Appraisal of pyrolytic techniques on different forms of organic matter from a Cretaceous basement in Central Spain

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Abstract—Pyrolytic techniques were used to characterize three different forms of fossil organic matter in Cerro de la Mesa (an important Cretaceous paleobotanic basement in Central Spain): two kerogens isolated from carbonaceous marls, and from lignitiferous layers, and well-preserved remains of the fossil Gymnosperm *Frenelopsis oligostomata*. By conventional flash pyrolysis the *Frenelopsis* remains released mainly alkyl-substituted phenols and polyaromatic compounds, whereas the organic matter from the lignitiferous layer is dominated by phenols and that from the carbonaceous marls by polycyclic and aliphatic compounds. Pyrolysis-thermochemolysis alkylation in the presence of tetramethylammonium hydroxide (TMAH) allowed the detection of additional diagnostic compounds, such as series of methylated fatty acids, benzenecarboxylic and phenolic acids, which revealed further differences between the three materials studied. The chemical characterization of the organic matter in addition to the micropaleontological study suggests that the *Frenelopsis* remains consist mainly of heavily altered lignin and cuticular lipid biomacromolecules, whereas the materials from the lignitiferous layers and the carbonaceous marls correspond to intermediate coalification stages of woody plants, the latter showing the greatest degree of selective preservation of aliphatic structures. The comparison of the above results with those obtained by thermochemolysis suggests that the latter technique produces independent and complementary reactions to conventional pyrolysis, providing additional information to an extent which depends mainly on the polyalkyl and oxidized character of the sample. © 1998 Elsevier Science Ltd. All rights reserved

Key words—Cretaceous palaeoflora, pyrolysis, thermochemolysis, kerogen, *Frenelopsis*, tetramethylammonium hydroxide

INTRODUCTION

The Upper Cretaceous basement in Cerro de la Mesa (Madrid) includes a large variety of palaeobotanical samples, consisting of mega- and microrests (palinomorphs) (Álvarez-Ramis, 1981; Álvarez-Ramis and Fernández Marrón, 1994; Álvarez-Ramis *et al.*, in press). One of the most interesting stratigraphic series as regards the presence of organic remains is found in the gray marls and in the lignitiferous levels, which have never been characterized from a geochemical viewpoint.

Analytical pyrolysis is a rapid and routine analytical technique. It has evident advantages in the case of insoluble macromolecular materials, such as kerogens, coals and humic substances (van de Meent *et al.*, 1980; Hatcher *et al.*, 1988; Tegelaar *et al.*, 1989a; van Aarsen *et al.*, 1991; Christiansen *et al.*, 1993; Almendros *et al.*, 1993; Martín *et al.*,

1994). The alternative use of thermochemolysis induced by alkylating reagents (formerly referred to as "simultaneous pyrolysis methylation") has led to additional improvements in the identification of the constituents of complex materials (Challinor, 1991; Hatcher *et al.*, 1995; McKinney *et al.*, 1995; Kralert *et al.*, 1995; del Rio *et al.*, 1996). However, the molecular characterization of the different forms of fossil organic matter has a series of well-known limitations since most classical chemolytic and pyrolytic techniques may exert selective effects depending on the chemical composition of these materials (Rullkötter and Michaelis, 1990). The very different behavior of lignin-type structures as regards to those derived from carbohydrate has been described extensively (Ralph and Hatfield, 1991; Almendros *et al.*, 1997), as have the non-diagnostic compound patterns yielded by most types of macromolecular polymethylene structures (Boon, 1989).

In this study, widely different types of organic matter accumulated in the Supracretaceous base-

ment of Cerro de la Mesa are analyzed. The samples selected ranged from amorphous organic matter in carbonaceous marls, to morphologically well-preserved branches of a fossil Gymnosperm. The study aims at quantifying any additional information provided by thermochemolytic degradation compared with conventional pyrolysis, as well as assessing to what extent such potential improvements may be sample-dependant.

MATERIALS AND METHODS

Location and lithostratigraphic features of Cerro de la Mesa quarry

The organic samples were taken from a limestone quarry located in Guadalix de la Sierra (Madrid) currently used to extract building materials. The coordinates of the basement are 40°47'37" N and 3°42'11" W (Greenwich). Layers of limestone, marl and sand, cyclically alternate with dolomitized limestones and lignitiferous layers. In particular, the marl levels and the thin carbonaceous levels are very rich in plant remains.

The lithostratigraphic series in Cerro de la Mesa consists of eight members. Marly materials dominate in the lower part (members 8 and 6), whereas limestones (in some cases dolomitized) are the most frequent materials in the upper parts. The subjacent marly sandy limestones (member 4) include thin discontinuous lignite layers.

From the palaeobotanical viewpoint, the greatest number of megaremaines corresponds to Gymnosperms, mainly *Araucariaceae*, *Taxodiaceae* and *Cheirolepidiaceae*. There was a reduced number of Angiosperm megarests, but they were very varied. The palynomorphs confirmed the taxa identified in the megarests. They corresponded mainly to *Araucariacites*, *Inaperturopollenites*, *Classopollis* and *Normapollens* (Álvarez-Ramis and Fernández Marrón, 1994; Álvarez-Ramis and Doubinger, 1994; Álvarez-Ramis *et al.*, 1997). The palynological analysis (Álvarez-Ramis *et al.*, 1989, 1994) attributed the age of Cerro de la Mesa to the Campanian–Maastrichtian interval: the most frequent pollens were from primitive Angiosperms (*Normapollens*), mainly *Interporopollenites*, *Papillopollis* and *Triatriopollenites*, and a lower proportion of *Vacuopollis*, *Complexiopollis* and *Atlantopollis*. There were *ca.* 25% pollens from Gymnosperms and *ca.* 9% of spores from vascular Cryptogams. Additional amounts (2–8%) of microrests from the Protista, Fungi and Animalia Kingdoms, with a large proportion of cysts from Dinoflagellates were observed. The dominance of Angiosperms as regards Conifers points to a warm humid climate in Cerro de la Mesa palaeoecosystem during the Upper Cretaceous. Its coastal location is suggested by the presence of internal lodges of *Foraminifera*,

dynocysts and euhyaline elements such as *Botryococacceae*.

One of the three samples used in the present study was taken from the 4th member—basically consisting of sandy limestones—and from the lowest level of lignites (sample L). Another sample of calcareous marls (sample CM) was taken from the 6th member. Just below, the layer of compacted marls included mummified branches of the Cheirolepidiaceae *Frenelopsis oligostomata* (Romariz) Alvin (sample F) (Álvarez-Ramis, 1981; Álvarez-Ramis *et al.*, 1982). Histological features and chemical characteristics of the latter sample were reported elsewhere (Almendros *et al.*, 1982, 1985).

Chemical analyses

For pyrolytic characterization, the organic matter in the sediment was isolated by physical methods and subjected to mild demineralizing treatments. In the case of the *Frenelopsis* remains, the branches were isolated from the calcareous rock, grounded in an agate mortar, decarbonated with 0.5 mol dm⁻³ HCl, and finally washed with deionized water on a sintered glass filter under reduced pressure. The same was done with the lignite fragments (L). In the case of sample CM and in order to concentrate the organic matter, the ground and decarbonated material was separated by flotation in an extraction funnel with a CHBr₃–CH₃CH₂OH mixture adjusted to a density of 1.9.

Analytical pyrolysis was carried out at 500°C at a rate of 20°C ms⁻¹ in a CDS Pyroprobe 190 unit equipped with a Pt-coil heater. Samples of 3 mg were pyrolyzed in a quartz tube in a He atmosphere and the volatile products were condensed in a cold trap submerged in liquid N₂. The products were recovered with methylene chloride, then injected in the splitless mode in to a Hewlett–Packard 5890 gas chromatograph, coupled to a 5791 A mass spectrometer. An OV-1 cross-linked capillary column was used (20 m, 0.2 mm internal diameter, 0.2 µm film thickness).

The injector temperature was set to 270°C and the oven temperature was programmed from 40°C to 100°C (rate = 32°C min⁻¹), then raised to 270°C at 6°C min⁻¹.

For pyrolysis–alkylation, samples of 4 mg were suspended in 25 µl of TMAH (25% water solution), and dried overnight in a desiccator at room temperature. The resulting product was transferred to the pyrolysis tube (Martin *et al.*, 1994, 1995a). The pyrograms obtained correspond to very complex mixtures: in many cases, two or more compounds overlapped in a single peak.

The identification was carried out using mass spectral diagnostic ions and chromatographic retention data. Total ion current profiles should not be used for quantitative determinations due to the above coelution problems: for this reason, ion pro-

files were monitored for the diagnostic ions of different aromatic and aliphatic series (e.g. phenols, naphthalenes), and the integrated peak area was used as a relative measure of compound concentration.

For aromatic compounds, the molecular ion was usually selected for the ion profile, whereas the ions at m/z 60 and m/z 83 were chosen for fatty acids and alkenes, respectively. In the case of alkanes, the ion at m/z 85 was selected instead of the more intense ions at m/z 57 or 43, due to the relatively higher abundance of the latter ions in the chromatographic background and the "hump" by cyclic compounds, mainly in sample F.

The peak area values were referred to the total ion counts in the pyrogram, obtained by integration of the whole chromatographic area (4–55 min range). The semiquantitative values obtained in this way are only an indication of the relative abundance of the compounds in each pyrogram, but are perfectly suitable to compare the relative yields of individual families of compounds in the pyrograms of the different samples, which is the main objective of the present study.

RESULTS AND DISCUSSION

Tables 1–3 show the relative abundances of the different products released by conventional pyrolysis (Fig. 1) and thermochemolysis with TMAH. Only the cyclic compounds are given in Table 1, showing the different patterns in terms of the degradation method. Table 2 shows the cumulative values for the main groups of molecules, including the alkyl series. Thermochemolysis with TMAH released a series of compounds, mainly in the form of methyl esters, not previously found after conventional pyrolysis, and listed independently in Table 3, Fig. 2.

Conventional pyrolysis

The most frequent pyrolysis products corresponded to series of alkyl-substituted polycyclic aromatic hydrocarbons (naphthalenes, anthracenes, phenanthrenes and pyrenes), in some cases including hydroaromatic rings (tetralins, fluorenes and indenenes) or heterocyclic rings (dibenzofuranes) and their OH-substituted derivatives (phenols, benzene-diols, naphthols and biphenols).

Sample L yielded mainly OH-substituted mono- and polycyclic compounds: aliphatic molecules were lacking, and the cresols produced the major chromatographic peaks. The high amount of benzene-diols is interpreted as characteristic of an intermediate stage of plant lignin coalification. The lignins are progressively demethoxylated and converted into polyphenol macromolecules (Hatcher *et al.*, 1988). However, small amounts of vanillyl and syringyl-type ketones similar to those produced by

pyrolysis of lignins were still present. This seems to point to the preservation of woody plant remains altered by moderate maturation processes. In particular, some tendency to greater relative abundance of syringyl-type ketones in sample CM may point to the dominance of angiosperm plants in this depositional environment. Characteristic of sample L was the presence of a molecular sulphur peak, with the typical mass spectral pattern of S_2 , S_4 and S_6 fragments. Nevertheless, no sulphur-containing organic compound other than dimethyltrisulphide was found in the pyrogram.

The sample CM yielded a small amount of oxygen-containing products (Tables 1 and 2) and no methoxyl-containing aromatic ketones. The pyrogram consists primarily of alkyl homologs of polycyclic aromatic hydrocarbons (1 to 4 benzene rings), C_3 naphthalenes being the most abundant aromatic products (Table 1). In particular, C_3 naphthalenes have been considered structures preexistent in geological samples, where they may have a varied origin, such as Angiosperm triterpenoids. The abundance of trimethylnaphthalenes is often reported in sediments derived from higher plants (Püttmann and Villar, 1987; Strachan *et al.*, 1988). On the other hand, some studies have suggested that polyaromatic structures present in the pyrolysates (alkylphenanthrenes and alkylanthracenes) are directly released by thermal evaporation from an organic matrix, possibly originating from woody plant tissues modified by paleofires (which conform to the non- and mono-alkyl substitutions found mainly in the 4-ring compounds) as well as by diagenetic aromatization of biogenic compounds from higher plants (Hartgers *et al.*, 1994). In addition to these compounds, sample CM also yielded large amounts of short-chain ($<C_{20}$) alkanes and olefins, with no odd-to-even C-number preference. This suggests a significant input of aliphatic (microbial and/or algal) biomass and/or an early diagenesis in the aquatic environment, inferred from the palaeobotanical data.

Finally, the pyrolysis patterns from the *Frenelopsis* remains (F) had a pronounced "hump" presumably consisting of random fragments from branched and/or cyclic aliphatic structures. The compound assemblages could be interpreted as the result of intense maturation of aromatic and recalcitrant lipid biomacromolecules (Almendros *et al.*, 1982, 1985; Álvarez-Ramis *et al.*, 1984): there was a large variety of aromatic and hydroaromatic oxygen-containing compounds, and additional yields of ketones, alkanes, and olefins (C_{11} – C_{23} alkane series with a maximum approximately C_{17} and some preference for the odd-C number homologues, and alkenes with a parallel distribution, and no clear even-to-odd C number preference). At least of weak m/z ion traces produced by alkyl compounds (not shown) were also very complex since they over-

Table 1. Compounds obtained from Supracretaceous kerogens from Cerro de la Mesa basin after conventional pyrolysis (Py) and thermochemolysis with TMAH

#	MW	Compound	Relative amount*					
			F		L		CM	
			Py	TMAH	Py	TMAH	Py	TMAH
1	92	Methylbenzene (toluene)	0.1					
2	106	Benzaldehyde	0.1					
3	126	Dimethyltrisulphide	1.2		0.1	0.0		
3	94	Phenol	0.1	0.6	17.1	19.3	1.9	
4	116	Indene	0.2	0.2		0.1	0.8	
5	130	Methylindenes	0.0	0.5				
6	108	Methylphenols (creosols)	2.6	0.8	28.4	24.2	3.5	
7	124	Phenol, 3-methoxy (guaiacol)			0.1			
8	144	C ₂ -Indene		0.4		0.4	0.3	0.2
9	122	C ₂ -Phenols (dimethylphenols + ethylphenol)	2.8	0.3	9.5	11.8	3.3	0.3
10	128	Naphthalene	0.2	0.6	0.1	0.6		0.1
11	136	C ₃ -Phenols	1.7	0.3	3.6	9.5	1.3	0.1
12	110	1,2-Dihydroxybenzene (benzenediols)			4.3			
13	158	C ₃ -Indenes		0.3		0.1	0.6	0.1
14	136	Ethanone, 1-(2-hydroxyphenyl)-		1.0	2.4			
15	134	Phenol, 2-(2-propenyl)-			2.0			
16	172	C ₄ -Indenes					0.1	
17	132	Naphthalene, 1,2,3,4-tetrahydro- (tetralin)	0.2	0.2	0.2		0.4	0.1
18	142	Methylnaphthalenes	0.3	1.0	0.3	1.1	2.2	1.3
19	150	4-Vinylguaiacol	0.1		0.2	3.1		
20	150	C ₄ -Phenols	0.7	0.1	1.6	1.7	0.2	
21	124	Methylbenzenediols			1.4			
22	148	1-Naphthol, 5,6,7,8-tetrahydro-	0.1		0.2			
23	146	Methyl(1,2,3,4-tetrahydronaphthalenes) (methyltetralins)	0.3		0.3	0.3	0.1	
24	138	C ₂ -Benzenediols (C ₁ -benzenediols)		0.2	0.2			
25	164	C ₅ -Phenols	0.3		0.3	0.2		
26	162	4-Methylcinnamic acid	0.1			1.9		
27	162	3-Methylcinnamic acid	0.1					
28	148	1-(2,4-Dimethylphenyl)ethanones	0.1		0.6			
29	156	C ₂ -Naphthalenes	1.4	1.3	0.5	0.9	8.0	1.3
30	220	Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)	0.2					
31	180	1-(2-Hydroxy-5-methoxy-4-methylphenyl)ethanone	0.4					
32	150	1-(4-methoxyphenyl)ethanone	0.2	0.2	0.6			
33	170	C ₃ -Naphthalenes	1.8	1.0	0.5	0.2	8.7	1.0
34	160	C ₂ -(1,2,3,4-Tetrahydronaphthalenes) (C ₂ -tetralins)	0.2	0.4	0.5	0.0	0.4	0.3
35	168	Dibenzofuran			0.2		1.3	0.2
36	144	Naphthol	0.1	0.1	0.7			
37	150	1-(4-Hydroxyphenyl)propanone			0.5			
38	166	Fluorene	0.5	0.2	0.3	0.5	1.2	0.3
39	174	C ₃ -Tetrahydronaphthalenes (C ₃ -tetralins)	0.3	0.2	0.3	0.5	0.7	0.1
40	180	Methylfluorenes	1.0	0.2	0.3	0.4	1.4	0.2
41	184	C ₄ -Naphthalenes	1.1	0.2	0.2	0.2	7.2	0.7
42	158	Methylnaphthol	1.1	0.2	1.6	0.8		
43	182	Methyldibenzofuran	0.1		0.2	0.4	0.7	0.1
44	182	Xanthene			0.2	0.2		0.1
45	170	1,1'-Biphenyl-4-ol			2.1	0.6		
46	172	C ₂ -Naphthol	0.6	0.4	0.3	1.4		
47	188	C ₄ -(1,2,3,4-Tetrahydronaphthalenes) (C ₄ -tetralins)			0.1		0.2	0.1
48	184	Methylbiphenylols			2.1			
49	196	1-(4-Hydroxy-3,5-dimethoxyphenyl)ethanone (acetosyringone)	0.1		0.5		0.8	
50	178	Anthracene	0.3	0.2	0.2	0.3	1.8	0.4
51	178	Phenanthrene	0.3	0.2	0.1	0.3	0.7	0.1
52	194	C ₂ -Fluorenes	0.3		0.2	0.1	3.5	0.6
53	186	C ₃ -Naphthols		0.2	0.5	0.8		
54	198	C ₅ -Naphthalenes	0.6		0.3		2.3	0.6
55	196	C ₂ -Dibenzofurans			0.1		0.3	0.6
57	192	Methyl TAH	0.8	0.5	0.3	0.6	3.2	0.6
58	202	Pyrene					0.6	0.1
58	182	Hydroxyfluorene			0.9			
59	208	C ₃ -Fluorenes	0.1		0.2			
60	216	Methylpyrene					0.7	0.2
61	210	Propiosyringone			0.6			
62	210	C ₃ -Benzofurans			0.6			
63	200	(Hydroxyphenyl)methylphenol			0.9			
64	206	C ₂ -TAH	0.7	0.2	0.2	0.3	3.8	0.1
65	256	S ₈			0.2			
66	196	Methoxyfluorene	0.1		0.3	0.3		
67	230	C ₂ -Pyrenes					0.3	0.2
68	214	Bis(hydroxyphenyl)-methanone			0.2			
69	244	C ₃ -Pyrenes					0.1	0.1
70	220	C ₃ -TAH	0.3	0.1	0.1	0.1	2.6	0.3
71	224	C ₄ -Dibenzofurans			0.1			0.1
72	234	C ₄ -TAH	0.1				1.2	0.1

*Semiquantitative data obtained from the ratio between peak areas in the ion chromatograms corresponding to the traces indicated in column "MW" and the total ion count in the chromatogram $\times 1000$. The figures (=relative amounts of each compound in the different samples) can be compared directly from column to column, but not vertically, due to the different response factors of the compounds in the MS detector. TAH: C₁₄-tricyclic aromatic hydrocarbons (phenanthrenes + anthracenes). Compounds representing less than 0.04% of the total ion counts are shown as blank cells. Compound numbers refer to Fig. 1.

Table 2. Relative yields* of the main groups of pyrolysis products from Supracretacic kerogens after conventional pyrolysis and thermochemolysis with TMAH

Compound	Relative amount*					
	F		L		CM	
	Py	TMAH	Py	TMAH	Py	TMAH
<i>n</i> -Alkanes	0.9	0.8	0.0	0.0	6.8	2.6
<i>n</i> -Alkenes	0.9	1.0	0.0	0.0	2.0	1.2
<i>n</i> -Fatty acids	0.0	0.0	0.0	0.0	0.0	0.0
Phenols	8.2	2.3	60.4	66.7	10.2	0.7
Benzenediols	0.0	0.0	5.8	0.0	0.0	0.0
Naphthalenes	5.4	4.1	1.9	3.0	28.5	4.9
Naphthols	1.8	0.8	3.1	3.0	0.0	0.0
Fluorenes	1.9	0.4	0.9	1.0	6.1	1.1
Biphenylols	0.0	0.0	4.2	0.6	0.0	0.0
Dibenzofurans + xanthenes	0.1	0.0	1.4	0.6	2.2	0.9
Naphthalenes + phenanthrenes	2.5	1.1	0.8	1.5	13.3	2.1
Pyrenes	0.0	0.0	0.0	0.0	1.7	0.5
Tetralins	1.0	0.7	1.3	1.0	1.8	0.5
Indenes	0.2	1.4	0.0	0.9	1.7	0.3

*Semiquantitative data obtained from the ratio between peak areas in the ion chromatograms corresponding to the traces indicated in column "MW" (Table 1) and the total ion count in the chromatogram $\times 1000$.

lapped with the series alkylaromatic compounds with which they had ions in common.

Thermochemolysis with TMAH

As expected, the differences between the pyrolytic patterns in the presence or not of TMAH depended on the samples that were compared. Mainly in samples F and CM, the release after the treatment

with the alkylating reagent, of additional thermochemolysis products caused a decrease in the relative yield of most groups of compounds (Table 3).

It is worthwhile indicating that some of the compound series (e.g. phenols, naphthols...) are not fully methylated after the TMAH treatment (i.e., the number of peaks in the pyrogram increased considerably because small peaks of the original

Table 3. Compounds exclusively obtained by thermochemolysis with TMAH of Supracretaceous kerogens

#	MW	Compound	Relative amount*		
			F	L	CM
1	122	Methoxy methylbenzenes	1.1	36.3	0.1
2	136	Benzenecarboxylic acid, methyl ester	0.1		0.2
3	136	C ₂ -Methoxybenzenes	0.6	3.1	
4	138	3-Methoxy-4-methylphenol (4-methylguaiacol)	0.2		1.4
5	150	C ₃ -Methoxybenzenes	0.4		0.2
6	134	Benzene, 1-ethenyl-4-methoxy-		0.9	
7	166	Methoxy benzenecarboxylic acid methyl ester	0.3	2.2	0.6
8	148	Benzene, 1-methoxy-4-(2-propenyl)-		7.1	
9	194	Benzene dicarboxylic acids, dimethyl esters	0.6	0.1	9.6
10	136	Benzaldehyde, 3-methoxy		7.1	
11	194	4-Methoxybenzenepropanoic acid, methyl ester	0.1		
12	196	Dimethoxybenzenecarboxylic acids, methyl esters	0.3		0.4
13	224	Methoxybenzenedicarboxylic acids, dimethyl esters	0.1	69.1	0.1
14	226	Trimethoxybenzenecarboxylic acid, methyl ester			0.2
15	172	2-Methoxy-3-methylnaphthalene		0.7	
16	252	Benzene tricarboxylic acids, trimethyl esters	0.4	0.6	
17	256	Tetramethoxybenzenecarboxylic acid, methyl ester	0.1		0.8
18	254	Dimethoxy benzenedicarboxylic acids, dimethyl esters	0.3	0.5	
19	184	1-1'-Biphenyl, 4-methoxy		2.0	
20	198	Methylbenzotriophene		0.4	
21	198	Benzene, 1-methyl-2-(4-methoxyphenoxy)		0.5	
22	212	Dimethyl dibenzotriophene		0.7	
23	228	Benzene, 1-methoxy-2-[(4-methoxyphenyl)methyl]		0.3	
24	242	Benzoic acid, 2-(2-methylphenoxy)-, methyl ester		0.4	
25	242	Benzoic acid, 2-(4-methylphenoxy)-, methyl ester		1.1	
Cumulative values					
Total <i>n</i> -fatty acid methyl esters			15.6	0.3	41.0
Total unsaturated fatty acid methyl esters			1.0	0.1	14.4
Total branched fatty acid methyl esters			1.0	0.1	6.9
Total fatty alcohols					2.3
Total benzenecarboxylic acids, methyl esters			1.3	0.7	9.8
Total phenolic acids, methyl esters			1.1	71.7	2.0
Total methoxybenzenes			2.1	39.4	0.3

*Semiquantitative data obtained from the ratio between peak areas in the ion chromatograms corresponding to the traces indicated in the column "MW" and the total ion count in the chromatogram $\times 1000$. The data were obtained by adding the peak areas for the different positional isomers. Compounds representing less than 0.04% of the total ion counts are shown as blank cells. Compound numbers refer to Fig. 3.

Fig. 1. Chromatographic separation (total ion counts) of pyrolysis products from different kerogen types from Cretaceous levels in Cerro de la Mesa (Guadalupe de la Sierra, Madrid). The chemical structure of the major pyrolysis compounds are indicated on the peaks. Homologues labelled by C number refer to alkanes. Numerals refer to Table 1.

Fig. 2. Chromatographic separation (total ion counts) of products obtained from Cretaceous kerogens (Fig. 1) after pyrolysis in the presence of tetramethylammonium hydroxide. The chemical structure of the major pyrolysis compounds are indicated on the peaks. Homologues labelled by C number refer to fatty acid methyl esters. Numerals refer to Table 3.

non-derivatized compounds frequently coexist with their corresponding methyl esters or methyl ethers). This fact (Tables 1 and 3) was also noted by Challinor (1995) and attributed to steric factors influencing the reaction of TMAH with the OH-phenolic groups but, to some extent, may also be due to competition between alkylation and thermoevaporization processes (Kralert *et al.*, 1995).

A noteworthy effect of the TMAH treatment was the release of an additional series of fatty acid methyl esters (even in sample L in which no polymethylene compound was detected after conventional pyrolysis). Sample F, which had previously yielded some quantity of alkyl products, released a fraction of fatty acid methyl esters more abundant than the original amount of polymethylene compounds. This may be a direct consequence of the fact that pyrolysis in the presence of TMAH produced not only the methylation of volatile pyrolysis products, but also chemical bond disruption especially transesterification reactions (de Leeuw and Baas, 1993). The series of fatty acid methyl esters (C_8 – C_{22}) had a clear biogenic signature: only two major peaks corresponding to the C_{16} and C_{18} methyl esters, and a large even-to-odd preference. The peaks were preceded by a small but conspicuous series of unsaturated homologues, the origin of which might be explained by thermally-induced processes, such as the six-membered ring rearrangement reactions in fatty polyesters, postulated for cutin preparations subjected to pyrolysis (Tegelaar *et al.*, 1989b) as well as by isomerization reactions of unsaturated fatty acids in the presence of an excess of TMAH reagent (Challinor, 1991).

This TMAH effect of "aliphatic enhancement" was more accentuated in sample CM, which yielded the greatest fraction of fatty acid methyl esters, including saturated, unsaturated and branched homologues, as well as a conspicuous series of primary alcohols (C_{18} – C_{25}) with a clear even-to-odd C preference and a maximum at C_{22} (shown in Fig. 2 as unlabeled peaks eluting after 40 min). This release of long-chain alcohols in addition to fatty acid methyl esters has also been reported by de Leeuw and Baas (1993) as a result of pyrolysis of wax esters in the presence of TMAH, and by Kralert *et al.* (1995) from a solvent-extracted brown coal of a comparatively high polymethylene character. The fatty acid methyl ester series in sample CM (C_9 – C_{24}) had a bell-shaped distribution and a striking even-to-odd carbon preference, with a maximum at C_{16} : the C_{18} and C_{14} peaks dominated in the m/z 74 ion trace. As in sample F, there were parallel series, including unsaturated homologues and minor peaks of branched acids, mainly C_{15} and C_{17} , which possibly correspond to *iso*- and *anteiso*-isomers. At least the major aliphatic compounds strongly suggest the remains of a very stable polymethylene network derived from altered plant bio-

polyester. In this sample (irrespective the pyrolytic procedure) the alkanes and alkenes ranged from C_{11} to C_{13} , with a maximum *ca.* C_{22} , and a clear even-to-odd C-number preference in the former case.

Table 3 shows another of the pyrolysis products obtained after the TMAH treatment, not found after conventional pyrolysis. In addition to the expected presence of methoxyalkylbenzenes (i.e., phenols converted into the corresponding methyl-ethers), there were additional yields of methyl esters of benzenecarboxylic and phenolic acids. This may indicate that such structures may preexist in oxidized domains of the kerogens (i.e., humic-like), and could not be detected by conventional pyrolysis due to factors such as thermal decarboxylation. A similar result was obtained by Hatcher and Clifford (1994) and Martin *et al.* (1994) after "in situ pyrolysis methylation" of soil humic acids which, in fact, is known to release benzenecarboxylic acids by mild transesterifying treatments, such as the BF_3 –MeOH complex (Almendros and Sanz, 1989). The production of methyl benzenecarboxylates after thermochemolysis has also been described in lignin preparations (which do not yield the corresponding acids after conventional pyrolysis) and has also been interpreted in the sense that such units preexist in lignin structure, but their relative amount was underestimated by thermal decarboxylation (Martin *et al.*, 1995b). Challinor (1995) attributed the presence of lignin-derived acids after thermochemolysis to a natural process as the heartwood ages. In particular, the highest boiling point volatile products (Table 3) structurally resembled lignin dimer units: sample L yielded characteristic hydroxy- and methoxyphenyl ethanones and propanones which are major volatile products from plant biomass combustion.

The fact that both benzenecarboxylic and phenolic acids were not found in non-methylated forms in conventional pyrolysis is consistent with the above-indicated thermal defunctionalization to yield other structures. The situation is different with compounds like phenols that were obtained by pyrolysis, both in the presence or not of alkylating reagents (Tables 1 and 2). In this study, partial methylation may be pointing to successive and/or independent competitive reactions depending on temperature, contact time of the TMAH and accessibility of the bonds to cleave. Such interpretation is in agreement with recent results by McKinney *et al.* (1995) who indicated that both transesterification (base-catalyzed hydrolysis) and cleavage of ether bonds are TMAH-induced reactions occurring at sub-pyrolysis temperatures, yielding a series of degradation products that, in the case of lignins, are similar to those obtained by classical alkaline CuO oxidation (Hatcher *et al.*, 1995). In particular, the acid/aldehyde ratios from the thermochemolysis

results (Table 3) points to a lower degree of oxidation and/or alteration of the lignin-derived matrix in the case of sample L.

Multivariate data treatment

Correspondence analysis (Nakache and Lebart, 1970) was applied in order to simplify the interpretation of all the pyrolysis results. In addition to the above-indicated "aliphatic enhancement" which characterized the TMAH treatment and absorbs most of the total inertia in any multivariate data treatment, there was an additional source of variance due to the different amounts of the molecules simultaneously present in the pyrolyzates obtained by both methods. Figure 3 shows the arrangement obtained for the samples (the different forms of organic matter subjected to pyrolysis with or without TMAH treatment) and the variables (the 27 most frequent pyrolysis compounds simultaneously present in the pyrograms obtained with the two methods). The program was made to extract two synthetic axes (embracing most of the information, respectively, 79% and 11% of the total inertia of the original data matrix) in order to present a two-dimensional representation where the lineal distances in the two-dimensional space defined by the axes indicate the similarity between the samples, in terms of the relative abundance of the different pyrolysis compounds. The coordinates of the latter suggest clusters for these descriptors in the vicinity

of the samples for which they are more diagnostic. Since the new axes obtained after correspondence analysis were variables not linearly correlated between them (as opposed to the original variables), they included information of a different kind (Sneath and Sokal, 1973): axis x is useful to define the differences between the three types of fossil organic matter, whereas axis y leads to the differentiation as regards to the effect of the TMAH treatment.

In this plot, it is clear that the additional effect of thermochemolysis was small in sample L, where the large yields of phenols was the most diagnostic feature. On the other side, sample CM is characterized by the dominance of polycyclic aromatic hydrocarbons, whereas sample F shows an intermediate composition, with major yields of pyrolysis products consisting of hydroaromatic rings, mainly fluorenes and tetralins.

As expected, the TMAH-induced effects on the pyrolytic patterns were largely dependent on the type of sample analyzed: in sample L, the small differences concerned some preference for the odd-C alkylphenols after the TMAH treatment. In sample F, there were higher amounts of short-chain naphthalenes. This was also the case of sample CM, where polycyclic aromatic compounds dominate vs biphenyls and dibenzofurans after the TMAH treatment.

Fig. 3. Factorial correspondence analysis showing the main sample-dependent differences between the aromatic assemblages obtained by conventional pyrolysis (circles) and thermochemolysis with TMAH (squares) (vertical axis) and between different kerogen types (horizontal axis). CM = kerogen in carbonaceous marls, L = lignitiferous layer, F = remains of the Cheirelepidiaceae *Frenelopsis oligostomata* (Gymnosperm).

The results obtained suggest that thermochemolysis with TMAH caused the release of additional compounds to those produced by conventional pyrolysis. In this study, the effects of TMAH on fossil insoluble organic matter were found to be: (i) largely sample-dependent, (ii) more or less partial as regards alkylation yield, and (iii) responsible for a more in-depth degradation through the previous chemolysis of structural domains the cleavage of which does probably not require the temperature of conventional pyrolysis.

The lack of fatty acids in conventional pyrolysis and the release of the corresponding methyl esters after TMAH treatment, also observed by Hatcher and Clifford (1994), may be interpreted by pyrolytic decarboxylation of fatty acids when esterified or entrapped in macromolecular networks, to yield alkenes or alkanes. In the present study the effect is more likely due to TMAH-induced transesterification reactions removing tightly bonded acids in e.g. sterically-protected ester forms. In fact, and since esters are expected to be saponified in the early diagenetic stages, their presence in ancient geological samples probably reflect recalcitrant association patterns between plant biomacromolecules leading to encapsulation of intramolecular bonds, a situation that has been pointed out to probably concur in *Agave* cuticle (McKinney *et al.*, 1996). In the present study, with *Frenelopsis* remains consisting mainly of well-preserved cuticular material (Almendros *et al.*, 1982), the microscopical observation of the other two samples also indicates cuticular fragments presumably including residual biopolyester moieties.

Also interesting after the TMAH treatment is the release of methyl esters of benzenecarboxylic and phenolic acids that are decarboxylated at elevated temperatures occurring during pyrolysis conditions (Martin *et al.*, 1994) and of volatile methoxylated (biphenyl or phenyl-phenoxy structures) resembling dilignol units of the lignin macromolecule.

Associate Editor—P. G. Hatcher

Acknowledgements—This research was funded by the Spanish CICYT under project AMB96-0384 and by the DGICYT under project PB92-0101.

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Appraisal of pyrolytic techniques on different forms of organic matter from a Cretaceous basement in Central Spain

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Abstract—Pyrolytic techniques were used to characterize three different forms of fossil organic matter in Cerro de la Mesa (an important Cretaceous paleobotanic basement in Central Spain): two kerogens isolated from carbonaceous marls, and from lignitiferous layers, and well-preserved remains of the fossil Gymnosperm *Frenelopsis oligostomata*. By conventional flash pyrolysis the *Frenelopsis* remains released mainly alkyl-substituted phenols and polyaromatic compounds, whereas the organic matter from the lignitiferous layer is dominated by phenols and that from the carbonaceous marls by polycyclic and aliphatic compounds. Pyrolysis-thermochemolysis alkylation in the presence of tetramethylammonium hydroxide (TMAH) allowed the detection of additional diagnostic compounds, such as series of methylated fatty acids, benzenecarboxylic and phenolic acids, which revealed further differences between the three materials studied. The chemical characterization of the organic matter in addition to the micropaleontological study suggests that the *Frenelopsis* remains consist mainly of heavily altered lignin and cuticular lipid biomacromolecules, whereas the materials from the lignitiferous layers and the carbonaceous marls correspond to intermediate coalification stages of woody plants, the latter showing the greatest degree of selective preservation of aliphatic structures. The comparison of the above results with those obtained by thermochemolysis suggests that the latter technique produces independent and complementary reactions to conventional pyrolysis, providing additional information to an extent which depends mainly on the polyalkyl and oxidized character of the sample. © 1998 Elsevier Science Ltd. All rights reserved

Key words—Cretaceous palaeoflora, pyrolysis, thermochemolysis, kerogen, *Frenelopsis*, tetramethylammonium hydroxide

INTRODUCTION

The Upper Cretaceous basement in Cerro de la Mesa (Madrid) includes a large variety of palaeobotanical samples, consisting of mega- and microrests (palynomorphs) (Álvarez-Ramis, 1981; Álvarez-Ramis and Fernández Marrón, 1994; Álvarez-Ramis *et al.*, in press). One of the most interesting stratigraphic series as regards the presence of organic remains is found in the gray marls and in the lignitiferous levels, which have never been characterized from a geochemical viewpoint.

Analytical pyrolysis is a rapid and routine analytical technique. It has evident advantages in the case of insoluble macromolecular materials, such as kerogens, coals and humic substances (van de Meent *et al.*, 1980; Hatcher *et al.*, 1988; Tegelaar *et al.*, 1989a; van Aarsen *et al.*, 1991; Christiansen *et al.*, 1993; Almendros *et al.*, 1993; Martín *et al.*,

1994). The alternative use of thermochemolysis induced by alkylating reagents (formerly referred to as “simultaneous pyrolysis methylation”) has led to additional improvements in the identification of the constituents of complex materials (Challinor, 1991; Hatcher *et al.*, 1995; McKinney *et al.*, 1995; Kralert *et al.*, 1995; del Rio *et al.*, 1996). However, the molecular characterization of the different forms of fossil organic matter has a series of well-known limitations since most classical chemolytic and pyrolytic techniques may exert selective effects depending on the chemical composition of these materials (Rullkötter and Michaelis, 1990). The very different behavior of lignin-type structures as regards to those derived from carbohydrate has been described extensively (Ralph and Hatfield, 1991; Almendros *et al.*, 1997), as have the non-diagnostic compound patterns yielded by most types of macromolecular polymethylene structures (Boon, 1989).

In this study, widely different types of organic matter accumulated in the Supracretaceous base-