge Clay Formation (e.g. oil B) (3). Less variation was apparent in the probable source of the asphaltene phase, with all of the oils yielding asphaltenes, which generate an *n*-alkane envelope with a relatively waxy nature, similar to that of Middle Jurassic sourced oils, suggesting that the initial pulse of oil was single sourced.

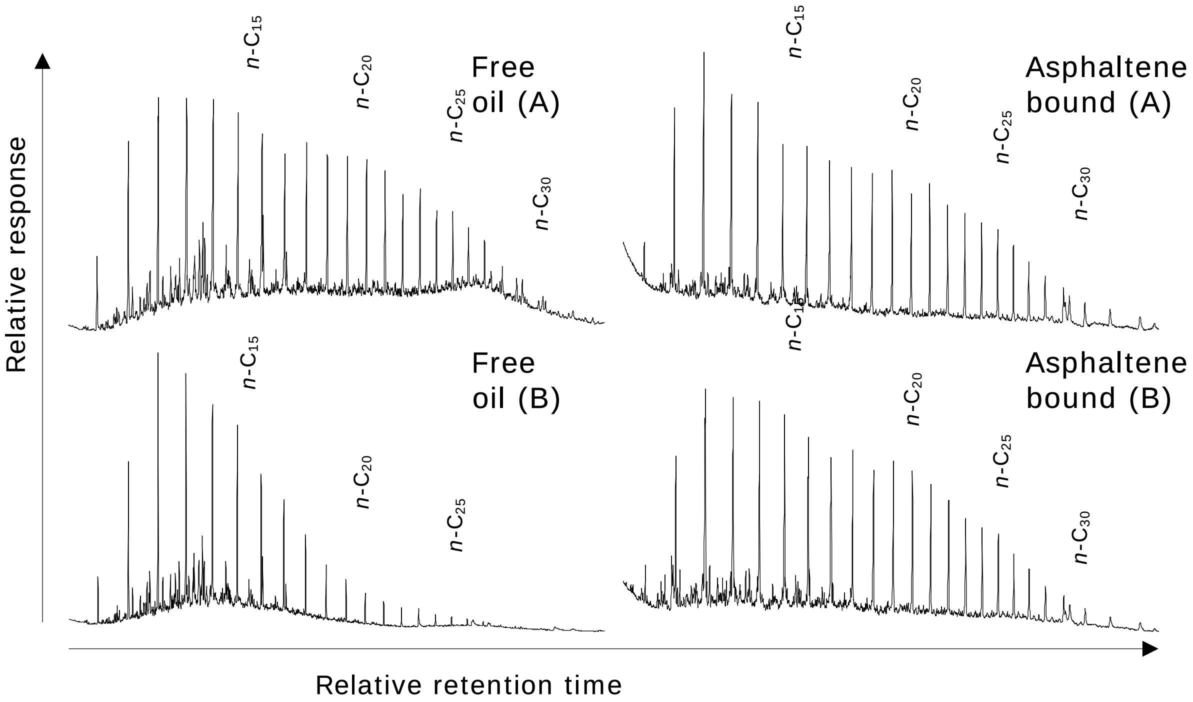


Fig.1. Gas chromatograms of the saturate hydrocarbon fraction from the free oil and aspahltene bound hypy products of 2 oils from the Clair Field

These interpretations will go on to be tested by assessing the compound specific stable isotopic composition of the biomarkers from the free and bound phases, together with those from source rock analogs. The asphaltenes adsorbed to oil stained reservoir cores, believed to represent the first charge of oil (2), will also be analysed.

References

[1] Love, G.D., Snape, C.E., Carr, A.D. and Houghton, R.C., 1995. Organic Geochemistry 23, 981-986.

[2] Russell, C.A., Snape, C.E., Meredith, W., Love, G.D., Clarke, E. and Moffatt, B., 2004. Organic Geochemistry 35, 1441-1460.

[3] Scotchman, I.C., Griffith, C.E., Holmes, A.J. and Jones, D.M., 1998. Organic Geochemistry 29, 671-700.

[4] Rooney, M.A., Vuletich, A.K. and Griffith, C.E., 1998. Organic Geochemistry 29, 241-254.

OGC-1: A reassessment of the source for a large, ultra-high pressured gas reservoir of China: clues from the associated condensates

Y. Sun[1], S. Xu[1], J. Chen[2], S. Zhang[2], D. Liu[1], P. Chai[1]

1) SKLOG, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Wushan, Guangzhou 510640, P. R. China (e-mail: ygsun@gig.ac.cn)
2) Research Institute of Petroleum Exploration and Development (RIPED), PetroChina, P. O. Box 910, Beijing 100083, P. R. China

The most exciting discovery of petroleum exploration at the end of last century in China is the Kela 2 gas field, located in the thrusting zones of the Kuche depression, Tarim basin, NW China. With about 280 billion m^3 of natural gas, this gas field is the biggest one discovered to date in China and becomes the main source for the "*Transport the Natural Gas from the West to East*" project in China. It is an anticlinal gas field, characterized by ultra-high pressure (Ac>2.0, Ac—the quotient of the measured pressure divided by the hydrostatic pressure). The gas contains more than 97% of methane and shows heavier carbon isotopic values of C_1-C_4 hydrocarbons (-28‰—17‰). Based on isotopic and compositional data, the natural gas was considered to be from Jurassic coal measures during catagenesis and metagenesis. However, mass balance calculations by Basin Modelling were not consistent with this conclusion (lower than the workable reserve)! This means that, except Jurassic coal measures, there should be other contributors and/or mechanisms involved for the gas generation and accumulation. Due to limited geochemical information from natural gas itself, it is still ambiguous and vigorously debated on the source of Kela 2 natural gas. In this presentation, we provide clues from the associated condensates to discuss the possibility of multiple sources for the Kela 2 gas field.

Molecular and isotopic geochemistry suggested that complex processes were involved for the generation and accumulation of condensates. A high C_{34}-homohopane and relatively high concentration of γ-cerane indicated a source of marine carbonates or evaporites (Carboniferous deposit?). Moderate maturity as revealed by molecular parameters and the occurrence of 25-norhopane suggested that it should be a residue of early-trapped oil that experienced biodegradation due to tectonic uplift at the end of Cretaceous Period. The rapid subsiding during the whole Cenozoic era prohibited further biodegradation with a reservoir temperature of up to 97-108°C.

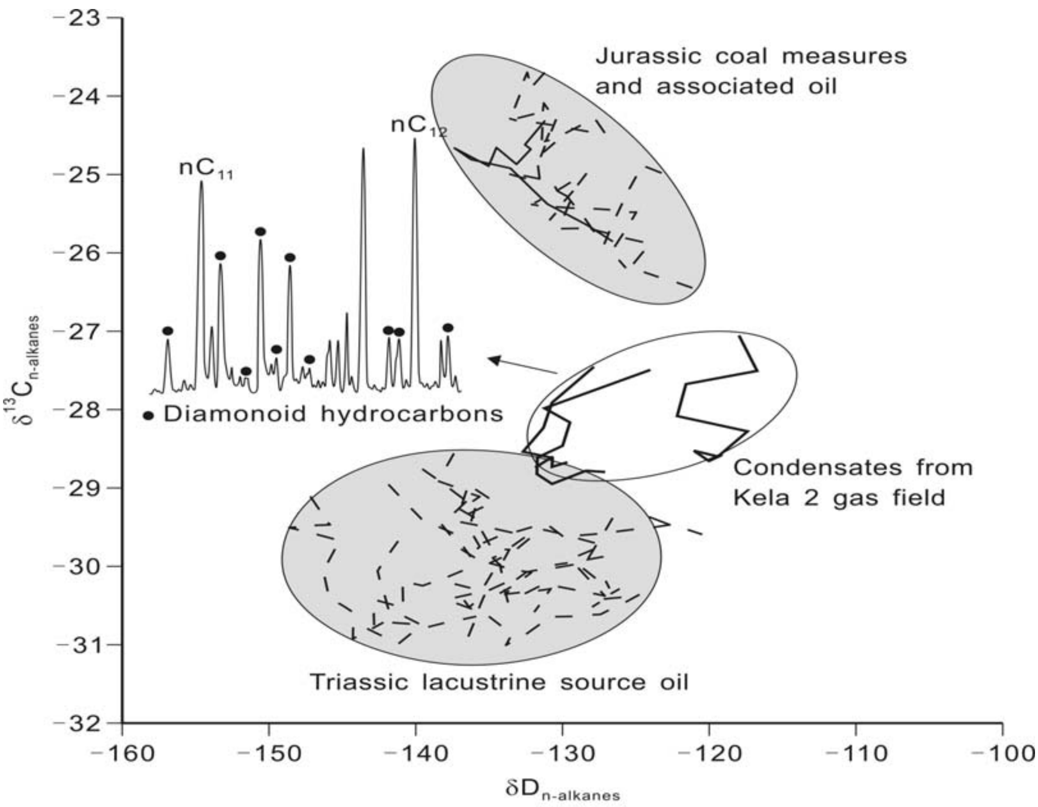


Fig. 1 Stable carbon and hydrogen isotopic profiles of nC13–nC20 from the Kela 2 condensates

Of the most interest is the high concentration of diamondoid hydrocarbons in condensates (Fig.1). The methyldiamantanes in condensates were dramatically concentrated to 1900ppm. Another prominent feature of light hydrocarbons is the abnormally high concentration of light aromatics (the ratio of toluene to n-C_7 up to 22). Although gas washing can be responsible for the enrichment of light aromatics and diamondoid hydrocarbons, there is little report on such a high concentration from the worldwide oil and we believe that, except fractionation, thermal alteration must take effects! In fact, using diamondoid hydrocarbon ratio proposed by Chen *et al.* (1996), the equivalent vitrinite reflectance of condensates reaches about ~1.7-1.9%. Furthermore, the stable carbon isotopic profile of *n*-alkanes showed two distinguishable stages: a steeply dipping $\delta^{13}C$ profile toward more negative values (-25 ~ -29‰) in the range of nC_{13} — nC_{19} and a relatively flat $\delta^{13}C$ profile (~-29‰) in the range of nC_{20} — nC_{30}. The data set strongly suggested that the condensates were mixed with different sources. According to the geological background and hydrocarbon-generated history, the low molecular weight part of condensates possibly generated from Triassic lacustrine source rocks at the stage of high to over maturation, or oil cracking, or a mixture of the Jurassic- and Triassic-sourced oils. Interestingly, GC/MS analysis of aromatic fractions revealed a series of unusually high molecular weight nonalkylated, pericondensed (i.e., fused six-membered ring aromatics) PAHs. These PAHs were few reported to occur in natural petroleum and they believed to be formed by ring condensation during progressive maturation (Sun *et al.*, 2002). In such a way, we infer Trassic-sourced oil cracking as a main factor responsible for the unusual distribution of light hydrocarbons. As showed in Figure 1, thermally induced changes in $\delta^{13}C$ and δD of *n*-alkanes are well overprinted in the range of nC_{13} — nC_{20}. The $\delta^{13}C$ of individual *n*-alkanes are enriched in 13C relative to that of unaltered Triassic-sourced oils with the excursion up to ~2-5‰ and the δD values with the excursion up to ~10-30‰, indicating a typical isotopic trend progressively shift towards heavier isotopic compositions with increasing thermal stress.

The integration of geological and geochemical data clearly showed that, except well-known Jurassic coal-genetic gas, oil-cracking gas also made an important contribution to the formation of the kela 2 gas field. Theoretically, pyrobitumen would be expected due to the hydrogen mass balance of oil cracking in reservoir. However, it is not the case of the aimed reservoir and suggests that oil cracking must occur in deeper reservoir or source body, which further evidenced by the relatively low homogenization temperature of fluid inclusions in diagenetic quartz overgrowths (100-140°C). This means that oil-cracking gas and associated condensates have the same filling history and the Kela 2 is a late accumulated gas reservoir. Geochemical evidences from fluid inclusions indicated that gas migrated into the reservoir in the last 5Ma and it coincides well with the development of the anticlinal structure of the Kela 2 (start at about 5 Ma b.p.). In conclusion, the deep natural gas kitchen evolves into vertical degassing features accompanied by tectonic uplift. The charge model for natural gas in this overpressured petroleum system suggested in which the tectonic uplift play an important role in the migration of gas and associated condensates into the trap. It also can conclude that the early-trapped residue oil has no genetic relationship with the Kela 2 natural gas.

References

Chen J, Fu J, Sheng G, Liu D, Zhang J, 1996. Organic Geochemistry 25, 179-190; Sun Y, Xu S, 2002. Geochim. Cosmochim. Acta 66, P. A753.

OGC-2: Biogenic and thermogenic coalbed gas in the Illinois Basin: insight from compound-specific carbon isotopic ratios

D. Strapoc[1], M. Mastalerz[2], A. Schimmelmann[1], C. Eble[3]

1) Indiana University, Dept. of Geological Sciences, 1001 E. 10th St., Bloomington, IN 47405 (e-mail: dstrapoc@indiana.edu)
2) Indiana Geological Survey, 611 N. Walnut Grove, Bloomington, IN 47405
3) Kentucky Geological Survey, University of Kentucky, Lexington, KY 40506

The coalbed gas potential in the Illinois Basin has been previously underestimated owing to the low rank of coals and their low thermogenic gas potential. Our recent compositional and isotopic data suggest that, in addition to thermogenic gas, these coals contain a significant contribution of biogenic gas, making the Illinois Basin (i) an important coalbed methane target and (ii) a natural laboratory to study gas generation and its geological controls on a basin-wide scale. Multiple drill sites in the SE Illinois Basin (Pennsylvanian age) provided gas samples from five Pennsylvanian-age coal beds. We determined (i) $^{13}C/^{12}C$ ratios in hydrocarbons C_1 (=CH_4), C_2, C_3, *i*-C_4, *n*-C_4 and in CO_2 and (ii) D/H ratios in C_1. The coal beds range from 100 to 350m in depth and represent high volatile bituminous coal (R_o 0.54 to 0.75%).

The assessment of biogenic versus thermogenic gas origins was aided by gas compositions and isotopic data from canister desorption experiments. For up to four months, we periodically collected coalbed gas samples from desorption canisters to assess prolonged compositional and isotopic fractionation during gas desorption. Methane desorbs more readily than CO_2 due to preferential adsorption of CO_2 over methane on coal [1]. The concentration of CO_2 in desorbing gas increases by 50% from the first to the fiftieth day of desorption. Desorbed C_1 and CO_2 become gradually ^{13}C-enriched by 2 and 9‰, respectively, as isotopically light molecules desorb from and/or diffuse faster out of coal. Our isotopic time-series of coalbed gas desorption data indicate that gas samples collected from desorption canisters between day 6 and day 12 of desorption (when approximately 50% of gas has been desorbed) express the weighted average isotopic values of the total desorbed gas.

The gases vary compositionally depending on coal maturity. For example, gas from 100m-deep Springfield coal from southwest Indiana having an R_o of 0.56% contains 98% C_1 and only trace amounts of C_{2+}, whereas the age-corresponding more mature coal bed in western Kentucky at a depth of 350m and R_o of 0.75% yields gas having 5.6% C_2 and 1.3% C_3. These Indiana and Kentucky coalbed gases also differ isotopically having $\delta^{13}C_{CH4}$ = -63.1‰ and -49.5, and $\delta^{13}C_{CO2}$ = 2.8‰ and -20.6‰, respectively (Fig. 1). Compositional and carbon isotopic differences are interpreted in terms of various origins and processes involved in gas genesis. Since our coals are at or above the threshold for thermogenic gas generation (R_o ~ 0.55%), the gases are usually of mixed thermogenic and biogenic origin, with the biogenic component being formed by a microbial CO_2 reduction pathway. Using Katz's approach [2] we estimate that the biogenic component is negligible in the highest-rank Springfield coal in western Kentucky. For lower-rank Springfield coal in Indiana and eastern Illinois, the contribution of biogenic gas ranges from 57% to 100%. Proportions of thermogenic versus biogenic gas for other coal beds show similar variability.

The general dependence between coal rank and coalbed gas origin cannot, however, account for all observed variations in the gas composition. We suggest that isotopic variations within coal beds may also be related to differences in the hydrogeologic setting. Infiltrating meteoric and ground waters could provide a conduit for inoculation with methanogenic bacteria. Access could have been provided by a tectonic or erosional uplift shortly after the Pennsylvanian or after the last Pleistocene deglaciacion and rebound [3]. Infiltrating water might also facilitate microbial oxidation of methane, resulting in the shift in isotopic composition of the gas in the roof rocks towards thermogenic values (Fig. 1).

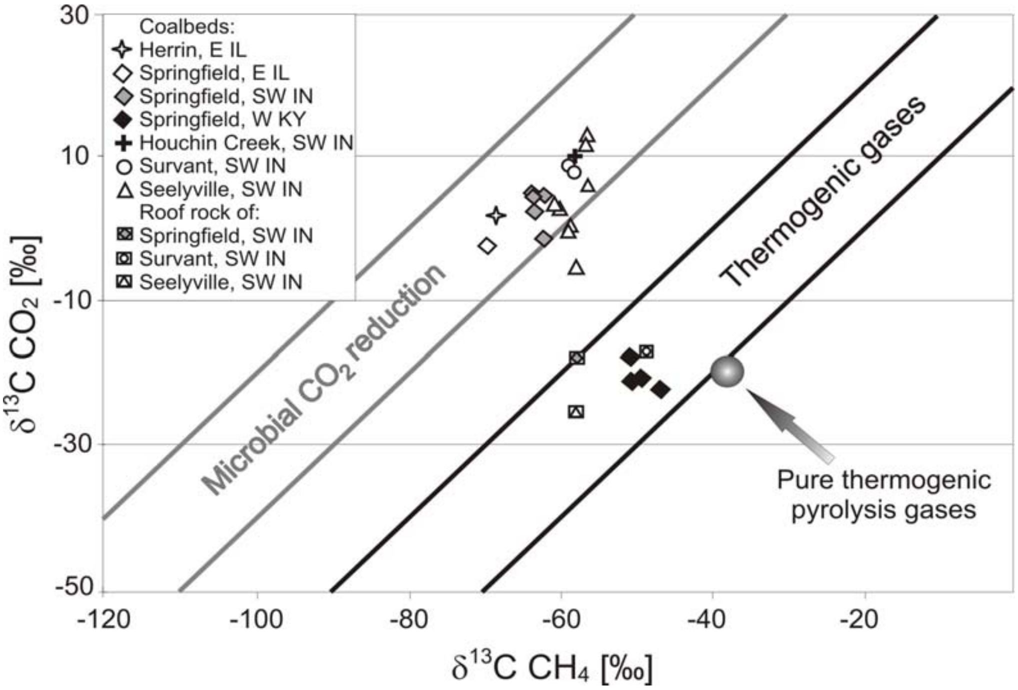


Fig. 1. Coalbed gas carbon isotopic data from the SE Illinois Basin. Genetic ranges of gases and pyrolysis data after Smith and Pallasser 1996 [4]

References

[1] Mastalerz M, Gluskoter H and Rupp J, 2004, Carbon dioxide and methane sorption in high volatile bituminous coals from Indiana, USA. International Journal of Coal Geology 60, 43-55.

[2] Katz B, Narimanov A and Huseinzadeh R, 2002, Significance of microbial processes in gases of the South Caspian basin. Marine and Petroleum Geology 19, 783-796.

[3] Martini AM, Walter LM, Ku TCW, Budai JM, McIntosh JC and Schoell M, 2003, Microbial production and modification of gases in sedimentary basins: Ageochemical case study from a Devonian shale gas play, Michigan basin. AAPG Bulletin 87 (7), 1355-1375.

[4] Smith JW and Pallasser RJ, 1996, Microbial origin of Australian coalbed methane. AAPG Bulletin 80(6), 891-897.

OGC-3: Predicting gas composition and its effect on petroleum phase behaviour during secondary migration

R. di Primio, B. Horsfield, A. Fuhrmann

GFZ-Potsdam, 14473 Potsdam, Germany

The possibility to model petroleum composition during hydrocarbon generation as well as the PVT behaviour of the fluids during migration is now available in modern basin modelling software packages. The main problem in determining petroleum compositions from pyrolysis results lies in the fact that while the gas to oil ratio (GOR) and the liquid composition can correctly be assessed, the gas composition, which primarily controls fluid phase behaviour, is always too wet (e.g. Mango, 1992; 1996; 2001). For hydrocarbon compositional predictions aiming at modelling petroleum phase behaviour during migration and entrapment, this implies that the predicted changes of petroleum physical properties during migration, including timing and volumetrics of phase separation, will be incorrect.

In the comparison of PVT data from natural petroleum maturity series provided by our industry sponsors and closed-system pyrolysis of the corresponding source rocks we have recognised that gas composition is strongly heating rate dependent. Based on these results alone we can conclude that kinetic descriptions of the generation of individual gas compounds as measured in the laboratory are invalid for geologic heating rates. Bulk oil and gas generation are, however, not heating rate dependent as discussed earlier by Dieckmann et al. (2000).

Interestingly, gas composition is systematically related to GOR in natural fluids, whereby correlation coefficients are excellent for unaltered fluids from individual source rock organofacies (Figure 1). This observation allows the difference between pyrolysate gas composition and live oil gas composition of samples related using their respective GORs to be characterised. Pyrolysis compositions were seen to systematically overestimate gas dryness at low conversion rates (corresponding to early-mature natural fluids) whereas the well-known too wet gas composition was seen to be typical for transformation ratios above roughly 30%.

The individual organic facies types analysed showed also differences in the degree of over- or underestimation of gas wetness as compared to the related natural fluids. We have tentatively related heating rate dependent compositional variability of the gas phase to a temperature prefference of radical reaction extent leading to wet gas dominated fluids at high temperatures and dry gas at lower (geologic) temperatures.

In an attempt to correct pyrolysis gas compositions we have trained neural networks to predict natural fluid composition based on closed system pyrolysis results. Neural network predictions resulted in a near perfect match to natural fluid compositions (error < 5%).

Integration of compositional predictions from the neural networks and compositional kinetic models for bulk gas and oil generation determined for the individual source rocks allowed the definition of multi-compound kinetic models which correctly reproduce petroleum composition and, hence, also phase behaviour. These models have been implemented and tested in basin and fluid flow modelling with excellent results regarding GOR, saturation pressure and API gravity prediction.

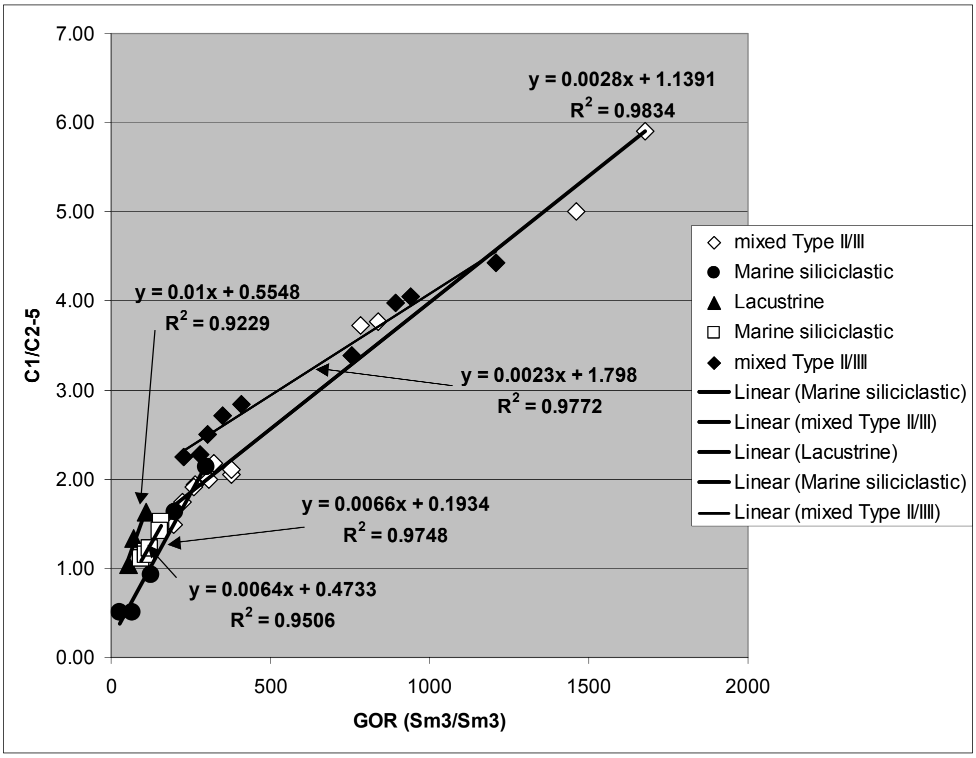


Fig.1. Correlation of GOR and gas dryness for petroleum fluids from different source rock types

References

Dieckmann, V., Horsfield, B. And Schenk, H.J., 2000. Heating rate dependency of petroleum-forming reactions: implications for compositional kinetic predictions. *Organic Geochemistry*, **31,** 1333-1348.

Mango, F.D., 1992. Transition metal catalysis in the generation of petroleum and natural gas. *Geochimica et Cosmochimica Acta*, **56,** 553-555.

Mango, F.D., 1996. Transition metal catalysis in the generation of natural gas. *Organic Geochemistry*, **24,** 977-984.

Mango, F.D., 2001. Methane concentrations in natural gas: the genetic implications. *Organic Geochemistry*, **32,** 1283-1287.

OGC-4: Using gas geochemistry to determine commingling in East Breaks 160 (Cerveza) Field, offshore Gulf of Mexico

R. Patience[1], C. Schile[1], E. Graven[1], K.K. Bissada[2]

1) Unocal, P.O. Box 5076, Sugar Land, TX 77487-5076, USA
2) Dept. of Geosciences, University of Houston, Houston, Texas, USA

Cerveza Field

The Cerveza Platform is located ~150 miles south of Houston, in 900 feet of water (Figure 1). The platform was set in 1981, followed by the drilling of 19 development wells. Production began in March 1987. The deepest production has been from the Late Pliocene *Globoquadrina altispira* (GA) and *Globorotalia miocenica* (GM) sands at depths of 6500-9200 feet TVD, which have produced over 30 billion cubic feet (BCF) of gas and 6 million barrels of oil (MMBO). The most prolific zones are the overlying Early Pleistocene *Hyalinea balthica* (HB) sands at depths of 5500-6200 feet, which have produced over 35 BCF and 5 MMBO. Minor production of 3.4 BCF has come from the shallower Middle Pleistocene *Trimosina A* (TA) sands at depths of 4100-4400 feet.

A persistent regulatory issue at Cerveza Platform has been the sustained gas pressure on many of the casing annuli. In some cases these sustained casing pressures (SCP) have reached over 1000 psi. When the pressures are bled off, they take several days to build back, indicating poor communication with the gas source. One explanation for the source of this gas is the blowout which occurred while drilling the A28 well in 1983 in the TA sands at roughly 4000'. This blowout may have charged shallower sands and thus resulted in SCP on many of the shallow drive pipes and conductors. However, this scenario does not explain the SCPs observed on many of the deeper intermediate casing strings.

Work program

To gain a better understanding of the source of the SCP, a work program was initiated to investigate the potential of gas isotopes as a means to track the source of the pressure. This was based on the knowledge that there are decreasing amounts of isotopically light, biogenic methane in the formation (tubing) gases with increasing stratigraphic age. TA contains the most biogenic gas with $\delta^{13}C$ values < -60‰ for methane, whilst GA and GM have $\delta^{13}C$ values for methane of around -48‰. Gas dryness (%methane/sum of %C1 to C5) declines from ~0.99 in TA to 0.91 in GA and GM. Hence, determining the isotopic and chemical composition of the casing gas should allow recognition of the source of the pressure. Six wells were chosen for gas analysis. A total of 26 casing gases and 6 formation (tubing) gases was analysed for chemical and isotopic composition.

Results & Discussion

Of the six wells, four gave results which could be readily interpreted in terms of allocating the source of the gas and hence the pressure. The fifth well showed no change in isotopic composition with depth. This well also had no formation gas sample, and so interpreting these data was problematic. The sixth well showed a zigzag pattern of changing isotopic composition with depth which could not be interpreted.

In the four wells with both systematic carbon isotopic changes and a formation gas sample, the pattern was the same in each case. The shallower the casing point, the more likely the gas was to come from the predominantly biogenic gas originally in the TA formation. In contrast, the deeper the casing point, the more likely it was that the gas came from the deeper HB or GA/GM formations. Thus the original hypothesis, whereby the blowout had charged shallower sands with gas which was in turn the source of the casing pressure, was not correct for the deeper casing points, since the pressure here was caused mainly by gas from the deeper (HB, GA, GM) formations. The conclusion was also that producing the formation gas and hence lowering the formation pressure should help to relieve the pressure on the casing.

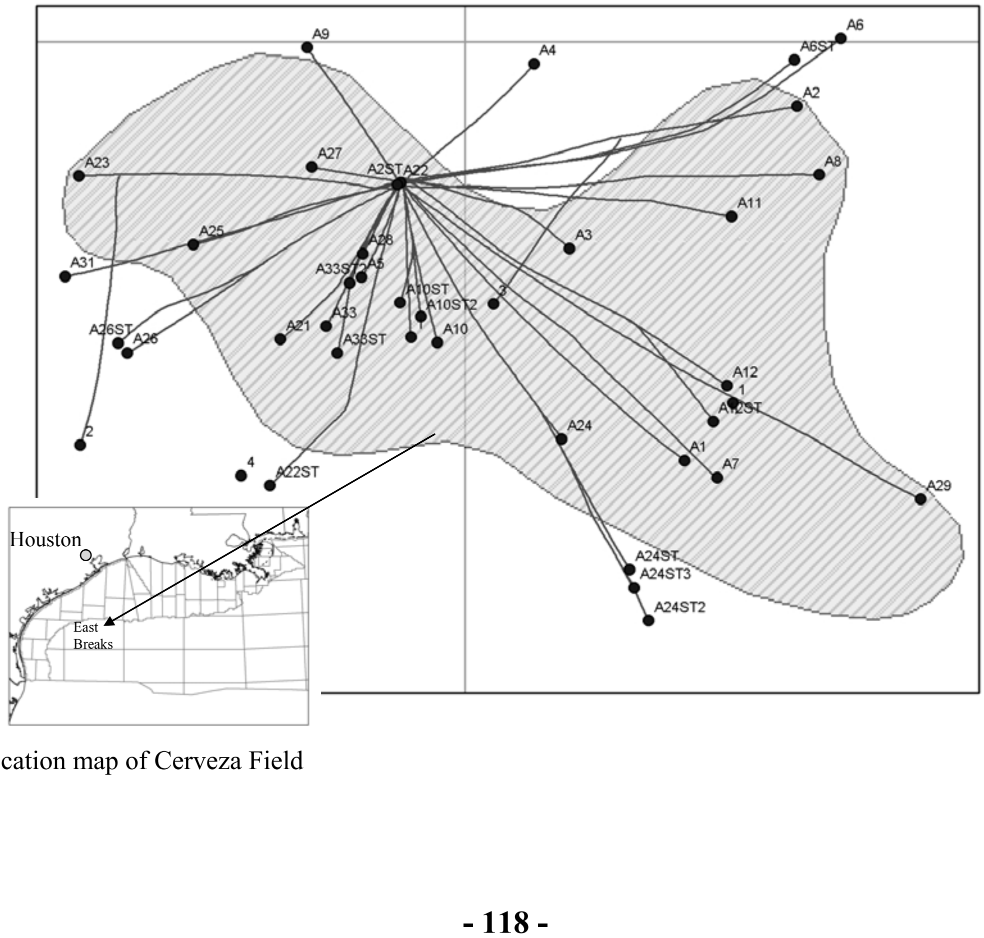


Fig.1. Location map of Cerveza Field

OGPR-1: Metal sulfide catalyzed geosynthesis of lipids from carbon oxides and hydrogen sulfide: implications for prebiotic chemistry and organic geochemistry

S. Dubant, P. Adam, P. Albrecht

Laboratoire de Géochimie Bioorganique, Université Louis Pasteur ECPM, 25 rue Becquerel, 67200 Strasbourg, France (e-mail : padam@chimie.u-strasbg.fr)

Compartimentalization is a prerequisite for the emergence of cellular life on earth. This role might have been insured by amphiphilic molecules due to their capacity to undergo self assembly . In this respect, *n*-carboxylic acids can be considered as the simplest structures able to fulfill the requirements for such a function. Therefore, a viable prebiotic pathway to their synthesis or that of related lipids would fill a huge gap in the first steps of life emergence on Earth. The possibility that the conditions prevailing in the environment of hydrothermal vents are likely to favour the abiotic geosynthesis of lipidic compounds has been investigated by means of laboratory simulation experiments. These experiments involving constituents of the fluids emitted in the sea by hydrothermal vents (metal sulfides and gases like H_2S, CO_2, CO, Merlivat *et al.*; 1987) have been performed under conditions compatible with those prevailing in the vicinity of these vents.

Laboratory experiments involving carbon oxides (CO_2 or CO), hydrogen sulfide and *in situ* precipitated metal sulfides (Fe, Ni, Co) in water at low temperature (90°C) resulted in the formation of several reduced C_1 to C_5 organic compounds (thiols, carboxylic acids, thioacids) by a combination of C-C bond forming reactions and reductive processes. It could be shown that carbon monoxide is a key intermediate in this abiotic synthetic process leading to organic compounds. It may have been available directly in the environment (e.g. volcanic gases). Otherwise, we also demonstrated that it can most probably be formed *in situ* from CO_2 and H_2 *via* the "water-gas shift" equilibrium in hydrothermal settings. H_2 might originate from reaction of hydrogen sulfide with iron sulfide leading to pyrite (Rickard and Luther; 1997) or from serpentinization (Berndt *et al.*; 1996). Among the minerals emitted by hydrothermal vents, nickel and cobalt proved to be more efficient catalysts (but less abundant) than iron, at least for the C-C bond forming reactions.

Simulation experiments performed on reference compounds showed that under the experimental conditions, any thiol can be homologated to a longer thiol or carboxylic acid possibly *via* the related thioester or thioacid. Since methanethiol, the simplest thiol, can be easily formed from carbon oxides (CO, CO_2) under the same conditions, this opens an iterative reaction pathway able to go from a C_1 carbon oxide to thiols and carboxylic acids with any chain length (Fig 1). This is a yet unprecedented process which is operative in water under geochemically plausible conditions. It could also be shown that the key reactions involved in this iterative chain elongation process, namely, the C-C bond forming reaction involving a thiol and CO and the subsequent reduction reactions are both catalysed by reduced metallic species (possibly metals at the degree of oxidation 0) formed by reduction of metal sulfides by H_2S. A complete catalytic pathway involving reduced metallic species and able to explain most of the observed reactions has been suggested.

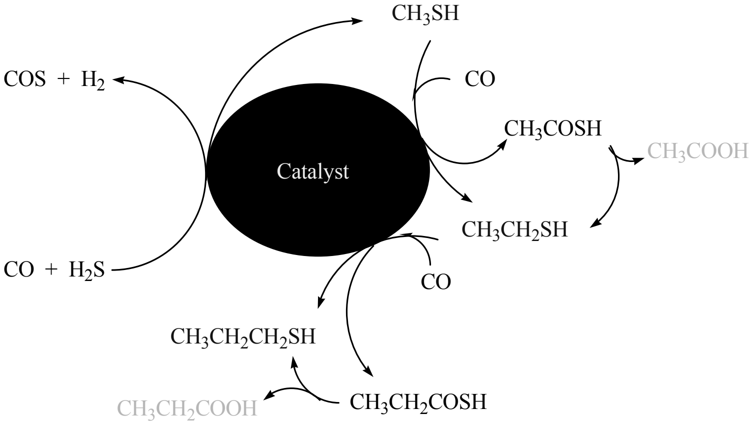


Fig.1. Summary of the processes leading from carbon monoxide to both thiols and carboxylic acids with any chain length

Besides, the same conditions may also result in the desulfurization of thiols (alkylthiols, aromatic thiols) and in the reduction-sulfurization of various functionalities (carbonyls, double bonds, etc.). Such a synthetic iterative pathway might therefore also explain to some extent the reported abiotic formation of saturated hydrocarbons observed in some particular geological settings. In addition, the particular reactions involved in this pathway might be effective in the sulfurization and reduction processes affecting organic matter in any natural sulfur-rich anoxic environment where metal sulfides are available.

References

Berndt M. E., Allen D. E., Seyfried, Jr, W E.; *Reduction of CO_2 during Serpentinization of Olivine at 300°C and 500 bar*; Geology **24**; 351-354 (1996).

Merlivat L., Pineau F., Javoy M.; *Hydrothermal Vent Waters at 13°N on the East Pacific Rise: Isotopic Composition and Gas Concentration*; Earth and Planetary Science Letters **84**; 100-8 (1987).

Rickard D. and Luther G. W. III; *Kinetics of Pyrite Formation by the H_2S Oxidation of Iron(II) Monosulfide in Aqueous Solutions Between 25 and 125°C: The Mechanism*; Geochimica et Cosmochimica Acta; **61**; 135-47 (1997).

OGPR-2: Branched alkanes in Precambrian manganese carbonates and modern hypersaline environments

M.B. Vogel[1], D.J. Des Marais[1], D. Zinniker[2], J.M. Moldowan[2]

1) Exobiology Branch, NASA Ames Research Center, MS 239-4, Moffett Field, California, 94305-1000, USA (e-mail: mvogel@arc.mail.nasa.gov)
2) Geological and Environmental Sciences Department, Stanford University, Stanford California, 94305-2115, USA

Branched alkanes are a prominent class of compounds in biomarker distributions in many Precambrian samples and in modern sediments [1], [2]. Carboxylic acid precursors and methyl- and dimethylalkanes are a significant lipid component of cyanobacterial cultures and both ancient and modern cyanobacterial mats [3], [4]. High concentrations of branched alkanes have been associated with redox gradients, anaerobic and/or microaerophilic environments, the presence of sulfur oxidants, and inputs by chemoautotrophic organisms [1], [5]. Critical questions concerning branched alkanes are whether these compounds derive from organisms using a specific metabolic pathway (i.e. sulfur oxidation, sulfate reduction, methanogenesis) and what factors contribute to their accumulation in sediment (composition of phototrophic biomass, oxide reduction, fermentation, etc.). Systematic description of branched alkanes is complicated by the diversity in position and structure of alkyl groups and a number of reports, especially concerning dimethylalkanes, have been subject to re-interpretation [6].

We report on a series of methyl- and gem-dialkylalkanes (GDAs) occurring in Precambrian rhodochrosites ($MnCO_3$) and modern cyanobacterial mats from salt crystallizers at Guerrero Negro, Baja California Sur, Mexico. Of the more than 19 series of compounds eluting between n-alkanes in rhodochrosite samples, 4 series of dimethyalkanes, 4 series of diethylalkanes and 2 series of butyl-, ethylalkanes were identified using GCMS-SIR, mass spectra and relative retention factors. Cyclohexanes and cyclopentanes are also present, as are homologous series of aryl-alkanes. Chromatograms recording higher molecular weight fragments indicate that the C_{16} – C_{19} homologs (hexadecane to nonadecane) are the most abundant, consistent with n-alkane distributions that also maximize at C_{16} - C_{19}. GDAs with functional groups at odd numbered carbon sites are more prevalent than those with functional groups at even number carbon sites. Most GDAs with alkyl groups at odd numbered carbons have extreme odd over even preference while GDAs with alkyl groups at even numbered carbons have extreme even over odd preferences.

The abundance and diversity of GDAs in manganese carbonates suggests an association with metal oxide reduction as well as the fermentative processes that involve sulfate reduction and methanogenesis. The biomass in rhodochrosites is expected to reflect the contributions of microbial consortia involved mainly in Mn reduction as this pathway is energetically more favorable than sulfate reduction in the anaerobic oxidation of organic acids. Sulfate reduction is inhibited by low electron donor availability in zones of the sediment column where Mn and Fe are available ([7] and references therein). Manganese reducing bacteria such as *Shewanella putrefaciens* are thus the anticipated biological sources of GDAs in rhodochrosite samples. Alternatively, the presence of GDAs may be due to similar preservation potential of anoxic environments where metal and sulfur are terminal electron acceptors. Querying hypersaline environments can provide constraints on the distinction between various bacterial and archaeal sources of GDAs. The Guerrero Negro crystallizer ponds offer voluminous cyanobacterial mats as sources for methyl- and dimethylalknes. High concentrations of sulfate and organic acids in the salinity continuum present a range of dissimilatory environments in which to document the chemolithotrophic and chemoörganotrophic affinities of GDAs.

References

[1] Kenig, F., Simons, D.H., Crch, D., Cowen, J.P., Ventura, G.T., Rehbein-Khalily, T., Brown, T.C. and Anderson, K.B., 2003. Branched aliphatic alkanes with quaternary substituted carbon atoms in modern and ancient geologic samples. Proceedings of the National Academy of Sciences 100, 12554 – 12558.

[2] Greenwood, P.F., Arouri, K.R., Logan, G.A. and Summons, R.E., 2004. Abundance and geochemical significance of C_{2n} dialkylalkanes and highly branched C_{3n} alkanes in divers Meso- and Neoproterozoic sediments. Organic Geochemistry 35, 331 – 346.

[3] Köster, J., Volkman, J.K., Rullkötter, J., Scholz-Böttcher, B.M., Rethmeier, J. and Fischer, U., 1999. Mono-, di- and trimethyl-branched alkanes in cultures of the filamentous cyanobacterium *Calothrix scopulorum*. Organic Geochemistry 30, 1367 – 1379.

[4] De Leeuw, J.W., Sinninghé Damste, J.S., Klok, J., Schenck, P.A. and Boon, J.J., 1985. Biogeochemistry of Gavish Sabkha sediments. In Freidman, G.M. and Krumbein, W.E., (Eds.) Hypersaline Ecosystems. Springer – Verlag, Berlin. pp. 350 – 367.

[5] Zinniker, D. (2005) New Insights into molecular fossils: Fate of terpenoids and the origin of gem-alkylalkanes in the geological environment: *Stanford University Ph.D Thesis*.

[6] Mycke, B., Michaelis, W. and Degens, E.T., 1988. Biomarkers in sedimentary sulfides of Precambrian age. Organic Geochemistry 13, 619 – 625.

[7] Lovely, D.R., Holmes, D.E., and Nevin, K.P., 2004. Dissimilatory Fe (III) and Mn (IV) reduction. Advances in Microbial Physiology 49, 259 – 287.

OGPR-3: A >90 million year molecular record of neoproteroic sponges (Porifera) in the South Oman Salt Basin

G.D. Love[1], E. Grosjean[1], D.A. Fike[1], J.P. Grotzinger[1], S.A. Bowring[1], D. Condon[1], A.N. Lewis[1], C. Stalvies[2], C.E. Snape[3], R.E. Summons[1]

1) Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, MA 02139, USA (e-mail: glove@mit.edu)
2) School of Civil Engineering and Geosciences, University of Newcastle upon Tyne, NE1 7RU, U.K.
3) Nottingham Fuel & Energy Centre, School of Chemical, Environmental and Mining Engineering, University of Nottingham, NG7 2RD, U.K.

The earliest, widely accepted, evidence for metazoa reported thus far in the geological record comes from sponge fossils, in the form of siliceous monoaxonal spicules and preserved larvae, recovered from the Upper Phosphorite Bed of the Doushantuo Formation China of 600-570 Ma (Li et al., 1998). This is at least as old as the oldest known Ediacaran impression so it is clear that metazoan radiation was initiated even earlier in the Neoproterozoic. The application of molecular biomarkers to the study of early metazoan evolution has much to commend it since primitive, soft-bodied animals are likely to have had poor preservation and no potential for leaving a trace fossil record. Here we report molecular evidence, in the form of uncommon sterane distributions in marine source rocks from the South Oman Salt Basin (SOSB), for a radiation in Porifera occurring prior to 630 Ma. The sample suite investigated spans a timescale of ca. 540-711 Ma from U-Pb geochronology of volcanic ash beds and detrital zircons.

Sponges are hosts to a large diversity of symbiotic microorganisms, encompassing microalgae, bacteria, archaea and fungi, and a variety of unusual and conventional steroid structures have been detected in their extracts (Aiello et al., 1999). So caution must be exercised in targeting fossil molecular markers for sponges. It appears, however, that 24-isopropylcholestanes are reliable molecular fossil markers for sponges (McCaffrey et al., 1994) since the precursor 24-isopropylcholesterols and related structures (Hofheinz and Oesterhelt, 1979) appear to be ubiquitous lipid components of the class *Demospongiae*, and these have not yet been reported as constituents of any other organisms.

MRM-GC-MS analysis of aliphatic hydrocarbon fractions has allowed investigation of the distributions of trace biomarker compounds, such as C_{30} steranes, which are not abundant enough to analyse in detail by conventional GC-MS. The ratio of 24-isopropylcholestane / 24-n-propylcholestane (for $\alpha\alpha\alpha$ 20S+20R isomers) was measured and found to be anomalously high (0.8-15) in all Neoproterozoic-early Cambrian SOSB sediments in comparison with Phanerozoic and mid-Proterozoic oils and bitumens which we have analysed and with those reported previously (typically <0.5) by McCaffrey et al. (1994). The 24-*n*-propylcholestanes are molecular markers for marine chrysophyte algae (Moldowan et al., 1990) and so provide a benchmark for inputs of sponge biomass, relative to these algae, to sediments through geological time. We propose that only a significant input from sponges could result in such a high value for this 24-iso / n-propylcholestane ratio. Hydropyrolysis (pyrolysis assisted by high hydrogen gas pressures-15 MPa) of extracted sediments and prepared kerogens indicates that 24-isopropylcholestanes are genuine, covalently-bound molecular components of immobile kerogen and not simply constituents of younger petroleum that have migrated into these older rocks. This is key evidence for proving that the 24-isopropylcholestane biomarkers were deposited synchronously with the host sediment. Unusually high relative of amounts of 27-norcholestanes and, as yet unidentified C_{19} steranes, which co-occur in SOSB bitumens and kerogens, may also reflect an input from sponges.

A marine source rock from the pre-salt Ghadir Manquil Fm. in the SOSB, deposited between the Marinoan (ca. 630 Ma) and Sturtian (ca. 712 Ma) glaciation events, contained abundant free and kerogen-bound 24-isopropylcholestanes (iso / n-propylcholestane = 3.1 for free steranes) and so this constitutes the oldest, presently known, evidence for metazoa in the geological record. This finding suggests that the initial radiation of Porifera, the most primitive metazoa, occurred prior to 630 Ma and may be a response to environmental conditions prevailing during the the Neoproterozoic C-cycle perturbations that signal major redox change in the ocean (Rothman et al., 2004). The timing of the sponge biomarker appearance corresponds remarkably well to divergence ages for *Demospongiae* based on the most recent molecular clock studies based on metazoan proteins (Peterson et al., 2004).

References

Aiello, A., Fatturusso, E., Menna, M., 1999. Steroids from sponges: Recent reports. Steroids 64, 687-714.

Holfheinz, W., Oesterhelt, G., 1979. 24-Isopropylcholesterol and 22-Dehydro-24-isopropylcholesterol, novel sterols from a sponge. Helvetica Chimica Acta 62, 1307-1309.

Li, C.-W., Chen, J.-Y., Hua, T.-E., 1998. Precambrian sponges with cellular structures. Science 279, 879-882.

McCaffrey, M.A., Moldowan, J.M., Lipton, P.A., Summons, R.E., Peters, K.E., Jeganathan, A., Watt, D.S., 1994. Paleoenvironmental implications of novel C_{30} steranes in Precambrian to Cenozoic age petroleum and bitumen. Geochimica et Cosmochimica Acta 58, 529-532.

Moldowan, J.M., Fago, F.J., Lee, C.Y., Jacobson, S.R., Watt, D.S., Slougi, N.-E., Jeganathan, A., Young, D.C., 1990. Sedimentary 24-n-propylcholestanes, Molecular Fossils Diagnostic of Marine Algae. Science 247, 309-312.

Peterson, K.J., Lyons, J.B., Nowak, K.S., Takacs, C.M., Wargo, M.T., and McPeek, M.A. (2004). Estimating metazoan divergence times with a molecular clock. Proceedings of the National Academy of Sciences, USA, 101: 6536-6541.

Rothman D. H., Hayes J. M., and Summons R. E., 2003. Dynamics of the Neoproterozoic carbon cycle. Proceedings of the National Academy of Science (USA) 100, 8124-8129.

ORP-1: A fill, spill and leak approach to pre-drill fluid property prediction

P.J. Hicks (Jr.)

ExxonMobil Upstream Research Company, P.O. Box 2189,URC S-139. Houston, TX 77252-2189 (e-mail: paul.hicks@exxonmobil.com)

Explorationists are often called upon to make pre-drill fluid property predictions. Fluid properties, including gas-oil-ratio, API gravity, viscosity, inerts and fluid type, are controlled by a number of chemical and physical processes. This paper discusses an integrative approach to modeling fluid type and fluid properties through time by accounting for migration including fill and spill relationships, PVT and in-reservoir fluid alteration processes. The approach works best under geologic conditions where the fill and spill relationships do not vary significantly through time.

A description of the modeling approach is as follows. The area and time range of interest is selected. Model areas typically include all traps in the drainage area which feed the traps of interest through fill and spill migration pathways. The time range is typically from the initiation of hydrocarbon generation or trap formation to present day. This time range is discretized and the trap pore volumes are initialized with all water. Then, for each trap at each time step:

1) Newly generated hydrocarbons in the drainage area migrate to the trap;
2) Hydrocarbons spilling to this trap from a downdip trap are added;
3) Any user-specified fluid alteration processes (such as in-reservoir cracking) are modeled;
4) The hydrocarbon fluid is flashed to paleo-pressure and temperature; hydrocarbon phases, densities, volumes and heights are estimated;
5) The capacity of the trap to hold the hydrocarbon volume and hydrocarbon column heights is evaluated and
6) Hydrocarbons leak through the top seal or spill to the next trap if the seal capacity or volumetric capacity, respectively is exceeded.

Present-day fluid properties are estimated from the compositions in each trap after the final time step at time 0 ma. The figure below illustrates the fill and spill relationships for a trap containing gas and oil.

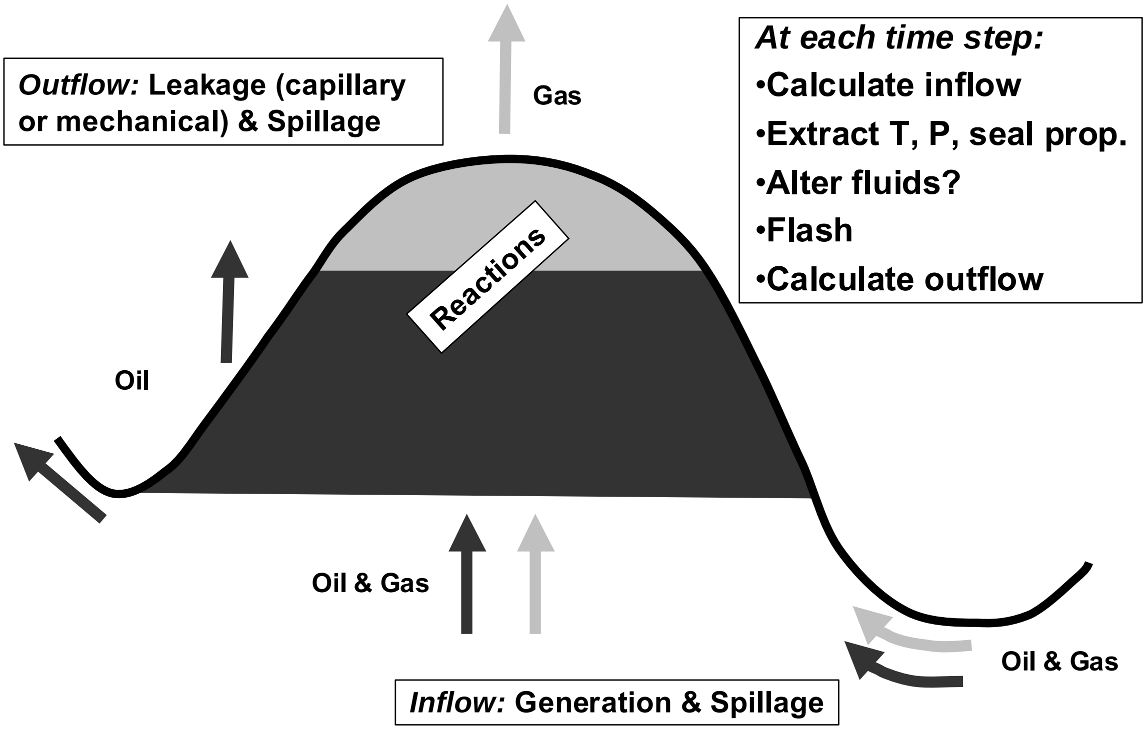


Fig.1. Fill and spill for a single two-phase trap

Inputs to a model include outputs from a 3-D basin model such as pressure, temperature and hydrocarbon yield histories through time. Additional key inputs include seal capacity (both mechanical and capillary); reservoir properties such as porosity, water saturation and net-to-gross; a PVT model; a drainage analysis; and models for any user-specified fluid alteration processes. Sensitivity studies can be conducted to investigate uncertainties in inputs such as migration efficiencies, source parameters, reservoir parameters, seal properties and fluid alteration processes.

Simple examples will be presented which illustrate the approach and the effect certain key variables have on predicted fluid properties.

ORP-2: Source facies identification from light hydrocarbon analysis – Implications for petroleum system analysis

D.M. Jarvie[1], R.J. Hill[2], K.F.M. Thompson[3], F.D. Mango[4], C. Jiang[1]

1) Humble Geochemical Services, P.O. Box 789, Humble, TX 77338 USA
2) US Geological Survey, Box 25046 Denver Federal Center MS 939 Denver, CO 80225 USA
3) Petrosurveys, P.O. Box 671264, Dallas, TX 75367 USA
4) Petroleum Habitats, 806 Soboda Ct., Houston, TX 77079 USA

Light hydrocarbon (LH) distributions are affected by source input including both organic and inorganic matrices, thermal maturity, alteration processes such as biodegradation, evaporative fractionation, thermochemical sulfate reduction, oil cracking, and by mixing of oils from the same or different sources. The goal of this study is to establish criteria for distinguishing source rock lithofacies from LH analysis of oil samples. However, it is also essential to understand and evaluate the impact of alteration and mixing processes on LHs.

In the Williston Basin, shale, carbonate, and *G. prisca* kukersite sourced oils are clearly segregated from one another using a ternary plot of C_7 hydrocarbons and all isomers (Jarvie, 2001). Mixtures of these oils based on LH analysis are also recognized. In a more recent study, terrigenous sourced oils from S.E. Asia were found to group with carbonate oils, as both exhibited 6 ring preference (RP). However, it was found that terrestrially sourced oils are dominated by methylcyclohexane (MCH), whereas carbonate oils are dominated by toluene (TOL). A ternary plot of MCH, TOL, and n-C_7 clearly segregates terrestrial, carbonate, shale, and *G. prisca* sourced oils (Fig. 1). Variable organofacies will affect this segregation as will fractionation and other alteration processes.

It is hypothesized that lithofacies assessment using LHs is influenced by kerogen composition and structure, thermal maturity, and other factors ranging from source rock mineralogy to Eh conditions during deposition of the source rock. For example, differences between carbonate and terrestrial source rocks are hypothesized to be a function of compositional and structural differences in the two different sources, but also due to the possibility of hydrogen abstraction by free sulfur in carbonates resulting in increased aromaticity. Reactions carried out in the presence of excess H_2 have shown a preference for MCH, whereas low H_2 results in increased TOL. Where terrestrial source rocks have more oil prone character, there is a primary difference in the LHs in the concentration of n-C_7 versus MCH.

While both carbonate and terrestrial oils both show 6 RP, differences between carbonate and shale sourced oils are apparent by selectivity for 3 RP in shales. The higher clay content of marine shales and the higher sulfur content of carbonates are inferred to result in different final LHs composition due to different isomerization pathways. In marine shales higher clay content is known to be related to increased diasterane content in biomarkers.

Alternatively, LHs show higher dimethylcyclopentane (DMCP) and isoalkane contents in marine or marly shales. DMCP concentration decreases with increasing thermal maturity, either as a function of ring opening or simply as a result of increased concentration of other C_7 hydrocarbons from thermal or catalytic cracking. It was also shown by Xiao and James (1997) that the invariance of the LHs could be explained by mineral acid catalysis. Increased isomerization is also shown by MSSV experiments using oil asphaltenes mixed with clays.

A statistical approach also provides results that allow oils to be segregated by isomeric distribution of LHs. Using polytopic variable analysis (PVA), LHs can be grouped by cyclopentane (CP), cyclohexane (CH), isoalkanes (ISO), paraffinicity, and aromaticity. CP dominated oils are derived from low maturity marine shales. CH dominated oils are higher maturity than CP dominated oils and have higher GOR values. Oils with high ISO yields are also marine shales of high maturity, but appear to reflect an alternate pathway to the CP dominated oils hypothesized to be due to mineral acid catalysis. Oils dominated by high n-alkane yields are typical of *G. prisca* sourced oils and certain lacustrine oils.

Slope factors and combined LH and additional analytical techniques are used to distinguish altered and mixed systems.

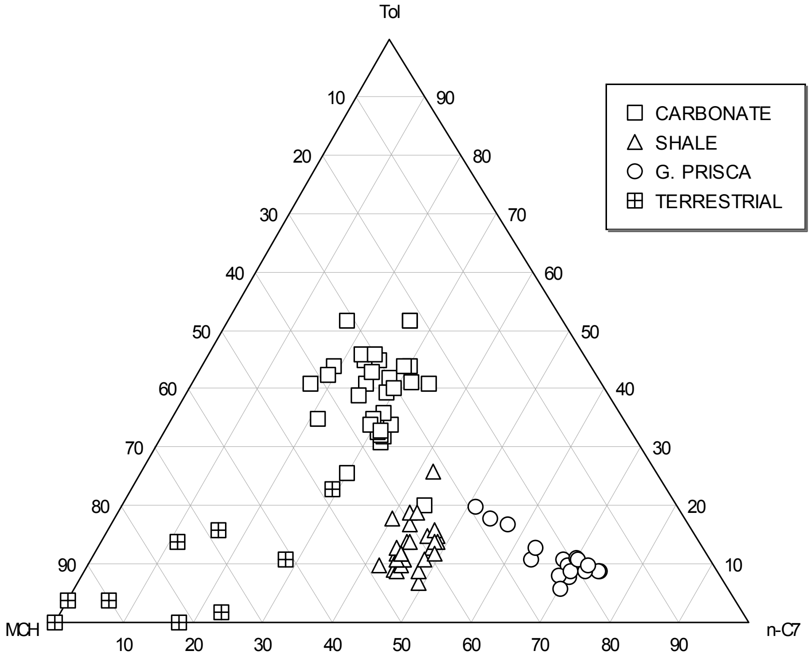


Fig.1. Ternary plot segregating pristine oils by source lithofacies

References

Jarvie, Daniel M., 2001, Williston Basin Petroleum Systems: Inferences from Oil Geochemistry and Geology, The Mountain Geologist, Vol. 38, No. 1, pp. 19-41.

Xiao, Yitian and A. T. James, 1997, Is Acid Catalyzed Isomerization Responsible for the Invariance in the Isoheptanes of Petroleum?, 18th Int'l Meeting on Organic Geochemistry, Abstracts Part II, pp. 769-770.

OOS-1: New oil-source correlations in the South Oman Salt Basin

E. Grosjean[1], C. Stalvies[2], G.D. Love[1], A.N. Lewis[1], Y.J. Hebting[1], D. Fike[1], P.N. Taylor[3], M.J. Newall[3], J.P. Grotzinger[1], P. Farrimond[2], R.E. Summons[1]

1) Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139, USA (e-mail: egrosjea@mit.edu)
2) Newcastle Research Group, University of Newcastle, Newcastle upon Tyne NE1 7RU
3) Petroleum Development Oman, PO Box 81, Muscat, PC 113, Sultanate of Oman

The South Oman Salt basin is a prolific petroleum-producing basin, host to the world's oldest known commercial deposits. Most of the South Oman oils have been proven to be associated with the source rocks of the Neoproterozoic to Cambrian Huqf Supergroup [1] but the assignment of oils to specific Huqf intervals or facies is hampered by the geochemical similarity of the organic matter across the whole Huqf sequence, a consequence of the limited biological diversity at the time of deposition.

This study was conducted to establish improved correlations between organic-rich rock units and reservoir fluids in the SOSB through a detailed chemostratigraphy, geochronology and organic geochemistry of the Huqf Supergroup, with a special emphasis directed towards the understanding of the Ara carbonate stringer play.

The Ara group, which spans the Precambrian-Cambrian boundary [2], is the terminal subdivision of the Huqf Supergroup and can be subdivided into two separate geological domains, a carbonate-prone area comprising two Carbonate Platforms, referred to as the North and South Carbonate Platforms, separated by a silica-prone Central Trough, otherwise known as the Athel domain. The carbonate platforms consist of a succession of six carbonate units, or stringers, each sandwiched by evaporites, whilst the time equivalent Athel domain contains, within the Ara evaporites, the Athel silicilyte as well as two organic-rich sediments, the U shale and the Thuleilat shale. The Ara group overlies source rocks of world-class quality of the pre-salt Nafun group, whose contribution to the South Oman oils remains unclear.

The South Carbonate platform has recently gained a renewed interest in exploration since the discovery of oil in carbonate stringers in 1996 and now represents the some of the most prospective plays in Oman. However, the charge scenario for these reservoirs is very poorly understood, especially with respect to contributions from the pre-salt Nafun group.

To improve the understanding of the South Oman petroleum systems, fifty-seven crude oils from carbonate stringer and silicilyte reservoirs and from post-salt Eastern Flank accumulations, as well as forty-six potential source rocks distributed across the Nafun and the Ara groups, were selected for detailed molecular geochemical and isotopic analyses.

Hierarchical cluster and principal component analysis based on biomarker ratios reveal that carbonate stringer oils form two geographically and stratigraphically resolved groupings and that they are genetically related to carbonate stringer kerogens. Moreover, unusual biomarkers, identified as C_{19} sterane isomers, show a distinctive pattern among carbonate stringer oils and rocks which is different from the distributions observed in Nafun sediments and in Ara rocks from the Athel basin and evidence of a self-charging mechanism for the carbonate stringer play (Figure 1). The precise structures of the novel C_{19} steranes and related C_{20} compounds remain to be determined.

Subtle aspects of the composition of oils in Ara carbonate reservoirs with direct access to Nafun source rocks suggests some degree of sourcing from this pre-salt sequence. The charge history of Phanerozoic reservoirs on the Eastern Flank of the SOSB is complicated by biodegradation and oil mixing processes. However, Athel source rocks were found to contribute largely to these oils with a variable input from the pre-salt Nafun rocks.

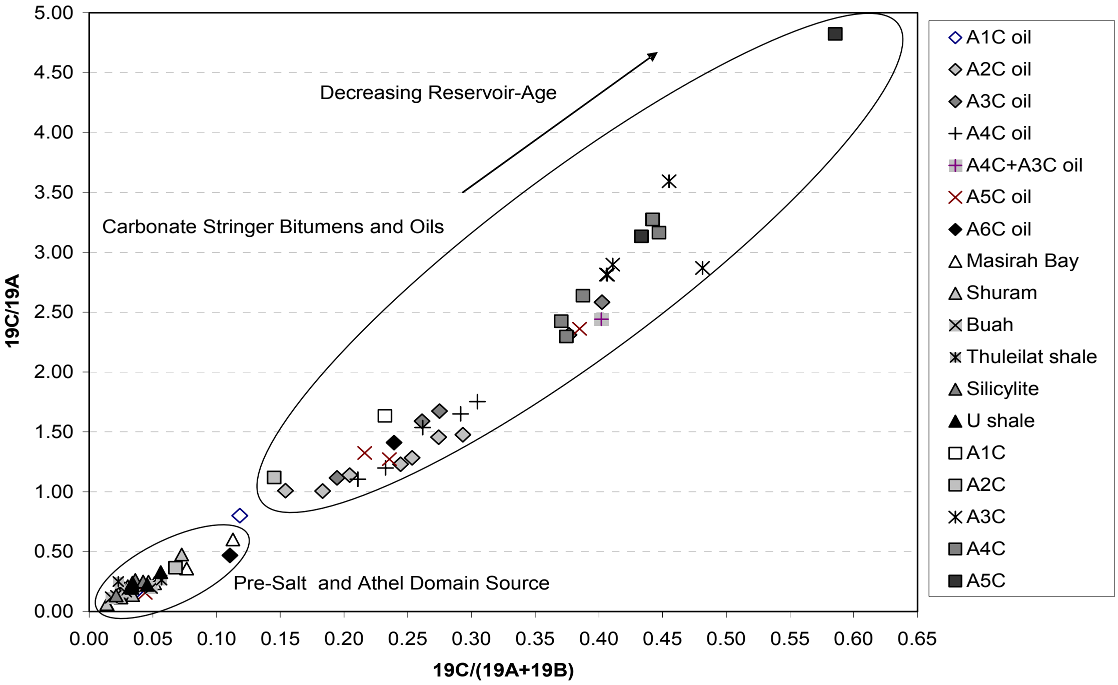


Fig.1. Cross-plot of ratios for three C_{19} sterane isomers for a selection of SOSB oils and source rock bitumens

References

[1] Grantham, P.J., Lijmbach, G.W.M., Posthuma, J., Hughes Clarke, M.W., Willink R.J., 1987. Origin of crude oils in Oman. Journal of Petroleum Geology 11, 61-80.

[2] Amthor, J.E., Grotzinger, J.P., Schröder, S., Bowring, S.A., Ramezani, J., Martin, M.W., Matter A., 2003. Extinction of Cloudina and Namacalathus at the Precambrian-Cambrian boundary in Oman. Geology 31, 431-434.

OOS-2: Characterization of sulfur in source rocks and petroleum reservoirs by Rock Eval analysis

F. Lorant[1], R. Antonas[2], J. Espitalie[2]

1) Institut Français du Pétrole, 1-4 avenue de Bois Preau, 92500 Rueil-Malmaison, France
2) Vinci Technologies S.A., 27 B rue du Port, 92022 Nanterre, France

Sulfur occurs in sedimentary basins under various forms and concentrations, which depend on the nature of original sediments and organic matters, and the conditions of deposition. Sulfur-containing minerals and organic matters are potentially subject to chemical reactivity, through processes that naturally may take place during the evolution of petroleum systems (*e.g.*, thermal decomposition of organic matter, sulfate reduction, either thermally or biologically activated, biodegradation of oils), or artificially may be induced during the exploitation of reservoirs, especially water and steam injection operations (*e.g.*, aquathermolysis of sulfur-rich heavy oils, pyrite oxidation). Such processes mostly result in generation of H_2S, sulfured heavy oils, occurrence of sulfur-rich tar mats and pyrobitumen, which all reduce the economic value of oil fields and are directly or indirectly hostile to the environment.

The presence of sulfur in sedimentary basins, especially in source rocks and reservoirs, therefore constitutes a risk in exploration and production, that is currently hardly appraised. Straightforwardly, one might expect that H_2S and sulfur-rich tar deposits are likely to be formed, via different processes, where significant concentrations in organic sulfur, and/or pyrite and/or sulfates occur. Accordingly, detecting at least these three forms of sulfur in source and reservoir rocks has a potential interest to (qualitatively)assess the risk of occurrence of H_2S and sulfured oils and tars.

For that purpose, a new analytical module dedicated to the determination of sulfur content in natural organic and mineral samples has been developed and coupled to a Rock Eval 6 apparatus. Sulfur is analyzed by oxidation of a few milligrams of sample, possibly preceded by a pyrolysis run, using an infrared detector calibrated for SO_2, CO and CO_2. Preliminary tests showed that the analysis of total sulfur is quantitative in most cases (Figure), expect for sulfates which require very high temperatures (> 900°C). The principle of this device being validated, various analytical methods (*i.e.*, sample preparation and temperature programs) have been calibrated in order to split the SO_2 signal, that is recorded continuously, into different peaks, and associate each peak to a specific form of sulfur (with a specific thermal reactivity). Based on this principle, organic sulfur can quantitatively be differentiated from iron sulfide minerals in kerogens. Additionally, running on the same sample a direct oxidation analysis, then a second analysis comprising a pyrolysis cycle followed by an oxidation cycle, organic sulfur can be split into a labile fraction, which is reactive to temperature (under pyrolysis condition) and can therefore be a source of H_2S, and a refractory fraction which remains in residual organic matter. The determination of labile versus refractory sulfur ratios in source rocks at various depth is potentially a promising approach to determine H_2S and sulfured oils kitchens in sedimentary basins. On reservoir cores, this method also provides an information on the probability of H_2S formation from heavy oils submitted to thermal recovery.

To date, this method requires technical improvements, especially to allow for sulfates to be quantified. The fast determination of sulfates concentrations in reservoirs should offer a new tool to investigate the probability of occurrence of thermal and bacterial sulfate reduction.

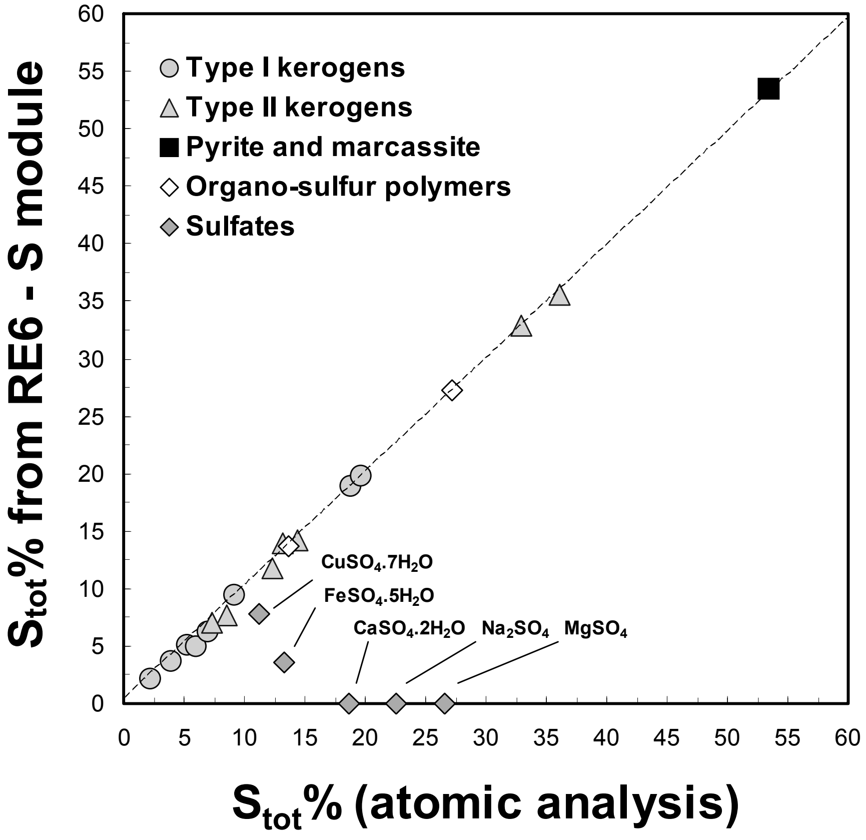


Fig.1. Comparison of total sulfur concentrations in various organic and mineral samples, obtained by Rock Eval 6 - S module analysis and direct atomic analysis.

OOS-3: Relationship between petroleum biomarker composition, depositional environment and age of the source rock (revisited)

S.M. Barbanti[1], J.M. Moldowan[2]

1) Petrobras Research and Development Center, Cidade Universitária, Ilha do Fundão, Rio de Janeiro, RJ 21949-900, Brazil (e-mail: barbanti.ufrj@petrobras.com.br).
2) Department of Geological and Environmental Sciences, Stanford University, Stanford, CA 94305-2115, USA.

A suite of 100 oil samples from diverse global locations, derived from a wide variety of source rock types with ages ranging from Precambrian to Miocene were analyzed for their biomarker compositions. The purpose of this work is to verify, substantiate or determine to what extent paradigms about biomarker composition hold up within such a diverse sample set, and to show relationships with environment and age that may not have been widely recognized previously. Analytical methods included gas chromatography-mass spectrometry (GC-MS) and metastable reaction monitoring (MRM)-GC-MS of saturate branched plus cyclic fractions and GC-MS of aromatic fractions.

Focal points for this oil compositional survey include some parameters that had only been tested previously on source rock suites, such as the oleanane index [oleanane/(hopane + oleanane)], triaromatic dinosteroids and 23,24-dimethylcholesteroids occurrence in their relative abundance with respect to geologic time. Other parameters where scant information is available about age-range and significance and abundance of occurrence in ancient oil and rock samples, such as bicadinane indices, tricyclic and tetracyclic plant diterpane ratios, and the C_{25} highly branched isoprenoid were surveyed. And finally, widely used biomarker parameters for maturity and source such as C_{27}-C_{28}-C_{29} sterane (Figure 1), diasterane and aromatic steroid distributions, hopane and rearranged hopane distributions and relative abundances, and gammacerane indexes versus other widely used biomarker parameters and against depositional environment were also surveyed. Only a few examples of the approximately 100 parameters surveyed can be mentioned here as examples.

Some of the more interesting findings to be discussed will be the relationship between bicadinane index (higher plant resins), oleanane index (angiosperm plant group), C_{30} sterane index (marine algal input) and the tetracyclicpolyprenoid index (possible marker for green algae), how they correlate with each other, environment, lithology and geologic age. Similarly how some parameters for depositional environment such as the gammacerane index (water stratification/anoxia), the homohopane index (anoxia), pristane/phytane, Ts/Tm and diasterane/sterane and diahopane/hopane ratios correlate with each other has not been well-explored in the past.

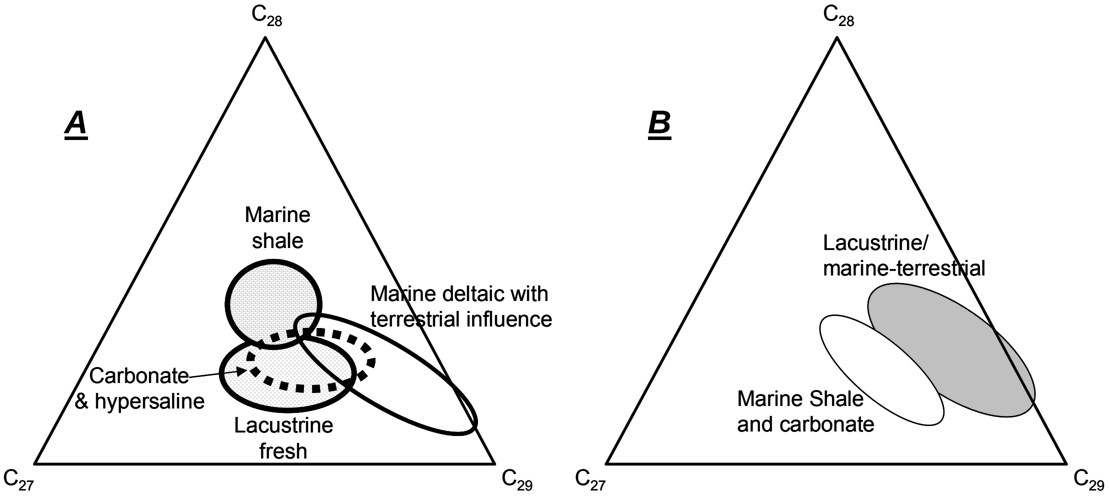


Fig.1. Distributions of C_{27}-C_{28}-C_{29} steranes from MRM-GC-MS analysis of oils displayed in Ternary diagrams show differences by age and depositional environment. Tertiary and Cretaceous oil samples (***A***) show separate, barely overlapping regions for oils from marine algal shale, marine carbonate or hypersaline environment, lacustrine and terrestrially influenced sources. Jurassic and Triassic oil samples (***B***) show a different distribution. During those Periods oils marine shale and carbonate oil sources are not distinguished by sterane distributions and lacustrine oils are relatively more abundant in C_{28}-steranes than are Cretaceous and Tertiary oils. Highest relative C_{28}-sterane abundances are recorded in Cretaceous and Tertiary marine shales, probably due to radiation of certain algae (diatoms?) that were neither abundant in carbonate/hypersaline environments nor prior to the Cretaceous Period

TOPIC SESSIONS

BIOGEOCHEMISTRY

OB1-1: The GCMS correlation of series of highly branched C_{3n} alkanes detected in extant and ancient sediments and polypropylene oligomers

P.F. Greenwood

CRC-Water Quality and Treatment and Curtin University of Technology, Perth, GPO Box 1987, WA 6845, Australia (e-mail: p.greenwood@curtin.edu.au)

Two distinct series of branched alkanes displaying an unusual C_{3n} sequence and GC characteristics indicative of a very high degree of branching were recently detected in several Neoproterozoic sediments ([1], [2]). The two C_{3n} series have now also been reported to occur in present day environments with Durkay [3] detecting them in very high abundances in the hydrocarbon fractions extracted from surface and groundwaters used to irrigate a Clare Valley (SA) winery. Bacterial microbes are one of the major sources of naturally occurring branched alkanes and the C_{3n} branched alkanes are thought to derive from a specific microbe(s). An association with fossilised or extant bacteria has been one commonality to their occurrence. Other anecdotal evidence (e.g. co-occurring biomarkers) supports a biological origin, as opposed to contaminant or analytical artifact.

The early elution of the C_{3n} series of branched alkanes, relative to *n*-alkanes of corresponding carbon number, equates to very negative relative retention factors (RRFs) becoming more negative with increasing carbon number. The RRF values of the C_{3n} series are even more negative than those of the highly branched isoprenoids ([2], [4], [5]). Apart from this observation, the GCMS data of the C_{3n} alkanes provided minimal structural information. Fragment ions diagnostic of specific structural units were not readily evident from their mass spectra.

Whilst many structural conformations fit the simple permutation of a C_{3n} ($3 \geq n \geq 12$) sequence and an increase in branching with each C_{3n} addition, a polypropylene (PP) related sequence is an obvious candidate. Similarities in the GCMS data of the C_{3n} branched alkanes and C_{3n} series of PP oligomers detected in the extract or pyrolysates of a commercially available polypropylene polymer (isotactic; Ave MW = 12,000) have been identifed. The PP data show complex product distributions with pronounced clusters of C_{12}, C_{15}, C_{18}, etc. (i.e., C_{3n}, $n \geq 4$) saturated and unsaturated PP oligomers. These include diastereoisomers (*meso* and *rac*) and other structural conformations arising from chemical inversion during polymerization [6].

GCMS data will be presented for several recognisable series of PP oligomers including the same two series of C_{3n} branched alkanes detected in the Neoproterozoic sediments [2]. Positive correlation was based on their co-elution and identical mass spectra. Similar RRF profiles were observed for all C_{3n} series of PP oligomers reflecting their consistent extension by addition of PP monomer units.

A mass spectral interpretation of the naturally occuring C_{3n} branched alkanes made on the basis of exclusively methyl branching and PP monomer extension suggest methyl groups are located at carbon positions 2, 3, ω4, ω3 and 5, 8, 11, etc for $\geq C_{15}$ members extending by mid chain addition of C_3 units (Figure 1). A 2,3-dimethyl unit at one terminal end and a 3,4-dimethyl unit at the other accounts for the consistently high relative abundance of C_nH_{2n+1} fragment ions where $3 \leq n \leq 6$. Secondary carbonium ions produced by cleavage either side of mid chain methyl groups of the proposed structure also accounts for the distinct series of C_{3n-1} (C_5, C_8, C_{11}, etc) and C_{3n} (C_6, C_9, C_{12}, etc) fragment ions. Unequivocal confirmation of this or any alternative structural assignment will require correlation to a synthesised aunthentic standard.

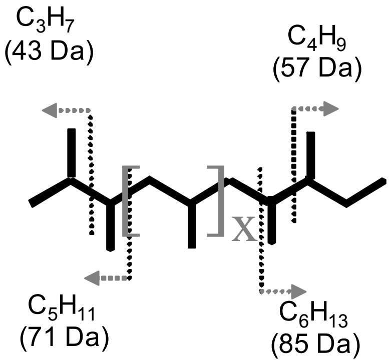


Fig.1. Tentative structure proposed for naturally occurring C_{3n} branched alkanes ($x \geq 0$)

References

[1] Arouri, K., Greenwood, P.F., Walter, M., 2000. Biological affinities of Neoproterozoic acritarchs from Australia: microscopic and chemical characterisation. Organic Geochemistry 31, 75-89.

[2] Greenwood, P.F., Arouri, K.R., Logan, G.A., Summons, R.E. 2004. Abundance and geochemical significance of C_{2n} dialkylalkanes and highly branched C_{3n} alkanes in diverse Meso- and Neoproterozoic sediments. Organic Geochemistry 35, 331-346.

[3] Durkay, M.S., 2002, Use of hydrocarbons in winery wastewater to establish hydraulic connectivity in a fractured Rock Aquifer, in a Clare valley winery, SA. Honours thesis, University of Adelaide, SA.

[4] Barrick, R.C., Hedges, J.I., Peterson, M.L., 1980. Hydrocarbon geochemistry of the Puget sound region - I. Sedimentary acyclic hydrocarbons. Geochimica et Cosmochimica Acta 44, 1349-1362.

[5] Prahl, F.G., Bennet, J.T., Carpenter, R., 1980. The early diagenesis of aliphatic hydrocarbons and organic matter in sedimentary particles from dabob Bay, Washington. Geochimica et Cosmochimica Acta 44, 1967-76.

[6] Tsuge, S., Sugimura, Y., Nagaya, T., 1982. Structural characterization of polyolefins by pyrolysis-hydrogenation glass capillary gas chromatography. Journal of Analytical and Applied Pyrolysis 1, 221-2294.

OB1-2: Use of paleochemotaxonomy for tracing paleobotanic and paleoclimatic changes during Jurassic

Y. Hautevelle[1,2], R. Michls[1], F. Malartre[3], A. Trouiller[2]

1) UMR 7566 CNRS G2R, Université Henri Poincaré, Nancy 1, BP 239, 54506 Vandoeuvre-lès-Nancy cedex, France (e-mail: Yann.Hautevelle@g2r.uhp-nancy.fr).
2) ANDRA, 1-7 rue Jean Monnet, 92268 Châtenay-Malabry, France.
3) UMR 7566 CNRS G2R, Ecole Nationale Supérieure de Géologie, BP 40, 54501 Vandoeuvre-lès-Nancy cedex, France.

Many geoterpenoids preserved in sediments derive from the degradation of bioterpenoids synthesized by vascular plants. Terpenoids analyses in extant plants, organic aerosols as well as fossil woods and resins yield valuable information on their specific plant sources and highlight the chemotaxonomic value of many compounds (Lockheart et al., 2000; Otto and Wilde, 2001, Otto and Simoneit, 2001). For example, cadinane-type sesquiterpenoids are widespread in the plant kingdom and are therefore unspecific. Nevertheless, other compounds are more specific like abietane or pimarane-type hydrocarbons (e.g. retene) which are biomarkers typical of conifers. Some are very specific and can be linked to specific families (e.g. cuparane-type sesquiterpenoids for Cupressaceae). Thus, the distribution of geoterpenoids preserved in sedimentary rocks reflects the paleodiversity of plants on emerged lands close to sedimentary basins at the time of sediment deposition and can be used as chemostratigraphic tool for tracing paleoflora changes. As evolution of vegetation is under climate control, chemostratigraphy based on vascular plant biomarkers can also be used in order to trace climatic changes during geological times.

This study concerns Callovo-Oxfordian series located in the North-East of Paris basin (France). The London-Brabant Massif was the nearest emerged land (Dercourt et al., 2000) and was covered by plants (Filicales, Cycadales, Ginkgoales, Coniferales…) which were the main source of the detrital organic matter preserved in the studied sedimentary series. 160 samples distributed through five wells drilled by Andra were investigated for vascular plants terpenoids. GC-MS analyses of claystones dated from middle Callovian to the end of lower Oxfordian are all characterized by high abundance of cadalene and by very low abundance of saturated, aromatic and functionalised diterpenoids. However, at the end of lower Oxfordian (*Cordatum* ammonite zone), the relative abundances of diterpenoids increase drastically and distributions of vascular plant biomarkers show a major change. This strong evolution is synchronous to the progressive installation of the Oxfordian carbonate platform. Diterpenoids are isomers of labdane, fichtelite, abietane, and norabietane monoene in the saturate fraction; retene, dehydroabietane, dehydroabietins, tetrahydroretene, simonellite, methylretenes in the aromatic fraction; methyldehydroabietate, dehydroabietal and dehydroabietic acid in the polar fraction. Most of these compounds derive from bioditerpenoids synthesized by all conifer families but some of them are more specific. Dehydroabietic acid is the direct degradation product of abietane acids which are much more abundant in Pinaceae. Furthermore, the absence of beyerane-, kaurane-, phyllocladane-type diterpanes and phenolic and ketophenolic abietanes certifies that the above described diterpenoids are not derived from other conifer families (Araucariaceae, Podocarpaceae, Cupressaceae, Taxodiaceae, Cheirolepidiaceae). This major evolution in vascular plant biomarkers distribution is interpreted as an increase of the Pinaceae proportion in the London-Brabant Massif. Pinaceae show morphologic adaptations to dry climate (needle-like leaves covered by a thick layer of epicuticular waxes, stomata sunken in wells and burrows) while other conifer families preferably colonize humid environments. Thus, we interpret the increased contribution of Pinaceae biomarkers at the end of the lower Oxfordian (*Cordatum* ammonite zone) as imprint of a dryer climate on the London-Brabant Massif.

This conclusion is also supported by geochemical, paleontological, palynological, paleobotanical and mineralogical data (Abbink et al., 2001; Rees et al., 2000; Pellenard et al., 2003). A comparable increase of the retene/(cadalene+retene) ratio was described by van Aarssen et al. (2000) in the Oxfordian of Western Australia. Similar evolution in land plant composition in far apart continents is an argument for identifying a worldwide paleoclimatic change during Oxfordian.

Our study proves that paleochemotaxonomy is an innovative and appropriate stratigraphic tool for tracing paleovegetation and paleoclimatic changes.

References

Abbink O. et al. (2001). Global Plan. Change, **30**, 231-256.
Dercourt J. et al. (2000). Atlas Peri-Tethys. MAP 9 : Middle Callovian.
Lockheart M.J. et al. (2000). Org. Geochem., **31**, 1223-1246.
Otto A. and Simoneit B.R.D. (2001). Geochim. Cosmochim. Acta, **65** (20), 3505-3527.
Otto A. and Wilde V. (2001). Bot. Rev., **67**, 141-238.
Pellenard P. (2003). Soc. Géol. Nord, Publication n°**31**, 362 p.
Rees P.M. et al. (2000). Available at http://pgap.uchicago.edu/Reesetal2000.html
van Aarssen, B.G.K. et al. (2000). Geochim. Cosmochim. Acta, **64** (8), 1417-1424.

OB1-3: Linking organic geochemistry and microbial ecology in the Black Sea

S.G. Wakeham[1], I.F. Putnam[1], K.M. Arzayus[1], E. Hopmans[2], S. Schouten[2],
J.S. Sinninghe-Damsté[2], X. Lin[3], G.T. Taylor[3]

1) Skidaway Institute of Oceanography, 10 Ocean Science Circle, Savannah, GA 31411 USA (e-mail: stuart@skio.peachnet.edu)
2) Royal Netherlands Institute for Sea Research, Department of Marine Biogeochemistry & Toxicology, PO Box 59, 1790AB Den Burg, Texel, The Netherlands
3) Marine Sciences Research Center, Stony Brook University, Stony Brook, New York 11794-5000, USA

The Black Sea is the largest marine anoxic basin in the world, and its water column has been the focus of intense biogeochemical study for several decades. The biogeochemical structure of the Black Sea consists of four distinct layers: (*1*) a euphotic zone characterized by active aerobic planktonic organic matter production and cycling processes; (*2*) a 20-30 m aphotic zone (the oxycline/upper nitracline) where O_2 deceases to about 10 µM and NO_3^- increases to 6-8 µM as sinking organic matter is remineralized aerobically; (*3*) the oxygen deficient (suboxic) layer of about 30 m defined by sharp decreases in nitrate and very low levels of O_2; and (*4*) a deep anoxic layer down to the sea floor with high concentrations of H_2S and NH_4^+ produced by anaerobic decomposition. The sub-oxic/anoxic interfacial zone involves a complicated series of bacterially-mediated iron, manganese and sulfur redox cycles, and the transition zone between oxic upper waters and anoxic bottom waters (the chemocline) is characterized by stratified microbial communities, consisting of aerobic, microaerophilic, and anaerobic guilds.

The utility of biomarkers as tracers of organic matter sources and microbial processes depends on linking biomarker distributions and microbial community composition and function. Here we describe just such a cross disciplinary investigation based on suspended particulate matter (spm) samples collected at high resolution across the chemocline in the Black Sea in 2003. A suite of microbial biomarkers have been measured on spm to assess how biomarkers are distributed throughout the water column, and fluorescent *in situ* hydridization (FISH) has been used to probe the abundances of major microbial groups at the same depths. Depth-distributions of biomarkers vary down the water column, indicative of the differing depth regions at which they are produced (Fig. 1, upper two rows of panels). Distributions of several microbial groups (Bacteria, Archaea, ε-proteobacteria, and sulfate reducers) also vary as a function of depth (Fig. 1, bottom row of panels) as microbial community structure and function shifts down the water column. Both biomarker and microbial group depth distributions reflect the geochemical zonation of the water column of the Black Sea. Statistical analysis using principle component analysis of biomarker data clearly differentiate the different biogeochemical environments present, with biomarkers clustering as a function of sample depth and water column geochemistry. On-going work will obtain stable carbon isotope values for key biomarkers and genetic sequencing of microbial groups.

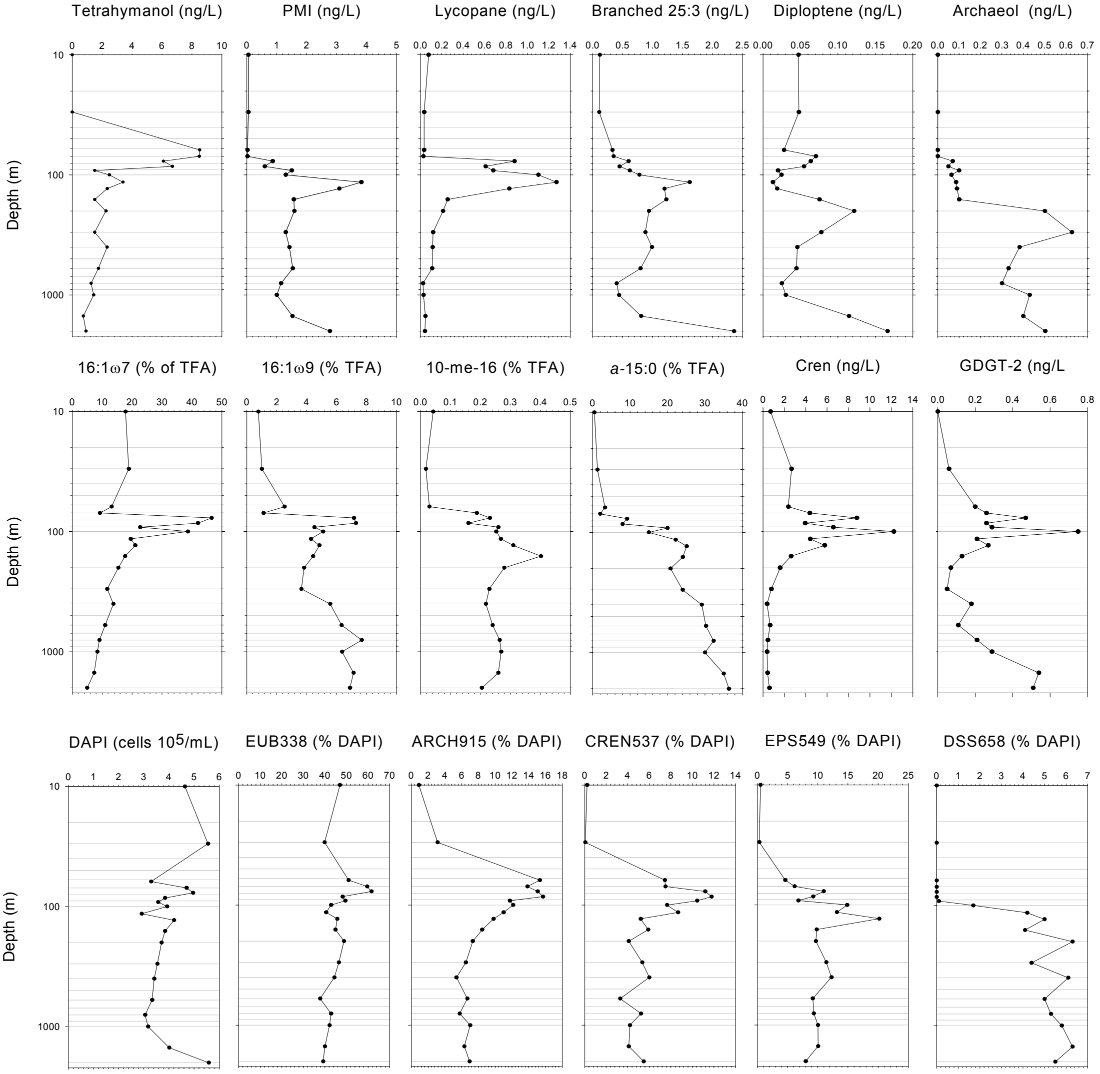


Fig.1. Biomarker distributions (upper two rows of panels) and microbial groups (lowest row of panels) in the Black Sea from cruise 172/8 of R/V Knorr in April 2003. Note the logarithmic depth scale to accentuate the chemocline. Biomarker concentrations are ng/L except for fatty acids which are expressed as percent of total fatty acids. Distributions of major microbial groups EUB, ARCH, CREN, EPS, and DSS were determined by FISH and are as a percent of the total DAPI-stained cells

OB2-1: A quantitative assessment of pressure-dependent changes in the membrane phospholipid composition of a piezotolerant deep sub-seafloor bacterium

K. Mangelsdorf[1], K.-G. Zink[1], L. Toffin[2]

1) GFZ Potsdam, Telegrafenberg, D-14473 Potsdam, Germany (e-mail: K.Mangelsdorf@gfz-potsdam.de)
2) Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Yokosuka Japan

With the finding of microbial communities in both deep marine and deep terrestrial sediments, the so-called "deep biosphere" (Pedersen, 1997; Parkes et al., 2000), the question arises, as to how these microorganisms are able to survive under such "extreme" environmental conditions. Inhabiting deep sedimentary successions requires an enormous adaptability of the microbial life to increasing temperature and pressure conditions.

The cellular lipid inventory of microorganisms, especially the membrane constituents, often gives evidence of such adaptation processes. A new quantitative approach was used to monitor adaptive changes in the cell membrane phospholipid composition of microbial cultures in response to different growth pressure conditions using HPLC-ESI-MS and MS/MS technique. The developed method on intact phospholipids allows the structural elucidation and the relative quantification of individual phospholipids and their acyl side-chain compositions thereby considering different response factors of individual phospholipid groups during the ESI-MS detection process. Both quantitative fatty acid combination patterns and fatty acid distribution patterns comparable to those from GC-MS analysis (PLFA) obtained after mild alkaline hydrolysis can be created.

A piezotolerant bacterium, strain LT25, was isolated from deep subsurface sediments (297 m below seafloor in 4790.7 m water depth) in the Nankai Trough offshore Japan (ODP Leg 190) and was subsequently cultivated under atmospheric (0.1 MPa) and high hydrostatic pressure conditions (25 MPa). The cell membrane of strain LT25 contains phosphatidylglycerols (PGs) and phosphatidylethanolamines (PEs) with saturated or mono-unsaturated fatty acids consisting mainly 14, 16 and 18 carbon atoms. The dominating phospholipid combinations are 16:0/16:1 and 18:1/16:1. A quantitative comparison of the phospholipids and their fatty acyl side-chain inventory illustrate complex restructuring processes in the microbial cell membranes of strain LT25 cultivated under different pressure conditions.

At constant ambient temperature sufficiently high pressure is suggested to cause the transition of the cell membrane lipids from the liquid to the solid-gel state, which would consequently result in a decrease of membrane fluidity. To maintain the membrane fluidity, strain LT25 seems to alter its membrane phospholipid composition by including more bulkyshaped phospholipids into the cell membranes to enhance the cell membrane disturbance and to prevent a tight membrane packing. Thus, the culture raised under high pressure conditions reveals a higher proportion of phosphatidylglycerols and of mono-unsaturated fatty acyl side-chains. The larger PG head group causes a higher disruption of the cell membrane packing than the PE head group due to the lower affinity of PGs to interact intermolecularly by hydrogen-bonding (Boggs, 1986). The incorporation of more *cis*-unsaturated fatty acids also disturbs the cell membrane ordering, because the *cis* double bonds cause a kink in the otherwise relatively straight side-chains, which prevents also a close packing of the phospholipid acyl ends. Since both changes counteract the effect of increasing pressure on cell membranes, an adaptive alteration of the cell membrane composition in response to increasing growth pressure conditions is suggested.

Additional experiments, for instance, on the thermophilic *Pyrococcus glycovorans* have shown that with increasing pressure the content of phosphatidylinositol-glycosaminyl-archaeol slightly increases relative to the dominant phosphatidylinositol-archaeol (>90%). The additional ring and with that the larger polar head group seem to prevent a closer cell membrane packing and to support the maintenance of the membrane fluidity. The investigation of the PL compositions of microbial cultures isolated from deep buried sediments or of laboratory cultures of potential contributors to the deep biosphere are currently underway.

References

Boggs, J.M., 1986. Effect of lipid structural modifications on their intermolecular hydrogen bonding interactions and membrane functions. Canadian Journal of Biochemistry and Cell Biology 64, 50-57.

Parkes, R.J., Cragg, B.A., Wellsbury, P., 2000. Recent studies on bacterial populations and processes in subseafloor sediments: A review. Hydrogeology Journal 8, 11-28.

Pedersen, K., 1997. Microbial life in deep granitic rock. FEMS Microbiology Reviews 20, 399-414.

OB2-2: Possible origin of 24-norcholesterol in marine environment

N. Suzuki, N. Yasuo, T. Nakajo, H. Shine

Division of Earth and Planetary Sciences, Graduate School of Science, Hokkaido University, N10 W8, Kita-ku, Sapporo, 060-0810, Japan (e-mail: suzu@ep.sci.hokudai.ac.jp)

The 24-norcholestane (C_{26}) (5α(H), 14α(H), 17α(H)-24-norcholestane) is known as characteristic sterane of diatomaceous siliceous rocks [1]. High abundance of 24-norcholestane or 24-nordiacholestane in the Cenozoic marine oils is well correspondent to the evolution of diatom [2]. Our recent study on Oligocene to Miocene diatomaceous siliceous rocks distributed in North Pacific revealed that 27-nor-24-methylcholestane (C_{27}) (27-nor-24-methyl-5α (H), 14α(H), 17α(H)- cholestane) is another sterane which is commonly present in siliceous rocks as well as 24-norcholestane. The 24-norcholestane and 27-nor-24-methylcholestane are empirically considered as possible diatom biomarkers.

Their possible precursory compounds, 24-norcholesterol and 27-nor-methylcholesta-5,22(E)-dien-3β-ol, occur in marine filter feeders, some diatom-rich algal assemblages, and separated diatoms collected in North Pacific and Bering Sea during cruise KH99-3 of the Hakuho Maru. We also analyzed some cultured diatoms (*Chaetoceros didymus*, *Chaetoceros sociale*, *Cosinodiscus marginatus*, *Cosinodiscus sp.*, *Rhyzosolenia setigera*, *Skeletonema sp.*, and *Thalassiosira sp.*) for these possible precursory sterols. However, 24-norcholesterol and 27-nor-methylcholesta- 5,22(E)-dien-3β-ol have not been detected in all the cultured diatoms.

Biodegradation of sterols in natural diatoms are carried out to clarify the origin of 24-norcholestane and 27-nor-24-methylcholestane often found in diatomaceous siliceous rocks. Natural diatom was collected by plankton net in Tomakomai bay, Hokkaido. The sample is markedly rich in *Cosinodiscus marginatus* as shown in Fig. 1. A part of the sample was quicly analyzed for sterols soon after the sampling. Result showed the absences of 24-norcholesterol and 27-nor-24-methylcholesterol in the natural *Cosinodiscus marginatus* (Fig. 1). Another part of natural *Cosinodiscus marginatus* in sea water of Tomakomai Bay were kept in the refregerator at 3ºC for 30 days. Natural *Cosinodiscus marginatus* after the low temperature biodegradation was similary analyzed for sterols. Result showed significant presences of 24-norcholesterol and 27-nor-24-methylcholesterol in the biodegraded sample as shown in Fig. 1. Other sterol cholesta-5,24-dien-3β-ol (C_{27}) was also newly detected in the biodegraded sample. Whereas, relative abundance of 24-methylcholesta-5,24(28)-dien-3β-ol (C_{28}) decreased markedly (Fig. 1).

Biodegradation experiment in the present study strongly suggests that bacterial demethylation of 24-methylcholesta-5,24(28)-dien-3β-ol at low temperature can be important porcess to form 24-norcholesterol and 27-nor-24-methylcholesterol. Cholesta-5,24-dien- 3β-ol, which has the same carbon sekeleton with 27-nor-24- methylcholesterol, also can be a precursory compounds of 27-nor-24-methylcholestane in siliceous sedimentary rocks. Our results showed both 24-norcholestane and 27-nor-24-methylcholestane can be biomarkers of some specific diatoms rich in 24-methylcholesta-5,24(28)-dien-3β-ol.

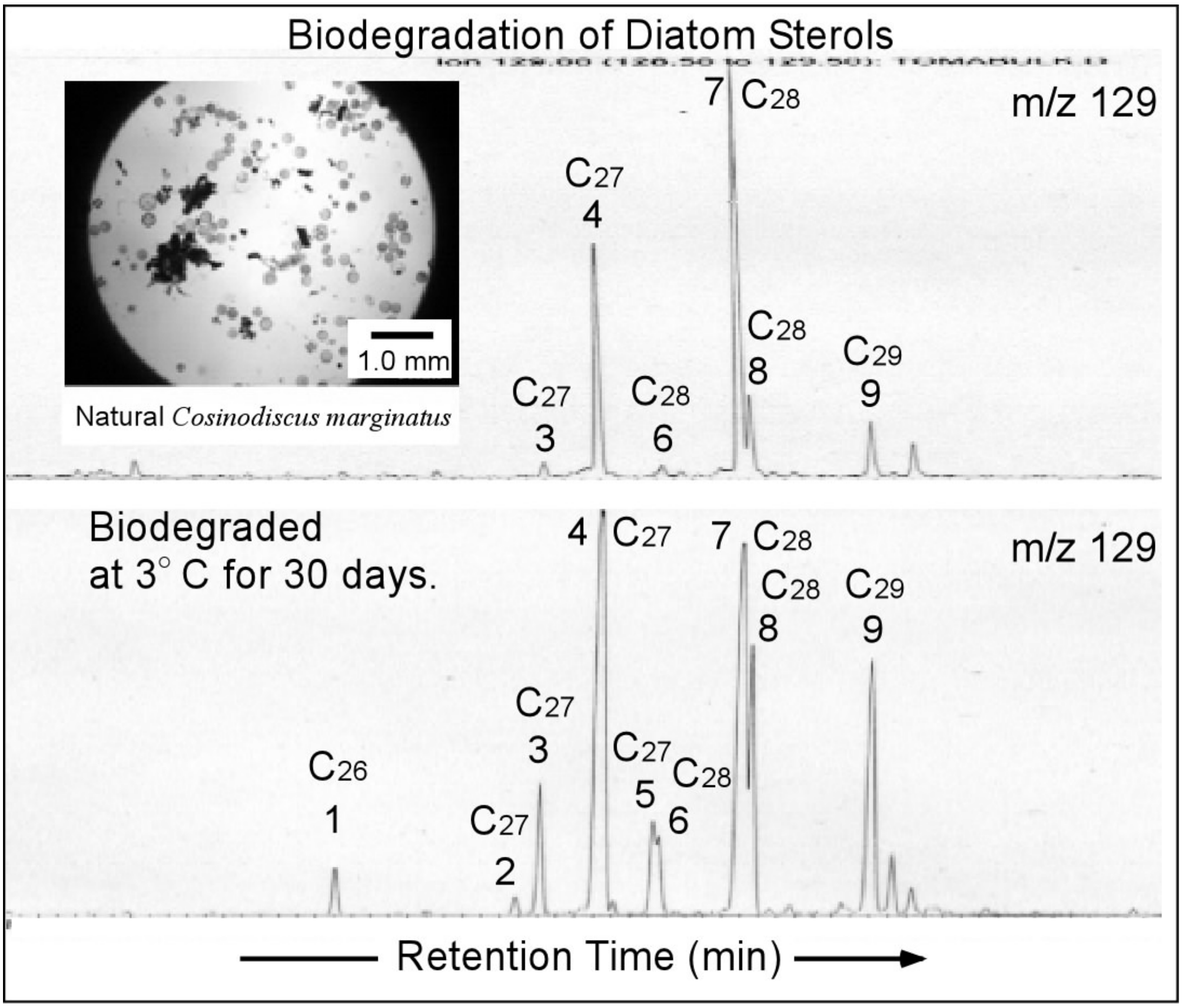


Fig.1. Biodegradation of sterols in natural diatom (Cosinodiscus marginatus) at 3ºC for 30 days. Formations of 24-norcholesterol (peak 1), 27-nor-methylcholesta-5,22(E)-dien-3β-ol (peak 2), and cholesta-5,24-dien-3β-ol (peak 5) proceeded with a marked decrease of 24- methylcholesta-5,24(28)-dien-3β-ol (peak 7). Other peaks are cholesta-5,22(E)-dien-3β-ol (peak 3), cholest-5-en-3β-ol (peak 4), 24-methylcholesta-5,22(E)-dien-3β-ol (peak 6), 24- methylcholest-5-en-3β-ol (peak 8), and 24-ethylcholest-5-en-3β-ol (peak 9), respectively.

References

[1] Suzuki, N., Yoshikazu, S. and Koga, O., 1993. Norcholestane in Miocene Onnagawa siliceous sediments, Japan. Geochimica et Cosmochimica Acta, 57, 4539-4545.
[2] Holba, A.G., Dzou, L.I.P., and Masterson, W.D. , 1998. Application of 24-norcholeatanes for constraining source age of petroleum. Organic Geochemistry, 29, 1269-1283.

OB2-3: Carbon isotopic constraints on the metabolism of archaea inhabiting deeply buried sulfate/methane transition zones

J.S. Lipp[1], J. Biddle[2,3], H.F. Sturt[4], R. Anderson[1,5], M. Elvert[1], J.E. Brenchley[2,3], C.H. House[3,6], K.-U. Hinrichs[1,4]

1) Organic Geochemistry Group, DFG-Research Center Ocean Margins & Dept. of Geosciences, University of Bremen, P.O. Box 330 440, D-28334 Bremen, Germany (e-mail: jlipp@uni-bremen.de)
2) Dept. of Biochemistry and Molecular Biology
3) PennState Astrobiology Research Center
4) Dept. of Geology and Geophysics, Woods Hole Oceanographic Institution, Woods Hole, MA, USA
5) Carleton College, Northfield, MN, USA
6) Dept. of Geosciences, Pennsylvania State University, University Park, PA, USA

Organic geochemical methods have become increasingly important for microbial ecology and biogeochemistry. Together with molecular biological techniques they can provide complimentary insights into the composition and metabolic activities of microbial communities in sedimentary environments. Although the deep biosphere may comprise a tenth of Earth's living biomass (Parkes et al., 2000) still little is known about the key processes and their significance for surface environments.

In deeply buried sediments recovered during ODP Leg 201 (D'Hondt et al., 2003), we analyzed intact membrane lipids (IPLs) using HPLC-ESI-MS^n. IPLs are particularly labile against hydrolytic cleavage of the polar headgroup and thus considered to be representative of live prokaryotes when found in environmental samples. At ODP Sites 1227, 1229 and 1230 off the coast of Peru, we targeted four sulfate/methane transition zones (SMTZ), in two of which cell counts were strongly elevated relative to the adjacent sedimentary strata (D'Hondt et al., 2003). The major IPLs detected were glyceroldialkylglyceroltetraethers (GDGTs) with glycosidic headgroups representative of archaea. Concentrations of these archaeal compounds are low and consistent with biomass estimates based on cell counts. Structural features such as a calditol based tetraether (cf. Sturt et al., 2004) and crenarchaeol with a glycosidic headgroup indicate the presence of crenarchaeal community members. Surprisingly, isotopic compositions of IPLs, conducted on biphytanes released from the IPLs after their isolation by preparative HPLC and subsequent ether cleavage, suggest that methane is not an important carbon source for these communities. The isotopic evidence based on lipids is backed up by isotopic compositions of intact archaeal cells using FISH-SIMS (cf. Orphan et al., 2001). Autotrophic carbon fixation appears unlikely given the observed relationships between isotopic compositions of DIC and archaeal biomass. Instead, the combined lines of isotopic evidence suggest that the bulk of the archaeal community is heterotrophic. Combined isotopic data from IPLs and whole cells provided novel information on the metabolism of uncultured archaea in deeply-buried sediments but also pose interesting new questions regarding the significance of strongly elevated cell numbers that exactly coincide with the SMTZs at Site 1229.

References

D'Hondt, S., Jørgensen, B.B., et al., 2003. Proceedings of the Ocean Drilling Program, Initial Reports. College Station, TX, Ocean Drilling Program.

Orphan, V.J., House, C.H., Hinrichs, K.-U., McKeegan, K.D., DeLong, E.F., 2001. Methane-Consuming Archaea Revealed by Directly Coupled Isotopic and Phylogenetic Analysis*. Science,* 293, 484-487.

Parkes, R.J., Cragg, B.A., Wellsbury, P., 2000. Recent studies on bacterial populations and processes in subseafloor sediments: A review. *Hydrogeology Journal,* 8, 11-28.

Sturt, H.F., Summons, R.E., Smith, K., Elvert, M., Hinrichs, K.-U., 2004. Intact polar membrane lipids in prokaryotes and sediments deciphered by high-performance liquid chromatography/electrospray ionization multistage mass spectrometry - new biomarkers for biogeochemistry and microbial ecology. *Rapid Communications in Mass Spectrometry,* 18, 617-628.

OB3-1: Non-isoprenoidal ether lipids in marine and terrestrial settings

R.D. Pancost[1], S.P. Kelly[1], G. Kaur[1], F. Brock[2], N. Banning[3], A. Weightman[3], J. Fry[3], J. Coleman[1], I. Bouloubassi[4], C.S. Boot[1], B. Cragg[2], J.L. Wadham[1], E.R.C. Hornibrook[1], R.J. Parkes[2]

1) Bristol Biogeochemistry Research Centre, University of Bristol, UK
2) School of Earth, Ocean and Planetary Sciences, University of Cardiff, UK
3) Cardiff School of Biosciences, University of Cardiff, UK
4) LPCM, Université P. et M. Curie, France

Despite extensive study, many aspects of microbially mediated anaerobic sedimentary processes remain unclear: primary substrates, pathways of carbon and electron flow between syntrophic organisms, and the role of newly discovered microorganisms remain debated. To better understand the relationships among sulfate reduction, methanogenesis and anaerobic oxidation of methane, we performed an interdisciplinary investigation of 6 continental shelf marine sites, 2 freshwater sites and 3 intermediate sites. At each, we determined: concentrations of HS^-, SO_4^{2-}, volatile fatty acids, methane and dissolved inorganic carbon; rates of methanogenesis (both acetate and CO_2/H_2 driven); and microbial assemblages using microbiological and biomarker approaches. We also performed pulse-chase experiments, in which ^{13}C-labelled substrates are traced into microbial biomarkers confirming inferred pathways of carbon flow. Here we discuss the results of these investigations with particular emphasis placed on the distributions and isotopic compositions of archaeal and bacterial biomarkers; the insights gained are then applied to two palaeoenvironmental investigations.

A range of biomarkers – all derived from bacterial or archaeal membrane lipids – were examined, including phospholipid fatty acids, archaeol and hydroxyarchaeol, hopanoids and non-isoprenoidal dialkyl glycerol diethers (DGDs). Of these, the archaeal lipids and structurally similar non-isoprenoidal DGDs proved most useful in evaluating sedimentary processes due to a lack of inputs from allochthonous sources. In all marine settings examined – each characterised by a diffusive flux of methane and, hence, slow AOM rates – archaeol and C_{33} DGDs are present, albeit at concentrations 1-2 orders of magnitude lower than observed at cold seeps. Hydroxyarchaeol is present at 4 of the 6 marine sites. However, archaeal lipids occur only near the sulfate-methane transistion zone (SMTZ); C_{33} DGDs, while most abundant at the SMTZ, are also present higher in the sedimentary column. Coupled with the low carbon isotopic composition (-55‰) of archaeol, these depth profiles provide some of the first evidence that microbial consortia in settings characterized by diffusive methane flux are similar to those observed at cold seeps. The presence of non-isoprenoidal DGDs at depths above the SMTZ and where archaeol is absent provides further evidence that they derive from SRB and are not obligately part of AOM consortia.

Similar biomarker assemblages are found in marine settings where methanogenesis occurs (and ^{13}C pulse-chase experiments confirm that the archaeal lipids derive from methanogens rather than methanotrophs). This association of bacterial and archaeal diethers with both processes could complicate interpretation of biomarker assemblages, but distinguishing features are evident. Non-isoprenoidal DGDs of inferred SRB origin are more abundant than archaeal lipids in settings where AOM does not occur. Moreover, where they could be determined, archaeal $\delta^{13}C$ values range from –28 to –35‰, inconsistent with a methanotroph source. Thus, methanogen and anaerobic methanotroph populations can be distinguished in the geological record but should be done cautiously. At the freshwater sites, non-isoprenoidal DGDs are absent as expected. In addition, hydroxyarchaeol was not detected, despite the presence of *Methanosarcinales* species, important producers of hydroxyarchaeol.

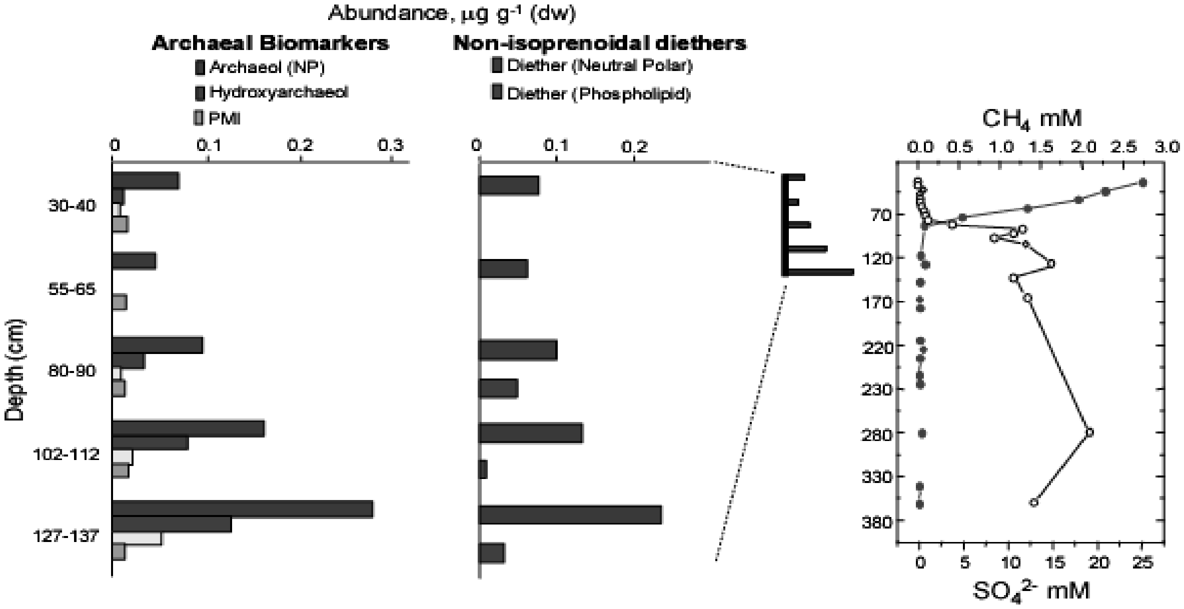


Fig.1. Depth profiles of biomarker abundances and methane and sulfate concentrations in sediments from the Skaggerak.

Insights from the modern ecological studies have been applied to sediments from the Amazon Fan and Benguela Upwelling System. Both sediments contain non-isoprenoidal DGDs and archaeol, with the former being among the most abundant polar lipids in some Benguela sedimentary horizons. In the Benguela sediments, the carbon isotopic compositions of both bacterial and archaeal lipids range from –28 to –37‰, indicating that they do not derive from AOM-related organisms and are instead associated with sulfate reduction and methanogenesis. Low biomarker abundances prevented application of a similar approach to Amazon Fan sediments but the relative abundances of the two compound classes (non-isoprenoidal diethers being more abundant than archaeol) are consistent with an origin from sulfate reducers and methanogens.

OB3-2: Specificity of molecular constitution of organic matter from Triassic formations in Southwestern Siberia

O.V. Serebrennikova[1], F. Czechowski[2], E.A. Belitskaja[1], T.J. Filippova[1], V.V. Evseev[1]

1) Institute of Petroleum Chemistry RAS, Tomsk, Russia (e-mail: ovs49@yahoo.com)
2) Wroclaw University of Technology, Wroclaw, Poland

The molecular constitution of organic matter (OM) in middle and lower triassic of southern part of western siberia is presented. The investigated core profile is formed of volcanic rocks interbedded with sand and clay layers (Fig. 1). Content of organic carbon (C_{org}) in clay layers ranges from 0.3 to 3.3%.

Sedimentation in early Triassic over the Siberia region took place in arid climate and was accompanied by volcanic activity episodes. During anisian climate had changed to humid and volcanic processes declined. These drastic changes between the middle and lower Triassic periods are also marked by the change in molecular constitution of OM in the respective clay formations. The results on OM molecular constitution in clay layers of the investigated profiles allowed to the following general characteristics:

(i) *Middle Triassic.* In OM are present abundant metalloporphyrins, mainly as complexes with nickel (0.1 - 64 μmol/g of OM), in which peripheral alkyl substituents are highly degraded. In upper part of the profile a homological composition of metalloporphyrins is characterised by a dominant homologue with summary peripheral alkyl substituents of 7 carbons, while in lower part of the profile it is characterised by 6 carbons (Fig. 1). Only rarely are present vanadylporphyrins with concentration below 0.7 μmol/g of OM. Among isoprenoid hydrocarbons high relative concentration reveal pristane (pr) and phytane (ph), while among hopanes - 17α(h),21β(h)-c30-hopane (ratio of ts/tm is 0.59). Steranes are absent in OM, whereas triaromatic C_{20} - C_{28} steranes and C_{15} - C_{20} sesquiterpanes are in higher concentration. Among polyalkyl naphthalene derivatives a highest concentration reveal 1,2,5-tmen and 1,2,5,6-+1,2,3,5-temen, while relative concentration of naphthalene is low (Fig.1). In comparison a relative concentration of phenanthrene is higher, where similarly as for methylnaphthalenes, the highest relative concentration among phenanthrene polyalkyl derivatives reveal has one isomer of the tetramethylphenanthrenes (Fig. 1). Polyaromatic hydrocarbons (PAH) are present in low concentration only in some samples.

(ii) *Lower Triassic.* Through the all profile steranes, hopanes and nickel porphyrins are absent in OM. Only in one sample were recorded abundant vanadylporphyrins. Characteristic is occurrence of a variety of aromatic compounds containing sulfur and oxygen in high concentration, and also sterols with a domination of stigmast-5-en-3β-ol (24s), fatty acids within homologues range C_5 - C_{24} as well as isopropyl ethers C_{12} and C_{14}. A relative concentration of pristane and phytane is lower compared to farnezane and norfarnesane. Composition of bicyclic aromatic compounds through the profile changes. In some samples it is similar as for middle Triassic OM, while in the others naphthalene, methyl- or dimethylnaphthalenes dominate. In the formation occurring directly on basaltic rocks with marks of lava flow biphenyl compounds dominate (Fig.1). In the majority of the samples phenanthrene compounds are represented by phenanthrene and methylphenanthrenes. Except in the three samples, occurrence of chrysophanol through the all profile is characteristic, and among aromatic hydrocabons PAH dominate and show a similar molecular composition (Fig.1). Often they also contain benz(c)phenanthrene and benz(ghi)fluoranthene.

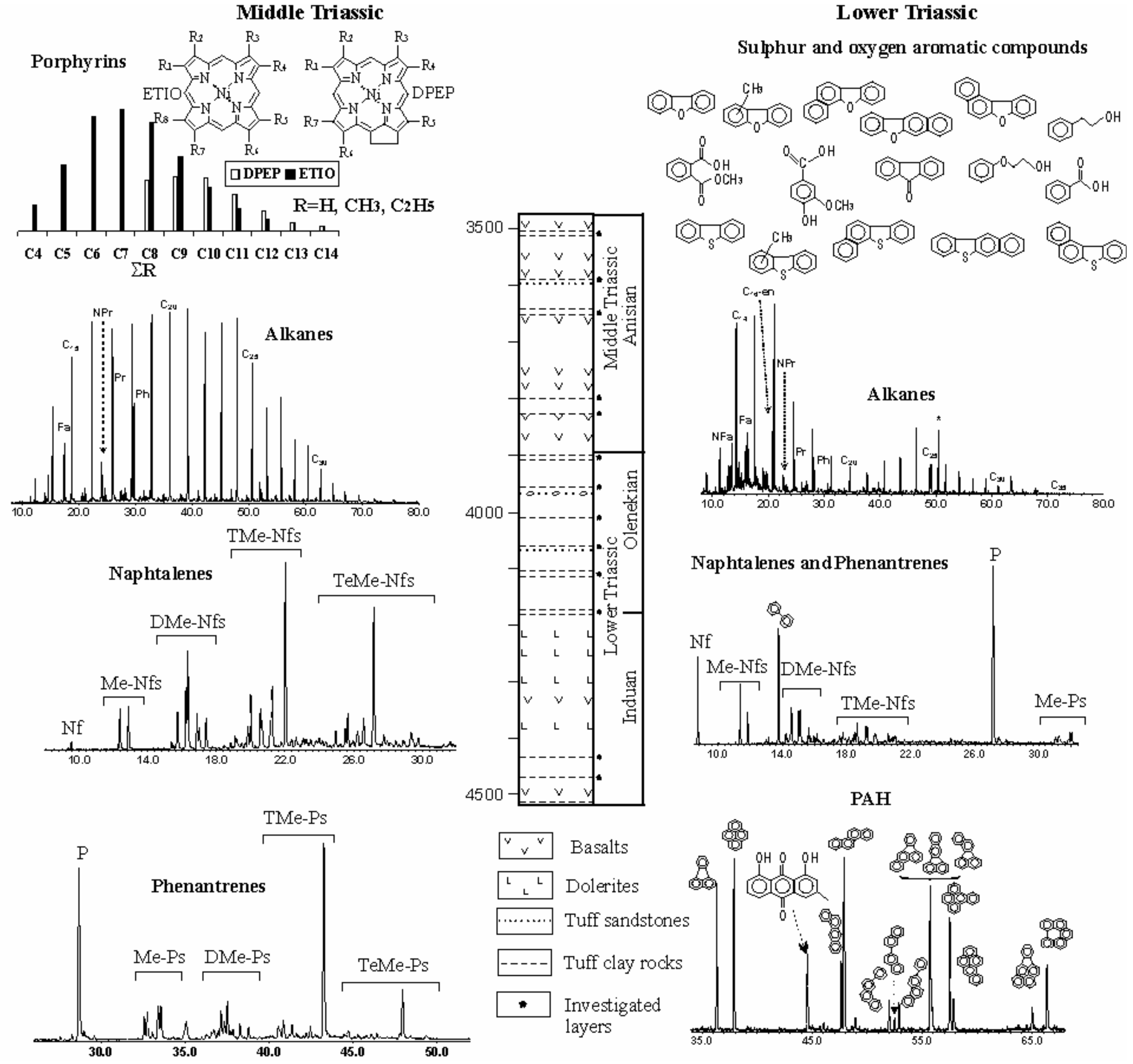


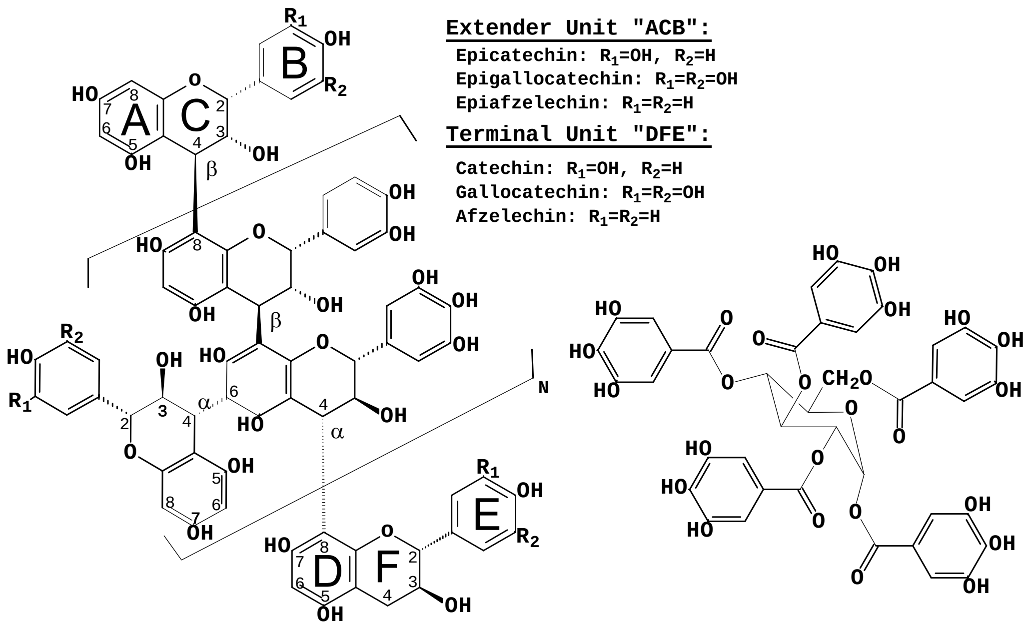
Fig.1. Molecular composition of selected group of compounds in OM of Triassic formations sequence of Western Siberia.

OM-1: Diagenesis through the lens of molecular-level tannin: tapping into the potential

P.J. Hernes[1,2], J.I. Hedges[1]

1) School of Oceanography, University of Washington, Seattle, WA 98195-7940 USA (e-mail: pjhernes@ucdavis.edu)
2) Department of Land, Air and Water Resources, University of California, Davis, CA 95616 USA

In terrestrial biomass, tannin is the third most abundant biochemical behind carbohydrates and lignin. However, in rapidly cycling leaves and needles, tannin is often more abundant than lignin, with ^{13}C-NMR measurements as high as 20%. Thus, the annual flux of tannin into the environment is substantial. Combined with its reactivity, there is great potential for tannin to influence biogeochemical cycling of carbon and nutrients. However, reactivity is dependent on structure (primarily due to hydroxylation patterns on the B-ring), and structure is source dependent.



Condensed Tannin **Hydrolyzable Tannin**

Utilizing a molecular technique for quantifying condensed tannin, we analyzed 117 tissues from 77 plants to ascertain the quantitative importance of tannin in these tissues as well as compositional information that should relate directly to reactivity. Molecular measurements yielded as much as 10.5 wt% tannin. Pine needles in general contained the most total tannin as well as the most reactive form of tannin with three hydroxyl groups on the B-ring. As a source indicator, tannin can be used to distinguish between different sources, but it is also clear that reactivity in the environment can readily alter these distinctions.

Early diagenetic behavior of tannin was studied in a series of degrading mangrove leaves from a tropical estuary. Tannin reactivity was intermediate between more conservative components like lignin and more labile components like cyclitols. Nitrogen immobilization, a net increase in total nitrogen from an exogenous source, was observed in these leaves and shows an inverse correlation with measurable tannin at the molecular level. Several trends point toward condensation reactions between tannin and nitrogen, including 1) ^{13}C-NMR data comparisons to molecular measurements, which shows that tannin is being chemically altered but not remineralized, 2) differential reactivity between tannin with di- and trihydroxylated B-rings, consistent with quinone formation, and 3) preferential loss of basic amino acids, which are normally preferentially preserved in sediments. The latter trend is also consistent with condensation reactions.

Tannin shows a strong affinity for mineral surfaces, which may in part account for the difficulties in measuring tannin in environmental samples. Tannin-mineral complexes could play a vital role in processes such as carbon sequestration, DOC transport and partitioning, organic contaminant transport and remediation, soil stabilization, and microbial community structure. Research is currently being conducted on batch sorption/desorption of tannin standards to clay minerals. New analytical methods will need to be developed to better quantify tannin in environmental samples, perhaps degradative methods to isolate the less reactive A-ring of the tannin monomers.

References

Hernes P.J. and J.I. Hedges (2004) Tannin signatures of barks, needles, leaves, cones, and wood at the molecular level. *Geochimica et Cosmochimica Acta,* **58**, 1293-1307.

Hernes P.J., R. Benner, G.L. Cowie, M.A. Goñi, B.A. Bergamaschi, and J.I. Hedges (2001) Tannin diagenesis in mangrove leaves from a tropical estuary: A novel molecular approach. *Geochimica et Cosmochimica Acta*, **65**, 3109-3122.

Hernes P.J. and J.I. Hedges (2000) Determination of condensed tannin monomers in plant tissues, soils, and sediments by capillary gas chromatography of acid hydrolysis extracts. *Analytical Chemistry*, **72**, 5115-5124.

OM-2: Covalent and non-covalent coupling of peptides with humic substances: implications for protein preservation in natural organic matter

P.G. Hatcher, P.-H. Hsu

Department of Chemistry, The Ohio State University, Columbus, OH 43210 USA

Since proteins and their constituent amino acids are the most abundant nitrogen-containing substances in natural organic matter (NOM), they are important sources of nitrogen in numerous sedimentary systems. Historically, proteins have been considered very labile, and consequently unlikely to survive during early diagenesis. Evidence is increasing, however, that some fraction of "proteinaceous" material is preserved in sedimentary environments (Pantoja and Lee, 1999; Nguyen and Harvey, 2001). While these recent studies revealed that high-molecular-mass proteinaceous material comprised a significant fraction of the nitrogen in some sediments, many questions remain as to the mechanisms by which proteins or peptides are preserved. Some suggest that organo-mineral associations constitute an important mechanism for preservation (Keil et al., 1994). Others suggest that aggregation of organic matter within mineral assemblages offers protection from degradation (Anarson and Keil, 2001) or encapsulation within macromolecular organic matter (Knicker and Hatcher, 1997; Nguyen and Harvey, 2001). Kirchman et al. (1989) suggested that proteins underwent some sort of covalent binding to macromolecular organic matter and resulting protection during degradation of phytoplankton in oceanic systems. We propose that protection of peptides from hydrolysis can be afforded by covalent linkage to the macromolecular SOM.

To demonstrate covalent linking of peptides to macromolecular organic matter, 2D HSQC (Heteronuclear Single Quantum Coherence) NMR spectroscopy was utilized in conjunction with an isotopic enrichment experiment. The 2D ^{15}N-^{1}H HSQC NMR spectroscopy observes protons directly bonded to nitrogens in molecules and is sensitive to covalent bonds adjacent to the observed nitrogen-proton pair. ^{15}N-^{1}H HSQC NMR spectroscopy is commonly utilized to examine protein structures, as changes in NMR spectra are observed when amino acid residues experience a change in their chemical environment. An ^{15}N-labeled tetrapeptide with the sequence of amino acids glycine-glycine-glycine-arginine (GGGR with only G labeled, Figure 1) was added to humic acids from a sample of Douglas fir wood showing the early onset of humification of lignin.

HSQC NMR provides direct spectroscopic evidence for the reaction of nitrogen-containing molecules with macromolecular organic matter in the form of lignin-derived humic acids. The ^{15}N-^{1}H HSQC NMR spectrum clearly reveal shifts in nitrogen-proton correlated signals that can only be interpreted as the formation of covalent and non-covalent bonds between peptides and humic acid molecules (Figure 1). The formation of new peaks and loss of intensity in existing peaks indicates that the covalent bonds involve the amide groups of the peptide. Broadened peaks suggest possible covalent, non-covalent, or charge-charge interactions. In ^{13}C-^{1}H HSQC NMR experiments, comparable peak shifts are also observed providing clear evidence that the covalent bonding occurring between peptides and humic substances is through a nucleophilic attack of the nitrogen in amide groups of the peptide to appropriate functional groups in humic substances.

We suspect that quinone structures are the most likely candidates for formation of adducts with peptides via the Michael reaction, considering the fact that such structures are known to exist in humic acids and their affinity for nucleophiles like peptides is well known (Mason and Liebler, 2000). These studies show that N incorporation into humic substances can readily occur by covalent coupling of peptides to the macromolecular framework through quinone-like functional groups.

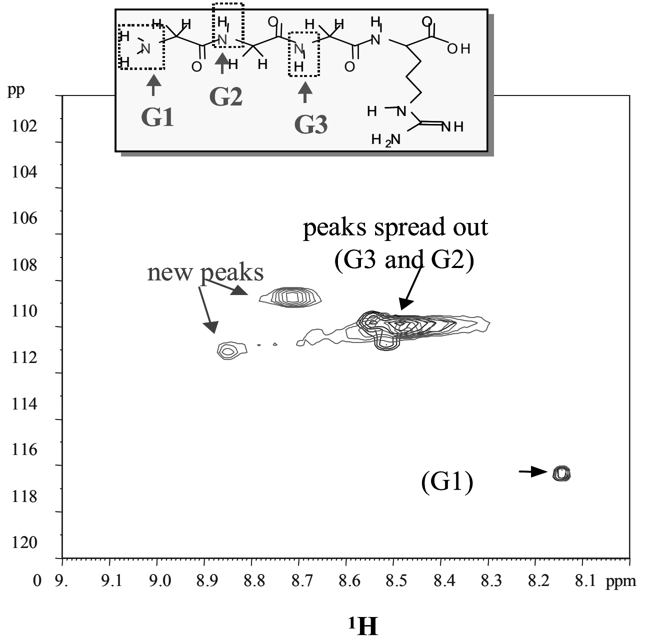


Fig.1. ^{15}N-^{1}H HSQC spectrum of the peptide GGGR, shown in the inset above, reacted with humic acids from a degraded wood sample from Mt. Rainier, Washington. The cross peaks for the unreacted peptide are shown in black and those for the peptide/HA mix (room temperature for 24 hrs) are shown in red. New cross peaks are shown indicating covalent binding. The broadened peaks are due to either covalent or non-covalent binding.

References

Anarson, T. S. and Keil, R.G., 2001. Organic-mineral interactions in marine sediments studies using density fractionation and X-ray photoelectron spectroscopy. Organic Geochemistry 32, 1401-1415.

Kirchman D. L., Henry D. L., and Dexter S. C., 1989. Adsorption of proteins to surfaces in seawater. Marine Chemistry 27, 201-217.

Keil R. G., Montlucon D. B., Prahl F. G., and Hedges J. I., 1994. Sorptive preservation of labile organic matter in marine sediments. Nature 370, 549-552.

Knicker H. and Hatcher P. G., 1997. Survival of protein in an organic-rich sediment. Possible protection by encapsulation in organic matter. Naturwissenschaften 84, 231-234.

Mason D. E. and Liebler D. C., 2000. Characterization of benzoquinone-peptide adducts by electrospray mass spectrometry. Chemical Research in Toxicology 13, 976-982.

Nguyen R. T. and Harvey H. R., 2001. Preservation of protein in marine systems: Hydrophobic and other noncovalent associations as major stabilizing forces. Geochimica et Cosmochimica Acta 65, 1467-1480.

Pantoja, S. and Lee, C., 1999. Molecular weight distribution of proteinaceous material in Long Island Sound sediments. Limnology and Oceanography 44, 1323-1330.

OM-3: Influence of climate indices on cross-linking between lignin and polysaccharides as revealed from $\delta^{13}C$ of wood hydropyrolysis residues

L.E. Beramendi-Orosco[1], D.J. Large[2], C.E. Snape[2], T. Drage[2], C.H. Vane[3]

1) Instituto de Geofisica, UNAM, Ciudad Universitaria, Mexico D.F. 04510, Mexico (e-mail: laura@geofisica.unam.mx)
2) Nottingham Fuel and Energy Centre, SChEME, University of Nottingham, Nottingham NG7 2RD, UK.
3) British Geological Survey, Keyworth Nottingham NG12 5GG, UK.

Hydropyrolysis (Hypy, i.e. pyrolysis under high hydrogen pressure) performed on cellulose and Klason lignin samples does not produce major isotopic fractionation that could affect the stable carbon isotope composition, $\delta^{13}C$, of the hypy residues (Beramendi-Orosco et al. 2005). What is more, the $\delta^{13}C$ of hypy residues from cellulose-Klason lignin mixtures were in the value range of the corresponding Klason lignin. This indicates that cellulose decomposed completely and that there are no major structural rearrangements, which could lead to carbon cross-linking between these two moieties, are produced by hypy. When performing this technique on wood samples, the $\delta^{13}C$ of the hypy residues are consistently enriched in ^{13}C relative to the corresponding Klason lignin and depleted relative to the original wood sample. This results from polysaccharide derivatives remaining in the residue, indicating the presence of cross-linking between lignin and polysaccharides (Beramendi-Orosco et al. 2005).

This research explores if the $\delta^{13}C$ signal from a tree ring sequence yields information on the influence of climate on cross-linking. Hypy was applied to a 54-year oak tree ring sequence, covering the period 1947-1999. The $\delta^{13}C$ signals obtained from the wood and hypy residues from the same tree ring sequence (Figure 1) have very similar profiles with a high correlation coefficient ($r = 0.93$, $P<0.001$) and a consistent offset in the hypy signal by an average of 1.20 ‰ (± 0.31 ‰). The new signal derived from this offset (Δwood-hypy) appears to have some periodic components.

Spectral analysis (periodogram and singular spectrum analysis (SSA) followed by the multitaper method (MTM)) of this Δwood-hypy signal revealed two significant periodicities, at about 5 and 3.6 years. These appear to be related to the North Atlantic Oscillation (NAO) and El Niño Southern Oscillation (ENSO) climatic indices. Fluctuations in the Δwood-hypy time series seem to be in phase with the NAO data for the period 1947-1965 and with ENSO for the years 1973-1999.

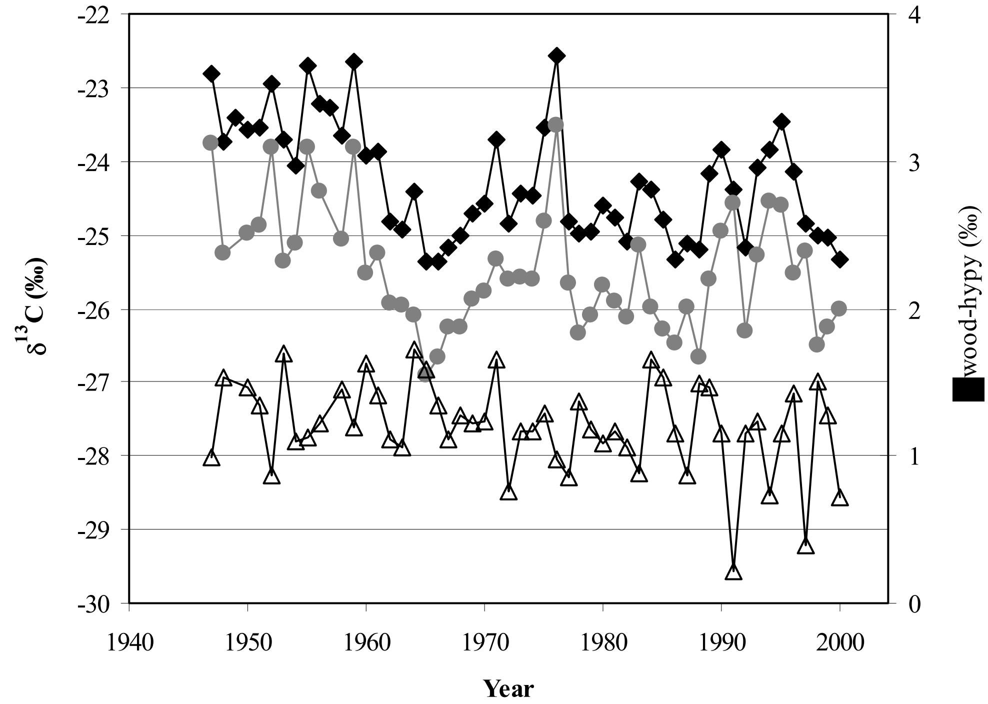


Fig.1. $\delta^{13}C$ time series tree ring wood (rhomboids), hypy residues obtained at 500 °C (circles), and offset between $\delta^{13}C$ of wood and hypy residues (Δwood-hypy, triangles)

A possible explanation to this apparent influence of climate indices on the degree of cross-linking between lignin and polysaccharides is currently being explored. Variations in syryngyl to guaiacyl lignin units ratios are being determined by a combination of TMAH thermochemolysis and solid state ^{13}C NMR.

References

Beramendi-Orosco L.E., Snape C.E., Large D.J. (2005). $\delta^{13}C$ of wood hydropyrolysis residues: evidence of cross-linking between lignin and polysaccharides. Organic Geochemistry (submitted).

OEB-1: Organic tracers for sources of atmospheric particulate matter - Current status for urban and global applications

B.R.T. Simoneit[1], M. Kobayashi[2], M. Mochida[2], K. Kawamura[2]

1) College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, OR 97331, U.S.A.
2) Institute of Low Temperature Science, Hokkaido University, Kita-ku, Sapporo 060-0819, Japan

Global and urban pollution of the atmosphere by particulate matter (PM) is a major research topic related to climate change and public health. The concept of source apportionment for particles in urban airsheds has been amply documented (1 and references therein). Currently new research directions on atmospheric PM are the composition of polar, water-soluble compounds(2-4) and the inputs and source strengths of soil and desert dusts in urban, rural and global regions. Thus, black carbon (soot), polar compounds, lipid components, and anthropogenic and synthetic compounds, besides PAH, are being characterized in global aerosols.

The current status of this research is illustrated here with the annual Asian dust storms transiting into the Pacific region. Samples were acquired as TSP (total suspended particles) or size segregated fractions of PM-10 or PM-2.5 (µm size cut) at ground stations, on ship and aircraft(5-7). The detection limits for the major tracer compounds are adequate to analyze PM from 1–100 m^3 of air. Total extracts and derivatized aliquots were analyzed by GC-MS. Typically the major inputs of organic compounds to these aerosols (Fig. 1) are: (1) natural emissions of terrestrial plant wax and marine lipids based on the alkanoic acid, alkanol, and alkane distributions; (2) smoke from biomass burning (mainly non-conifer fuels) using levoglucosan and dehydroabietic acid as tracers; (3) soil resuspension due to spring agricultural activity as inferred from major primary and reduced sugars (e.g., sucrose, glucose, sorbitol); and (4) urban/industrial emissions from fossil fuel use based on petroleum biomarkers. Significant secondary products derive from the oxidation of organic compounds during long-range transport and consist of dicarboxylic, aromatic, and hydroxycarboxylic acids. The same compound distributions are found aloft in the aircraft samples, except the polar compounds are enhanced over the lipids.

In summary, it is routine to monitor major organic tracers for dominant sources of aerosol PM on urban to global scales using ground stations (also towers), ships or aircraft. The major sources for PM are natural emissions from vegetation (wax), urban activity (traffic, industries, etc.), fires (wildfires, garbage burning, etc.), and soil and desert sand resuspension (agriculture, construction, wind erosion). The novel concepts are: (1) organic compound tracers are specific for many emission sources, and (2) burning of refuse, wildfires, and controlled combustion, steam strip fuel-specific tracers as the natural products, altered derivatives and depolymerization compounds into aerosols.

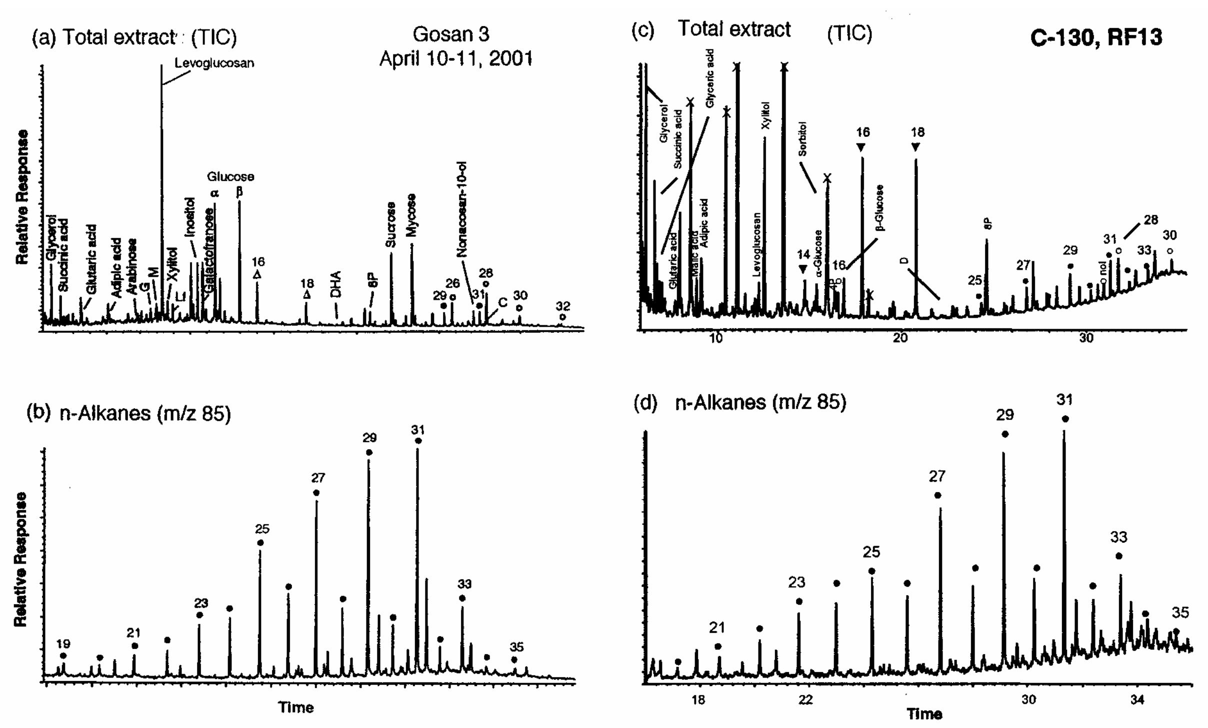


Fig.1. Examples of salient features of the GC-MS data for total extracts of aerosol samples: (a) Gosan, Korea, TIC; (b) Gosan, *m/z* 85, key ion for *n*-alkanes; (c) aircraft C 130 research flight 13, Yellow Sea, TIC; and (d) *m/z* 85, RF13 (numbers refer to carbon chain length of homologous compounds, •=*n*-alkanes, °=*n*-alkanols, Δ or ▼=*n*-alkanoic acids, G=galactosan, M=mannosan, DHA=dehydroabietic acid, Lf=1,6-anhydro-β-D-glucofuranose, 8P=dioctyl phthalate, C=cholesterol, X=silicones)

References

(1) Schauer, J. J., et al. (1996). Atmos. Environ., 30, 3837–3855.
(2) Graham, B., et al. (2002) J. Geophys. Res. 107(D20), 8047, doi:10.1029/2001JD000336.
(3) Simoneit, B. R. T., et al. (1999). Atmos. Environ., 30, 173–182.
(4) Simoneit, B. R. T., et al. (2004a). Environ. Sci. Technol., 38, 5939–5949.
(5) Mochida, M., et al. (2003). J. Geophys. Res. 108(D23), 8368, doi:10.1029/2002JD003249.
(6) Simoneit, B. R. T., et al. (2004b) J. Geophys. Res. 109, D19S10, doi:10.1029/2004JD004598.
(7) Simoneit, B. R. T., et al. (2004c) J. Geophys. Res. 109, D19S09, doi:10.1029/2004JD004565.

OEB-2: Aromatic sulphur compounds in UCMs from crude oils – A cause for environmental concern?

V. Reineke[1], J. Rullkötter[1], E.L. Smith[2], S.J. Rowland[2]

1) Institute of Chemistry and Biology of the Marine Environment (ICBM) Carl von Ossietzky University of Oldenburg, P.O. Box 2503, D-26111 Oldenburg, Germany (e-mail: v.reineke@icbm.de)
2) Petroleum and Environmental Geochemistry Group, School of Earth, Ocean and Environmental Sciences, University of Plymouth, Drake Circus, Plymouth, PL4 8AA, UK

Gas chromatograms of crude oils – and especially biodegraded ones – are often dominated by a “hump“ of an unresolved complex mixture (UCM) beneath the resolved peaks. One-dimensional chromatographic techniques cannot resolve the thousands of substances because of their similar chemical and physical properties. A large amount of these individual compounds – with each isomer present in a low concentration – have yet to be identified although comprehensive two-dimensional GCxGC-ToF-MS already allows classification of compound groups [1].

Whenever crude oil is spilled, a considerable proportion of these compounds is resistant to biodegradation and accumulates in the environment [2]. The toxicity of many single compounds, e.g. the genotoxic potential of PAHs present in crude oils, is known. Thus, it is important to determine the ecotoxic potential of the vast mixtures of hydrocarbons in the UCM.

For this study, the total and the monoaromatic hydrocarbon fractions, separated from two oil pairs by liquid chromatography, were examined. Each oil pair consists of a moderately biodegraded and an unbiodegraded oil from the same oilfield. A pair of moderately mature crude oils with a high sulphur content (3%) was chosen from the Santa Maria Basin (Monterey Formation, California). The second pair is represented by mature oil from the Vienna Basin (Austria) which has a low sulphur content (0.2%). The fractions of aromatic hydrocarbons, including sulphur-containing compounds eluting in this fraction, were obtained by MPLC and normal phase HPLC and analysed by GC-MS.

Besides the expected differences in alkyl benzene and toluene distributions, GC-MS analysis of the aromatic fractions (ion chromatograms of m/z 111) showed differences in sulphur-containing aromatic compounds in the two Monterey oils related to the difference in the extent of degradation. There were no sulphur compounds within the detection limit in the aromatic hydrocarbon fractions of the two Vienna Basin oils.

In order to test the ecotoxicity of the different mixtures, tests were performed with the blue mussel *Mytilus edulis* at different aqueous concentrations of the aromatic hydrocarbon mixtures. The hydrocarbons the mussels were exposed to cause narcosis, i.e. the bioassay was performed on a sublethal level. The biological effect measured was the reduction of feeding rate, which is a parameter used in the calculation for the so-called scope for growth index, which is widely used to indicate mussel health [3]. After the tests, the mussel tissue was extracted to quantify body burdens of accumulated hydrocarbons. Previous studies have shown that a monoaromatic UCM isolated from a Gullfaks crude oil did cause a reduction of feeding rate of about 40% [4].

After 24 h exposures, the mixture of aromatic compounds isolated from the Monterey oils had reduced the feeding rate by up to 40% compared to control mussels. However, the aromatic mixtures isolated from the Vienna oils did not show any significant toxic effect. Thus, the difference in toxicity may mainly be ascribed to organic sulphur compounds. So far, few data are available on the ecotoxicity of alkylated thiophenes and benzothiophenes. Tissue extracts of the exposed mussels are now examined for compounds which might be responsible the differences in toxicity. A special focus lies on identifying organic-sulphur compounds in the aromatic hydrocarbon fractions of the Monterey oils.

References

[1] Sutton, P.A., Smith, E.L., Booth, A.M., Rowland, S.J., Lewis, C.A., Lewis, A.C., Hamilton, J., 2003. GCxGC-ToF-MS identification of compounds in the toxic hydrocarbon unresolved complex mixture (UCM) of crude oils. Poster presentation. 1st International Symposium on Comprehensive Multidimensional Gas Chromatography, Volendam, The Netherlands, March 2003.

[2] Rowland, S.J., Donkin, P., Smith, E., Wraige, E., 2001. Aromatic hydrocarbon “humps” in the marine environment: unrecognized toxins? Environmental Science and Technology 35, 2640-2644.

[3] Widdows, J., Donkin, P., Brinsley, M.D., Evans, S.V., Salkeld, P.N., Franklin, A., Law, R.J., Waldock, M.J., 1995. Scope for growth and contaminant levels in North Sea mussels (*Mytilus edulis*). Marine Ecology Progress Series 127, 131-148.

[4] Smith, E.L., 2002. Unresolved complex mixtures of aromatic hydrocarbons in the marine environment: toxicity, solubility and photodegradation studies. PhD Thesis, University of Plymouth.

OEB-3: Analysis of undisturbed layers of a waste core – Insights into the contamination history of a waste deposit landfill

J. Schwarzbauer, S. Heim, R. Littke

Institute of Geology and Geochemistry of Petroleum and Coal, RWTH Aachen University, Lochnerstrasse 4-20, D-52074 Aachen, Germany (e-mail: schwarzbauer@lek.rwth-aachen.de)

Organic matter in waste deposit landfills is composed of the original waste constituents as well as of transformation products as a result of intense chemical and microbial processes within the deposit body. Mode and kinetics of the reactions depend mainly on the specific conditions with respect to temperature, pressure, microbial communities and oxygen availableness. In particular the build up of individual waste layers, one upon the other, over a long filling period causes significant alterations of the surrounding environment with time. Furthermore, these systems allow to investigate the time depending occurrence and subsequent transformation processes by investigating individual layer separately. This approach was used for the presented study by analysing both the mobile liquid phase (leakage water) and the immobile solid matter of discrete layers of a waste deposit landfill. For these purposes a unique drilling experiment was conducted in 2002 producing an undisturbed waste core of 80m length representing a deposit filling time between 1974 and 2000.

Comprehensive GC/MS analyses were applied to leckage water and solid waste samples of individual core slices of approx. 5m thickness. The analyses revealed a complex mixture of natural compounds as well as xenobiotics including their transformation products (see Fig. 1). A time correlated evaluation of concentration profiles of specific compounds allowed insights into principal transformation processes on a molecular level and provides general information on generation processes of leakage water constituents. Such information is of principal environmental interest, because the discharge of waste deposit derived emissions to the soil and corresponding groundwater is frequently reported.

Bulk parameters (e.g TOC values) revealed sligthly varying chemical properties of the individual waste layers. The concentrations of individual contaminants differed in the same order of deviation. However, the concentration profiles were not congruent to the TOC-profile. Hence, variation due to inhomogeneous deposition of waste is assumed to be a major factor influencing the contamination level of waste layers (see Fig. 2).

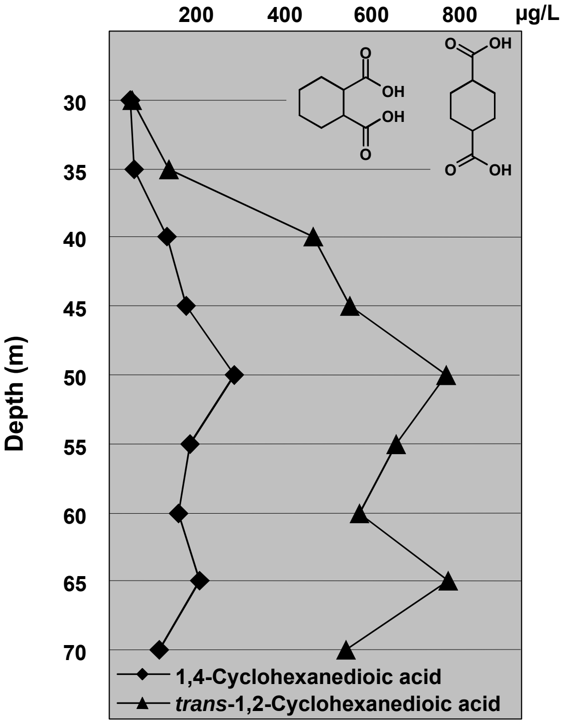


Fig.1. Transformation processes within the deposit are illustrated in Fig. 1 by concentration profiles of specific transformation products. The hydrolysed and hydrogenated metabolites of phthalic and terephthalic acid esters (widespread used as polymer additives) appeared with increasing concentrations towards the bottom of the waste core, reflecting an ongoing degradation of these plasticizers with time and depth.

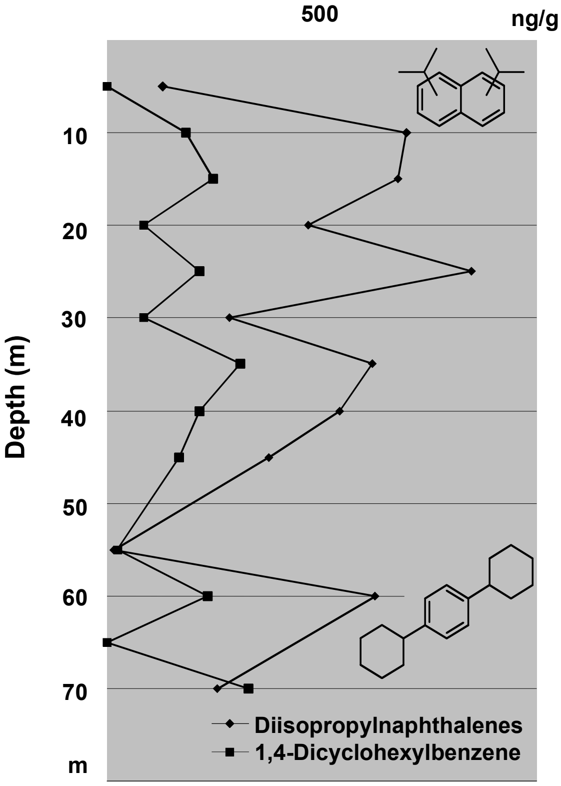


Fig.2. Complementary, in waste layers decreasing concentration of further technical additives, the di-*iso*-propylnaphthalenes and 1,4-dicyclo-hexylbenzene, were detected. However, the concentration profiles are characterized by higher variations as compared to leakage water analyses. This might be the result of the inhomogeneity of the solid waste deposition.

OPC1-1: Constraints in the use of alkenones as proxies of surface marine salinity

J. Bendle[1], A. Martínez-García[2], A. Rosell-Melé[2]

1) Organic Geochemistry Group for the Study of the Ocean and the Atmosphere, Institute of Low Temperature Science, Hokkaido University, Sapporo, 060-0819, Japan
2) Institute of Environmental Science and Technology, Autonomous University of Barcelona, Bellaterra 08193, Catalonia, Spain (e-mail: antoni.rosell@icrea.es)

At present there are no well-established sea surface salinity (SSS) proxies available to paleoceanographers. This would allow to obtain information on past evaporation, precipitation and runoff inputs to the surface ocean mixed layer and - combined with estimates of past sea surface temperature (SST) - the investigation of paleodensities and past boundary conditions for deepwater formation. In this communication we evaluate further the use of an alkenone based index as a potential SSS proxy.

The alkenone unsaturation index $U_{37}^{K}{}'$ has been widely adopted as a proxy to estimate past SSTs. This index measures the relative abundance of the di- and tri-unsaturated C_{37} alkenones ($C_{37:2}$, $C_{37:3}$) in sediments. In the Nordic Seas alkenone SST indices are subject to increasing error in regions where present SST falls below ~6°C (annual mean 0-30m) [e.g. *Rosell-Melé*, 1998]. Coincidentally, in these sub-polar and polar regions the abundance of $C_{37:4}$, relative to the other C_{37} alkenones (%$C_{37:4}$) increases significantly [e.g. *Rosell-Melé*, 1998]. In the northern latitudes, some studies have highlighted an empirical relationship between %$C_{37:4}$ and sea surface salinity (SSS) [*Harada et al.*, 2003; *Rosell-Melé*, 1998; *Rosell-Melé et al.*, 2002; *Sicre et al.*, 2002]. Moreover, some have applied the %$C_{37:4}$ measurement downcore as a tentative proxy to infer paleo-salinity variations [e.g. *Bard et al.*, 2000; *Rosell-Melé et al.*, 2002]. On a global scale it has been demonstrated that there is no discernable relationship of %$C_{37:4}$ to SSS [*Sikes and Sicre*, 2002]. However, in the Nordic Seas and North Atlantic, %$C_{37:4}$ in surface sediments does show a correlation to ocean atlas SSS [*Rosell-Melé*, 1998; *Rosell-Melé et al.*, 2002].

In this paper we further investigate the potential in %$C_{37:4}$ by reporting the values of this index measured in situ in the surface waters of the Nordic Seas and the Southern Ocean (Atlantic sector). We have also studied a range of coastal environments off Northwest Scotland which are representative of a range of marine/brackish to isolated/lacustrine conditions.

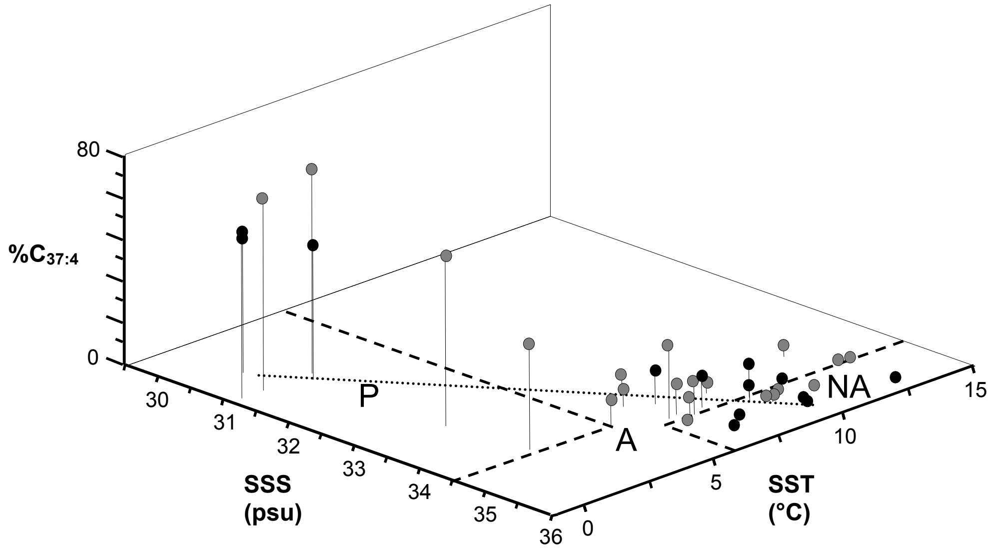


Fig.1. Distributions of %$C_{37:4}$ in the surface waters of the Nordic Seas. %$C_{37:4}$ vs temperature and salinity with major water masses delimited (P: Polar; A: Arctic; NA: North Atlantic) (dark dashed line)

Unusually high percentages of the tetraunsaturated alkenone were measured in the Polar waters, with %$C_{37:4}$ of up to 77% in 80% of sea-ice cover of the East Greenland Current (e,g, Fig. 1). Values of %$C_{37:4}$ across the transects studied show a strong association with water mass type. Analysis of coccoliths in filters indicated that calcified *Emiliania huxleyi* could not be discounted as the biological precursor of alkenones in all the water masses. In some instances values of %$C_{37:4}$ in sea surface POM are also much higher than those in surficial sediments. In the coastal sites, the results suggest an excellent efficiency for %$C_{37:4}$ at predicting the original depositional conditions of the sediments.

The results prevent confirmation of %$C_{37:4}$ as a quantitative palaeo-SSS proxy given the multivariate nature of the data sets. However, %$C_{37:4}$ can be used to reconstruct the type of water mass in the original setting (i.e. marine vs freshwater). This can be applied to reconstruct the relative extension of polar water masses in the Atlantic, or as an indicator of sea-level change in sediment cores in coastal isolation basins. Therefore, %$C_{37:4}$ can be used as a qualitative palaeo-SSS proxy.

References

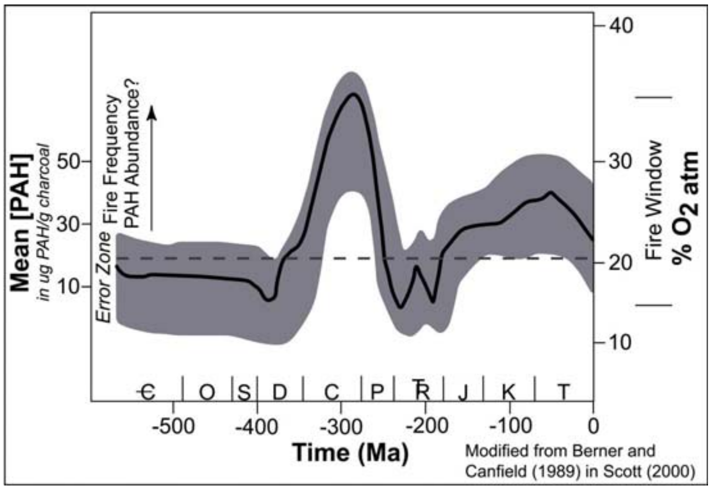
Bard, E., F. Rostek, J.-L. Turon, and S. Gendreau, *Science*, 289, 1321-1324, 2000.
Harada, N., K. H. Shin, A. Murata, M. Uchida, and T. Nakatani, *Geochim. Cosmo. Acta*, 67, 1507-1519, 2003
Rosell-Melé, A., *P aleoceanography*, 13, 694-703, 1998
Rosell-Melé, A., E. Jansen, and M. Weinelt, *Global and Planetary Change*, 34, 143-152, 2002
Sicre, M.-A., E. Bard, U. Ezat, and F. Rostek, *Geochemistry, Geophysics, Geosystems*, 3, 10.1029/2001GC000159, 2002.
Sikes, E. L., and M. A. Sicre, *Geochemistry Geophysics Geosystems*, 3, art. no.-1063, 2002

OPC1-2: Empirical and experimental observations on the occurrence of pyrogenic PAH: implications for paleoatmospheric oxygen reconstruction

P.J. Schuneman, M.E. Uhle

The University of Tennessee, Department of Earth and Planetary Sciences, 1412 Circle Drive, 306 EPS Bldg., Knoxville, TN 37996, USA

Theoretically, the concentration of oxygen in the atmosphere may have dramatically fluctuated throughout the Phanerozoic (Figure 1; Berner and Canfield, 1989). Because oxygen is a critical component to any fire, major fluctuations in atmospheric oxygen level may have significantly affected the intensity and frequency of biomass burning events, suggesting that wildfires would have been more prevalent at times of elevated oxygen content (Scott, 2000). Abundances of fossil charcoal in the geologic record qualitatively reflect this relationship. Land plants had evolved by the Silurian, and the earliest true forests had evolved by the mid-Devonian, while oxygen levels were still low. Fuel accumulations and oxygen content in the atmosphere probably did not reach sufficient levels to sustain burning until the late-Devonian. There are only one or two isolated samples of fossil charcoal of this age (Scott, 2000). By the time oxygen levels had risen to ~35% in the Carboniferous (Berner and Canfield, 1989), fossil charcoal is globally abundant (Scott, 2000). During the Triassic, oxygen levels had fallen to ~15%, and fossil charcoal is nearly absent from the rock record (Scott, 2000). Based on the empirical association between modeled oxygen level and charcoal abundance, an implicit relationship between biomass burning and oxygen level exists. By focusing on a distinct set of combustion-derived organic compounds, polycyclic aromatic hydrocarbons (PAH), the qualitative nature of this relationship can be approached quantitatively. During times of elevated oxygen level, biomass burning events are facilitated, and therefore, a greater proportion of PAH are expected.



Modified from Berner and Canfield (1989) in Scott (2000)

Fig.1. Modeled atmospheric oxygen concentrations throughout the Phanerozoic: error zone in gray; average values in solid black line; modern concentration in dashed line (21%). Mean PAH concentration based on sum of U.S. EPA Priority 16 PAH concentrations from samples of Carboniferous, Triassic, and Modern ages.

To test the hypothetical relationship between atmospheric oxygen level and PAH production, charcoals were collected from rocks of Carboniferous and Triassic age, which relate to the highest (35%) and lowest (15%) levels of atmospheric oxygen (Berner and Canfield, 1989). Carboniferous samples were collected from the Joggins Formation of Nova Scotia, and Triassic samples were collected from the Chinle Formation of Petrified Forest National Park, Arizona. Modern charcoals, known to have formed in an atmosphere of 21% O_2, were collected from Zion National Park, Utah. Preliminary results of PAH extracted from these samples substantiate the relationship between modeled oxygen level and PAH production.

Carboniferous charcoals have the highest concentrations of total PAH, followed by modern charcoals, and Triassic charcoals contain the lowest concentrations of total PAH. This trend in PAH concentration corresponds with oxygen levels. Total PAH concentrations from Carboniferous samples average 50.12 µg/g (4.22 -234.61 µg/g); Triassic samples average 8.76 µg/g (7.08-11.26 µg/g); and modern samples average 15.26 µg/g (6.23-22.43 µg/g). The relationship between total mean PAH concentration and oxygen content (Figure 1) is linear with an r-squared value of 0.93. Multivariate statistical analysis of the entire data set shows that one principal component accounts for 90% of the total variance. This component may be oxygen content.

To more accurately assess the role of atmospheric oxygen concentration to PAH production, a set of combustion experiments has been designed. Because fires exist at the interface of sufficient heat, fuel, and oxygen, more than simply oxygen content will be considered. In a quartz glass tube, dry vegetation (fuels) collected from Zion National Park will be combusted at a range of temperatures under varying levels of atmospheric oxygen. By isolating the individual role of oxygen concentration to PAH production, through the experimental design and multivariate statistical analyses, a more detailed reconstruction than those offered by theoretical models of atmospheric oxygen fluctuations may be obtained.

OPC1-3: The calibration and application of TEX_{86} in lacustrine systems: a powerful tool for independent continental paleotemperature reconstruction

L.A. Powers[1], J.P. Werne[1], T.C. Johnson[1], E.C. Hopmans[2], J.S. Sinninghe-Damsté[2,3], S. Schouten[2], I.S. Castañeda[1]

1) Large Lakes Observatory, University of Minnesota, 10 University Drive, Duluth, Minnesota 55812, USA (e-mail: powe0285@umn.edu)
2) Royal Netherlands Institute for Sea Research, Department of Marine Biogeochemistry and Toxicology, P.O. Box 59, 1790 AB Den Burg, Netherlands
3) Utrecht University, Faculty of Geosciences, PO Box 80.021, Utrecht, Netherlands

The development of the TEX_{86} paleotemperature proxy [1] in lacustrine systems [2] provides a new independent paleothermometer, providing for temperature reconstructions only limited by the length of modern and ancient lacustrine sedimentary records. We have developed a new calibration for the TEX_{86} paleotemperature proxy from a climatically diverse suite of globally distributed lacustrine systems (N=12). The results of this calibration show a strong linear relationship between TEX_{86} values and published mean winter lake surface temperatures (TEX_{86}= 0.017*LST+0.28 R^2=0.97). The TEX_{86} index as it currently stands appears to work only in large volume lakes, which are typically the best integrators of regional climate variability. The "marine" crenarchaeota responsible for producing the tetraether membrane lipids used in the TEX_{86} index do not appear to be ubiquitous in lakes as previously thought, or are not in great enough abundance to be detected in the sediments of some, especially small, lakes. In contrast to the aquatically derived tetraether lipids, we have found terrestrial tetraether lipids in all lacustrine sediments analyzed thus far. We believe that the terrestrial tetraethers are primarily produced by soil bacteria or archaea. In very few cases the presence of terrestrial tetraethers and/or tetraethers produced by methanogenic archaea, co-occurring with the aquatic tetraethers, confuse the TEX_{86} signal. Here we explore the relationship between surface temperature and tetraether abundance, attempting to minimize the influence of the terrestrial tetraethers on the temperature signal.

We have also applied TEX_{86} to lacustrine sediments from Lake Malawi, East Africa, to develop a high-resolution paleotemperature record from the LGM to the present. We find a ~4 ºC overall warming since the LGM, with temperature reversals of more than 2 ºC during the Younger Dryas (12.5 ka BP) and in the early Holocene (Fig.1), possibly associated with the 8.2 ka event. The warmest Holocene temperatures in this part of Africa appear to have occurred around 5000 years ago. The onset of warming in the Lake Malawi basin coincides with the BYRD oxygen isotope record of warming in Antarctica. While the range of temperatures observed in this study is not surprising, the timing of post-glacial warming, the thermal response to the YD, and the Holocene history of warming and cooling trends are providing important new insights into tropical climate dynamics on centennial to millennial scales.

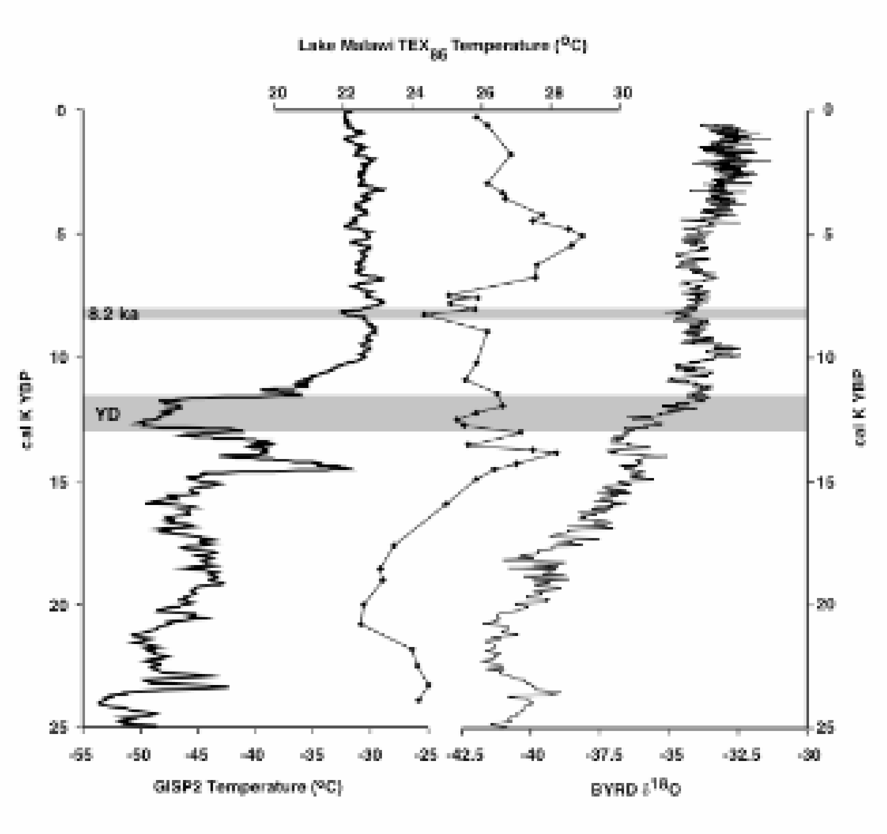


Fig.1. Lake Malawi TEX_{86} temperature curve plotted with GISP2 temperature curve [3] and Byrd oxygen isotope record (on the GISP2 timescale) [4,5] and supplemental Holocene data provided by Dr. Sigfus Johnsen. Two major events are highlighted, the Younger Dryas (YD), and the cooling at 8.2 ka. The uppermost 40 samples are from core M98-1P and the last 3 samples are from core M98-2P (for age models see http://www.ngdc.noaa.gov/paleo/datalist.html). Standard deviations of at least duplicate analyses for all samples are < ± 1 ºC.

References

1. Schouten, S., Hopmans, E. C., Schefuss, E. & Sinninghe Damsté, J. S. Distributional variations in marine crenarchaeotal membrane lipids: a new tool for reconstructing ancient sea water temperatures? *Earth and Planetary Science Letters* 204, 265-274 (2002).
2. Powers, L. A., Werne, J. P., Johnson, T. C., Hopmans, E. C., Damsté, J. S. S. & Schouten, S. Crenarchaeotal membrane lipids in lake sediments: A new paleotemperature proxy for continental paleoclimate reconstruction? *Geology* 32, 613-616 (2004).
3. Alley, R. B. (IGBP PAGES/World Data Center for Paleoclimatology, Data Contribution Series #2004-013, NOAA/NGDC Paleoclimatology Program, Boulder CO, USA, 2004).
4. Blunier, T. & Brook, E. J. (IGBP PAGES World Data Center-A for Paleoclimatology, NOAA/NGDC Paleoclimatology Program, Boulder, CO, USA, 2001).
5. Johnsen, S. J., Dansgaard, W., Clausen, H. B. & Langway Jr., C. C. Oxygen isotope profiles through the Antarctic and Greenland ice sheets. *Nature* 235, 429-434 (1972).

OPC2-1: Abrupt wind regime changes in the North Atlantic during the past 28.000-60.000 years

C. Lopez-Martinez[1], J.O. Grimalt[1], M.J. Vautravers[2]

1) Institute of Chemical and Environmental Research (CSIC) 08034-Barcelona
2) Godwin Laboratory, University of Cambridge, Cambridge

C_{25}-C_{33} odd carbon numbered *n*-alkanes and C_{22}-C_{30} even carbon numbered *n*-alkan-1-ols are components of higher plant waxes (Eglinton & Hamilton, 1967) that have been successfully used for the estimation of inputs from continental sources in paleoclimatic and paleoceanographic studies (e.g. Gagosian & Peltzer, 1986; Poynter *et al.,* 1989; Villanueva *et al,* 1997). Here we report the first reconstruction of terrestrial material inputs in the western subtropical North Atlantic for the Marine Isotope Stage 3 (MIS 3) in which abrupt climatic events are recorded (see reviews in Leuschner & Sirocko, 2000 and Voelker *et al.,* 2002).

The studied ODP core Site 1060 is located at the Blake Outer Ridge (30º46'N, 74º28'W, 3481 m depth) (Fig. 1), within the subtropical gyre, under the influence of the Gulf Stream (Keigwin *et al.,* 1998). In winter, the Site is affected by the westerlies, whereas in summer wind blows along the coast, following the Gulf Stream direction (http://ferret.pmel.noaa.gov/Ferret/LAS/LAS_servers.html) (Fig. 1). The results are compared with previously reported $U^{K'}_{37}$-SST, faunal proxies and IRD records from the same core (Vautravers *et al.,* 2004).

During MIS 3 sea surface temperatures measured from C_{37} alkenones (SST-UK'$_{37}$) exhibited a strong parallelism with the abrupt D/O changes observed in the $\delta^{18}O$ ice composition in GRIP. They fluctuated between 16.3ºC and 21.6ºC following abrupt warming and cooling of about 3.5ºC in less than 400 yr (Fig. 1). However, during the interstadials SST-UK'$_{37}$ involved relative constant values with abrupt starts and ends while D/O $\delta^{18}O$ in GRIP exhibited progressive temperature decreases after abrupt warming transitions.

Higher plant *n*-alkanes and *n*-alkan-1-ols also exhibited an abrupt pattern following D/O $\delta^{18}O$ in GRIP. Increases of these terrigenous compounds are coincident with cold events, marked by $U^{K'}_{37}$-SST minima and abundance of cold water foraminifera species maxima (Fig. 1). Major terrestrial material inputs rapidly rise at the beginning of most Greenland Stadials (GSs), coinciding with the decline of $U^{K'}_{37}$-SST. Fluxes increases of more than four times for the *n*-alkan-1-ols and of three times for the *n*-alkanes can be found in less than 400 years, like at the beginning of GS-13 that coincides with Heinrich 5 (Fig. 1). Even in only 150 years, *n*-

alkan-1-ols fluxes could increase six times and *n*-alkanes, more than five times, like when starting GS-9, coinciding with HE 4 (Fig. 1).

In this study, fluxes of terrigenous biomarkers have been used to evaluate changes in the wind system strength during MIS 3. A strong correlation is found between terrigenous fluxes oscillations and the Polar Circulation Index (PCI) in GISP2 showing that the wind changes measured in Blake Outer Ridge were general of the Northern Hemisphere.

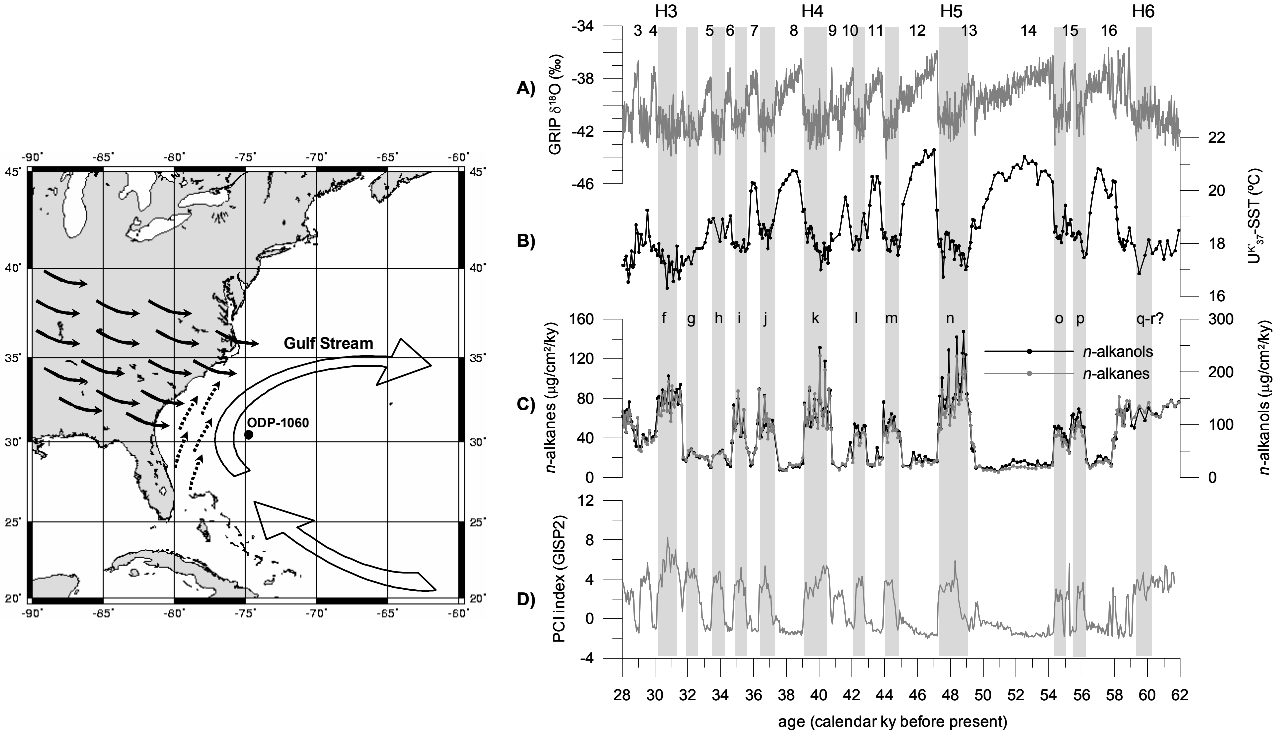


Fig. 1. Map showing the location of core ODP Site1060 in the Blake Outer Ridge. White arrows indicate surface ocean circulation. Black continuous and discontinuous arrows indicate wind direction in winter and summer, respectively. **(A)** Atmospheric $\delta^{18}O$ in GRIP; Heinrich events are indicated on top (H); isotopically defined Greenland Interstadials (GIS) are also indicated; **(B)** $U^{K'}_{37}$-SST profile; **(C)** C_{23}-C_{33} *n*-alkanes and C_{20}-C_{30} *n*-alkan-1-ols fluxes; they are labelled following Rohling *et al.* (2003); **(D)** Polar Circulation Index (PCI) in GISP2 (Mayewski *et al.,* 1997). All profiles are based on the timescale of Shackleton *et al.* (2004). Shaded areas indicate cold events (Heinrich events and Greenland Stadials)

References

Eglinton, G., Hamilton, R.J., (1967) *Science*, 156, 1322-1335.
Gagosian, R.B., Peltzer, E.T., (1986) *Org. Geochem.* 10, 661-669.
Keigwin, L.D., *et al.* (1998) *Proc. ODP, Initial Reports, 172*. ODP, College Station TX.
Leuschner, D.C., Sirocko, F., (2000) *Quat. Sci. Rev.* 19, 243-254.
Mayewski, P.A. *et al.* (1997) *J. Geophys. Res.* 102, 26345-26366
Poynter, J.G., *et al.* (1989) *Paleoclimatology and paleometerology: Modern and past patterns of global atmospheric transport* (Ed. by M. Leinen, M. Sarnthein), pp. 435-462. Kluwer Academic Publishers, Dordrecht.
Rohling, E.J., *et al.* (2003) *Clim. Dyn.* 20, 257-267.
Shackleton, N.J., *et al.* (2004) *Quat. Sci. Rev.* 23, 1513-1522.
Vautravers, M., *et al.* (2004) *Paleoceanography*, 19(PA2011), doi:10.1029/2003PA000966.
Villanueva, J., *et al.* (1997) *Geochim. Cosmochim. Acta*, 61(21), 4633-4646.
Voelker, A.H.L., *et al.* (2002) *Quat. Sci. Rev.* 21, 1185-1212.

OPC2-2: Reconstructing abrupt climate changes over the European land mass during the late Holocene using biomarker analysis of ombrotrophic peats

E.L. McClymont, L.A. Avsejs, C.J. Nott, Z.E. Roberts, F.D.M. Volders,
R.D. Pancost, R.P. Evershed

Organic Geochemistry Unit, School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK
(e-mail: erin.mcclymont@bris.ac.uk)

Ombrotrophic peats provide valuable stratigraphic archives of past climate change, due to the influence of climate on bog vegetation and hydrology. Biomarker proxies show potential for reconstructing past changes in vegetation and water table depth, and for recording meteorological change directly (e.g. temperature, precipitation; [1]). These proxies can be particularly important where peat humification has destroyed or decayed the macrofossil record. Here, we test, apply and develop further organic geochemistry techniques to reconstruct past climate change at a selection of ombrotrophic peat bogs across Europe (Figure 1). Our analyses form part of the multi-proxy EU programme ACCROTELM (Abrupt Climate Change Across The European Land Mass), enabling us to test our molecular proxies against other palaeoenvironmental records in different regions/environmental settings and for different time intervals during the Holocene.

We have collected ACCROTELM cores at sites with high peat accumulation rates. For example, cores of 4 m and 7 m have been collected at Butterburn Flow (UK) and Kontolanrahka (Finland) respectively, which span at least the late Holocene (the last 5000 years); these complement existing datasets derived from two additional UK peats (Bolton Fell Moss and Walton Moss). Age models have been reconstructed at each site using AMS ^{14}C dating of macrofossil remains, wiggle-matched to the tree-ring ^{14}C calibration curve to provide high-resolution and robust chronological control (e.g. [2]). At the ACCROTELM sites, peat accumulation rates are around 0.1 cm a^{-1}, and thus, our analyses at 1-cm intervals enable high resolution (decadal-scale) to be achieved. The cores have been analysed for macrofossil, pollen and testate amoebae, revealing that vegetation and bog surface wetness has varied significantly during the late Holocene. Here, we present high resolution data focussing on two periods of rapid climate change, both involving a shift toward cooler European climates: first, the Medieval Warm Period and Little Ice Age (800-1800 calendar years AD); second, the Sub-boreal/Sub-Atlantic transition (1000-500 calendar years BC).

Biomarker proxies complement macrofossil and pollen data, facilitating the reconstruction of past environmental change in late Holocene peat deposits. 5-*n*-alkylresorcinol concentrations double to >200 μg g^{-1} as sedge inputs increase from <20% to

>60%. Shifts from low (~20%) to high (100%) inputs of *Sphagnum* are identified by order of magnitude increases in the C_{23}/C_{31}-*n*-alkane ratio, reflecting the dominance of the shorter *n*-alkane homologues in *Sphagnum* species. The relative abundance of the *Sphagnum* acid pyrolysis product 4-isopropenylphenol is also able to track subtle variations in *Sphagnum* inputs, of <10% (Figure 1). Biomarker transformation products and biomarker carbon and hydrogen isotopic compositions provide further insight into past climate. δD variations of 15-40 ‰ in the C_{23}-*n*-alkane record reveal major climate shifts over the last 5500 years, including the shift toward cooler and/or wetter climate at the Subboreal/Subatlantic transition ca. 3000 years ago and those associated with the Medieval Warm Period and Little Ice Age.

To further evaluate the biomarker proxies, we have assessed the impact of peat formation (through the decomposition of surface plant material) on biomarker distributions in the top 20 cm of the peat profile. While we identify changes in biomarker distributions associated with peat formation, these do not impact the aforementioned biomarker proxies. Therefore, the data presented here demonstrates that organic geochemical analyses are effective in tracing past environmental change in ombrotrophic peat archives, including the relatively subtle climate shifts characteristic of Holocene climate.

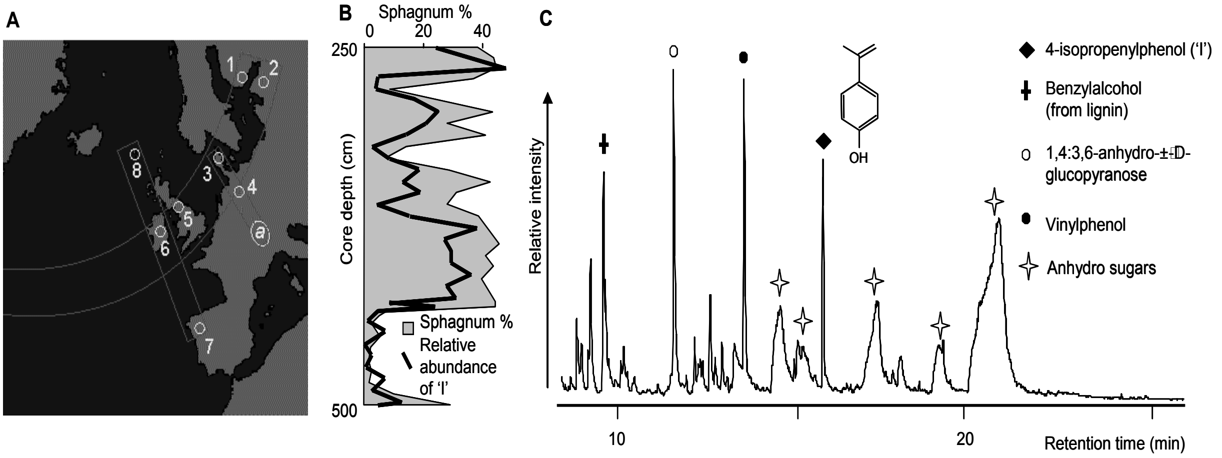


Fig.1. A) ACCROTELM Project Sites; B) and C) Application of the pyrolysis product 4-isopropenylphenol to reconstruct past *Sphagnum* inputs to peat samples. B) Relative abundance of 4-isopropenylphenol and *Sphagnum* down-core, Bolton Fell Moss, UK; C) Pyrogram (total ion current) of a lipid-extracted Finland peat, showing 4-isopropenylphenol.

References

[1] Xie, S., Nott, C. J., Avsejs, L. A., Maddy, D., Chambers, F. M., and Evershed, R. P. (2004). Molecular and isotopic stratigraphy in an ombrotrophic mire for paleoclimate reconstruction. *Geochimica et Cosmochimica Acta* **68**, 2849-2862.

[2] Mauquoy, D., van Geel, B., Blaauw, M., Speranza, A., and van der Plicht, J. (2004). Changes in solar activity and Holocene climatic shifts derived from ^{14}C wiggle-match dated peat deposits. *The Holocene* **14,** 45-52.

OPC2-3: From the Cretaceous Paleoequator to the Arctic: sea-surface temperature reconstruction in a greenhouse world based on the TEX$_{86}$-proxy

A. Forster, S. Schouten, J.S. Sinninghe-Damsté

Royal Netherlands Institute for Sea Research (NIOZ), Department of Biogeochemistry and Toxicology, P.O. Box 59, 1790 AB Den Burg, Texel, The Netherlands (e-mail: forster@nioz.nl)

The tetraether index of 86 carbon atoms (TEX$_{86}$) is a novel organic sea surface temperature (SST) proxy based on the distribution of core-membrane lipids specific for marine Crenarchaeota. The TEX$_{86}$ utilizes the ability of Crenarchaeota to adjust the composition of their glycerol dialkyl glycerol tetraether (GDGT) membrane lipids in response to changes in the water temperature by the number of cyclopentane rings incorporated. In today's oceans Crenarchaeota are ubiquitous and form an important component of the aquatic picoplankton. On a global scale, their indicative GDGTs are present in a wide variety of marine surface sediments, which have been employed to calibrate the TEX$_{86}$ SST-proxy for temperatures ranging from 0 to 29 °C.

Although established for Recent marine settings, the TEX$_{86}$ appears also to be applicable in the geological past because fossil GDGT lipids have been detected in marine sediments as old as Upper Jurassic. Especially the middle Cretaceous represents a time in Earth history characterized by extreme global warmth so that records of paleo-SSTs from the mid-Cretaceous oceans are considered to be important for the understanding of greenhouse climate conditions and related processes of climate change. As an organic SST-proxy, the TEX$_{86}$ has the advantage that it can be applied in carbonate free sediments or settings where carbonate diagenesis or other factors as sea-water pH or salinity are precluding or biasing conventional paleothermometry based on stable oxygen isotopes determined from carbonates or calcareous microfossils.

It is critical for the applicability of the TEX$_{86}$ that the investigated sediments contain sufficient amounts of organic matter (>0.1% TOC), are thermally immature (hopane $17\alpha,21\beta(H)$-22S/(22S + 22R) ratios <0.1 or $\beta\beta/(\beta\beta + \alpha\beta + \beta\alpha)$ ratios >0.5) and that the reconstructed paleotemperatures fall within the calibrated temperature range of the proxy. The importance of the latter point is illustrated by the difficulties with TEX$_{86}$-based paleo-SSTs reconstructions for extreme warm settings above 30 °C like in the Cretaceous. They require the calibration of the proxy for higher SSTs than those encountered in the modern marine realm, where even tropical SSTs are not exceeding 30 °C. This "high-end" temperature calibration is currently undertaken by growing modern marine Crenarchaeota in water of tropical origin (Seychelles) at controlled temperatures between 25 to 40 °C under laboratory conditions.

Results of the TEX_{86} high temperature calibration will be presented and discussed in connection with examples of TEX_{86}-based paleo-SST-reconstructions obtained from Cretaceous black shales derived form various locations ranging from the paleo-tropics (Albian to Santonian, Demerara Rise, ODP Leg 207: 32 to 35 °C) to the polar region (Lower Maastrichtian, Arctic Ocean: 15 °C).

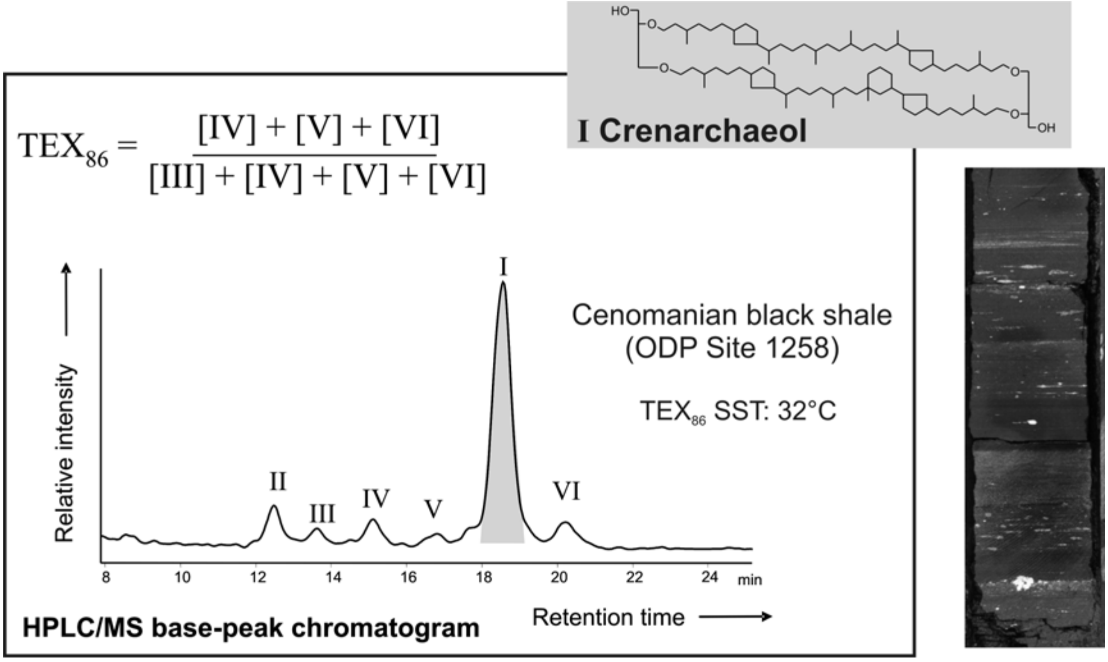


Fig.1. Typical distribution of crenarchaeal glycerol dialkyl glycerol tetraethers (GDGT's) detected by HPLC/MS analysis in a Cenomanian black shale from ODP Leg 207 Site 1258. Compounds employed to reconstruct sea-surface temperatures (SST) based on the TEX_{86} proxy are indicated

OPC2-4: Recent advances in TEX_{86} paleothermometry

S. Schouten[1], C. Wuchter[1], C. Huguet[1], S.G. Wakeham[2], S. Bohaty[3], J. Zachos[3],
E. Hopmans[1], J.S. Sinninghe-Damsté[1]

1) Royal Netherlands Institute for Sea Research, Department of Marine Biogeochemistry & Toxicology, PO Box 59, 1790 AB Den Burg, The Netherlands
2) Skidaway Institute of Oceanography, USA
3) Department of Earth Sciences, University of California Santa Cruz, USA

One of the major contributions of organic geochemistry to other scientific disciplines was the discovery of the sea surface temperature proxy $U^{K'}_{37}$. This proxy has considerable advantages over inorganic SST proxies because knowledge of the original sea water composition is not necessary. Throughout the past 18 years since the initial discovery many studies have been performed to test the robustness of the $U^{K'}_{37}$ proxy. Most of them have shown that it reflects annual mean SST and can be used to reconstruct SST over the last 6 Ma or so. However, there is still a need for additional SST proxies as alkenones are not always present in sediments and rarely extend further back in time than the Pliocene. Recently we proposed a new organic SST proxy, the TEX_{86}, based on the relative abundance of tetraether membrane lipids of marine crenarchaeota. As with their hyperthermophilic relatives, the marine crenarchaeota adjust their membrane lipid composition to ambient water temperature, i.e. at higher temperatures, greater proportions of tetraethers containing cyclopentane rings are biosynthesized. An initial core top study has shown that the TEX_{86} is linearly correlated to annual mean SST. However, before this new proxy can be confidently applied, as was the case with the $U^{K'}_{37}$, studies need to be performed to test its robustness. Here we report the latest studies on TEX_{86} and show that it can be used to reconstruct SST over the last 140 Ma.

One important consideration is the robustness of the analytical techniques. Initially a full scan mass spectrometry technique was used resulting in analytical reproducibility's in the TEX_{86} of ca. ±0.03 or ±2°C. Improvements in LC conditions and the use of a single ion monitoring technique have led to an analytical reproducibility of the TEX_{86} of ca. ±0.01 or ±0.8°C. To investigate the impact of different analytical instruments on TEX_{86} precision, a set of core tops, spanning the full range of TEX_{86}, was measured on an Agilent LC/MSD and a Thermofinnigan LC/TripleQMS. TEX_{86} values on both machines were linearly correlated with a slope near 1 and r^2 of 0.96 suggesting no instrument biases. The effect of extraction techniques were also investigated and showed that there is no systematic bias in TEX_{86} values between ultrasonic, Soxhlet and Accelerated Solvent extraction.

We also performed studies using mesocosm enrichment cultures and particulate organic matter (POM) from different oceanic provinces, in addition to extending the original core top study. The results show that the TEX_{86} is linearly correlated with sea water temperature in mesocosms, POM as well as core tops (Table 1). The linear equations between SST and POM and core top are not significantly different, but the intersect in the mesocosm correlation is substantially lower, due to the low abundance of the regioisomer of crenarchaeol. POM TEX_{86} correlated well with *in situ* temperature for depths shallower than 100m. However a poor correlation for depths>100m suggests that tetraether lipids present in POM at these depths are largely derived from dead cell material originating at the sea surface, since TEX_{86} for POM >100m did correlate with SST. Statistical analysis of the extended core top calibration shows that the standard error of the estimate is now 0.026 or 1.7 °C, only slightly larger than that of the $U^{K'}_{37}$ (1.5 °C).

Table 1. Correlations of mesocosm, POM and core top TEX_{86} with temperature

Sample	*Correlation*	r^2	*No. samples*
Mesocosm	$TEX_{86} = 0.015\ (\pm 0.02)*T + 0.10\ (\pm 0.05)$	0.80	16
POM	$TEX_{86} = 0.017\ (\pm 0.01)*T + 0.28\ (\pm 0.02)$	0.80	65
Core top	$TEX_{86} = 0.016\ (\pm 0.01)*T + 0.25\ (\pm 0.01)$	0.94	103

The TEX_{86} proxy has been applied to several climatically important time periods. Reconstructions of SST in the Arabian Sea during the last 30 Ky show that SST in this area was ca 3 °C colder during the Last Glacial Maximum and that the evolution of SST paralleled ice core records from Antarctica. Miocene SST evolution was reconstructed for Pacific coastal waters and showed warm SST (23 °C) during the early Miocene and cooling to modern day SST in the late Miocene, but well after the Middle Miocene cooling event. We will also present TEX_{86} analysis of sediments deposited during the Paleocene/Eocene Thermal Maximum at several paleolatitudes which show considerable warming during this event.

OPE1-1: Selective degradation of organic compounds in sediments from the California Borderland Basins: evidence from compound specific $\Delta^{14}C$ and $\delta^{13}C$ analyses

G. Mollenhauer, T. Eglinton

Woods Hole Oceanographic Institution, Marine Chemistry and Geochemistry, Mails Stop #4, Woods Hole, MA 02543-1543, USA (e-mail: gmollenhauer@whoi.edu)

The study was designed to investigate the influence of bottom water oxygen content, advection and bioturbation on the distribution and composition of sedimentary organic matter. Compound-specific radiocarbon and stable carbon isotope data were obtained on various phytoplankton and vascular plant derived biomarkers, including alkenones and fatty acids extracted from sediments from the Santa Barbara and Santa Monica Basins. We investigated core-top and pre-bomb sediment intervals at sites from the periphery and depocenter of the basins deposited under oxic and anoxic bottom water conditions. Lipid radiocarbon contents were compared with those of co-occurring planktic foraminifera and bulk OC.

Pearson et al. (2000, 2001) report good agreement in radiocarbon content between planktic foraminifera and phytoplankton derived sterols from the central Santa Monica Basin and demonstrated the potential of the latter as tracers for ^{14}C of surface water dissolved inorganic carbon. In contrast, our results reveal that another suite of algal biomarkers – the alkenones – are systematically depleted in radiocarbon with respect to foraminifera. Bulk OC generally has the lowest radiocarbon levels of all sediment constituents measured. We interpret these differences in ^{14}C content as a function of the lability of different organic compounds, with less refractory compounds (e.g. sterols) being enriched in radiocarbon with respect to more recalcitrant biomarkers (alkenones). Short chain (C_{14}, C_{16}, C_{18}) fatty acids decrease rapidly in abundance both in absolute terms and relative to longer chain ($>C_{22}$) homologues from core-top to pre-bomb samples. This loss is associated with a stable carbon isotopic depletion of these compounds, indicating preferential preservation of terrestrially-derived fatty acids. Greater preservation of labile organic compounds observed at the anoxic depocenters results in the presence of “younger” biomarkers. $^{230}Th_{xs}$ derived focusing factors suggest significant sediment focusing to occur at all sites in both basins. Together, these data point to a strong advective control on the ages of the more refractory alkenones, while more labile compounds are derived dominantly from the overlying water column. Bioturbational processes could not be detected as a significant factor influencing the radiocarbon signature of sediments in the California Borderland Basins.

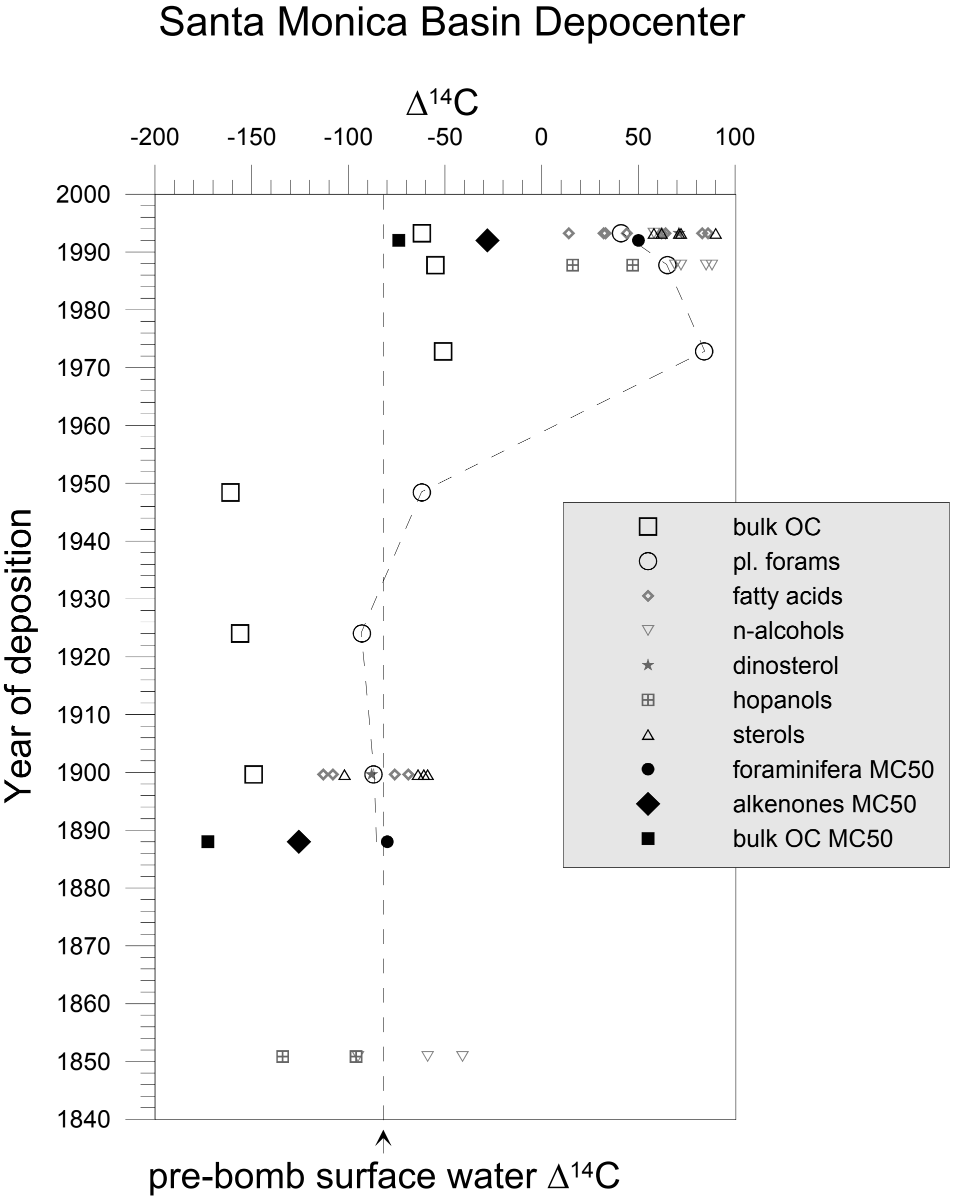


Fig.1. Summary of radiocarbon data from Santa Monica Basin depocenter cores collected on R/V R. Revelle at 33°44.0°N, 118°50.0'W, 905 m and on R/V New Horizon at 33°46.1'N, 118°49.0'W, 900 m (open symbols: Pearson et al., 2001; closed symbols: this study), on their respective time scale based on ^{210}Pb stratigraphy. Foraminifera record radiocarbon content in surface water DIC and trace the bomb-spike. Alkenones are more radiocarbon depleted than the other biomarkers.

References

Pearson et al., 2000: An organic tracer for surface ocean radiocarbon, Paleoceanography 15(5), 541-550.

Pearson et al., 2001: Origins of lipid biomarkers in Santa Monica Basin surface sediment: A case study using compound-specific Δ^{14}C analysis, GCA 65 (18), 3123-3137.

OPE1-2: The Continental residence time of terrestrial biomarkers as determined by molecular level radiocarbon analysis. A case study from the Pettaquamscutt River Basin (USA)

P.F. Poussart, N.J. Drenzek, A.L. Lima, T.I. Eglinton, C.M. Reddy, K.A. Hughen

Department of Marine Chemistry & Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA, 02543, USA (e-mail: ppoussart@whoi.edu.)

Fatty acids are a major component of epicuticular leaf waxes produced by terrestrial plants and are delivered to aquatic sediments by both aeolian and fluvial transport (Conte and Webber, 2002; Minor et al., 2001). Leaf waxes are commonly used to reconstruct changes in the biosphere and/or atmospheric circulation because the distributions and stable carbon and hydrogen isotopic composition of long chain homologues encode important biogeochemical information and are generally well preserved in sediments (Schefuss et al., 2003). However, the temporal relationship of fatty acid storage and transport relative to concomitant organic and inorganic material remains poorly understood. There is increasing evidence that both marine and terrestrial biomarkers can be pre-aged by up to several thousand years prior to burial in marine sediments (Ohkouchi et al., 2002; Drenzek et al., In prep.) due to temporary storage on the continents, sediment redistribution by bottom currents, or influence by fossil carbon sources. In particular, the delivery of terrestrial compounds to marine sediments may be retarded during transit through intermediate carbon reservoirs including forest litter, soils, river and lake beds, and wetlands. Significant 'residence times' for terrestrial materials could therefore decouple climatic signals from different geochemical proxies deposited at the same site. Drainage basin properties, such as size and relief, as well as climate conditions and land-use practices, are each likely to strongly influence timescales of terrigenous organic carbon transport and delivery to the marine environment.

We measured the radiocarbon and stable carbon isotopic signatures of long chain fatty acids extracted from annually laminated estuarine sediments in an effort to quantify this residence time. The down core $\Delta^{14}C$ profiles for several homologues were compared within a simple model framework to that of the atmospheric $\Delta^{14}C$ history during the latter part of the 20th century. Above-ground nuclear weapons testing initiated in the 1940s elevated the atmospheric $^{14}CO_2$ concentration in the Northern Hemisphere, peaking in 1963 at double the pre-anthropogenic value. Since then, this excess radiocarbon has been taken up rapidly by the terrestrial and marine environments, simultaneously labeling the corresponding biomass and producing an exponential decline in atmospheric $^{14}CO_2$. Thus by comparing the timing and magnitude of the radiocarbon 'bomb spike' for long-chain fatty acids and other higher plant biomarkers with that of the atmosphere, the time between biosynthesis and sedimentary incorporation of these molecular proxies of terrestrial vegetation can be ascertained. A simple geochemical box model that compares the shape of each curve prior to, during, and following the bomb ^{14}C peak is used to quantitatively interpret the molecular signature in terms of: transport pathway and delivery rate, contamination from fossil sources, and distinction between steady state and non-steady state behavior (e.g., resulting from changes in land use within the drainage basin). This approach takes advantage of the large magnitude of the atmospheric signal (1000 ‰) relative to instrumental error (5 ‰), sufficient to detect decadal scale residence times.

Results from the Pettaquamscutt River Basin in Rhode Island (USA) will be presented within the context of an ongoing study that includes four additional sites spanning 40º of latitude and representing a wide range of drainage basin and climatic conditions. In addition, the distributions and stable carbon isotopic compositions of fatty acid homologues will be presented with an eye to assessing land use practices that might have influenced their corresponding residence times. The results of this study carry significant implications for the interpretation of terrestrial organic biomarkers used to reconstruct environmental conditions on Earth's continents in the past.

References

Conte, M.H. and Weber, J.C., 2002. Plant biomarkers in aerosols record isotopic discrimination of terrestrial photosynthesis. Nature 417, 639-641.

Drenzek, N.J., Montlucon, D.B., Yunker, M., Macdonald, R., Eglinton, T.I. A coupled molecular isotope approach to constraining the origin of sedimentary organic carbon in the Beaufort Sea. In prep.

Minor, E.C., Boon, J.J., Harvey, H.R., Mannino, A., 2001. Estuarine organic matter composition as probed by direct temperature resolved mass spectrometry and traditional geochemical techniques. Geochimica et Cosmochimica Acta 65, 2819-2834.

Ohkouchi, N., Eglinton, T.I., Keigwin, L.D., Hayes, J.M., 2002. Spatial and temporal offsets between proxy records in a sediment drift. Science 298, 1224-1227.

Schefuss, E., Ratmeyer, V., Stuut, J.B., Jansen, J.H.F., 2003. Carbon isotope analysis of *n*-alkanes in dust from the lower atmosphere over the central eastern Atlantic. Geochim. Cosmochim. Acta 67, 1757-1767.

OPE1-3: Transgression/regression cycles on Continental shelves – A modulator of varying atmosferic CO_2 levels?

T. Boski, L. Albardeiro, D.Moura, C. Veiga-Pires, H.Martins

CIMA – Centro de Investigação Marinha e Ambiental, Universidade do Algarve, Campus de Gambelas, 8000 FARO, Portugal (e-mail: tboski@ualg.pt)

It is generally accepted that the carbon storage within the principal earth surface reservoirs vary in a multitude of time scales hence it must be strongly affected by the sea-level changes, thus it is to large extent controlled by glacial-interglacial cycles. Nonwithstanding, the well documented variability of the atmospheric CO_2 partial pressure (p) (eg. 3), which occurred during the Quaternary climatic oscillations, remains still an unsolved question. The complexity of environmental changes provoked by the climatic oscillations implies also, that several processes and complex feedbacks must be involved in controlling of atmospheric CO_2 levels in the range from 200 ppmV during the glacial periods to 270 ppmV during the interglacials (1).

Several authors (eg. 2) pointed out that the terrestrial organic matter is an essential fertilizer of the seas, which is processed essentially within the coastal zone of the ocean. The sea level and hence the position of river mouths with respect to shelf break must to large extent control the proportion between two parts of this fertilizer: one which may be quickly buried in coastal traps and the another which may be delivered to the open ocean and fuel the "biological pump".

Higher burial rate of terrestrial OM leads to lower primary production in the ocean and therefore an increase in atmospheric p CO_2. Ca 35 600 000 km^2 of continental shelves where submerged during the post glacial transgression which took place since the LGM ca 18 000 yrs BP until the Middle Holocene. On one hand the shallow water continental margins belong to the most fertile areas in terms of organic carbon (OC) production but from the other, may also function as very efficient organic carbon traps. Estuaries, deltas and lagoons are among the most effective OC storage sites, due the fast sediment accumulation rates.

In order to assess the changes of OC storage in the coastal areas, the OC content must be integrated with sediment accumulation rates at the continental margins. In this study, the organic matter content was determined in several hundreds of samples taken from cored boreholes which crossed the entire estuarine infill sequences of Guadiana, Arade and Boina rivers, in Algarve (S.Portugal). These ^{14}C dated sedimentary sequences represent the time span from ca 13000 yr cal BP to present and constitute one of the longest records from nonglaciated terrains. The obtained data indicate that until ca 7000 yr cal BP, i.e. during the period of fast sea level rise, organic carbon accumulated at an average rate of 280 gm^2 yr^{-1}. In the Middle and Upper Holocene, when the sea level rise was not exceeding 25cm/century the organic carbon accumulation rate dropped to an average value of 80 gm^2 yr^{-1}.

Considering that the terrestrial organic matter supports directly the primary production in the ocean, it is postulated that an enhanced burial of POM in the coastal areas during the period of fast postglacial sea level rise is responsible for decrease of primary productivity in the open ocean and consequent transfer of 200 Gt of C to the atmosphere.

References

(1) Barnola, J.M., Anklin, M., Porcheron, J., Raynaud, D., Schwander, J., Stauffer, B., 1995. CO2 evolution during the last millennium as recorded by Antarctic and Greenland ice. Tellus, 47, 264 –b272.

(2) Hedges, J.I., Keil, R.G., Benner, R., 1997. What happens to the terrestrial organic matter in the ocean. Organic geochemistry, 27, 195 – 212.

(3) Petit, J.R., J. Jouzel, D. Raynaud, N.I. Barkov, J.-M. Barnola, I. Basile, M. Bender, J. Chappellaz, M. Davis, G. Delayque, M. Delmotte, V.M. Kotlyakov, M. Legrand, V.Y. Lipenkov, C. Lorius, L. Pepin, C. Ritz, E. Saltzman, and M. Stievenard. (1999). Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica. Nature 399: 429-436.

OPE2-1: Biomarkers in bacterial fossils: observations from the 25 million years old Enspel formation

J. Toporski[1], C. Ostertag-Henning[2], J. Eigenbrode[3], G. Cody[3], A. Steele[3]

1) Christian-Albrechts-University Kiel, Department of Geosciences, Olshausenstrasse 40, 24098 Kiel, Germany (e-mail: jtoporski@min.uni-kiel.de)
2) Westfälische-Wilhelms University Münster, Department for Geology and Paleontology, Corrnesstrasse 24, 48149 Münster, Germany
3) Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road NW, Washington DC 20015, USA

Bacterial biomarkers have long been known and characterized and their information contents systematically been utilized and explored, particularly in the petroleum exploration industry and related research areas. A specific class of molecules, the hopanes, could be identified as purely deriving from bacterial sources, specifically as derivatives from hopanoid cell wall components (Rohmer et al., 1984). This was long unknown and only much later after the discovery of the hopanes were bacterial organisms identified that biosynthesize the precursor molecules of the compounds found in the fossil record. These compounds have been described to be preserved in a great variety of different environments from recent lake sediments (e.g. Innes et al., 1997) to Precambrian rocks from Australia (Brocks et al., 1999).

Here we report the results from a study of fossil bacterial biofilms from the Upper Oligocene (ca. 25 Ma) Enspel formation in Germany. The presence of these exceptionally well-preserved bacterial fossils from this formation has been reported in the literature (Wuttke, 1997; Gibson et al., 2001; Westall et al., 2001; Toporski et al., 2002). The fossil bacterial biofilms are found associated with macrofossils (primarily fish and tadpole) from these volcanoclastic lacustrine sediments, replacing the soft tissues of macroorganisms. In situ analysis of small fragments of fossil bacterial biofilm using Time of Flight – Secondary Ion Mass Spectrometry (ToF-SIMS) indicated – amongst others - the presence of hopane-type compounds (Toporski et al., 2002) in these very organic carbon-rich (up to ca. 50% TOC) samples (Schweizer et al., in press). We therefore attempted to investigate the composition of the extractable organic compounds in the bacterial biofilm and the surrounding sediment and characterize possible difference between both materials. Samples were collected during the field season 2002. Upon identification in the field, samples were immediately put onto dry ice and kept frozen until sample preparation for GCMS analysis to prevent the samples from alteration and/or contamination. After thawing and gentle drying, fossil bacterial biofilm samples were separated from the sedimentary matrix under a light microscope. 60 mg of fossil bacterial biofilm was separated from the mineral matrix using clean tools and ground to a fine powder. 2 grams of surrounding sediment not adjacent to the fossil were sub-sampled and ground to a fine powder. Samples were then organic solvent extracted (Dichloromethane and methanol). The samples were subsequently separated into several fractions using silica gel column chromatography (non-polar to polar; after Ostertag-Henning, 2001). The first (aliphatic) faction was further prepared for analysis using gas chromatography – mass spectrometry.

Initial results show distinct differences in the composition of organic compounds extracted from the fossil bacterial biofilm and the sedimentary matrix. Three main distinctions can be observed:

1) The distribution of the *n*-alkane series: *n*-alkanes in the biofilm show a "regular" distribution in the chromatogram (increasing intensity to C_{24} followed by a decrease in intensity), whereas even carbon number *n*-alkanes are significantly lower in the sediment than odd carbon number *n*-alkanes.

2) A homologous iso-alkane series is present in the extracts form the biofilm, which cannot be observed in the sediment (possibly a 5,5 diethylalkane).

3) Distinct variation between biofilm and sediment can be observed in hopane distribution and intensities of peaks in the chromatogram. Hopenes dominate the sediment, whereas hopanes are more prevalent in the fossil bacterial biofilm. Methyl hopane appear in the sediment but not in the biofilm.

These observations indicate that the development of both pools of organic compounds developed largely independently, and little – if any – transfer of compounds between materials seems to have occurred. Different starting materials lead to different compounds in both materials, which here indicates that bacterial biomarkers are directly associated with bacterial fossils. In our paper we will present the above results and initial interpretations of our observations.

References

Brocks JJ, Logan GA, Buick R and Summons RE (1999): Archean molecular fossils and the early rise of eukaryotes. *Science* **285**, 1033-1036.

Gibson E.K., McKay D.S., Thomas-Keprta K., Wentworth S.J., Westall F., Steele A., Romaneck C.S., Bell M.S., and Toporski J. (2000) Life on Mars: Evaluation of the Evidence within Martian Meteorite ALH84001, Nakhla, and Shergotty. *Precambrian Research*, **106**, 15-34.

Innes HE, Bishop AN, Head IM and Farrimond P (1997) Preservation and diagenesis of hopanoids in recent lacustrine sediments of Priest Pot, England. *Org. Geochem.* **26**, 565-576.

Ostertag-Henning, C. (2001) PhD Thesis, Erlangen University, Institute for Geosciences, Erlangen, Germany.

Rohmer, M., Bouvier-Nave, P., Ourisson, G., 1984. Distribution of hopanoid triterpenes in prokaryotes. *Journal of General Microbiology* **130**, 1137–1150.

Schweizer MK, Wooller MJ, Toporski J, Fogel ML and Steele A. Reconstruction of an Oligocene lacustrine ecosystem using C and N stable isotopes. *Paleo3,* in press.

Toporski J., Steele A., Westall F., Avci R., Martill M., and McKay D.S. (2002) Morphological and spectral investigation of exceptionally well preserved bacterial biofilms from the Oligocene Enspel formation, Germany. *Geochim. Cosmochim. Acta*, **66**, 1773-1791.

Westall F., Steele A., Toporski J., Walsh M.M., Allen C., Guidry S., McKay D.S., Gibson E., and Chafetz H. (2000) Polymeric substances and biofilms as biomarkers in terrestrial and extraterrestrial materials. *Journal of Geophysical Research - Planets*, **105**, 24,511-24,527.

Wuttke M. (1997) Die Fossillagerstätten Enspel und Messel. *Spektrum der Wissenschaft* **3**, 110–112.

OPE2-2: A 10 million year, high-resolution record of carbon and hydrogen isotope ratios of leaf waxes from Arabian Sea ODP Site 722: implications for the late Miocene C_4 plant expansion

Y. Huang, S. Clemens, W. Liu, Y. Wang, W. Prell

Department of Geological Sciences, Brown University, RI 01912 (e-mail: Yongsong_Huang@brown.edu)

The Siwalik paleosol sequence in Pakistan and India and the Bengal Fan sediment record indicate a major expansion of C_4 plants during the late Miocene, approximately 8 to 5 millions year ago. However, the depositional environments of paleosol sequences and deep-sea fans result in significant uncertainties in chronology and sediment discontinuities. The paleosol isotopic data and Bengal Fan records are also regional in nature. Here we report new high-resolution carbon and hydrogen isotopic measurements of higher plant biomarkers from marine sediments in the Arabian Sea (ODP 722B). This site is situated at 2000 m water depth on the Owen Ridge, isolated from turbidite deposition on the adjacent Indus Fan. Continuous deposition allows more accurate age control, based on nannofossil stratigraphy. The principal source of terrestrial input to the site is from aeolian sources associated with monsoon circulation, which results in the transport of plant leaf waxes from adjacent continental regions, especially the Arabian Peninsula, the Middle East, and the Indian subcontinent. Therefore, our data represent the first integrated large scale changes of C_3 and C_4 plants on these continental regions.

We analyzed ca 200 samples for isotope and alkenone ratios and quantified alkenone and leaf wax abundances for the last 10 million years in the ODP 722B (Fig.1). Our results show that C_4 plants expanded from ca. 25 % at 10 Ma to about 65 % at 5 Ma. C_4 percentage continued to rise slowly from 5 Ma, reaching 75% at 0.8 Ma, when a reversal occurred. Hydrogen isotope ratios of leaf waxes show a similar trend of increase from 9 to 6 Ma (40 ‰ rise), which is followed by a more gradual increase from 6 to 0.8 Ma (30 ‰ increase), and then a reversal toward present. We also studied lake surface sediments from 30 lakes lying on a transect from Houston, TX to Phoenix, AZ. The relative humidity levels in the summer growth season change from 85 % in Houston to ca. 30 %, in Phoenix. The D/H ratios of leaf waxes extracted from lake sediments show that hydrogen isotopic fractionation of leaf waxes (relative to precipitation) from higher plants decrease with decreasing relative humidity (ca. 70 ‰ drop along the transect) (Huang et al., in prep.). Therefore, the hydrogen isotopic ratios of leaf waxes in ODP722B suggest a major increase in continental aridity between 8 to 6 Ma (increase by 40 ‰), which is followed by a slower rate of aridity increases from 6 to 0.8 Ma (increase by 30 ‰) when a reversal occurred. The sea surface temperature changes using the UK37 ratios also suggest little changes in SST from 10 to 6 Ma, which is inconsistent with a large pCO$_2$ decrease between 8 to 6 Ma. Overall, our isotopic and SST results suggests an increase in continental aridity and summer monsoon strength (more seasonal precipitation, rather than a global change in atmospheric *p*CO$_2$, played the dominant role on the rise of C$_4$ plant during the late Miocene.

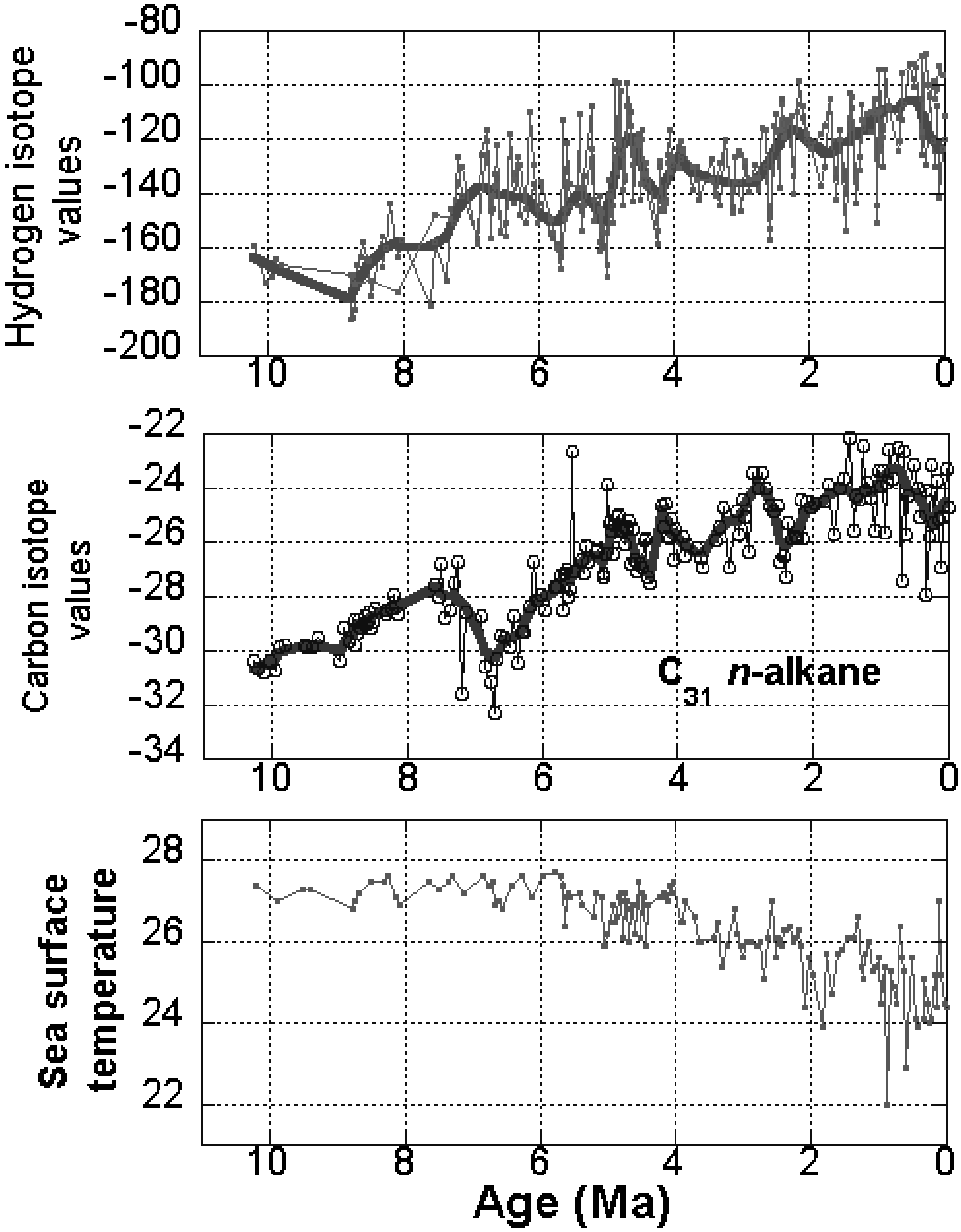


Fig.1. Carbon and hydrogen isotope ratios of C$_{31}$ *n*-alkane, and alkenone sea surface temperature from ODP722B for the last 10 million years

OPE2-3: Molecular records of Euxinia and protracted environmental disturbance from Permian to early Triassic sediments at Meishan, South China

R.E. Summons[1], C. Cao[2], G.D. Love[1], K. Grice[3], E. Grosjean[1], Y. Jin[2]

1) Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, MA 02139, USA (e-mail: rsummons@MIT.EDU)
2) Nanjing Institute of Geology and Palaeontology, Nanjing 210008, China
3) Curtin University of Technology, Perth, WA 6845, Australia

The Late Permian mass extinction was most extensive in Earth's history, resulting in around 90% of marine animal species, and many terrestrial taxa, becoming extinct. The most likely explanations involve disruptions to the biosphere occurring at a time when land masses merged to form the vast super-continent Pangaea and left fragile ecosystems particularly vulnerable to environmental perturbations. Shallow and deep water anoxia, global warming, Siberian Trap volcanism, collapse and oxidation of methane hydrates, sea level change and bolide impact have all been proposed as possible causes of the extinction event (summarised by Benton, 2003).

Samples from outcrop, and from a new core drilled through the Permian-Triassic (P-Tr) Boundary at the type marine section at Meishan, have been examined for biomarker and isotopic evidence of environmental and associated biotic change. Late Permian sediments from Meishan Beds 22-30 are characterized by indicators of anoxia including low Pr/Ph ratios and abundant aryl iosprenoids and isorenieratane derived from the precursor carotenoid isorenieratene. These latter biomarkers, derived from brown species of green sulphur bacteria (Chlorobiaceae), are considered reliable indicators of euxinic water columns where hydrogen sulfide extends into the photic zone. The highest abundances of Chlorobiaceae biomarkers occur through Beds 24 to 27 and so bracket the major extinction horizon evident in ash Bed 25. Additional sub-maxima of Chlorobiaceae biomarker abundances, at Beds 30, 35 and 37 in the Early Triassic and coincident with monotonous bivalve debris suggestive of mass extinction, indicate that pulses of photic zone euxinia occurred after the Permian events and may have caused the protracted recovery in biodiversity.

The prevalence of aryl isoprenoids and isorenieratane is also recorded in a recently cored borehole, Hovea-3, of the Perth Basin, Western Australia (Grice et al., 2005). This suggests similar palaeoenvironmental conditions prevailed across the Tethys Ocean during and immediately after the P-Tr Boundary. In particular, the presence of biomarkers for Chlorobiaceae at two separate locations indicates that water column euxinia was pervasive during and after the extinction event and suggest that sulfide may have been a key toxic agent, as proposed by Kump et al. (2003). Widespread outcropping of anoxic sulfidic waters onto continental shelves compromised aerobic habitats and might ultimately have allowed a hydrogen sulfide plume to influence continental regions and compromise terrestrial organisms. Supporting evidence for widespread euxinia comes from $\delta^{34}S$ isotope studies on sulfate and sulfide minerals at P-Tr sections from numerous locations worldwide (e.g. Korte et al., 2004; Nielsen and Shen, 2004).

On passing up into the Early Triassic, anomalously high hopane/sterane in Beds 29-39 (with ratios >100 in beds 35 and 36) and 2-methylhopane indices are indicative of cyanobacterial blooms dominating the phytoplankton communities in the aftermath of the extinction, with only minor inputs from planktonic algae. This is most likely a response to nutrient limitation, in particular low dissolved nitrate, and possibly iron, concentrations in aquatic environments arising from enhanced denitrification during extended periods of euxinia. Cyanobacteria with a capacity to directly fix N_2 would possess a distinct advantage over algae in establishing blooms throughout and after the oceanic anoxic event.

A pronounced negative C-isotopic excursion of around 4 per mil for kerogen is evident reaching a maximum near the top of bed 26 (black shale layer). This, and roughly parallel shifts in carbonate $\delta^{13}C$, have been observed in other P-Tr sections worldwide. The carbon isotopic excursions, and accompanying anomalies in nitrogen and sulfur isotopes, indicate there was a major reorganisation of the global carbon cycle over the P-Tr Boundary. Biomarker and carbon isotope patterns found for Meishan have much in common with those observed at Oceanic Anoxic Events such as those of the Early Aptian and Toarcian (e.g. Schouten et al., 2000).

References

Benton, M.J., 2003. In: When life nearly died. Thames & Hudson Ltd., London.

Grice K., Cao C., Bőttcher M.E., Twitchett R.J., Grosjean E., Summons R.E., Turgeon S.C, Dunning W. and Jin Y., 2005, Anaerobic Photosynthesis in an Early Triassic Sea: Sluggish Ocean Circulation in a Greenhouse World. *Science* 307, 706-709

Kump, L.R., Pavlov, A., Arthur, M., Kato, Y., Riccardi, A., 2003. Death by hydrogen sulfide: a kill mechanism. GSA Abstracts with Programs 35, p. 203.

Korte, C., Kozur, H.W., Joachimski, M.M., Strauss, H., Veizer, J., Schwark, L., 2004. Carbon, sulphur, oxygen and strontium isotope records, organic geochemistry and biostratigraphy across the Permian/Triassic boundary in Abadeh, Iran. International Journal of Earth Sciences 93, 565.

Nielsen, J.K., Shen, Y., 2004. Evidence for sulfidic deep water during the Late Permian in the East Greenland Basin. Geology 32, 1037-1040.

Schouten, S., van Kaam-Peters, H.M.E., Rijpstra, W.I.C., Schoell, M, Sinninghe Damsté, J.S, 2000. Effects of an Oceanic Anoxic Event on the stable carbon isotopic composition of early Toarcian carbon. American Journal of Science 300, 1-22.

OBD1-1: Quantifying the mass loss of light hydrocarbons during in-reservoir biodegradation using their stable isotopic compositions

A. Vieth, H. Wilkes

GeoForschungsZentrum Potsdam, Organische Geochemie, Telegrafenberg, D-14473 Potsdam
(e-mail: vieth@gfz-potsdam.de)

The biodegradation of hydrocarbons in petroleum reservoirs leads to substantial change of petroleum composition and quality and decreases the economic value of crude oil. The strongest change of petroleum quality occurs in the initial phase of biodegradation. To adequately assess this very important part of oil biodegradation, focus has to be placed on the light hydrocarbons.

To quantify the mass loss of individual constituents of crude oil that occurred in the reservoir due to biodegradation, the decrease in concentration of these components alone is not sufficient, because the concentration is always related to the overall oil composition which may be affected by various alteration processes. However, biodegradation goes along with an enrichment of the heavier stable isotopes in the residual fraction of the organic substrates. Therefore, carbon and hydrogen isotopic compositions of certain alkylbenzenes (BTEX) could be used to trace biodegradation in laboratory experiments and studies on contaminated aquifers (e.g. Mancini *et al.*, 2002; Meckenstock *et al.*, 1999). Using the Rayleigh-equation, the changes of isotopic composition and concentration are correlated by the isotope fractionation factor. This factor has to be determined for every compound in separate degradation experiments. With the knowledge of individual fractionation factors, quantification of the amount and rate of biodegradation of BTEX in a contaminated aquifer was possible from the carbon isotope ratios (Vieth *et al.*, 2005).

To investigate the effect of biodegradation on the isotopic composition of the light hydrocarbons crude oil samples from the Gullfaks oil field, offshore Norway were taken. The Gullfaks oil field is known to represent a good example of in-reservoir biodegradation. Along the biodegradation gradient, as indicated by increasing ratios of phy/*n*C_{18}, the concentration of light-hydrocarbon *n*-alkanes (e.g. *n*C_5, *n*C_6, *n*C_7) decreases (Figure 1A). This decrease in concentration goes along with an enrichment in ^{13}C of the residual *n*-alkane fraction (Figure 1A). Application of the Rayleigh-equation clearly demonstrates the good correlation of decrease in concentration and change in the carbon isotopic composition (Figure 1B). Thus, if appropriate isotope fractionation factors for the *n*-alkanes are available, quantification of in-reservoir mass loss of individual compounds is possible by applying this Rayleigh-approach. For example, using the experimentally determined isotope fractionation factor for *n*-hexane under anoxic conditions (Vieth et al., unpublished results) a 75% loss of this hydrocarbon is determined for the most heavily degraded Gullfaks oil.

This presentation will show how to use the carbon isotope ratios of various light hydrocarbons including but not limited to *n*-alkanes to better assess in-reservoir biodegradation, but will also discuss the chances and limitations of this stable isotope approach when applied to such complex systems like oil reservoirs are. Currently hydrogen isotopic composition of light hydrocarbons in the same samples is under investigation. The combined evaluation of carbon and hydrogen isotope data will provide new and more detailed insight into the microbially mediated processes in reservoirs.

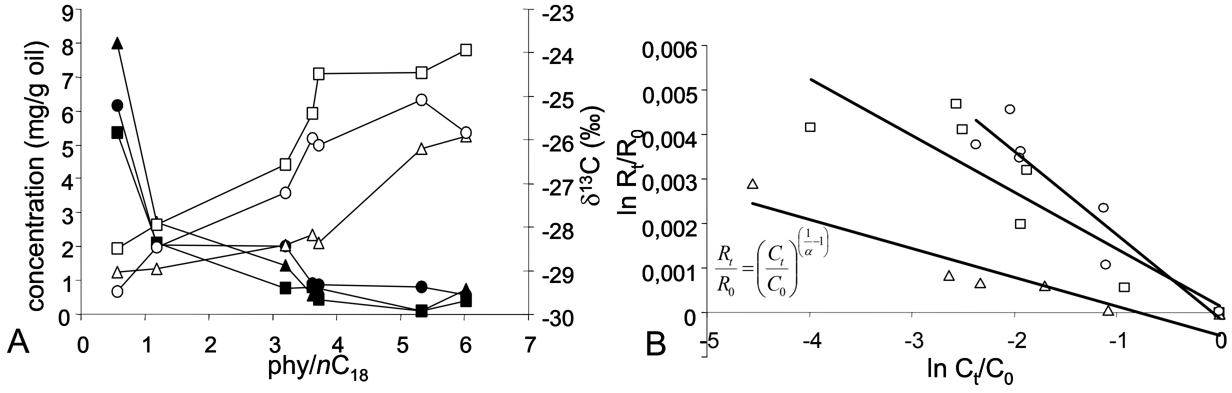


Fig.1. A) Concentration (closed symbols) and carbon isotope ratios (open symbols) of nC_5 (squares), nC_6 (triangles) and nC_7 (circles) in 7 crude oil samples from Gullfaks oil field, offshore Norway; B) concentrations and carbon isotope ratios of nC_5 (squares), nC_6 (triangles) and nC_7 (circles) were plotted according to the Rayleigh-equation. The coefficients of determination (R^2) of the linear regression lines for nC_5, nC_6 and nC_7 are 0.77, 0.88 and 0.88, respectively

References

Mancini, S.A., Lacrampe-Couloume, G., Jonker, H., Van Breukelen, B.M., Groen, J., Volkering, F., Sherwood Lollar, B., (2002) Hydrogen isotopic enrichment: An indicator of biodegradation at a petroleum hydrocarbon contaminated field site. *Environmental Science & Technology*, 36(11), 2464-2470.

Meckenstock, R.U., Morasch, B., Warthmann, R., Schink, B., Annweiler, E., Michaelis, W., Richnow, H.H., (1999) C-13/C-12 isotope fractionation of aromatic hydrocarbons during microbial degradation. *Environmental Microbiology*, 1(5), 409-414.

Vieth, A., Kästner, M., Schirmer, M., Weiss, H., Gödeke, S., Meckenstock, R.U., Richnow, H.H., (2005) Monitoring in-situ biodegradation of benzene and toluene by stable carbon isotope fractionation. *Environmental Toxicology and Chemistry*, 24(1), in press.

OBD1-2: Some unexpected biodegradation features in oils from a Brazilian marginal basin

H.L.B. Penteado[1], J.P. Lopes[1,2], S.M. Barbanti[1,2]

1) Petrobras/CENPES/PDEXP/GEO, Cid. Universitária, Rio de Janeiro, CEP 21949-900, Brazil
2) COPPE/UFRJ/LAMCE, Cid. Universitária, Rio de Janeiro, PO: 68552, CEP 21949-900, Brazil

Oil composition and physical properties are key factors for the economic value of petroleum accumulations. Most of the heavy oils in the offshore Brazilian marginal basins have been interpreted to be the result of mixing between biodegraded and non-biodegraded oils (with low and high API gravities, respectively), and the relative amount of each one controls the overall oil quality (Cerqueira *et al.*, 2001). Therefore, a better understanding of the biodegradation and mixing processes is of utmost importance for the explorationists in order to minimize the risk of discovery of subcommercial heavy-oil accumulations. The main objective of this study is to investigate the sequence of biodegradation in two oilfields in a Brazilian marginal basin, and to correlate geochemical parameters derived from biomarkers with API gravity.

Several crude oil samples were chosen from different production wells in both oilfields. In the studied fields, oil API gravities range from 12 to 30, and biodegradation levels from 1 to 6 in the Peters & Moldowan (1993) scale. Whole oils were analyzed by gas chromatography (GC). Saturate, aromatic and NSO compounds were separated by medium pressure liquid chromatography (MPLC). The saturate fractions were analyzed by gas chromatography-mass spectrometry (GC-MS) to obtain biomarker signatures (terpanes and steranes), and the stable carbon and hydrogen isotopic composition of individual *n*-alkanes. Metastable reaction monitoring-gas chromatography-mass spectrometry analyses (MRM-GC-MS) were undertaken to investigate the homologous series of demethylated hopanes.

Biodegradation has been generally interpreted to follow a sequence defined by a gradual decrease of *n*-alkanes from low to high molecular weight compounds. However, two biodegradation pathways were observed affecting compounds on the GC traces of oils from the studied fields. One biodegradation path, which seems to occur in early stages of bacterial attack, concerns the consumption of *n*-alkanes from *n*-C_8 to *n*-C_{12}, with *n*-C_{10} more severely biodegraded. A second biodegradation pathway involves the consumption of high molecular weight normal alkanes proceeding towards lighter *n*-alkanes. Thus, the GC traces present an intermediary step in which *n*-alkanes are almost restricted to the *n*-C_{10}/*n*-C_{18} range. Later on, the progressive depletion in normal paraffins leads to oils with GC traces in which isoprenoids are the major resolved compounds. Further evolution in biodegradation intensity produces oils with GC traces consisting in a hump almost devoid of identifiable compounds on its upper region.

Carbon and hydrogen isotopic ratios have been determined for normal and branched paraffins of oils from the studied fields. For each of the fields, samples with varying API gravities present similar profiles of stable isotopic for carbon and hydrogen in normal and branched alkanes. Thus, the similarity in isotopic composition would suggest charging of a relatively homogeneous oil during reservoir filling. In this case, biodegradation intensity did not affect considerably the isotopic signature of paraffins.

A relationship could be established between biodegradation intensity given by various molecular parameters and API gravity for each oilfield. The series of demethylated hopanes has been identified by MRM-GC-MS analyses in all samples, regardless of the aspect of the GC trace and the API gravity. Nevertheless, demethylated hopanes become more abundant in both absolute and relative terms in samples in which normal paraffins are present in small amounts or absent. Therefore, the formation of demethylated hopanes would be related to bacterial activity in a situation of depletion of normal and branched alkanes. Two hypotheses can be advanced for the generalized presence of demethylated hopanes. On the one hand, it is possible that a certain background amount was present in the original oil since the onset of reservoir filling. In this case, the biodegraded series could be interpreted as the product of different extents of biodegradation intensity on a pristine oil already containing demethylated hopanes. On the other hand, reservoir filling can be envisaged as a continuous process in which alternate discrete events of charging and biodegradation follow in close succession. According to the latter model, the more biodegraded oils would be the result of a mixing process in which biodegradation events overcome the charging rate during reservoir filling.

References

Cerqueira, J.R., Trindade, L.A.F., Elias, V.O. (2001) Estimating API gravity based on oil shows in cuttings and core samples from Brazilian basins. Abstracts of the 20th International Meeting on Organic Geochemistry, 10-14 September, 2001, Nancy, France, v.1, p. 483.

Peters, K., Moldowan, J.M. (1993). The Biomarker Guide. Prentice-Hall, New Jersey, 363 pp.

OBD1-3: Low temperature pyrolysis. The UCM and biomarker regeneration from biodegraded oils

A.G. Holba[1], L.I. Dzou[2], R. Tharp[3], D. Stansbury[3], P. Walker[3], S.R. Palmer[3]

1) ConocoPhillips Petroleum Co., Houston, TX, USA (e-mail: albert.g.holba@conocophillips.com)
2) BP America Inc., Houston, TX, USA; [3]Baseline Resolution Inc., The Woodlands, TX, USA.

Gas chromatography of some oils shows a baseline shift often described as an "unresolved complex mixture (UCM)" or "hump". We propose that relatively low temperature pyrolysis (LT-Py) of high molecular weight material, either in the injector or the column of the gas chromatograph, often contributes to the observation of UCM. This view is supported by the fact that UCM can be enhanced or suppressed by changes in temperature programming.

The observation of LT-Py can be turned to advantage for regeneration of biomarkers from the purified nonhydrocarbon fractions of severely biodegraded oils or contaminated oils. Asphaltenes are precipitated by excess pentane and the polar (NSO or resin) fraction is isolated by column chromatography. For test samples this process was repeated to insure that no contamination of biomarker from the hydrocarbon fractions are present. The isolated nonhydrocarbon fractions are then heated at low temperature in MSSV tubes for relatively short time periods. The tubes are opened and processed by normal sample preparation for biomarker analysis. Gas chromatography/mass spectrometry of the resulting hydrocarbon fractions provides biomarker patterns that are very similar to those of the undegraded or uncontaminated oil.

Heating of the nonhydrocarbon fractions to temperatures that generate an oil-like pattern of *n*-alkanes (temperatures > 300°C) leads to cracking of biomarkers and patterns that are rarely encountered in petroleum. The liberation of hydrocarbon biomarkers from nonhydrocarbon fractions under mild conditions implies that carbon-carbon bonds are not likely to be broken in the process. For biodegraded oil, the liberated hydrocarbon biomarkers must have been protected by the three dimensional structure of the nonhydrocarbon macromolecules. In practice, the regeneration of biomarkers from the nonhydrocarbon fractions works best for young oils (e.g. Tertiary) that have never been subjected to prolonged exposure to high temperatures in the subsurface over geologic time.

OBD2-1: Diamondoids as bioremediation indicators for diesel spills

C. McIntyre[1], P. Harvey[2], I. Snape[2], S.C. George[1]

1) CSIRO Petroleum, PO Box 136, North Ryde, NSW 1670, Australia (e-mail: cameron.mcintyre@csiro.au)
2) Human Impacts Research, Australian Antarctic Division, Channel Highway, Kingston, TAS 7050, Australia

Biodegradation of petroleum can be assessed by the removal of various classes of hydrocarbons in a quasi-stepwise fashion ordered by their level of resistance (Volkman et al., 1984; Trolio et al., 1999; and references within). The resistance of aliphatic and aromatic hydrocarbons to microbial action typically increases with the number of rings and alkyl substituents: e.g. *n*-alkanes and methylnaphthalenes are highly susceptible, while diasteranes and aromatic steroids are highly refractory. Diamondoids, which are a class of saturated hydrocarbons containing fused cage structures, remain in crude oils when other compounds have been removed by biodegradation (Grice et al., 2000). Applications of the biodegradation scheme include assessment of crude oil quality and the environmental impact of oil spills. In this contribution we have analysed petroleum contaminants extracted from soil cores taken from a diesel spill site at the main powerhouse on the World heritage-listed Macquarie Island in the Southern Ocean. The aim was to characterise the nature and extent of contamination and identify compounds that could be used to assess the extent of bioremediation during trials and clean-up operations, diamondoids being a particular focus.

The site is characterised by an older, larger spill of diesel which is heavier than the Special Antarctic Blend diesel (SAB) used today. This is overlain by a smaller, fresh spill of SAB. Contaminants in the upper layers of cores from the old spill are moderately biodegraded, and biodegradation decreases with depth, with some samples appearing virtually unaffected. Several cores show stratification consistent with restricted migration of the fuel into deeper layers and an addition of fresh soil over the original surface layer. Aromatic hydrocarbons are largely absent from the soil samples, except from those with the most concentrated contaminants. This is consistent with water washing of the site by the 920 mm of rainfall the Island receives each year, but as yet it is unknown if other processes such as aerobic oxidation or sequestration have had a significant impact on the aromatic hydrocarbons. Samples from the fresh spill generally contain pristine SAB, with low to high molecular weight aromatic hydrocarbons present. Therefore if water washing is a significant process at the site, then this spill poses an immediate environmental hazard.

The major compounds remaining in the most biodegraded upper layers that are useful bioremediation indicators were bicyclic alkanes, diamondoids and hopanes (Fig. 1).

Consistent with Volkman et al. (1984), samples from deeper layers had *n*-alkanes removed first and acyclic isoprenoids later, making these classes, as expected, more useful during earlier stages of bioremediation. Tetralins and diamondoids occurred over a range of molecular weights that were useful for assessing if the samples had undergone evaporation, as lighter compounds were depleted in surface samples. Aromatic hydrocarbons were considered unsuitable as they are rapidly removed from the system. The major finding of this study is that the relative abundance of diamondoids is a useful indicator of the extent of biodegradation and hence bioremediation in the fuel spills at this site. An advantage of using diamondoids rather than hopanes is that they fall within the main molecular weight region of the refined fuels, whereas hopanes do not and are sometimes not present.

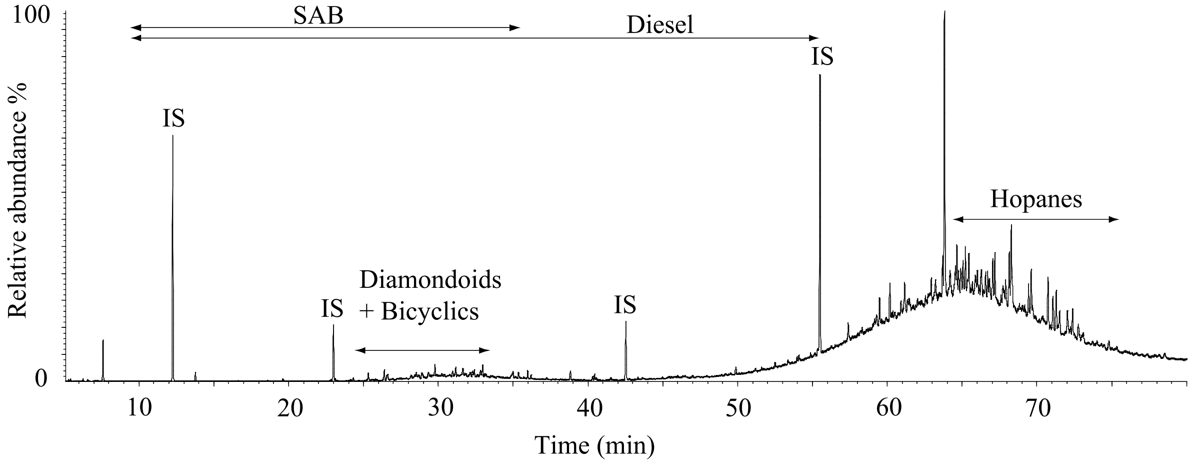


Fig.1. Chromatogram of a biodegraded diesel extracted from soil showing the location of refractory hydrocarbons. The elution ranges of compounds in the raw fuels are indicated

References

Grice, K., Alexander, R., Kagi, R. I. (2000). Diamondoid hydrocarbon ratios as indicators of biodegradation in Australian crude oils. *Organic Geochemistry* **31**, 67-73.

Trolio, R., Grice, K., Fisher, S. J., Alexander, R., Kagi, R. I. (1999). Alkylbiphenyls and alkyldiphenylmethanes as indicators of petroleum biodegradation. *Organic Geochemistry* **30**, 1241-1253.

Volkman, J. K., Alexander, R., Kagi, R. I., Rowland, S. J. and Sheppard, P. N. (1984). Biodegradation of aromatic hydrocarbons in crude oils from the Barrow Sub-basin of Western Australia. *Organic Geochemistry* **6**, 619-632.

OBD2-2: Early production of polar products from the Boom Clay kerogen (Mol underground laboratory) upon thermal stress in relation with nuclear waste disposal

I. Deniau[1,2,3], F. Behar[2], C. Largeau[3], C. Beaucaire[1], H. Pitsch[1]

1) IRSN/SARG, BP 17, 92262, Fontenay-aux-Roses, France (e-mail: isabelle-deniau@enscp.fr)
2) IFP, Geochemistry Division, Rueil-Malmaison, France
3) LCBOP, CNRS UMR 7573, ENSCP, 11 rue P. M. Curie, Paris 05

Burial in geological formations, especially in clay, is among the main solutions currently considered for the long-term disposal of high-activity nuclear waste. The Boom Clay Formation (Oligocene) has been extensively studied as a potential host rock for such disposal. These studies included *in situ* experiments, focused on clay mineralogy and physico-chemical features, performed in the underground laboratory located at a depth of 230 m at Mol (Belgium). Bulk studies showed the presence of substantial amounts of organic matter (OM), average content of ca. 3 wt%, in the Boom Clay (e.g. Van Geet et al., 2003). As commonly observed in sedimentary rocks the OM is dominated (over 80 wt% by kerogen). This kerogen would be submitted to some thermal stress upon disposal of “hot” radioactive waste and thus may release some liquid and gas compounds. The latter may influence the effectiveness of the geological barrier through a number of processes.

Accordingly, we undertook a detailed study of the kerogen isolated from representative core samples collected in the Mol underground laboratory. Classical geochemical studies (Deniau et al., 2001, 2004) showed this is a low maturity type II kerogen with an especially high oxygen content (O/C ratio of 0.27) and some moieties exhibiting low thermal stabilities. Such features supported the idea that thermal degradation of the Boom Clay kerogen could be an important feature in relation with the efficiency of long-term disposal.

Therefore, the aim of the present work was to derive detailed molecular and kinetic information on the production of liquid and gaseous compounds, upon the type of thermal stress that the “near field” clay would undergo during disposal. Emphasis was put on low molecular weight oxygen-containing components. Indeed, the latter may influence the confinement properties of the clay barrier and the radionuclide transport through various processes like changes in PCO_2, in pH and in complexation ability.

Gas production was examined by closed isothermal pyrolyses, using 30 time/temperature conditions, with focus on mild conditions starting from 150 °C/1 h. The gas fractions generated were quantified and analysed by GC. The *in situ* production of CO_2 was simulated, using the kinetic parameters (Fig.) derived from these experiments, for the type of thermal stress that would occur upon disposal (foreseen to be around 80°C for centuries to millenia).

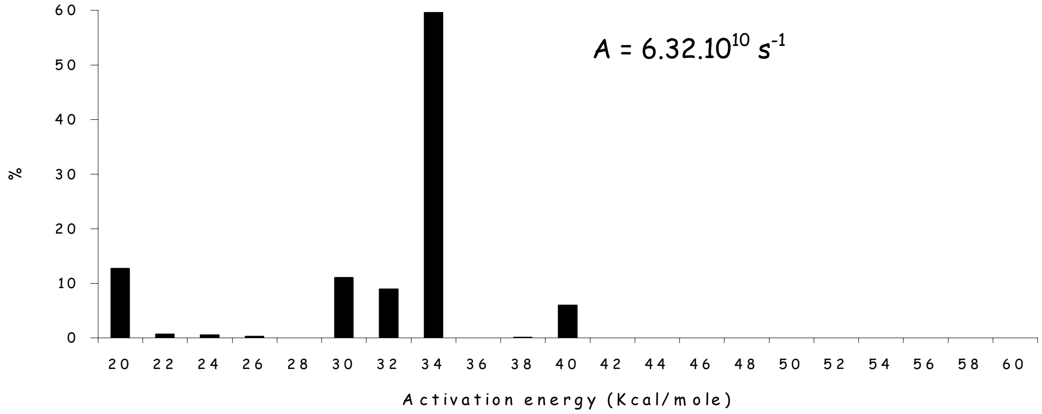


Fig.1. Activation energy distribution and frequency factor determined for "labile CO_2" production from the Boom Clay kerogen. The bulk of the distribution occurs for low values (30-34 kcal/mole range), furthermore a substantial contribution is noted for an especially weak value (20 kcal/mole) corresponding to a very early "flash" CO_2 production

This study showed the occurrence of CO_2-generating groups exhibiting a (very) weak thermal stability in the Boom Clay kerogen. Substantial amounts of CO_2 corresponding to about 20 % of the total oxygen content of the kerogen are thus generated under mild thermal stress. This simulation indicated that "labile" CO_2 production, taking place at time scale of only tens to a few hundred years could influence the effectiveness of the clay barrier, especially through acidification and large changes in bicarbonate concentration in interstitial water. The soluble fractions generated from the kerogen, were also examined and shown to contain a wide variety of low molecular polar O- and/or N-containing compounds, including mono- and dicarboxylic acids and phenols.

All these observations indicate that the production of polar liquid and gaseous compounds from the Boom Clay kerogen, when submitted to a low thermal stress, has to be taken into account to assess the effectiveness of the geological barrier. The present data will be integrated in performance assessment models to evaluate the efficiency of the Boom Clay as main barrier during the long-term disposal of high-activity radioactive waste.

References

Deniau, I., Derenne, S., Beaucaire, C., Pitsch, H., Largeau, C., 2001. Morphological and chemical features of a kerogen from the underground Mol laboratory (Boom Clay Formation, Oligocene, Belgium): structure, source organisms and formation pathways. Organic Geochemistry 32, 1343-1356.

Deniau, I., Derenne, S., Beaucaire, C., Pitsch, H., Largeau, C., 2004. Occurrence and nature of thermolabile compounds in the Boom Clay kerogen (Oligocene, underground Mol Laboratory, Belgium). Organic Geochemistry 35, 91-107.

Van Geet M., Maes N., and Dierckx A. (2003) Characteristics of the Boom Clay organic matter, a review. *Royal Belgian Institute of Natural Sciences, Geological Survey of Belgium, Professional Paper 2003/1,* ***N°298,*** Brussels, Belgium, 23 pp. ISSN 0378-0902.

OBD2-3: Lignite mineralization in lignite-containing mine sediment with contrasting redox conditions

A. Chabbi[1,2], C. Rumpel[3], J.A. González-Pérez[4], F.J. González-Vila[4]

1) Department of Soil Protection and Recultivation, BTU Cottbus, Cottbus, Germany
2) INRA, UEFE, Lusignan, France (e-mail: Abad.Chabbi@lusignan.inra.fr)
3) CNRS, Laboratoire de Biogéochimie des Milieux Continentaux, Grignon, France
4) Instituto de Recursos Naturales y Agrobiología de Sevilla, IRNAS-CSIC, Sevilla, Spain

Degradation of organic substances in soils and sediments is strongly dependent on the environmental condition governing the abundance and activity of microorganisms. In the Lusatian mining district (Germany), lakes associated with coal or lignite mining has unique pH and reducing sediment conditions which govern organic matter degradation or transformation. In this environment, lignite is present in addition to recent plant litter. Aromatic lignite was found to be subject to microbial decomposition in soil, which is highly, oxidized [1]. Decomposition is however limited under reduced conditions. Oxygen release by the roots of pioneer plants colonizing the littoral area changes the redox potential within the rhizosphere [2] and may therefore alter the extent of decomposition of geogenic carbon, which would largely be preserved under reducing conditions. The aim of the study is to examine the influence of pH and sediment redox on the oxidation of lignite carbon present in mine sediment and recent organic matter.

The influence of sediment pH and redox conditions on the oxidation of lignite and sediment organic carbon was studied using a series of laboratory microcosms. The experiment was conducted over 450 days in reducing sediment suspensions maintained at four redox potential (-170, 0, +350 and +500 mV) and two pH levels (3.2 and 5.3). Carbon and lignite mineralization was determined over time by ^{14}C analysis, DOC (dissolved organic carbon) production and pyrolysis-GC/MS spectroscopy.

More than 50 % of carbon mineralization occurred during the first 200 days of incubation. Maximum mineralization occurred under the more oxidized sediment conditions (+350 and +500 mV). The amount of CO_2 produced was greater at pH 5.3 as compared to pH 3.2 showing that low pH reduces organic matter mineralization regardless of sediment redox potential. ^{14}C analysis showed that lignite carbon was mineralized at each redox potential level studied. The average decay rate was estimated in 12 mg lignite C kg^{-1} yr^{-1} under oxidizing conditions vs 2.4 mg lignite C kg^{-1} C yr^{-1} under reducing conditions. Lignite carbon contributed substantially to total CO_2-C emissions (20 %) and to DOC (> 70%). Under the lowest redox level (0 and -170 mV) lignite carbon accumulated in dissolved form. The concentrations of DOC were inversely related to the intensity of sediment redox potential ($r^2 = 0.96^{**}$, n=6, **p<0.05) (Fig. 1). This suggests that the initial cleavage of macromolecules by hydrolytic enzymes from aerobic heterotrophic organisms occurs more aggressively than by enzymes of anaerobic hydrolytic bacteria unable to oxidize certain class of organic compounds.

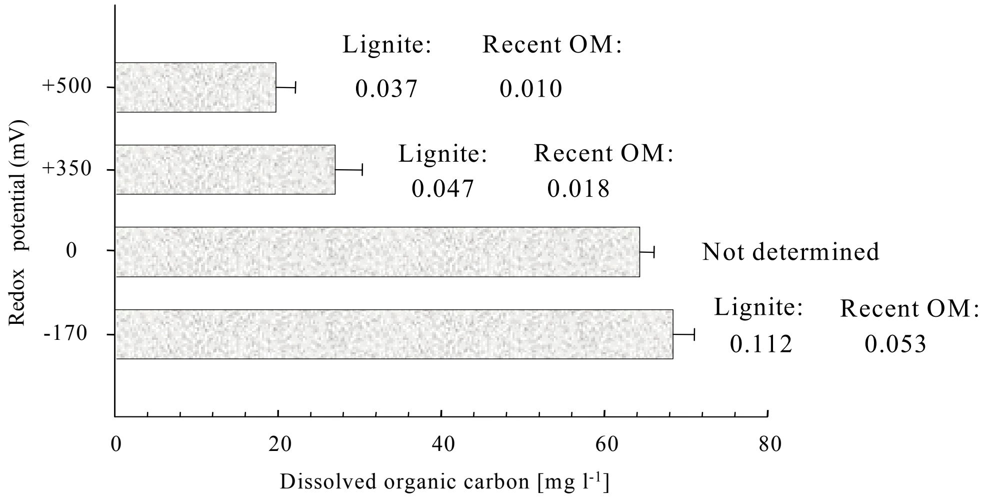


Fig. 1. Concentration of DOC sediments with contrasting redox conditions

Pyr GC-MS analysis was used to further characterize DOC collected from the incubated sediment. Single ion monitoring (SIM) for aromatic compounds (ion at m/z 91) show a well resolved alkylbenzene series in the DOC pyrolysates from the more reducing condition (-170 mV). This would indicate the occurrence of an alkaline ionization of acidic groups in the low-rank coal (xylite) producing water-soluble humates. The absence of oxygen to further degrade the aromatic compounds would favor a selective preservation of these compounds. The fact that accumulation of aromatic moieties was not observed in the DOC under more oxidizing conditions (+350 mV) would indicate the occurrence of a rapid mineralization by depolimerization of the lignite and the degradation of the resulting aromatic compounds. Our study has three implications: (1) geogenic carbon, e.g. lignite may be decomposed under inoxic conditions, (2) plant oxygen release e.g. in the littoral area of lakes may accelerate this decomposition, (3) changes in redox potential from reducing to oxidizing conditions may cause a rapid mineralization of lignite degradation products, resilient at low redox values, in the form of water-soluble coal humates, and a CO_2 liberation.

References

[1] Rumpel, C., Kögel-Knabner, I., 2002. Organic Geochemistry 33, 393-399.
[2] Chabbi A., 1999. The New Phytologist 144/1, 133-142.

OSB1-1: The fate of Rubisco in soils

H.R. Mottram, R.P. Evershed

Organic Geochemistry Unit, Bristol Biogeochemistry Research Centre, School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK.

Ribulose-1,5-bisphosphate carboxylase/oxygenase (RubiscoCO) is probably the most abundant protein in the world (Ellis 1979). Located within the chloroplasts of cells, this enzyme forms the bridge between life and the lifeless by creating organic carbon from atmospheric carbon dioxide. This process, which consumes around 10^{11} tonnes of CO_2 per year (Schneider, 1992), represents the most important pathway by which inorganic carbon enters the biosphere, with as much as 95% of all carbon fixation by C_3 plants occurring in this way (Raven 1995). With an estimated 40 million tonnes of RubisCO present worldwide, this protein represents a highly significant, bio-available pool of organic nitrogen, but little is known of its fate in the environment. It is known that during leaf senescence, 50-80% of the RubisCO is hydrolysed and reabsorbed by the plant prior to abscission (Kolb and Evans, 2002). However, a significant proportion of the protein remains in the senescing leaf when it falls to the ground, providing a considerable input of organic nitrogen.

Nitrogen availability is the limiting factor for growth and biomass production in almost all environments and hence is a key element in controlling the diversity, dynamics and functioning of many marine, freshwater and terrestrial ecosystems (Vitousek *et al.*, 1997). However, in sharp contrast to the carbon cycle, we are still far from a quantitative understanding of the nitrogen cycle. In particular, little is known about the nature, availability or mobility of organic N. Since RubisCO represents such a large pool of organic N which is available to the biosphere, it is essential to investigate its fate at a molecular level. What is its residence time in soil? What are the pathways and relative rates of mineralization or uptake by plants and bacteria? This study is addressing such questions by tracing the fate of stable isotopically-labelled RubisCO.

Plants will readily incorporate ^{13}C and ^{15}N into their tissues when provided with stable isotopically-labelled substrates and hence highly enriched ^{13}C and ^{15}N-labelled RubisCO has been isolated from perennial ryegrass (*Lolium perenne*) grown on $^{15}NH_4$ and $^{13}CO_2$. Following purification with gel filtration, this labelled protein has been added to a grassland soil held in lysimeters, with or without ryegrass. Simulated rainfall is added and soil, roots and shoots sampled at time intervals ranging from hours to days. Leachates and evolved gases are being collected. The bulk $\delta^{13}C$ and $\delta^{15}N$ values of the major soil fractions, the plant roots and shoots, the leachates and any gaseous emissions are being used in conjunction with elemental analysis, and the $\delta^{15}N$ values for ammonium and nitrate in the soil and leachate to perform mass balance calculations.

The decay of the labelled, intact RubisCO in the soil and the potential production of peptidic fragments is being followed using MALDI-TOF mass spectrometry. The total protein is being extracted from the soil and the RubisCO isolated using gel electrophoresis. Since the protein will be uniformly labelled the level of incorporation will be determined from the increase in molecular mass.

In addition, gas chromatography/combustion/isotope ratio mass spectrometry (GC/C/IRMS) is being used to follow the incorporation of ^{13}C and ^{15}N into amino acids, both free and peptidic, in the soil, leachates and plant roots and shoots. Since proteins are believed to be degraded by the action of proteases which initially break peptide bonds, we would anticipate an initial incorporation into the soil free amino acid pool as the labelled protein is degraded, followed by a decrease as the free amino acids are either lost through leaching, taken up by the plant or are metabolised/catabolised by soil micro-organisms. Analysis of plant root and shoots will allow plant uptake to be measured, whilst the $\delta^{13}C$ and $\delta^{15}N$ values of amino sugars in the soil, which are bacterial and fungal biomarkers, will enable the relative uptake by microorganisms to be followed. Carbon flow into the microbial biomass will also be followed by compound-specific stable isotope analysis of phospholipids fatty acids.

References

Ellis, R. J. (1979). The most abundant protein in the world. *Trends in Biochemical Science* **4**, 241–244.

Kolb, K. J. and Evans R. D. (2002). Implications of leaf nitrogen recycling on the nitrogen isotope composition of deciduous plant tissues, *New Phytologist*, **156**, 57-64.

Raven J. A. (1995). Photosynthetic and non-photosynthetic roles of carbonic anhydrase in algae and cyanobacteria, *Phycologia* **34**, 93-101.

Schneider, G., Lindqvist, Y. and Brändén, C.-I. (2002). RubisCO: Structure and Mechanism. Annual Review of Biophysics and Biomolecular Structure, **21**, 119 43.

Vitousek, P. M. *et al.* (1997) Human alteration of the global nitrogen cycle: Sources and consequences, *Ecological Applications*, **7**, 737-750.

OSB1-2: Influence of change in land use on the abundance and composition of the refractory organic macromolecular fraction of a sandy spodosol (Landes de Gascogne, France)

K. Quénéa[1,2], S. Derenne[1], C. Largeau[1], A. Mariotti[2]

1) LBCOP,UMR CNRS 7573, ENSCP, 11 rue Pierre et Marie Curie 75231 Paris cedex 05, France
(e-mail : katell-quenea@enscp.fr)
2) BiomCO, INRA-CNRS-UPMC, bât EGER, 78850 Thiverval-grignon, France

Soil organic matter (SOM) represents by far the largest surficial pool of organic carbon of continents and is thought to play an important role in the global carbon cycle. In fact, this pool exhibits large variations, in relation with changes in land use and/or environmental conditions, so that SOM can act as a large source or sink for atmospheric CO_2. Our studies on SOM are focused on the insoluble and refractory (i.e. resistant to drastic laboratory hydrolyses) macromolecular components. Indeed, a number of studies on sedimentary OM demonstrated that this type of components exhibit a conspicuous resistance upon fossilisation. Thus, the non-hydrolysable highly aliphatic biomacromolecules, cutans and suberans, occurring in the cuticles and suberized layers of some higher plants, respectively, can survive, almost unaffected, deposition in sediments and fossilisation. This raises two important questions about SOM: does a tight relationship between a high resistance to laboratory hydrolyses and a high resistance to degradation under natural conditions exist for some SOM components as well? and what is the fate of the refractory fraction of SOM upon change in land use when this change promotes bulk SOM degradation ?

In the present work we examined the refractory organic macromolecular material (ROM) isolated from a typical sandy spodosol (Cestas, "Landes de Gascogne", south-west France) from a plot that was cleared 22 years ago and since then continuously used for intensive maize cropping. The ROM was quantified and the respective contributions of components inherited from the initial forest soil and of maize-derived components were assessed through $\delta\ ^{13}C$ measurements. The molecular composition of the ROM was determined via a combination of spectroscopic (FTIR and solid-state ^{13}C NMR) and pyrolytic (conventional pyrolysis and thermally assisted hydrolysis and methylation) methods. The results were compared with those previously obtained (Quénéa et al., 2004) for the ROM isolated from the soil of an adjacent reference plot where the natural vegetation (pine forest) of the area was preserved.

It thus appeared that:

- The ROM accounts for a substantial part (ca. 20%) of the total OM of the cultivated soil.

- This ROM shows a heterogeneous composition with important contributions of lignin and suberin and, probably, of melanoidin-type components, and minor contributions of polysaccharides, cutans and condensed fatty acids from bacteria and higher plants.

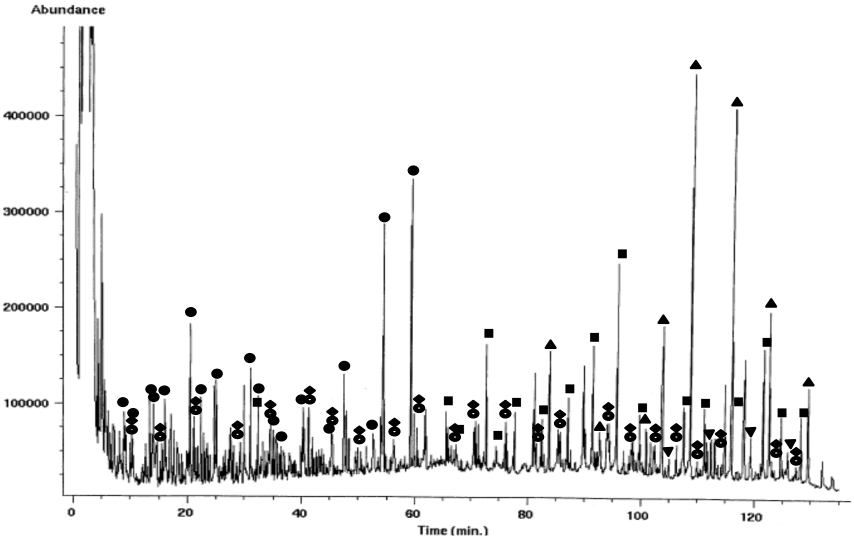


Fig.1. Total ion current trace of the 650°C Curie point pyrolysate, in presence of TMAH, of the ROM from the Cestas cultivated soil (*n*-alkanes (♦), ω-hydroxyacids (▲), carboxylic acids (■), methoxybenzenes (•)).

- Extensive degradation of the ROM inherited from the forest soil (ca. two thirds) occurred upon cropping. A conspicuous uncoupling is thus observed between the resistance of this material to drastic laboratory hydrolyses and its resistance to degradation under natural conditions. These observations, added to recent ones on other types of soils (Poirier et al., 2002, 2003), suggest that such uncoupling is a general feature of SOM thus making a remarkable difference with sedimentary OM.
- A low input of maize components occurred in the ROM of the cultivated soil so that, in spite of large degradation of the refractory carbon inherited from the forest soil, the latter is still predominant (ca. 85%) in this ROM,
- Differential degradation took place in the ROM inherited from the forest soil, some components are entirely degraded while others exhibit some increase in relative abundance.

References

K. Quénéa, S. Derenne, C. Largeau, C. Rumpel, A.Mariotti 2004. Spectroscopic and pyrolytic features and abundance of the macromolecular refractory fraction in a sandy acid forest soil (Landes de Gascogne, France). Organic Geochemistry (in press)

Poirier N., S. Derenne, J. Balesdent, A. Mariotti, D. Massiot, C. Largeau, 2003. Isolation and analysis of the non-hydrolysable fraction of a forest soil and an arable soil (Lacadée, southwest France). European Journal of Soil Science 54, 243-255.

Poirier N., S. Derenne, J. Balesdent, J. N. Rouzaud, A. Mariotti, C. Largeau, 2002. Abundance and composition of the refractory organic fraction of an ancient, tropical soil (Pointe Noire , Congo). Organic Geochemistry 33, 383-391.

OSB1-3: Cluster-size of aromatic domains in charred humic material and its impact on the stability of pyromorphic soil organic matter

H. Knicker[1], G. Almendros[2], F.J. González-Vila[3]

1) Lehrstuhl für Bodenkunde, Technische Universität München, 85350 Freising-Weihenstephan, Germany
2) Centro de Ciencias Medioambientales, CSIC, Serrano 115B, 28006 Madrid, Spain
3) Instituto de Recursos Naturales y Agrobiología de Sevilla, CSIC, P.O. Box 1052, E-41080 Sevilla, Spain.

After wildfires, the incorporation of charred materials into the soil organic matter is expected to increase the stable C-pool and thus, to have a long term impact on C-sequestration. Charred organic matter is assumed to contain highly condensed aromatic clusters with a considerable proportion of core C, for which the distances to the next protons exceed the length of three to four bonds. Such C were found to be underrepresented in solid-state cross polarization magic angle spinning (CPMAS) ^{13}C NMR (Smernik et al., 2002). On the other hand, no appreciable loss in detectability of aromatic C of charred peat subjected to 500°C for 1 h under N_2 was detected (Freitas et al., 1999). After increasing the temperature to 900°C and 1000°C the use of the CP technique was completely unsuccessful. From this report it may be referred that the presence of higher proportions of large graphitic domains is limited to soot and material produced under coking conditions at elevated temperatures above 700° C. Under aerobic and wildfire conditions, most of the organic matter has been mineralized or volatilized at those high temperatures. Thus, the input of soot remaining from the burnt vegetation to the fire-affected soil may be lower than often assumed.

To elucidate the impact of charring on the condensation process, charred peat, produced under laboratory conditions and charred plant remains collected from a natural fire-affected soil from Southern Spain were analyzed by elemental analysis and various NMR techniques. Additionally, commercially available barbeque charcoal was examined. The solid-state ^{13}C NMR spectra were obtained on a Bruker DSX 200 spectrometer using the cross polarization (CP) magic-angle spinning (MAS) technique. For comparison, Bloch decay ^{13}C NMR spectra were obtained from selected samples. Condensation degrees of the aromatic fractions were determined by elemental analysis and dipolar dephasing (DD) NMR experiments. A brief characterization of the relaxation and CP behavior allowed conclusions about the mobility of different molecular domains.

The aromatic portion of the barbeque char and the peat showed atomic H/C ratios between 0.4 and 0.6 revealing that in average every second to third C is connected to a proton. Assuming graphite-like aromatic clusters, this allows for maximal size of ten rings (atomic H/C = 0.4). DD NMR data confirm with clusters of 6 rings which are connected by approximately two bridging C. Alternatively, benzanthracene-like structures with 3 to 5 bridging C are possible. The relatively small clusters disagree with a highly condensed aromatic structure commonly proposed for Black Carbon. On the other hand, comparably small cluster sizes were determined for various natural coals (Abelmann et al., 2003). Although their cross polarization and relaxation times were found to be in the range of our chars, their proportion of slowly polarizing aromatic C was considerably higher (Abelmann et al., 2004), indicating a lower content of crystalline domains.

The small cluster size of the aromatic domains in charred plant residues may explain previous findings which resulted in a questioning of the high stability and inertness of Black Carbon. Compared to predominantly graphitic structures, their surfaces is easier attacked and oxidized. Oxidized char was also detected in Australian soils (Skjemstad et al., 1996). In fact, (Haumaier and Zech, 1995) extracted aromatic clusters rich in carboxylic groups from oxidized charred residues. They concluded that such structures should also occur in fire-affected soils with subsequent high rate of oxidation. Those carboxyl groups were suggested to be involved in organo-mineral complexation (Glaser et al., 2000) but may also allow a fast colloidal transport into deeper horizons by the leaching soil solution.

References

Abelmann, K., Knicker, K., Kögel-Knabner, I., 2003. Mitteil. Deutsch. Bodenkundl. Gesell. 102, 157-158.
Abelmann, K., Totsche, K.U., Knicker, H., Kögel-Knabner, I., 2004. Solid State Nucl. Mag. Res., 25, 252-266.
Freitas, J.C.C., Bonagamba, T.J., Emmerich, F.G., 1999. ^{13}C high-resolution solid-state NMR study of peat carbonization. Energy and Fuels, 13, 53-59.
Glaser, B., Balashov, E., Haumaier, L., Guggenberger, G., Zech, W., 2000. Org. Geochem. 31, 669-678.
Haumaier, L., Zech, W., 1995. Org. Geochem. 23, 191-196.
Skjemstad, J.O., Clarke, P., Taylor, J.A., Oades, J.M., McClure, S.G., 1996. Austral. J. Soil Res. 34, 251-271.
Smernik, R.J., Baldock, J.A., Oades, J.M., Wittaker, A.K., 2002. Solid state Nucl. Mag. Res. 22, 50-70.

OSB2-1: Lignin monomers display contrasted and specific turnover rates in a cultivated soil

M.-F. Dignac, H. Bahri, C. Rumpel, D.P. Rasse, G. Bardoux, A. Mariotti, C. Chenu

Laboratoire de Biogéochimie des Milieux Continentaux (BioMCo), UMR INRA CNRS Université Paris VI,
78850 Thiverval-Grignon, France (e-mail: dignac@grignon.inra.fr)

Lignins are constitutive biopolymers of higher plants possessing a macromolecular polycondensed aromatic structure. Lignins are often considered as slowly biodegradable relative to total plant organic matter. They may preferentially feed C into long-residence time pools of soil organic matter (SOM), therefore contributing to carbon storage in soils.

The fate of lignins under field conditions has been studied in both cultivated and forest soils by molecular analysis after CuO oxidation (e.g. Kögel, 1986). However, a simple quantification of lignin phenols does not permit the determination of their turnover rates in soils. Such an assessment requires isotopic tracer analyses.

Natural ^{13}C labelling of plant-derived material in a vegetation succession of C3 and C4 plants is a powerful technique to measure *in situ* turnover times of SOM (Balesdent et al., 1987). The difference in isotopic ^{13}C signatures observed between C4 plants such as maize (δ^{13}C -12‰) and C3 plants such as wheat (-27‰) is maintained when residues are decomposing in soils. A soil continuously cultivated with C3 plants adopts δ^{13}C value of about -27‰. When this soil is cropped with C4 plants, a progressive increase in its ^{13}C content is observed, due to the substitution of C3- by C4-derived SOM. The turnover rate of SOM may be assessed through this shift in δ^{13}C. The specific isotopic signatures of C3 and C4 plants hold true at the molecular level, implying that this labelling technique can be applied to individual families of molecules through compound specific isotope analysis.

The objective of our study was to compare the specific turnover rates of individual lignin monomers in soils in order to improve our understanding of lignin biodegradation processes. Many studies on SOM turnover using stable isotopes only compare one duration of C4 cropping to the control C3 soil, which implies strong hypotheses on the kinetics. To overcome this limitation, we used natural ^{13}C labeling of SOM generated in a 9 year chronosequence of maize C4 crop replacing the previous wheat C3 crop at the Closeaux experimental field, in France (Dignac et al., 2005). Soils having received from 0 to 9 years of maize cropping after wheat were thus available. We quantified soil lignin monomers released by CuO oxidation and measured their ^{13}C content by gas chromatography coupled via a combustion interface to isotope ratio monitoring mass spectrometry (GC/C-IRMS).

The phenolic monomers obtained after CuO oxidation have a vanillyl (V), syringyl (S) or cinnamyl (C) structure, and derive from guaiacyl, syringyl and p-coumaryl units respectively (Hedges and Mann, 1979). The vanillyl and syringyl phenols have aldehyde, ketone and acid forms. We calculated the proportion of C4-derived lignin during the first nine years of maize cropping by applying the isotopic mass balance equation (Balesdent and Mariotti, 1996) to each lignin monomer (Figure).

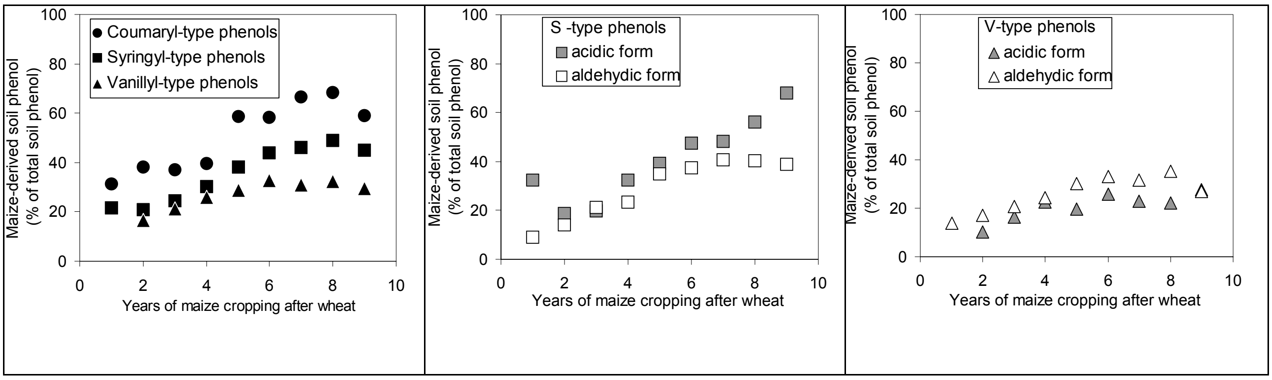


Fig.1. Proportion of maize-derived phenols with years of maize cropping for coumaryl, syringyl and vanillyl-type phenols (left), for acidic and aldehydic forms of S-type phenols (middle) and of V-type phenols (right)

Recent contributions to phenolic carbon pools in soils were consistently higher for the more reactive syringyl and cinnamyl units than for the more recalcitrant vanillyl structures (Figure). Consequently, the turnover rate of vanillyl units may be slower than those of syringyl and cinnamyl units. Vanillyl units are released by CuO oxidation from guiacyl type lignins which have a higher degree of cross-linking compared to syringyl-type. A preferential degradation of syringyl *vs.* vanillyl structural units was previously suggested by Ertel and Hedges (1985). Acidic and aldehydic forms displayed different incorporation kinetics for both syringyl and vanillyl structures (Figure).

None of the observed kinetics had a linear shape. This observation underlines the importance of accurately computing the kinetic parameters of SOM for the first years of vegetation change, which requires comprehensive ^{13}C-SOM time sequences such as provided by the Closeaux experimental design.

References

Balesdent, J., Mariotti, A., Guillet, B., 1987. *Soil Biology & Biochemistry*, 19: 25-30.

Balesdent, J. Mariotti, A., 1996. In: *Mass spectrometry of soils.* T.W. Boutton, S.I. Yamasaki (Eds), Marcel Dekker Inc., New York USA, pp. 83-111.

Dignac, M.F., Bahri, H., Rumpel, C., Rasse, D.P., Bardoux, G., Balesdent, J., Girardin, C., Chenu, C., Mariotti, A., 2005. *Geoderma*, in press.

Ertel, H., Hedges, J.I. 1985. *Geochimica et Cosmochimica Acta,* 49: 2097-2107.

Hedges, J.I., Mann, D.C., 1979. *Geochimica et Cosmochimica Acta*, 43: 1803-1807.

Kögel, I., 1986. *Soil Biology & Biochemistry*, 18: 589-594.

OSB2-2: Chemical composition and age of organic carbon pools in topsoil and subsoil horizons of acid forest soils with different pedogenesis

S. Spielvogel, J. Prietzel, I. Kögel-knabner

Lehrstuhl für Bodenkunde, Department für Ökologie, Technische Universität München, 85350 Freising-Weihenstephan, Germany (e-mail: spielvogel@wzw.tum.de)

Recent carbon inventories have shown that significant amounts of organic matter (SOM), even though at low concentrations, can be stored in subsoils (Batjes, 1996; Jobbagy and Jackson, 2000). However, the chemical composition of subsoil organic carbon is almost unknown. In the presented study we characterize the chemical composition of the bulk soil organic matter in the mineral horizons of three different acidic soil types under Norway spruce forest. Our objective was to assess the quantity and chemical composition of SOM stored in the subsoil (B horizon and BwC horizon) compared to the topsoil (A horizon and forest floor). Samples were taken from the forest floor, the A and B horizons of ten Dystric Cambisols, ten Dystric Cambisols with low bulk density and ten Entic Podzols, respectively. They were analysed for concentrations and contents of nitrogen and carbon; additionally chemical structure of SOM was investigated by ^{13}C CPMAS NMR spectroscopy. Two profiles per soil type were analysed for radio carbon age by accelerator mass spectrometry and for the contribution of lignin to the carbon pool using the CuO oxidation technique according to Kögel and Bochter (1985) as a relative measure of lignin and its degree of structural alteration.

More than 45 % of the organic carbon and nitrogen pools of the mineral soil of the Cambisols is stored in the Bw and BwC horizons and up to 70% in the Bsh, Bhs and Bs horizons of the Podzols. Radiocarbon age increased with soil depth, and the organic carbon in the BvC horizon of the Cambisols had an apparent age of several thousand years (2000 to 3900 years B. P.). However, the organic carbon stored in the Bsh horizon of the analyzed Podzol is much younger than the organic carbon stored in the B horizons of the two Cambisols, reflecting the different pedogenetic history of the soils. The young age of the deeper horizons of the Podzol can be explained by the vertical translocation of DOC during podzolization.

The structural analyses indicate a similar chemical composition of the organic matter in the forest floor of all three soil types. However, in the mineral soils especially in the B horizons, the chemical composition of the SOM differed according to the different pedogenetic processes operating in the three soil types. The contribution of alkyl carbon to total OC increases with soil depth in the Dystric Cambisols and the Dystric Cambisols with low bulkm density whereas the contribution of O-alkyl carbon decreases. Consequently for the Cambisols the alkyl C/O-alkyl C ratio increased with soil depth and correlated significantly with the radiocarbon age ($p \leq 0.05$). In the Podzols, the contribution of O-alkyl C also decreases in the forest floor and the A-horizons with depth. In contrast to the Cambisols, however, it slightly increases again in the Bsh horizons. The contribution of alkyl C shows an opposite feature. The higher contribution of O-alkyl C and carboxylic carbon in the spectra of the Bsh horizons of the Haplic Podzols, may be due to carbon leaching during podzolization. In the Bhs and Bs horizons of the Podzols and the BwC horizons of all soil types, most of the organic carbon was mobilized after demineralisation by treatment with 10% hydrofluoric acid (HF) and may therefore probably represent organic matter adsorbed to the soil minerals.

The contribution of vanillyl- + syringyl- + cinnamyl-units shows the same pattern in the Haplic Podzol and the Dystric Cambisol profile. It decreases with depth whereas the acid to aldehyde ratio of the CuO oxidation products vanillyl (Ac/Al)v and syringyl (Ac/Al)s increases, indicating an increasing state of decomposition of the lignin with soil depth (Rumpel 2004). However, in the Dystric Cambisol with low bulk density the (Ac/Al)v and (Ac/Al)s ratios decrease again in the BvC horizon. The reason could be the input of fresh root litter which may be more abundant at this site.

Our data indicate that there is a strong influence of soil forming processes on the composition of organic carbon in subsoils.

References

Batjes N. H. (1996): Total carbon and nitrogen in the soils of the world. European Journal of Soil Science 47, 151-163.

Jobbagy E. G. and R. B. Jackson, (2000): The vertical distribution of soil organic carbon and its relation to climate and vegetation. Ecological Applications 10, 423-436.

Kögel I. and R. Bochter (1985): Characterization of lignin in forest humus layers by high-performance liquid chromatography of cupric oxide oxidation products. Soil Biology and Biochemistry 17, 640-673.

Rumpel C., K. Eusterhues and I. Kögel-Knabner (2004): Location and chemical composition of stabilized organic carbon in topsoil and subsoil horizons of two acid forest soils. Soil Biology and Biochemistry 36, 177-190.

OSB2-3: Incorporation of CO_2 into soil microbial biomass and its conversion to soil organic matter

A. Miltner[1], R. Kindler[1], C. Hoffmann-Jähniche[1], H.-H. Richnow[2], F.-D. Kopinke[3], M. Kästner[1]

1) Department Bioremediation, UFZ - Centre for Environmental Research Leipzig-Halle, 04318 Leipzig, Germany (e-mail: anja.miltner@ufz.de)
2) Department Isotope Biogeochemistry, UFZ - Centre for Environmental Research Leipzig-Halle, 04318 Leipzig, Germany
3) Department Environmental Technology, UFZ - Centre for Environmental Research Leipzig-Halle, 04318 Leipzig, Germany

In the past years, it has been assumed that most soil microorganisms are heterotrophic and thus CO_2 producers, because the net carbon dioxide flux goes from the soil to the atmosphere. Therefore it has been neglected that the opposite flux (CO_2 fixation by non-autotrophic soil microorganisms) also takes place and may, although not quantitatively dominant, significantly affect the isotopic composition of the soil microflora and later on of the soil organic matter. In addition, this process may alter the risk assessment of bound residues as determined by non-extractable radioactivity remaining in soil after incubation with radiolabelled pollutants, because this radioactivity may, at least partly, originate from bacteria which incorporated radioactive CO_2 which was produced during mineralization of the radiolabelled compound. We therefore investigated this process by incubating soil with radiolabelled $^{14}CO_2$ to determine the dynamics of the process and with stable isotope labelled $^{13}CO_2$ in order to trace the fate of the assimilated C. We performed the experiment in the dark to exclude phototrophic processes. In addition, the heterotrophic microbial activity was enhanced by adding farmyard manure as an easily available C source. We found that CO_2 was incorporated from the atmosphere into the microbial biomass. The process proceeded with a relatively high rate at the beginning and slowed down towards the end of the experiment, but continued even after 81 days. The amount of CO_2 fixed at the end of the experiment corresponded to about 0.05% of the soil organic carbon or 7% of the microbial biomass. A closer examination of the fate of the label revealed that the labelled C was incorporated into biomolecules such as amino acids and fatty acids, but to a much lower degree into amino sugars which indicates starvation metabolism. The distribution of the label in the soil fatty acids indicated that (1) a wide range of microorganisms contributed to the process, because all fatty acids with 20 or less C atoms were significantly enriched in ^{13}C, and (2) a part of the C incorporated initially into the biomass was already present in the pool of non-living organic matter, because in addition to phospholipid fatty acids (characteristic for living cells), a significant amount of label was found in the non-phospholipid fraction of fatty acids which is not associated to living biomass. The labelling pattern of the amino acids indicated that oxaloacetate was an important metabolite of the CO_2 fixation, because those amino acids derived from it (asparagine and aspartate) carried the highest label. Oxaloacetate is the main product of anaplerotic reactions, which are required by all organisms to replenish the citric acid cycle when substances of this cycle are used for biosynthesis of amino acids or porphyrins. The main process is the carboxylation of pyruvate or phosphoenolpyruvate to oxaloacetate, which can be directly transaminated to yield aspartate. Although we cannot exclude other processes such as chemoautotrophic reactions or the synthesis of pyrimidine and purine nucleotides, our data suggest that soil microorganisms are able to incorporate C from CO_2, that anaplerotic reactions contribute significantly to this process, and that part of the C originally incorporated into the biomass has been converted to non-living organic matter already after 81 days.

TOPIC SESSIONS

METHODS & NEW TRENDS

OMN-1: Scanning for indigenous biomass contributions in petroleum and coals Using LC-MS techniques

T.B.P. Oldenburg[1], S.R. Larter[1], H.Huang[1], K. Kaster[2], G. Voordouw[2], A. Rowan[3], I.M. Head[3], J. Lipp[4], K.-U. Hinrichs[4], T. Thielemann[5]

1) Petroleum Reservoir Group (PRG), Department of Geology and Geophysics, University of Calgary, Canada
2) Department of Biological Science, University of Calgary, Canada
3) NRG petroleum group, School of Civil Engineering and Geosciences, Univ.of Newcastle upon Tyne, UK
4) Research Centre Ocean Margins (rcom), University of Bremen, Germany
5) Bundesanstalt für Geowissenschaften und Rohstoffe (BGR), Hannover, Germany

Most of the world's petroleum is partially biodegraded. This is of considerable importance as biodegradation reduces the economic value and causes problems during petroleum production and refining. Although microbial activity in deep sediments was reported over 75 years ago and while dramatic geochemical and microbiological advances in our understanding of the deep biosphere have occurred, relatively little is known about the microbial populations involved in subsurface hydrocarbon degradation. A better understanding of microorganisms resident and active in petroleum microcosms, their physiological properties and then geochemical roles will aid both oil exploration and production. While microbiology has been able to isolate microorganisms from deep sediments contamination is a major problem, especially in petroleum reservoirs where drilling mud contamination is common. Intact polar membrane lipids (IPLs) have better prospects in some settings as biomass chemotaxonomic indicators as they can accumulate in the oil column in the reservoir. We describe method developments for the detection of IPLs of microorganisms, such as phospholipids and corresponding archaea-related tetraethers, at natural abundance levels in petroleum systems. Developments in liquid-chromatographic mass-spectrometry (LC-MS) techniques allow us to now detect relatively low concentrations of biomass and we investigated in combination with microbiological 16S rRNA genes analysis several samples from natural methanogenic environments, heavily biodegraded oil fields, methane-enriched coal mine waters and oil storage tanks. The objective was to determine IPLs and relate their occurrence to the diversity of microorganisms in fossil fuel reservoirs.

Figure 1 shows a typical analysis of the IPLs of a subsurface sulfate reducing archaea notified from a North Sea oil reservoir illustrated as a two-dimensional density map. We describe our approach and show the ease with which chemotaxonomic interpretation can be obtained from fossil fuel reservoirs.

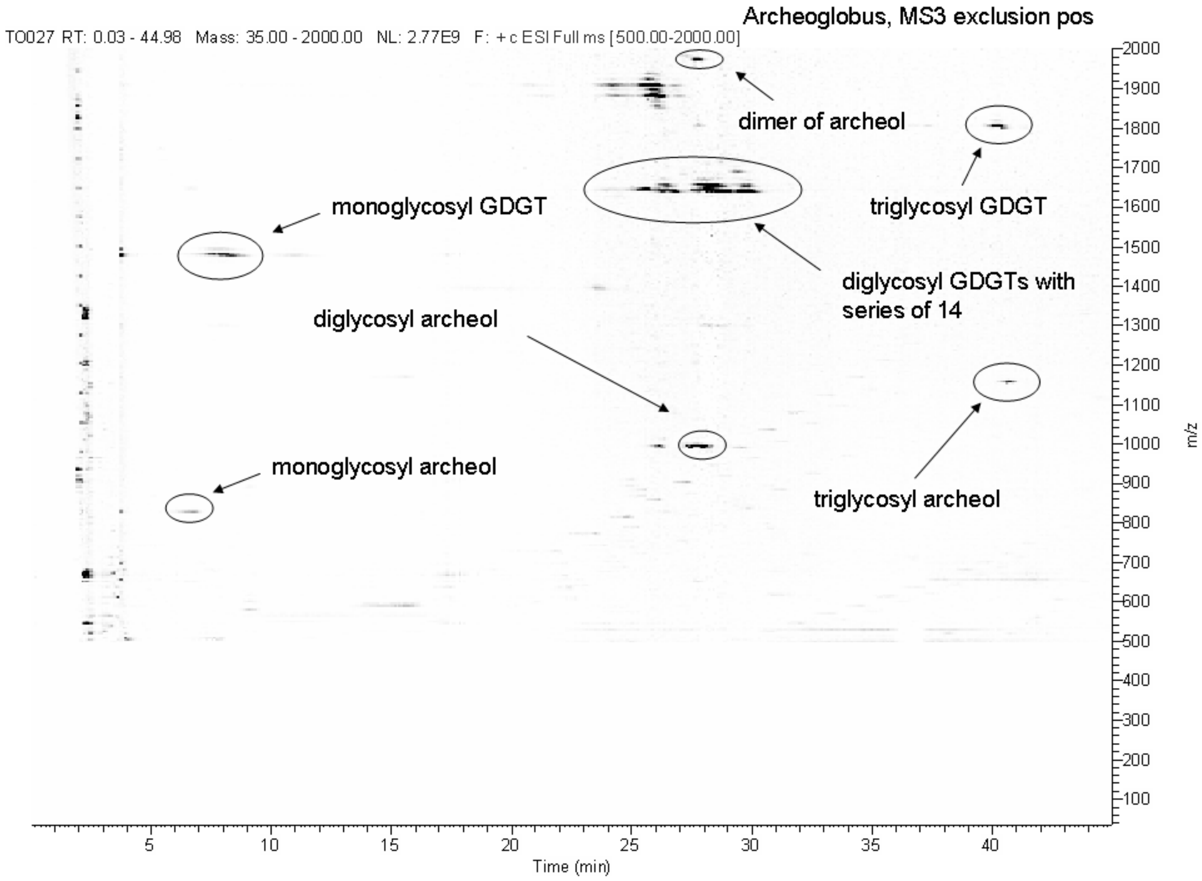


Fig.1. Two-dimensional density map illustrating the intact polar lipids (archaeal lipids) of an Archaeoglobus detected from a North Sea oil reservoir

OMN-2: Recurring molecular themes in the Ultrahigh Resolution Mass Spectra of aquatic humic substances from a variety of sources

W.T. Cooper[1], L.B. Tremblay[1], J. Chanton[2], T. Dittmar[2], T.R. Filley[3]

1) Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306-4390, USA (e-mail: cooper@chem.fsu.edu)
2) Department of Oceanography, Florida State University, Tallahassee, FL 32306-4320 USA
3) Department of Earth and Atmospheric Sciences, Purdue University, West Lafayette, IN 47907-2051, USA

The combination of electrospray ionization and ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) has revolutionized the characterization of humic substances. Indeed, high-field (9.4 Tesla) FT-ICR MS can now fully resolve individual compounds in complex humic mixtures [1,2], providing a level of molecular detail thought impossible just a decade ago. For example, we have argued that our ultra-high resolution ($m/\Delta M > 10^5$) mass spectra, which reveal the presence of molecular families in aquatic humic and fulvic acid mixtures, indicate that humic compounds are relatively small covalent structures with a high degree of molecular order and almost polymeric character [3].

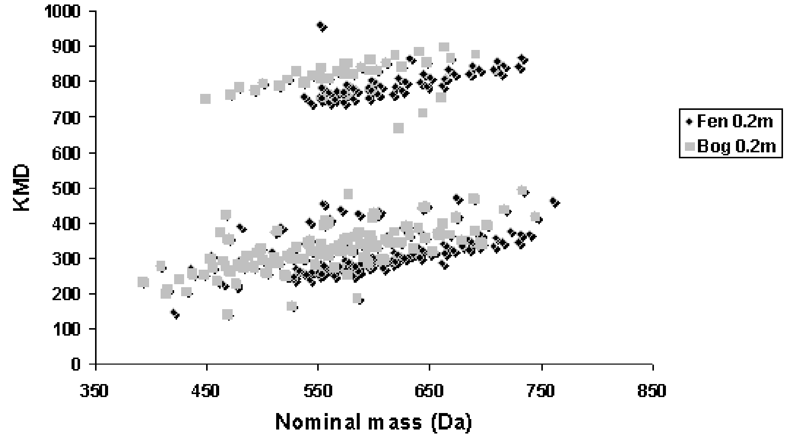


Figure 1: *Kendrick plot (Kendrick mass defect, KMD, vs. nominal IUPAC mass) for DOM from the surface porewaters of a peatland fen and bog.*

In this presentation we will highlight the molecular information that ultrahigh resolution ESI-MS can provide about humic mixtures. For example, controlled studies of lignin degradation by the brown rot fungus *G. trabeum* resulted in mass spectra that were remarkably similar to those of riverine humic and fulvic acids. Because of the complexity of the raw mass spectral data, trends in molecular formulas using Kendrick plots and point out how data in this format can be interpreted. By overlaying Kendrick plots for degraded lignin, fulvic acids and humic acids we will demonstrate the remarkable similarities in molecular composition of these highly complex but apparently linked natural mixtures.

We will also show how this ultrahigh resolution MS data can be used to trace organic matter as it moves along tempero-spatial gradients, using DOM from two unique and quite different sources: peatland fens and bogs in Northern Minnesota (US) and mangrove-fringed estuaries in Northern Brazil. Analysis of DOM isolated from pore mangrove pore waters and an adjacent estuary allowed us to identify molecular tracers that are specific for following the coastal outwelling of mangrove-derived DOM into the ocean. We will also show molecular differences in soil pore water DOM from a peatland fen and bog (Figure 1), and document the changes that occur in DOM as it moves through both horizontal and vertical gradients in these different peats formations.

Finally, we have not ignored other data that suggest humic mixtures are comprised of much larger molecules and/or aggregates. For example, size-exclusion chromatography with ESI-MS detection has revealed what appear to be large fulvic acid molecules based on SEC retention but which do not appear as high-molecular weight ions in the corresponding mass spectra [4,5]. We will thus attempt to reconcile our high resolution mass spectrometry information with classical models of humic and fulvic acid structure and aggregation, as well as recent suggestions regarding the presence of tannin- and terpenoid-like structures in riverine humics.

References

[1] Stenson, A.C., Landing, W.M., Marshall, A.G., Cooper, W.T. 2002. Ionization and Fragmentation of Humic Substances in Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. Analytical Chemistry, 74, 4397-4409.

[2] Kujawinski, E.B., Hatcher, P.G., Freitas, M.A. High-resolution Fourier transform ion cyclotron resonance mass spectrometry of humic and fulvic acids: Improvements and comparisons. Analytical Chemistry, 74, 413-419.

[3] Stenson, A.C., Marshall, A.G., Cooper, W.T. 2003. Exact Masses and Chemical Formulas of Individual Suwannee River Fulvic Acids from Ultrahigh Resolution Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry, Analytical Chemistry, 75, 1275-1284, 2003.

[4] Reemtsma. T., These, A. 2003. On-line coupling of size exclusion chromatography with electrospray ionization-tandem mass spectrometry for the analysis of aquatic fulvic and humic acids. Analytical Chemistry, 75, 1500-1507.

[5] These, A., Reemtsma, T. 2003. Limitations of electrospray ionization of fulvic and humic acids as visible from size exclusion chromatography with organic carbon and mass spectrometric detection. Analytical Chemistry, 75, 6275-6284.

OMN-3: Carbon isotopic compositions of volatile fatty acids in sediment/pore-water systems measured by Isotope-Ratio-Monitoring Liquid Chromatography/Mass Spectrometry

M. Elvert[1], V. Heuer[1], X. Prieto Mollar[1], L.R. Hmelo[1], M. Krummen[2],
J.M. Hayes[3], K.-U. Hinrichs[1,3]

1) Organic Geochemistry Group, DFG-Research Center Ocean Margins & Dept. of Geosciences, University of Bremen, P.O. Box 330 440, D-28334 Bremen, Germany
2) Thermo Electron Cooperation, Finnigan Advanced Mass Spectrometry, Hanna-Kunath-Strasse 11, D-28199 Bremen, Germany
3) Dept. of Geology & Geophysics, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA

In recent decades, our understanding of biogeochemical processes has benefited enormously from the information encoded in the stable carbon isotopic composition of organic molecules. For low-molecular-weight metabolites, δ^{13}C values are routinely acquired for methane and used to examine details of its production and consumption. On the other hand, systematic information about the isotopic compositions of volatile fatty acids (VFAs) and other water-soluble metabolites in natural environments is very rare. The isotopic composition of acetate, a ubiquitous intermediate in anaerobic metabolism, is affected by biological processes that produce and/or consume it (Blair et al., 1992; Gelwicks et al., 1989; 1994). Therefore, δ^{13}C values of acetate extracted from natural systems are potentially powerful probes to decipher the dominant carbon-transforming processes *in situ*.

The lack of information about carbon isotopic variations of VFAs in natural environments is due to a lack of methods suitable for their analysis at typical natural concentrations (i.e., µmolar in sediment pore-waters). We have developed a new analytical protocol for sensitive and accurate carbon isotopic analysis of VFAs by isotope-ratio-monitoring liquid chromatography/mass spectrometry (irm-LC/MS). This technique is based on the new Finnigan™ LC IsoLink interface that couples an HPLC to commonly used irm-MS-systems (Krummen et al., 2004). Our protocol requires only minor manipulation of the pore-water sample prior to analysis and avoids complex purification and derivatization steps. We are able to obtain reproducible and accurate results for direct injections of acetate dissolved in artificial seawater at concentrations ranging from 50 to 1000 µM (Fig. 1). This range can be extended by concentrating or diluting the sample prior to analysis. Samples with initial concentrations of acetate as low as 2 µM are concentrated by lyophilizing pore-water samples at pH 13. Our technique extends the previously accessible concentration range by more than an order of magnitude to lower concentrations and thus will enable systematic analysis of the variability of δ^{13}C in most sedimentary environments. Currently, we are investigating marine sediments taken from both the deep subsurface and the sediment-water interface. Our field data and laboratory-based experiments indicate wide variations in the isotopic composition of acetate. For example, we find δ^{13}C values to be generally lower in sulfate-reducing sediments compared to methanogenic sediments. This presumably indicates that the carbon isotope effect associated with acetoclastic methanogenesis is higher than that associated with the consumption of acetate by sulfate-reducing microorganisms. We will present results from aqueous fluid samples that originate from coastal, open-ocean, and deeply-buried sedimentary environments. We will highlight the potential of VFA stable isotopes as indicators of predominant biogeochemical processes in natural environments.

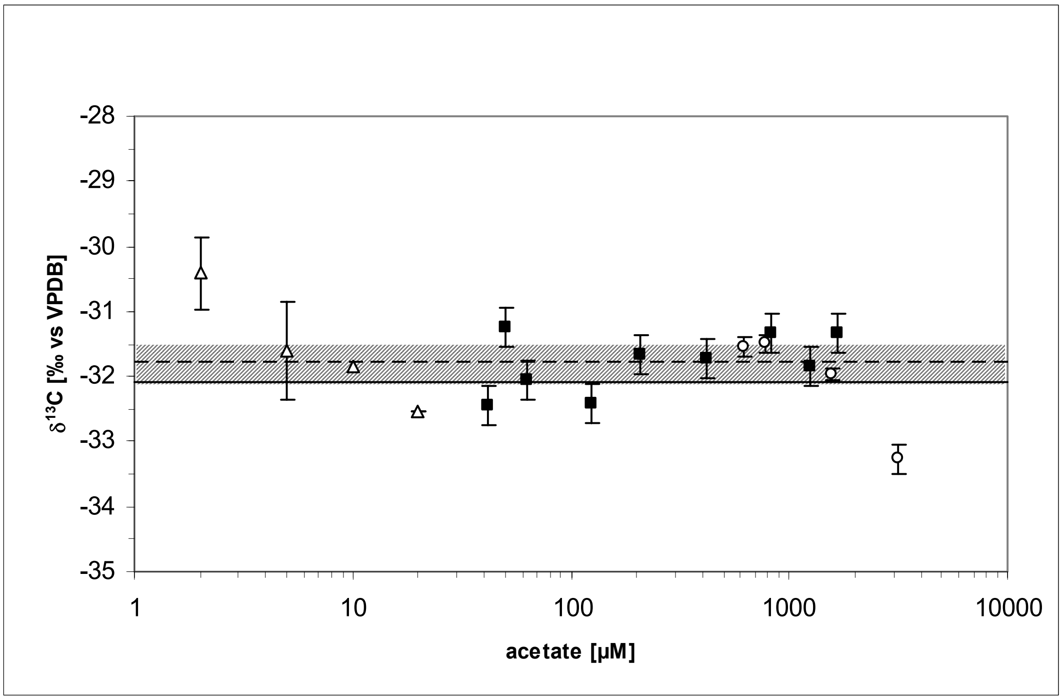


Fig.1. Carbon isotopic analysis of acetate by irm-LC/MS yields a mean δ^{13}C value of -31.8‰ (n = 31, dashed line) for 2 to 3125 μM aqueous solutions prepared from a pure Na-acetate salt. With the precision (95% confidence interval) of the analysis being ± 0.3‰ (n = 31, shaded area), irm-LC/MS results agree well with the δ^{13}C value of -32.08 ± 0.08‰ (n = 3) determined for pure Na-acetate by irm-EA-MS (solid line). Open triangles represent 2-20 μM acetate solutions, analyzed after 12.5-fold pre-concentration. Solid squares symbolize 42 - 1667 μM standards. Open circles designate 625 – 3125 μM solutions obtained from 12.5-fold pre-concentration of 50-250 μM standards and document negligibility of isotopic fractionation. The analyzed concentration range is equivalent to 30 - 3750 ng of carbon delivered to the ion source

References

Blair, N.E., Carter Jr., W.D., (1992) The carbon isotope biogeochemistry of acetate from a methanogenic marine sediment. *Geochimica et Cosmochimica Acta*, 56, 1247-1258.

Gelwicks, J.T., Risatti, J.B., Hayes, J.M., (1989) Carbon isotope effects associated with autotrophic acetogenesis. *Organic Geochemistry*, 14(4), 441-446.

Gelwicks, J.T., Risatti, J.B., Hayes, J.M., (1994) Carbon isotope effects associated with aceticlastic methanogenesis. *Applied and Environmental Microbiology*, 60(2), 467-472.

Krummen, M., Hilkert, A.W., Juchelka, D., Duhr, A., Schlüter, H.-J., Pesch, R., (2004) A new concept for isotope ratio monitoring liquid chromatography/mass spectrometry. *Rapid Communications in Mass Spectrometry*, 18, 2260-2266.

POSTER COMMUNICATIONS

TOPIC SESSIONS

OIL, GAS & COAL GEOCHEMISTRY

PGG1-1: Facies, thermal maturity and correlation of source rocks and crude oils in the Western Depression of the Liaohe Basin, P.R. China using molecular markers

A. Fuhrmann[1], J.F. Lopez[2], B. Horsfield[1], H. Wilkes[1], L. Hu[3]

1) GeoForschungsZentrum Potsdam, D-14473 Potsdam, Germany (e-mail: furmi@gfz-potsdam.de)
2) Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany
3) Exploration & Development Research Institute, Liaohe Oilfield Subcompany, PetroChina, Panjin, Liaoning 124010, P.R. China

The Liaohe Basin is a Tertiary rift and one of the most important petroleum bearing Cenozoic sedimentary basins in NE China. Normal gravity oils as well as heavy to extra-heavy oils are produced in the Western Depression of this basin. Previous studies have shown that lacustrine oil shales and mudstones in the fourth (ES_4) and third (ES_3) members of the Eocene-Oligocene Shahejie Formation are major source rocks which have generated significant amounts of petroleum (e.g. Chen et al., 1999). However, only few investigations have attempted to link source rocks and crude oils and thus the origin of petroleums in large parts of the Western Depression remains unresolved. As part of a larger project of evaluating the petroleum system we present regional variations of source rock and crude oil biomarker characteristics which are based on an excellent coverage with core samples and oils from most of the major producing areas in the Western Depression.

Thirty source rock and twenty-five oil samples were selected for a geochemical characterisation using gas-chromatography and gas chromatography-mass spectrometry. The oils chosen for detailed facies and maturity investigations have a biodegradation ranking 0-1 according to the Peters & Moldowan biodegradation scale. Crude oils from the Shuguang and Gaosheng areas were most likely expelled from source rocks deposited in a restricted and stratified paleolake setting which can be deduced from a relatively high gammacerane content, low amounts of diasteranes, relatively low pristane/phytane ratios and high concentrations of β-carotane. By comparison, most oils from the Lengjiapu area are characterised by relatively high C_{29}-diasterane/regular sterane ratios and pristane/phytane ratios and a depletion of gammacerane, thereby suggesting source rock deposition in a freshwater dominated lake setting.

All available oils can be categorized as "immature oils" based on sterane maturity parameters C_{29}-sterane $20S/(20S+20R)$ and $\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$ which are both less than 0.4. However, these low maturity levels are not supported by other ratios as those based on methylphenanthrenes and benzocarbazoles which indicate a higher thermal maturation. In addition, our investigations have shown that the C_{29}-diasterane/regular sterane and the

Ts/(Ts+Tm) ratios are not helpful for maturity estimations due to the influence of facies. However, two parameters based on ring D aromatised 8,14-secohopanoids and C_{31}-C_{34} benzohopanoids show very sensitive changes with increasing maturity for source rocks from the Western Depression (Figure 1).

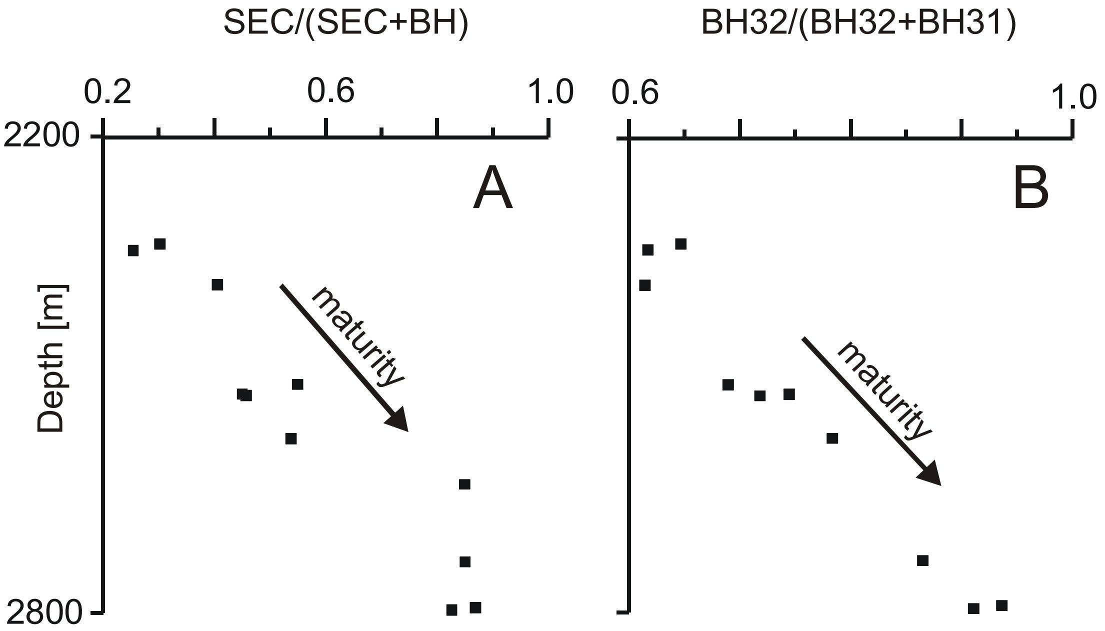


Fig.1. Monoaromatic hopanoids in ES_4 source rock extracts (Dujiatai sub-member). A, MAH ratio based on ring D aromatised 8,14-secohopanoids (SEC) and benzohopanoids (BH) after He and Lu (1990). B, Benzohopane ratio based on C_{31} and C_{32} benzohopanoids (BH)

References

Chen, Z., Yan, H., Li, J., Zhang, G., Zhang, Z., Liu, B., 1999. Relationship between Tertiary volcanic rocks and hydrocarbons in the Liaohe Basin, People´s Republic of China. AAPG Bulletin 83, 1004-1014.

He, W., Lu, S., 1990. A new maturity parameter based on monoaromatic hopanoids. In: Durand, A., Behar, F. (Eds.), Advances in Organic Geochemistry 1989. Organic Geochemistry 16 (4-6), pp. 1007-1013.

PGG1-2: A fast method for the detection of thiadiamondoids as molecular marker of thermochemical sulfate reduction

R. Galimberti[1], F. Zecchinello[1], M. Nali[1], N. Gigantiello[2], L. Caldiero[2]

1) ENI E&P, Basin Geology Dep., Via Maritano, 26, San Donato Milanese, MI, 20097 Italy
2) EniTecnologie, Via Maritano, 26, San Donato Milanese, MI, 20097 Italy

Thermochemical Sulfate Reduction (TSR) is a high temperature process occurring in some carbonate reservoirs that can lead to sour (H_2S and CO_2 rich) petroleum accumulation.

During TSR petroleum compounds react with sulfate minerals (primarily anhydrite) to form H_2S and calcium carbonate. Beside the main products, TSR can originate new organic sulfur compounds of the thiaadamantane series which have been proposed by different authors as molecular markers for this kind of oil alteration (Hanin et al., 2002 and 2003; Dessort et al., 2004).

The mentioned research groups have detected thiaadamantanes in altered oils by GC-MS after a pre-concentration by chromatography over silver nitrate impregnated silica gel.

Here we propose a new and simpler method based on the direct analysis of the oil by Gas Chromatography coupled with Tandem Mass Spectrometry (GC/MS-MS). The oil sample is only diluted by solvent or deasphalted when necessary, avoiding any possible loss of the lighter thiadiamondoids during the solvent evaporation. The thiaadamantane and its alkylated derivatives (C_1, C_2, and C_3 substituted) are detected by a Single Reaction Monitoring acquisition using the abundant molecular ion as the parent ion and the most abundant or most specific fragment ion (m\z 79 or 93 or 125) as shown in Fig.1.

The new method has been tested on a set of samples confirming that only oils altered by TSR contain significant quantities of thiadiamondoids.

In addition, the simultaneous acquisition by GC/MS-MS of ions related to thiophene derivatives, has allowed to test the hypothesis that thiadiamondoids are formed through a sulfurisation processes different from those of the earliest diagenesis. In fact there is no relation between the content of “classic” organic sulfur compounds and the presence of thiadiamondoids.

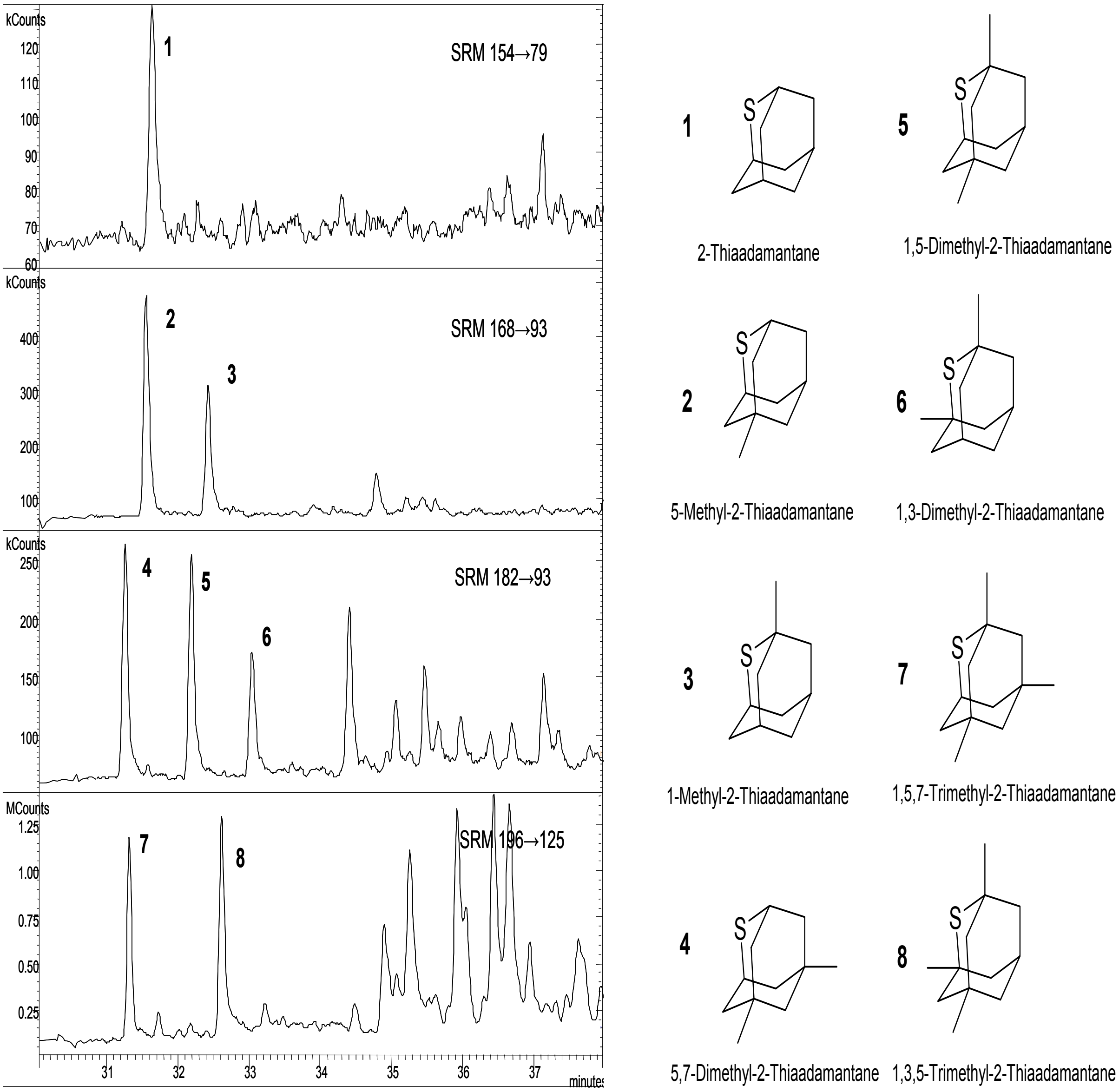


Fig.1. Single Reaction Monitoring chromatogram of an oil sample altered by TSR. The tentative identification of the different isomers is based on the data published by Dessort et al. (2004)

References

Hanin, S.; Adam, P.; Kowalewski, I.; Huc, A.Y.; Carpentier, B.; Albrecht, P.; (2002). Bridgehead alkylated 2-thiaadamantanes: novel markers for sulfurisation processes occurring under high thermal stress in deep petroleum reservoirs.
Journal of Chemical Society, Chemical Communication, 1750-1751.
Hanin, S.; Adam, P.; Kowalewski, I.; Carpentier, B.; Huc, A.Y.; Albrecht, P.; (2003). Alkylated 2-thiaadamantanes: molecular markers for thermochemical sulfate reduction.
21st International Meeting on Organic Geochemistry, Krakow – Poland.
Dessort, D.; Montel, F.; Caillet, G. ; Lescanne, M. ; (2004). Organic geochemistry of oils and condensates associated to sour gas in Gulf.
The 6th Middle East Geosciences Conference and Exhibition, GEO 2004, Bahrain.

PGG1-3: The history of Lomovoe oilfield filling based on molecular parameters

I.V. Goncharov, N.V. Oblasov, S.V. Nosova, V.V. Samoilenko

TomskNIPIneft, 72 Av. Mira, Tomsk, 634027, Russia (e-mail: GoncharovIV@nipineft.tomsk.ru)

Knowledge about composition and properties of produced oil are very important from the position of recovery and oil treatment organization. On the other hand, molecular composition can bear important information about field filling history and migration routes. It can be used for oil search in a region.

Lomovoe oil field is located in the South-East of Western Siberia (Russia). Production horizon is U1 of Verhnevasugan formation. Lomovoe field differs markedly from other fields of this area. GOR varies between 50 and 315 m^3/t (figure 1). This fact appreciably complicates field development. GC/MS analysis of 55 oils was carried out for the purpose of determination the reasons for different GOR values.

Analysis data show that composition of oils from different parts of the field differ in some geochemical parameters. Pristane to phitane ratio values (Pr/Ph) vary from 1.22 to 2.40, the ratio of pristane and phitane sum to that of n-C17, and n-C18 (Ki) varies from 0.62 to 0.86. The ratio 4-methildibenzothiophen to 1-methildibenzothiophen (4MDBT/1MDBT) lies within the range of 1.51 and 2.25.

The variation of Pr/Ph ratio definitely indicates that Lomovoe oil field has been formed due to generation of different source rocks of different nature. At that oils with the largest values of Pr/Ph ratio have the largest values of Ki and GOR, and occupy the roof and northeastern parts of the field.

Distribution of 4MDBT/1MDBT ratio values along the field turned out to be somewhat different than the other parameters. The largest values of this ratio occupy southern part of the field but 4MDBT/1MDBT ratio increases from the south-east to the north-west at the other part of the field.

Analysis Data of neighboring Grushevoe oil field show similar behavior of geochemical parameters. Oils from southeastern part have high Pr/Ph, Ki and 4MDBT/1MDBT ratio values, but oils from northwestern part have low values of these ratios (figure 1).

Field filling history can be reconstructed based on these findings. On the first stage, Lomovoe field had been filled due to oil generation of Togur formation, which located approximately 300 m lower then Vasugan and Bazhenov formations. Pristane dominates over phitane in oils related to Bazhenov formation [1].

On the second stage, when organic matter of overlying Bazhenov formation had matured to “oil window”, field started filling by oils with low GOR and Pr/Ph. Oil related to Bazhenov formation fills up the field from South and North. Analysis of rock extracts indicates that maturity of organic matter differs in the North (Ki=0.7-0.9, 4MDBT/1MDBT=0.9-1.5) and in the South (Ki=0.5-0.7, 4MDBT/1MDBT=2.11-2.50). In so doing, it explains the increase of 4MDBT/1MDBT ratio from the south-east to the north-west along the field.

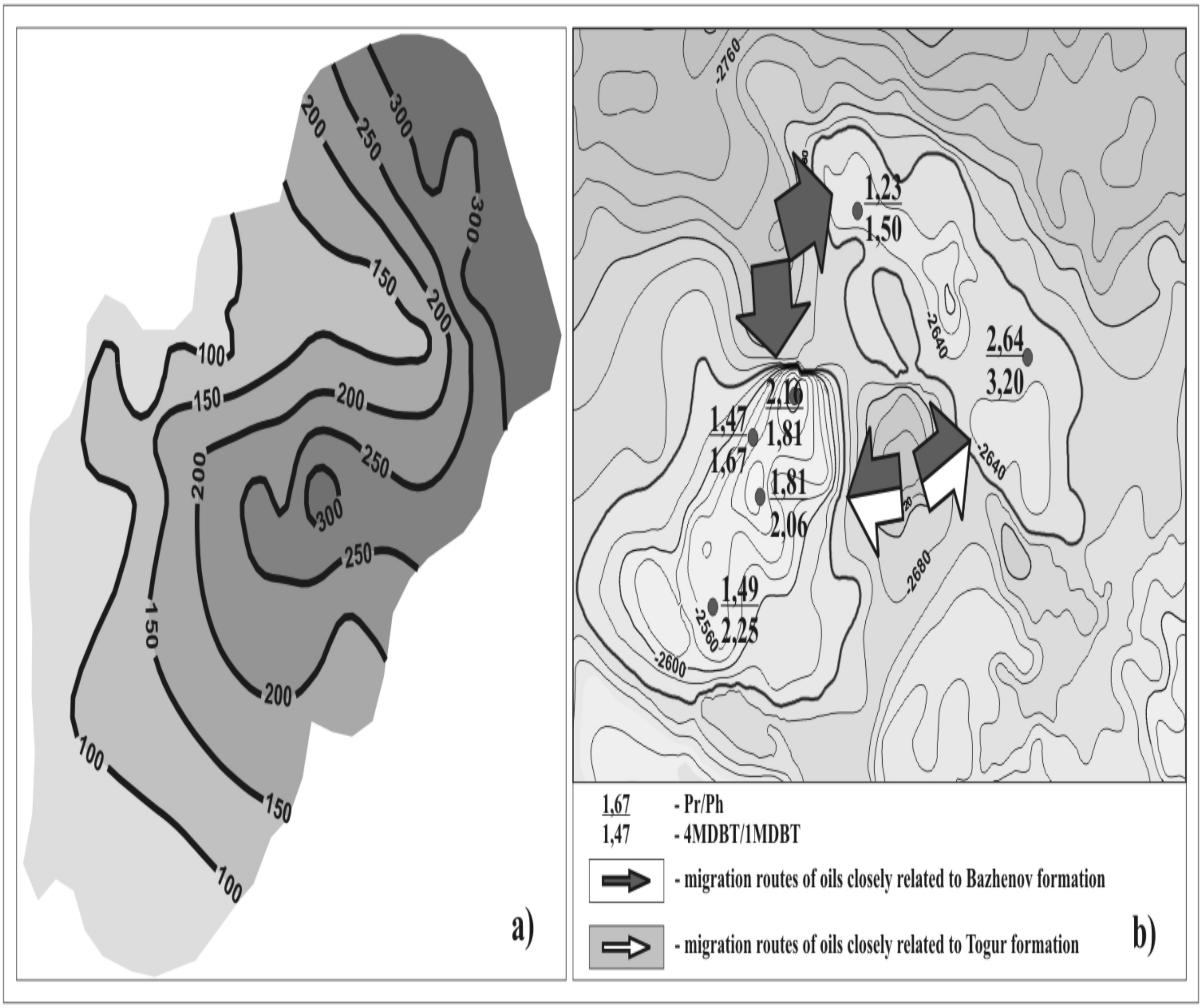


Fig.1. GOR (a) and filling scheme of Lomovoe oil field

References

[1] Goncharov, I., Gorodnikov, M., Novikova, N., Lopatin, N., Emec, T., 2001. The nature of oils in Tomsk region. 20th International Meeting on Organic Geochemistry, Nancy, pp.179-181

PGG1-4: Investigation on catalytic abiogenous synthesis of hydrocarbon masses on the ores of the Earth's crust

K.G. Ione, V.M. Mysov

STC "Zeosit", Pr. Akad. Lavrentieva, 6, Novosibirsk, 630090, Russia (e-mail: zeosit@batman.sm.nsc.ru)

The conventional models for the origin of the hydrocarbon deposits in the Earth's crust imply biogenic mechanisms of the Earth's oil-gas lens formation. However, a great scope of investigations has been carried out in the recent years on the hydrocarbon mixtures' catalytic synthesis from CO, CO_2 and H_2 gases over bi-functional catalytic systems including metal components as well as acid-base type components (clays, zeolites).

The Earth's atmosphere is supposed to have contained CO, CO_2 along with H_2 1-1.8 milliard years ago while its oxygen content was then about 0.001 of the modern one. Moreover, the data on the chemical compositions of the abyssal areas of the Earth regarding the presence of the nickel-iron-ore formations and of Co, Mo, Zn, Cr-containing ores as well as the data on chemical composition of the abyssal strata atmosphere rich in the CO_2, CH_4 and H_2 gaseous mixtures allow considering the above areas as the regions of potential proceeding of the said catalytic processes.

It can be suggested that the highly exothermic reactions of the hydrocarbons and water synthesis from CO, CO_2 and H_2 in the areas of nickel-iron-ore formations were of a global character on the Earth.

The present paper summarizes the data on the lab-scale hydrocarbon synthesis from CO, CO_2 and H_2 over metal-containing catalysts (covering Fe, Ni, Co, Mo, Zn, Cr etc.) as well as various ores, namely haematite, goethite, magnetite, chromite, olivinite, lherzolite xenolith, magnetite+zeolite, magnetite+silicoaluminophosphate, hornblende, chrome-diopside, basalt, almandine, serpentinite. The compositions of the synthesised hydrocarbon mixtures are compared with those of the natural gas-condensate deposits.

The conclusion is made that catalytic hydrocarbon synthesis allows obtaining the natural variations of hydrocarbon mixtures – from predominantly methane to the liquid hydrocarbon mixtures (C_{20+}) with various contents of olefins, n-alkanes, iso-paraffins, and aromatic hydrocarbons.

The supposition is discussed that the processes of hydrocarbon synthesis from CO_2, CO_4 and H_2 mixtures over inorganic catalysts and ores may simulate the macro-geochemical processes having proceeded in the Earth's crust at different stages of its geochemical history.

Besides, the following fact is to be taken into account while comparing the probabilities of the biogenic and the abiogenous ways of the natural hydrocarbon mixtures synthesis. For the biogenic version of hydrocarbon synthesis, the carbon dioxide and water bonding reactions proceed in the endothermic way requiring an energy source. Their intensity in the oxygen-free atmosphere would be low. However with the abiogenous hydrocarbon synthesis, the reactions proceed with a considerable heat release and therefore thermodynamically are highly probable. The intensity and probability of these processes in the primary atmosphere conditions must have been quite high.

If the described scheme of forming the natural oil-and-gas lenses proves to be highly probable, a new approach to searching oil-and-gas deposits and estimating their volumes might be developed on the base of analysis of the nickel-iron-ore formations layout combined with that of the high-temperature geological areas.

PGG1-5: Diamondoids occurrence and distribution in oils from Brazilian and Colombian basins

L.S. Jesuino[1], J.B. Tamanqueira[1], D.A. Azevedo[2], F.T.T. Gonçalves[3,4], L. Landau[1]

1) LAMCE/COPPE/Universidade Federal do Rio de Janeiro, I-2000, sala I-214, P.O.Box. 68552,21949-900, Brazil (e-mail: ljesuino@lamce.ufrj.br)
2) Departamento de Química Orgânica, Instituto de Química, Universidade Federal do Rio de Janeiro, Brazil
3) GIMAB/LAB2M/COPPE/UFRJ, Centro de Tecnologia, Bloco I-2000 (anexo), Rio de Janeiro, Brazil, 21949-900
4) PGT-Petroleum Geoscience Technology Ltd., Rua 2 s/n, Incubadora de Empresas da Coppe, Cx. Postal 68.568, Rio de Janeiro, Brazil, 21945-970

Diamondoids comprise a class of saturated polycyclic hydrocarbon compounds with a diamond-like structure that occur naturally in petroleum. Highly stable, diamondoids are more resistant to thermal and biological destruction than other hydrocarbons. Diamondoids-derived parameters have been used in the assessment of the degree of thermal evolution and extent of secondary cracking of light oils and condensates and in the recognition of mixtures of oils from distinct migration pulses [2]. Combined with biomarker data, diamondoids have been also applied to characterize mixtures of oils from distinct migration pulses with contrasting maturity levels in a single petroleum accumulation. Previous studies have demonstrated that the integration of bulk, biomarker and diamondoid analysis from oil samples is a powerful tool for the understanding of petroleum systems dynamics (petroleum generation, cracking, migration, alteration and remigration).

In this study, diamondoids occurrence and distribution was investigated for a set of representative oil samples from sedimentary basins of the eastern Brazilian margin and a Colombian basin. Selected samples were submitted to liquid chromatography using a silica gel column. Saturated and aromatic hydrocarbons and NSO compounds fractions were eluted using *n*-hexane, *n*-hexane:dichloromethane and dichloromethane:methanol, respectively. Saturates fractions were analyzed using a Hewlett-Packard 5890 series II gas chromatograph coupled to a Hewlett-Packard 5972 mass selective detector. All diamondoids were identified by comparison of their mass spectra and relative retention times with reported literature data ([1] e [4]) and authentic standards. They were quantified by internal standard and external calibration curves with authentic diamondoids standard.

Analytical results allowed the characterization of diamondoids hydrocarbons distributions in the selected samples. The determination of diamondoid hydrocarbon ratios (e.g. methyl adamantane and methyl diamantane indices) and biomarker ratios led to a more refined maturity assessment of the analyzed oils and condensates. The combination of diamondoids data with source-dependent biomarker parameters also allowed the characterization of different oil families and their possible source rocks. The results of this study have corroborated the importance of applying biomarker and diamondoid analysis for the understanding of petroleum systems dynamics in sedimentary basins.

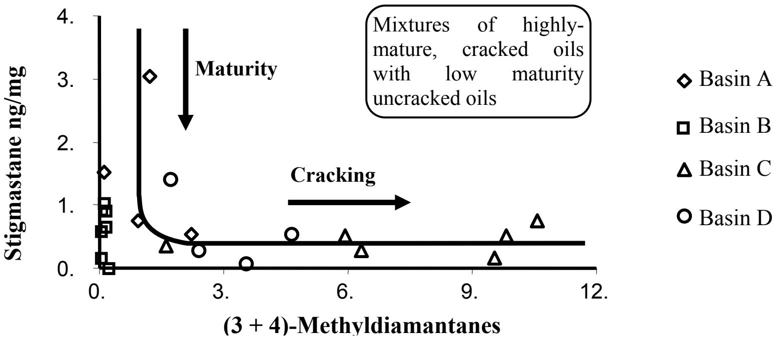


Fig.1. Correlation between biomarkers (stigmastane) and diamondoids (methyldiamantanes) concentration in oils of different thermal maturities, which shows that the biomarkers decrease in concentration with thermal maturity as the diamondoids increase

Acknowledgments

Brazilian National Petroleum Agency (ANP, PRH-02) and Petrobras for the Master scholarships, Geochemical Solutions International (GSI) and PGT-Petroleum Geoscience Technology.

References

[1] Chen, J., Fu, J., Sheng, G., Liu, D., Zhang, J., 1996. Diamondoid hydrocarbon ratios: Novel maturity indices for highly mature crude oils. Organic Geochemistry 25, 179-190.

[2] Dahl, J., Moldowan, M., Peters, K., Claypool, G., Rooney, M., Michael, G., Mello, M.R., Kohnen, M., 1999. Diamondoid hydrocarbons as indicators of natural cracking. Nature 399, 54-56.

[3] Grice, K., Alexander, R., Kagi, R., 2000. Diamondoid hydrocarbons as indicators of biodegradation in Australian crude oils. Organic Geochemistry 31, 67-73.

[4] Wingert, W.S., 1992, G.C.M.S. Analysis of Diamondoid Hydrocarbons in Smackover Petroleums, Fuel 71, 37-43.

PGG1-6: Alkyltriaromatic steroids in the Cambrian oil shales and crude oils in the Aldan Anticlise Northen slope, Siberian platform

V.A. Kashirtsev[1], A.E. Kontorovich[2], O.N. Chalaya[1],
I.N. Zueva[1], I.K. Ivanova[3], A.G. Alexeev[3]

1) Institute of Oil and Gas Problems, Siberian Branch of the RAS, Oktyabrskaya st., 1, Yakutsk, 677891, Russia, (e-mail: i.n.zueva@ipng.ysn.ru)
2) Institute of Oil and Gas Geology, Siberian Branch of the RAS, prosp. Akad. Koptyuga 3, Novosibirsk, 630090, Russia
3) Ykutian State University, Kulakovskogo st., Yakutsk, 677891, Russia

The chloroform extracts (bitumoids) of samples from Cambrian oil shales and crude oils from hydrogeological wells drilled in the northern slope of Aldan anticlise had been studied. Using the GC-MS investigation allowed to identify the new homologous row of alkyltriaromatic steroids in the bitumoids and crude oils.

Mass-chromatograms by m/z 191 and m/z 217, 231, 245, 259, 273 showed ideally the same distribution of terpane, sterane and triaromatic (TA) steroid biomarkers as for the bitumoids of the Sinskaya formation as for the samples of crude oils of the Kutorginovaya formation. The obtained results may concern as an evidence of genetic correlation source rocks of the oil shale formation and crude oils in the Lower and Middle Cambrian reservoirs.

Mass-chromatogram by m/z 231 showing intensity of ionization current exceeds the same for m/z 217 and other fragmentograms almost ten times (Fig. 1). It may indicate the concentrations of triaromatic steroids C_{28} (R and S) predominate over steranes and other triaromatic steroids concentrtions.

Peaks of triaromatic steroids (20 and 21) on mass-chromatogram m/z 217 with molecular ion 358 have been identified as TA-steroids C_{27} with absent methyl group at C_{17}. Peaks 24-29 with main molecular ions m/z 386, 400, 414 have been determined as triaromatic steroids with alkyl chain at ring A (Fig.1). From literature it is known the data on TA-steroids C_{29} with methyl group are rare. Identification of TA-steroids C_{30} and C_{31} in composition of oil shales and crude oils in the northern slope of Aldan anticlise makes them as remarkable in the row biomarkers for genetic family of the Cambrian crude oils.

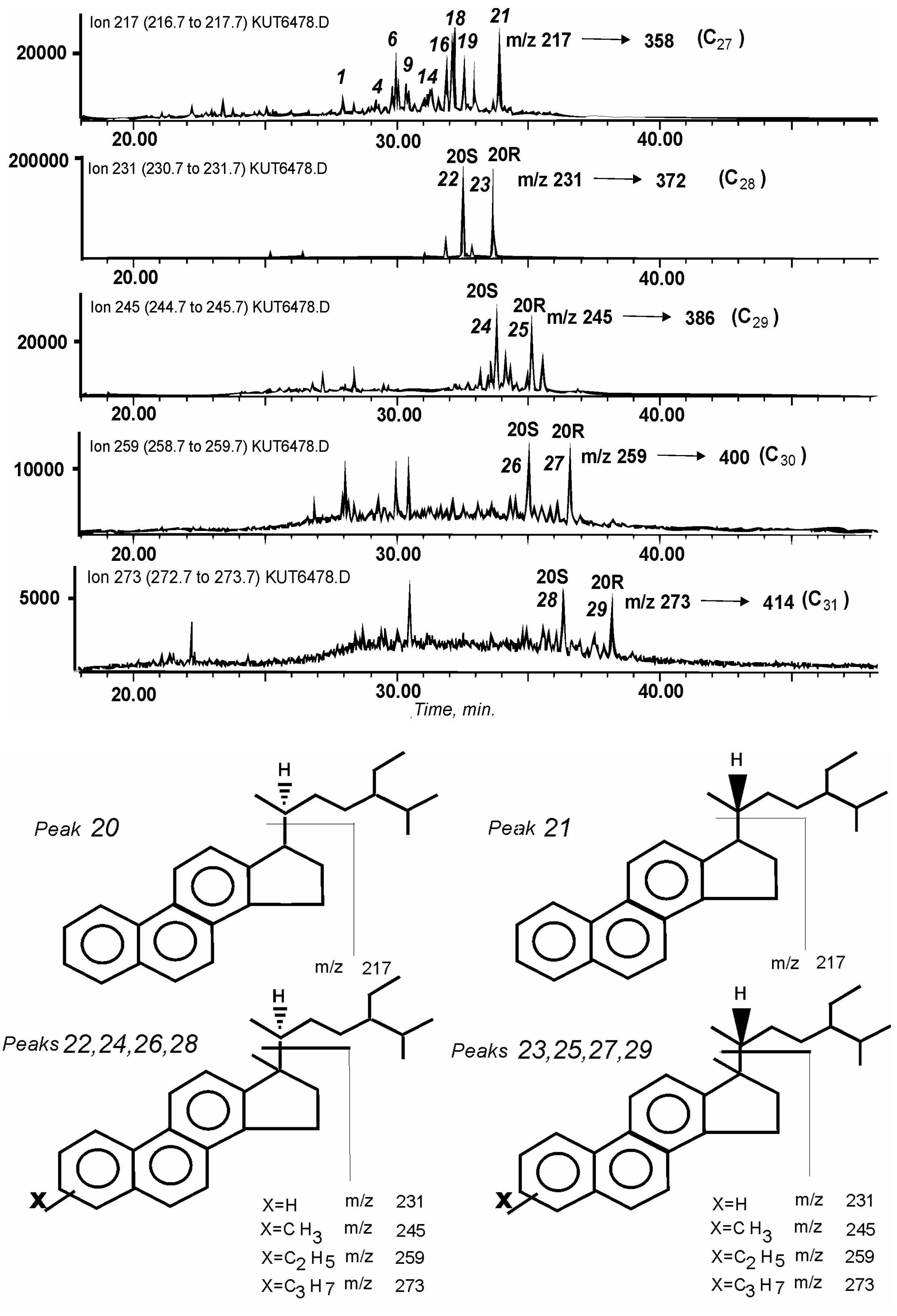


Fig.1. Mass-chromatograms by m/z 217,231,245,259,273 for saturated + aromatic fraction of hydrocarbons in the Cambrian oil shales and crude oils in the Aldan anteclise.
Peaks 1-19 – steranes; 20-29 – triaromatic steroids.

PGG1-7: Alkylcyclohexanes and alkylbenzenes of terrigenous oils in the Vilyui basin, Siberian platform

V.A. Kashirtsev, A.F. Safronov, O.N. Chalaya,
S.H. Lifshits, I.K. Ivanova, I.N. Zueva

Institute of Oil and Gas Problems, Siberian Branch of the RAS, Oktyabrskaya st., 1, Yakutsk, 677891, Russia, (e-mail: i.n.zueva@ipng.ysn.ru)

Crude oils in the Eastern part of Siberian platform are divided into several genetic groups based on bulk properties, carbon-isotope compositions and biomarker distributions. One group in the Vilyui basin characterized by “heavy” carbon-isotope composition, high wax (except biodegraded oils) and low sulfur content, high Pr/Ph ratios and absence of tricyclic terpanes and C_{35} homohopanes. These characteristics suggest that the oils were generated mainly from terrigenous organic matter in source rocks deposited under highly oxic conditions.

The composition and distribution of alkanes, alkylcyclohexanes and alkylbenzenes for these Upper Paleozoic-Mesozoic crude oils had been studied.

For the Upper Jurassic crude oils (the Berge field on the top of figure 1) n-alkanes dominate (about 75% per total content of identified hydrocarbons). Maximum of distribution locates in range n-C_{18}, n-C_{19}, pristane predominates over phytane, coefficient odd/even is equal 1. Skaning saturated + aromatic fraction by ions m/z 82, m/z 92 we identified alkylcyclohexanes and alkylbenzenes in range C_{15}-$C_{35.}$ Its distribution is similar n-alkanes distribution but predominance odd over even homologs has been detected.

The Permian crude oils (the Srednetyung field on the middle of figure 1) also contain high content of n-alkanes (about 64% per total content of identified hydrocarbons). Maximum of distribution locates near n-C_{23}, pristane also predominates over phytane, coefficient odd/even is equal 1. Distribution of alkylcyclohexanes (m/z 82) is the same as alkylbenzenes (m/z 92).

Thus the distribution feature of alkylcyclohexanes and alkylbenzenes have been detected to be similar as n-alkanes distribution. It may explain by cyclization with subsequent dehydration normal chain structures in process of hydrocarbon generation.

As concerned biodegraded crude oils (the Zapadno-Tyung field on the bottom of figure 1) alkylcyclohexanes and alkylbenzenes have been removed before of n-alkanes and isoprenoids. The mass-chromatogram m/z 82 showed presence of bicyclohexyl stuctures and m/z 92 - cyclohexylbenzenes as residues.

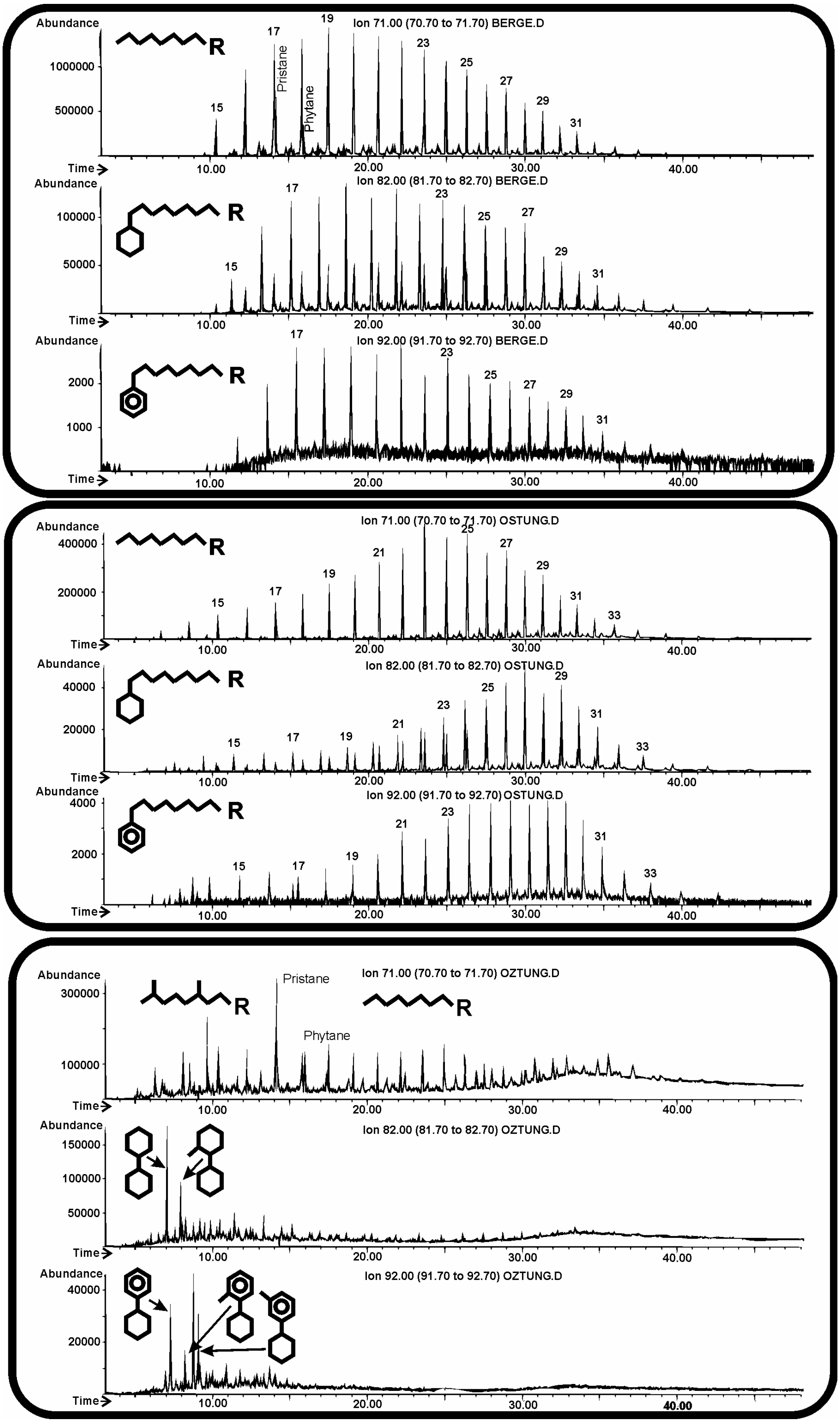


Fig.1. Mass chromatograms m/z 71, 82 and 92 showing alkanes, alkylcyclohexanes and alkylbenzenes distribution in crude oils of the Vilyui basin

PGG1-8: Mechanism of methylated polyaromatics pyrolysis at low conversion

J.P. Leininger[1], F. Lorant[1], F. Behar[1],C. Minot[2]

1) Institut Français du Pétrole, Geology and Geochemistry Division, 1-4 avenue de Bois-Préau, 92852 Rueil-Malmaison, France (e-mail: J-Philippe.LEININGER@ifp.fr)
2) Laboratoire de Chimie Théorique, Case 137, Université Pierre et Marie Curie, 75252 Paris Cedex 05, France

Recent studies showed that thermal stability of aromatic hydrocarbons is a key parameter to explain the composition of oils in deep reservoirs (Vandenbroucke et al., 1999; Behar et al., 1999). Within the aromatic fraction, the mechanism of thermal conversion of methylated polyaromatics remains unexplained so far, especially the primary reactivity processes. Smith et al. (1992), Behar et al. (1999) and Lorant et al. (2000) previously derived, from pyrolysis experiments, bulk rate equations for the thermal decomposition of methylated aromatics. However, apparent kinetic parameters, as well as molecular and mass balances were not elucidated by any free-radical kinetic scheme. The extrapolation of empirical rate equations to geological thermal gradients was consequently still subject to uncertainty.

Therefore, the next stage after these studies was to elaborate a free-radical kinetic model for the pyrolysis of methylated aromatics. For that purpose, a set of experimental data was generated, in order to explore low conversion reactivity processes (0 to 10%). Then, once the mechanism established, rate constants of specific elementary reactions were evaluated by quantum mechanical simulations (De Bruin et al., 2004).

Pyrolysis experiments were conducted on a neat model compound, the 1-methylnaphthalene (1-MNa), at 380, 400 and 423°C, under a constant-pressure (100 atm), in batch reactors. Under such experimental conditions, 1-MNa globally decomposed according to a first-order rate law. Corresponding activation parameters, estimated at $E = 47.5$ kcal.mol^{-1} and $A = 7.6\times10^{9}$ s^{-1}, were consistent with those previously determined by Behar et al. from 9-methylphenanthrene. For conversions in the range 0.5 - 5% (at 380 and 400°C), 1-MNa was mostly converted into naphthalene, methane and C_{14+} compounds, identified as di(alphanaphthyl)ethane and dinaphthylmethane isomers. hydrogen gas was a minor reaction product. Neither 1-MNa isomerization nor formation of dimethylnaphthalenes isomers were observed below this level of conversion. Generation of 2-methylnaphthalene and dimethylnaphthalenes isomers appeared respectively for conversions higher than 30% and 20%. Additionally, key information on preferential initiation and propagation reactions were deduced from these data.

This experimental study, together with quantum mechanical simulations (Density Functional Theory) to evaluate kinetic parameters of key-elementary steps leaded us to proposing a primary mechanism, based on free-radical reactions, accounting for the pyrolysis of 1-MNa. Generalization of this latter kinetic scheme to larger methylated polyaromatics, as well as consequences for the occurrence of such compounds in geological settings is discussed.

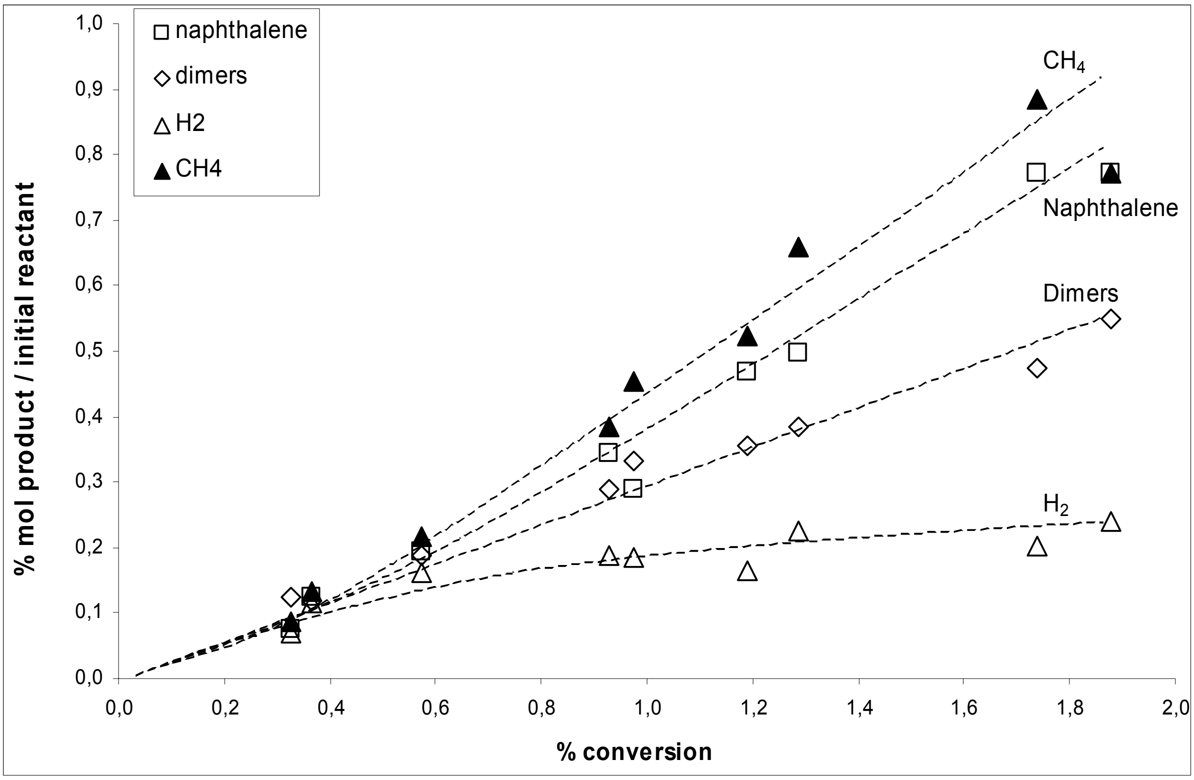


Fig.1. Molar ratios between 1-MNa conversion products at low conversion

References

Vandenbroucke M., Behar F., Rudkiewicz J.L. (1999) Kinetic modelling of petroleum formation and cracking: implication from the high pressure/high temperature Elgin field. Org. Geochem., 30(9), 1105-1125.

Behar F., Budzinski H., Vandenbroucke M., Tang Y. (1999) Methane generation from oil cracking: kinetics of 9-methylphenanthrene cracking and comparison with other pure compounds and oil fractions. Energy & Fuels, 13 (2), 471.

Smith C.M., Savage P.E. (1992) Reactions of polycyclic alkylaromatics. 4. Hydrogenolysis mechanisms in 1-alkylprene pyrolysis. Energy & Fuels, 6, 195.

Lorant F., Behar F., Vandenbroucke M., McKinney D.E., Tang Y. (2000) Methane generation from methylated aromatics. Energy & Fuels, 14, 1143.

De Bruin T., Lorant F., Behar F., Toulhoat H., Goddard III W.A. (2004) Reaction kinetics of elementary processes involved in the thermal decomposition of 9-methylphenanthrene using Density Functional Theory. J. Phys. Chem. A. 108 (46); 10302-10310.

PGG1-9: Using gas chromatography to assess the impact of diesel-oil mud in the oil Properties

J.P. Lopes [1,2], M.D. Rangel[1], H.L.B. Penteado[1], A.J.M. Vieira[1]

1) PETROBRAS R&D Center, Ilha do Fundão, Quadra 7, 21949-900, Rio de Janeiro, Brazil, (e-mail: joelma.coppetec@petrobras.com.br)
2) COPPE/UFRJ, State University of Rio de Janeiro, , Ilha do Fundão, Quadra 7, 21949-900, Rio de Janeiro, Brazil

Diesel-oil mud is the traditional oil mud and has a history of excellent performance for drilling difficult wells. It has been used because the base oil is a low-cost and widely available motor fuel. In-gauge holes can be drilled through all types of shales, salt, gypsum and other difficult strata using diesel-oil mud systems. It is often the mud of choice for drilling high-pressure, high-temperature zones. Although diesel-oil muds have been widely used, their impact on the physicochemical properties of the reservoir oil has not been adequately evaluated.

Oil sample properties are among the most important information to appraise the economic value of an accumulation. This work aims at showing the gas chromatogram and API variations due to the influence of contamination by diesel-oil mud. Gas chromatography parameters have been used in an attempt to predict the percentage of diesel in the tested oil.

API gravities and gas chromatography (GC) traces were obtained for five samples. The samples are described as follows: tested oil with diesel contamination, representative crude oil from the same field of the previous sample, diesel oil, and artificial mixtures of crude oil plus 3% and 6% of diesel. The artificial diesel mixtures were made in order to compare the features of the gas chromatograms of the samples and to verify the effect of diesel contamination on the oil density.

The representative crude oil is biodegraded (Peters and Moldowan (1993) scale level 6) with an API gravity of 11.6. On the other hand, the tested oil shows the presence of *n*-alkanes in the gas chromatogram and higher API gravity (13.2), although both oils were collected from the same reservoir (Fig.1). These observations suggest that the tested oil has been contaminated by diesel-oil mud.

The best gas chromatogram correlation was observed between the tested oil and the crude oil plus 6% diesel (Fig.1). This result suggests that the diesel contributes more than six percent in the total volume of the tested oil. Using the *n*-alkanes heights provided by the gas chromatograms, the ratios (n-C_{17}/n-C_{30}) for each sample were calculated. T the linear equation between the ratios and the percentage of diesel added to the mixtures indicates that the percentage of diesel in the tested oil is 8% (Fig.1). The linear correlation between API gravity and percentage of diesel added to the samples corroborates this value.

Small amounts of diesel oil mud admixed with crude oil can change significantly the original imprint of the oil. Ratios of compounds from gas chromatograms of representative oil, diesel oil and several mixtures were useful to predict the amount of diesel that contaminated the formation oil.

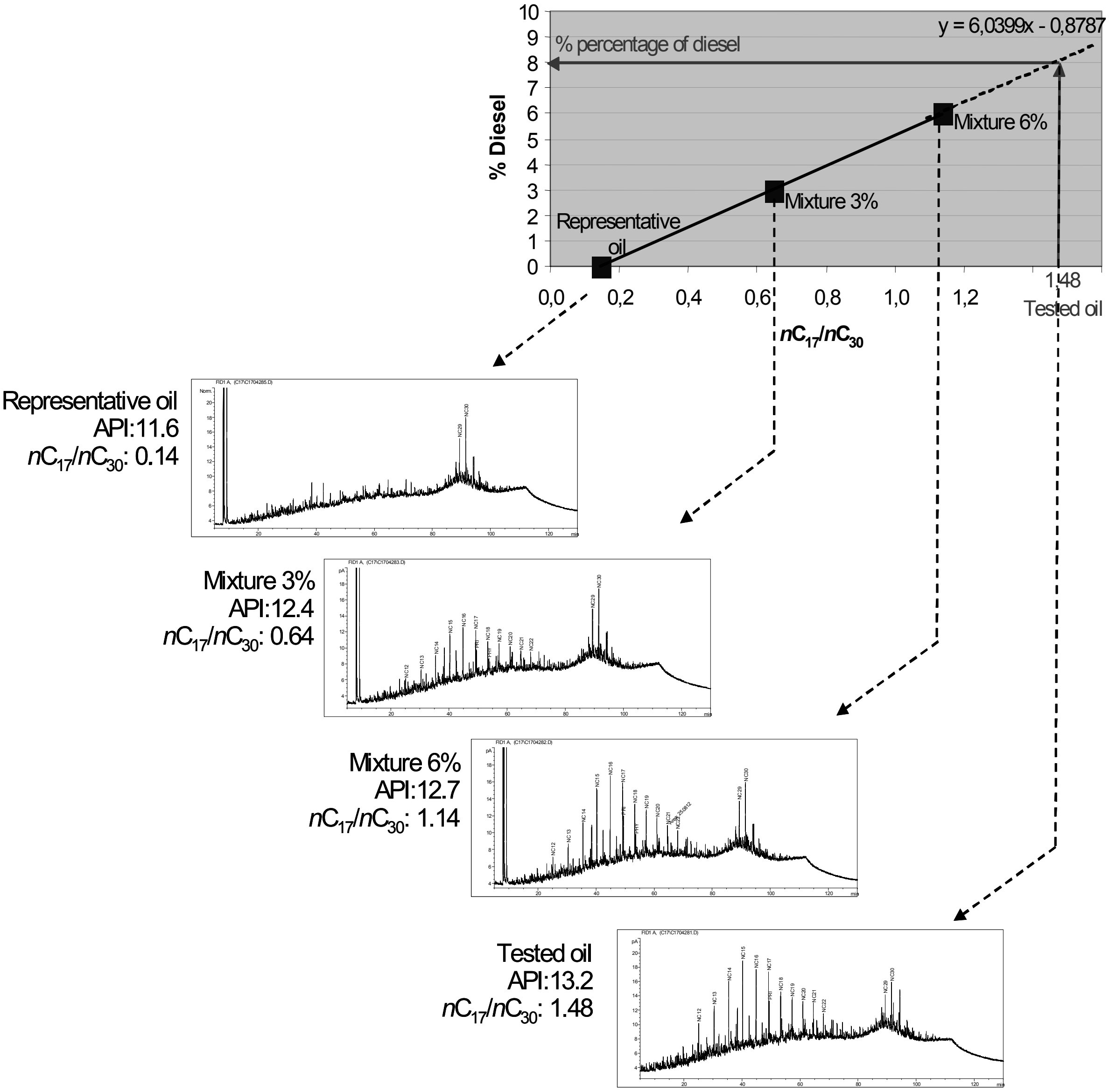


Fig.1. Correlation using the *n*-alkanes heights (n-C_{17}/n-C_{30}) provided by the gas chromatograms and the percentage of diesel added to the mixtures. Linked to the graph, gas chromatograms of the following samples: tested oil with diesel contamination, representative crude oil from the same field of the previous sample and artificial mixtures of crude oil plus 3% and 6% of diesel

References

Peters, K.E., and Moldowan, J. M., (1993) "The Biomarker Guide". New York. Englewood Cliffs e Prentice Hall, N J, p.363.

PGG1-10: Bicadinanes in high latitude oils

H.P. Nytoft, J.A. Bojesen-Koefoed, F.G. Christiansen

Geological Survey of Denmark and Greenland (GEUS), 10 Øster Voldgade, DK-1350K Copenhagen, Denmark
(e-mail: hpn@geus.dk)

Bicadinanes are pentacyclic hydrocarbons having 30 carbon atoms. They are formed from polycadinene resins which are mainly produced by angiosperm trees of the tropical Dipterocarpaceae family, and which yield bicadinanes upon maturation. Dipterocarpaceae probably originated in western Malaysia during late Cretaceous or early Palaeogene time but did not become widespread until the Miocene. The occurrence of bicadinanes in oils generally follows the present distribution of the Dipterocarpaceae (e.g. India, Bangladesh, Indonesia, Vietnam, Southern China, Papua New Guinea) although a few exceptions have been reported (Australia, New Zealand). Here we demonstrate the presence bicadinanes in high latitude oils (central West Greenland and the Beaufort-Mackenzie Delta, Canada), and thus present the first discovery of these compounds outside the Austral-Asian region.

Five distinct oil types have been identified on northwestern Disko and western Nuussuaq, central West Greenland. Three of these oils, the ‘Marraat type’ of early Paleocene age, the ‘Niaqornaarsuk type’ of Campanian age and the ‘Kuugannguaq type’ of Albian age are high-wax oils which have all the characteristics of terrigenous oils including predominance of C_{29} steranes and high hopane/sterane ratios. Reanalyses of these oils using GC-MS-MS produced 412 > 369 mass chromatograms that were remarkably similar to those of oils from south east Asia suggesting the presence of bicadinanes. The *trans-trans-trans*-bicadinane (T) was unambiguously identified by full scan analysis of fractions obtained by reverse phase HPLC-separation of a biomarker concentrate from the ‘Marraat oil’. Other bicadinanes having similar mass spectra and at least one ring-methylated bicadinane (C_{31}) were also detected. A low content of bicadinane T was also detected in the Amauligak oil, Beaufort-Mackenzie Delta. The distribution of bicadinanes in the three Greenland oils is dominated by bicadinane T. The bicadinane maturity index BMI-1 (T/T1+R) is between 2.0 and 2.5.

Both the Marraat and Niaqornarssuk oils contain oleananes and lupanes which are general markers for angiosperms, but no correlation between the content of bicadinanes and oleananes/lupanes could be established. In fact, the Kuugannguaq oil, which is otherwise devoid of angiosperm-derived biological markers, had the highest bicadinane content (highest bicadinane/hopane ratio).

The source of bicadinanes in these arctic oils is not known. It seems unlikely, that Dipterocarpaceae have reached Greenland in late Cretaceous or early Palaeogene times although conditions allowed megathermal (frost intolerant) angiosperms to extend much farther north than at present. The bicadinanes in the Greenland oils probably arose from some other family of resin-producing angiosperms, although its precise identity still eludes us.

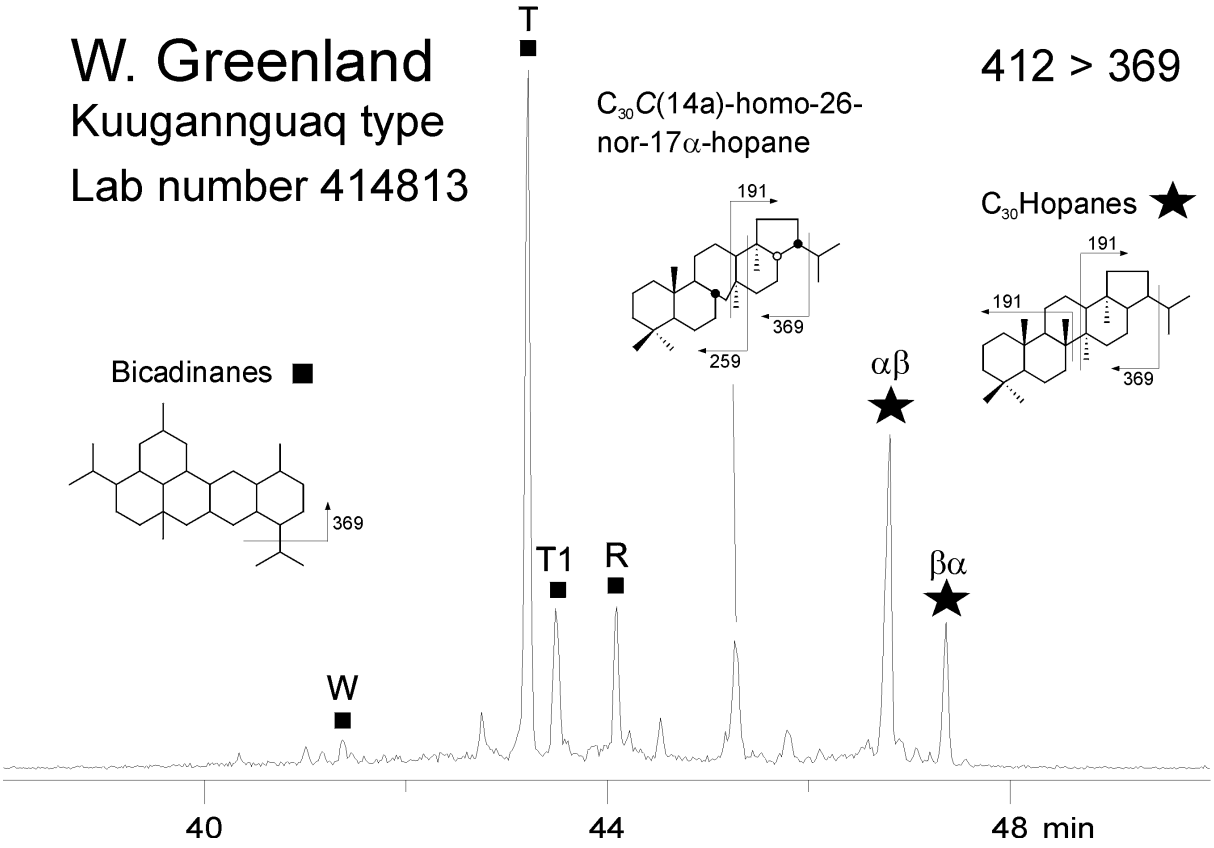


Fig.1. 412 > 369 transition showing the distribution of bicadinanes and C_{30} hopanes in the Kuugannguaq oil, West Greenland

PGG1-11: Alkyl monoaromatic hydrocarbons in Meso-Paleozoic oils (Russia)

G. Pevneva, J. Golovko, E. Ivanova, A.Golovko

Institute of Petroleum Chemistry SB RAS, 3 Academichesky Ave, 643021, Tomsk, Russia (e-mail: luvn@ipc.tsc.ru)

Petroleum aromatic hydrocarbons (AHCs) play an essential role in caustobioliths genesis. The complexity of the aromatic hydrocarbons composition and analysis, poor knowledge of mechanisms of their generation in the processes of dia- and catagenesis, as well as lack of information on AHCs distribution and molecular composition in oils and DOM, suppress an application of the composition data of AHCs in terms of the reconstruction of oil generation environment. Individual composition of alkyl monoaromatic hydrocarbons and their statistical analysis have been studied in 61 oils from Meso-Paleozoic deposits of West Siberia and 5 Paleozoic oils of the Volga Ural Basin for the purpose to define similarities and differences in their distribution depending on depositional environment.

For preliminary comparison of oils the distribution of n-alkanes, one of the widely used class of hydrocarbon-biomarkers has been analysed. The distribution of n-alkanes showed unimodal pattern with maximum at C_{10}-C_{15} in all crudes, where pristane predominate over phytane. The data on the n-alkane distribution indicate the significant sapropelic input to the initial OM and varying redox depositional environment of the source organic matter.

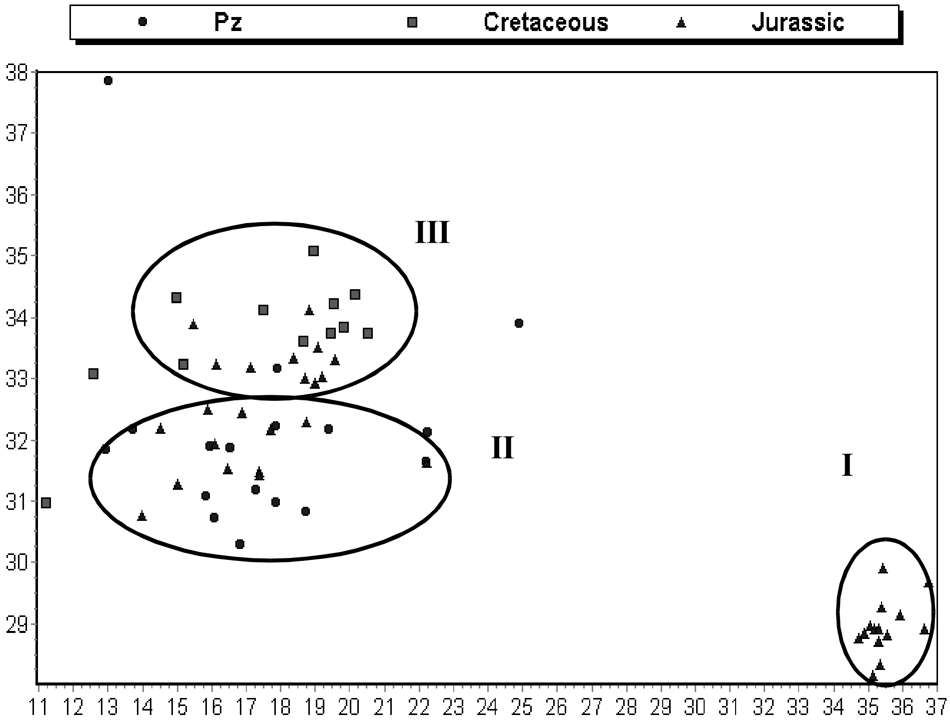
Along with n-alkanes, the alkyl benzenes, which preserved the structure moieties of the initial biomolecules, can serve as an indicator of the oil genesis since unsaturated fatty acids are their biochemical precursors.

In the monoaromatic fraction the n-alkyl, iso-methylalkyl, ethylalkyl benzenes, o-tolylalkanes and phenylalkanes were identified. The homologous series of alkyl benzenes in most of the oils were shorter than those of n-alkanes and consisted of C_{13}-C_{26} hydrocarbons.

Basically, the amount of the low-molecular weight alkyl benzene homologs with a carbon number 13-15 is maximal and the sharp decline starting with C_{16}-C_{17} can be observed on the distribution pattern.

Thus, in the oils studied the low-molecular weight alkyl benzenes were found to prevail which also indicates the significant marine OM contribution. This data correlate with n-alkanes distribution. The alkyl benzene composition data in the oils let us to conclude that deposition of the initial organic matter mainly occurred in the shallow marine and littoral environment.

The principal component analysis (PCA) was applied to the group composition of the alkyl benzenes data and showed the differences of the alkyl benzenes composition in the oils recovered from the reservoirs of different ages. Distribution of oils into families on the coordinates of two principal components demonstrated, that the Middle Jurassic oils combined into Family I. Family II was generated by the Paleozoic oils of West Siberia and Volga Ural, as well as by the Low Jurassic oils. The Upper Jurassic and Cretaceous oils combined into Family III, which indicate their similar alkyl benzenes composition.



Thus, alkyl benzenes along with n-alkanes can serve as an indicator of oil generation. Moreover, as the product of secondary transformation of the components of the initial OM alkyl benzenes provide information on maturation processes.

References

Korzhov Yu. V., Golovko A. K. 1992. Composition of alkylbenzenes as an indice reflecting transformation processes of organic matter from oil-produsing deposits (in Rus). Geochemistry 2, 279-283.
Gelpi E., Schneider H., Mann J., Oro J. 1970. Hydrocarbons of geochemical significance in microscopic algae. Phytochemistry 9, P.603-612 .
Tissot B. P., Welte D. H. 1981.Petroleum formation and occurence. 500 pp.

PGG1-12: Some geochemical regularities in vanadium and nickel distribution in naphthides

S.A. Punanova

Institute of Problems of Oil and Gas, Russian Academy of Sciences, ul. Gubkina 3, Moscow, 119991 Russia
(e-mail: punanova@mail.ru)

The content of V and Ni as the well-studied elements reaching 60% in oil ashes is a very important characteristic. Oils from individual petroleum provinces or complexes show specific V and Ni contents and V/Ni ratios, thus representing kinds of metallogenic provinces. These parameters are used for comparison of different oils or oils with organic matter (OM) in rocks as indicators of the environment of oil formation, facies conditions, and genetic type of initial OM, and are most closely related to physicochemical properties of oils.

As was corroborated by numerous investigations, the rocks containing OM of the sapropel type commonly are two to three times richer in V and Ni than the sedimentary rocks with OM of humic and mixed sapropel-humic type. Bitumoids extracted from the sapropel-type OM contain V and Ni in much greater amounts with prevalence of V over Ni (V/Ni > 1). At the same time, bitumoids from rocks containing admixture of humic OM are enriched in Fe and depleted in V and Ni with prevalence of Ni over V (V/Ni < 1).

The Paleozoic sequences in the Volga-Ural and Timan-Pechora provinces and some regions of the Caspian province, like the Bazhenovo Formation in the western Siberia, are largely composed of marine rocks with sapropel-type OM. Bitumoids and oils from these rocks are enriched in V and Ni with V/Ni > 1. The Mesozoic and Cenozoic sequences in the Fore-Caucasus, central Asia, western Siberia, and some other provinces contain either the purely humic OM or sapropel-type OM with substantial admixture of humic component. Oils and bitumoids in these sequences are characterized by lower V and Ni contents with V/Ni ratio below 1.

These data indicate that the V/Ni ratios in oils and in bitumoids from petroliferous rocks vary in the direct proportion. The coherent variation of V/Ni ratio is explained by consistence between the trace element contents in oils and prevailing OM in source rocks.

The V and Ni contents and V/Ni ratio in oils continuously decrease from Paleozoic to Cenozoic sequences [Punanova, 1974]. This trend is traced for oils from CIS countries and the North America [Hyden, 1961].

Depletion of oils in V and Ni with time was most likely related to evolution of life on the Earth, particularly by the conquest of land by higher plants and formation of soil. The expansion of higher plants over continents was accompanied by enrichment of soils in humic components. The soils readily accumulating trace elements became gradually more efficient barriers for element migration to sedimentary basins. Moreover, the earlier marine organisms and algae contained more V and Ni than the higher land species. The areas of exposed mafic and ultramafic rocks as the main sources of V and Ni in the zone of supergene migration [Punanova, Katchenkov, 1984] were substantially reduced due to gradual waning of the geosynclinal regime on the planet.

However, the V and Ni variations in oils could depend not only on the primary processes of petroleum formation, but also on the secondary alteration of naphthides during their migration toward the pools, catagenesis, and hypergenesis [Punanova, 1998]. The asphaltic and resinous components of oils and related trace elements can be redistributed in these processes, i.e., lost during migration and catagenetic alteration and gained as residues during supergene alteration and biodegradation. Because V is linked with heavier components of oils than Ni, the V/Ni ratio changes. Furthermore, the secondary accumulation of V in oils with strong increase in V/Ni ratio could be also possible. Unusual V and Ni distribution in oils of some provinces can be accounted for by such a secondary alteration of naphthides.

Some authors hold to another viewpoint. They suppose that the redox processes developing in sediments during the diagenetic stage of lithification control the V/Ni ratios in oils. Acording to Lewan [1984], the V/Ni ratio with prevalence of V or Ni is determined by environments of source rock accumulation. The Eh-pH diagrams presented by Lewan ascertain the factors controlling the metal ratios in oils and their correlation with sulfur contents. content and V/Ni ratio. The Paleozoic oils are not universally rich in V and Mesozoic-Cenozoic oils are not always depleted in V. It is quite probable that the redox conditions of sedimentation play an important role in concentration of these metals. Lopez et al. [1995] comprehensively studied the oil differentiation in the Maracaibo Basin in Venezuela and correlated oils using V and Ni distribution in them and in their components: resins and asphaltenes. Vanadium and nickel show a strong positive correlation both in oils and their components.

Thus, our analysis of numerous data on V and Ni contents and V/Ni ratios in naphthides demonstrated that these parameters:

(1) Characterize the facies and mechanism of the initial organic matter formation;

(2) Are controlled by conditions of source rock formation, particularly, by Eh and pH;

(3) Indicate secondary alteration of naphthides during migration, catagenesis & biodegradation;

(4) Reflect evolution of the organic wealth on the Earth from Paleozoic to Cenozoic.

PGG1-13: Organic matter in salt from the Verkhnekamsk deposit (solid and liquid organic matter, oil and gas inclusions)

S. Shanina

Institute of Geology of Komi Science Center of RAS, Pervomayskaya 54, 167982, Syktyvkar, Russia

Verkhnekamsk deposit of potassium salt is located in the central part of a Solikamsk depression of the Near Ural foredeep and it represents thick salt sediments consisting of underlying rock salt, potassium and potassium-magnesium salts and covering rock salt. The organic matter of the salt thickness is represented by several forms of presence: dispersed organic substance in clay-anhydrite layers, rock salt, sylvinite and carnallite rocks, fossilized wood, oil shows in salt rocks and hydrocarbons in microinclusions of salt minerals.

To study structure and quantity of organic matter in salt samples contents of organic carbon, chloroform and alcohol-benzol bitumoids were determined, distribution of aliphatic and polycyclic hydrocarbons with GC and GC-MS analyses were studied. Research of inclusions was carried out on the chips of salt samples using methods of opening of inclusions in liquid, luminescent microscopy and gas chomatography.

Dispersed organic matter. It is pointed out, that organic matter is a component of the insoluble remains of the salt rocks. More often to greater contents of insoluble remains correspond greater contents of organic matter and gases of microinclusions. The contents of organic carbon ranges from 0.38 up to 1.54 %. In a potash deposit concentration C_{org} is higher, than it is in thickness of underlying rock salt. Positive correlation of contents of C_{org} in the insoluble remains with contents of iron oxides in it observed.

While studyng organic matter of the insoluble remains of salts it is established, that it is autochtonous. Phytpoplankton serves a basic source of its accumulation. Transformation of organic matter occured under reduction conditions. No doubt, process of the radioactive decay of the radionuclides ^{40}K with additional heat emission influenced on structure of organic matter in potassium salts.

Organic matter and precious metals in salts. As a result of the studies high contents of Au, Pt and Pd were registered in the insoluble remains of sylvinite, basic form of existence of which are organic compounds. It is determined, that the most amount of gold is concentrated in sylvin and carnallite presumably as carbonilhalogenic compounds. Platinum metals are concentrated in the insoluble remains of sylvins and also associated with an organic phase. As precious metals are correlated with organic matter, which is syngenetic to salt rocks then precious metals are syngenetic to salt rocks too.

Organic inclusions in salt minerals. Liquid inclusions of hydrocarbons are determined only in recrystallized halite which is a secondary structure of rock salt. Three types of hydrocarbon inclusions are determined. The first type is represents spherical droplets of hydrocarbons locating in two or three-phase large inclusions representing yellow microdroplets of oily liquid, most often with a dark rim of bitumen substances or their relicts. In their structure oily-resin compounds prevail. The second type of inclusions is characterized by the presence of a colorless liquid phase as hydrocarbons of petrol structure. Frequently, lumps of bitumen of brown or black color which are identical to the above described droplets stick to their internal surface. There are inclusions with a continuous rim of yellowish or dark brown compounds around the salt brine and with oily-resin composition.

Formation of organic microinclusions in salt minerals of the Verkhnekamsk deposit is associated with transformation of organic matter of salts during post-sedimentation processes.

The special attention involves distribution of gas hydrocarbons in composition of microinclusions of salts. Rather frequently there are higher concentrations of hydrocarbons of structure C_2–C_4 in them and there are hydrocarbons of oil series (C_4–C_8). Such higher values of syngenetic gas hydrocarbons can quite correspond to a zone of a "petroleum window”. This fact can serve as the proof that in salt sediments there were all necessary conditions for transformation of the buried organic matter into hydrocarbons and generation of micropetroleum.

PGG1-14: Multivariate statistical methods applied to interpretation of saturated biomarkers (Velebit oil field, Pannonian basin, Serbia)

T. Šolević[1], K. Stojanović[1,2], B. Jovančićević[1,3],
A. Kronimus[4], J. Schwarzbauer[4]

1) Center of Chemistry, IChTM, Njegoševa 12, 11001 Belgrade (e-mail: tsolevic@chem.bg.ac.yu)
2) Department of Medicine, University of Belgrade, Višegradska 26, 11000 Belgrade
3) Department of Chemistry, University of Belgrade, PO Box 158, 11001 Belgrade, Serbia & Montenegro
4) Institute of Geology and Geochemistry of Petroleum and Coal, Aachen University, Lochnerstrasse 4-20, D-52056 Aachen, Germany

Saturated biomarkers (*n*-alkanes, isoprenoids, steranes and triterpanes) in crude oils of Pliocenic age, taken from 25 oil wells in the oil field of Velebit, the most important one in Serbian territory, were analyzed using gas chromatography-mass spectrometry (GC-MS). The absence of *n*-alkanes and undisturbed distributions of isoprenoids, steranes and triterpanes, pointed out to minimal degree of biodegradation.

This paper gives results of our effort to make a detailed classification of samples based on source and maturation parameters using multivariate statistical methods - factor analysis and cluster analysis (programme SPSS 10.0 for Windows; Belonin *et al.*, 1982; Reimann *et al.*, 2002; http://www.psychstat.smsu.edu/multibook/mlt04.htm). Discriminant function analysis was excluded since it demands the existence of some previous classification (http://www.psychstat.smsu.edu/multibook/mlt03.htm). In case of cluster analysis, Square elucidation cluster method with Between-groups linkage and Pearson measures as well as Ward cluster method were used with the aim to determine which one of aforementioned methods of cluster analysis is in the best accordance with factor analysis and gives the best dendogram and because of that can be regarded as the most applicable to interpretation of saturated biomarkers in geochemical research.

Factor analysis on source and maturation parameters of saturated fraction was first to be performed. In case of source parameters it revealed 2 significant factors. The first one was marked by high loadings (higher than $|0.7|$) on oleanane/C_{30}hopane, gammacerane/C_{30}hopane and C_{29}hopane/C_{30}hopane parameters, while the second one was marked by content of C_{27} and C_{29} regular steranes (loadings higher than $|0.9|$). Factor analysis on maturation parameters gave 3 significant factors. The first one was marked by C_{30}moretane/C_{30}hopane, C_{29}moretane/C_{30}hopane, C_{29}Ts/C_{29}hopane and $C_{27}\beta\alpha$(S)diasterane/ $C_{29}\alpha\alpha$(R)sterane parameters (loadings higher than $|0.7|$). The second one was completely marked by sterane maturation parameters $C_{29}\beta\beta(R)/C_{29}\alpha\alpha(R)+C_{29}\beta\beta(R)$ and $C_{29}\alpha\alpha(S)/C_{29}\alpha\alpha(R)+C_{29}\alpha\alpha(S)$ (loadings higher than $|0.9|$), while the only significant parameter in the last, third factor was Ts/Tm+Ts. Classification of samples, based on source and maturation parameters, was performed constructing correlation diagram of two the most significant factors. According to their position in the diagram, samples are classified into three groups, but due to their closeness, it was difficult to draw a sharp line between them.

In order to make a more detailed classification, the same set of parameters was subjected to cluster analysis using three aforementioned methods. Firstly, classification of parameters was done with aim to compare the distribution of parameters in factors (using factor analysis) and their grouping in dendograms (using cluster analysis) and in case of source as well as maturation parameters, Square elucidation cluster method with Between-groups linkage and Ward method were in good accordance with factor analysis. Thereafter, samples were classified on the basis of source and maturation parameters. In case of source parameters, both methods gave very clear dendograms and showed to be in good accordance with results of factor analysis. But in case of maturation parameters, Ward method resulted in clearer dendogram and better accordance with factor analysis. Because of that, this method was chosen and combining factor and cluster analysis, investigated oils were precisely classified into 5 groups, based on maturation and source parameters (Table 1).

Table 1. Classifications of investigated oils

Classification based on source parameters		**Classification based on maturation parameters**	
Group	Samples	Group	Samples
I	4, 5, 6, 8, 9, 10, 13, 14, 16 and 19	I	4, 5, 6, 8, 9, 10 and 14
II	2, 7, 12, 15, 17, 18 and 22	II	7, 13, 15, 20, 23 and 24
III	1, 3 and 11	III	11, 12, 17, 21 and 22
IV	20, 21, 23 and 24	IV	1, 2, 3, 16, 18 and 19
V	25	V	25

These results show that some samples are in different groups (according to their source and maturation parameters) which points to the existence of a large number of source rocks as well as the effects of mixing during migration.

References

Belonin, M.D., Golubeva, V.N., Skublov, G.T., 1982. *Principal Component Analysis in Geology*, Nauka, Moscow (In Russian).

Globočanin, D., Škrbić, B., Miljević, N., 2004. Principal component analysis for soil contamination with PAHs. *Chemometrics and intelligent laboratory systems* **72**, 219-223.

Reimann, C., Filmoser, P., Garrett, R.G., 2002. Factor analysis applied to regional geochemical data: problems and possibilities. *Applied Geochemistry* **17**, 85-206.

http://www.psychstat.smsu.edu/multibook/mlt03.htm

http://www.psychstat.smsu.edu/multibook/mlt04.htm

PGG1-15: New approach to maturity investigation of Banat depression crude oils (Southeastern part of the Pannonian basin, Serbia) based on distribution of naphthalene and phenanthrene isomers

K. Stojanović[1,2], B. Jovančićević[2,3], D. Vitorović[2,3],
J. Golovko[4], G. Pevneva[4], A. Golovko[4]

1) Faculty of Medicine, University of Belgrade, Višegradska 26, 11000 Belgrade
2) IChTM, Chemistry Centre, POB 815, 11000 Belgrade
3) Faculty of Chemistry, University of Belgrade, POB 158, 11000 Belgrade, Serbia and Montenegro
4) Institute of Petroleum Chemistry, 3, Academichesky Ave., 634055, Tomsk, Russia

A new approach based on maturation changes of naphthalene and phenathrene isomers, proposed in this paper, is aimed at more reliable maturity correlation between crude oils, as well as indirect estimation of catagenetic evolution stage of their corresponding source rocks. Banat depression crude oils (southeastern part of the Pannonian Basin, Serbia) were used as substrates. Fourteen samples (V1-V14) originated from the Province of Vojvodina localities which represent the greatest part of the depression (north of the Danube River), and nine samples (PO1-PO9) came from Sirakovo and Bradarac-Maljurevac localities, which belong to a separate, smaller Drmno depression, close to the City of Požarevac.

Phenanthrene and naphthalene isomers were identified by GC analysis of bi- and tricyclic aromatic hydrocarbon fractions (Model 3700, quartz capillary column, SE-54; He; FID). A great number of maturation parameters were calculated from abundance and distribution of identified compounds. A factor analysis (SPSS 10.0 programme for Windows) was then carried out in order to define parameters which optimally characterize the maturity of examined crude oils. Methyl-, dimethyl- and trimethylnaphthalene parameters, as well as parameters based on distribution and abundance of methyl- and dimethylphenanthrene isomers, were equally represented in the parameters' selection.

Parameters based on $\alpha \rightarrow \beta$ isomerization of methyl group in phenanthrene and naphthalene rings, i.e., parameters MPI 3, MPR 1, MNR, DNx and TNy (Radke, 1987; Stojanović *et al*., 2003) were shown to be most significant (>0.8 loadings in factor 1). Based on this set of parameters the examined crude oils were classified into four maturity groups. The second important group (>0.8 loadings in factor 2) included parameters based on alkylation-dealkylation processes in methylphenanthrenes, i.e., parameters [P], MDR and MTR (Stojanović *et al*., 2001; Jovančićević *et al*., 2003). They also led to classification of the investigated crude oils into four maturity groups. By comparing the classifications based on isomerization and dealkylation parameters, no differences were observed with crude oils originating from the Vojvodina part of the Banat depression, in contrast to crude oils from the Drmno depression, which demonstrated certain differences in the arrangement into four groups.

In order to explain these discrepancies, a factor 1/factor 2 diagram was constructed (Fig. 1), i.e., a diagram of methylnaphthalene and methylphenanthrene isomerization reactions *vs*. methylphenanthrene dealkylation processes which only begin at the stage of "oil window" maximum (Radke, 1987). Such an approach, based on combination and simultaneous consideration of a great number of maturation parameters, enabled, on the one hand (Fig. 1a), a more precise, and thus more reliable classification of the examined crude oils, although again into four I→IV maturity decreasing groups (sample PO8 gravitates towards group III). On the other hand (Fig. 1b), it indirectly led to estimation of the catagenetic stage characterizing the corresponding source rocks. Namely, a positive correlation between the factors defined by alkylarene isomerization and dealkylation reactions, observed with Vojvodina crude oils, suggested that their source rocks already reached the "oil window" stage (Ro≥0.80). On the other hand, high negative correlations between these two factors, observed with Drmno depression crude oils, suggested that phenanthrene alkylation reactions are still taking place, and hence that the corresponding source rocks did not yet attain the "oil window" maximum (Ro≈0.70).

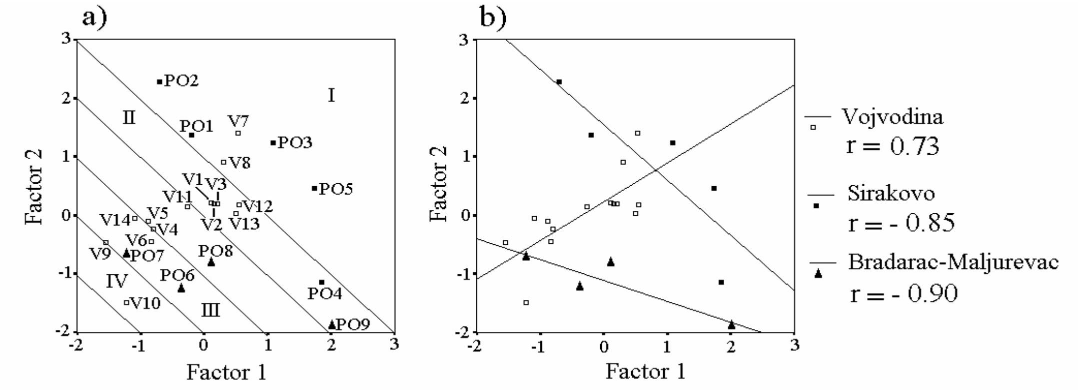


Fig.1. Factor 1/Factor 2 correlation diagrams

References

Jovančićević, B., Stojanović, K., Golovko, J.A., Pevneva, G.S., Golovko, A.K., 2003. Dealkylation of alkylnapthalenes and alkylphenanthrenes in the evaluation of thermal maturity of Vojvodina petroleums (southeastern part of the Pannonian Basin, Serbia). Proceedings of the 5th Interantional Conference "Oil and Gas Chemistry", Tomsk, Russia, September 22-26, 2003, pp. 17-19 (In Russian).

Radke, M., 1987. Organic geochemistry of aromatic hydrocarbons. In: Radke, M. (Ed.), Advances in Petroleum Geochemistry. Academic Press, London. pp.141-205.

Stojanović, K., Jovančićević, B., Pevneva, G.S., Golovko, J.A., Golovko, A.K., Pfendt, P., 2001. Maturity assessment of oils from the Sakhalin oil fields in Russia: phenanthrene content as a tool. Organic Geochemistry **32**, 721-731.

Stojanović, K., Jovančićević, B., Golovko, J.A., Pevneva, G.S., Voronetskaya, N.G., Golovko, A.K., 2003. New di- and trimethylnaphtalene parameters for the evaluating the thermal maturity of oils from southeastern part of Pannonian basin (Serbia). Proceedings of the 5th International Conference "Oil and Gas Chemistry", Tomsk, Russia, September 22-26, pp. 23-26 (In Russian).

PGG2-1: Biomarker composition of Nigerian beach tars

E.J. Ukpabio[1], F.E. Asuquo[2]

1) Production Chemistry Laboratory . SPDC . Portharcourt ,Nigeria (e-mail: elijahukpabio@yahoo.com)
2) Institute of Oceanography , University of Calabar, Nigeria

Black asphalt bitumens regularly strand on Nigeria beaches. Their presence usually triggers allegations of oil pollution by the producing communities. Nigerian beach tars sampled from 2000 to 2003 were analysed for their biomarker composition. Three distinct sources of tars are identified based on the presence/absence of oleanane, gammacerane, bisnorhopane and other source indices such as $C_{29/30}$ hopane, $C_{35/34}$ hopanes, and pristane/phytane

Group 1: The diagnostic features of tars in this group are the conspicuous presence of oleanane, (oleanane /C_{30} hopane >40%), high pristane/phytane (1.5-3), $C_{35/34}$ hopane <1.0, C_{30}/C_{29} hopane > 1,Ts/Tm 0.41 and traces /complete absence of bisnorhopane and gammacerane. These features correlate these tars to the oils of the Niger Delta petroleum province.

Group 2: These tars are distinguished by the presence of bisnorhopane (BNH index >25%), hop/sterane < 2, C_{35}/C_{34} hopane > 1.0, pristane/phytane -1.0, $C_{29/30}$ hopane 0.40, Ts/Tm of 0.44 and complete absence of oleananes. These features together with the complete absence of oleananes are probably the features of oils sourced from organic matter deposited in highly anoxic setting earlier than Upper Cretaceous-Tertiary ages.

Group 3 tars are characterized by high amount of gamacerane (>25), traces of both oleanane (8.6) and bisnorhopane indices (8.0), hop/sterane < 10, C_{27}/C_{29}sterane > 1, pristane/phytane 1.0. These are the diagnostic features of oils sourced from predominant marine organic matter (with traces of terrestrial contribution) deposited in hypersaline environment. The presence of oleananes, though small, supports Upper Cretaceous -Tertiary origin of oils.

The conspicuous presence of gamacerane and bisnorhopanes implies that groups 1 and 2 tars as residues of oil spills outside the Niger Delta province but transported by ocean current into Nigerian marine environment.

The implications of these in apportioning blames and settling claims in cases of oil pollution in Nigeria are discussed.

PGG2-2: Composition and origin of fuel from Scott's expedition to Antarctica

H. Volk[1], C. McIntyre[1], B.D. Batts[2], S.C. George[1]

1) CSIRO Petroleum, PO Box 136, North Ryde, NSW 1670, Australia (e-mail: Herbert.Volk@csiro.au)
2) Department of Chemistry, Division of Environmental and Life Sciences, Macquarie University, North Ryde, NSW 2109, Australia

In the summer of 1911/1912 Captain R.F. Scott attempted to be the first person to reach the South Pole. To assist the expedition in the setting up of base and field camps, in the exploration of the region and the collection of geological samples, Scott took with him three newly developed motor driven sledges and 2.5 tons of petrol (Mountevans, 1953). Photographs show that the fuel drums were packed in wooden boxes labelled "SHELL". The sledges were plagued with problems, including being extremely difficult to start, having very poor traction on the ice and constantly requiring mechanical repairs, and were abandoned part-way through the journey to the pole. As a result, the loads they were carrying then had to be carried by the expeditioners, causing unexpected hardship and no doubt contributing to the ultimate failure of the expedition and death of the five men. During the summer of 1988/89, a New Zealand Antarctic Division conservation team removed left-over petrol from Scott's Cape Evans hut. Although the hut was in a state of near perfect preservation, the petrol tins and drums were considered an environmental hazard. In this contribution, we have analysed the chemical composition of the gasoline Scott took to Antarctica, and discuss its tentative source (Volk *et al.*, 2005).

The gasoline consists predominantly of C_5 - C_9 alkanes, and aromatic compounds such as benzene, toluene, ethylbenzene and xylenes. The distribution of aromatics, *n*-alkanes, branched alkanes and cyclic alkanes is similar to unbiodegraded oils and condensates. In refinery terms the fuel can be classified as a straight run gasoline. A palaeo-temperature derived from the 2,4-/2,3-dimethylpentane ratio is ~137ºC, typical of oils sourced at about 1% vitrinite reflectance, and this maturity is corroborated by alkylnaphthalene and alkylphenanthrene maturity parameters. One major difference in chemical composition between Scott's fuel and that of a modern day gasoline used under Antarctic conditions is in the proportion of low boiling components in the fuels. Approximately 47% of modern Antarctic Blend consists of compounds boiling at or below 68.7ºC (*n*-hexane), whilst only 20% of Scott's fuel boils in this range. These low boiling compounds make engine starting easier under cold conditions. It is not likely that these compounds were lost by evaporation from the sample, as the fuel was stored in tightly stopped bottles under very cold conditions.

The overall chemical composition of Scott's fuel indicates that it may have been too heavy for usage in polar regions.

The branched and cyclic fraction of the topped fuel residue contains oleanane and other angiosperm plant markers, the bicadinane polyprenoids W, T, R (dipterocarp hardwood markers) and abundant aromatic higher plant markers cadalene and 1,2,7-trimethylnaphthalene. The occurrence of abundant bicadinanes in oils is confined to some SE Asian oil provinces with Tertiary source rocks and a strong terrestrial signature. At the beginning of the 20th century, oil fields in SE Asia were amongst the biggest resources of the Royal Dutch Shell Group. Given the findings of our analyses and the photographs taken in Scott's hut, it is likely that the fuel was distilled by the Royal Dutch Shell Group from a crude oil derived from terrestrially-influenced, Tertiary source rocks in SE Asia, or was carried by a vessel that had previously been used to transport or store such crude oils.

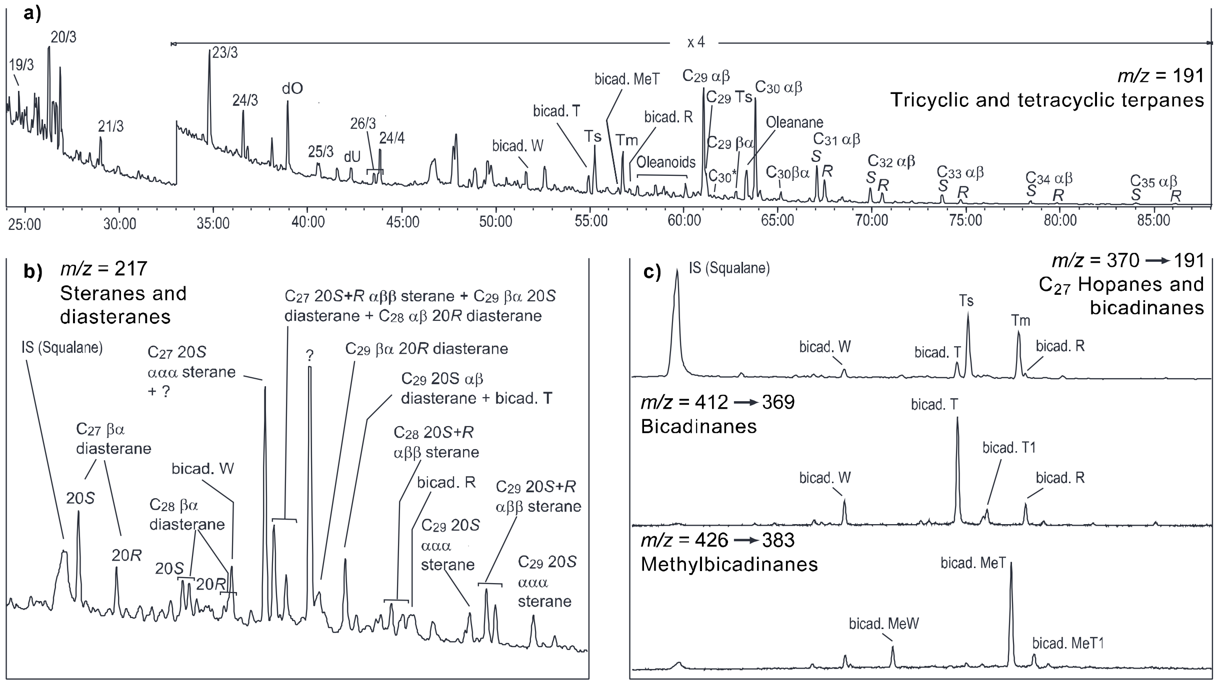


Fig.1. Partial mass chromatograms of the branched and cyclic fraction showing (a) the terpane distribution, (b) the sterane and bicadinane distribution, and (c) partial MRM chromatograms showing the distribution of C_{27} hopanes, bicadinanes and methylbicadinanes

References

Mountevans, A.L., 1953. South with Scott. Collins, London.

Volk, H., McIntyre, C., Batts, B. D. and George, S. C. (2005) Composition and origin of fuel from the hut of explorer Robert Falcon Scott, Cape Evans, Antarctica. *Organic Geochemistry* **36**, 655-661.

PGG2-3: The catalytic effects of minerals on the formation of diamondoids during kerogen pyrolysis

Z. Wei, J.M. Moldowan, J. Dahl

Department of Geological and Environmental Sciences, Stanford University, Stanford, CA 94305, USA

Nanometer-sized polycyclic diamondoids occur as complex mixtures of compact and caged polycycloalkane molecules. Their lower members have been successfully synthesized via carbonium ion rearrangements under laboratory conditions (e.g., Schneider et al., 1966; Olah et al., 1989) by treating a wide variety of organic molecules with super-acid catalysts. Although diamondoids have long been known to be widespread in petroleum, rock and coal extracts in various amounts (e.g., Landa, 1933; Dahl et al., 1999), how these molecules are form remains unknown. Thus, we investigated the role of naturally occurring minerals as catalysts in the formation of diamondoids.

Hydrous and anhydrous pyrolysis were performed on two type-I kerogens isolated from the Irati oil shale and limestone, Brazil, and one Monterey type II-S kerogen, with and without various minerals, including montmorillonite, $CaCO_3$, anhydrite ($CaSO_4$), S^0, and their associated mixtures. Diamondoids were detected in all the kerogen pyrolysates and quantified using several deuterated diamondoid standards and SIR-GCMS.

Our preliminary results indicate that the occurrence of diamondoids in the kerogen pyrolysates results from the thermal decomposition of kerogen regardless of the availability of water. Montmorillonite greatly promotes the formation of diamondoids probably because of its super-acid properties (Figure 1). We believe that during pyrolysis, possible organic precursors (e.g. cyclic alkenes) released from the kerogen come into contact with super-acid sites on the montmorillonite. The subsequent rearrangements of certain strained polycyclic carbonium-ion intermediates produce the experimentally observed large quantities of diamondoids upon pyrolysis. In contrast, calcium carbonate inhibits the formation of diamondoids, both alone and in the presence of montmorillonite. The addition of elemental sulfur to both calcium carbonate and the mixture of montmorillonite and calcium carbonate can slightly increase the amount of diamondoids in kerogen pyrolysates. Similar results are observed in the anhydrite catalytic reaction with kerogen in the presence of water. However, the catalytic activity of montmorillonite is substantially suppressed in the presence of elemental sulfur. This effect is not well understood and we are running further experiments to try to understand the effects of elemental sulfur.

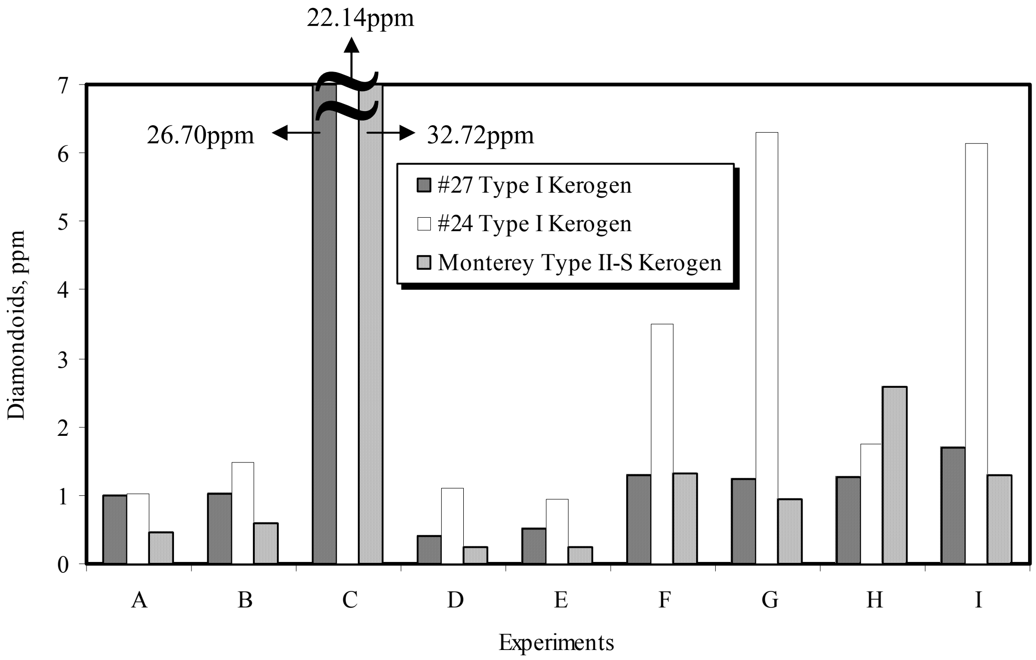


Fig.1. The concentrations of diamondoids (3-+4-methyldiamantanes) formed from kerogen pyrolysis in the absence and presence of different mineral catalysts at 340°C for 72 hours. A: kerogen+H_2O (1:10); B: kerogen only; C: kerogen+H_2O+montmorillonite (1:20:20); D: kerogen+H_2O+$CaCO_3$ (1:20:20); E: kerogen+H_2O+montmorillonite+$CaCO_3$ (1:20:2:18); F: kerogen+H2O+anhydrite (1:20:20); G: kerogen+H_2O+montmorillonite+$CaCO_3$+S^0 (1:20:2:18:2); H: kerogen+H_2O+montmorillonite+S^0 (1:20:20:2); I: kerogen+H_2O+$CaCO_3$+S^0 (1:20:20:2)

References

Dahl, J.E., Moldowan, J.M., Peters, K., Claypool, G., Rooney, M., Michael, G., Mellos, M., and Kohnen, M., 1999. Diamondoid hydrocarbons as indicators of oil cracking. *Nature*, **399**, pp.54-56.

Landa, S., and Machacek, V., 1933. Adamantane, a new hydrocarbon extracted from petroleum. *Collection Czechoslov. Chemical Communications*, **5**, pp.1-5.

Olah, G.A., Wu, A., Farooq, O., and Prakash, G.K.S., 1989. Single-step reductive isomerization of unsaturated polycyclic to $C_{4n+6}H_{4n+12}$ diamondoid cage hydrocarbons with sodium borhydride/triflic acid. *Journal of Organic Chemistry*, **54**, pp.1450-1451.

Schneider, A., Warren, R.W., and Janoski, E.J., 1966. Formation of perhydrophenalenes and polyalkyladamantanes by isomerization of tricyclic perhydroaromatics. *Journal of Organic Chemistry*, **31**, pp.1617-1625.

PGG2-4: Carboxylic acid distribution and possible origin in oils and source rocks from different lacustrine sedimentary basin, China

S. Zhou[1,2], P. Farrimond[2], H. Zou[1]

1) Key Laboratory of Gas Geochemistry, Lanzhou Institute of Geology, Chinese Academy of Sciences, Lanzhou 730000, China
2) Fossil Fuels and Environmental Geochemistry, Drummond Building, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, UK

Carboxylic acids, major constitutes of all living organisms, can survive in a low temperature anaerobic environment for geologically long periods of time. Although these compounds are not routinely analyzed in petroleum exploration, they are useful indicators to assess organic matter origin, maturity, petroleum migration and biodegradation. Previously early studies, including fields and experimental observation, showed that decarboxylation of fatty acids were a major mechanism of *n*-alkanes formation. But when kerogen was accepted as major source of petroleum hydrocarbons, the role of carboxylic acids was less discussed in the petroleum generation. In this study thirteen crude oils and seven sedimentary rock samples from different lacustrine basins were used, and their quantitative composition and significance (mainly n-acids and hopanoic acids) were discussed in relation to the corresponding hydrocarbons in order to assess possible relationships between both classes of compounds.

Four series of carboxylic acid were identified, which included monocarboxylic acids (C_{12}-C_{32}), isopreoid acids (C_{14}-C_{21}), homologous series of iso (C_{12}-C_{35}) and anteiso (C_{12}-C_{30}) and hopanoic acids(C_{28}-C_{33}/C_{34}, no C_{29}). Although oils were collected from different depositional environments, their distribution of n-fatty acids are characterized by a predominance of n-C_{16} and n-C_{22} acid with bimodal distribution and strong even/odd predominance, especially in lower molecular weight fatty acids. Despite n-fatty acid distribution are similar in these oils, but their n-alkanes and isopreoid alkanes distribution are obviously different. Whether even or odd carbon preference for n-alkanes, their corresponding n-fatty acid distribution possesses higher even/odd predominance, thus the n-alkanes distribution cannot be explained by decarboxylation of carboxylic acids. Also, carbon number distribution of *n*-alkanoic acids in source rocks, whether in lower molecular weight fatty acids or in higher molecular weight fatty acids, displays inconsistence with the *n*-alkane distributions, indicating that there are no correlation between the origin and geochemical behavior of the n-acids and the *n*-alkanes in these samples. Moreover, *n*-alkanoic acid concentrations in immature source rock samples are higher than that in oils, but biodegraded oils did not contain higher *n*-alkanoic acids.

There are two series of 2-metheyl alkanioc acid and 3- metheyl alkanioc acid detected in some oil and source rock samples. Because Branched acids are abundant in a number of bacteria, thus the presence of these two series compounds may suggest considerable bacterial activity in sedimentary environment, the abundant hopanoid occurred in these samples also support this suggestion.

Jaffé et al.(1988) indicated that carboxylic acids can be used as indicators of oil migration, but our data indicate that there are multiple sources for hopanoic acids in these oils, such as original organic matter, incorporated contaminations during oil migration, etc. It was also observed that hopanoic acids with the 17β(H),21(β) stereochemistry were in all biodegraded oils, which were thought to be mainly derived from the bacteria. In source rock samples, the hopanoic acids display similar isomeric distributions to the hopanes; the more mature samples are dominated by 17α(H)β(H)-hopanes and 17α(H)β(H)-hopanoic acids, whilst the least mature are dominated by the 17β(H)21(β)-isomers of both compound types. Furthermore, immature source rocks contains more abundant hopanoic acids compared with the oils, thus if oils migrate through immature source rocks, it is possible that some less stable components will incorporate in oils.

PGG2-5: Aromatic hydrocarbons in crude oils and source rocks from different sedimentary environments

E.A. Belitskaja, O.V. Serebrennikova

Institute of Petroleum Chemistry RAS, Tomsk, Russia (e-mail: helene@ipc.tsc.ru)

Aromatic hydrocarbons (AHs) have attracted considerable attention in recent years as important components ubiquitous in source rocks and crude oils. They can provide significant information on oil migration, thermal maturity and oil-source correlation.

The purpose of this study was to determine geochemical characteristics of these aromatic compounds in crude oils and source rocks from different sedimentary environments. The aromatic fractions of source rocks and crude oils were analyzed using gas chromatography-mass spectrometry technique.

We have studied AHs distribution in the source rocks and crude oils within one of the depressions located in the southeastern part of Western Siberia. The sedimentary rocks from the Early Cretaceous to Early Jurassic are mainly presented by clay and sand argillites and were investigated in the interval of 2370-3352 m. The crude oils were investigated in the interval of 2492-3280 m. The most of the investigated samples of crude oils have the marine origin. The two crude oils have the terrestrial one.

AHs such as naphthalenes, dibenzothiophene, biphenyl, dibenzofuran, fluorine, phenanthrenes, retene, fluoranthene, pyrene, benzoanthracene, chrysene, benzofluoranthenes, benzopyrenes, perylene and their alkyl derivatives have been found to be present in the investigated samples.

By contrasting of aromatic hydrocarbons in crude oils and source rocks from different sedimentary environments, obvious differences in their distribution can be seen. It is established, that naphthalenic and phenantrenic structures prevail in the composition of AHs. The relative abundance of the naphthalene series in the aromatic fractions of marine oils is higher than that of terrestrial oils and source rocks. Their average content makes 59,39 and 45,97 % from sum AHs, accordingly. The average content of phenantrenes changes from 21,41 up to 30,27 %. In the oils and source rocks of the continental genesis the content of naphthalenes makes 34,78 and 23,32 %, and phenantrenes - 30,01 and 35,57 %, accordingly.

By studying and contrasting naphthalene and its alkyl derivatives, it is found that among naphthalene series of both in marine and in terrestrial crude oils, C_2- and C_3-naphthalenes are the predominant. The relative high abundances of C_4-naphthalenes are marked in the samples of terrestrial origin. Alkyl derivatives of phenantrenes prevail among phenantrene series too. The abundance of C_1- и C_2-phenantrenes prevails among them. In the samples of marine origin C_1- phenantrenes are the predominant, and in the samples of terrestrial one – C_2-phenantrenes and the high content of C_3-phenantrenes are marked.

The mean value of the total naphthalene/phenanthrene ratio (ΣN/ΣP) of marine oils changes from 1,59 up to 5,41, and in source rocks – from 1,08 up to 1,22. The content of naphthalenes in the oils and rocks of terrestrial origin decreases, and content of phenanthrenes – increases and the ratio ΣN/ΣP makes 0,94-1,03 and 0,39-0,92, accordingly.

Fluorene, dibenzofuran, dibenzothiophene and their alkyl derivatives were abundant in the investigated source rock and crude oil samples. Their relative abundances in the aromatic fractions vary from 3 to 6%. The contents of dibenzothiophenes in the samples of marine genesis is increased, it is especially evident in the source rocks. The content of the dibenzofurans and dibenzothiophenes, on the contrary is increased in samples of a terrestrial origin.

In the AHs composition of the oils and source rocks retene was occurred. The content of retene in oils of terrestrial origin is higher than in those of marine origin. The average content it in oils changes from 0,28 up to 1,78 %. The relative content of retene in source rocks – from 0,03 to 0,55 %. The abundance of biphenyls in oils of different genesis practically does not change and makes 2,86 and 2,96 % from sum AHs, and in source rocks - 5,00 and 11,99 % with the maximal contents in source rocks of terrestrial genesis.

Also the prevalence of tetra- and pentacyclic AHs in samples of the terrestrial origin above samples marine is marked. The average contents of these compounds in oils and source rocks of marine genesis make 1,12 and 2,06 %, and terrestrial- 4,62 and 4,98 %, accordingly.

Thus, studying of individual composition of AHs allows receiving the specific information on conditions of sedimentary environments, to determine type initial organic matter and maturity. The crude oils and source rocks of marine origin have the following distribution of aromatic hydrocarbons: byarenes > tryarenes > polyarenes. The crude oils and source rocks of terrestrial origin have the following distribution of aromatic hydrocarbons: tryarenes > byarenes ≥ polyarenes.

PGG2-6: The principal compositional and structural features of petroleum high-molecular heteroatomic compounds

A.K. Golovko, L.V. Gorbunova, V.F. Kamyanov, T.A. Filimonova

Institute of Petroleum chemistry, Siberian Branch of Russian Academy of Sciences 3, Academichesky av., 634021, Tomsk, Russia

Experimental data on structural group composition and macro-structural characteristics of the resins and asphaltenes from large number (over 150 samples) of crude oils extracted on the oil-fields of Pannonian (Serbia), South-Caspian, West-Siberian and other Eurasian oil-bearing basins are summarized. The products of chromatographic separation of resins and asphaltenes from several representative petroleums are characterized by the same structural parameters.

It was established that resin molecules isolated from deasphaltenized oils by means of adsorption procedure contain, on the average, 1-3 structural blocks each consisting of 0-3 aromatic and 0-5 naphthenic rings in such combinations that total number of cycles in each block does not exceed 5-6. Mono-block resin molecules are identical to all known types of strongly adsorbable, low-molecular N-, S- and O-containing petroleum components. The rest part of resins is complicated mixture of two- or three-block molecules, which in fact should be attributed to petroleum high-molecular compounds (PHMC); their average molecular masses do not exceed 1000-1500 a.m.u. Aliphatic chains in resin molecules are very multifarious and can contain 1-15 and more C-atoms depending on the chemical type of initial petroleum.

Asphaltenes differ from resins by larger average numbers of structural blocks in (up to 5), by predominantly tri- and/or tetracycloaromatic nature of blocks in the molecules, by lesser substitution factors of aromatic nuclei and lesser proportions of C-atoms in saturated fragments. Mean masses of asphaltene molecules measured by cryoscopy in naphthalene do not exceed 2500 a.m.u. Distributions of asphaltene and resin samples depending on the mean values of all their compositional and structural parameters mutually overlap, observed differences between these kinds of PHMC being only in the quantitative proportions of average magnitudes and in occurrence frequencies of some or other values of these compositional and structural parameters.

In structural respect, the blocks of PHMC molecules are similar to petroleum hydrocarbons and heterorganic compounds and cover all the natural diversity of their structural types. The exceptional multiformity of the possibilities of combining different numbers of different structural blocks by different inter-block bonds explains a complexity of molecular composition of PHMC.

Owing to strong intermolecular interactions, PHMC molecules in the petroleums form various assotiates and polymolecular particles including prototurbostratal quasicrystalline “batches” and multi-batch aggregates, especially in asphaltenes. Through spontaneous decay and formation of such particles the petroleums have character of dynamically equilibrium polydisperse systems.

The main regularities in the compositional and structural variations of PHMC were established depending on depth factors. On the whole, a decrease in average content of PHMC in crude oils, in their mean molecular masses, in the content of polar components in the PHMC composition, and in the average number and size of polyarenic nuclei in their molecules is observed when increasing geological age and burial depth of oil-bearing rocks. These trends and also an enrichment of PHMC molecules with paraffin fragments and an impoverishment with naphthenic structures, or, in other words, the general "methanization" of petroleum composition with increasing of deposit burial depth are traceable only in thick terrigenous rock complexes. PHMC molecules are markedly enriched with naphthenic structures when initial petroleum was deposited in carbonate layers, both at West-Siberian platform and at geosynclinal South-Caspian province. An anomalous increase in content of naphthenic rings in the PHMC of crude oils extracted from deeply buried terrigenous Mesozoic horizons on West-Siberian oil-fields can be caused by an influx of organic substances emigrated from subjacent Paleozoic carbonate strata.

In the resins from petroleums accumulated in cracky argillites of Bazhenovskaya suite (West Siberia) there is significant predominance of alkylaromatic compounds devoid of naphthenic cycles. Apparently, this may be interpreted as evidence for an intensificetion of the processes leading to "methanization" of petroleum composition under conditions provoked lithification of clays. "Methanization" process leads to the increase of portions of paraffinic C-atoms both in hydrocarbon and resinous fractions of petroleums generated in geologically younger Cainozoic deposits, whereas in more ancient Mesozoic petroleums maximum proportion of paraffinic C-atoms in resins is characteristic of petroleums which are naphthenic by their hydrocarbon composition. All these regularities are also pronounced for petroleum asphaltenes, but more weakly than for resins, because of "natural selection" ensuring the unifying of molecules to form asphaltenes (asphaltenic "batches") according to the presence of large polyarene nuclei and, to much lesser degree, according to other structural characteristics.

Consisting of chemically labile hetero-organic substances, PHMC are subjected to compositional and structural transformations which are more rapid and substantial as compared with petroleum hydrocarbons and are more responsible to any changes of strata conditions.

Geo-chemical investigations of PHMC can furnish new rich information regarding the questions of petroleum generation and transformations in earth entrails as well as new additional criteria for differentiation of crude petroleums and other natural hydrocarbon systems.

PGG2-7: Geochemical controls on carboxylic acids distribution in crude oils and impact on performance of inner sealing sheath of flexible pipe

I. Kowalewski[1], N. Rouquette[2], P. Schaeffer[2], P. Albrecht[2], S. Pignoc[3], A. Driancourt[1]

1) Geology-Geochemistry Division, IFP, BP311, 92506 Rueil-Malmaison, France
2) Bioorganic Geochemistry Laboratory, CNRS UMR 7509, ECPM, 25 rue Becquerel, 67200 Strasbourg, France
3) FlexiFrance 76580 Le Trait, France

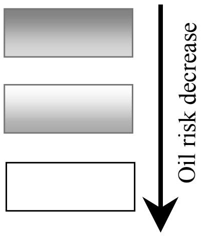
Acidic crudes are characterized by a low API gravity (<20), a high viscosity and a high sulfur content. Their role can be significant in terms of corrosion and materials life time (during production, transportation and/or refining), of environment (waste-waters processing) and of oil quality (weaker economic value). Crudes are considered as acidic when their total acid number (TAN) exceeds 0.5 mg KOH/g as determined by non-aqueous titration. The use of a global acidic parameter (TAN) is very often insufficient to accurately predict the properties of the acidic crude oils. For a given TAN value, acidic crudes may exhibit during production completely opposite behaviour in terms of emulsion (stable vs. unstable emulsion), and corrosion (heavy vs. low hydrolysis of flexible pipe internal coating). The corrosion effect based on natural and artificial samples indicates that the ageing evolution of the polyamide constituting, in some designs, the inner sealing sheath of offshore flexible pipe (assimilated to a change in polymer mechanical properties and measured by inherent viscosity) clearly depends on the chemical types of acidic compounds within the samples. Therefore, in order to better predict the effect of acidic crudes, a detailed molecular knowledge of acids appears to be a paramount prerequisite.

A set of crude oils selected according to geochemical criteria such as organic matter deposition settings, thermal and biological alterations were characterized in order 1) to identify and tentatively quantify the acidic compounds, and 2) to tentatively correlate the geochemical properties with the acidic content. Moreover, the repartition of acids in crudes and the influence of acid molecular weight on polymer ageing were investigated related to distillation cuts (375^-, 375-520, 520^+).

The results indicate that the risk of acidic crudes can be tentatively predict from geochemical parameters such as organic matter type and extent of biodegradation (Table 1). Moreover, it appears that TAN is not an accurate measurement of oil acidity and depends on the origin of acidity (biodegradation or immaturity).

Table 1. Acidic oil prediction as a function of geochemical criteria

Geochemical criteria	n-alkanes	saturates/ aromaticss	resins/ asphaltenes	S weight %	TAN (mg KOH/g oil)
Type I	C20>C10	>2	>10	<0.5	<0.5
Type I-biodegraded	absent	>2	≥10	<0.5	>0.5
Type II-immature	C20≥C10	<2	<10	>1	>>0.5
Type II-mature	C20<C10	<2	<10	>1	<0.5
Type II- biodegraded	absent	<2	<10	>1	>>0.5
Type IIS	C20<C10	<2	<10	>1	>0.5
Type III	C20>C10	>2	>10	<0.5	<0.5
Type I et III- mature	C20<C10		<10	<0.5	<<0.5
Type III- biodegraded					-



PGG2-8: Identification of 17,21-Secohopanoic Acids in Source Rocks and Crude Oils

X. Pan, R.P. Philp

School of Geology and Geophysics, University of Oklahoma, Norman, OK 73019

A series of 17,21-secohopanes ranging from C_{24} to C_{27} were found as degradation products of hopanes in crude oils by Aquino Neto et al. (1983). In this paper we present the first evidence for the occurrence of a novel series of compounds, 17,21-secohopanoic acids (C_{25}-C_{27}, C_{30}, C_{31}), which are possibly related to the hydrocarbons (Fig. 1A).

17,21-Secohopanoic acids have been found to date in a mature oil from West Siberia, an immature oil from the Uinta Basin, the Green River Shale, and tar balls from the Seychelle Islands. In the mature West Siberian oil, the C_{31} 17,21- secohopanoic acids occur as the S and R epimers (Fig. 1B). In the Green River shale, only the C_{30} 17,21-secohopanoic acid was found. C_{25} and C_{26} 17,21-Secohopanoic acids were detected in the immature oil from the Uinta Basin, which was sourced from the Green River Shale. C_{25}-C_{27} 17,21-Secohopanoic acids were found in a tar ball from the Seychelle Islands. In the hydrocarbon fractions of the above mentioned oils, the Green River Shale extract and tar balls, there were no tetracyclic hydrocarbons present corresponding to the decarboxylation products of 17,21-secohopanoic acids apart from trace amounts of the C_{24} tetracyclic terpane. This observation would suggest that the 17,21-secohopanoic acids are not necessarily precursors of the tetracyclic terpanes.

Carboxylic acids were extracted with formic acid in chloroform from KOH impregnated silica gel loaded with rock extracts or crude oils. The acids were subsequently derivatized, purified, and analyzed by GC, and GC/MS. The mass spectra of secohopanoic acids are characterized by a base peak of m/z 191 and some other characteristic fragment ions at m/z 329, 371, 399 (Fig. 1). By analogy with previously published spectra of the C_{24}-C_{27} 17,21-secohopanes (Aquino Neto et al., 1983), m/z 329 for C_{25},C_{26} 17,21-secohopanoic acids corresponds to the A,B,C,D ring fragment after loss of the side chain, m/z 371 for C_{30} 17,21-secohopanoic acids corresponds to the A,B,C,D ring fragment with the side chain cleaved at the C21-C22 bond. M/z 399 for C_{31} 17,21-secohopanoic acids corresponds to the A,B,C,D ring fragment with the side chain cleaved at the C_{22}-C_{29} bond.

The occurrence of 17,21-secohopanoic acids in source rocks, crude oils of different maturity, and biodegraded tar ball implies that these compounds may be formed via a number of different mechanisms. The prominent C_{31} 17,21-secohopanoic acids found in the West Siberian crude may be formed by microbial oxidation of hop-17(21)-ene or other hopane precursors and preserved under anoxic conditions. Highly anoxic conditions prevalent during the deposition of the source material for these oils is suggested by a predominance of the C_{35} extended hopanes over the C_{34} hopanes. In the Green River Shale, the 17,21-secohopanoic acid may be a product of early diagenesis from an abundant hopanoid source (such as hopenoic acids). The C_{30} 17,21-secohopanoic acid disappeared after 72 hours of pyrolysis of Green River Shale at 310°C, which could be due to its low thermal stability, explaining why no 17, 21-secohopanoic acids were found in mature crude oils from the Uinta Basin. Thus secohopanoic acids may be useful as a maturity indicator in the early stages of diagenesis. The shorter side chain C_{25} and C_{26} 17, 21-secohopanoic acids in the Uinta Basin oil may result from maturation processes and the C_{25}-C_{27} 17, 21-secohopanoic acids in the tar ball samples microbial oxidation of the hopanes.

In summary, the presence of the 17,21-secohopanoic acids in the Green River Shale extract suggest as least in some cases the acids reflect a direct source input. However in certain cases the acids may also be formed as a result of hydrocarbon oxidation. Variation in depositional environments and redox conditions are probably responsible for variations in the acid distribution in the oils from different sources.

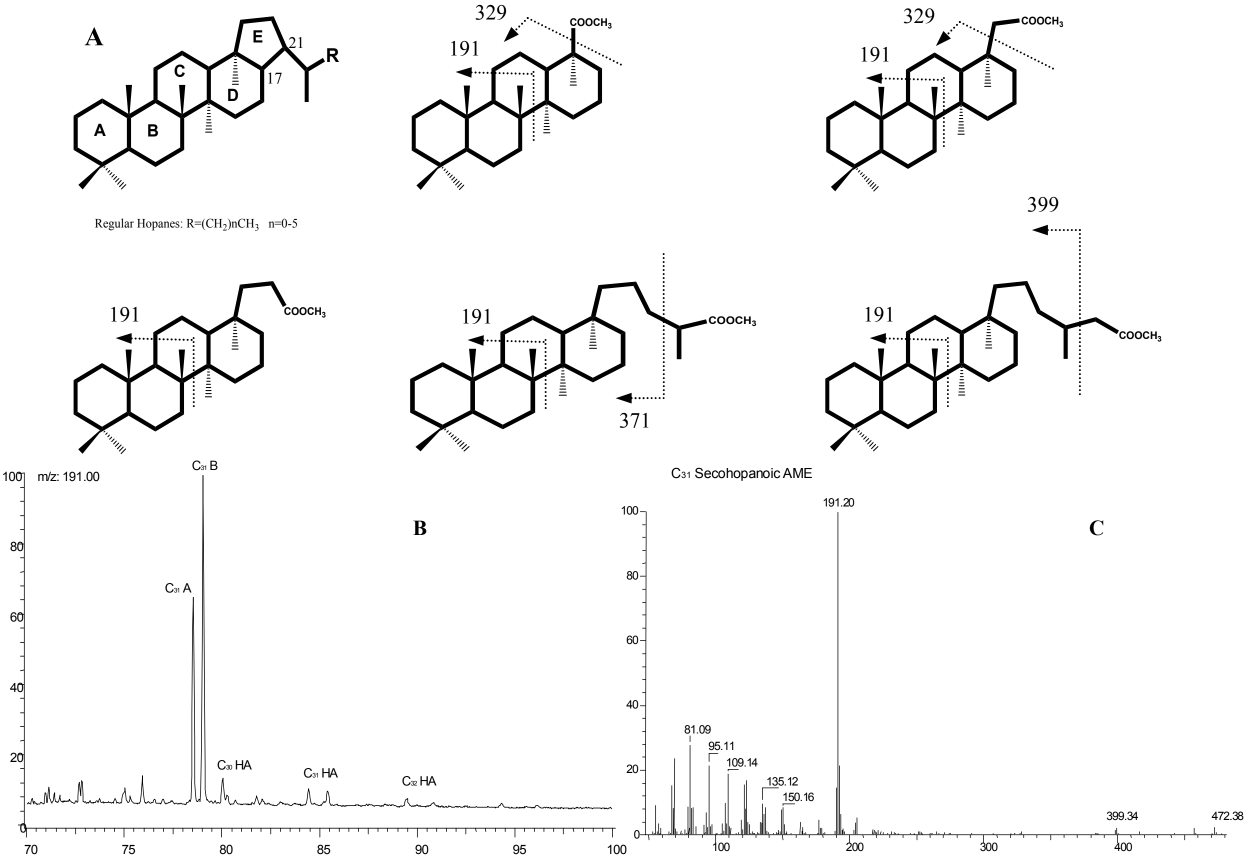


Fig.1. A: Structure of regular hopanes and the C_{25}, C_{26}, C_{27}, C_{30}, C_{31} 17,21-secohopanoic acids. B: m/z 191 mass chromatogram illustrating the distribution of the acids isolated from the West Siberian oil (C_{31}A, C_{31}B: C_{31} 22S, 22R 17,21-secohopanoic acid respectively: C_{30}HA-C_{32}HA: normal hopanoic acids). C: Mass spectrum of the C_{31}A of the West Siberian oil.

References

Aquino Neto, F. R., Trendel, J. M., Restle, A., Connan, J., Albrecht, P. A., 1983. Occurrence and formation of tricyclic and tetracyclic terpanes in sediments and petroleums. Advances. Organic Geochemistry. Proceedings of the 10th International Meeting on Organic Geochemistry, Norway, 659-667.

PGG2-9: Using information on oilfield formation water heterogeneities to improve reservoir and production management of the Oseberg Field, Norwegian Continental Shelf

E. Rein[1], V. Hatlø[2], E. Moldrheim[3], E. Hodneland[3]

1) Hydro Operations & Production, Research Centre, P. O. Box 7190, N-5020 Bergen (e-mail: Elin.Rein@hydro.com)
2) University of Bergen, Department of Chemistry, P. O. Box 7800, N-5020 Bergen
3) Hydro Operations & Production, P. O. Box 7190, N-5020 Bergen

Formation water compositional heterogeneities have been documented to exist in some oilfields (Smalley, 1995). These heterogeneities are to some extent products of interactions of formation waters with reservoir minerals, and water chemistry may thus be used as natural tracers in produced water allocation. As oil fields approach tail-end production, the management of associated water production may be a challenging and costly task. Improved understanding of water ingress in complex production wells will then be of key value.

In the present study we describe the use of detailed water chemistry data for production allocation of associated water on the North Sea Oseberg Field. The Oseberg reservoir consists of Middle Jurassic sandstones and the main oil-producing units are the Tarbert, Ness and ORE formations. The reservoir burial depth is 2200 – 2800 m TVD MSL and the reservoir temperature is around 100 °C. The oil production on the Oseberg Field started in 1988, and gas and water injection has been performed since 1989 to improve production by pressure support. Many of the production wells on the Oseberg field are completed in several reservoir formations or have more than one well trajectory, and production allocation is generally model-based due to the high cost of production logging operations. Produced water sampling and analysis has been performed on the field since 1993 as a part of scale prevention strategy, and in the present study compositional water data from 41 wells (600 samples) were used.

Multivariate statistical methods and cross-correlations were used to evaluate the compositional water data and to determine water chemistry characteristics for each of the producing formations. In this aspect, only wells producing from a single formation was used. The cat ions Na^+, K^+, Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+} were, as expected due to water-mineral reactions, the ones discriminating between waters from the various reservoir formations on the Oseberg Field. Cat ion parameters were created with the purpose of giving the best possible separation between the Tarbert, Ness and ORE formations in the Oseberg compartments (Figure 1). Following this “end member” determination, production allocation using water chemistry data was performed on 14 Oseberg wells completed for production in more than one formation. The results confirmed the reservoir production model for 10 of the wells, and gave new information contradicting the model for 4 of the wells. In two wells where the model predicted water production both from the ORE and the Ness formations the water data showed that the water originated from the ORE formation. In one well the water data showed an ORE origin whereas the model predicted Tarbert Fm. water, and in another well the water data suggested an ORE origin where the model stated Ness water production. Results from this study have proved valuable in the reservoir and production management of the Oseberg field. The results have given information on adjustment of oil-water contacts. Areas/formations with no water production are identified and this knowledge may be used to promote candidate areas for infill drilling to increase oil recovery. Results from the study have also been used for a well intervention decision on plugging back a water producing zone in a production well. The use of natural water tracers for qualitative production allocation is a low cost method that may be used in other oil fields.

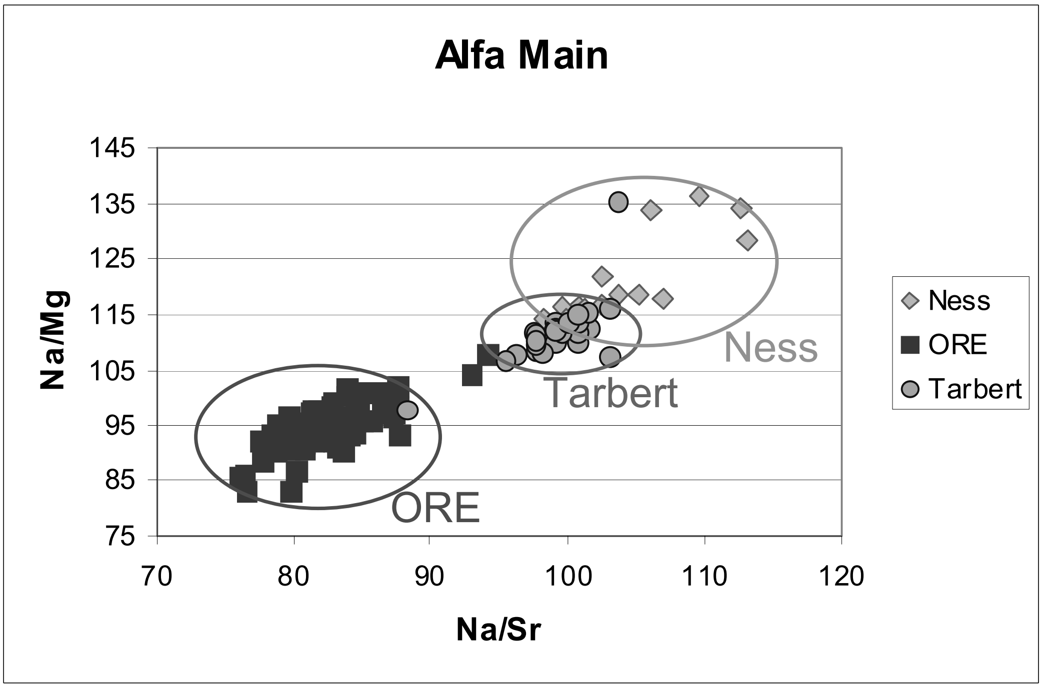


Fig.1. Cross plot of water cat ion parameters, samples from the Oseberg field, Alfa Main compartment

References

Smalley P.C, Dodd T. A., Stockden I. L., Råheim A. and Mearns E. W. (1995) Compositional heterogeneities in oilfield formation waters: identifying them, using them. *The geochemistry of reservoirs. Geol. Soc. Special Publication.* No. **86**, 59-69.

PGG2-10: Biomarkers in ancient oils

E. Ablia, I. Slivko, M. Sokolova

Moscow State University (MSU). Faculty of Geology, Moscow, Rusia (e-mail: eaablia@geol.msu.ru)

The interesting analysis of individual hydrocarbons in oils from the most ancient Upper Proterozoic reservoirs of Pripiat basin deposits, deposits of Kama depression, deposits of the Siberian platform and "ancient" oil of Danilovskoe oil-show (Moscow region) is executed. Research of composition by traditional methods (the general composition, the gas-liquid chromatography) reveals the close affinity of these oils composition. The executed primary balance analysis of hydrocarbons distribution by results of high resolution mass-spectrometry shows that in "ancient" oils composition differences can be detected. The features of the some "most ancient" oils geochemical individuality by biomarkers distribution character are received. The reliable indicator of the initial organic matter type is the sterane hydrocarbons distribution of C_{27} and C_{29} compositions. The C_{27} sterane testifies to the greater contribution of algal organic matter and C_{29} –of land plant.. Thus it is necessary to note, that recently the oils of obviously marine origin (Pre-Cambrian age) are detected, but with prevalence of "continental" homologe C_{29}. As a rule, it speaks about influence of specific organisms existing in Pre-Cambrian, for example some species of blue-green and diatom marine algae. In Siberian and Kama region oils we see it - the expected prevalence of “non-marine” C_{29} homologe. In our samples the prevalence of marine C_{27} sterane is marked in Pripiatskiye and Danilovskaya ancient oils At the same time all oils have visible content of 12, 13 methyl-alcanes. The very high concentration of gammacerane (G) is distinctly identified in these oils. It is not present in others oils. It is considered, that its appreciable concentration is the certificate of salty, hypersalty conditions of sedimentation basin. Probably, the uncharacteristic distributions of sterane homologes in some oils (from marine organisms) in residual organic matter of ancient sedimentation basins are connected to specificity of the organisms lived in fresh-water conditions.

PGG2-11: Biomarkers in laboratory oil mixes

E. Ablia, M. Podolskaya, I. Slivko, M. Sokolova

Moscow State University (MSU). Faculty of Geology, Moscow, Rusia (e-mail: eaablia@geol.msu.ru)

The traditional representations about phasic transformation of organic matter (OM), about generation definite oils by this OM and formation of oil composition caused by genotypes of OM and its mature stages lay in a basis of the classical concept of HC's formation processes. Formation of complex HC systems (which the fluids of the certain deposits finally are) occurs at mixture of different oils fluids generation stages, sometimes various OM even one autonomous fluid-dynamic system of petroleum basin.

The complex of detailed researches (with high resolution GC-MS Thermo Finnigan MAT 900 system based on standard analytical procedures) of some synthetic oil mixes, the modeled analogues of natural HC solutions has been executed. In the beginning the composition of HC of each "crude" oil and the hexane-cleared fraction of each oil was investigated. The first group of investigated oils have rather close range of physical and chemical properties (the average density, the rather low of). The second group of light oils are the practically without asphaltenes and sulfur. The all investigated oils have of a close genotype. The initial organic matter was marine with a small quota of Mesozoic land plant OM. The basic distinctions in maturity of initial organic material – the practically "non-mature" oil (the conventional R^o is till 0.35) (the Okruznoe deposit, the Sakhalino-Okhotskiy basin) and oil enough a high degree of maturity of initial organic matter (the conventional R^o is till 0.6) (the Pushkarskoye deposit, the Tersko-Caspian basin) have been identified in the first group (according to sterane and hopane coefficients) (tab. 1). It is necessary to note, that the «aromatic coefficients of a maturity» (the calculated by them conventional R^o is till 0.6) for the first oil are not comparable with biomarker's maturity coefficients. The second group oils have a high maturity of initial OM.

Then synthetic oil mixes with enough perceptible distinctions in individual hydrocarbons distribution has been executed. In the beginning oil mixes have been created. The mixes were created in various proportions. A method of mixes creation is volumetric. The hydrocarbons distribution of the received real mixes is designed, the real geochemical coefficients of these hydrocarbons distribution are counted. The mathematical modelling of possible hydrocarbon structure of the created mixes has been executed, the "virtual" geochemical coefficients of these hydrocarbons distribution (the genetic and maturity coefficients) are counted. In result the some differences of modeling and real coefficients of hydrocarbons distribution have been revealed (tab.1). The change of some coefficients strictly corresponds with weight ratio of initial oils and fractions. The nonlinear change of coefficients is marked according to oils or fractions weight ratio for lines - (Ph+Pr/C17+C18, Ts/Tm, 27/29 steranes, moretaneC30/ hopaneC30). The "deficiency" of the some hydrocarbons is counted. Probably, the ambiguous characteristics of individual compounds distribution in initial oils and mixes are caused intercomponental fractionation the some hydrocarbons at laboratory oils mixture (for example in asphaltene - resin fractions). It is possible in nature conditions. These phenomena can bring some fluctuations in real hydrocarbons distribution. At execution of geological reconstruction it is necessary to allow the interpretation of the geochemical data smartly and fully.

Ratios	1	2	3	4	5	6
iC19/iC20	1,25	1,80	1,73	1,45	1,88	1,50
iC19/C17	0,22	2,00	0,74	0,29	0,77	0,31
iC20/C18	0,19	1,17	0,44	0,22	0,45	0,22
2C27/C26+C28	1,00	1,05	1,07	1,10	1,10	1,07
C15-C19/C25-C29	0,82	1,96	0,94	0,92	2,85	1,21
Ts/Tm	1,52	0,48	0,71	1,68	0,77	1,40
M30/H30	0,11	0,21	0,18	0,18	0,18	0,15
H29/H30	0,44	0,67	0,56	0,56	0,61	0,51
35(S+R)/31(S+R)	0,42	0,26	0,31	0,39	0,35	0,38
35(S+R)/34(S+R)	1,12	0,88	1,10	1,10	1,09	1,13
α29S/α29S+α29R	0,54	0,34	0,35	0,52	0,38	0,52
α27S/α27S+α27R	0,41	0,31	0,32	0,31	0,31	0,37
β29(S+R)/α29(S+R)+β29(S+R)	0,62	0,27	0,36	0,56	0,35	0,57
β27(S+R)/α27(S+R)+β27(S+R)	0,67	0,20	0,22	0,43	0,22	0,42
α27S/α29S	0,37	1,51	1,59	0,69	1,71	0,84
α27R/α29R	0,64	1,75	1,83	1,65	2,38	1,58
α27R, %	0,34	0,44	0,44	0,45	0,50	0,45
α28R, %	0,12	0,30	0,31	0,27	0,30	0,26
α29R, %	0,54	0,26	0,24	0,28	0,20	0,29
(26+27)DMN/(2*15DMN)	1,81	1,61	1,64	1,67		
(3+2)MP/(3+2+9+1)MP	0,46	0,51	0,50	0,47		
2 MP/(3+2+9+1)MP	0,25	0,27	0,27	0,25		

1- Crude oil Pushcarskoe, J3
2- Crude oil Okruzgnoe, N2
3- 1and 2 Mixture (1:1)
4- 1and 2 Mixture (20:1)
5- Mixture of 1Hexane fraction and 2 Hexane fraction (1:1)
6- Mixture of 1Hexane fraction and 2 Hexane fraction (20:1)

PGG2-12: Autonomous fluid systems – Biomarkers based evidence

E. Ablia, M. Podolskaya, I. Slivko, M. Sokolova

Moscow State University (MSU). Faculty of Geology, Moscow, Rusia (e-mail: eaablia@geol.msu.ru)

The autonomous zones of the monotypic fluids vertical moving are well identified by materials of organic matter detailed geochemical researches within the contours of a wide range of deposits in vertical columns-projection of an oil deposit. One of such examples is considered by us on a Jurassic-Cretaceous section of one deposit well in West-Siberian basin.

The oils from the upper intervals of a section (2500м), the organic matter of coaly detritus (coal interlayer) from samples of under-laying intervals - 2660м, samples of average section sandstones - 2700м, the carbonaceous sandstone and fragments of the black argillite in the same sample - an interval 2900м, the bituminous flinty-carbonaceous argillite - an interval 2950м, the Middle Jurassic rocks samples (from 3500м) are analysed.

The interesting character of some hydrocarbons groups distribution in oils compositions, in organic matter, extracted from rocks and coaly detritus is revealed. The precise proximity of basic biomarkers distribution in samples of all investigated section is traced. As a whole it is possible to speak about marine initial organic matter. The character of the aromatic hydrocarbons distribution is very close. The character of the basic "biomarkers of a maturity" distribution assumes the close and high degree of organic matter hydrocarbons maturity, extracted from all rocks (taking place in various thermal zones). In pure differences of coaly detritus extracts the uncharacteristic hydrocarbons for continental organic matter of normal oil type are revealed.

It is possible to assume the *through* migratory character of hydrocarbons in all investigated samples of this section from a uniform source. The active sorption processes are revealed by a coal matrix of migrating hydrocarbons of oil type.

PGG2-13: Identification of the acidic and neutral biomarkers in oils from the Estreito-Guamaré trend, Potiguar basin, Brazil

A.A. Da Silva[1], L. Koike[1], F.A.M. Reis[1], E.V.S. Neto[2], S.G. Lima[1], J.A.D. Lopes[3]

1) Instituto de Química, Universidade Estadual de Campinas, CP 6154, Campinas, 13083-970, SP, Brazil
(e-mail: luzia@iqm.unicamp.br)
2) Petrobrás/Cenpes/PDExp/GEO, Rio de Janeiro, Brazil
3) Universidade Federal do Piauí

The Potiguar Basin is located in the Brazilian equatorial margin and has an area of about 48,000 km^2. It is boarded on the west and the south by the Precambrian basement and extends north and east to the edge of the continental shelf (Bertani *et al.*, 1990). Geochemical studies have classified the main families of the Potiguar oils as marine-evaporitic, lacustrine and mixed oils (Mello *et al.*, 1988; Santos Neto *et al.*, 1990).

In this work, we present the geochemical results of a study using representative samples of two lacustrine and two mixed (marine-evaporitic + lacustrine) samples both from fields near the coast, and two marine-evaporitic oils from fields located inland about 55 km from the coast. All samples were collected along the Estreito-Guamare (EG) fault lineament that spreads along a NE-SW direction. The main objectives in this study are to characterize the samples accordingly to their neutral and acidic biomarker contents, and to compare them with a suite of marine-evaporitic oils from the Fazenda Belém (FB) field that were presented by Lopes *et al.* (1999).

The analytical protocol used in this study was previously published by Koike *et al.* (1992). Other geochemical data, such as the biodegradation levels that are similar for the oils from FB and EG trend, were obtained from the available literature. In the neutral fraction, the EG marine-evaporitic oils showed lower concentrations of sesquiterpanes, tricyclic terpanes and hopanes compared with those found in the FB oils. The steranes and alkyl steranes series were found in the EG and FB oils. Fatty acids from C_{13} to C_{27} and hopanes from C_{28} to C_{33} were detected in the acidic fractions from EG oils. However, sesquitepanes and tricyclic terpanes are absent.

The comparison of acidic biomakers found in the studied oils families showed higher concentrations of fatty acids and lower abundance of sesquiterpanes, tricyclic terpanes and steranes. Relatively lower concentrations of fatty and tricyclic terpanic acids were found in the marine-evaporitic and mixed oils. Hopanic and steranic acids with similar concentrations were detected in all samples.

Special attention was devoted to the geochemical analyses to identify the alkyl sterane series. In a previous analysis of Fazenda Belem oils, 25 alkylsteranes (two with 5β(H) configuration) and 48 carboxyalkylsteranes (nine with 5β(H) configuration) were detected. Futhermore, 8 alkylsteranes plus 8 carboxyalkylsteranes were identified by co-injection. Recently, 10 new members (eight with 5β(H) configuration) have been identified in Fazenda Belem oils by Lima et al. (2004). The present work reports the identification of eleven alkyl-steranes (four with 5β(H) configuration) and seventeen carboxyalkyl steranes (eight with 5β(H) configuration) in samples collected along the Estreito-Guamare (EG) fault. Nine alkyl steranes and ten carboxyalkyl steranes have also been detected. The results show a high concentration of these compounds in marine-evaporitic and mixed oils, which are rarely found in lacustrine oils.

Acknowledgements

The authors wish to thank PETROBRAS for authorization to publish these results.

References

Bertani, R. T., Costa, I. G., Matos, R. M. D., 1990. In: Raja Gabaglia, G. P. and Milani , E. J. (Eds)., *Origem e Evolução das Bacias Sedimentares Brasileiras*: Petrobrás , 291-310, Rio de Janeiro.

Koike, L.; Rebouças, L.M.C.; Reis, F.A.M.; Marsaioli, A.J., 1992. *Organic Geochemistry*, **18,** 851-860.

Lima, S. G.; Koike, L. Santos Neto, E.V.; Cerqueira, J. R.; Reis, F. A. M., 2004. *9th Latin American Congress on Organic Geochemistry*, Merida, Mexico, 210,221,255,256.

Lopes, J. A. D.; Santos Neto, E. V.; Mello, M. R.; Koike, L.; Marsaioli, A. J.; Reis, F. A. M., 1999. *Chemical Geology*, **158**, 1-20.

Mello, M. R.; Gaglianone, P.C., Brassell, S.C., Maxwell, J.R., 1988; *Marine and Petroleum Geology*, **5**, 205-224.

Santos Neto, E. V.; Mello, M. R.; Rodrigues, R. 1990. *XXXVI Congresso Brasileiro de Geologia Proceedings,* **1**, 974-985.

PGG2-14: Parameters for the process of cumulative filling and mixing of reservoir oil inputs

V. Hatlø[1], T. Barth[1], M. Erdmann[2]

1) University of Bergen, Department of Chemistry, P .O. Box 7800, N-5020 Bergen, Norway
(e-mail: Vibeke.Hatlo@kj.uib.no)
2) Norsk Hydro Research Centre, P. O. Box 7190, N-5020 Bergen, Norway

The processes of secondary migration and filling of permeable reservoirs is complex. Most reservoirs receive multiple charges, continuously or periodically, of gradually more thermally mature petroleum. The composition of petroleum within reservoirs is consequently a mixture of different hydrocarbon fluids expelled from source rocks at different times and temperatures. Mixing processes in permeable reservoirs will tend to cancel out the heterogeneities of petroleum compositions over geological time, and result in oil with an average thermal maturity (England et al., 1987; George et al., 1998). The various molecular maturity indicators may differ widely between the end-member values of the mixed oils (Huang et al., 2004). Fluid inclusion and PVT analysis are useful methods for relative maturity estimation, recognition of mixing effects and evaluation of complex reservoir filling histories (Di Primio et al., 1998; George et al., 2004). However, a better chemical understanding of the progressive compositional change in oil charge going into the reservoir can improve the models.

The principal objective of this study is to find chemical properties of the oil which can be determined by molecular level analysis, and which reflect the geological transformation processes. This can lead to new chemical indicators for evaluation of mixing. Methods for oil characterisation, including NMR, GC of light hydrocarbons and GC-MS, will systematically be tested for their potential to provide information on cumulative filling and mixing of fluid input from a source rock into a reservoir. The methods are initially applied to an artificial set of mixed oils made by 2-3 end-members with varying degree of maturity. North Sea oils generated from the Draupne formation have been chosen since this system is extensively studied. A reference data set is also produced by hydrous pyrolysis of a Draupne formation source rock. Both the mixed oils and the pyrolysates are analysed by NMR, GC and GC-MS.

Analysis of the oil using NMR is especially of interest. In contrast to chromatographic analysis based on separation, NMR reflects the total oil composition. ^{1}H-NMR and ^{13}C-NMR give bulk structural parameters such as average chain lengths of saturates, including both alkane molecules and alkyl substituents on ring structures, the average number of substituents on aromatic rings and average aromaticity. This structural information has previously shown to be highly related to the maturity of oil samples (Hatlø, 2004). NMR measurements are performed on a Bruker 500 Plus spectrometer. Quantitative ^{13}C-NMR spectra (Figure 1) are recorded by using an inverse gated pulse sequence to suppress the Nuclear Overhauser Effect, and with addition of a relaxation agent Cr(acac)$_3$.

The parallel approach of using NMR and light hydrocarbon composition data will provide independent data sets that can be treated statistically. All results will be analysed with statistical software suited for chromatographic and spectroscopic data complex mixtures, to identify indicators of mixing.

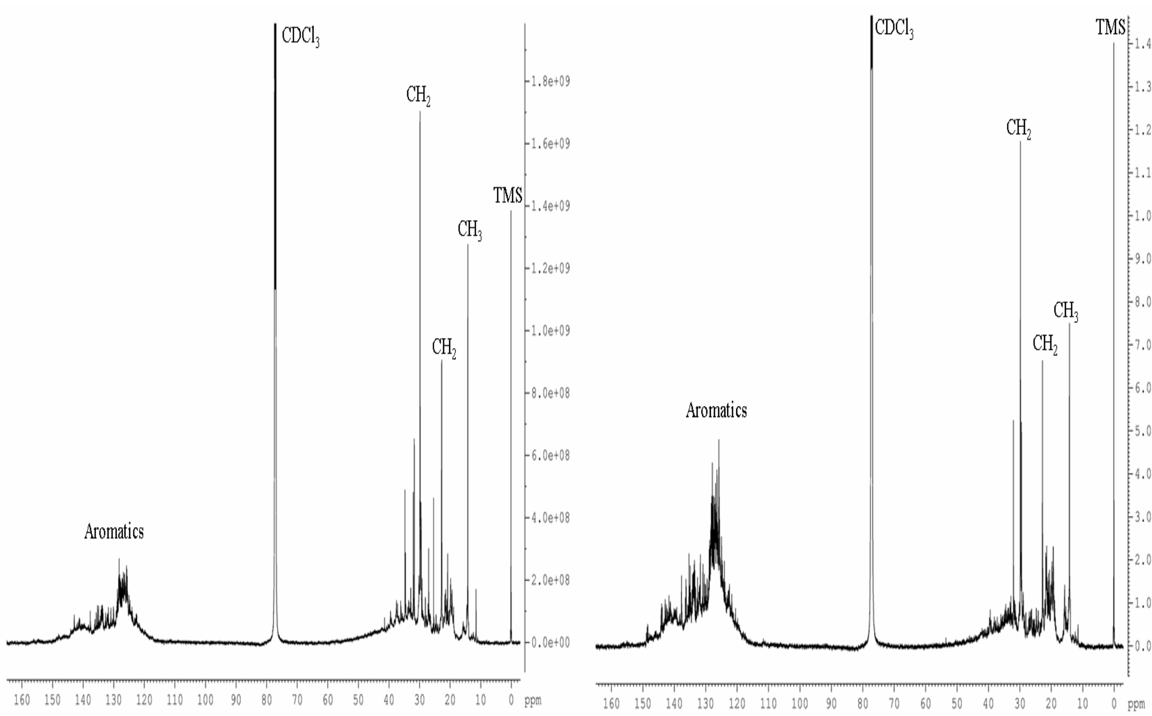


Fig.1. ^{13}C-NMR spectra of the aromatic fraction of a North Sea oil before and after artificial maturation by hydrous pyrolysis

References

Di Primio, R., Dieckmann, V. and Mills, N. (1998) PVT and phase behaviour analysis in petroleum exploration. Organic Geochemistry 29, 207-222.

England, W. A., Mackenzie, A. S., Mann, D. M. and Quigley, T. M. (1987) The movement and entrapment of petroleum fluids in the subsurface. Journal of the Geological Society of London 144, 327-347.

George, S. C., Lisk, M., Summons, R. E. and Quezada, R. A. (1998) Constraining the oil charge history of the South Pepper oilfield from the analysis of oil-bearing fluid inclusions. Organic Geochemistry 29, 631-648.

George, S. C., Ahmed, M., Liu, K. and Volk K. (2004) The analysis of oil trapped during secondary migration. Organic Geochemistry 35, 1489-1511.

Hatlø, V. (2004) Characterisation of crude oils before and after pyrolysis using NMR and standard geochemical methods. MSc. thesis, Department of Chemistry, UoB (in Norwegian).

Huang, H., Larter, S. R., Bowler, B. F. J., Oldenburg, T. B. P. (2004) A dynamic biodegradation model suggested by petroleum compositional gradients within reservoir columns from the Liaohe basin, NE China. Organic Geochemistry 35, 299-316.

PGG2-15: Sludging tendency of Permian basin oils during production stimulation

R.J. Hwang

ChevronTexaco Energy Technology Company, San Ramon, CA 94583, USA

Many oil fields in the Permian Basin in West Texas have experienced "sludging" problems associated with acid treatment for production stimulation. Crude oils in these producing fields form acid sludge upon contact with acid commonly used for stimulation. In numerous producers, the sludge appears to be quite voluminous, viscous, and stable. It has great potential to plug pore throats, vugs, caverns, and fractures, resulted in a great reduction in rock permeability. It also produces skin damage that significantly reduce permeability in the near well bore area. Acid sludge reportedly has caused well damages that often offset the benefit of acid stimulation. Despite its negative impact on oil production, acid sludge has not been well characterized and, more importantly, sludging tendency of crude oil has not been well understood.

To characterize acid sludge and to evaluate sludging tendency of Permian Basin oils, oil samples from twenty-five wells in six Permian fields that had not been acid treated were selected for detailed characterization before and after the oils reacted with acid in the laboratory. Acid solutions used in the testing were typically 15 % HCl with or without iron. All the oils ranging from heavy to light crude were found to form acid sludge in various amounts when mixed with acid. The acid sludge was similar among all the oils, and appeared as a tight and stable emulsion. The emulsion was viscous, occupied the entire acid/oil volume, and showed very little or no break at ambient or reservoir temperatures. The emulsion appeared to become more stabilized and viscous with increasing total iron concentration in the acid.

Microscopic examinations of acid-crude oil mixtures revealed that, prior to contact with acid and iron, the oils exhibited no emulsion or solids. When mixed with an iron-free acid, a water-in-oil emulsion was generated, but with no obvious solid particles. When an acid-free iron solution was added to the oil, dark-brown solid particles were formed, but with no emulsion. Only when both acid and iron were present, both emulsion and solids were formed. The solids were closely associated with the emulsion droplets, which helped to stabilize the emulsion. Through additional geochemical characterization, acid sludge was shown to be a viscous emulsion stabilized by asphaltene-rich organic solids. For all the acid sludges generated, they are richer in asphaltenes and resins than their parent crude oils. The sludges also contain significant amounts of saturated and aromatic hydrocarbons.

Quantitative determination indicates amounts of acid sludge formed from various Permian crudes are proportional to the content of asphaltenes and resins but inversely proportional to the paraffinic content of the crude oils. Thus the Permian crudes that contain more asphaltic components will have a greater tendency to form acid sludge when treated with iron-laden acids. In addition, a positive correlation between amounts of acid sludge formed and base numbers of crude oils has also been observed. Overall the sludging tendency of a curde oil increases with the content of asphaltenes and resins, base number of the oil, and ferric ion content in the acid.

PGG2-16: Biomarkers derived from terrestrial higher plants in crude oils from Hokkaido, Japan, and Sakhalin, the Far East Russia

Y. Suzuki

Institute of Geo-resources and Environment, (Geological Survey of Japan), National Institute of Advanced Industrial Science and Technology (AIST), Higashi 1-1-1 Central 7, Tsukuba, Ibaraki 305-8567, Japan
(e-mail: yu-suzuki@aist.go.jp)

Introduction

Several oil and gas-fields are distributed in Central Hokkaido, Northern Japan, and in Northern Sakhalin, Far East of Russia which is a geologically north extension of Hokkaido. Biomarker analyses were carried out for several crude oils from these areas and the existence of diterpnoid was checked for influences of coals or terrestrial higher plants source rocks.

Samples and method

3 crude oils were sampled from small oil-fields in Tempoku Area, Northern part of Central Hokkaido, which are Yuchi, Wakkanai and Toyotomi. Other 2 oils were collected from the Atuta and the Barato oil-field in western part of Central Hokkaido. Reserver rocks of these 5 oil-fields are sandstones in Miocene formations and properties of crude oils were shown by Waseda et al. (1998).

3 crude oils from Sakhalin were collected at the Okha oil-field, the Nutovo oil-field and the Katangli oil-field along the eastern coast of northern Sakhalin. These samples had been collected by Kita-Sakhalin Oil Co. of Japan in 1930's.

Condensate samples from Yufutu oil and gas-field, which was assumed that their source rocks were coals, and several coals samples from the Ishikari coal-field in central Hokkaido and from the Tempoku Area, were also analyzed for oil and coal source-rock correlations

Analytic methods in this study are conventional methods that are shown in some guidebooks and papers. Biomarkers analyses have been done with saturated hydrocarbon fractions in this study.

Results and Discussion

Ion-chromatograms of m/z 191 from Yuchi, Toyotomi and Atuta crude oil are shown in fig.1. Diterpane compounds, which are most useful terrestrial plants indicators, were found in m/z 191 and 123 ion-chromatograms and their Occurrence in each sample is summarized in table 1. From our results of biomarker analysis, source rocks of crude oils in Tempoku and condensate from Yufutu are strongly suggested their influence of terrestrial higher plant inputs. Paleogene coals from the Ishikari coal-field are also rich in diterpanoid, but Crude oils from Atsuta and Barato have no or few diterpanoid showing coals or terrestrial organic matters origin. Sakhalin crude oils are similar as Atuta and Barato oils in biomarkers. This result of Central Hokkaido is good concordant with the results of sterane compositions analysis by Waseda et al.(1998).

In Tempoku area coal seams were deposited in two geological horizons. The coal-bearing Souya Formation is exposure on surface widely, but the other one, the Haboro Formation, is not exposed on surface, and it was confirmed only in deep-drilled wells by JNOC. The geologic age of Haboro Formation is Paleogene and it is correlated to the strata of Ishikari coal-field. Both coals in Tempoku area contained diterpanoid, but maturity indexes by phyllocladanes isomerization (Alexander et al., 1987) are suggested that the Soya Formation is not reached oil-generation degree, but Ishikari coals have already reached to oil generation zone. It is inferred that source rocks in Tempoku area is correlated to coals of deeper Habaro Formation. Oils in the Haboro Formation were migrated to shallow formations vertically along some faults.

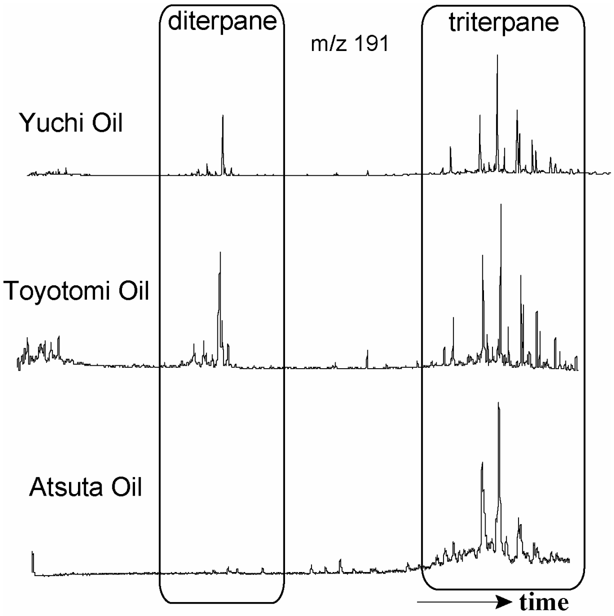


Fig.1. m/z191 Ion-chromatogram of Yuichi, Toyotomi and Atuta oil

Hokkaido	
Tempoku(North)	
Yuchi	O
Wakkanai	O
Toyotomi	O
Central	
Barato	+
Atuta	X
South	
Yufutu	O
Sakhalin	
Okha	X
Nutvo	+
Katangli	+

Table 1. Existence of Diterpanoid
O: abundant +; rare X; none

References

Waseda, A. and H.Nishita(1998); Org. Geochem., Vol.28,No.1/2,27-41
Alexander,G., I.Hazai,J.Grimalt and J.Albaiges(1987);Geochem. Cosmochem. Acta, Vol51, 2065

POS1-1: Carbon and sulfur transformations in hydrous pyrolysis experiments of Senonian (Ghareb) bituminous rock: source of Dead Sea area asphalts and oil shows?

A. Amrani[1], E. Tannenbaum[2], M. Lewan[3], M. Vairavarmurthy[4], Z. Aizenshtat[1]

1) Casali Institute of Applied chemistry and Department of Organic chemistry. The Hebrew University of Jerusalem, 91904 Jerusalem, Israel (e-mail: zeev@vms.huji.ac.il)
2) Kimron Company, 19A Hahistadrot st. hod Hashraon 45270 Israel
3) U.S. Geological Survey, Box 25046, MS977, Denver, Colorado 80225, USA
4) Department of Energy Sciences & Technology, Brookhaven Nat. laboratory, Upton N.Y. 11973-5000 USA

The present study aims at the use of the hydrous pyrolysis method (Lewan, 1993) as a proximate simulation of maturation to provide a better of understanding the mechanisms prevailing at deeper depths of burial due to the rifting and plugging of salt. The experiments were carried out to cover kinetic controlled and thermally dominated processes, following both inorganic and organic transformations in gas, liquid and solid phases. Figure 1a,b shows the transformations of kerogen through bitumen to oil and organic bound sulfur to H_2S. These transformations were monitored by both carbon and sulfur isotopes. For each temperature of HP carbon and sulfur gases were analyzed and the residual kerogen in rock was examined by Rock-Eval after extraction of the bitumen. For some selected experiments, kerogen was isolated and examined by XANES for the sulfur functionality. The overall hydrocarbon distribution of the obtained oils (260- 365ºC) was compared with petroleum samples of the Dead Sea Area as well as the biomarkers profiles (mostly steranes and hopanes). In addition, the formation of the very high amounts of asphaltic matter (extractable bitumen) is similar to the immature asphalts naturally occurring in the area. The use of the above parameters with the C and S stable isotopes provides a deeper understanding of the thermally controlled mechanisms. The functionality changes for both carbon and in particular, sulfur is currently investigated. Studies of organic matter in both bituminous rocks of the Ghareb Formation as well as asphalts and petroleum shows of the Northern Negev and the Dead Sea area in Israel have been previously published (Spiro, et al*.,* 1983a and 1983 b; Tannenbaum, et al., 1987). These sedimentary rocks were suggested as possible source rocks for the formation of the immature asphalts and the more matured oils found in geographical proximity. Hydrous pyrolysis (HP) experiments conducted on similar members of the Ghareb Formation from the Jordan side of the Rift valley were discussed by Koopmans et al., 1998. Despite the geographical proximity and the similar depositional environments proposed for the various Ghareb formation studied sites, we find that the $\delta^{34}S$ values for the kerogens span in the range from -10‰ for Amiaz to +4‰ at the Nabi Musa deposit no detailed information has been obtained for the Jordan (Ghareb Formation). The present work will combine all the data obtained to support the source rock asphalts and oils correlation for the Dead Sea Area. The mechanisms suggested will be discussed as for other basins with type II-S kerogens hence offering better Basin Evaluation parameters.

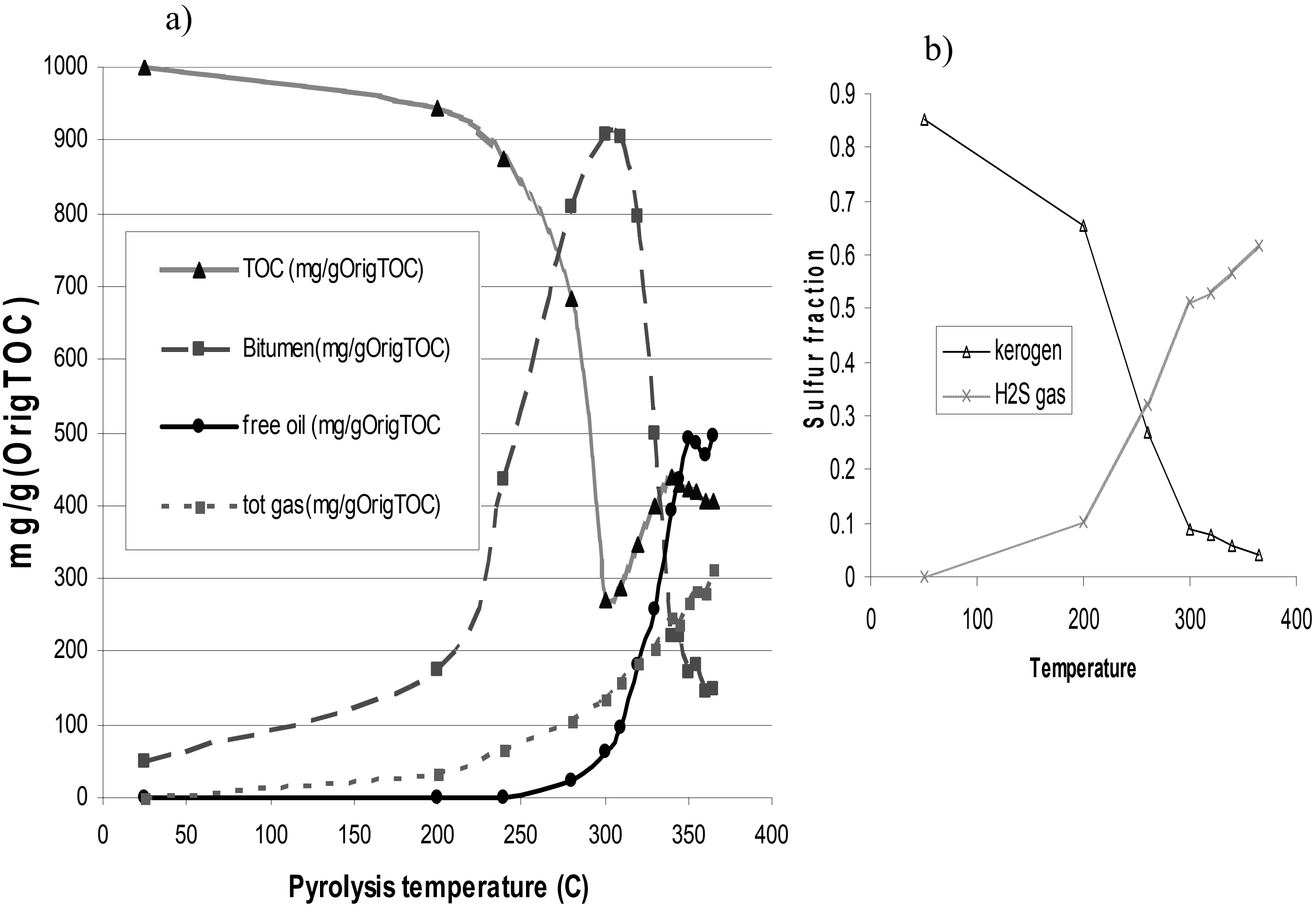


Fig.1. a. Organic matter transformation as function of hydrous pyrolysis various fractions as marked on graph (normalized for original on unheated sample TOC).b. Major changes in sulfur transformations from organically bound S to H_2S normalized to total sulfur content in original rock.

References

Lewan M.D. (1993) Laboratory simulation of petroleum formation :hydrous pyrolysis. In *organic geochemistry* (ed. M.H. Engel and S.A. Macko), pp.419-442.

Spiro B., Dinur D. and Aizenshtat Z. (1983a) Evaluation of source, environments of deposition and diagenesis of some Israeli "oil shales": n-alkanes, fatty acids, tetrapyrroles and kerogen. *Chem. Geol.* 39, 189-214.

Koopmans M.P., Rijipstra W.I.C., de Leeuw J.W., Lewan M.D. and Sinninghe Damsé J.S. (1998) Artificial maturation of immature sulfur-and organic matter-rich limestone fron the Ghareb Formation, Jordan. *Org. Geochem.* 28, 503-521.

Spiro B., Welte D.H., Rullkotter J. and Schaeffer R.G. (1983b) Asphalts, oils and bituminous rocks from the Dead Sea Area: a geochemical correlation study. *Am. Assoc. Petroleum Geologists.* 67, 1163-1175.

Tannenbaum E., Starinsky A. and Aizenshtat Z. (1987) Light oils transformation to heavy oils and asphalts. In: Meyer, R. F. (Ed.), Exploration for Heavy Crude Oils and Natural Bitumen. Studies in Geology Am. Assoc. Petroleum Geologists, Series 25, Tulsa, pp. 221-231.

POS1-2: Stable sulfur isotopes partitioning during simulated petroleum formation as determined by hydrous pyrolyses of Ghareb Limestone, Israel

A. Amrani[1], M. Lewan[2], Z. Aizenshtat[1]

1) Casali Institute of Applied chemistry and Department of Organic chemistry. The Hebrew University of Jerusalem, 91904 Jerusalem, Israel
2) U.S. Geological Survey, Box 25046, MS977, Denver, Colorado 80225, USA

The $\delta^{34}S$ of sulfur rich kerogens and oils is controlled by two major stages: sulfur incorporation during early diagenesis at relatively low temperatures and sulfur decomposition and re-reaction during catagenesis at higher temperatures (Aizenshtat and Amrani, 2004a,b). The present work is focused on the thermal behavior of both organic sulfur and inorganic sulfur species and the stable sulfur isotopes partitioning during thermal alteration. Hydrous pyrolysis experiments (200-365ºC) were carried out on organic and sulfur rich containing type II-S kerogen (11.8% S w.w) sample from Ghareb Formation North Negev Israel. This carbonate rich limestone belongs to the Dead Sea Senonian bituminous section. Most of the sulfur in the rock (85%) is bonded to the organic fraction. The most dominant sulfur transformation is due to cleavage of the sulfur cross linked kerogen to form $H_2S_{(gas)}$. Up to 70% of the organic sulfur is released, as $H_2S_{(gas)}$ that is isotopically lighter than the sulfur in the kerogen. The organically bonded sulfur is enriched up to 2‰ in ^{34}S compared with the initial $\delta^{34}S$ values during thermal treatment. The $\delta^{34}S$ values differentiation between the three main organic fractions (kerogen, bitumen and expelled-oil) is within 1‰. Neither thermochemical reduction (TSR) nor formation of sulfate or isotopic changes was observed during the experiments. Secondary and heavier pyrite formed (Fig.1) up to 300ºC experiments. This secondary formed pyrite is isotopically heavier than the unheated pyrite and partially decomposes above 300ºC. The early released sulfur reacted with available iron to form the secondary pyrite and is the most ^{34}S depleted, about 21‰ lighter than the organic bound sulfur. The large isotopic effect for the early formed H_2S is due to the non-equilibrium system, upon creation of larger partial pressure of $H_2S_{(gas)}$, retro-reactions with the organic matter cause isotope mixing. The results obtained in the present study are discussed as for relevance to catageneteic thermal processes and kerogen-oil-H_2S-pyrite correlations. Caution should be used when using pyrite-kerogen correlations for reconstructing diagenetic conditions in mature reservoirs. The thermally formation of pyrite can erase this diagenetic isotopic and quantity signature of pyrite. The main transformations kerogen-bitumen-oil can be recorded by using both sulfur content and $\delta^{34}S$ of each phase in combination with $H_2S_{(gas)}$

isotopic data. This shows that sulfur isotopes are sensitive indicators during catagenesis structural changes. Thermaly formed H_2S in association with oil should be isotopically lighter or similar to oil. It is concluded that small isotopic differentiation obtained for all organic species can be adapted to closed reservoirs conditions. However, in other cases, petroleum reservoirs, separated from their source rock, indicate that the migration of oil is open-system processes that may cause significant isotopic discrimination between the oil and its source kerogen. The magnitude of this discrimination is suggested to be highly dependant on the mineral facies of each reservoir because of secondary formation of pyrite.

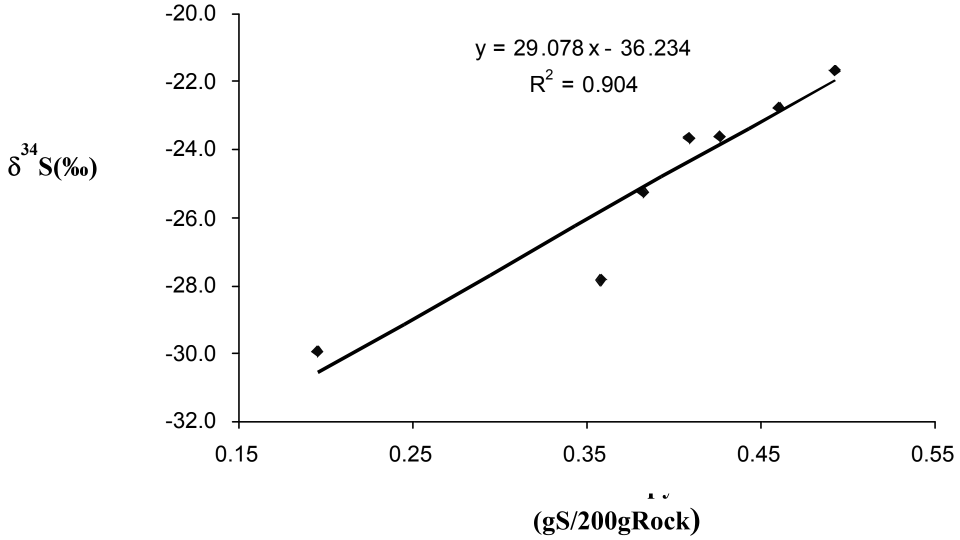


Fig.1. Secondary formed pyrite during hydrous pyrolysis experiments. The $\delta^{34}S$(‰) of pyrite as a function of pyrite amount normalized to total sulfur in the rock

References

Aizenshtat, Z. and Amrani, A**.,** (2004a) Significance of $\delta^{34}S$ and evaluation of its imprint on sedimentary organic matter I. The role of reduced sulfur species in the diagenetic stage: a conceptual review. In Hill, R.J. et al. (Eds.).Geochemical Investigations: A tribute to Isaac R. Kaplan, The Geochemical Society, Special Publication No. 8, pp 15-33.

Aizenshtat Z. and Amrani A.,(2004b) Significance of $\delta^{34}S$ and evaluation of its imprint on sedimentary organic matter II. Thermal changes of Type II-S Kerogens Catagenetic stage controlled mechanisms. Study and conceptual overview. In Hill, R.J. et al. (Eds.).Geochemical Investigations: A tribute to Isaac R. Kaplan, The Geochemical Society, Special Publication No. 8, pp 35-50.

POS1-3: The $\delta^{34}S$ values of the early-cleaved sulfur upon thermal alterations as determined by closed and open systems pyrolyses

A. Amrani[1], S.A. Ward[1], M. Lewan[2], Z. Aizenshtat[1]

1) Casali Institute of Applied chemistry and Department of Organic chemistry. The Hebrew University of Jerusalem, 91904 Jerusalem, Israel
2) U.S. Geological Survey, Box 25046, MS977, Denver, Colorado 80225, USA.

In the present study, we performed pyrolysis experiments under low temperatures (130-300°C) and used several pyrolysis methods (closed ampoules and continues-flow; hydrous and dry) on sulfur rich organic matter. These experiments are needed for better understanding of the kinetics that dominate thermal sulfur isotopic discrimination. Therefore, immature asphalts, kerogens (Senonian) and petroleum, from the Dead Sea area as well as synthetic sulfur cross-linked polymers (Krein and Aizenshtat, 1995; Amrani and Aizenshtat, 2004) and monomers were used for the experiments. In addition, we performed isotope-mixing experiments (closed ampoule) to demonstrate the active role of reduced sulfur species during heating experiments. The continues flow pyrolysis and the kinetic closed pyrolysis (up to 4 hours), showed that the early thermally released sulfur (H_2S) is isotopically much lighter in comparison to the unheated organic sulfur by 6-13‰. When reaction time is prolonged, (Fig.1) the isotopic differences are minimized. This is due to both isotopic mixing and release of heavier isotopes as the pyrolysis advances. Isotope mixing experiments conducted (200°C closed ampoule) between sulfur containing synthetic polymer with initial $\delta^{34}S_{VCDT}$ value of +3.5‰, and added aqueous ammonium sulfide solution (4 folds of sulfur content) with a distinct $\delta^{34}S$ of +33.3‰ showed that $H_2S_{(gas)}$-sulfur$_{(organic)}$- $H_2S_{(aq)}$ were partly isotopically mixed after 4 hours and were totally mixed after 48 hours pyrolysis. The character of the pyrolysis system is very important and is controlled by different parameters leading to significant changes in the $\delta^{34}S$ values for the obtained pyro-products open or closed systems. Open systems consist of vessels from which the volatile pyro-products can escape from the system thus, avoid secondary reactions. Closed systems are sealed environments that confine all reactants and products to a restricted volume. At the beginning, the thermal alteration the "closed" system is actually "open" because the pressure is still building up and there are minimal back reactions. Since the released sulfur species at elevated temperatures become chemically highly active (Krein and Aizenshtat, 1995), the type of reaction conditions is imperative. If the system, is totally open the kinetic control will be dominant leading to the highest isotope discrimination between the released sulfur species (e.g. H_2S) and the residual organic sulfur. In closed systems, the thermodynamic control will re-equilibrate all species, minimizing the isotope effect (Aizenshtat and Amrani, 2004b). The geological environment during the catagenetic stages is dominated by gradual temperature increase and sedimentary modifications. Generation and early migration of petroleum in the source rock and on its route to the reservoir is intermittently close or opened systems, i.e. differential removing of the early produced H_2S out of equilibrium hence increasing the isotopic discrimination recorded between kerogens, asphalts and oils.

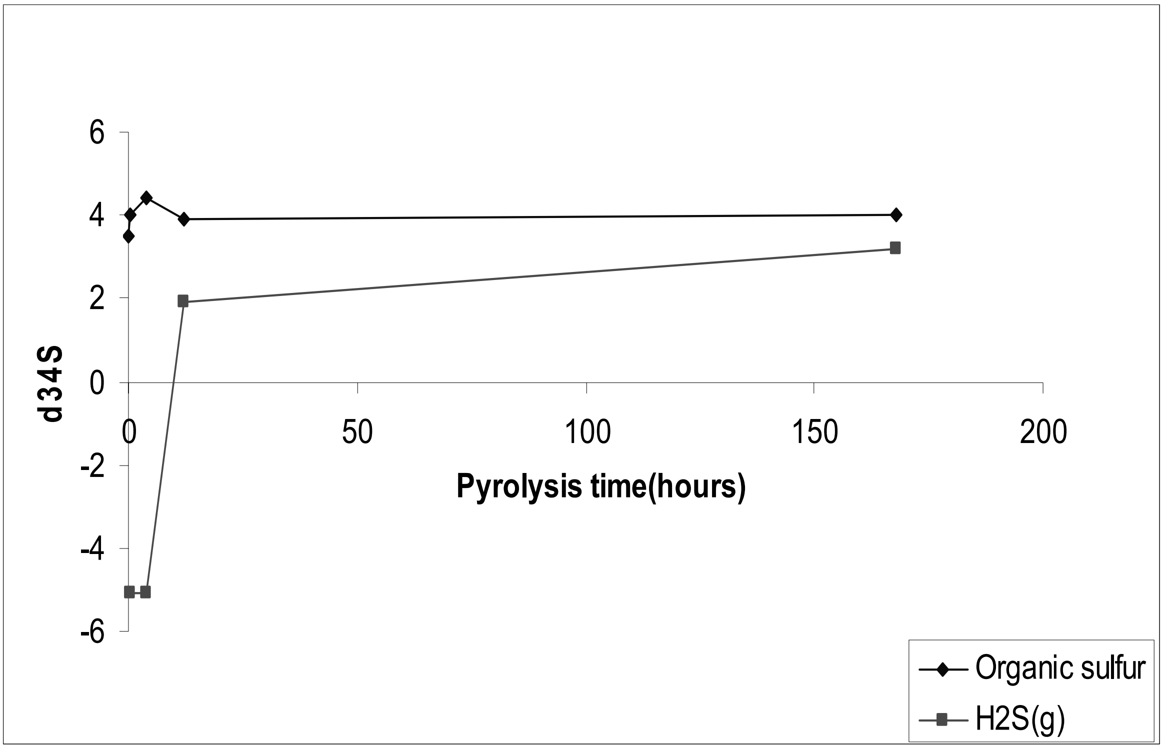


Fig.1. Kinetics of dry pyrolysis experiments (200°C), in closed ampoule for polysulfide cross-linked polymer with initial $\delta^{34}S$ value of 3.5‰

References

Aizenshtat Z. and Amrani A.,(2004) Significance of $\delta^{34}S$ and evaluation of its imprint on sedimentary organic matter II. Thermal changes of Type II-S Kerogens Catagenetic stage controlled mechanisms. Study and conceptual overview. In Hill, R.J. et al. (Eds.).Geochemical Investigations: A tribute to Isaac R. Kaplan, The Geochemical Society, Special Publication No. 8, pp 35-50.

Amrani, A. and Aizenshtat Z., (2004b) Reaction of polysulfide anions with αβunsaturated isoprenoid aldehydes in aquatic media: simulation of oceanic conditions. *Org. Geochem.* 35, 909-921.

Amrani, A. and Aizenshtat Z., (2004a) Mechanisms of sulfur introduction chemically controlled: $\delta^{34}S$ imprint. *Org. Geochem.* 35 1319-1336.

Krein E. B. and Aizenshtat Z. (1995) Proposed thermal pathways for sulfur transformation in organic simulation macromolecules: laboratory simulation experiments. In: Vairavamurthy, M. A., Schoonen, M. A. A. (Eds.) Geochemical Transformation of Sedimentary Sulfur. American Chemical Society Symposium Series 612, Washington, D.C. pp. 110-137.

POS1-4: Stable hydrogen isotope ratios of petroleum hydrocarbons to evaluate the thermal history of highly-mature and pre-Devonian sedimentary organic matter

D. Dawson, K. Grice, R. Alexander

Stable Isotope and Biogeochemistry Group, Centre for Applied Organic Geochemistry, Department of Applied Chemistry, Curtin University of Technology. GPO Box U1987 Perth, WA 6845, Australia (e-mail: d.dawson@curtin.edu.au)

Stable hydrogen isotope ratios of sedimentary hydrocarbons can provide information about the depositional environment associated with their precursors, reflecting the isotopic composition of meteoric (source) waters (e.g. [1]). This is based on the assumption that the δD signature of the precursor is preserved throughout sedimentation and the associated diagenetic processes leading to petroleum formation. It is thought that diagenetic effects over extended periods of geological time promote significant hydrogen exchange between organic hydrogen and surrounding environment (e.g. [2], [3]). Thermal maturation in particular has been found to play a significant role in the alteration of indigenous δD signatures ([4], [5]).

Recent work ([6]) demonstrates the use of δD values of sedimentary hydrocarbons (*n*-alkanes, pristane and phytane) to evaluate the maturity of a series of source-rocks (Early Triassic) and crude oils (Late Permian–Late Jurassic) from Western Australia. Distinct δD signatures were observed for immature source-rocks where pristane (Pr) and phytane (Ph) were significantly depleted in deuterium (D) relative to the *n*-alkanes. With increasing maturity the difference between the δD values of *n*-alkanes and isoprenoids reduces as Pr and Ph become progressively enriched in D. The *n*-alkane–isoprenoid δD signature of the crude oils, including one from a different source facies, was similar to mature-late mature source-rocks representative of the peak oil-generative window. The enrichment of D in isoprenoids was attributed to isotopic exchange associated with thermal maturation ([5], [6]). This work included a comparison of the δD values of Pr and Ph with the traditional maturity parameters Ts/Tm (18α(H)/ 17α(H)-trisnorhopane ratio) and R_e (equivalent vitrinite reflectance) (Fig. 1). The average δD values of Pr and Ph correlate well with $\%R_e$, as does Ts/Tm, clearly showing that the isotopic enrichment in isoprenoids is proportional to maturation.

The measurement of δD values of sedimentary hydrocarbons may be a useful maturity parameter which also accounts for source-effects ([6]). These measurements are currently being trialed on a series of Late Jurassic sediments covering a wide maturity range ($\%R_o$ = 0.6–1.6), as well as on several pre-Devonian sediments and crude oils, and a Proterozoic hydrothermal ore deposit. Preliminary data obtained for hydrocarbons from post-mature sediments (R_o = 1.6%) shows that the trend of enrichment of D in isoprenoids continues, indicating the measurements will be useful for highly-mature sedimentary organic matter. If successful, this new technique will prove useful in cases where biomarker maturity parameters are ineffective, e.g. at higher maturity levels (i.e. $\%R_o > 1$) where their associated reactants and products either equilibrate, or are thermally degraded. In addition, this new maturity measurement could be applicable to pre-Devonian sedimentary organic matter, unlike vitrinite reflectance which cannot be measured in pre-Devonian source-rocks because the higher-plant precursors of vitrinite had not yet evolved.

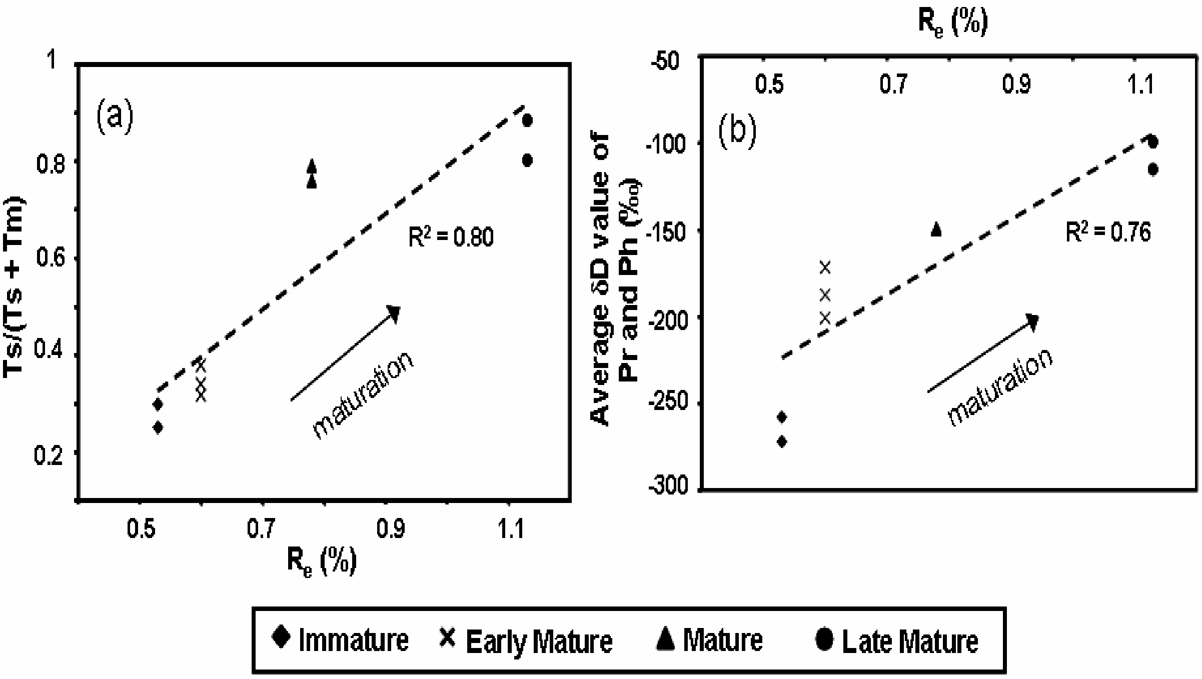


Fig.1. Plots of (a) Ts/Tm, and (b) average δD value of pristane (Pr) and phytane (Ph), versus the equivalent vitrinite reflectance (R_e) values for the Perth Basin sediments

References

[1] Dawson, D., Grice, K., Wang, S.X., Alexander, R., Radke, J., 2004. Stable hydrogen isotopic composition of hydrocarbons in torbanites (Late Carboniferous to Late Permian) deposited under various climatic conditions. Organic Geochemistry 35, 189-197.

[2] Alexander, R., Kagi, R.I., Larcher, A.V., 1984. Clay catalysis of alkyl hydrogen exchange reactions – reaction mechanisms. Organic Geochemistry 6, 755-760.

[3] Sessions, A.L., Sylva, S.P., Summons, R.E., Hayes, J.M., 2004. Isotopic exchange of carbon-bound hydrogen over geologic timescales. Geochimica et Cosmochimica Acta 68, 1545-1559.

[4] Rigby, D., Batts, B.D., Smith, J.W., 1981. The effect of maturation on the isotopic composition of fossil fuels. Organic Geochemistry 3, 29-36. 3, 29–36.

[5] Dawson, D., Grice, K., Alexander, R., 2005. Effect of maturation on the indigenous δD signatures of individual hydrocarbons in sediments and crude oils from the Perth Basin (Western Australia). Organic Geochemistry 36, 95–104.

[6] Dawson, D., Grice, K., Alexander, R., 2005. Stable hydrogen isotope ratios of sedimentary hydrocarbons: A potential method for assessing thermal maturity? The APPEA Journal, in press.

POS1-5: Kinetic simulating experiment on carbonate source rocks and the isolated kerogens

X. Geng, A. Geng, Y. Xiong, J. Liu,
H. Zhang, Q. Zhao

The State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Wushan, Guangzhou 510640, P.R. China (e-mail: gxinh@gig.ac.cn)

The thick marine carbonate rocks spread widely in China. It is characterized by low TOC, high maturity and long geological history. There is no obvious development in the exploration of oil & gas in the carbonate strata up to now. Therefore, more works are needed for the assessment of carbonate source rocks in China.

Previous works showed that rock matrix in shale has little effect on the parameters when determining overall pyrolysis kinetics and there is no difference between kinetic parameters determined on the whole rock and the isolated kerogen (Reynolds and Burnham,1995). What is the situation for carbonate rocks? Here is a primary answer.

A marine carbonate source rock sample for the simulating experiment was collected from the Lucaogou Formation in upper Permian of Santanghu basin, NW China. The basic geochemical data of the sample are as follows: Ro=0.53%, Tmax=441 ºC, S1+S2=22.01mg/g, HI=251mg/g. The total organic carbon of the kerogen isolated from the source rock is 62.7%.

The experiment was carried out in a pressurized closed experimental system. The prepared source rock sample and kerogen sample were sealed in gold tubes (40 mm×4 mm i.d.) charged with argon. Each of the gold tube was placed in a stainless steel autoclaves. The pressure was kept at 50Mpa. The temperature was programmed to increase at a rate of 2 ºC/h and the other at a rate of 20 ºC/h . For each of the two heating series, 10-100mg samples were loaded into gold tubes under anhydrous conditions.

The gas produced in the pyrolysis was divided into two groups: methane and C_{2-5}. The kinetic parameters were calculated through a special kinetics software. For methane generation, A is about $6.05\times10^{15}S^{-1}$ for the carbonate source rock and $4.80\times10^{15}S^{-1}$ for the isolated kerogen, while E is 45-69 kcal/mol (with main frequency at 69 kcal/mol) for the carbonate source rock and 44-68 kcal/mol (with main frequency at 68 kcal/mol) for the kerogen. As to the kinetic parameters of C_{2-5} hydrocarbon generation, A is $1.53\times10^{21}S^{-1}$ for the carbonate source rock and $1.06\times10^{21}S^{-1}$ for the isolated kerogen, while E is 57-78kcal/mol(with main frequency at 75 kcal/mol) for the carbonate source rocks and 65-75 kcal/mol(with main frequency at 75 kcal/mol) for the kerogen.

The values of kinetic parameters for the carbonate source rocks are a litter larger than that for the kerogen at the same experimental condition. Based on the calibrated kinetic parameters, a series of simulating calculations are carried out for the actual geological condition. A model to predict the methane and C_{2-5} generation is shown in Fig.1, calculated at a presumed geologic heating rates of 1.5 ºC/My. The result shows that there are some differences between the carbonate source rock and corresponding isolated kerogen in the cumulative fraction and generating rate. The carbonate source rock need higher temperature to generate gaseous hydrocarbons than the isolated kerogen. It is suggested that kerogen isolation may not be necessary to derive valid kinetic parameters if the catalytic effect of mineral is taken account.

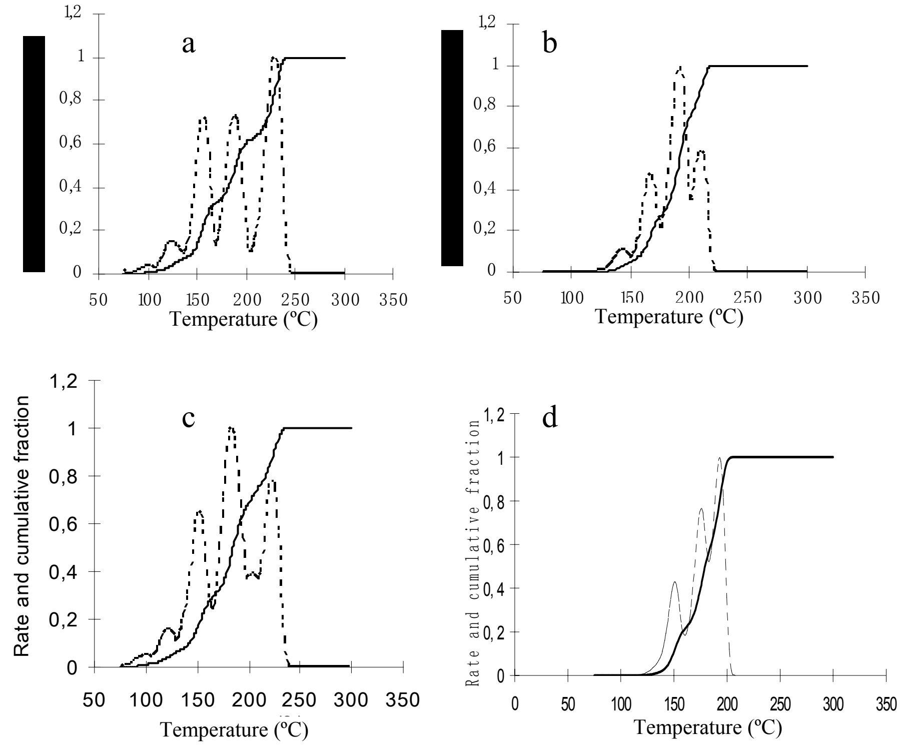


Fig.1. Relation of the temperature and cumulative fraction and generating rate: (a)C_1 from sourc rock; (b)C_{2-5} from sourc rock; (c)C_1 from kerogen; (d)C_{2-5} from kerogen

References

Reynolds J G. and Burnham A K. Comparison of kinetic analysis of source rocks and kerogen concentrates. Organic Geochemistry, 1995,23(1), 11-19.

POS1-6: Thermal effects of basaltic sill emplacement into source rocks on maturity & hydrocarbon generation

J.H. Hubred[1], D.A. Karlsen[1], S. Dahlgren[2]

1) Department of Geosciences P.O.Box 1047, Blindern, N-0316 Oslo, Norway (e-mail: jornar@geo.uio.no)
2) Norwegian Petroleum Directorate, P.O.Box 600, N-4001 Stavanger, Norway Present address: County councils of Buskerud, Telemark and Vestfold, Svend Foynsgt. 9 Fylkeshuset, N-3110 Tønsberg, Norway

In sedimentary basins sills have a tendency to become emplaced in litholgies of lower mechanical competence, like shales, which can possess source rock qualities.

In this study we have been investigating the thermal effects of thick sills on sedimentary rock units at Svalbard, Norway. We believe this study to be directly relevant for sills in large scale sedimentary basins. If sills were emplaced in contact with the source rocks at great burial depth a "source rock on a hot plate" type of situation could arise with a temperature-heat history quite unlike that of small dykes in shallow, water-rich sediments. An additional effect could be related to a regional increase in heat flow if the sills are in a sense "symptoms" of massive ingenious activity as known from other regions.

It is well proven that thin sills and dykes can locally mature source rocks, increase biomarker ratio in extractable compounds and at the same time cause systematic increases in kerogen maturity parameters. Since few organic geochemistry results on large scale sills have been published it was not clear to us if massive sills simply could be viewed as a upscalling phenomena of the smaller dyke and sill systems..

Samples were collected from eight different profiles with sills. The Triassic Botneheia black shale source rock formation, with dominantly marine kerogen, were collected from the hills of Botneheia (Central Spitsbergen), Teistberget (eastern Central Spitsbergen), Krefftberget and Høgrinden (Barentsøya Island). Samples were also collected from the Jurassic Janusfjellet black shale (with dominantly terrestrial kerogen) from Domen (eastern Central Spitsbergen) and the Wilhelmøya Island. Samples from identical black shale units in nearby sections not thermally affected by the sills were also collected and used for comparison.

Organic petrographical descriptions, vitrinite reflectance, Rock Eval, TC and TOC were determined on all 170 samples, whereas metamorphic phase petrology, EOM, Iatroscan TLC-FID, GC-FID, GC-MS and isotopic studies of C and O (in carbonates, kerogen and extracts) were conducted on 48 selected samples.

The vitrinite reflectance (%R_o) profiles show the typical inverted profile closer to the sills i.e. the vitrinite values are as low as 1.5 at 2m from a 23m thick sill, 5 at 5m, decreasing to 3.5 at 10 meters before reaching the background value of 0.8 at about 20m distance from the sill.

However, no trends in biomarker maturity of the extracts could be detected over the same profile. These results were in the beginning difficult to understand but lead us to suggest that the generative process caused violent mobilization of water, at the same time as generation of light hydrocarbons took place, transporting these light hydrocarbons away. Low maturity biomarkers have at a later stage back diffused from the lower maturity, unaffected shales into the thermally affected shales following cooling of the intrusions. The composition of generated hydrocarbons extracted from the rock samples indicates that hydrocarbon generation by sills may be a less than perfect analogue for "normal" hydrocarbon generation in subsiding basins.

Results from this study would not only be relevant for sill intruded sedimentary basins but would possibly also be relevant for deep water exploration e.g. the Atlantic volcanic margin were sediments have experienced increased heat flows due to magmatic underplating.

POS1-7: Relationship between TOC contents and palynofacies distribution of a paleogene section from Jequitinhonha basin, Brazil

T.R. Menezes[1], C.V. Araujo[2], O. Strohschoen Jr.[3], J.R. Maizatto[4], C.C. Lana[3]

1) Fundação COPPETEC, Av. 1, Qd 7, Ilha do Fundão, Rio de Janeiro, Brasil, CEP: 21949-900
(e-mail: taissar.Fundacao_Padre@petrobras.com.br)
2) GEOQ/CENPES/PETROBRAS, Av. 1, Qd 7, Ilha do Fundão, Rio de Janeiro, Brasil, CEP: 21949-900
3) BPA/CENPES/PETROBRAS, Av. 1, Qd 7, Ilha do Fundão, Rio de Janeiro, Brasil, CEP: 21949-900
4) Fundação FADESP, Av. 1, Qd 7, Ilha do Fundão, Rio de Janeiro, Brasil, CEP: 21949-900

This study comprises the analyses of total organic carbon, Rock-Eval pyrolysis, and palynofacies characterization in 150 cuttings samples from Paleogene section from two exploratory wells of Jequitinhonha Basin. The palynofacies characterization was based on quantitative analyses of the particulate organic matter. Additional palynological and paleobathymetric analyses based on foraminifera were carried out to paleonvironmental assesment of the section.

Four and three palynofacies association were identified in the wells 1 and 2, respectively: The *palynofacies association 1* (Paleocene) presents the highest relative amounts of equant-opaque phytoclasts. Fewer sporomorphs (dominated by pollen grains) and dinoflagellates, non-fluorescent amorphous organic (AOM) were identified, as well as moderate percentage of non-opaque-biostructured phytoclasts. The *palynofacies association 2* (Paleocene in well 1 and Oligocene-Eocene in well 2) reveals a more mixed composition (non-opaque- bioestructured phytoclasts + opaque phytoclasts), and a lower relative amount of AOM and palynomorphs. In the *Palynofacies associations 3 and 4* (Eocene in well 1 and Oligocene in well 2) there is a predominance of non-opaque phytoclasts and an increase of non-fluorescent AOM, sporomophs (dominated by spores), marine microfossils (dinoflagellates and prasynophites) and fungal remains.

The TOC contents of the section from well 1 vary from 0.16 to 1.6%, and TOC values from well 2 vary from 0.23 to 2.48%, with the highest values corresponding to the samples with predominance of refractory material. The Hydrogen Indices are low and Oxygen Indices are high ranging from 48 to 283 mg CO_2/g and 96 to 336 mg CO_2/g, respectively, characterizing the abundant terrestrial organic matter input to the sections and indicating poor hydrocarbon source rock characteristics.

The studied sections represent a marine paleoenvironment with a strong terrigenous influence according to the palynofacies results. This interpretation is supported by the foraminifera data which point to upper/middle bathyal conditions. Selective preservation of phytoclasts seems to reflect the proximal-distal depositional trend in the studied section, corroborated by the varying proportions of main palynomorph groups.

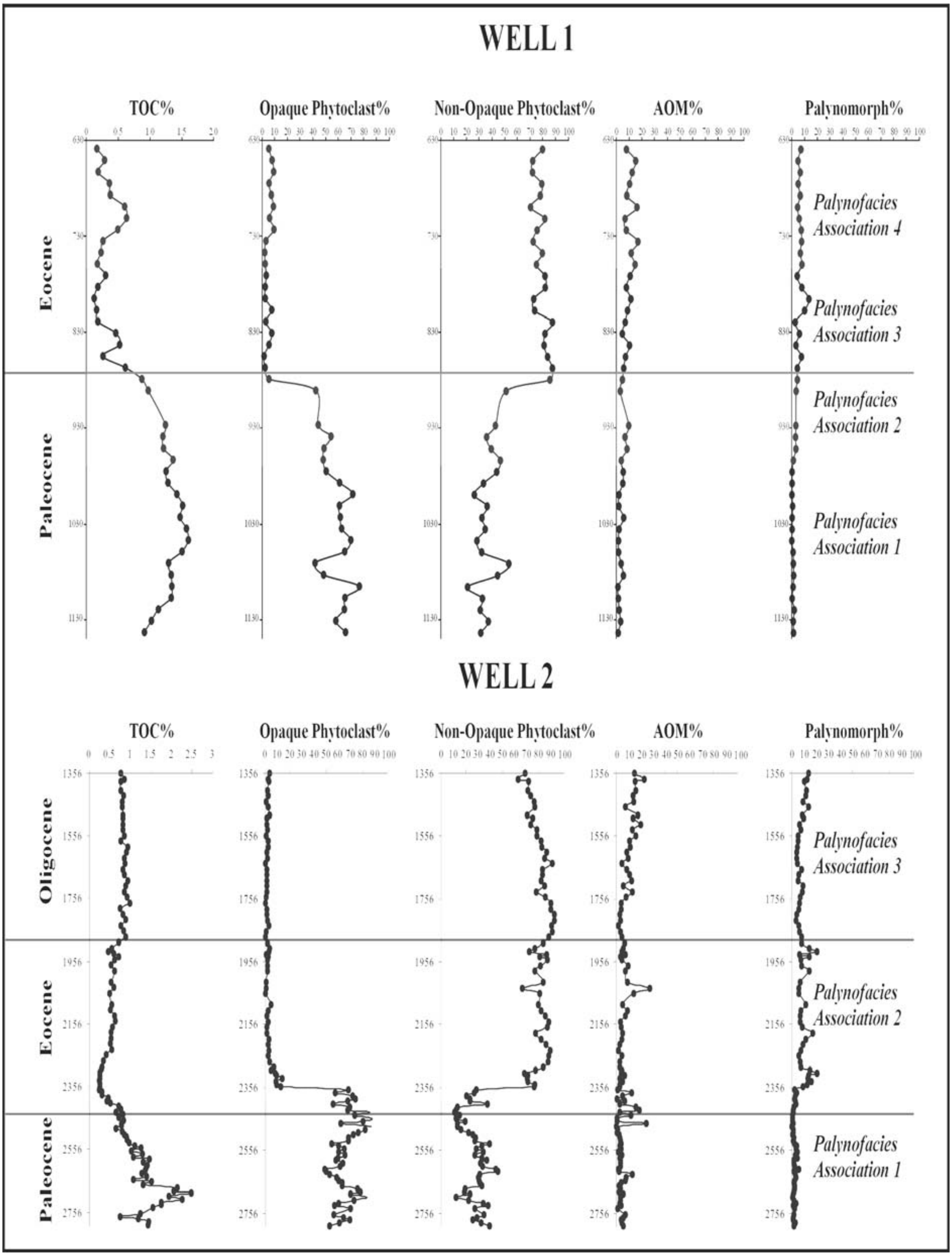


Fig.1. Palynofacies and geochemical parameters from studied sections from Jequitinhonha basin

POS1-8: Hydrocarbon generation in high thermal maturity samples

L.R. Snowdon[1], L.D. Stasiuk[2]

1) Snowdon Research Ltd., 4904 Brockington Rd. NW Calgary, Alberta Canada T2L 1R6 (e-mail: Snowdon_research@shaw.ca)
2) Geological Survey of Canada, 3303 – 33rd Street NW, Calgary, Alberta Canada T2L 2A7

Nine high thermal maturity coals and coaly samples (random vitrinite reflectance values of 1.3% - 3.6% Ro_R) from diverse geographic areas have been pyrolyzed to 800 °C in a Rock-Eval® 6 instrument to determine their residual hydrocarbon generation potential. Hydrocarbon yields (S2) ranged from 3.5 mg HC/g rock (Ro_R = 1.7%, TOC = 16%) to 130 mg HC/g rock (Ro_R = 1.35%, TOC = 71%) when the maximum pyrolysis temperature was set at 800 °C. The highest maturity sample in the set (Ro_R = 3.6%, TOC = 81%) yielded 11.3 mg HC/g rock, a value comparable to a reasonable petroleum source rock.

All of the samples provided a well defined S2 peak (Fig. 1) with reproducible temperatures at the maximum generation rate (Tpeak) for heating rates ranging from 25 °C/min to 2 °C/min. At a heating rate of 25 °C/min, Tpeak values ranged from 518 to 660 °C. Tpeak is used rather than Rock-Eval® Tmax because the temperature errors of the latter are unknown at very high temperatures whereas the measured temperatures of the Rock-Eval® 6 instrument are considered to be accurate because of the geometry of the pyrolysis oven. Tpeak increases systematically with increasing reflectance up to about 2.6% Ro_R, after which Tpeak remains approximately constant at 660 °C. This suggests that the chemical structures being thermally degraded to release the volatile products observed in the FID (flame ionization detector) are essentially similar in all samples above 2.6% Ro_R.

A single rock sample (Ro_R = 2.2%, TOC <1%), known to have Type III kerogen, yielded a Tpeak of 760 °C at a heating rate of 25 °C/min. The FID trace shows a narrow, well defined, high temperature peak following a broad, multi-modal hydrocarbon yield at lower pyrolysis temperatures. Coincident with this high temperature hydrocarbon peak, the infrared detector shows a CO_2 peak resulting from the decomposition of carbonate minerals. Thus the very high temperature hydrocarbons are interpreted to be the result of the release of volatile hydrocarbons due to the thermal decrepitation of fluid inclusions from the carbonate.

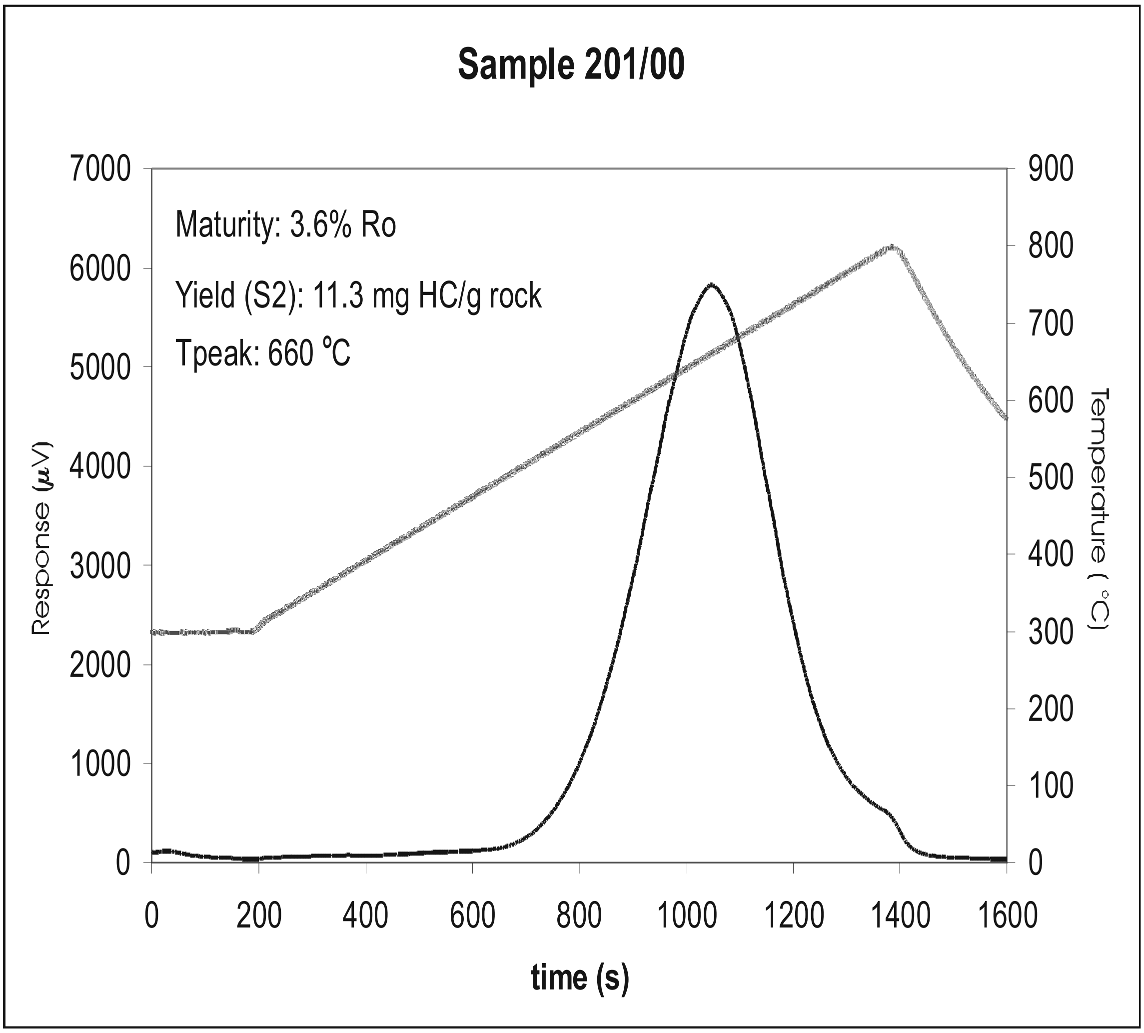


Fig.1. Rock-Eval 6 FID trace from 300 °C to 800 °C for a high maturity coal sample

POS1-9: Comparative characteristic of nitrogen compounds in oils and dispersed organic matter of Upper Jurassic rocks in the Southeast of West Siberia

S.S. Yanovskaya, T.A. Sagachenko, O.V. Serebrennikova

Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences, 3, Academichesky Avenue, 634021, Tomsk (e-mail: dissovet@ipc.tsc.ru)

Detailed information about compositions of oils and dispersed organic matter (DOM) in source rocks is considered as an important part of the complex studies aimed to solve the problem of oil origin, to estimate oil-and-gas content in separate territories and to predict qualitative compositions of hydrocarbon fluids in exploratory areas. The paper presents the results obtained in the study of regularities of nitrogen compounds (NC) distribution in oils and DOM of Upper Jurassic rocks located in the southeast of West Siberia. The features of NC structure and distribution are used to characterize evolutionary stages of oil generation (Vinogradova T.L. et al., 2002) and processes of initial and secondary migrations (Yamamoto M, 1992; Larter S. R. et al., 1996). Upper Jurassic deposits are considered as the basic source formations in West Siberia.

We have studied 35 rock samples and 12 oil samples recovered from the corresponding areas. The samples under study were confined to different tectonic zones. They also differed in depth of occurrence of enclosing sediments and in pristane-phytane ratio (Pr/Ph). Bitumoids differed in maturity (from anomalous high maturity to immature) and in a type of the initial organic matter (sapropelic and humus).

NC occurring in rock DOM and oils were presented by basic, weak-basic and neutral substances. The content of NC of all types was higher in DOM as compared with that in oils. It may probably be associated with adsorption of a part of polar compounds on the rock at the initial migration (Yamamoto M, 1992). The analysis of NC distribution in DOM and oils in the territory under study showed that the concentration of organic NC was higher in the samples occurring in the в arch limits as compared with those confined to depressions.

Redox conditions in sedimentation basin were found to affect NC distribution in oils and in rock DOM. For DOM we determined direct relation between the content of nitrogen-containing components of all types and the values of this quantity. As to oils the relation was inverse.

NC content in DOM of sapropelic type was on average lower as compared with that in DOM of humus type. The highest concentration of nitrogen-containing components was observed in bitumoids of moderate maturing. The highest portion of bases was found in the samples of high maturing.

Low-molecular nitrogen bases were separated from DOM and oils using a solution of sulphuric acid in acetic acid, where the ratio of mineral and organic acids and water was equal to 26: 60: 15 (% wt.). The concentrates were separated by liquid-adsorption chromatography on silicic acid. Compound desorptions were carried out with hexane-toluene (1:1), toluene, toluene-diethyl ether and alcohol-toluene (1:1).

It has been determined that both in oils and DOM low-molecular nitrogen bases are presented with strong- and weak-basic components. Their content in oils is lower as compared with that in DOM. General character of chromatographic fractionation of the separated compounds testifies to similarity of qualitative compositions of low-molecular nitrogen bases in oils and in DOM. Nitrogen compounds of the two first fractions are presented with strong bases only. A major portion of these compounds contains a screened nitrogen atom and is concentrated in the least polar fraction. Weak bases are predominantly eluted with toluene-diethyl ether mixture. According to the data of non-aqueous potentiometric titration and of high-grade IR-spectroscopy strong bases in oils and DOM are presented with pyridine benzologues, whereas weak bases contain amides and nitrogen-containing acids. Oils and DOM differ in the contents of different types of low-molecular nitrogen bases.

References

Vinogradova T.L., Chakhmachev V.A., Agafonova Z.G., Yakubson Z.V. (2001). Hydrocarbon and heteroatomic compounds – indicators of thermal maturity of organic matter in rocks and naphthides. Oil and Gas Geology. № 6. P. 49 – 55.

Yamomoto M. (1992). Fractionation of azaarenes during oil migration. Organic Geochemistry. V. 19, P. 389 – 402.

Larter S.R., Bowler B.F., Li M., Chen M., Brincat D., Bennett B., Noke K., Donohoe P., Simmons D., Kohnen M., Allan J., Telnaes N., Horstad I. (1996). Molecular indicators of secondary oil migration distances. Nature. V. 383. P. 593 - 597.

POS1-10: Detailed Geochemical Evaluation Green River Shale core: implications for an unconventional source of hydrocarbons

B.M. Jarvie[1], D.M. Jarvie[1], H. Alimi[1], C. Jiang[1], J.D. Burgess[1], R.J. Drozd[1], R.J. Hill[2]

1) Humble Geochemical Services, P.O. Box 789, Humble, TX 77338 USA
2) US Geological Survey, Box 25046 Denver Federal Center MS 939 Denver, CO 80225 USA

Oil shale resources are significant world wide and have been utilized in Russia and Germany as an energy source, although in the United States, exploitation has been limited. A large effort was undertaken in the 1970's and 1980's to develop the Eocene Green River Shale oil-shale resources in the US, but low oil prices rendered the resource uneconomic. Work at Lawrence Livermore National Laboratory showed the impact of the inorganic matrix on the decomposition rates, product yield and type of products that could be generated during oil-shale retorting, but only limited evaluation of the detailed organic and inorganic geochemical characteristics of the Green River Shale are available (Horsfield et al., 1995 and Ruble et al., 2001).

Detailed geochemical analyses of the Green River Shale were performed on a full core of the Lower Green River Formation (1200 ft.) taken from Chevron Marsing #16 well. This well was drilled in Wasatch County, Utah in the southwestern Uinta Basin. Detailed lithofacies, depositional sequences, and stratigraphy were published by Wiggins and Harris (1996). The objectives of this study are to detail the entire Green River section by classical geochemical methods comparable to those used by Horsfield et al. (1994) and to evaluate the implications of geochemical variations for development of the Green River Shale as an unconventional resource.

Samples were taken from the core at discrete intervals, although coal lenses and unusual features were also sampled. Five coal lenses in the core allowed the thermal maturity to be measured with a high degree of certainty. The samples were analyzed for total organic carbon (TOC) and Rock-Eval parameters and a geochemical log of oil yields and hydrogen indices generated (Figure 1).

Based on the screening results additional samples were taken for solvent extraction and the extracted rock analyzed for kinetic parameters using the single run approach of Waples (2002) followed by multiple heating rate analyses and processing in discrete and Gaussian models and with specific activation energy and Arrhenius factor pairs for each 10% reacted (Friedman, 1963; Dieckmann, 2005).

Solvent extracts were fingerprinted and paraffin envelopes as well as peak ratios showed considerable variation. Pristane-to-phytane ratios varied from 0.50 to 1.75. Paraffin profiles ranged from unimodal to trimodal. Sandy intervals were much less complicated having a unimodal, primarily n-paraffin distribution. Biomarker results showed that *b*-carotane was present in most, but not all samples. In the marginal lacustrine sequence the *b*-carotane yields showed inverse correlation to oxygen indices.

Light hydrocarbon data generated from microscale sealed vessel (MSSV) maturation shows distinct differences in various organofacies of the GRS. Enhanced aromaticity (toluene/n-C_7) was noted in select samples. These data as well as biomarker and nitrogen data reflect not only differences in the organofacies, but also variable mineralogy and depositional environments. Combining the organic geochemical results with mineralogical data will further enhance the understanding of the Green River petroleum system and its development in the United States as a source of oil and gas.

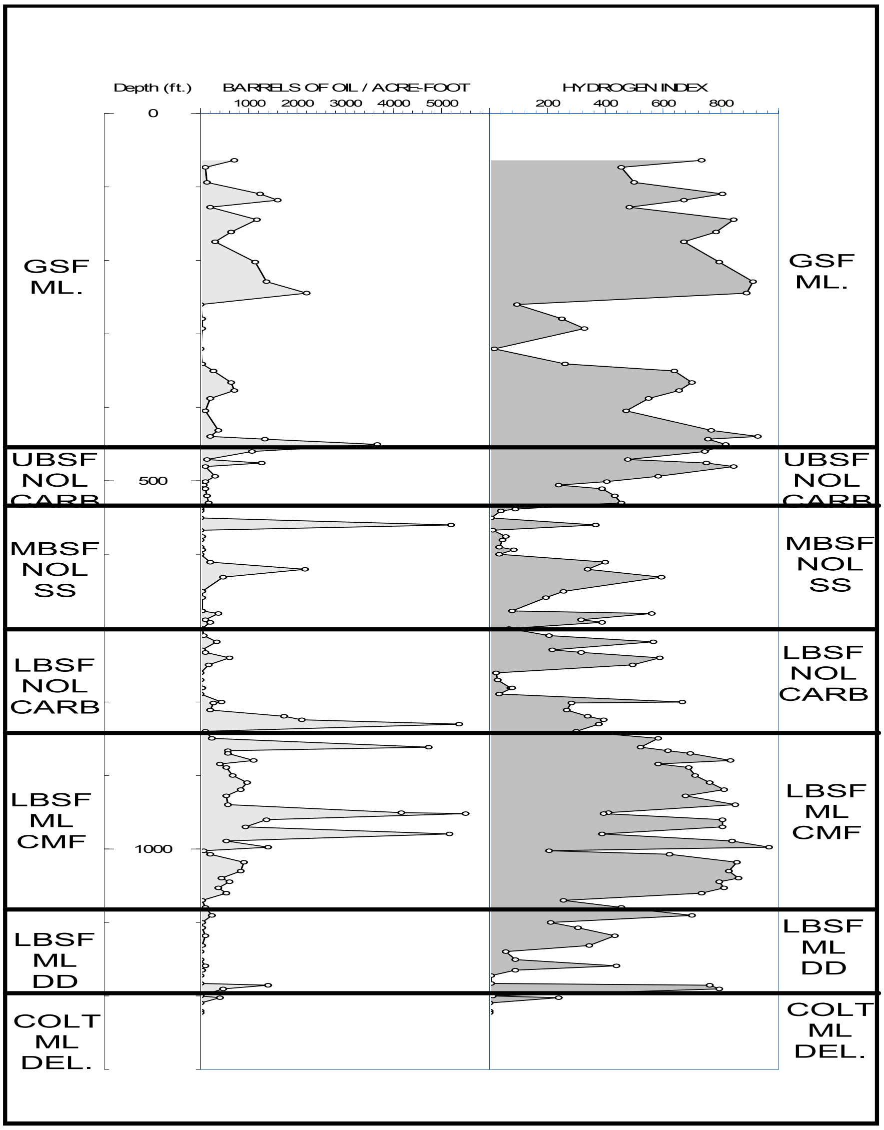


Fig.1. Chevron Marsing #16 well profile showing calculated hydrocarbon yields from Rock-Eval S2 converted to barrels of oil per acre-foot and hydrogen indices. Abbreviations for units and depositional environment are: GSF ML = Green Shale Facies Marginal Lacustrine; UBSF NOL CARB = U. Black Shale Facies Nearshore Open Lacustrine Carbonate; MBSF, NOL, S = M. Black Shale Facies, Nearshore Open Lacustrine, Sand; LBSF NOL CARB = L. Black Shale Facies; LBSF ML CMF = L. Black Shale Facies, Marginal Lacustrine, Carbonate Mud Flat; LBSF ML DD = L. Black Shale Facies, Marginal Lacustrine, Distal Deltaic; COLT ML D = Colton, Marginal Lacustrine, Deltaic

References

Burnham, *A. K.,* R. L. Braun, T.T. Coburn, E.I. Sandvik, D. J. Curry, B.J. Schmidt, R.A. Noble, 1996, An Appropriate Kinetic Model for Well-Preserved Algal Kerogens, *Energy Fuels*, No. 10, pp. 49-59.

Dieckmann, V., 2005, Modelling petroleum generation from heterogeneous source rocks: The influence of frequency factors on activation energy distributions and geological predictions, Marine and Petroleum Geol., *in press.*

Friedman, H.L., 1963, Kinetics of Thermal Degradation of Char-Forming Plastics from Thermogravimetry. Application to a Phenolic Plastic, Jour. Polymer Sci., No. 6, pp. 183-195.

Horsfield, B., D.J. Curry, K. Bohacs, R. Littke, J. Rullkotter, H.J. Schenk, M. Radke, R.G. Schaefer, A.R. Carroll, G. Isaksen, and E.G. Witte, 1994, Organic geochemistry of freshwater and alkaline lacustrine sediments in the Green River Formation of the Washakie Basin, Wyoming, U.S.A., Org. Geochem., Vol. 22, No. 3-5, pp. 415-440.

Ruble, Tim E., Lewan, M. D., and Philp, R. P., 2001, New insights on the Green River petroleum system in the Uinta basin from hydrous pyrolysis experiments, AAPG Bulletin, Vol. 85, No. 8 (August 2001), pp.1333-1371.

Waples, D.W., J. Pacheco, and A. Vera, 2002, A new method for kinetic analysis of source rocks: development and application as a thermal and organic facies indicator in the Tithonian of the Gulf of Campeche, Mexico, 8th Latin American Congress on Organic Geochemistry, Cartegena, Colombia, October 20-24th, 2002, Abstracts Book, pp. 296-298.

Wiggins, W.D. and P.M. Harris, 1994, Lithofacies, Depositional Cycles, and Stratigraphy of the Lower Green River Formation, Southwestern Uinta Basin, Utah: Notes for SEPM Core Workshop—Lacustrine Source-rock Depositional Environments, AAPG Annual Meeting, 22 p.

POS1-11: Formation of organic matter from the Upper Jurassic oil shales of Sysola shale-bearing basin (Russia)

N.S. Burdelnaya, D.A. Boushnev

Institute of Geology of Komi SC RAS, Russia (e-mail: burdelnaya@geo.komisc.ru)

The aim of the present work is the study the OM composition of J_3v_2 of the sediments with different TOC in the rocks from outcrops of oil shale deposits of the Sysola shale-bearing region. TOC content changes from 0.2 to 40.8 %. The analysis of hydrocarbon fraction of bitumen reveals the presence of two maximums of *n*-alkanes – low-molecular C_{15}-C_{19} are characteristic for sapropelic OM accumulated in sea basin, and the predominance of C_{27}-C_{31} *n*-alkanes, characteristic for humic continental OM. Low/high-molecular H/C ratio is low which testifies to the proximity of the sea palaeobasin to the source of terrigenous OM. From the distribution of ααα20R steranes of the saturated bitumen fraction two types of facies can be determined where OM, deposited in open sea conditions, and OM, deposited in bay or estuarine, accumulated (Fig. 1).

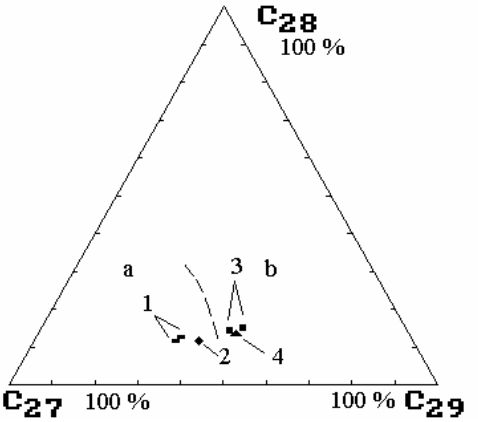


Fig.1. Triangular diagram showing proportions of C_{27}, C_{28} and C_{29} regular steranes in two facies Sysola shale-bearing basin (Russia): a – OM, deposited in open marine conditions; b – OM, deposited in bay (1 – Koygorodok, 2 – Sinegor'e, 3 – Vazhyu, 4 – Ib)

The lower values of the pristan/phytan indicate that a reduction conditions play an important role during deposition of the oil shales. The aromatic fraction analysis reveals the derivatives of isorenieratene which is a specify indicator anoxic water column that extended into photic zone. In the composition of clayey rocks bitumen the low-molecular monoaromatic derivatives of isorenieratene are determined; in the composition of oil shales di- and triaromatic derivatives with a higher molecular weight are marked; and also the isorenieratene is determined – the saturated analogue of isorenieratene, which testifies to weak destructive-transforming processes characteristic of low TOC sedimentation.

The results of the element analysis reveal the kerogen of type II (Vazhyu, Koygorodok) and type II-III (Ib, Sinegor'e). Due to S_{org}/C_{org} ratio exceeds 0.04 the kerogen is related to type II-S (see the table).

Table. Bulk data of samples investigated

sample	Kgs	V-1/2	V-1/3	V-1/5	V-1/7	V-2/3/1	V-2/4/1	K-1/1	K-/3/2	K-1/5/2	S-6/8
Litology	Oil shale	Clayey shale	marl	Oil shale	Bituminous shale	Shale Clay	Carbonate shale	Clayey Shale	Oil shale	Shale clay	Oil shale
section	Ib	Vazhyu	Vazhyu	Vazhyu	Vazhyu	Vazhyu	Vazhyu	Koygo-rodok	Koygo-rodok	Koygo-rodok	Sinegor'e
C_{org}, %	35.34	9.13	2.68	33.55	16.98	3.74	19.27	12.11	20.80	5.57	23.00
H/C	0.85	1.34	1.24	1.26	1.35	1.06	1.12	1.37	1.19	1.51	0.93
S_{org}/C_{org}	0.047	0.032	0.050	0.063	0.045	0.021	0.032	0.039	0.039	0.044	0.027

The results of the quantitative analysis of kerogen pyrolysis products from the Upper Jurassic shale-bearing strata with different TOC concentrations, reveal a regular change of pyrolysate composition and TOC concentration alteration in the initial rocks. Thus, while changing TOC from 1 to 40.8% a sharp increase of thiophene index occurs – which is an indicator of content of organic sulfur in the structure of kerogen. Simultaneously a linear increase of relation 2,5-DMT/(2-ET+2,3-DMT+2,4-DMT) occurs, that is the part of so called "linear short-chain thiophenes". Parallel to this, together with TOC increase the linear decrease of absolute values of *n*-alkyl aliphatic structures is observed which testifies to decreasing concentration of lipid components of kerogen together with the TOC rise. We have also determined a regular change of the content of sulfurous components in pyrolysate products of kerogen together with TOC rise in rocks. Among the organic sulfur compounds *n*-alkylthiophenes predominate. In the rocks with the greatest TOC bi- and tricyclic structures predominate which contain thiophene and aromatic cycles which is related to the change of direction of thermal destruction of organic sulfur fragments of the kerogen with the rise of the quantity of sulfide bridges.

Thus, it can be supposed that 1) the shale-bearing sediments formation is connected with coastal regions which are the sources of terrigenous removal; 2) the presence of anoxic conditions together with a high bioproductivity during sedimentation in the Sysola depression resulted in shale-bearing sediments formation; 3) a high sulfur content of OM is connected with the preservation of the given OM in the conditions of early diagenetic intensive sulfurization.

Acknowledgements

This work is supported by RFBR grant (05-05-65018) and "Russian Science Support Foundation".

POS1-12: Organic geochemical study of sediment from Sangkarewang formation, West Sumatra, Indonesia

R.Y.P. Burhan[1], S.R. Putra[1], Y. Zetra[1], F. Riandra[2]

1) Chemistry Department, Sepuluh Nopember Institute of Technology, Kampus ITS Keputih, Surabaya 60111, Indonesia (e-mail : pburhan@chimie.its.ac.id)
2) Research Institute of Petroleum Exploration and Development "LEMIGAS", Jakarta, Indonesia

Introduction

The Ombilin basin, West Sumatra, Indonesia is a Tertiary intermountain basin located within the Barisan Mountain Range of West Sumatra. The oldest Tertiary unit, the Sangkarewang formation, presumably in Paleocene age, consists of lacustrine shales, where fish fossils have been found. The basin is well known for coal mining carried out since 1891 in Sawahlunto area [1]. The stratigraphic description estimated that the Ombilin basin may have received up to 4600 m of Tertiary sediments during its depositional history. These sediments were deposited in a stable lacustrine environment, which were significant for the hydrocarbon potential since lacustrine rocks are known to be excellent oil source rocks in many other basins worldwide [2]. The aim of the present study is to confirm the source of the organic matter, investigate the palaeoenvironmental conditions, to understand the transformation which occurs at the molecular level. So, we can consider that the Ombilin basin has a great potential and commercial values.

Results and discussion

Two sediments from Sangkarewang formation have been selected. They are sediments from Sitangkai and Kolok Tengah. The shale of Sitangkai has total organic carbon (TOC) of 4.03 %, hydrocarbon source potential (S_2 from Rock-Eval pyrolysis) 16.32 kg HC per ton rock and hydrogen indices (HI) 405 mg HC per g TOC, potential yield (PY) 16.90. And the shale of Kolok Tengah with TOC 2.88 %, S_2 7.54 kg HC per ton rock and hydrogen indices (HI) 262 mg HC per g TOC, potential yield (PY) 7.61. This indicates that the sediments from Sangkarewang formation have a great potential as a hydrocarbon source [3].

The organic matter from two samples of sediments were extracted and fractionated into different classes of components. GC-MS analysis revealed that both samples contain the *n*-alkanes distributions range from C_{14} to C_{35}, and pristane/phytane (Pr/Ph) ratios is 2.47 for Sitangkai and 3.27 for Kolok Tengah. The alkane distribution and Pr/Ph ratios suggested that the predominance of the biomass indicated lacustrine source for the oils as results of algal degradations [4].

The pentacyclic terpanes distributions ranges from C_{27} to C_{32}. These terpanes constitute of hopanoid derived from bacterial origin which related to depositional conditions in lake. These terpanes revealed that there was a weaker terrestrial influence on the depositional environment. The large predominance of the C_{30} $\beta\alpha$-hopane homologue in the hopane distribution points out to highly functionalized precursors abundant in methanotrophic bacteria [5]. And lower thermal maturity of the sediments reveal the characteristics of coal formation or sediments associated with the coal. The geochemical characteristics of the sediments shows that they will be thermally mature and finally considered to have potential values.

Conclusions

The studies of the organic matter from the Sangkarewang Formation sediments have reveals high amounts of hydrocarbon source potential. The *n*-alkane and hopanoid contents reflects that the sediments are in the start of the oil window and in a high thermal maturity. These sediments is considered to have great potential and commercial values

References

[1] Koning, T. (1985) Petroleum geology of the Ombilin intermontane Basin, West Sumatra, Proc. 14th Indonesian Petroleum Association Convention, Jakarta, 117-140

[2] Fouch, T. D. (1982) Character of ancient petroliferous lake basin s of the world, AAPG Bull., 66, 1680-1681

[3] Petersen, H. I. Nytoft, H. P. and Nielsen, L. H. (2004) Characterisation of oil and potential source rocks in the northeastern Song Hong Basin, Vietnam : indications of a lacustrine-coal sourced petroleum system, Org. Geochem., 35, 493 - 515

[4] Pang, X., Li, M. Li, S., Jin, Zh., Xu, Zh. and Chen, A. (2003) Origin of crude oil in the Jinhu Depression of North Jiangsu-South Yellow Sea Basin, Eastern China. Org. Geochem.,34, 553-573.

[5] Neunlist, S. and Rohmer, M. (1985) Novel hopanoids from the methyotrophic bacteria Methylococcus capsulatus and Methylomonas methanica. (22S)-35-aminobacteriohopane-30,31,32,33,34-pentol and (22S)-amino-3β-methyl bacteriohopane-30,31,32,33,34-pentol. Biochem. J., 231, 635-639

POS1-13: Organic matter maturation and the acquisition of chemical remanent magnetizations in the Sawtooth Mountains, Montana

M.H. Engel[1], R.D. Elmore[1], V.J. O'Brien[1], L.A. Totten[1], K. Imbus[2], J.E. Zumberge[2]

1) School of Geology & Geophysics, University of Oklahoma, Norman, OK 73019 USA
2) GeoMark Research, 9748 Whithorn Dr., Houston, TX 77095 USA

The occurrence of chemical remanent magnetizations (CRMs) in sedimentary rocks affords a unique opportunity to constrain the ages of post-depositional events such as fluid migration (e.g. Blumstein et al., 2005), organic matter maturation (e.g. Blumstein et al., 2004) and illitization (e.g. Gill et al., 2002; Woods et al., 2002). This is because pole positions determined for the CRMs can be interpreted with respect to the apparent polar wander paths that have been established for the continents (e.g. Van der Voo, 1993) for the Phanerozoic.

Whilst pervasive CRMs in mountain belts have been commonly attributed to orogenic fluids (e.g. Oliver, 1992), alternative mechanisms have been sought for regions where no obvious connection exists (e.g. Elmore et al., 2001). Here we report the results of a combined organic geochemical and paleomagnetic study in an attempt to determine the causes of CRMs in an eastern region of the northern Cordillera in North America. The Sawtooth Mountains occur within the Disturbed Belt in northwestern Montana and consist of a series of thrust faulted and folded sediments (Precambrian to Cretaceous in age). Cretaceous age organic-rich shales (Blackleaf Formation, Marias River Shale, Telegraph Creek Formation) and organic-rich, *in situ* carbonate concretions within the shales were collected from outcrops in the region. Samples were also collected from the Ellis Group (Jurassic), the Madison Group (Mississippian) and the Jefferson Formation (Devonian). Organic matter type, maturity and source rock potential were determined by Rock-Eval pyrolysis, biomarker distributions (GC/MS) and stable carbon isotopes. Paleomagnetic, rock magnetic and petrographic analyses were performed on the same sets of samples.

Based on Rock-Eval (Tmax) and biomarker ratios (e.g. C_{30} Dia/C_{30} hopanes vs C_{27} Dia/C_{27} regular steranes, C_{27} Ts/Tm vs C_{29} Ts/Tm), it appears that sample thermal maturity increases towards the mountain front. Although preliminary results indicate the presence of CRMs in samples of both lower and higher maturity, magnetic intensity is higher in the latter, indicating a possible connection with organic matter maturation. Whilst the role of orogenic fluids and clay diagenesis on the precipitation of authigenic magnetic mineral phases can not be entirely excluded at this time, the results of this study support previous observations that a complex interplay involving organic matter maturation may play an important role in magnetite authigenesis. If true, then the timing of organic matter maturation will be able to be constrained by the paleomagnetic method proposed herein. Establishing the timing of diagenetic events will be very beneficial for ongoing hydrocarbon exploration in this region.

References

Blumstein, A.M., Elmore, R.D., Engel, M.H., Elliot, C. and Basu, A. (2004) Paleomagnetic dating of burial diagenesis in Mississippian carbonates, Utah. J. Geophys, Res. 109, B04101,doi:10.1029/2003JB002698,2004.

Blumstein, R.D., Elmore, R.D., Engel, M.H., Parnell, J. and Baron, M. (2005) Date and origin of multiple fluid flow events along the Moine Thrust Zone, Scotland. Jour. Geol. Soc. London, in press.

Elmore, R.D., Kelley, J., Evans, M. and Lewchuk, M. (2001) Remagnetization and orogenic fluids: Testing the hypothesis in the central Appalachians. Geol. J. Int. 144, 568-576.

Gill, J.D., Elmore, R.D. and Engel, M.H. (2002) Chemical remagnetization and clay diagenesis: testing the hypothesis in the Cretaceous sedimentary rocks of northwestern Montana. Physics and Chemistry of the Earth 27, 1131-1139.

Oliver, R. (1992) The spots and stains of plate tectonics. Earth Sci. Rev. 2, 77-106.

Van der Voo, R. (1993) Paleomagnetism of the Atlantic, Tethys and Iapetus Oceans. Cambridge Univ. Press, Cambridge, p. 78.

Woods, S., Elmore, R.D. and Engel, M.H. (2002) Paleomagnetic dating of the smectite to illite conversion: Testing the hypothesis in Jurassic sedimentary rocks, Skye, Scotland. J. Geophys, Res. 107, 10.1029/2000JB000053.

POS1-14: Experimental generation and transport of petroleum in oil shales

E. Eseme, R. Littke, B.M. Krooss, J. Schwarzbauer

Institute of Geology and Geochemistry of Petroleum and Coal, Aachen University, Lochnerstr. 4-20, D 52056 Aachen, Germany (e-mail: eseme@lek.rwth-aachen.de)

Cylindrical plugs of Permian to Miocene lacustrine and shallow marine oil shales (Torbanite, Messel, Himmetoglu, Condor and Posidonia) were subjected to unconfined compaction tests with maximum temperatures of 350°C and axial loads of 8 MPa. These samples were characterised alongside corresponding original samples. Integrated geochemical and petrologic techniques were employed in order to assess the response of their organic matter to thermal stress and evaluate the transport of mobilised organic matter within the matrix in bulk rock samples. Infra-red spectroscopy revealed that little changes occurred in the organic matter which is dominated by functional groups characteristic of types I and II kerogen. This observation is consistent with the findings of previous studies on kerogen. Principal noticeable changes in the spectroscopic data (Fig.1) included the incidence of aromatic functional groups at 700-900 cm^{-1}, and decrease in aliphatic bands (2800-2950 cm^{-1}). Rock-Eval pyrolysis provided the basis for numerical estimation of the transformation ratio and this ranged from 4% in the Torbanite to 53% in the Posidonia shale from S. Germany. The expulsion efficiency showed a strong correlation to the transformation ratio with values from 40% (Torbanite) to 106 % (Posidonia shale). Hg-porosimetry showed an increase in porosity from 12 % in the Posidonia shale to 31% in the Torbanite. The increase in porosity results from generation and subsequent expulsion. The high expulsion efficiency of the Himmetoglu oil shale along with a decrease in porosity suggests collapse in response to axial stress after expulsion and is attributed to its low matrix strength. Scanning electron microscopy (secondary electron mode) revealed pore coalition by a micro-fracture in post deformation Posidonia shale from N. Germany and confirms that organic matter blocks pores in source rocks and enhances porosity during generation as a result of conversion (Fig.2). Migration avenues involve intergranular pores, isolated fractures as well as fracture connected pores. Expulsion is thought to be controlled by the proximity of pores and organic matter within the matrix. The association of organic matter to the distribution of pores controls bitumen network formation while fracture generation seems to be the principal expulsion mechanism.

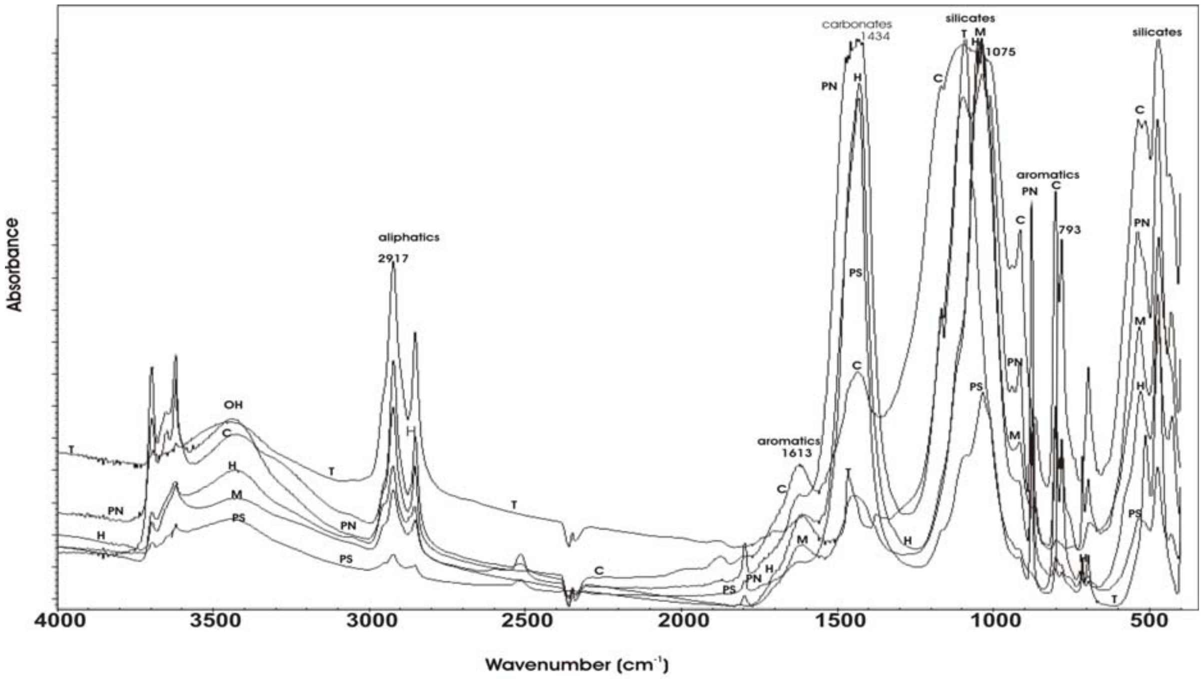


Fig.1. FT-IR spectra of post deformation samples of oil shales (T = Torbanite, PS = Posidonia shale from S.Germany, PN = Posidonia shale from N.Germany, M = Messel, H = Himmetoglu, and C = Condor) showing principal functional groups related to organic matter as well as major minerals

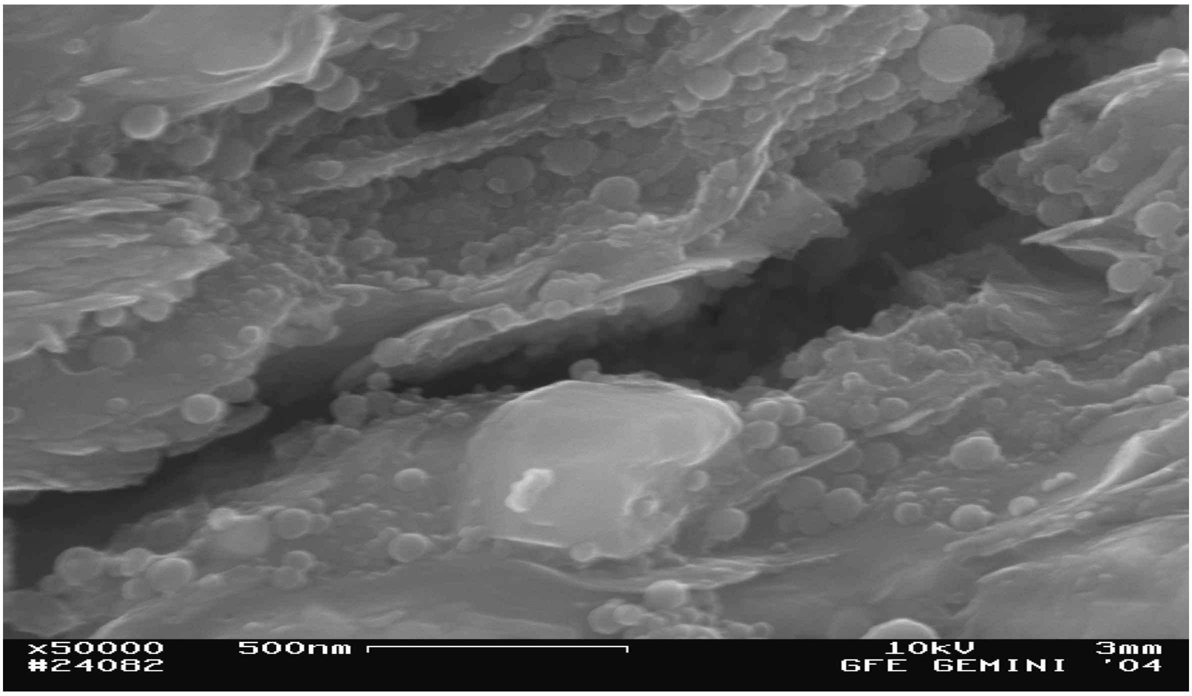


Fig.2. High resolution electron micrograph (secondary electron mode) showing micro fracture with maximum fracture width of about 200nm that connects 2 pores in the Posidonia shale from N.Germany after deformation with thermal stress up to 350°C

POS1-15: Hydrocarbon generation and expulsion using hydrous pyrolysis experiments – two examples from Brazilian source rocks

N. Franco[1], G. Machado[1], H. Penteado[2], W. Kalkreuth[1]

1) Geosciences Institute, UFRGS, Av. Bento Gonçalves 9500, Bairro Agronomia, CEP: 91501-970 Porto Alegre, RS. Brazil
2) Cenpes-Petrobrás, Rio de Janeiro, RJ. Brazil

Simulation of the generation and expulsion of oil was performed on immature samples of source rocks using the hydrous pyrolysis technique, with the objective of establishing the compositional, molecular and isotopic changes that occur between retained and expelled oil related to changes in maturity levels alone at the moment of expulsion and not to secondary processes such as washing and biodegradation as observed in nature (Peters, *et al.*, 1990, Lewan, 1985). The samples come from the Permian Irati Formation of the intracratonic Paraná Basin and from a Cretaceous source rock of a Marginal Basin of Brazil.

To determine the changes between retained and expelled oils different experiments at 2000psi and 350ºC were performed, varying the reaction time at the maximum temperature of 1 hour up to 98 hours, creating several levels of organic matter maturation.

To reach the objective of this study, geochemical parameters commonly used as indicators of maturation (Ro, Tmax, HI and biomarkers) and organic matter source (hop/ste, % steC_{27}, % steC_{29}) were determined. In addition, the molecular orientation in the kerogen was determined by using a high resolution transmission electronic microscopy technique (HRTEM).

The parameters obtained from the geochemical analyses such as TOC, Tmax and vitrinite reflectance (Ro) for both samples before and after the hydrous pyrolysis experiments showed that the organic matter was successively transformed into hydrocarbons with increase of reaction time. This transformation was also corroborated with the increase observed in the transformation ratio of the organic matter (TR).

The maturity level of the organic matter increased significantly with increasing reaction time as indicated by Tmax, HI, steC_{29} 20S/(20R+20S) and αββ/(αββ+ααα), whereas data obtained from other maturity parameters such as the Pr/Ph, Pr/n-C17 and Ph/n-C18 ratios in the retained and expelled oils in both samples did not show a clear tendency regarding the influence of reaction time.

Regarding organic matter sources, the ratios of biomarkers in both basins showed an increase of the ratio hop/ste with the increase of the reaction time in the experiments. The duration of reaction time also had a significant effect of sterane distribution. The relative proportion of C_{29} sterane was found to decrease with reaction time, whereas the C_{27} sterane was found to increase. The changes found in the relative abundance of these steranes caused by maturation can lead to erroneous conclusions about the organic matter source.

The compositional variations between retained and expelled oils indicated, that in general, the retained oils show a relative enrichment of the NSO fraction caused by the preferential expulsion of the lighter compounds (saturates and aromatics) during the primary migration of the generated oils. As a consequence the expelled oils show a greater concentration of lighter fractions and a relative low proportion of the heavier fraction (NSO).

Comparing the chromatograms of expelled and retained oils from the Irati source rock (Paraná Basin), it was observed that in the stages of low level of organic matter maturation the expelled oil is enriched in n-alkanes of low molecular weight when compared to the retained oil, suggesting that the expelled oil shows a relatively greater maturation when compared to the oil retained in the rock which expelled it. In later stages, both the expelled and retained oils showed a very similar maturation level. This pattern was not as well documented in the chromatograms of the Marginal Basin samples.

Stable carbon isotope analysis indicated enrichment of the ^{13}C isotope with increasing reaction time in both retained and expelled oils derived from the Irati source rock, whereas the samples from the Marginal Basin did not show a clear trend in isotope composition.

HRTEM analyses indicated an increase of structural ordering of the aromatic compounds with the increase of organic matter thermal evolution.

References

Lewan, M.D., 1985. Evaluation of petroleum generation by hydrous pyrolysis experimentation. Philos. Trans. R. Soc. London Ser. 315, 123-134.

Peters, K.E., Moldowan, J.M., Sundararaman, P., 1990. Effects of Hydrous pyrolysis on biomarker thermal maturity parameters: Monterey phosphatic and siliceous members. Organic Geochemistry 15 (3), 249-265.

POS1-16: Fractionation of stable isotopes in strong redox gradients – basic principles for petroleum geochemistry applications

H. Johansen

Institutt for Energiteknikk, P.O.Box 40, N-2027 Kjeller, Norway

Stable isotopes commonly show strong fractionation when bond breakage and formation is associated with a change in redox state for the element of interest. This is particularly evident for C and S, which show multiple redox states and are involved in many different bonding configurations. Redox reactions in sedimentary fluids are effectively visualized in pH-pe diagrams. Superposition of fields of predominance for the most common natural solid and fluid C and S species show that sedimentary fluids are likely to be constrained to a relatively narrow diagonal band with negative slope in pH-pe space. Because pH and pe are significantly affected by both mineral reactions and by organic reactions, pH-pe diagrams have the power of representing complete rock-fluid systems.

For both isotope systems, the strongest variation in isotopic signatures for both reduced and oxidized species, is expected in an intermediate redox-pH domain with approximately equal concentrations of reduced and oxidized species. The magnitude of the fractionation factor is very sensitive to reaction rates. The domains of strong isotope fractionation sensitivity is somewhat different for C and S. This implies that a dataset which contains sufficient isotope and concentration data for both reduced and oxidized C and S species, will commonly allow a fairly accurate definition of the pH-pe state of the environment. This can in turn be used to make predictions about the saturation and distribution of gas, oil and water in time and space. Redox reaction rates are strongly dependent upon the quantity of water relative to oil/gas, and the size and configuration of the fluid interface. Because many redox transitions are rather slow, isotope and concentration data of redox species also carry information about rates of transport which control reactions. This means that migration, mixing and segregation rates can in principle be deduced from isotope and concentration data. Several important oil industry applications in exploration, production and acid gas sequestration will benefit from an improved model for redox isotope fractionation. The presentation contains several examples from various basinal environments, ranging from near surface to deep burial, where the above principles are applied. C and S isotopes are most directly controlled by the redox reactions, but also H and O isotopes are commonly affected by the same transitions.

When reservoir intervals with high initial oil saturation are depleted during production, the water cut will increase. Experience from the Norne Field in the Norwegian Sea shows that C isotope changes of TIC (total inorganic carbon) in the water are associated with the increase in water cut. Fluorescence and isotope data suggest that increased TIC is the result of a redox reaction at the oil-water interface, and that it is thus predictable from redox reaction principles. Fluorescence of produced water is likely to be significantly affected by the type and quantity of hydrocarbons in close contact with the water. C isotopes of TIC, and water fluorescence colour and intensity, can thus be used as an early warning for increase of water cut.

During future reinjection of acid gases like CO_2 and H_2S into aquifers and reservoirs to reduce atmospheric emissions, the behaviour and distribution of the injected gases can in principle be monitored by C and S isotopes, provided that mixing with naturally occuring gas, and the operation of reactional sources and sinks can be accounted for. A leakage plume from such a repository is likely to present a very distinct redox boundary. A model to predict isotope values associated with such a boundary is a necessity for monitoring.

Stable isotope data are routinely used to identify the source and maturity of accumulated gas for exploration purposes. These interpretations are commonly compromised by the occurrence of biogenic gas or the products of biodegradation in the reservoir. Bacterial activity is to a large extent controlled by the superimposed redox environment, and also by the availability of inorganic nutrients in the water phase. Redox isotope fractionation principles are thus highly relevant for the correct interpretation of natural gas origin.

The above examples suggest that stable isotope fractionation interpreted in a framework of redox reactions offers a great potential for important new and improved petroleum geochemical applications.

POS2-1: Molecular comparison of pyrolysate compositions from adjacent lacustrine oil shales and coals (NW Anatolia, Turkey)

A. Jurisch[1,2], F. Leistner[1], U. Mann[1], R.G. Schaefer[1],
N. Volkmann[2], M.N. Yalçın[3]

1) Forschungszentrum Jülich, Institut Sedimentäre Systeme, D-52425 Jülich, Germany
(e-mail: u.mann@fz-juelich.de)
2) Technische Universität Bergakademie Freiberg, Institut für Geologie, D-09596 Freiberg, Germany
3) Istanbul University, Department of Geological Engineering, TR-34850 Avcılar-Istanbul, Turkey

Neogene sediments of NW Anatolia (Turkey) represent a highly variable succession of siliciclastics and limestones with local high organic matter contents up to oil shales and coal deposits [1]. In order to evaluate the quantitative and qualitative range of the individual admixtures of organic matter, beside bulk parameters, the molecular pyrolysate compositions of different rock and kerogen types were compared to each other.

In total, more than 200 rock samples were studied along a 30m section from the Göynük and a 13m section from the Seyitömer area. Compositional variations of the sediment input were assigned macro- and micro-petrographically and by measurement of the carbonate content. Kerogens were characterised by total organic carbon, total sulphur and Rock-Eval pyrolysis. Selected rock samples were investigated in detail by temperature programmed open-system pyrolysis-gas chromatography [2].

Both sections investigated represent a similar sequence of limestones and siliciclastics, but generally with slightly elevated carbonate contents in the Seyitömer area. In total, the investigated sediments yield extreme variations of 0.7-67% in organic carbon, 0.1-7.4% in sulphur and 14-987mg HC/g TOC in hydrogen index. In detail, especially the relative molecular compositions of the individual pyrolytic degradation products from temperature programmed pyrolysis-gas chromatography are able to differentiate the relative amounts of sapropelic versus humic organic matter. Distinct differences become obvious from compound classes (aromatic hydrocarbons, n-C_{6-32} alkanes+alkenes and C_{6-32} unidentified resolved compounds normalized to 100%), and especially from ratios of alkanes+alkenes to aromatic compounds (Table 1). According to the variation of compound classes, most characteristic are the differences in the amount of C_{6-32} n-alkanes. The variation of sapropelic versus humic organic matter is also expressed by a variation of 0.08-5.30 of the ratio of C_{6-14} n-alkanes to aromatics as well as individual molecular ratios of the pyrolysates (Table 1). In both shales and limestones, the range of 40-90% is very broad. According to characteristics of the depositional environment [3], it is suspected that the variation of the relative amounts of unidentified resolved compounds is closely related to the paleoredox conditions.

In total, the investigated sedimentary rock sequences could be differentiated in detail not only in respect to their different organic matter types but also according to the environmental and preservation conditions of the sedimentary sequences.

Table 1. Ratios of n-alkanes, n-alkenes and other resolved peaks to adjacent aromatics or aromatic groups according to the composition of the respective pyrolysates of individual sample lithologies and kerogen types (nd = not determined)

Ratio of n-Alkanes to Aromatics	**Shale, Limest. A**	**Humic Coal A**	**Shale, Limest. B**	**Humic Coal B**	**Oil Shale**	**Sapr. Coal**
C_{6-32} (all resolved peaks) / Aromatics(1)	2.14	8.38	8.38	12.49	19.01	29.82
C_{6-14} *n*-Alkanes / Aromatics(1)	0.08	0.19	1.09	1.41	4.13	5.30
***n*-Hexane / Benzene**	0.03	0.18	0.37	0.57	1.31	1.58
(*n*-Hexane + *n*-Hexene) / Benzene	0.08	0.39	1.05	1.14	4.35	3.82
***n*-Heptane / Toluene**	0.05	0.08	0.27	0.31	1.02	1.57
(*n*-Heptane + *n*-Heptene) / Toluene	0.09	0.13	0.63	0.53	2.50	3.32
***n*-Octane / (C_2-Benzenes(2) + Styrene)**	0.10	0.10	0.19	0.26	0.47	0.74
(*n*-Octane + *n*-Octene) / (C_2-Benzenes(2) + Styrene)	0.15	0.15	0.40	0.46	1.14	1.50
***n*-Undecane / Methylnaphthalenes(3)**	nd	nd	0.39	0.82	1.25	1.90
(*n*-Undecane + Undecene) / Methylnaphthalenes(3)	nd	nd	1.07	1.85	3.20	3.88

(1) Benzene+ Toluene+Ethylbenzene+ m-Xylene+ p-Xylene+ o-Xylene+ Naphthalene+ 1-Methylnaphthalene+ 2-Methylnaphthalene

(2) Ethylbenzene + m-Xylene + p-Xylene + o-Xylene

(3) 1-Methylnaphthalene + 2-Methylnaphthalene

References

[1] Yalçın, M.N, Mann, U., Bulkan, Ö., Dikmen, D., Disko, U., Hosgörmez, H., Nazik, A., Nickel, B., Schaefer, R.G., Sengüler, I., Wilde V., Willsch, H. (2003) Significance of sediments palynomorphs and lipids in relation to environmental conditions in two Neogene lacustrine basins in NW Anatolia. 21st Int. Meeting on Org. Geochemistry, September 8-12, 2003, Kraków-Poland, Book of Abstracts Part II, 305-306.

[2] Horsfield, B., Disko, U., Leistner, F. (1989) The micro-scale simulation of maturation: outline of a new technique and its potential applications. Geol. Rundschau, 78,171-182.

[3] Mann, U. (2004) MioEcoChange: Synopsis and perspective. Workshop on Miocene Paleo Ecosystem Changes. Turkish-German Co-operation in Science and Technology: Istanbul Üniversitesi – Forschungszentrum Jülich, Istanbul University, Engineering Faculty, Department of Geological Engineering, Istanbul, Turkey, 06.-08.06.2004.

POS2-2: Alternative mode of naphthenic oil formation in the depths

V.F. Kamyanov, A.K.Golovko

Institute of Petroleum chemistry, Siberian Branch of Russian Academy of Sciences 3, Academichesky Ave, 634021, Tomsk, Russia (e-mail: golovko@ipc.tsc.ru)

The transformations of oils composition in the depths are accounted for microbiological or catagenetic processes. The formation ways and the main features of naphthenic oils are very often associated with microbiological factors only ([1] et al.). It is well-known that microorganisms are able to assimilate fast aliphatic hydrocarbons, especially n-alkanes, and much more slower to consume cyclic compounds; therefore the biodegradation results in dewaxing and thereby enriches oil with naphthenes.

A rate of oil biodegradation is rather low even under favorable conditions ([2], [3]). The activity of microorganisms must be the most effective at moderate depths of occurrence, that is considered as the main reason of naphthenic oil distribution in the upper horizons of many multiplay oil fields. At great depths the conditions are less favorable for bacterial activity, that is why oil compositions are mainly changed due to thermal and thermocatalytic (catagenetic) processes of larger molecules destruction, disclosing or dehydroaromatization of saturated cycles and other reactions, which do not promote the increase of naphthenes in the system, i.e. the formation of naphthenic oils. On this ground other possible ways of naphthenic oil generation were not properly considered except biodegradation of initially paraffinic organic matter.

We believe that L. Moore ([4]) was much more correct, claiming that in fact only the differences in the initial composition of organic matter buried in sediments could be associated with biological factors, and all subsequent changes of organic matter depended on thermobaric conditions only, properties of oil-bearing rocks and other geological indices.

It should be noted, that changes in a chemical type of oils from naphthenic to methanic with the depth of occurrence are characteristic of terrigenous sedimentary strata. Oils from carbonate beds are often rich in paraffin hydrocarbons even at moderate depth of occurrence (less than 1000 m).

Adhering to the positions of both biodegradation and catagenesis theories it is impossible to explain the existence of quite paraffinless and naphthenic oils in the deep-occurred (4000 m and more) beds, whereas the upper horizons in the same oil field contain the oils with higher alkane concentrations.

Bradarats oil-field (Serbia) is a striking example of non-participation of microbiological processes in the forming of naphthenic oil composition, where at the depths of ≈ 1800 and 2300 m one found oils containing 57.6 and 88.6 wt % of naphthenes in the compositions of gasoline hydrocarbons of C_7-C_{11}, respectively ([5]).

It is possible to remove the difficulties mentioned above taking into account that oil composition can also change due to some molecules differentiation, depending on their shapes. Such differentiation may occur during hydrocarbon fluid emigration from the initial source rock.

It is obvious, that voluminous polycyclic and to a lesser degree branched isoalkane molecules considerably prevent consolidation of stratified clay minerals containing water and organic matter in the interlayer spaces of crystals, as compared with practically planar molecules of n-alkanes and condensed polyarenes. Such compression of plastic clays with release of fluid components always occurs with the depth of rock submersion and pressure rise. A difference ΔP between values of rock pressure on the fluids sealed within clay particles and hydrostatic pressure in the pores of adjacent collector is considered as a motive force for fluid emigration process.

Therefore it is clear that polycyclic molecules begin to release from clay particles at already shallow depths (at lower ΔP values), whereas for the release of n-alkanes and polyarenes higher ΔP values (greater depths) are required.

Mathematical analysis ([6]) showed, that under real deep conditions only peripheral parts of plastic clay layer at most 21 m thick are squashed. Therefore if the thickness of oil-producing layer exceeds 40-45 m (20-22 m on top and bottom), then oils rich in polycyclic components can be retained in the source clays and begin to release into reservoirs only at sufficiently great depth.

The mechanism of hydrocarbon differentiation is unrealizable in such inductile oil-generating rocks as carbonates or argillites.

Based on the stated considerations all known peculiarities of hydrocarbon compositional changes occurring in oils in the depths become more clear and explainable.

References

[1] Tissot, B.P., Welte D.H., 1984. Petroleum Formation and Occurrence. Springer, New York.

[2] Rozanova, Ye.P., Kuznetsov, S.I., 1974. Microflora of oil-fields. Nauka, Moscow. (in Russian)

[3] Connan J., Restle A. and Albrecht P., 1980. Biodegradation of crude oil in the Aquitain basin. In: Adv. Org. Geochem., 1979 – Pergamon Press, Oxford, pp. 1-17.

[4] Moore L.M., 1969. Geomicrobiology. In: Eglinton, G., Murphy, M. (Eds.) Organic geochemistry. Methods and results. Springer Verlag, Berlin-Heidelberg-New York.

[5] Ercegovac, M., Grubić, A., Djoković, I., Kuzljević, B., Marović, M., Vitorović, D., Branković, M., Grkavac, S., Kostić, A., Prstojević, B., 1993. Contribution to better understanding of geological and geochemical properties characterizing Drmno depression (Serbia) from the aspect of oil-gas potential. Annales Geologiques de la Peninsule Balkanique, Belgrade, v.57, pp. 373-393.

[6] Smith J.E., 1971. Relation between petroleum reservoir rocks and source rocks. J. Int. Assoc. Math. Geol., v. 3, № 2, pp.183-192.

POS2-3: Geochemical and petrographical study of Irati and Ponta Grossa formations, Paraná basin, Brazil

M. Kern, R. Pacheco, N. Franco, W. Kalkreuth

Instituto de Geociências, UFRGS, Av. Bento Gonçalves, 9500, 91501-970 Porto Alegre, RS, Brazil

The principal aim of this study is the geochemical and palynological characterization of the two main sequences of potential source rocks of the Paraná Basin. The basin is a huge intracontinental sedimentary area located in the southeast center portion of the South-American continent, with about 1.700.000 km^2 of territorial surface (Zalán *et al.,* 1990).

The chrono-stratigraphical framework of the Paraná basin is characterized by six second order or supersequences (in the sense of Vail *et al*., 1977; Milani, 1997), each of them comprising a geological record in the order of some tens of millions years. Source rocks of the Ponta Grossa Formation occur in the second supersequence (Paraná-D), whereas source rocks of the Irati Formation are developed in the third supersequence (Gondwana I (Upper C - Lower Tr).

The geochemical and palynological characterization of the source rocks is based on an extensive sampling representing the whole area of occurrence of the sedimentary rock sequence along a SW-NE transect spanning a distance of 5000 km. The sample material was collected from outcrop locations, surface mines, and core from exploration boreholes made in the eighties and provided by the Geological Survey of Brazil (CPRM) and the National Department of Mineral Production (DNPM).

The results of the geochemical analyses show that the rocks are composed of different types of Kerogens (I, II and III) in various proportions. The total organic content (TOC) content of the Irati Formation rocks is high, reaching values up to 21 wt.%, with an average value of 5 wt.%. As for the Hydrogen Index (HI) the preliminary results indicate a great scatter, with the highest values determined in rocks collected in São Mateus do Sul area, reaching 750 mgHC/gTOC.

For the Ponta Grossa Formation, the TOC values in general are lower and reach a maximum of 1.81 wt.%, with an average value of 0.71 wt.%. The HI values do not show a great variation, the highest values identified were in the order of 440 mgHC/gTOC. These relatively low values of TOC and HI obtained for the Ponta Grossa Formation are probably in part due to oxidation processes at the outcrop locations.

Different stages of thermal evolution were also identified based on Rock Eval Pyrolysis (Tmax ^{o}C) and Spore Colour Index (SCI). Tmax and SCI show that most of the analyzed samples are immature, but there are certain areas, where there are in the initial stage of the mature zone. These areas are still being investigated in greater detail and results will be represented at the meeting.

Palynofacies data were obtained by counting 500 particles of disperse organic matter (kerogen) in each sample according to methodology proposed by Tyson (1995) and Mendonça Filho (1999). The data show that the source rocks are composed essentially by a complex and heterogenic mixture, which can be subdivided into three distinct groups of morphological constituents: (a) Phytoclasts, (b) Palynomorphs and (c) Amorphous Organic Matter (AOM). The data are expresses in percentages with the objective of characterizing and quantifying the existing variations for each analyzed sample. The AOM is in general the predominant constituent reaching in the Irati Formation samples up to 90 Vol.% and in the Ponta Grossa Formation samples up to 87 Vol.%. Phytoclasts and palynomorphs in general occur in minor amounts, although a few samples are characterized by a larger input of these constituents (66 Vol.% and 46 Vol.% respectively).

The two analyzed source rocks show potential for the generation of hydrocarbons, with the black shales of the Irati Formation having the greatest hydrocarbon generation potential. The correlation between optical and geochemical parameters was of good quality. The integration of the geochemical and petrographical data will contribute to an assessment of paleofacies and paleoenvironments of the source rocks, as defined by concepts of sequence stratigraphy.

References

Mendonça Filho, J. G. 1999. Aplicação de estudos de Palinofácies e Fácies Orgânicas em Rochas do Paleozóico Superior da Bacia do Paraná, Sul do Brasil. Instituto de Geociências. Universidade Federal do Rio Grande Do Sul, Ph.D. Thesis, 2 Vol.

Milani, E. J. 1997. Evolução Tectono-Estratigrafica da Bacia do Paraná e seu Relacionamento com a geodinâmica fanerozóica do Gondwana Sul-Ocidental. Instituto de Geociências. Universidade Federal do Rio Grande do Sul, Ph.D. Thesis, 2 Vol.

Tyson, R. V. 1995. Sedimentary Organic Matter: Organic Facies and Palynofacies. Chapman & Hall. London, 615p.

Vail, P.R.; Mitchum, R.M.; Thompson, S. 1977. Seismic stratigraphy and global changes of sea level, part 3: relative changes of sea level from coastal onlap. In: Payton, C.E. (ed.). Seismic stratigraphy - applications to hydrocarbon exploration. Tulsa, Oklahoma, American Association of Petroleum Geologists, p. 63-81 (AAPG Memoir, 26).

Zalán, P. V., Wolff, S., Astolfi, M. A. M., Vieira, I. S., Conceição, J. C. J., Appi, V., Santos Neto, E. V., Cerqueira, J. R., Marques, A. 1990. The Paraná Basin, Brazil. *AAPG. Mem*. N.51, P.681-708.

POS2-4: Optical characterization of hydrogenized dispersed organic matter applied to source rocks of Mexico

J.A. Pérez-Ortiz, E. Gutiérrez-Mejia, L. López-López

Instituto Mexicano del Petróleo. Laboratorio de Petrografía Orgánica, Pachuca, Hgo. México (e-mail: jortiz@imp.mx)

ABSTRACT. Optical studies performed on 184 core and cutting samples determined, in base to their organic content, the presence of excellent indicators of liquid condensated and gaseous hydrocarbons mainly the ones from Upper Jurassic and Upper Cretaceous layers. One of the most important observations are the news horizons of the Tertiary (Paleocene – Eocene) as new structures of petroleum interest. Therefore, exhaustive studies were performed in order to determine the highly hydrogenised organic matter contained in the sediments (type) and thermal evolution (maturity) as well as the relation between the organic particles and the mineral matrix. This played an important roll in the determination of the hydrocarbon generative potential and to define three natural systems in the studied wells. This same study was extended to various petroleum basins in the country that share the same characteristics.

INTRODUCTION. Optical studies using reflected light (%Ro) and fluorescent light (%I) on the lignocelulosic (vitrinite/huminite) and liptinitic (alginate, resinite, cutinite) macerals, were carried out, in order to define the organic richness as well as their vertical distribution and thermal evolution of coal particles, contained in Upper Jurassic and Upper Cretaceous rocks and in sediments of Tertiary age. Studied samples proceed from wells of three sedimentary petroleum basins located on coastal plain and the Gulf of México.

Manzanal-1 and Piramide-1 wells are located in the northern of Tampico-Misantla Basin, Limon-1 well is located in the Papaloapan-Veracruz Basin, and Guacamaya-1 well within Sound of Campeche, offshore of the Sureste Basin.

DEDUCTIONS. We deduct the organic components materials can be related to lagoonal-marine sedimentary environments for the Upper Jurassic and Upper Cretaceous in Manzanal-1, Piramide-1, Limon-1 wells as well as for the Tertiary in Guacamaya-1 well (Paleocene-Eocene).

The Upper Jurassic organic matter in Guacamaya-1 well is marine with contribution of terrigenous in some horizons.

In manzanal-1 and Piramide-1 wells the Lower Cretaceous organic facies are also related to marine environments.

CONCLUTIONS. According to the generative potential, the quality of the dispersed organic matter and the thermogeological conditions we conclude that the best identified source horizons are:

- The Upper Jurassic in Manzanal-1 (0.65 %Ro), Piramide-1 (0.85 %Ro) and Guacamaya-1 (0.60 %Ro) wells.
- The Lower Cretaceous in Manzanal-1 (0.62 %Ro), Piramide-1(0.75 %Ro), and the Middle Cretaceous in Guacamaya-1 (0.55 %Ro).
- The Upper Cretaceous in Limon-1 and Manzanal-1 wells (0.60 %Ro) and Piramide-1 well (0.70 %Ro).
- For the Tertiary we observed excellent quality organic matter in the Paleocene-Oligocene for Manzanal-1, Piramide-1 (0.45 %Ro) and Guacamaya-1 (0.40 %Ro) wells.

References

Bradley, W. H. (1924), Amer, J. Sci., 5th Series, 8, 228.
Combaz, A. , (1962), C.R. Acad. Sci. París, 253,1977.
Durand, B. Espitalié, J., Nicaise, G. and Combaz, A., (1972), Rev. Inst. Franc. Du Pétrole, XXVII, 865.
Gadel, F. Et Ragot, J.P., (1974), in: Advances in Organic Geochemistry 1973,620, Editions Technip, París.
Pérez Ortiz, J.A., (2000) Caracterización Geoquímica de los Campos Petroleros de la Cuenca Tampico-Misantla
Pérez Ortiz, J.A., (2000) Estudio Integral de la Cuenca Papaloapan-Veracruz
Pérez Ortiz, J.A., (2001) Evaluación Óptico-Geoquímica de los Campos de la Sonda de Campeche.
Pérez Ortiz, J.A., (2001) Caracterización Óptica de los Hidrocarburos del Campo Jujo-Tecominoacán, Cuencas Terciarias del Sureste.
Pérez Ortiz, J.A., (2002) Estudio Optico-Geoquímico de los Campos Arroyo Zanapa, Juspi y Sitio Grande.
Teichmuller, M. and Ottenjahn, K., (1977) Erdol Und Kohle, 30, 387.
Tissot, B. and Weltw, D.H. (1978), Petroleum Formation and Ocurrence, Springer Verlag Press.

POS2-5: Environmental control on the gas potential of Cretaceous and Tertiary source rocks in the Mackenzie Delta, Northwest Territories Delta (Canada)

A. Saison, V. Dieckmann, B. Horsfield

GFZ, Telegrafenberg, 14473 Potsdam

The Mackenzie Delta (Northern Canada) is among the major gas hydrate provinces in the world. Gas hydrate occurrences are widespread in the subsurface up to depths of 1200m. Free Gas and clathrated gas is mainly of thermal origin from the cracking of sedimentary organic matter. Due to the low maturity gradient of sediments drilled in the Mackenzie Delta has been proposed that the gas was formed from marine sediments deeper that 6000m. However, it has also been shown that terrestrial sediments within the Mackenzie Delta contain in-situ hydrocarbons which are formed at shallower depths (Snowdon, 2002).

The major aim of the present study is to identify the effects of thermal transformation processes on shallow terrestrial sediments in the Mackenzie Delta. We focus first on the impact of depositional facies variations on organic matter transformation to hydrocarbons within the deltaic sediments and then present the results of artificial maturation experiments on immature coal and terrestrial shales from different organic rich sequences.

Seventy-seven samples covering the whole area of the delta have been studied. These represent five organic rich formations (Kugmallit, Richards, Taglu, Aklak and Smoking Hills sequences), as well as different depositional environments inside these formations, from delta plain to slope/base of slope. Their composition was evaluated by Rock-Eval Pyrolysis, organic petrography, open and closed system pyrolysis-GC, Pyrolysis-GC-MS and thermovaporisation. 10 samples pyrolyzed under open-system conditions at different heating rates (0.1, 0.7 and 5.0) in order to determine kinetics parameters. In addition to these analyses, two selected samples were heated to 10 different stages of artificial maturation under closed system conditions to trace structural and kinetic transformations.

The studied sample set indicates that the organic rich sediments are extremely heterogeneous in terms of depositional environment and organic matter transformation behaviour.

Indeed, not only the sedimentary organic matter preserved in the sequences shows characteristics typical for type II and III source rocks, but a given depositional environment presents different structural and kinetic properties from one sequence to another. Furthermore, unexpected trends, depending on depth and/or locations, observed within the sequences, likely highlights the state of trangression or regression of the delta. This in turn has a strong impact on the petroleum formation predictions, with onset temperatures which vary between 90 and 140°C under geological conditions, and with various distribution of activation energies. Even on regional scale lateral variations in hydrocarbon formation behaviour within the different sequences are very common. This in turn implies that overall petroleum generation models, which cover the whole Mackenzie Delta are by far not simplistic to predict gas formation characteristics on smaller regional scale.

However artificial maturation in closed system couple with bulk kinetics on the residual artificially matured sample and additional structural analysis allows us to draw a scheme of maturity-related evolution of the source rock in term of structural rearrangements and hydrocarbon generation characteristics for the Smoking Hills, Upper Cretaceous sequence in the south of Richards Island and the Kugmallit, Oligocene sequence within the Kugmallit Bay. These maturation experiments are balanced with natural in-situ gas occurrences and show that a specific portion of gas within the gas hydrate zone may also be formed from sediments as shallow as 3000-4000m.

Based on these results a pattern of organic facies characteristics and variations, and petroleum generation of the Cretaceous and Tertiary sediments in the Mackenzie Delta will be presented.

References

Snowdon, L.R., (2002) Natural gas composition in a geological environment and the implications for the processes of generation and preservation; reply. *Organic Geochemistry*, 33(1), 85-88.

POS2-7: Organic geochemical study on Hungarian oil shales

C. Sajgó[1], A. Brukner-Wein[1], M. Hetényi[2]

1) University of Szeged, H-6701 Szeged PO Box 651, Hungary (e-mail: sajgo@sparc.core.hu)
2) Inst. for Geochemical Research, Hung. Acad. of Sci., H-1112 Budapest Budaörsi út 45, Hungary

In our earlier studies, we demonstrated several organic geochemical parameters of different Hungarian oil shale occurrences (e.g. Brukner-Wein and Hetényi, 1993; Brukner-Wein et al., 2000; Hetényi et al., 2002), but we have not compared them yet on a common basis. In this paper, we focus on atomic ratios and pyrolysis results of the studied deposits to compare the organic facies in the oil shales.

In table I, the most important averaged data are summarised. Over 60 selected samples used come from 7 representative oils shale deposits of Hungary.

Table 1. Elemental ratios and pyrolysis results of representative Hungarian oil shales

location	age	[1]TOC %	[2]HI	[3]T_{max}	[4]H/C	[4]N/C	[4]S_{org}/C	[5]o/x	[6]phenol %	[7]mthio/tol	[8]pr/C_{17}
Pula	Pliocene	16.92	603	440	1.60	0.016	0.0063	3.84	18.5	0.87	0.34
Gérce	Pliocene	6.85	588	424	1.53	0.025	0.0058	2.39	23.3	0.55	0.16
Várkesző	Pliocene	10.03	525	431	1.42	0.027	0.0091	1.69	43.1	0.18	0.49
Egyházaskesző	Pliocene	8.15	405	431	1.38	0.021	0.0273	0.60	43.5	0.20	0.75
Várpalota	Miocene	15.63	722	420	1.46	0.025	0.0540	0.95	42.2	0.62	0.42
Mecsek	Jurassic	7.26	417	425	1.22	0.024	0.0300	0.99	22.7	1.43	0.57
Rezi	Triassic	7.24	743	402	1.39	0.017	0.0766	0.64	17.3	1.79	1.24

[1]TOC: total organic carbon, [2]HI: (mgHC/gTOC) , [3]T_{max}…(°C), [4]H/C, [4]N/C, [4]S_{org}/C: atomic ratios of kerogens; [5]o/x: *n*-octene/(*m*+*p*)xylene ; [6]phenol %: normalised on the basis of ∑*n*-octene+(*m*+*p*)xylenes+phenol contents in pyrolysate ; [7]mthio/tol: 2-methylthiophene/toluene in pyrolysate; [8]pr/C17: ∑prist-1-ene + prist-2-ene +pristane/∑*n*-heptadecane + *n*-heptadecene in pyrolysate.

The oil shales of Pula, Gérce, Várkesző and Egyházaskesző were deposited in *maar-type* craters about 4 million years ago, in small area (0.3-2.1 km^2), their thickness attaining a maximum of 70 m. The diatomaceous oil shale of Várpalota deposited on Badenien coal seam in *lagoonal* environment, its thickness reaching a maximum of 45 m in about 50 km^2. The Jurassic oil shales of Mecsek area deposited in shallow marine environment during Toarcian age in several small basins. The Rezi carbonate-rich oil shale was deposited in toe of the platform slope during late Triassic (Norian-Rhaetian), its thickness 200 m and the most organic-rich section represents a third of the deposits.

The rank of maturation of the studied samples is similar, the level is about the middle of diagenesis, so the majority of insolubilisation, polycondensation and polymerisation have taken place, but onset of hydrocarbon generation has not yet started. The Tmax values did not represent the level of maturity but they demonstrate the organic facies of samples, with special respect to their S_{org} contents.

On the basis of H/C atomic ratios, the kerogens are belonging to Type I and Type II. This observation is also corroborated by *n*-octene/(m+p)xylenes ratios but HI values suggest partly different classification (e.g. in cases of Várpalota and Rezi samples).

On the basis of their relative phenol contents, the samples form 3 groups, firstly as a consequence of the terrestrial contribution to their organic matter, secondly the influence of the oxidative processes suffered.

The ratio of pr/C17 (Table I and Fig. 1), representing the relative richness of acyclic isoprenoids suggests that the isoprenoids did not come from chlorophyll or from other N-rich precursor (comparing with N/C ratios and relative phenol contents) predominantly.

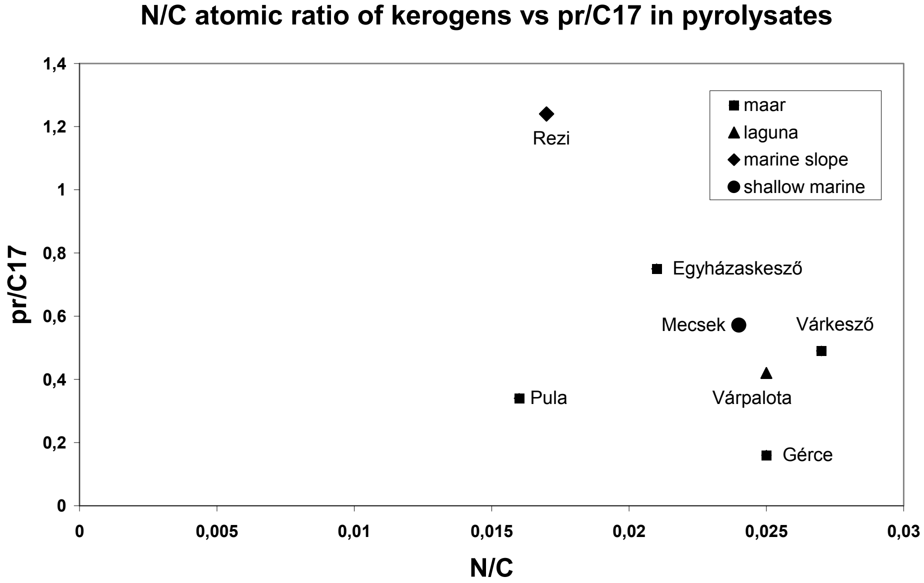


Fig.1. Relationship between average N/C atomic ratios and the pr/C17 ratios (∑prist-1-ene + prist-2-ene +pristane/∑*n*-heptadecane + *n*-heptadecene) in pyrolysates of different Hungarian oil shale deposits

Further details of hydrocarbon generating features and organic facies (mainly the incorporation of S_{org}) will be discussed, and we shall focus on the similarities and differences.

Acknowledgements

This work was funded through grant: OTKA T 034579 and T 034168 from the Hungarian National Science Foundation.

References

Brukner-Wein A, Hetényi M Relationship of the organic geochemical features of two maar-type Hungarian oil shales. Acta Geologica Hungarica, 36/2, 223-239 1993

Brukner-Wein A, Sajgó Cs and Hetényi M. Comparison of Pliocene organic-rich lacustrine sediments in twin craters. Organic Geochemistry, 31/5, 453-461 2000

Hetényi M, Brukner-Wein A, Sajgó Cs, Haas J, Hámor-Vidó M, Szántó Zs and Tóth M Variations in organic geochemistry and lithology of a carbonate sequence deposited in a backplatform basin (Triassic, Hungary). Organic Geochemistry , 33/12, 1571-1591 2002.

POS2-7: Organic petrology of Mesozoic marine source rocks in the Qiangtang basin, Tibet, SW China

J. Tu[1,2], S. Zhang[1,2], D. Liu[3], L. Bian[4]

1) Research Institute of Petroleum Exploration and Development, PetroChina, Beijing 100083, China (e-mail: jqtu@yahoo.com.cn, jqtu@petrochina.com.cn)
2) Key Laboratory of Petroleum Geochemistry(KLPG),CNPC,Beijing 100083,China
3) China University of Geosciences,Beijing 100083,China
4) Nanjing University,Nanjing 210093,China

The Qiangtang Basin, Tibet, SW China covers an area of 185,000 sq. km and is one of the largest continetal basins,which is the poorest in exploration (no drilling up to now) and the least knowing for Mesozoic Marine source rock in the world.

The Mesozoic marine source rocks in the Qiangtang Basin mainly include Upper Triassic basinal argillutites and marls (Xiaochaka Formation, T_{3x}), Middle-Jurassic platform carbonates and mudstones (Buqu Formation,J_{2b}) and Upper Jurassic platform carbonates (Suowa Formation,J_{3s}). In additional, Middle-Jurassic lagoonal argillutites and oil shales (Xiali Formation, J_{2x}) is another important source rock in the mid-western part of the Qiangtang Basin,

The maceral classification of the Mesozoic marine source rocks has been suggested on the basis of a great deal of data from both optical and chemical analysis for outcrop samples in the Qiangtang Basin. The maceral groups are divided into three groups: Primary morphological organic matter, primary amorphous organic matter and secondary organic matter. The difference in the assemblage and distribution of maceral has been occurred among these different source rocks. Thus the type and content of maceral vary according to the depositional environment, the precursor and the maturation degree of source rocks.

The precursors of the hydrocarbon-generating maceral of Mesozoic marine source rock have already been separated and identified. They include dinoflagellate, acritarch, macroalgae, sporopollens, cuticle of land plants and zooclast, etc. The main precursors for oil-generating maceral are macroalgae (phydophyta and phaeophyta), dinoflagellate and classopollis. Phodophyta is the most important precursor for oil-generating rocks in the basin.

The amorphogen is the preponderant hydrocarbon-generating maceral in the Mesozoic source rocks in Qiangtang Basin. Three different types of amorphogen maceral are identified mainly by their precursors: sapropelic amorphinite, macroalgal amorphinite and humic amorphinite. It is their different precursor that the difference shows in the optical and chemical characters among them, reflecting the big difference among their hydrocarbon-generating ability and process. Sapropelic amorphinite (Type I organic matter), which precursor is planktonic algae, can possess long-time and powerful oil-generating ability,whereas humic amorphinite (Type II_2 organic matter),which precursor is the mixture of high plant and plankton, can only possess short-time and low oil-generating ability. Macroalgal amorphinite (Type II_1 organic matter), which precursor is benthic macroalgae (Phodophyta and Phaeophyta) , can possess longer-time and morepowerful oil-generating ability than humic amorphinite,whereas less than sapropelic amorphinite.

Micrinite and exsudatinite have already been identified under microscope in the Mesozoic marine source rocks, suggesting the oil generated at one time in the Qiangtang Basin. Micrinite can been nearly seen in these three sets of main source rock if the source rock reached at higher maturation. Exsudatinite, which developed from the epidermis or zooclast has also been identified. It is well known that the genesis of these two secondary maceral is related to that of fluid petroleum.

POS2-8: Source rocks of the Sarawak basin, Malaysia: variation in hydrocarbon composition in relation to depositional setting

P. Abolins[1], W.H. Abdullah[2]

1) PETRONAS Carigali Sdn Bhd, Technical Geoscience Department, Tower 2, PETRONAS Twin Towers, Kuala Lumpur City Centre, 50088 Kuala Lumpur, Malaysia
2) Department of Geology, University of Malaya, 50603 Kuala Lumpur, Malaysia

Sarawak, an oil and gas producing state of Malaysia, is situated on the northwest margin of Borneo in Southeast Asia. The Sarawak basin is currently a passive margin basin that initiated, as a Foreland basin, during early Tertiary and underlies most of offshore, and parts of onshore, Sarawak. The basin is divided into several tectonostratigraphic provinces, each with their own characteristic reservoir type and trapping style. However, a common element that runs through the basin is the source rock interval, which is the late Oligocene – early Miocene sequence.

A palaeogeographic reconstruction at the time of source rock deposition, as schematically shown in Figure 1, consists of a northwest trending coastline, essentially perpendicular to today's coastline. Well penetrations have confirmed this palaeogeography, with coals and carbonaceous shales penetrated in the lower coastal plain strip. The number of coals and the richness of shales reduce to the north and east where the environment becomes increasingly marine.

The Balingian Province, towards the south of the Sarawak basin, provides strong evidence for coal as an important source rock for oil. These late Oligocene to Lower Miocene coals were deposited within a coastal plain paralic setting. Palynomorph analyses confirm the marginal marine origin of these coals. Based on lithofacies association, macerals types and biomarker distribution, at least two distinct coal facies were identified from the onshore analogue i.e. mangrove-derived coals or coaly shales and marine-influenced fresh water coals. The mangrove-derived coals are generally thin and are very rich in mineral matter and in liptinite content which is high in suberinitic constituents. The fresh water coals are dominated by vitrinite with very low mineral matter and low liptinite content. Oleanane is common in both types of coals. The coals possess good oil generating potential. Their HI values range between 250-450 and give high EOM yields. Onshore, the thermal maturity of these coals ranges between 0.35-0.55%Ro.

The hydrocarbon distributions appear to be strongly governed by paleogeography. Fields situated above the lower coastal plain trend are generally oil bearing, whereas a prominent gas trend occurs to the east and north in the Central Luconia province in which the fields are positioned above increasingly marine source rocks with an absence of coal.

The quality of coals, and the richness of associated shales, decreases very rapidly from the west to east, emphasizing the paleogeographic control on the source rock deposition. This is supported by the oil composition. Biomarker distributions for the Balingian and Central Luconia oils and condensates indicate a gradual reduction in terrigenous input from west to east (B-B' in Figure 1). The relative abundance of biomarkers such as oleanane and bicardinanes decrease towards the east, whereas compounds such as C_{27} steranes increase relative to C_{29} steranes, and C_{30} steranes occur to the east. There is less variation in biomarker distributions observed on the NW-SE trend (A-A' in Figure 1), consistent with a northwest-southeast trending palaeo coastline. Thus, oil and gas distribution, supported by biomarker fingerprints as well as petrological and lithofacies studies agree with the proposed paralic coastal plain depositional model for source rocks of the Balingian Province. Whereas a more strongly marine-influenced source rock is responsible for condensates of the Luconia province.

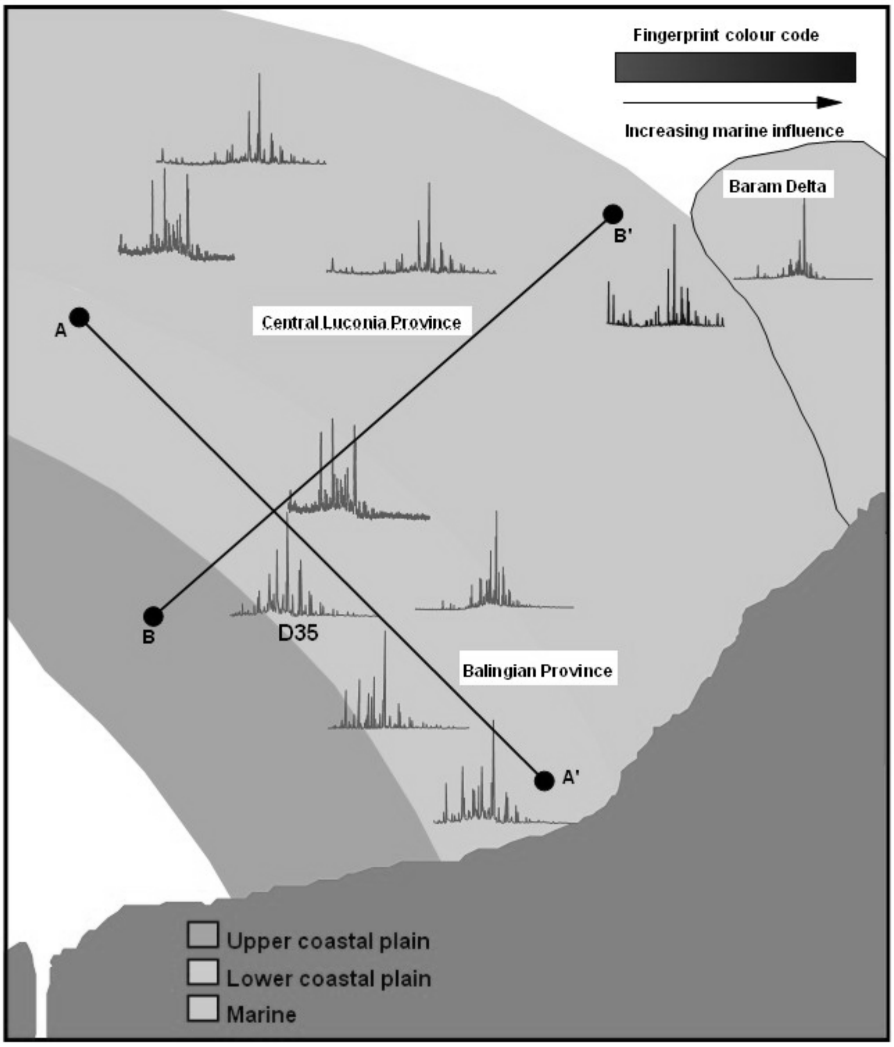


Fig.1. Schematic palaeogeographic reconstruction for late Oligocene and early Miocene relative to today's coastline. Biomarker distributions are triterpanes (m/z 191) for oils and condensates in early to middle Miocene reservoirs charged from the underlying source

POS2-9: Kumsk suite - high-potential source rock in the Caucasian-Scythian region

L. Distanova, O. Bazhenova

Moscow State University, Geological faculty, Vorobjevy Gory, Main building, sector “A”-619
(e-mail: bazh@geol.msu.ru)

Kumsk suite (middle Eocene, bartonski layer) is widely spread within the limits of the continental part of the Crimean-Caucasian region and within the limits of the Black Sea. Lithological composition of the strata is rather constant – dark-layered bituminous marls and carbonate clays with thin seams of sands and siltstones. Thickness of Kumsk sediments is changeable: from 50 to 260 m. Kumsk suite is distinguished as one of the most high-potential source rocks in the sedimentary sequence of the studied region.

Object of geochemical investigation were rocks and oils of Kumsk suite of the Western and Eastern Precaucasus and Crimea (sequences at r. Heu, r. Pshish, r. Belaya (the Western Precaucasus), outcrop on Cherkey-HPS (Dagestan) and Kazantash (Crimea).

TOC content in marls of Kumskaya suite varies in wide ranges from 0,2 to 8,1% (average 1,5-3%). Genetic potential (S_1 +S_2) changes from 0,4 to 28,3 $^{kg\ HC}/_{t,\ rock}$, that is characterizing generation potential from low up to excellent.

Values of hydrogen index HI in the studied sequences are low: 10-250 $^{mg\ HC}/_{g\ OM}$, characteristic of low OM quality (kerogen type III), only in the western sequences kerogen of II type, performing high oil-generation potential (HI=450-600 $^{mg\ HC}/_{g\ OM}$).

In the studied sequences OM is immature. By T_{max} = 415 - 420°C and productivity index values [OPI=S1 / (S1+S2) =0,01-0,02], katagenesis degree of OM has not reached the level of the "oil window", except exposures of Charkey - HPS (Dagestan) where $T_{мах}$ = 440°C, so in this area the strata is being buried deeper.

Bitumen content in the studied samples amounts 0,035-0,1%, β is equal to 0,64-2,3 % - evidence of syngenetic nature of bitumen. By GH data distribution of n-alkanes is 2-modal with maximum on C_{16}-C_{18} and C_{28}-C_{29}, Pr/Ph=0.55, $^{even\ HC}/_{odd\ HC}$=1.1. Distribution character of steranes is similar – C_{27}:C_{28}:C_{29} is accordingly 31:17:55 (average values). Prevailing of ethylcholestane (C_{29}), higher concentration of high-molecular n-alkanes, variations in TOC concentrations and genetic potential values are probably caused by both different bioproductivity and by sharp changes of diagenetic conditions.

Accumulation of Kumsk deposits proceeded in marine basin of Eastern Perithetis. In the northern part Kumsk deposits are light-coloured, less bituminous that is connected with their accumulation in oxidizing conditions.

The deepest sites of sedimentation are situated mainly in the area of Eastern Precaucasus, in Western Precaucasus - to Adagum-Athipski trough deflection. Accumulation conditions of OM in Kumsk time were extremely favorable – marine basin with normal water salinity, humid climate. Big quantity of OM led to creation of reducing conditions, to what low sustained values of Pr/Ph ratio in bitumen (average 0,55) testify. The studied sequences belong to the coastal part of the Kumsk basin, in the southern direction improvement of OM quality is observed, and it is necessary to expect more sustained values of genetic potential; so on the most part of the area the suite could be considered as high-potential oil-generating sequence.

Kumsk suite is oil-bearing in Western Precaucasus (Zapadno-Athipskaya, Severskaya, Levkinskaya areas). Based on GC data of the middle part of the oil, n-alkanes are represented by long-chain alkanes (C_{12}-C_{31}) with maximum on C_{12}-C_{14} - in the field of low-molecular alkanes. Such one-modal distribution with prevailing of low-molecular homologues testifies of algae planktonogenic initial matter. Pr/Ph changes from 1,8 to 2,2, even HC/odd HC=0.17-1.15.

By distribution character of steranes $C_{27,}$ C_{28} and C_{29} in the oils - their equal parity 32:31:35 - corresponds to the mixed type of OM and its marine conditions of sedimentation. Kumsk sequence is poor at reservoirs; they are of bad quality (pore-fractured clayey siltstones). Microoil emigration from these reservoirs is very complicated. But at the same time high tectonic activity of the region in Late Alpine is being that mobilizing factor that led to forming of oil and gas condensate fields in Kumsk suite and also in the others.

POS2-10: Petroleum generating potential of marine-influenced organic-rich sediments from the Middle Miocene Belait formation of Brunei Darussalam, NW Borneo

W.H. Abdullah

Department of Geology, University of Malaya, 50603 Kuala Lumpur

Three coals, one coaly shale and one mudstone from the Middle Miocene Belait Formation of Muara District, Brunei Darussalam were analysed by means of organic petrological and organic geochemical methods. The aim of this study was to evaluate the petroleum generating potential of these sediments. All of the samples analysed are low thermal maturity, sub-bituminous rank with mean vitrinite reflectance (%Ro) of 0.40 - 0.49%. The TOC content is between 2.39 - 65.21 wt%.

The Belait Formation sediments were deposited in estuarine to shallow marine conditions and are dominated by tidally deposited sandstones and mudstones with significant occurrence of coals and coaly shales. These coaly sediments contain abundant mangrove pollen and are thus interpreted as being mangrove coals. The coal seams are generally thin (about 0.3 to 1.0 m thick) and occur within an intertidal succession consisting of tidal flat sandstones and mudstones with common occurrence of coal clasts. The occurrence of the mineral jarosite supports the marine influenced nature of these sediments.

The petrographic and the geochemical evidence both indicate that, among all the sediments analysed, the coals possess the greatest petroleum generating potential. They are rich in liptinitic constituents that constitute up to 50% of the coals. This is supported by moderate to high hydrogen indices (HI) of 233 to 794 and by Py-GC programs displaying mixed assemblages of aromatic hydrocarbons and n-alkane/alkene doublets extending beyond n-C_{30}. One coal sample analysed possesses a maceral assemblage dominated by resinite and vitrinite, and yielded a very high HI of 794. The Py-GC pyrogram, however, is dominated by aromatic compounds with very low concentration of n-alkane/alkene doublets. This sample is therefore not considered oil-prone and demonstrates the need for integrated petrological and geochemical assessments. Poor petroleum generating potential is expected from the mudstone and silty shale samples based on low HI of 63 and 138, respectively.

Based on petrographic observations, the organic matter considered to be the most oil-prone at low thermal maturity are the macerals suberinite and bituminite. Bituminite in these sediments appears to be an intermediate oil-rich constituent that subsequently expels its liquid hydrocarbons in the form of oil smears or as exsudatinite. The exsudatinite commonly impregnates and/or brecciates the predominantly vitrinite dominated coal matrix. Oil haze and oil globules are other common liquid hydrocarbon generative features observed in these oil-prone coals of Brunei Darussalam.

Stable carbon isotope fractionation and organic sulphur content in hydrous pyrolysis (24 to 108 hours and 300 to 365 °C) immiscible oils, bitumens and kerogens from the Oligocene Menilite shales of the Polish Flysch Carpathians

M.J. Kotarba[1], M.D. Lewan[2], D. Wieclaw[1], J.B. Curtis[3]

1) AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, Al. Mickiewicza 30, 30-059 Krakow, Poland
2) U.S. Geological Survey, Federal Center, MS 977, Denver, CO 80225, USA
3) Colorado School of Mines, Dept. of Geology and Geological Engineering, Golden, CO 80401, USA

This paper addresses the aspects of carbon isotope fractionation and changes of organic sulphur content in kerogen, bitumens and immiscible oils from Oligocene Menilite Shales during simulation of maturation processes by means of hydrous pyrolysis (HP) experiments of different times (24, 36, 48, 72 and 108 hrs) and temperature (300, 310, 320, 330, 340, 350, 360 and 365°C). The Polish part of the Flysch Carpathians consist of several nappes composed of Cretaceous to Late Miocene strata generally claystones, mudstones and sandstones, and belongs to one of the largest petroleum provinces of Central Europe. The Menilite Shales are considered to be the best source rock in the Flysch Carpathians. Based on results of previous work (Curtis et al., 2004), from among the total collected 32 Menilite Shales samples, two sample sites (ST-4 from the Skole nappe and RR-45 from the Silesian nappe) were selected for HP experiments. After re-sampling, they were labeled as ST-4(u) and RR-45(2), respectively. Geochemical indices and ratios for the ST-4(u) and RR-45(2) unheated samples are as follows: TOC content 17.2 and 17.3 wt.%, hydrogen index 731 and 601 mg HC/g TOC, organic S content in kerogen 9.8 and 3.0 wt.%, organic S content in bitumens 4.8 and 0.90 wt.%, $\delta^{13}C$ values of saturates -34.5 and -29.3‰, $\delta^{13}C$ values of aromatics -32.0 and -28.5‰, respectively. The ST-4(u) and RR-45(2) samples are comprised of type IIA (II-S) and type IID kerogens, respectively. The kerogens were thermally immature, with T_{max} values of 414 and 431°C, respectively.

Organic sulphur content in bitumens for ST-4(u) sample increase with the growing temperature of HP experiments, and maksimum value of 7.94 wt.% achieved at 350°C/72hrs. The highest organic sulphur contents (0.5 and 0.7 wt.%) are typical of oils generated from ST-4(u) sample at the lowest temperatures (300 and 310°C), which may be explained by the breaking of relatively weak sulphur bonds - abundant in type IIA (II-S) kerogen.

In RR-45(2) samples analysed after HP experiments, the content of organic sulphur in immiscible oils and bitumens increases with the increase of their temperature, and the highest values were observed at 365°C/72hrs: 0.97 and 9.56 wt.%, respectively. However, no influence of the duration time of HP experiments on sulphur content in immiscible oils and bitumens was observed. This effect can be explained by the presence of sulphur-carbon bonds in type IID kerogen, the destruction of which requires considerable quantities of energy.

δ^{13}C values of pyrolytic products of ST-4(u) and RR-45(2) samples vary as follows: bitumens from -32.9 (300°C/72hrs) to -27.6‰ (365°C/72hrs) and from -30.3 (300°C/72hrs) to -29.0‰ (340°C/108hrs), respectively; immiscible oil from -31.8 (300°C/72hrs) to -27.8‰ (365°C/72hrs) and from -30.5 (300°C/72hrs) to -28.8‰ (350°C/72hrs), respectively. The difference between δ^{13}C values of saturates and aromatics at end member HP experimental temperatures (300 and 365 °C) for 36, 48, 72 and 108 hours duration time are always much higher in the case of type IIA kerogen than in the case of the type IID kerogen. Fig. 1 depicts the stable carbon isotope fractionation effects for aromatics and saturates at 72 hours duration time of the HP experiments.

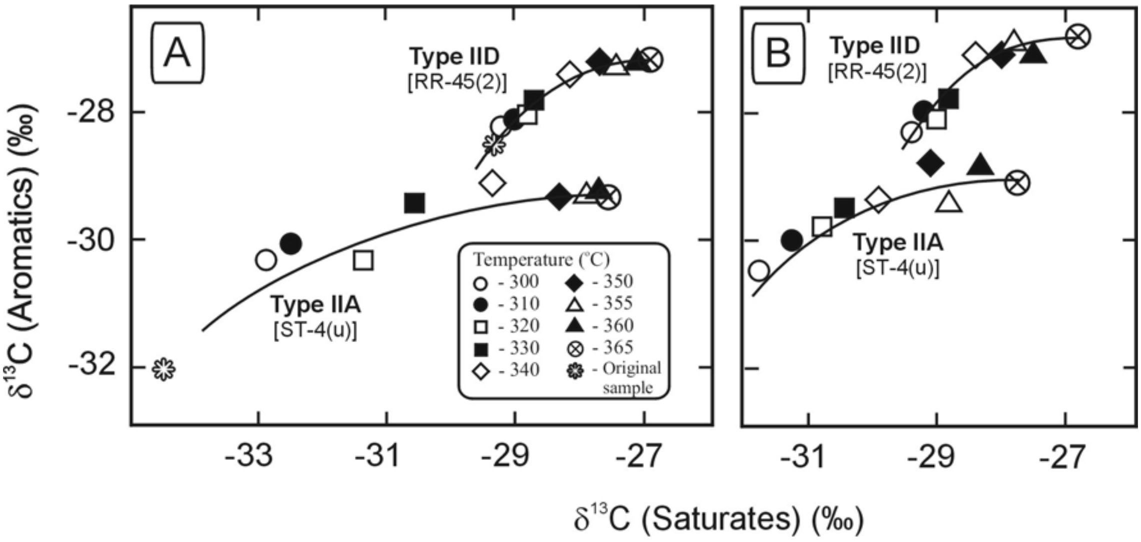


Fig.1. Stable carbon isotope composition of aromatics versus saturates for (A) bitumens extracted from unheated RR-45(2) and ST-4(u) samples and from the same samples after hydrous pyrolysis experiments for 72 hrs and 300 to 365 °C, and for (B) immiscible oils from the same hydrous pyrolysis experiments

References

Curtis, J.B., Kotarba, M.J., Lewan, M.D., Więcław, D., 2004. Oil/source rock correlations in the Polish Flysch Carpathians and Mesozoic basement and organic facies of the Oligocene Menilite Shales: insights from hydrous pyrolysis experiments. Org. Geoch., 35, 1573-1596.

POS2-12: Potential hydrocarbon generation in the Lake Baikal Rift, Eastern Siberia

A.G. Polozov[1], D.K. Martikhaeva[1], V.A. Makrygina[1], A.P. Giże[2], P.A. Hall[3], K. Hall[3]

1) Institute of Geochemistry, Siberian Branch of RAS, Irkutsk, Russia
2) School Earth, Atmospheric and Environmental Sciences, University of Manchester, Manchester, M13 9PL, UK3) Hall Analytical, Millbrook Business Estate, Wythenshawe, Manchester, M23 9YJ, U.K.

Petroleum shows in Siberia have been interpreted as derived from PreCambrian algal source rocks. In a detailed study of high grade metamorphic rocks (amphibolite facies) exposed along the west coast of Lake Baikal, initial petroleum traces were detected which can not be assigned to anthropogenic contamination.

The petroleum yields are highest in fault zones, and least biodegraded in the finest fractures (Figure 1a). The oil is characterized by a predominance of nC_{20-21} normal alkanes, together with isoprenoids (farnesane, pristane and phytane), steranes (C_{27}, significant C_{28}, and C_{29}), diasteranes, and pentacyclic triterpanes (with only trace gammacerane). Mild biodegradation has occurred in petroleum trapped in coarser fractures.

Subsequently, three petroleum seepages trapped under winter ice from the eastern shore and southern basin of Lake Baikal were analysed (Figure 1b). All seepages show more intensive biodegradation than the petroleum in the onshore metamorphic rocks, with almost complete loss of normal and isoprenoid alkanes. Relatively high molecular weight polycyclic aromatic hydrocarbons (e.g. benzopyrenes and coronene) are of concentrations comparable to the pentacyclic triterpanes. Although there are differences in the sterane and diasterane distributions, the pentacyclic triterpane distributions in the seepages are very similar to those in the onshore metamorphic rocks.

The Lake Baikal rifting commenced in the Oligocene, with sedimentation continuing to the present. It is suggested that the petroleum detected in the onshore metamorphic rocks and the Lake Baikal seepages are from similar sources. The sterane distributions suggest a mixed aqueous and terrestrial source, and therefore sterane distributions suggest a mixed aqueous and terrestrial source, and therefore a source younger than the Precambrian, but compatible with the recent rifting.

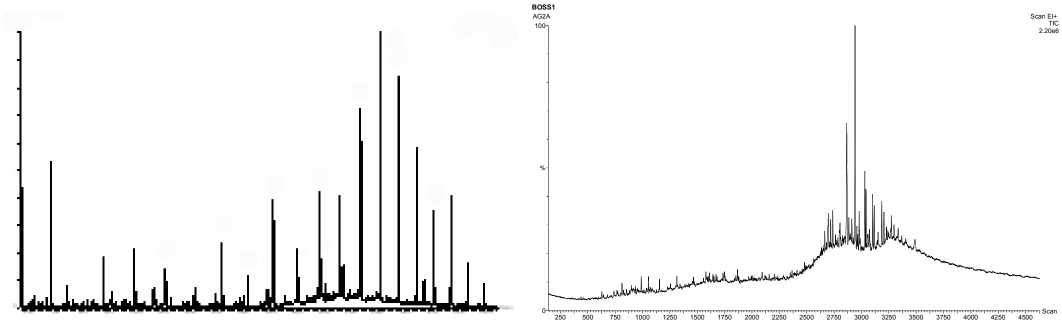


Fig.1. a (left) is a selected ion chromatogram (m/e 43+57+71+85+99) showing a mildly biodegraded petroleum in metamorphic rocks (location 2417). Figure 1b (right) is a total ion chromatogram of a Lake Baikal seepage, in which extensive biodegradation has resulted in loss of normal and isoprenoid alkanes

The heat flow in Lake Baikal has been reported as uneven[1]. The background heat flow is 50–70 mW/m^2, but locally is 1–8 W/m^2. Heated fluids have been reported along fault zones, and recent volcanic activity has occurred. It is suggested that locally the Lake Baikal sediments may have entered the oil window as a result of the elevated thermal activity. A similar situation occurs in the East African Rift. Although we acknowledge that the PreCambrian contains significant petroleum source rocks, recent source rocks (Oligocene and younger) are considered responsible for the petroleum in the fractured metamorphic rocks adjacent to Lake Baikal , and the seepages within Lake Baikal.

References

[1] Golubev, V.A., Klerkx, J., Kipfer, R., 1993. Heat flow, hydrothermal vents and static stability of discharging thermal water in Lake Baikal (South-Eastern Siberia), Bull. Centres Rech. Explor.-Prod. Elf Aquitaine Prod. 17, 53–65.

POS2-13: Geochemical preconditions of oil-bearing strata on the Western Greenland margin

E. Poludetkina[1], J. Boesen-Koefoed[2]

1) UNESCO-MSU Centre for Marine Geology and Geophysics, Faculty of Geology, Moscow State University, Vorobjevy Gori, Moscow 119899, Russia (e-mail: poludetkinaelena@mail.ru)
2) Geological Survey of Denmark and Greenland, Thoravej 8, DK2400, Copenhagen NV, Denmark

West Greenland has been perspective object for searching of hydrocarbons for the last 30 years. Oil seepages are widely spread on northwestern Disco and Nuussuaq, central part of West Greenland. Geochemical analyses suggest existence of several petroleum systems in the underlying Cretaceous and Paleocene fluvio-deltaic to marine sediments and even in the deeper strata. Thus, the tasks of investigation during the 4th Leg of TTR-13 cruise was concerned to searching of possible indications of hydrocarbon fluids unloading to the sea bottom and investigation of source-rock formations on the western Greenland margin. A collection of rocks from the outcrops (presumably, original deposits) was gathered and investigated.

Depositional environments and sedimentation history of the studied rocks have been interpreted from organic geochemical data (extraction, GC, MS, pyrolysis Rock Eval, bituminological analysis), lithological investigations and age determination. Igneous rocks were studied in order to verify possible migration of oils through them. As a result, in the studied basalts allochtonous bitumoid ($\beta \rightarrow 100\%$), probably migrated from the underlying sedimentary sequence was found.

Sedimentary samples observed are represented mainly by gray to dark gray high maturity limestones with clayey-silty admixture, and by carbonate clays, siltstones and sandstones. TOC content is changing in different samples from 0,1% to 0,7%. By Rock-Eval data practically all the rocks have low genetic potential S1+S2 (0,1-0,41 $^{kg,\ HC}/_{t,\ rock}$). HI=10-500 $^{mg,\ HC}/_{TOC,\ g}$, PI=0,02-0,38; Tmax varies from 410 to 450^{0}C with minor deviations – therefore thermal maturity of the source rocks is low, corresponding to the upper part of the oil window or even less. MS investigations showed that practically all the samples are situated in the area of marine OM with admixture of continental OM. Differences are observed in Ordovician black clayey limestones: S1+S2=3,2-16,5 $^{kg,\ HC}/_{t,\ rock}$; TOC=0,8-3,2%, Tmax=429-432^{0}C. By character of n-alkane distribution we can assume first stage of bitumoid biodegradation. Pr/Ph=2,6, the chromatogram is characterized by large quantity of Pr and Ph. Pr/nC17==2,4; Ph/nC18=1,85 ratios tells about OM of mixed origin. Ro=0,81 – 0,83 and Ki ratios approve that these rocks are situated in the upper part of the oil window.

Concluding, litho-geochemical investigations allowed to characterize practically all the rocks from the studied stations to be with low oil-gas-generating potential. But in the studied strata there is layer (layers) of Late Ordovician with high oil-generating potential characterized by the samples with high TOC content and high HI value (up to 488). Clayey-limestone rocks of this type are characterized by mixed kerogen with continental admixture, thermal maturity is corresponding to the upper part of the oil window. Oil-and gas-generating potential of these rocks could be estimated as high (7,9 – 48,2 $^{mg,\ HC}/_{g,\ TOC}$). So presumably such rocks in the basins of the Labrador Sea and West Greenland can generate both gaseous and liquid hydrocarbons nowadays. Such implications are very encouraging for future exploration offshore Labrador and West Greenland, since it demonstrates the source rock capable to generate liquid hydrocarbons exists in the region and contradicts the idea that this area is being only gas-prone.

POS2-14: Biological markers distribution in Bahloul source rock extracts from Central-Northern Tunisia

H. Affouri[1], M. Montacer[1,2]

1)Université de Sfax, Faculté des Sciences de Sfax, Département des Sciences de la Terre, Adresse : Route Soukra Km 3,5 ; BP 802, 3018 Sfax, Tunisie, Unité de Recherches « Géoressources, Environnements naturels et Changements globaux (GEOGLOB) (e-mail : hassene_affouri@yahoo.fr)
2)Université de Gabès, Cité Riadh, Zerig 6072 Gabès, Tunisie

During the late Cenomanian–Early Turonien (C/T boundary) organic rich facies were deposited under anoxic bottom water conditions in central and northern Tunisia : the Bahloul formation [1]. It is well known as source rock for oil generation in Tunisia [2].

Detailed geochemical analyses have been performed on more than 80 samples collected from the outcrops of this formation in central and northern Tunisia. The aim was to study the organic matter repartition and its thermal evolution. This organic matter is found to be very rich in biological markers, mainly steranes and terpanes ([3], [4], [5], [6], [7]). These markers were used to study the organic matter evolution degree as well as the depositional environments of this formation in the different studied areas.

Organic matter characterization using Rock-Eval pyrolysis and gas chromatography techniques displays that it was of type II marine planktonic origin. Furthermore, organic matter evolution indicates an advanced thermal maturity in many areas. This was particularly the case in Kef and Kalaat Senan.

Moreover, the dominance of the ββ-steranes configuration (peaks R and S), the presence of tricyclic terpanes ($C_{23/3}$ to $C_{29/3}$, peaks 3 to 8) and the high Ts/Tm ratios (peaks 9/10), indicates a high level of thermal maturity in Kef and Kalaat Senan areas (fig.1 C) in agreement with Rock-Eval pyrolysis and gas chromatography analyses. Biological configuration is found to be dominant in samples of central and northern Tunisia (fig.1 A) indicating a low maturity level of organic matter. Well preserved sterane and methyl-sterane (fig.1 B) molecules suggested an anoxic water column. High hopanes/steranes ratios from central Tunisia are with agreement of highly bacterial activity in sediments.

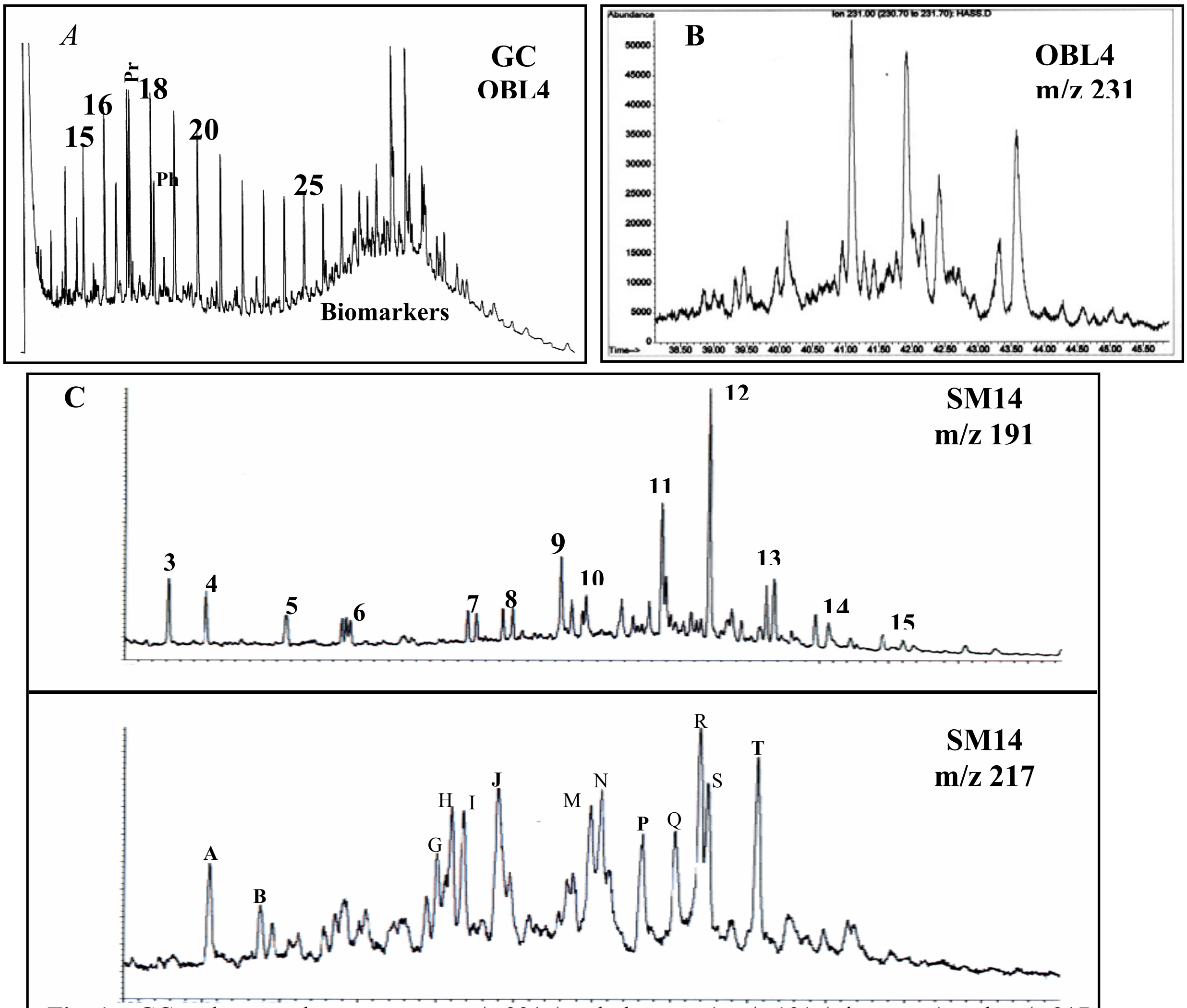


Fig. 1 – GC and mass chromatograms m/z 231 (methylsteranes) m/z 191 (triterpanes) and m/z 217 (steranes) of Bahloul source rock extract from central Tunisia (A and B) and from Kalaat Senan area (C)

References

[1] Burollet, P. F., (1956) – Contribution à l'étude stratigraphique de la Tunisie centrale. Ann. Mines et Géol.,Tunisie, n° 18, 350 p.

[2] Ben Ferjani, A., Burollet, P.F., Mejri, F., 1990. Petroleum geology of Tunisia. E.T.A.P, (Ed.) Tunis, 1990, 194 p.

[3] Affouri, H. 2004. Etude géochimique des faciès roches mères d'hydrocarbures et réservoirs potentiels dans le cadre de l'exploration pétrolière en Tunisie septentrionale. Thèse de Doctorat, Univ. Tunis El Manar, F.S. Tunis.

[4] Affouri, H., Montacer, M., 2002. Organic geochemistry characterisation of two oil source rocks in northern Tunisia. 6th international conference on the Geology of the Arab Word (GAW-6), Cairo University, February 2002, Abstract.

[5] Affouri, H., Montacer, M., Ghanima R. Saidi M., 2002. Bahloul and Bou Dabbous source rock biomarkers correlation with reservoir oils and surface oil seeps. The eighth Tunisian Petroleum Exploration & Production Conference, EPC 2002, poster session, Abstract, ETAP, Tunisia

[6] Montacer, M., 1995. Comparative organic geochemistry of two Tunisian oil source rocks (Bahloul and Bou Dabbous) as an approach of oil exploration in northern part of Tunisia. Proceedings of the seminar on source rocks and hydrocarbon habitat in Tunisia, ETAP, memoir n°9, 1995, pp. 45-47

[7] Montacer, M., Disnar, J. R., Orgeval, J. J., Trichet, J., 1988. Relationship between Zn-Pb ore and accumulation process: Example of Bou Grine deposit (Tunisia). Organic Geochemistry 13, n° 1-3, 423-431.

POS2-15: Importance of the paleothermometers that can be used for the study of the organic matter content in the potential generating rocks with low level of maturity

J.A. Pérez-Ortiz[1], L.F. Fuentes-Pacheco[2], E. Gutiérrez-Mejía[1], L. López-López[1]

1) Instituto Mexicano del Petróleo. Laboratorio de Petrografía Orgánica. Pachuca, Hgo. México
(e-mail: jortiz@imp.mx)
2) Petróleos Mexicanos. Exploración y Producción. Gerencia de Análisis Técnicos. Villahermosa, Tab. México
(e-mail: ffuentesp@pep.pemex.com)

In this study is presented the thermal setting determined by means of the optic analytic results focused to the samples of three wells, "X", "Y" and "Z", to which, them they were carried out optic studies in light reflected (% Ro), fluorescent light (% I) and light transmitted of the content of the organic materials of the lignocellulosic and liptinitic type (bitumen solids), including the results of the analyses performed by means of the application of pyrolysis, chromatography, biomarkers and isotopic analysis for samples of rock and oil of the wells cited.

The objective of such analysis they have permitted to test new applications of geochemical and optician analysis to support a congruent history, detailing the vertical distribution and the thermal evolution of the diverse carbonaceous particles contents in the Jurassic, Cretácicas and Tertiary rocks in 88 samples of cutting and core of the wells "X" and "Y" located in the Coastal Plain of the Gulf of Mexico and the well "Z", located in Chiapas.

These studies are with the purpose to determine the state of evolution and maturity, as well as the degree of alteration to relate to the formation damage in this part of the basin. It is appreciated the state of immaturity of the algal-laminated facies with values of IH from 600 to 700. The organic facies are cellulosic and lignocellulosic type and present values of vitrinite reflectance (% Ro) from 0.20 to 0.33. Fig. 1.

In the oils is observed high content of the contaminants additives and abundant asphaltens, for which is observed that this material is originated *in situ* with values of 7º API. The production of fluids is low and is observed that they are found highly altered by the presence of meteoric and injection water, that in this area is abundant. Fig. 2. The study of the oils it gives as a result that they originate from an alteration process of the crude oil, what causes as consequence, heavy oils and relatively enriched in aromatic-asphaltic compounds rich in sulfur and ºAPI smaller.

These oils were generated of suboxic to anoxic marine carbonated facies, which can be corroborated for the results of the analyses of gas chromatography and mass spectrometry. Defined relations are observed, as the case of the relation of the C_{29} hopane greater C_{30}

hopane, that as a group with other biomarkers they relate them to environments marine generators of the Tithonian. Fig. 3.

The organic matter dispersed fossil found in the wells represents an excellent paleothermometer, since the temperature-time that has modified its physiochemical and biological properties permits us to visualize the way of the transformations diagenetic of the organic matter represented with an increase in the reflecting power of the organic materials.

The organic sediments characterized in the wells "X" and "Y" they were analyzed as a group by presenting the same type of organic matter dispersed fossil and different thermal values with respect al well "Z". The specific characteristics for the intervals of geochemistry interest in the sedimentary columns studied have shown us that: 1) in the carbonated intervals with clayey horizons of Thitonian Jurassic age of the wells "X" and "Y", is shown algal matrix with lignocellulosic fragments, as well as of bitumen; 2) in the carbonated interval of the Middle Cretaceous it more is the amorphous organic material on the lignocellulosic and in the interval of Oligocene was observed a mixture of both, amorphous material and lignocellulosic. With respect to well "Z", without any doubt, the only part studied presents lignocellulosic matter with small contribute of bitumen that is possible to identify in the algal matrix. Fig. 4.

With respect to potential generator of these three wells can be concluded that the wells "X" and "Y" have excellent values in the Middle Cretaceous and Oligocene would be able to expect a good potential as generators of light hydrocarbons. In the well "Z", nevertheless, the conditions of maturity aim at deeper horizons Upper Jurassic and with smaller probability the Middle Cretaceous.

References

Barbosa, C. F. 2000. Exploración y Reservas de Hidrocarburos en México. Col. J. Silva H. / Porrúa Libro 385.pgs.

Birkle, P. y Portugal M. E. 2001. Caracterización Química e Isotópica de los acuíferos profundos del Campo Cactus. IIE. CFE. Informe inédito.

Bradley, W. H., (1924), Amer, J. Sci, 5th Series, 8, 228.

Combaz, A., (1962), C. R. Acad Sci. Paris, 253, 1977.

Durand, B., Espitalie, J., Nicaise, G. And Combaz, A., (1972) Rev. Inst. Franc. du Pétrole, XXVII, 865.

Gadel, F. Et. Ragot Gadel, F. Et Ragot, J.P., (1974), in: Advances in Organic Geochemistry 1973,620, Editions Technip, París.

Guzmán, V. M., Pérez, O. J. A. y Olivo, B. E., 2000. Geoquímica de Yacimientos Campos Cactus – Nispero – Rio Nuevo – Sitio Grande. IMP. Proyecto F.00517. Informe Inédito.

Sosa, P. A. y Ramírez, G. F. 1997. Evaluación del potencial generador del Jurásico Superior Tithoniano del área del Comalcalco Tab. PEP. Mermoria del 1er Encuentro de la Estratigrafía, Sedimentología, Diagénesis y Petrofísica de las rocas del Jurásico Superior en México, Tampico,Tamps: 109-113.

Teichmuller, M. and Ottenjahn, K., (1977) Erdol Und Kohle, 30, 387.

Tissot, B. and Weltw, D.H. (1978), Petroleum Formation and Ocurrence, Springer Verlag Press.

PRG1-1: Simulated Maturation of Sulfur–Rich Asphaltite by Hydrothermal Conversion

V.R. Antipenko[1], O.A. Golubina[1], I.V. Goncharov[2], S.V. Nosova[2], J.V. Rokosov[3]

1) Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences, 3, Academichesky Avenue, 634021, Tomsk (e-mail: dissovet@ipc.tsc.ru)
2) Tomsknipineft, Tomsk, Mira Street, 72
3) Institute of Coal and Coal Fuel Chemistry SB RAS

Previously we (Antipenko V.R. et al., 2003) reported about a lower thermal maturity of petroleum, which formed vein Ivanovskoye deposit of sulfur–rich asphaltite. Asphaltite hydropyrolysis can provide additional information about its genesis.

The present work is aimed to reveal directions and scales of compositional changes occurring in hydrocarbon and heterorganic components of the natural asphaltite during its hydrothermal conversion, which simulates thermal maturing of organic matter.

The experiments on hydrothermal conversion of natural asphaltite (40 g) were carried out in a rotating (200 rev/min) autoclave at 400 °C in the presence of nitrogen gas (5 MPa) and 0.3 L of 5% KOH aqueous solution. The rotating autoclave was 0.5 L in volume and it was made of stainless steel. A sample was kept at the designed temperature during 30 and 60 min. The pressure in the autoclave within the experiment was 40–42 MPa. Then during 80 min the autoclave was cooled with compressed air up to 40 °C and unloaded. A reactor pot was washed with hot benzene. After precipitation of asphaltenes from a benzene–soluble product with a chromatographic method we separated aliphatic and aromatic hydrocarbon fraction (oils), which then were divided into polar and non–polar parts by column liquid chromatography on silica gel. GC/MS – analysis of these fractions was carried out using Hewlett Packard 6890/5973. As a result mass–chromatograms and mass–fragmentograms have been recorded for alkanes, alkenes, terpanes, steranes, alkylbenzens, naphthalenes, phenanthrenes, anthracenes, benzothiophenes, dibenzothiophenes, carbazoles, benzocarbazoles and thiophenoles. One compared analyses data of oils, obtained in different tests with the data obtained for oils of the initial asphaltite.

The data testify that molecular compositions of all analyzed compound classes in oils separated from the products of hydrothermal conversion noticeably differ from the compositions of the compounds occurring in oils of the initial asphaltite. In particular, one can observe benzocarbazoles, thiophenoles and alkenes, which were absent in oils of the initial asphaltite. It is determined by the fact that compositions of the compounds occurring in the products of hydrothermal conversion are formed due to superposition of two processes. First, their generation is caused by destruction of both asphaltenes and resins of asphaltite. Second, isomeric compositions of the obtained compounds and of those occurring in oils of the initial asphaltite change under the influence of temperature. It is just impossible to split distinctly the contribution of each process to the formation of the compositions of hydrocarbon and heterorganic compounds in the products of hydrothermal conversion. In particular, in a number of cases an increased portion of lower molecular homologues (tri- and pentacyclic terpanes, steranes, n- and iso-alkanes, carbazoles) can be explained by cracking of high-molecular homologues. At the same time it can reflect compositional features of the initial organic matter, remained in the structures of asphaltenes and resins. One can also predicate that the effect of thermal transformation of the compounds generated by asphaltite under the conditions of hydrothermal conversion is sufficiently exhibited. It is indicated by regular change in a number of widely used parameters of thermal maturity (MNR, % n-C_{20+}, Pr/n-C_{17}, Ph/n-C_{18}, n-C_{19}/n-C_{31}, MPI-1, MPI-2, MDR_1, $MDR_{2,3}$, MDR_4, 1-MC/(1-MC+1-EC). However it attracts attention that tendencies towards the change of several parameters of the thermal maturity, namely Ts/(Ts+Tm), M_{30}/H_{30}, $\alpha\alpha 20S/(20S+20R)$, $\beta\beta/(\beta\beta+\alpha\alpha)$, MDR and MDR′, benzothiophenes/dibenzothiophenes, B[a]C/(B[a]C+B[c]C), do not closely agree with the desired ones. Anomalously high contents of anthracene, 2-methylanthracene and benzo[b]carbazole are among other unusual compositional features of the obtained products. Such features are typical for some petroleums (Li M. et al., 1998). In the above paper it was explained by the fact that such unusual petroleums were generated by high-temperature, short–term pyrolysis of thermally immature organic matter. Therefore, the data obtained in the study are the evidence of the previous conclusion (Antipenko V.R. et al., 2003) about a lower thermal maturity of petroleum, which formed Ivanovsky asphaltite deposit.

References

Antipenko, V.R., Semennikova, O.A., Nosova, S.V., Goncharov, I.V., 2003. Composition and Genesis of Ivanovskiy Asphaltite. 21st Inter. Meeting on Organic Geochemistry, 8-12 September, 2003, Krakow, Poland. Abstracts, Part II, 241–242.

Li, M., Osadetz, K.G., Yao, H., Obermajer, M., Fowler, M.G., Snowdon, L.R., Christensen, R., 1998. Unusual crude oils in the Canadian Williston Basin, Southeastern Saskatchewan. Organic Geochemistry 28, 477–488.

PRG1-2: Geochemical characterisation of crude oils from the Mittelplate oil field, Germany: implications for oil quality distribution and field development

C. Brinzer, E. Mueller

RWE Dea AG, Ueberseering 40, 22297 Hamburg / Germany (e-mail: Christian.Brinzer@rwedea.com)

The Mittelplate oil field, located in the tidal zone off the western coast of Schleswig-Holstein, is Germany's largest oil field with original oil in place (OOIP) reserves of about 100 mill. metric t. Sulphur-rich, aromatic heavy oils are produced from interbedded sandstones of Middle Jurassic age drilled at depths ranging between approximately 1800-3000 m TVD. Average oil gravity ranges from 0,91-0,94 g/cm³ with corresponding sulphur contents of 2,6-18,2% and GORs of 11,5-22,5 Sm³/Sm³. The field is characterized by two stacked reservoir sections with independent oil-water contacts which onlap on the western margin of the Büsum salt plug. A general increase of oil quality from bottom to top reservoir levels controls field development concepts since oil quality has a major impact on well planning, recoverable reserves and economic modeling.

Geochemical analyses ($\delta^{13}C$ isotopes GC, GCMS) of crude oil samples from 25 wells were performed in order to investigate on the oil quality variation in the Dogger and Wealden Formations. All samples show a homogeneity in terms of geochemical facies parameters which suggests the Lower Jurassic Posidonia Shale as an early to beginning peak oil window mature (VR_o range approximately 0.7-0.8%) single common source. Varying intensities of crude oil alteration due to biodegradation and/or water-washing can be excluded as a cause for the range of oil qualities. Trends of various biomarker based maturity parameters indicate decreasing oil maturity with increasing depth, which correlates closely with vertical oil quality distribution. The presence of these maturity trends excludes a homogenisation of the oil column by means of segregation, diffusion and/or convective mixing. It is assumed that expulsion sequence, secondary migration processes and sequential filling of the individual reservoirs determine the present vertical oil quality distribution. Oil of an early generation phase migrated first to the structurally and stratigraphically lowest reservoir sandstones that are located closest to the source rock. After saturation was reached the sequential filling of the superimposed reservoirs continued independent of the stratigraphic level of the reservoirs. Oils produced from shallowest depths show highest maturities and improved oil quality. Also, within individual reservoir sections a similar maturity gradation can be observed. Apparently, the geochemical signature of the oils did not change since filling of the reservoirs began in Upper Cretaceous and Lower Tertiary times, respectively, and systematic vertical distribution of geochemical and physical properties are preserved. In contrast to oils of the shallower reservoirs, oils in the stratigraphically oldest and structurally deepest Middle Jurassic reservoir levels very close to the oil-water contact show geochemical characteristics indicating initial oil degradation.

Based on geochemical analyses and data interpretation in a structural-geological context a basic concept for hydrocarbon generation, timing and reservoir filling processes in the Mittelplate field area was established. The integration of crude oil PVT data provides a consistent explanation of oil quality distribution. Probabilistic prediction of oil PVT properties for field development and depth estimates of producible oil is now possible using linear relationships of depth, maturity and quality of the oils. However, analyses point to potential degradation processes in the deepest reservoir section, which potentially limits the depth of producible oil and influence recoverable reserve estimates.

The concept of oil emplacement also provides criteria to evaluate basin and fluid flow models and modeled PVT properties of reservoired oil. Based on measured oil maturity, OOIP reserve estimates and quantitative source maturity modeling calculations of hydrocarbon volumes available for charging of additional or secondary plays is possible. Additionally, the correlation with geochemical parameters was used to evaluate oil qualities when only small amounts of sample material are available or fluid sample quality was poor. Results of the analyses provide a basis for planning, sample selection and evaluation of production allocation/commingled production studies.

PRG1-3: Effects on geochemical parameters caused by mixing of lacustrine and marine oils

J.R. Cerqueira, E.V. dos Santos Neto, J.V.P. Guzzo

Petrobras Research Center, Av. Hum, Quadra 7, 21949-900, Rio de Janeiro, RJ, Brazil

Results of geochemical analyses such as gas chromatography, biomarkers, carbon and hydrogen isotopic ratios, are very useful tools for the evaluation of petroleum systems. They contribute for petroleum exploration providing important information in order to assess the paleoenvironment, age, kerogen composition and thermal evolution of the source rocks, allowing oil-to-oil and oil-to-source rock correlations.

In the South Atlantic basins, petroleum was derived from Lower and Upper Cretaceous source rocks, deposited in a syn-rift saline lacustrine and in a post-rift marine paleoenvironments, respectively (Mello et al., 1994, Schiefelbein et al., 1997 and Wiles et al, 1998). Normally, crude oils accumulated in the Lower Cretaceous to Tertiary reservoirs have geochemical characteristics of a particular source rock. However, sometimes they do not show any distinctive biomarker evidence of their origin, making difficult the interpretation of the geochemical data.

In order to deconvolute the sources of mixed lacustrine and marine oils, four mixtures of representative samples of each end-member were prepared in laboratory in different proportions (20%, 40%, 60% and 80%). These mixtures were analyzed by gas chromatography, medium pressure liquid chromatography, gas chromatography-mass spectrometry (saturates biomarkers) and isotope ratio monitoring-gas chromatography-mass spectrometry ($\delta^{13}C$ and δD of individual *n*-alkanes).

The results showed a trend in direction to the end-members, but each mix did not present remarkable biomarker characteristics indicating a predominance of lacustrine or marine oil. In some cases it is difficult to determine its origin, i.e, whether it is lacustrine, marine or mixed, observing only the biomarker or isotopes results of one single mixture. For example, figure 1 shows that only using the comparison of all the results together it is possible to define correctly the origin of each sample and the proportion of its mixture.

In conclusion, we propose that studies involving the relative contribution of different sources for mixed oils can be significantly improved with the use of a data base with analytical results of artificial mixtures, prepared with representative end-member.

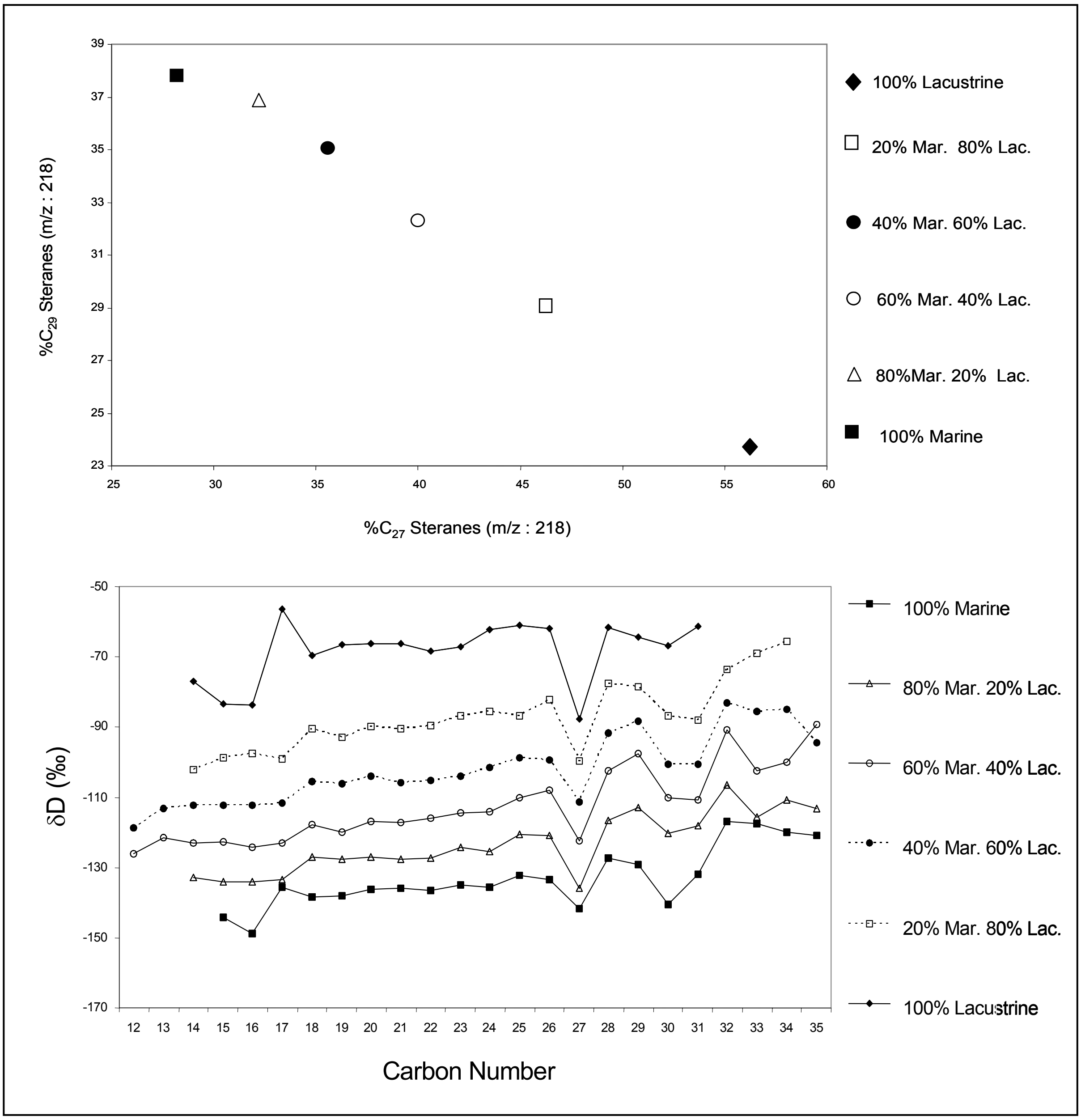


Fig.1. Cross-plots of geochemical parameters showing the percentages of C_{29} and C_{27} steranes and hydrogen isotopic composition of *n*-alkanes in the oil mixtures

References

Mello, M. R., Mohriak, W. U., Koutsoukos, E. A. M. and Bacoccoli, G., 1994. Selected petroleum systems in Brazil. In: Magoon, L. B. and W. G. Dow, eds., The petroleum system - from source to trap: AAPG Memoir 60, 499-512.

Schiefelbein, C. F., Zumberge, J. E., Cameron, N. C. and Brown, S. W. 1997. Petroleum Systems in South Atlantic Margin. Extended Abstracts Volume of Hedberg Research Symposium, Rio de Janeiro, Brazil.

Wiles, R. L. F., Peper, A. S. and Cawley, S. J., 1998. Source rocks of petroleum in the South Atlantic Margins. Extended Abstracts Volume of 1998 AAPG International Conference & Exhibition, Rio de Janeiro, Brazil, 422.

PRG1-4: Compositional alteration of crude oils from different petroleum systems during initial biodegradation

R. Elias[1], A. Müller[1], A. Vieth[1], A. Riva[2], H. Wilkes[1]

1) GeoForschungsZentrum Potsdam, Telegrafenberg, D-14473 Potsdam, Germany
(e-mail: elias@gfz-potsdam.de)
2) ENI-Agip Divisione E&P, Via Maritano 26, 20091 San Donato Milanese, Milan, Italy

Biodegradation of hydrocarbons in petroleum reservoirs is an important alteration process of enormous economic importance. While the mechanisms and effects of aerobic biodegradation of petroleum are long-known and well-studied, the alteration of hydrocarbons due to anaerobic degradation of crude oil is a discovery of the last decade. Only recently, a reasonable pathway for complete bacterial oxidation of *n*-alkanes to carbon dioxide under strictly anoxic conditions has been proposed [3]. This is relevant to petroleum exploration, because it is unlikely that in subsurface petroleum reservoirs oxygen is available for a volumetrically significant aerobic biodegradation of hydrocarbons. However, the detailed processes taking place during biodegradation of petroleum in reservoirs still remain obscure. Extremely little is known about possible differences in alteration mechanisms and degradation rates under variable *in situ* conditions.

Here we present preliminary results of a study focussing on specificities of compositional alteration of crude oils in different petroleum systems caused by biodegradation. The main objective of this study is to gain a better understanding of biodegradation effects on oil quality with the ultimate goal to develop tools for the prediction of oil quality from molecular composition. A representative set of initially biodegraded crude oils from different petroleum systems was selected representing degradation levels of 1-4 on the Peters & Moldowan scale [1] and very slight to slight on the scale of Wenger and co-workers [2]. We assume that the loss of major oil components occurs essentially within these stages of biodegradation which therefore are likely to cause the most significant decreases in oil quality. The phytane/*n*-octadecane ratio, being applicable to biodegradation levels below 4 on the Peters and Moldowan scale, is a widely used biodegradation indicator. Figure 1 illustrates that major losses of *n*-octadecane occur when the phytane/*n*-octadecane ratio changes only slightly. Loss of *n*-octadecane for a given sample was calculated by comparison with the least degraded end member in the respective subset. The calculation is based on the assumption that *n*-octadecane in the end members and phytane in any sample were not affected by biodegradation which may not be true in all cases. The same is conceptually applicable to any type of major oil constituent. This implies that mass loss of main petroleum constituents occurs during stages of biodegradation which, according to conventional classification schemes, would be regarded as marginal. Such apparently strongly underestimated effects of very initial biodegradation will be addressed in this presentation. The molecular characterisation of our sequences of degraded oils provides evidence that the depletion order of specific types of petroleum constituents may be different in different petroleum systems. Possible controls on these specific patterns of compositional alteration will be further investigated and discussed in this presentation.

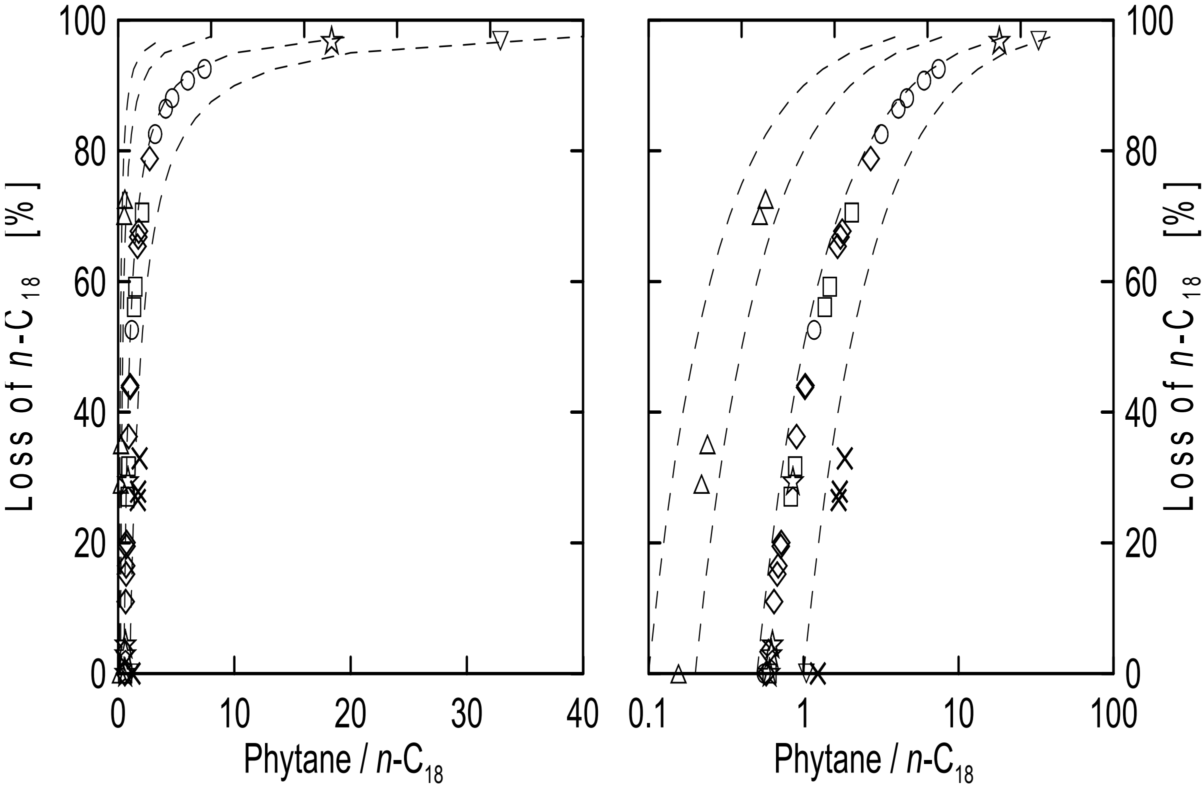


Fig.1. Plot of loss of *n*-octadecane vs. phytane/*n*-octadecane for crude oils from seven petroleum systems as indicated by different symbols. The dashed lines represent calculated values for oils of different initial composition (initial phytane/*n*-octadecane ratio 0.1, 0.2, 0.5 and 1.0 from left to right, respectively)

References

[1] Peters, K. E., Moldowan, J. M., 1993. The Biomarker Guide. Englewood Cliffs, Prentice Hall.

[2] Wenger, L. M., Davis, C. L., Isaksen, Gary H., 2001. Multiple controls on petroleum biodegradation and impact on oil quality. Society of Petroleum Engineers Paper 71450.

[3] Wilkes, H., Kühner, S., Bolm, C., Fischer, T., Classen, A., Widdel, F., Rabus, R. 2003. Formation of *n*-alkane- and cycloalkane-derived organic acids during anaerobic growth of a denitrifying bacterium with crude oil. Organic Geochemistry 34, 1313-1323.

PRG1-5: High-molecular weight hydrocarbons distribution in marine oils, Volga-Ural basin, Russia

J. Golovko[1], R.P. Philp[2], G.S. Pevneva[1]

1) Institute of Petroleum Chemistry SB RAS, 3 Academichesky Ave, 643021, Tomsk, Russia
(e-mail: luvn@ipc.tsc.ru)
2) University of Oklahoma, 100 East Boyd St., Norman, OK 73019, USA

High-molecular weight hydrocarbons (HMWHCs) are ubiquitous in crude oils and typically reflect both the source material and depositional environment of the source rocks. HMWHCs can be extremely significant since they lower the pour point of the crude oil and can be responsible for wax deposition problems that occur during production, transportation and refining of crude oils all over the world. An improved knowledge of the genesis and behavior of these compounds in oils is particularly important for Russia where operation of many oil fields proceeds for a long period of time under negative temperatures.

HMWHCs have been isolated from 8 Paleozoic oils collected from 4 oil fields in the Volga-Ural region, one of the largest Russian oil-and-gas bearing basins. The oils are of high viscosity and have a relatively high asphaltene (3.3–10.1wt.%) and wax content (3.7–15.6wt.%). The oils were sourced from marine organic matter and one from the Novolobaitovskoye field was biodegraded and contained 25-norhopanes.

HMWHCs are complex mixtures of compounds above C_{40}, including n- and iso-alkanes, alkylcycloalkanes, alkylaromatic hydrocarbons. The relative proportions of these various components will define when the wax deposits start to appear. For example, n-alkanes have higher melting points than iso-alkanes and addition of a long alkyl side chain to the cycloalkane structure lowers the melting point in comparison to the n-alkane of corresponding carbon number.

In the Volga-Ural oils the wax fraction was dominated by n-C_{19}-C_{44} alkanes (24-46wt.%) with an even/odd carbon predominance between C_{26} and C_{30}. In samples from the Novolabitovskoye and Allagulovskoye oilfields the relative amounts of n-alkanes increases with depth. Such an increase was not observed in the Mordovoozerskoye oil field. The concentration of HMWHCs in the biodegraded Novolabitovskoye oil does not exceed 4.7wt.%, whereas in the non-biodegraded sample from the same oil field their abundance is 15.1wt.%. The n-alkanes in the biodegraded oil represent 46wt.% of the HMWHC fraction but in the non-biodegraded oil only represent 29.4wt.%. The non-degraded oil is located close to the source organic matter and as a result the initial composition of HMWHCs is well preserved. The HMWHC components in the biodegraded oil reflect the composition of organic matter more distant from the source and representative of both the biodegraded and initial organic matter. The relatively high concentration of HMW n-alkanes in this oil probably caused by adsorptive precipitation of branched and cyclic alkanes in rocks during migration enhancing the concentration of the n-alkanes.

The homologous series of alkylcyclopentane extends to C_{48} in Volga-Ural oils with an even over odd carbon number predominance. For most of the oils the carbon preference indices for C_{42}-C_{46} was >1 as previously reported for oils of marine source from other regions. The biodegraded Novolabitovskoye oil was an exception, where CPI^a ~1 was probably caused by generation of the initial organic matter in a freshwater lacustrine environment.

The branched compounds present in the HMW fractions of oils are generally dominated by monomethyl branched alkanes (MA) though HMW di- and trimethylalkanes, suggested to be possible precursors of HMWHCs in oils, have been observed in some insect species and cyanobacteria. The concentrations of 2-MA and 3-MA dominate over other branched hydrocarbons. Identification of other homologous series or individual methyl alkanes was troublesome because of their low concentrations as well as poor chromatographic separation. The relative concentrations of 2-MA and 3-MA are similar, therefore they assumed to be generated by common source through the same series of reactions. Despite of the different chemical nature of reservoir rocks and temperature gradient, distribution of MA is similar in the oils. Even the biodegraded oil does not show significant differences reflecting the stability of the HMWHCs to biodegradation.

The relative concentrations of HMWHCs in the oils from Volga-Ural Basin and their distributions indicate similar depositional environments for the initial organic matter as well being characteristic of the oilfields being studied.

References

Hsieh, M., Philp, R.P., 2001. Ubiquitous occurrence of high molecular weight hydrocarbons in crude oils, Organic Geochemistry 32, 955-966.

Kenig, F., Sinninghe Damste, J.S., Kock-van Dalen, A.C., Rijpstra, W.I.C., Huc, A.Y., de Leeuw, J.W., 1995. Occurrence and origin of mono-, di- and trimethylalkanes in modern and holocene cyanobacterial mats from Abu Dhabi, United Arab Emirates. Geochimica et Cosmochimica Acta 59, 2999-3015.

Tuo, J., Philp R.P., 2003. Occurrence and distribution of high molecular weight hydrocarbons in selected non-marine source rocks from the Liaohe, Qaidam and tarim Basins, China. Organic Geochemistry 34, 1543-1558.

PRG1-6: Low- and high-molecular weight hydrocarbons in heavy oils

J. Golovko, G. Pevneva, A. Golovko

Institute of Petroleum Chemistry SB RAS, 3 Academichesky Ave, 643021, Tomsk, Russia
(e-mail: luvn@ipc.tsc.ru)

Nowadays, the study of heavy oils ubiquitous in oil-and-gas bearing basins all over the world is under high interest. To those refer oils with the high content of high-molecular paraffins (waxes), asphaltenes and resinous compounds obtained with hot extraction from SiO_2 gel in the Soxhlet apparatus. Their density varies from 0.870 g/cm^3 in heavy oils up to 0.895 g/cm^3 and higher in bituminous oils. The low-molecular weight hydrocarbons reflect the initial OM nature. In the oils changed their original composition under various processes effect in rocks, such information can be obtained on high-molecular weight hydrocarbons (HMWHCs). In such cases the data on their composition are inestimable in geochemical study.

Low- and high-molecular weight HCs have been studied in 4 heavy West Siberian oils: Van Egan, Pravdinskaya, Kalinovaya, Urmanskaya (density of 0.873-0.954 g/sm^3).

The low-molecular weight n-alkanes prevail in crude oils. The even over odd C_{18}-C_{30} n-alkanes predominance indicate marine genesis of Pravdinskaya oil. Only Van Egan oil differs by the absence of n-alkanes as well as iso-alkanes, which is caused by biodegradation. On the terpane distribution Urmanskaya, Pravdinskaya and Kalinovaya oils are similar to the most West Siberian oils previously studied. The significant destruction of the hopane series as well as 25-norhopane series occurrence, generated by the microbial removal of the methyl group at C_{10} and indicating heavy biodegradation, observed in Van Egan oil in the present study and also noted by other authors. Relatively high gammacerane concentration in these oils caused by reducing environment with the enhanced salinity and probably lacustrine environment of the initial OM generation.

The C_{30} steranes, known as 24-n-propylcholestanes and indicating marine depositional environment identified in Pravdinskaya and Van Egan oils. Their origin relate to 24-n-propylcholesteroles, which present in algae and sea invertebrates.

The geochemical parameters on the saturated and aromatic hydrocarbons reflecting both an origin, and a thermal maturity of the oils under research were calculated. In the biodegraded Van Egan oil with the enhanced concentration of the cyclic and cycloaromatic compounds the identification of alkyl aromatic HCs was impossible due to their small amounts. On the base of the parameters C_{29}S/R, $C_{29}\beta\alpha/\alpha\alpha$, C_{30} Moretane/C_{30} Hopane,

C_{31}(22S), MNR, DNR2, MPI1, PR1, *etc.* it was shown that Cenomanian Pravdinskaya oil is of the same thermal maturity level with Paleozoic Kalinovaya and Urmanskaya oils.

As far as it is considered that HMWHCs are more stable and reflect the initial OM genesis, the HMW n-alkanes, monomethyl alkanes and alkylcyclopentanes of the wax fractions were studied. The n-alkanes amounts increase with a thermal maturity enhancement of the oils studied and is maximal in Urmanskaya oil. The even HMW n-alkanes are predominant in Pravdinskaya oil. The relative amount of monomethylalkanes and alkylcycloalkanes correlation with a thermal maturity of oils was not observed. Their maintenance probably caused by the initial OM composition. It is interesting, that in Van Egan oil the relative amount of the wax fraction is high (11.3 wt.%), but no homologous series, neither individual HCs were identified by HTGC. Whereas, there is a point of view that HMWHCs are less/do not undergo biodegradation we assumed to identify some HCs. However, HMWHCs in this oil appear to be a mixture of cyclic hydrocarbons showing poor GC separation.

The carbon preference index CPI^a (CPI^a (C_{42}-C_{46})) > 1 in Pravdinskaya oil indicate marine depositional environment of the initial OM, and CPI^a ~1 in Urmanskaya and Kalinovaya oils: fresh-water lacustrine environment. The monomethylalkane distributions are similar and apparently of a common origin.

The hydrocarbon composition differences of the oils caused by the initial OM source as well as conditions of oil occurrence, in particular a chemical composition of reservoir rocks and reservoir temperature. Kalinovaya and Urmanskaya oils were generated by the same source, and the differences of their hydrocarbon distributions caused by their different maturity. Van Egan and Pravdinskaya oils generation proceeded in the different environment with the high input of marine OM. The HMWHCs along with LMWHCs reflect the depositional environment of these oils, however, in case of heavy naphthenic oils they cannot be applied since consist of unresolved mixture of cyclic and cycloaromatic hydrocarbons.

References

Peters, K.E., Kontorovich, A.E., Andrusevich, V.A., Moldowan, J.M., Huizinga, B.J., Demaison, G.J., Stasova, O.F., 1991. Biomarker hydrocarbons in oils and rocks from the Middle Ob region of West Siberia, Russia. Geology and Geophysics (in Rus) 10, 3-33.

Kashirtzev, V.A., Kontorovich, A.E., Philp, R.P., Chalaya, O.N., Zueva, I.N., Ivanova, I.K., Memetova, N.P., 2001. Biodegradation of saturated cyclic chemofossils. Geology and Geophysics (in Rus) 11-12, 1792-1800.

Hsieh, M., Philp, R.P., 2001. Ubiquitous occurrence of high molecular weight hydrocarbons in crude oils, Organic Geochemistry 32, 955-966.

PRG1-7: Using asphaltene-bonded biomarkers released by RICO reaction to identify source and filling direction of biodegraded oil reservoir— The application to the PL19-3 oilfield

G. Xu

Petroleum Geology Research and Central Laboratory, Research Institute of Petroleum Exploration and Development, No.20 Xueyuan Road P. O. Box 910, Beijing 100083, P.R.China (e-mail: guanjun_xu@263.net)

The source of the biodegraded oil of the PL19-3 oilfield, the largest heavy oil reservoir located in Bozhong depression of Bohaiwan Basin, East China, has been in dispute since its discovery in 1999. In this paper, asphaltenes of the biodegraded oil and source rocks from PL19-3 and other wells in the depression have been analyzed by RICO method (Ruthenium-Ions-Catalyzed-Oxidation) in order to evaluate its source and petroleum filling direction. The analysis of the biomarkers bonded on the asphaltene suggests that the source rock of the Lower Member of the Dongying Formation is the main contributor to the oil of the PL19-3 oilfield, and that the oil charge direction is running from north to south.

Ten oil and six rock samples were analyzed using RICO method previously published and ZSM adduction is added before GC-MS determination.

The analysis results show that both the ratios of $\sum C_{21}$-/$\sum C_{22}$+ and C_{21}+C_{22}/C_{28}+C_{29} of the n-alkanoic acids in RICO products of the oil from PL19-3 oilfield are lower than those of the oil from QHD32-6 oilfield, suggesting that there are less short n-alkyl side chains in the asphaltene of the PL19-3 oil than that of QHD32-6 crude oil. The distributions of steranoic acid (as methyl esters) are $C_{28}>C_{30}>C_{29}$ in the oil from PL19-3 oilfield, while the distributions are $C_{28}>C_{29}>C_{30}$ in the samples from QHD32-6 oilfield (Fig.1). The distributions of the source rocks in the Lower Member of the Dongying Formation are consistent with that of PL19-3 oilfield. In addition, the methyl sterane bonded on the asphaltene of the oil from PL19-3 oilfield, with methyl sterane/sterane values of 0.36~0.38, is lower than that of the oil from QHD32-6 oilfield, whose values are 0.41~0.42. Therefore the sources of the two oilfields are different.

Isomerization parameters of steroids and hopanoids bonded on asphaltenes exhibit lower thermal maturity than those of the counterpart in the saturate because of the suppression of isomerization of bonded-sterane. The ratios of (C_{31}+C_{32}+C_{33}) 22S/(S+R) hopanoic acid of the oil of PL19-3 oilfield, ranging from 0.54 to 0.58, are lower than those of the oil of QHD32-6 oilfield, ranging from 0.59 to 0.60. The values of C_{30} 20S/(20S+20R) steranoic acid of the oil from PL19-3 oilfield, with values ranging from 0.19 to 0.27, are also lower than those of the oil from QHD32-6 oilfield whose values range from 0.29 to 0.32. The relationship between the values of (C_{31}+C_{32}+C_{33}) 22S/(22S+22R) hopanoic acids and the values of the C_{28}/C_{30} steranoic acid indicates that the oil from the PL19-3 has more terrestrial inputs and lower maturity than that of the QHD32-6. This is also consistent with the source input and maturity of the two sets of source rocks, the Lower Member of the Dongying

Formation and the Third Member of the Shahejie Formation, respectively. So, it can be concluded that the oil of the PL19-3 originates mainly from the Dongying Formtion and the oils of the QHD32-6 from the third Member of the Shahejie Formation.

The values of C_{30} 20S/(S+R) steranoic acid of the oil from wells PL19-3-8, PL19-3-2, PL19-3-5, PL19-3-4, which are arranged from south to north, are 0.19, 0.20, 0.24, 0.27, respectively. Consequently, this indicates the oil charge direction is from north to south that is from well PL19-3-4 to well PL19-3-8.

From the biomarkers bonded on the asphaltenes, it can be concluded that the oil of the PL19-3 with relative lower maturity and more terrestrial inputs has close genetic relationship with the source rock of the Lower Member of the Dongying Formation, and that its charge direction is from north to south.

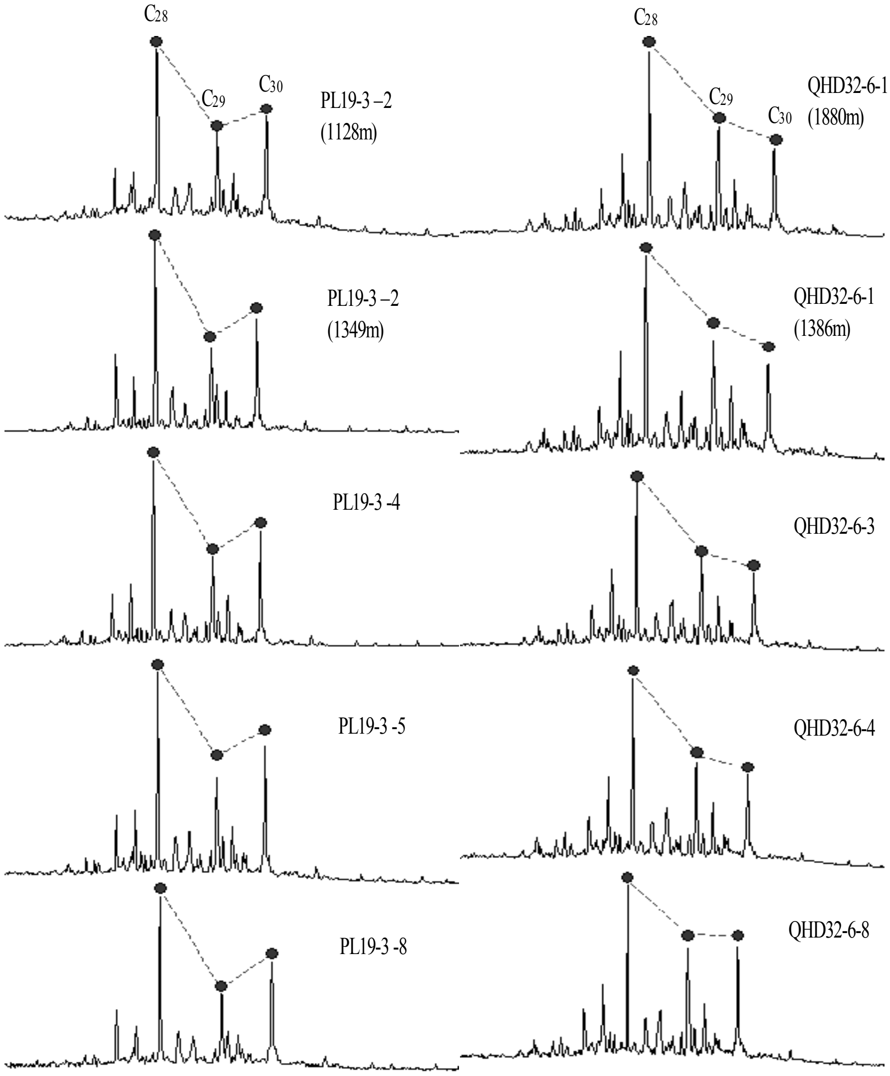


Fig.1. Partial mass chromatograms of m/z 275 showing the distributions of steranoic acid (as methyl esters) in the samples from PL19-3and QHD32-6 oilfields. C_{28},C_{29},C_{30} refer to steranoic acid after RICO treatment

PRG1-8: Sulfur Fingerprinting of Crude Oils for Reservoir Characterization

R.J. Hwang

ChevronTexaco Energy Technology Company, San Ramon, CA 94583, USA (e-mail: RJHW@chevrontexaco.com)

Analysis of organic sulfur compounds using gas chromatography- atomic emission detector (GC-AED) was completed on a series of oils samples from a giant field in Middle East to evaluate the potential of sulfur fingerprinting of crude oil in characterizing reservoir connectivity and compartmentalization. AED features high selectivity and sensitivity for detecting multiple elements generated from dissociation of compounds induced by high temperature helium plasma. Its responses to sulfur spices are linear and compound-independent, allowing a quick assay of distribution of sulfur compounds (sulfur fingerprint) in a crude oil. This paper presents a case study in evaluating applicability of sulfur fingerprinting in reservoir characterization by analyzing a suite of oils collected from a field with well characterized reservoirs in Middle East.

A giant field in Middle East produces sulfur rich, medium gravity oils from D and H reservoirs. The major reservoir (D) is over 70 km in length and 10 km in width, and consists of highly porous and permeable carbonate sands, whereas the underlying H consists of porous calcareous mudstones with low matrix permeability. Highly uniform bulk geochemical and molecular properties of D oils shown in a previous study indicate laterally connectivity throughout the D reservoir, which is supported by pressure and production data (Hwang and Baskin, 1994). However, hydrocarbon differences determined from gas chromatographic and biomarker analyses indicate that some H oils are compositionally distinct and vertically separated from D oils by a layer of impermeable carbonates and some are in vertical communication through a fracture network in the southern part of the field.

The sulfur chromatograms generated by GC- AED analysis of the oils were compared in great details with an in-house computer program designed for the rapid correlation of oil fingerprints. Like hydrocarbon compositions, sulfur fingerprints of the D oils are uniform, consistent with the laterally connected reservoir for the D zone. The results also show that the D oils can be differentiated from H oils where the reservoirs are vertically segregated, and cannot be differentiated where the reservoirs are vertically continuous. The study has demonstrated that sulfur fingerprinting can be an effective tool for characterizing reservoir connectivity and compartmentalization, particularly for the fields where oils are biodegraded or contaminated by synthetic-oil-based mud. With higher resistance to biodegradation, sulfur fingerprints are easier than conventional hydrocarbon fingerprints for correlating oils with different degrees of biodegradation. Further, the general absence of sulfur compounds in widely used synthetic-oil-based muds makes sulfur fingerprinting a highly valuable tool for correlating heavily contaminated oils.

Reference

Hwang, R. J., and D. K. Baskin, 1994, Reservoir connectivity and oil homogeneity in a large scale reservoir: *in* Proceedings of AAPG Middle East Geosciences Exhibition & Conference, Bahrain, vol.2, pp. 529-541.

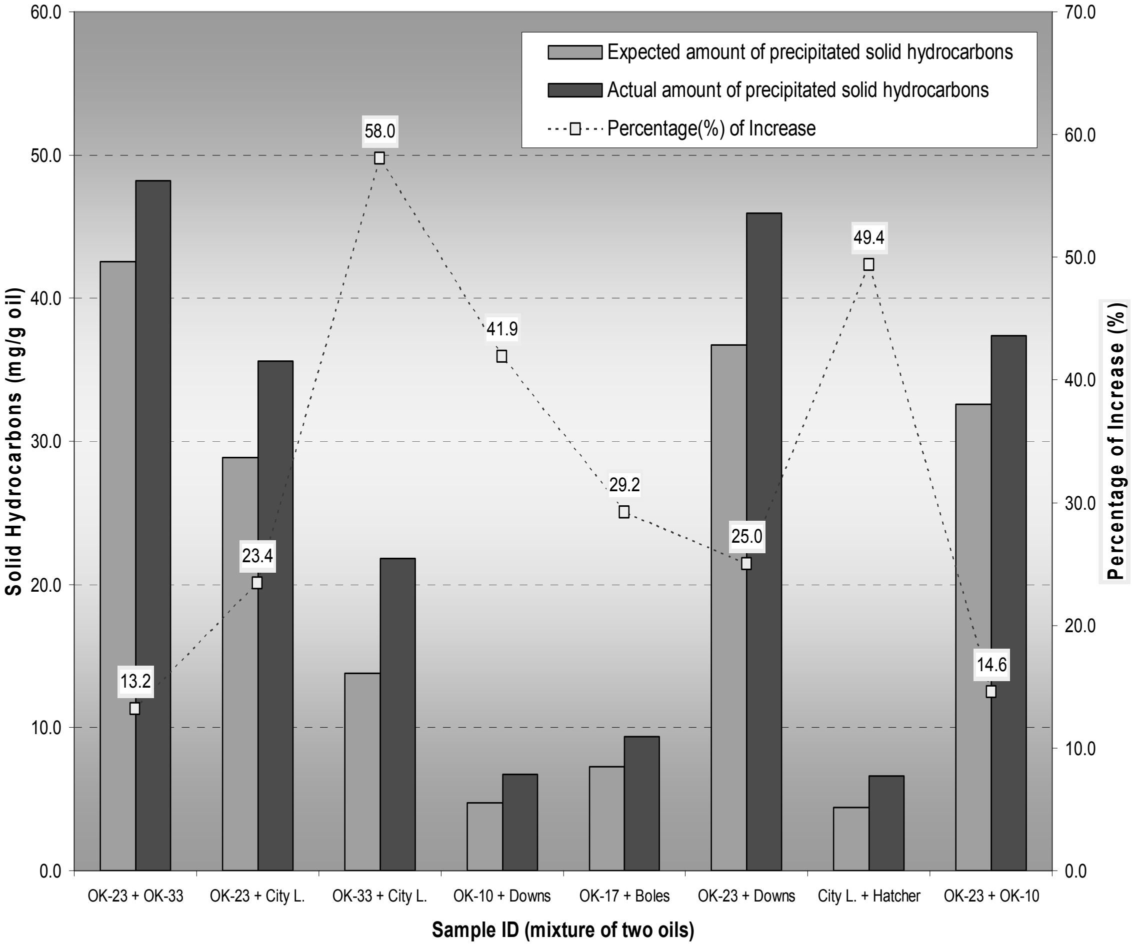
PRG1-9: Mixing of crude oils and deposition of solid hydrocarbons in the Hitch sandstone reservoir, southwest Kansas

D. Kim, P.R. Philp

School of Geology and Geophysics, University of Oklahoma, Norman, OK 73069, U.S.A.

A suite of crude oils and their respective core extracts from Upper Mississippian sandstone reservoirs in the Hitch and Etzold fields (southwest Kansas) were analyzed by various geochemical techniques to study the geological and geochemical controls on the formation of solid hydrocarbons. The occurrence of solid hydrocarbons was unexpected because the Anadarko Basin and its shelf areas are known for the production of gas and light oil. Solid hydrocarbons were deposited in the lower part of the reservoir and are significantly enriched in paraffinic waxes and asphaltenes. The presence of solid hydrocarbons impacts oil production economics by forming horizontal barriers in the reservoir, which prevent crude oils from flowing during production. The solid organic materials account for about 50 wt. % of the total hydrocarbons. Half of the solid materials are insoluble in a mixture of dichloromethane and methanol using conventional Soxhlet extraction. The solid hydrocarbons can be explained by mixing of oils of different geochemical compositions, for example a light paraffinic oil vs. an asphaltene-rich oil. The mixing model is supported by comparable geochemical analyses of crude oils and source rocks in adjacent areas with the geochemical signature of the Hitch oils. Based on their biomarker and carbon isotopic compositions, it is concluded that the Hitch crude oils are mixtures of hydrocarbons from Ordovician and Devonian (Woodford Shale) source rocks.

A simple laboratory mixing experiment, using several different types of oils, indicates that compositional changes after oil-mixing are insignificant, but the amount of solid organic material precipitated increased up to 60 wt. % more than expected (Fig. 1). The oil-mixing resulted in slight ^{13}C depletion in saturate and aromatic compounds of unprecipitated hydrocarbons. The precipitated solid hydrocarbons consisted of 25-45 wt. % of paraffinic waxes and 55-75 wt. % of asphaltenes. There is no clear evidence to support other potential solid deposition mechanisms such as biodegradation or thermal alteration for the Hitch oils. The formation of solid hydrocarbons in the Hitch field is believed, therefore, to be caused by mixing of oils from multiple source rocks filling the reservoir over an extended period of time. In addition, regional pressure and temperature drops caused by post-Laramide erosion may have contributed to a phase change in the reservoir fluid to precipitate solid hydrocarbons.



Sample ID	Well Name	Location (County)	Source Rock	Geochemical Characteristics
OK-10	Gail Moore #1	Dewey, OK	M. & U. Pennsylvanian marine black shale	Light oil, low asphaltene and wax content
OK-17	Inman "J" #1	Major, OK	Pennsylvanian	Relatively waxy crude
OK-23	Joachim #1	Woods, OK	Woodford Shale	Asphaltene-rich oil
OK-33	Wyman "B" #1-28	Woodward, OK	Morrowan or Atokan shale	Waxy crude oil
City L.	City of Liberal C1	Seward, KS	Ordovician	High CPI value, paraffinic oil
Downs	Downs No. A-1	Seward, KS	N/A	Very dark-colored oil, high conc. of NSOs and wax
Boles	Boles "F"	Seward, KS	N/A	Wax & asphaltene precipitation problem
Hatcher	Hatcher B	Seward, KS	N/A	

Fig.1. Bar diagram for the amounts of solid hydrocarbons after mixing of oils of different geochemical compositions. The amount of solid hydrocarbons expected to precipitate after mixing of two oils (which was calculated by sum of the solid hydrocarbons from each oil before mixing) versus the amount of solid hydrocarbons precipitated after oil mixing

PRG1-10: Structural alteration of native solid hydrocarbons by thermolysis

O. V. Kovaleva

Institute of Geology, Komi Scientific Center, Ural Division, Russian Academy of Sciences, 54 Pervomaiskaya St, Syktyvkar, 167982, Russia (e-mail: OlgaKovaleva@geo.komisc.ru)

A vast experimental material on the chemical structure of natural solid hydrocarbons (bitumens) has been accumulated to date using IR spectroscopy. However, there are no data in the literature on the chemical structure and supermolecular organization of bitumens subjected to high-temperature pyrolysis. The purpose of this work was to study the effect of temperature on the structural changes in natural bitumens of the carbonization series: asphalt – asphaltite – kerite – anthraxolite and solid products of their thermal treatment. Studies were carried out using IR spectroscopy and pyrolysis gas chromatography.

The spectral factors characterizing the chemical structures of bitumens were determined as the ratio between absorbances at maximums of the corresponding absorption bands: aliphatic (720, 1380, 1465 cm^{-1}) and aromatic moieties (1600 cm^{-1}) and sulfoxide groups (1030 cm^{-1}). The following factors were used: $C_1=D_{1600}/D_{720}$ (aromaticity), $C_2=D_{1710}/D_{1465}$ (oxidation), $C_3= D_{720} + D_{1380})/D_{1600}$ (aliphaticity), and $C_4 = D_{1030}/D_{1465}$ (sulfurization).

It was established, that the IR spectroscopy and pyrolysis-gas chromatography study of the temperature effect on the structural transformations of bitumens in the carbonization series asphalt–asphaltite–kerite–anthraxolite has shown that the heat treatment of bitumens at high temperatures (500^{o}C) leads to a considerable change in their molecular structure. It has been found that low-molecular-mass saturated are primarily produced upon the thermal degradation of bitumens. In addition, insignificant amounts of unsaturated, aromatic, and cyclic hydrocarbons are formed, which evidently indicates the occurrence of the hydrogen redistribution process under the pyrolysis conditions. The main starting material for hydrogen redistribution is high-molecular-mass naphthenic hydrocarbons producing lower hydrocarbons, predominantly paraffinic and aromatic hydrocarbons. Light hydrocarbons, which volatilize upon pyrolysis, contain a lower relative amount of carbon and more volatile foreign compounds, which is indicated by a decrease in the aliphaticity factor and degrees of oxidation and sulfurization. The residual substance is gradually enriched in carbon and is the most associated product of thermal decomposition. Its formation is accompanied by the molecular dissociation that yields bonds predominantly between carbon atoms. This process proceeds through the formation of aromatic rings, which are grown together to form polycyclic structures, which is accompanied by an increase in the intensity of absorption bands of polynuclear aromatic structures at 900–700 and 600–400 cm^{-1} and the appearance of new bands in these IR spectral regions of the pyrolysis products of bitumens. Then, these planar molecules are stacked, thus leading to further compacting of the molecular structure of the material. A single mechanism can be established for the transformation of bitumens both in the initial state and after pyrolysis, which manifests a tendency to form a thermodynamically stable structure. This mechanism suggests changes that resulting in structure ordering, wherein thermal treatment enhances this process. In summary, the general character of thermally induced changes in the composition and structure of bitumens in the series asphalt–asphaltite–kerite–anthraxolite can be presented as follows: – loss of volatile products formed as a result of hydrogen redistribution, as well as destruction of N,S,O hetero bonds; – molecular association and formation of the homeopolar framework of molecules as fused polycyclic aromatic structures; – molecular-structure condensation due to the formation of giant planar molecules resembling the structure of atomic layers in a graphite crystal (Fig.1).

The results obtained confirm the idea that the thermal treatment is an important factor in the maturation of organic matter.

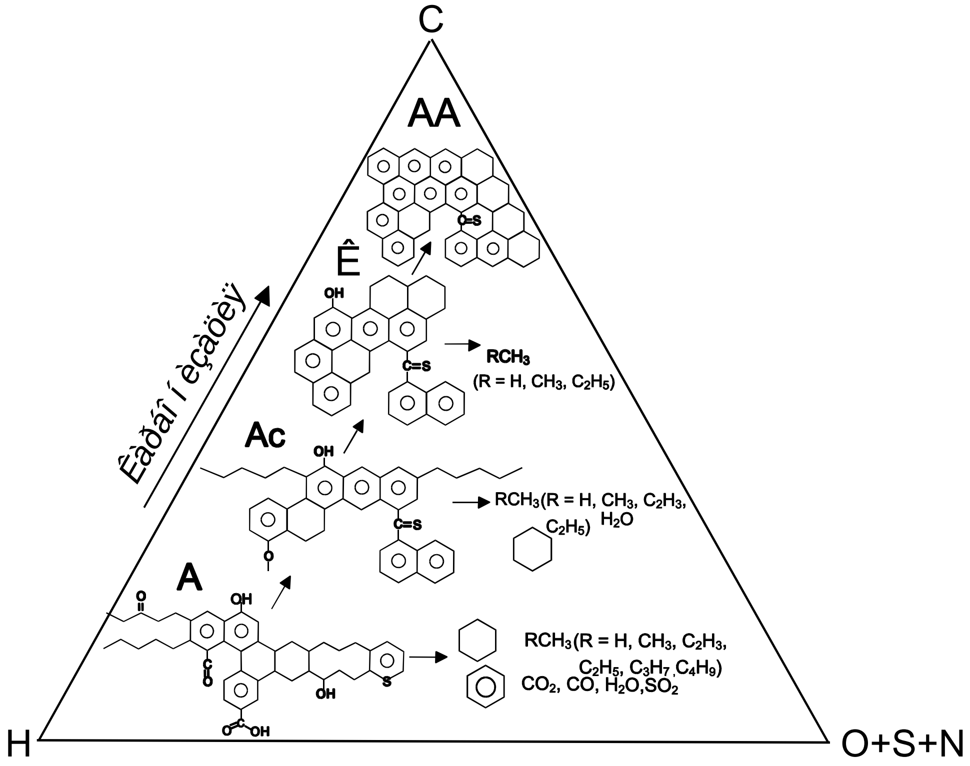


Fig.1. Model of structural transformation solid hydrocarbons on molecular level.
A – asphalts; Ac – asphaltites; K – kerite; AA – anthraxolite.

PRG1-11: Geochemical factors controlling H_2S production in petroleum reservoirs during steam injection process: TSR experimental simulation

I. Kowalewski, V. Lamoureux-Var, F. Lorant

Geology-Geochemistry Division, IFP, BP311, 92506 Rueil-Malmaison, France

The thermo-reduction of sulphates (TSR) is a set of abiotic reactions that naturally occurs in deep petroleum reservoirs (depth >3000m, temperature >100°C) and lead to the accumulation of H_2S, as a result of sulphates decomposition followed by oxidation of in situ organic matter. This process is also responsible for the formation of CO_2 , the deposition of pyrobitumen, the occurrence of organosulphur compounds, and the precipitation of carbonates. The economic impact of TSR is thus very clear since, on the one hand the presence of high H_2S amount, sour toxic and corrosive gas, returns the reservoirs operating conditions more difficult and that, on the other hand, the TSR carries out to the destruction of a part of the hydrocarbon resources by their dilution by H_2S and CO_2 gas.

TSR can also artificially be induced by the injection of hot water or hot steam during Enhanced Oil Recovery (EOR) operations in shallow reservoirs containing heavy oils (API gravity < 20). Due to the high temperature (150°C <T<300°C) reached in the reservoirs during water and steam flooding, chemical reactions involving reservoired oil, water and mineral matrix enriched in sulphates can lead to a significant increase of H_2S production (Hyne et *al*., 1994; Hoffmann et *al*., 1994; 1995).

In order to better understand TSR mechanisms and to tentatively estimate the risk of H_2S occurrence during hot water or steam stimulated enhanced recovery operations, experimental pyrolysis experiments were undertaken as close as reservoir conditions during hot water injection (i.e., mineral: 70% vol., porosity: 30% including 24% vol. of oil and 7% vol. of water). The purpose of this set of experiments was to measure H_2S production rates at various temperatures, then to derive a numerical model of H_2S formation due to artificial TSR to be used in reservoir simulators. The three primary processes involved in TSR, i.e. (1) oxidation of organic matter, (2) sulphate reduction and (3) thermal cracking in absence of sulphur, were independently simulated in laboratory conditions. Each set of experiments was then compared to the complete TSR phenomena, in order to determine which of these three reactions kinetically controls the bulk rate of H_2S formation. Artificial simulation for each primary reaction and complete TSR were conducted using a mixture of saturated hydrocarbons mixture (nC_8-nC_{14}), using an inert closed system pyrolysis at a temperature ranged from 150 to 320°C for different residence times. Different amounts of elemental sulphur (used here as reaction initiator), de-ionised water and mineral ($MgSO_4$) were tested. In order to get a complete mass balance, specially on sulphur-containing species, two pyrolysis experiments in similar conditions were necessary for the separation and quantification of all pyrolysis effluents. Gases were quantified by gas chromatography using an external standard after separation in a vacuum line. C_6-C_{14} fractions were quantified by gas chromatography after recovering the C_{6+} effluents with n-pentane. The C_{14+} fraction was recovered by extraction in dichloromethane, fractionated by liquid chromatography into saturates, aromatics and NSO compounds. Finally, insoluble residues recovered by filtration were analyzed by Rock-Eval and the elemental composition was determined.

Results showed (1) that thermal reduction of sulfates occurred in our experimental conditions, generating high amounts of H_2S and (2) that organosulphur compounds are neo-formed (figure). Using an initial amount of elemental sulphur of ~ 5 weight % of organic sulphur, which is similar to concentrations observed in sulphur-rich accumulations, like in oils derived from Type II/II-S organic matters, or in biodegraded oils, we found that the reduction reaction occurred within a relatively short period (3 days at 320°C). Contrary to recent results published by Cross et al. (2004), low elemental sulphur concentration (≈ 3% of total sulphur) was enough to generate TSR in laboratory conditions. The role of initial S amount, as well as water and mineral amounts on the rate of H_2S formation will be presented and discussed.

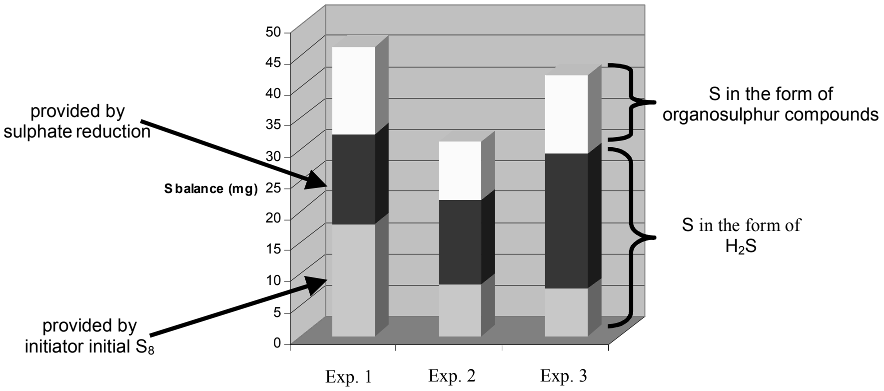


Fig.1. Sulphur balance of experimental simulation of complete TSR mechanism at 320°C

Acknowledgements

We would like to thank C. Leblond and E. Tocqué for their precious help in laboratory work.

References

Hyne JB, Greidanus J.W., Tyrer J.D., Verona D., Rizek C., Clarke R.A., Koo J. (1984). Aquathermolysis of Heavy oils. *In "2nd Int. Conf.: The Future of Heavy Crude and Tar Sands"*, Mc Graw-Hill, NY. p. 404-411.

Hoffman G.G., Steinfatt I. and Strohschein A. (1994). The role of sulphur and its organic as well as inorganic compounds in Thermal Recovery of Oil. *5th Int. Sympo*sium. *Chemistry in the Oil Industry.* Charlotte Mason College. Ambleside. Great Britain. p. 188-206.

Hoffman G.G., Steinfatt I., Strohschein A. (1995). H_2S Formation in Thermal Oil Recovery processes – as seen from the chemical point of view. 6th Unitae et al Heavy Crude and Tar Sands Int. Conf.. Houston. p. 317-327.

Cross M.M., Manning D.A.C., Botrell S.H., Worden R.H. (2004). Thermochemical Sulphate Reduction (TSR): Experimental determination of reaction kinetics and implications of the observed reaction rates for petroleum reservoirs. *Org. Geochem*. **35**. p. 393-404.

PRG1-12: Different occlusion characteristics of asphaltenes: some implication concerning asphaltene structural features and its secondary evolution processes in the oil reservoir

Z. Liao[1,2], A. Geng[1], A. Graciaa[2], H. Zhou[3], A. Laporte-chrostowska[4], P. Creux[2]

1) State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, P. R. China (e-mail: zw_liao@hotmail.com)
2) Laboratoire des Fluides Complexes, UMR 5150 TOTAL-CNRS-UPPA, BP 1155, 64013 Pau Cedex, France
3) Total, CSTJF, Avenue Larribau, 64018 Pau Cedex, France
4) Laboratoire de Chimie Théorique et Physico-Chimie Moléculaire, UMR CNRS 5624, University of Pau, BP 1155, 64013 Pau Cedex, France

Due to the structural characteristics of asphaltenes, some of the other compounds such as hydrocarbons could be occluded inside asphaltene structures. These occluded compounds can be considered as the "original oil" derived from kerogen, and then have a special significance in the related geochemical studies. The mild oxidation degradation of asphaltenes could properly release these occluded hydrocarbons, making it possible directly to study these compounds without interference from the segments chemically bonded to asphaltene molecule. Interference from adsorbed and/or co-precipitated components can be avoided by applying an asphaltene purification procedure. A comparative study has been performed on 6 crude oil samples, V1, V2 and ZL from Venezuela, C1 and C2 from Congo, and JAC from Canada.

The preliminary experimental results indicated that different asphaltenes could occlude different kind of compounds, and the amount of the occluded compounds is different, too. For example, from the oxidation products of V1 and V2, a lot of saturated hydrocarbons have been obtained, including a complete distribution of normal alkanes up to more than C_{30} and abundant of polycyclic saturated hydrocarbons such as terpanes and steranes. These compounds have been interpreted as the occluded “original oil” derived from kerogen based on the experimental procedure used in this work. With respect to samples ZL and JAC, only some polycyclic saturated hydrocarbons (terpanes and steranes) have been found from the oxidation products of asphaltenes, whereas no enough normal alkanes were detected. As to samples C1 and C2, neither enough *n*-alkanes nor terpanes/steranes has been properly detected from the oxidation products of asphaltenes, in fact almost no saturated hydrocarbons has been found from the oxidation products.

The different occlusion properties of asphaltenes are maybe associated with the different structural characteristics of asphaltenes and/or the secondary evolution processes occurred inside oil reservoirs. For example, due to the different structural characteristics of asphaltenes and the different secondary evolution processes in the oil reservoir, the protection efficiency from asphaltene structures could be different, and then the occluded compounds inside asphaltenes could be well retained (V1 and V2), partly lost (ZL and JAC) or almost totally lost (C1 and C2).

However, these different occlusion results may be related to the original source material of asphaltenes. At the stage of asphaltene generation from kerogen, maybe a lot of saturated hydrocarbons, only some polycyclic or almost no saturated hydrocarbons has been co-generated and at the same time has been well occluded inside asphaltene structures. In order to obtain a better understanding for these different experimental results, the further work is underway.

PRG1-13: Compound-specific stable carbon and hydrogen isotope ratios as a diagnostic oil-source correlation tool in the Canadian Beaufort-Mackenzie basin

M. Li[1], Y. Xiong[1,2], L. Snowdon[1], D. Issler[1]

1) Geological Survey of Canada, 3303-33 St. NW Calgary, Alberta T2L 2A7, Canada (e-mail: mali@nrcan.gc.ca)
2) State Key Laboratory for Organic Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China

Compound-specific hydrogen and stable carbon isotopes were measured for *n*-alkanes in source rocks and oil samples from the Canadian Beaufort-Mackenzie Basin. Four types of potential petroleum source rocks were identified. First, the Tertiary source rocks in the Richards and Taglu formations are characterized by a clear odd-even *n*-alkane predominance, high pristane/phytane ratios (>3), abundant oleanane and bisnorlupanes, and a C_{29} sterane dominance, reflecting terrigenic organic matter in a fluvio-deltaic setting. The $\delta^{13}C$ values of *n*-alkanes in these rocks range from –28 to -31‰, being more negative with increasing carbon number. The δD values of *n*-alkanes in these extracts range from -100 to -250‰, also displaying more negative values with increasing carbon number. Such depletion in deuterium reflects the environmental water being dominated by freshwater. In addition, a zigzag pattern for the *n*-alkane δD values was observed in the Tertiary rock extracts with low maturity levels. Second, the Upper Cretaceous marine source rocks in the Boundary Creek and Smoking Hills formations are characterized by relatively low pristane/phytane ratios (1.06 to 1.84), lack of *n*-alkane carbon number preference, and a signature 1:1:1 relative abundance for C_{27}:C_{28}:C_{29} steranes, reflecting dominantly marine algal contribution. The $\delta^{13}C$ and δD values of *n*-alkanes from the Upper Cretaceous source rocks do not change with carbon number, ranging from –30 to -33‰ and –160 to -210‰, respectively. While the narrow ranges in the $\delta^{13}C$ and δD values for different alkane homologues are typical of marine organic input, the depletion in D in the Upper Cretaceous extracts is possibly related to freshwater discharge into the ancient North American Seaway. In contrast, two distinctive source rocks are recognized in the Lower Cretaceous and older strata. The mature source rocks in the Jurassic Husky Formation are relatively enriched in both ^{13}C and deuterium of *n*-alkanes. Their $\delta^{13}C$ values vary from –25.5 to -27.5‰, with flat or slightly negative slope toward higher homologue. Their δD values range from –75 to -115‰, showing slightly positive slope toward higher homologue. Whereas, samples from the Husky Formation with slightly low thermal maturity show lower *n*-alkane $\delta^{13}C$ (–28.5 to -30.5‰) and δD values (–125 to -170‰).

Based on the chemical and isotopic compositions, the discovered oils in the Beaufort-Mackenzie Basin generally fall into one of the three oil families. The first oil family includes those light oils and condensates in the Lower Cretaceous reservoirs from the Parsons/Siku /Kamik discoveries. The relatively high maturity levels (as reflected by bulk parameters and sterane isomerization ratios) and a dominance of C_{29} steranes indicate that the oils were derived from highly mature nonmarine source rocks. The $\delta^{13}C$ values of the *n*-alkanes in this oil family range from –25.5 to -27.5‰, similar to those in the mature Husky Formation source rocks. The δD values of these oils (-105 to -130‰) are around 20‰ lower than those in the mature Husky Formation source rocks, suggesting that these oils were derived from a Lower Cretaceous and Jurassic source rock with significant freshwater organic input. The second oil family includes those from the Tuktoyaktuk Peninsula-South Delta, located on the southern and eastern flanks of the basin. Their biomarker distributions correlate well with the source rocks in the Upper Cretaceous Boundary Creek and Smoking Hills formations. However, their *n*-alkane $\delta^{13}C$ values (-29 to -31‰) and δD values (-115 to -170‰) are significantly higher than those of the studied source rocks, suggesting that the effective source rocks of the oils are located in different sedimentary facies of the Upper Cretaceous strata. The third oil family includes those in the Tertiary reservoirs in the more central part of the basin. These oils show diversity in chemical and isotopic composition due to the possible effects of maturity, mixing and post-generation factors such as biodegradation. Most of the oils are characterized by relatively high pristane/phytane ratios, high concentrations of 18α(H)-oleanane and bisnorlupanes and a C_{29} sterane predominance, indicating a higher plant input in the Tertiary deltaic strata. While the biomarker concentrations decrease with increasing maturity, the $\delta^{13}C$ and δD values of n-alkanes in crude oils were not significantly affected by thermal maturation and migration. Therefore, a combination of the stable carbon and hydrogen isotopic compositions of the oils potentially provides powerful tools for the definition of petroleum systems through better constrained oil-oil and oil-source correlations.

PRG1-14: Evidence of mature oils with low-maturity biomarkers in Brazilian marginal basins

J.P. Lopes [1,2], H.L.B. Penteado[1], M.D. Rangel[1], J.V.P. Guzzo[1],
H.G.M. Aguiar[2]

1) PETROBRAS R&D Center, Ilha do Fundão, Quadra 7, 21949-900, Rio de Janeiro, Brazil
(e-mail: joelma.coppetec@petrobras.com.br)
2) COPPE/UFRJ, State University of Rio de Janeiro, , Ilha do Fundão, Quadra 7, 21949-900, Rio de Janeiro, Brazil

The comprehension of the thermal evolution of oils using maturity biomarkers is crucial to understand the maturity of the source-rock areas during petroleum expulsion, and thus processes in petroleum system. The main objective of this study is to highlight the occurrence of "immature oils" in Brazilian basins. This kind of oils is characterized by high contents of saturates and API gravities as well as biomarkers indicative of relatively low thermal evolution. These oils have been observed in several Brazilian marginal basins, both onshore and offshore.

Along its migration pathways, an oil can sweep away bitumen or oil from source rocks that have different biomarker fingerprints. Moreover, a reservoired oil can be "contaminated" by biomarkers from surrounding or intercalated source rocks (Curiale, 1991; Pang *et al.*, 2003). Depending on the quantity and thermal evolution of the oil admixed to the originally migrated oil, source and maturity biomarkers of the resulting mixture might be significantly affected.

Most Brazilian lacustrine oils have relatively low concentrations of steranes. However, it was observed that some of them have unusually high concentrations of steranes probably due to bitumen contribution. In order to test the hypothesis of bitumen contamination, ten lacustrine oil samples were collected from different intervals in a specific oilfield in northeastern Brazil. All oils present similar gas chromatogram features and bulk oil parameters. Nevertheless, an oil produced from a reservoir surrounded by marine source rocks contains biomarkers suggestive of low maturity and from a marine source. A source-rock extract close to this oil-producing interval shows sterane signatures identical to that of the oil. The discrepancy in the steranes fingerprint of the oil in relation to other related oils in the field can be explained by a mixture of a lacustrine oil with low amounts of steranes (≈ 100 ppm) with a marine source-rock bitumen containing greater concentrations of steranes (≈16000 ppm).

In order to observe the variation of the physicochemical parameters due to bitumen contamination, four artificial mixtures were prepared between a representative lacustrine oil and a marine source-rock extract (bitumen) and geochemical analyses undertaken. These mixtures contain 2.5, 5, 7.5 and 10% of bitumen. The results show that small amounts of highly concentrated biomarkers from the immature source rock can significantly change the original imprint of the oil (Figure 1).

This study provides further evidence of "immature oils" in other Brazilian fields. The large variation observed in the steranes concentrations in oils suggests that contaminations during migration or after accumulation might be quite a widespread phenomenon, and that care must be taken when using steranes maturity parameters, especially in lacustrine and highly mature oils.

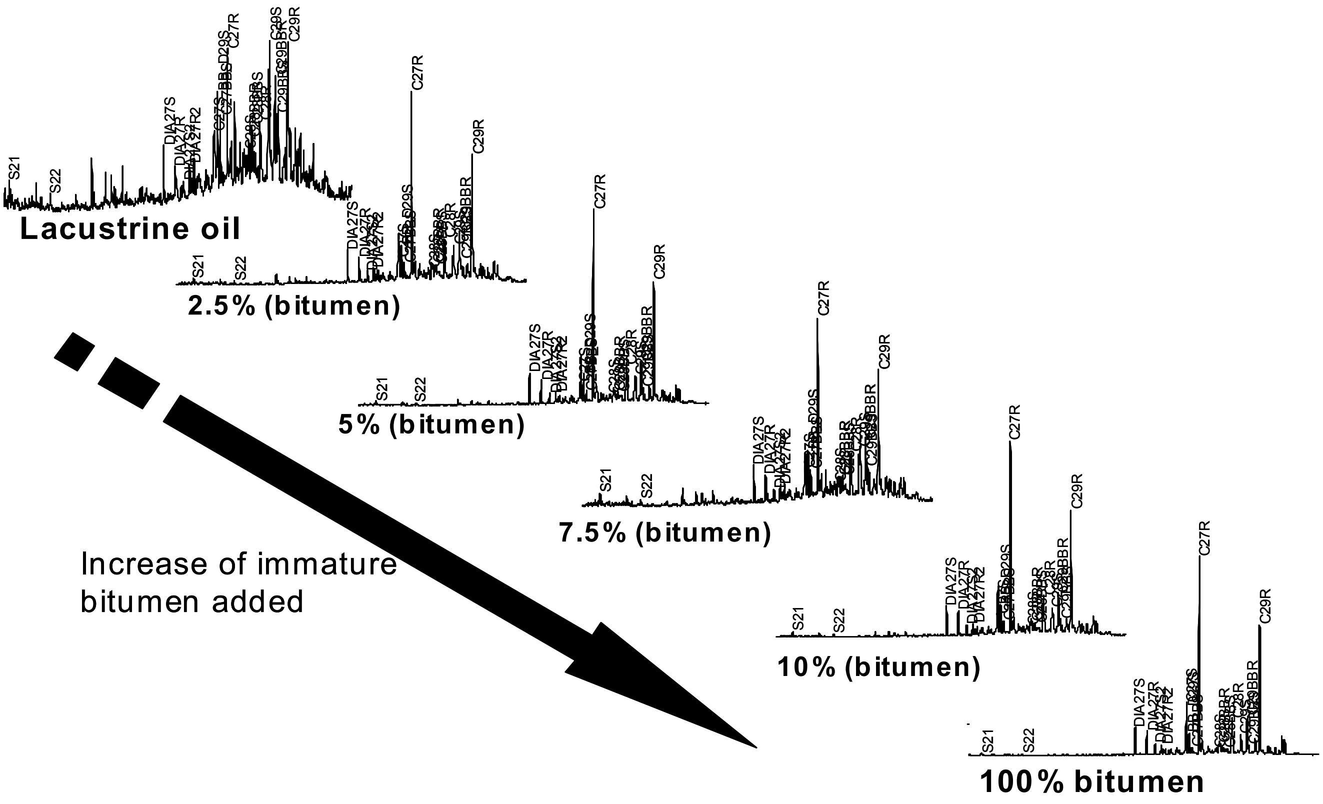


Fig.1. Fragmentograms m/z 217 of artificial mixtures of a lacustrine oil and bitumen

References

Curiale, J. A., 1991. The petroleum geochemistry of Canadian Beaufort Tertiary "non-marine" oils. Chemical Geology 93, 21-45.

Pang, X., Li, M., Li, S., Jin, Z., 2003. Geochemistry of petroleum systems in the Niuzhuang south slope of Bohai Bay Basin. Part 2: evidence for significant contribution of mature source rocks to "immature oils"in the Bamianhe field.Organic Geochemistry 34, 931-950.

PRG1-15: Evaluation of reservoir compartmentalization in the deep-water Gulf of Mexico oil fields through the integration of seismic, pressure, PVT and geochemical data

A.V. Milkov, L. Dzou

BP America, 501 Westlake Park Blvd, Houston, TX 77079, USA (e-mail: alexei.milkov@bp.com)

Evaluation of reservoir compartmentalization is one of the key objectives during appraisal and development of oil and gas fields. Petroleum industry deploys a variety of tools to identify and characterize fluid flow barriers within a reservoir. Slices of seismic amplitudes, spectral decomposition and coherency are commonly studied to locate structural (separated by faults) and stratigraphic (separated by pinch-outs and mud channels) compartments. Large pressure shifts and variations of pressure gradient between wells are usually interpreted to indicate compartments. PVT properties (GOR, API gravity, density of dissolved gas, saturation pressure) are used to distinguish a continuous hydrocarbon column from the one dissected by lateral or vertical fluid flow barriers and baffles. Finally, geochemical data (oil and gas fingerprints, biomarkers) are applied with an underlying assumption that fluids with significantly different compositions should be located in different reservoir compartments.

Deep-water Gulf of Mexico field examples available within BP suggest that none of the individual tools listed above can provide a reliable prediction of reservoir compartmentalization if used in isolation. The reasons for that are natural. Not all faults and mud channels are sealing. Pressures in different hydrocarbon compartments can equilibrate through a common aquifer. Variations in PVT and geochemical properties of fluids may be a result of charge history or on-going post-accumulation processes (e.g., biodegradation) and insufficient time available for complete mixing of fluids. Therefore, it is proposed that a true understanding of reservoir compartmentalization can be achieved only through an integration of all available datasets. Such an integrated compartmentalization model is more reliable when it is coupled with the model of petroleum charge and post-accumulation history, and they together explain the observed variations in data. Failure to obtain and integrate proper geological, geophysical, PVT and geochemical information at appraisal and development stages may result in a non-optimal positioning of production wells and, as a result, a more expensive recovery.

PRG1-16: Relationship between oils in granite basement and in Miocene and Oligocene reservoirs at White Tiger oil field

Y.V. Savinykh, D.H. Luong, V.K. Utoplennikov,
V.I. Urmancheev, T.L. Dong

105, Le Loi Street, Vung Tau City, NIPI, JV Vietsovpetro, Vietnam

The White Tiger oil field, located on the shelf of South-Chinese Sea (Vietnam), contains hydrocarbon accumulations in Miocene, Oligocene sediments and fractured basement rock. The origin of oil in the basement is still insufficiently determined.

This paper is made on the basis of the result of analysis of crude oil samples taken from the White Tiger Field named LM-45, LM-16 (Lower Miocene), LO-93, LO-14 (Lower Oligocene), BS-56, BS-03, BS-02, BS-05 (Basement).

The obtained results can help come up with the following comments on the general characteristics and the geochemical features of the eight oil samples having been analyzed.

Gas Chromatography Fingerprinting Analysis of the eight surveying oils was not all similar, but three oil GCFA forms were detected, they look quite different from each other. Moreover, the differentiation among them is so big that they can be identified and classified in 3 different groups, corresponding to three different reservoirs as follows:

- ☐ Group 1: Includes two samples (LM-45 and LM-16) which have been described as Miocene oils.
- ☐ Group 2: Includes two samples (LO-93 and BS-03), which have been described as Oligocene oil and Basement oil respectively.
- ☐ Group 3: Includes four oils (BS-56, LO-14, BS-02 and BS-05), which have been described as Basement oil, excluding the sample LO-14 which has been described as Oligocene oil.

The similarities of the sample LO-93 and BS-03 are not only clearly proved by GCFAs but also by other analytical results.

The ratios of Pristane/Phytane reveal that the environment where the oil was generated is of the low oxidizing one. However, the Miocene oils present a reducing level, being smaller than the others.

GC-MS analysis (m/z 217) shows the distribution of the C_{27}-C_{28}-C_{29} Sterane with a predominance of C_{27} sterane compared to C_{28} and C_{29} sterane of eight oil samples. This indicates that these oil samples belong to two differential relative zones in which the Miocene oil samples (LM-45 and LM-16) are of open marine origin while the six others are of the transitional origin between the open marine and the estuarine (table).

Index	LM-45	LM-16	LO-14	LO-93	BS-56	BS-03	BS-02	BS-05
Pr/Phy	2.4	2.1	2.0	1.9	1.9	1.9	1.9	1.9
Alkind Index	48.4	50.0	56.7	52.2	51.2	51.6	51.3	51.7
Oleanane Index	3.9	3.9	17.8	9.4	9.5	10.6	10.4	9.9
Hopane/Sterane	85.3	85.6	48.6	71.6	70.0	65.1	63.2	66.5
$4MeC_{30}$ Sterane	51.6	45.3	81.1	106.2	108.0	87.5	95.2	95.2
C27 Sterane	53.9	51.6	41.8	42.3	46.1	44.1	43.1	42.9
Ts/(Ts+Tm)	0.51	0.51	0.44	0.57	0.57	0.56	0.56	0.55
MPI-1	0.70	0.72	1.61	0.95	0.99	0.99	0.98	0.97
MDR-1	0.74	0.75	0.50	0.50	0.58	0.59	0.61	0.64

Series of biomarker parameters obtained when analyzing C_{15}^{+} saturated fraction by GC-MS have reconfirmed the above comments; and further more, the dominance of charging the organic matter of the marine phase over the terrestrial phase can be recognized.

The thermal maturity of the surveyed oil samples is evaluated through the obtained values of following main geochemical parameters: Alkind Index, Methyl Phenanthrene Index (MPI-1),

1-Methyldibenzothiophene Ratio (MDR-1), Ts/(Ts+Tm). The above data help to come up with the comment that in general the oils of the White Tiger field were generated from the organic matters with the maturity degree from moderate to the relatively high

Eight oil samples analyzed by Gas Chromatography Fingerprint may be separated into three different groups as above mentioned. Such a group classification is not fully correspondent to the made description of the lithological name for the production reservoir target where oil samples were collected.

PRG1-17: Microbial alteration of crude oils: chain length dependency of *n*-alkane degradation

A.-K. Scherf[1], H. Wilkes[2], J. Rullkötter[1]

1)Institute for Chemistry and Biology of the Marine Environment (ICBM), Carl von Ossietzky University of Oldenburg, P.O. Box 2503, D-26111 Oldenburg, Germany (e-mail: annka.scherf@icbm.de)
2) GeoForschungsZentrum Potsdam, Section 4.3: Organic Geochemistry,D-14473 Potsdam, Germany

Biodegradation of crude oils is one of the most important alteration processes in petroleum reservoirs [1]. It is assumed, that the microbial degradation of crude oil may occur under aerobic as well as anaerobic conditions [2]. Aerobic degradation requires oxygen-containing meteoric water to reach the reservoir. However, there is increasing evidence, that in-reservoir-biodegradation of crude oils is an anaerobic process in most cases. Biodegradation in reservoirs takes mainly place next to the oil-water contact, and diffusion of alteration products into the oil column may contribute to the compositional alteration of the oil [3].

The microbial alteration of crude oil hydrocarbons is known to be a sequential process. The biodegrading microbes have a pronounced preference for *n*-alkanes, followed by branched and cyclic hydrocarbons. The corresponding effects on crude oil composition, i.e. the extent of depletion of the hydrocarbon compound classes, relate to the biodegradation levels of Peters and Moldowan [4]. In more recent studies is has been shown, that the process of biodegradation is not strictly sequential with respect to compound classes but occurs quasi-stepwise, i.e. there is overlapping biodegradation of hydrocarbon types. So far, the quasi-stepwise degradation of *n*-alkanes has generally been assessed in terms of chain-length groups (C_1-C_5, C_6-C_{15}, C_{15+}) rather than individual homologues: short-chain *n*-alkanes are degraded earlier and faster than the long-chain homologues.

In this study a sequence of crude oil samples from the Foinaven Complex, West-Shetland Basin, has been analysed. The crude oil samples are slightly to moderately biodegraded according to the biodegradation ranking of Peters and Moldowan [4]. The *n*-alkanes are partially removed, and only in the most heavily biodegraded oil isoprenoids have also been attacked. Furthermore, all analysed crude oils are depleted in the *n*-C_{15-} fraction. Comparison of the content of individual *n*-alkanes in all crude oil samples, internally calibrated to the isoprenoid content, revealed systematic changes. For the C_{15} to C_{33} *n*-alkanes a clear chain length dependency of relative biodegradation rates has been observed (Fig. 1). These data provide evidence that bioavailability of hydrocarbon substrates plays an important role with respect to the compositional alteration of crude oil during biodegradation in petroleum reservoirs.

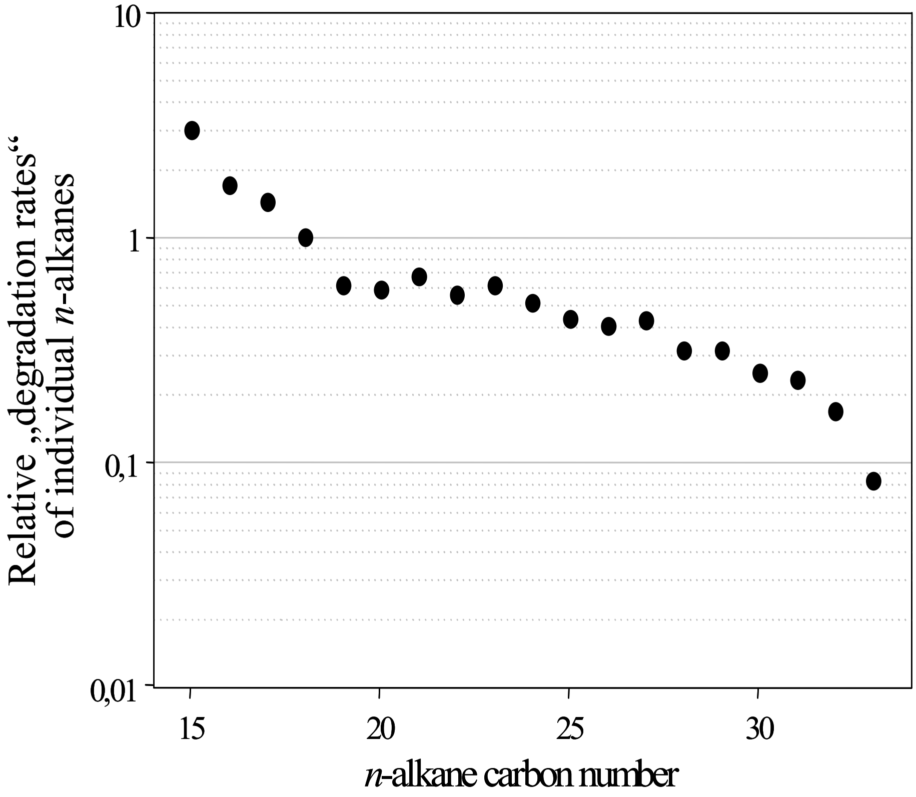


Fig.1. Relative degradation rates of individual *n*-alkanes in crude oils from the West-Shetland Basin

References

[1] Connan, J., 1984. Biodegradation of crude oils in reservoirs. In Brooks, J., Welte, D. (Eds.) Advances in Petroleum Geochemistry, Vol. 1. Academic Press, London, pp. 299-335.

[2] Wenger, L.M., Isaksen, G.H., 2002. Control of hydrocarbon seepage intensity on level of biodegradation in sea bottom sediments. Organic Geochemistry 33, 1277-1292.

[3] Huang, H., Bowler, B.F.J., Oldenburg, T.B.P., Larter, S.R., 2004. The effect of biodegradation on polycyclic aromatic hydrocarbons in reservoired oils from the Liaohe basin, NE China. Organic Geochemistry 35, 1619-1634.

[4] Peters, K., Moldowan, J.M., 1993. The Biomarker Guide**.** Prentice Hall, New Jersey.

PRG1-18: Reservoır geochemıstry of Cendere, Kuzey Karakus, Karakus and Guney Karakus oıl fıelds, SE Turkey

O. Soyhan, C. Soylu, S. Sayılı

Turkish Petroleum Corporation, Research Center, M. Kemal Mah. 2. Cad. No. 86, 06520 Esentepe, Ankara, Turkey (e-mail: osoyhan@tpao.gov.tr)

Reservoir geochemistry study has been performed on 62 oil samples collected from Cendere, Kuzey Karakus, Karakus ve Guney Karakus oil fields which are located at 14 km northeast of Adiyaman in SE Turkey.

These fields are the most important oil fields in SE Turkey producing nearly 10.000 bbls/day. The main reservoirs in these oil fields are Cretaceous-aged Derdere and Karababa formations.

The Halpern parameters (1995) and the statistical methods have been used to determine the chemical differentiation between the oils and thus to identify the reservoir continuity.

Two different types of oil populations have been designated in the studied oil fields. These types are named as Type-A and Type-B. Integration of the reservoir geochemical data with geological data revealed that the differentation of the oil types resulted from the differences in the producing units and thus there is a vertical compartmentalization.Type-A oils are produced from Derdere and Type-B oils are produced from Karababa Formation.

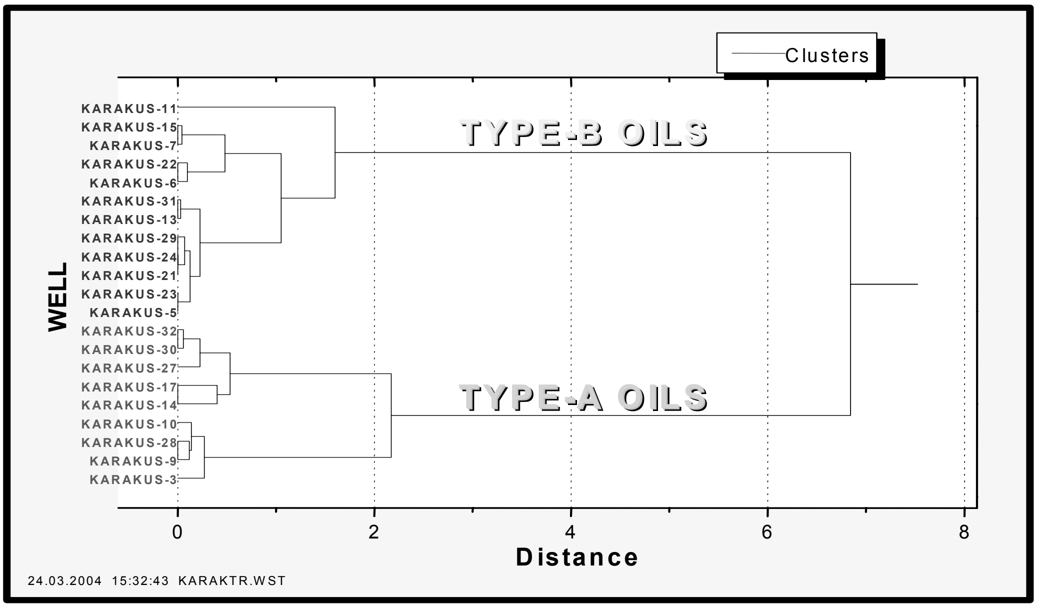


Fig.1. Dendogram of the oils of Cendere and Kuzey Karakus oil fields

References

Halpern, H. I., 1995. Development and Application of Light-Hydrocarbon-Based Star Diagrams, AAPG Bul., V. 79, No. 6, p. 801-815.

PRG1-19: Reservoır geochemıstry of Sılıvanka oıl fıeld, SE Turkey

O. Soyhan[1], S. Sayılı[1], A. Akalın[2]

1) Turkish Petroleum Corporation Research Center, M. Kemal Mah. 2. Cad. No. 86, 06520 Esentepe, Ankara, Turkey (e-mail: osoyhan@tpao.gov.tr)
2) Turkish Petroleum Corporation, Exploration Group, M. Kemal Mah. 2. Cad. No. 86, 06520 Esentepe, Ankara, Turkey

Silivanka Oil field is located at 30 km northwest of Siirt and 13 km southwest of Kozluk district in SE Turkey. The oil discovery was in 1962 in Silivanka-1 well and total production of this field was 11.729.140 barrels until today. Oil production continues 600 barrels/day. The reservoir units in this field are Beloka and Garzan formations.

8 oil samples from Silivanka oil field and additional Dogu Silivanka-2 oil was used in this study.

The aim of this study is to evaluate the reservoir continuity by using the differentations in the light end of the oil samples and to determine if there is a compartmentalization or not. The other aim is to determine the filling directions of this field.

The Halpern parameters (1995) and the statistical methods have been used to determine the chemical differentiation between the oils and thus to identify the reservoir continuity. Two different types of oil populations have been designated in the studied oil Fields. These types are named as Type-A and Type-B.

The biomarker parameters used to determine the migration directions are C_{31} ($17\alpha 21\beta$ S/$17\alpha 21\beta$ R), C_{32} (22S/22S+22R), C_{29} ($\beta\beta/\beta\beta+\alpha\alpha$) and C_{29} (20S/20S+20R) ratios. These ratios are basically maturation parameters. The main idea lying under using these maturation parameters is that, the changes occurring in these parameters shouldn't be related with maturation, since the oils migrating are subjected to temperatures less than they were in the source rocks. These parameters are know as increasing with increasing migration distance, hence showing migration and filling directions, not the maturation patterns.

As a result, two compartments and two different types of oil populations have been determined in Silivanka Oil Field. The impermeable fault located at the southern part of the Type-A oils is thought to be the main reason for this compartmentalization.

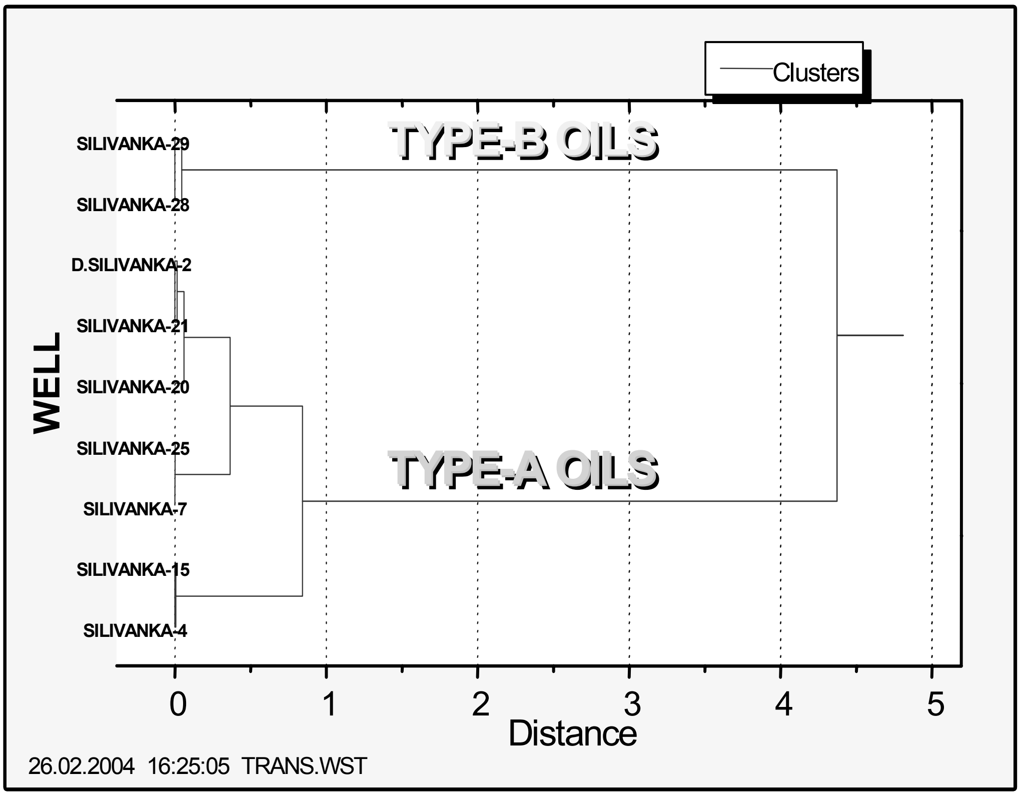


Fig.1. Dendogram of oils of Silivanka Oil Field

It is also found that the migration directions are from Northwest-North-Northeast to the areas, where Silivanka-4, Silivanka-7 and Silivanka-20 wells are located.

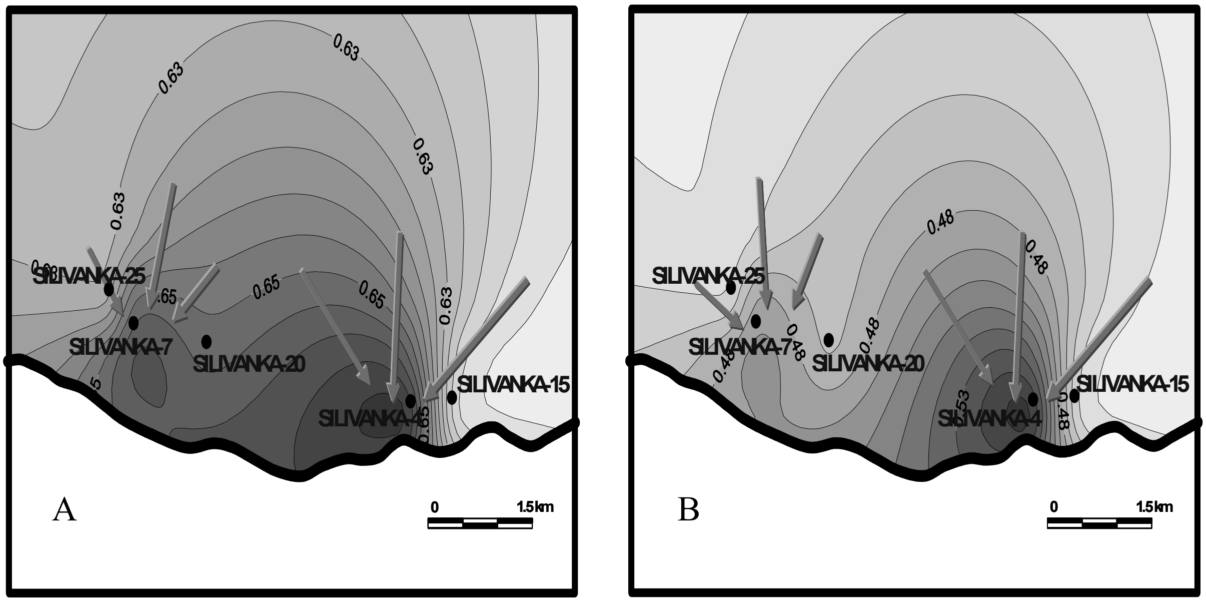


Fig.2. Distribution map of A) C_{32} (22S/22S+22R) ratio, B) C_{29} (BB/BB+αα) ratio of Silivanka oils

References

Halpern, H. I., 1995. Development and Application of Light-Hydrocarbon-Based Star Diagrams, AAPG Bul., V. 79, No. 6, p. 801-815.

PRG1-20: Stable carbon and hydrogen isotopic fractionations of individual *n*-alkanes accompanying biodegradation: evidence from a group of progressively biodegraded oils

Y. Sun[1], Z. Chen[2], S. Xu[1], P. Cai[1]

1) SKLOG, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Wushan, Guangzhou 510640, P. R. China (e-mail: ygsun@gig.ac.cn)
2) Exploration and Development Research Institute of Liaohe Oil Field Branch Company, PetroChina, Panjing, Liaoning 124010, P. R. China

Seven crude oils of known source and maturity, representing a natural sequence of increasing degree of biodegradation, were collected from reservoirs in the Liaohe Basin, NE China, in an effort to determine the magnitude and direction of isotopic shift of carbon and hydrogen in individual *n*-alkanes during microbial degradation. The results show that biodegradation has little effect on the carbon isotopic composition of the whole oil. However, a sequential loss of *n*-alkanes leads to 13C depletion of bulk residual saturate fraction. The stable carbon isotopic compositions of aromatics and macromolecular organic matter (resins and asphaltenes) follow a pattern with an overall trend towards 13C enrichment of 0.8-1.7‰ in the residues. The stable carbon and hydrogen isotope values of individual *n*-alkanes demonstrate that they follow different trends during biodegradation. No significant carbon isotopic fractionation occurs for *n*-alkanes during slight to moderate biodegradation. However, there is a general increase of up to 4‰ in the $\delta^{13}C$ values of low molecular weight *n*-alkanes (C_{15}-C_{18}) during heavy biodegradation. In contrast, no isotopic fractionation occurs for higher molecular weight *n*-alkanes (≥ C_{19}) (Fig.1a). The hydrogen isotope compositions of *n*-alkanes show a

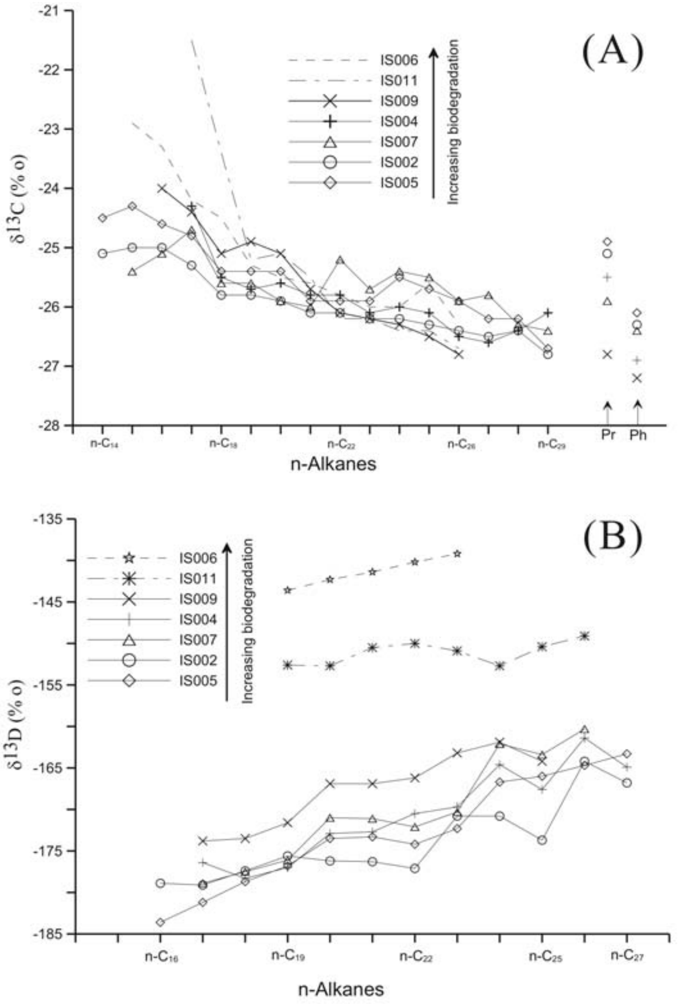


Figure 1 Stable carbon and hydrogen profiles of n-alkanes from a naturally progressive biodegradation sequence

significant fractionation as moderate biodegradation proceeds, resulting in an enrichment in D of up to ~35‰ upon heavy biodegradation (Fig.1b).

Because biodegradation can alter commonly used maturity and correlation parameters, it is critical to develop geochemical parameters independently of biodegradation. A few studies have shown that stable carbon isotopic compositions of *n*-alkanes are not affected by biodegradation and thus can be used to correlate biodegraded oils with their source. However, most published work limited their investigation to a moderate level of biodegradation due to the difficulty of *n*-alkane recovery from heavily biodegraded oils. It has not been well established whether the isotopic compositions of compounds of interest (*e.g.* *n*-alkanes) would be affected by more severe biodegradation. The present study provides a robust base for compound specific analysis as a tool for correlating heavily biodegraded oil with its source by using the conservative characteristic of $\delta^{13}C$ values of high molecular weight *n*-alkanes ($\geq C_{19}$). The hydrogen isotopic compositions of *n*-alkanes are more sensitive to biodegradation than carbon isotopes because of the larger relative mass difference between deuterium and hydrogen compared to ^{13}C and ^{12}C, and possibly more complicated process involved during microbial degradation. Therefore, the use of *n*-alkane δD values as an oil/oil and oil/source correlation tool is currently limited to petroleum reservoirs with non-biodegraded to slightly biodegraded oils.

Theoretically, stable carbon and hydrogen isotope fractionations of organic compounds accompanying biodegradation are strictly controlled by kinetic isotope effects during initial transformation and the process is similar to Rayleigh distillation. If the biodegradation process indeed follows the Raleigh model, an exponential isotopic enrichment or depletion would be expected in the residual reactant reservoir as the product removed. The calculation showed that the carbon isotopic fractionation factor (α) for C_{17} *n*-alkane is 0.98, indicating a single biodegradation step responsible for this fractionation. In the same way, we made calculations for hydrogen isotopic fractionation on C_{17} and C_{22} *n*-alkanes. The result showed that the hydrogen isotopic fractionation observed does not fit the theoretical model. There are poor correlation between $\ln [(\delta + 1000) / (\delta_i + 1000)]$ and $\ln F$ during the course of the biodegradation for nC_{17} ($R^2 = 0.70$) and nC_{22} ($R^2 = 0.36$). One possibility is that changes in δD values are correlated with biodegradation, but not caused by biodegradation. The kinetic results open the possibility of quantitative assessment on the extent of biodegradation using a Rayleigh model if the petroleum reservoir in question is a relatively closed system.

PRG1-21: Hydrogen isotope systematics of individual hydrocarbons in gasoline fraction of Western Canada sedimentary basin oils

M.J. Whiticar, P. Eby

Biogeochemistry Facility, School of Earth and Ocean Sciences, University of Victoria, Victoria, BC, V8W 2Y2, Canada (e-mail: whiticar@uvic.ca)

In a previous paper, Whiticar and Snowdon, reported the carbon isotope characterization of 42 oils/condensates in the Western Canada Sedimentary Basin [1]. We extend that Compound Specific Isotope Correlation (CSIC) study to include the stable hydrogen isotope ratios ($^2H/^1H = D/H$) of individual hydrocarbon species from pentane to nonane on the same sample suite. We have developed an on-line SPME-GC-Reduction-IRMS analytical platform to routinely make D/H measurements on C_5-C_9. These initial measurements have produced surprising and exciting results. The overall range in δD_{cpd} values is between ca. –22‰ and –395‰ (vs. V-SMOW, Figure 1). Between compounds in any given oil the average δD_{cpd} range is ca. 250‰, and the largest range is 373‰. Comparing the same compound in different oils shows a remarkable consistency, i.e., pattern of excursions in δD_{cpd} for specific compounds is generally mirrored in most oils. However, for any specific compound a δD_{cpd} range of 50‰ to 200‰ is observed. Compound classes (e.g., n-alkanes) show intriguing systematic shifts with carbon number. In particular isomers of can consistently have dramatically different D/H ratios. Of further interest is the possible connection between the carbon and hydrogen isotope ratio signatures. These various aspects, and their consequence on understanding the process of petroleum formation and oil fingerprinting are examined.

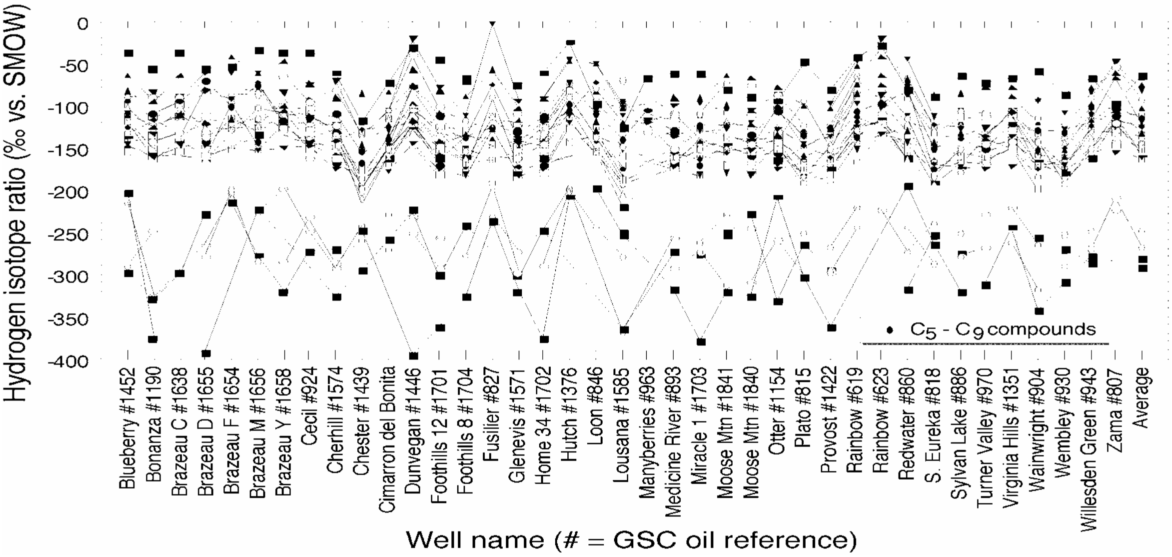


Fig.1. General hydrogen isotope (δD_{cpd}) isotopograms for specific compounds in 42 oils from WCSB.

References

[1] Whiticar, M.J. and L.R. Snowdon, 1999. Organic Geochemistry 30 (9), 1127–1161.

PRG2-1: Depositional and diagenetic history of the Mauddud formation in the Great Burgan field in Kuwait

F.H. Abdullah

Kuwait University, Earth & Environmental Science Department, P.O Box 2457 Mishrif, 40176 Kuwait (e-mail: tamam@kuc01.kuniv.edu.kw)

The Mauddud Formation is one of the major Cretaceous oil reservoirs in Kuwait. It is mainly composed of alternative carbonate and clastic intervals but dominated with carbonate. Oil is produced from the northern fields in the State of Kuwait. In the southern parts the thickness of the formation is less than the northern parts. In the Great Burgan Field (Burgan, Ahamdi, Magwa fields) south Kuwait the formation is relatively thin with a thickness varies between 26-80ft. Maximum thickness is in Magwa oil field and minimum in the Burgan Field. The reservoir part of the formation consists of clean to clay bearing packstones and rare, sandstone. The clastic part of the formation is composed of fine, greenish-brown glauconitic sands mixed with shale. It contains abundant microfossils and some pyrite

The purpose of this study is to identify depositional and diagenetic history of the Mauddud formation in the Great Burgan Field. This was carried out by studying the nature of the rock and correlating it with the type of incorporated organic matter.

A total 15 core samples from Ahmadi Field, 13 samples from Magwa Field and 9 samples from Burgan Fields were prepared for pyrolysis using RE6. The kerogen samples which has been extracted from rock samples by acid maceration process using HCl and HF acids were mounted on microscopic slide for petrographic studies using transmitted microscope.

A total of 9 samples from Ahmadi Field, 7 samples from Magwa Field and 6 samples from Burgan Field were studied in detail using thin section under polarized and transmitted light microscopic. Detailed study for distinctive rock thin section were carried using SEM technique.

Petrographic result shows that the formation is dominated by packstone limestone deposited during transgression period. These carbonate rocks alternated with clastic thin layers that varies in their grain size from coarse sand to fine clay laminated shale. Thus, the rock is interchanging between carbonate and clastic rocks cycles, reflecting sea transgression and regression periods. The thickness of these cycles varies in the three oil fields with maximum thickness in Magwa Field. During these cycles, the area has been affected by short periods of unconformities that is later shed the depositional environment with clastic rock during regression periods.

Pyrolysis results show that the formation has migrated oil mostly in the carbonate section with kerogen mainly in the shale parts. The kerogen show immature type II-III. The organic matter is dominated by marine amorphous type with minor concentration of terrestrial particles especially in the clastic parts. These might be vitrinite woody, spores and pollen as well as cuticle particles. The organic matter, particularly marine type, suffered biodegradation. The biodegradation is highest in both Burgan and Ahmadi fields and sometimes attacked the terrestrial parts also, which is an indication of oxic water condition. In Migwa Field, the organic matter is more preserved with almost 90% concentration of amorphous sapropelic type in the shale rock and they are mixed with 10% vitrinite, spores and pollen grains. This may indicates that at that time the Magwa Field was deeper than both Burgan and Ahmadi fields which resulted in deeper water level in the Magwa field area. Such variation in water depth was either related to topographic sea bottom variation or variation in structural growth between these anticline structure fields.

The amorphous marine part is less preserved in the bottom parts than the top parts of the shale section. This might be an indication that the sea water transgression with time caused reduction in the oxygen level in the depositional environment and thus more preservation of the organic matter.

During regression periods the underlying carbonate rocks suffered diagenesis which caused an increase in porosity followed by periods of recrystallization and destruction of these moldic and vuggy porosity. Leaching process for the carbonate rocks was in two stages, the first stage was related to short interval unconformities and the effect of meteoric water, the second could happed just before the oil invasion and resulted in preservation of these pore space compared to the previous recrystallized moldic porosity. The migrated oil has been generated from deeper source rocks resulted in the preservation of the secondary porosity.

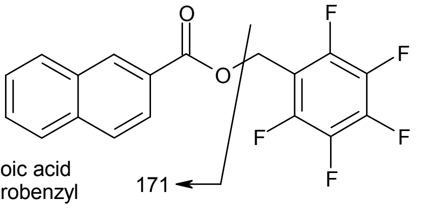
PRG2-2: Detection of acidic metabolites of anaerobic hydrocarbon degradation using negative-ion chemical ionisation mass spectrometry

C. Aitken[1], M. Jones[1], S. Larter[1,2]

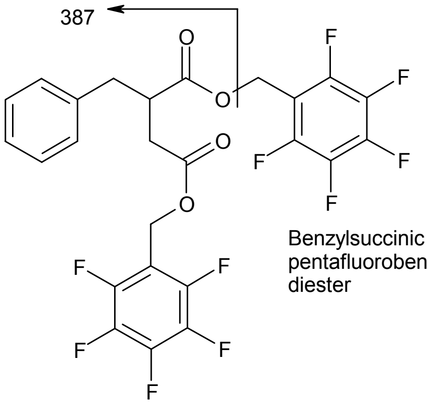
1) University of Newcastle upon Tyne, School of Civil Engineering and Geosciences, Drummond Building, Newcastle upon Tyne, NE1 7RU, UK (e-mail: C.M.Aitken@newcastle.ac.uk)
2) University of Calgary, Petroleum Reservoir Group, Dept of Geology and Geophysics, Calgary, AB, T2N 1N4, Canada

Hydrocarbon biodegradation is a common occurrence in shallow petroleum reservoirs which has been known for many years and which has huge economic implications, yet the mechanisms of this process are still not fully understood. Evidence for anaerobic hydrocarbon degradation in oil reservoirs in the form of naphthalene carboxylic acid and reduced naphthalene carboxylic acid metabolites have recently been identified from many degraded oils from around the world. Other anaerobic hydrocarbon metabolites such as aromatic and aliphatic succinic acids as well as naphthalene carboxylic acids and reduced naphthalene carboxylic acids have been reported from the anaerobic oxidation of hydrocarbons using laboratory enrichment cultures and from studies of anoxic zones in petroleum contaminated aquifers. An extensive laboratory study of anaerobic crude oil degradation under iron III-reducing, sulphate-reducing and methanogenic conditions is now underway and preliminary findings have revealed the formation of cycloalkyl, aromatic, and polycyclic aromatic succinate metabolites under all three reducing conditions.

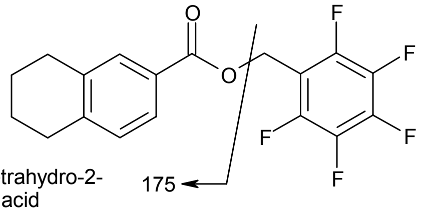
The search for succinates, reduced naphthoic acids, and other metabolites of hydrocarbon degradation has usually involved the use of gas chromatography- mass spectrometry with electron impact ionisation to analyse the methylated acid fractions. However, these metabolites are often in very low abundance and so in order to increase analytical sensitivity and specificity to allow a more detailed investigation of the occurrence of these metabolites, alternative derivatization procedures have been utilised. In particular, those allowing the use of negative-ion chemical ionisation (NCI) mass spectrometry and employing esterifying reagents such as pentafluorobenzylbromide (PFBBr) and 1,1,1,3,3,3-hexafluoroisopropanol (HFIP), have been investigated. The efficiency of the derivatization process is dependent of the derivatization conditions used and the NCI mass spectra from a variety of monocarboxylic and succinic acid metabolite model compounds show fragmentation modes that vary considerably with compound type as well as type of derivative. In NCI mode pentafluorobenzyl (PFB) esters of carboxylic acids such as 2-naphthoic acid and the reduced 2-naphthoic acids show simple mass spectra with no evident molecular ion and a large base peak corresponding to the carboxylate anion. The spectrum for the PFB diester of benzylsuccinic acid, which has two carboxylic acid functional groups, also shows no evident molecular ion but gives a large base peak corresponding to the loss of only one of the two PFB functional groups. In NCI mode, fragmentation patterns for HFIP esters of mono- and dicarboxylic acids are more complex. Large peaks corresponding to molecular ions are evident for HFIP esters of 2-naphthoic acid and reduced 2-naphthoic acids whereas the diester of benzylsuccinic acid gives only a very small molecular ion peak and a large base peak corresponding to the loss of one of the ester functions. Examples of derivatized metabolite compounds and their corresponding major NCI ions are given below. This information on the NCI spectra of halogenated derivatives of these compounds is being used for the detection and quantification of anaerobic hydrocarbon metabolites in a variety of laboratory microcosm and field degraded crude oils in order to gain a better understanding of the mechanisms of this important process.



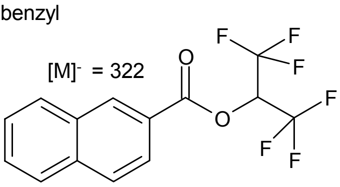
2-Naphthoic acid pentafluorobenzyl ester



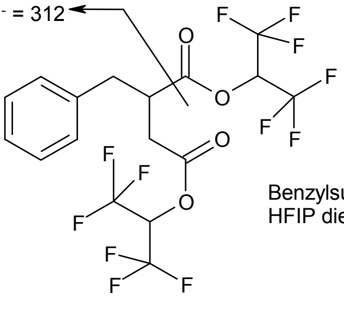
Benzylsuccinic acid pentafluorobenzyl diester



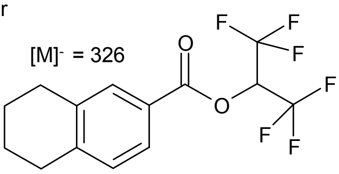
5,6,7,8-Tetrahydro-2-naphthoic acid pentafluorobenzyl ester



2-Naphthoic acid HFIP ester



Benzylsuccinic acid HFIP diester



5,6,7,8-Tetrahydro-2-naphthoic acid HFIP ester

PRG2-3: Influence of Production activities on the field crude oil composition

N. Cañipa-Morales[1], A. Pérez-Ortiz[1], L. López-López[1], E. Gutierrez-Mejía[1], J. Mandujano-Velazquez[1], N. Pintado-Moscoso[2]

1) Instituto Mexicano del Petróleo, Parque Industrial Canacintra, Mineral de la Reforma, Hgo., México, C.P. 42083 (e-mail: acanipa@imp.mx)
2) PEMEX Exploración y Producción, Reforma, Chiapas

Hydrocarbon production activity requires the application of more and more power tools to increases petroleum field recovery. The methods normally used are water injection, gas injection, chemical stimulation, etc. Sometimes, the use of these methods without compatibility studies prior to be applied can generate an adverse effect on the crude oil composition altering their composition and instead of solve the production problem, it becomes in an additional problem to solve.

In this work, 65 crude oil samples and 102 cores were analyzed and we report the results obtained from the CGC-FID, CGC-MSD, MS, fluorescent and reflected light optical analysis. Samples were collected from wells provided of a pneumatic pumped system and some of those were chemically stimulated.

According to the results, crude oils have marine carbonate origin related with tithonian organic facies. In general terms, the maturity of oils seems to belong to the maximum oil window generation source rock. Some crude oils exhibit evidences of mixture and biodegradation, this explains the high sulfur contents and the aromatic-asphaltic nature of the oils.

Oils from wells which were chemically stimulate, show similar composition than those from pneumatic pumped wells, nevertheless, the most relevant difference is the presence of variables amounts from 2 to 40 % of heavy organic matter that is dispersed in the oil during sampling, but spontaneously precipitates at room temperature. This organic material contains a mixture of very heavy paraffins and asphaltenes which we presume are formed during chemical stimulation of the wells. From these results, it is highly advisable to perform laboratory tests in order to know the chemical compatibility of the petroleum field and the chemical agent prior to apply it at the field scale.

PRG2-4: Bitumens in North Sea Jurassic sandstone reservoirs: evidence for low temperature degradation rather than oil cracking

A.D. Carr[1], I.C. Scotchman[2], W. Meredith[3], C.E. Snape[3]

1) Advanced Geochemical Systems, 1 Towles Fields, Burton-on-the-Wolds, LE12 5TD, U.K.
(e-mail: andrew.carr@which.net)
2) Statoil, Statoil House, 11A Regent Street, London, SW1 4ST, U.K.
3) Nottingham Fuel & Energy Centre, School of Chemical, Environmental and Mining Engineering, University of Nottingham, NG7 2RD, U.K.

While Upper Jurassic (Fulmar and equivalent) sandstones are major oil and gas condensate reservoirs in the North Sea, many reservoirs also contain small but still significant amounts of bitumens. These bitumens have been described as pyrobitumens by Isaksen, (2004), resulting from the cracking of an earlier oil charge to generate gas condensate and bitumen. However, analytical data from the bitumens supporting this formation mechanism have not been published. Vandenbroucke et al. (1999) also suggested that the Elgin/Franklin complex (Fulmar) gas condensates were derived by the thermal cracking of an earlier oil charge and produced a kinetic degradation model showing that the gas condensate composition could have been derived by the oil cracking process. Again the bitumen is assumed to be the thermal residue produced by the cracking process, although Vandenbroucke et al. (1999) did not present analytical data from either the bitumens generated in the laboratory during the oil cracking reactions, or from the bitumens in the Elgin/Franklin complex. The increase in temperature that occurred during the rapid Plio-Pleistocene subsidence in the Central Graben would have provided the thermal energy necessary for such oil cracking processes.

Within the Fulmar reservoirs, bitumens often impregnate the microporosity within the diagenetic illite cements (Wilkinson et al., 1997), and these bitumens therefore provide a key to understanding of the formation of the hydrocarbon charges and the timing of the diagenetic cements, both of which are very important to the economic success of the petroleum system. However, the analysis of the bitumens is very difficult using conventional petroleum geochemical techniques, due to their insolubility in most organic solvents. The problem with the bitumen insolubility can be overcome by using hydropyrolysis (hypy). Love et al., (1995; 1997) showed that low extrabilities of immature and overmature kerogens could be increased by using the catalytic hydrogenation technique (hypy), and consequently the biomarker characterisation of the insoluble bitumens should be feasible using this approach.

Using both drill cuttings and core fragments, bitumen-stained samples were successively extracted using *n*-heptane, toluene and DCM/methanol. Asphaltenes were precipitated from the DCM/methanol extracts using *n*-heptane; the hypy analysis of the asphaltenes follows that described by Meredith (2004). The analysis is complicated by the use of oil-based drilling muds and this has necessitated assessing the overall maturity of the aromatic hydrocarbons released by hypy. Both GC-MS and NMR indicate that the bitumens compromise aromatic hydrocarbons of mid-maturity, as opposed to the high maturity (with high concentrations of parent PAHs) expected if the bitumens formed by thermal cracking of an oil. Indeed, the bitumen hypy aromatics have the same maturities as mid-mature oils found in many of the North Sea reservoirs and a formation mechanism is described in which the bitumens formed as result of an early oil charge that was subsequently degraded during the period of uplift and erosion that generated the base Cretaceous unconformity. This is significantly earlier than predicted by conventional basin modelling, and was modelled using a thermal history derived from tectonic modelling with maturity calibrated by the PresRo® kinetic model. Thermal cracking of oils was prohibited by the high fluid pressures that developed during the Plio-Pleistocene subsidence.

References

Isaksen, G. H. 2004. Central North Sea hydrocarbon systems: Generation, migration, entrapment, and thermal degradation of oil and gas. *AAPG Bulletin*, 88, 11, 1545–1572.

Love, G.D., Snape, C.E., Carr, A.D. and Houghton, R.C. 1995. The release of covalently-bound biomarker hydrocarbons via pyrolysis at high hydrogen pressure (hydropyrolysis). *Organic Geochemistry*, 23, 981-986.

Love, G.D., McAulay, A., Snape, C.E. and Bishop, A.N. 1997 Effect of process variables in catalytic hydropyrolysis on the release of covalently-bound aliphatic hydrocarbons from sedimentary organic matter. *Energy & Fuels* 11, 522-531.

Meredith, W., Russell, C.A., Cooper, M., Snape, C.E., Love, G.D., Fabbri, D. and Vane, C.H. 2004. Trapping hydropyrolysates on silica and their subsequent thermal desorption to facilitate rapid fingerprinting by GC-MS. *Organic Geochemistry*, 35, 61-72.

Vandenbroucke, M., Behar, F. and Rudkiewicz, J-L. 1999. Kinetic modelling of petroleum formation and cracking: implications from the high pressure/high temperature Elgin Field (UK, North Sea) . *Organic Geochemistry,* 30, 1105-1125.

Wilkinson, M. and Haszeldine, R.S. 1997. Discussion on aluminium loss during sandstone diagenesis. J. Geol. Soc., London, 154, 747-751

PRG2-5: Are sulphur-rich oils more susceptible to biodegradation than other oils?

M. Fowler[1], M. Obermajer[1], S. Larter[2]

1) Natural Resources Canada, Geological Survey of Canada Calgary, 3303-33rd St. N.W. Calgary Alberta T2L 2A7
(e-mail mfowler@nrcan.gc.ca)
2) Department of Geology and Geophysics, University of Calgary, Calgary Alberta T2L 1N4 Canada

Subsurface biodegradation is now widely believed to occur through the action of anaerobic bacteria at shallow depths and low (< 80°) temperatures. Other controls on biodegradation that have been suggested include charge timing, presence or absence of a significant water leg, access to electron acceptors, nutrient availability, and water salinity. Here we consider another factor that appears to influence the susceptibility of an oil to biodegradation and which does not seem to have received so much attention - the composition of an oil and by inference the nature of its source rock. Intuitively, oil composition would be expected to have some affect on the susceptibility of an oil to biodegradation as some compounds are more easily degraded than others, a trend that is the basis for ranking the extent of biodegradation. Here we provide empirical evidence that demonstrates; (i) in some situations sulphur-rich oils appear to be more prone to biodegradation than low sulphur oils and (ii) the occurrence of some unbiodegraded, low sulphur oils in shallow reservoirs that cannot easily be explained by "paleopasturization" of the reservoir ([1]).

Oil is produced from very shallow Devonian Dundee - Detroit River oil reservoirs in the Michigan Basin, southwestern Ontario. These reservoirs are at depths of less than 150 m and yet this oil does not appear to be biodegraded, although there is some evidence for water-washing. As these reservoirs are not thought to have experienced temperatures of more than 60°C, the lack of biodegradation cannot be attributed solely to paleopasteurization. We discuss the likely geological and geochemical constraints on limiting biodegradation in this setting. The oils are low S oils with an average saturated/aromatic hydrocarbon ratio of 1.7 that are derived from Devonian clastic source rocks. Slightly biodegraded high S oils that have a Silurian carbonate source rock occur in the same area in deeper (400-600 m) Silurian reservoirs. Both oil families are thought to have been generated during the Upper Paleozoic.

In the east central part of the Western Canada Sedimentary Basin, extensively biodegraded oils occur in Lower Cretaceous and Mississippian reservoirs at depths of less than 1000 m. The source rock for these oils is the Latest Devonian-Earliest Mississippian Exshaw Formation that generates high S oils. Slightly shallower (700-800 m) Viking Formation reservoirs in the same area contain low S, unbiodegraded to mildly biodegraded oils derived from Upper Cretaceous clastic source rocks. The regional maturity for Lower Cretaceous strata in this area is less than 0.4% Ro suggesting that paleopasturization could not have occurred.

In the Oriente Basin of Ecuador, two oil families occur in reservoirs of the Cretaceous Napo Formation. The two oil types are sourced from different carbonate and clastic intervals within the Napo Formation. Although both oil types occur in stratigraphically equivalent reservoirs in different compartments of the same field, only the sulphur-rich carbonate sourced oils are biodegraded while none of the low sulphur, clastic sourced oils have been found to be biodegraded in these or other fields.

We have observed other examples that show a similar pattern of carbonate derived sulphur -rich oils being preferentially degraded relative to low sulphur, clastic sourced oils, or where unbiodegraded low sulphur, waxy oils occur in shallow reservoirs where paleopasturization would seem unlikely. Hence at least in some situations, the composition of an oil appears to affect its susceptibility to biodegradation and thus may be another factor to consider when examining the risk of biodegradation. At present, we do not have an explanation for this, which runs counter-intuitive to what might be expected based on the susceptibility of different compound classes to biodegradation. It is possible that the greater susceptibility to biodegradation of S-rich oils could be related to the type of microorganisms responsible for the biodegradation in these reservoirs (e.g. sulphate-reducers), to the greater solubility of some S (and N and O) compounds and hence their greater bioavailability, or to some other facet of the oil's composition.

References

[1] Wilhelms, A., Larter, S.R., Head, I., Farrimond, P., di-Primio, R. and Zwach, C. (2001) Biodegradation of oil in uplifted basin prevented by deep-burial sterilization. Nature vol. 411, p. 1034-1036.

PRG2-6: Factors Controlling The Quality Of Oils From The Oriente Basin, Ecuador

M. Fowler[1], M. Obermajer[1], M. Dashwood[2], J. Cody[2]

1) Natural Resources Canada, Geological Survey of Canada Calgary, 3303-33rd St. N.W., Calgary Alberta T2L 2A7, Canada (e-mail: mfowler@nrcan.gc.ca)
2) EnCana Corporation, P.O. Box 2850, 421 7th Ave. S.W., Calgary, Alberta T2P 2S5 Canada

The Oriente Basin of Ecuador is one of the most productive of the South American Sub-Andean basins. A large number of oils (87) have been collected from Cretaceous Napo and Hollin Formation reservoirs from the northern and central part of the basin. These oils show a range of gravities, 11.3-33.6E API, that significantly impact the economics of their production and transportation. The object of this study was to investigate the factors controlling oil quality.

The oils were analysed using a range of techniques including elemental sulphur analysis, whole oil gas chromatography, gasoline range gas chromatography, fractionation and subsequent analysis of saturate and aromatic fractions by gas chromatography and gas chromatography - mass spectrometry. The data obtained indicates that of the four inter-related factors controlling oil quality, source and biodegradation are the most important, while maturity and water-washing have a lesser effect.

The analysed oils belong to two main oil families. Shallower reservoirs in the central and southern part of the study area contain >F=-type oils which are generally low gravity, high sulphur oils. Geochemical characteristics indicate their source is a carbonate-dominated interval deposited under highly anoxic conditions. Most of the oils in the northern area and in deeper reservoirs further south are >G=-type oils. These tend to be higher gravity, lower sulphur and hence better quality than F oils. Their source rock was deposited in a less oxidising, more clastic-influenced paleoenvironment. Many reservoirs contain a mixture of the two oil types. The maturity of all the oils is fairly low suggesting they were generated in the early to middle part of the oil window. In fields containing F and G type oil, the latter is generally slightly more mature. Based on this oil maturity characteristic, and the stratigraphic occurrence and geochemical characteristics of the oils, it is believe that the two source rocks are not stratigraphically far apart within the Upper Cretaceous Napo Formation with the G source occurring lower within this unit. Lower maturity equivalents of the probable source of the F oils, with very high TOC contents and HI values, outcrop in the area of the Napo River. The source of the G oils has not been conclusively demonstrated to date.

The quality of many, but not all the F oils is further reduced because they have been biodegraded. G oils have not been affected by this process, even when they occur in the same reservoir intervals at similar depths in another block of the same field. This possibly reflects the influence of source rock type on the susceptibility of an oil to biodegradation. The present day depth of all reservoirs is too great for biodegradation to be a currently active process, implying that it took place in the past. Some reservoirs contain a mixture of biodegraded and unbiodegraded hydrocarbons suggesting that a second pulse of hydrocarbons arrived when the reservoir was at a depth and temperature too great for biodegradation to occur.

Almost all the F and G oils in the deeper Hollin Formation reservoirs have been extensively water-washed but not biodegraded. This process seems to have improved their quality by removing the more water-soluble aromatics and NSO compounds, hence reducing their sulphur content.

PRG2-7: Integrated geochemical methods for recognition of oil-condensate mixtures: implications for basin scale petroleum processes

R. Hill[1], D. Jarvie[2], Z. Wei[3], J. Dahl[3], M. Moldowan[3]

1) USGS, Box 25046, MS 939, Denver, CO 80225
2) Humble Geochemical Services, Humble, TX 77338
3) Department of Geological and Environmental Sciences, Stanford University, Stanford CA, 94305

Oil-condensate mixtures are difficult to recognize, due to our limited understanding of the genetic significance of condensate hydrocarbon composition. Recognition of petroleum mixtures has important implications for petroleum system definition and the interpretation of basin scale processes. Recent advances in our discernment of shale, carbonate, *G. prisca* kukersite, and terrigenous source rock facies from light hydrocarbon distribution have led to the development of criteria for recognizing oil-condensate mixtures. The ability to decipher oil-condensate mixtures ultimately yields greater insight into the processes that control petroleum composition. The goal of this study is to demonstrate how the integration of routine biomarker, light hydrocarbon, diamondoid and compound specific isotope analyses can be used to interpret petroleum mixing and basin scale petroleum processes.

Biomarker and bulk geochemical analyses of oils allow us to interpret the lithology, redox and salinity conditions, organic matter type, and approximate geologic age of their source rocks. However, biomarker interpretations are limited for light oils and condensates that are devoid of biomarkers or contain these compounds in low concentrations. Light hydrocarbon distributions are affected by organic matter type, inorganic matrices, thermal maturity, and petroleum alteration processes. Shale, carbonate, *G. prisca* kukersite, and terrigenous sourced oils can be clearly differentiated from one another using ternary plots of C_7 hydrocarbon isomers (Jarvie, 2001; Hill et al., 2005) and can reveal source facies not apparent from biomarker analysis. The integration of facies interpretations from biomarker and light hydrocarbon analyses can be used to identify oil-condensate mixtures and their respective source rock types. This provides insight into the active petroleum generating source rocks in the basin, particularly those petroleum systems that may only generate condensates. Confirmation of mixing processes is provided by compound specific isotope analysis. When combined with diamondoid interpretations, the relative significance of oil cracking as source of petroleum condensate can be evaluated. Integration of all of the geochemical data with the geology of a basin facilitates the interpretation of the major petroleum systems, basin scale petroleum migration, oil cracking, petroleum mixing processes, and the likelihood of deep petroleum potential.

References

Jarvie, Daniel, 2001. Williston basin petroleum systems: Inferences from oil geochemistry and geology. The Mountain Geologist 38, 19-41.

Hill, Ronald J. , Jarvie, Daniel M. , Henry, Mitchell, and Pollastro, Richard M., 2005. Oil and Gas Geochemistry and Petroleum Systems of the Fort Worth Basin. Submitted to AAPG Bulletin.

PRG2-8: Use of organic geochemistry in allocation of production: application in the Chihuido de la Sierra Negra-Lomitas field, Neuquina basin, Argentina

I. Labayén[1], M. Fasola[1], A. Del Monte[2], R. Castelo[2], E. Lovrincevich[2]

1) CTA-REPSOL YPF, Baradero s/n, 1925 Ensenada, Buenos Aires, Argentina
(e-mail: Mefasolaf@repsolypf.com)
2) REPSOL YPF, Rincón de los Sauces, Neuquén, Argentina

The organic geochemistry has been traditionally used in the exploratory area, but in the last years some novel applications of potential utility for reservoirs and production have been published. One of those applications is the allocation of commingled production in multilayered reservoirs.

This work was carried out in the Oil Field Chihuido de la Sierra Negra-Lomitas in the Neuquina basin (Figure 1a), where most of the wells are finished in commingled production from Avilé, Troncoso and Rayoso Formations (Figure 1c).

The objective of this work is to develop a method that allows to discriminate the contribution of the different producing layers in production petroleum samples. From the analysis of the results corresponding to production oils of individual layers and to synthetic mixtures of laboratory, the following conclusions were obtained:

- With the chromatographic analyses is possible to differentiate not altered oils from Avilé and Troncoso Formations from biodegraded oils produced in Rayoso Formation. But this methodology is not enough to differentiate between not altered oils from Troncoso and Avilé Formations.
- The contents of Vanadium, Nickel and Sulphur discriminate non biodegraded oils produced in Avilé and Troncoso Formations (Figure 1d).
- By the successful solving of synthetic mixtures, it is verified the applicability of this analytical methodology to discriminate the individual contributions of each production layer (Figure 1b).

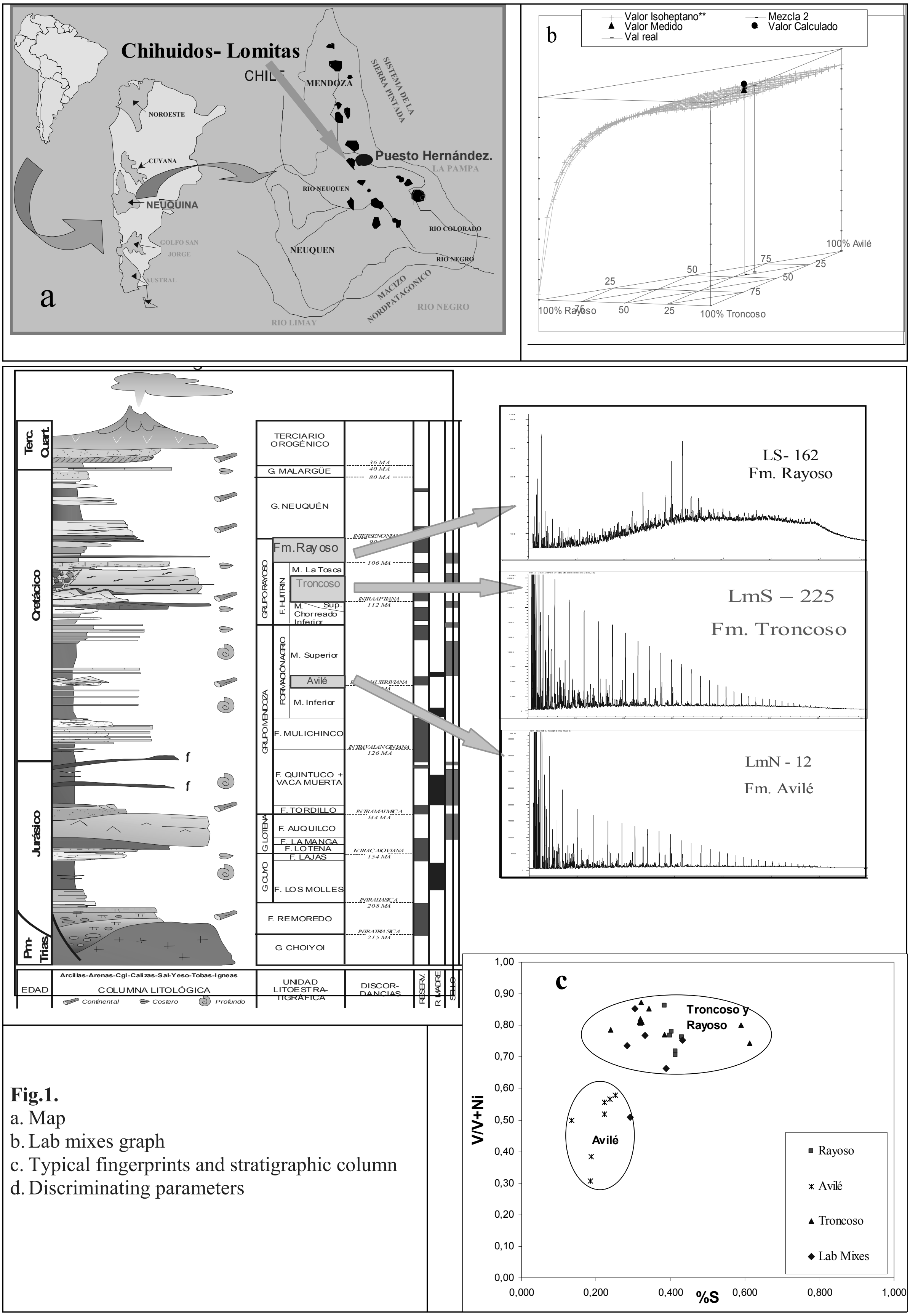


Fig.1.
a. Map
b. Lab mixes graph
c. Typical fingerprints and stratigraphic column
d. Discriminating parameters

PRG2-9: The use of alkylbenzene ratios for the determination of reservoir fluid communication

S.R. Palmer, P. Walker, R. Tharp, D. Rocher

Baseline Resolution, 8701 New Trails Drive, The Woodlands, TX 77381 (e-mail: SPalmer@brilabs.com)

The physical communication or connectivity relationships between the various geologic features that make up an oil bearing formation or reservoir is an important issue since it has a large impact on the costs of petroleum exploration and production. Since typical geophysical methods for determining reservoir communications are often very expensive, an opportunity exists for organic geochemical analysis to be used for this purpose. Organic geochemistry can help establish the extent of reservoir communication by investigating the differences and/or similarities in various properties between crude oils, or families of crude oils, obtained from different locations within the study area. However, there are many occasions where it is difficult to distinguish one oil from another purely based on simple bulk geochemical property measurements. Hence, detailed chemical analysis becomes necessary to distinguish these oils. Traditionally this differentiation has been accomplished by high resolution gas chromatography of the whole oil. While this approach is often sufficient to distinguish samples, this is not always the case in the Gulf of Mexico where common source rocks and reservoir filling histories make comparisons difficult. A new alternative approach focuses on the measurement of a series of alkylbenzene ratios used for resolving and reproducibly measuring C_8, C_9 and $>C_9$ alkylbenzene homologues. Examples of the chromatography achieved, highlighting the baseline resolution of all C_8 and C_9 alkylbenzenes, including meta and para xylene will be given. The precision of the analytical method has been established at the < 0.2% RSD for all combined ratio measurements. The long term stability of the method will be presented and how this impacts cost reduction efforts and timeliness of reservoir communication studies. Data will be shown that demonstrates the ability to distinguish families of oils from each other that are difficult to differentiate on the basis of other analytical methods (see figure 1).

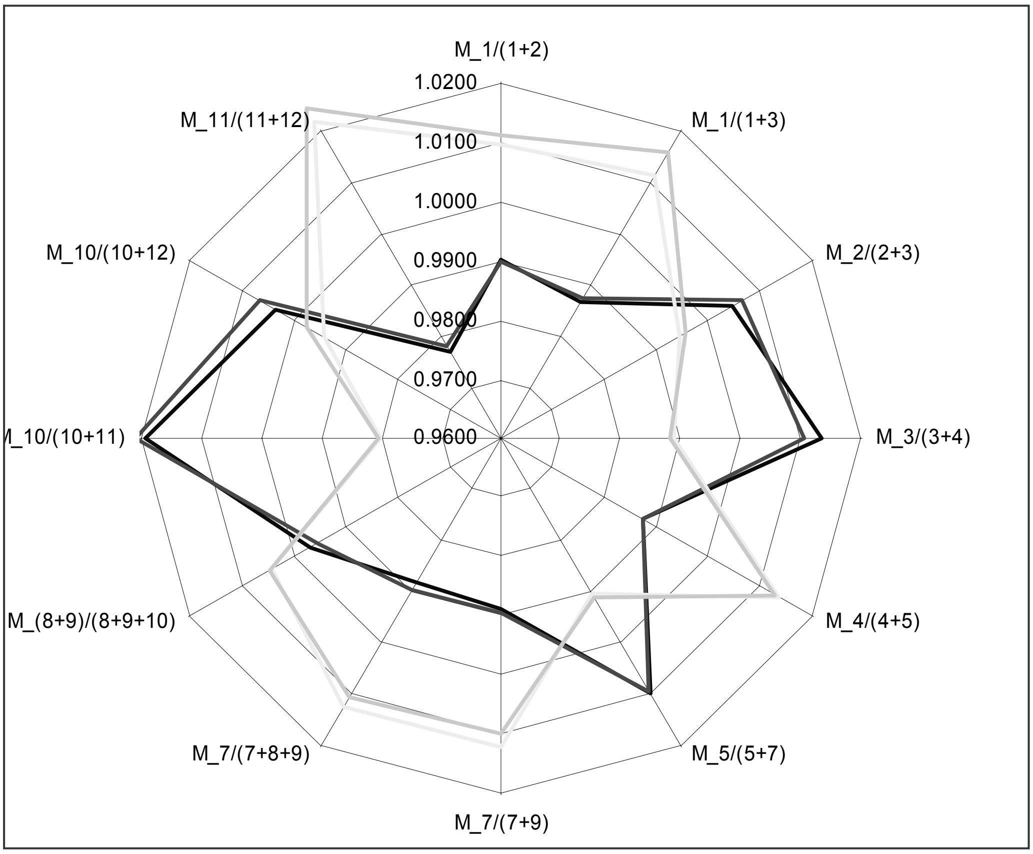


Fig.1. Example star plot showing the ability to distinguish families of crude oils based on differences in their alkylbenzene ratios

PRG2-10: Does dissolved oxygen in the water of Açu formation (Potiguar basin, Brazil) affect biodegradation of its petroleum?

P.F. Parente[1], F.F. Lima Neto[2], L. Landau[1]

1) COPPE/UFRJ, Laboratory for Computation Methods in Engineering-LAMCE, PO: 68552, 21949-900, Rio de Janeiro, Brazil (e-mail: patifp@lamce.ufrj.br)
2)Petrobras/CENPES/PDP/TEP, Ilha do Fundão, Quadra 7, 21941-598, Rio de Janeiro, Brazil

Most of the Brazilian oil production comes from offshore fields located at very deep waters. Unfortunately that oil is generally too heavy, increasing production, transportation and refining costs. Until now the biodegradation process is not well understood: some people claim that aerobic bacteria play an important role in this process, but others argue that dissolved oxygen is consumed by oxidation reactions as water percolates down dip in the basin, so it will not be available to sustain such kind of life, and so anaerobic bacteria are responsible for oil biodegradation.

The onshore Potiguar basin (Fig. 01), located at Northeast Brazil, represents a special case as most of its oil production comes from reservoirs also saturated by fresh waters of meteoric origin. Potiguar oils have different extents of biodegradation, some being very heavy, requiring steam injection to be economically produced, whereas others are very light in spite of its very low gas-oil ratio. This region suffers with repeated drought, and the most important water resources are the same sandstone that produces oil. As a matter of fact, it was an artesian well that led to petroleum discovery in the 80's.

The objective of this study is to understand biodegradation in this basin, comparing the dissolved oxygen in its waters with the quality of the oil produced in different fields. Other parameters, like temperature, pressure, salinity, and physicochemical analyses will be taken to support our conclusion.

Our results could help to choose areas less prone to biodegradation processes, even at very deep waters in offshore basins. And they could also help to better manage the most important aquifer of the region.

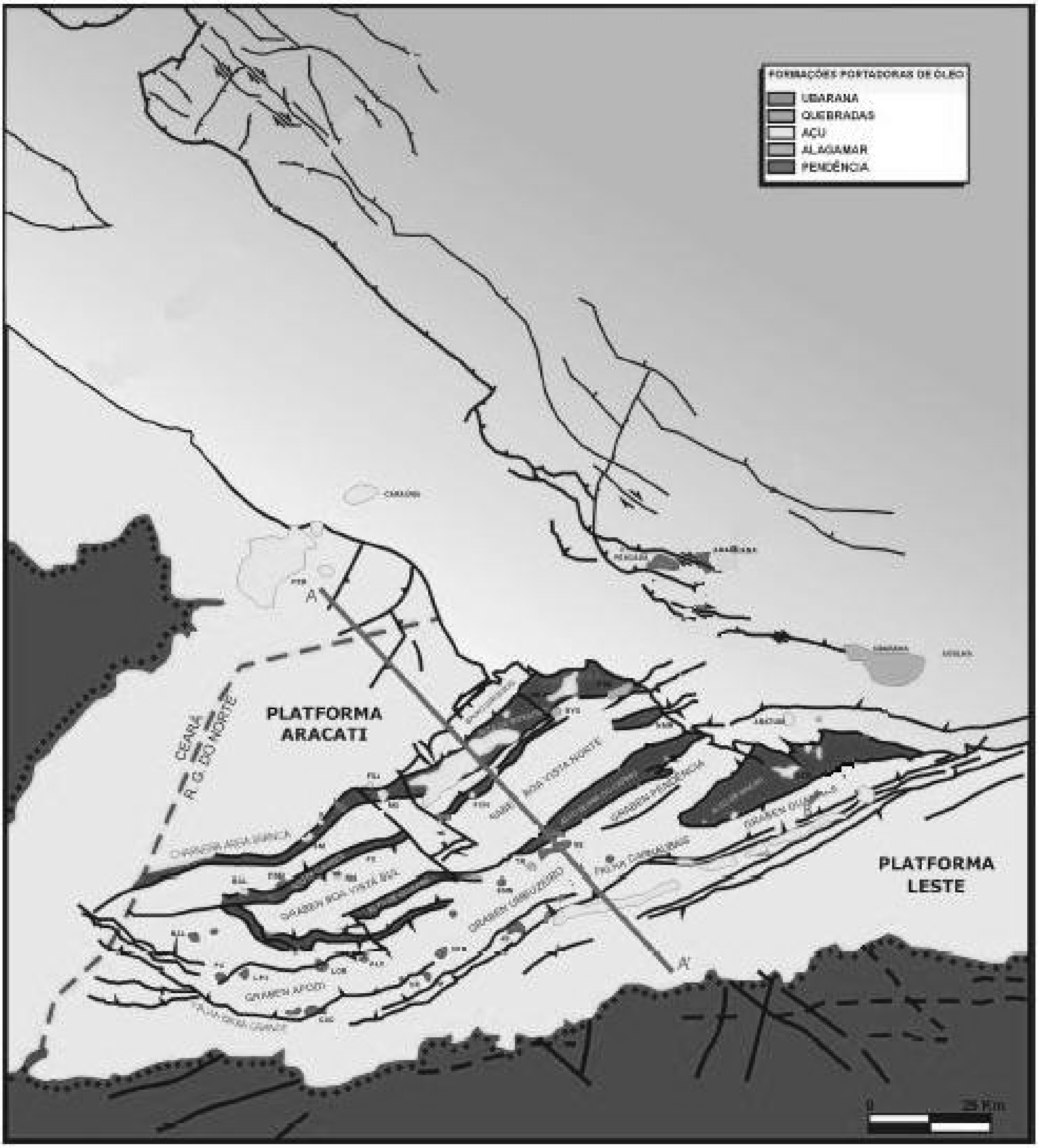


Fig.1. Location map of Potiguar Basin showing its structural framework and major oil fields (source: ANP)

References

Bertani, R. T.; Costa, I. G. ; Matos, R. M. D. Evolução tectono-sedimentar, estilo estrutural e habitat do petróleo na Bacia Potiguar. In: RAJA GABAGLIA, G. P.; MILANI, E. J. (Eds.). **Origem e Evolução de Bacias Sedimentares**. Petrobras: Rio de Janeiro, 1990, p. 291-310.

Milani, E. J.; Zalán, P.V. - POTIGUAR Basin in **The Geology of Paleozoic Cratonic basins and Mesozoic Interior Rifts of Brazil**: Brazilian Geology, part 1. Rio de Janeiro: ABGP, 1998. p.149-158.

Souto Filho, J. D., et al. Alagamar-Açu Petroleum system, onshore Potiguar Basin, Brazil: a numerical approach for secondary migration. In: MELLO, M. R.; KATZ, B. J. (Eds.). **Petroleum Systems of South Atlantic margins**. Tulsa: The AAPG, 2000. p.151-158. (AAPG Memoir 73)

ANP (Agência Nacional de Petróleo) – Potiguar Basin map at www.brasil-rounds.gov.br/geral/ATIV_secoes_e_cartas.asp.

PRG2-11: Biodegradation of crude oil on the Norwegian Continental Shelf

B.S. Pedersen[1, 3], N. Mills[2], H. Wilkes[3], T. Barth[1]

1) Department of Chemistry, Univeristy of Bergen, Allegt 41, N-5007 Bergen, Norway
(e-mail:bent.pedersen@kj.uib.no)
2) Applied Petroleum Technology, Postboks 123, N-2027 Kjeller, Norway
3) GeoForschungsZentrum Potsdam, Section 4.3 Organische Geochemie, D-14473 Potsdam, Germany

In-reservoir biodegradation of crude oil has a huge impact on oil recovery and oil quality, and a number of parameters currently used for assessing oil quality are known to be negatively affected by bacterial alteration. Although much is known about the bulk effects of crude oil biodegradation, little is known about the controls which govern this process. Based on the assumption that components in crude oils are biodegraded sequentially, different classification systems describing the extent of biodegradation have been suggested. The most commonly used [1] has, however, limited applicability for the oil industry, because of the emphasis on heavy and severe biodegradation. Therefore, another scheme with more focus on the less severe levels of biodegradation has been proposed [2]. Biodegradation in the Barrow Island Oilfield in Australia has been studied with emphasis on initial biodegradation [3], but available field and lab data are inconsistent with regards to the sequence of components degraded. Thus, detailed studies of in-reservoir biodegradation of crude oil will be important in clarifying the important controls on crude oil biodegradation.

In this study we look closer into the biodegradation of oils on the Norwegian continental shelf. Data from GC analysis of oils from a large database have been studied with emphasis on biodegradation, and the results are interpreted relative to available models of sequential biodegradation. The aim is to find similarities and dissimilarities in the biodegradation scheme of crude oils with respect to specific characteristics of the studied petroleum systems.

Several samples of biodegraded oils from the Heidrun and Draugen fields are part of the dataset, along with samples biodegraded to different extents from, among others, Midgard, Tyrihans, Skarv and Norne.

This study will present profiles of representative oils and multivariate models are used to identify the components that show systematic variation. The potential presence of different regimes of biodegradation in terms of primary degradation of aromatic or aliphatic compounds will be given special attention.

As an example, a PCA model of all the data from whole oil GC and GC of the saturate fraction is shown in Figure 1. Using the model one can see that the Heidrun samples, as expected, are depleted in the *n*-alkanes and most of the light aromatic hydrocarbons, while the non-biodegraded oils have larger amounts of these compounds. Most of the branched- and cyclic alkanes are less susceptible to biodegradation. Not all the differences between the samples in this plot are due to biodegradation, but the model does make a good starting point for the analysis. The probable interpretation with respects to biodegradation is indicated by an arrow.

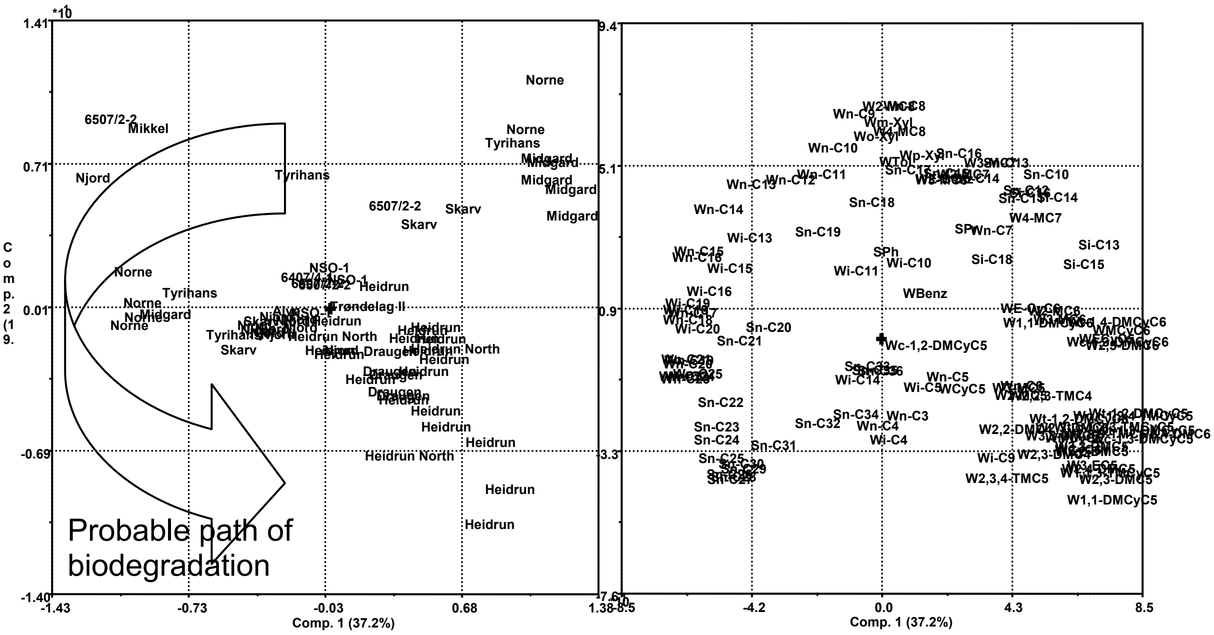


Fig.1. A PCA model of the samples represented in this study. The data used in this are both from GC of whole oils and saturates. Therefore there is a double series of *n*–alkanes (squares) in the loadings plot to the right. The arrow indicates the probable path of biodegradation

References

[1] Peters, K., Moldowan, M.J., 1993. The Biomarker Guide. Prentice Hall, Englewood Cliffs.

[2] Wenger, L.M., Isaksen, G.H., 2002. Control of hydrocarbon seepage intensity on level of biodegradation in sea bottom sediments. Organic Geochemistry 33, 1277-1292.

[3] George, S.C., Boreham, C. J., Minifie, S. A., Teerman, S. C., 2002. The effect of minor to moderate biodegradation on C-5 to C-9 hydrocarbons in crude oils. Organic Geochemistry. 33 1293-1317.

PRG2-12: Origin and alteration of oils and oil seeps from the Sinú-San Jacinto basin, Colombia

C. Sánchez, A. Permanyer

Universitat de Barcelona, Barcelona, Catalonia, Spain (e-mail: sanchezgelvez@yahoo.com)

In the Sinú-San Jacinto Basin (located in the Northwest of Colombia), the presence of liquid hydrocarbons has been recognized in subsurface as well as in surface (oil seeps and crude emanations through mud volcanoes). Origin of oils has not been clearly established so far, particularly in the south part of the basin.

The candidate source rocks in the basin are the Oligocene-early Miocene Ciénaga de Oro Formation (immature terrestrial organic matter) and the Cansona Formation (marine organic matter within oil window) from upper Cretaceous.

In this study, production oil samples, seeps and source rock extracts were analyzed by GC and GC/MS, and $\delta^{13}C$ was determined, with the aim to identify source facies. The sulphur content and gravity data were also considered. Biodegradation that affects some seep samples and the current feeding processes of crude at surface, were also characterized.

Two organic facies were identified: the first one is constituted by terrestrial organic matter deposited in marginal marine to deltaic environments, in suboxic conditions and siliciclastic features (Fig. 1). The second facies is made up of marine organic matter deposited in marine carbonated platform to pelagic environments, in anoxic conditions (Fig. 1). The oils from the first organic facies are paraffinic and present low sulphur contents, whereas the oils from the second organic facies present a paraffin-naphthenic composition and high sulphur contents.

The geochemical analyses allowed demonstrating that the crude from the first facies presents a good correlation with the extracts from the Oligocene-early Miocene source rock, deposited along the whole basin. The second facies presents a good correlation with the extracts from the upper Cretaceous source rocks, deposited just along the folded belt of San Jacinto (east side).

Oil seeps have been affected by moderate to strong biodegradation, leading to alteration or disappearance of selected biomarkers. The seeps presenting moderate biodegradation are characterized by the absence of n-alkanes and the partial degradation of isoprenoids, while the seeps strongly biodegraded show total absence of n-alkanes and isoprenoids, strong degradation of steranes and hopanes, and moderate degradation of diasteranes.

The biomarkers analyses of some oil seeps strongly biodegraded, allowed to identifying the presence of the $C_{29\text{-}25}$ norhopane. Moreover, the presence of saturate hydrocarbons in some of these samples, gives evidence of a current feeding process by fresh oil, rich in low molecular weight paraffin.

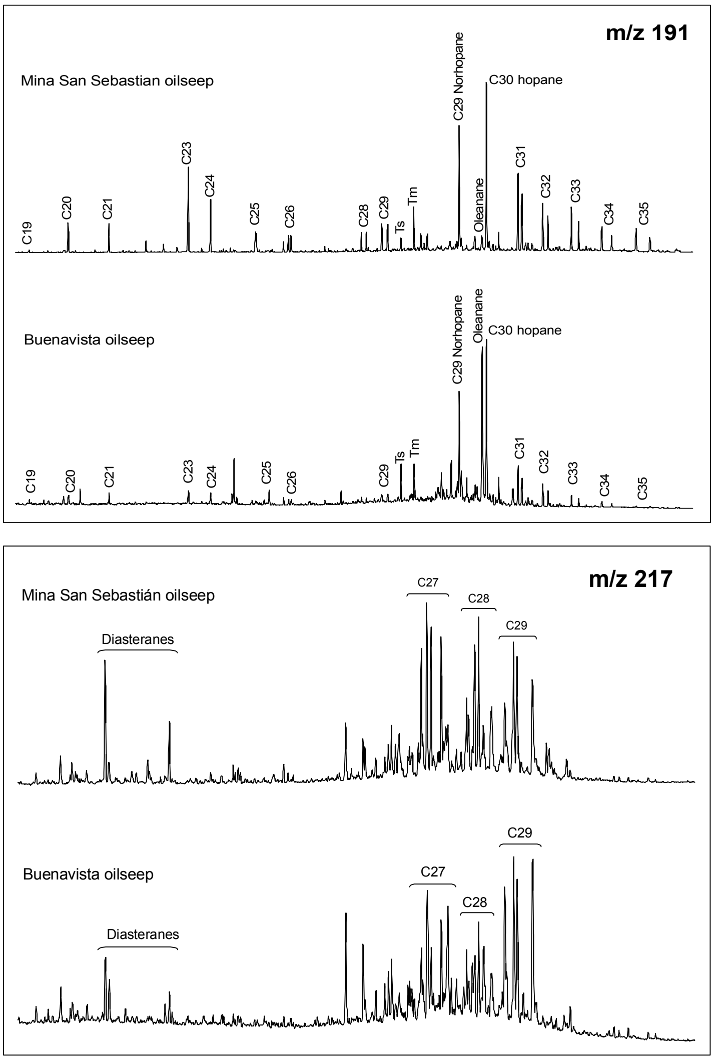


Fig.1. Mass chromatogram from triterpanes (up) and steranes (down) of oil seeps from two different organic facies. Mina San Sebastian oil seep denote a marine source (low oleanane and predominance of C_{28} over C_{29} steranes), and Buenavista oil seep showing a terrestrial organic matter input (high oleanane and predominance of C_{29} over C_{28} steranes)

Acknowledgements

This work was financed by the DURSI of the Catalonian Government (2001SGR00075 "Grup de Geologia Sedimentaria"), and Project BTE2003-06915 from the Spanish Ministry of Science and Technology.

PRG2-13: Comparative study and optimization of asphaltenes and maltenes quantification for diffferent API petroleums

C. Zúñiga-Santillán, N. Cañipa-Morales, Y. Contreras-Santiago, K. Magos-Carmona

Instituto Mexicano del Petroleo, Km. 7.5 Carretera Pachuca-Cd. Sahún, Parque Industrial Canacintra, Mineral de la Reforma Hgo., México, C.P. 42083 (e-mail: czuniga@imp.mx)

Precipitation and quantification of asphaltenes and maltenes are of great importance in the petroleum industry because depending on the petroleum type and the particular condition that every petroleum field has, different precipitation of organic materials phenomena occurs which can cause production conflicts. In order to know the causes that generate the drop in production, pipe line clogs, and to predict asphaltenes precipitation, the reliable determination of asphaltenes is a useful head start tool.

By definition the asphaltenes are n-heptane insoluble components of the crude oil but soluble in toluene. Despite this, many laboratories use the n-hexane or n-pentane as a routine precipitant agent in the quantification process. For this reason, it is important to study the solvents influence on the separation of these components due to the fact that asphaltenes are determined mainly by their raw solubility properties and not by a chemical structure in particular.

In this approach we study the effects of five precipitant agents (n-pentane, n-hexane, n-heptane, n-octane and n-nonane) and their impact on asphaltenes obtained for different petroleum API samples. Likewise, we evaluate the recovered percentages of maltenes and asphaltenes obtained by the traditional procedure at room temperature and at cryogenic conditions using the five different solvents and the different API density petroleum samples.

Based on the results, we found a generalized behavior for all petroleum samples. The obtained asphaltenes percentage is gradually increased by using the lighter precipitant agent. The recovered percentages of asphaltenes at room temperature are as good as at cryogenic conditions in terms of repeatability and reproducibility for all solvents and different API gravities petroleum samples. Thus, it is more convenient to use the cryogenic method in order to decrease time process and to increase the laboratory productivity.

PRG2-14: TAN and TBN determination of acids and bases in crude oils compared with extraction and molecular analysis

T. Barth, K. Erstad, T. Negash

Department of Chemistry, University of Bergen, Allègaten 41, N-5007 Bergen, Norway
(e-mail: Tanja.Barth@kj.uib.no)

Acidic compounds in petroleum are a matter of concern in the processing of crude oils because of their corrosive properties and their contribution to increased viscosity and emulsion stability. Basic compounds are also of interest from a quality perspective due to their high nitrogen content and catalyst poison properties. The conventional methods used by petroleum chemists to determine the content of acids and bases are based on non-aqueous titration, which gives a measure of the total content of acidic groups in the oil as the "total acid number" or TAN (ASTM664-89) and the content of basic groups as the "total base number" or TBN (ASTM D 2896-85). These methods give no information on the chemical structures of the acids or bases, and only to a limited degree information on the strength (pK_a values) of the acidic and basic compounds.

The most frequently used analytical procedures in organic geochemistry combine physical fractionation of samples with molecular analysis by chromatography coupled to mass spectrometry (GC-MS or, more recently, LC-MS). Such analytical schemes have been applied to the analysis of both acids [1, and references therein] and bases [2], [3]. The analyses have given a certain degree of understanding of the chemical structures of the acidic and basic compounds, though especially for biodegraded oils, the attempts at molecular level characterisation are mostly not successful. The quantitative aspects of the geochemical analysis of acids and bases have, with a few exceptions, not been discussed.

Recently there has been concern that the acid number does not show a clear correlation with the corrosiveness of oils, and there is thus a need for more specific analytical information. At the same time, quantitative approaches in geochemical investigations show that often only a small proportion of the acids in crude oils are found in the fractions that are suitable for analysis using the established procedures with extraction, derivatisation and GC-MS analysis. There is therefore a need for a clear understanding of the scope of both types of method, so that all the available information can be combined and exploited optimally in the characterisation of crude oils with regard to amount and chemical structure of acids and bases.

The results from extensive titration analysis of a set of crude oils from the Norwegian continental shelf will be presented. In addition, model compounds have been titrated by the TAN and TBN procedures, and the range of acid and base strengths covered in the titration procedures is thus determined. Surprisingly, at the conditions used in TAN determinations, phenolic compounds are not registered. Thus a major group of compounds registered as acids in other procedures are excluded from the TAN values. The ability of the titration system to differentiate between strong and weak acids and bases has also been determined, and average pK_a values for the crude oil bases are calculated from the half-neutralisation potential.

Back titration procedures have been used to see if the oils contain compounds that already are internally neutralised, e.g. carboxylic acid anions, protonated bases or stable ion pairs. The results show only a small increase in the TAN and TBN values in back titration, except for the biodegraded oils where the TBN values in some cases decrease to below 50 % of the initial value. This indicates a lack of chemical stability relative to pH changes for the bases that are present in the oil after in-reservoir biodegradation.

Results from extraction and analysis of acids and bases will be presented and compared to the TAN and TBN results. The recovery of acids or bases by extraction is quantified by titration. The molecular weight ranges of the extracts have been determined by gel permeation chromatography (GPC). Extracts are further characterised using infrared spectroscopy, and GC-MS when applicable. The distribution between acids and bases in the asphaltene and maltene fractions has been determined for some of the oils. The results are discussed in terms of compound types, effects of biodegradation on the amounts and composition of both acids and bases, and their effects on the physical properties of crude oil that are important during pipeline transport, for storage stability and quality evaluation.

References

[1] Barth, T., Høiland, S., Fotland, P. Askvik, K.M., Pedersen, B.S. and Borgund, A.E. 2004 Acidic compounds in biodegraded petroleum. Organic Geochemistry 35, 1513-1525.

[2] Merdringnac, L., Behar, F., Albrecht, P., Vandenbroucke, M. 1998 Quantitative extraction of nitrogen compounds in oils: Atomic balance and molecular composition. Energy & Fuels 12, 1342-1355

[3] Erstad, K. 2004 Baser og asfaltener i petroleum (Bases and asphaltenes in petroleum) Thesis, Department of Chemistry, University of Bergen, Norway. 173 pages (in Norwegian).

PRG2-15: Charge histories of Ness and Tarbert sands, Northern Oseberg area, using reservoir geochemistry

B. Dahl[1], W. Mathiassen[1], I. Meisingset[2]

1) Department of Geology, Bergen University, 5007 Bergen, Norway (e-mail: birger.dahl@geo.uib.no)
2) Aker Kvaerner Geo AS, P.O. Box 242, Lilleaker, 0216 Oslo, Norway

The main objectives of reservoir geochemical studies are usually to understand the accumulation history (filling, loss, refilling, etc.) of fields or particular reservoir compartments [1]. The results of such studies can be applied to both field development planning and exploration.

The present study has addressed the dynamics of the filling of Ness and Tarbert channel sands in parts of the Oseberg Alpha structure and the adjacent satellites in order to understand the relative distribution of petroleum and water in a fairly complex sand-shale reservoir. Conventional geochemical techniques (thermal and solvent extraction, GC, GC-MS, etc) have been used. The results have been compared with porosity and permeability in order to use Augustsons [2] method to identify “live” versus residual oil columns as well as water zones.

The project identified water zones in oil legs formerly believed to be continuous. Remnant oil zones below present-day water contacts were encountered that suggest adjustment of the oil-water content, either through structural rearrangement or leakage through the cap rock. Traces of biodegraded oils combined with interpretations following Augustsons method [2] support emptying and recharge of the structure. Two oil families were encountered.

References

[1] Dahl, B. and Yukler, M.A. (1991). The Role of Petroleum Geochemistry in Basin Modelling of the Oseberg Area, North Sea. In: R.K. Merrill (Ed.) AAPG Treatise of Petroleum Geology Handbook. Source and Migration Processes and Evaluation Techniques. American Association of Petroleum Geologists, Tulsa, pp 65-85.

[2] Augustson, J.H. (1992) A method on classification of oil traps based on heavy oil contents in cores with relevance to filling and drainage of Barents Sea oil bearing structures. In: Artic Geology and Petroleum Potential. Proceedings of the NPF conference, Tromsø, 1990.

PRG2-16: A tale of two Eromanga oil fields: a comparison of the hydrocarbon charge histories of sandstone reservoirs at Strzelecki and Acrasia

L. Kramer[1], D.M. McKirdy[1], K.R. Arouri[1], L. Schwark[2], D. Leythaeuser[2], P.J. Boult[3]

1) Organic Geochemistry in Basin Analysis Group, School of Earth and Environmental Sciences, University of Adelaide, SA 5005, Australia (e-mail: liza.kramer@adelaide.edu.au)
2) Department of Geology, University of Cologne, Zülpicherstrasse 49a, 50674 Cologne, Germany
3) Petroleum Group, Office of Minerals and Energy Resources, PIRSA, GPO Box 1671, Adelaide, SA 5001, Australia

The majority (but by no means all) of the oil pooled in the Jurassic-Cretaceous Eromanga Basin is sourced from Permian humic coals and carbonaceous shales of the Patchawarra and Toolachee Formations in the underlying Cooper Basin. The remainder (i.e. hydrocarbons indigenous to the Eromanga Basin) are derived mostly from the non-marine organic-rich shales and siltstones of the Jurassic Birkhead and Cretaceous Murta Formations. Thus, each Eromanga oil accumulation needs to be considered individually to determine the number, extent and timing of charges from pre-Permian, Permian, Jurassic and Cretaceous source rocks.

The multi-reservoir Strzelecki oil and gas field is located on the southern margin of the Nappamerri Trough, a major hydrocarbon kitchen in the Cooper/Eromanga petroleum province of central Australia. Its oil-bearing Mesozoic sandstones (Hutton, Birkhead, Namur) contain oil of mixed Permian and Jurassic source affinity. In this study, we compare its charge history with that of the recently discovered, less well understood, Acrasia oil field. The Acrasia structure is a simple anticline formed over the 'Candra Dome', located on the opposite flank of the Nappamerri Trough in the northeast Cooper/Eromanga Basin. The 'Candra Dome' is a long-lived relatively stable feature, little affected by the widespread Tertiary uplift evident elsewhere. Therefore it represents a good focus for oil migrating out of the adjacent Patchawarra Trough and the contiguous Arrabury Trough. The principal oil-bearing reservoirs at Acrasia are the Tinchoo Formation (Middle Triassic) and Hutton Sandstone (Middle Jurassic), although oil was also recovered on DST of the Early Jurassic Poolowanna Formation.

With a view to reconstructing the hydrocarbon charge history of sandstone reservoirs, core plugs of each reservoir at Strzelecki-4, 5 and 6 were extracted in a high-pressure solvent flow-through extraction cell. This device sequentially recovers individual oil charges from the intact pore systems of a reservoir rock, in the reverse order of their arrival at the trap. A different procedure (viz. sequential Soxhlet extraction) was employed to retrieve residual oils from Tinchoo and Hutton core chips from Acrasia-1. In both methods, initial extraction with dichloromethane retrieves the oil that is freely mobile in the pore network ('free oil' = final charge). The subsequent chloroform/methanol extracts represent the part of the oil that is immobile due to adsorption on pore walls ('adsorbed oil' = initial charge) or retained in smaller, less accessible pores. Analysis of the 'free' and 'adsorbed' oils allowed 1) determination of their source and maturity signatures; 2) differentiation of the initial and final charges at different stratigraphic levels within each oil column; and 3) their comparison with DST oils from Strzelecki, Acrasia and adjacent fields.

The residual oils exhibit systematic variations in yield and bulk composition within each oil column. A minor upward decrease in thermal maturity (~0.02–0.03% R_c) is evident in the Hutton and Namur oil pools at Strzelecki. However, at any given level, there is generally no significant difference in either maturity or source affinity between the 'free' and 'adsorbed' oils. On a larger scale, the 'free' oils display a field-wide maturity differential: Hutton, 0.87%; Birkhead, 0.86%; and Namur, 0.94% R_c. In terms of their source affinity, the relative Araucariacean input is Birkhead > Hutton > Namur. All three oil pools comprise mixtures of intra-Jurassic (probably Birkhead) and Permian hydrocarbons. In the Strzelecki oil field, the major contribution (65–80%) appears to have come from source rocks in the Toolachee Formation of the underlying Cooper Basin. The analysis of the residual oils at Acrasia manifests a marked source and maturity differential between 1) Acrasia and Strzelecki; and 2) Triassic and Jurassic oil pools. In the Acrasia oil field, the Permian input to the Triassic and Jurassic reservoirs is substantially higher (>85%). This Permian charge (probably Patchawarra-sourced) is more mature than that at Strzelecki.

PRG2-17: Biodegradation, mixing and lithological controls in the Heidrun field

T.L. Leith[1], D.A. Leith[2]

1) Statoil Research Centre, Postuttak N7005 Trondheim, Norway (e-mail: t-leith@online.no)
2) Åsgård RESU B, Statoil, Stjørdal, Norway

The initial charge to the Heidrun Field probably occurred during the Eocene-Oligocene predominantly by spill from the Smørbukk/Smørbukk Sør structures to the south. This initial charge event(s) was subsequently biodegraded due to the temperature of the reservoir at the time, and has subsequently mixed with the current, non-degraded charge which started ca. 2 Ma and is probably continuing at present.

The gas cap seems likely to have been emplaced as a separate event. Biodegradation of the initial oil charge may have resulted in volume loss which has not yet been fully replenished.

Mixing is most pervasive in the Fangst Group/uppermost Tilje Formation, but does not extend into the lower Tilje/Åre Formation over much of the field. Mixing in the Åre Formation is apparently restricted to the I-segment north of 6507/8-1, the crest of the structure (e.g. 6507/7-6) and along the western margin of the Q segment. Different mixing profiles may be observed in the Tilje and Åre Formation reservoirs. Boundaries between mixed and non-mixed tend to be more abrupt in the Tilje Formation reservoirs, where they are typically associated with segment-wide permeability barriers. Boundaries in the Åre Formation tend to be more gradational, reflecting a general absence of horizontal permeability barriers, although local lithological heterogeneity may be reflected in “bypass” intervals.

The Heidrun North structure seems not to have received the late oil charge, but has received the same gas charge as the rest of the field. This segment appears to be undergoing biodegradation at the present day. The occurrence of a major charge directly from the west is currently unproven and can, at present, only be based on the occurrence of "anomalous" compound-specific isotope data in a few western wells, e.g. 6507/7-5, 6507/7-4.

PRG2-18: Formation and thermal evolution of insoluble reservoir bitumen in Angolan carbonate reservoirs

A. Mort[1], F. Laggoun-Défarge[1], I. Kowalewski[2], A.-Y. Huc[2],
J.-N. Rouzaud[3], F. Muller[1]

1) ISTO, UMR 6113, Université d'Orléans, 45067 Orléans Cédex 2, France
(e-mail: andrew.mort@univ-orleans.fr)
2) IFP Geology & Geochemistry, 1 et 4 avenue de Bois Préau, 92852 Rueil Malmaison, France
3) Ecole Normale Supérieure 24 Rue Lhomond, 75231 Paris Cédex 5, France

Pyrobitumen resulting from the thermal cracking of crude oil is a frequent occurrence in petroleum reservoirs. Despite the detrimental implications of pyrobitumen for the poroperm qualities of the reservoir; little is known about the evolution of pyrobitumen properties as a function of increasing thermal stress.

A suite of pyrobitumen-bearing reservoir cores from the carbonate Jurassic Pinda formation in offshore Angola has been studied using geochemical and petrographic techniques (including elemental analysis, Rock Eval pyrolysis, GC, FTIR, XRD, SEM, TEM) in order to characterise the physical, chemical, and optical properties of the pyrobitumen as fully as possible. The 11 core samples contain pyrobitumen at reflectance values ranging from 0.55-2.24%R_o and display varying degrees of solubility in dichloromethane (DCM) from 98% insoluble bitumen to 45% insoluble (Fig.1), indicating a substantial spread of maturities. However, these indicators of maturity, and further classical maturity indicators such as the H/C and T_{max} show surprisingly poor mutual agreement.

The reliability of maturity parameters such as vitrinite reflectance, T_{max}, H/C, has been proven by their widespread and long-standing application to coals and kerogens. However, the discordance shown by these parameters (e.g. bitumen reflectance and bitumen solubility in DCM) indicates that thermal evolution of solid bitumens is not a straightforward process based on cracking and condensation reactions alone. Given that reflectance values for solid reservoir bitumens with equivalent degrees of insolubility display substantial variation, it appears that additional reaction pathways are responsible for the thermally driven insolubilisation of crude oil in petroleum reservoirs.

Despite reflectance values in excess of 2.2%R_o, and low H/C ratios between 0,6 and 0,8, condensed polyaromatic structures remain poorly ordered, as indicated by XRD analysis of the molecular structure (maximum stack height of basic structural units (BSUs) implies only 7-8 aromatic layers). Although the FTIR spectra show development of these condensed polyaromatic structures, the retention of large amounts of the aliphatic fraction even at high values of reflectance and low H/C is one of the most striking features of the bitumen samples.

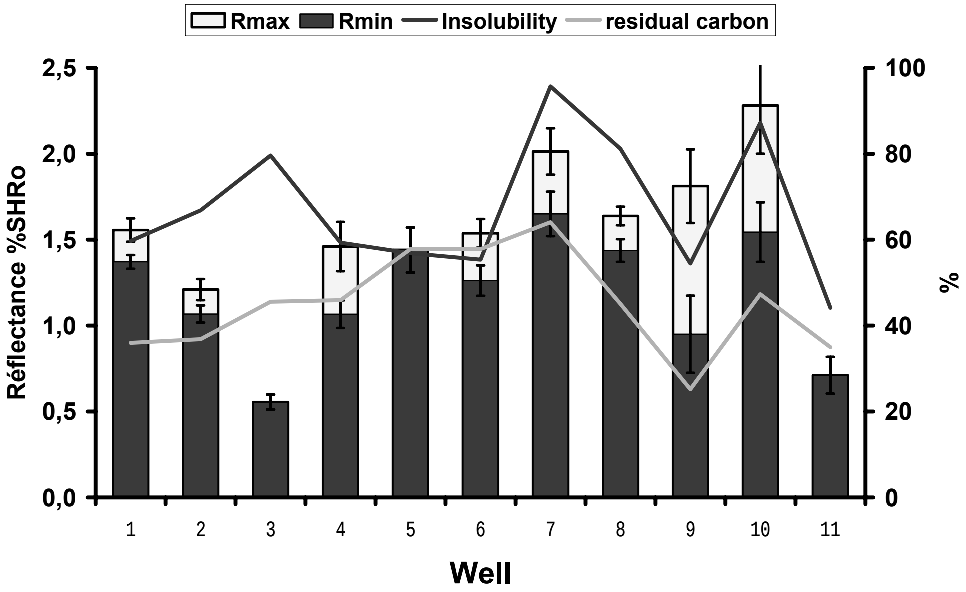


Fig.1. Reflectance and solubility data for a suite of solid reservoir bitumens from offshore Angola

Bitumen structure was studied at multiple scales to elucidate the relative order of condensed polycyclic aromatics. TEM *a posteriori* analysis of cokes obtained by pyrolysis of bitumens reveals that the maximum degree of order of BSUs to form molecular orientation domains (MODs) is attained when the semi-coke precursor is oxygen-depleted and hydrogen rich. On a microscopic scale, observation in polarised light reveals varying degrees of bireflectance (anisotropic, mostly fine mosaic optical textures) in all but the 3 most immature samples.

Development of highly reflective, optically anisotropic microtextures has previously been attributed to bitumens originating from “normal” oils rather than NSO-rich heavy oils (Stasiuk, 1997) but the geochemical evidence points to a significant influence of the NSO component in precocious insoluble bitumen formation in this series. Photonic microscopy of the bitumen *in situ* also provides corroborative evidence for a heavy precursor (e.g. gravitational segregation of polar fraction, EDS compositional analysis), and suggests collateral influences on bitumen formation such as oil-mineral interactions and the depletion of light hydrocarbons by thermochemical surface reduction (TSR) in this sample series.

The origin of insoluble bitumen is thus unlikely to be identifiable by a single means of analysis (e.g. petrography) but must be elucidated from a wide body of evidence.

PRG2-19: Genetic mechanisms of the heavy oils in the North Steep Slope of Dongying Depression, Bohai Bay Basin, East China

S. Li[1,2], X. Pang[1,2], G. Qiu[3], Y. Gao[3]

1) Key Laboratory for Hydrocarbon Accumulation in Petroleum University, Ministry of Education P.R.China
2) Basin and Reservoir Research Center; Beijing; 102249
3) Shengli Oilfield Company Limited , SINOPEC, Dongying 257015 , China

Considerable heavy oils were discovered in the North Steep Slope(NSS) of Dongying Depression, Bohai Bay Basin, China. Most of the heavy oils are characterized by low concentrations of saturated hydrocarbons (28.7%~38%) with relative high content of NSO compounds and asphaltens (33.5%~47.8%), and exhibit typical features of the heavy oils resulting from with secondary alteration, which include short of low molecular weight compounds of saturated and aromatic fractionation as well as occurrence of 25-norhopanes. Quite a few quantity of relative normal oils are also discovered in the NSS. One abnormal phenomenon is that the normal oils are observed in the upper layer (Es_1 member of the Tertiary Shahejie Formation), whereas the heavy oils in the underlying layer (i.e.Es_3 member of the Shahejie Formation). It was also observed in one well (Zx41) that the heavy oils even located in the middle position of the relative normal oils.

25-norhopanes indicating serious biodegradation usually were detected in several oil samples with *n*-alkanes and/or isoprenoids unmoved in the NSS, suggesting the oils with different degree of secondary alteration were mixed commonly. It was presumed that there is probably two main periods of oil charging in the area, which are possibly responsible for the reversion of the heavy and normal oils. However, results of inclusion component and paleotemperature analysis expose no essential differences among the inclusions in the sand reservoir of both the heavy and normal oils, and the oils in the NSS are charged within 5 My up to now.

Various fan reservoir with high porosity and permeability are well developed in the NSS, which are consisted of coarse sand and conglomerate. Most of the oil pools are buried shallowly with poor cap rock property and lateral plugging condition. Additionally, there are several uncomformities including weathering crust of Ordovician burial hill and complex faults developed in the NSS. All of these make water washing and biodegradation easy to happen and should be essential fators for the formation of the heavy oils in the NSS.

Conclusionly, several geological and geochemical factors as the following have a controlling on the physical properties of the oils in the NSS: 1) porosity and permeability of oil reservoir; 2) whether or not an oil pool contact with substantial water immediately; 3) properties of upper and lateral seal of reservoir; 4) differential degree of biodegradation and water washing; 5) the time of oil charging. Among which, 1), 2) and 3) are suggested to be the dominant factors having impact on oil physical properties. Compared with oil pools for Es_1, reservoir of Es_3 generally have characteristics of much higher level of porosity (up to 40%) and permeability (up to $20000 \mathrm{x} 10^{-3} \mu m^2$), which make it easy to transport meteoric water. Additionally, most of the oil pools of Es_3 contact with substantial water pool immediately, which make the oils subject to stronger secondary alteration than that of Es_1 oils. We suggest that it is differential biodegradation and water washing controlled by the special geological background of the NSS that resulting in the formation of the heavy oils and the inversion of the heavy oils and the normal oil apparently in the NSS.

PRG2-20: Variability of molecular maturity parameters in isothermal source rocks — Implications for assessing the thermal maturity of oils

H. Volk[1], S.C. George[1], M. Ahmed[1], R. Sykes[2]

1) CSIRO Petroleum, PO Box 136, North Ryde, NSW 1670, Australia. (e-mail: Herbert.Volk@csiro.au)
2) Institute of Geological & Nuclear Sciences, PO Box 30-368, Lower Hutt, New Zealand

The thermal maturity of oils is routinely assessed using molecular maturity parameters to estimate the maturity of their source rocks at the time of expulsion. Many of these parameters are based on the molecular distribution of aromatic hydrocarbons and aliphatic biomarkers. However, it is well known that maturity parameters differ in their sensitivity ranges, and are influenced by factors such as heating rate, source rock facies and the diagenetic evolution of source rocks. In order to study the effects of source rock facies and diagenesis, coal extracts have been investigated from the Eocene Mangahewa Formation, the main petroleum source rock unit in the onshore Taranaki Basin, New Zealand. The formation consists of intercalated terrestrial and marginal marine sediments deposited under variably brackish conditions in a coastal plain environment. Three closely spaced (within 5 m) and therefore isorank, high volatile bituminous coal seams have been analysed from the Ohanga-2 well. Seams 10 and 11 were divided into 7 and 10 serial ply samples, respectively, while 5 ply samples were collected from the top 0.69 m of Seam 12. "Whole seam" samples were prepared by proportionally recombining ply samples. Seams 10 and 11 are more strongly marine-influenced than Seam 12, as judged by, *inter alia*, total sulphur content (S_{total}), and are consequently more perhydrous. Each seam also has internal variation in the degree of marine influence, generally being stronger towards the roof and floor. Expelled liquids are likely to be more similar to "whole seam" samples than individual ply samples. In addition to variable degrees of marine influence, the three seams also record differences in angiosperm vs gymnosperm input, probably representing variable biomass input and selective preservation.

Many commonly used molecular maturity parameters are highly variable within the sample set and hence, not suitable for predicting thermal maturity. The methylphenanthrene index-1 (MPI-1) ranges from 0.27 to 0.84 (Fig. 1a), corresponding to vitrinite reflectance equivalent (VRE) values of 0.56–0.91% (Radke and Welte, 1983). The controlling methylphenanthrene (MP) isomer in this dataset is 2-MP (Fig. 1b). Other investigated aromatic maturity parameters are also variable, with the exception of trimethylnaphthalene ratio-2 (TNR-2). A correlation of TNR-2 with vitrinite reflectance (Radke et al., 1984) yields VRE values (0.77–0.82%), similar to the measured vitrinite reflectance values (0.74–0.78%) of the least perhydrous Seam 12 samples. The sterane maturity parameter C_{29}

ααα 20*S*/(20*S*+20*R*) falls in a narrow range between 0.48 and 0.50, with slightly lower values in the less marine-influenced Seam 12. Values for the C_{29} αββ/(αββ+ααα) sterane maturity parameter are similar for Seams 10 and 11 (0.45 and 0.51), but significantly lower in Seam 12 (0.36–0.38). Ts/Tm values are very low, but show a strong positive correlation with S_{total} (Fig. 1d). This positive correlation also holds for C_{30} and C_{31} hopane / moretane ratios, whereas the C_{29} hopane/moretane ratio is invariant and is therefore a potential candidate for assessing thermal maturity in this case.

This study has highlighted the facies-dependence of many commonly used molecular maturity parameters, but conversely has identified several parameters that appear to be more robust indicators of maturity. The findings of this study are supported by an additional dataset for Mangahewa coals from Toko-1, Cardiff-1 and Waihapa-1 wells, onshore Taranaki Basin.

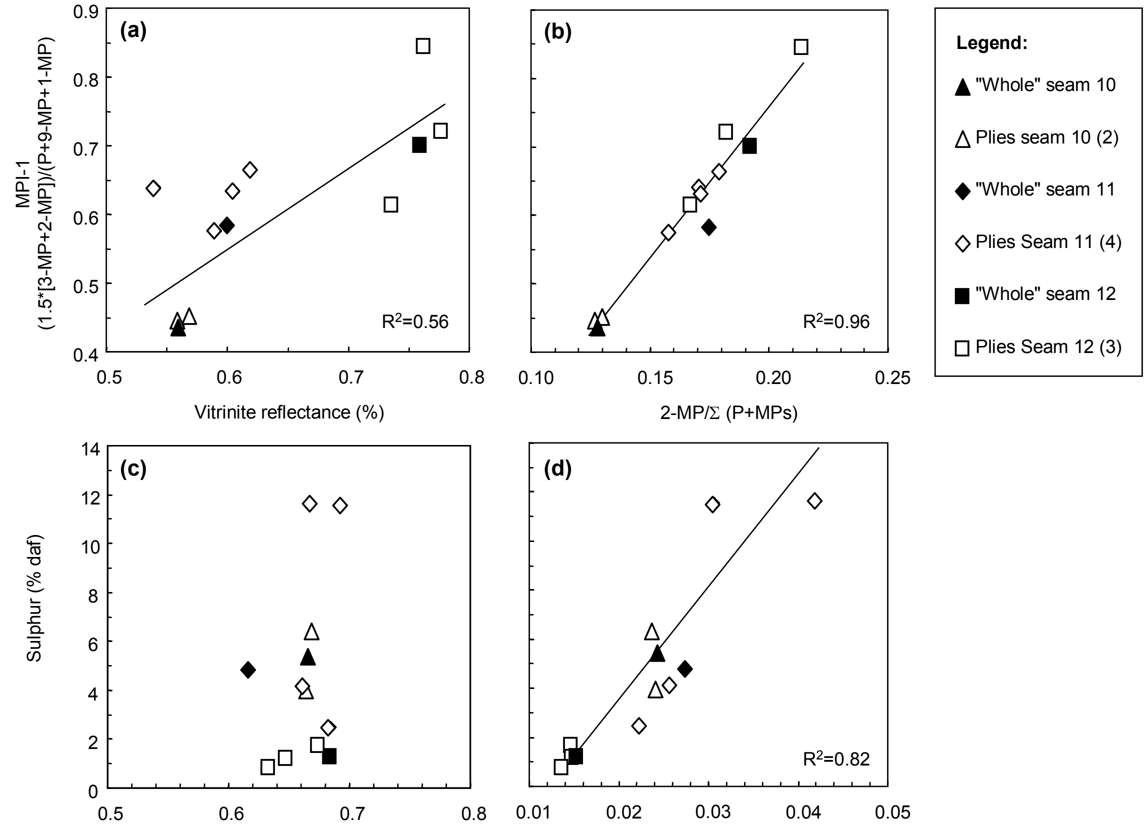


Fig.1. Relationship of MPI-1 with (a) vitrinite reflectance and (b) 2-MP/(Σ P+MPs). Relationship of S_{total} with (c) TNR-2 and (d) Ts/Tm. Sulphur values are on a dry, ash-free basis (% daf)

References

Radke, M., Leythaeuser, D., Teichmüller, M., 1984. Organic Geochemistry 6, 423-430.
Radke, M., Welte, D.H., 1983. Advances in Organic Geochemistry*,* John Wiley, Chichester. pp. 504-512.

PRG2-21: Reservoir petroleum inclusion GOR characteristics and geological significance from the Lunnan Low Uplift of the Tarim Basin

X. Xianming[1], H. Yunxia[1], X. Zhongyao[2], S. Zhiguang[1]

1) State Key Laboratory of Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640 (e-mail: xmxiao@gig.ac.cn)
2) Exploration and Development Institute, Tarim Petroleum Company, CNPC, Kerle 841000

There have been different opinions about the origin of petroleum property variations in the Lunnan Low Uplift of the Tarim Basin. In this paper, a software PVTsim was applied to investigate the compositions of the petroleum fluid inclusions in different sets of reservoir rocks from this area. The results have shown that there are three phases of petroleum inclusions in the Ordovician carbonate reservoirs and two types of petroleum inclusions in the Carboniferous and Triassic sandstone reservoirs. The three phases of the petroleum inclusions from the Ordovician reservoir rocks have similar compositions with the type 1 petroleum inclusions from the carboniferous and Triassic reservoir rocks, but the type 2 petroleum inclusions from the carboniferous and Triassic reservoirs is characterized by higher content of C_1 and higher GOR values. With the combination of the geological background, it has been inferred that the current petroleum pools in the Lunnan Low Uplift were formed mainly by two phases of petroleum charges, one is normal oils and another light oils, and both occurred during late Tertiary. The light oils came from eastern-south direction, and migrated and charged into the reservoirs upward and toward northern west directions. On the basis of this, it has been believed that the multiphases of the petroleum charges and some composition dissipation caused by the preserved condition changes would be the main reason of the petroleum property variations in the petroleum pools in this area.

PBS-1: Tertiary saline lacustrine petroleum geochemistry in Qaidam basin, NW China

A. Su[1], D. Liang[1], S. Zhang[1], Y. Zhu[2], D. Peng[3], H. Huang[4]

1) PetroChina Research Institute of Petroleum Exploration and Development, Beijing; 100083, China
(e-mail: aiguosu@hotmail.com)
2) Zhejiang University, Hangzhou, 310027, China
3) PetroChina Qinghai Oilfield Company, Dunhuang, 736202, China
4) University of Calgary, Alberta T2N 1N4, Canada

The Tertiary saline lacustrine sediments in western part of the Qaidam interior basin contain low amount of organic matter but form large quantity of commercial oil and gas accumulations. This paper systematically investigates oil and gas geological and geochemical features in the study area in aspects of the Tertiary lacustrine water salinity stage classification and spatial distribution pattern, sedimentary organic matter formation nature, organic matter richness and control factors, hydrocarbon generation mechanism and evolution model, petroleum geochemical characteristics, source rock system classification and correlation, petroleum migration, hydrocarbon generation evaluation and oil and gas exploration targets.

1. Base on inorganic elemental analysis such as chlorine anion content, boron content etc., the Tertiary ancient salinity calculation formula and classification criteria in the study area are established. Tertiary lacustrine salinity shows general increase trend from west to east geographically and increase from ancient to present chronically.
2. The saline lacustrine source rocks have type αorganic matter with less than 5% of morphologic macerals. However, their mineral bitumen matrix contents are high (2%~45%), and organic maceral compositions are dominated by sapropel components. Such kind of organic composition, with high hydrocarbon generation potential, is critical for hydrocarbon generation from saline lacustrine source rocks in study area.
3. The most distinct characteristic of the Tertiary source rocks is low organic matter content (TOC with average value of 0.46%~0.58%) and relatively high soluble organic fraction content (bitumen A with average value of 0.110%~0.163%). The relationship between TOC content and chorine anion concentration reflects that moderate salinity is favourite for organic matter preservation in sedimentary rocks but high salinity is harmful for good source rock development.
4. Base on geochemical profiles in the study area, oil and gas generation model can be established for the saline lacustrine source rock in the Qaidam basin. This model suggests that large quantity of oil and gas generated from low organic matter content source rocks in the

saline lacustrine basin not only due to special precursor composition within source rocks, but more importantly saline water body is good for original organic matter (especially soluble organic matter) preservation.

5. Oil biomarker compounds and isotopic data from saline lacustrine oils in the study area and fresh lacustrine oils in northern margin of the Qaidam basin are investigated. Correlation analysis indicates clearly geochemical characteristic difference between fresh water and saline water origin oils, ie., the saline lacustrine oils are of high K1 values (Mango,1990), high branched isoprenoid alkane contents and even over odd predominance within range of C_{18}~C_{28} n-alkanes, et al.

6. The oil and gas occurrence in the western Qaidam basin was controlled by source rock intervals in geological history and depositional phases in spatial. The southern and the northern parts of the saline basin have different source rocks, and deep and shallow source rocks have different origins. Oil-source correlation results suggest that oils discovered in the southern part of the basin are mainly derived from the Lower Tertiary E_3 source rocks, those discovered in the northern part mainly from the Upper Tertiary N_1/N_2 source rocks.

7. The study of neutral nitrogen compounds and biomarker correlation not only indicate the main source kitchen but also show several sub hydrocarbon generation centres divided due to depositional phase variations and migration directions from hydrocarbon generation centres towards marginal structural highs.

8. Finally, the Tertiary saline lacustrine source rock organic matter richness and maturity evaluation criteria are established. Meanwhile, oil and gas exploration targets are proposed for the study area on the base of source rock distribution and hydrocarbon generation capability evaluation.

References

Mango F D.,1990. The origin of light hydrocarbons in petroleum: A kinetic test of the steady-state catalytic hypothesis. Geochimica et Cosmochimica Acta, 54:1315~1323.

PBS-2: Hydrocarbon content of organic matter and oils of the Anadyr basin

O.K. Bazhnova, T.A. Kirjukhina, E.N. Poludetkina, N.P. Fadeeva

Geological Department of the Moscow University, Vorobjovy Gory, MGU, 119234, Moscow, Russia

Anadyr basin is located in the outermost north-eastern part of the Asian continent; considerable part is located on the Bering Sea shelf. The basin is bounded on the east and north by the Okhotsk-Chukotsk volcanic belt. Anadyr basin is filled with up to 8.000 meters of Tertiary sediments. Two oil-gas fields have been already discovered in this basin (Verhne-Telikajskoe and Verhne-Echinskoe). Semicommercial inflows of oil and gas were obtained from Cretaceous to Neogene deposits.

Oils are usually light, resinous, viscous to non-viscous, lightly sulphureous. The characteristic feature is very high content of paraffins (up to 25%). This fact and absence of connection between physical properties with the depth testify about distribution of migration prosesses. Prevailing of methane hydrocarbons is observed in hydrocarbon content both in benzene and in distillate fractions. N-alkane distribution is mostly one-modal, with maximum on C_{23}, C_{22} and less on $C_{16.}$ Distinguishing feature of oils of the Anadyr basin is harsh prevailing of pristane under phytane, Pr/Ph=7-8 (variations between 3-13). Oils are relatively isotopically light ($\delta^{13}C$= - 27.9 - -28,2‰).

Hydrocarbon content of bitumen from Sobolkov suite – main productive horizon of Verhne-Telekajskoe area - was investigated, at that extract from open and closed pores consistently extracted from the non-splintered and splintered rock was studied separately.

In group content of hydrocarbons part of n-alkanes in the saturated fraction reaches 35%, their maximum concentration in most of the samples is marked for the n-alkanes of C_{19} – C_{24} content (27-63%), in some samples content of hard hydrocarbons reaches 63%.

Bitumen in open and closed pores are radically different by the distribution character of n-alkanes and by the value of Pr/Ph ratio. Value of this parameter in the closed pores is generally <1. Differences in content are caused by the genetic differences. Extract in open pores is usually migrational, in the closed pores there could also be autigenic and migrational bitumen of earlier generation.

By Pr/Ph ratio all the studied samples were included into 2 groups: I - Pr/Ph>3 - with essential part of continental OM, and II - Pr/Ph<3 – presumably marine. Groups are divided by the distribution character of steranes and some other polycyclic coefficients, but they are absolutely not connected with the distribution character of n-alkanes. By distribution of sterane biomarkers OM of rocks on Verhne-Telekajskij area are divided on 2 groups: 1 – with prevailing of sterane C_{29} – considerable part of continental OM, 2 – with equivalent concentrations of these hydrocarbons, that marks marine facies of OM accumulation. For the first group lower values of sterane/hopane ratio (0,1–0,2), tricyclic and pentacyclic hydrocarbons (0,01–0,03) are observed. For the second group these values are slightly higher: 0,3–0,4 and 0,04– 0,08 accordingly. Correlation of these groups by Pr/Ph ratio and sterane distribution is not monosemantic: all the samples of the second group by steranes have low values of Pr/Ph ratio, i.e. are dated to the second, "marine" group. The samples with the hightened content of ethylcholestane are dated by Pr/Ph ratio both to the first "continental" and second "marine" groups. It is especially displayed by the bitumoid from the closed pores, characterized by the higher values of ethylcholestane, but lower (less than 1) Pr/Ph ratio.

Studied oils are closer to the first genetic group by both indexes (table), but differ from the bitumen by the higher content of ethylcholestane, so they could be referred to one genetic group (12:18:70**)** accordingly.

Initial matter of the Anadyr basin is mostly continental, but apparently noticeably bacterially reworked. Evidence of that is absence of remarkable peak in C_{27}-C_{29} area and C_{23} distribution maximum. Such maximum is often marked in the coal strata. In presumed oil-maternal strata similar character of n-alkanes character is marked, Pr/Ph ratio is also very high (6-7), though it is lower than in oils. Oils with Pr/Ph>10 are rarely met. They are known in some Kz basins, for example oils in Veiber and Sredne-Kunginsk areas of Western Kamchatka, Northern Vjetnam, in Upper Cretaceous and Eocene deposits of Gipslend basin and Paleogene deposits of Kuper area, Australia.

Table.1. Distribution character of alkane biomarkers.

Area	well	Depth, m	suite	Pr/Ph	Pr/n-C_{17}	Ph/n-C_{18}	C_{max}
Verhne-Echinsk.	13	1443-1486	N_{av}	10.5	1.07	0.10	C_{23}
" – " – " -	"-"	1522-1528	"-"	12.9	0.90	0.09	C_{23}
" – " – " -	"-"	1491-1499	" –"	8. 3	0.90	0.07	C_{23}
Vost.-Telekajsk	2	1843-1875	N_{sb}	3.3	0,7	0,2	C_{23}
Verhne-Telekajsl	9	1863-1875	" – " –	7.6	0,8	0,3	C_{23}
" – " – " -	4	1818-1826	" – " –	9.1	0.9	0.08	C_{23}
" – " – " -	10	2121-2134	" – " –	7.7	0,97	0.11	C_{23}
Oljhovaja	1	2244-2273		6.8	1.7	0,26	C_{23}
Izmennaja	10	2034-2085	Pg_{mn}	6.2	1.4	0.30	C_{23}
" – " – " -	" – " –	2085 -2834	" – " –	9.3	1.4	0.22	C_{23}

References

Gurko N.N. et.al. Nefti I kondensati osadochnih basseinov Chukotki I Kamchatki. Tihookeanskaja geologija, 1986, #4. pp. 111 – 116.

PBS-3: A Mesozoic Davis Strait? – an example of the use of molecular markers in paleogeographic reconstructions

J.A. Bojesen-Koefoed, H.P. Nytoft, F.G. Christiansen

Geological Survey of Denmark and Greenland (GEUS), 10 Øster Voldgade, DK-1350K Copenhagen
(e-mail: jbk@geus.dk)

The paleogeography of the Labrador Sea – Davis Strait - Baffin Bay area, situated between Canada and Greenland, is not well understood. Published reconstructions are demonstrably wrong, and filtered gravimetry data plus recent seismic surveys show the presence of deep interconnected Mesozoic or perhaps even older sedimentary basins in areas previously believed to be underlain by younger oceanic crust. The region is a frontier area for petroleum exploration, with only 6 exploration wells drilled, none of which tests strata older than the Santonian. Exploration models rely heavily on the presence of yet unproven Mesozoic age marine source rocks in the vast offshore areas. Consequently, understanding the paleogeography, at least with respect to the distribution of Mesozoic marine sediments or the possible existence a seaway, connecting a ”proto-Atlantic” to a ”proto-Arctic Ocean” is crucial for assessment of the region’s prospectivity for exploration.

A such seaway will be partially analogous to the well-known ”Cretaceous Western Interior Seaway” (CWIS) of the USA and Canada, and although the CWIS is a foreland basin developed in front of the cordillera rising to the west, and the ”paleo-Davis Strait” is a rifted margin, the same mechanisms responsible for the development of prolific marine Cenomanian-Turonian age petroleum source rock in the CWIS, can be expected to have operated in a hypothetical ”paleo-Davis Strait” as well. Evidence for the existence of a Mesozoic marine passage between Canada and Greenland comes from several sources including seismics and gravity data, as mentioned above, palynological data, that show reworked marine palynomorphs in Santonain and younger strata, and organic geochemistry, that will be discussed here.

Seepages of several different types of oil have been discovered in the Disko-Nuussuaq-Svartenhuk Halvø region, central West Greenland. A number of samples represent a marine shale derived oil of unknown origin, but the oil was presumably generated from Cretaceous age (Cenomanian-Turonian) marine shales similar to the deposits known from the basal part of the Kanguk Formation, Ellesmere Island, Nunavut. Canada. Cenomanian-Turonian age oils are well known from the CWIS and from the Canadian Arctic, and a characteristic feature of these oils is a high proportion of C_{28} regular steranes. This characteristic is recurring in several West Greenland oils. For comparison, a series of oil samples was analysed: Cenomanian–Turonian age oil samples from the CWIS and the Canadian Arctic, Paleozoic oil from Newfoundland, Cretaceous oil from the Scotian shelf, and Upper Jurassic oils from the Jeanne d'Arc Basin and the North Sea. Age-specific biological marker data (24-nordiacholestane ratios) show that most of the West Greenland yield similar source ages as Cenomanian-Turonian age oils from the CWIS. The indications provided by age-specific markers and the overall characteristics of the West Greenland oils, compounded by geophysical and palynological evidence support the existence of marine conditions in the Davis Strait region during the Cretaceous.

A few samples, however, yield considerably higher ages corresponding to the Upper Jurassic, similar to oils from the Jeanne d'Arc Basin and the North Sea. These samples primarily represent an isolated population of partially biodegraded oils, occurring in a setting geologically detached from the remainder of the oil samples. The samples do not show high levels of dinosteranes, that are characteristic of Upper Jurassic oils from the Jeanne d'Arc Basin, but their marine-derived nature may hint at the presence of marine conditions conducive for deposition of petroleum source rocks in the region already during the Upper Jurassic.

In summary, the combined evidence from geophysics, palynology and geochemistry suggest that a seaway hosting environments favourable for deposition of petroleum source rocks existed between Canada and Greenland as early as the Cretaceous, or perhaps even during the Upper Jurassic.

PBS-4: Organic geochemical study of the organic-rich facies in the lacustrine sequences of the Crato formation (Aptian-Albian, Araripe basin, NE Brazil)

A.G. Borrego[1], V.H. Neumann[2], L. Cabrera[3], C.G. Blanco[1]

1) Instituto Nacional del Carbon (CSIC), Apartado 73, 33080 Oviedo (Spain) (e-mail; angeles@incar.csic.es)
2) Dept of Geology, Federal Univ. of Pernambuco, Av. Acad. Helio Ramos, S/N, Recife-PE, 50.740-530, Brazil
3) Group of Geodynamics and Basin Analysis. GRQ 94-1048. Dept of Dynamic Geology, Geophysics and Palaeontology, Universitat de Barcelona, 08028 Barcelona (Spain)

A wide array of cyclically arranged facies varying from marginal to inner lacustrine were deposited as result of long lasting evolution of a Cretaceous lacustrine depositional system in the Araripe Basin, NE Brazil [1]. Three main patterns of organic matter accumulation/preservation can be broadly outlined: i) oxic-suboxic marginal to inner lacustrine facies with low organic matter content (TOC=1-4%) dominated by higher land plant components; ii) anoxic inner lacustrine oil shale facies (TOC=5-19%) dominated by lamalginite with very scarce telalginite (*Botryococcus).* Differences in lamalginite preservation were observed varying from well-preserved, long, anastomosing lamellae with intense yellow fluorescence to shorter laminae with weaker and red-shifted fluorescence, which could be linked to variations in the oxygen content of the bottom waters; iii) anoxic inner lacustrine carbonate dominated facies with low organic content (TOC< 4%) dominated by poorly preserved, often pyritized higher plant fragments (Cheirolepidiacea). Samples from well preserved and poorly preserved lamalginite (samples A and B, respectively) and a limestone (sample C) were selected for the geochemical study in order to investigate the effect of the organic matter assemblage on the biomarker fingerprint.

Samples were ultrasonically extracted with dichloromethane and the aliphatic fractions eluted with *n*-hexane were separated for analysis. The gas chromatographic/mass spectrometric (GC/MS) analyses were carried out on a Finnigan MAT 8200 mass spectrometer using a capillary column coated with SE-54 stationary phase, He as carrier gas and heating rate of 4 ºC/min from 50 to 280 ºC.

The TIC aliphatic profiles in Figure 1 shared some general characteristics although significant differences could be observed among the three samples. The *n*-alkane ranged from n-C_{14} to n-C_{31} with variable relative abundance. The three profiles were bimodal peaking at n-C_{17} (major peak in the three chromatograms) and either at n-C_{24} or n-C_{25}. Slight even predominance was observed in the medium boiling point region (n-C_{20}- n-C_{28}) in sample A whereas the sample with reddish fluorescing lamalginite showed strong odd predominance (sample B). The limestone with abundant higher land plant debris (sample C) showed also

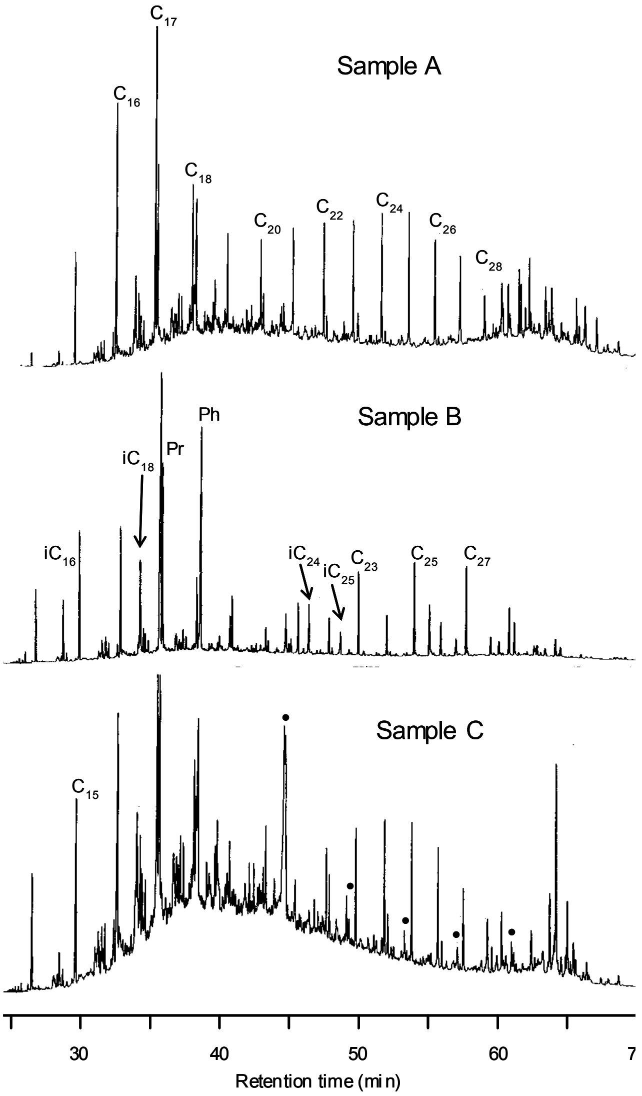


Fig.1. TIC traces of the samples. C_n=n-alkane of n carbon number; iC_n=regular acyclic isoprenoids, Pr=pristane, Ph=phytane, solid circle=mono-methylalkane

slight even predominance. Regular isoprenoids (iC_{16}, norprinstane, pristane and phytane) were present in the three samples and also the iC_{24} and iC_{25} members were identified in sample B. Pristane/phytane ratios over 1 were observed for samples A and C whereas in sample B phytane was more abundant than pristane. A series of 3-methyl-alkane (C_{19} to C_{25}) was present in the samples, these compounds being particularly abundant in sample C where the members up to C_{29} were identified. Only the mono-methylalkanes with an odd number of carbon atoms as reported for insect-derived waxes were present in the samples [2].

The m/z 191 traces showed similar peaks in the three samples with differences in their relative abundances. Prominent peaks corresponding to the 17β(H),21β(H)-isomers were identified and also those with moretane configuration indicating a very low maturity for the samples in agreement with huminite reflectance (~0.25%). The sterane fingerprints in the m/z 217 traces also shared some common characteristics with prominent peaks corresponding to the 5α(H),14α(H),17α(H)-isomers.

Overall the differences in the biomarker composition between the samples are more subtle than those observed in their petrographic components (algal/bacterial vs. higher plant remains). Particularly in sample C the compounds appear to be more related to higher plant fragments bacterial alteration since no typical biomarkers for higher plants were detected.

References

[1] Neumann V.H., Borrego A.G., Cabrera L., Dino R. 2003 Int. J. Coal Geol. 54, 21-40.
[2] Kenig F. 2000 Org. Geochem. 31, 237-241

PBS-5: Geochemical characteristics of the hydrocarbons in the Ulleung basin, offshore Korea

T.J. Cheong[1], Y.J. Lee[1], S.J. Park[2], S.S. Yi[2]

1) KIGAM, Gajeong-dong 30, Yuseong-gu, Daejeon, 305-350 Korea (e-mail: cheong@kigam.re.kr)
2) KNOC, Gwanyang-dong 1588-14, Dongan-gu, Anyang, Gyeonggi-do, 431-711 Korea

Seventeen exploratory wells have been drilled in the Block VI-1 of offshore Korea, which is located in the southern part of the Ulleung Basin. Gas show has been recognized from most of the wells and condensate accompanied in some wells. Commercial discovery of gas, accompanied by condensate, has been made from Gorae V well.

The hydrocarbon gases from the Gorae and Dolgorae wells occupy from 92.87% to 100% of reservoir gases, and non hydrocarbon gas contents are less than 8%. Reservoir hydrocarbon gases mainly consist of methane ranging from 84.19% to 95.97% and ethane ranging from 3.80% to 5.82%. Nitrogen and carbon dioxide are also present as non hydrocarbon gases. On the basis of hydrocarbon gas composition, the hydrocarbon gases from the Ulleung Basin can be classified as wet gas.

The condensate of DST #2 and #3 in the Gorae V well mainly contains C_5 - C_{10} normal alkane and has API 51-53°. The condensate seems to be generated from source rock containing mainly coaly matter according to the high pristane/phytane ratio (6.5 - 6.7) and oleanane index (38 - 45). However, detection of 24/(27+24)-nordiacholestane and C_{30} sterane indicate influence of marine environment. Ternary diagram of $C_{27-28-29}$ sterane may also indicate the influence of marine environment.

Correlation between the thermal maturation level of the condensates and that of organic matter in the sediments reveals that a depth of the generation of liquid hydrocarbons can be inferred to 3,000 m for the Gorae V well. Condensate from the Gorae I well contains relatively heavy normal alkane compared with that of Gorae V; C_{13} normal alkane is the highest and C_{32} normal alkane was detected. Hydrocarbon contains 65% of saturated hydrocarbon, 33.8% of aromatics and 1.2% of NSO compound. The condensate seems to be originated from type III organic matter on the basis of high pristane/phytane, pristane/nC_{17} and phytane/nC_{18} ratio. Evidence of marine organic matter input was not detected in the condensate of the Gorae I well. Carbon isotope of the methane indicates that hydrocarbon gas was generated by cracking of oil or kerogen at catagenesis stage or oil generation stage.

Considering the different source and thermal maturity of hydrocarbon, it is suggested that reservoir hydrocarbons of the Ulleung Basin were generated from at least two different source rocks of terrestrial origin dominantly.

PBS-6: Petroleum geochemistry of the Wessex basin (Dorset, UK)

P. Farrimond[1,4], M. England[1], R. Paterson[1,2], M. Erhuma[1], A. Hindle[3]

1) NRG, School of Civil Engineering & Geosciences, Drummond Building, University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU, UK (e-mail: paul@igiltd.com)
2) Dept. of Earth Sciences, Wills Memorial Building, University of Bristol, Queen’s Road, Bristol, BS8 1RJ, UK
3) Egdon Resources (U.K.) Ltd., Suite 2, 90-96 High Street, Odiham, Hampshire, RG29 1LP, UK
4) Geochemical Interpretation Ltd., Hallsannery, Bideford, Devon, EX39 5HE

The Wessex Basin, located mainly onshore in the south of England (Dorset), is a classic area for petroleum geochemical study, with all the various components of the petroleum system being exposed at the surface. In addition, many exploration wells have been drilled in the area since 1937, providing subsurface material and data, and the subsurface structure is well constrained due to extensive seismic surveys. The basin also contains the largest onshore oilfield in Western Europe: Wytch Farm. However, despite the wealth of available information, important questions remain, and ongoing exploration to identify new oil accumulations and to reappraise earlier undeveloped discoveries provides the motivation for our research. Here we present results from several studies addressing the following aims: (1) defining lateral variability in source rock maturation and hydrocarbon generation, (2) correlating the various oils and seeps in the basin, and (3) determining whether the apparent lack of biodegradation seen in the produced oils is due to “palaeopasteurisation” of reservoirs.

The three source rock intervals (Lower Lias, Oxford Clay and Kimmeridge Clay) are all good Type II marine source rocks, but are all immature at outcrop. The source kitchen lies just offshore (to the south), but geochemical analysis of samples from a number of onshore wells indicates that the Lower Lias may have just entered the oil window in some onshore areas. Uplift during the Tertiary inversion of the basin terminated oil generation, and it is likely that only the Lower Lias reached the oil window in this area.

The Wessex Basin contains two major petroleum plays: the Triassic Sherwood Sandstone and the Jurassic Bridport Sands. Aliphatic hydrocarbon fractions of numerous produced oils, DST oils and stained sands from both core and outcrop have been analysed by gas chromatography-mass spectrometry to provide biomarker data on source rock facies and maturity. Principal components analysis clearly distinguished two main groups of oils, corresponding to the Sherwood and Bridport plays, the latter being of consistently lower maturity, and interpreted as reflecting earlier oil generation in the basin. The presence of oil-cemented clasts in a Wealden (Lower Cretaceous) conglomerate at Mupe Bay confirms that some oil was indeed generated well before the Tertiary uplift, and this oil correlates well with the oils of the Bridport play. The fact that the oil in the Sherwood reservoir at Wytch Farm is of higher maturity, and records later generation, is consistent with the interpretation that oil could not migrate into the Sherwood Sandstone until a later phase of basin subsidence, when juxtaposition of the Lias source rock with the stratigraphically lower Triassic reservoir was achieved. The observed maturity differences between some of the Dorset coastal “seeps” are also explained by timing of relative fault placement to open migration paths.

Significantly, none of the produced oils in the Wessex Basin are biodegraded, despite their low reservoir temperatures (40-65 ºC). This is explained by the concept of palaeopasteurisation, whereby the reservoirs were previously buried to depths where the temperatures exceeded the temperature (*ca*. 80 ºC) at which hydrocarbon-degrading bacteria are killed (Fig.1). Although subsequent uplift in the Tertiary led to cooler temperatures, the reservoirs had been effectively pasteurised and have clearly not been recolonised by hydrocarbon-degrading bacteria. Interestingly, DST oils from two wells drilled into the Bridport reservoir at Waddock Cross show some evidence for biodegradation, possibly due to shallower burial, and consequently inefficient palaeopasteurisation of this reservoir (Fig.1) which lies further west of the producing fields. This interpretation indicates that reservoir burial history reconstructions may be important to give pre-drill predictions of biodegradation in other prospects in the Wessex Basin.

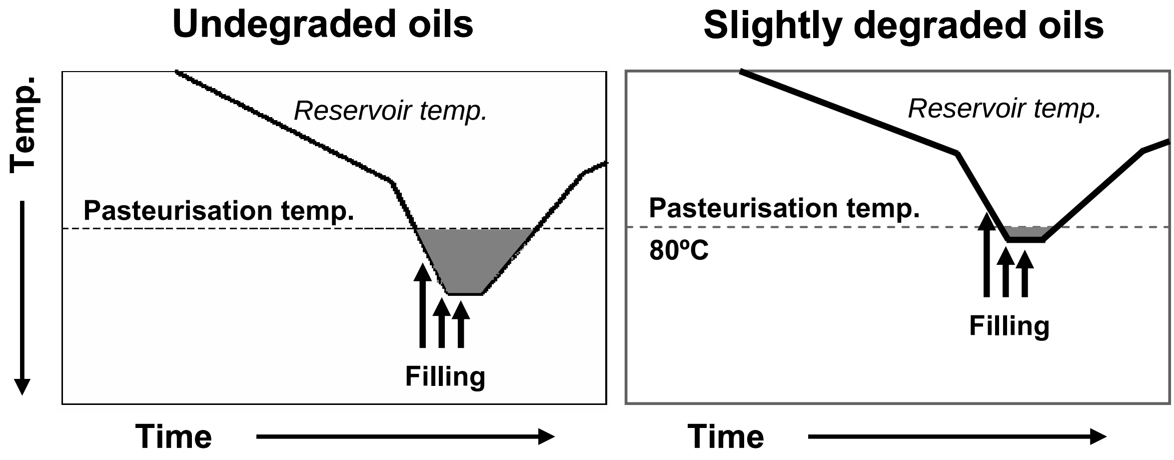


Fig.1. Different reservoir burial scenarios: for the undegraded oils filling occurred at reservoir temperatures >80°C, whilst for the slightly degraded oils shallower burial of the reservoir resulted in some filling commencing at lower temperatures, allowing some biodegradation to occur.

PBS-7: Petroleum characterisation of Salambo formation by organic petrography and organic geochemistry (Gulf of Gabes - Tunisia)

H. Inoubli

Entreprise Tunisienne D'activités Pétrolières , 27 bis Avenue Khereddine Pacha , Tunis , TUNISIA

The combination of petrographic and geochemical results allows better petroleum characterisation of the Oligocene-Miocene lithostratigraphic level (Salambo Formation) known only in boreholes of the East Southern Gabes basin throught the Tunisian-Lybian boundary.

Organic matter from five wells has been analyzed by the the Rock-Eval pyrolysis and microscopically in transmitted and reflected lights .This study leds to the understanding of the marly Salambo Formation petroleum characteristics and its possible capacity to generate oil or gas.

This Oligocene-Miocene column is, in general, poor in organic matter (TOC is less than 0.5%); nevertheless the unit below 2000 m (Lower Salambo Formation) is the exception; organic matter is well preserved (TOC is ranging from 0.66 to1.97 % and PP is up to 1.5 Kg of HC/t of rock).

In general, this organic matter is a mixture of type III and II kerogens, dominated by herbaceous palynomorphous and ligno-cellulosic tissus with some amorphous material. Below 2000 m, and mainly for the wells located relatively in the North of Gabes basin, the maceral composition is dominated by the amorphous bodies (more than 50% of the total maceral composition). This characterise an open marine deposit environment.

The oil window starts at about 2000 m ($0.67\ \% < R° < 1.02\ \%$ and Tmax =435°C); up to this level the Salambo Formation is immature ($R° < 0.43\%$ and $416°C < Tmax < 427°C$).

In addition to the poven source rocks within the area which are the early Turonian Bahloul and the Ypresian Bou Dabbous Formations, and due to its good geochemical quality below 2000 m and its vertical and lateral extension, the Lower Salambo Formation might locally play a role in the petroleum history of the Gabes basin.

To confirm, even more, the petroleum interest of this horizon, this study must concern others tunisian and especially lybian wells which cross the Oligocene-Miocene column, along the Tunisian-Lybian boundary.

PBS-8: Organic geochemistry and organic petrography of petroleum systems in the Western Kamchatka coastal margin, Russian Far East

M. Li[1], L. Stasiuk[1], R. Maxwell[2], F. Monnier[2], O. Bazhenova[3]

1) Geological Survey of Canada, 3303-33 Street NW Calgary, Alberta, Canada (e-mail: mali@nrcan.gc.ca)
2) CEP-International Petroleum Ltd., 2050, 140 – 4th Ave, Calgary Alberta T2P 3N3, Canada
3) Moscow State University, Russia

This paper describes the organic geochemistry and organic petrography of the petroleum systems in the Western Kamchatka coastal margin, Eastern margin of the Okhotsk Sea, Russian Fast East. This coastal margin is a back arc basin with over seven kilometers of Tertiary sediments. The stratigraphic and structural framework of the basin is remarkably similar to the South Sumatra back arc basin. A significant gas (Nizhne Kuakschikskya) and several oil discoveries have been made from Paleocene syn-rift fluvial and marginal marine sandstone reservoirs in the Snatolsky and Napanskaya formations. This work was based on a recent sample collection consisting of a large number of drill-stem-test fluids, cores and outcrop samples.

The physical properties of petroleum fluids discovered in the Western Kamchatka vary considerably, from tarball, heavy oil, to gas and condensate. Based on whole oil gas chromatograms, gasoline range hydrocarbons, saturate gas chromatograms and aliphatic biomarkers, at least four oil families have been identified in the study area. Oils in Family I display a wide variety in physical properties, including heavy waxy oils and light condensate oils. A humic coal origin for these oils is indicated by the extremely high pristane/phytane ratios (7.72-9.25), moderate C_{29} diasterane/C_{29} sterane ratios (around 1), and the dominance of C_{29} over other homologous steranes and diasteranes in these oils. Oils in Family II contain substantial amounts of light end components on the whole oil gas chromatograms. These oils are characterized by relatively high pristane/phytane ratios (4.75-4.84), moderate C_{27}/C_{29} sterane ratios (0.7-0.8), and the overwhelming dominance of diasteranes over regular steranes, correlating well with those of marginal lacustrine shales commonly associated with coal seams. Oils in Family III typically show moderate pristane/phytane ratios (around 2), a dominance of C_{27} over C_{28} and C_{29} steranes, and the presence of abundant short-chain steranes and extended chain tricyclic terpanes indicative of significant *Tasmanite* contribution. In contrast, oils in Family IV display rather low pristane/phytane ratios (<1), the presence of C_{30} desmethylsteranes, and a characteristic $C_{28}>C_{29}>C_{27}$ sterane pattern. This type of biomarker distribution has been observed from Upper Cretaceous marine source rocks in many sedimentary basins around the world, possibly due to the emergence of coccolithophorids and silicoflagellates as prominent contributors to the lipid budget of marine sediments.

The Paleocene-Eocene reservoirs in the study area are in unconformable contact with the Cretaceous strata. As no well has penetrated the Mesozoic strata, only Tertiary rock samples were collected for geochemical analyses. Available Rock-Eval/TOC data indicate that effective and organic-rich petroleum source rocks in the "oil-window" exist in the Snatolsky and Napanskaya formations. While some of the Paleogene source rocks are gas prone, others (coal and carbargilite) exhibit good oil source potential. For example strata from the Irgirninvayam River Delta contain coals with Type III kerogen and carbonaceous shales with Type II kerogen with TOC values ranging from 7 to 37 % and hydrogen indices between 340 and 500 mg HC/g TOC. The shales are of freshwater origin, enriched in sporinites, pollen, and cutinite although they also contain a significant amount of perhydrous vitrinite, most likely derived from leafy matter. Vitrinite reflectance for the Irgirninvayam shales, and associated coals, ranges from 0.45 to 0.58 %Ro. Higher maturity shales (0.70 %Ro vitrinite) from the Rassoshina-Napanskaya River area have 24-28 % TOC, Type II/III kerogen, hydrogen indices range from 116 to 250.

Biomarker fingerprinting of these sediments correlates well to some recovered oils from the basin (families I - III) and are similar to oils and extracts from the Talang Akar Formation in Indonesia. In addition an organic-rich diatomite, Miocene in age, equivalent to the main source rock of the Sakhalin field located on the western margin of the Okhotsk sea, is suspected to be present in the basin but may not be sufficiently mature to have generated large volumes of oil. The Biomarker fingerprinting of oil recoveries, corroborates the Paleogene origin of the Families I - III oils, but the chemical compositions of the Family IV oils suggests also the possible presence of so-far unpenetrated Cretaceous marine source rocks in the basin.

PBS-9: Organic geochemistry of the petroleum systems in the Zhanhua depression, Bohai Bay basin (China)

M. Li[1], X. Pang[2], D. Chen[2], S. Zhang[3], Y. Wang[3], D. Shi[3]

1) Geological Survey of Canada, 3303-33 St. NW Calgary, Alberta T2L 2A7, Canada
(e-mail: mali@nrcan.gc.ca)
2) Key Laboratory for Petroleum Formation Mechanisms of the Chinese Ministry of Education, Petroleum University (Beijing), Beijing 102200, China
3) SINOPEC Shengli Oilfield Company, Dongying, Shandong 257000, China

The Zhanhua Depression is one of the most prolific petroleum provinces in the Bohai Bay Basin, eastern China, with over 76% of the proven petroleum reserves occurring in the Neogene Guantao and Minhuazhen formations. Detailed geological and geochemical mapping of the Phanerozoic strata in this basin reveals that oil shales and dark mudstones in the Es_4, Es_3 and Es_1 members of the Eocene-Oligocene Shahejie Formation have excellent potential as petroleum source rocks. Regional distributions of total organic carbon content, kerogen type and thermal maturation indicate that abundant mature source rocks are present in several discrete sag areas bounded by extensive basement-related fault networks. In contrast, source rocks along the paleo-topographic highs are currently immature with respect to the generation of conventional oils. This study examined the key molecular characteristics for the common isoprenoid, hopanoid and steroid biomarkers, in relation to source facies variations in lacustrine sediments. The hydrocarbon source potential and expulsion efficiency for each of the source rock units were evaluated, which integrated the source rock characteristics with regional thermal subsidence and sediment burial. An important observation made during this study is the striking contrast between the source potential and proven oil reserves within each stratigraphic section, illustrating how significant the migration of hydrocarbon fluids derived from deep mature source kitchens through over 2000 m of fine-grained formations must have been to form several giant oil accumulations in the shallow strata.

The chemical compositions of crude oils from over 20 oilfields in the Zhanhua Depression, Bohai Bay Basin, were studied in order to understand their genetic relationships, thermal maturity and biodegradation ranking. Molecular geochemical parameters indicate the presence of three possible oil families in reservoirs ranging from Paleozoic (basement) to Neogene. A number of biomarker features support deposition of the source rocks for these oils under a wide range of depositional environments. Most of the oils belong to the FL family, and display characteristics consistent with a dominantly freshwater (to slightly brackish water) lacustrine source rock in the Es_3 member of the Shahejie Formation. The somewhat geographically restricted SL family oils are apparently linked to saline lacustrine, carbonate-evaporite source rocks distributed mostly in the upper Es_4 member of the Shahejie Formation from the Bonan-Gubei sag areas. The thermally less mature BL family oils occur mostly within the Es_1, Es_2 or Dongying Formation reservoirs near the central sag areas, and show close affinities to the interbedded or intercalating Es_1 calcareous mudstones and oil shales deposited in a slightly saline to dominantly brackish water lacustrine setting. The SL and FL family oils are generally mature, whereas most of the BL family oils usually show low maturity. Oil-source correlation demonstrates strong genetic relationships between the mature Es_4 and Es_3 source rocks of the Eocene-Oligocene Shahejie Formation in the sag areas and the oils accumulated in the shallow Neogene petroleum plays.

The geochemical data provide strong support for two sharply contrasting hydrocarbon migration scenarios: (1) short distance lateral migration is dominant in the central sag areas; and (2) the fault-fracture mesh facilitated vertical migration, and coupled with the regional porous Guantao Formation sand sheets, makes the structural, stratigraphic and lithological features over basement high blocks the focal points for petroleum accumulation. These results support the concept of the "Neogene fault-fracture mesh petroleum plays" proposed recently [1] and the vital role that the faults and fracture systems have in controlling hydrocarbon migration conduits and accumulation habitat in this rift basin. With the recent discovery of several giant oilfields in the shallow Neogene reservoirs both onshore and offshore Bohai Bay Basin, this geochemical work helps the exploration geologists to modify and clarify long held traditional concepts of petroleum play types in this basin, and expand upon the new exploration horizons of the shallow subtle petroleum traps.

References

[1] Zhang, S.W., Wang, Y.S., Shi, D.S., Xu, H.M., Pang, X.Q., Li, M., 2004. Fault-fracture mesh petroleum plays in the Jiyang Superdepression of the Bohai Bay Basin, eastern China. Marine & Petroleum Geology 21, 651-668.

PBS-10: Saturated hydrocarbons of oil-producing rocks of the Cambrian Kuonamka formation (Eastern Siberian platform)

T.M. Parfenova, E.N. Ivanova, E.A. Zubova

Insitute of Petroleum Geology, Siberian Branch of the RAS, 3 prosp. Akad. Koptyuga, Novosibirsk, 630090, Russia (e-mail: ParfenovaTM@uiggm.nsc.ru)

Applying modern analytical methods, we investigated organic matter from the Lower-Middle Cambrian rocks of Kuonamka Formation in the eastern Siberian Platform. The rocks were sampled in the exposures on the right bank of the Molodo River (the left inflow of Lena R.). We divided them into groups and subgroups according to the content of organic carbon and studied the contents and distribution of they saturated biomarker hydrocarbons.

Group I – highly carbonaceous black shales – argillaceous and argillaceous-siliceous rocks ans silicites, often bearing carbonates (calcite), enriched in organic carbon (usually C_{org} > 10%). The organic matter (OM) is characterized by a bimodal distribution of n-alkanes and higher concentrations of tricyclanes as compared with total hopanes. This group is subdivided into two subgroups according to lithology: Ia and Ib.

Group II – carbonaceous rocks – includes with different proportions of argillaceous, carbonate, and siliceous matter, usually containing < 10% C_{org}. *n*-Alkanes show a unimodal distribution. Hopanes and homohopanes dominate over tricyclanes. This group is divided into three subgroups according to lithology: IIa (rocks of mixed composition), IIb (dolomitic limestones), and IIc (cherts).

Below, we will consider the HC distribution in two groups of rocks.

The GL chromatograms are hump-shaped because of the abundance of nonseparated and thus undeterminable naphthenes among the saturated HCs. There are also C_{14-35} *n*-alkanes and C_{15-25} isoprenoids on the background of the naphthene humps. The average Pr/Ph ratio in the bitumens varies from 1.1 to 1.5. The average Pr/*n*-C_{17} and Ph/*n*-C_{18} ratios vary from 0.5 to 0.8. Note that usually the *n*-C_{27}/*n*-C_{17} ratio increases in passing from carbonaceous to highly carbonaceous rocks. The carbon preference index (CPI) varies from 0.9 to 1.1. The group I bitumens have higher CPI than the group II ones; only dolomitic limestones have CPI > 1.

The steranes are dominated by ethylcholestanes (C_{29}) and cholestanes (C_{27}). The steranes are dominated by C_{29} (> 40 rel.%) in all rocks except for the Ia ones (C_{29} < 40 rel.%). With decreasing C_{org} contents in the rockes, the concentrations of ethylcholestane increase from 32 to 54 rel.%. The concentrations of methylcholestane (C_{28}) are minimum and vary from 16 to 26 rel.% (average is 20 rel.%). The between sterane isomers and stereoisomers are commensurate in all rocks and depend neither on the OM concentration nor on the rock composition. The concentration of pregnanes in the saturated HC fraction increases with the content of OM in the rock, and the sterane/pregnane ratio correspondingly decreases. Tricyclanes are polycyclic HCs making up > 30% of the detected terpanes. The concentrations of tricyclanes increase (up to 50% and more) with the content of OM in the rock. In passing from rocks of mixed composition (Ia, b) to carbonate and siliceous varieties (IIa, b, c), the portion of light C_{19-20} tricyclanes decrease and that of heavy C_{28-31} ones increases. Tetracyclanes are scarce in the studied bitumens, 2-3% of all terpanes. Among the C_{24}, C_{25}, C_{26}, and C_{27} homologues, the former is predominant (on the average, 67 to 79 rel.%). The saturated HC fractions of the studied bitumens contain all hopane homologues: norhopanes (C_{27-29}), hopane (C_{30}), and homohopanes (C_{31-35}). The hopanes are dominated by C_{30}, C_{29} norhopane is less abundant, and trisnorhopanes (Ts, Tm – isomer of C_{27}) are still scarcer; Ts/Tm = 0.5-0.7. The bitumens of all the studied shales show similar distributions of hopanes, but the content of trisnorhopanes is higher in the samples enriched in C_{org}: up to 22 rel.% in the Ia rocks against 12 rel.% in the IIc carbonaceous silicites. The contens of homohopanes decrease with increasing their molecular weight: $C_{31}>C_{32}>C_{33}>C_{34}>C_{35}$. All the rocks have $C_{35}/C_{34} < 1.0$, except for two samples with $C_{35}/C_{34} > 1.0$. With increasing concentration of tricyclanes, the content of homohopanes in the terpane fraction decreases from 30 to 10%. We have also detected gammacerane in the terpane fraction. As a rule, it amounts to no more than 1% of total terpanes.

Conclusions. Studying the organic geochemistry of the Kuonamka Formation rocks by modern analytical methods provided new data on the syngenetic OM of Cambrian deposits. Steranes and terpanes identified in the saturated bitumen fraction evidence that the OM of the Kuonamka paleosea is of planktonic-bacterial nature. The contents and proportions of homohapanes and gammacerane in the terpane fraction indicate that the OM accumulated in aeration environments with normal water salinity, which were seldom changed by stagnant environments. The abundance of saturated HCs in the bitumens is shown to be correlated with the concentrations of organic carbon. The alternation of abnormally OM-enriched (C_{org}>10%) and depleted (C_{org}<10% and < 5%) rocks in the Lower and Middle Cambrian deposits seems to be due to changes of communities of microorganisms that produced biomarker HCs and to changes in the rate of sedimentation.

PBS-11: The Hydrocarbon Occurrences of the Mrah Area in the Hayan Block-Syria

I. Stanković, L. Rumenjak, D. Španić, T. Troskot-Ćorbić, M. Maričić, V. Čuljak

INA- Oil Industry, Corporate Processes, Research and Development Sector, Rock and Reservoir Fluid Research Laboratory Department, Geology and Geochemistry Section, Geochemical Laboratory, 10002 Zagreb, Lovinciceva 1, Croatia (e-mail: irenka.stankovic@ina.hr)

The Hayan concession block in central Syria belongs to the Palmyride region. Exploration activities of INA Naftaplin were focused on many prospects in the Hayan block. The aim of our interest is the Mrah area situated on the northern «Jihar« flank. Very little data are available on the presence of source rocks and hydrocarbons from this area. The main targets of exploration were the Kurrachine Dolomite Formation sediments, the prominent reservoir rocks in the area.

In the studied area Mrah-1 and Mrah-2 exploration wells were drilled to total depths of 2490m and 3043m respectively, terminating in the Kurrachine Dolomite Formation, which dates from the Middle Triassic period. Geochemical investigations of cuttings and cores have shown only limited quantities of organic matter. The average TOC ranges from 0,24 to 0,46%. The increased values of total organic carbon (TOC>0,3 %) are linked to claystone/shale layers within the sediments of the Middle Triassic age. In spite of this, the Rock Eval pyrolyses data (S_2<2mgHC/g rock) show low petroleum generating capability along the whole well profile. The low hydrocarbon generation potential of the Middle Triassic sediments is the result of oxic to suboxic depositional conditions, which altered hydrogen rich organic matter into unfavorable organic facieses.

The microscopic examination of kerogen has demonstrated the predominance of amorphous, unstructured organic matter with only sporadic traces of fusinite, liptodetrinite, vitrinite and reworked vitrinite. Considering all optical examinations and maturity parameters, organic matter has reached the high maturity stage of catagenesis (1,2 to 1,3 %R_0) (TAI from $3^{-}$to 4^{-})([1], [3]).

Low gas content was registered in shallower sediments but gas concentration increased with depth, especially within the Kurrachine Dolomite Formation. The gases are wet with significant content of high homologues, which indicates their thermal maturity and secondary, migrated origin ([3]).

The presence of bitumen in the form of lamination and impregnation was also registered in both Mrah wells. The bitumen yields are rather high and varied from 368 to 1884 ppm. High EOM/TOC ratios (average 241mgHC/gTOC), and high content of the n-alkanes (77,7-91,9%) point to their secondary, migrated origin([2], [3]). Fingerprint of bitumens shows differences in their molecular parameters and highlights the differences of organic matter type and their precursors, as well as environmental conditions and thermal maturity level. Dissimilar bitumen characteristics could be explained as the result of hydrocarbon migration processes, which took place during different geological periods. We hope that additional exploration activities will confirm economical hydrocarbon reserves in this area.

References

[1] Engel, M. H. & Macko, S. A. (1993): Organic Geochemistry-Principles and Applications (Topics in Geobiology, v. 11), Plenum Press, New York and London

[2] Powell, T. G. (1988): Some Aspects of the Hydrocarbon Geochemistry of the Middle Devonian Barrier-Reef Complex, Western Canada. In J. G. Palacas, ed., Petroleum geochemistry and source rock potential of carbonate rocks: AAPG Studies in Geology, 18, p. 45-62.

[3] Waples, D.W. (1985): Geochemistry in Petroleum Exploration. IHRD, Boston, 232 p.

PBS-12: Two contrasting scenarios for thermochemical sulfate reduction and sour gas accumulation: case studies in the Chinese sedimentary basins

S. Zhang[1], M. Li[2], G. Zhu[1], J. Li[1], J. Dai[1]

1) CNPC Key Laboratories for Petroleum Geochemistry, PetroChina Research Institute of Petroleum Exploration & Development, Beijing 100083, China (e-mail: sczhang@petrochina.com.cn)
2) Geological Survey of Canada, 3303-33 Street NW Calgary, Alberta T2L 2A7, Canada

Concentrations of H_2S in natural gas vary significantly (0-98%). The presence of H_2S in the natural gas not only reduces the heat value of the gas, but also affects every aspect of field operations from drilling, transport to processing. A sour gas-well blowout occurring on December 2003 near the city of Chongqing was the worst oilfield disaster in China. In order to minimize the risk of encountering high H_2S gas in future exploration and assess the cause of field souring during production, it is essential to gain a clear understanding of origin and geological controls of H_2S in petroleum. This paper reports the results and interpretations from case studies in several sedimentary basins in China and describes two contrasting geological scenarios for thermochemical sulfate reduction (TSR) and sour gas accumulation.

The first scenario is exemplified by the sour gas accumulation in the Zhaolanzhuang field of the Jinxian Sag, Bohai Bay Basin. This field produces gases with 40-92% H_2S. The Jinxian Sag is one of the many Mesozoic-Cenozoic faulted depressions developed due to the extension behind magmatic arcs on an active plate margin. The primary sour gas habitat includes the Eocene-Oligocene Kongdian Fm (Ek) and the Es4 member of the Shahejie Fm, deposited in the early stage of rift development characterized by the formation of coarse clastics and evaporites. Significant sour gases are often produced together with sulfur-rich heavy oils with less than 12 ^{o}API. The co-produced waters are of $CaCl_2$ type, rich in total dissolved solids. The occurrence of the high sulfur oils and H_2S-rich gases coincides with that of the Ek_1-Es_4 evaporite, indicating a possible genetic relationship. Molecular evidence for the origin of the heavy oils from a hypersaline lacustrine source rock include relatively low pristane/phytane ratios, high gammacerane/hopane ratios, and extremely high (pregnane + homopregnane)/C_{27}-C_{29} sterane ratios. The low abundance of n-alkanes relative to acyclic isoprenoid/cyclic alkanes in the oils was more likely the result of early generation from a sulfur-rich kerogen, rather than oil biodegradation in the reservoir. The availability of extensive cores and other fluids in the Zhaolanzhuang Field also enabled us to obtain valuable sulfur isotope data from various geological substrates. The results show that both H_2S and CO_2 are present in high concentrations in the gas samples, and in addition to secondary calcite, abundant elemental sulfur was also observed, either in thick or thin layers, in anhydrite, sandstone and argillaceous siltstone samples within the sour gas payzones. The

δ^{34}S values of the anhydrite samples in the Ek_1 - Es_4 source rocks range from 30 to 35‰, reflecting the characteristics of oceanic waters during the deposition of these strata. In contrast, the δ^{34}S values of elemental sulfur in the Zhaolanzhuang Field range from 0.76 to 22.29‰, roughly within the range for H_2S obtained in laboratory thermal experiments (11.33-18.30‰). As H_2S and elemental sulfur formed by BSR generally show δ^{34}S values within –30 to 10‰, our data clearly suggest a TSR origin for the sour gas accumulation in the Zhaolanzhuang Field.

The second scenario is represented by the enormous sour gas accumulations recently discovered from the northeastern Sichuan Basin, SW China. Each of the five largest gas pools contains over 50 bcm (or 1.8 tcf) of proven gas reserves. Results obtained from this study demonstrate the presence of two types of natural gas accumulations in the Lower Triassic oolitic reservoirs. Both types contain highly mature thermogenic gases, with the hydrocarbon source rocks in the Upper Permian strata. Natural gases from the area south of the ancient Kaijiang-Liangping Seaway are generally sweet gases formed as the result of thermal maturation, in contrast to those sour gases discovered north of the Seaway that were clearly products of both thermal maturation and thermochemical sulfate reduction of early accumulated oils in the Feixianguan Fm reservoirs. The origins of the gases are supported by their chemical and stable carbon isotope compositions, as well as the occurrence of pyrobitumens in the reservoir. The distribution of the gas accumulations is controlled dominantly by the combination of lithologic and structural factors, and the regional variation in the concentrations of H_2S in the gases is clearly related to the presence and thickness of anhydrite-bearing evaporitic rocks interbedded or intercalated with oolitic reservoirs.

The minimum temperature to initiate TSR was controversial for many years. Recent work suggests that TSR begins in the range of 127-140 ^{o}C, depending on the hydrocarbons in the reservoir, and that higher temperatures are required to initiate TSR for methane than heavier hydrocarbons. As the current temperatures of the Zhaolanzhuang sour gas reservoirs are 75-90 ^{o}C and have never been above 100 ^{o}C, the H_2S in this case was derived from a deeper source, or from TSR reactions of heavier hydrocarbons in crude oils with anhydrite. In contrast, results from1-D basin modeling indicate that the sour gas accumulations in the eastern Sichuan Basin have involved much higher temperatures (100-200 ^{o}C), and represent the products of both thermal maturation and TSR of early accumulated oils that had migrated considerable vertical distances.

PBS-13: Geochemical characterization of lacustrine oils in Recôncavo basin, Brazil

H.G.M. Aguiar[1], H.L.B. Penteado[2]

1) COPPE/UFRJ, Laboratory for Computation Methods in Engineering-LAMCE, PO: 68552, 21949-900, Rio de Janeiro, Brazil (e-mail: hgma@coc.ufrj.br)
2) Petrobras/CENPES/PDEXP/GEO, Ilha do Fundão, Quadra 7, 21949-900, Rio de Janeiro Brazil (e-mail: hpenteado@cenpes.petrobras.com.br)

The Recôncavo Basin covers an area of approximately 11.500 km^2 in the state of Bahia, in northeastern Brazil. The basin has the shape of a half graben, with regional dip towards its eastern depocenters. The source rocks of the oils in the Recôncavo Basin are the shales of the Candeias Fm. (Tauá and Gomo members) deposited in lacustrine fresh to brackish water environments. The geochemical datas of oils indicate lacustrine origin.

Among 163 oil samples, there are three oil families, henceforth named groups 1, 2 and 3. Mass chromatograms m/z 191 and 217 of representative samples from each of the three oil families can be seen in Fig.1. The steranes configuration was the principal criterium for the differentiation of the oil families (m/z 217 fragmentograms in Fig.1). Maturation levels are quite distinct in the oils. Oils of group 1 are characterized by a low relative concentration of diasteranes and a predominance of C_{29} steranes index. In the group 2 oils, diasteranes are relatively more abundant, and $C_{27}\alpha\alpha R$ and $C_{29}\alpha\alpha S$ are the most common isomers. A low relative concentration of diasteranes, a predominance of $C_{27}\alpha\alpha R$ and $C_{29}\alpha\alpha R$ among steranes, and a low abundance of $\alpha\beta\beta$ steranes compared to their $\alpha\alpha\alpha$ counterparts are the main features of the group 3 oils. Whereas hopanes are not particularly useful for grouping, group 3 oils stand out for their higher gammacerane indices and for their greater abundance of normal and extended tricyclics.

High API gravities (25-42^0) and tricyclics/pentacyclics ratios suggest that the group 3 oils are very mature. However, steranes isomerization ratios ($C_{29}\alpha\beta\beta/(\alpha\alpha\alpha+\beta\beta\beta)$ and$C_{29}S/(S+R)$) indicate a low thermal evolution. This inconsistency might be due to a contamination of a highly mature oil with low concentrations of biomarkers by bitumen. The incorporation of biomarkers from bitumen or from a relatively less mature oil could occur during secondary migration or, most probably, from contamination of reservoired oils by surrounding potential source rocks. Source-rock extracts will be analyzed in order to verify whether the oil compositional differences are linked to lateral variations in organic facies of the Tauá and Gomo members (Candeias Fm.) or to distinct geochemical features observed vertically along the source-rock sequences.

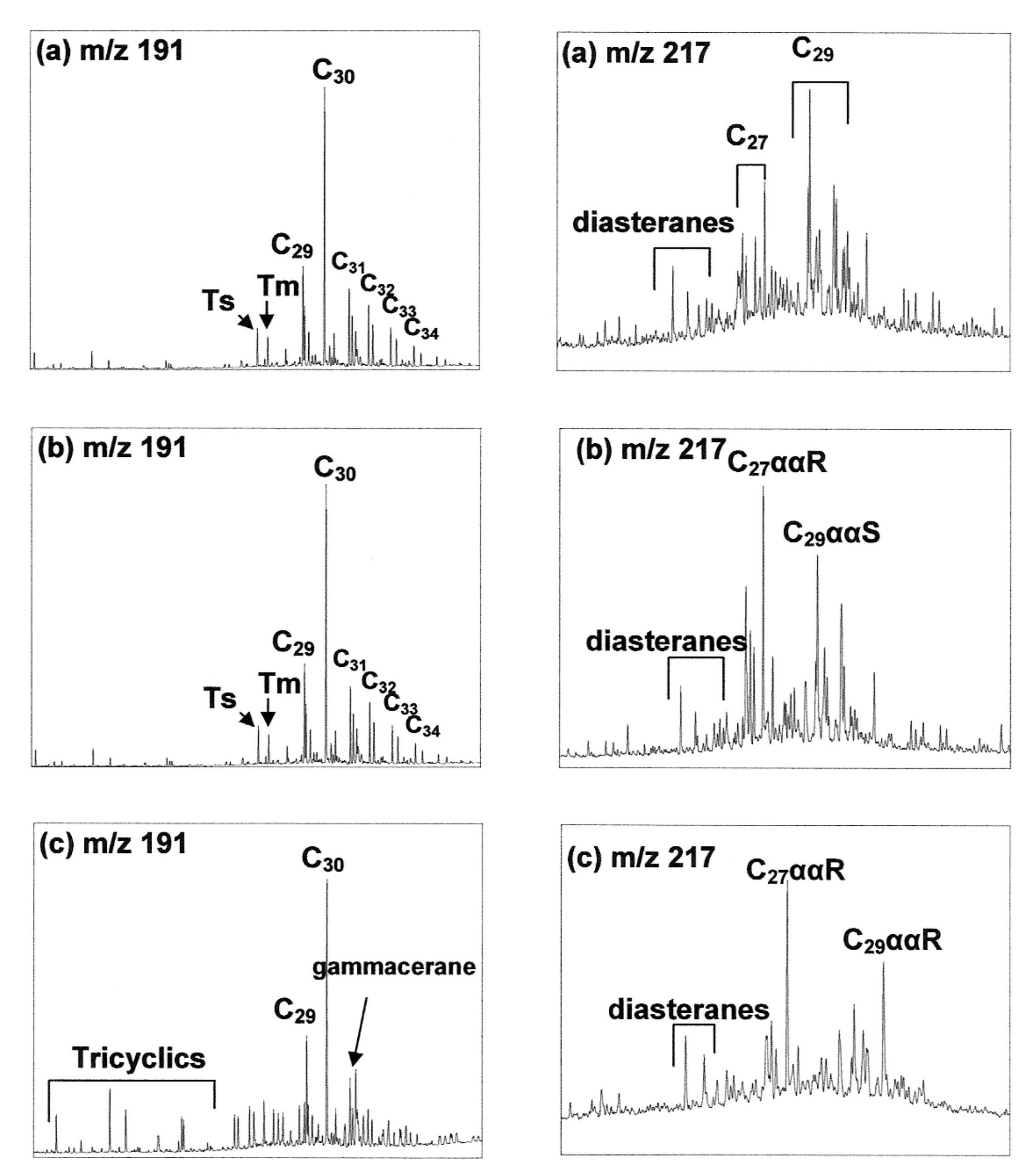


Fig.1. Mass chromatograms m/z 191 (hopanes) and m/z 217 (steranes) of families of lacustrine oils in the Recôncavo Basin: (a) group 1, (b) group 2, (c) group 3

PBS-14: Hydrocarbon charge modelling in deepwater NW Sabah, Malaysia

A. Anuar, P. Abolins

PETRONAS Research & Scientific Services Sdn Bhd, Lot 3288 & 3289, Kawasan Institusi Bangi, Off Jalan Ayer Itam, 43000 Kajang, Selangor Darul Ehsan, Malaysia (e-mail: azlinaa@petronas.com.my)

Perhaps the single most fundamental question in any prospective basin is whether or not we have source rocks and what are their quality, distribution, and maturity? In most frontier basins, and even in some well explored basins, we are generally not fortunate enough to be able to provide many definitive answers for the simple reason that the source rocks have never been penetrated. In such situations, analogue studies can provide useful insights into likely source rock facies. In the deepwater of NW Sabah, three (3) possible source rock facies have been recognised based on analogue studies which incorporated field observations and laboratory analysis of the West Crocker Formation in Kota Kinabalu, Sabah (Azlina Anuar & Peter Abolins, 2003). The three source facies studied were: bathyal pelagic shales, slumps and debris flows, and levee and overbank shales. Of these, the slumps and debris flows were observed to be the organically richest facies and the only facies that broadly correlated with the oils of NW Sabah.

In order to test this conceptual model for source rock deposition in deepwater NW Sabah, a pilot area basin modelling study was undertaken. The selected pilot area incorporated both explored (for calibration) and frontier areas of offshore NW Sabah. The objectives of the study were (1) to demonstrate that the conceptual model could reproduce the known hydrocarbon distribution in the pilot area, and (2) assess hydrocarbon charge likelihood in unexplored areas of was selected for basin modelling. The tools and concepts used included 1D, 2D and 3D basin modelling, a robust conceptual source rock depositional model and personalised kerogen kinetics.

To ensure that the constructed basin model accurately reflects the underlying geological model, much time was spent incorporating our new understandings of NW Sabah source rock distribution into the basin model. This included incorporating expected Total Organic Carbon content, kerogen types and kinetics for each of the main source rock facies into litho-facies maps. The facies maps were then assigned geochemical properties typical of each facies as defined by the source rock conceptual model described above. A basal heat flow map constructed from the results of 1D modelling was imposed on the geological model as the bottom boundary condition. A sediment–water interface temperature map was constructed based on water depth and represents the top boundary condition.

The results from the modelling agreed reasonably well with observed hydrocarbon distribution confirming that the new source rock depositional model was an improvement over earlier models and demonstrating the importance of understanding source rock distribution during basin assessments. The deepwater pilot study area was subsequently divided into three regions based upon the anticipated available charge: oil charged, gas charged, and mixed oil and gas charged regions. There were occasional situations where observed oil and gas distributions do not agree with that predicted; there is a likelihood that they are caused by top seal issues and/or a manifestation of phase behaviour affects. Work continues in attempting to understand such situations.

References

[1] Azlina Anuar & Peter Abolins, 2003. A field investigation of source facies occurrence in an ancient deepwater turbidite fan system of Northwest Borneo. In, Book of Abstracts Part II, 21st International Meeting on Organic Geochemistry, European Association of Organic Geochemists, 8-12 Sept 2003, Krakow, Poland. pp. 50-51.

PBS-15: A geochemical overview of oils and condensates of the Barents Sea region

P.B. Hall, M. Bjorøy, I. Ferriday

Geolab Nor AS., P.O. Box 5740, 7437 Trondheim, Norway

Thirty-two oils from seventeen wells from the Norwegian sector of the Barents Sea have been assessed to determine their source/maturity/alteration history. There are a number of potential source rocks in the area, from the Cretaceous (Knurr Fm.), Upper Jurassic (Hekkingen Fm.) to Triassic (Anisian-Ladinian). In addition there are potential Palaeozoic source rocks, in the Permian (Tempelfjord Gp.), Carboniferous and possible Devonian (Domanik facies) source rocks. The most prolific source rocks are those from the Mesozoic, with the Upper Jurassic Hekkingen Fm. being the most widespread and the richest, although not everywhere is it the most oil prone source rock. Most of the oils come from the

Because of the significant uplift and subsequent erosion during the Tertiary, maturation of source rocks was halted or at least reduced in parts of the Barents Sea. However, many of the oils are high API gravity crude oils or condensates and based on routine petroleum geochemical analyses they have a wide range of maturities (based mainly on conventional parameters from GC and GC-MS analyses) from early oil window to condensate window maturity (0.6%Ro to 1.3%Ro equivalent). The oils can be divided into at least two separate groups (from bulk stable carbon isotope data and, saturated and aromatic hydrocarbon GC and GC-MS). They also show evidence of reservoir alteration (waterwashing, migration contamination etc.). Discussion will concentrate on reasons for the observed groupings, including the most probable source rock(s) and kitchen areas for these oils. The effects of mixing and alteration as well as uplift and cap rock leakage on the composition of the oils will also be addressed.

PBS-15: Temporal resolution of an oil-charging history – A case study from the Gidgealpa field

C. Hallmann[1], K. Arouri[2,3], D. McKirdy[2], L. Schwark[1]

1) Geological Institute, University of Cologne, Germany (e-mail: Hallmann.C@gmx.net)
2) Geology & Geophysics, School of Earth & Environmental Sciences, University of Adelaide, SA 5005, Australia
3) Department of Geology, United Arab Emirates University, Al-Ain, UAE

The Gidgealpa Field in the southern Cooper and Eromanga Basins, South Australia, was the scene of complex petroleum fluid flow. Hosting oil pools in stacked fluviatile sandstones, it is a typical example of many oil fields in these contiguous basins. However, this field is located above a basement ridge, comprising steeply dipping Early Palaeozoic sediments and volcanics of the Warburton Basin, that is onlapped and overlain by the mainly terrestrial sedimentary sequences of the Cooper (Permian-Triassic) and Eromanga (Jurassic-Cretaceous) Basins. The latter attain their greatest thicknesses (up to 4 km total) in the adjacent Patchawarra and Nappamerri Troughs. Oil and gas-condensate generation from four accepted source units and two discrete hydrocarbon kitchens resulted in a complex charging history. Furthermore, coal seams in reservoir units are capable of contaminating reservoired oils with indigenously produced petroleum; and a fifth (Cambrian) source unit was proposed [1,2].

Source rock extracts, DST oils and residual oils, obtained by sequential flow-through extraction of sandstone cores, were separated into SARA compound classes. Saturates and aromatics were analysed for hopanoid, steroid and *Araucariacaean* biomarkers by GC-MS. The polar fraction was enriched in carbazoles using a two-step solid phase extraction before being analysed by GC-MS.

Residual oils revealed palaeo-petroleum charges and palaeo-oil columns that would have been diluted beyond detectability when using conventional destructive extraction of sandstone cores. While the source affinity of the oils (Jurassic *versus* pre-Jurassic) was established using the abundance of *Araucariacean* conifer-specific aromatic biomarkers, the location of the source kitchen was indicated by the benzocarbazole $a/(a+c)$ ratio (BCR), which does not depend on either maturity or facies in the studied oils.

The reconstructed charging history reveals two discrete petroleum charges from Jurassic source rocks in separate hydrocarbon kitchens. A locally sourced charge (BCR_{mean} = 0.42) was later displaced by a longer distance migrated charge (BCR_{mean} = 0.17). While pre-Jurassic oil and gas-condensates that are reservoired in Permian sandstone units were generated in the vicinity of the study area, Permian oils from a more distant source kitchen lost their gases and entered the study area laterally (Fig. 1). Furthermore, an input from the Warburton Basin was noticed in a few residual oil samples, providing the first conclusive evidence for the petroleum generation potential of marine pre-Permian source rocks.

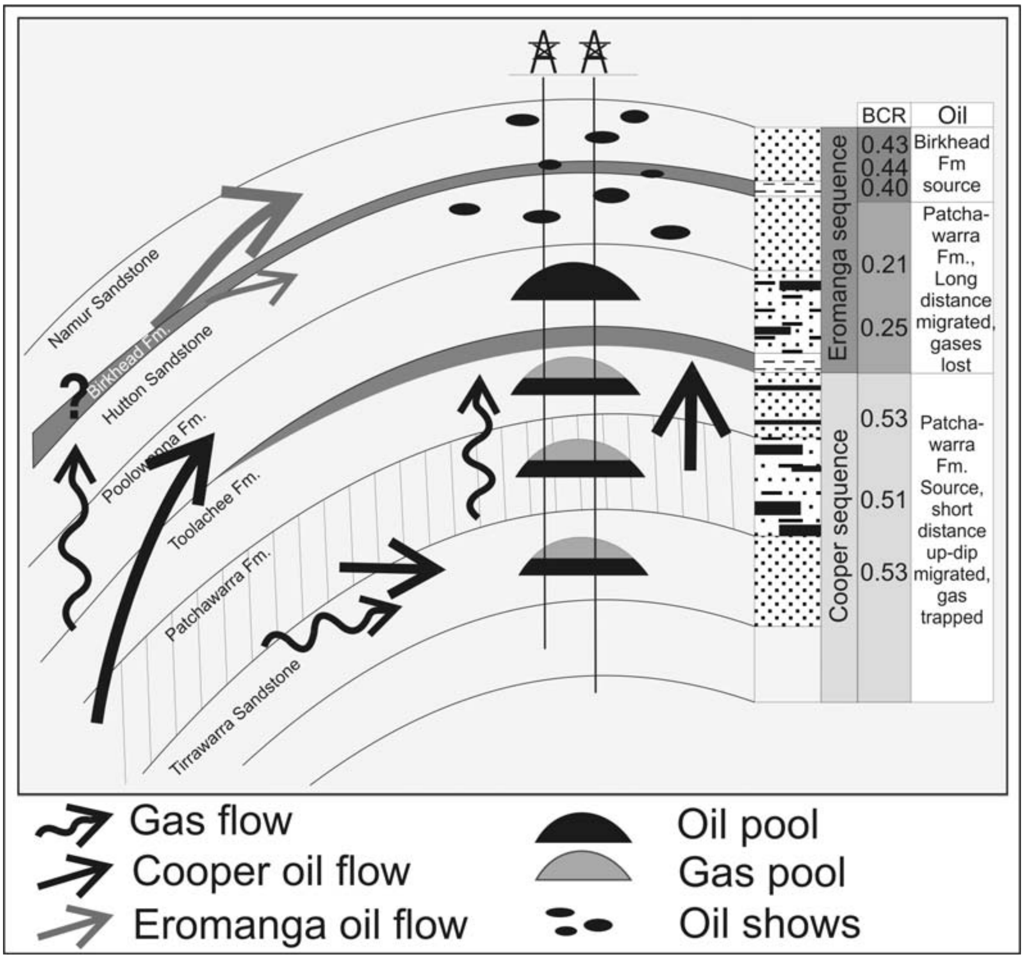


Fig.1. Reconstructed charging history for the southern dome of the Gidgealpa Field

References

[1] Schwark, L., Hallmann, C., Arouri, K.R. and McKirdy, D.M. (2005) Elucidating multifactorial controls of carbazole distribution (to be submitted to Geochimica et Cosmochimica Acta).

[2] Hallmann, C., Arouri, K.R., McKirdy, D.M. and Schwark, L. (2005) The petroleum generation potential of Warburton Basin source rocks, recognised by carbazole signatures in Cooper Basin residual oils. Central Australian Basins Symposium 2005. Accepted for oral presentation.

PBS-17: Can we correlate liquid hydrocarbons accumulations with Miocene source rocks in Eastern part of the Carpathian Foredeep, Poland?

I. Matyasik, A. Steczko

Oil & Gas Institute, PL-31503 Krakow, Poland Cracow (e-mail: Matyasik@inig.pl)

The Carpathian Foredeep is one of the largest sedimentary basins in Central Europe, stretching from Austria to Romania. In Poland, the foredeep hosts many commercial accumulations of methane-rich natural gas and some petroleum accumulations reservoired in Miocene sands. Many of the gas accumulations are associated with liquid hydrocarbons. Microbial methane is generated at depths of less than about 2400 m below the Miocene seafloor. Four zones representative for the dispersed organic matter characteristics are distinguished in the outer Miocene basin. Two zones are typical of the part of the foredeep north off the edge of the Carpathian overthrust closed to the Tarnów and Mielec-Lezajsk area. Two other zones Rzeszow and Przemysl are present at and under the Carpathian orogen overthrust.

Until present it is poorly understood, which source rocks contribute liquid hydrocarbon accumulations and how expelled hydrocarbons reach the respective reservoirs.

This paper summarizes new results of geochemical analysis of the liquid hydrocarbons from eastern part of the Carpathian foredeep (Rzeszow area) and presents a working hypothesis about possibilities of generation these liquid hydrocarbons from Miocene source rocks at early mature stage.

According to rock samples results (Rock-Eval, GC, GC-MS) organic matter in this area has not reached the conventional oil window.

Miocene rocks in the interval of 1200-3200 are marginally mature with T_{max} in range 429-439^{o}C and characterize by small differences in geochemical quality. The TOC values range from 0,5-0,8%, hydrocarbon-generative potential for all samples is evaluated as low. S_1+S_2 ranges from 0,6-1.0 mg HC/g rock (except one sample from the deepest interval Jodlowka-7, with value 17,7 mg HC/g rock.), with a Hydrogen Index ranging from 84-261 mg HC/g TOC.

Based on these data and biomarker maturity parameters most Miocene rock samples belong to gas prone type III (humic) with rare admixtures of type II kerogene in deeper facies closed to the Przemysl area. Relative high pristane/phytane ratios (1,1 – 2,6), abundance of oleanane, cadalene and retene indicates terrestrial origin of organic matter and oxic depositional environment. We consider the Miocene strata to be a significant gas source in

Rzeszow region and have also been identified as having minor liquid hydrocarbon source rock potential especially in Przemysl area.

Ten samples of liquid hydrocarbons from Rzeszow, Przemysl and Lubaczow area were examined in an effort to determine the causes of compositional differences among them. Compositional variability in the physical properties, carbon isotope ratios and molecular distributions suggests that at least two sub-groups occur in the sample set. The sub-groups are characterized by differences mainly in abundance of light hydrocarbon ($< n\text{-}C_9$), distribution of n-alkanes, pristane/phytane ratio and abundance of biomarkers (hopanes and steranes).

Group I consist of nine samples of "oils" which occur mainly in the Rzeszów and Przemysl area. These "oils" are characterized by high concentration of pristane ($1<Pr/Ph<11$) and low concentration of n-alkanes. Pristane and phytane are predominant over all n-alkanes. Saturate/aromatic ratios are variable in range from 4,7 to 20,7. Light hydrocarbons ($<n\text{-}C_9$) are present in very low abundance with heptane value (H) from 2 to 10. All biomarkers are absent in all samples. Aromatic are dominated by cadalene and retene.

To Group II belongs only one sample - oil from Zalazie well reservoired at the deepest interval (2600 m) among all of examined samples. The n-alkane distribution is in range from $n\text{-}C_{11}$ to $n\text{-}C_{32}$ (CPI=1), with pristane/phytane =3,6. Low molecular weight aromatic hydrocarbons are rich in benzene and toluene and Heptane value is high (H=31). The aliphatic fraction is characterized by relative low contribution of biomakers. This oil contains characteristic biomarker –oleanane. Aromatic fraction is dominated by alkylated naphtalenes.

These results show that this oil was generated from the source rock which was at the higher stage of thermal maturity than source rocks for previous described oils.

Are these "liquid hydrocarbons" (Group I and Group II) related to a different source rocks? "Oils" from Group I are immature or/and are affected by biodegradation?

Is migration (migration-fractionation) induced compositional changes in these "oils"?

The answers on these considerations will have an important impact on future exploration in this region.

PBS-18: An organic geochemical study of Palaeozoic sediments and petroleums from the Scandinavian on- and offshore areas

J.H. Pedersen[1], D.A. Karlsen[1], R. di Primio[2], J.E. Lie[3], H. Brunstad[3]

1) Department of Geosciences, University of Oslo, P.O. Box 1047 Blindern, N-0316 Oslo, Norway
(email: j.h.pedersen@geo.uio.no)
2) GeoForschungsZentrum Potsdam, Telegrafenberg, D-14473 Potsdam, Germany
3) RWE Dea Norge AS, P.O. Box 243 Skøyen, N-0213 Oslo, Norway

In Lower Palaeozoic times, large parts of the Scandinavian region of the NW Europe were covered by the Iapetus Ocean. Shales, mudstones and carbonates were deposited on the mainland of Scandinavia, and in offshore areas east, south and west of the Scandinavian mainland. Some of these sediments, like the Upper Cambrian – Lower Ordovician Alum Shale, have certainly generated petroleum. On- and offshore oil and gas fields in the Baltic countries Latvia and Lithuania are sourced from Cambrian, Ordovician and Silurian marine shales. In Scandinavia, insoluble bitumens, oil stains and oils in inclusions found on the Scandinavian onshore prove that Lower Palaeozoic petroleum systems have been active in this region. Insoluble bitumen found in Upper Palaeozoic reservoir sandstones in the Norwegian North Sea suggests that Lower Palaeozoic petroleum also have been present in the North Sea region. This study presents an evaluation of Palaeozoic source rocks, bitumens and oil stains from Norway, Sweden, Scotland and Spitsbergen in order to evaluate the source rock properties and distribution of Palaeozoic source rocks in the Scandinavian on- and offshore region.

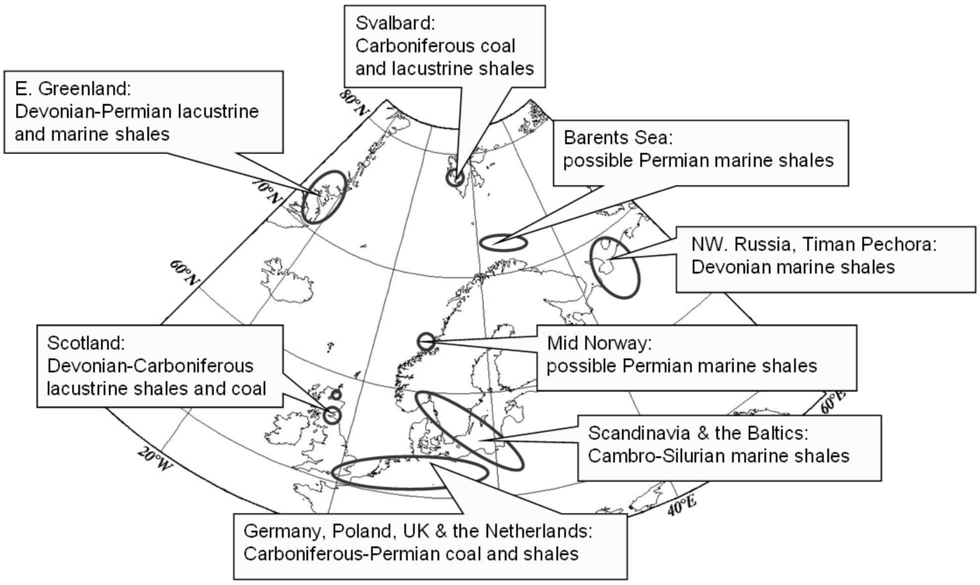


Fig.1. Occurrences of Palaeozoic source rocks in the North West Europe

PBS-19: Source rock - oil correlation in the Eastern flank of the Upper Magdalena Valley basin, Colombia

M. Torres[1], A. Permanyer[1], C. Mora[2]

1) Universitat de Barcelona, Catalonia, Spain (e-mail: albert.permanyer@ub.edu)
2) PGT Ltda., Colombia

In order to assess the hydrocarbon generation potential of La Luna and Tetuán Limestone Formations (Cenomanian-Coniacian) and establish source rock-oil correlations in the Eastern flank of the Upper Magdalena Valley Basin (Colombia), a series of analyses (including Rock-Eval pyrolysis, gas chromatography (GC), gas chromatography - mass spectrometry (GC-MS) and $\delta^{13}C$ isotopes) were carried out on 17 cuttings samples from Encanto-1 well and 6 oil samples from wells Encanto-1 and Encanto-2.

A good generation potential is observed in rocks from La Luna and Tetuán Limestone Formations (S2 up to 20.56 mgHC/g rock). Thermal maturity ranges from immature in La Luna Formation to mature (oil window) in the Tetuán Limestone Formation.

According to biomarker analysis (particularly Pristane/Phytane ratios lower than 3, terpane C_{24}/C_{23} and C_{26}/C_{25} ratios between 0.4 and 0.6, low Ts/Tm values and high Gammacerane Index), source rock intervals in La Luna and Tetuán Limestone Formations were deposited in a predominantly marine-carbonate rich environment, with occasional terrestrial contribution as shown by the high C_{29} sterane percentages (above 50%).

Oil samples from Encanto-1 well are of marine deltaic origin (Pr/Ph between 3 and 5.5 and C_{29} sterane percentages around 70%), with contribution of terrestrial organic matter ranging from high to moderate, therefore allowing to identify two different oil families, informally named A and B respectively. These oils could have been generated by more proximal facies from La Luna Formation present in the south-eastern part of the studied area, where the supply of terrestrial organic matter is more important.

Oils in Encanto-2 well (family C) show C_{27}, C_{28} and C_{29} sterane percentages of around 30%, Pr/Ph ratio between 1 and 1.4, tricyclic triterpanes C_{26}/C_{25} lower than 1 and high Gammacerane Index values, all of which indicative of a fully marine source rock, probably of carbonate-rich nature, suggesting a correlation between these oils and the source rocks from La Luna and Tetuán Limestone Formations.

Oils from families A and B, present in Encanto-1 well are characterized by the following ratios: C_{29} $\beta\beta/C_{29}$ $\beta\beta\alpha\alpha$between 0.62 and 0.75, C_{29} 20S/20S+20R above 0.51, hopane C_{31} values around 60%, whereas in oil family C (Encanto-2 well) the ratios are: C_{29} $\beta\beta/C_{29}$ $\beta\beta\alpha\alpha$ between 0.36 and 0.41, C_{29} 20S/20S+20R between 0.28 and 0.35 hopane

C31 values around 40%. All of the above allowed concluding that thermal maturity is higher in oils from families A and B (Encanto-1 well) than oil from family C.

In summary three different hydrocarbon families are identified (A, B and C). Oils belonging to families A and B were generated from marine source rocks with high content of terrestrial supply, probably corresponding to a proximal facies of the La Luna Formation, known to exist in the south-east of the studied area. Oils from family C were generated from marine source rocks and show a good correlation with the extracts obtained from source rocks of La Luna and Tetuan Limestone Formations. In terms of thermal maturity oils from families A an B are more mature than those from family C.

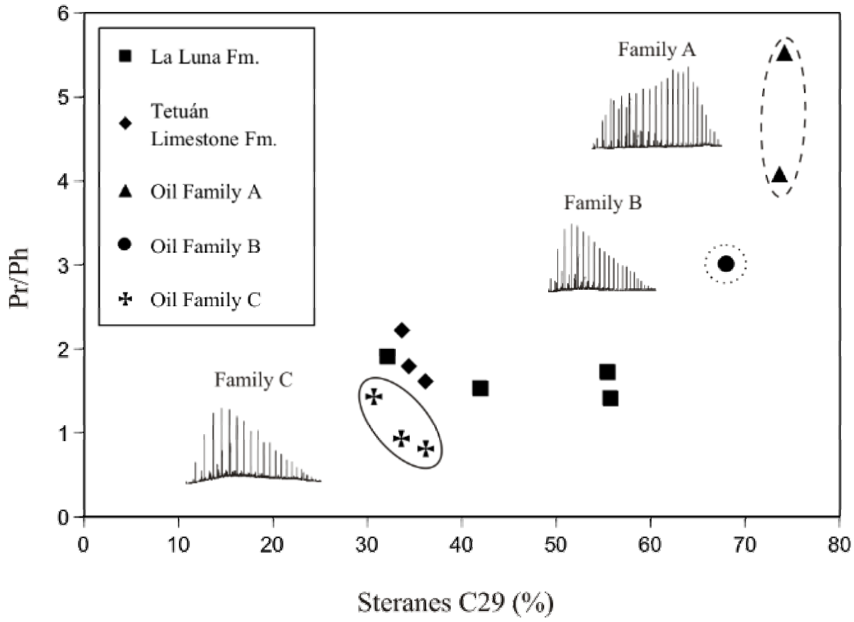


Fig.1. % C_{29} steranes vs. Pr/Ph diagram from La Luna and Tetuán Limestone Formations extracts, and oil samples from Encanto-1 and Encanto-2 wells

Acknowledgements

Authors are grateful to Sipetrol S.A providing rock and oil samples. This work was financed by the DURSI of the Catalonian Government (2001SGR00075 "Grup de Geologia Sedimentaria"), and Project BTE2003-06915 from the Spanish Ministry of Science and Technology.

PBS-20: Oil-source rock correlation of oils from the northern part of Pechora basin

O.V. Valyaeva

Institute of Geology of Komi Science Center of RAS, 54-Pervomayskaya St, Syktyvkar, Russia
(e-mail: valyaeva@geo.komisc.ru)

The Khoreyver depression is located in the northern part of Pechora basin (Russia) where almost all of the oil reserves occur within carbonate reefs of the Upper Devonian. A lot of 25 oil samples from this territory were examined by gas-liquid chromatography (GLC), but only 6 of them turned out to be singenetically to Upper Devonian containing deposits.

They are: 2-Yanemdeyskaya, 1-Syurkharatinskaya, 2-Syurkharatinskaya, 10-South-Syurkharatinskaya, 20-Noth-Sykhoreyskaya and 65-Upper Kolvinskaya wells. Several parameters derived from gasoline-range hydrocarbon and chromato-mass-spectrometry (GC-MC) analyses of the oils are given in Table 1.

Table 1. Average geochemical parameters

geochemical parameters	Oils	bitumen's
αββ C_{27}, %	25.48	25.94
αββ C_{28}, %	21.34	19.11
αββ C_{29}, %	53.18	54.48
Sterane/hopane	0.03	0.11
$C_{35}/(C_{31}-C_{35})$ (hopane)	0.17	0.06
DiaS/regS	0.12	0.18
Pr/Ph	0.53	1.8
n-C_{31}/n-C_{19}	0.15	0.15
Pr/n-C_{17}	0.25	0.75
2*n-C_{17}/(n-C_{16}+n-C_{18})	1.29	1.13
Parameters of thermal maturity		
20S/(20S+20R)	0.38	0.51
αββ/(ααα+αββ)	0.52	0.51
22S/(22S+22R)	0.55	0.59
K_1	2.66	4.99

diaS/regS – C_{27} diasterane/ regular sterane ratio. All GC-MC parameters were calculated using peak heights on appropriate m/z 191 or 217 mass fragmentograms.

The n-alkane distributions of the oils have a maximum in the C_{15}-C_{20} range. 2*n-C_{17}/(n-C_{16}+n-C_{18}) – 1.29, a low pristan/n-C_{17} (0.28) and n-C_{31}/n-C_{19} (0.15) ratios are characteristic for organic matter (OM) derived from alga's. For that oils low ratio steranes to hopanes are very typical (0.04 or less), that can indicate high bacterial input in sedimentated organic matter or high degree of OM transformation in early diagenesis stage. A low pristan/phitan ratio (Pr/Ph) – 0.28 and $C_{31}/(C_{31}$-$C_{35})$ homohopanes ratios – 0.17 were thought to be indicative of reduce condition environments of OM. whereas, a higher concentrations of steranes as compared with diasteranes were inferred to be characteristic of carbonate source rocks. Oils have identical character of regular steranes distribution: $C_{29}>C_{27}>C_{28}$. The 20S/(20S+20R), αββ/(ααα+αββ), K_1=5α14β17β(20R+20S)/5α14α17α20R ratios for C_{29} steranes and 22S/(22S+22R) ratio for C_{31} hopanes were used to define the maturity levels of oils. The maturity of studing oils is corresponded to the beginning of oil window.

Source rocks for oils in this region are the organic-rich carbonate of Domanic and Famenian age from West-Osoveyskaya, South-Khosedayuskaya, West-Vissertynskaya and Yaneityvisovskay areas. The TOC content in the rocks varies from 1.99 to 14.16, TGP varies from 7.94 to 32.19, PI – 0.1-0.18 and T_{max} – 433-443^{0}C. Chloroform-soluble organic matter (bitumen) of rocks was investigated by GLC and GC-MC. Main characteristics of this analysis you can see in Table 1. The best oil-source rock correlation is shown by αββ C_{27}, C_{28} and C_{29} steranes distribution. Differences in n-alkane and i-alkane distribution in oils and bitumen are influenced by oils and bitumen's alterations during primary migration.

Consideration of classic biomarker permits to evaluate genetic peculiarity of oils.

PBS-21: Characterizing the oil source of the Lower Paleozoic Tarim basin by oil geochemistry of the Tahe oilfield

C.-J. Wang[1], F.-Q. He[2], C.-G. Wang[3], T.-G. Wang[1]

1) Laboratory of Geochemistry & Environmental Sciences, Faculty of Geosciences, China University of Petroleum, Beijing, 102249 (e-mail: wchj333@126.com)
2) Department of Oilfield Exploration and Production, China Petroleum & Chemical Corporation, Beijing, 100029
3) Institute of Oil Exploration and Production, China Petroleum & Chemical Corporation, Beijing, 100083

Oil source problem has been being the bottleneck restricting the oil exploration in the Paleozoic Tarim basin in China for nearly twenty years. Oil source problem is substantially of sedimentary-organic facies, while the key to understand the sedimentary-organic facies is the study of oil geochemistry for this huge and complex basin. Oils from Tahe oilfield, the biggest one in the Tarim basin, with normal maturities (medium-mature to mature) predominantly, much lower than that from Lunnan and Tazhong oilfields, should contain the most convincing proofs of the oil source, and should be the most important study objects for Tarim oil source determinating. More than 110 oils from this oilfield were studied and the sedimentary-organic facies of the source rocks or the oil source are characterized as following:

1. Pr/Ph value of the oils varies from 0.7 to 1.1, with an average of 0.89, indicating the source rocks deposited in reductive environments.

2. High values of C_{35}/C_{34}Hop, predominantly of 1~1.3, indicating reductive depositional environments and carbonate-predominated sediments.

3, The composition of steranes in the oils are homogeneously characterized with the typical "V" type of C_{27}-C_{28}-C_{29} fingerprint in relative abundance. The distribution of tricyclic terpanes are also homogeneous with the low C_{21}/C_{23}Tri value.

4. High abundance of isorenieratene derivatives (ID) of photosynthetic green sulphur bacteria *chlorobiaceae* (mainly the series of 1-alkyl-2,3,6-trimethylbenzenes), with C_{13}~C_{23}ID/(P+MP) predominantly as high as 1.0~2.0, with an average of 1.47 for 75 Ordovician reservoired oils, strongly indicate the photic zone euxinia and water column stratification developed during organic matters depositing.

5. The series of dibenzothiophenes are also abundant in these oils, with MDBT/MP value predominantly as high as 0.8~0.9, and $\sum$DBT/$\sum$(DBT+DBF+F) value up to 0.65~0.80, showing carbonate-predominated source rocks deposited in reductive environments.

6. The oils are ^{13}C-depleted, with $\delta^{13}C_{oil}$ ranging from -33.3‰ to -32.2‰, which indicates the depositional condition of the source rocks is reducing, in some extent.

7. Ts/(Ts+Tm) value mainly ranging from 0.25 to 0.35, not only indicates the oils are of medium-maturated, but also implies that the source rocks are predominantly carbonates.

8. The maturity of the Tahe oils are predominantly equivalent to Ro0.8~1.0%. All the oils are analogous in molecular geochemical characteristics, and thus are regarded as one oil family, which means Tahe oils are of very similar oil sources.

To summarize, the Tahe oil source rocks are organic-rich and carbonate-predominated (possibly interbedded with argillaceous carbonates) which deposited in anoxic-dysoxic periodically euxinic conditions. Such sedimentary-organic facies are most probably developed in platform depression or marginal slope. But, it is clear that there is no evidence to support argillaceous shales just like that of the Saergan Formation and the Yingan Formation as source rocks for the Tahe oils, and oil-source correlation also indicates that the Tahe oils have no relationship with the over-mature Cambrian argillaceous shales, and no indications for hydrocarbon contribution from the huge volume of O_{2-3} organic-lean clastic rocks (“black sheet”) in the great Manjiaer depression.

Based on the oil source characteristics of the Tahe oils, with more extensive oil-source correlation, we propose that the above oil source concept should be most extensively applicable to the whole Lower Paleozoic Tarim Basin, which means we have not revealed the true source rocks for the recovered oils, and the good source rocks must occur in the Middle-Upper Ordovician strata.

PBS-22: Oil and gas potential mapping of the Upper Jurassic source rocks using accumulation rates, Danish Central Graben

B. Dahl[1], C. Andersen[2], E. Thomsen[2]

1) Department of Geology, Bergen University, 5007 Bergen, Norway (e-mail: birger.dahl@geo.uib.no)
2) Geus, 2400 Copenhagen NV, Denmark

Volumetric assessments of generated petroleum are needed in order to carry out prospect evaluations. For the increasing demand of predictability with respect to trap content compositions (gas versus oil) oil and gas potential maps can be produced for application in the volume assessment process.

A recent method [1] proposed for application in source potential mapping is used to assess the original oil and gas potentials in source rock horizons based upon Rock-Eval potential (S_2) and total organic carbon (TOC) values. The method assumes that kerogens consist of mixtures of end-members with assigned hydrogen index values. Based on suggested algorithms, the average amounts of oil-prone, gas-prone and inert organic material over source rock intervals are determined in TOC units. The method uses regression lines from plots of remaining hydrocarbon potentials (S_2) versus total organic carbon (TOC). A computer program "Kerdet", where appropriate S2 TOC populations can be encircled graphically prior to method execution, have been applied.

It is obviously of great advantage to map source rock properties within isochronous or time-stratigraphic layers since it allows comparison of the depositional processes that occurred simultaneously at different locations. The detailed time- and sequence-stratigraphic subdivisjon of the Upper and Middle Jurassic in the Danish Central Graben reported by Andsbjerg and Dybkjær [2] was therefore applied. Accumulation rates of oil prone and gas prone organic constituents have been calculated for each of the 25 system tracts in more than 30 wells and these results formed the basis for the mapping.

The mapping of organic accumulation rates using the hydrogen index end-members suggested by Dahl et al. [1] method, leads to very simple algorithms for petroleum mass calculations:

$$HC(oil) = Fc(oil) * \Delta t * Tr(oil)$$

$$HC(gas) = Fc(gas) * \Delta t * Tr(gas)$$

where HC is the generated mass, Fc the organic accumulation rate, Δt the time interval and Tr the transformation ratios.

Due to application to basin modelling the system tracts had to be merged into 4 mega-sequences that correspond to the seismic resolution and the conceptual subdivision of the Upper Jurassic layers.

The map preparation is supported by the paleo-topography of the basin inferred from the isopach maps of the 4 isochronous units and the paleo-geographic maps of Andsbjerg and Dybkjærv [2].

Some general observations have emerged during the course of this study:

- The preservation of organic carbon was dependent on the clasitc sedimentation rates [3] and suggests optimum TOC values at LSAR (linear sediment accumulation rates) around 30 m/mill years for the uppermost Farsund formation.
- The amounts of organic material produced in the water column have a tendency to increase in the deepest parts of the basin. This is probably due to a combination of better conditions for preservation of the organic matter and an effect of topographical focusing. Very high clastic input to the basin, particular from slump deposits, etc can, however, dilute the organic matter and reduce the apparent organic sedimentation rate.
- The terrestrially derived (gas prone) material tends to be enriched along the paleo-shoreline and the concentration or “flux” declines with increasing distance from the shoreline. High clastic input can also dilute the organic material and lower the apparent organic flux.

References

[1] Dahl, B., Bojesen-Koefoed, J., Holm, A., Justwan, H., Rasmussen, E. and Thomsen, E., 2004. A new approach to interpret Rock-Eval S2 and TOC data for kerogen quality assessment. Org. Geochem. 35, 1461-1477.

[2] Andsbjerg, J.and Dybkjær. K. 2003 Sequence stratigraphy of the Jurassic of the Danish Central Graben. In: The Jurassic of Denmark and Greenland eds. F..Surlyk and I. O..Ineson. pp 265-300.

[3] Ibach, L.E.J. 1982 Relationship between Sedimentation Rate and Total Organic Carbon Content in Ancient Marin Sediments. AAPG Bull. 66, 170-188.

PBS-23: Potential petroleum systems in the Labrador and Baffin Shelf areas, offshore North Eastern Canada

M. Fowler[1], L. Stasiuk[1], M. Avery[2]

1) Natural Resources Canada, Geological Survey of Canada Calgary, 3303-33rd Street N.W. Calgary, AB T2L 2A7 (e-mail: mfowler@nrcan.gc.ca)
2) Natural Resources Canada, Geological Survey of Canada Atlantic, 1 Challenger Drive, Dartmouth, NS B2Y 4A2

Between 1971 and 1983, 31 wells were drilled on the Labrador Shelf and southeast Baffin Shelf area of Canada=s Atlantic offshore. This activity resulted in seven significant discoveries of mostly light oil, condensate and gas. Subsequent activity in this frontier area was low until recently. However, rising commodity prices as well as the well-documented oil seeps across the Davis Strait in western Greenland has prompted a reassessment of its petroleum potential. There is very limited petroleum geochemical data available for this area with the last significant paper ([1]) published over twenty years ago. Here we use new data obtained from organic geochemical and organic petrological analysis of DST liquids and cuttings to comment on possible source rocks and what this implies about the nature of potential reserves.

Liquids from DSTs were obtained from Bjarni, Gudrid, Hopedale, North Leif and Snorri wells drilled on the Labrador Shelf, and from Hekja on southeast Baffin Shelf. These are mostly unbiodegraded light oils with North Leif being much more waxy oil than the others, reflecting its lower gravity. All of these samples have high pristane/phytane ratio (>3) indicating that they were sourced from intervals deposited under relatively oxidising conditions, probably with a major contribution of terrestrial organic matter. Biomarkers are in very low concentrations in most of these oils with the exception of North Leif which shows characteristics of a low maturity terrestrial source. Based mainly on aromatic parameters, the Hopedale oil from the Labrador Shelf is more mature than the other samples, being generated in the later part of the oil window while the others were likely generated at lower maturity. These oils do not appear to have the same source as a heavily biodegraded seep sample from Scott Inlet, northeast Baffin Island, which biomarkers suggest is possibly related to the presumed Upper Cretaceous-sourced Greenland oil seeps.

Rock-Eval analysis of cuttings from Labrador Shelf wells to date, indicate that the best potential source rocks occur in the Lower Cretaceous Bjarni Formation at Herjolf and North Leif. At Herjolf this unit has a thickness of at least 500 m with an average TOC content of about 5% and contains Type III/II and III kerogen. The maturity of the upper to lower

Cretaceous at these locations ranges between about 0.40 to 0.70-0.80 % vitrinite reflectance. In the southeast Baffin Shelf area, the only potential source rocks occur at Hekja and Raleigh with ~100 m of early to middle Eocene-Late Paleocene coaly siliclastics and coals containing Type III and liptinite enriched Type II-III kerogens. Petrologically, these samples are dominated by vitrinite, sporinite, cutinite as well as some resinite and exsudatinite. Vitrinite reflectance of Pliocene to early Paleocene strata ranges is 0.22 to 0.28% and from 0.55 to 0.72% for Eocene to Paleocene units. The type of organic matter in the source rocks is largely prone to significant gas- (condensate) generation at the observed maturity, suggesting that these or similar units are the source rocks of hydrocarbons discovered in this area.

References

[1] Powell, T.G. and Snowdon, L.R. (1983) A composite hydrocarbon generation model: Implications for evaluation of basins for oil and gas. Erdöl und Kohle v. 36, p. 163-170.

PBS-24: Integrated approach to characterize non-marine "dual petroleum systems" in Southeast Asia

A. Okui

Idemitsu Oil and Gas Co., Ltd.2-5, Toranomon 2-Chorme, Minato-ku, Tokyo, 105-0001, JAPAN (e-mail: okui@iog.idemitsu.co.jp)

It was thought that Miocene coal is main source rock in the basins in and around Indochina Peninsula in Southeast Asia. However, detailed investigation by the state-of-art geochemical analysis such as GC-MS-MS and diamondoids on crude oils and condensates suggested wide distribution of Oligocene lacustrine source rock in these basins. In addition, the analytical results indicated that different type of fluids (oil, condensate and gas) generated from 2 source rocks mixed during their migration and trapping in these basins. These results demonstrated that the petroleum system originated from Oligocene lacustrine source rock play much more important role in these basins.

This conclusion was also confirmed by multi-dimensional basin modeling. The modeling also suggested that the timing of generation and migration from 2 source rocks with trap formation is the key factor to deliver oil, condensate and gas in these basins.

The understanding of this kind of complex dual petroleum systems will give new insights to petroleum potential of the basins in Southeast Asia.

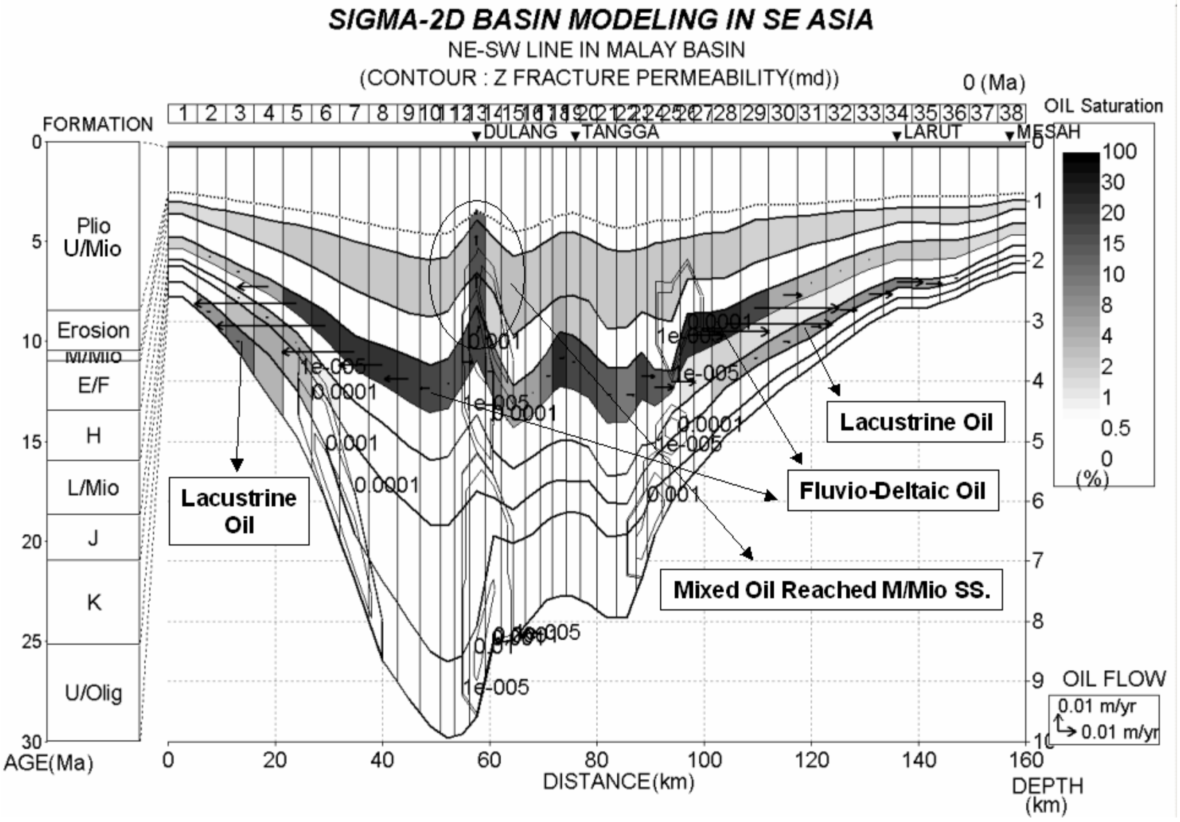


Fig.1. Two-dimensional basin modeling in the Malay basin, Malaysia

PBS-25: Carbon isotope and Cambrian oil families in the Baltic sedimentary basin

O. Zdanaviciute

Institute of Geology and Geography, T. Sevcenkos 13, 03223 Vilnius, Lithuania (e-mail: zdanaviciute@geo.lt)

The discovered oil and gas accumulations in the Baltic Syneclise mostly are related to Middle Cambrian sandstone beds and only some of them occur in Ordovician limestone and Silurian reefs. Moreover, small oil extractions were given from fractured Precambrian crystalline basement and Devonian sediments. According to the distribution of source rocks, oil reservoirs and seals the Cambrian, Ordovician and Silurian oil-bearing complexes are distinguished in the Baltic Syneclise. Based on the organic matter type, quantity and thermal maturity data, several source rock intervals have been determined within the Palaeozoic deposits. The source rocks includes the Cambrian argillite and clayey aleurite, black argillite of Ordovician Mossen and Fjacka Formations and dark grey clayey Llandovery–Ludlow complex. According to B.Tissot et al. [1] classification the kerogen of the mentioned source rocks may be ascribed to the II marine type. It is predominated by syngenetic, sapropel, marine organic matter and "vitrinite-like" macerals, and charred remains of fauna.

The crude oil within the Baltic Syneclise has moderate densities (26–42 ^{o}API) and contains low or average values of asphaltenes (0–3%) and a small value of sulphur (0.04–0.44%). The content of saturated HC makes up 42–78%. The ratio of saturated and aromatic HC reaches 2.2–5.2. The gas-chromatographic analyses of crude oils from the Baltic Syneclise showed that oil composition is dominated by (C_{13}–C_{19}) n-alkanes, with the maxima at C_{15} and reduced abundance in the range C_{20}–C_{35}. The ratio of odd and even n-alkanes calculated for C_{22}–C_{32} n-alkanes is close to unity. The content of isoprenoides is considerably smaller than that of n-alkanes, and their ratio is very stable (0.39–0.52). Pristane and phytane ratio also is very stable and ranges from 2.07 to 2.65. The Baltic oils are, as many Paleozoic oils, characterised by very low concentrations of sterane and triterpane, the distributions, which show limited variability. In general, notable features include prominence of tricyclic triterpanes, comparatively low hopane to sterane ratios and low proportions of extended hopanes. Classification of such oils by standard biomarker techniques is often difficult [2], [3].

This paper presents stable carbon isotope composition of crude oils from Lithuanian oil pools (table 1). Interpretation of preliminary data suggests that the distinction of the oil classes (A and B) that established in Cambrian reservoirs is related to variation in petroleum compositions caused by differences in level of thermal maturity in response to the location of prominent kitchen areas, and other structural elements, biodegradation, and presumed variations in source rock age and facies. Oils from Girkaliai, Nausodis, Vilkyciai, Sakuciai, Siupariai, Degliai fields are more mature and existed at rather high temperatures. Oil from the Antkoptis, Genciai, Uoksai, Pociai oil fields is attributed to transition zone.

Table 1. Stable carbon isotope composition of crude oils from eastern part of the Baltic Syneclise.

Well, Reservoir	Depth, m	Crude oil δ^{13}C‰, PDB	Well, Reservoir	Depth, m	Crude oil δ^{13}C‰, PDB
Girkaliai-2, Cm	1896–1930	-30,40	Siupariai-1, Cm	1975–2005	-29,90
Girkaliai -1, Cm	1737–1738	-30,28	P.Siupariai-1, Cm	1975–2005	-30,27
Nausodis-1, Cm	1820–1829	-30,57	Degliai-9, Cm	2012–2015	-30, 27
Vilkyciai-9, Cm	1965–1990	-30,56	Antkoptis-1	1900–2003	-31,52
Pociai-1, Cm	1975–1995	-31.00	Genciai-3	1832–1848	-31,22
Sakuciai-1, Cm	2005–2080	-30,24	Uoksai-1	2187–2200	-31,22

References

[1] Tissot, B.P., Demaison, G., Espitalie, J. and Combaz, A. 1974. Influence of the nature and diagenesis of organic matter in formation of petroleum. AAPG Bulletin 58, 499–506.

[2] Zdanaviciute O. and Bojesen-Koefoed J.A. 1997. Geochemistry of Lithuanian oils and source rocks: a preliminary assessment. Journal of Petroleum Geology 4, 381–402.

[3] Zdanaviciute O., Lazauskiene J. 2004. Hydrocarbon migration and entrapment in the Baltic Syneclise. Organic Geochemistry 35, 517–527.

PBS-26: Paleostructural evolution and geochemical characterization of the Silurian bed source basin of Sbaa, Algerian Sahara

M. Sadaoui

Department Layers. Faculty of Hydrocarbons and the Chemical. University M'Hamed Bougara. Boumerdes. AIgeria (e-mail: sadaoui2001@yahoo.fr)

The gas discovery in 1954 in the Western Sahara has classified this area like a gas-bearing zone. However, the discovery of oil layers in the Eighties in the Basin of Sbaa, would have called into question the theories which allowed this area to a gas-bearing province.

This work concerns a paleostructural study and the qualitative characterization of the Silurian bed rock. The sedimentary cover is principally Palaeozoic, it is not very thick and was truncated by frequent erosions.

Although forming integral part of the basin of Timimoun, the Basin of Sbaa is distinguished like an entity, as well on the paleogeographic level as on the plans structural and oil. It was developed in the site of an old furrow subsident, which occurred with the favour of great faults of the substratum, which played in faults of collapse.

For the characterization of the organic matter of the Silurian bed rock, several taken samples of the surveys were analysed and observed under the microscope. Silurian clays are widespread in all the Basin, their thickness varies from 110 m in the South East to 790 m in Western North.

The interpretation of the geochemical results shows that the values of the TOC vary from 1.2 to 3.8 % and the Kerogen is of type II and III. The generation of hydrocarbons began with Carboniferous and the liquid hydrocarbons generated by Silurian clays in the North East underwent a dry gas cracking, while in the Western South and the West, Silurian is in the oil phase. The inversion of the relief, with the uplift of Ougarta in the Visean, allowed the Basin to receive a significant volume of sediments during this same period and like in the Mesozoic one. That has contributed to the maturation of the organic matter in these zones with weak maturation.

PPM-1: Blender: a surface geochemistry tool to sample interstitial hydrocarbons in soils and piston core sediments

C.S. Bandeira de Mello[1], R.C.S. Gonçalves[2], D.J. Miller[2], J.B.L. Francolin[2]

1) Instituto Alberto Luiz Coimbra de Pós-Graduação e Pesquisa de Engenharia – COPPE – UFRJ. Cidade Universitária (e-mail: bandeira.coppe@petrobras.com.br)
2) Centro de Pesquisas Leopoldo Migueiz de Mello CENPES / PETROBRAS / GEO. Cidade Universitária, Ilha do Fundão, quadra 7, radial 7, Rio de Janeiro, Brazil, cep: 21949 900

At present time, the search for oil and gas in Brazilian sedimentary basins is carried out mainly in deep offshore waters. Such fact results in very expensive operations. For this reason the optimization of indirect tools may represent savings in terms of time and money. The Center of Excellence in Geochemistry from the Petrobras Research and Development Center – CENPES is engaged in this big effort. The blender method has been used worldwide to measure the occluded hydrocarbons that are not obtained by the common headspace analysis. The evaluation of the results was accomplished by comparing the blender and headspace analysis from the same samples. The experiments provided interesting and important results in oil research in a Brazilian sedimentary basin. A total of fifty three (53) samples were used in dry and wet soil conditions. The samples were blended in different times varying from one to twenty minutes and analyzed by Gas Chromatography – GC.

The main results from the study were: Blender concentrations showed average values 5.6 times larger than the headspace, when blended in dry conditions, and 3.2 times larger when blended with water. In sandy samples, the blending with water produced more consistent results than with the dry samples. In clayey samples, the dry samples showed more consistent results depicting a slower increment rate of gas concentration than in the sandy samples. The ideal average blending time for best contrasts in concentration are considered to be around 5 minutes. The results in an offshore area of the Santos Basin showed geochemical blender anomalies following similar trends to those indicated by the adsorbed hydrocarbons results.

This paper discusses the experiments obtained with blender in several kinds of soil samples in Brazil. In the test phase samples in different conditions and different blending times were used. The results from these tests were very important for a better evaluation of gas and oil exploration in the offshore Santos Basin, Brazil, using piston core samples.

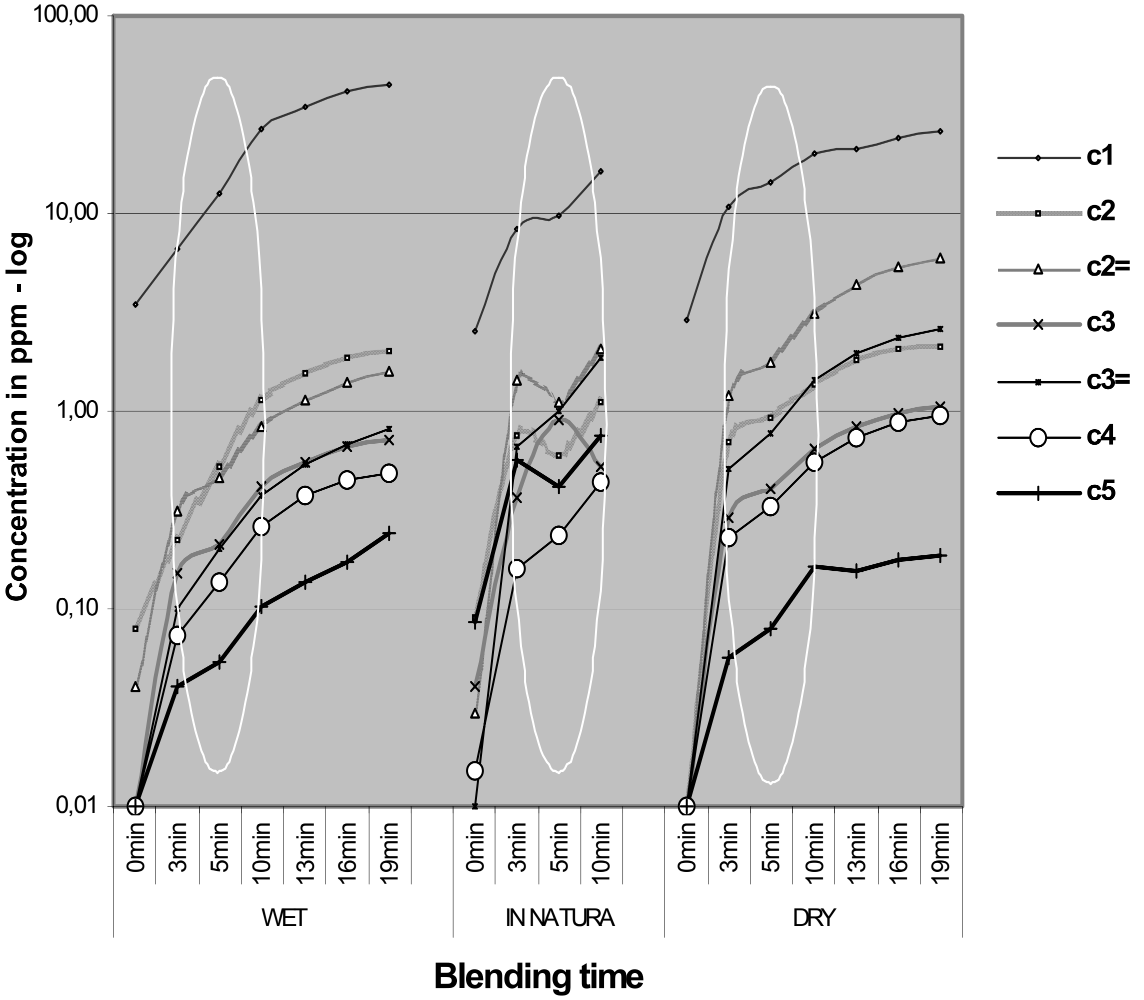


Fig.1. Mechanical break up time and gas concentrations, considering samples *in natura*, wet and dry conditions. (C1 methane, C2 ethane, C2= ethene, C3 propane, C3= propene, C4 butane and C5 pentane).

PPM-2: An integrated multi-component model for petroleum generation, expulsion, and cracking

D.J. Curry[1], A.E. Bence[1], C.C. Walters[2], S.R. Kelemen[2], H. Freund[2]

1) ExxonMobil Upstream Research Company, P.O. Box 2152, Houston, Texas 77252, U.S.A.
2) ExxonMobil Research and Engineering Company, Rte 22E, Annandale, New Jersey 08801, U.S.A.

A key objective in modeling hydrocarbon systems is the prediction of the volumes, timing, fluid properties, phase behavior, and preservation of petroleum in a basin. The volume and timing of petroleum generation can be predicted using simple, two-component models (i.e., oil and gas). However, predictions of fluid properties, phase behavior, and extent of preservation require more complex multi-component models that can predict the compositions of expelled and retained fluids. We have developed a compositional model for petroleum generation, expulsion, and cracking within the source rock and fluid cracking within the reservoir to address these needs.

The construction of a compositional model for use in a basin simulator requires compromises between the rigorous specification of solid and fluid components and reaction networks and the practical programming limitations. In our integrated model, the components and the reaction network are optimized for prediction of fluid properties, phase behavior, and cracking behavior while remaining flexible in parameterization. The model contains 12 components that include hydrocarbon gases, light oil, C_{15}+ fractions, and solids. In the model, the hydrocarbon and polar (NSO's + asphaltenes) components and solid residues are initially generated by the source kerogen and a fraction of each fluid component is then expelled preferentially. The retained fluids can then be cracked to lighter components and solid residues if sufficient temperatures are reached. Condensation reactions and branched reaction pathways are not used.

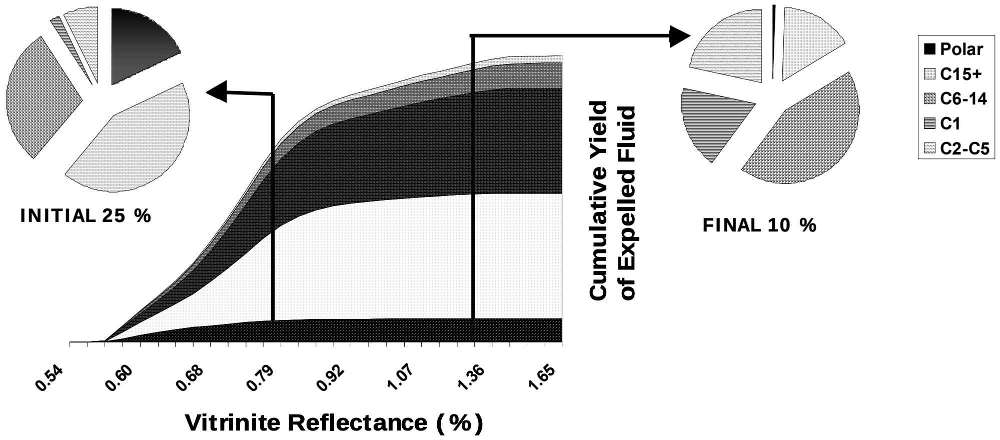
The primary generation reactions were calibrated by Microscale Sealed Vessel (MSSV) experiments conducted on three Type II kerogens (two from the North Sea, one from Canada), one Type I kerogen, and one Type IIIC (oil-prone) coal. The calibration showed that parameterization of reaction network can be simplified using bulk (global) generation kinetics to model primary generation of the hydrocarbon components, rather than determining individual kinetics for the generation of each component, particularly for Type II and Type I organic matter. The reaction stoichiometries (i.e., component yields) can be determined using appropriate experimental methods or default values for different organic matter types (determined from the calibration experiments) can be used.

The expulsion/retention model is based on Regular Solution Theory and was calibrated with experimental and published data. In the expulsion model, the concentrations and compositions of the expelled fluids vary with the composition of the generated fluids, the composition of the previously retained fluids, and level of maturity of the kerogen.

Secondary cracking kinetics and stoichiometries for the fluid and solid components were calibrated using MSSV 1 data. Since saturate and aromatic species have significantly different cracking kinetics, the secondary cracking kinetics for the liquids and solids incorporate multiple pre-exponential factors as well as distributed energies of activation.

Geologic calibration of laboratory-based model is a crucial step in validating hydrocarbon systems models. Although volumetric audits of hydrocarbon systems are difficult, the integrated multi-component model was validated using a combination of geological observations including the fluid compositions and properties of both expelled and retained fluids at different levels of maturity. For example, the compositions of the fluids expelled from Type II kerogen during the initial 25 % and last 10 % of expulsion are similar to natural systems (Fig. 1).

Fig. 1: Variation in composition of expelled fluids with increasing level of maturity (Type II organic matter)



Additional fluid compositions and fluid parameters, such as the composition of the retained fluids (e.g., 93 mole % methane at Ro = 1.83 %) and the changes in API gravity, polar fraction concentrations, and C_6+ fraction concentrations and properties during expulsion, closely resemble natural systems. Low temperature (pre-cracking) validation also included comparison of pressure-volume-temperature (PVT) behavior of the predicted fluids to reservoir fluids of similar maturity. Similarly, the fluid compositions and PVT behavior predicted by the reservoir fluid cracking model closely resemble fluids from similar sources observed in high temperature reservoirs.

PPM-3: Geochemical study of natural shows of gas and surface OM in the regions of hypothetical oil-and-gas accumulations, West Siberia, Russia

A. Golovko, G. Pevneva, E. Ivanova, J. Golovko, N. Savinikh

Institute of Petroleum Chemistry SB RAS, 3 Academichesky Ave, 643021, Tomsk, Russia
(e-mail: luvn@ipc.tsc.ru)

Study of the surface gas and oil shows and of the gases of the snow cover and surface air allows revealing their nature (subsurface or biological). Their study together with gases and bitumoids dispersed into rocks and water perform the information for a preliminary forecast of the zones of the hypothetical oil-and-gas accumulations, approximate depths and age of the reservoir rocks of the regional oil-and-gas-bearing complexes. In the regions of the Ob River valley on the territory of the Tomsk Oblast (West Siberia, Russia) one has revealed natural gas shows and, hypothetically, oil shows in the form of opalescent films on the water surface. In accordance with the data of prospecting seismology and geophysical exploration, the deposits on this territory could be oil- or gas-bearing ones. Therefor, a study of the surface gas shows was performed. The samples of the natural gas shows and oil-like films were taken from water surface in summer and fall period, from July to October.

Chloroform extracts of the films sampled from water stream surface were studied with gas-liquid chromatography, which demonstrated that normal and iso-hydrocabons (HC), as well as naphthenic HC, were present in their compositions (see Figure). Background water samples taken in winter and summer in the main beds of the Ob and Ushayka Rivers were analyzed to compare them with the films taken in the places of gas shows.

All the films and background extracts contain n-alkanes from C_{10}-C_{12} to C_{33}-C_{35} with the bimodal distribution and the maximums at C_{16}-C_{20} and C_{26}-C_{29}. Some samples show the odd C_{25}, C_{27}, C_{29} n-alkanes predominance. The distributions of alkanes in the films and background samples are similar. The insignificant differences observed in the alkanes distribution probably caused by the various contributions of the higher plants, size and activity of the microbial populations in the reservoirs studied.

Hydrocarbon biomarkers were also identified in the water films. Practically in all the films the tricycloterpanes are present in small amounts, the content of C_{30} hopane is maximal, 17α(H)-diahopane and gammacerane are present, the ratio of C_{28}/C_{29} steranes is 0.6-0.9.

The data obtained on the content and distribution of saturated hydrocarbons (alkanes and cyclic HC) in the films and background samples does not evidence a depth source of the film components in the water streams on the territory studied.

In the gas samples, N_2, O_2, H_3, CO_2, CH_4 and traces of C_2-C_3 hydrocarbons were detected. Nitrogen fraction in gases is maximal, reaching 91 wt.% in some samples. Methane is present in all the samples in the amounts from traces to 63 wt.%, its concentrations in the samples with a low content increasing from July to September. In the gas samples with high methane content its seasonal variation is insignificant. The presence of trace amounts of ethane and propane is confirmed by mass-spectrometry however no significant concentrations of the homologues of methane and inert gases, which could confirm the depth origin of these gases, were established. The presence of hydrogen is not characteristic for gas or oil-and-gas pools and most likely hydrogen in the samples studied is a product of biochemical OM transformations.

The isotopic composition of methane $\delta\ ^{13}C$ in average -65.6, -69.4 ‰ and only in the one sample -55.6‰, the predominance of CO_2 light carbon isotopes and seasonal variations of CO_2/CH_4 ratio in gas samples point to its biogenic origin.

Research performed on the composition of the gas from natural surface and 'oil-like' films from the surface of water basins allowed to make a conclusion on their biogenic origin and did not confirm the expected forecast on the presence of the hydrocarbon accumulations in the deposits of the territory studied.

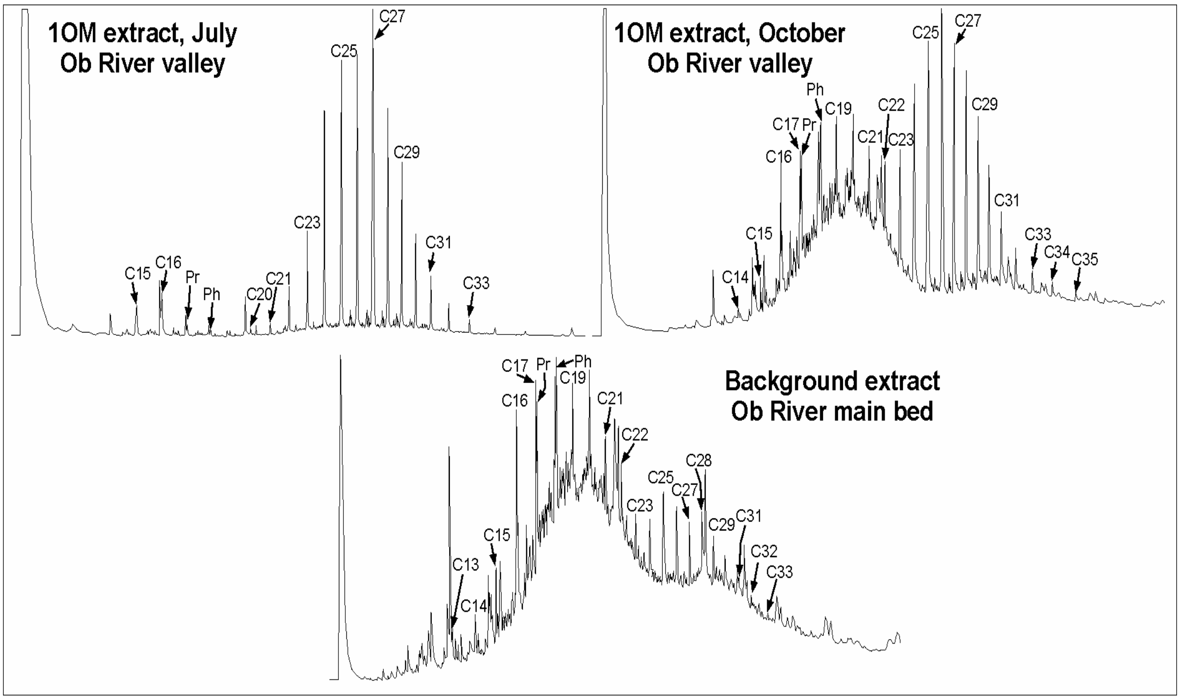


Fig.1. GC chromatograms of the film extracts sampled from the water surface in the places of gas shows, and of the background sample.

PPM-4: 3D petroleum secondary migration modeling of the Jurassic petroleum system in part of the West Siberia basin

I.V. Goncharov[1], A.G. Romanov[2], A.N. Gagarin[1], D.J. Carruthers[3], P.W.M. Corbett[2],
A.P. Afanasenkov[1]

1) TomskNIPIneft, 72 Av. Mira, Tomsk, 634027, Russia (e-mail: GoncharovIV@nipineft.tomsk.ru)
2) Institute of Petrolem Engineering, Heriot-Watt University, Edinburgh, UK, EH14 4AS
3) Permedia Research Group, Ottawa, Canada

3D oil migration modeling of the region of a junction of the Kaymissov Arch and the Nyurol Depression of the Western Siberia Basin has led to increase understanding of the migration routes and definition of oil migration fairways.

The evaluation was based on a 2D seismic sub-regional database coupled with a profound geochemical dataset. In order to assess the various aspects of the petroleum system, the following elements were evaluated: (1) source rock quality and distribution; (2) thermal history and maturation; (3) oil-source rock correlations; (4) palaeotopographic restoration and structural decompaction; and (5) reservoir distribution and connectivity. The elements were then integrated to provide a quantitative analysis of petroleum migration for the petroleum system by use of a percolation modeling approach.

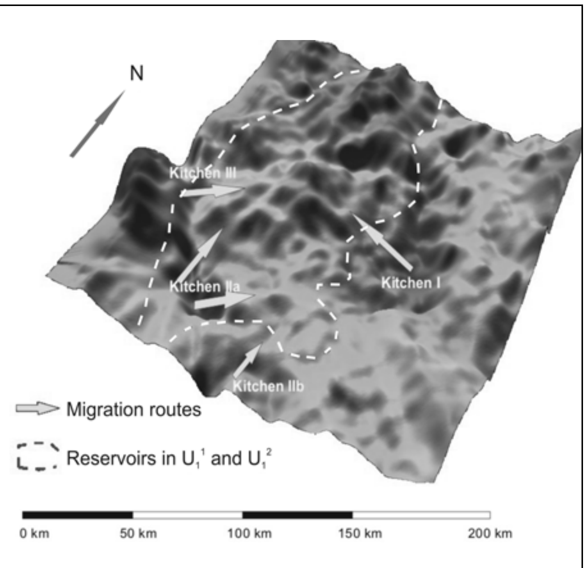
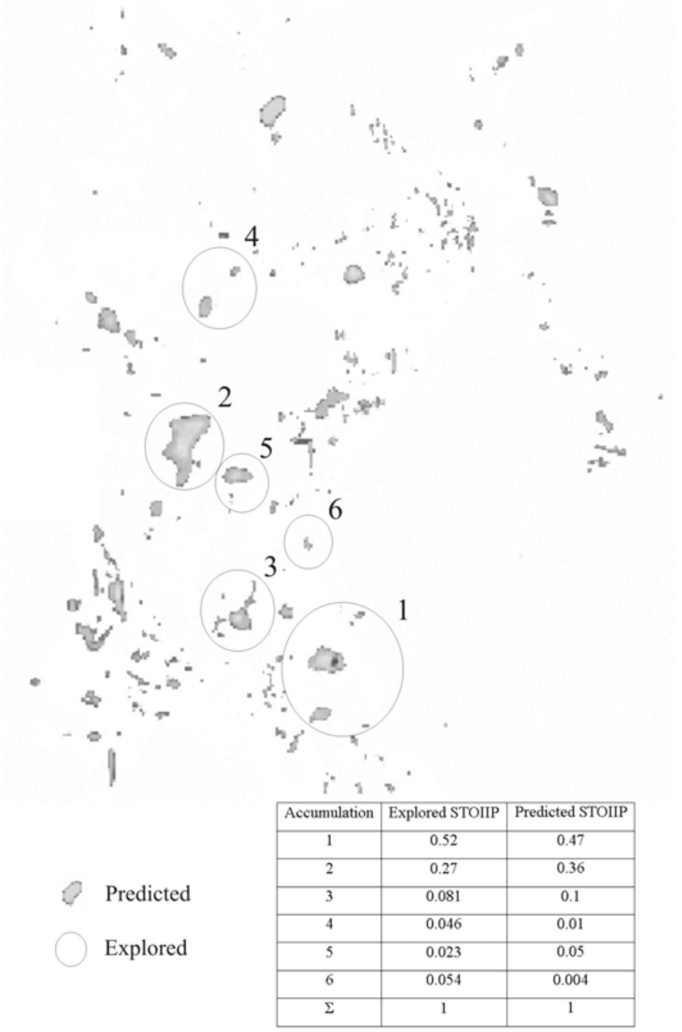


Fig.1. General migration routes

The majority of discovered fields lie on local highs. Migration modeling demonstrates that they were filled by oil generated from a number of depressions. The migration paths are suggested to be stratigraphically downwards from the Volgian, Bazhenov Formation source rock into the Oxfordian, Vasyugan Formation sandstones.

Besides the qualitative appraisal of migration routes and petroleum presence, petroleum accumulations were quantitatively estimated using the model-based approach. Since conventional fluid flow modeling approaches based on the full D'Arcy Law is computationally ineffective for models containing more than a few million cells, i.e. for typical basin scale models, a computational approach based on invasion-percolation technique was employed [1]. It honors a special gravity and capillary dominated flow regime of petroleum migration.

Our study suggests that oil migrates vertically downwards from the Bazhenov Formation source rock into adjacent sandstones, from where lateral migration occurs within the Upper Jurassic U_1 Formation sandstones. Thereafter petroleum moves up-dip in and may migrate from one reservoir level to another depending upon lithological “windows” in interformational seals. Major fill–spill routes are a common feature of this prolific petroleum province. It was concluded that three separate kitchen areas contributed filling traps of the srtudied area (fig.1). Besides that, possible prospects confined to beach sand reservoir pinchout, in U_1^2 and U_1^1 (Vasyugan Formation) have been predicted and probable STOIIP values have been assessed (fig.2).



Accumulation	Explored STOIIP	Predicted STOIIP
1	0.52	0.47
2	0.27	0.36
3	0.081	0.1
4	0.046	0.01
5	0.023	0.05
6	0.054	0.004
Σ	1	1

Fig.2. Predicted and explored discoveries

Thus a multi-layer, multi-directional, migration system has been understood using a 3D geological-based model. Combination of geochemical and petrophysical data provided additional information and supported model predictions. The key to successful modeling lay in having sufficiently accurate data available to build realistic geological models for this area.

For the first time it has been possible to quantitatively assess and visualize the complex petroleum system of the area and to gain an insight into how this system may have developed through geological time.

References

[1] Carruthers, D. J., 2003. Modeling of secondary petroleum migration using invasion percolation techniques, in Duppenbecker, S., and Marzi, R., eds., Multidimensional basin modeling, AAPG. Datapages Discovery Series No. 7, pp. 21-37.

PPM-5: Isotopic fractionation effect of primary migration in simulation experiments of selected terrestrial source rocks

Y. Liao, A. Geng

The State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Wushan, Guangzhou 510640, P.R. China (e-mail: liaoyh@gig.ac.cn; asgeng@gzb.ac.cn)

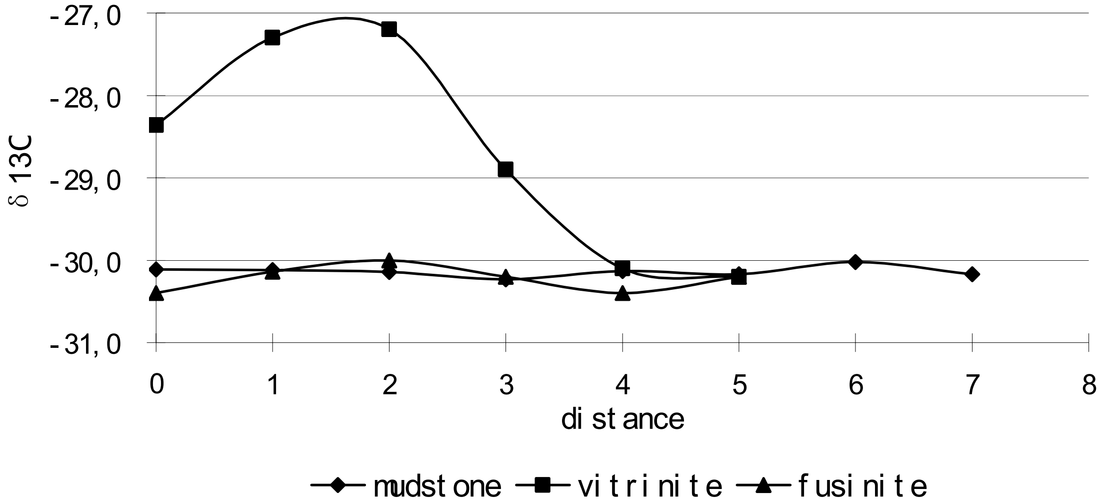
Previous Data ([1]) shows that there exists isotopic fractionation effect in expulsion of petroleum from terrestrial source rocks, especially for vitrinite-rich coals. The isotopic compositions of expelled n-alkanes are lighter than those of extracted n-alkanes from pyrolysis residue, especially for vitrinite-rich coal. In this simulation system the hydrocarbons generated early may be expelled out early, so both maturation and adsorption-desorption process may contribute to isotopic differences between expelled n-alkanes and extracted n-alkanes from residue. It is hard to tell how much of such isotopic difference is contributed by maturation and how much is contributed by adsorption-desorption process in primary migration just from these data.

A simulation experiment in the same semi-close system is designed to make clear how much the isotopic fractionation effects are contributed by adsorption-desorption process in primary migration. A mudstone, a vitrinite-rich coal and a fusinite rich coal were chosen for the simulation. All the source rocks are powdered to 80 mesh and then soxhlet extracted for 72 hours with chloroform. 25 mg deuterated normal pentadecane (n-$C_{15}D_{32}$) was added into 5g extracted source rocks as petroleum source layer (layer 0). The powdered extracted source rocks were than placed into a cylinder to make a distance for primary migration. It was separated into several migration layers and they were termed increasing numbers according to their distance from source layer. Each migration layer is about 1.8-2.0 cm thick. The system was kept isothermal and the pressure is 700atm. The gas and liquid products can flow out of the system through a hole at opposite direction to the source layer. All layers were powdered and soxhlet extracted and the n-$C_{15}D_{32}$ of each layer was examined by GC-C-IRMS.

For the mudstone after the system was kept isothermal at 320° for 36 hours about half of the n-$C_{15}D_{32}$ was expelled out of the system and some of the n-$C_{15}D_{32}$ was retained in the source layer and migration layers, respectively. The $\delta^{13}C$ of the n-$C_{15}D_{32}$ that are remained in each layers are very alike, no obvious isotopic fractionation effect exist.

After vitrinite was kept at 320° for 168 hours the n-$C_{15}D_{32}$ almost didn’t migrate because of the strong adsorptive capacity. To desorb the n-$C_{15}D_{32}$ from vitrinite and make it move in migration layers, new vitrinite was tested and the temperature was increased to 350° and kept isothermal for 96 hours. For the $\delta^{13}C$ of n-$C_{15}D_{32}$ in vitrinite, layer 1 is -27.3‰, layer

4 and expelled n-$C_{15}D_{32}$ are both -30.1‰. N-$C_{15}D_{32}$ in layer 1 is around 2.8 ‰ richer in ^{13}C than layer 4. For vitrinite the isotopic fractionation effect in primary migration is large. The adsorptive capacity of the fusinite is weak, about half of the n-$C_{15}D_{32}$ was expelled out after 8 hours at 320°, isotopic fractionation effect is not obvious.



isotopic fractionation effect in primary migration

For comparison, n-$C_{15}D_{32}$ was also sealed in glassy tubes and kept isothermal at 320° and 350° for 72 hours, respectively. Cracking of the n-$C_{15}D_{32}$ exists at both 320° and 350°. The δ^{13}C values become a little heavier, -30.0‰ at 320° and – 29.9‰ at 350°, the original n-$C_{15}D_{32}$ is -30.5‰. Cracking makes n- $C_{15}D_{32}$ about 0.6‰ richer in ^{13}C at 350°.

Simulation experiments above suggest that scatter of hydrocarbons in source rocks can cause isotopic fractionation effect in those rocks having strong adsorptive capacity and poor generation potential like vitrinite, liquid hydrocarbons are difficult to expel out and thus isotopic fractionation effect may exist in primary migration. For mudstones that have good oil potential and poor adsorptive capacity, there is no obvious isotopic fractionation effect. In geological conditions, much hydrocarbon generates before expulsion, usually oil phase primary migration is the major way and diffusion is not significant, the chromatography-like effect is small and the isotopic fractionation effect may be much smaller than in experiment.

References

Yuhong Liao, Ansong Geng, Yongqiang Xiong, Dehan Liu, Jialan Lu, Jinzhong Liu, Haizu Zhang, Xinhua Geng, 2004. The influence of hydrocarbon expulsion on carbon isotopic compositions of individual n-alkanes in pyrolysates of selected terrestrial kerogens. Organic Geochemistry 35, 1479-1488.

PPM-6: Investigation on hydrocarbon migration direction of the Silurian Paleo-pools in Tarim basin, Northwest China

L. Luofu[1,2], H. Hoiland[2], H. Hong[1], C. Lixin[1], C. Yuanzhuang[1], Z. Suping[1], L. Chao[1], L. Shuangwen[1]

1) Key Lab for Hydrocarbon Accumulation Mechanism in Petroleum University, Ministry of Education; Basin and Reservoir Research Center, University of Petroleum, Beijing, China, 102249
2) Department of Chemistry, University of Bergen, Allegt. 41–N-5007, Bergen-Norway

Tarim Basin is a multi-cyclic superimposed basin, and in geologic history, it underwent intense tectonic destruction of several times. This results in difficulties in the study of migration of hydrocarbons, especially the hydrocarbons generated in the Early Paleozoic. The present research achievements show that the first-stage oil-gas pool formation both in the Tazhong and Tabei Uplifts of the Tarim Basin took place in the later Caledonian period (mainly at the end of Silurian), and these hydrocarbons are the products generated and expelled from the Middle—Lower Cambrian source rocks and were trapped mainly in Silurian and Ordovician reservoir beds. Both Tabei and Tazhong areas had incipient uplifting at the end of Ordovician or even earlier, and during the later Caledonian their structural heights were increased largely, i.e. the formation time of these two uplift areas should be earlier than that of the first-stage oil-gas pool formation, which provided a favorable geological background for migration and accumulation of hydrocarbons from the basin platform to the uplifts. After the first-stage oil-gas pool formation, Tazhong and Tabei areas rose in a large scale and suffered serious denudation. This caused the Silurian paleo oil-gas pools to be damaged in varying degree in the Devonian period, resulting in the loss of hydrocarbons and the residual of heavy components, forming the widely distributed asphaltic sandstones. Therefore, the asphalts in the Silurian sandstones should keep information about the basin's first-stage oil-gas pools formation, and a detailed study on the geological and geochemical characters of the Silurian asphalts is of significance in understanding the hydrocarbon migration direction and distance.

The hydrocarbon reservoir formation in the Areas around Awati Sag was in Hercynian period. In Hercynian, the Manjiaer Sag rose and the Awati Sag subsided, and the latter became the major oil-generation sag. In the later Hercynian, the formed Silurian hydrocarbon reservoirs around Awati rose to the surface and were denuded into asphaltic sandstones.

The neutral nitrogen compounds of carbazole-type have proved to be a useful geochemical index for hydrocarbon migration studies through several years' exploration activity because of their stability and difference of polarity. In this paper, the migration direction of hydrocarbons is studied by making use of the characteristics of carbazole-type compounds, which entered the Silurian reservoirs of the Tazhong and Tabei areas during the first-stage oil-gas pool formation period and of the Areas around Awati Sag during the second-stage, aiming to supply data for study of the formation mechanism of paleo pools and for the establishment of hydrocarbon pools formation model. Totally 60 rock samples of the Silurian asphaltic sandstones were collected and were analyzed by Gas chromatography—mass spectrometry, etc. Results from this paper have shown that carbazole-type nitrogen compounds have a high thermal stability and are relatively stable towards oxidation and bio-degradation, and they still have large amounts and complete distribution of homologues in the dry asphalts. These compounds are of significance in the study of hydrocarbon migration of paleo-pool. The parameter of carbazole-type amount is the most powerful one; the trimethyl carbazole (A)/(C), benzocarbazole [a]/[c] and alkyl carbazole/(alkyl carbazole+ benzocarbazole) ratios also show a satisfactory effect.

Based on this study and the comparison with some Chinese basins, one can find that the hydrocarbons trapped in Silurian reservoirs in the basin platform (Tazhong and Tabei) of Tarim during the first-stage oil-gas pool formation and those in the Areas around Awati Sag during the second-stage pool formation underwent long distance migration. They migrated vertically through the thick Cambrian, Ordovician and part of Silurian. More importantly, these hydrocarbons underwent long distance lateral migration from the source areas (middle─lower Cambrian in Manjiaer Sag and Awati Sag, respectively) to the Silurian reservoirs in the two uplifts of Tazhong and Tabei, and the Awati Sag's margins.

During formation of the Silurian paleo-pools in the Tazhong Uplift at the end of Silurian, the hydrocarbons were mainly from the middle─lower Cambrian source rocks in Manjiaer Sag, and they migrated towards southwest─south entering the Tazhong Silurian reservoirs first, then further migrated along the Silurian reservoirs in two directions, from northwest to southeast along the high positions of the Structural Belts, and from northeast to southwest, respectively, towards the Silurian pinchout boundary in Tazhong (i.e. migrated in the updip direction). Hydrocarbons may also have migrated vertically along faults in short distance from the Cambrian directly located under the Tazhong to the Silurian reservoirs.

The hydrocarbons in the Silurian of Tabei Area also underwent a long-distance migration during formation of the Silurian paleo-pools at the end of Silurian. The hydrocarbons were mainly from the middle─lower Cambrian source rocks in Manjiaer Sag, and they migrated towards the northwest entering the Tabei Silurian reservoirs first and then continued to migrate towards the northwest into traps along the Silurian reservoir beds.

The hydrocarbons in the Silurian paleo-pools around Awati Sag were mainly from the lower─middle Cambrian source rocks in Awati Sag during Permian, and these hydrocarbons migrated from the generation center to the marginal areas of the Sag in every direction.

PPM-7: Change of geochemical parameters during phase behaviour of oil

D.H. Luong, Y.V. Savinykh, P.D. Hai, V.I. Urmancheev, T.L Dong

105, Le Loi Street, Vung Tau City, NIPI, J.V.Vietsovpetro, Vietnam

The understanding of phase differentiation of oil components during production has great value for successful exploration of a hydrocarbon basin. Results of biomarker analysis of oil from the "abnormal" well H003 in the White Tiger oil field (Vietnam) are presented in this paper. Analysis of oil sample taken the top of the well at the moment of its first opening (the sample is named H003top) has shown high content of light fraction and low oil density (0,80 g/sm^3, against 0,83 g/sm^3 for oil in the surrounding wells). In our opinion, it has taken place because the saturation pressure of the oil was equal to or greater than pressure in the well. The oil sample from bottom of the well taken in 6 months later (the sample is named H003bottom) has the same density as oils in the surrounding wells. Main objective of this study is to examine the effect of phase behaviour of oils on their geochemical features.

Analyzing the geochemical parameters of the oil samples we have the following two conclusions:

- The values of geochemical parameters are *identical* for oils H003top and H003bottom. These parameters are geochemical indexes Pr/Phy, Pr/nC_{17}, Phy/C_{18}, MPI-1, $T_s/(T_s+T_m)$. These indexes showed that the oils were formed in similar depositional environment and have identical thermal maturity level. In triangle diagram in coordinates: the content sterane C_{27}-C_{28}-C_{29} for oils H003top and H003bottom are located in the same area that is evidence of a simple source of initial organic matter.

- The value of parameters *varies* from samples H003top and H003bottom. Oil H003top is more enriched with light fractions and sulfurous components. Geochemical parameters (Indexes: C_{23}Heilantane/C_{30}Hopane, Hopane/Sterane, 4-MeC_{30}Sterane, Oleanane/Hopan) are different for samples H003top and H003bottom. The triangle diagram in coordinates: content Normal C_7 - Mono Branched Alkanes - Poly Branched Alkanes shows position of oils H003top and H003bottom in various areas of the diagram that specifies a various level of their transformation. These results indicate that oils H003top and H003bottom possibly had different sources of organic matter and were formed in different depositional environment and thermal maturity.

Thus, geochemical parameters of oil depend on sampling condition and first of all, phase behaviour of oils.

PPM-8: Understanding synchronisation and migration processes associated to the Caribbean Tectonic during the Oligocene to Miocene in Eastern Venezuelan basin

C. Olivares, W. Rodriguez, L. Duerto, I. Rojas, J. Noya

Petróleos de Venezuela. División Oriente Puerto La Cruz. Edo. Anzoátegui. Estudios Regionales. Gerencia Técnica de Exploración (e-mail: Olivaresck@pdvsa.com)

The presence of all essential elements (source, reservoir, and seal rocks, and overburden) and processes (trap formation, generation and migration) required for a petroleum system to exist does not necessarily ensure the presence of hydrocarbon accumulation. A timely convergence among such elements and processes, as well as appropriate preservation conditions, are also crucial factors for the existence of hydrocarbon reserves.

Due to the complex tectonic evolution of the Eastern Venezuelan Basin during Meso-Cenozoic times, it underwent multiphase source rock burial and trap development histories, bringing some difficulties in the estimation of timing between hydrocarbon charge and trap formation. An integrated approach that encompassed basin modelling techniques (1D and 2.5D) as well as structural information was applied in the northwestern side of the eastern Venezuelan mountain front in order to understand the spatial and temporal relationships among the elements and processes of the petroleum systems involved.

Oil-seep-source rocks correlation studies have been proven so far (Stouffer *et. al*., 1998, Vivas, 1999, among others); in order of importance, the chances for oil and gas generation in the area is as follows: 1. - Type-II oil marine prone Upper Cretaceous; 2. - Type- III-terrestrial gas prone Oligocene, and 3. - Type II/III gas-oil prone Early Miocene. An integrated geochemical and geological model has been developed to reconstruct the expulsion, migration and entrapment history of hydrocarbons of the former source rocks in one structure located at the Northweast side of the Eastern Venezuelan mountain front.

This structure is an anticline located at the Southeast of Barcelona, with the Urica lateral fault system towards the North, and the Capiricual *inverse* fault towards the South, acting as its main limits. In this area extension occurred during the Early Paleogene, when it was partially inverted at the end of the Oligocene-Early Miocene. A mild inversion together with anticline formation and partial erosion occurred during the Early Miocene. At the time of Middle Miocene the most important compressive event in this area occurred, during which the Maturin foredeep (Di Croce, 1995) and the Interior Foothills were formed (Chevalier *et al*., 1995).

The stratigraphic sequence preserved in the area contains abundant potential reservoir and seal rocks, including Cretaceous, Paleogene and Neogene intervals. Erosion and uplift (*ca*. 10-12My) are the main factors that impact the hydrocarbon generation and expulsion. Complementary 1D (3 wells and 12 virtual points were modelled using basin mod) and 2.5D models (migration maps) were used to integrate the burial and thermal histories with the kinetic parameters of the potential source rocks, providing the following times of hydrocarbon generation and expulsion: Late-Middle Eocene and Middle-Late Miocene associated to the Upper Cretaceous source rock interval, and Late Miocene to Pliocene related to the Paleogene source rock intervals. Oil and gas are the hydrocarbons expected.

In order to visualise secondary migration from the Upper Cretaceous and Late Oligocene source rocks interval, a series of migration lines tendency maps were constructed during the Middle-Late Miocene (Critic time for both source rocks and trap formation) using and integrated 2.5 Basin View-Basin Flow modelling software. The results show that migration started since 20My (for the Upper Cretaceous source rock) to charge Cretaceous and Oligocene reservoirs and at 15My for the Early Miocene reservoirs, following the structural dipping of the area towards the N-NW where the Capiricual structure has been interpreted. For the Late Oligocene source rock, migration started at 11My and reaches the structure at 8My and is concentrated towards the depocenters located at the N-NE of the area. These findings point out to an effective synchronisation for hydrocarbon charge in the structure interpreted.

References

CHEVALIER Y., E. ÁLVAREZ & G. HERNÁNDEZ. 1995. A transverse section from the Orinoco Oil Belt to the El Pilar Fault System. IX Congreso Latinoamericano de Geología, Caracas. Guía de excursión, Nov. 9-10.

STOUFFER, S., MELLO, M.R., SANCHEZ., H., CHIGNE, N. 1998 “Geochemical Characterisation of crude oils from Eastern Venezuelan Basin” .AAPG International Conference and Exhibition. Extended Abstract. Río de Janeiro, Brazil.

VIVAS. M.A. 1999 Caracterización Geoquímica de Rocas e Hidrocarburos Líquidos y gaseosos como fundamento de los Sistemas Petroleros en la región norcentral de la Cuenca Oriental de Venezuela. Tesis de Maestría. Universidad Federal de Río de Janeiro.

DI CROCE, J., 1995, Eastern Venezuela Basin:Sequence Stratigraphy and structural evolution, PhD Thesis, Rice University, 225 pp.

PPM-9: Estimating hydrocarbon expulsion from the Shahejie formation in the Niuzhuang South Slope of Bohai Bay basin, E China

X. Pang[1], M. Li[2], S. Li[1,2], Z. Jin[1,3]

1) Key Laboratory for Petroleum Formation Mechanisms of the Chinese Ministry of Education, Petroleum University (Beijing), Changping, Beijing 102200, China (e-mail: pangxq@bjpeu.edu.cn)
2) Geological Survey of Canada, 3303-33 Street NW Calgary, Alberta T2L 2A7, Canada
3) SINOPEC Petroleum E&D Research Institute, Beijing, China

A potential source rock becomes an effective hydrocarbon generator and expeller only after it reaches sufficient burial depth and a maturity level beyond the “hydrocarbon generation threshold”. This concept is the basis for identifying the effective petroleum source rocks by oil-to-source rock correlation of geochemical parameters. In recent years, however, the generation of hydrocarbons at abnormally low thermal maturity has been proposed, resulting in so-called “immature oils” that contain unstable biomarker configurations normally found only in immature sediments. To the best of our knowledge, previous studies of “immature oils” deal with evidence for possible early generation, but the discussions seldom touch upon key issues related to the hydrocarbon expulsion thresholds and the quantitative importance of hydrocarbons generated from immature *versus* mature source rooks.

The Niuzhuang South Slope, located in the Dongying Depression of Bohai Bay Basin is one of the most important petroleum provinces in China that have been reported to produce “immature oils”. It was suggested that oils produced from the Bamiange Field originated from shallow algae-rich Es_4 shales of the Eocene-Oligocene Shahejie Formation, with maximum burial depth of less than 2700 m (or <0.5% Ro). The suggested source area is distributed between the Bamianhe and Wangjiagang fields and does not include the mature source kitchen in the Niuzhuang Sag. Immature SOM that had never been incorporated into kerogens was thought to have contributed over 75% of the identified oil reserves in this field, whereas the remainder was attributed to mature source rocks.

We described the distributions and diagnostic molecular features of petroleum source rocks in the study area (Li et al., 2003, Organic Geochemistry 34, 389-412). Based on detailed examination of crude oils from the Bamianhe Field, we demonstrated that the suggested source for the immature oils was not supported by molecular parameters across different oil fractions (Pang et al., 2003, Organic Geochemistry 34, 931-950). In this paper, we present a quantitative evaluation of hydrocarbons generated and expelled from all possible source rocks in the studied drainage area. Expulsion intensities for all of the source rock units were contoured, using an in-house developed software package. The intensity of hydrocarbon expulsion is controlled by several geological factors, including source rock thickness, TOC content, kerogen type, and thermal maturity. Our results show that hydrocarbon expulsion intensity for the mudstones in the Es_4 member of the Shahejie Formation increases with increasing burial depth toward the Niuzhuang Sag, whereas the shales (dominantly oil shales) within the same stratigraphic interval along the South Slope have much lower expulsion intensities due to their smaller thickness. The lower and middle parts of the Es_3 members of the Shahejie Formation generally show higher combined values of the expulsion intensities than the Es_4 member at any location. The oil shales and mudstones have different centers of hydrocarbon expulsion. In addition, the upper part of the Es_3 member displays little hydrocarbon expulsion potential due to its generally low thermal maturity. Two observations can be made from the above data. First, the Es_4 shales, Es_4 mudstones, Es_3 shales, and Es_3 mudstones roughly contribute 8, 42, 16 and 34% of the total expelled hydrocarbons, respectively. Thus, mudstones rather than oil shales are the most important source rocks. Second and perhaps more important, the proportions of the expelled hydrocarbons from the shallow source rocks (<2700 m depth) account for less than 0.1% to 17 % of the total estimated hydrocarbon expulsion in each straigraphic unit. Thus, while the saline to brackish water lacustrine Es_4 shales along the Niuzhuang South Slope generate and expel some hydrocarbons during early thermal maturation, their proposed effectiveness as a major source for economic oil accumulations in the Bamianhe field needs to be reevaluated.

PPM-10: Petroleum migration and accumulation in Gaoyou depression, East China

Y. Zheng[1], H. Huang[2], Y. Wang[1]

1) China University of Mining and Technology, Beijing, 100083 (e-mail: my.lu185@126.com)
2) China University of Geosciences, Beijing, 100083

The intention of this paper is to investigate the feature of petroleum migration and accumulation in Gaoyou Depression, East China. There are three difference source rocks and associated oils in it. The composition of oil influenced by the depositional environments, degree of thermal maturation, mixing and secondary alteration etc. Depositional environments and thermal maturity of organic matter with minor effects of biodegradation control the oil and gas compositions in the Gaoyou Depression.

Various geochemical methods can describe the regular changes in petroleum migration. Oil physical property variations during migration indicate the direction and pathway of oil migration. Migration coefficient proposed by Kaximov is one of methods to evaluate oil migration degree. GC-traces of saturated hydrocarbons shift regularly from back peaks dominated pattern to double-peaks or even front peak with increasing migration distances, which can be used as supplementary migration indicator. Sterane isomer ratios also reflect the characteristics of oil migration in some degree. According to light hydrocarbon migration parameters defined by Thompson, coupled with geological conditions in Gaoyou depression, four migration index of light hydrocarbons are proposed to study the characteristics of oil migration.

Dimethylcarbazoles in nitrogen-bearing compounds have three types such as “shielded”, “semi-shielded” and “exposed”. Their relative concentrations decrease with increasing migration distance but different type of isomers show different characteristics with nitrogen shielded isomer being enriched in oil phase and exposed isomers being enriched in mineral phase.

Relative concentrations between alkylated phenols in ortho position and non-ortho positions of oxygen-bearing compounds show similar variations as nitrogen-bearing compounds. Their concentrations and different isomer ratios can be applied to study petroleum migration distance. The ratios of ortho alkylated phenol to non-ortho alkylated phenols vs. depth reflects more dramatically non-ortho alkylated phenol concentrations decrease with decreasing burial depth, indicating oil migrates from deep to shallow strata. The concentrations of alkylated phenols show similar nature as these of carbazoles and are also applicable to study oil migration direction.

Three main migration-accumulation models were established on the base of secondary migration and a variety of case histories in the Gaoyou depression. One is dominated by lateral migration in reservoirs (model I), another is vertical migration along faults (model II), and the third is the combination of I and II (model III). Model I occurs generally in gentle slope zone and model II occurs more frequently in deep depression, while model III seems prevalent in all structural units.

PPM-11: Surface geochemistry from deep water offshore Brunei

M. Bjorøy[1], I.L. Ferriday[2]

1) Surface Geochemical Services AS, P.O.Box 5740, 7437 Trondheim, Norway
2) Geolab Nor AS. P.O. Box 5740, 7437 Trondheim, Norway

Surface geochemical prospecting involves the search for near-surface or surface anomalies of hydrocarbons, which could indicate the occurrence of petroleum accumulations in the sub-surface. The methodology, as applied in offshore basins, covers a range of techniques, from observation of visible oil seepage at the surface to detection of micro-seeps in near surface sediments using sensitive analytical techniques. This paper shows the results from a detailed analytical study in deep water offshore Brunei, where the analytical results are discussed and the surface geochemical results are integrated with the geology using 3D seismic.

A surface geochemical study was undertaken over the deep water area offshore Brunei in 2001, on behalf of the Petroleum Unit of Brunei. The planned sample locations were partly based on a 3D survey undertaken over a part of the study area closest to shore and partly based on a regional 2D survey for the area furthest from shore. A total of 200 first-priority sample locations and 13 second-priority locations were selected. Of these, 189 cores were recovered having sufficient material for geochemical analyses, from an average water depth of 1640 m. Sampling was undertaken using a gravity corer with a 4 m core barrel, the average core length being 3.2 m. Three of the cores contained gas hydrates, which were also collected for analysis. One of the cores contained oil, so abundant as to be exuding from the core liner after the core had been brought up on deck. A strong smell of hydrocarbons was detected in approximately 20 cores. Samples from the anoxic part of the cores were collected, put in pre-cleaned cans, flushed with nitrogen, sealed and frozen to – 80 °C within minutes after the cores were retrrieved. After the survey was completed the samples were packed into special cooler boxes with dry ice for transport to the laboratory.

A complete geochemical analysis program was undertaken, i.e. headspace-, occluded- and adsorbed gas GC, TOC and TC of the clay/silt (< 63 μm) fraction, solvent extraction, and GC and TSF analysis of the extract (EOM). Following this, GC-IRMS of gases and GC-MS of the EOM was performed on those samples that showed indications of petrogenic hydrocarbons.

The abundance of gases in the headspace gas, the occluded gas and the adsorbed gas are lower than what is normally found for other studied areas, e.g the North Atlantic and the Barents Sea, Bjorøy and Ferriday, (2001). The abundance of adsorbed gas is particular low. Similar low abundances of adsorbed gas have also been recorded in other areas of the South China Sea, Abrams, (1996). This was previously interpreted to signify that there were no active seeps in the area. Our study shows this to be incorrect for the area studied. The present data shows that the percentage of mineral (carbonate) carbon in the < 63 µm fraction is markedly lower in the offshore Brunei samples compared with what is found for other areas, e.g. the North Atlantic and the Barents Sea. Similar low abundances are also found in other samples from the South China Sea. The lower abundance of adsorbed gas is therefore possibly due to a low abundance of carbonate, and lower adsorbtive capacity for the sediments of this area. A number of samples show active seepage of gaseous hydrocarbons. Before the survey was undertaken, the general belief was that the deep water area offshore Brunei would be a gas province at best. None of the analyzed samples in this study contained dry petrogenic gas. The samples having petrogenic gas contained oil-associated gas based on the composition and stable carbon isotope values of the gases.

Based on the GC analyses, a total of 40 samples contained seeped, variably biodegraded liquid hydrocarbons. Some of these samples were already described as containing live oil during the sampling.

GC-MS analyses of both biomarkers and aromatic compounds were undertaken on the EOM of all the samples that were interpreted from the gas chromatograms to contain seeped hydrocarbons. These data show the hydrocarbons in all the registered seeps to have been generated from the same terrestrial/deltaic type of source rock. There is, however, a large variation in the maturity of the liquid hydrocarbons, from the lower part of the oil window to the condensate window. Some locations situated close together show seeps with a significant variation in the maturity that would indicate more than one source rock formation in the basin, but with the same type of kerogen.

Based on all the analytical data, an evaluation of the sample sites was undertaken. A map showing the summary results from this is shown in Figure 1. Registered seeps have been tied in with structures determined from the 3D seismic. Some of these structures have been drilled after the survey was undertaken. At the time of writing the abstract, there has been considerable agreement between the drilling results and the results of the surface geochemical survey.

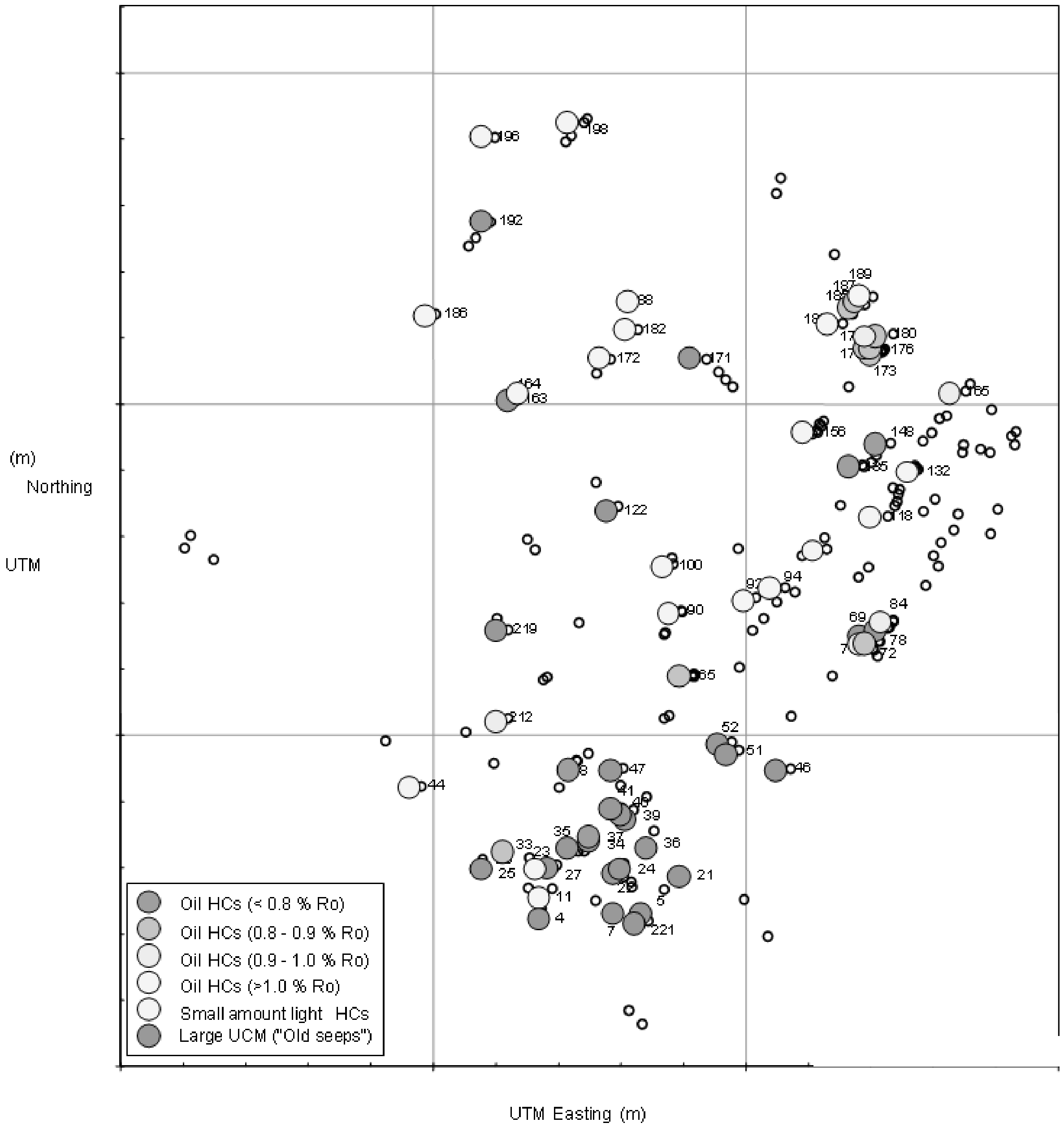


Fig.1. Summary Map of Hydrocarbons in Cored Sample Sites, Offshore Brunei

PPM-12: The origin of hydrocarbons in the Gorleben salt dome, a 3D basin modelling study

B. Cramer, P. Gerling, O. Bornemann

Federal Institute for Geosciences and Natural Resources (BGR), Hannover, Germany
(e-mail: B.Cramer@bgr.de)

The Gorleben salt dome in Lower Saxony, Germany, is a more than 10 km long wall shaped halokinetic structure built up with evaporitic rocks of Upper Permian age (Zechstein). In the last decades the Gorleben salt dome was investigated intensively for evaluating its potential as repository for nuclear waste.

As it is generally known from salt mining, also in salt from Gorleben natural gas and liquid hydrocarbons were recovered. These comparatively small amounts of petroleum were found locally as separate phase or more closely bound to the rocks where they had to be release through dissolution of the salt. In most cases geochemical analysis of the hydrocarbons prove their thermal origin. Molecular composition and stable carbon isotope analysis of the natural gas point to a source rock dominated by marine sedimentary organic matter within the oil window (0.8 to 1.2 % Ro). Because no relevant source rock is known from the sedimentary strata within the rim synclines of the diapir the hydrocarbons were proposed to origin from below the base of the salt. Possible source rock formations are the organic rich Stassfurt-Carbonate at the base of the evaporitic sequence and the Permian marine shale Kupferschiefer.

To investigate the importance of these source rocks, the timing of petroleum generation, and the processes of hydrocarbon migration into the diapir, an integrated 3D basin modelling (PetroMod, IES Jülich) was applied for the Gorleben salt dome and adjacent areas. In a cube of 20 x 20 x 4 km the geological history was reconstructed laying special emphasis on the timing of salt movement. For this purpose, thickness variations in the rim synclines of the salt structure were investigated in detail to calculate changes in salt thickness. The thermal history of the salt dome was reconstructed using vitrinite reflectance data from two deep wells penetrating the domes flanks.

As a result, the ascending Gorleben salt structure is shown to act as important thermal anomaly since more than 200 million years. In consequence, maturity of organic matter at the base of the salt structure today clearly displays the areas of the former primary salt pillow and of the recent salt dome. The modelled maturity range of both proposed source rock formations matches the vitrinite reflectance values derived from natural gas geochemistry. Both formations generated petroleum in the same order of magnitude. Migration into the surrounding rocks through phase flow of hydrocarbons was restricted. The Kupferschiefer was effectively sealed at the top preventing larger scale upward movements of petroleum. This finding coincides with the molecular composition of condensates which argue for only minor contributions of hydrocarbons from pre-Zechstein source rocks.

The most intense petroleum generation from the Stassfurt-Carbonate proceeded during the Upper Jurassic (Malm). At this time the primary salt pillow reached its maximum extent and the basal rocks entered their deepest burial. Because of the comparatively low content of organic matter, even at that time the Stassfurt-Carbonate did not produce enough hydrocarbons to initiate an effective expulsion. With the break-through of the salt dome during the Upper Jurassic, hydrocarbon generation in the sediments ceased. The subsequent halokinetic movements incorporated also rocks of the Stassfurt-Carbonate into the diapir. With this mass movement of the source rock petroleum was locally squeezed into the surrounding salt.

In conclusion, the hydrocarbons found in the evaporitic sequences of the Gorleben salt dome today origin from the Stassfurt-Carbonate and are older than about 150 million years. They migrated through the tight salt into the diapir mainly through the mechanism of halokinetic movement of the source rock. A mass balance for the entire model results in a maximum average hydrocarbon concentration in the salt dome of about 40 ppm by weight.

PPM-13: Competing mechanisms of geochromatography

C. Hallmann[1], K. Arouri[2,3], D. McKirdy[2], L. Trindade[4], L. Schwark[1]

1) Geological Institute, University of Cologne, Germany (e-mail: Hallmann.C@gmx.net)
2) Geology & Geophysics, School of Earth & Environ. Sci., University of Adelaide, SA 5005, Australia
3) Department of Geology, United Arab Emirates University, Al-Ain, UEA
4) Petrobras-CENPES, Rio de Janeiro, Brazil

During the primary and secondary migration of petroleum, fractionation occurs on a molecular level due to preferential adsorption of certain molecular species on mineral phases, water or solid organic matter. This process was termed *geochromatography* by Kroos *et al.* [1]. Although Mackenzie *et al.* [2] recognised the fractionation of *n*-alkanes during expulsion, most subsequent studies have focussed on polar species such as phenols, quinolines and carbazoles, the latter being the most prominent.

Fractionation of alkylcarbazoles has been attributed to the degree to which alkyl groups shield the nitrogen atom that has the ability to form hydrogen bonds with cations in clay minerals and solid organic matter. The fractionation of benzocarbazoles, as expressed by the benzocarbazole *a/(a+c)* ratio, however, breaks this rule since the nitrogen-exposed benzo[c]carbazole was observed to become enriched in oils upon migration, relative to the nitrogen-shielded benzo[a]carbazole. Other fractionation mechanisms must thus be active. Larter *et al.* [3] noted a difference in the effective dipole moment and geometry of the rod-shaped benzo[a]carbazole versus the sub-spherical benzo[c]carbazole.

Observations made during studies of the distribution of carbazoles in oils from the Recôncavo Basin (Brazil) and the Cooper/Eromanga Basins (Australia) shed further light on the fractionation of benzocarbazoles.

Oil samples from the Recôncavo Basin, Brazil, exhibit a strong positive correlation between the benzocarbazole *a/(a+c)* and the 1-/9-methylphenanthrene ratios, suggesting a size-exclusion fractionation effect. Benzo[a]carbazole and 1-methylphenanthrene fit into “natural molecular sieves” and are successively filtered out of a migrating oil charge. Coaly source rocks from the Cooper/Eromanga Basin exhibit a decreasing benzocarbazole a/(a+c) ratio with increasing maturity.

We suggest the possibility of competing fractionation mechanisms. In source rocks that contain abundant organic matter, like coaly source rocks in the Cooper and Eromanga Basins, the size-exclusion effect might be outcompeted by hydrogen bonding on solid organic matter. This will lead to benzocarbazole a/(a+c) ratios that decrease with increasing maturity, which is in contrast to the trend generally observed in clastic source rocks. The dominating mechanism might be ultimately determined by the characteristics of the source rock, in particular its concentration of dispersed organic matter, its pore size distribution and the availability of cations for binding of hydrogen.

References

[1] Kroos, B.M., Brothers, L. and Engel, M.H. (1991) Geochromatography in petroleum migration: a review. In: England, W.A. and Fleet, A.J. (Eds), Petroleum Migration. Geological Society Special Publication 59, 149-163.
[2] Mackenzie, A.S., Price, L., Leythaeuser, D., Muller, P., Radke, M. and Schaeffer, R.G. (1987) The expulsion of petroleum from Kimmeridge Clay source rocks in the area of the Brae Oilfield, U.K. Continental Shelf. In: Brooks, J. and Glennie, K.W. (Eds), Petroleum Geology of North West Europe. Graham and Trotman, London, pp. 865-877.
[3] Larter, S.R., Bowler, B.F.J., Li, M., Chen, M., Brincat, D., Bennet, B., Noke, K., Donohoe, P., Simmons, D., Kohnen, M., Allan, J., Telnaes, N. and Horstad, I. (1996) Molecular indicators of secondary oil migration distances. Nature 383, 593-597.

PPM-14: Identifying diagnostic compositional features in gasoline range hydrocarbons using genetic algorithm optimisation with procrustes criterion

N. Pasadakis[1], K.G. Osadetz[2], M. Obermajer[2], A. Kardamakis[1]

1) Mineral Resources Engineering Department, Technical University of Crete, Chania 73100 Greece
2) Geological Survey of Canada, 3303 - 33rd Street NW, Calgary, AB T2L 2A7, Canada

In this study, we have applied multivariate statistical analysis to explore the specific petroleum-petroleum correlations in Williston Basin. Petroleum system definition and analysis use composition links between petroleum and source kerogen. Compounds with relatively low abundance, high molecular weight and complicated structure, such as polycyclic alkanes, are the preferred basis for petroleum family definition. This is because the biochemical, sedimentological and physical processes singly or competitively affecting their compositional variations are well understood.

It is, however, especially important to explore the value of the more abundant and thermally stable components of petroleum in order to confirm and extend classifications and analyses that are commonly based on the low-abundance, complicated and thermally unstable biological marker compounds. Gasoline range hydrocarbons (GRHC's), up to n-octane, have been shown to carry important information regarding the source of, and processes affecting, petroleum systems in the Williston Basin (Obermajer et al., 2000). As the thermally most persistent fraction, these compounds have the best possibility of providing classification information over a wide range of thermal maturities. Principal Component Analysis refinement of the Williston Basin oils families (Pasadakis et al., 2004) documented that GRHC's can be excellent indicators for certain processes, compositional mixing in particular, enhancing overall the interpretation of petroleum systems.

Here, we present a method for the reduction of the number of original GRHC variables that shows the equivalent information regarding oil affiliation can be obtained from both a reduced number of the original GRHC compounds, as well as, from the whole data set. Most of the information and variation of the GRHC fraction compounds are carried by a restricted set of approximately 10 compositional components, while the information carried in the remaining 25, or more, commonly analysed GRHC compounds is redundant. The method used is based on the Procrustes Criterion combined with the application of Genetic Algorithms to select an optimal compositional variable subset. The proposed method was applied on both, GRHC single data sets derived from four separate, extensively studied and well defined, compositional oil families from Williston Basin, as well as on the whole data set. The restricted set of original compositional molecular species that carry most of the significant information are, more or less, consistently the same whether analyzing separate oil families or the complete set. N-octane, 3-methylheptane, methylcyclohexane, n-heptane, n-hexane, cyclohexane, benzene and toluene, among others, are the components carrying the most significant compositional information. Such analyses indicate that it may be possible to employ a universal select set of GHRC compounds to confirm biomarker-based classifications, which have been shown susceptible to errors and revision due to both mixing and thermal degradation.

References

Obermajer, M., Osadetz, K. G., Fowler, M. G. and Snowdon, L. R., (2000). Light hydrocarbon (gasoline range) parameter refinement of biomarker-based oil-oil correlation studies: an example from Williston Basin. Organic Geochemistry 31, 959-976.

Pasadakis, N., Obermajer, M. and Osadetz, K. G., (2004) Definition and Characterization of Petroleum Compositional Families In Williston Basin, North America Using Principal Component Analysis, Organic Geochemistry, 35, 453-468.

PPM-15: Crude oil predictions of source rock depositional environments help constrain paleoclimatic models

J.E. Zumberge[1], C.R. Scotese[2], S.W. Brown[1], H.A. Illich[1]

1) GeoMark Research Ltd., 9748 Whithorn Dr., Houston, TX 77095 USA
(e-mail: jzumberge@geomarkresearch.com)
2) PALEOMAP Project, 700 Tanglewood Lane, Arlington, TX 76012 USA

Marine shale, marl, carbonate and lacustrine source rock types of various geological ages can be predicted using terpane and sterane biomarkers in corresponding crude oils. Paleo latitude and longitude locations of over 1800 crude oils comprising more than 130 known petroleum systems are calculated based on the present day oil location and the age of the corresponding source rock deposition. The oils can then be plotted on appropriate rotated plate reconstructions depicting paleo topography, bathometry, SST, prevailing wind directions, and areas of upwelling. When considering paleo latitudes, carbonate source rocks throughout the Phanerozoic were deposited within 25 degrees of the paleo equator. Key tri- and tetracyclic terpane ratios potentially distinguish between warm, shallow intra-shelf source rock environments and cold, deeper-water upwelling areas of source rock deposition.

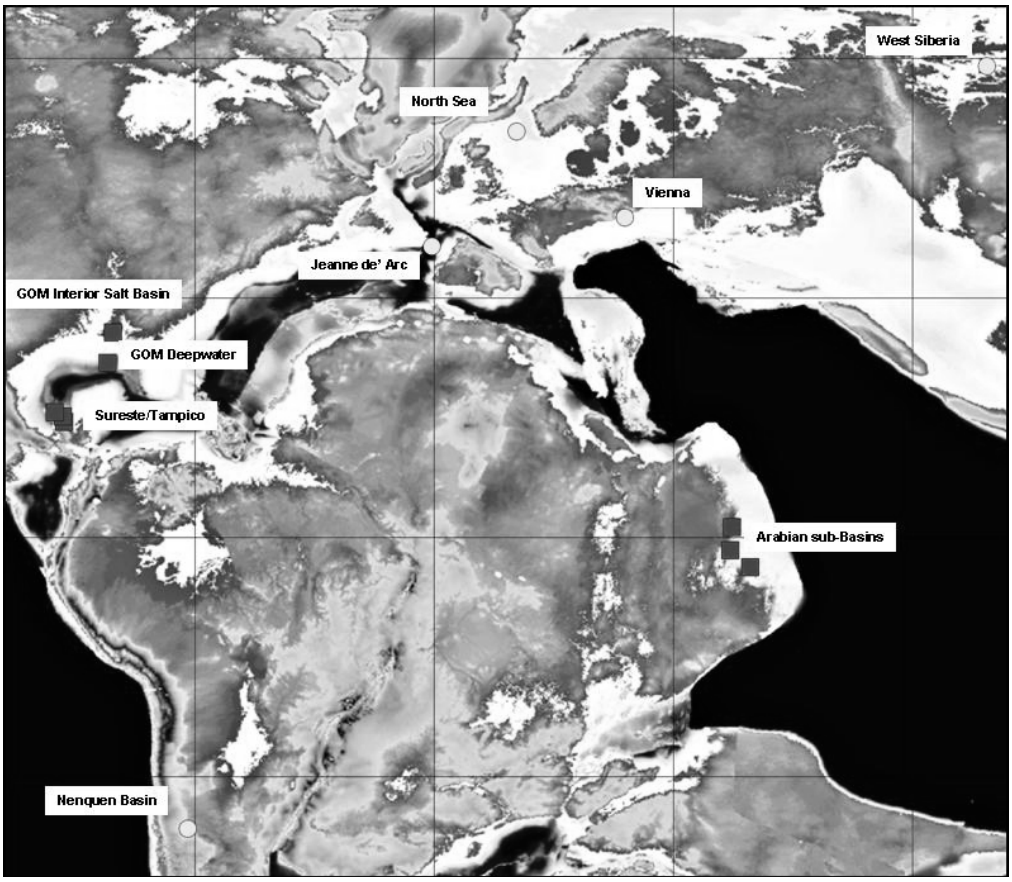


Fig.1. Upper Jurassic petroleum systems: distal marine shale (circles) and carbonate (squares) source rock environments.

PG-1: Genetic characterization of natural gases by stable carbon and hydrogen isotope composition in the Southern part of the Pannonian basin, Croatia

V. Culjak, I. Stankovic, D. Spanic, S. Cadez

INA- Oil Industry, Corporate Processes, Research and Development Sector Rock and Reservoir Fluid Research Laboratory Department, Geology and Geochemistry Section, Geochemical Laboratory, 10002 Zagreb, Lovinciceva 1, Croatia (e-mail: veronika.culjak@ina.hr)

The southern, marginal part of the Pannonian Basin is located in the Republic of Croatia. This area is a hydrocarbon producing area consisting of gas, gas-condensate and oil-gas fields. Several depressions and sub-depressions are situated in the region. The large gas and gas-condensate fields are located in the northern, central part of the Drava Depression and small gas-condensate fields were recognized in the Mura Depression, in the marginal western part of the studied areas. The Sava Depression and the eastern, elevated part of the Drava Depression are also producing areas consisting of numerous small oil and oil-gas fields.

Research on chemical components, as well as carbon and hydrogen isotopic composition of the natural gas show that gases are predominantly of thermogenic origin. Gas and gas condensate fields in the central part of Drava and Mura Depressions contain wet gases (C_{2+} 3.4 –15.7%). Stable carbon and hydrogen isotopic ratios of methane vary between ($\delta^{13}C$ –31.1 and –42.1‰; δD –157 and –167‰). According to Schoell, (1983) these gases are classified as "migrated, thermogenic condensate associated gases"([3]). The source rocks of these gases are mostly clastics from the Lower Miocene to the Badenian age. Organic facies of source rocks indicate terrigenous precursor, type III kerogen, which reached the gas-condensate window stage of thermal alteration. Gases in these fields contain inorganic constituents including CO_2, H_2S, N_2, He and Hg. Concentrations of CO_2 vary over a wide range (0.2 to 67.3%). High concentrations of CO_2 are related to carbonate rocks and specific thermodynamic conditions of reservoirs.

Gases in small gas and oil-gas fields in the eastern Drava and the Sava Depression are wet. Stable carbon isotopic ratios of methane vary in a range between $\delta^{13}C$ –39.8 and –47.9‰. For hydrogen the corresponding ratios are between δD –163 to –170‰. These gases can be classified as thermogenic, petroleum-associated gases. Geochemical data indicate the presence of oil-prone source rocks which are from the Badenian to the Pannonian age. Smaller numbers of gases are biogenic/diagenetic and mixed gases. The origin of these gases is a result of microbiological activity or mixing (combination) of thermogenic and biogenic gases.

References

[1] Baric, G., Mesic, I. and Jungwirth 1998. Petroleum geoshemistry of the deep part of the Drava Depression, Croatia. Organic Gechem. Vol 29, No. 1-3, pp 571-582.

[2] Baric, G. 1996. Organic geochemistry in the rationalization of oil and gas exploration and production. Geologica Croatica, 49(2), 191-195.

[3] Schoell, M. 1983. Genetic characterization of natural gases. American Association of Petroleum Geologists Bulletin, 67, 2225-2238.

[4] Tissot, B. P. (1984) recent advances in petroleum geochemistry applied to hydrocarbon exploration. American Association of Petroleum Geologists Bulletin 68, 545-563.

PG-2: The origin of hydrocarbon gases in the South-East of Western Siberia (Russia)

I.V. Goncharov, V.G. Korobochkina, N.V. Oblasov, S.V. Nosova, V.V. Samoilenko

TomskNIPIneft, 72 Av. Mira, Tomsk, 634027, Russia (e-mail: GoncharovIV@nipineft.tomsk.ru)

Many oil and oil-gas condensate fields have been explored on the territory of Tomsk region which is a part of Western Siberia. GOR of these fields varies from 27 to 170 m^3/t (in average among the fields) with the exception of gas condensate fields. Composition of gases varies sharply but the main component remains methane. Methane content lies in the range from 50 to 85 %vol. Therefore, the question about the reasons of GOR variation and different composition of gases arises.

A wide range of geochemical parameters is employed for oil-oil and oil-source rock correlation and they are based on the features of liquid hydrocarbon compositions. The number of such parameters for gases is less than for oils. Today, the isotopic composition of hydrocarbon gas components is the best tool for correlation [1], [2], [3]. The carbon isotopic composition of gaseous petroleum components of some oil fields was determined. It varies in a wide range, however, difference between the maximum and the minimum values decreases gradually with the increase of molecular weight of gaseous component.

Gases fall into three main groups according to results of isotopic composition determination (figure 1). The first group (Upper Jurassic) consists of gases which relate to oils by Bazhenov formation (low maturity and marine origin) and occur in Upper Jurassic and Cretaceous deposits only. These gases are characterized by the largest content of light ^{12}C isotope in all gaseous components.

The second group is comprised of gases related to source rock by Palaeozoic formation. High maturity and marine type of organic matter are the cause of high $\delta^{13}C_{Methane}$ values and relatively low $\delta^{13}C$ values of gaseous components from ethane to pentane, compared to gases of Bazhenov formation. Usually, oil and gas in the same bed are related to the same source rock. Nevertheless, gases of some gas condensate fields are typical representatives of Palaeozoic gases and they are deposited in Upper Jurassic. But the composition of oils indicates that oils of these fields were generated by Bazhenov formation. Thus carbon isotopic composition of gases and molecular parameters of oils unambiguously indicates that liquid and gaseous components of reservoir fluid of these fields have different origin.

Last group is represented by gases related to source rocks of Lower Jurassic. Lower Jurassic source rocks are mainly lake, off shore and nonmarine deposits. Oxidative depositional environment and origin of organic matter caused high $\delta^{13}C$ value of heavy gaseous components [4]. However, different $\delta^{13}C$ values of methane clearly indicate different maturity level.

Figure 1 shows that five samples are not included in any group and take intermediate position. Most likely they are mixture of gases with different origin and catagenesis.

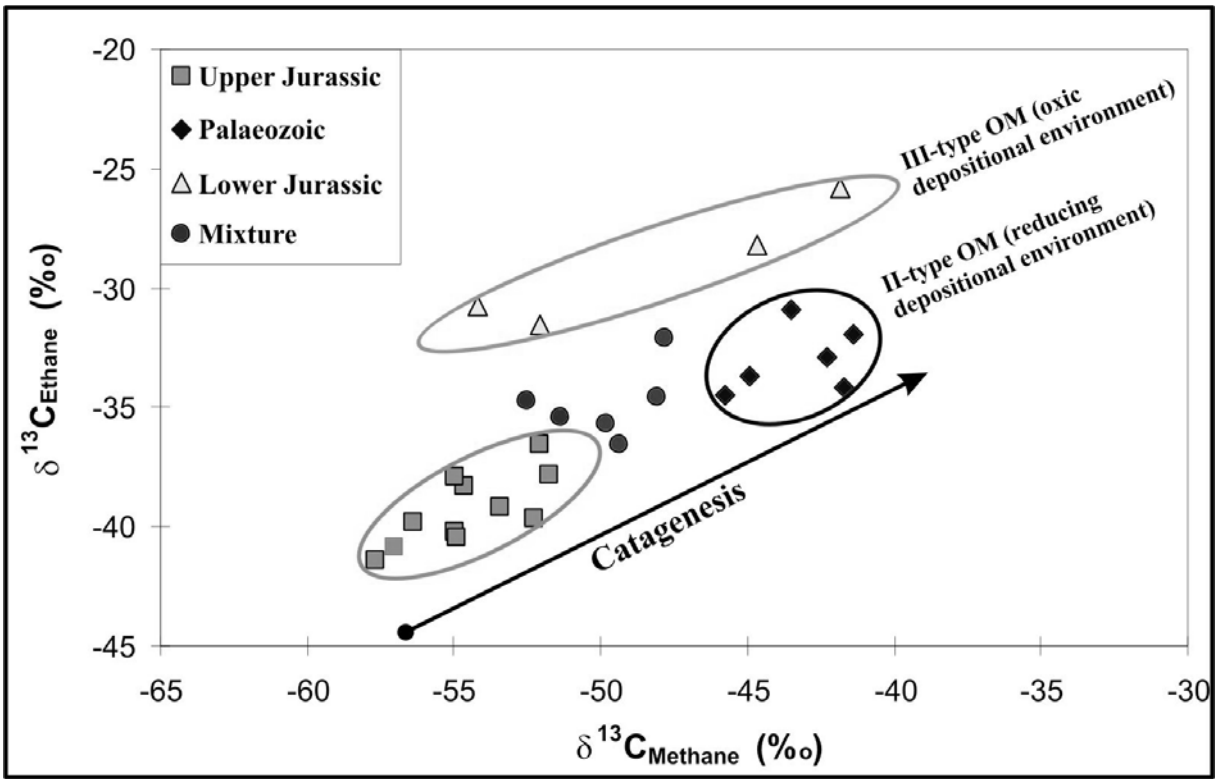


Fig.1. Ethane vs. methane carbon isotopic composition West Siberian gases

References

[1] Galimov, E.M., 1988. Source and mechanisms of formation of gaseous hydrocarbons in sedimentary rock. Chemical Geology. V.1. №3. pp. 77-95.

[2] Berner, U. and Faber, E., 1996. Empirical carbon isotope/maturity relationships for gases from algal kerogens and terrigenous organic matter, based on dry, open-system pyrolysis. Org. Geochem. 24, 10/11, pp. 947-955

[3] Kotarba, M., Lewan, M., 2004. Characterizing thermogenic coalbed gas from Polish coals of different ranks by hydrous pyrolysis. Org. Geochem. 35. pp. 615-646

[4] Goncharov, I.V., 1987. Geochemistry of oils in West Siberia. Moscow, Nedra, 181.

PG-3: Unusual natural gas resources of Hamitabat-(Eocene-Oligocene) (!) gas system of the Thrace basin: implication to future exploration activity

K. Gürgey[1], P. Philp[2], C. Clayton[3]

1) Pamukkale University Geological Engineering Department Kınıklı Kampus 20017 Denizli -Turkey
2) School of Geology and Geophysics, University of Oklahoma, Norman, OK 73019, USA
3) High Bank House, Eardiston, Tenbury Wells, Worcestershire, WR15 8JJ, UK

The Tertiary Thrace Basin located in the northwestern part of Turkey comprises 9 kilometers of clastic-stratigraphic column ranging in age from Early Eocene to Recent age. 15 natural gas, 10 associated condensate, and 5 oil samples collected from the 13 different fields along the NW-SE extending zone of the northern portion of the basin were evaluated on the basis of their chemical / biomarker and individual carbon isotopic compositions.

Methane gas in the Thrace basin appears to show three types: Type-1 methane is bacteriogenic (Corrected $\delta^{13}C_C$ = -61.48‰; Silivri Field) and found in Oligocene reservoirs as a mixture with the thermogenic Type-2 methane. They formed most likely from Upper Oligocene coal and shales deposited in marshy-swamp environment of fluvio-deltaic settings. Methane in the Type-2 ($\delta^{13}C_C$ = -35.80 ‰; Hamitabat Field) and Type-3 ($\delta^{13}C_C$ = -49.10‰; Değirmenköy Field) gases is thermogenic and share the same origin with the Type-2 and Type-3 C_{2+} gases. The Type-2 C_{2+} gases are the major and common gas type and cover 63% of the gas fields in the Thrace basin. They are produced overwhelmingly from both Eocene and Oligocene reservoirs. These gases were almost certainly generated from isotopically heavy terrestrial kerogen ($\delta^{13}C$ = -21 ‰) of the Eocene deltaic Hamitabat shales. The Type-3 C_{2+} gases, produced from one field, were generated from isotopically lighter marine kerogen ($\delta^{13}C$ = -29 ‰) of the Lower Oligocene Mezardere shales deposited in pro-deltaic settings.

The bulk and individual *n*-alkane isotopic relationships between the rock extract, gase, condensate, and oils from the basin recealed two types of condensates and oils, which can be linked genetically to the Type-2 and -3 thermogenic C_{2+} gases. This finding is strongly supported by biomarker composition of the oils.

Maturity assessments on the Type-1 and -2 thermogenic gases based on their estimated initial kerogen isotope values ($\delta^{13}C$ = -21 ‰; -29 ‰) and maturity specific biomarker distribution of the oils and associated condensates reveal that all the hydrocarbons in the Thrace basin are the products of primary cracking at an early stage maturation (R_{eq} = 0.60 - 0.81%) and subsequent expulsion. An open - system condition required for such an early-mature hydrocarbon expulsion was probably provided by deep-seated faulting system of the basin. A model was then developed to predict distribution of the active kitchen volume of the Hamitabat formation using estimated maturity levels on the basinwide %Ro – Depth profile (n=274).

An attempt was made to assess the quantity of natural gases generated from active kitchen area, the quantity of already discovered natural gases, material-balance calculations and finally suggest possible accumulation sides in the Thrace basin for future natural gas exploration activities.

Results show that the calculated quantity of natural gases generated from the active kitchen area of Hamitabat formation reaches the value up to 110 B m^3. The quantity of already discovered natural gas and natural gas- equivalent oil, on the other hand, is about 18.5 B m^3. Hence, 91.5 m^3 undiscovered natural gas appears to be present the Thrace basin. The question is “where did this huge amount of natural gas go? Investigation concerning this question shows that the most plausible locality for accumulation is the various coal seams present in the Oligocene Danişmen formation. This hypothesis is supported by isotopically identified Hamitabat sourced natural gas samples from sandstone reservoirs between the coal seams in all over the basin, for example, in the Karacalı gas field.

PG-4: The geochemical characteristics of natural gas and its charging history in the Eastern part of Tarim basin in China

H. Guoyi, L. Zhisheng, L. Xia, X. Zengye, M. Chenghua, Z. Ying

Research Institute of Petroleum Exploration and Development (Langfang), PetroChina

The well Mandong 1 and the well Yingnan 2 in the different traps have been drilled in the eastern part of Tarim basin and commercial gases were produced from these two wells. The geochemical characteristics of natural gas have been studied in details and it is very helpful to explore gas fields in this area.

Mudstone and carbonate in Cambrian-Lower Ordovician is mainly source rock. The maturity is over than 1.5%VRo. Another source rock is coal from Lower and middle Jurassic. The maturity is less than 0.7%VRo.

There are two distinct characteristics for gas component. The relative content of methane is less than 76.8% and the relative content of C_2^+ is very high. The ratio of C_1/C_{1-5}^+ is less than 0.9. The relative content of N_2 is the highest among all non-hydrocarbon compounds and the average content is about 11%.

The $\delta^{13}C$ value of natural gas is very low. The value range of $\delta^{13}C_1$is from -36.2‰ to -39.3‰,and that of $\delta^{13}C_2$is from -30.9‰ to -39.0‰.But the value of δD_{CH4} is very high. The value range of δD_{CH4} is from -147.8‰ to -154.4‰.

Among all light hydrocarbons the relative content of cycloalkanes is the highest. But the relative content of aromatics is the lowest. According to the analytical result of geochemical characteristics of natural gas, we conclude that the origin of natural gas in the eastern part is from the Cambrian-Ordovician source rock and the maturity of natural gas is over maturity.

In addition, the study result of geothermal history and the homogenization temperature of the fluid inclusion show that these gas reservoirs were formed during Neogene.

PG-5: The index optimization and application of the biomaker of nature gas in the gas source correlation

L. Jian[1], L. Xia[1], Z. Ying[1], L. Zhisheng[1], W. Xiaojuan[2]

1) Research Institute of Petroleum Exploration & Development, Langfang, PetroChina, Hebei, China, 065007
2) University of Petroleum (Beijing), China, 100083

Same as the biomarker of the extract of rock and of the crude oil, the biomarker of nature gas is a molecular fossil which can represent the carbon skeleton of the organic matter. It concludes sterene, hopane, light aromatic hydrocarbon etc. It is an important index to the gas correlation and type distinguished that can not only inflect the type of the mother material also the evolution extent, migration extent and secondary function.

For the content of the biomarker of gas is small, the research and application of this is little. This article optimized the analysis methods of biomarker of natural gas. The result is that the freezing method is an efficiency method of biomaker of gas for its pollution is little. The nature gas flow into cold trap to be concentrated and then heated up to flow into GCMS to detect biomarker and the Pr and the Ph are analyzed by Agilent GC 6890. To analyze biomaker of the coal bed methane and oil prone gas, the nature gas and crude oil in a same well, the biomarker of gas reflects the humic type signature in the coal bed methane, and sapropel type signature in the oil prone gas. Biomakers of the oil and the gas in a same well are not similar. All these indicate that biomaker of gas is taken by the gas itself and can use as an index of the gas source correlation.

The value of the tricycle tepane C_{19} / C_{23} and tricycle tepane C_{26} / four cycled Tepane C_{24} are efficient index to indicate different types of source rocks suck as coal and limestone by research on the biomarker of different kinds of source rocks. The above values of typical coal formed gas are similar with those of coal and those of oil prone gas are similar with limestone source rocks.

The relative content of Sterene C_{27}~C_{29} and the value of Pr/Ph are also good indexes in gas rock correlation.

The contents of different type of gas are determined by above parameters of Ordos basin. Combined with carbon isotope composition of natural gases, the relative contents of different kinds of natural gases are calculated by following model:

$$\text{Coal fromed gas (\%)} = 6.1426\ \delta^{13}C_2\ (‰) + 227.09$$

$$\text{Coal formed gas (\%)} = 7.1425\ \delta^{13}C_3\ (‰) + 237.28$$

Gases in middle gas filed of Ordos basin are mainly mixed gases by above calculation model. The proportion of the coal formed gas is different from different areas with higher in north and east than that in south and west.

PG-6: Paleo-pressure calculation of P_1s_2 and the relationship study between the paleo-pressure and the gas accumulation of Ordos basin

Luoxia[1], Shanxiuqing[1], Lijian[1], C. Honghan[2], Hguoyi[1], Machenghua[1], W. Xiaojuan[3]

1) Research Institute of Petroleum Exploration & Development, Langfang, PetroChina, Hebei, China
2) China Geosciences of University (WuHan), Hubei,China
3) University of Petroleum (Beijing), China

The Ordos basin, with relative stable geological structural setting, slight structural activity, few interior faults, is the one of the largest basins in China at present. Many gas fields with reserve more than $10000\times10^8m^3$ have been discovered in Ordos basin. For example, ChangQing gas filed whose reservoir strata are is Majiagou formation, Ordovician, lower Paleozoic and Suligemiao,Yuling and Wushengqi gas fields whose reservoir strata are Permo-Carboniferous, upper Paleozoic. Characteristics of Upper Paleozoic gas fields are low porosity (ranging from 4% to 12%), low permeability (ranging from $0.1\times10^{-3}\mu m^2$ to $1\times10^{-3}\mu m^2$) and low-pressure (ranging from 6.94MPa to 36.32Mpa). The gradient of the formation pressure ranges from 0.38Mpa/100m to 1.09Mpa/100m. The mean pressure gradient is 0.89Mpa/100m.

What the reason of low pressure is, how the evolution of pressure did, what the relationship between pressure and gas accumulation is are still hot points of Ordos basin.

This paper taks focus on the pressure evolution of P_1s_2, the reservoir of Yulin gas field. Distribution of present pressure shows that the fluid static pressure ranges from 20MPa to 30MPa, gradient of formation pressure ranges from 0.8Mpa/100m to 1.05Mpa/100m (mainly between 0.9 Mpa/100m and 0.95Mpa/100m).

Fluid inclusion PVT simulation is applied in this paper to get Paleo-pressure. A lot of data are got through 110 fluorescence samples (P_1s_2 formation) analysis, 76 fluid inclusion samples (P_1s_2 formation) analysis and 20 individual inclusion Laser-Raman samples analysis. Paleo-pressures are calculated by VTFLINC software.

Paleo-pressure and coefficient of pressure increased progressively from J_1 to K_1. It is shows that it had being similar tendency of Paleo-pressure that was lower in north and higher in south since T_3 to J_{2+3}. While, those tendency changed into lower in east and higher in west at the end of K_1. The scope of Paleo-pressure and coefficient of pressure were between 20 and 30Mpa and between 0.9 and 1.1 at the end of late Triassic system separately. Correspondingly, they were between 20 and 36Mpa and between 0.95 and 1.2 at the end of early Jurassic system, between 28 and 42Mpa and between 1.05 and 1.3 during the middle-late Jurassic system and between 34 and 46Mpa and between 1.05 and 1.4 at the end of earlier Cretaceous system.

According to the Formula PV=ZnRT and present characteristics of Yulin and Sulige gas fields (two big gas fields of Ordos basin), it is found that temperature, Z coefficient, disperse of gas fields are main factors to make pressure towards low. Compare with other factors, disperse of gas field is the key factor to make pressure towards low. Coal bed methane could be a part of supplementary gas to the gas field.

Evolution of pressure is closely related to the gas accumulation. Paleo-pressure increased progressively from J_1 to K_1, correspondingly, accumulation of gas increased progressively. Gas fields were being at dissipated stage from K_1 to now. Lower disperse areas of the basin could be determined by present pressure and Paleo-pressure. The distributions of these areas are partial. Presented gas fields are located in these areas.

PG-7: Correlation of gases with source rocks in Sonliao basin, China

Luoxia, Lijian, Liurenhe, Lizhisheng, Huguoyi, Liuchenglin, Machenghua, W. Xiaojuan

Research Institute of Petroleum Exploration & Development, Langfang, PetroChina, Hebei, China, 065007

Songliao basin is the one of the most important basin of China. Daqing oil field is located in this basin. In addition, many gas fields (pools) such as Changed, Wangjiatun, Shengping and Xushen1 gas fields have been discovered in this basin (mainly around Xujiaweizi depression).

This paper mainly focused on the geochemical characteristics of gases whose reservoirs are from K_1q_1 to basement. The relative contents of hydrocarbon of natural gases are from 0.062% to 99.57% (main in 90%-100%). The ratios of C_1/C_{1-5}^+ rang from 0.9-1.0(mainly 0.97~0.99). The relative content of CO_2 of natural gases are 0~90 (mainly 0%~2%).$\delta^{13}C_1$, $\delta^{13}C_2$, $\delta^{13}C_3$ of natural gas rang from -16‰ to -30‰, from–19.2‰ to –35.92‰ and from –24.1‰ to –36.67‰ separately.

Two types of source rocks those are mudstone with TOC 1.5%, high-post maturity and Type α~β of K_1sh and coal with high-post maturity of K_1sh and K_1h_2. Different types of source rocks have different geochemical characteristics by different types of source rocks thermal simulation experiment. The value of $\delta^{13}C_1$ of thermal gas from mudstone thermal simulation is lighter (ranging from -31‰ to –41.1‰) than that of from coal thermal simulation (ranging from -24‰ to –34.4‰) at the similar maturity stage. Also, the phenomenon of $\delta^{13}C_2 > \delta^{13}C_3$ of thermal from mudstone thermal simulation at post maturity stage appeared but not appearance in coal thermal simulation.

So, correlation of natural gas with source rocks by the relationship between $\delta^{13}C_1$ and $\delta^{13}C2$ and the relationship between $\delta^{13}C_2$ and $\delta^{13}C3$ in this paper.

Gas from coal is called coal-formed gas. That from mudstone is called humic prone gas in this paper.

It is turned out that abiogenic gas, humic prone gas, coal formed gas and mixed gases are all existed in Xujiaweizi area. Some gases in Changde and Wangjiatun gas fileds are mainly abiogenic gas with $\delta^{13}C_1$ (from-15.8‰ to -22.8‰) >$\delta^{13}C_2$ (from -19.2‰ to 26.2‰)>$\delta^{13}C_3$ (from-24.3‰ to -30.7‰)>$\delta^{13}C_4$ (from -27.2‰ to -30‰). Others are mixed gases with $\delta^{13}C_1$ (from 26‰ to -30‰) and $\delta^{13}C_2$ (from 22‰ to -33‰). Well xushen1 is mixed with coal-formed gas and humic prone gas. The values of $\delta^{13}C_1$, $\delta^{13}C_2$, $\delta^{13}C_3$, $\delta^{13}C_{i4}$ and $\delta^{13}C_{n4}$ are -29.6‰, -33.0‰, -34.6‰, -34.9‰ and -35.2‰ separately. The value of $C_1/(C_1\text{-}C_5)^+$ is more than 0.97. While, gases of Shengping gas filed are mainly coal formed gas. The values of $\delta^{13}C_1$, $\delta^{13}C_2$, $\delta^{13}C_3$, and $\delta^{13}C_4$ are from -21.76‰ to -27.53, from -26.46‰ to -26.53‰, from -28.03 to -27.93‰ and from -28‰ to -28.53‰ separately.

PG-8: Compound specific carbon and hydrogen isotopic composition of Rotliegend gases in the Voelkersen Gas field, NW Germany: applications in field characterization and drilling operations

E. Mueller, T. Scholz

RWE Dea AG, Ueberseering 40, D-22297 Hamburg (e-mail: eric.mueller@rwedea.com)

The Voelkersen Gas field (NW Germany) produces thermogenic dry gas from multiple eolian Rotliegend reservoir sandstone sections at depths > 4700 m. The gas is composed of an average 87 vol.% CH_4 and 11 vol.% N_2 with the remainder consisting of C2+ and minor traces of CO_2 (< 0,6 vol.%) and He (< 0,06 vol.%), respectively. The gas is generated from semi-anthracitic to anthracitic Upper Carboniferous coals underlying and adjacent to the reservoir sections. No or very minor condensates are associated with the gas production. The Voelkersen field, located in a graben to halfgraben structural setting, is dissected by a complex transpressional wrench fault system. Smaller scale compartmentalization comprises facies changes and minor subseismic faults as well as further partitioning by fractures and cataclastic bands. Seismic reservoir imaging is impeded by Zechstein salt overlying the Rotliegend, and reservoir continuity predictions are particularly difficult due to complex diagenetic modifications of the reservoir sands. However, recognition of compartmentalization is critical for well placement, well testing and general field development models. Gas isotope analysis was performed to support field modelling efforts, for development of a compartment identification tool while drilling and during well testing; application for potential commingled production investigations was intended for the production phase.

Initial GCIRMS online analysis of gas samples from nine production wells showed a significant variability of carbon isotopic composition which coincided with field compartmentalization concepts. While conventionally used methane carbon isotopic composition showed little variance, the ethane to pentane hydrocarbon isotope values varied considerably and compartments were found to be distinguishable based on complete carbon isotopic C1-C5 profiles. The normal- and *iso*-configurations of butane and pentane as well as comparison of butane and ethane in particular discriminated individual compartments. Trace concentrations of propane to pentane limited reliability of Deuterium analysis but variations of methane and ethane composition suggested an even larger variability in hydrogen isotopic gas composition.

Isotope gas composition appeared to remain unchanged during gas processing in the surface flow line as comparisons of analyses of samples taken before and after cold condensate separation indicate. Similar isotopic signatures of test gases (taken after well cleanout and flush production, respectively) and production gases taken from the same well substantiate the assumption that production gas analysis is representative for reservoir gas composition.

Offline methane and ethane analyses and enrichment of propane to pentanes in production gas samples taken roughly a year after the first study confirmed the earlier results. However, the study also revealed that ethane to pentane showed a large variability of gases from different compartments in terms of the deuterium composition. Compartment distinction based on δD C1-C5 composition is more consistent and obvious compared to carbon isotope analysis. Differences with a ΔD up to 95‰ of butane, *n*-butane and *n*-pentane between samples and of up to 42‰ of *iso*- and straight chain isomers in individual samples render hydrogen isotopic analysis particularly useful for compartment identification.

Carbon and hydrogen isotope measurements on mudgas samples were performed during drilling operations in a recent well. The well was designed to access a reservoir section wedged between field compartments which are known to produce gases with significantly different isotopic signatures. The purpose of the mudgas isotope analysis was the assignment of the drilled section to either of the neighbouring compartments. Unfortunately, casing was set immediately above the reservoir and materials used interfered with the gas analysis. Gases liberated from connector grease (temperature at casing shoe approximately 130-140°C) apparently contaminated the mudgas. However, the vastly different isotopic composition identified in neighbouring compartments was still considered useful to assign the drilled compartment based on mudgas isotopic composition. This assignment led to the decision to cancel a planned deviation of the well and initiate completion.

Open-system non-isothermal pyrolysis experiments [1] showed generation of ^{12}C enriched methane and ethane from Upper Westphalian coals at temperatures >600°C and >500°C, respectively, and characteristic inflexion trends towards heavier isotopic gas composition with increasing maturity. The differences in isotopic signatures of the C2+ species of the Rotliegend gases may thus be caused by maturity dependent generation from specific "precursor pools" present in the local kitchen source rock.

References

[1] Gaschnitz, R., Krooss, B.M., Gerling, P., Faber, E., Littke, R., 2001. On-line pyrolysis-GC-IRMS: isotope fractionation of thermally generated gases from coals. Fuel, 80, 2139-2153.

PG-9: Unusual hydrogen content and its isotopic composition in biogenic gases of the Qaidam basin, Western China

Y. Shuai[1], S. Zhang[1], A. Su[1], H. Huang[2]

1) CNPC Key Laboratories for Petroleum Geochemistry, PetroChina Research Institute of Petroleum Exploration & Development, Beijing 100083, China (e-mail: sczhang@petrochina.com.cn)
2) Department of Petroleum Geology, China University of Geosciences, Beijing 100083, China

The Quaternary and Upper Tertiary in eastern Qaidam basin has an economically significant source of biogenic gas. Sebei gasfield alone, the biggest one ever discovered in China, contains 2×10^{12} m^3 of dry gas reserves. In order to understand gas origin and generation mechanism, detailed examination of chemical and isotopic compositional changes from canned cuttings at new drilled productive Well Xinse 2 was carried out using GC and GC-IRMS.

Carbon isotope compositions of methane from Well Xinse 2 are typical of the established range for biogenic gas ($\delta^{13}C_1$ = -65 ~ -69‰ PDB). However, the hydrogen isotope values of methane (δD_{CH4}) vary significantly at shallow interval (< 400 m) and remain constant at deep profile (Fig. 1). Two distinct gas generation processes were inferred that acetate fermentation prevails at shallow interval while carbon dioxide reduction dominates at deep profile.

Unusual high contents of H_2 were detected throughout the profile. The H_2 contents are particularly high in interval of 800 ~ 1000 m, about 2 ~ 20 times as much as CH_4. Meanwhile only trace amounts of CO_2 were detected in most gas samples. Such composition reflects microbial methanogenesis by carbon dioxide reduction, which can be expressed as:

$$CO_2 + 4H_2 === CH_4 + 2H_2O$$

Both CO_2 and H_2 serve as direct reaction precursors for CH_4. Unusual high content of H_2 in biogenic gas is an intermediate stage of methanogenesis while CO_2 was largely consumed. We suggest that biogenic gas generation is more likely a dynamic process and it is still going on in the Qaidam basin. The hydrogen isotope ratios of H_2 provide the most compelling evidence of methanogenesis conversion of the H_2 into CH_4. The measured values from H_2 are around -710 ~ -740‰ (SMOW), which are much more depleted in deuterium than the methane (Fig. 1). The fractionation of hydrogen isotopes between H_2 and CH_4 arising from methanogenesis was found over 400 per thousand. Such large fractionation implies that deuterium should be preferentially consumed by the H_2-dependent methanogenesis, which leads the residual part of unconsumed H_2 rich in light hydrogen.

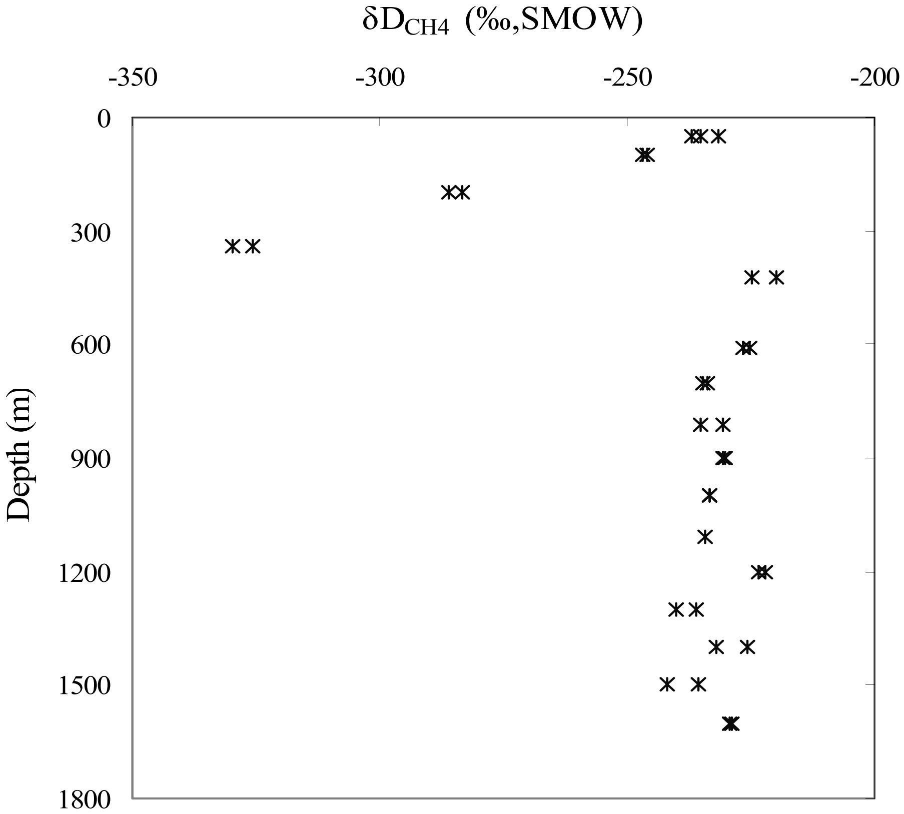


Fig.1. The δD$_{CH4}$ profile at Well Xinse 2

PG-10: Gas alteration and maturation trends in the Western Canada sedimentary basin from three mud gas depth profiles

B.J. Tilley, K. Muehlenbachs

Department of Earth and Atmospheric Sciences, University of Alberta, 1-26 Earth Sciences Bldg., Edmonton, Alberta T6G 2E3, Canada (e-mail: btilley@ualberta.ca)

Alteration and maturation trends of isotopic and molecular compositions of mud gas have been examined from three mud gas depth profiles (Figure 1a) in the Western Canada Sedimentary Basin. Each well penetrates a similar Mississippian or Triassic to Cretaceous stratigraphic section in the foreland basin, but occurs in a different post-depositional tectonic setting. The OJAY well occurs in the easternmost part of the disturbed belt (eastern British Columbia), where the lower of two stacked thrust sheets is sampled. The Kakwa well occurs in the undisturbed 'Deep Basin' of Alberta, about 100 km east of the OJAY well. Here, gas generated from abundant Cretaceous coals and reservoired in low porosity-permeability sandstones, created what is known as the 'Deep Basin Gas Trap' (Masters, 1984). The Belloy well is located about 150 km updip from the Kakwa well, where the sedimentary section is significantly thinner in the Peace River Arch area.

A delta C1 versus delta C2 cross plot (Figure 1b) shows that the gases have multiple origins and have suffered complex alterations. Shallow gas at Belloy is predominantly biogenic. Pre-Cretaceous gas at Belloy and Ojay is sourced from type II kerogen. Cretaceous gas at Ojay is sourced from type III kerogen, whereas Cretaceous gas at Belloy is predominantly biodegradaded. Gas at Kakwa is cross-formationally homogenized into three distinct gas compositions. Late stage kerogen cracking and gas cracking has altered both type II and type III kerogen sourced gas at Ojay. Delta C2 versus delta C3 cross plots support these interpretations. Plots of ln (c1/c2) versus the difference in delta C1 and C2 indicate that gas in pre-Cretaceous sediments evolved in an open system, whereas gas in the Gething Formation at Ojay underwent gas cracking in a closed system. The variable composition of gas in other Cretaceous sediments at Ojay is a function of the timing of gas expulsion from the local coals and the trapping efficiency. In general, regional maturation in the area represented by the three mud gas depth profiles is consistent with burial history. Gas migration, except at Kakwa, has been negligible.

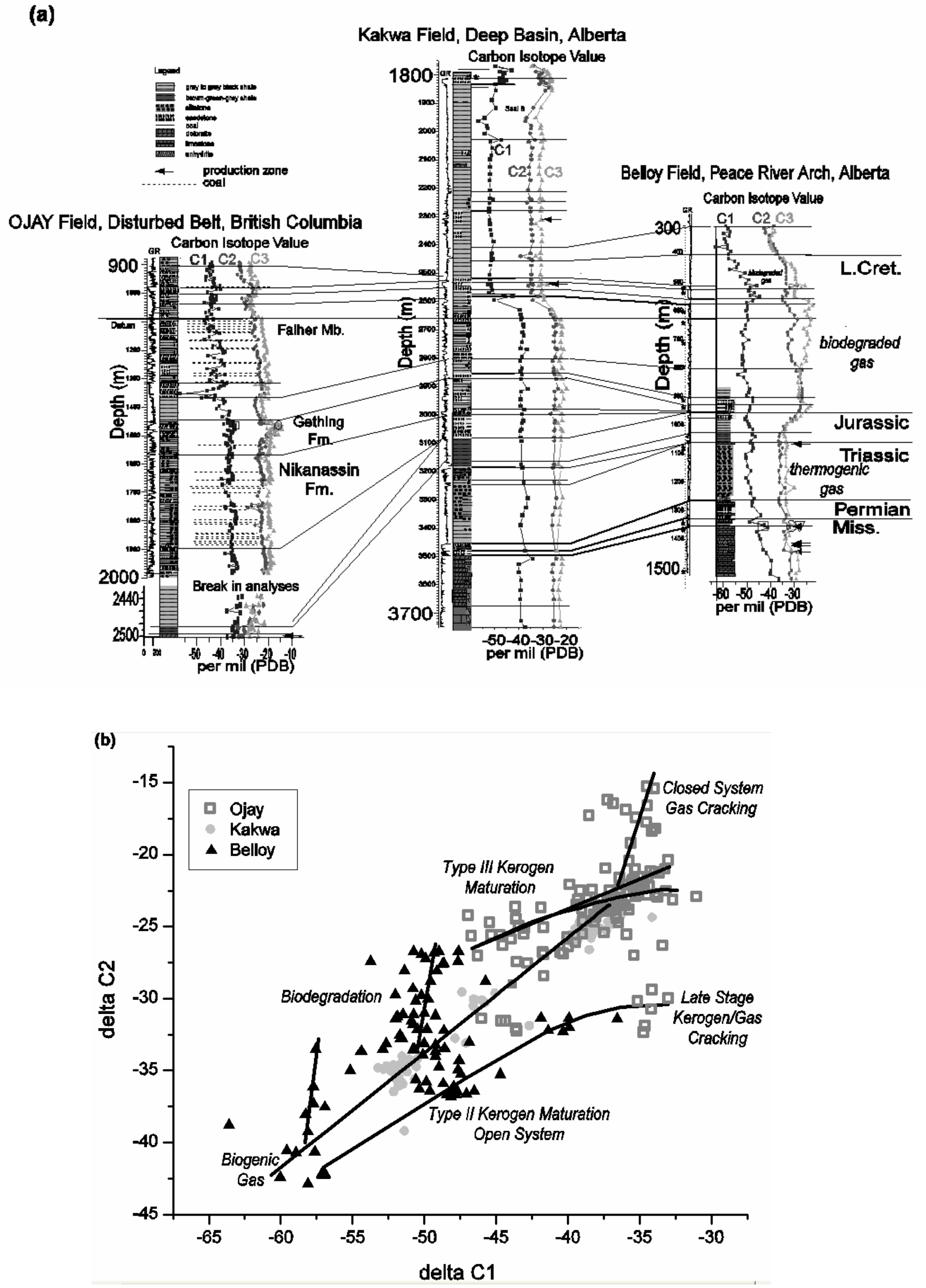


Fig.1. (a) Stratigraphic cross section of three carbon isotope mud gas depth profiles across the western part of the Western Canada Sedimentary Basin. (b) Delta C1 vs delta C2 cross plot of mud gas data from the three depth profiles showing the complex combination of maturation trends

PG-11: Methane generation from Miocene lacustrine sedimentary rocks containing different types of organic matter

M.N. Yalçın[1], R.G. Schaefer[2], U. Mann[2]

1) Istanbul University, Department of Geological Engineering, 34850 Avcilar-Istanbul, Turkey
2) Forschungszentrum Jülich GmbH, ICG-V: Sedimentäre Systeme, 52425 Jülich, Germany

The Middle to Late Miocene was a period when many lakes of different size and type covered almost the entire western Turkey. Respective sedimentary successions of these lakes are characterized by a close neighbourhood of coals and oil shales/oil marls (Yalçın et al., 2003). Whereas coals are bearing mostly humic organic material, the organic content of oil shales/oil marls are sapropelic. Sediments with a mixed type of organic matter do also exist. Total organic carbon (TOC) contents of these rocks vary from a few percent to 70 %. The entire sedimentary sequence is immature, as indicated by Rock-Eval T_{max} values below 435 ^{o}C. Hence, the sedimentary rocks of the Miocene lakes in western Turkey studied, provide an useful suite of immature samples to quantify by laboratory measurements the methane generation as a function of type and amount of organic matter.

In this study ten selected samples from Göynük and Seyitömer basins, which contain different types and amounts of organic matter, have been analysed by programmed-temperature open-system pyrolysis in order to determine the methane generation potential and its reaction kinetics. Effects of organic matter richness and type on methane generation is investigated. Open-system pyrolysis is performed at heating rates 0.1, 0.7 and 5.0 °C/min, combined with a gas chromatograph in order to quantify simultaneously the gases generated (Schaefer et al., 1999). For the determination of the kinetic parameters, the single pre-exponential (frequency) factor and activation energy distribution approach described by Schaefer et al. (1990) is applied.

TOC and Rock Eval hydrogen index (HI) values of the samples range between 3 and 61 weight-% and 107 – 941 mg HC/g TOC, respectively. Source area, some additional geochemical properties and the total methane generation potential of the samples are given in Table 1. Rock weight based methane generation potential data show a strong variation between 0.44 and 15.60 mg methane/g of rock, whereas, on the other hand, the respective TOC-normalized values vary only between about 14 to 35 mg methane/g TOC. These TOC-normalized potentials are discussed in relation to the total hydrocarbon potential as measured by Rock-Eval HI values. Here, it exists an obvious correlation between the percentage of methane generation potential in respect to the total hydrocarbon generation potential and type of organic matter. Whereas by Type III organic matter upto 27 % of the total HC-generation potential belongs to methane, the respective value is only 2 % for Type I kerogen. In addition, the kinetic parameters (frequency factor and activation energy distributions) of the investigated lacustrine sedimentary rocks are presented and compared with source rocks of different geologic origin.

Table 1. Bulk geochemical properties and total methane potential of the samples as obtained from temperature-programmed open-system pyrolysis.

Code	Sample	Basin	TOC	HI	Tmax	TS	CaCO3	Total methane generated	
			(%)	(mgHC/ g TOC)	(°C)	(%)	(%)	[mg/ g rock]	[mg/ g TOC]
E50325	H1	Göynük	7.13	107	433	0.65	4.71	2.10	29.45
E50335	H10	Göynük	5.25	707	430	0.50	59.58	1.34	25.52
E50338	H13	Göynük	60.70	941	430	3.34	7.50	11.80	19.43
E50339	H14	Göynük	52.15	134	419	2.67	16.67	12.30	23.58
E50341	H16	Göynük	7.22	358	415	0.36	0.79	2.55	35.32
E50649	AS 11	Seyitömer	52.00	183	404	1.14	13.33	15.60	30.00
E50659	AS 29	Seyitömer	34.45	912	437	1.86	24.58	6.36	18.46
E50660	AS 31	Seyitömer	6.81	911	434	0.43	39.50	1.38	20.26
E50669	TR 3	Seyitömer	14.20	178	417	0.18	4.17	4.17	29.37
E50672	TR 7	Seyitömer	3.06	395	422	6.66	78.25	0.44	14.38

References

Schaefer, R. G., Schenk, H. J., Hardelauf, H. & Harms, R. (1990) Determination of gross kinetic parameters for petroleum formation from Jurassic source rocks of different maturity levels by means of laboratory experiments. In: *Advances in Organic Geochemistry 1989* (Durand, B. & Béhar, F., eds), Pergamon Press, Oxford, 115-120; and *Organic Geochemistry,* 16, 115 - 120.

Schaefer, R. G., Galushkin, Yu. I., Kolloff, A. & Littke, R. (1999) Reaction kinetics of gas generation in selected source rocks of the West Siberian Basin: Implications for the mass balance of early-thermogenic methane. *Chemical Geology,* 156**,** 41 - 65.

Yalçın, M.N., Mann, U., Bulkan, Ö., Dikmen, D., Disco,D., Hoşgörmez, H., Nazik, A., Nickel, B., Schaefer, R.G., Sengüler, İ., Wilde, V., Willsch, H., (2003) Significance of sediments, palynomorphs and lipids in relation to environmental conditions in two Neogene lacustrine basins in NW Anatolia. *21st International Meeting on Organic Geochemistry, 8-12 September, 2003, Krakow, Poland, Book of Abstracts Part II,* 305-306.

PG-12: Simulation experiments of TSR process and the investigation on thermodynamics and kinetics

C. Yue, S. Li, K. Ding, N. Zhong

State Key Lab of Heavy Oil Processing, University of Petroleum, Beijing 102249, China

The reactions of thermochemical sulfate reduction (TSR) could take place in the geological deposits. TSR may form sour gas reservoirs by the oxidation of organic matter, which results in the destruction of natural gas and the formation of metal sulfide. Therefore, the investigation of TSR process is necessary to determine the geochemical depth limit for natural gas, and to investigate the geochemical cycle of sulfur. In this paper, thermal simulation experiments on the reactions of hydrocarbon-$CaSO_4$ and H_2S-MeO (Me = Fe, Pb, Zn) were carried out using autoclave at high temperature and high pressure. The products were characterized by some advanced analytical methods, such as microcoulometry, gas chromatography, XRD, FT-IR and mass spectrometer. The thermodynamics and kinetics were discussed by means of experimental results.

It is hard to detect the products of the hydrocarbon-$CaSO_4$ reactions at the temperature of less than 400° in lab. When the simulation temperature ranges from 450° to 700°, the reactions can take place obviously. The main products consist of hydrogen sulfide, calcium carbonate and water. Thermodynamic result shows that the reactions occur spontaneously and that the increasing temperature is favorable. The temperature of 450-700° in lab corresponds to the temperature of 160-200° in geology settings. Therefore, the hydrocarbon-$CaSO_4$ reactions can proceed in deep carbonate reservoirs, a probable way to result in the natural gas destruction. The activation energies for the reactions of CH_4-$CaSO_4$, C_2H_6-$CaSO_4$ and C_3H_8-$CaSO_4$ are 152.9kJ/mol, 131.0kJ/mol and 120.6kJ/mol, respectively.

The metal sulfide can be generated at low temperatures. Temperature and water medium are the important factors that affect the composition of reaction products. The products of H_2S-Fe_2O_3 and H_2S-Fe_2O_3-H_2O systems are complex Fe-s compounds. The most stable product is FeS_2. The reactions can proceed spontaneously and increasing temperature is disfavorite for the reaction systems. The determination of the geochemical depth limit for natural gas and the investigation of geochemical cycle of sulfur can both be related to the formation of sulfide deposits. Accoding to the kinetic results, the activation energies for the formation of FeS_2 and the disappearance of Fe_2O_3 in H_2S-Fe_2O_3 system are 26.2kJ/mol and 24.4kJ/mol, while those in H_2S-Fe_2O_3-H_2O system are 21.9kJ/mol and 21.2kJ/mol.

PG-13: The origin of natural gases in Kuqa depression, Tarim basin, NW China

Y.-R. Zou[1], P. Peng[1], Y. Shuai[1,2]

1) The State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640
2) The Research Institute of Petroleum Exploration and Development, PetroChina, Beijing 100083

The Kuqa depression, northwards bounded by the South Tianshan Mountain, is a secondary structural unit within the northern Tarim Basin, NW China. Significant natural gas, condensate resources have been discovered in the Kuqa depression. This depression is divided into three structural belts, i.e. the Kelasu–Yiqikelik belt, the Qiulitak belt and the Front Uplift belt. A special distribution pattern of gases chemical and isotopic compositions has been observed in this depression. Dry, isotopically heavy gases occur in the Kelasu substructure belt, while wet, isotopically light gases are in the Yiqikelik substructure belt and condensate in the Front Uplift.

Both the chemistry and the isotopic signatures of the gaseous hydrocarbon provide the information of gases genesis and evolution. In the present paper, pyrolysis experiment of Jurassic coal under confine system, GC and GC-IRMS analysis of pyrolysates and kinetic modeling on gases generation and carbon isotope of methane / ethane have been carried out. The results show that the relationships of $\delta^{13}C_1$-%Ro, $\delta^{13}C_2$-%Ro and Transformation Ratio-%Ro are independent of heating rates for a given source rock; the gases occurred in this depression are thermogenic (Fig 1a) after Prinzhofer et al.(1995); two directional trends shown on the diagram C_2/C_1-$\delta^{13}C_1$ with increasing maturity are related to the organic matter types. Group 1 is coal gas; Group 2 is gas associated with oil and mixed with different origin (Fig. 1b), as Prinzhofer et al.(1997) demonstrated.

A plot with gas expulsion threshold (Ritter et al., 2005), carbon isotope ratios of C_1-C_2 and vitrinite reflectance is employed to identify the origin of gases in the depression (Fig. 1c). The gases are related to different source rocks. The gases in the Kelasu substructure belt are related to the Jurassic coal measure; the gases in the Front Uplift belt are generated from the Triassic strata, while those of the Yiqikelik substructure belt are associated with both strata, depending on the borehole locations. The gas origins of two large-size gas fields, Kela 2 and Dina 2, are different. The gases generated from the Jurassic coal are accumulated in the Kela 2 gas pool from 12Ma to the maturity level of 2.3%Ro reached. The Kela 2 is predominated by coal-derived gas. The gases of Dina 2 field are characterized by wet gases and relatively light carbon isotope values, mainly from the Triassic lacustrine organic matters.

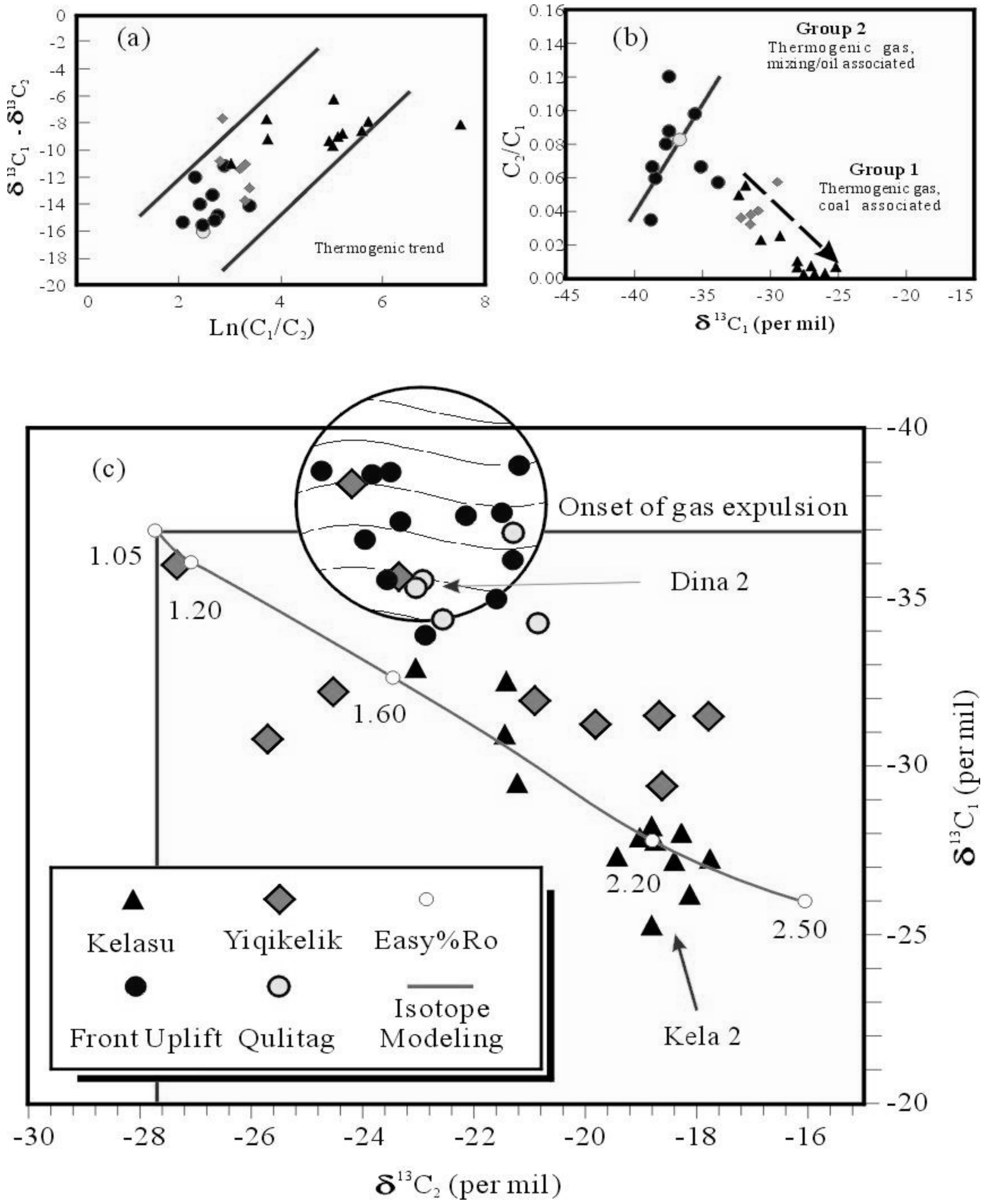


Fig.1. (a) Diagram of δC_1-δC_2 versus $\mathrm{Ln}(C_1/C_2)$ showing that the gases from the Kuqa depression are thermogenic(Prinzhofer et al., 1995). (b) Two group trends are demonstrated with increasing maturity and methane carbon isotope ratio. (c) A plot with C_1-C_2 isotope, Easy%Ro and gas expulsion onset is used to distinguish from the gases origins in such a large district as the Kuqa depression

Acknowledgement

This work was supported financially by the National Key Foundation Project (Grant: 2001CB209101) and the Natural Sci. Foundation of China (Grant No. 40272067; 40072053).

References

Prinzhofer, A. and Huc, A.Y. (1995) Genetic and Post-Genetic Molecular and Isotopic Fractionations in Natural Gases, Chemical Geology, 126(3-4): 281-290.

Prinzhofer, A. and Pernaton, E. (1997) Isotopically Light Methane in Natural Gases: Bacterial Imprint or Fractionation? Chemical Geology, 142, 193-200.

Ritter, U. and Grover, A., 2005. Adsorption of petroleum compounds in vitrinite: implications for petroleum. expulsion from coal. International Journal of Coal Geology, 62:183-191.

PG-14: Gases of the kerogen pyrolysis products

D. Bouchnev, S. Shanina

Institute of Geology of Komi Science Center of RAS, 54-Pervomayakaya St., Syktyvkar, Russia

The investigation of the kerogen structure is usually performed by the geopolymer destruction by thermal or chemical techniques followed by the products analysis. The gazes of the pyrolysis products are not common compounds to be analyzed. Nevertheless their composition and yield are correlate to the kerogen structure, as it seems. The investigation of gazes forming during pyrolysis of different kerogens allows us to understand the genesis of gazes.

To perform pyrolysis we used GC coupled with pyrolytic and cryogenic units. Kerogen (apr. 5 mg) was deposited in quartz reactor, and was pyrolysed at 600 ^{o}C during 10 min. HP Plot-Q capillary column was used to separate the pyrolysis products and FID as well as TCD were used to quantify organic and inorganic gazes (Bushnev and Shanina, 2005).

Two series of kerogen samples were investigated. The first set represents by kerogens isolated from J_3v_2 oil shales and clays from Sysola region (Bushnev and Burdel'naya, 2003), the initial rocks contain 0.8-33 % TOC. The OM is characterized by high S_{org} content so OM of oil shale is type II-S. The natural sulfurisation of lipids and carbohydrates also was the very important process of J_3v_2 OM accumulation. The second kerogens set represents by D_3dm samples of Ukhta region (Bushnev, 2002). TOC content in the Devonian rocks set is not so high and type II (II-III) of kerogen is determined here.

H_2, CO, CO_2, H_2S, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, n-C_4H_{10}, i-C_4H_{10} as well as H_2O were detected in almost all pyrolysis products. N_2 was not detected. The absence of molecular nitrogen in the kerogen pyrolysis products could by explain by labile nitrogen compounds destruction at early diagenesis stage and high stability of residual nitrogen kerogen units. The H_2 formation by H_2O and metal reactions was exclude during blank experiments so H_2 is formed by kerogen decomposition, and possible way is the free radical destruction of the aliphatic chains.

CO could be formed by CO_2 and C reactions, but we exclude this way of CO formation. The investigation of kerogens isolated from oil shale heated in the conditions of aqueous pyrolysis shows that CO/CO_2 ratio increases in samples heated at higher temperatures and we could conclude the different CO and CO_2 formation ways during kerogen pyrolysis (Bushnev *et al.*, 2004). It is possible to suggest that CO forms by mono-oxygen kerogen groups like ether as well as ketons and CO_2 is formed by bi-oxygen kerogen groups destruction. The present conclusion permits to use CO and CO_2 contents in pyrolysis products of kerogen to elucidate the type of the oxygen containing functional kerogen groups.

The hydrogen sulfide yield has a strong correlation with thiophene ratio (TR) measured by off-line pyrolysis. Really, thermal decomposition of organic-sulfur compounds leads to H_2S generation. But not only organic sulfur of the kerogen is the principal source of the hydrogen sulfide. One of more pyrite rich kerogen sample (K-1/6/2) shows extremal yield of the H_2S. Thus we could not simply use the hydrogen sulfide yield upon pyrolysis to S_{org} determination.

CH_4, C_2H_4, C_2H_6, C_3H_8 and C_3H_6 yields are in good correlation with the yield of *n*-alkanes/*n*-alkenes-1 sum upon off-line 400 ^oC pyrolysis (C_{14}-C_{30}) so we could conclude that the formation of long and short n-alkyl chains relates to the one process of free-radical destruction. Butanes do not correlate to n-alkanes/n-alkenes-1 sum, but they shows very good positive correlation to C2 thiophenes ratio of 2,5-DMT/(2-ET+2,3-DMT+2,4-DMT) measured by off-line pyrolysis for J_3v_2 sample set. The above mentioned C2 thiophenes ratio has, as was shown by van Kaam-Peters *et al.* (1997), very good correlation to sulfurized carbohydrate remains in kerogen structure. Thus C_1-C_3 gazes on the one hand and C_4 gazes on the other have different source in the kerogen structure. The D_3dm sample set shows strong negative correlation of butanes and 2,5-DMT/(2-ET+2,3-DMT+2,4-DMT) thiophenes ratio.

References

D.A. Bushnev, N.S. Burdel'naya, S.N. Shanina, and E.S. Makarova Generation of Hydrocarbons and Hetero Compounds by Sulfur-Rich Oil Shale in Hydrous Pyrolysis // Petroleum Chemistry Vol. 44, No. 6, 2004, pp. 416-425.

D.A. Bushnev and N.S. Burdel'naya Organic Sulfur Compounds from the Upper Jurassic Shale Bearing Strata of the Sysola Region // Petroleum Chemistry Vol. 43, No. 4, 2003, pp. 230-239.

D.A. Bushnev The Composition of Biomarkers in Bitumen and Pyrolysis Products of Kerogen from the Pechora-Basin Upper Devonian Deposits // Petroleum Chemistry Vol. 42, No. 5, 2002, pp. 291-305.

D.A. Bushnev and S.N. Shanina Gazes in the pyrolysis products of kerogen from an organic carbon rich deposits // Geochemistry International, 2005, № 3 (in press).

PG-15: A new approach for geochemical correlation of gases and condensates from the Burgos basin, Mexico

T. Carrillo Hernández[1], M. Guzmán Vega[1], A. Prinzhofer[2], A.Y. Huc[2], M. Escudero[1]

1) Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas 152, Col. San Bartolo Atepehuacan, 07730, México, D. F., México (e-mail: tcarrill@imp.mx)
2) Division of Geology-Geochemistry, Institut Français du Pétrole, 1 and 4 avenue de Bois Préau, 92852, Rueil Malmaison Cedex, France

The origin of gas accumulations without associated oil found in sedimentary basins is controversial. However, the concepts of gas generation and migration of gas fluids have been reviewed with improvements in the quality of laboratory experimental data, and new techniques which provide better approaches on the origin and evolution of the gases.

Hypotheses that explain the occurrence of gas without associated oil:

- High thermal maturity of source rock.
- Preponderant contribution of source rock type III.
- Late formation of trap where only the most thermally mature fluids are accumulated (gas and condensate).
- A segregation phase during the migration between the source rock and the reservoir that produce the gas accumulation in the relatively superficial environments.

The Burgos basin represents an ideal natural laboratory to test the different concepts and hypotheses proposed. The known reservoirs in the Burgos Basin produce only gases and condensates (PEMEX, 1989).

The Burgos Basin is located in northeastern extreme of Mexico, and it belongs to the Gulf of Mexico basins. The stratigraphic column includes sediments from Jurassic to Miocene, arranged in strips with a NNW-SSE orientation, in such a way that the strips stratigraphically older lie to the west, and the younger ones to the east. The maximum thickness sediment, in the center of the basin, is 10-km approximately (Santiago et al., 1984).

The aims of this study have been: a) to establish the existence of genetic relationships between the gases and condensates found in the Burgos Basin, b) to propose an explanation for the absence of oil in the basin and c) to establish a technique for the isotopic molecular analysis of condensates.

The study of the chemistry and carbon isotopic ratio in the gases and condensates from the Burgos Basin gives estimations about the maturity and the relative directions of migration (Carrillo Hernández, T., 1999).

This study has shown that the natural gases originate from organic matter of high thermal maturity and that they have been formed mainly from primary cracking (around 80%). The behavior of these gases is like an open system (Prinzhofer et al., 1997, Lorant et al., 1998), with a fast expulsion of produced hydrocarbons (instantaneous gas). In addition, for the first time, the new information given by the analysis of gases and condensates has made possible the definition of the genetic relationship between the gases and associated condensates studied, based on their isotopic values (Figure 1). The very strong abundance of gas in relation to the condensate is explained by primary cracking of late maturity type III organic matter. Therefore it is possible that the humic organic matter of deltaic series of the Tertiary is the origin of the gases and condensates from the Burgos Basin.

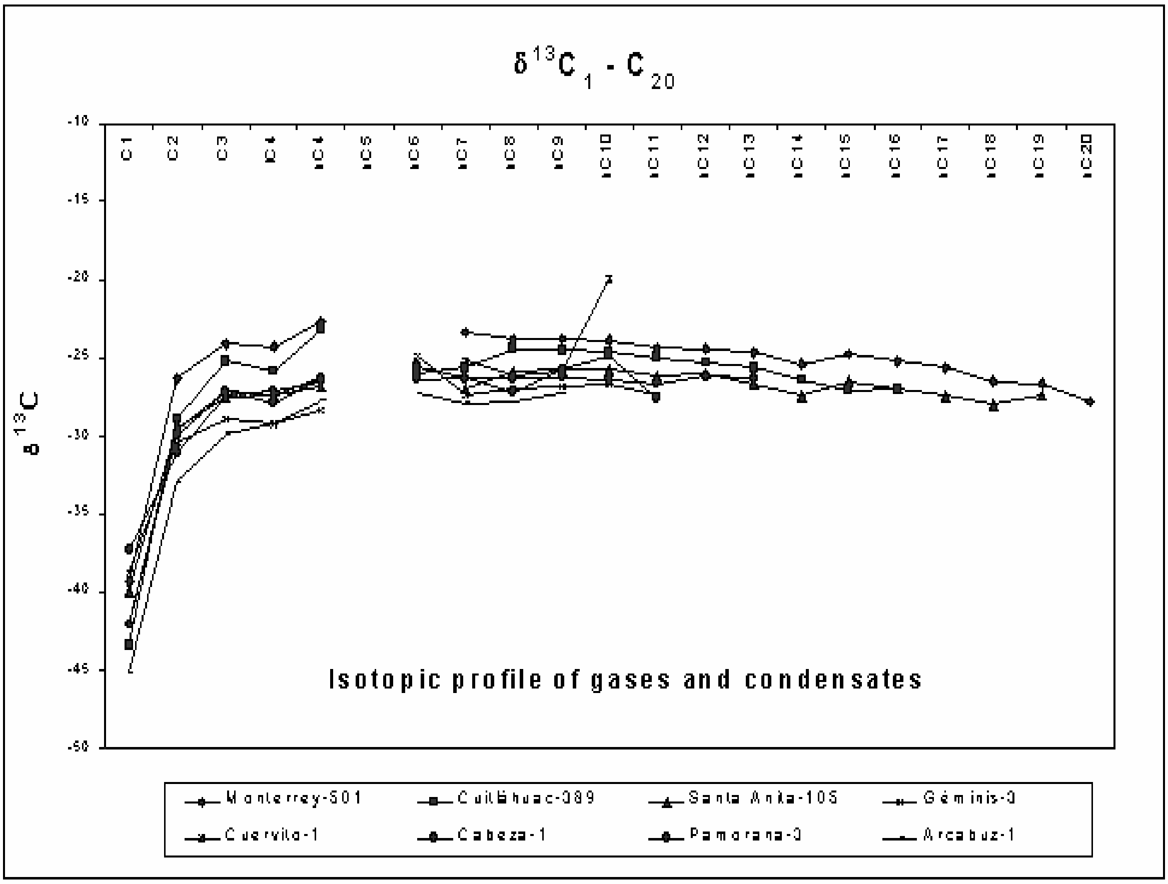


Fig.1. Isotopic profile of gases and condensates from the Burgos Basin

References

Carrillo Hernández, T. 1999. Etude Géochimique de Gaz et Condensat du Bassin de Burgos (Mexique). Report of DEA (master's degree). Intitut Français du Pétrole, Rueil Malmaison, France, pp. 61.

Lorant, F., Prinzhofer, A., Behar, F., Huc, A. Y. 1998. Carbon isotopic and molecular constraints on the formation and the expulsion of thermogenic hydrocarbon gases. Chemical Geology, 147, 249-264

PEMEX. Autores varios. 1989. Cuenca de Burgos (Informe Inédito).

Prinzhofer, A., Pernaton, E., Lorant, F. 1997. Efficiency of gas accumulation in a reservoir: chemical and isotopic controls. Report of Inst. Français du Pétrole, Div. Géologie-Géochimie, Rueil Malmaison, France.

Santiago, A. J., Carrillo, B. J., Martell, A. B. 1984. Geología Petrolera de México. Schlumberger, pp.1-36.

PG-16: Methane generation during dry open-system pyrolysis, insights from isotope specific reaction kinetic modelling

B. Cramer[1], Y. Sun[2]

1) Federal Institute for Geosciences and Natural Resources (BGR), Hannover, Germany
(e-mail: B.Cramer@bgr.de)
2) SKLOG ,Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Wushan, Guangzhou 510640, P. R. China

Methane generation and associated stable carbon isotope fractionation were investigated applying dry open-system pyrolysis to three types of sedimentary organic matter: Jurassic coal measures as prominent gas-prone source rock in the Tarim Basin, a pure vitrinite sample, and asphaltene extracted from marine sourced oil. As shown in Figure 1 the dynamics of methane generation and $\delta^{13}C$ trends differ significantly for the three samples. The asphaltene is distinguished by the highest methane potential (48 mg/g_{TOC}) followed by the vitrinite (28 mg/g_{TOC}) and the coal with a low potential of only 14 mg/g_{TOC}. Temperatures of maximum methane generation are similar for the vitrinite and the asphaltene with 465 °C at 0.2 K/min heating (Figure 1) but lower than for the coal (535 °C). Whereas methane generation from asphaltene ceases at about 650°C, the coaly organic matter investigated here continues to produce methane up to more than 750 °C.

Despite the differences in methane generation, $\delta^{13}C$ trends of methane from the coal and the vitrinite run almost parallel with two minima and one maximum and a constant offset of methane from the coal of about +2 ‰ (Figure 1). For these samples the phase of main methane generation is characterised by an almost linear increase of $\delta^{13}C$ values. In contrast, methane from the asphaltene is significantly lighter reaching $\delta^{13}C$ values of -45 ‰ and the isotope trend does not show the maximum at the late stage of methane generation.

For analyzing the mechanisms of methane generation from the three types of organic matter, the reaction kinetic approach previously presented by Cramer ([1]) was applied. This model is based on the concept of a certain number of reactions contributing to the generation of methane, each reaction distinguished by an initial pool of precursor sites with a defined stable carbon isotope signature and a common reaction rate determining step. For each reaction the mathematical model defines Gaussian distributed activation energies, a single pre-exponential factor, an initial isotope ratio of the precursor and a single difference in activation energy between the heavy and the light isotope species. Applying this model, methane generation and isotope trends of methane from each sample can be explained by three reactions, proceeding subsequently with increasing temperature. For the asphaltene the first two reactions by far dominate the release of methane. The main production peak is explained as an overlap of these two reactions with a weak inflexion in methane's $\delta^{13}C$ trend (Figure 1, at 475 °C). The third reaction is proven by the inverse isotope trend above 560 °C.

This third reaction is more obvious for methane from the coal and the vitrinite sample (Figure 1). Here the obvious shoulder at late stage of methane generation coincides with a distinct isotope trend at temperatures above maximum $\delta^{13}C$. For the coal sample the first reaction seems to have the lowest methane potential.

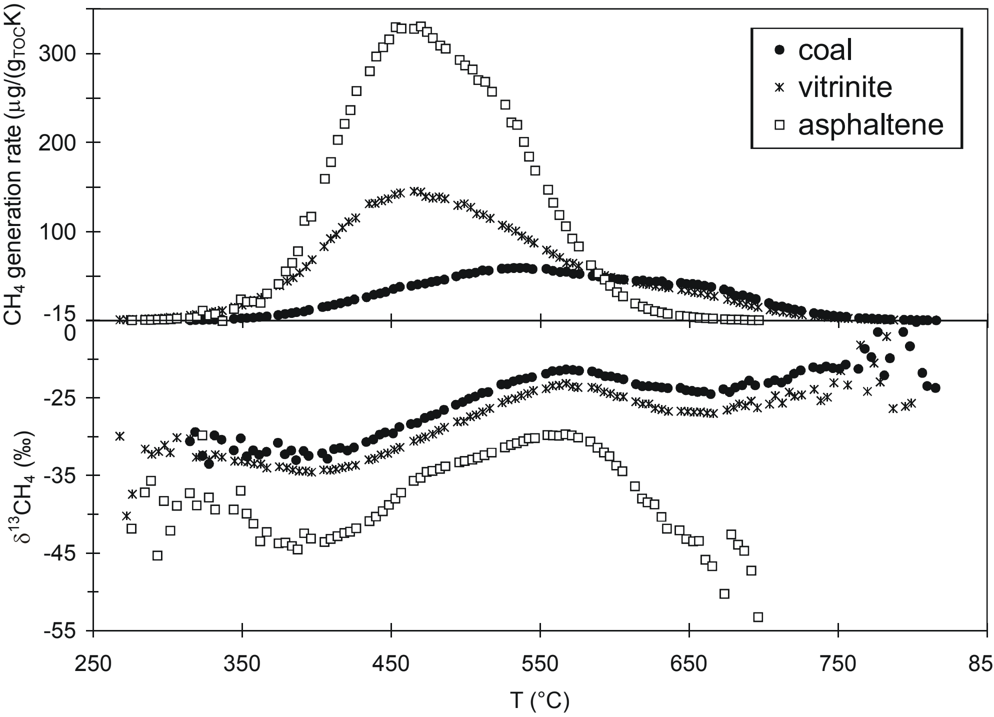


Fig.1. Comparison of methane generation rates and $\delta^{13}C$ values of methane from a natural coal, pure vitrinite, and asphaltene during dry, open-system pyrolysis with 0.2 K/min linear heating

As interpretation of these findings we propose that the first reaction represents the release of methane by cracking of short chain groups distributed in the macromolecular network with weak bonds like hydrogen bonds or covalent bonds. This process is important for the asphaltene and the vitrinite sample compared to the coal. The second reaction generates methane by cracking of side-chains bounded to aromatic structures. For all three samples investigated this process seems to be of significant importance. For the third reaction we propose ring-open followed by condensation reactions which are most obvious for the coal and the vitrinite.

References

[1] Cramer, B., 2004. Methane generation from coal during open system pyrolysis investigated by isotope specific, Gaussian distributed reaction kinetics. Organic Geochemistry, 35 (4): 379-392.

PG-17: Origin of carbondioxide and hydrocarbon gases in Dodan and Silivanka fields (SE-Turkey)

H. Hoşgörmez[1], M.N. Yalçın[1], C. Soylu[2]

1) Istanbul University, Engineering Faculty, Geology Dept,TR-34850, Avcılar, Istanbul, Turkey
(e-mail: hosgorme@istanbul.edu.tr)
2) TPAO Research Center, Mustafa Kemal Mah. 2. Cad, No:86, 06520 Ankara, Turkey

Gas occurrences in the Dodan and Silivanka fields near Batman in Southeastern Turkey are located within the same carbonate reservoir rock, namely the Garzan formation. Although both fields are situated within the same petroleum system, compositions of produced gases are different. Whereas in the Dodan field CO_2 is the major constituent of the produced gas, in the Silivanka field hydrocarbon gaseous (HCs) are the major component. The aim of this study is to investigate differences in gas composition and to determine the origin of the gases in these fields. For this purpose gas samples were analyzed for their molecular and isotopic composition. The gas from the Dodan field consists of 83 % CO_2 and only 4.5 % HCs, whereas the gas produced in the Silivanka field contains 2% CO_2 and 95 % HCs. The isotopic composition of HC gases in both fields indicates a thermogenic origin (Figure 1). Gas from the Dodan field is isotopicaly heavier and has a higher methane content than the Silivanka gas. The isotopic composition of CO_2 in both fields with values of -1.7 %o and -1.5%o, suggests an abiogenic origin from marine limestones. CO_2 from carbonates can either be formed by thermal decarbonation of calcite at high temperatures (200-250 ^{o}C) or by neutralization of carbonates with acids [1], [2], [3], [4]. In both fields reservoir temperatures are far below the required temperatures for thermal decarbonation. Consequently, neutralization with acids has to be the major mechanism of CO_2-formation. Neutralization of carbonates of the Garzan formation is probably caused by H_2S, which forms a certain part of the gas in the Dodan field. The respective chemical reactions leading to CO_2 formation from calcite may be defined by as;

$CaCO3 + H2S \rightleftharpoons Ca^{+} + HCO_3^{-} + HS^{-2}$ "neutralization reaction" or as;
$CaCO3 + H2S + 2O2 \rightarrow CaSO4 + CO2 + H2O$ "redox accompanied neutralization reaction"

The occurrence of H_2S in sedimentary rocks is explained either by reduction of sulfate from pore water or by thermal degradation of reservoired oils [2]. As described in the following formula the respective reaction of sulfate reduction also leads to CO_2-generation.

$SO4^{-2} + 1.33(CH_2) + 0.66H_2O \rightarrow H_2S + 1.33CO_2 + 2OH^{-}$

However, we believe that the contribution of this reaction to H_2S and CO_2 occurrences was limited, since the isotopic ratio of CO_2 clearly indicates an abiogenic source.

Consequently, thermal degradation of reservoired oil can be considered as the main mechanism of H_2S formation within the Garzan formation as described by Hunt (1996) [2].

$$C_{100}H_{170}S_{1.4} \rightarrow 23\ CH_4 + 0.7\ H_2S + C_{77}H_{77}S_{0.7}$$

High sulfur content (4.3-4.6 %) of oils in the Dodan field and lower sulfur content of oils in the Silivanka field (0.61-2.92%) [5] support such degradation. Therefore, it could be concluded that the differences in gas composition in both fields are due to the different levels of degradation of oils. Advanced thermal degradation of sulfur-rich oils in the Dodan field led to the formation of higher amounts of H_2S and subsequent CO_2 formation by simple or redox–accompanied neutralization of calcite. Less degradation and lower sulfur oils in Silivanka field restricted H_2S and subsequent CO_2 formation here. This conclusion is supported by the fact that both the isotopic composition and relative percentage of methane in the Dodan field is slightly modified by methane generated during degradation of oils (Figure 1).

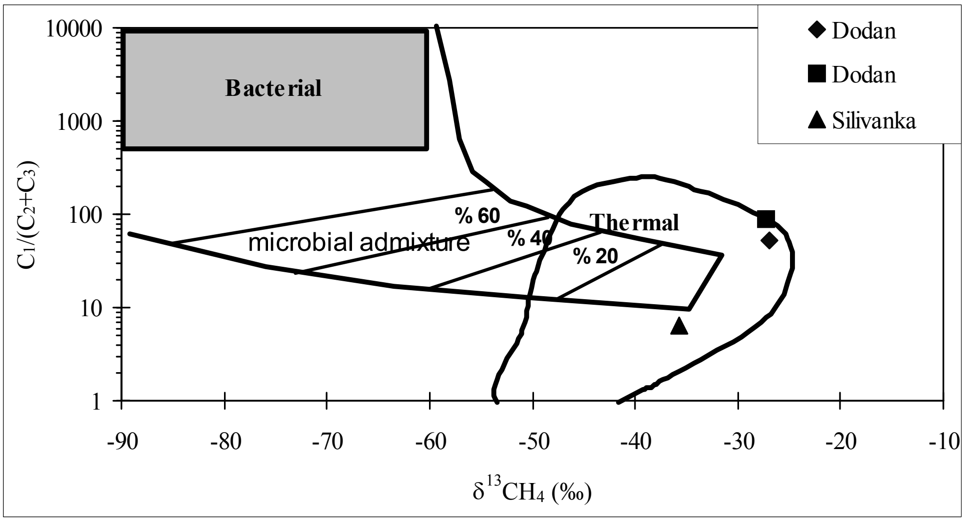


Fig.1. Genetic characterization of gas occurrences in Dodan and Silivanka fields according to molecular ratio (C_1/C_2+C_3) versus $\delta^{13}C$ isotopic composition of methane

References

[1] Manahan, S.E., 1993, Fundementals of Environmental Chemistry. CRC press, pp. 394-404
[2] Hunt, J. M., 1996, Petroleum Geochemistry and Geology. 2nd Ed. San Francisco: Freeman, pp 743.
[3] Welhan, J., 1988, Origins of methane in hydrothermal systems. Chemical Geology, 71, pp. 183-198.
[4] Minissale, A., Evans, W., Magro, G., Vaselli, O., 1997, Multiple source components in gas manifestations from north-central Italy. Chemical Geology, 142, pp. 175-192.
[5] Gürgey, K., 1991, Genetic classification of the SE Turkey oils and delination of source rocks types with the use of biological markers. METU, PhD. Thesis, 320 p.

PG-18: Geochemical characterization of gas system associated to oil biodegradation in the Liaohe basin, NE China

H. Huang[1,2], T.B.P. Oldenburg[1], B. Bennett[1], J. Adams[1], K. Noke[1], S. Larter[1,3]

1) Petroleum Reservoir Group(PRG), Department of Geology and Geophysics, University of Calgary,
844 Campus Place Northwest, Calgary, AB T2N 1N4, Canada (email: huah@ucalgary.ca)
2) China University of Geosciences, Beijing 100083, China
3) NRG, University of Newcastle upon Tyne, UK

A suite of oil associated gases from the Liaohe basin NE China, which have similar maturity and source origin but with varying degrees of biodegradation, have been analyzed for gas composition as well as for the $\delta^{13}C$ of C_1-C_4 and CO_2 and δD of C_1-C_3. Isotopic compositions of the studied gas samples show wide variations ($\delta^{13}C_1$ from −43.2‰ to −54.8‰, $\delta^{13}C_2$ from −28.5‰ to −38.3‰, $\delta^{13}C_3$ from −16.8‰ to −29.3‰, and $\delta^{13}nC_4$ from −20.4‰ to −26.4‰). Most gas samples display clear geochemical evidence of alteration by biodegradation, with relatively high dryness ($C_1/C_{1\text{-}4} > 92\%$), high ratios of isobutane/*n*-butane (0.8-2.0), high $\Delta^{13}C$ (C_3–C_2) values (> 5‰), and high $\Delta D(C_2\text{-}C_1)$ values (> 30‰). The carbon isotopic compositions of ethane, propane, and butane in the biodegraded gases are 3-5‰ heavier than these in non-biodegraded gases, but methane isotope signatures are variably heavier or lighter than these in non-biodegraded gases. Carbon dioxide contents and isotopic values provide evidence for gas origin and its isotopic variation. Gases with isotopically heavy carbon dioxide (> +8‰), isotopically light methane (< -54‰) and high carbon dioxide content (2-5%) indicate that secondary biogenic methane was generated from CO_2 reduction under anaerobic conditions. Gases with low carbon dioxide content (< 2%), coupled with heavy carbon dioxide (> +8‰) and heavy methane (> -45‰), probably indicate high degrees of CO_2 conversion to methane and later stages of methane generation. However, the presence of isotopically heavy methane (> -45‰) and isotopically light carbon dioxide (< -8‰) with low concentration of carbon dioxide (< 2%) are indicative of mixing of different phases of generated methane and carbon dioxide (Fig. 1).

It seems likely that most of the variations in isotopic signatures of biodegraded oil related gases can be described by various sequential biodegradation-carbon dioxide reduction and gas mixing processes. Methanogenesis through carbon dioxide reduction does not necessary produce isotopically-depleted methane. The methanes become richer in ^{13}C when large fraction of carbon dioxide is reduced to methane, resulting in newly generated methane sometimes heavier than the original thermogenic methane. Mixing of newly generated methane with thermogenic methane already in place in the reservoir can cause very complicated isotopic signatures. We discuss the origin of the gases in the Liaohe basin using geological, geochemical and isotope mixing models for the basin.

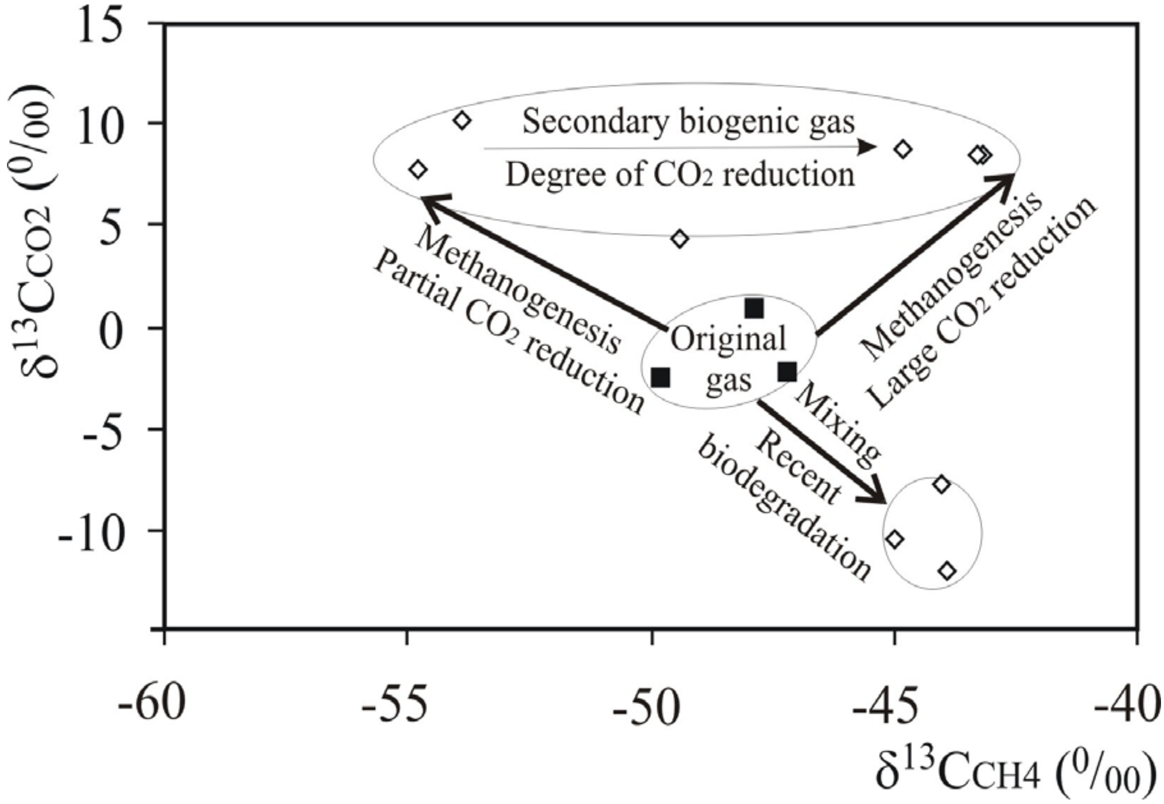


Fig.1. The isotopic compositions of methane and carbon dioxide in oil associated gases from the Liaohe basin suggest that methane was generated by CO_2 reduction and its isotope signature was affected by degree of methanogenesis and mixing

PG-19: Geochemical indicators for formation of natural gas hydrates in the Southeastern Ulleung basin, East Sea off the east coast of Korea

B.J. Ryu, J.H. Kim, Y.J. Lee, T.J. Cheong

Petroleum and Marine Resources Research Division, Korea Institute of Geoscience and Mineral Resources (KIGAM), 30 Gajeong-dong, Yuseong-gu, Daejeon, 305-350 Korea (e-mail: bjryu@kigam.re.kr)

Studies on natural gas hydrates have been performed in Korea Institute of Geoscience and Mineral Resources (KIGAM) with financial supports from Ministry of Commerce, Industry and Energy (MOCIE) and Korea Gas Corporation (KOGAS) since 2000. As the parts of this project, research surveys involving core sampling of the shallow sediments and detailed grids of 2-D multichannel seismic lines, etc. have been carried out in deep-water East Sea off the east coast of Korea by using R/V Tamhae-2 (IGT: 2085 GRT, length: 64 m, breath: 15 m) of KIGAM.

To evaluate the potential for the formation and presence of natural gas hydrates in the southeastern Ulleung Basin, 5 piston cores recovered from the water depth of 2283 ~ 2450 m were analyzed in this study. Average contents of total organic carbon (TOC) of the analyzed core sediments range from 1.73% to 2.39% that suggest a good condition for the formation of natural gas hydrates. Two core sediments associated with horizontal cracks recovered in the southern part of the study area show high concentrations of residual hydrocarbon gas (up to 197.07 ml HC gas/liter wet sediments) mainly composed of methane that could also favorable for natural gas hydrates formation. The lack of higher hydrocarbons and the stable carbon isotope ratios (-86.5 ~ -69.5‰) indicate that the gas is primarily biogenic origin. The horizontal cracks would be formed by gas expansion from dissociated natural gas hydrates. Moreover, bottom simulating reflectors (BSRs), the most important geophysical indicators for presence of natural gas hydrates are commonly found on seismic sections acquired in the areas where the 03GHP-01 and 03GHP-02 cores were recovered. In spite of high TOC contents, the low concentrations of residual hydrocarbon gas of the core sediments recovered in the northern study area would be related with the depth of sulfate methane interface (SMI). The measured SMI depths in the southern part of the study area are deeper than those in the northern part.

PG-20: Gas expulsion from coals (Brent and Åre Fm NOCS); New proofs and understanding

D.A. Karlsen[1], S.E. Ohm[1,2]

1) Department of Geosciences, P.O.Box 1047, University of Oslo, Blindern, N-0316 Oslo, Norway
2) ConocoPhillips Norge, P.O.Box 220, N-4098 Tananger, Norway (e-mail: sverre.e.ohm@conocophillips.com)

Much has been published regarding hydrocarbon generation in coals as a result of *in-vitro* or similar artificial pyrolysis and extraction techniches. The literature becomes, however, sparse when it comes to documentation of actual natural expulsion products from coals. We have in this study analysed gas composition and isotope values of gas liberated from coals by simple crushing (Brent coal n=5 and Åre coal n=5, NOCS), i.e. residual gas from coals at "oil-window" maturity . These values were compared to those representing gas from fluid inclusions. The fluid inclusions were formed *in-situ* in sandstones in contact with the coals. Thus, the strategy was to utilize gas trapped in water/gas inclusions as gas became liberated in nature from the coals. The gas liberated by crushing of the coals was found to be isotopically identical to that liberated from inclusions. This strongly suggests the gas in the inclusions to have been derived mainly from the coals. Furthermore, the methane was found in all but one case to be isotopically very light with $\delta^{13}C$ values in the range of -58 to -72‰, whilst for ethane, values fell in the much heavier and "normal" and expected range of -24 to -32‰. Similarly, for propane the $\delta^{13}C$ values fell mostly between -24 to -34‰ and for the butanes between –23 to - 34‰. The methane liberated from the coals by gentle crushing and from inclusions is isotopically very different from most of the gas discovered on the norwegian continental shelf (NOCS) in which methane generally fall in the range of -42 to -45‰. It is, furthermore, very much lighter than the gas traditionally expected to be formed form coals if one consider the most commonly used characterization diagrams published over the last 3 decades. Note that the optically measured vitrinite reflectivity of the coals (n=10) range from 0.5-0.6 (n=2) to 1.3%Ro, with most of the samples around 0.8 to 1% Ro, corresponding roughly to the mid-oil-window maturity. These coals are therefore generally not immature, nor highly mature (in the dry gas window).

All inclusion samples contain dominantly methane (between 70 to 90%). Gas from the coals was compositionally much wetter. This is due to selective loss of methane and ethane which both have the same small kinetic diameter. Propane and butane (plus hexanes and higher homologues) with their larger kinetic diameters were more effectively retained in the coals during expulsion in nature and during core retrieval and storage.

It could be argued that gas liberated by crushing potentially could have been affected by isotope fractionation during desorption. As, however, the carbon isotope data for gas species are similar in coals and inclusions we believe to have proven that desorption processes are of little if any importance.

Based on the identical carbon isotope composition of inclusion gases and gas liberated by crushing of coals, it is clear that we must adopt a much more humble position than to state that the gas in traps in these regions is necessarily always 100% Upper Jurassic ‘hot-shale’ derived in origin.

As to the origin of the gas, data presented in this study show that methane from coals can have isotopically light values, at least up to a maturity of c. 1% Ro, and that also the relatively minor amounts of ethane, propane and butanes generated from these coals have isotope values similar to that found for marine Type II kerogen derived gas species.

It is clear that this place a whole new perspective, not only from an academic point of view as to the gas isotope values in coals, but also to prospectivety and trap filling off Mid-Norway and most likely along the whole NOCS.

CONCLUSIONS

1. Coals with “oil- window” maturities liberate isotopically light methane upon crushing.

2. Water/gas inclusions formed in sandstones in close proximity to the coals contain isotopically light methane of the same type as found in the coals.

3. The release of methane in nature from coals is not associated with carbon isotope fractionation.

4. The data from the coals proves that methane and ethane, which have identical kinetic diameters, are preferentially lost from coals compared to higher homologous.

5. We may have to consider that traps, earlier believed to contain gas from the Upper Jurassic ‘Hot-shales” may in fact have received gas, and in cases are receiving methane from the coaly Brent/Åre Fm.

6. The heavy coal isotope signature was in this study only found for an inertinitic coal. Hence, coals with different maceral (vitrinite and some hydrogen rich macerals) compositions give off isotopically lighter methane. Hence we need to consider in more detail the coal lithotypes before predicting the carbon isotope values for the gas most probably given off in an exploration region.

PG-21: Early versus late generation of gas from coals and marine source rocks

F. Lorant[1], F. Behar[1], M.D. Lewan[2]

1) Institut Français du Pétrole, 1-4 avenue de Bois Preau, 92852 Rueil-Malmaison, France
2) US Geological Survey, PO Box 25046, Denver, CO 80225-0046, USA

The contribution of primary cracking in source rocks to thermogenic gas generated within sedimentary basins is still subject to controversy. Classical scheme of gas generation, like that provided by Tissot and Welte (1984), infer primary cracking gas would mostly occur at low to mild thermal maturity levels, while gas generated after the catagenesis zone would rather originate from oil secondary cracking, either in source rocks or in reservoirs. Published studies based on artificial maturation experiments seem to agree with this concept: hydrocarbon gas generation from type III kerogens would mostly be completed at vitrinite reflectance values between 1.8 and 2.0%Ro (*e.g.*, Rohrback et al., 1984; Kotarba and Lewan, 2004). Moreover, gas yields measured during oil cracking experiments are usually much higher than those generated during primary cracking (*e.g.*, Behar et al., 1992; Henry and Lewan, 2001). Consequently, primary cracking in 'oil-prone' source rocks is a source of thermogenic gas that is often neglected.

However, the use of this type of gas formation scheme in basin simulators usually fails to account for the very large volumes of hydrocarbon gas (compared to oil volumes) often observed in natural reservoirs. A possible explanation to that underestimation, is that in addition to early gas, the late gas potential of source rocks (*i.e.*, gas generated at vitrinite reflectance values higher than ~1.4%Ro), especially those of type-I and II, might have a significant contribution to thermogenic gas (Lorant and Behar, 2001). If so, then both early and late gas potentials should be taken into account systematically.

In order to better quantify the potential of primary cracking gas in source rocks, contributions of 'early' gas (< 1.4%Ro) and 'late' gas (>1.4%Ro) were experimentally investigated. Early gas generation was studied in the range 0.3 - 0.8 %Ro by running pyrolysis experiments at low temperature (175 to 325°C), in order to avoid any contribution of secondary cracking, on an immature coal (Wilcox Fm, USA) and a type-II kerogen concentrate (Toarcian Shale, France). Pyrolyses were all conducted in a closed system, without addition of water, using 2cc sealed gold tubes (IFP device) and 20cc stainless-steel vessels (USGS device). Corresponding late gas yields were first evaluated using previously published experimental data, obtained from naturally mature samples (Lorant and Behar, 2002). Then, additional pyrolysis runs were performed on mature kerogens, artificially prepared from the two immature samples.

For both samples, early gas potential was largely dominated by non-hydrocarbons (> 90 vol%), mostly CO_2. CO_2 generation occurred first, followed by methane, then C_{2+} hydrocarbons. Observed yields of methane hardly reached 5 mg/g of organic carbon from the immature coal, while more than 15 mg/gC of this gas were generated from the type-II kerogen. The early hydrocarbon gas potential from the 'oil-prone' sample thus appeared to be greater than that of the 'gas-prone' sample.

However, a reverse tendency was observed for late gas (the composition of which was dominated by both methane and CO_2). A late methane potential of ~ 17 mg/g of *initial* organic carbon was found for the type-II kerogen, while the coal sampled generated over 35 mg/g of *initial* carbon in the maturity range 1.4 to 4.0 %Ro. It is worth noticing that due to high pyrolysis temperatures (400 to 500°C), gas generation remained significant even after 2.0 %Ro. In this regards, the geological significance of a part of recorded late methane yields is probably questionable.

This work showed that both early and late gas potentials in source rocks may significantly contribute to thermogenic gas in sedimentary basins. Corresponding kinetic parameters, plus additional data from other samples will be presented and discussed.

Acknowledgements

The authors are very grateful to Augusta Warden for technical assistance during this work.

References

Henry A.A., Lewan M.D. (2001) Chapter D, Comparison of kinetic-model predictions of deep gas generation. In: T.S. Dyman and V.A. Kuuskraa, eds., Geological studies of deep natural gas resources: USGS DDS-67, CD-ROM.

Kotarba M.J., Lewan M.D. (2004) Characterizing thermogenic coalbed gas from Polish coals of different rank by hydrous pyrolysis. Organic Geochemistry, 35, 615-646.

Lorant F., Behar F. (2002) Late generation of methane from mature kerogens. Energy Fuels, 16, 2, 412-427.

Rohrback B.G., Peters K.E., Kaplan I.R. (1984) Geochemistry of artificially heated humic and sapropelic sediments-II: Oil and gas generation. AAPG Bulletin, 68, 961-970.

Tissot B.P., Welte D.H. (1984) Petroleum formation and occurrence, 2nd edition, Springer Verlag, Berlin.

PG-22: A new genetic scheme for natural gas formation and isotopic evidence for oil cracking as a potentially significant source of natural gas in sedimentary basins

Y. Tang[1], M. Schoell[2]

1) Power Environmental Energy Research Center, California Institute of Technology, 738 Arrow Grand Circle, Covina, CA 91722, USA (e-mail: tang@peer.caltech.edu)
2) GasConsult International Inc. 2808 Adeline St. #3. Ca 94703-2224, USA

The positive identification of the source rock(s) of natural gas in a sedimentary basin is still mostly based on empiric models. We developed a method based on laboratory simulation of gas formation and isotope compositions of gas components that allows the correlation of gases to their source(s) and an assessment of amount of gas (gas potential) and time of gas formation. From these experiments we developed a new genetic scheme of gas formation (Fig.1).

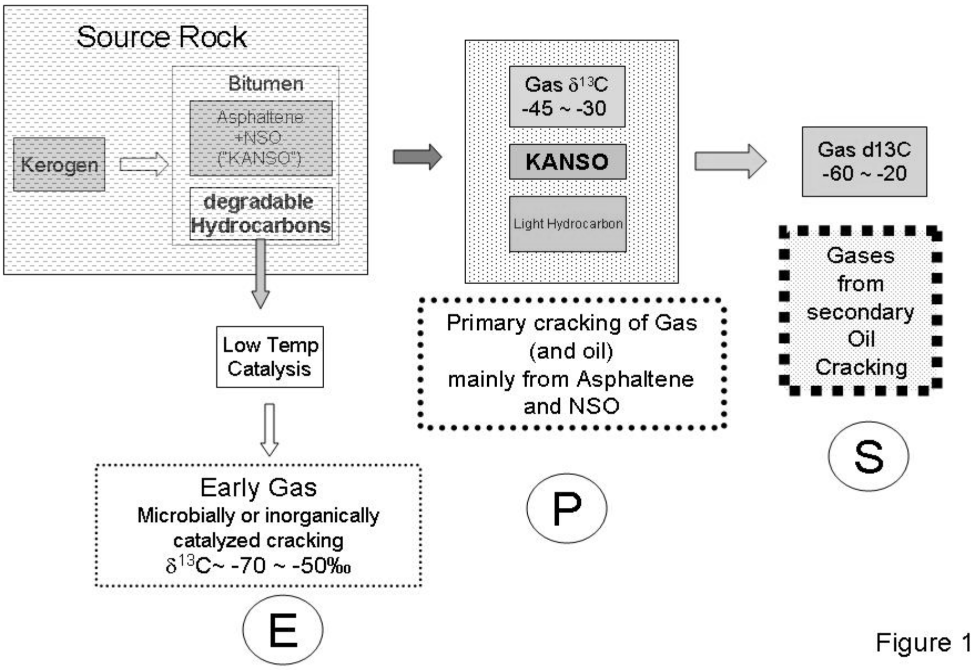
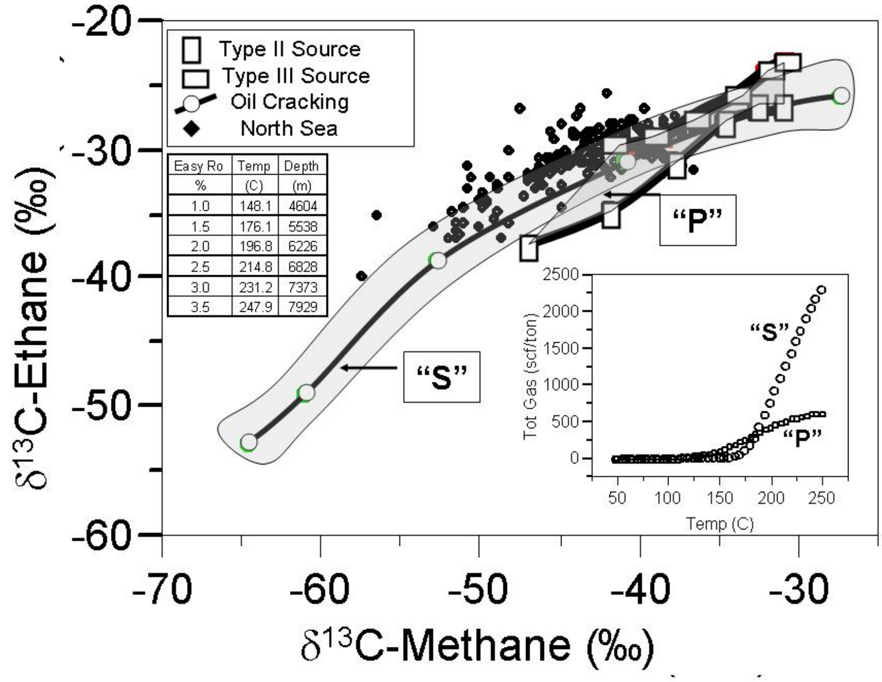


Fig.1. Genetic scheme of gas formation. KANSO depicts the conversion of **K**erogen to **A**sphaltenes and **NSO** compounds as intermediary precursors for primary cracking of gas

We differentiate three principal types of gases:

1) **Early Gas ("E"):** These gases form through low temperature reactions, very likely either biologically or inorganically catalyzed degradation processes of bitumen. Examples are bacterial gases and low-temperature (40 to 80C) shale gases. (e.g. Rowe and Muehlenbachs, Organic Geoch. 30, 861 to 871, 1999).

2) Gas from **Primary Cracking** of KANSO (“P”) form at temperatures starting around 100^{o}C gases form through primary cracking of asphaltenes and NSO compounds
3) Gases from **Secondary Cracking** of oils (“S”) form at temperatures starting around 150^{o}C.One of our findings is that gases from secondary cracking of oils have a high gas potential (inset Fig.2) and are systematically depleted in ^{13}C in methane and ethane compared to gases from primary cracking of KANSO (Fig 2).



Easy Ro	Temp	Depth
%	(C)	(m)
1.0	148.1	4604
1.5	176.1	5538
2.0	196.8	6226
2.5	214.8	6828
3.0	231.2	7373
3.5	247.9	7929

Fig.2. Methane and ethane isotope calibrations and gas potential (inset) for primary cracking of type II and type III kerogens (“P”) and secondary cracking of oil (“S”). The inset Table gives the used Ro steps and corresponding data (Calibration data are compilations for generic Type II and II and oil cracking from the GOR 1.47 software)

Comparing natural gas data with our calibrations, we find for example that gases from the North Sea fit either a type III calibration or are more ^{13}C-depleted than gas from primary cracking. We infer from this observation that secondary cracking is an important source for natural gas in the North Sea as has been recently empirically deduced for the Central North Sea (G.H. Isaksen, 2004, AAPG Bull. 88, 1545-1572, 2004). This may have important implications for gas potential estimates as the gas potential from oil cracking is about 4 times that of gas formation from primary cracking of organic matter in gas source rocks (Inset Fig.2). Isotope calibrations provide, therefore, a means for a better assessment of the amount of gas that can be formed in a sedimentary basin (gas potential) and the prediction where the highest gas potential can be found.

PG-23: Methane formation in the Nile Delta (Egypt): thermogenic versus microbial mechanisms

C. Vandré[1], B. Cramer[2], P. Gerling[2], J. Winsemann[1]

1) IGP - Institute for Geology and Palaeontology, University of Hannover, Callinstrasse 30, D-30167 Hannover, Germany (e-mail: c.vandre@bgr.de)
2) BGR - Federal Institute for Geosciences and Natural Resources, Stilleweg 2, D-30655 Hannover, Germany

Large delta systems have proven to be important oil and gas provinces. The Nile delta, which represents the SE part of the eastern Mediterranean basin, is an emerging gas province and one of the most promising areas for future petroleum exploration in northern Africa. In the last years, drilling in the western offshore delta encountered several new commercial gas/condensate discoveries. To determine whether microbial or thermogenic processes are the dominant source of methane, a regional study was performed on the geochemistry of gases and condensates (samples were kindly provided by RWE Dea Egypt and BP Egypt) from major producing Neogene intervals. Main constituents of the gas are methane (> 91 vol. %) up to pentane with traces of carbon dioxide and nitrogen. Chemical and stable isotope ratios of the natural gases and condensates suggest several genetic systems which appear to correlate with the regional stratigraphy: shallow microbial gas generation ($\delta^{13}CH_4 < -60$ ‰) in Plio-Pleistocene sediments; a variable mixture of microbial and thermogenic gases ($\delta^{13}CH_4$ between -45 ‰ and -60 ‰) trapped mainly in Pliocene rocks, and thermogenic gas ($\delta^{13}CH_4$ between -30 ‰ and -45 ‰) occurring in the Pre-Miocene to Miocene section. The mixed and the thermogenic gases are frequently accompanied by condensates (41-56 °API).

In addition to the processes of thermogenic gas generation by cracking of kerogen and microbial gas generation by microbial decomposition of dispersed sedimentary organic matter, isotope geochemical data support the assumption of methane generated by microbial degradation of thermogenic hydrocarbons (*secondary microbial methane*). The mechanisms and the importance of this process were recently discussed controversially in several studies ([1], [2], [3], [4]). Our data indicate that all Neogene gas and gas/condensate accumulations in the Nile Delta investigated are influenced by microbial alteration. Biodegradation of the condensates led to the preferential loss of higher n-alkanes. Anomalously heavy isotope compositions of both propane (Fig.1) and n-butane suggest microbial oxidation of these wet gas components [5]. In contrast, ethane and pentane seem to be less intensively affected. Unaltered gases (Group 2, see Fig.1) are commonly found in association with altered condensates. This indicates that during initial stages of microbial alteration, condensates are selectively attacked. In case of gas accumulations without condensates, propane is most intensively affected (Group 1, see Fig.1).

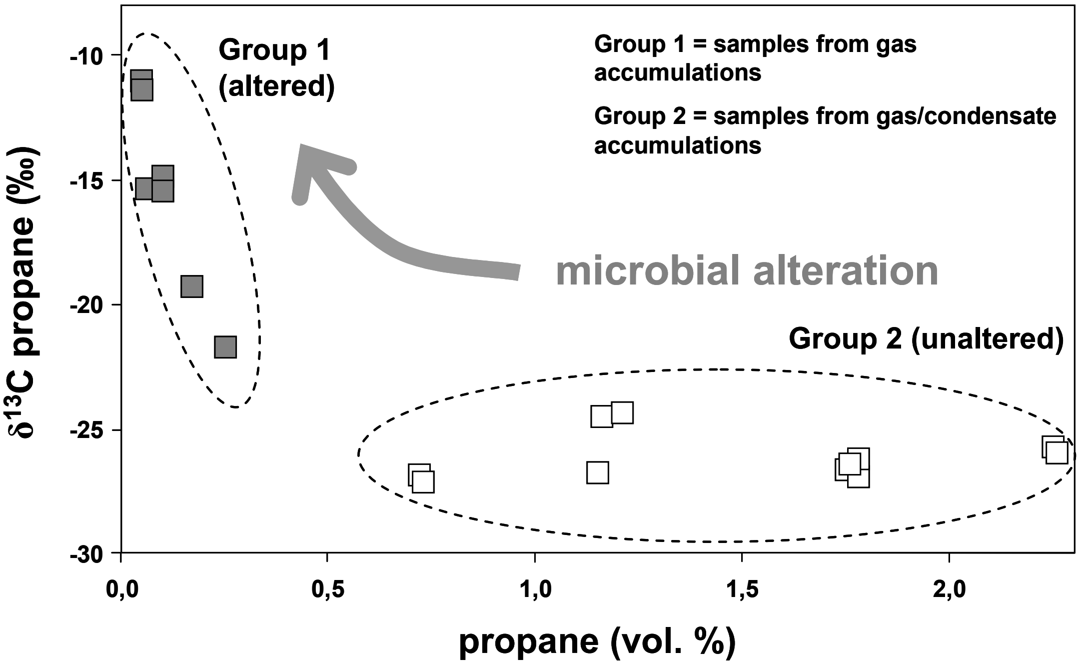


Fig.1. Plot of $\delta^{13}C$ versus vol. % of propane showing the influence of microbial alteration on propane from natural gas in the western Nile Delta

References

[1] Clayton, C.J., Hay, S.J., Baylis, S.A., Dipper, B., 1997. Alteration of natural gas during leakage from a North Sea salt diapir field. Marine Geology 137, 69-80.

[2] Zengler, K., Richnow, H.H., Rosselló-Mora, R., Michaelis, W., Widdel, F., 1999. Methane formation from long-chain alkanes by anaerobic microorganisms. Nature 401, 266-269.

[3] Pallasser, R.J., 2000. Recognising biodegradation in gas/oil accumulations through the $\delta^{13}C$ compositions of gas components. Organic Geochemistry 31, 1363-1373.

[4] Martini, A.M., Walter, L.M., Ku, T.C.W., Budai, J.M., McIntosh, J.C., Schoell, M., 2003. Microbial production and modification of gases in sedimentary basins: A geochemical case study from a Devonian shale gas play, Michigan basin. American Association of Petroleum Geologists Bulletin 87, 8, 1355-1375.

[5] James, A.T., Burns, B.J., 1984. Microbial alteration of subsurface natural gas accumulations. American Association of Petroleum Geologists Bulletin 68, 8, 957-960.

PG-24: Indigenous and imported gases in the Pannonian basin system

I. Vető

H-1026 Budapest, Balogh Ádám u. 18/c (e-mail: vetoi@mafi.hu)

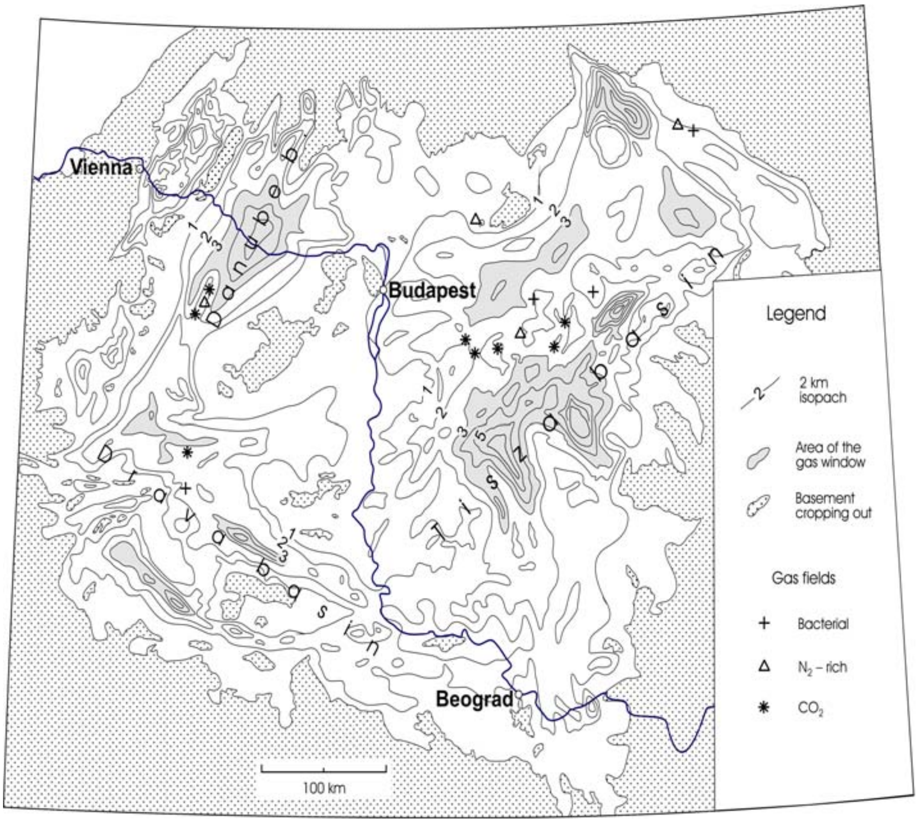
Here a synthesis of data and interpretations published partly in journals of the 8 countries sharing in the basin system is attempted.

Dispersed and water-dissolved gases According to head space studies thermal gas generation starts in the 700-1300 m depth interval. Due to their strong retention by kerogen early thermogenic HC-gases enter the aquifers in insignificant amounts. In aquifers of the upper 2 km the bulk of the water-dissolved CH_4 is of bacterial origin. Bacterial methanogenesis was mostly an early, shallow process but late, deep fermentation played a non-insignificant role. Bacterial processes, maturation, and carbonate decomposition in the basement are important sources of water-dissolved CO_2. Variations of up to several orders of magnitude in CH_4 and CO_2 concentrations reflect dilution by infiltrating glacial-age meteoric waters.

Indigenous gas fields Source rocks are in the gas window below 3-3.5 km depth, the mild Vienna basin excepted. Pliocene and Quaternary were/are the main times of gas formation. According to high $\delta^{13}C_{methane}$ values, the bulk of the gas is of late catagenetic origin and in case of some fields as much as 3.5 km of vertical migration has occurred. In agreement with absence of evaporites, most of the fields contain only traces of H_2S, but some deep fields in the Drava and Vienna basins, trapped in anhydrite-bearing Triassic basement, consist of sour gas. Bacterial gases, accumulated in both sands and lignites, comprise about 5% of the reserves. Despite the great volume of overmature sediments in the Danube basin, no indigenous gas fields are known in it. This fact reflects absence of good source rocks.

Imported gases Terranes building up the basement contain source rocks with varying type and richness of kerogen which had attained different maturities before the basin system started to develop. Due to early Miocene thrusting, fast burial and/or high heat flow some of the terrane source rocks have been strongly reheated, which resulted in generation of important amounts of catagenetic and metagenetic gases. Renewal of maturation in immature late Jurassic black shales in the deep basement of the mild Vienna basin led to formation of commercial gas (and oil) fields in both Neogene reservoirs and the overthrusted Triassic basement. In the north of the hot Tisza basin a similar scenario resulted in generation of late catagenetic gases and N_2-rich metagenetic gases (HC gas / N_2 = ~2.5) in the already mature early Jurassic coaly sequence. These gases migrated through the overthrusted U. Cretaceous-Paleogene flysch basement and accumulated in Neogene reservoirs. Small fields of N_2-rich gases are known also in other parts of the basin system. Due to high heat flow, temperature prevailing in the lower crust made/makes possible intense decomposition of carbonates, resulting in formation of considerable reserves of CO_2 throughout the basin system, the mild Vienna basin excepted.

High $\delta^{13}C$ values, low Ar and He-contents and high $^3He/^4He$ ratios measured in some fields support their deep, carbonate decomposition origin. Mixing of N_2-rich gases and CO_2, reaching the traps in different times, is recorded by some multipay fields.



	Indigenous gases Gm^3		imported gases Gm^3		
basin	bacterial	catagenetic	catagenetic	N_2-rich	CO_2
Vienna	insignificant	insignificant	44	no	no
Danube	no	no	no	1	min. 10
Drava	min. 6	min. 50	no	no	min. 15
Tisza	min. 20	max. 320	min. 5	10	35

Ackmowledgements

The support of the OTKA (Grant T 048829) is acknowledged.

References

Ballentine et al. 1991 *Earth and Planetary Science Letter*, 105, 229-246., Baric et al. 1998 *Organic Geochemistry*, 29, 571-582., Clayton et al. 1990 *Organic Geochemistry*, 15, 233-247., Fedor F 2003 Thesis of University of Miskolc, Kárpáti et al.. 1999 *Organic Geochemistry,* 30, 701-712. Koncz and Etler 1994 *Organic Geochemistry*, 21, 1069-1080. Ladwein 1988 *AAPG Bull*., 72, 586-599. Sherwood Lollar et al. 1997 *Geochim. Cosmochim. Acta*, 61, 2295-2307. Vető et al. 1997 18th *Int. Meeting on Org. Geochem*., Maastricht, Abstracts, p. 229-230. Vető et al. 2004 *Organic Geochemistry*, 35, 713-723.

PG-25: Experimental study of n-octadecane thermal cracking

H. Zhang, A. Geng, Y. Xiong, J. Liu

State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Wushan, Guangzhou 510640, China (e-mail: asgeng@gis.sti.gd.cn)

Recently Gas generation from the late cracking of crude oils in reservoir is considered one of important source of thermogenic gas. Crude oils as a special gas precursor, shows different gas-generation characteristics from those of kerogen. Therefore, the study of oil cracking (including the gas-generating potential of the oil, chemical and isotopic compositions of residual oil) can not only improve our understanding of the genesis of natural gases, but also provide practical application tools for the source identification and quantitative assessment of oil-derived gases. The aim of this work is to determine the molecular and stable carbon isotope compositions of pyrolysates from normal octadecane and to study methane generation kinetic and carbon isotope fractionation of gaseous hydrocarbon generated from n-C_{18} cracking.

Pyrolyses were carried out in anhydrous closed system (gold tubes) under a constant pressure of 50 MPa at heating rates of 20°C/h and 2°C/h. Yields and $\delta^{13}C$ values of gaseous hydrocarbons in pyrolysates are shown in Fig. 1.

Based on gas compositions, gas chromatograms and total ion current plot of residual liquid hydrocarbons, it is clear that the main temperature range for thermal cracking of n-octadecane occurs from 350 to 480°C, corresponding to a maturity of 0.9 to 2.0%Ro. At the initial stage of n-octadecane cracking, polymerization concurs to form C_{18+} n-alkanes with n-octadecane cracking. Above 460°C, cyclization and aromatization of n-alkanes lead to abundant aromatic compounds for which alkylation, dealkylation, and aromatic ring condensation occurrs resulting in gaseous hydrocarbons and coke with increasing pyrolysis temperature. At two heating rates, gas yields are very small at low levels of thermal stress (%Ro<1.0, 400°C). With increasing thermal stress, n-C_{18} cracks to form C_1, C_{2-5}, C_{6-17}, C_{18+}, aromatic compounds and coke fractions. Methane and coke increase continually as thermal stress increases, which shows that methane and coke are the thermodynamically stable end products expected from n-C_{18} cracking. Pyrolysis yields were used to model methane generation with a series of parallel, first-order reactions with activations energies between 64 and 75 kcal/mol and a single frequency factor of 1.59×10^{15} s^{-1}. Extrapolation of these parameters to geologic heating rates suggests that gas from saturated hydrocarbons cracking begins to generate at 170°C during geological times but a great deal generates at 200°C. This results show that secondary cracking of saturated hydrocarbons, a major fraction in reservoir oils, does not produce a large proportion of gas even in deep conditions.

With the increase of the degree of thermal evolution, early in the pyrolysis process, methane, ethane and propane become depleted in ^{13}C. After reaching a minimum of $\delta^{13}C$ value, methane, ethane and propane become enriched in ^{13}C as thermal evolution increases. At higher pyrolysis temperatures ethane and propane become depleted in ^{13}C again (Fig. 1). Cracking and polymerization in the relatively low temperatures are probably causes for the first carbon isotope composition reversal of gaseous hydrocarbons. Disproportionation reactions of aromatics at high temperature are probably a main reason of the secondary carbon isotopic composition reversal of gaseous hydrocarbons.

In addition, the heating rate has a significant effect on the variation of carbon isotope composition of gaseous hydrocarbons, e.g. with the increase of the heating rate, the $\delta^{13}C$-trend of pyrolysis gas will shifts toward higher temperatures (Fig. 1). The magnitude of difference between $\delta^{13}C_{ethane}$ and $\delta^{13}C_{propane}$ increases in a closed system as thermal stress increases.

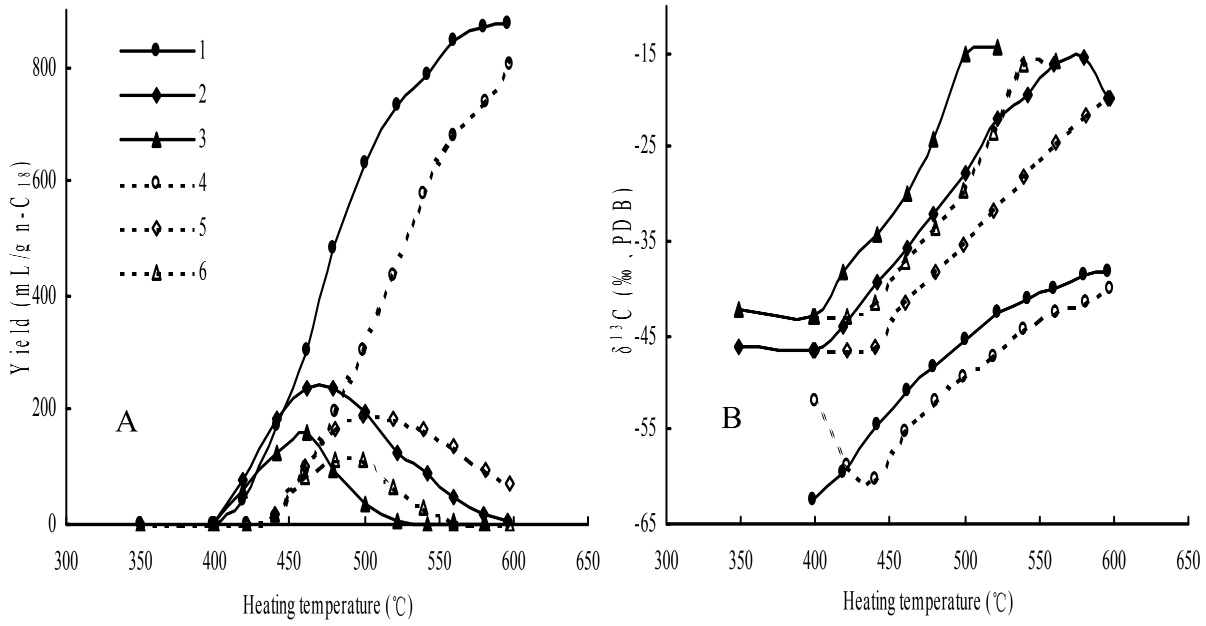


Fig.1. Yields and $\delta^{13}C$ values of gaseous hydrocarbons C_1-C_3 during n-octadecane cracking: A; yields of gaseous hydrocarbons B; $\delta^{13}C$ values of gaseous hydrocarbons. 1.2°/h, methane; 2. 2°/h, ethane; 3. 2°/h, propane; 4. 20°/h, methane; 5. 20°/h, ethane; 6. 20°/h, propane.

PG-26: Sorption of methane and carbon dioxide in hard coals and its consequences for gas storage

P. Baran, G.S. Jodłowski, A. Nodzeński, M. Wójcik

University of Science and Technology – AGH, Faculty of Fuels and Energy, al. A.Mickiewicza 30, 30-059 Kraków, Poland (e-mail: jodlowsk@uci.agh.edu.pl)

Introduction

Measurements of the sorption isotherms of carbon dioxide and methane on Polish hard coals, as well as analysis of the sorption phenomena by the Multiple Sorption Model elaborated in the Faculty are presented. The aim of this work is to obtain detailed insight into the mechanism of co-sorption of CH_4 and CO_2 from the mixture and elaboration of the theoretical description of the process. The preliminary investigations allow some conclusions on methane storage or carbon dioxide sequestration.

Experimental

Sorption isotherms of CO_2 and CH_4 were measured on the high pressure equipment under the following conditions: pressure range to 3.6 MPa and temperatures 293 K or 303 K [1]. Coal samples (hard coals or active carbons) were cleared of sorbed molecules at low pressure (10^{-3} Pa) before measurements. The obtained sorption isotherms were converted to their numerical representations (about 30 points) for computation. The unique multiple sorption model (MSM) was used for the theoretical analysis of the sorption process [2]. The model takes into account the simultaneous occurance of the wide variety of phenomena: absorption and adsorption, as well as swelling subsystem, as an intermediate phenomenon. The adsorption model was developed to the polylayer model with a limited capacity of the subsequent layers [3,4,5]. In order to include multilayer sorption the gases MSM model is extended with special equation of gas state [6].

Results

From investigations it may be derived that significant difference between location process of the CO_2 and CH_4 occur. In the case of carbon dioxide adsorption and absorption are equivalent phenomena (see the Figure 1). On the other hand, methane sorption process consists mainly of adsorption and, to a limited extend, expansion (i.e. swelling of coal mass and contraction of porous structure). In this case penetration of bulk of the coal mass could be neglected.

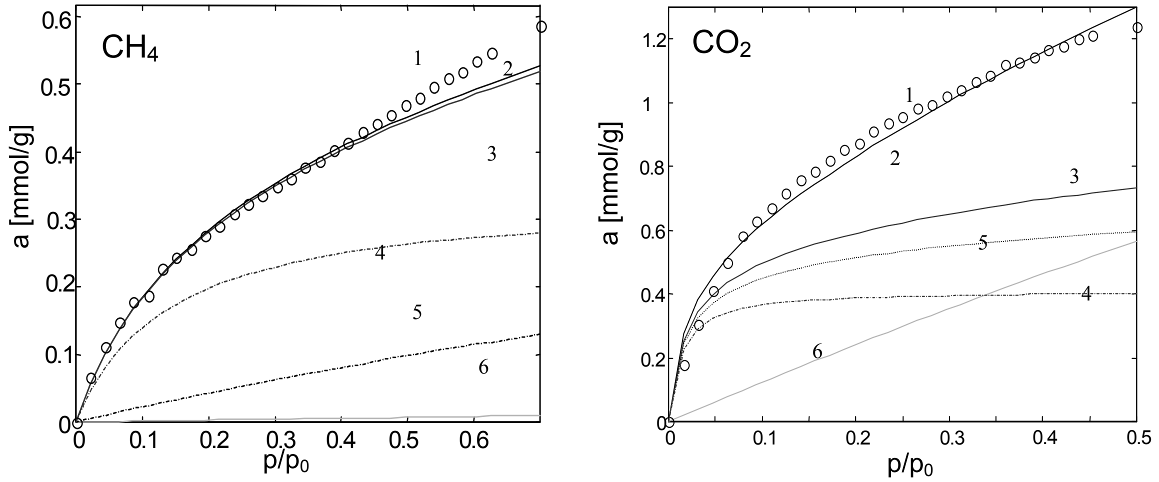


Fig.1. Multiple sorption isotherms of the CH_4 and CO_2 on the low rank coal (80.88 % C^{daf}): 1 – empirical sorption, 2 – theoretical sorption, 3 – total adsorption, 4 – monolayer adsorption, 5 – expansion isotherm (swelling), 6 – absorption (all lines denote theoretical - computed values)

Conclusions

From the point of view of methane storage and sequestration of carbon dioxide, the occurring phenomena in the sorption process are advantageous. The penetration of coal mass by the molecules of CO_2 leads to higher capacity of the gas in the mine area. The lack of penetration of the methane molecules into the bulk of hard coal in combination with swelling and contraction of pore structure results in lower risk of leaking of the gas pumped to the mine. Thus, it may be assumed that exploited – closed mines could be a reservoir for the gas storage or carbon dioxide sequestration.

Acknowledgements

This work is carried out with the financial support of Polish State Committee for Scientific Research, project No. 4T 12A 02027.

References

[1] Milewska-Duda J., Duda J., Nodzeński A., and Lakatos J., Langmuir, 2000, **16**,5458 – 5466
[2] J.Milewska-Duda, J.Duda, Langmuir, 1993, **9**, 3558-3566.
[3] J. Milewska-Duda, J.Duda, G.Jodłowski, M.Kwiatkowski, Langmuir 2000, **16**, 7294-7303
[4] Janina Milewska – Duda, Jan T. Duda, Colloids and Surfaces A, **208**, 71-81 (2002)
[5] Janina Milewska – Duda, Jan T. Duda, Applied Surface Science, **196**, 115-125 (2002)
[6] J. Milewska-Duda, J.Duda, G.Jodłowski, M.Wójcik, Langmuir 2000, **16**, 6601-6612

PG-27: Sorption of small molecules of organic substances in hard coals

G.S. Jodłowski, J. Milewska - Duda, M. Wójcik

University of Science and Technology – AGH, Faculty of Fuels and Energy, al. A.Mickiewicza 30, 30-059 Kraków, Poland (e-mail: jodlowsk@uci.agh.edu.pl)

Introduction

Behavior of the complex molecules on sorbent surface is very interesting from the point of view of theoretical models of adsorption. When constructing a thermodynamical model, some simplifying assumptions are usually made. The multiple sorption model (MSM) elaborated at the Faculty contains some simplifications [1-5]. The aim of this work is to investigate of the properties of sorption systems consisting of hard coals and different type organic molecules. Additionally properties of the model are tested for more complex molecules.

Measurements

Sorption isotherms of hexane, heptane, octane, cyclohexane and benzene on different rank hard coals were measured using the following procedure. Samples of coals were inserted into liquid microburettes equipment, the grain size of the coal probe being about 0.2 mm. The samples were degassed at pressure of 10^{-3} Pa, and then sorption isotherms at the room temperature were measured.

Hard coal structure is partially elastic, so one could expect absorption or swelling phenomena proceeding slowly. In order to take it into account, each experimental point of the isotherm was measured for ca two days.

Computations

The empirical isotherms were used for comparative simulation experiment; the basis at which were known trends in hard coal structure versus coal rank and properties of the sorbate the MSM model was used. It is a complex tool in which absorption and adsorption phenomena, as well as expansion of coal matter, are taken in to account [1-6]. The computation procedure was carried out until agreement of empirical and simulated isotherms is reached.

Model enables us to differentiate between absorption, adsorption and expansion subsystems from sorption process with a detailed porous system description. The results of the computations allow the conclusion that chain molecules (e.g. hexane) take the plate-like or globular shape and their behavior in the adsorption system is similar rather to benzene than to cyclohexane [7]. On the other hand monolayer capacities calculated from the hexane and cyclohexane isotherms are nearly the same. These facts in connection with total adsorption capacity of hexane which is ten times greater, shows that adsorption of hexane is evidently multiplayer. Moreover hexane molecule locate differently on the surface: a part of molecule introduces the pore, while a part is on the external surface or is not adsorbed being the adsorption center for next molecules.

Conclusions

The ring molecules (e.g. cyclohaxane or benzene) could be considered as a spherical-like, while the chain molecules lead to complications. A simplifying assumption on the negligibility of molecules location order is not precise and should be reconsidered. Nevertheless, the MSM is a useful tool for analysis of sorption process of complex sorbents such as hard coal.

Acknowledgements

The work was carried out under financial support of University of Science and Technology – AGH Statutory Research No. 10.10.210.52.

References

[1] J.Milewska-Duda, J.Duda, Langmuir, 1993, **9**, 3558-3566
[2] J. Duda, J. Milewska-Duda, Journal of Mathematical Chemistry, 1995, **17**, 69 – 109
[3] J. Milewska-Duda, J.Duda, G.Jodłowski, M.Kwiatkowski, Langmuir 2000, **16**, 7294-7303
[4] Janina Milewska – Duda, Jan T. Duda, Colloids and Surfaces A, **208**, 71-81 (2002)
[5] Janina Milewska – Duda, Jan T. Duda, Applied Surface Science, **196**, 115-125 (2002)
[6] J. Milewska-Duda, J.Duda, G.Jodłowski, M.Wójcik, Langmuir 2000, **16**, 6601-6612
[7] M.Żyła, G.S.Jodłowski, M.Wójcik, Fyzika. Chemie. Sbornik Prací Prirodovedecké Fakulty Ostravské Univerzity. 1999, **7,** 15-32.

PG-28: Origin and accumulation model of the AK-1 natural gas pool from the Tarim basin, China

X.M. Xiao[1], Q.H. Zheng[1], Y.C. Tang[2], R.W.T. Wilkins[3]

1) State Key Laboratory of Organic Geochemistry, Guangzhou Institute of geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China (e-mail: xmxiao@gig.ac.cn)
2) Petroleum Energy and Environmental Research Center, California Institute of Technology, 20970 Currier Rd, Walnut, CA 91789, USA
3) CSIRO Petroleum , P. O. Box 136, North Ryde, NSW, Australia

The AK-1 Gas Pool is the first commercial gas pool recently discovered in the Kashi Depression, northwest Tarim Basin. The geochemical data show that the pool is characterized by a very dry hydrocarbon gas with an average dry index >0.995, a very heavy methane carbon isotopic value with an average $\delta^{13}C_1$ of -25‰, and an abnormally heavy $\delta^{13}C_2$ with an average $\delta^{13}C_2$ - $\delta^{13}C_1$ value of 3.9‰. For the main production reservoir there is a high content of CO_2 with a $\delta^{13}C_{CO2}$ value of -8.6‰. These features indicate that the hydrocarbon gas from the gas pool was originated from multiple sources, and that the CO_2 is of mixed inorganic and organic origin. There are two possible source areas: the lower block of the AK-1 overthrust structure and the central area of the Kashi Depression. In these areas two sets of source rocks are developed - lower Carboniferous mudstone and lower and middle Jurassic coal measures, typically with type II and type III kerogens respectively. Both the reservoir fluid inclusion data and the trap structure evolution indicate that the gas pool was formed during the Pliocene- Quaternary. On this basis, geological models of methane generation and carbon isotopic fractionation of the two sets of source rocks from the two source areas were established. By comparison of modeled results with the geochemical characteristics of the gas pool, it can be inferred that the source rock of the gas pool is the lower Carboniferous mudstone, and the main source area is in the lower block of the AK-1 overthrust structure with a secondary source area in the center of the Kashi Depression. The pool gas may be regarded as a late stage cumulative gas, the structure trapping gas from the source rock with a methane conversion rate of 0.64-1.0 in the lower block of the AK-1 overthrust structure together with some very dry hydrocarbon gas, N_2, and inorganic CO_2 from the thermal decomposition of carboniferous carbonate rocks in the central area of the Kashi Depression.

Keywords: AK-1 Gas Pool, Kashi Depression, Tarim Basin, gas source, gas accumulation model.

PC-1: Quantitative organic sulphur functionality study of Bulgarian low rank coal lithotypes by reductive pyrolysis off-line coupled with GC/MS

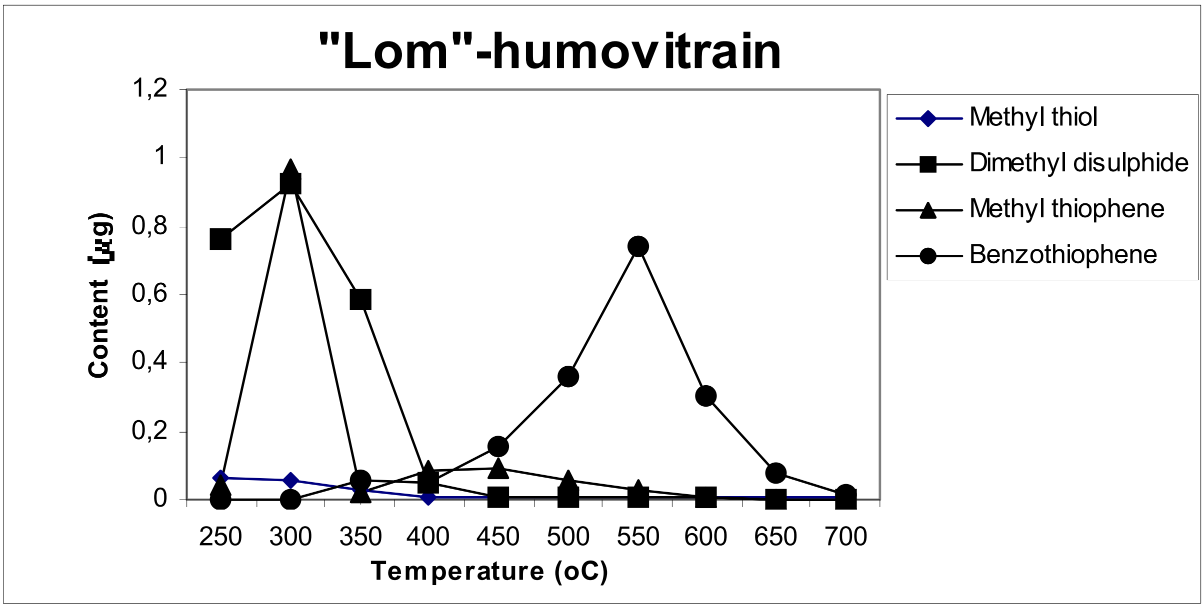
S. Marinov[1], M. Stefanova[1], V. Stamenova[1], L. Gonsalvesh[1], R. Carleer[2], J. Yperman[2]

1) Inst.Org.Chem.Bulg.Acad.Sciences, Sofia 1113, Bulgaria (e-mail: stif@bas.bg)
2) Lab.Appl.Chem., CMK, Limb.Univ.Centrum, B-3590, Diepenbeek, Belgium

The organic sulphur functionality study was performed on the three main lithotypes of low maturity "Lom" coal (lignites), North Bulgaria, i.e. humovitrain, xylain and humoclarain. Dominated "Lom" coal lithotypes were humoclarain (>60%), followed by xylain and humovitrain. The content of fusain plus semifusain was ~1%. The age of the coal-bearing basin measured for "Lom" lignites was Dacian and in thickness strata it range from 15 to 40m [1]. This basin has not industrial importance. The aim of the investigation was a quantitative organic sulphur functionality study on basic "Lom" lignite lithotypes by atmospheric pressure-temperature programmed reduction (AP-TPR)-GC/MS techniques.

Lithotypes were hand picked and optically defined by MPT 2 Opton device. Preliminary treatments by dilute 5% HCl for carbonate removal and depyritization by ferric sulphate refluxing to avoid undesirable influence on sulphur AP-TPR profile interpretation were performed. Contents of S-organic in the treated lithotypes were the highest in the homogeneous lithotypes humovitrain and xylain, ~2.5 %. The performance of the AP-TPR experiments was described in a previous study [2]. The system was now supplementary "off-line" connected to GC/MS to analyze evolved gases. The analyses were run in discrete temperature intervals each 50^o +/- 15^oC starting from 250 ^oC. The volatiles were collected up to 700 ^oC by means of cooled Tenax tubes. After collection, a thermal desorption step was carried out for transferring the volatiles towards the GC-MS apparatus [3]. SIM monitoring, using clusters of specifing mass fragments that related to individual organic sulphur compounds allowed a dedicated detection of these compounds. The following ions were considered: *m/z* 47 +14n for thiols; *m/z 62* + 14n for aliphatic sulphides; *m/z* 94 for disulphides; *m/z* 84 + 14n for thiophenes; (with n = number of CH_2 units) and *m/z* 134 for benzo[b]thiophenes. Each Tenex tube was spiked with 5µl d6-Benzene methanol solution to obtain quantitative results for the target sulphur species. The highest amounts of these sulphur compounds were found for methylthiol, methylthiophene, benzothiophene and dimethyldisulphide. Dimethyldisulphide maximized at 300-350 ^oC and dominated at low temperature region for all studied lithotypes in their kinetograms. Trisulphides were found only for xylain in minor amounts. Thiophenes and their alkylated homologues were identified in the lower temperature range. Benzothiophene appeared at low temperature but its concentration increased with temperature and the maxima was found at 500-600 ^{o}C for all lithotypes. Sulphur analogues of polycyclic aromatic compounds could not be expected bearing in mind the immaturity of studied coals. On the figure below, some distributions of the highest abundant sulphur species in the humovitrain sample in micrograms as a function of the temperature are shown.

The proposed AP-TPR-GC/MS "off-line" coupling enriched our knowledge not only of the organic sulphur forms in immature coal lithotypes but also improved the knowledge of sulphur speciation in the solid materials.



References

[1] Šiškov G.D., Stefanova Y.S., Angelov A.T., 1984. Petrological characteristics of coals from Lom basin, North Bulgaria. C. R. Bulg. Acad. Sci. 5, 779-781.

[2] Yperman J., Maes I.I., Van den Rul H., Mullens S., Van Aelst J., Franco D.V., Mullens J., Van Poucke L.C., 1999. Sulphur group analysis in solid matrices by atmospheric pressure-temperature programmed reduction. Anal. Chem. Acta 395, 143-155.

[3] Marinov S.P., Stefanova M., Kostova I., Stamenova V., Carleer R., Yperman J., 2005. Peculiarities of sulphur functionalities in the Thracian coal province, Bulgaria. Bullet. of Geosciences (Czech Geol. Surv. ISSN 1214-1119), 80, №1, 33-38.

PC-2: Lignite carboxylic acid moieties view by CuO oxidation and thermochemolysis

M. Stefanova

Institute of Organic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev str. Bld. 9, Sofia 1113, BULGARIA (e-mail: maia@orgchm.bas.bg)

In a suite of studies lithotypes of extremely immature Bulgarian lignite “Maritza-Iztok”, R_o=0.18%±0.02, were under consideration. The compositions of extractable portions, biomarker assemblages, products of desulphurisation, etc. were under study. Later on, the contents of preserved lignin structures in Miocene-aged lithotypes were determined by CuO oxidation and analysis of products by capillary zone electrophoresis and GC-MS [1]. In the present study an attempt to assess carboxylic acid moieties in lignite by oxidation and thermochemolysis will be done.

The results of conventional pyrolysis of lignite lithotypes revealed the lack of carboxylic functions. To overcome the drawbacks of the pyrolytic technique it was replaced by thermochemolysis. In the presentation the results on lignite thermochemolysis will be interpreted in comparison with the data of CuO oxidation. The study will be performed on macroscopically distinguishable a hand picked lignite lithotypes. Bulgarian Neogene coals are described by very low exploration characteristics but in them still the relationship with the progenitors can be recognised [2]. The geochemical parameters, EPR data, biomarkers distributions were already described [3]. Our preliminary attempt to use thermochemolysis for lignite characterisation unambiguously confirmed diagenetically altered gymnospermous lignin as main structural unit of lignite organic matter.

Experiments were performed on homogeneous, i.e. xylain, humovitrain and heterogeneous lithotypes, i.e. liptain and humoclarain. A sequence of extraction and hydrolysis in alkaline media gave as possibility to obtain residues completely insoluble in organic media. Subsequently initial lithotypes and insoluble products were subjected to thermochemolysis with tetra methyl ammonium hydroxide (TMAH).

It is documented that with coalification lignin biopolymer is altered and carboxylic acid functions are increased. The process could be appreciated by the ratio Ac/Ad, where Ac described carboxylic acid-containing lignin phenols and Ad, aldehyde-containing phenols, respectively. Calculated values for the ratios obtained after CuO oxidation and thermochemolysis were compared. Data for λ content of lignin phenols released per 100 mg C) determined by CuO will be listed as well. The results will be discussed in relation with the contents of acid, i.e. G_6 (3,4-dimethoxybenzoic acid, methyl ester), G_{12} (3-(3,4-

dimethoxyphenyl)-propanoic acid, methyl ester), and G_{24} (3,4-dimethoxyphenylacetic acid, methyl ester) [4].

With the advance of gelification and humoclarain formation the magnitudes for Ac/Al increased, documented by the two methods. The following values were calculated for humoclarain: 0.87 (by CuO oxidation), 2.7 (by thermochemolysis). The values for the homogeneous lithotypes were comparable (0.64÷0.67, by CuO technique,) and completely coincided (1.7, by thermochemolysis,). With coalification the side chains in phenyl propanoic units were altered resulting in complete disappearance of G_{12} and G_{24} as was observed by thermochemolysis. The values for λ determined by CuO oxidation were as follows: xylain, 11.3, humovitrain, 8.4, liptain, 7.8, and humoclarain, 2.6

Fatty acids, methyl esters were the other carboxylic functionality registered. An appreciable variety was determined in initial humoclarain: $n\text{-}C_{10} \div n\text{-}C_{34}$, with strong dominance of “even” members; α,ω-di C_{21} to α,ω-di C_{29}. Succinic acid was highly abundant in all pyrolysis products, an indication for $-CH_2-$ bridges in lignite organic matter. Fatty acids moieties were capable of identification only in heterogeneous lithotypes.

References

[1] Stefanova, M., Maman O., Guillet, B., Disnar, J.R., 2004. Preserved lignin structures in Miocene-aged lignite lithotypes. Fuel 83, 123-128.

[2] Stefanova, M. 2004. *Taxodium dubium* as progenitor of Bulgarian Neogene coals. Ext.Abst.Book, 10th Int. Conf. Geol. Soc.Greece, Thessaloniki, 602.

[3] Stefanova, M., Czechowski, F., Marinov, S., Jezierski, A., 2001. Molecular study of brown coal lithotypes from Miocene Maritza-East deposit, Bulgaria. Abstr. Book 20th IMOG 1, 269-270

[4] McKinney, D.E., Hatcher, P.G., 1996. Characterization of peatified and coalified wood by tetramethyl hydroxide (TMAH) thermochemolysis. Int. J. Coal Geology 32, 217-228.

PC-3: Aliphatic chains in coals of different age: controls on the ability to generate liquid hydrocarbons

H.I. Petersen, H.P. Nytoft

Geological Survey of Denmark and Greenland (GEUS), 10 Øster Voldgade, DK-1350 Copenhagen K, Denmark (e-mail: hip@geus.dk)

The length of aliphatic chains in the coal structure is a determining factor for the type of petroleum generated during thermal maturation. A potential for liquid hydrocarbon generation necessitates the presence of long-chain *n*-alkanes. Aliphatic chains occur attached to the aromatic rings or as crosslinks in the macromolecular coal matrix. The length and amount of the *n*-alkanes is thus a function of the overall chemical composition of the vegetational input to the original peat. Worldwide major coal-sourced oil accumulations have generally been associated with Cenozoic coaly source rocks. In contrast, Carboniferous coals have principally been related to gas accumulations. This could imply an overall floral control on the generation potential, which is linked to the evolution of higher land plants. The present study investigates the aliphatic components of various coals with special reference to the age of the coals in order to assess the principal type of petroleum generated by coals from the major coal-forming periods (Carboniferous, Permian, Jurassic, Cenozoic).

Estimation of the relative proportions and lengths of the aliphatic chains in the coal structure have been achieved by Fourier Transform Infrared Spectroscopy (FTIR) and Ruthenium Tetroxide Catalysed Oxidation (RTCO). The relative proportion of long-chain *n*-alkanes (oil-proneness) was obtained by measuring the peak amplitude (normalised to g $\text{coal}_{\text{d.a.f.}}$) at 2850 cm^{-1} (symmetric CH_2) in the aliphatic stretching region in the FTIR spectra. Gas-proneness was determined from the 2955 cm^{-1} band (asymmetric CH_3). The RTCO method results in the liberation of aliphatic chains from the coal matrix as fatty acids, that upon esterification were analysed by GC-MS (internal standard added) (m/z 74).

The majority of the coal samples analysed are at or close to their maximum Hydrogen Index (HI_{max}), which provides the best measure of the generation potential. In addition, only samples with approximately similar HI are compared as these coals should have more or less equal proportions of hydrogen available for hydrocarbon formation. Peaks in the FTIR spectra related to aliphatic CH_2 are generally more prominent for Cenozoic and Jurassic coals. Hence, overall the estimated proportion of aliphatic hydrogen and CH_2 in Carboniferous and Permian coals is lower than in the younger coals. In addition, the length of the aliphatic chains are generally shorter in the Palaeozoic coals. This is demonstrated by the distribution of the aliphatic chains in the m/z 74 chromatograms of the esterified fatty acids. Due to the internal standard, the chromatograms are comparable. Within each HI group of coals the proportion of aliphatic chains with a carbon number >20 is much higher in the younger coals, in particular in those of Cenozoic age (Fig. 1). The aliphatic chains also extend to the highest carbon numbers in the Cenozoic coals, i.e. up to about C_{35}. In the Carboniferous and Permian coals they are generally not exceeding C_{24}, and the amount of C_{20-24} is overall very low.

The obtained results suggest that the evolution of higher land plants towards much more diversified plant communities from the Palaeozoic to the Cenozoic had an overall impact on the coals ability to generate liquid hydrocarbons due to a change to a generally more aliphatic organic matter input to the original peats.

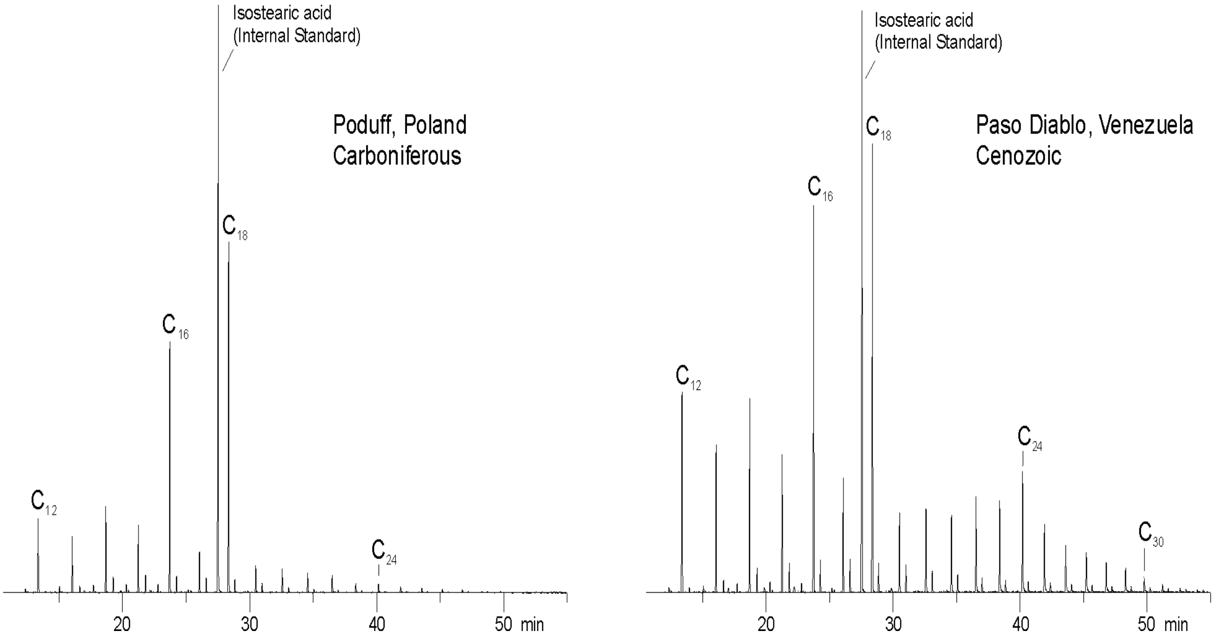


Fig.1. Distribution of esterified fatty acids (m/z 74) obtained by RTCO of a Carboniferous (HI=290; H/C=0.76) and Cenozoic (HI=270; H/C=0.83) coal

Acknowledgements

The study was carried out during a Carlsberg Research Foundation grant (ans-1293; ans-1293/20) to H.I. Petersen.

PC-4: Fractionation of petroleum during expulsion from coal: How much is due to molecular retention processes?

U. Ritter, A. Grøver

Sintef Petroleum Research, S P Andersens vei 15b, N7465 Trondheim, Norway
(e-mail: ulrich.ritter@iku.sintef.no)

Experimental evidence suggests that coal is able to generate considerable amounts of C15+ hydrocarbons and NSO compounds. Yet there is much circumstantial and some direct evidence that coal is mainly responsible for gas- and condensate fields. Adsorption has frequently been suggested to account for retention in coal, but the concepts brought forward to date are rather unspecific and not quantifiable. This presentation looks at the interaction of adsorption and absorption in coal and suggests quantifiable processes of fractionation.

Vitrinite is distinctly porous from the nano- to micrometer scale. Basic structural units (BSU) with widths around 1 nm and d002 spacing of 0.34 to 0.38 nm in bituminous coal and anthracite make up nanoporosity. If pore diameter approaches the diameter of molecules and the adsorption system is dominated by van der Waals forces, the Dubinin-Radushkevich (D-R) equation can be applied

$$W = W_m \cdot \exp\left[-\left(\frac{R \cdot T \cdot \ln\left(\frac{C_e}{C_s}\right)}{\beta \cdot E_o}\right)^n\right]$$

(*W*: amount adsorbed, *Wm:* maximum capacity of the micropores, *R:* gas constant, *Ce*: equilibrium concentration, *Cs:* solute solubility at temperature *T (K)*, *β*: Affinity Coefficient, *Eo:* Characteristic Energy, *n*: exponent).

The Characteristic Energy is mainly a function of pore size to molecular size. The Affinity Coefficient (*β*) is a function of the molecular properties, most simply related to molar vol. (*MV*).

$$\beta = \frac{MV_c}{MV_{benz}} \quad (MVc\text{: compound, } MV_{benz}\text{ : benzene})$$

Solubility in kerogen can be quantified by a solubility parameter

$$\delta = \left[\frac{\Delta E - R \cdot T}{MV}\right]^{1/2} \quad (\Delta E\text{ : energy of vaporisation})$$

Gas and light non-saturates have the lowest Adsorption Affinities, i.e. are least well adsorbed (Figure 1). Light saturates and heavy non-saturates have somewhat higher and heavy saturates and asphaltenes have the highest *β*. Within each of these groups adsorption affinity increases with increasing molecular weight. In contrast, solution in the kerogen matrix *(δ)* retains aromatics better than aliphatics and light compounds better than heavy ones.

We used proprietary software *PriMig*, together with a ten-component generation-, cracking-, and distribution model, to validate the processes, which to date reveals the following relationships:

An absorption model based on Polymer Solution theory only, fails to eliminate heavy compounds sufficiently. A model based on D-R theory only leads to rather aromatic oils and condensates. However, a combination of adsorption- and absorption processes explains why coal expels gas, even if its chemical model may suggest generation of large amounts of C15+ hydrocarbons.

Coals with >5% porosity expel gas irrespective composition of the original chemical generation model. Coals with initial potential around 300 mg/gTOC and with porosity <2% expel high-GOR petroleum fluids. GOR decreases with increasing initial potential.

The sequence of events simulated by the model is: after a molecule is cleaved from the kerogen, it will be embedded inside the cross-links according to Polymer Solution theory. Molecules not accommodated there enter the vitrinite nanopores where they will be retained according to the D-R equation. Availability of nanopores in vitrinite, swelling ratio of the vitrinite matrix and liptinitic macerals, will determine which of the processes will dominate the direction of fractionation.

The results obtained to date are encouraging and point in the right direction. Improved quantitative predictions need better knowledge of multi-component swelling ratios and adsorption, as well as temperature-and maturity-dependence of adsorption and solution systems. The presentation shows the newest available modelling examples of model’s application and validation.

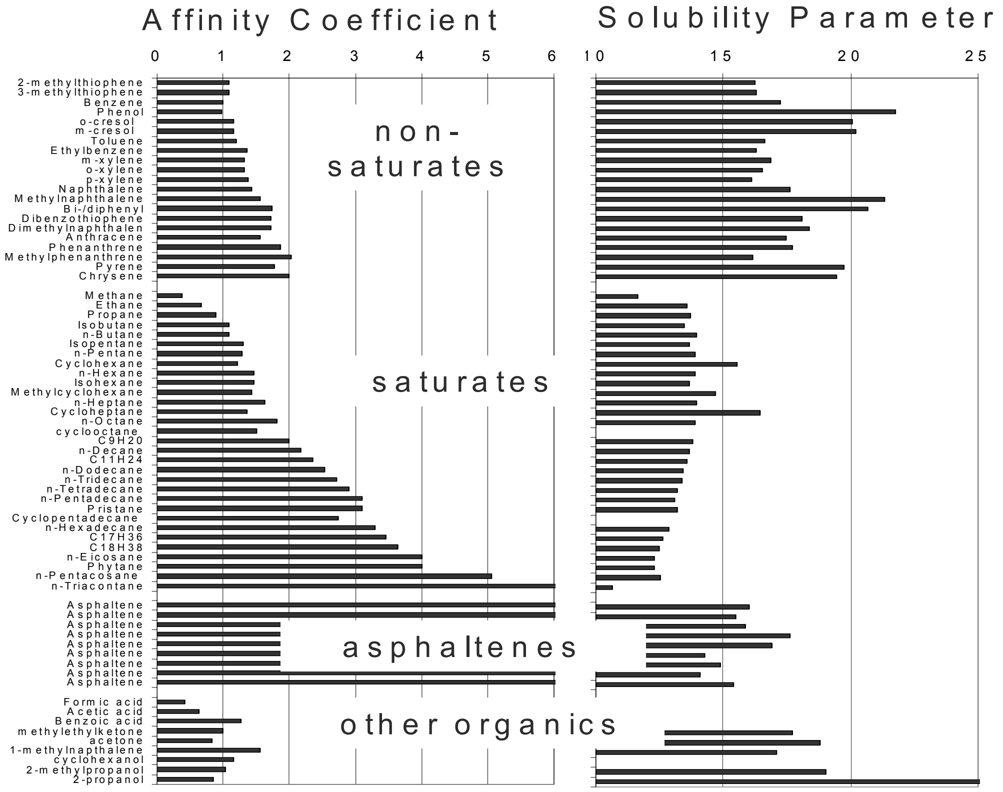


Fig.1. Molecular sorption parameters. The unit of the Solubility Parameter is $MPa^{1/2}$. For hydrocarbons, molecular weight increases towards the bottom of the figure. The Affinity Coefficient influences nanopore adsorption, the Solubility Parameter controls polymer solution

PC-5: Effects of marine influence on the paraffinic oil potential of humic coals: Eocene Mangahewa formation, Taranaki basin, New Zealand

R. Sykes[1], P.E. Johansen[2], L.R. Snowdon[3]

1) Institute of Geological and Nuclear Sciences, PO Box 30-368, Lower Hutt, New Zealand (e-mail: R.Sykes@gns.cri.nz)
2) Applied Petroleum Technology, Instituttveien 18, PO Box 123, 2027 Kjeller, Norway
3) Geological Survey of Canada, 3303-33rd St. N.W., Calgary, Alberta, T2L 2A7, Canada

Globally, many humic coals that have sourced or have the potential to source paraffinic crude oils are paralic. Synsedimentary marine influence typically enriches coals in hydrogen and sulphur, but the implications for paraffinic oil potential remain uncertain. George et al. (1994), for example, concluded that brackish conditions had reduced the paraffinic oil potential of Permian coals in the Sydney Basin, Australia, as a result of bacterial reworking of aliphatic groups. In contrast, Sykes (2004) found no evidence that brackish conditions had directly affected the paraffinic oil potential of Late Cretaceous coals in the Canterbury Basin, New Zealand, despite significant enrichment in hydrogen.

In this study, we have investigated the effects of marine influence on the paraffinic oil potential of 18 well-characterised coals from the Eocene Mangahewa Formation, Taranaki Basin, by undertaking quantitative thermal extraction- and pyrolysis-gas chromatography and comparing results with those for Late Cretaceous Rakopi Formation coals and coaly mudstones from the same basin that have negligible marine influence (Sykes et al. 2004). Both formations are major coaly source rock units and are inferred to have sourced both paraffinic oil and gas/condensate accumulations within the basin (Killops et al. 1994). The Mangahewa Formation contains up to 900 m of coastal plain coal measures, with up to 50 coal seams and net coal thicknesses reaching almost 200 m. Stratigraphic variations in coal sulphur content and occurrences of dinoflagellate cysts, mangrove pollen and *Ophiomorpha* burrows indicate frequent marine flooding of the Mangahewa coastal plain and widespread development of brackish conditions. The sampled coals, from Waihapa-1, Cardiff-1 and Toko-1 wells, are all vitrinite-rich (81–91% mineral matter-free), inertinite- (4–13%) and liptinite- (2–11%) poor, and are of similar maturity [Rank(S_r) 10.2–11.3, equiv. R_o ca. 0.65–0.75%], close to the onset of oil expulsion. Total sulphur contents range from 0.63 to 4.41% (dry, ash-free), indicating variation from slightly to strongly marine-influenced. Rock-Eval HI, atomic H/C, volatile matter and vitrinite fluorescence intensity all show strong, positive correlations with sulphur content — and hence with marine influence — whereas vitrinite reflectance and Rock-Eval T_{max} display negative correlations.

HI values range from ca. 209 to 324 mg HC/g TOC. Pyrolysate-GC yields are somewhat less, from 142 to 206 mg/g TOC (including unresolved complex mixture – UCM), indicating that a significant proportion of the total pyrolysate is not GC-amenable. Pyrolysate-GC yields increase with sulphur content, with much of the increase consisting of UCM, which increases from 37 to 90 mg/g TOC. The total ($n\mathrm{C}_{6+}$) and non-volatile ($n\mathrm{C}_{15+}$) paraffinic oil yields are relatively low for all of the Mangahewa samples, with yields of 13.1–23.5 and 4.9–11.2 mg/g TOC, respectively, compared to 21.0–38.7 and 12.1–24.0 mg/g TOC, respectively, for the Rakopi samples. The paraffinic oil potential of the Rakopi samples is controlled primarily by the abundance of leaf-derived liptinite macerals (cutinite and liptodetrinite; Sykes et al. 2004), and the low abundance of these macerals in the Mangahewa samples appears to be the main cause of the relatively low paraffinic oil potentials. Multivariate analysis (HCA and PCA) supports the conclusion that marine influence does not have a major, direct effect, either positive or negative, on the paraffinic oil generating potential of the Mangahewa coals. However, the increase in pyrolysable carbon that results from marine influence would presumably promote saturation of adsorption sites within the coal pore system and thereby facilitate the expulsion of paraffinic oil.

References

George, S.C., Smith, J.W., Jardine, D.R., 1994. Vitrinite reflectance suppression in coal due to a marine transgression: case study of the organic geochemistry of the Greta Seam, Sydney Basin. The APEA Journal 34/1, 241–255.

Killops, S.D., Woolhouse, A.D., Weston, R. J.; Cook, R. A., 1994. A geochemical appraisal of oil generation in the Taranaki Basin, New Zealand. American Association of Petroleum Geologists Bulletin 78, 1560–1585.

Sykes, R. 2004. Peat biomass and early diagenetic controls on the paraffinic oil potential of humic coals, Canterbury Basin, New Zealand. Petroleum Geoscience 10, 283–303.

Sykes, R., Snowdon, L.R., Johansen, P.E., 2004. Leaf biomass—a new paradigm for sourcing the terrestrial oils of Taranaki Basin. *In:* Boult, P.J., Johns, D.R. & Lang, S.C. (Eds), Eastern Australasian Basin Symposium II. Petroleum Exploration Society of Australia, Special Publication, 553–574.

PC-6: The New Zealand coal band – Molecular compositional changes of a complete maturity series and their potential for feeding the deep biosphere

T.T.A. Vu, K.-G. Zink, V. Dieckmann, F. Gaidies, K. Mangelsdorf, B. Horsfield

GeoForschungsZentrum Potsdam, Section 4.3, Telegrafenberg, 14473 Potsdam, Germany
(e-mail: anhtiem@gfz-potsdam.de)

Organic matter transformation in the biosphere is a fundamental process within the global carbon cycle. It is well established that the shallow biosphere in the first metres of sediment is exclusively controlled by biotic processes whereas much less is known about the deep biosphere which may be fed by abiotic organic matter transformation. This is due to subsurface depths of this zone which can extend to several hundred to thousand metres, the high quality sampling requirements and also due to the heterogeneous character of geological systems which does not allow the precise evaluation of substrate forming processes.

The New Zealand coal band (Suggate, 2000) however seems to represent an appropriate candidate for such research because it covers the complete maturity range from peat to anthracite, thus from early diagenetic to early metagenetic coalification levels. Structural rearrangements are exclusively controlled by physicochemical transformation processes, and the associated loss of low molecular weight (LMW) compounds (CO_2, acetate, methane, hydrogen, etc.) might provide major substrates for microorganisms living in adjacent strata. In this context, a drilling campaign (DEBITS) has been conducted in order to sample both lignite/coal layers and fine/coarse grained sediments to investigate the interaction between “feeder” and “consumer” lithologies.

We report here detailed organic-geochemical investigations on samples of the coal band sequence from Cretaceous to Tertiary covering a maturity range from rank 0 to rank 12 (Suggate, 2000). We will focus on the molecular compositional changes within the coal band sequence especially the influence of organofacies changes on the different maturity levels to correlate molecular maturity parameters with the rank classification of the New Zealand coals. Second, it will be of interest to ascertain the release of LMW compounds from aromatics and heterocompounds with increasing maturity concerning their feeding potential for deep subsurface viable microorganisms.

The sample series consists of two sets providing material which on the one hand was stored for several years under room temperature and on the other hand material of the same rank sequence which was recently sampled and immediately stored in liquid nitrogen. Both sample sets are therefore also analysed with regard to any alteration processes of organic compounds, i.e. oxidation, due to their storage conditions. This aspect will provide important information about the degree of influence on different maturity parameters.

So far the investigation of the continuous maturity sequence of the New Zealand coal band reveals increasing TOC values from 36 to 70 % with increasing rank, and bulk organic δ^{13}C-isotope values shifting to heavier values (from – 28 to –25.5 ‰) already in the early maturity stage. Extraction yields and asphaltene precipitation imply high contents of waxy and highly polar compounds, and the asphaltene proportion decreases in average from 70 % to 35 % with increasing maturity as expected. From Rock-Eval experiments it had been shown already that the hydrogen index (HI, mgHC/gTOC) slightly increase from the immature peats to the higher rank coals which can be explained by an early diagenetic reorganization of kerogen where hydrogen-rich labile compounds are incorporated into the insoluble kerogen structure (Schenk & Horsfield, 1998; Killops et al., 2002).

The DEBITS borehole, drilled down to 148 m, with Pleistocene and Eocene/Oligocene age can be linked to the coal band sequence. The borehole samples cover rank 0 - 1 above, and rank 5 - 6 below, an unconformity (gap from late Oligocene to mid-Miocene), respectively. This unconformity separates the samples series into an upper part with immature peats and coarse grained sediments and into a deeper interval consisting of coal, silt- and mudstone which was subsided and elevated again meeting high temperatures, thus paleopasteurisation is probable.

References

Killops, S., Jarvie, D., Sykes, R., Funnell, R., 2002. Maturity-related variation in the bulk-transformation kinetics of a suite of compositionally related New Zealand coals. Marine and Petroleum Geology 19: 1151-1168.

Schenk, H.J., Horsfield, B., 1998. Using natural maturation series to evaluate the utility of parallel reaction kinetic models: An investigation of Toarcian shales and Carboniferous coals, Germany. Organic Geochemistry 29: 137-154.

Suggate, R.P., 2000. The Rank(Sr) scale: its basis and its applicability as a maturity index for all coals. New Zealand Journal of Geology & Geophysics 43: 521-553.

PC-7: Hydrocarbons generation by applying artificial confined pyrolysis to coals from the Asturian Central Coal basin (Spain), Sabinas-Piedras Negras (Mexico) and Donets (Ukraine) basins

D. Alsaab[1], L. Martínez[1], A. Izart[1], M. Elie[1], I. Suárez-Ruiz[2], N. Piedad-Sánchez[1], F. LannuzeL[1], C. Menetrier[1]

1) UMR G2R/7566 - Géologie et Gestion des Ressources Minérales et Energétiques. Faculté des Sciences. Université Henri Poincaré, Nancy 1. BP-239, Boulevard des Aiguilletes, 54506 Vandoeuvre-lès-Nancy Cedex France (e-mail: Dani.Alsaab@g2r.uhp-nancy.fr)
2) Instituto Nacional del Carbón - CSIC. Francisco Pintado Fe 26, 33011 Oviedo, Spain

A confined pyrolysis was carried out inside gold cells under a pressure of 700 bars at different temperatures (330°C, 360°C and 400°C) and periods of time (24h, 120h and 720h). The aim of this coal maturation in laboratory conditions was to estimate the level of hydrocarbon production in sedimentary basins, and to predict the generation of oil and gas under variable geological conditions. To achieve this objective, coals from three coal basins were chosen: Sabinas-Piedras-Negras (Mexico), Donets (Ukraine) and the Asturian Central Coal Basin (Spain). These experiments were accompanied by a study of the petrographic (%R_r vitrinite reflectance mean, %R_r max, %R_r min and the anisotropy) and geochemical (T_{max}) changes to which the samples were subjected during the artificial maturation process.

By means of the artificial maturation process, from lower to higher temperature, it was possible to follow the evolution of the macerals. This was achieved by analyzing the raw coal and the solid residues after pyrolysis. It was found that whereas the vitrinite content increased, the liptinite contents decreased. The vitrinite reflectance of the solid residues (%R_r vitrinite reflectance) also rose as the temperature and duration of pyrolysis increased. Organic geochemistry exhibits a similar trend in the evolution from oil windows to gas windows. Molecular geochemistry confirms the trend by revealing a decrease in total extract yields and changes inside the aliphatic and polar compounds as the temperature and time increase. The transformation of aliphatics and polars at high temperature can be attributed to aromatization and condensation.

The volume of methane was calculated for each experiment. By using the METAGAZ Model simulation, for %R_r = 1.16, the production of methane was found to be 12.4 m^3/ton of coal and 4.5 m^3/ton of coal in the case of samples from the Asturias Basin with a % R_r of 1.18% (Piedad-Sanchez et al., in press). With an increase in coal rank (reflected by the vitrinite reflectance value) the methane production increases, as shown by the results obtained: 27 and 11m^3/ton of coal for the Asturias and Sabinas coals (Rr = 1.5%) respectively and 28-33 m^3/ton for the Donets coals. For R_r=2.5% the production of methane was found to be 100m^3/ton of coal for the Mahakam coal (Behar et al., 1995) 175 m^3/ton of coal for Flores (1998), and 90- 102 m^3/ton of coal for the Donets coals. Finally for a vitrinite reflectance of 2.98%, the production of methane obtained was 56.5 m^3/ton of coal in the case of coals from the Asturias basin. The differences in the amount of methane production were obtained with artificial maturation of the coals from the Asturias and Sabinas basins using the METAGAZ model and previously published data (Behar et al.,1995 and Flores, 1998). The Donets coals, on the other hand, exhibited the same values for gas production as the coals from the Mahakam delta, whereas those of the Flores (1998) were found to be lower.

In the case of the Donets Coal Basin (Ukraine) and the Asturian Central Coal Basin (Spain) two maps relating to CH_4 coal production and CH_4 coal adsorption were made. Coal gas production and adsorption were studied in order to compare and analyze gas migration and potential areas for coal gas exploitation were established. A similar study is in progress in the Sabinas-Piedras Negras Basin (Mexico) which will provide a solution to the problem of gas migration in this basin.

Because of this study of coal samples from different basins using an approach based on confined pyrolysis it has been possible to establish a relationship between gas generation, types of organic matter (different maceral compositions) and the age and thermal history of each basin.

References

Behar, F., Vandenbroucke, M., Teermann, S.C., Hatcher, P.G., Leblond, C., Lerat, O., 1995. Experimental simulation of gas generation from coals and a marine kerogen. Chemical Geology 126, 247-260.

Flores, R.M., 1998. Coalbed methane: From hazard to resource. International Journal of Coal Geology 35, 3-26.

Piedad-Sánchez, N., Martínez, L., Suárez-Ruiz, I., Izart, A., Elie, M., Menetrier, C., Lannuzel, F., 2005. Artificial maturation of high volatile bituminous coal from Asturias (NW Spain) in a confined pyrolysis system. Part II: gas production during pyrolysis and numerical simulation. Journal of Analytical and Applied Pyrolysis (in press).

PC-8: Variability of coalification parameters and CH groups content of thermally metamorphosed Tertiary coal from Tanjung Enim Area, South Sumatra basin, Indonesia

H. Amijaya, J. Schwarzbauer, R. Littke

Institute of Geology and Geochemistry of Petroleum and Coal, Aachen University Lochnerstrasse 4-20, 52064 Aachen, Germany (e-mail: littke@lek.rwth-aachen.de)

The coalification parameters of a series of thermally metamorphosed coals from the Tertiary Muara Enim Formation which was intruded by andesitic bodies in Tanjung Enim Area, South Sumatra Basin, Indonesia was studied by means of vitrinite reflectance, carbon content and volatile matter content. The random vitrinite reflectance values of studied coals vary from 0.5 to 5.2% and the carbon contents range between 75.5 and 96.8 wt.%, indicating a drastic increase of coalification towards the intrusion. Increasing coalification is also indicated by a decrease in volatile matter content from 45.8 to 4.5 wt.% (daf). The parameters allowed calculation of maximum paleotemperatures.

The CH groups content was determined by Fourier Transform infrared spectroscopy (FTIR). The aromatic CH stretching (3100 - 2990 cm^{-1}) and aliphatic CH streching (2990 – 2700 cm^{-1}) areas were calculated and compared to selected coalification parameters. A distinct aromatic CH signal is recognizable very well in the sub-bituminous and bituminous coals. In the anthracite coal, it is only marginally detectable. There is a progressive decrease in the aliphatic CH content of coal as the rank increases. Two peaks at around 2900 cm^{-1} and 2850 cm^{-1} which are both related to CH_2 and to a lesser extent CH_3, are dominant. However, the aromaticity parameter (the ratio of aromatic to aliphatic CH) is also increasing with increasing coalification, except at the meta-anthracite stage, where the aromaticity parameter is very low since the CH spectra bands almost disappear.

Furthermore a variety of biomarker parameters measured on aliphatic and aromatic hydrocarbons by gas chromatography was additionally determined and correlated to vitrinite reflectance and maximum paleotemperature.

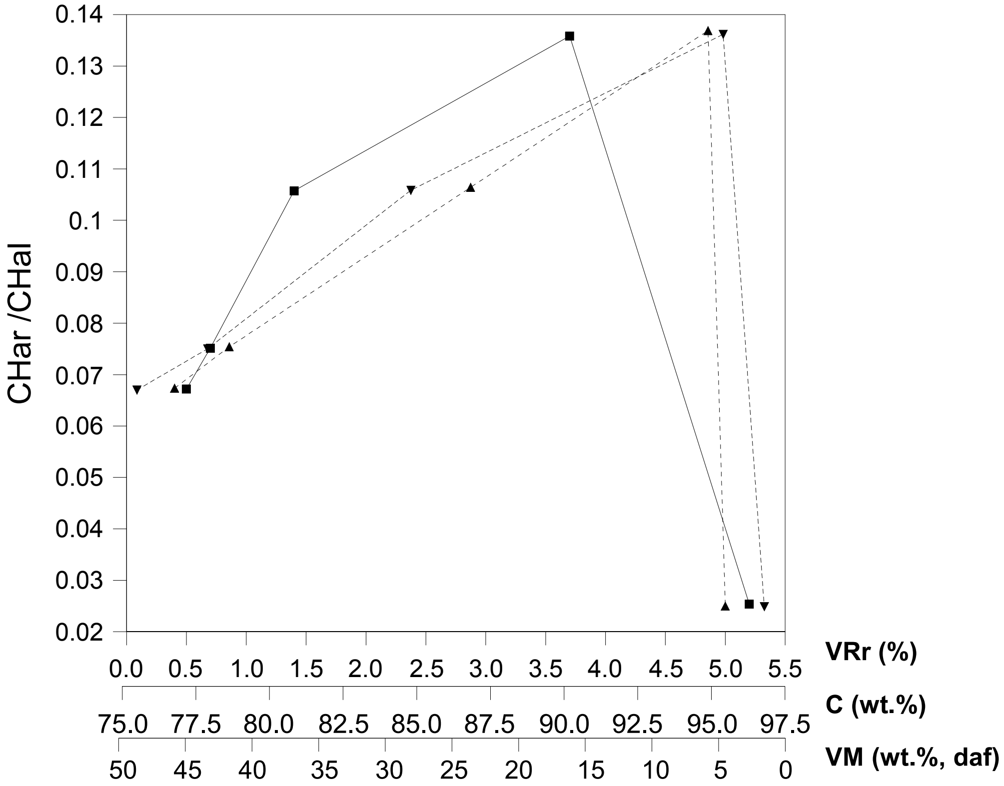


Fig.1. Change of the ratio of aromatic CH to aliphatic CH with increasing coalification indicated by random vitrinite reflectance (■), carbon content (▼) and volatile matter (▲). Note: the scales of the coalification parameters do not correlate each other.

PC-9: Compound specific carbon stable isotope analysis on biomarker of Late Palaeozoic coals

R. Meier[1], J. Schwarzbauer[1], P. Weniger[1], H. Strauß[2], R. Littke[1]

1) Institut of Geology and Geochemestry of Petroleum and Coal, RWTH-Aachen University, Lochnerstr. 4-20, 52056 Aachen (e-mail: meier@lek.rwth-aachen.de)
2) Lehrstuhl für Regionale und Historische Geologie, Westfälische Wilhelms-Universität Münster, Corrensstr. 24, 48149 Münster

Biomarker compounds provide information on the contribution of different groups of organisms to the organic matter, its thermal maturity, the palaeoclimatic or paleoenvironmental conditions. Applying compound specific isotope analysis (CSIA) on individual compounds further information on paleoenvironmental conditions can be obtained. Therefore, the present study focused on CSIA of aliphatic biomarkers in late palaeozoic coals including *n*-alkanes, acyclic isoprenoids, hopanoids and fatty acids.

The coal samples were extracted, fractionated and the aliphatic fraction were analysed by GC/MS as well as GC/irmMS. Furthermore, bound compounds as released after alkaline hydrolysis were included. Qualitative and isotopic results of *n*-alkanes and fatty acids reveal the importance of a combined interpretation of biomarker data and isotopic values in order to differentiate biogenic and thermogenetic contributions. Comparison of free and bond *n*-alkanes revealed comparable δ^{13}C-values and, consequently, similar isotopic trends. However acyclic isoprenoids (mainly phytane, pristane and norpristane) reflected much better the plant derived contribution to the organic matter. In comparison to bulk δ^{13}C-values a significant shift to lighter values were observed, but the general variations were comparable. However, in the paleozoic time, no general to higher or lighter δ^{13}C-values of the plant derived compounds was observed. Short time variations in the range of approx. 3‰ were also reflected by bulk δ^{13}C-values. These variations might be attributed to changes in the paleaoclimatic or paleoenvironmental conditions. Regarding the hopanoids, which reflect the microbial contribution to the organic matter, isotopic ratios between approx. 32 ‰ and 45 ‰ were measured, reflecting a secondary transformation of biogenic organic matter. These shifts pointed out the usefulness of isotopic analysis to differentiate various pools of organic matter.

PC-10: Cretaceous and Paleogene coals in Japan as source rocks of natural gas and petroleum

H. Oda

Institute for Geo-Resources and Environment, Geological Survey of Japan, AIST 1-1-1 Higashi, Tsukuba, Ibaraki 305-8567, Japan

Introduction:

In Japan there were once numerous coalfields. And most of them are closed now. However the coal resources are still calculated as more than 20 billion tons. So we are hopeful to find the petroleum and natural gas resources generated from these coals. But it is necessary to develop the unique evaluation method of Japanese coals. Because Japanese coals are richer in hydrogen than other coals and they contain “degradinite”. So the authors have investigated the characteristics of Japanese coals which generate petroleum and natural gas.

The MITI Sanriku-Oki borehole was drilled in 1999 to a depth of 4,500 m to explore offshore gas resources derived from the Cretaceous and the Oligocene coals and coaly shales. The borehole site is located 857 m deep below the sea level and about 60 km offshore Hachinohe City, Aomori Prefecture, north Japan. And the coal bearing beds correlated with formations of the MITI Sanriku-Oki are exposed inland along the coast. The authors have been conducting a sequence stratigraphic, sedimentological, and geochemical study for the reconstruction of sedimentary facies and organic features of the natural gas reservoirs derived from coal and coaly shale in this area. The data of vitrinite reflectance of these coals indicate around 0.5 %, showing that these coals are still immature However Rock-Eval data show between 100 and 180, showing these coals are classified as organic type II / III. Coals from Kuji area, north Japan, are still immature but high potential for petroleum and natural gas resources. There are numerous coalfields in Japan. So they can be new targets for petroleum and natural gas explorations.

Geologic Settings and Coal Samples:

Upper Cretaceous Kuji and lower Oligocene Noda Groups are distributed along Iwate Sanriku coast, north Japan. Kuji Group is dated as Early Campanian from molluscan biostratigraphy including *Inoceramus*. And the Noda Group is correlated with the Lower Oligocene. Both groups were not tectonically modified, but show slightly inclination eastward. In 1999 the MITI Sanriku-Oki was drilled offshore Hachinohe City and natural gas derived from coals and/or coaly shales were explored in this site.

Kuji Group is overlain by Cretaceous Miyako Group and granite, and it inclines northeastward. Kuji Group is divided into three formations: Tamagawa, Kunitan, and Sawayama Formations. Lithological change of Kuji Group is interpreted as transgressive sequence including peat, medium-to-coarse sandstone, trough cross-stratified sandstone, hummocky cross stratified sandstone, and bioturbated sandstone. Kunitan Formation contains various coal beds. But this thickness is very thin, around 50 to 60 cm and coal ranks are low. Peat layers were deposited in river mouth and natural levee of swamp. Coal beds of Kuji Group are characteristic with bearing a lot of amber.

Noda Group overlays Kuji Group with unconformity. And it is divided into two formations: Minato and Kuki Formations. Noda Group is correlated with the lower Oligocene by fossil flora, which are similar to those of Ishikari coalfield in Hokkaido, north Japan. Minato Formation is characterized by abundant round pebble layers deposited in river channels. And it also has various coal beds which are about 60 cm in thickness and continuous. Lithlogical cycles are observed in Minato Formation including conglomerate, sandy tuff, siltstone and mudstone, showing deltaic formation.

Source Rock Potential of Coals from Kuji Coalfield

The authors have performed vitrinite reflectance (Ro) measurements for 12 samples and Rock-Eval pyrolysis analyses for 8 samples from Kuji coalfield. Ro data of coals from the Cretaceous Kuji Group range from 0.29 to 0.45 %. Hydrogen index (HI) data of them are between 46 and 122 mgTOC/gTOC, total organic carbon contents (TOC) ranging from 40 to 64 %. And Ro data of coals from the Oligocene Noda Group range from 0.35 to 0.45 %. Hydrogen index (HI) data of them are between 34 and 172 mgTOC/gTOC, TOC values are ranging from 31 to 64 %.

As a result, all coals of Kuji coalfield are less than 0.6 % (oil window) and immature mainly because burial depth is shallow there. Thus oil and gas will not be generated from coals in this area. However they could be good source rocks. Because organic types of them are classified as type II/III with medium-to-high HI values. This idea is supported by amber in those coals. In addition, from MITI Sanriku-Oki borehole they succeeded in producing natural gases from the Cretaceous and the Oligocene coals and or coaly shales. It implies that coals in Kuji coalfield can generate oil and natural gas if they are buried deep enough.

Discussion:

Japanese Paleogene coals mainly consist of two groups of maceral constituents, telinite/collinite and degradinite. Intercellular spaces of telinite and collinite were filled with substance dominant in aliphatic compounds, derived from the algae and/or bacteria and diagenetic transportation of plant biopolymers under the anaerobic condition. In the case of telocollinite, the intercellular spaces were completely filled with and are no longer readily distinguishable from cell walls under anaerobic condition. Also, “degradinite” was originated from residue probably derived from the algae and/or bacteria and the other residue of degraded plant materials.

Activities of petroleum explorations have been focused on backarc (Sea of Japan) side in Japan. Because the back-arc basins of Japan have good reservoirs, the Neogene “Green Tuff”. And partly because coals have not been considered as good source rocks in Japan without enough source rock evaluation. However, in the forearc (Pacific Ocean) side of Japan there are a lot of sedimentary basins bearing coalbeds, deposited in Cretaceous and Paleogene. Source rock potentials of Cretaceous and Paleogene coals from forearc basins, especially in Ishikari, Kushiro, Kuji, and Joban coalfields, north Japan, can be good enough to generate oils and natural gases. So it is necessary to develop the unique evaluation method of Japanese coals to explore potential petroleum and natural gas resources in Japan. And this method will be applied to coalfields including in Brazil, Colombia, Indonesia, and so on.

Ro data of coals from Kuji coalfield show that these are still immature However Rock-Eval data imply that these coals are classified as organic type II/III and have high potential for petroleum and natural gas resources. There are numerous coalfields in Japan. So they can be new targets for petroleum and natural gas explorations.

PC-11: Origin and distribution of biomarkers in the Utrillas coal basin

M.A. Olivella, R. Gorchs, F.X.C. de las Heras

Escola Universitària Politècnica de Manresa (U.P.C.), Av Bases de Manresa 61-73, 08240-Manresa, Catalonia (Spain) (e-mail: heras@emrn.upc.es)

The Utrillas coal facies belongs to the Maestrazgo Basin and is located in NE Spain. It contains lignite and leonardite facies and was deposited during the middle Albian (Lower Cretaceous, 105 Ma) in proximal areas of a delta estuary with abundant sulphur. The high sulphur content is possibly due to an influx of sulphate, resulting from weathering of Triassic gypsum from the catchment's area into the delta estuary. The depositional environment of that basin originated bituminous shales and coals some of them are object of economic exploitation.

Their organic matter has been object of scattered reports. In short, bulk pyrolysis parameters and microscopical observation in Utrillas basin has been studied together with the inorganic and the insoluble organic fraction. Also, their sulphur functionality has been described recently by XANES.

We have analyzed the organic soluble extract of the Utrillas coals by GC-MS in order to characterize their aliphatic, aromatic and organosulphur compounds. Distribution of biomarkers allows to recognize different inputs and to assess their depositional palaeoenvironment and degree of maturity.

In particular homologous series of thienylhopanes with 30-(2'-methylenethienyl) and 30-(2'-(5'-methylenethienyl)hopane structures related with sulphur incorporation in eubacterial functionalized precursors are present. The presence of biomarkers such as unsaturated linear alkylbenzenes recently described, facilitates the recognition of the palaeodepositional environment where they sedimented.

The abundance of unsaturated biomarkers such as diacholestenes and hopenes is indicating low maturity coals. In the same sense, different aromatic ratios such as the methylphenanthrene index are suggesting diagenesis in the initial stage.

PC-12: Organic geochemistry and coal petrology of Tertiary brown coal in the Soko mine, Soko Banja basin, Serbia and Montenegro

D. Životić[1], H. Wehner[2], O. Cvetković[3], B. Jovančićević[3,4], I. Gržetić[4], W. Hiltmann[2], G. Scheeder[2], A. Vidal[2], A. Šajnović[3]

1) Faculty of Mining and Geology, University of Belgrade, Djušina 7, 11000 Belgrade, Serbia and Montenegro (e-mail: draganar@rgf.bg.ac.yu)
2) Bundesanstalt für Geowissenschaften und Rohstoffe, Stilleweg 2, 30655 Hannover, Germany
3) Center of Chemistry, IChTM, Studentski trg 16, 11000 Belgrade, Serbia and Montenegro
4) Faculty of Chemistry, University of Belgrade, Studentski trg 16, 11000 Belgrade, Serbia and Montenegro

The organic geochemical and petrological study was performed on coal samples from the Soko mine, Soko Banja basin, Serbia. Ten coal samples and two carbonaceous clay samples were collected from fresh, working faces in the underground brown coal mine, from different parts of the main coal seam. The results of organic geochemistry and coal petrology are summarized in Table 1.

The Lower Miocene brown coal of the Soko mine is a typical humic coal with huminite concentration of up to 76.2 vol. %, liptinite less than 14 vol.%, and inertinite less than 11 vol.%. In the xylite-rich coal [1], ulminite is the most abundant maceral. The most abundant maceral in the matrix coal is densinite, with variable amount of ulminite, and clay minerals. Sporinite and resinite are the most common macerals of the liptinite group. Mineral-bituminous groundmass, impregnation of detrohuminite [2] with bituminite, identified in some coal samples, and carbonaceous marly clay, indicate sub-aquatic origin and strong bacterial decomposition. Inertodetrinite is the most abundant maceral of inertinite group. Huminite reflectance (eu-ulminite B) ranges from 0.29 to 0.57 %, which is typical for an immature to early mature stage of organic matter.

The organic matter (OM) ranges from 45.86 to 93.20%, in which alkanes (AL) make 1.0-20.1%, aromates (AR) 1.3-14.7%, asphaltenes (AS) 28.1-76.2%. Saturated hydrocarbon fractions include n-C_{15} to n-C_{32} with odd carbon number predominance in almost all samples, and CPI from 0.71 to 6.47. The n-C_{27} and n-C_{29} alkanes are extremely high in some samples, as a contribution of epicuticular waxes from higher plants.

Acyclic isoprenoid hydrocarbons are minor constituents in aliphatic fraction, and the pristane/phytane (Pr/Ph) ratio varies between 0.56 and 2.14. Low pristane/phytane ratio (< 1) indicates the anaerobic conditions during sedimentation, and values over 1 the oxic conditions [3].

The most abundant diterpanes are tricyclic (abietane and dehydroabietane) and tetracyclic (16α(H)-phyllocladane). In some samples the diterpanes are dominant constituents of alkane fraction. The dominance of abietane and 16α(H)-phyllocladane in aliphatic fraction reflects a high contribution of *Gymnosperms* in sediment forming plant community.

Policyclic alkanes of the triterpane type (*m/z* 191) are important constituents of alkane fractions. Typical hopanes of the Soko Banja coal are the αβ- and ββ-type hopanes from C_{27} to C_{33}, but without C_{28}. In the fraction of pentacyclic triterpanes the C_{30}17α(H)21β(H)-hopane and C_{29}17β(H)21α(H)-normoretane are more abundant then less thermodynamically stable C_{30}17β(H)21β(H)-hopane. However, the ratio of ββ/αβ hopane (C_{30}17β(H)21β(H)-hopane/ C_{30}17α(H)21β(H)-hopane), and $C_{30}M/C_{30}H$ (C_{30}17β(H)21α(H)-moretane/C_{30}17α(H)21β(H)-hopane), also indicate an immature to early mature stage of organic matter or diagenetic alteration of the biomass.

The aim of the study was to investigate the coal facies, obtain more information on the molecular compositions of the aliphatic fractions, and interpretation of the peat forming environments.

Table 1. The results of organic geochemistry and coal petrology of the Soko Banja basin. %Rr - Average huminite reflectance

Sample	Lab. No.	Lithotype	OM (%)	$\%R_r$	AL (%)	AR (%)	AS (%)	Pr/Ph	CPI	ββ/αβ hopane	$C_{30}M/C_{30}H$
Soko1	211149	Xylite-rich coal	92.45	0.34	15.1	7.6	46.9	1.14	0.71	0.18	0.04
Soko2	211150	Xylite-rich coal	93.20	0.40	4.1	7.3	56.0	0.86	1.68	0.41	0.06
Soko3	211151	Xylite-rich coal	84.47	0.35	5.8	8.1	49.3	1.39	1.84	0.22	0.02
Soko4	211152	Matrix coal	75.88	0.32	20.1	14.7	28.1	1.55	1.78	0.29	0.05
Soko5	211153	Matrix coal	89.48	0.42	5.1	3.2	70.4	3.13	5.90	0.21	0.08
Soko6	211154	Matrix coal	82.85	0.42	4.6	6.0	53.2	2.40	3.55	0.41	0.10
Soko7/1	211155	Xylite-rich coal	89.30	0.48	6.0	6.4	67.1	0.56	4.76	4.14	0.21
Soko7/2	211156	Matrix coal	89.21	0.38	5.4	2.9	63.9	2.11	6.47	0.34	0.04
Soko8	211157	Xylite-rich coal	90.43	0.41	1.5	2.1	76.2	2.14	1.86	0.56	0.04
Soko10/1	211158	Carbonaceous marly clay	45.86	0.35	3.8	5.4	60.3	1.44	4.55	0.71	0.13
Soko10/2	211159	Carbonaceous clay	46.38	0.35	4.9	5.2	50.6	1.90	3.50	0.34	0.06
Soko11	211160	Xylite-rich coal	88.23	0.47	1.0	1.3	54.2	1.78	1.65	0.62	0.03

$$\mathrm{CPI} = \frac{1}{2}\frac{(C_{17}+C_{19}+C_{21}+C_{23}+C_{25}+C_{27}+C_{29}+C_{31})}{(C_{16}+C_{18}+C_{20}+C_{22}+C_{24}+C_{26}+C_{28}+C_{30})}+\frac{(C_{17}+C_{19}+C_{21}+C_{23}+C_{25}+C_{27}+C_{29}+C_{31})}{(C_{18}+C_{20}+C_{22}+C_{24}+C_{26}+C_{28}+C_{30}+C_{32})}$$

References

[1] Taylor, G. H., Teichmüller. M., Davis, A., Diessel, C. F. K., Littke, R. and Robert, P., 1998. Organic Petrology. Gebrüder Borntraeger-Berlin-Stuttgart.

[2] Sykorova, I., Pickel, W., Christanis, K., Wolf, M., Taylor, G. H., Flores, D., 2005. Classification of huminite-ICCP System 1994. Int. J. Coal Geol., 62, 85-106.

[3] Peters, E.K., and Moldowan, M.J., 1993. The Biomarker Guide, Interpreting Molecular Fossils in Petroleum and Ancient Sediment. Prentice Hall, New Jersey.

BIOGEOCHEMISTRY

PBG1-1: Organic Geochemistry—A Retrospective

K.A. Kvenvolden

U.S. Geological Survey, Menlo Park, CA 94025 and Institute of Marine Sciences, University of California, Santa Cruz, CA 95064

The historical beginnings of organic geochemistry are vague, but there is a general consensus that the work of Alfred Treibs, carried out in Germany in the 1930s, formally established the field. He discovered porphyrin pigments in shale, crude oil, and coal, and demonstrated that these compounds were degradation products of chlorophyll and hemin, thus linking geomolecules to biomolecules.

For the next thirty years, organic geochemistry was undertaken, at least in the United States, mainly in the petroleum industry, where the focus was on the molecular constituents of petroleum, source rocks and sediments, and geochemical prospecting. However, during this time, academic interest in organic geochemistry was stimulated, and in 1959 organic geochemistry was formally recognized as a geoscience discipline with the organization of the Organic Geochemistry Division (OGD) of the Geochemical Society. OGD first met in 1960 at the annual meeting of the Geological Society of America.

The 1st International Meeting on Organic Geochemistry (IMOG) was held in Milan, Italy, in 1962, and IMOG continued to be convened every other year, leading to this occasion of the 22nd IMOG in Seville, Spain, in 2005. Gordon Research Conferences devoted specifically to organic geochemistry began in 1968 and have been held on alternate years for 19 times at the Holderness School in New Hampshire. The European Association of Organic Geochemists (EAOG) was established in 1983, and the journal *Organic Geochemistry*, started in 1978, was designated the official publication of EAOG in 1988.

Many individuals have contributed over the years to the advances in organic geochemistry. In this retrospective, a photographic record of 132 of these people is organized into twelve categories (Biomarkers, Coal, Crude-oil, Entrepreneurs, Environment, Geomolecules, Isotopes, Natural-gas, Organic-matter, Pyrolysis, Sediments, and Source-rocks), showing some of the diversity of topics in this geoscience discipline. For almost 50 years, organic geochemistry has been a recognized geoscience, and great satisfaction can be taken in the progress that has been made in understanding the role of organic materials in geological and cosmological processes.

PBG1-2: Source and diagenesis of organic matter from the Middle Jurrassic epicontinental basin of Poland

L. Marynowski[1], M. Zatoń[1], M.O. Jędrysek[2], C. Grelowski[3]
S. Kurkiewicz[4]

1) University of Silesia, Faculty of Earth Sciences, Będzińska 60, 41-200 Sosnowiec, Poland
(e-mail: marynows@wnoz.us.edu.pl)
2) Lab. of Isotope Geology and Geoecology, University of Wrocław, Cybulskiego 30, 50-205 Wrocław, Poland
3) PETROGEO Ltd., Pl. Staszica 9, PL-64-920 Piła, Poland
4) Med. Univ. Silesia, Dept. Mol. Biol. Biochem. & Biopharm., Narcyzow 1, 41-200 Sosnowiec, Poland

During the Middle Jurassic time, the Submediterranean epicontinental Polish Basin, which is the easternmost part of the Mid-European Epicontinental Basin - had transgressive character despite two, short regressive episodes. These episodes took place on the Lower/Upper Bajocian boundary (*subfurcatum* Zone) and in the Lowermost Callovian (*herveyi* Zone).

Samples from the two different regions of the central part of the Middle Jurassic Basin of Poland were collected. In the southern part the samples were collected from brick-pits exploiting the Upper Bajocian and Bathonian sedimentary rocks represented by dark-grey clays with many levels of massive siderites, and carbonate concretions. This complex is known as the Ore-Bearing Częstochowa Clay Formation. In the northern part the samples were collected from four boreholes: Okonek 1, Brzozówka1, Czarne-4 and Czarnowo-1 drilled through clays of the Polish Lowland.

Organic matter (OM) from both: the southern and the northern part of Poland is immature. Values of T_{max} obtained from Rock Eval analysis are between 415 and 425°C. This is in agreement with the high concentration of biomarkers with biological configurations, such as ββ-hopanes, hop-13(18)-enes and hop-17(21)-enes, diasterenes and traces of sterenes present in clays, concretions and wood fragments.

Values of $CPI_{(25-31)}$ considerably higher than 1, together with abundant perylene, fichtelite, cadalene, dehydroabietane, simonellite and retene occurrences suggest predominance of terrestrial organic matter.

One of the most abundant group of biomarkers, present in all samples are $\Delta^{13(17)}$diasterenes. Diasterenes are products of early diagenetic acid-catalysed backbone rearrangement of sterenes [1]. Abundance of individual diasterenes with 27, 28 and 29 carbon atoms differs significantly between samples (Fig. 1). Samples of wood practically do not contain $\Delta^{13(17)}$diasterenes with 27 carbon atoms in the molecule. In contrast, distribution of $\Delta^{13(17)}$diasterenes in the clays is dependent on samples location in the basin (Fig. 1). Clays from the Polish Lowland contain relatively higher amount of C_{29}-$\Delta^{13(17)}$diasterenes than clays from the Częstochowa Clay Formation, whereas samples from the Holy Cross Mts. are intermediate between two above mentioned area.

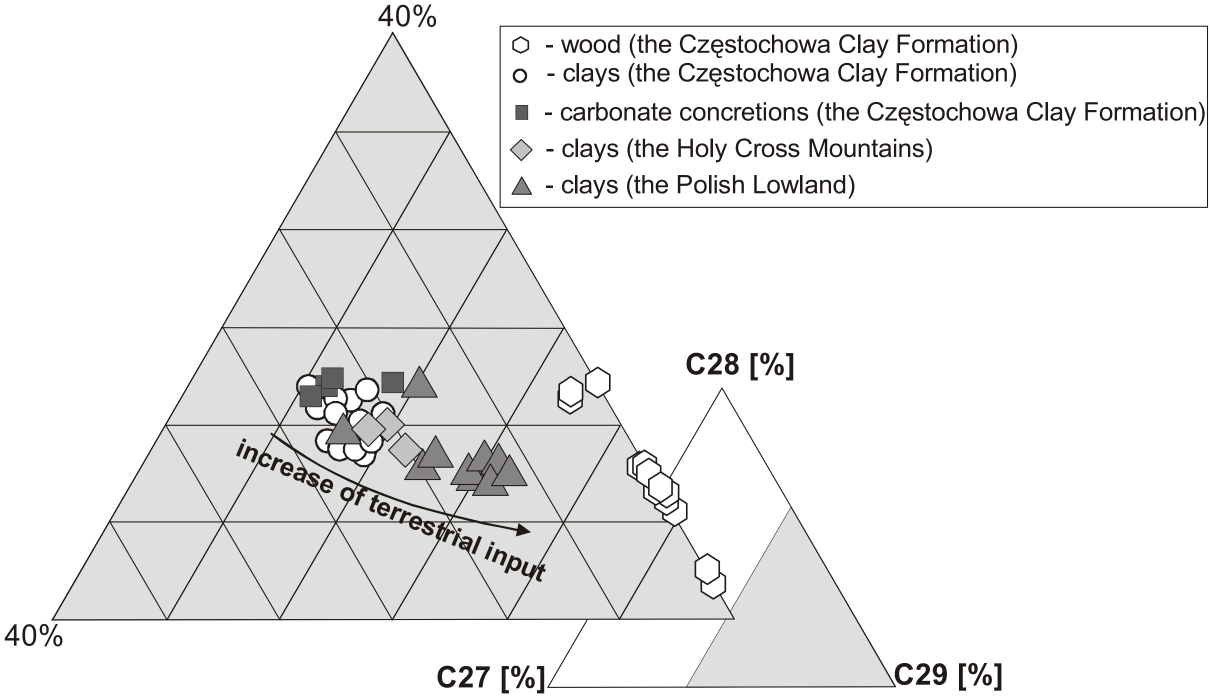


Fig.1. Composition of C_{27}, C_{28} and C_{29} (20S+R), $\Delta^{13(17)}$diasterenes in the Middle Jurrassic Epicontinental Basin of Poland (note that all wood samples contain almost exclusively C_{29} $\Delta^{13(17)}$diasterenes)

There are many known exceptions from the generally accepted view that C_{29} sterols are derived solely from higher plants [see 2]. However, taking into account high concentration of C_{29} -$\Delta^{13(17)}$diasterenes in the wood fragments (Fig. 1) and uniform distribution of diasterenes in the whole investigated areas, we conclude that $\Delta^{13(17)}$diasterenes with 29 carbon atoms are mainly of terrestrial origin in this case. This confirms the results of Brassell et al. [3]. If increasing concentration of C_{29} -$\Delta^{13(17)}$diasterenes indicates increase of terrestrial input, this terrestrial OM would have originated from enhanced transport of organic matter from the land situated at northern bank of the basin, that is the Fennoscandian Shield. During Jurassic, the Fennoscandian Shield was the large land mass, which could have provided much greater amount of terrestrial OM than the southern Bohemian Massif.

References

[1] Rubinstein, I., Sieskind, O. & Albrecht, P. 1975. Rearranged sterenes in a shale: Occurrence and simulated formation. Journal of Chemical Society; Perkin Transfer I, 1833-1836.
[2] Peters, K.E. & Moldowan, J.M. 1993. The biomarker guide. Interpreting molecular fossils in petroleum and ancient sediments. Prentice-Hall, Englewood Cliffs, NJ. 363 pp.
[3] Brassell, S.C., Eglinton, G. & Mo, F. J. 1985. Biological marker compounds as indicators of the depositional history of the Maoming oil shale. Organic Geochemistry **10**, 927-941.

PBG1-3: Effect of UVB irradiation on Cu^{2+}-binding organic ligands and Cu^{2+} speciation in alpine lake waters of New Zealand

S.G. Sander, J.P. Kim, B. Anderson, K.A. Hunter

Marine and Freshwater Chemistry, Department of Chemistry, University of Otago, P.O.Box 56, Dunedin, New Zealand (e-mail: sylvias@alkali.otago.ac.nz)

It is well-established that natural organic matter (NOM) ligands in lake waters form strong complexes with Cu^{2+}, controlling the speciation and bioavailability of this metal ion[1,2]. The biologically active forms of Cu(II) are considered to be free Cu^{2+} ions and kinetically labile complexes formed with simple, mainly inorganic, ligands[3]. In seawater, Cu(II) is also mostly bound to strong NOM ligands of apparent biological origin[4] which appear to be produced by phytoplankton species including bacteria[5], perhaps as a response to Cu(II) toxicity. However the origin of strong Cu(II)-binding NOM in lakes is less clear. In the past we observed variations in the concentrations of strong Cu(II)-binding NOM ligands in two New Zealand alpine lakes which seemed to show a seasonal pattern[6]. We hypothesised that these seasonal changes might be driven either by enhanced UV irradiation in summer or by seasonal changes in phytoplankton community structure.

To evaluate our hypthesis we measured the Cu^{2+}-NOM speciation in a time series of samples collected throughout the summer UV maximum period (austral summer 2002/03) for six alpine lakes on the South Island, New Zealand. Total dissolved Cu ($[Cu]_T$), the concentration of strong Cu^{2+} binding ligands ($[L]_T$) and their conditional stability constant K" were determined in surface samples of all six lakes, using competitive ligand equilibration with salicylaldoxime and detection by cathodic stripping voltammetry (CLE-CSV). All lakes exhibited appreciable concentrations of a strong Cu^{2+} binding ligand with similar K" values and concentrations always exceeding $[Cu_T]$, thus dominating Cu^{2+} speciation. A typical ligand titration data set is shown in Fig. 1.

Four of the lakes (Hayes, Manapouri, Wanaka and Te Anau) showed no appreciable trend in $[L_T]$ throughout the summer, while in two others (Lakes Wakatipu and Hawea) $[L_T]$ increased steadily throughout this period. Laboratory UVB irradiation of lake water samples using a 400 W mercury lamp with a Pyrex glass filter (wavelength >280 nm) showed that Cu^{2+} binding ligands are destroyed by UVB radiation, causing $[L]_T$ to decrease with a rate of -0.588 nmol L^{-1} h^{-1} (r^2= 0.88). From this we calculate that the in situ ligand destruction rate by UVB in summer for surface waters of these lakes is too small to significantly affect $[L_T]$, and conclude that variations in ligand concentrations must result from seasonally variable biological factors, influencing ligand production and/or microbial ligand destruction.

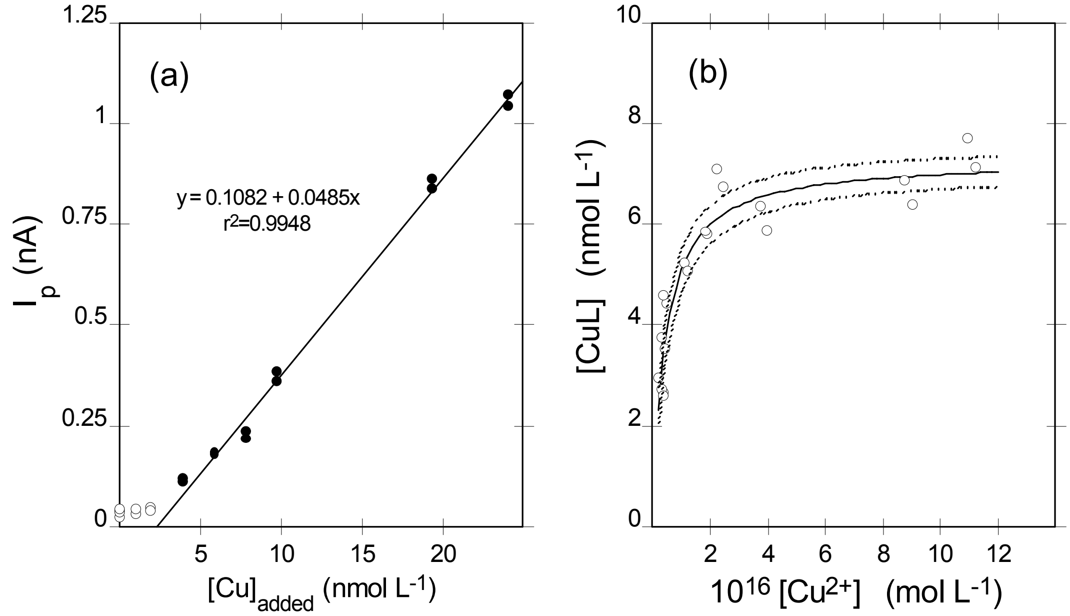


Fig.1. (a) Typical Cu^{2+}-ligand titration curve showing CSV peak current I_p as a function of the concentration of added Cu(II); (b) Gerringa plot to calculated values of K" and $[L_T]$

Acknowledgements

This research was supported by a grant from the New Zealand Foundation for Research, Science and Technology through collaboration with the National Institute for Water and Atmospheric Research (NIWA).

References

[1] E. Achterberg, C. van den Berg, M. Boussemart and W. Davison, 1997 Speciation and cycling of trace metals in Esthwaite Water: A productive English lake with seasonal deep-water anoxia, Geochim. Cosmochim. Acta, 61, 5233.

[2] H. Xue, A. Oestreich, D. Kistler and L. Sigg, 1996, Free cupric ion concentrations and Cu complexation in selected Swiss lakes and rivers, Aquat. Sci. 58, 69.

[3] P. B. Kozelka and K. Bruland, 1998, Chemical speciation of dissolved Cu, Zn, Cd, Pb in Narragansett Bay, Rhode Island, Mar. Chem., 60, 267.

[4] K. W. Bruland, J. R. Donat and D. A. Hutchins, 1991, Interactive influences of bioactive trace metals on biological production in oceanic waters, Limnol. Oceanogr., 36, 1555.

[5] J. W. Moffett, R. G. Zika and L. E. Brand, 1990, Distribution and potential sources and sinks of copper chelators in the Sargasso Sea, Deep Sea Res., 37, 27.

[6] K. B. Averyt, Kim, J. P. and Hunter, K. A., 2004, Effect on pH of strong binding copper ligands in lakesLimnol. Oceanogr., 49, 20.

PBG1-4: Discovery of strong copper-binding organic matter in the mixing zone of hydrothermal fluids and sea water

S.G. Sander[1], K.A. Hunter[1], A. Koschinsky[2]

1) Marine and Freshwater Chemistry, Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, New Zealand (e-mail: sylvias@alkali.otago.ac.nz)
2) Geosciences and Astrophysics, School of Engineering and Science, International University Bremen IUB, Campus Ring 8, D-28759 Bremen, Germany (e-mail: a.koschinsky@iu-bremen.de)

The discovery of abundant life around marine hydrothermal sites has amazed not only the first discoverers of these peculiar biogeochemical niches. Organisms inhabiting these extreme environments are able to cope with temperatures up to 115°C, strongly acidic and reducing conditions, and potentially toxic concentrations of metals. Yet despite these harsh conditions, the biomass around these sites is orders of magnitude higher than that of the surrounding marine environment. It is particularly difficult to understand how this abundant and diverse biomass is possible in the presence of such high concentrations of metal ions that are normally toxic to marine life.

Although many metals in seawater are essential for biological processes because of their role as catalysts, enzyme co-factors, active redox pair, and stabiliser of protein structures, they may become toxic by e.g. blocking functional groups of enzymes, inhibiting transport systems, or displacing essential metals from their native binding sites[1]. It is known that some acidophilic bacteria and archaea do have basic mechanisms that convey an increased level of cellular resistance to metals[1]. However, in the ocean the biological availability of metals is controlled by metal-binding organic matter[2]. Some metal-binding organic matter appears to be deliberately produced by organisms to sequester an essential element (e.g. Fe-binding siderophores)[3] or to detoxify a specific metal (e.g. Cu^{2+}) [4]. Other metal-binding organic matter appears to be produced mainly by the degradation of organic matter, much like soil humus[5]. Whatever the origin, without the protection afforded by metal-binding organic matter, biology in the ocean would be killed off by metal toxicity. So, how do the abundant organisms (including higher eukaryotes, molluscs, fishes and crustaceans etc.) in hydrothermal systems survive their toxic metal-rich environment?

We have demonstrated for the first time, using samples from two different hydrothermal locations (Logatchev field (14º45'N) on the Mid-Atlantic-Ridge, and Brothers volcano area on the Kermadec Arc, Pacific ocean) using voltammetric techniques, that high concentrations of strong copper-binding organic matter are being generated in hydrothermal vents as indicated by the correlations between organic ligand concentrations and hydrothermal fluid percentage in the samples. In the Logatchev samples copper ligand concentrations between 10 and 100 nM were found. The Brothers volcano samples had much higher copper ligand concentrations (up to 3 μM) and showed strong pH dependence. The stability constants of the copper binding ligands are high compared with those found in ambient seawater.

A key question is whether this metal-binding organic matter is specifically produced by the micro-organisms living in the hydrothermal system as a detoxifying mechanism (biotic), or whether the metal-binding organic matter is produced by the chemical action of high temperature and low pH reducing conditions on organic matter (abiotic). Besides the potential role as detoxification agents, organic ligands also influence the thermodynamic characteristics of the dissolved metals (complexed metals have different Gibb's Free Energies of formation etc. than free metal ions) and are therefore also important with respect to precipitation-dissolution and sorption-desorption equilibria of these metals.

Acknowledgements

This work was funded by a University of Otago Research Grant. Thanks are due to Captain M. Kull, the officers and the crew of the R/V METEOR as well the ROV crew (Universität Bremen) for their excellent co-operation during the M60/3 cruise, which was funded by The German Research Foundation (DFG) within Priority Program 1144. We also would like to thank the Captain, officers and crew of the Yokosuka. Special thanks to Gary Massoth and Mathew Scott for taking sampels during that cruise and supplying additional information of the samples.

References

[1] Dopson, M., Baker-Austin, C., Koppineedi, P.R., Bond, P.L., 2003. Growth in sulfidic mineral environments: metal resistance mechanisms in acidophilic micro-organisms. Microbiology. 149, 1959-1970.

[2] Hunter, K. and Boyd, P., 1999. Biogeochemistry of trace metals in the ocean. Marine and Freshwater Research. 50, 739-753.

[3] Rue, E.L. and Bruland, K.W., 1995. Complexation of iron(III) by natural organic ligands in the Central North Pacific as determined by a new ligand equilibration/adsorptive cathodic stripping voltammetric method. Marine Chemistry. 5, 117-138.

[4] Moffett, J.W. and Brand, L., 1996. Production of strong, extracellular Cu chelators by marine cyanobacteria in response to Cu stress. Limnology and Oceanography. 41, 388-395.

[5] Stevenson, F.J., 1970. Binding of Metal Ions by Humic Acids. Environmental Biogeochemistry. 2, 519-540.

PBG1-5: Effects of adsorbed humic acids on iron oxide and alumina surface properties: investigation of interparticle forces in natural waters

S.G. Sander, L. Mosely, K.A. Hunter

Marine and Freshwater Chemistry, Department of Chemistry, University of Otago, P.O.Box 56, Dunedin, New Zealand (e-mail: sylvias@alkali.otago.ac.nz)

In natural waters, colloidal particles are characterized by extreme complexity and diversity. However, their surface properties appear to be rendered quite uniform by ubiquitous surface films of natural organic matter (NOM) that envelop the particles[1]. Thus, almost all particles, regardless of inherent mineral type, are found to be negatively charged because of the ionization of acidic carboxyl acid groups (pK ~ 4.5) on the NOM dominating the surface chemistry[2]. The NOM coating on natural particles is highly heterogeneous in size and chemical properties[3]. Usually such NOM is characterized on an operational basis with common groupings being humic and fulvic acids and these have different size characteristics when derived from different sources[4]. These molecules have been shown to contain various functional groups and structures (e.g. phenolic groups, quinone structures, nitrogen and oxygen as bridge units, and carboxylic acid groups) the exact nature of which is often difficult to determine.

In this work, the nature of interparticle forces acting on colloid particle surfaces with adsorbed surface films of the internationally used humic acid standard material, Suwannee River Humic Acid (SHA), has been investigated using an atomic force microscope (AFM)[5]. Two particle surfaces were used, alumina and a hydrous iron oxide film coated onto silica particles. Adsorbed SHA dominated the interactive forces for both surface types when present (see Fig. 1). At low ionic strength and pH >4, the force curves were dominated by electrostatic repulsion of the electrical double layers, with the extent of repulsion decreasing as electrolyte (NaCl) concentration increased, scaling with the Debye length (κ^{-1}) of the electrolyte according to classical theory. At pH 4, electrostatic forces were largely absent, indicating almost complete protonation of carboxylic acid (-COOH) functional groups on the adsorbed SHA. Under these conditions and also at high electrolyte concentration ([NaCl] > 0.1 M), the absence of electrostatic forces allowed observation of repulsion forces arising from steric interaction of adsorbed SHA as the oxide surfaces approached closely to each other (separation < 10 nm). This steric barrier shrank as electrolyte concentration increased, implying tighter coiling of the adsorbed SHA molecules. In addition, adhesive bridging between surfaces was observed only in the presence of SHA films, implying a strong energy barrier to spontaneous detachment of the surfaces from each other once joined. This adhesion was especially strong in the presence of Ca^{2+} which appears to bridge SHA layers on each surface.

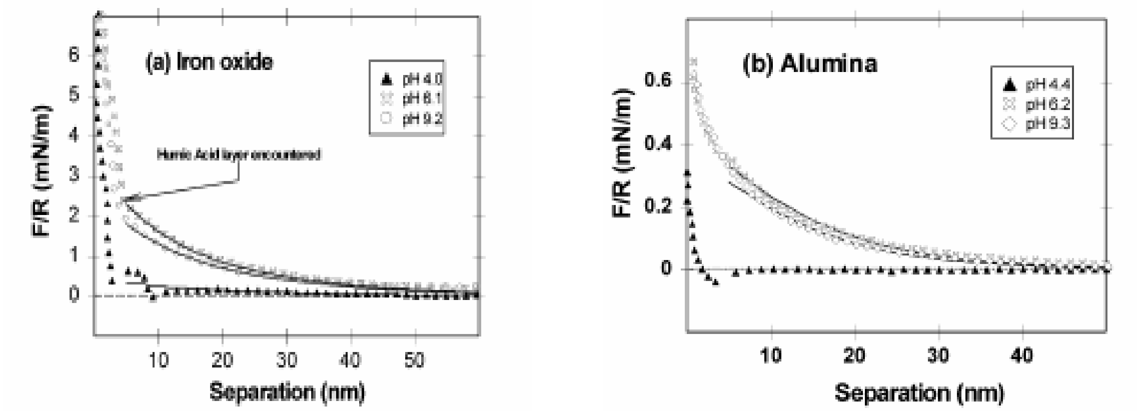


Fig.1. pH-dependence of the normalized force, F/R, as a function of surface separation after adsorption of Suwannee River Humic Acid, a) iron oxide, b) alumina surfaces. Solid lines are calculated from DLVO theory

In summary, we were able to show that the properties of iron hydroxide and aluminium oxide colloids after exposure to SHA are very similar in their force characteristics confirming general observations and previous results[1,2]. These have considerable potential for better understanding of particle interactions in natural waters. Furthermore, we have shown that the behaviour of SHA with respect to colloid particle interactions with the two oxide surfaces we have studied is very similar to that exhibited by marine and freshwater NOM[6]. Thus we suggest that SHA provides a suitable and conveniently available model material for the further study of colloid properties in natural waters, especially by AFM techniques.

Acknowledgements

We are grateful to the Marsden Fund of the Royal Society of New Zealand for financial assistance.

References

[1] Hunter, K. A.,1980. Microelectrophoretic properties of natural surface active organic matter in coastal seawater. Limnology and Oceanography 25, 807-822.

[2] Hunter, K. A. and P. S. Liss, 1979, The surface charge of suspended particles in estuarine and coastal waters, Nature 282, 823-825.

[3] Perminova, I. V., F. H. Frimmel, et al., 2003. Molecular Weight Characteristics of Humic Substances from Different Environments As Determined by Size Exclusion Chromatography and Their Statistical Evaluation, Environmental Science and Technology 37, 2477-2485.

[4] Santschi, P. H., J. J. Lenhart, et al., 1997, Heterogeneous processes affecting trace contaminant distribution in estuaries: The role of natural organic matter. Marine Chemistry 58, 99-125

[5] Sander, S., L. Mosley, Hunter K.A., 2004. "Simulations of inter-particle forces in natural waters: Effects of adsorbed humic acids on iron oxide and alumina surface properties." Env. Sci. Technol. 38, 4791-4796.

[6] Mosley, L., K. Hunter, et al. 2003, Forces between colloid particles in natural waters. Environmental Science and Technology 37, 3303-3308.

PBG1-6: Abiotic Carbon in Areas of Thermal Systems Discharge in Mid-Atlantic Ridge

V.N. Sharapov[1], K.G. Ione[2], V.M. Mysov[2], M.P. Mazurov[1]

1) Institute of Geology SB RAS, Pr. Akad. Koptyuga, 3, Novosibirsk 630090, Russia
(e-mail: vik@uiggm.nsc.ru)
2) SEC Zeosit SB RAS, Pr. Akad. Koptyuga, 3, Novosibirsk 630090, Russia

Free carbon, as a solid dispersed in rocks, is widely spread in the Earth's crust and in the upper mantle. It can be of interest as an indicator of degassing in the abyssal strata of the Earth and of the nature of fluid flows. In the present report, the authors focus on some characteristic features in the structure and genesis of the graphite rock mass detected in three different points of the Mid-Atlantic Ridge (1). To this effect, an investigation of the natural samples was made and the process of carbon condensation from gaseous phase separating from basalt melt was both numerically and experimentally simulated. The diagnostics of phases was made with a scanning electronic microscope LEO 1430VP, equipped with an EDX spectrometer OXFORD. An X-ray phase analysis, Raman, IR, EPR spectroscopy, and electron probe micro-analysis were also used.

The studied samples of natural carbon are of two types, porous and compact. The samples of the porous type appear as silver-black matter with the volume of pores exceeding 80%. By their texture features, these samples can be subdivided into three groups. The first group is aggregates of hexagonal plates packed in rows and loops of sizes varying from tenths of micron to mm. They form a frame with numerous expansions and necks. In the vicinity of the necks the carbonaceous mass is built up with crystals of calcite, halite, chlorite, and in some places with numerous microfossils. The second group is aggregates of tightly packed micro-spheres. The third species is compact masses of homogenous carbon with a conchoidal surface partly split with a net of micro-fractures encrusted with plates of graphite and micro-crystals of halite and calcite. The compact clusters of carbon appear as graphite micro-xenoliths in vitreous basalt.

The process of carbon deposits formation was simulated in a laboratory installation by SEC Zeosit SB RAS during a research on synthesis gas conversion on some natural mineral samples (2, 3). The duration of the experiments was 10 to 40 hours, the pressure values were 30 and 80 bar, the range of temperatures was 250 to 600°C, and the molar composition of the gaseous mixture was 67% of H_2, 32.8% of CO, 0.2% of N_2. It was found that, along with catalytic synthesis of hydrocarbons, a highly condensed carbon phase is deposited on the minerals. When using a scanning electron microscope, separate particle, tenths of micron in size, can be clearly distinguished, conglutinated in aggregate spheres about 2 μm in diameter. ″Biomorphic″ carbon aggregates also occur, having the shape of worms, sticks, and cones about 1-5 μm in length and 0.2-0.3 μm in diameter. When compacted, these particles turn into plates and flakes; with further sintering, they turn into a tighter aggregate. The more the carbonisation degree, the more the variety is of the shapes of catalytic carbon. Along with carbon, the reaction products include spheres and dendrites of γ-Fe about 0.2 μm in diameter as well as irregular-shaped particles of cohenite, wustite and magnetite. According to Raman spectroscopy both in the natural and laboratory samples, modifications of carbon are highly disordered graphite. This is indicated by two wide lines in the range 1330 and 1590 cm^{-1}.

The numerical simulation of the physical-chemical processes has been carried out using SelectorWin (4) program for temperature range 200 to1200˚C and pressure range 40 bar to 45 kb**.** Two schemes have been used. The first one is "fixed", i.e. models a hetero-phase equilibrium under fixed temperature and pressure in the above ranges, for the molar quantities C (0.1 – 10), H (1.5 – 15), Cl (0.05 – 0.5), F (0.01 – 1), S (0.01 – 0.1), N (0.02 – 0.1) and 1 kg of rock. The second scheme was of continuous flow type, where gas flow of the above composition passed from a magma reservoir through 38 reactor stages of the "rock massif – fracture – rock massif" type. The interval for time steps varied from 5 to 100. Performing this task allowed us to get a more precise and detailed representation of the thermodynamic modelling results for possible compositions of the mantle fluids in the lithosphere section (5),, and to determine the range of stability of free carbon. During condensation, the phase composition of the mineralization that accompanies the carbon deposition essentially depends on the ratio of concentrations C, H, Cl, F, and S in the magma fluid being detached. Both experimental and numerical modelling confirm the hypothesis of abiotic origin of carbon in the areas of thermal systems discharge in Mid-Atlantic ridge as a result of interaction of reduced abyssal fluids with basalts and serpentinites of the ocean bed.

Acknowledgements

This work was supported in the framework of the RAS Project N° 6.1.1 and of RFBR Project N° 04-05-64107.

References

1. Dynamics of ore-magma systems in spreading zones / V. N. Sharapov , V. A. Akimtsev, V.N. Dorovsky et al., Novosibirsk, UIGGM SB RAS, 1999, 414p. (in Russian).
2. Ione K.G. Mysov V.M. et al., About possibility of catalytic abiotic synthesis of hydrocarbons in the earth crust // Chemistry for sustainable development, 2001, № 9, p.129 – 143.
3. Patent 2180651 RF, 2002 (in Russian).
4. Karpov I.K., Chudnenko K.V., Kulik D.A., Bychinskii V. A. The convex programming minimization of five thermodynamic potentials other then Gibbs energy in geochemical modeling // Amer. J. Sci., 2002, v.302, № 4, p. 281 – 311.
5. Zubkov V.S. Composition and forms of fluids of C – H – N – O – S system on PT conditions of upper mantle // Geochemistry, 2001, № 2, p. 131 – 145 (in Russian).

PBG1-7: The geochemistry of the organic matter (OM) of the Upper Quaternary glacial sediments of the Peri-Polar Urals

L.A. Anischenko, S.S. Klimenko, D.A. Bouchnev

Institute of Geology KSC UB RAS, Russia, Syktyvkar

The area of investigation is confined to the basin of river Yunyakha of the Peri-polar Urals. It is located 90 km south-eastward from the city of Vorkuta. The loams of glacial sediments of the last covering glaciation are studied. In the loams the abundance of pebble and single boulders, abundant plant detritus, Quaternary high plant pollen are observed. TOC content is from 1.8 to 2.2%. HI ranges within 245 - 340 mgOM/gTOC. The HI values allow to classify the OM as III-II. The OM is not mature which is proved by Rock-Eval analysis. The temperature of HC maximal output T_{max} ranges within 419-425 deg. C. Free+sorbed/pyrolized (S2) HC ratio does not exceed 0.9 (S_1/S_1+S_2 = 0.06-0.088). In all samples n-alkanes highly dominate (Fig.1). The oddness factor for C_{29} changes from 4.3 to 7.7. The lowest value is determined in the sample with HI at 340 mgOM/gTOC.

HC biomarkers testify to the heterogeneous content of OM producing bitumen. The major part of TOC are comprised by high plant derivatives. N-alkanes C_{25}-C_{35} forms more than 70% of the fraction volume. The oddness factor is great in this component interval which is characteristic for humic TOC. The greatest values correspond to C_{31} or to C_{27}. In the first case a low HI value (HI=245) and a high value of Pr/C_{17} = 0.6 are observed. Together with nC_{27} predominance the increased HI value (HI = 340 and 263 accordingly) and the predominance of n-alkanes C_{23} and C_{25} are determined which conforms to the showings of eksinite matter (Table 1). Isoprenoid components are determined in minor quantity with the predominance of pristan together with low HI values. An interesting feature is a small even nC_{16} predominance ($2*nC_{16}/C_{15}+C_{17}$=1.15-1.19) which may be due to bacterial contribution to HC producing. A general feature of the HC under study is the absence of naphthene background in chromatograms.

Resume:

Glacial sediments accumulate mainly humic matter with a slight admixture of type II products. OM in glacial sediments is not practically oxidized.

Table 1. The results of geochemical investigation

N образца	OM, %	HI, мг/г	S_1, мг/г	T_{max}, °C	Pr/Ph	Pr/C_{17}	Ph/C_{18}	$\frac{2\text{н}C_{17}}{\text{н}C_{16}+\text{н}C_{18}}$	$\frac{2\text{н}C_{16}}{\text{н}C_{15}+\text{н}C_{17}}$	$\frac{2\text{н}C_{29}}{\text{н}C_{28}+\text{н}C_{30}}$	Maxi-mum
12-71	2.2	245	0.56	419.6	0.700	0.6	0.18	0.90	1.18	6.27	C_{31}
10-43	1.8	340	0.58	423.3	0.387	0.26	0.81	1.11	1.19	4.30	C_{27}
16-18	1.8	263	0.46	423.2	1.090	0.28	0.30	1.15	1.15	7.70	C_{27}

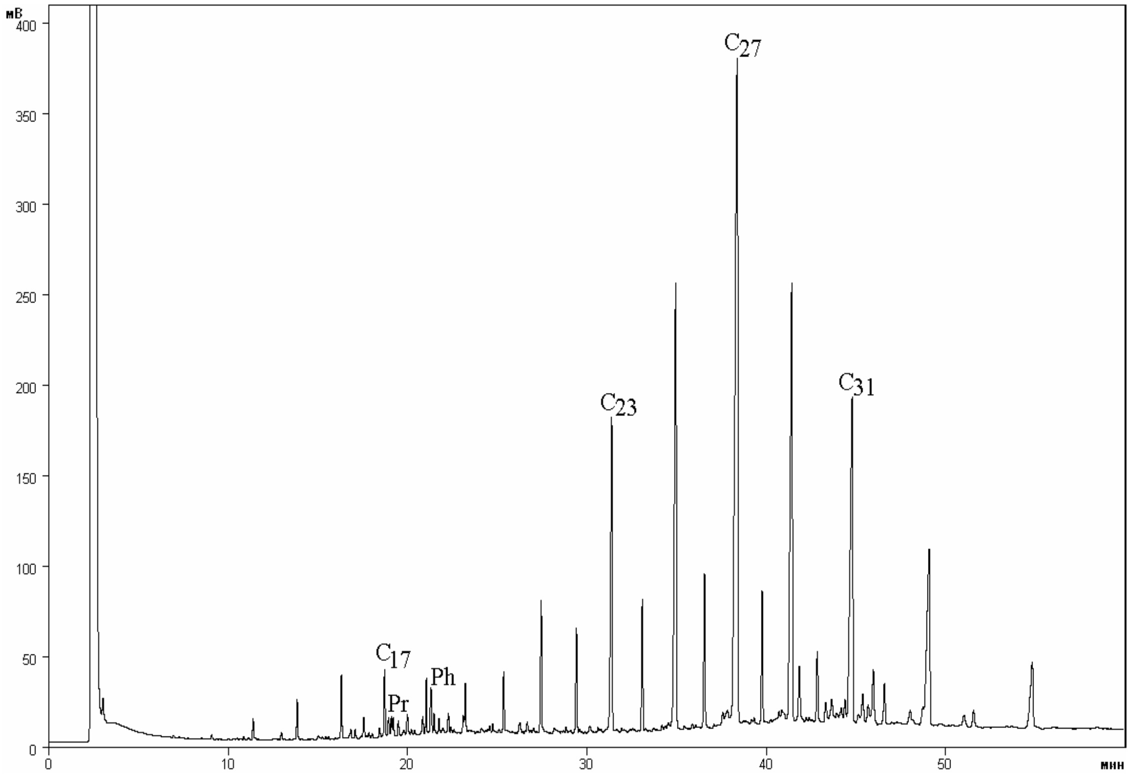


Fig.1. Chromatogram of M-N fraction of chloroform bitumen of sample 10-43

PBG1-8: Carbon isotopic composition of extracted and bound OM in sediments of hypersaline lake Karachi, West Siberia

V.N. Burkova, E.A. Kurakolova

Institute of Petroleum Chemistry SB RAS, 634021, Tomsk, Russia (e-mail: ovs@ipc.tsc.ru)

Intensive studies of carbon isotope distribution in sedimentary OM as a whole or in its individual components are aimed at identification of their sources and distinguishing thin differences in their composition. The greater part of such researches was carried out using freely extracted OM.

Our study is focused not only on soluble fractions of OM but also upon insoluble ones, i.e. bound with mineral and protokerogen matrixes, and residual OM as well. The objects of the study are bioproducers and sediments of hypersaline lake Karachi, West Siberia. The sediments were recovered at the depths 0-1.20 m. Lipids were extracted with equi-volumetric mixture of chloroform and methanol after successive solution of minerals, aluminum silicate and carbonate, with mineral acids and saponification of protokerogen with diluted alkaline solution. All operations were realized at low temperature.

Carbon isotopes of lipids and residues of biomass fall within the narrow range of δ^{13}C values from –26 to –27 ‰. Planktonic organisms such as *Microcystis sal.* and *Artemia sal,* have heavier isotopic composition, while saprophytic bacteria – lighter.

There is no difference in isotopic compositions between biomass and residual OM of bottom sediments. This fact reflects the latest stage of protokerogen formation. Residual OM of submerged cores is enriched with light carbon isotopes (from -25.5 ‰ to -28.0 ‰). Sedimentary lipids contain light carbon isotopes even to a greater extent than residual OM (from -27.5 ‰ to -31.7 ‰), at that lipids included into protokerogen matrix are the lightest ones (-29.8 ÷ -31.7 ‰). Such isotope distribution holds its regularity out up to the depth of 0.70 m, agrees with that of marine deposits (Galimov and Kodina, 1982) and is stipulated by carbon isotope fractionation during diagenesis.

The closeness in carbon isotopic composition of soluble lipids and bound with minerals proves their common source and the same mechanism of sorption of soluble lipids on the mineral surfaces. On the contrary, enrichment with light carbon isotopes of lipids included into protokerogen up to -2 ‰ in comparison with other lipid fractions may be explained by presence of mainly neutral components within protokerogen structure.

It is known (Galimov and Kodina, 1982) that humic acids tend towards complexation with liophobic compounds, alkanes, fatty acids and pigments among them, which form the basis of the future source-rock bituminous portion. An experiment carried out to simulate such a process has demonstrated a possibility to involve freely extracted lipids inside humic acids structure. These lipids are chiefly nonpolar components since the portion of carboxylic groups in lipids enclosed into protokerogen becomes two times less than it was in the original soluble lipid fraction. As to HCs enclosed into protokerogen they are predominantly low-molecular, unsaturated, linear and even-numbered as compared with those of original freely extracted lipids. All these HCs included into protokerogen are lighter in their isotopy than their counterparts are.

The fractionation of lipids between soluble portion and that in protokerogen is surely conditioned by cell sizes of protokerogen and by the interaction, which fixes lipids within protokerogen cells. The links are likely to be of the type as n-alkanes have with molecular sieves, forming clathrates.

There is a trend of carbon isotopic lightening from 1 to 3 ‰ in all fractions of sedimentary OM, which is observed as sediment cores approach the depth of 0.7 m. This phenomenon is conditioned by increase of terrestrial input in the earlier periods of depositing, as it is confirmed by hydrocarbons distribution, and also by intensification of diagenetic transformation that is accompanied by loss of heavier carbon isotopes with polar ingredients.

The established above regularities are inverted in the lowest core which occurs at depth from 0.7 m to 1.20 m. Isotopic compositions of both residual OM and the lipid fraction included in protokerogen grow heavier comparing with those in the overlaying cores, but insignificantly. Contrariwise, carbon isotopies of other lipid fractions become heavier than residual OM (-24.0 ÷ -25.5 against -27.7 ‰, respectively), even heavier than biomass and much heavier than corresponding lipid fractions in overlaying core (-24.0 ÷ -25.5 against -29.6 ÷ -30.8 ‰, respectively).

The received results may be explained by the fact that the lowest sediment layer deposited during preindustrial period, more than 200 years ago, when atmospheric CO_2, used by phototrophs, was heavier in isotopy up to -3 ‰. Another factor affecting the isotopic composition of sedimentary OM was the less degree of salinity at the early stage of lake evolution. It was actually up to 2 times less than it is nowadays. Marine plankton is known as organisms greatly enriched with heavy carbon isotopes. Both factors could favour OM isotopy weighting. But residual OM and lipids in protokerogen seem not to be affected by these factors so much as other lipid fractions.

The third factor is the greater terrestrial input into sedimentary OM in the lowest core as it appears from the HCs. Higher terrestrial plants are lighter in carbon isotopic composition than marine plankton and could affect the carbon isotopy of residual OM and protokerogen lipids in case lignin was the basis of humic acids in the lowest core.

PBG1-9: The fate of organic matter in mangrove sediments under variable environmental conditions (French Guiana)

E. Lallier-Vergès, C. Marchand, P. Albéric, J-R. Disnar

Institut des Sciences de la Terre d'Orléans, UMR 6113 CNRS-Université d'Orléans, Bâtiment Géosciences, 45064 Orléans, France (e-mail: Elisabeth.Verges@univ-orleans.fr)

During the 4 last years, a National research Program for Coastal Environment (PNEC) was partly devoted to the littoral of French Guiana. Several field trips allowed the sampling of twinned sedimentary cores from sediments with or without vegetal cover, and of various vascular plants specific to these swamps. An elemental, pyrolytic and optical study of total sedimentary organic matter (OM), completed with stable isotope and molecular analyses, was performed on these sets of samples and coupled with a study of pore waters (physico-chemical properties and dissolved OM study) collected in the mean time, during contrasted seasons. The development and age of mangrove marshes and forests was assessed by parallel studies performed by ecologists (F. Fromard, University Paul Sabatier, Toulouse, France).

The main purpose of this study was to assess the origin of the sedimentary OM and its fate (Hedges et al. 1997) considering the various diagenetic processes present in the brackish to hypersaline mangrove sediments characterised by great changes in the redox conditions. Several specific results of this work have already been published, namely: the physico-chemical conditions of these environments during the wet and dry seasons, the composition of bulk OM, the organic content of pore-waters linked to degradation processes and finally the behaviour of carbohydrates and lignin during early diagenesis (Marchand et al., 2003; 2004; 2005; in press). Here, we present an integrated conceptual model for organic sedimentation and diagenesis in French Guiana mangroves, taking into account as far as possible, the whole range of results.

The studied mangroves are located: i) on the right bank of the Sinnamary River, near Kourou, ii) at the mouth of the Kaw River, near Cayenne. They develop on the upper intertidal zone of 30 km long mud banks that can reach up to 5 km in width and that move upwards to the North West due to the huge discharge of the Amazone River. This moving occurs with a fifty years cyclicity, which is a quite critical point for economical development of the Guiana's littoral.

We demonstrate that the OM composition depends on both the topography of the formations and the age of the ecosystems, which will directly determine the origin of the OM. Close to the sea, algal mats develop on the top of just accreting littoral deposits. Along a sea-land transect, the forest is the dominant organic source, it becomes denser and denser with increasing age, thickening litters and soils. The underlying fine-grained clay sediment only contains minute refractory debris of higher plants supplied with clay minerals by the Amazonian current.

Based on the study of both pore-waters and sediments, we determined very different bio-geochemical processes depending on the locations studied. We showed that these processes are clearly linked to interacting parameters among them: climate, forest and soil development, vegetal species, tides and bioturbation intensity.

The climate plays a main role on the establishment of environmental conditions by directly driving sediment water-saturation seasonal changes. Consecutively, an oxidation front affects the sediment once a year in the most seaside locations. Moreover, these places are also submitted to the daily running off of the uppermost sediments due to tides and to the bioturbation effects. Far from the littoral, where tides and crabs are non effective, the nearly permanent water-saturation of the sediments induces medium stable conditions. The succession of seasons leads to a stratification of redox processes (oxic-suboxic-anoxic) and to strong variations of surface sediments salinity. In buried wet sediments, pyrite framboids assess the occurrence of marked sulfate reduction conditions.

The mangrove vegetation is the major organic source in these environments. Its distribution is the other main parameter determining the environmental conditions and OM evolution. It supplies organic carbon into the sediment, via the litters, under the form of fresh ligno-cellulosic debris. We characterized the OM evolution by the following markers: 1) palynofacies constituants %, 2) TOC%, HI (mgHC/gTOC), C:N ratio and $^{13}\partial$C values, 3) total sugars and phenols %, 4) $(Ad/Al)_v$ and S/V ratios, 5) fucose and rhamnose contents. Their distribution obeys a combined vertical/horizontal trend revealing that the sedimentary OM is degraded through a succession of oxic-suboxic-anoxic processes depending on both the location and the age of mangroves. Additionally, it has been shown that the vegetation is locally able to increase the salinity of pore waters as a result of evaporation-transpiration process. *A. germinans* specific from young littoral mangroves may also introduce O_2 into the sediment through its very specific root system inducing oxidative conditions.

Moreover, this study illustrates that both lignin and cellulose from vascular plants, can be rapidly degraded (10 yrs scaled) in waterlogged, brackish to hypersaline sediments.

References

- Marchand et al. (2003) *Estuarine Coastal Shelf Sciences* **56**: 119-130; (2004) *Marine Geology* **208**: 361-381; (2005) *Geochim. et Cosmochim. Acta* **69**: *131-142, Marine Chemistry* (in press*);* Hedges et al. (1997) *Organic Geochemistry* **27**, 195-212.

PBG1-10: Positioning of the Silurian-Devonian boundary at the North Rim of the Arabian Plate (Hazro Area, SE Anatolia, Turkey): an organic-geochemical assignment

U. Mann[1], R. Brocke[2], U. Herten[1], O. Kranendonck[1]

1) Forschungszentrum Jülich, Institut Sedimentäre Systeme, D-52425 Jülich, Germany
(e-mail: u.mann@fz-juelich.de)
2) Forschungsinstitut Senckenberg, Paläobotanik, D-60325 Frankfurt, Germany

In the Hazro area of the Turkish border fold zone (SE Anatolia, Turkey), the exact position of the Silurian-Devonian (S-D) boundary is still under debate. Biostratigraphic approaches failed up to now due to completely missing index fossils (e.g. conodonts, graptolites) and the incomplete distribution of palynomorphs (e.g. chitinozoans, acritarchs). According to the geological information from this area near the north rim of the Arabian plate, the S-D boundary should be positioned within the local Upper Dadas Fm. which represents a subunit of the Silurian to Devonian Diyarbarkir Group ([1], [2]. Based on Acritarch assemblages, the Dadas Fm. is of Wenlockian to Lochkovian age [3].

In order to localise the S-D boundary, we have tested the sedimentary sequence for a specific isotopic trend in relation to the global bioproductivity event at the S-D boundary [4], [5], [6]. However, no comparable isotopic excursion of organic and/or carbonate carbon could be revealed [7].

At the GSSP of the S-D boundary (Prague Basin, Czech Republic), the high bioproductivity signal of the S-D boundary is expressed by a bloom of prasinophytes [8]. Thus, a second approach to locate the S-D boundary tried to obtain a characteristic algae bloom signal via biomarker analyses. A maximal signal of this kind was established by the ratio of regular steranes to 17α(H)hopanes [9] which could be confirmed by scanning electron microscopy at the respective bedding planes at a depth of 66m of borehole Fetlika-1 (Fig. 1).

By combining the biomarker results with carbon isotope trends [7] and a sedimentary facies analysis [9], it became obvious that the position of the high sterane/hopane ratio just marks the onset of the global high bioproductivity peak. The principal signal at the S-D boundary, however, is not preserved. It falls into parts of an eroded sedimentary sequence, i.e. bioclastic limestones representing a transgressive lag deposit, and thus a pronounced, but up to now not yet realized sequence boundary.

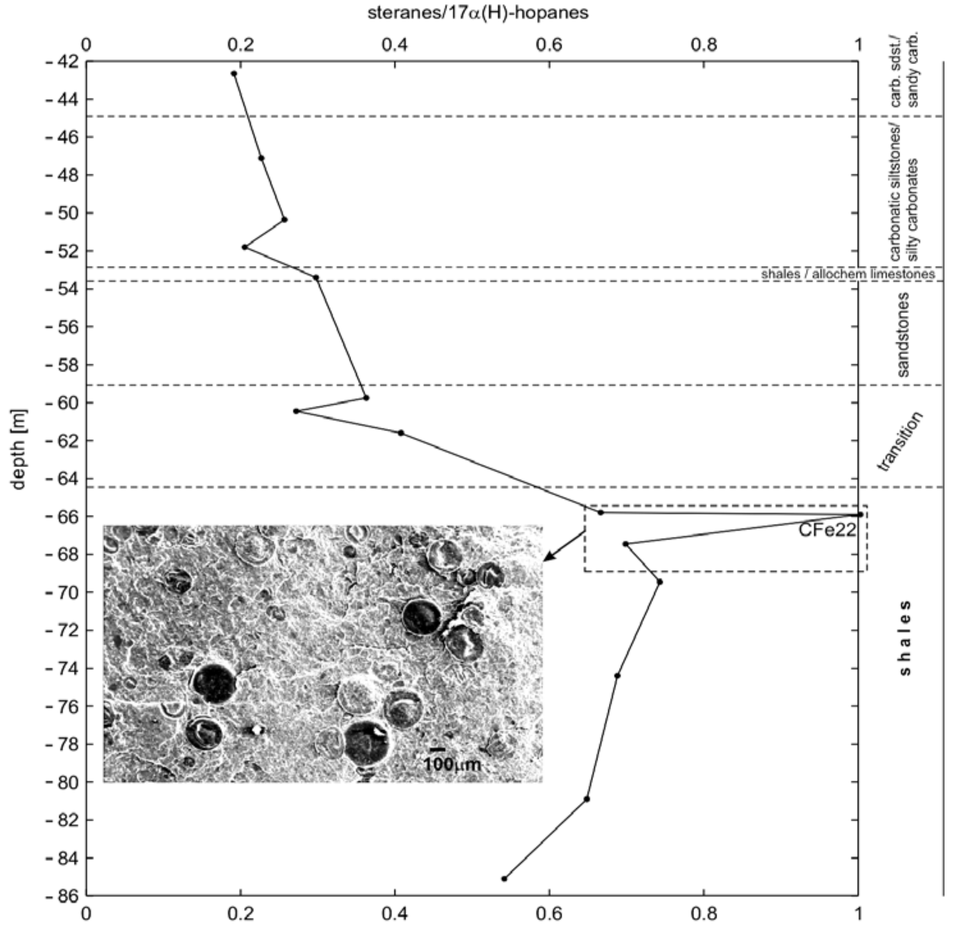


Fig.1. Variation of the relative amounts of algal versus bacterial organic matter within the sedimentary sequence of the 42-86m depth interval from borehole Fetlika-1 (SE Anatolia) as expressed by the ratio of steranes to 17α(H)hopanes which indicates a maximum algal contribution in sample CFe22 at approximate 66m depth and which is confirmed by scanning electron micrographs of abundant *Tasmanites* phycomata accumulated on the respective bedding plane (photomicrograph courtesy of Turkish Petrol. Corp., Research Centre, Ankara)

References

[1] Bozdoğan, unpublished.

[2] Fontaine, J. M., Brunton, C. H., Lys, M., Rauscher, R. and Balkas, O. 1980. Données nouvelles sur la stratigraphie des formations paléozoiques de la plate-forme arabe dans la région d´Hazro (Turquie). CR Acad Sc Paris 291, Série D, 917-920.

[3] Bozdogan, N. and Ertug, K. 1997. Geological Evolution and Paleogeography of the Southeast Anatolia in the Paleozoic. In: *Early Paleozoic Evolution in NW Gondwana*, *3*, *Special Publication* (Ed. by M. C. Göncüoglu & A. S. Derman). Turkish Assoc. of Petroleum Geologists, Ankara.

[4] Saltzman, M. R. 2002. Carbon isotope (δ^{13}C) stratigraphy across the Silurian-Devonian transition in North America: evidence for a perturbation of the global carbon cycle. Palaeogeography Palaeoclimatology Palaeoecology, **187**, 83-100.

[5] Herten, U., Mann, U. and Yalçın, M.N. 2004. Chemostratigraphic localization of the Silurian/Devonian boundary in the Palaeozoic of Istanbul (Esenyalı, Pendik-Istanbul) by stable carbon isotope composition. *In*: Proceed. of the Int. Symp. on Earth Sciences, Sept. 8-10, 2004, Istanbul (Turkey), 321-334.

[6] Buggisch, W. and Mann, U. 2004. Carbon isotope stratigraphy of Lochkovian to Eifelian limestones from the Devonian of central and southern Europe. Int. Journ. of Earth Sciences, **93**(4), 521-541.

[7] Herten, U. 2005. Global and environmental significance of increased bioproductivity during late Silurian/early Devonian time. Ph. D. Thesis, RWTH Aachen University, in preparation.

[8] Brocke, R., Fatka, O. & Wilde, V. (2003): Palynomorphs from the Silurian/Devonian Boundary GSSP at Klonk (Czech Republic). Terra Nostra, **5**, 32-33.

[9] Kranendonck, O., 2004. Geo- and biodynamic evolution during late Silurian/early Devonian time (Hazro area, SE Turkey). Schriften des Forschungszentrums Jülich, Reihe Umwelt/Environment, Volume 49, 268p.

PBG1-11: Terrestrial Organic Matter Transport: a Comparison Between Tropical and Temperate Rivers

P.M. Medeiros[1,2], B.R.T. Simoneit[1,2]

1) Environmental Sciences Graduate Program, Oregon State University, Corvallis, OR 97331, USA (e-mail: simoneit@coas.oregonstate.edu)
2) College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, OR 97331, USA

Riverine organic matter is of geochemical interest both as an integrator of processes within drainage basins and as a source of terrestrial organic matter (TOM) to continental margin sediments, ultimately preserved in the geological record(1). The total riverine organic flux derives largely from forested catchments, which export roughly 0.12 Gt (Gt = $1x10^{15}$ g) OC yr^{-1} in the tropics, whereas temperate forests contribute about half this flux(2). The major source of TOM is vascular plants, which are confined essentially to land and produce a host of unique compounds which can be used as sensitive biomarkers for tracing terrestrial origins. The main objective of this study is to identify the dominant biomarkers in river/estuarine systems from different climatic regions, and to assess the metabolic and redox alteration processes that affect organic components as they transit from land to sea. Sediment samples were collected in small rivers draining northern São Paulo State (Brazil) and western Oregon (USA), and analyzed as total and silylated total extracts by gas chromatography-mass spectrometry. Fatty acids (16:0, 16:1, 18:0, 18:1, 18:2) and cholesterol were by far the dominant biomarkers found in sediments from Brazilian rivers (Fig. 1a). This indicates an extensive microbiological activity in tropical conditions. Higher plant biomarkers (sitosterol, brassicasterol, campesterol) were also important organic tracers detected, followed by lower amounts of plant wax lipids (mainly *n*-alkanols). Besides those major and minor biomarkers, indicators of anaerobic alteration (phytadienes) and sugars such as glucose and inositol (ubiquitous in origin) and mycose (a fungal metabolite product) were also found in the Brazilian river sediments. In contrast, the major biomarker contributions found in Oregon river samples were sterols and triterpenoids (sitosterol, campesterol, lupenone) derived mainly from the vegetation bordering the rivers, followed by *n*-alkanols and *n*-alkanes from epicuticular plant wax. Autochthonous production (fatty acids and cholesterol) were important organic tracers detected only in higher altitude systems (e.g., spring bloom of algae, Deschutes River, ~1000 m). Resin acids (e.g., dehydroabietic acid, a biomarker for conifers) were expected to be the major tracer input to these sediments, as the dominant vegetation cover of temperate drainage areas is conifers. However, resin acids were detected at only trace levels (Fig. 1b). Therefore, during normal river flow conditions terrestrial organic signatures in the Brazilian river sediments are overwhelmed by organic compounds derived from autochthonous microbial activity due to low river discharges. In the Oregon Rivers only organic biomarkers derived from the surrounding vegetation along the riparian zone of the rivers studied are transported downstream.

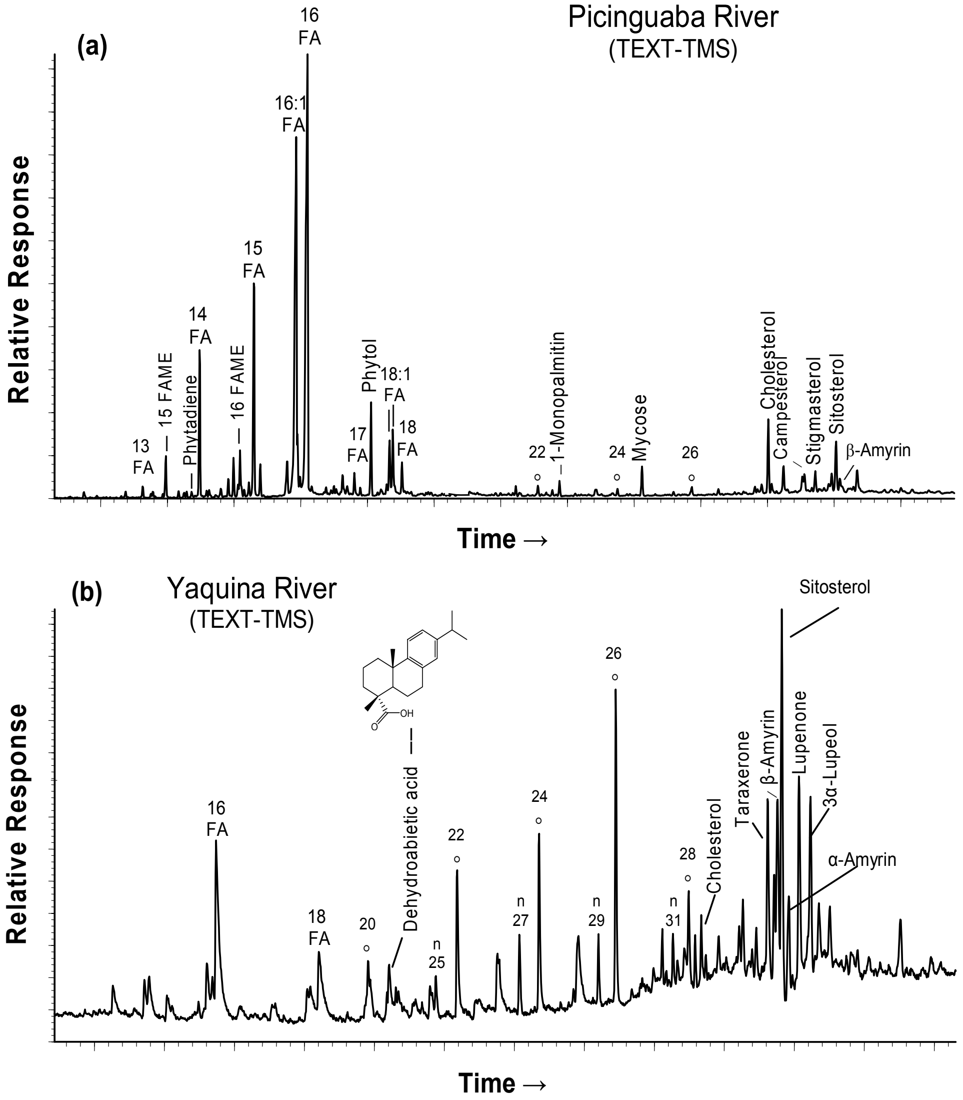


Fig.1. Silylated total extract chromatogram of (a) Picinguaba River sediment, São Paulo, Brazil, (b) Yaquina River sediment, Oregon, USA. Symbols: FA = fatty acid, ∘ = *n*-alkanol, n = *n*-alkane

References

(1) Hedges, J.I., Keil, R.G., Benner, R., 1997. What happens to terrestrial organic matter in the ocean? Organic Geochemistry 27, 195-212.

(2) Schlesinger, W.H., Melack, J.M., 1981. Transport of organic carbon in the world's rivers. Tellus 33, 172-187.

PBG1-12: Use of biomarker isomerisation ratios in estimating paleo thermicity and erosion: limitations and applications to the Paris Basin

C. Ménétrier[1], M. Elie[1], A. Le Solleuz[1], L. Martinez[1], P. Faure[1], C. Rigollet[2]

1) UMR CNRS 7566 G2R, BP. 239, Université Nancy I, 54506 Vandœuvre-lès-Nancy Cedex, France (e-mail: cedric.menetrier@g2r.uhp-nancy.fr)
2) Gaz de France, Direction Exploration Production, 361 Avenue du Président Wilson, 93211 St Denis La Plaine cedex France

Thermal and burial history modelling of sedimentary basin need to use maturity indicators that recorded the past thermal history of sediments, and whose evolution profiles with depth may be used to estimate the amount of sediments removed by erosion. Amongst other organic indicators, biomarkers can be used to establish thermal history of sedimentary basin. The breaks in the expected depth profile of vitrinite reflectance are commonly used to estimate the paleo-erosion. Although these organic indicators are proved to be powerful tools in petroleum exploration, cautions are needed in their using for thermal modelling. One of these limitations, widely demonstrated, is due to thermal stability of indicators as a function of burial depth of sediments. No limitations are known concerning the samples collected on the edge of sedimentary basin, and mature biomarker patterns which may be observed are frequently attributed to reworked organic material. It has been demonstrated that long-time storage under uncontrolled atmosphere can induce drastic modifications of organic signal similar to those observed during thermal maturation. Without this information, care must be taken in isomerisation reactions selected when collecting old core samples to avoid any dramatic error in estimating paleotemperature and erosion.

Paleo thermicity and erosion are presently studied using both S-R and ββ-αβ-βα isomerisation reactions of hopanes in the central and eastern parts of the Paris basin where a major episode of erosion occurred. Callovo-Oxfordian argillaceous rocks collected in HTM 102 borehole recently drilled in the northeast of the Paris Basin (France) were studied. Toarcian and Callovo-Oxfordian natural series, collected from older boreholes and whose most of cuttings were stocked in glass flasks, were also examined. Artificial maturation experiments were performed by heating Callovo-Oxfordian immature sample under isothermal conditions in gold tubes at temperatures ranging between 160 and 380°C for 24 h. Additional experiments in ventilated oven were carried out in ventilated oven at 130°C for 2 to 1024 hours to determine biomarkers reactivity to oxidising conditions. To evaluate the influence of the time/temperature pair used during the oxidation experiments, the powdered fresh sample was introduced in a gold tube, closed under argon atmosphere then placed in the ventilated oven at 130°C for 1024 h. All samples were extracted with dichloromethane, the extracts were fractionated in asphaltenes, saturates, aromatics, and resins. Aliphatic fractions were analysed by gas chromatography-mass spectrometry. Based on the heating experiments, kinetic parameters (i.e. activation energy and pre-exponential factor) were determined for isomerisation reactions. The obtained kinetic models were integrated to 1D and 2D thermal model (PetroMod, IES GmbH) and used to reconstruct the burial and thermal history of the Paris basin in the area of interest. Thermal reconstruction is performed by adjusting determined biomarkers ratios and simulated present day profiles vs. depth.

In the central part of the Paris basin, maximum paleotemperatures of burial estimated using S/R isomerisation ratios of C_{31} hopanes and C_{29} steranes are in agreement with temperatures inferred from previous studies, mainly based on fluid inclusions. Most isomerisation ratios for cuttings collected in the eastern part of Paris Basin are more mature than expected regarding other maturity indicators. When using these ratios, thermal modelling indicates that the eastern part of the Paris basin would have reached the oil generation window. This result is erroneous since petroleum has never been found and the biomarker isomerisation ratios for samples from borehole HTM 102 evidence for a low maturity level of organic material. The high values of cuttings, leading to an overestimation of uplift, are attributed to the occurrence of photo oxidation because these samples were kept in glass bottles and in uncontrolled conditions. Artificial oxidation in ventilated oven reveals that alteration status of organic matter increases with oxidising time, involving similar transformations to those observed in heating experiments. On the other hand, sample closed in gold tube under argon and placed in ventilated oven at 130°C for 1024 h is unaffected by oxidation compared to fresh samples. Isomerisation ratios indicate that simulation match rather well the natural behaviour of sediments stored for several years under uncontrolled conditions, and that ββ-αβ-βα isomerisation reactions are much sensitive to oxidizing conditions than S-R isomerisation. The samples have been selected and an attempt of thermal history reconstruction was made using αβ, αβ and ββ isomers. Calculated maximum temperature is 45±10°C, which is consistent with values derived from independent methods (fluid inclusions, fission tracks).

Then, a careful distinction between maturity and alteration status is needed when thermal history of sedimentary basin is reconstructed from old core samples. In respect to thermal stability, more sensitive isomers to oxidising alteration can be used to estimate paleotemperature and paleo-erosion of formations on the edge of sedimentary basins.

PBG1-13: Compound-specific radiocarbon dating of organic compounds in the oceanic sediments: tools for assessing chronology, transport processes, and biogeochemical cycles

N. Ohkouchi[1,2], D. Montlucon[1], T.I. Eglinton[1]

1) Woods Hole Oceanographic Institution, Woods Hole MA 02543, USA
2) Institute for Research on Earth Evolution, Yokosuka 237-0061, Japan

Compound-specific radiocarbon dating is a relatively new tool for organic geochemistry. It has proven to be useful for studying many aspects of biogeochemical investigations. For example, radiocarbon dating of short-chain (C_{14}, C_{16}, and C_{18}) fatty acids can be used to constrain sediment chronologies, such as those on the Antarctic margin which lack foraminiferal carbonate (Ohkouchi et al., 2003). However, molecular-level radiocarbon studies have also demonstrated that molecular stratigraphic records can be strongly influenced by sediment redistribution phenomena. Sediments deposited on the Bermuda Rise in the North Atlantic, and at the Benguela Upwelling region in the South Atlantic, contain C_{37}-C_{39} alkenones that are significantly (1000-8000 yr) older than coexisting planktonic foraminiferal tests (Ohkouchi et al., 2002; Mollenhauer et al., 2003). Lateral transport of alkenones associated with sediment resuspension and redistribution is invoked to explain these age offsets. In contrast, the ^{14}C analyses of sedimentary alkenones from other sites, including the Santa Barbara Basin, the Gulf of Mexico, and the North Indian Ocean yield almost equivalent ages to those of the coexisting planktonic foraminifera. These results indicate that caution is needed when interpreting biomarker records in sediments and underline the importance of understanding sedimentological processes.

Further information can be obtained on the sources and cycling of organic matter when the molecular ^{14}C approach is extended to other molecular markers. Radiocarbon measurements on vascular plant biomarkers can allow for refined assessment of the proportions of marine and terrigenous organic carbon inputs to ocean sediments, as well as the timescales involved in transfer of terrestrial molecular signatures to marine sediments. When coupled with $\delta^{13}C$ and D/H isotopic information on the same compounds, interpretation of the provenance and proportions of organic matter inputs can be further refined.

In this paper, we will describe results from molecular multi–isotopic (esp. ^{14}C) investigations of organic matter in sediments from a range of depositional settings in order to illustrate the utility of these approaches for biogeochemical investigations. Particular emphasis will be placed on the use of this information to understand depositional processes and to aid in refined interpretation of the sedimentary record.

References

Mollenhauer, G., Eglinton, T. I., Ohkouchi, N., Schneider, R. R., Müller, P. J., Grootes, P. M., and Rullkötter, J. (2003) *Geochim. Cosmochim. Acta* **67**, 2157-2171.

Ohkouchi, N., Eglinton, T. I., Keigwin, L. D., and Hayes, J. M. (2002) *Science* **298**, 1224-1227.

Ohkouchi, N., Eglinton, T. I., and Hayes, J. M. (2003) *Radiocarbon* **45**, 17-24.

OBG1-14: Organic matter of the Cenozoic bottom sediments (sedimentary cover) within the Mendeleev Rise (Arctic Ocean)

V. Petrova, G. Batova, M. Galishev, A. Kursheva, E. Kostyreva

VNIIOkeangeologia, 1, Angliysky ave., St.Petersburg; 190121, Russia (e-mail: geochem@vniio.nw.ru)

A study of a distribution and composition of the dispersed organic matter (OM) of the Quaternary deposits was carried out from the data of bottom testing, obtained during the cruise R/V “Academician Fedorov”, on the “Mendeleev Trough - Mendeleev Rise - Podvodnikov Trough sub latitudinal transect” (2000).

The analytical scheme has included a definition of a content of TOC and $CaCO_3$, a determination of a group composition of OM, a degree of its katagenetic transformation using data Rock-Eval pyrolysis, group and molecular composition of OM components, including hydrocarbon biomarkers as well. In this case methods of preparative chromatography, GC, HPLC and GC-MS were used.

It is established that OM is of the same type in composition for the whole stratigraphic section of Holocene-Pleistocene deposits. The following features are typical for it: low content of soluble components (<10%), abnormally high bituminisity (β=5-10%) and content of hydrocarbons (up to 30 mg/g TOC). Even (OEP<1), short-chain (n-$C_{14,16}$) compounds of linear structure (Ki=0,4) dominate in the composition of aliphatic hydrocarbons. Polyaromatic hydrocarbons are mainly presented by phenanthrene holonucleus structures.

Given parameters are absolutely non-typical for moderm bottom sediments, and most likely they are typical for the deeply transformed OM of the sedimentary rocks. This opinion is supported by a wide range of temperatures of the OM pyrolysis (Tmax), which reach in a number of samples 500^0C, as well as values of biomarker indicators of OM maturity (sterane and hopane ratios) corresponding to the level of catagenesis (20S/20S+20R=0,42-0,46; Ts/Tm = 0,56-0,73).

To reveal genesis of OM of the Mendeleev Ridge sediments, a comparison has been carried out of its main parameters and characteristics of possible primary sources. In our opinion, the most probable suppliers of the sedimentary material in the investigated region are:

- Ice transfer and/or water masses Transpolar Drift and the Beaufort Gyre (terrigenous OM);
- Atlantic or Pacific water masses penetrating along the continental slope edge (marine OM);
- Washout and redeposition in situ of local deluvial material.

A comparative analysis of average geochemical parameters of terrigenous OM of quaternary deposits of the Amerasian shelf, surface bottom sediments of the Beaufort Sea with the sedimentary deposits of the Mendeleev Rise shows their principal difference. For instance, the content of Corg in them as higher as on order, and the hydrocarbon content as lower as an order. The group and molecular compositions of HC are also considerably different. In modern terrigenous OM, formed by products of transformation of terrestrial biota, odd (OEP=3,5) long-chain (n-C_{27-31}) unbranchy n-alkanes (Ki=0,8) prevail. Polyaromatic hydrocarbons are mainly presented by chrysene and perylene structures. Values of Tmax (350^0C) and biomarkers ratios (20S/20S+20R=0,20-0,35; Ts-Tm=0,22) correspond to a diagenesis stage of the OM transformation. Likeness of OM parameters of bottom deposits of the Mendeleev Rise with the sediments of the Eurasian continental margin, OM of which are formed using terrigenous and marine compounds (β=1%, ΣHC=1mg/g TOC; n-alkanes max=C_{17-19}+C_{27-31}; OEP=2,0 Ki=0,6) is also not observed.

Hence the investigations carried out do not allow to trace a direct genetic connection OM of the Mendeleev Rise bottom sediments with the modern terrigenous and hydrobiontic sedimentary material. A significant degree of the OM transformation, analogous to the katagenetic maturity of upper Paleozoic – lower Mesozoic deposits of the Siberian Platform, evidently, shows a considerable part of the redeposition processes in their formation.

PRG1-15: Geochemical modelling of the hydrothermal alteration of komatiites and the abiogenic production of organic carbon in the Archean

L. Richard[1,2], M. Van Zuilen[3], C. Biache[1], M. Crovisier[1],
T. Filhine-Tresarrieu[1], M. Franiatte[1], N. Kammer[1]

1) Université Henri Poincaré (Nancy), Département des Sciences de la Terre, 54506 Vandoeuvre-lès-Nancy cedex, France
2) Géologie et Gestion des Ressources Minérales et Energétiques, UMR 7566 CNRS, 54506 Vandoeuvre-lès-Nancy cedex, France
3) Centre de Recherches Pétrographiques et Géochimiques, UPR 2300 CNRS, 54501 Vandoeuvre-lès-Nancy cedex, France

Recent studies on the origin of carbonaceous material in > 3 billion-year-old Archean rocks from the Pilbara craton (Western Australia) have resulted in considerable controversy between partisans of a biogenic origin (Schopf et al., 2002) and their opponents arguing in favor of a hydrothermal, high-temperature abiogenic reduction of carbon dioxide by hydrogen (Brasier et al., 2002). Beyond this debate, defining the oxidation-reduction conditions under which hydrocarbons and other simple organic compounds may have formed on the early Earth as a result of fluid-rock interactions has profound implications for the origin and evolution of life. Taking *n*-dodecane ($C_{12}H_{26}$) as an example, the abiogenic synthesis of hydrocarbons in hydrothermal systems may be written as:

$$12\ CO_{2(aq)} + 37\ H_{2(aq)} \rightarrow C_{12}H_{26(l)} + 24\ H_2O_{(l)}\ ,$$

the aqueous hydrogen being produced by a decomposition of water associated to the oxidation of iron in the fayalite component of olivine according to:

$$\underset{\text{(fayalite)}}{3\ Fe_2SiO_{4(c)}} + 2\ H_2O_{(l)} \rightarrow \underset{\text{(magnetite)}}{2\ Fe_3O_{4(c)}} + 3\ SiO_{2(aq)} + 4H_{2(aq)}$$

In order to evaluate the potential for the prebiotic synthesis of hydrocarbons in ancient hydrothermal systems, we have carried out mass transfer calculations describing the alteration of komatiites by hydrothermal seawater at 200°C. The composition of the reacting komatiite used in the calculations is given in Table 1. The reacting fluid has the composition given by Bischoff and Seyfried (1978). The evolution of the composition of the fluid is represented in Figure 1, where the concentrations in major elements have been plotted as a function of the logarithm of the reaction progress variable (ξ). Also indicated in Figure 1 is the alteration assemblage produced as a result of the hydrothermal alteration of the komatiite. This assemblage consists of quartz, calcite, clinochlore, talc, magnetite, and *n*-dodecane. Mass balance estimates based on our calculations indicate that the abiogenic production of 10^{-2} mole of organic carbon requires the hydrothermal alteration of ~ 56 cm^3 of komatiite.

Mineral	Formula	Vol. %	mol %
Olivine	$Mg_{1.9}Fe_{0.1}SiO_4$	30	49.36
Pyroxene	$CaMg_{0.9}Fe_{0.1}Si_2O_6$	30	32.69
Glass	$Ca_{0.901}Mg_{0.166}Fe_{0.065}Na_{0.171}K_{0.008}Al_{1.255}Si_{4.448}O_{12}$	40	17.95

Table 1. Mineralogical composition of the reacting komatiite (after Thompson et al., 2003)

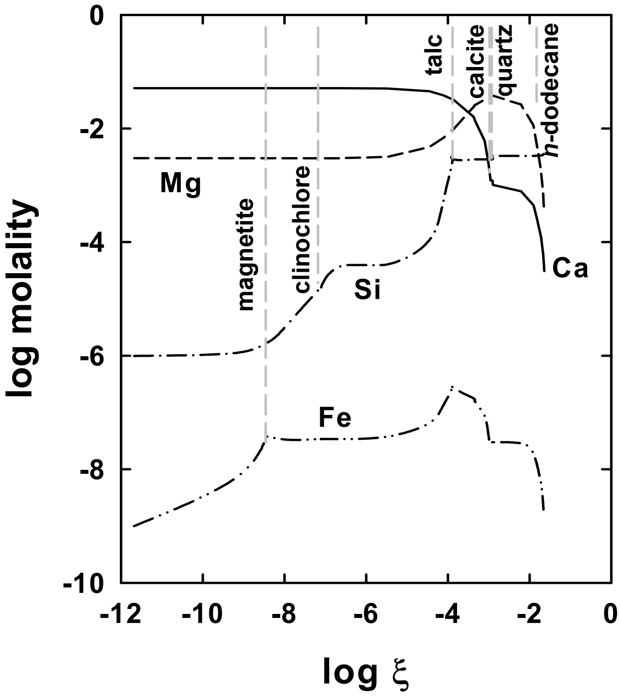


Fig.1. Evolution of the logarithm of the molality of major elements in the hydrothermal fluid as a function of the logarithm of the reaction progress variable (ξ). The dashed vertical lines correspond to the apparition of the reaction products.

References

Bischoff J.L. and Seyfried W.E. (1978) Hydrothermal chemistry of seawater from 25° to 350°C. *American Journal of Science* 278, 838-860.

Brasier M.D., Green O. R., Jephcoat A. P., Kleppe A.K., Van Kranendonk M. J., Lindsay J. F., Steele A., and Grassineau N. V. (2002) Questioning the evidence for Earth's oldest fossils. *Nature* 416, 76-81.

Schopf J. W., Kudryavtsev A.B., Agresti D. G., Wdowiak T. J., and Czaja A. D. (2002) Laser-Raman imagery of Earth's earliest fossils. *Nature* 416, 73-76.

Thompson M.E., Kareem K.M., Xie X., and Byerly G.R. (2003) Fresh melt inclusions in 3.3 Ga komatiitic olivines from the Barberton Greenstone Belt, South Africa. *Lunar and Planetary Science* XXXIV, 2112.pdf.

PBG1-16: Prebiotic reactions and synthesis of organic compounds under hydrothermal conditions

A.I. Rushdi[1], B.R.T. Simoneit[1, 2]

1) Environmental and Petroleum Geochemistry Group, College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, OR 97331, U.S.A.
2) Department of Chemistry, College of Science, Oregon State University, Corvallis, OR 97331, U.S.A.

Prebiotic synthesis of organic compounds under hydrothermal conditions is of interest to cosmochemists, astrobiologists and biogeochemists. Prebiotic chemistry comprises abiotic synthesis of organic compounds in various geological settings such as volcanoes, marine hydrothermal systems, gas seeps from ophiolites, meteorites, and other bodies in the solar system. CO_2, CO, CS_2, COS and NH_3 are common components of such geological locales. These species have been used as starting materials in prebiotic synthesis experiments to produce organic products (e.g., Hennet et al., 1992; McCollom et al., 1999). Thus, it is encouraging to test their reactivities in reductive aqueous thermolysis.

We have produced organic lipids from aqueous solutions of oxalic acid, carbon disulfide or ammonium bicarbonate at temperatures from 150-350°C. The lipids from oxalic acid solutions consisted of n-alkanols, n-alkanoic acids, n-alkyl formates, n-alkan-2-ones, n-alkanes and n-alkenes, typically to C_{30} with no carbon number preferences (Rushdi and Simoneit, 2001, Fig. 1). The yields from carbon disulfide in acidic aqueous solutions consisted of cyclic thioalkanes, alkyl polysulfides, and thioesters with numerous other minor compounds (Fig. 2). The products from oxalic acid and ammonium bicarbonate solutions were homologous series of n-alkyl amides, n-alkyl amines (Rushdi and Simoneit, 2004, Fig. 3), n-alkanes and n-alkanoic acids, also to C_{30} with no carbon number predominances.

Dehydration (condensation) reactions also take place under hydrothermal conditions as tested by model reactions to form ester, amide, nitrile and ether bonds (Rushdi and Simoneit, 2004, Fig. 4). For example, hexadecanedioic acid with aqueous NH_4HCO_3 yields the amido-acid and dinitrile, and hexadecanamide is hydrolyzed to the acid and dehydrated to the nitrile, wax ester and the C_{16} amide (Fig. 4). In another example, ethylene glycol condenses with a fatty acid to produce the mono- and diacyl glycolyl esters and the corresponding wax ester. This indicates that glycerol may also condense with fatty acids under hydrous thermocatalytic conditions to form triglycerides (fats).

In conclusion, abiotic formation of aliphatic lipids and secondary reactions (e.g., dehydration) are feasible under hydrothermal conditions. Further studies are needed to examine the abiotic synthesis and reactions of organic compounds under various hydrous thermocatalytic conditions.

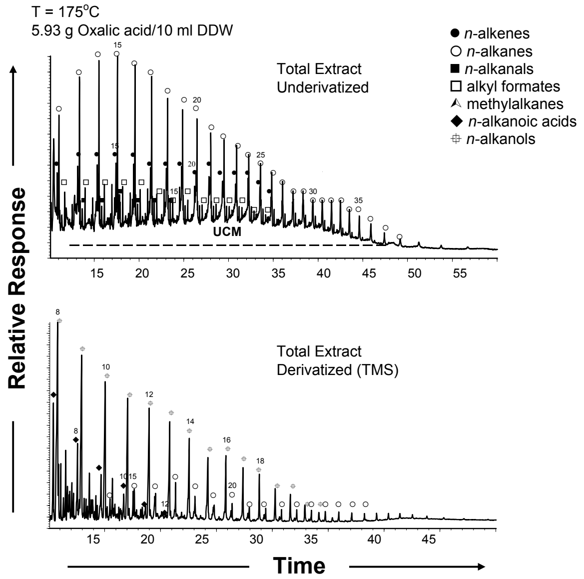


Fig. 1. GC-MS total ion current traces (TIC) for the extracts of products from synthesis experiments with aqueous solutions of oxalic acid at 175°C

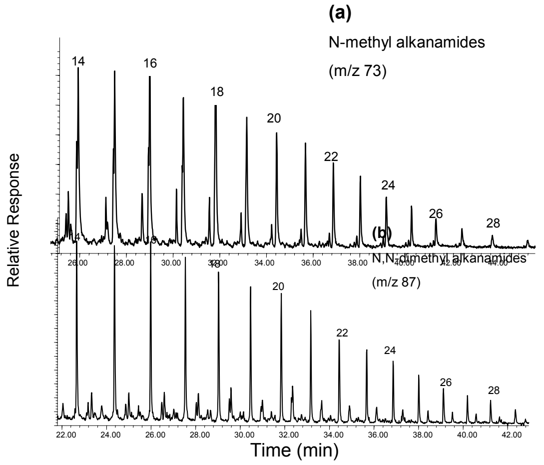


Fig. 3. GC-MS results of abiotic synthesis of amides from an aqueous mixture of oxalic acid and NH_4HCO_3 heated for 72 hours at 300°C: (a) N-methyl alkanamides and (b) N,N-dimenthyl alkanamides

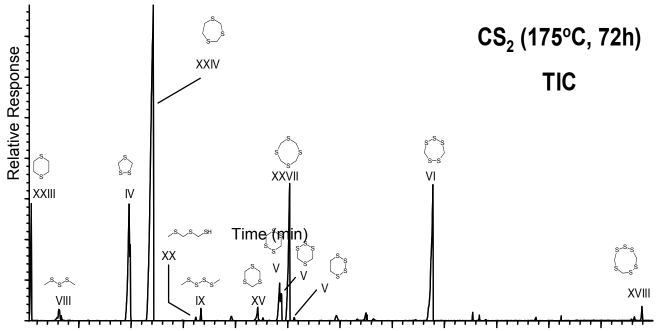


Fig. 2. GC-MS (TIC) traces for an extract of products from thermosynthesis experiments with aqueous solutions of CS_2 and oxalic acid at 175°C

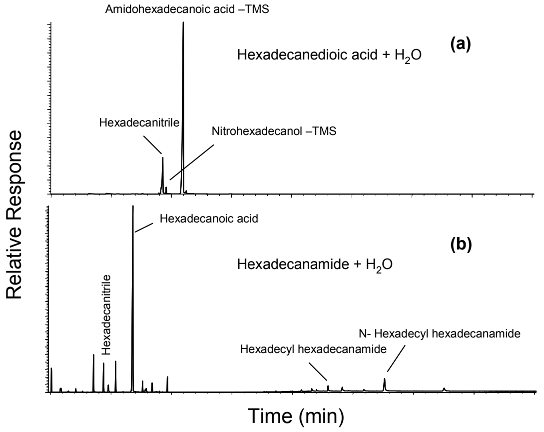


Fig. 4. GC-MS TIC traces of hydrous pyrolysis of: (a) aqueous mixture of palmitic acid and NH_4HCO_3 and (b) palmitamide in water

Acknowledgement

We thank the National Aeronautics and Space Administration of financial support (Grant NAS5-13502).

References

Hennet, R. J.-C., Holm, N. G., and Engel, M. H. (1992). *Naturwissenschaften* 79, 361.
McCollom, T. M., Ritter, G., and Simoneit, B. R. T. (1999). *Origins of Life and Evol. Biosphere* 29, 167.
Rushdi, A. I. and Simoneit, B. R. T. (2001). *Origins of Life and Evol. Biosphere* 31, 103.
Rushdi, A. I. and Simoneit, B. R. T. (2004). *Astrobiology 4(2):* 213-226

PBG2-1: Stable hydrogen isotopic fractionation patterns of long chain alkenones

S. Schouten[1], J. Ossebaar[1], M. Kienhuis[1], J. Bijma[2]

1) Royal Netherlands Institute for Sea Research, Department of Marine Biogeochemistry & Toxicology, PO Box 59, 1790 AB Den Burg, The Netherlands
2) Alfred Wegener Institute for Polar and Marine Research, PO Box 12 01 61, D-27515 Bremerhaven, Germany

The oxygen and hydrogen isotopic composition of seawater is directly correlated to salinity and the isotopic composition of sea water can therefore be used to reconstruct this physical parameter, e.g. by ^{18}O analysis of foraminifera. Hydrogen isotopic compositions of water may be recorded in the non-exchangeable hydrogen in biological organic matter, although with a considerable biosynthetic isotopic fractionation effect due to the production of NADPH from NADP, leading to an initial depletion of ca. 170‰ in the primary photosynthate (reviewed by Hayes, 2001). However, analysis of hydrogen isotopic compositions of fossil organic matter is complicated by the large potential for exchange of hydrogen after deposition of the initial organic matter. A more advanced method for reconstructing ancient δD values of organic matter and waters is now available through some recent technical innovations, i.e. compound-specific hydrogen isotope analysis. Through this technique δD values of individual compounds may be determined with an accuracy of 3-5‰. Thus, compound-specific hydrogen seems to be a unique tool to reconstruct deuterium contents of ancient waters and thereby salinity.

Similar to stable carbon isotopes, the δD values of individual compounds cannot be straightforwardly interpreted without knowledge of the effects of biosynthetic pathways and environmental parameters. Preliminary results, using cultures of a diverse set of microrganisms and re-evaluation of earlier work, suggest that the stable hydrogen isotopic composition of lipids in organisms are primarily a function of their biosynthetic pathways and not so much of the carbon acquisition mechanisms (in strong contrast to ^{13}C-contents of lipids). Thus, before δD values of individual compounds can be used to reconstruct the δD values of water, culture and field studies need to be performed.

In this project we investigate the relationship between the hydrogen isotopic composition of long chain alkenones, well known biomarkers derived from haptophytae algae, and the hydrogen isotopic compositions of sea water with the aim to use this to reconstruct paleohydrological changes in marine environments. Paul (2002) performed an initial investigation of the hydrogen isotopic fractionation of C_{37} alkenones using a culture of *Emiliania huxleyi* grown in waters of different stable hydrogen isotopic compositions.

Fractionation between δD of C_{37} alkenones and growth water was relatively consistent at. ca. 232‰. We extended these original observations by growing cultures of *E. huxleyi* and *Gephyrocapsa oceanica* at different salinities and different temperatures. Interestingly, a strong correlation was observed between the fractionation of $\delta D_{alkenones}$ vs. $\delta D_{growth\ water}$ and salinity for both C_{37} and C_{38} alkenones. However, there is a distinct off set between the correlation for *E. huxleyi* and *G. oceanica* suggesting that the fractionation is varying with algal species. No correlation was observed between the fractionation of $\delta D_{alkenones}$ vs. $\delta D_{growth\ water}$ and culture temperature. In contrast, the U^{K}_{37}' values of C_{37} alkenones for both hapotphytes were strongly linearly correlated to temperature and not to salinity, as has been documented in numerous studies. These results suggest that the $\delta D_{alkenones}$ may be used to quantitatively reconstruct past salinities.

We will now focus on hydrogen isotope patterns in the water column, the transfer of the δD biomarker signal to the sediment and the sedimentary δD signal it self. To this end, particulate organic matter, sediment traps and surface sediments from several oceanic sites with contrasting salinities will be investigated to see whether the relationship between δD values of alkenones and salinity is preserved. If so, paleosalinities of marine settings may be reconstructed by compound-specific hydrogen isotope analysis of long chain alkenones.

References

Hayes, J.M. (2001) In: Stable Isotope Geochemistry (Eds. Valley, J.W., Cole, D.R.) The Minerological Society of America, Washington, 225-277.

Paul, H (2002). PhD thesis, Swiss Federal Institute of Technology, pp.149.

PBG2-2: Organic matter of East Siberian metal-bearing Formations

O.V. Serebrennikova[1], V.K. Nemerov[2], V.V. Evseev[1], D.I. Vekulenkova[1]

1) Institute of Petroleum Chemistry SB RAS, Tomsk, Russia (e-mail: ovs49@yahoo.com)
2) Institute of Geochemistry SB RAS, Irkutsk, Russia

The composition of carbohydrates and trace elements in neoproterozoic (Kachergatska – NP$_3$, Uluntuyska and Khomolkinska – NP$_{2–3}$ Formations) and Lower-Middle Cambrian (Kuonamska Formation) black shales of East Siberia (Fig.1) was analyzed during our work.

Fig.1. Sampling location used in this study

Kuonamska Formation (R° is about 0.5 %, TOC – 13-22 %). The content of the following elements in the layers of high carbonaceous clayey shales is maximum (ppm): Ti – 2000-6000, V – 400-5000, Ba – 600-1000, P – 200-1000, Sr – 200-6000, Mo – 30-600, Cr – 60-400, B – 60-400, Cu – 50-400, Ni – 50-300, Zr – 80-300. The concentration of Ag varies from 0,20 ppm up to 2,0 ppm and of Au – 0.0015-0.05 ppm. With the increase of TOC and extractable organic matter (EOM) contents in the layers the rapid growth of concentration of V, Cr, Mo, Cu, Ag and Au was discovered as far as the increase in concentration of Ti, B, Ni, Zr, Ga, Sc, Pb, Zn, As, Nb, Ce, Yb. The concentration of Ba, Sr and P decreased. The composition of EOM also changed. The relative content of isoprenoid alkanes to n-alkanes (Ki = 0,60-0,25), the amount of the Pr/Ph ratio (1,2-1,9) and the content of vanadyl porphyrin (0,05-4,70 μmol/g EOM) essentially are decreases. The C$_{13}$-C$_{14}$ homologues predominate over the n-alkanes of all the studied samples.

Kachergatska Formation (R° is about 2.5, TOC – 20-40 %). The Carbonaceous clayey shales are enriched with (ppm): Ti – up to 10000, Ba – 800, P – 600, V – 400, B – 400, Cr – 200, Zr –200. The concentration of Ag makes up 0,4 ppm, Au – 0,0012-0,0070 ppm. The chain-length distribution of n-alkanes is bimodal with the main maximum falling at C_{26} and extra maximums falling at C_{14} and C_{16}. The amount of the ratio Ph/Ph is about 0.9, Ki = 0.46.

Uluntuyska Formation (TOC = 1.5 to 5 %). The layers of metamorphic carbonaceous flinty shales are characterized by the lowest content of Ti (1000 ppm) among the studied samples. The following elements are dominating (ppm): V – 400, P – 300, Ni – 150 and Cr – 150. The concentration of Ag reaches 1,0 ppm, of Au – 0,0016 ppm. The chain-length distribution of n-alkanes is bimodal with the main maximum falling at C_{14} and extra maximums falling at C_{26}. The amount of Ph/Ph is about 1.6, Ki = 0.54. The content of alkylnaphthalenes with methylnaphtalenes dominating increased in EOM.

Khomolkinska Formation (TOC = 5 to 20 %). The enclosing metamorphic carbonaceous rocks of gold deposit are enriched with (ppm): Ag - 6, Ti -3500, As - 550, Ba - 500, P -300, Ni -280, Cr - 120, Zn - 130. The character of the chain-length distribution of n-alkanes and isoprenoids is similar to that described for Uluntuyska formation. The content of alkylnaphthalenes is also increased in EOM but with dimethylnaphthalenes dominating. With the increase of content of TOC and EOM in Neoproterozoic (NP_{2-3}) shales, as well as in the series of Upper-Middle Cambrian shales, the increase in content of the majority of elements is observed in the layers. It is especially pronounced for Au, Ag, As, Pb, Ga, Sc. At the same time a decrease in content of V, Sr and Mo is observed.

PBG2-3: Free and bound carboxylic acids in carbonaceous chondrites

J.S. Watson[1], Z. Martins[2], O. Botta[3], P. Ehrenfreund[2], I. Gilmour[1], M.A. Sephton[1,4]

1) Planetary and Space Sciences Research Institute, Open University, Milton Keynes, MK7 6AA, UK
(e-mail: j.watson@open.ac.uk)
2) Astrobiology Laboratory, Leiden Institute of Chemistry, 2300 RA Leiden, The Netherlands
3) International Space Science Institute, 3012 Bern, Switzerland
4) Department of Earth Science and Engineering, Royal School of Mines, Imperial College, London, SW7 2BP, UK

Geological processing has long-since obliterated the Earth-based record of pre-biotic chemical evolution. However, remains of the materials that were involved in the construction of the Earth are preserved in ancient asteroids, fragments of which are naturally-delivered to the Earth as meteorites. Carbonaceous chondrites are a particularly primitive class of meteorite that contain 2 to 5 wt. % carbon, most of which is present as organic matter (Sephton, 2002). There have been relatively few studies of polar moieties in the macromolecular organic matter in carbonaceous chondrites (e.g. Hayatsu et al., 1980). NMR data suggests that there are various oxygen-containing functionalities in Murchison (e.g. Cody et al., 2002).

A HF/HCl residue from a sample of Murchison meteorite was subjected to thermochemolysis followed by analysis by GC-MS and GC-IRMS. The most abundant compound released by thermochemolysis was benzoic acid and other abundant compounds include methyl and dimethyl benzoic acids. Short chain α,ω-dicarboxylic acids (C_{4-8}) were also released from the macromolecule similar to those observed in solvent extracts of the same meteorite. Other compounds detected include fluoranone, dimethylsulfone and aromatic hydrocarbons. The distribution of the C_1 and C_2 benzoic acids (BA) contain all possible structural isomers (except the ethyl BA; see Fig 1). The most abundant isomers include 3,4-dimethylbenzoic acid (DMBA), 3,5-DMBA, 2,6-DMBA and phenylacetic acid. By contrast the most abundant organic acids in the free fraction are the aliphatic C_4-C_9 α,ω-dicarboxylic acids with all structural isomers present. Aromatic acids detected include benzoic acid, C_1 benzoic acids and phthalic acids; no C_2 benzoic acids or naphthoic acids were detected unlike the bound fraction.

There are two possible mechanisms for the formation of meteoritic organic acids; firstly irradiation of cosmic ices by UV or cosmic particle radiation and secondly and more likely, oxidation of free hydrocarbons or of macromolecular material. Bound acids will be formed from free acids being transesterfied into the macromolecule. The aliphatic acids will probably be destroyed by further oxidation whereas the aromatic acids require ring cleavage for complete oxidation and are therefore more resistant to complete mineralisation. The origin and significance of bound organic acids within meteorites and their relationship with the free carboxylic acids within carbonaceous chondrites will be discussed.

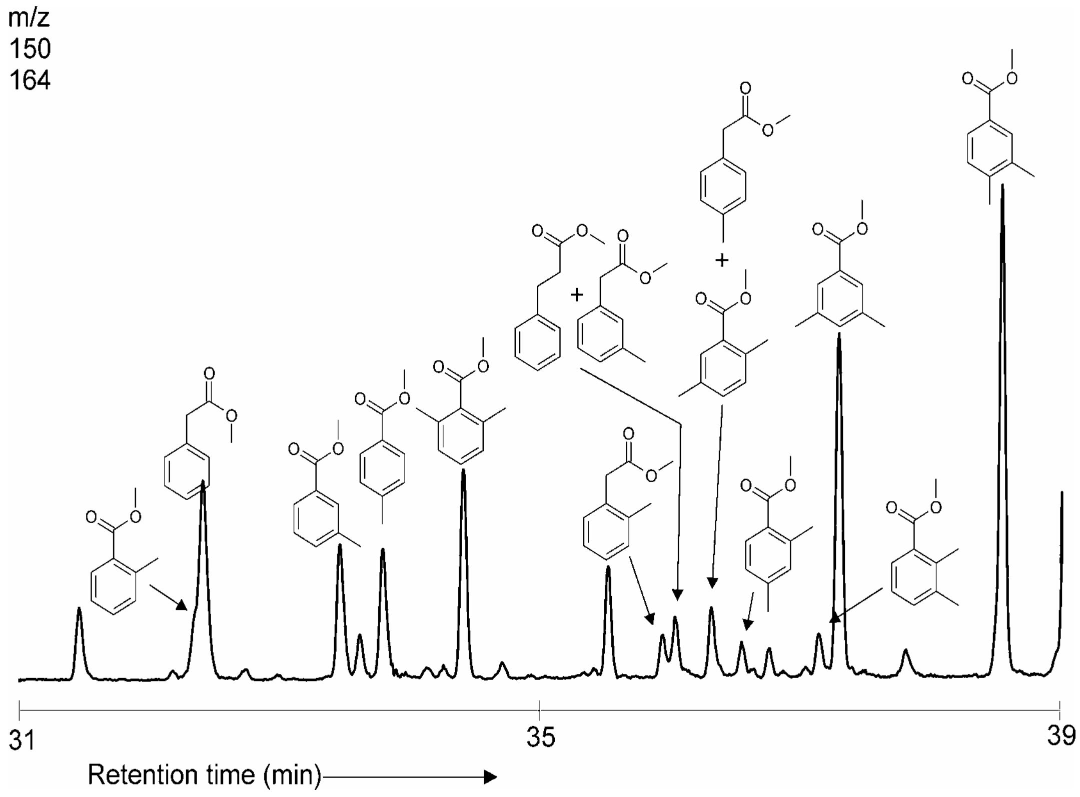


Fig.1. Partially reconstructed mass chromatogram (*m/z* 150 + 164) displaying the C_1 and C_2 benzoic acids (as methyl esters) released upon thermochemolysis of HF/HCl residue from Murchison

References

Cody G. D., Alexander C. M. O., Tera F., 2002. Solid-state (^{1}H and ^{13}C) nuclear magnetic resonance spectroscopy of insoluble organic residue in the Murchison meteorite: a self-consistent quantitative analysis. Geochimica et Cosmochimica Acta 66, 1851-1865.

Hayatsu, R., Winans, R.E., Scott, R.G., McBeth, R.L., Moore, L.P., Studier, M.H., 1980. Phenolic ethers in the organic polymer of the Murchison meteorite. Science 207, 1202-1204.

Sephton M.A., 2002. Organic compounds in carbonaceous meteorites. Natural Product Reports 19, 292-311.

PBG2-4: Composition of organic matter in Cretaceous sediments of the ICDP-Chicxulub drill core YAX-1

H. Wilkes, A. Fuhrmann, V. Lüders, V. Dieckmann, B. Horsfield

GeoForschungsZentrum Potsdam, Organische Geochemie, Telegrafenberg, D-14473 Potsdam, Germany
(e-mail: wilkes@gfz-potsdam.de)

The formation of the Chicxulub impact structure at the Yucatan peninsula, Mexico, is related to a meteoritic impact at the Cretaceous-Tertiary (KT) boundary 65 Ma ago. The relevance of this impact for mass extinction at the KT boundary is currently a matter of extremely controversial scientific discussion. The ICDP-Chicxulub drill core Yaxcopoil-1 (*Yax-1*), drilled between December 2001 and February 2002, penetrated through 600 m of carbonates and evaporites (sulphates) very probably of Cretaceous age. The sequence, in particular the interval at 1300-1510 m, contains numerous layers rich in organic matter (OM) which are displaced by brittle shear zones and locally offset by clastic dyke breccias (Fig. 1). The cross cutting relationship clearly indicates that layers rich in kerogen existed prior to the dykes and thus prior to the impact. Meteoritic impacts are believed to cause hydrothermal fluid circulation in the crater fill and surrounding rocks due to the release of large amounts of thermal energy during the impact and conductive cooling from the central uplift of the impact crater. The occurrence of significant amounts of OM in the drill core YAX-1 provides an unique opportunity to study impact-related hydrothermal alteration of indigenous OM. Our investigations aim at understanding the various factors that control the composition of OM at Chicxulub. This not only includes the role of hydrothermal processes but also that of other key factors such as the source of OM and the depositional environment.

Seventeen samples from the interval 900-1508 m were evaluated by organic geochemical methods because there were visible signs of enrichment in OM (indigenous and/or migrated), and the characteristic odour of crude oil was present. Organic petrology revealed a clear predominance of aquatic macerals such as alginite and lamalginite. The contents of total carbon, total organic carbon, and total sulphur varies between 0.4 and 12.6%, 6.8% and 0.16%, and 0.16% and 6.9%, respectively. In accordance with carbonate rocks in general, the yields of bitumen were relatively high, approximately equalling those of the insoluble kerogen component. However, the bitumens were unusually rich in polar compounds and asphaltenes, and strongly depleted in saturated hydrocarbons, thus more closely resembling hydrothermal petroleums or high temperature pyrolysis products than most petroleum source rocks, produced petroleums and residual oil in reservoirs. The composition of biomarkers in the saturate and aromatic hydrocarbon fractions gave mixed maturity signals, but pointed to a vitrinite reflectance equivalent of 0.8%. In subsiding sedimentary basins this would correspond to a temperature of 110-120°C. This approximate temperature is supported by the majority of fluid inclusion homogenization temperatures in abundant fissure calcites (~100°C). Facies-indicative parameters pointed to the source of the bitumen having been deposited in a clay-free, reducing environment, and were different to those reported for petroliferous basins in Mexico. In the aromatic hydrocarbon fractions phenanthrene concentration was clearly elevated in comparison to the methylphenanthrenes which might point to a significant pyrogenic contribution to the aromatic hydrocarbons. Pyrolysis gas chromatography of the kerogen fraction demonstrated the presence of alkyl, aryl and thiophenic moieties, and a strong inference (high abundance of 1,2,3,4-tetramethylbenzene) that deposition had occurred under conditions of photic zone anoxia. While no definitive statement can be made at this stage as to how much of the bitumen is indigenous or migrated, it is clear that at least 40% of the OM (the kerogen fraction) had to have been present in the analysed sediments at the time of the meteorite impact.

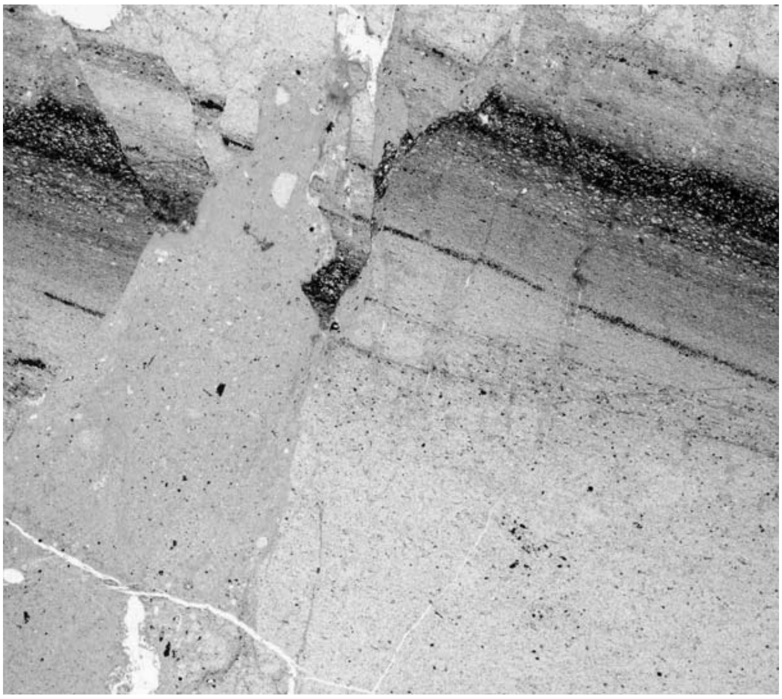


Fig.1. Clastic dike cuts layered carbonate. Dark layers are rich in organic matter (kerogen/bitumen); Yax-1_1316.05 m. Width of photograph 2.2 cm

PBG2-5: Terrestrial-plant derived leaf waxes in boundary layer aerosols: estimators of carbon isotopic discrimination of terrestrial photosynthesis on large regional scales

M.H. Conte, J.C. Weber

Ecosystems Center, Marine Biological Laboratory, Woods Hole MA 02543 USA (e-mail: mconte@mbl.edu)

Changes in the concentration and carbon isotopic composition of atmospheric CO_2 can be used to partition the terrestrial and ocean carbon sinks because terrestrial photosynthesis strongly discriminates against ^{13}C whereas discrimination during ocean uptake is negligible. This approach, though powerful, depends upon the accurate knowledge of the temporal and large spatial scale variation in terrestrial photosynthesis discrimination (Δ), a formidable challenge due to heterogeneity of terrestrial ecosystems. A promising new atmospheric tracer approach (Conte and Weber, Nature **417**, 639-641, 2002) uses the isotopic composition of higher plant derived leaf wax aerosols to derive direct estimates of isotopic discrimination of terrestrial photosynthesis (Δ) on large regional space scales and at ~monthly resolution. This method exploits the specificity of plant biomarker emissions with the integrating properties of atmospheric mixing.

Studies at Howland Forest, Maine USA (a transitional boreal forest) and Toolik Lake, Alaska USA (tundra) have focused upon the processes linking photosynthetic isotopic discrimination with the isotopic composition of plant wax aerosols in the boundary layer. We measured the molecular and isotopic composition of waxes in canopy foliage and also continuously collected wax aerosols above the canopy over the growing season. At Howland, the wax aerosol composition indicated major inputs from both the northern mixed hardwood forests upwind of Howland and local coniferous forests, confirming that the “footprint” of the wax aerosols in boundary layer air masses is of a regional scale. In July 2002, a smoke plume from forest fires in Quebec passed over the Howland site. The plume contained greatly elevated concentrations of both organic carbon and plant wax compounds, and allowed an independent estimate of wax biosynthetic fractionation relative to fixed carbon. The wax aerosol-based estimate of Δ ($18.0 \pm 0.5‰$) closely agrees with direct and model-based estimates of Δ for northern mixed forest ecosystems, and provides additional evidence that the weighted isotopic composition of plant waxes in the atmosphere reflects the Δ of the source vegetation.

PBG2-6: Wildfire contribution to long-range transport of terrestrial plant biomarkers

M.H. Conte[1,3], J.C. Weber[1], P. Medeiros[2], B.R.T. Simoneit[2]

1) Ecosystems Center, Marine Biological Laboratory, Woods Hole MA 02543 USA (e-mail: mconte@mbl.edu)
2) College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis OR 97331 USA
3) Bermuda Biological Station for Research, Ferry Reach St. Georges GE01, Bermuda

Our studies of biogenic aerosols at Bermuda, Howland Maine USA (a transitional boreal forest), Toolik Lake Alaska USA (tundra) and Gainesvilled Florida USA (a southern pine forest) have focused upon how the molecular and isotopic composition of higher plant-derived biomarker compounds (e.g. epicuticular waxes) present in continental air masses reflect terrestrial ecosystem source regions. On several occasions, smoke plumes from distant wildfires have passed over the sampling sites. Aerosols collecting during these periods have contained very high concentrations of levoglucosan (a product of cellulose combustion) as well as greatly elevated concentrations of other uncombusted terrestrial plant-derived compounds such as monosaccharides (glucose, glucopyranose, galactose, arabinose) and leaf waxes (C_{20-35} n-alkanols, n-alkanes, n-alkanoic acids, nonacosanol). Additionally, aerosol samples affected by wildfire plumes have exhibited wax/organic carbon ratios 3-5 times higher than ambient, indicative of steam stripping of waxes and other volatile products during the burn process. Similar findings of have been reported elsewhere (e.g. Kawamura *et al. Global Biogeochem. Cycles*, *17*(1), 2003). These data show that wildfires, through the processes of volatilization and enhanced convection, greatly enhance the long-range atmospheric transport of terrestrial biomarkers. Furthermore, they suggest that variations in past frequency and global distribution of biomass burning events may be major controls on the concentration and composition of terrestrial biomarkers in oceanic sediments.

PBG2-7: Nature, genesis and sources of the carbonaceous polymorphs tracing the 4-kyr BP impact

M.-A. Courty[1], M. Fedoroff[2], K. Grice[3], P. Greenwood[3], M. Mermoux[4], G. Sagon[5], D. Smith[6], M. Thiemens[7], M. Walls[8]

1) UMR 5198, CNRS-IPH, Centre Européen de Recherches Préhistoriques. Avenue Léon-Jean Grégory, 66720 Tautavel, France (e-mail: courty@tautavel.univ-perp.fr)
2) Lab. d'Electrochimie et de Chimie analytique. ENSCP. 11 rue Pierre et Marie Curie, 75231 Paris, France
3) Dpt Applied Chemistry Univ. Technology, Perth, Australia
4) LEPMI-ENSEEG, Domaine Universitaire, BP75, 38042 Saint-Martin d'Hères, France
5) LADIR, CNRS, rue Georges Urbain, 94407 Vitry-sur-Seine, France
6) MHN, Laboratoire de Minéralogie, 61 rue Buffon, 75005 Paris, France
7) Depart. of Chemistry and Biochemistry, University of California, San Diego 92093, USA
8) Université d'Orsay, Bât. 510, Orsay, France

The cause of the 4-kyr BP sharp event remains a contentious issue. For example, the co-occurrence of a dust peak, low lake levels, forest reduction and ice retreat at c.a. 4-kyr BP throughout tropical Africa and West Asia has been widely explained as the effects of an abrupt climate change. Severity and persistence of the drought is assumed to have precipitated the collapse of civilizations in the Aegean world, Mesopotamia, Palestine, Egypt, Indus valley, Central Asia, China. In contrast, detailed study of soils and archaeological records provided evidence that the 4-kyr BP was due to an impact, and not a climate change. Flash heating and violent turbulence generated by pulverisation at the soil surface of a hot impact melt were suggested to have locally damaged habitations, destabilised landscapes and induced soil erosion.

To investigate further these scenarios the organic materials trapped within the 4-kyr BP strata have been collected and their morphology and molecular composition studied. This organic material represents the first opportunity to directly study the molecular and morphological characteristics of carbonaceous compounds associated with an impact ejecta. Rapid burial of the 4- kyr BP surface led to good preservation and careful control of sampling procedures discounts the possibility of pollution by industrial source(s). The data has identified the unique transformation of terrestrially-sourced organic compounds. The co-occurrence of nano-sized diamonds, graphitic carbon and amorphous carbon together with polycyclic aromatic hydrocarbons (PAHs) species within the 4-kyr BP assemblage, in particular within the tektite-like flow-glass buds and re-crystallized micro-breccias, was recognized by high-resolution Raman microspectroscopy. Clusters of nano-sized crystallized carbon are detected in the carbon-rich silicate flow glass by TEM and electronic diffraction. Impact by-products are distinct from the composition of the host materials but reflect a chemical resemblance between distant regions and demonstrate their exogenous origin from a unique source of mixed compositions. The low $\delta^{13}C$ values (-25 to -31‰) of the melt-incorporated carbon is consistent with a terrestrial organic source. The two clusters of ^{14}C age dating obtained on the carbon-rich glass suggest mixing of fresh biomass and combusted fossil hydrocarbons. A similar association of diamond-rich carbon polymorphs in the heated host materials, linked with anomalous isotopically light carbonates (-25 ‰) suggests instantaneous interaction between a gas-rich fluid and the local carbonates along fine pores when the impact ejecta reached the soil surface as a hot combustion bed.

The most common type of scattered carbonaceous grains occur as stacked vesicular green fibres (VFGCG) speckled by metal droplets. Based on molecular and compound specific stable carbon isotopic analyses, VFGCG displays a unique phenolic distribution. The dominance of just a few specific alkylphenolic isomers is not typical of known terrestrial precursors, although their $\delta^{13}C$ signatures is consistent with a C3 terrestrial source. The simple dimethyl and trimethyl phenol profiles may reflect the most thermally stable isomers and are probably derived from a terrestrial source subjected to thermal processes. Single wall graphitic nano-tubes and crystallized nano-sized domains of carbide carbon (possibly carbyne species) were detected in the acid residue of VFGCG by high resolution TEM and Energy Loss Spectroscopy. These structural features suggest that VFGCG has derived from the thermal decomposition of a vapour-rich carbon solution in which super saturation of droplets resulted in the growth of carbon nanofibers as Vapour-Liquid-Solid whiskers.

Brittle carbonaceous aggregates that occur in the 4-kyr BP burnt soil surface at Dja'dé (NE Syria) along with BVCG and VFGCG grains. Py-GC-MS and py-GC-IR-MS analysis documents a molecular composition typical of kerogen, most probably algal-derived as indicated by the presence of C_{20+} *n*-alkanes/*n*-alk-1-enes. Their low $\delta^{13}C$ signatures support an algal organic origin. The low ^{14}C value is consistent with combusted fossil material. The anomalous isotopic composition of sulfur inclusions points to an intriguing mass independent fractionation. This suggests formation of the sulfur-rich kerogen via a gas-phase (SO_2) that suffered photolytic transformation when the ejecta cloud was launched beyond the O^2-O^3 shield of UV.

The widely distributed grains and the glass-incorporated carbon polymorphs are thought to share a common origin from thermal decomposition of two distinct organic sources: fresh biomass and combusted fossil material. This first report of the organic composition of an impact ejecta has identified the unique transformation of terrestrially-sourced organic compounds.

PBG2-8: The carbon isotopic composition of organic matter from Miocene lacustrine sediments (Göynük, NW-Turkey): a function of quality and/or preservation?

H. Hoşgörmez[1], U. Herten[2], U. Mann[2], R.G. Schaefer[2], M.N. Yalçın[1], Ö.B. Yeşiladalı[1]

1) Istanbul University, Engineering Faculty, Geology Dept,TR-34850, Avcılar, Istanbul,Turkey
(e-mail: hosgorme@istanbul.edu.tr)
2) Forschungszentrum Jülich, Institut Sedimentäre Systeme, D-52425 Jülich, Germany

Miocene lacustrine sediments from the Himmetoglu Basin in the Göynük area are characterized by organic rich sediments of varying amounts of organic matter and rapidly alternating types of algal and terrestrial plant origin [1]. This sample set with total organic carbon contents of 1.5-67% and hydrogen index values of 63-941mg HC/g TOC provides an ideal suite to investigate the effects of organic matter quality and preservation differences on the carbon isotopic composition of organic matter. In detail, the isotopic composition of 83 samples is correlated to individual bulk organic geochemical properties of the kerogen and to parameters characterizing the redox conditions during deposition.

The isotopic composition of organic carbon exhibits a negative correlation to hydrogen indices (Fig. 1a). This means that kerogens with low hydrogen indices are typical of ^{12}C-depleted organic matter from terrestrial plants [2]. However, because the isotopic composition exhibits a quite obvious scattering, other factors must also be related to this relationship. In order to check the correlation to the different preservation conditions for organic matter, we have tested the paleo-redox conditions of the depositional environment as a potential modifier for the carbon isotope composition. As the respective paleo-redox proxy, we applied the amount of pyrite sulphur. Since oxygen-deficient environments are characterized by enhanced pyrite formation [3], we could conclude that more oxic environments as indicated by low amounts of pyrite sulfur are represented by lighter isotope values (Fig. 1b). However, also at this correlation, severe disturbances can be observed. This may result from limitations of the pyrite sulphur by the amount of sulphate available for reduction. Furthermore, the amounts of reactive iron and organic matter may have effects on the above relationship, although limitations of both can generally be neglected in lacustrine sediments.

In addition to the above discussed xy-correlations, several selected sample sequences will be presented in order to demonstrate specific trends in respect to changes of organic matter type and depositional environment.

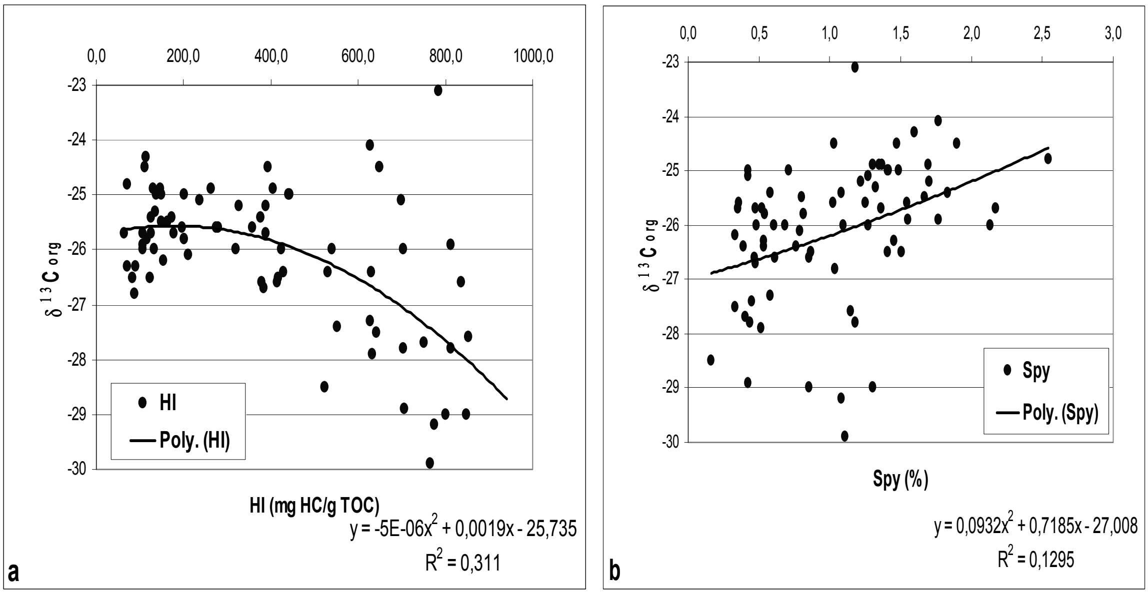


Fig.1. a) Relationship between $\delta^{13}C_{org}$ isotopic composition and hydrogen index (HI) values of organic matter and b) pyrite sulphur (Spy) in lacustrine sediments from Goynuk

References

[1] Yalçın, M.N., Mann, U., Bulkan, Ö., Dikmen, D., Disco,D., Hoşgörmez, H., Nazik, A., Nickel, B., Schaefer, R.G., Şengüler, İ., Wilde, V., Willsch, H., 2003, Significance of sediments, palynomorphs and lipids in relation to environmental conditions in two Neogene lacustrine basins in NW Anatolia. 21st International Meeting on Organic Geochemistry, 8-12 September, 2003, Krakow, Poland, Book of Abstracts Part II, 305-306.

[2] Ariztegui, D., Chondrogianni, C., Lami, A., Guilizzoni, P., Lafargue, E., 2001, Lacustrine organic matter and the Holocene paleoenvironmental record of Lake Albano (central Italy). Journal of Paleolimnology 26, 283–292.

[3] Berner, R. A., Raiswell, R. 1983, Burial of organic carbon and pyrite sulphur in sediments over Phanerozoic time: a new theory. Geochimica and Cosmochimica Acta *47,* 855-862.

PBG2-9: Inferring ancient food-chain dynamics from the fluctuating isotopic compositions of specific organic compounds

D.H. Rothman[1], R. Summons[1], J.M. Hayes[2]

1) Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139 U.S.A. (e-mail: dan@segovia.mit.edu)
2) Department of Geology and Geophysics, Woods Hole Oceanographic Institution, Woods Hole, MA 02543

Changes in the isotopic compositions of bulk sedimentary carbon are commonly used to infer past changes in the global carbon cycle. When both inorganic and organic carbon are analyzed, coevolving changes have revealed aspects of the dynamical interactions between these two bulk reservoirs (Rothman et al., 2003). Of at least as much interest, however, are the interactions *within* the organic reservoir. Here, by application of a new model to specific geochemical event sequences, we show how such interactions can be inferred from the changing isotopic compositions of specific organic compounds (i.e., “molecular fossils” or “biomarkers”).

Previous work (Hayes, 1990) has identified particular compounds whose carbon-isotopic compositions covary with primary (i.e., photosynthetically derived) and secondary (i.e., not primary) organic carbon as a whole. We model the evolution of these isotopic compositions as carbon flow on an elementary food chain. Three results are obtained. First, the prediction of a particular steady-state representation of the data provides a method for estimating the relative burial fluxes of primary and secondary sedimentary organic carbon. Second, we provide a means for interpreting non-steady-state, dynamical fluctuations, in analogy with methods already employed to explain the large fluctuations in the isotopic composition of carbonate carbon in the Neoproterozoic (Rothman et al., 2003).

The third result relates the fluctuations of the difference between primary and secondary isotopic compositions to community-level metabolism. Changes in the accumulation of such “trophic isotope effects” have previously been related to changing food-chain lengths (Logan et al., 1995). A theoretical model suggests, however, that such changes may also result from changes in the gross growth efficiency of organisms within the food chain (i.e., the fraction of consumed carbon converted to new biomass), along with other factors, such as respiratory loss, that not only limit the length of food chains, but also determine the magnitude of the trophic isotope effects.

We apply these ideas to biomarker data traversing the Cenomanian-Turonian oceanic anoxic event (Hayes et al., 1990), the Proterozoic-Cambrian transition (Logan et al., 1997), and other major biogeochemical transitions. The Proterozoic-Cambrian case exhibits a significant change in the apparent primary burial fraction across the Proterozoic-Cambrian boundary. The Cenomanian-Turonian anoxic event displays a dynamical signature roughly consistent with the Proterozoic data. Using our model, we relate these observations to changes in community-level metabolism, and suggest that a particular class of changes in the biomarker isotopic compositions is indicative of anoxic environments.

References

Hayes, J. M., Freeman, K. H., Popp, B. N., and Hoham, C. H. Compound-specific isotopic analyses: A novel tool for reconstruction of ancient biogeochemical processes. *Advances in Organic Geochemistry* **16**, 1115–1128 (1990).

Logan, G. A., Hayes, J. M., Hieshima, G. B., and Summons, R. E. Terminal Proterozoic reorganization of biogeochemical cycles. *Nature* **376**, 53–536 (1995).

Logan, G. A., Summons, R. E., and Hayes, J. M. An isotopic biogeochemical study of the Neoproterozoic and Early Cambrian sediments from the Centralian Superbasin, Australia. *Geochimica and Cosmochimica Acta* **61**, 5391–5409 (1997).

Rothman, D. H., Hayes, J. M., and Summons, R. E. Dynamics of the Neoproterozoic carbon cycle. *Proceedings of the National Academy of Sciences USA* **100**, 8124–8129 (2003).

PBG2-10: Preliminary organic geochemical analysis of surficial marine sediments from the Makassar Strait, Indonesia

J. Sáenz[1], D. Montluçon[1], D. Oppo[1], Y. Rosenthal[2], B. Linsley[3], Y.S. Djajadihardja[4], A. Ridlo[4], F. Syamsudin[4], T. Eglinton[1]

1) Woods Hole Oceanographic Institution, USA Fye, MS 4, Woods Hole, MA 02543
(e-mail: jsaenz@whoi.edu, jpsaenz@mit.edu)
2) Rutgers University Institute for Marine and Coastal Sciences, New Brunswick, NJ, USA
3) SUNY Albany Department of Earth and Atmospheric Sciences, Albany, NY, USA
4) Indonesian Ministry of Science and Technology, Jakarta, Indonesia

Instrumental records of the past several decades demonstrate that changes in El Niño Southern Oscillation (ENSO) have significant effects on extra-tropical climate, and it is possible that longer (e.g., centennial) scale shifts between El Niño-like and La Niña-like states play a role in initiating abrupt global climate change events. ENSO variability has a profound effect on tropical sea surface temperature (SST) and rainfall distribution and these parameters may provide key information about past ENSO variability.

In the present study, we provide biogeochemical data from an array of core top and near surface sediment samples taken from the shallow depths of the Makassar Strait in 2003 during a collaboration between US (led by Rutgers U.) and Indonesian (led by the Indonesian Ministry of Science and Technology) scientists. The Makassar Strait is the main conduit for Indonesian Throughflow (ITF), and temperature in its thermocline varies on interannual time scales due to the influence of ENSO on changes in the transport of warm ITF. ENSO-related shifts of the Western Pacific Warm Pool also drive rainfall variations in the region. Thus, SST and aridity records from these cores may provide insight into past ENSO behavior.

The goal of this study is to evaluate the potential for high-resolution down core reconstructions of paleo-SST and aridity in this region using marine and terrestrial molecular biomarkers. The samples were recovered from sites located off the western Sulawesi margin, and are characterized by high sedimentation rates (>30 cm/kyr) and high organic carbon content, making them ideal for high-resolution molecular stratigraphic studies. In order to reconstruct changes in continental aridity, which is closely linked to ENSO variability, we are measuring downcore variations in the concentrations of polycyclic aromatic hydrocarbons (PAHs) as a proxy for frequency of forest fires, and the stable carbon and hydrogen isotopic composition of vascular plant wax biomarkers, which reveal changes in vegetation type and relative humidity. As an independent proxy for SSTs (to complement those derived from foraminiferal Mg/Ca) we are exploring the applicability of the tetraether index derived from the membrane lipids of marine crenarchaeota (TEX_{86}) for these tropical waters. Because of the strong currents associated with passage of the ITF through the Makassar Strait, we are also examining the potential for sediment redistribution to influence downcore variations through radiocarbon measurements. Preliminary data from surface and near-surface sediments indicate the presence of a broad suite of organic compounds that are well preserved and in sufficient abundance required for our proposed measurements.

PBG2-11: Application of optical, chemical and thermal methods to the analysis of inorganic and organic constituents in phosphatic pellets (Tunisia)

A. Ben Hassen, J. Trichet

ISTO, Institut des Sciences de la Terre d'Orléans, Rue de Saint-Amand, Bâtiment Géosciences, BP 6759, 45067 Orléans Cedex 2 (e-mail: Aida.Ben_Hassen@univ-orleans.fr)

A study of "pellets", phosphatic grains whose size lie between 50 and 200 µm, of the Tertiary Gafsa Metlaoui basin (Tunisia) has been performed by X-ray diffraction, IR spectroscopy, CNS elementary analysis, microscopy (photonic, conventional MEB and Cryo-MEB), Rock-Eval pyrolysis.

The X-ray diffraction shows that the fundamental mineral within these phosphatic pellets is "carbonate-fluorapatite" or "francolite".

This francolite is characterized by low values of its cell parameters **a** and **c**: the **a** parameter is comprised between 9.291 and 9.322 Å and the **c** parameter between 6.874 to 6.899 Å. The comparison with other natural and synthetic similar apatitic compounds (francolite and fluorapatite) shows isomorphic substitutions in the crystal lattice of the pellets francolite and, in particular, the introduction of carbonate ions into the crystal lattice. This substitution of ions PO_4^{3-} by ions CO_3^{2-} is confirmed by the infra-red spectroscopy which shows low contents of CO_2 (from 2.75 to 3.82% of total sites), i.e. a carbonate fluorapatite of the type B ([2]).

Mineralogical and chemical studies let us to establish a structural formula for an apatite within a studied sample as: $(Ca_{4,63}\ Mg_{0,13}\ Na_{0,22})\ ((PO_4)_{2,51}\ (CO_3)_{0,48})\ (OH_{0,77}F_{0,23})$.

Observations under conventional MEB show a characteristic hexagonal shape for apatite minerals. Detailed examination of these minerals shows that each large mineral is formed by smaller hexagonal crystals (lower than 1µm in larger dimension). In certain cases, we observed, between the apatite microcrystals, stick forms with a median contraction, suggesting bacterial bodies.

In pellets, carbon is divided into organic and mineral carbon. Knowing the values of total carbon by LECO-2000 analysis, it was possible to obtain the mineral carbon content by deducing the organic carbon content from the total organic content. The organic carbon content varies within pellets from 0.11 to 1.74 %.

The organic matter appears as constituted by tangled filaments binding apatite crystallites. The observation in Cryo-MEB gives evidence of the presence of filamentous, intrapelletal, organic matter.

The study of the organic matter with Rock-Eval VI pyrolysis confirmed the origin of the organic matter associated with phosphatic pellets, i.e. its marine planktonic origin ([1], [3]).

Interestingly, the Rock-Eval technique allows the distinction of the CO_2 liberated by the pyrolysis of the intrapelletal organic matter from the CO_2 produced during the thermal cracking of the carbonate-fluorapatite.

In addition, it leads to the following fundamental result: values of HI, OI and Tmax confirm the humic (i.e. very poorly evolved in the range of diagenesis as well as from a thermal point of view) character of the organic matter contained in pellets. This character is typical of an organic matter which has been entrapped in a mineral (apatitic) network and whose diagenetic evolution has been empeached. Let us recall that the Tunisian phosphatic ores are Early Tertiary in age and that the presence of a humic organic matter within the pellets is in contradiction with such an age as well as with the kerogen nature of the organic matter within the sedimentary matrix embedding the pellets. As such apatite and its associated organic matter constitute a typical "organo-mineral" association.

References

[1] BELAYOUNI H. and TRICHET J. (1983) Preliminary data on the origin and diagenesis of the organic matter in the phosphate basin of Gafsa (Tunisia), In *"Adv. Org. Geochem. 1981*", ed. by Björoy et al., John Wiley and Sons eds., p. 328-335.

[2] BENALIOULHAJ S. (1989) Géochimie organique comparée des séries du bassin phosphaté des Oulad-Abdoun et du bassin de schistes bitumineux de Timahdit (Maroc). Implications dans la phosphatogenèse. *Thèse de Doctorat es-Sciences, Université d'Orléans*, 242 p.

[3] NATHAN Y.(1990) Humic substances in phosphorites: occurrence, characterization and significance. In Phosphorite Research and Development. *Geol. Soc., Sp. Publ., No. 52, ed. by Notholt A.J.G. and Jarvis I.*, p. 179-191.

PBG2-12: Radiocarbon ages and biomarker compositions of organic matter in size-fractionated sediments from the Washington Margin

M. Uchida[1,5], T.I. Eglinton[2], J.M. Hayes[1], L. Coppola[3], Ö. Gustafsson[4], P. Andersson[3]

1) Woods Hole Oceanographic Institution, Department of Geology & Geophysics, Woods Hole, MA 02543, U.S.A. (e-mail: uchidamao@aol.com; uchidama@jamstec.go.jp)
2) Woods Hole Oceanographic Institution, Department of Marine Chemistry & Geochemistry, Woods Hole, MA 02543, U.S.A.
3) LIG, Swedish Museum of Natural History, Box 50007, 10405, Stockholm, Sweden
4) Stockholm University, Institute of Applied Environmental Research (ITM), 10691 Stockholm, Sweden
5) Japan Agency for Marine-Earth Science and Technology, Yokosuka, 237-0061, Japan.

In order to examine relationships of organic matter source, molecular composition, and diagenesis with particle size in modern marine depositional regimes, 7 surface sediment samples were collected from water depths of 70 m to 2700 m along an E-W transect from the mouth of the Columbia River, across the Washington continental margin to the Cascadia Basin in the N.E. Pacific. The sediments were hydrodynamically separated into various coarse (>250, 100-250, 63-100, 38-63 and <38 μm) and two fine (38->1m/d and 38-<1m/d) fractions using sieving and SPLITT (split flow thin cell) fractionation, respectively. The sieve-SPLITT method was recently tested and validated by using a variety of natural sediments [1], demonstrating that many biogeochemical processes governed by particle dynamics could be examined using this approach. The mass distribution of sieve fractions indicates that sediments from the Washington shelf are dominated by large particles (>250 μm) whereas fine particles (<38 μm) are predominant in slope and Cascadia Basin sediments. This is consistent with the natural grain size distribution occurring in Washington margin sediments [2]. Total Organic Carbon (TOC) contents of the sediments generally follow the same distribution as the mass. With the exception of inner shelf stations, most TOC resides in the fine fraction and ranges around 1.5-3%. Radiocarbon ages of TOC ranges from 1190 yrs BP to 4320, with older ages further from the coast. The age distributions of grain-size fractions were systematically youngest in the most fine fraction (<38μm). The 38->1m/d fractions were systematically younger than 38-<1m/d fractions. Stable carbon isotopic measurements reveal an increase in δ13C values of TOC from the shelf to the Cascadia Basin (from -25 to -22 ‰), suggesting a transition from terrestrial to autochthonous marine sources. Variations in biomarker compositions between grain-size fractions and in bulk-phase organic matter will also be discussed in the context of the radiocarbon and $\delta^{13}C$ results. Moreover, compound-specific radiocarbon and stable carbon data of grain-size fractionated sediments from shelf and slope sites will be discussed in the light of transportation process and fate of organic matter in the conference.

References

[1] Coppola, L., Gustafsson, Ö., Andersson, P., Larsson, J. and Axelsson, P. *Water Research* submitted.
[2] Keil, R.G., Tsamakis, E., Fuh, C.B., Giddings, J.C. and Hedges, J.I. (1994) *GCA* **58,** 879-893

PBG2-13: Relationships Between the Radiocarbon Age and Modes of Association of Natural Organic Matter in Coastal Sediments

H.K. White, C.M. Reddy, T.I. Eglinton

Department of Marine Chemistry & Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA (e-mail: hwhite@whoi.edu)

We have investigated the relationships between radiocarbon (^{14}C) age and the different modes of association of organic matter (OM) present in surficial sediments from a variety of coastal sites that range in terms of inputs and depositional conditions. Radiocarbon is a sensitive tracer of OM with variations in its natural abundance reflecting the age and origin of material. In order to investigate isotopic variability within different sedimentary OM pools, sediments were sequentially treated first by solvent extraction to examine non-covalently associated compounds followed by saponification to cleave ester-linked moieties. In some cases, the saponified residues were subject to ether cleavage. Radiocarbon analysis was performed on the bulk sediment, sediment residues and select extracts. The molecular composition of the extracts was examined using gas chromatography/mass spectrometry (GC/MS) and the relative contributions of terrestrial and marine biomarkers released from the sequential chemical treatments was assessed. For select sites, pre-anthropogenic sediment horizons were also studied to examine diagenetic influences on relationships between age, chemical association and reactivity of sedimentary OM.

Radiocarbon abundances of the bulk organic carbon of the unextracted, extracted and saponified sediment residues are shown for surface sediments from a variety of representative sites in Figure 1. For the majority of sites shown and that we have examined, the bulk unextracted sediments have a $\Delta^{14}C$ range of ~ -50 to -150‰ and reflect a mixture of modern, pre-aged and fossil OM of marine and terrestrial origin. Exceptions include salt marsh sediments from West Falmouth, MA (USA) that is more enriched (+44‰) and shelf sediments from the Eel River Margin, which is more depleted (-320‰). The enrichment in the former is likely due to incorporation of recently synthesized terrestrial biomass (*Spartina alterniflora* roots) into the sedimentary matrix. The depletion at Eel River Margin is likely due to a natural input of fossil carbon.

In general, there is little difference between ^{14}C abundances for the unextracted and solvent extracted sediments for the majority of sites that we have examined (e.g., West Falmouth, Figure 1). However, slight offsets are observed, and these are highlighted by Lowes Cove and the Washington Margin (see Figure 1), where solvent extracted residues are significantly more depleted than the unextracted sediment. This reflects the weak association and facile removal of more recently synthesized material by solvent extraction. GC/MS analyses of the total lipid extracts (TLE) provide insights into the source of materials removed by solvent extraction. In each case, varying proportions of terrestrial, marine and fossil OM are indicated by the distribution of *n*-C12 to *n*-C34 fatty acids and alkanols and the abundance and carbon preference index (CPI) of *n*-C23 to C33 *n*-alkanes. The dominance of long-chain fatty acids in the Washington Margin TLE indicates that the shift in $\Delta^{14}C$ reflects significant input of recently synthesized terrestrial OC. The reverse is true for the Eel River Margin where the unextracted sediment is considerably more depleted than the extracted sediment residue. With respect to the latter, *n*-alkanes in the TLE with a low CPI (1.6) betray the presence of petrogenic hydrocarbons associated with the supply of OM from erosion of ancient sedimentary rocks on the adjacent continent.

Similar offsets are observed in $\Delta^{14}C$ at most sites between the solvent extracted and saponified sediment residues. With the exception of the Washington Margin, the $\Delta^{14}C$ of the saponified sediment residue is more depleted than the extracted residue indicating removal of more ^{14}C enriched material. GC/MS analysis shows that the saponification extracts are mainly composed of short-chain fatty acids from *n*-C12 to *n*-C24 with an even/odd dominance indicating a predominantly marine signature. These observations provide clear evidence for the protection of labile marine carbon by chemical binding.

In the case of the pre-anthropogenic sediments, the offsets between sediments and their corresponding residues are more subtle. Where offsets are observable, the saponified sediment residue is always the most depleted in ^{14}C suggesting that in general the sequential chemical treatments remove more recently synthesized organic matter. Continuing work involves compound-specific ^{14}C analysis of select extracts to provide a molecular-level basis for these findings.

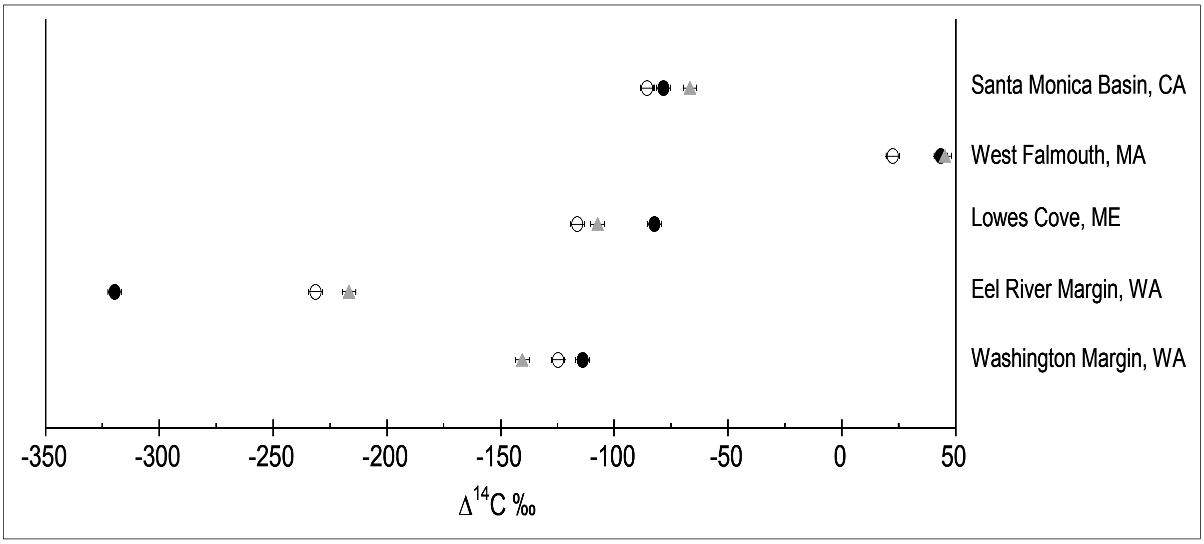


Fig.1. $\Delta^{14}C$ of the total organic carbon of the unextracted sediment (filled black circles), solvent-extracted sediment residues (filled grey triangles) and saponified sediment residues (unfilled circles) for a selection of pristine surface sediments

PBG2-14: Organics temporal changes in the Têt prodelta upper deposit (Gulf of Lions - NW Mediterranean sea): relation between the sediment dynamic events and the biogeochemical properties

R. Buscail[1], F. Bourrin[1], J. Guillen[2], G. Jeanty[1], G. Sarragoni[1]

1) Centre de Formation et de Recherche sur l'Environnement marin (CEFREM), UMR CNRS 5110- Université de Perpignan, 52 Avenue Paul Alduy, 66860 Perpignan cedex, France
2) Institut de Ciencies del Mar (C.S.LC.), Passeig. Maritim de la Barceloneta, 37. 08003 Barcelona, Spain

The importance of short-term processes, such as floods or storms, on organics temporal changes in the Têt prodelta upper deposit was studied in the framework of the EU EUROSTRATAFORM Project (EVK3-CT-2002-00079). The Têt prodelta is a small, event-dominated system, located at the southwestem part of the Gulf of Lions. An annual survey (oct. 2003-sept.2004) of upper deposit was investigated with sediment cores (0-20 cm) hand-sampled by scuba divers, at 28 m depth, in order to a good preservation ofthe sediment-water interface.

Physico-chemical conditions (redox, water content, porosity, grain size fraction) and biogeochemical characteristics (org C, N, C/N, lipids, sugars, amino acids) were analysed in order to evaluate their temporal changes in relation with sediment dynamic events. Current and wave measurements by a wave-gauge ADCP and seafloor erosion/accretion by altimeters contributed to estimate quantitatively and qualitatively sediment input phases during flood event and erosion phase during storm events. Two severe storms occurred on 4 December 2003 and 21 February 2004, displayed similar vawes characteristics: maximum Hs higher than 7 m, Tp> 12s and vawe direction around 90 degrees. Main environmental differences both storm events correspond to the amount of water and sediment discharge from the Têt river. The december event corresponded with high water and sediment discharge period (253 m^3/s and 715 mg/l) ("wet storm") while the water and sediment discharge were moderate during the February event (43 m^3/s and 49 mg/l) ("dry storm").

Temporal changes of the physico-chemical conditions and the biogeochemical properties characterised the 6 cm upper deposit. Usually, below the oxidised superficial layer (0-1 cm), the oxidation-reduction profiles decrease regularly between surface and 10-12 cm deep. After the winter storms, a thicker layer of 6 cm was oxidised. Surface sediment resuspension induced by active currents during the storms contributed to oxidise this layer. A water content enriched layer (320% d.w.) resulted of the December flood material deposit. The accumulation of fine particles after the "dry storm" of February was accompanied by a low water content enrichment (from usually 40% to 46% at this period). After the December storm, porosity reached a mean value of 1.14 in the upper 2 cm, against the average of 0.65

for the other months. Below in the mud-silts, porosity decreased with a mean value of 0.60 from October to April. During summer period, this layer was more compacted (0.57) in relation to the sedimentary stability. On the other hand, porosity increased to a mean value of 0.66 in the underlaying mud in relation to a finer grain size. The upper 6 cm were concerned by important temporal changes in OC, N, C/N ratio. The highest contents characterised the December flood (2.2% d.w.), i.e. five more times higher than for the other months (average content of 0.43%). After the winter storms, the sediment comprised between 2 and 5 cm showed the highest impovershiment in OC (0.2%) and in ON (<0.002%). This organic matter impovershisment can be related to resuspension which by chemical oxidation of the organic compounds accelerate the degradation. After the "dry storm", the comparison between February and March OC% and ON% profiles showed the disappearance of 1 cm thick layer resuspended and exported by the currents. Along the annual survey, OM in surface sediment showed a degraded state (C/N =15), excepted in December (C/N= 11) in relation to an enriched-N soil organic matter input by the river. In the medium muddy-silt deposit, the C/N ratios were ranging from 12 to 23. The zigzag pattern of their distribution was in relation to the alternative wentworth of silty mud and muddy silt layers. Relatively low C/N=10-12 values characterised the fastIy deposited underlaying mud.

Relationships between sugars, lipids, amino acids and OC allowed to underline two important notions: quantity expressed by OC content and quality (labile or refractory character) which do not follow the same trend. Quantity and quality are a consequence of sediment dynamic event differences in the origin of the OM and in the residence time at the sediment-water interface.

Results from this study indicate that in the Têt prodelta upper deposit organic matter is drastically degraded during each storm events and only an ephemeral organic-enriched deposit can be created after flood events. Organic matter transfer across the continental shelf, from the river to the slope, follows a complex, multi-step pattern that needs an interdisciplinary approach.