Experimental Impact Shock Chemistry on Planetary Icy Satellites

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ABSTRACT

We present new experimental results on impact shock chemistry into icy satellites of the outer planets. Icy mixtures of pure water ice with CO_2 , Na_2CO_3 , CH_3OH and $\text{CH}_3\text{OH}/(\text{NH}_4)_2\text{SO}_4$ at 77K were ablated with a powerful pulsed laser - a new technique used to simulate shock processes which can occur during impacts. New products were identified by GC-MS and FTIR analyses after laser ablation. Our results show that hydrogen peroxide is formed in irradiated H_2O / CO_2 ices with a final concentration of 0.23%. CO and CH_3OH were also detected as main products. The laser ablation of frozen H_2O / Na_2CO_3 generates only CO and CO_2 as destruction products from the salt. Pulsed irradiation of water ice containing methanol leads also to the formation of CO and CO_2 , generates methane and more complex molecules containing carbonyl groups like acetaldehyde, acetone, methyl formate, and a di-ether, dimethyl formal. The last three compounds are also produced when adding ammonium sulfate to H_2O / CH_3OH ice, but acetone is more abundant. The formation of two hydrocarbons, CH_4 and C_2H_6 is observed as well as the production of three nitrogen compounds, nitrous oxide, hydrogen cyanide and acetonitrile.

Key Words: Ices; Impact processes; Prebiotic chemistry

1. Introduction

Ice is largely widespread in the Solar System, being present on planetary surfaces (e.g. Earth, Mars), on the surfaces of the planetary satellites (e.g. most of the moons of the giant planets) and on small bodies such as comets, and Edgeworth-Kuiper belt objects. Icy moons of the outer Solar System reveal a variety of ice compositions as summarized in the first part below, show evidence on their surfaces of the action of many endogenic and exogenic processes, and therefore are particularly attractive planetary objects for future space missions.

Ices compositions of outer planet icy satellites

Spectroscopic observations of most of the outer planet satellites show evidence of abundant H₂O ice on the Galilean satellites (Io, Europa, Ganymede and Callisto), Saturn's large satellites (Titan, Rhea, Iapetus, Dione, Tethys, Enceladus, Mimas, Hyperion and Phoebe), those of Uranus (Titania, Oberon, Umbriel, Ariel and Miranda) and the Pluto's moon Charon (Cruikshank et al., 2005, 1998; Griffith et al., 2003; Owen et al., 1999).

O₂ has also been spectroscopically detected in the surface of Ganymede (Calvin and Spencer, 1997) and O₃ in the spectra of Ganymede (Noll et al., 1996), Dione and

Rhea (Noll et al., 1997a).

Frozen carbon dioxide has been detected on many satellites in the outer Solar System. McCord et al. (1997, 1998) detected frozen CO₂ on the surfaces of the Jovian satellites Europa, Ganymede, and Callisto using the reflectance spectra returned by the Galileo Near Infrared Mapping Spectrometer (NIMS). Grundy et al. (2003) detected it on the surface of Ariel and Cruikshank et al. (1993) on the surface of Triton by spectral observations from Earth-based facilities. Buratti et al. (2005) and Clark et al. (2005) have observed frozen CO₂ using the VIMS instrument aboard the Cassini spacecraft on Iapetus and Phoebe respectively. And Grundy et al. (2006) also observed frozen CO₂ from ground-based FTIR/SpeX analyses on the surfaces of Umbriel and Titania.

Another oxidant, H₂O₂, has been spectroscopically observed in the Europa NIMS spectra with an estimated concentration of $0.13 \pm 0.07\%$ (Carlson et al., 1999b).

The icy surfaces of the outer planet satellites may also contain other non-water ice constituents composed of carbon-, sulfur-, and nitrogen- bearing molecules including some hydrated salts and also may incorporate silicates, as described below. The exact chemical composition of some of these components is still under debate because of the uncertainties in the band assignments of the spectra.

Sulfur in the form of solid SO₂ has been directly evidenced on Io from strong absorption bands in the mid-IR and near-UV reflectance spectrum (see review from Nash and Betts, 1998) and as well on Europa, Callisto and Ganymede (Domingue et al., 1998; McCord et al., 1998; Noll et al., 1997b, 1995) from UV spectra. More generally,

sulfur species have been indicated as good candidates for the surface material of icy satellites (McCord et al., 1997). McEwen (1986) show that longitudinal distributions in reflectance in the visible and near-UV are consistent with the presence of sulfur-rich species as components in the ice of Europa's surface. H_2SO_4 matches also some absorptions features in the NIMS reflectance spectra for Europa (Carlson et al., 1999a) and SH-bearing molecules in the spectra of Ganymede and Callisto (McCord et al., 1997).

From a cosmic abundance point of view, N atoms should be also present on icy satellites in the outer Solar System (Lewis, 1971). Cosmochemical models of the solar nebula suggest that NH_3 would be among the most abundant and refractory substances to condense, preferentially in the dihydrate form, after water ice in a solar nebula cooled in thermodynamic equilibrium, and therefore would be stable and form significant part of some of the outer satellites (Pollack et al., 1976; Lewis, 1972). Alternatively, ammonia monohydrate or dihydrate could be brought towards the surface by complex geology activity like cryovolcanism (Kragel, 1995; Stevenson, 1982; Lewis, 1971). There is little or no spectroscopic evidence of ammonia in the icy satellites of the outer planets. Only few spectral interpretations (Cruikshank et al., 2005; Emery et al., 2005) have correlated some features with possibly ammonia as a trace constituent in water ice. Other N-bearing candidates for icy satellites, particularly for Europa, Ganymede, Callisto, Titan and Phoebe, are components with $\text{C}\equiv\text{N}$ structural group (McCord et al., 1997).

Besides CO₂ and C≡N group, carbon on the icy surface of the outer Solar System satellites may be present as organic material containing hydrocarbons. For example, it is proposed that they may have accumulated on the surfaces of Europa, Callisto and Ganymede, from asteroids or cometary impacts (Pierazzo and Chyba, 2002; McCord et al., 1997). For these Galilean satellites, no specific organic molecules have been precisely detected but CH- components have been indicated as possible candidates in their spectra (McCord et al., 1997). Organic material is also proposed as plausible constituents (ranging from nitriles to complex tholins) in water ice of Saturn's icy moons, i.e. Titan, Enceladus, Dione, Rhea, Hyperion, Iapetus, Phoebe (McCord et al., 2006; Ostro et al., 2006), and in two Uranian satellites, Titania and Oberon (Grundy et al., 2006; Roush et al., 1998). Triton is the only case where frozen organic material in the form of methane frost has been spectroscopically observed (Cruikshank and Apt, 1984).

Models of the evolution of the Galilean satellites and their possible oceans predict that salts may be also important constituents (Kargel et al., 2000; Kargel, 1991). On the surface of icy moons, such material may exist as hydrates or frozen brines (Kargel, 1991). The analysis of reflectance spectra from the Galileo mission near infrared mapping spectrometer (NIMS) shows evidence of hydrated salt minerals on Europa's surface and Epsomite (MgSO₄•7H₂O), hexahydrite (MgSO₄•6H₂O) and natron (Na₂CO₃•10H₂O), exhibiting severe distorted water bands, provide the closest match to Europa spectra according to McCord et al. (1999, 1998).

Silicates and/or hydroxylated silicates could also be constituents included in the water ice of some Saturn's icy satellites (Ostro et al., 2006) and Uranian satellites like Miranda (Bauer et al., 2002). Also for the three Galilean satellites, Europa, Ganymede and Callisto, the absorption feature at visible wavelengths in their spectra that is not attributable to water ice has been proposed, among different candidates, to be possibly due to silicate minerals and iron-bearing minerals (Clark et al., 1986; Clark, 1980), but until now no firm identification has been made.

Impacts and chemistry

A wide variety of impact craters has been observed on icy satellites of the outer Solar System (several references are listed in Dypvik et al., 2004; Melosh, 1989; Chapman and McKinnon, 1986) showing evidence for impact activity over in the past, with different degrees of intensity depending on the planetary satellites. Impact cratering is not the only outcome of an impact event. Depending on the energy density level, shattering (break down of the parent body into smaller pieces) and dispersing events (most energetic events leading to the escape of excavated fragments from the main body) can also occur (Benz and Ausphaug, 1999). Particularly for impacts on minor icy bodies such as the smaller planetary satellites, the result of an impact can also be a catastrophic disruption (Burchell et al., 2005; Arakawa et al., 2002; Benz and

Asphaug, 1999). Besides those physical phenomena, it is widely suggested that impacts may induce chemical synthesis, in the atmosphere or on the surface of the target planetary body (Managadze et al., 2003a, b; Blank et al., 2001; Chyba and Sagan, 1992; Bar-Nun et al., 1970).

In the atmosphere of planetary bodies (like the early Earth, Mars, Titan), the chemical effects of impact by extraterrestrial objects have been studied, discussed in detail, and related to atmospheric changes such as atmospheric erosion, i.e. substantial losses of the atmosphere (e.g. Chyba and Sagan, 1992; Chyba, 1990; Melosh and Vickery, 1989) but also have been associated with atmospheric shock synthesis (Oberbeck et al., 1989; McKay et al., 1989, 1988; Jones and Lewis, 1987; Prinn and Fegley, 1987; Fegley et al., 1986; Bar-Nun et al., 1970). In this perspective, impacts could have been an exogenic source of ingredients for the origin of life, and atmospheric impact shock synthesis in primitive environments could have the highest specific production efficiency compared to the other main energy sources of prebiotic organics (Chyba and Sagan, 1992). Numerical calculations have estimated that 10^{13} kg.yr⁻¹ of organic matter may have been delivered to the early Earth during the heavy bombardment before 3.8 Ga (Chyba et al., 1990).

Impacts, resulting in enormous release of energy, could be also a source of local or global endogenic chemical transformations of the surface depending on the scale of an impact (Gerasimov et al., 1998). Gerasimov and others (1998) have described them in detail as summarized next. Giant impacts of large bodies may result in a global

change of the overall chemical (and physical) situation on the planet or satellite (e.g. global melting of the planetary body, change of its elemental bulk inventory, loss of most of the primary atmosphere). Hypervelocity impacts between asteroids and/or comets also may lead to catastrophic change of the body, whereas large scaled impacts, i.e. impact of an asteroid size body (1 - 10 km in diameter) will not result in noticeable global changes in the state of the solid planetary material, but may provide a deep and long imbalance causing mass extinction and changes in sedimentary processes. Finally, high-velocity impacts of micrometeorites (size of some microns), occurring only on atmosphereless bodies provide erosion of the surface material (Gerasimov et al., 1998).

When impacting the surface, part of the kinetic energy of the impactor is imparted to the atmosphere as kinetic energy in the high-velocity ejecta plume and other part is transferred to the ground (Prinn and Fegley, 1987; Borucki et al., 2002), liberating a great deal of stress energy in the atmosphere and into the surface. The chemistry induced during the surface impact is basically triggered by this stress energy released in the form of shock vaporization of the impacting body and the solid targets generating a vapor plume, high-temperature melting and heating of the surface material (Mukhin et al., 1989). It has been suggested that post-impact shock synthesis of organics may occur (Chyba and Sagan, 1992; Freund et al., 1986). And particularly, for some icy satellites, it has been proposed that meteorite impacts could be a source for organic synthesis in ices (Borucki et al., 2002; Thompson and Sagan, 1991). Borucki et al (2002) have shown in laboratory experiments by impacting ice that the impact-

triggered release of stress energy in the ice exceeds the kinetic energy of the impacting body and thus they concluded that it could be a major source of energy driving a diverse series of chemical reactions in the fracture zone beneath the crater. Such a hypothesis has been motivated by Borucki and co-authors upon recent observations of the Jovian satellites' surface, Europa. On Europa, colored material darker than water ice has been localized at impact sites, like Tyre and Pwyll sites (Borucki et al., 2002). This material exhibits spectral commonalities such as asymmetric 1.4 and 2.0 μm infrared H_2O bands and visible coloration characterizes each site where morphologies suggest tectonic and impact disruption of largely water ice topmost crust (Fanale et al., 2000). Borucki et al. (2002) support the idea that this coloring agent in Europa's icy surface could be an indigenous complex organic material that is ionized by the energy of impacts and crustal fracture, or that it may be synthesized from the raw materials present in the target and/or impactor.

On the small inner Jovian satellites, Metis, Amalthea and Thebe, impact could possibly also affect their surfaces. Indeed, their leading sides are significantly brighter than their corresponding trailing sides by 25 to 30%. A possible mechanism for these common leading/trailing asymmetries has been proposed to be the strong effect from preferential impact of macroscopic meteoroids bombardment of the leading sides (Simonelli et al., 2000). Nonetheless, it is proposed that for other Jovian satellites like Ganymede, Callisto and Europa, energetic ions and electrons may also be effective for asymmetric observations of their surface composition (Cooper et al., 2001; Calvin and

Spencer, 1997).

The chemical modification of icy planetary surfaces in the outer solar system has been principally considered due to processing induced by UV photolysis, radiation of protons and electrons and thermal energy as volcanic hot springs, hydrothermal vents, and volcanic plumes (see multiple references cited in Schmitt et al., 1998). Nonetheless, as stated earlier, impacts could be also especially advantageous as an energy source to drive chemical reactions in surfaces. One can expect impact process onto ice as being an efficient energy for driving interesting chemistry. Impacts in ices can ensure that the frozen materials in the icy surfaces are eventually exposed, for a limited period of time, to aqueous melt in impact craters and ejecta. One can therefore imagine that the frozen materials included in the ice may undergo hydrolysis and other reactions under such conditions (Chyba and Sagan, 1992). Ice can melt and vaporize more easily than many other solids on a planetary surface. The presence of water with other materials containing carbon, nitrogen and sulfur offers a favorable initial “soup” for generating more complex organics and inorganics, and maybe essential compounds for the origin and evolution of life.

When referring to the literature, one observe that most of the experimental research applied to impacts on surfaces has been developed to study and understand the process of crater formation and the physical and geophysical characteristics of cratering by hypervelocity impacts, on rocky solids (Melosh, 1989 and many references therein), on water ice (Grey and Burchell, 2003; Burchell et al., 2001; Koschny et al., 2001;

Croft et al., 1979) and other ices (Grey and Burchell, 2004).

On the contrary, few experimental works on chemistry induced by impacts on solid surfaces, which are not related to shocks synthesis during atmospheric entry, are referred. The published experimental studies have focused mainly on two studies: (1) assessing the feasibility of the delivery of organics to the early Earth by cometary impacts, (2) studying the chemical conditions of the vapor plume of hypervelocity impacts. The reported laboratory experiments related to the studies (1) have tested the recovery of carbonaceous meteoritic samples experiencing shocks at high pressures (Peterson et al., 1997; Tingle et al., 1992), and the survivability and reactivity of prebiotic compounds (like amino acids in aqueous medium) under conditions relevant to cometary impact (for example Blank et al., 2001). Regarding the recovery of meteoritic material, there was reported little to large changes, depending on the peak pressures, in the organic constituents of meteoritic samples. The survivability experiments have shown that significant fraction of amino acids survived in all experiments and new reaction products were formed. Experimental studies type (2) have investigated the shock vaporization of terrestrial rocks and minerals, meteoritic samples and other carbonaceous material (Brinckenhoff et al. 2005; Managadze et al., 2003a, b; Kadono et al., 2002; Gerasimov et al., 1998; Dikov et al., 1994; Mukhin et al., 1989) and have reported a wide range of products formed in simulated vapor clouds.

The only laboratory works examining some chemistry by impacting ices are briefly reported as abstracts by Willis et al. (2005, 2004). They have used laser ablation

of methane-coated mineral target, and H₂O and D₂O coated copper target cooled to 77K to simulate the impact of ice particles onto the Cosmic Dust Analyzer (CDA) aboard the Cassini spacecraft. The objective of their experiments was only to calibrate the Cassini CDA instrument for ice particles as it was done previously for minerals. They have indeed done chemical analyses but their goal was not to study the chemistry occurring in planetary ices from direct meteoritic impact effect.

We note therefore a lack of information and experimental work done in laboratory on the study of the chemical synthesis conducted by impact shock on icy planetary surfaces.

Our experiments rely on a new approach to testing in the laboratory the chemistry induced on ices by micrometeorites impact shocks. We will study for different ices (1) the nature of the gas phase formed above the icy solid phase at low temperature (77K) due to simulated shocks, (2) the nature of volatiles evaporated at room temperature (293K) when the ablated ice has melt, and (3) the nature of dissolved trace volatiles in the liquid melt. Such type of studies may allow us in the future to further understand the optical features on the surfaces of icy satellites and the hydrolysis produced during liquid phase after impact melt. Our experiments are based on the pulsed laser ablation technique and GC-MS and FTIR analysis methods, as we describe in the next part.

2. Experimental Method

Impact shock in the laboratory was simulated using a powerful pulsed laser. Such a laser has been previously used to imitate impact processes providing an impact-like impulsive input of energy (Ohno et al., 2004; Managadze et al., 2003a, b; Kadono et al., 2002; Gerasimov et al., 1998). Part of these works have consisted in studying the vapor cloud generated by irradiating anhydrite, gypsum, olivine, basalt, and carbonaceous material. Recent study has measured the pressure of an impact vapor cloud (Langenhorst et al., 2003). Other workers have used such a laser for simulating micrometeorite bombardment during space weathering (Bentley et al., 2003; Sasaki et al., 2001).

Studies performed by these researchers have shown this new technique to be a good analogue of real impact events, causing heating, melting and vaporization followed by subsequent re-condensation. Shock effects in minerals during impact phenomena have been simulated with laser ablation in experimental work done by Langenhorst et al. (2003, 1999) who have concluded from a detailed and critical analysis of different methods (measuring shock pressures and surface temperatures) that the laser technique is instructive and powerful in reproducing of shock phenomena. In particular, compared to other techniques for simulating impacts (e.g. high explosive and light gas gun experiments), laser irradiation using high-power lasers in conjunction with

short wavelengths and extremely short pulse durations, in the nanoseconds range, allows the generation of the most extreme shock pressures in the laboratory, up to 75000 GPa (Cauble et al., 1993), what approaches the natural impact shock conditions. However, natural impacts generate shock waves which last distinctly longer than those in laser experiments. Also it has been shown by Kostin et al. (1997) that a laser pulse couples quite differently to the target than does a solid impactor: its energy is absorbed much more efficiently and over a shallower region.

In the laboratory, impact processes are still preferentially reproduced by small-scale hypervelocity impact experiments using single or two-stage light gas gun implying impact velocities between 1 to 8 km s⁻¹ (Croft, 1981; Burchell et al., 1998, 2001). Cratering mechanics, dynamics of ejecta and expansion of the vapor plume are the physical phenomena examined with such experimental simulations. The analysis of the chemical aspects are quite restricted because of the uncontrolled input of contaminants in the target due to the powder breech system, some metallic or polycarbonate projectiles and rifle barrel. In contrast, laser experiments are free from contamination and the additional use of a closed pre-evacuated system eliminates possible environmental contaminants. Moreover, the laser allows very rapid, repeatable experiments in a day, whereas gun experiments are more limited in time, firing at the maximum 2-4 shots per day.

Measuring the chemical effects of hypervelocity impacts (generally referred as impacts at speeds of more than 1 km s⁻¹) is challenging, especially at cometary and dust

particle velocities well above 20 km s^{-1} where impact guns cannot easily reach (Brinckenhoff et al., 2005). Pulsed laser ablation is a novel and promising experimental technique to study chemical processes in hypervelocity impacts (Brinckenhoff et al., 2005; Managadze et al., 2003a, b; Roybal et al., 1995; Mukhin et al., 1989). The correspondence of high irradiance in pulsed laser ablation ($> 1 \text{ GW cm}^{-2}$) with hypervelocity impacts up to 10^2 km s^{-1} has been confirmed recently by Kadono et al. (2002) and Sugita et al. (2003). Until now, these studies tend to demonstrate that pulsed laser ablation better simulate microgram-mass micrometeorites impacts onto atmosphere-free bodies than large impacts (Langenhorst et al., 2003; Gerasimov et al., 1998).

We used the same solid-state Q-switched Nd-YAG pulsed laser (model DCR-1A, Quanta-Ray) as used by Borucki et al. (1996) installed at NASA Ames Research Center. The pulsed laser delivers a beam at a wavelength of 1064 nm with a pulse duration of 10 ns and pulse repetition rate of 10 Hz. The absorption of the laser energy at the specimen surface produces an expanding vapor plasma above the surface, giving rise to high pressures which, in turn, drives a shock wave into the target material (Pirri, 1977). Owing to the short laser pulse of the order of nanoseconds, the shock wave generated is also extremely short lived and decays rapidly as it propagates into the sample (Langenhorst et al., 2003). In such conditions, most of laser pulse radiation is absorbed by the induced plasma (Pirri, 1977) and therefore the transmission of light

through the target material is irrelevant. We have examined in our experiments the transmitted energy through pure water ice at 1.064 μm (laser beam wavelength), during the plasma generation. For this, we made optical measurements of the incident power of the infrared laser beam and the transmitted power using optical head detector connected to an optical high-power meter. The measured transmitted energy amounted to only 10%. The laser beam was directed and focused via mirrors and lenses onto the surface of the ice which was located inside a closed Pyrex flask maintained at 77K during the entire irradiation time (see Fig. 1).

We decided to study ices of $\text{H}_2\text{O} / \text{CO}_2$ (10:1), $\text{H}_2\text{O} / \text{Na}_2\text{CO}_3$ (10:1), $\text{H}_2\text{O} / \text{CH}_3\text{OH}$ (10:1), and $\text{H}_2\text{O} / \text{CH}_3\text{OH} / (\text{NH}_4)_2\text{SO}_4$ (10:1:1). Icy samples were prepared inside the flask by freezing 30 ml aqueous solutions slowly at 77K, using a liquid nitrogen bath. Aqueous solutions were prepared by diluting in desire proportions ultra-pure reactant solution of methanol (Aldrich ACS spectrophotometric grade $\geq 99.9\%$) with deionized water 18.2M Ω , or by dissolving reactant powders of sodium carbonate (Aldrich ACS reagent, anhydrous, 99.95-100.05%) or of ammonium sulfate (Aldrich ACS reagent, 99.99%) with deionized water 18.2M Ω . When aqueous solutions were mixtures of water and CO_2 , dry ice previously weighted for having the desired mixing ratios was added, dissolved and homogeneously mixed in the deionized water. Frozen aqueous solutions were then pump-thaw degassed at 10^{-3} Torr at 77K, then backfrozen at 77K and ultimately pumped down to approximately 10^{-5} Torr. This allows removing any oxygen and nitrogen from the water ice.

In our experiments, we irradiated ices of ~ 2.5 cm thick by the pulse laser beam at different spots on the icy surface, with an input energy of each laser pulse of 200 mJ, and a total irradiation time of 30 min. Our focused spot size is determined to be 400 μm in diameter based on the measured spot size for pulsed laser plasma of Borucki et al. (1996) corrected for the difference in focal length. This leads to an energy deposition rate (or irradiance) of about $1.6 \times 10^{10} \text{ W cm}^{-2}$. As mentioned previously irradiance in pulsed laser ablation higher than 1 GW cm^{-2} corresponds to hypervelocity impacts up to $\sim 10^2 \text{ km s}^{-1}$ (Sugita et al., 2003; Kadono et al., 2002).

[Figure 1]

After irradiation, the first step was to examine the gas phase at 77K which was formed during the laser ablation at low temperature (77K) above the icy solid phase. For this, the glass flask kept in liquid nitrogen bath was connected to a high vacuum line and the gas phase contained inside was expanded into a high vacuum line evacuated to 10^{-6} Torr, then extracted with a gas-tight syringe for injection in the GC-MS instrument (Agilent, HP 5890 II GC – HP 5971 MSD). A fused silica capillary chromatographic column (Agilent GS-Q, 30 m $\times$ 0.32 mm ID) was used to allow the good elution and separation of a large variety of molecules like CO_2 , nitrogen oxides, water, organics (e.g. hydrocarbons C1- C12, nitriles, sulphur compounds). Helium was used as carrier gas with a flow of 1.9 ml/min and a temperature program of the GC oven was established to improve the molecules separation. The initial temperature was 40°C for 4 min, then increased at a rate of 15°C/min up to 240°C and finally isothermal at 240°C

for 4 min. Each separated molecule was transferred to the quadrupole mass spectrometer of the GC-MS instrument, operating in electron ionization (EI) mode. The mass spectrum of each molecule allows its identification by analyzing the ion masses of the molecule fragments and by comparing this fragmentation pattern with the mass spectral database by National Institute of Standard (NIST). Usual detectable amount of components with the GC-MS is at ppb level.

A detachable infrared single pass gas cell, with 10 cm path length and ZnSe windows (25 mm O.D.) at each extremity, was also connected to the vacuum line allowing the gas products transfer and analysis by FTIR. The measurement conditions of the FTIR spectrometer (Nicolet, Nexus 670) were set up in the spectral range from 400 to 4000 cm^{-1} , with a resolution of 2 cm^{-1} and 128 scans. The FTIR spectrometer allows molecules detection of microgram amount.

After the gas phase examination, the second step was to inspect the volatiles evaporated when the ablated ice has melt at room temperature (293K). This volatile fraction was collected for GC-MS and FTIR analysis in the same way as we did and explained for the first step of the gas phase examination.

Then, the last step was to examine the dissolved trace volatiles in the liquid melt which did not evaporate earlier at 293K. We used the technique of fractional distillation as described in Khare and Dondero (1977). It consisted of evaporating from the aqueous phase (liquid melt), fractionating and concentrating the trace dissolved volatiles using a series of cold traps connected from one end to the flask containing the liquid melt and

the other end to the vacuum manifold. The ramp of low-temperature baths used were -23°C obtained with a mixture of carbon tetrachloride and dry ice (for retaining water), -78°C with acetone and dry ice (retaining a fraction of volatiles), and finally -196°C with liquid nitrogen (capturing most of the organics and gases). By warming the traps at room temperature, volatiles from each trap were then released successively in the vacuum line and analyzed by GC-MS and FTIR.

For the sensitive GC-MS detection of hydrogen peroxide dissolved in the aqueous phase, we use the method described by Kobayashi and Kawai (1982). We have decided to apply this analytical process in our experiments because it allows the highly sensitive detection of H₂O₂ in aqueous solution at very low concentrations (up to ppb level). Indeed, we were unable to detect hydrogen peroxide in the gas phase by FTIR (technique by which it is usually identified), nor the examination by Raman spectroscopy of H₂O₂ dissolved in the liquid melt was successful. We explain it by a H₂O₂ production in our experiment below the detection limits of our both spectrophotometers (1 % and 0.5 % concentration for the FTIR and Raman instruments, respectively). Analyzing H₂O₂ directly by GC-MS was not possible as H₂O₂ is corrosive material for the chromatographic columns. Therefore we had to look for another method from Kobayashi and Kawai (1982) which has been successfully used in environmental analyses. It involves the specific enzymatic conversion by methanol-catalase system of hydrogen peroxide to formaldehyde (reaction 1 below). Formaldehyde is then

derivatized with pentafluorobenzyl hydroxylamine (PFBOA) and its derivative, PFBOA formaldoxime (reaction 2), is eluted in a DB-1MS column supplied by Agilent (30 m × 0.25 mm ID, 0.25 µm film thickness). In this case, the temperature program of the GC column oven was isothermal at 60°C for 2 min, then increased at a rate of 10°C/min up to 100°C and finally isothermal at 100°C for 4 min. PFBOA formaldoxime was selectively identified by the mass spectrometer of the GC-MS instrument with its specific fragment ions of masses 181, 195, 225 in the mass spectra (previously provided by Sugaya et al., 2001).

PFBOA

PFBOA Formaldoxime

For each experiment, a blank test was performed. The blank experiments for each ice composition correspond to the non-irradiated ices. The ice was not irradiated but the same procedure used for preparing the irradiated samples was followed, and the analysis conditions by GC-MS and FTIR were the same in both blanks and samples runs. For a complete control of the experiments, we have the blank runs of (1) the GC-MS column without injecting any samples, and (2) to examine possible contamination from the flask, a GC-MS run was made of the air in the flask after evacuating to 10^{-6} Torr, and finally (3) the IR gas cell was similarly examined for contamination.

3. Results and Discussion

We have impacted different ices containing C, H, N, O elements. Ice subjected to laser ablation revealed small circular zones of few millimeters diameter as pulse footprints of the beam spots on the sample. We have observed that some shocked material was ejected. The icy mixtures and the products detected after irradiation are reported in Table 1. Each experiment with a different ice composition was repeated three times resulting in unchanged GC chromatograms and FTIR spectra, which confirms the reproducibility of our results.

[Table 1]

3.1. H_2O / CO_2 ice

Laser ablation of 10:1 icy mixture of H_2O / CO_2 at 77K (Fig. 2b and 3b) shows the synthesis of the oxidants CO and CH_3OH . The detection of both products was distinct. First laser ablation of frozen H_2O/CO_2 leads to ejection of CO. CO molecules have been identified in the gas phase at 77K directly after irradiation by infrared spectroscopy, as observed by the CO absorption band at 2140 cm^{-1} in the spectrum (Fig.

2b). The peak at 2349 cm^{-1} (C=O asymmetric stretching vibration of CO_2) in the non-irradiated spectrum is due to incomplete removal of air from the spectrometer. In the irradiated spectrum, the same CO_2 band has a negative peak due to imbalance of purging between the non-irradiated and irradiated scans. CH_3OH was released in the gas phase at 293K, after melting the ice at room temperature and was detected by GC-MS. Figure 3 shows the chromatograms obtained without irradiating the ice (blank run, Fig. 3a) and after irradiation (Fig. 3b). Methanol is identified with its peak at 10.7 min. Other peaks in non-irradiated and irradiated spectra correspond to air (N_2 and O_2) at 1.4 min which is omnipresent as a source of instrument leakage, CO_2 at 2.03 min and water at 6.05 min, initial reactants in the ice.

[Figure 2]

[Figure 3]

We can compare our results to other experiments using other energy sources applied to H_2O / CO_2 ices in the laboratory, i.e. UV and ionizing radiations. In these experiments CH_3OH is not formed but rather carbonic acid and formaldehyde (Strazzulla et al., 2005; Gerakines et al., 2000; Moore and Hudson, 2000; Moore and Khanna, 1991; Pironello et al., 1984). This may suggest that impact shock simulated by laser ablation implies different chemical reactions than in other irradiations. This is expected, since in our simulations we are dealing with shock effects (shock wave compression and shock heating) and not with electron bombardment or the photon absorption process. It has been assumed, in a first approximation, that photons and fast

charged particles produce the same effects at the surface of the bombarded solid ice (Salama, 1998). The major difference of these two processes concerns the depth at which these effects can happen: UV photons dominate ice processing in the top layers of the surface (few fractions of μm) and energetic charged particles in deeper layers (Salama, 1998). Nonetheless, for the case of carbonic acid, one may not exclude the possibility that it could have been formed in our experiments. However at ambient temperature, H_2CO_3 dissolved in water dissociates rapidly into CO_2 and H_2O . Therefore when melting the ice at room temperature, on warming H_2CO_3 may have decomposed in the aqueous phase.

Motivated by the detection of hydrogen peroxide on Europa (Carlson et al., 1999b), as a second part of our experiments on H_2O / CO_2 ice, we have looked for H_2O_2 formation. The determination of H_2O_2 was done in a separate experiment using the enzymatic technique described in Section 2 under Experimental Method. The detection and identification of hydrogen peroxide in our experiments are illustrated in Figures 4 and 5. It shows the chromatograms of the aqueous phase obtained before (Fig. 4a) and after the laser irradiation (Fig. 4b). PFBOA formaldoxime, derivative for detection of formaldehyde produced selectively from hydrogen peroxide, was formed after 30 min irradiation. It was clearly identified at 6.54 min and from its distinguishing mass spectrum (Fig. 5), with a chromatogram peak abundance about 50 times higher in the irradiated ice spectrum (Fig. 4b) than in the non-irradiated one (Fig. 4a). In our experiments, the final concentration of H_2O_2 was determined as $0.23\% \pm 0.10\%$, or 2.3

$\times 10^{-3}$ ml H_2O_2 per ml of H_2O_2 in the $\text{H}_2\text{O}/\text{CO}_2$ icy mixture.

[Figure 4]

[Figure 5]

It has been demonstrated by laboratory experiments that, on the surface of icy satellites, energetic ion irradiation onto pure water ice, $\text{H}_2\text{O} / \text{O}_2$ and $\text{H}_2\text{O} / \text{CO}_2$ ices produces hydrogen peroxide (Loeffler et al., 2006; Gomis et al., 2004; Moore and Hudson, 2000). Such results have supported the hypothesis that H_2O_2 detected by space observations on the Galilean moons, e.g. Europa, is very probably formed by ion energies characteristics of magnetospheric ions from Jupiter.

The production of hydrogen peroxide in our new experiments may give rise to new ideas regarding the chemistry occurring at the surface of icy satellites such as Europa which shows various cratering features. Impact processing could be another source of H_2O_2 on Europa.

Beyond these first results, further laboratory studies are needed to provide complete data on the molecular production and destruction in $\text{H}_2\text{O} / \text{CO}_2$ ices. For example, specific issues needed to be addressed are the experimental measurement of hydrogen peroxide variation with CO_2 concentration and if longer and more complex carbon chains can be formed with increasing CO_2 abundance.

3.2. $\text{H}_2\text{O} / \text{Na}_2\text{CO}_3$ ice

We have irradiated ice mixtures of H_2O / Na_2CO_3 10:1 in order to compare the results with H_2O / CO_2 ices as both ices contain a source of oxidized carbon. After irradiation, we could observe a yellow coloration of the ice at the impact point region. The coloration disappeared when melting the ice. This yellow material may have sublimated when the temperature of the ice was increased, but we did not detect anything other than CO_2 in the gas phase at room temperature. Alternatively, it could have dissolved in water, but the analysis of the liquid phase did not show any new component. We have not succeeded in identifying this material. It may have been produced in undetectable amounts. Observations of Europa's surface reveal that the saltiest areas are red and yellow. Kargel (1998) wonders if the energetic ionizing radiation environment on Europa could partly alter the salts to red and yellow substances. From our experimental observation, we can also inquire about this possible alteration of carbonates from impact processing effect.

The only new species detected from ablated H_2O / Na_2CO_3 ices were carbon monoxide in the gas phase at 77K by FTIR (Fig. 6.1) with its absorption band at 2140 cm^{-1} and carbon dioxide in the gas phase at 293K by GC-MS eluted at 1.78 min (Fig. 6.2b). The peak at 1.3 min in both irradiated and non-irradiated ice spectra (Fig. 6.2a and 6.2b) is the omnipresent air from small leakage of the instrument. CO and CO_2 molecules are the principal decomposition products of the carbonate anion CO_3^{2-} . Unlike the experiments with CO_2 in ice, methanol was not formed in carbonated ice.

[Figure 6]

Laser ablation of frozen sodium carbonate in ice results primarily in the destruction of the salt into CO and CO₂. This leads us to suggest that impacts into ice containing Na₂CO₃ could have provided a local source of carbon monoxide released locally around craters on Europa. For the case of carbon dioxide, under Europa's low temperature surface (100-120K), CO₂ released may be trapped by the icy crust.

The coloration of the ice could be a preliminary indication that chemical synthesis has occurred but, at this first experimental stage, the results are not definitive and further experiments are needed.

3.3. *H₂O / CH₃OH / (NH₄)₂SO₄ ice*

Such icy mixture has been chosen for studying the synthesis of ices containing carbon, nitrogen and sulfur elements which we expect to be more complex and interesting for supplying molecules important for the origin, evolution and sustainability of life. Such ices are usually made in the laboratory for studying the chemistry of cosmic ices like interstellar ices and dust (Bernstein et al., 2002a, b). However it could also be used to represent a simplified Europa, Ganymede, or Callisto ice.

One component of icy material in comets is methanol, with an abundance that is a few percent relative to H₂O. Therefore it is plausible that CH₃OH could have been delivered on impact to icy moons and included in small amount in their frozen surfaces.

Following interpretations on the possible presence of nitrogen components in

some icy moons (as described in earlier in part 1), we have decided to include NH_3 in the icy composition and we have assumed that, after reaction with some form of sulfur, this NH_3 may end up as ammonium sulfate.

The laser ablation of H_2O / CH_3OH / $(\text{NH}_4)_2\text{SO}_4$ ice (10:1:1) leads to a rich variety of new compounds. It produces in the gas phase CH_4 and CO at 77K, identified by FTIR with the absorption band at 2140 cm^{-1} for CO and the C-H stretching vibration of methane at 3017 cm^{-1} (Fig. 7). The IR bands at 2849 cm^{-1} and 2918 cm^{-1} in both spectra, non-irradiated (Fig. 7a) and irradiated (Fig. 7b) are background artifacts (disturbing bands) from the KBr window of the infrared spectrometer. CO_2 and N_2O are released from the melted ice in the gas phase at 293K (Fig. 8). The synthesis of more complex molecules containing alkyl, carbonyl and nitrile groups is also observed by GC-MS analysis of the trace volatiles extracted from the aqueous phase (Fig. 9 and Fig.10). Methane (Fig. 7) and ethane (Fig. 9) were the only hydrocarbons formed, no unsaturated hydrocarbons have been detected. But longer carbon chains have been produced (Fig. 10): acetone (CH_3COCH_3), methyl formate (HCOOCH_3) and dimethyl formal ($\text{CH}_3\text{OCH}_2\text{OCH}_3$).

Nitrogen compounds were also found. In the chromatogram (Fig. 10), a peak at 13.2 min has been assigned to acetonitrile (CH_3CN) with characteristic peak masses at 41 (molecular ion) and 40 (fragment ion) in the corresponding mass spectrum.

[Figure 7]

[Figure 8]

[Figure 9]

[Figure 10]

The CH₃CN detection has led us to think that hydrogen cyanide (HCN), simpler nitrile, may have also formed. But there was no visible peak for HCN in the resulting chromatogram. Indeed, with this chromatographic column, HCN elutes practically at the same time as methanol. The methanol peak is so abundant that it hides the HCN peak. So we have extracted from the chromatogram the specific ions for HCN (mass 27 and mass 26) and CH₃OH (mass 31) and we have found a trace peak for HCN just before the peak of methanol, as illustrated in Fig. 11. We can therefore state that hydrogen cyanide was produced in trace amounts in our experiment.

[Figure 11]

3.4. *H₂O / CH₃OH ice*

The laser ablation of H₂O / CH₃OH (10:1) results first in the formation of CH₄ and CO in the gas phase at 77K (Fig. 12), then CO₂ was evaporated at 293K (Fig. 13). The three molecules are decomposition products of methanol. Secondly, the ablation of this ice leads to the synthesis of acetone (CH₃COCH₃), methyl formate (HCOOCH₃) and dimethyl formal (CH₃OCH₂OCH₃) extracted from the aqueous phase (Fig. 14). Acetone was found much more abundantly in ices containing ammonium sulfate. This was not the only difference. Acetaldehyde (CH₃CHO) was a new species volatilized

from the aqueous phase and detected during the GC-MS analysis with a peak at 10.6 min (peak 1 in Fig. 14).

[Figure 12]

[Figure 13]

[Figure 14]

Again, we can compare our results with experiments done with other energy sources applied to ices. In the laboratory, the UV photolysis of $\text{H}_2\text{O} + \text{CH}_3\text{OH}$ ices shows the formation of CO , CO_2 , CH_4 , HCO radical and H_2CO at $< 20\text{K}$ (Allamandola et al., 1988). The same products are identified from ion irradiation at $< 20\text{K}$ with the new production of ethanol and acetone (Moore et al., 1996; Moore et al., 1991). In both cases, formaldehyde was the dominant volatile species identified.

CO_2 is seen in the ice on the leading side of Europa (Carlson, 2001), where micrometeoroid infall is greater than on the trailing side. One mechanism proposed for the presence of this frozen CO_2 is the ion irradiation of a carbonaceous surface layer that arises from micrometeoroids infall (Carlson, 2001, 2002). From our experimental results where CO_2 is formed from ablated $\text{H}_2\text{O} / \text{CH}_3\text{OH}$ ice, we can propose that it may be also plausible that CO_2 could be formed around craters sites of Europa from impacts into ice containing methanol. It is probable that methanol could be produced in Europa's icy surface by the irradiation of high energy charged particles on water ice containing CO . Indeed, Moore et al. (1991, 2003) have experimentally shown that CH_3OH is produced by ion irradiation from $\text{H}_2\text{O} / \text{CO}$ ices. CO has not been detected on Europa

but experimental works (Strazulla et al., 2005; Gerakines et al., 2000, 1996; Moore et al., 1991; Moore and Khanna, 1991) have demonstrated that it could be produced by ion irradiation and by UV photolysis of H₂O / CO₂ and CO₂ ices. These ices have been spectroscopically observed on Europa (as indicated in part 1).

This scenario of the production of carbon dioxide by impacts of water ices containing methanol could be also applicable to Ganymede and Callisto, where carbon dioxide on their icy surfaces and impact crater features have been observed (see references pointed out in part 1).

4. Conclusion

Our laboratory simulations using laser ablation coupled with GC-MS and FTIR technique demonstrate a novel experimental method to study the chemistry in ices induced by impact shock. Our results confirm that chemistry is occurring in laboratory simulated impact shocks. Impact shock of ices of pure water with components, i.e. ices containing H, C, O, N simple compounds induces the production of more complex molecules, some of biological interest like nitriles. Another important result shows that H₂O / CO₂ ice subjected to laser ablation can form hydrogen peroxide, whose production has been related exclusively to ion irradiation of these ices (by protons and He ions).

The chemical influence of ionizing radiation and ultraviolet photolysis on frozen water and mixed ices has been investigated for many years by performing laboratory experiments (Strazulla et al., 2005; Gerakines et al., 2000; Moore and Hudson, 2000; Moore et al., 1991; Allamandola et al., 1988; Pironello et al., 1984). Our experimental results indicate that ices subjected to impact shocks also leads to the synthesis of new species. Icy planetary surfaces may not only be modified chemically by exposure to UV photons and high-energy charged particles, but meteoritic bombardment could possibly also participate in the chemical modification. Our experimental simulation could provide new information on the likely processes affecting the icy shells of icy satellites. It may be of great interest for studying chemical composition and evolution of the surface ices of satellites like Europa, Ganymede, Callisto, and Titan. In order to strongly support this hypothesis and estimate the relevance of impact processing compared to other energy sources, undoubtedly further laboratory investigations should be performed, as well as computer modeling.

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Table 1

New molecular species identified after laser ablation of different icy mixtures in the gas phase at low temperature (77K), from evaporation of volatiles from the melted ice at 293K and finally extracted, fractioned and concentrated from the liquid melt (aqueous phase). The detection and identification was performed by GC-MS and FTIR analyses. Ratios of components in icy mixtures are indicated in parenthesis.

Initial Ice	FTIR gas phase 77K	GC-MS volatiles evaporated 293K	GC-MS Dissolved trace volatiles extracted from aqueous phase
H ₂ O + CO ₂ (10:1)	CO	CH ₃ OH	H ₂ O ₂
H ₂ O + Na ₂ CO ₃ (10:1)	CO	CO ₂	—
H ₂ O + CH ₃ OH + (NH ₄) ₂ SO ₄ (10:1:1)	CH ₄ , CO	CO ₂ , N ₂ O	C ₂ H ₆ , CH ₃ COCH ₃ , HCOOCH ₃ , CH ₃ OCH ₂ OCH ₃ , HCN, CH ₃ CN
H ₂ O + CH ₃ OH (10:1)	CH ₄ , CO	CO ₂	CH ₃ COCH ₃ , HCOOCH ₃ , CH ₃ OCH ₂ OCH ₃ , CH ₃ CHO

Figure captions

Figure 1. Schematic illustration of the experimental set-up for laser ablation experiments on ices. Ices were ablated by a Nd-YAG pulsed laser during 30 min. The laser beam at 1.06 μm beam wavelength was focused on the ice surface using a plano-convex lens of 20 cm focal length. The laser pulse was 200 mJ, pulse duration 10 ns and pulse repetition rate 10Hz. Spot size was determined to be 400 μm in diameter and the energy deposition rate $1.6 \times 10^{10} \text{ W cm}^{-2}$.

Figure 2. Infrared spectra of $\text{H}_2\text{O} + \text{CO}_2$ (10:1) before (a) and after (b) laser irradiation showing CO formation in the gas phase at 77K. The measurement conditions of the FTIR spectrometer were a spectral range from 400 to 4000 cm^{-1} , a resolution of 2 cm^{-1} and 128 scans. The bands at $\sim 2350 \text{ cm}^{-1}$ in both (a) and (b) are due to CO_2 in the FTIR spectrometer.

Figure 3. Chromatogram of $\text{H}_2\text{O} + \text{CO}_2$ (10:1) before (a) and after (b) laser irradiation showing CH_3OH release in the gas phase at 293K. The column used was an Agilent GS-Q, 30 m $\times$ 0.32 mm ID with a helium flow of 1.9 ml/min and the temperature program of the GC oven was established as isothermal at 40°C for 4 min, then increase at a rate of 15°C/min up to 240°C and finally isothermal at 240°C during 4 min. Abundance ($\times 10^4$) means that the y-coordinate units have to be multiplied by 10000 for having the

correct value.

Figure 4. Chromatogram of $\text{H}_2\text{O} + \text{CO}_2$ (10:1) before (a) and after (b) laser irradiation confirming H_2O_2 formation in the aqueous phase. The peak in (b) at 6.5 min is 50 times larger than the peak in (a) before irradiation. The column used was a DB-1MS column supplied by Agilent (30 m $\times$ 0.25 mm ID, 0.25 μm film thickness) and the temperature program of the GC oven was established as isothermal at 60°C for 2 min, then increase at a rate of 10°C/min up to 100°C and finally isothermal at 100°C during 4 min.

Figure 5. Mass spectrum of peak eluted at 6.5 min in chromatogram of Figure 4b, confirming PFBOA formaldoxime, and thus the synthesis of H_2O_2 .

Figure 6. Analysis of $\text{H}_2\text{O} + \text{Na}_2\text{CO}_3$ (10:1) before (a) and after (b) laser irradiation showing CO and CO_2 formation. Spectrum 6.1- CO was detected by FTIR in the gas phase at 77K. The bands at $\sim 2350\text{ cm}^{-1}$ in both (a) and (b) are due to CO_2 in the FTIR spectrometer. Chromatogram 6.2- CO_2 released in the gas phase at 293K was identified by GC-MS. The measurement conditions of the FTIR spectrometer were the same as described in Fig. 2. The peak at 1.25 min in both (a) and (b) is the peak at the dead time corresponding to the non-retained fraction which is, in this case, the air ($\text{N}_2 + \text{O}_2$) fraction. The column type and GC conditions were the same as described in Fig. 3. Abundance ($\times 10^3$) means that the y-coordinate units have to be multiplied by 1000 for

having the correct value.

Figure 7. Infrared spectra of $\text{H}_2\text{O} + \text{CH}_3\text{OH} + (\text{NH}_4)_2\text{SO}_4$ (10:1:1) before (a) and after (b) laser irradiation showing CO and CH_4 formation in the gas phase at 77K. The measurement conditions of the FTIR spectrometer were the same as described in Fig. 2.

Figure 8. Chromatogram of $\text{H}_2\text{O} + \text{CH}_3\text{OH} + (\text{NH}_4)_2\text{SO}_4$ (10:1:1) before irradiation (a) and after laser irradiation(b) showing CO_2 and N_2O formed during the experiment at 77K and detected after evaporated when the ice has melt at room temperature (293K). The trace peak of CO_2 in the chromatogram of the non-irradiated ice is due to room air leaking while injecting the sample. The column model and GC conditions were the same as described in Fig. 3. Abundance ($\times 10^4$) means that the y-coordinate units have to be multiplied by 10000 for having the correct value.

Figure 9. Chromatogram of $\text{H}_2\text{O} + \text{CH}_3\text{OH} + (\text{NH}_4)_2\text{SO}_4$ (10:1:1) before (a) and after (b) laser irradiation showing the formation of ethane extracted and concentrated from the aqueous phase after melting the ice at room temperature. The column type and GC conditions were the same as described in Fig. 3. Abundance ($\times 10^3$) means that the y-coordinate units have to be multiplied by 1000 for having the correct value.

Figure 10. Chromatogram of $\text{H}_2\text{O} + \text{CH}_3\text{OH} + (\text{NH}_4)_2\text{SO}_4$ (10:1:1) before (a) and after

(b) laser irradiation showing the formation of acetone and other traces organic compounds. On the right side is an expanded vertical scale of the dashed framed area of the left top chromatogram to show the production of the traces compounds. All those compounds were extracted, fractionated and concentrated from the aqueous phase after melting the ice at room temperature (293K). The column type and GC conditions were the same as described in Fig. 3. Abundance ($\times 10^4$) means that the y-coordinate units have to be multiplied by 10000 for having the correct value.

Figure 11. Extracted ion chromatograms for detecting hydrogen cyanide formed after ablating by laser the ice of $\text{H}_2\text{O} + \text{CH}_3\text{OH} + (\text{NH}_4)_2\text{SO}_4$ (10:1:1).

Figure 12. Infrared spectra of $\text{H}_2\text{O} + \text{CH}_3\text{OH}$ (10:1) before (a) and after (b) laser irradiation showing CO and CH_4 formation in the gas phase at 77K. The measurement conditions of the FTIR spectrometer were the same as described in Fig. 2.

Figure 13. Chromatogram of $\text{H}_2\text{O} + \text{CH}_3\text{OH}$ (10:1) before (a) and after (b) laser irradiation showing CO_2 formation in the gas phase at 293K. The column type and GC conditions were the same as described in Fig. 3. Abundance ($\times 10^5$) means that the y-coordinate units have to be multiplied by 10^5 for having the correct value.

Figure 14. Chromatogram of $\text{H}_2\text{O} + \text{CH}_3\text{OH}$ (10:1) before (a) and after (b) laser

irradiation showing the formation of organic compounds extracted from the aqueous phase after melting the ice at room temperature. The column type and GC conditions were the same as described in Fig. 3. Abundance ($\times 10^3$) means that the y-coordinate units have to be multiplied by 1000 for having the correct value.

Fig 1

Fig 2

Fig 3

Fig 4

Fig 5

PFBOA formaldoxime

Fig 6

6.1

6.2

Fig 7

Fig 8

Fig 9

Fig 10

1- Methyl formate	4- unknown
2- Acetonitrile	5- unknown
3- Dimethyl formal	6- unknown

Fig 11

Fig 12

Fig 13

Fig 14