

Effect of mineral matrixes on the chemical evolution of organic molecules under simulated Mars surface UV radiations conditions with the MOMIE experiment

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Abstract

Organic molecules are currently one among the priority targets of the Mars surface exploration. Indeed, organic molecules could have been produced endogenously at the time the surface conditions of Mars were favourable to the development of a prebiotic chemistry and the emergence of life. Organics are also still brought continuously to the surface through meteoritic impacts^{[1][2]}. All this organic material can be kept buried and mixed in the Mars regolith where it can be submitted to harsh conditions (UV radiation, oxidants and energetic particles) that appeared with the magnetic field and atmosphere loss. Our work investigates the effect of various minerals on the chemical evolution of organic matter under simulated Mars surface UV radiation with the MOMIE laboratory experiment. These experiments are dedicated to help the interpretation of the past, present and future *in situ* analyses of Martian soil and rocks towards organic molecules.

1. Introduction

The search for organic molecules at the Mars surface is one among the main science goals for the Mars exploration. These molecules could be clues of past or present habitability and they are potentially present at the surface/subsurface of Mars. However, the current environmental conditions at the Mars surface (UV radiation^[3], oxidants^[4] and energetic particles^[5]) induce physico-chemical processes that may affect organic molecules. This is the reason why we study for years the evolutionary pattern of organics under the influence of current surface environmental conditions with the MOMIE^[6] (Mars Organic Molecules Irradiation and Evolution) laboratory experiment. This study aims at estimating the potential for organic molecules to be preserved in the regolith, their potential evolution into secondary chemical species. In this contribution, we will focus on the influence of the presence of minerals on the

evolution of organics under simulated Mars surface conditions.

2. The MOMIE experiment

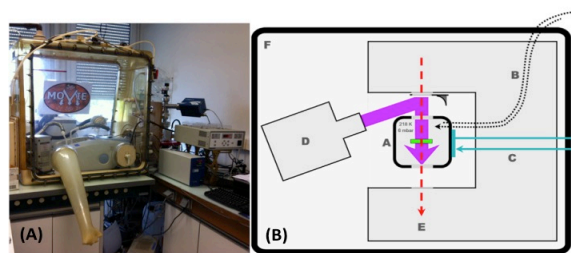


Figure 1: (A) Close view of the MOMIE experiment. (B) Scheme of the MOMIE top view with: A Reactor housing the samples. B Gas circulation system. C Cryostat. D Xenon arc lamp. E FTIR spectrometer. F Glove compartment.

The MOMIE simulation setup (Figure 1) is a Martian chamber where we introduce an organic molecules or an organic molecules and mineral mixture thick deposit (on an MgF2 window) in a reactor which is maintained at $-55^{\circ}\text{C} \pm 1^{\circ}\text{C}$ using a cryostat and $6 \text{ mbar} \pm 2 \text{ mbar}$ thanks to a gas circulation system. Then the samples are irradiated by a Xenon arc lamp (190-400 nm) reproducing the Sun UV irradiation that reaches the Mars surface. A temporal follow-up is made by a FTIR spectrometer in order to estimate the degradation kinetic of target molecules (quantitative analysis) and their transformation in solid or gaseous products, or in stable products (qualitative analysis).

3. Work in progress

Ferrous oxides are present everywhere at the surface of Mars, mainly as hematite (Fe_2O_3), goëthite (FeOOH) and magnetite (Fe_3O_4)^[7]. These minerals can generate oxydo-reduction reactions at their surfaces. Could they have a photocatalytic or a photoprotective effect on kinetic degradation of organic molecules? To answer this question, we are

(synthesized by LRS) on adenine samples under simulated Mars surface UV radiations conditions. The detailed results of these simulations will be presented at the conference.

4. Future work

After the experiments with adenine-hematite intimate mixture samples, we propose to investigate other characteristic Martian minerals effect on the chemical evolution of organic matter.

4.1 Phyllosilicates

First results about chemical evolution of organic molecules in presence of nontronite have been ever discussed^[8]. Phyllosilicates are exciting targets, known to concentrate and preserve organics on Earth thanks to their lamellar structure, even in oxidizing environments^[9]. We choose to work with nontronite which is a ferrous smectite type detected on Curiosity landing site by OMEGA and CRISM hyperspectral imagers^[10]. In addition, Curiosity has found Griffithite in Yellowknife Bay^[11]. It will also be interesting to investigate the effect of this mineral detected *in situ* on the evolution of organic molecules under UV irradiation.

4.2 Sulfates

An other mineral formation constitutes the Mount Sharp: sulfates. So, we propose to study a monohydrated sulfate, the kieserite and a polyhydrated sulfate, the hexahydrite to see if there is a different effect of the mineral hydration on the chemical evolution of the organic molecules contained in the mineral matrix.

4.3 Minerals-perchlorates interaction

Perchlorates seem to be present everywhere on the surface of Mars and could be at the origin of the chlorinated compounds detected by SAM (Sample Analysis at Mars) instrument onboard the Curiosity rover^[12]. They would have an important effect during high-temperature pyrolysis and would be very oxidizing. We propose to check if these perchlorates can have this oxidizing effect in the temperature conditions (-55°C) of the Mars surface studying the effect of the minerals-perchlorates interaction on the chemical evolution of organic molecules followed by the MOMIE experiment.

Acknowledgements

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Research at a European Planetary Simulation Facility

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Abstract

This unique environmental simulation facility is capable of re-creating extreme terrestrial, Martian and other planetary environments. It is supported by EU activities including Europlanet RI and a volcanology network VERTIGO. It is also used as a test facility by ESA for the forthcoming ExoMars 2018 mission. Specifically it is capable of recreating the key physical parameters such as temperature, pressure (gas composition), wind flow and importantly the suspension/transport of dust or sand particulates.

This facility is available both to the scientific and Industrial community. The latest research and networking activities will be presented.

1. Activities Overview

This environmental simulator facility is utilized for a broad range of research programs including; the study of other planets (such as Mars), for recreating extreme terrestrial environments, or in specific investigations involving aerosols and other forms of particulate transport.

This facility is part of a European network (VERTIGO) recently established to investigate the dynamics within volcanic ash clouds and pyroclastic flows including a detailed study of electrification.

The facility is also involved in the new Europlanet 2020 Research Infrastructure through which a trans-national access program will allow numerous research groups access to this facility, mostly involving specific Martian environment studies.

Other activities include the development, testing and calibration of sensor and planetary lander systems, both for ESA and NASA. Currently testing for missions ExoMars and Mars2020 are scheduled.

2. Design and Operation

The simulator consists of an environmental (thermal-vacuum) chamber within which a re-circulating wind

tunnel is housed [1,2,6]. The wind is generated by a set of two fans which draw flow down the 2m×1m tunnel section and return it above and below. The test section can be fully removed for access. Wind speeds in the range 1-25 m/s have been demonstrated.



Figure 1 The main Planetary Simulation Facility.

Cooling is achieved by a novel liquid nitrogen flow system which has achieved temperatures below -150°C, an electric heater system is also employed. The inner chamber is thermally isolated from the vacuum chamber.

A server based control system provides both control over wind flow, temperature, pressure, lighting, etc., but also acts as a data logger.

3. Planetary Simulation

The combination of low pressure, low temperature, composition and aerosol injection is ideal for recreating the environment of the upper atmosphere (for example of the gas giants).



Figure 2 Planetary Simulator design.

With also control of wind flow this facility is well suited for recreating the environment at the surfaces of Mars, Earth and Titan.



Figure 3 wind tunnel test section showing LED based illumination system (solar simulator).

4. Atmospheric Aerosols

A unique capability of this wind tunnel facility is the production and controlled study of suspended particulates (dust, ash, sand, etc.). This type of experiment is a continuation of a large body of research performed over the past decade studying dust aerosols, specifically granular electrification, erosion and deposition rates [1,2,3,4]. This research has direct relevance to aerosol studies on Earth which impact air quality, the environment and climate.

An advanced type of Laser aerosol and (2D) wind flow sensor is used for detailed study and control of these environmental parameters.

In recent studies this technology has been used to measure the settling rates of micron sized ($0.25 - 40 \mu\text{m}$) spherical silica particles at pressures below where conventional Stokes settling theory is valid and the so called Cunningham correction (or slip factor) are usually used. This work has direct relevance and applicability to aerosols in the upper atmospheres (above troposphere) of any/all planetary atmospheres.

5. Dust and Sand transport;

The interaction of wind and the planetary surface, specifically the transport of sand and dust is fundamental to understanding the evolution of the planets surface and atmosphere. Laboratory studies of the entrainment, flow, deposition and erosion are scarce and empirical in nature. The effects of low

atmospheric pressure, composition, temperature and even gravity can now be studied in detail. For example detailed measurements of sand grain trajectories are now being made under Martian pressure and composition in wind tunnel studies. This has direct relevance to the recent and still poorly understood observations of active sand transport at the Martian surface.

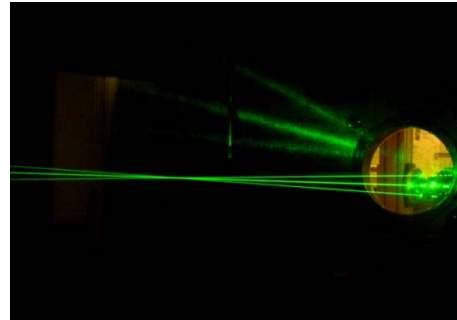


Figure 4 Laser based wind/dust sensor used for aerosol studies.

6. Conclusion

This planetary simulation facility has many unique features which make it well suited for both research applications and the development/testing of instrumentation. Details of this laboratory facility will be presented and some of the most recent activities will be summarized. For information on access to this facility please contact the author.

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Constraining the source of chlorinated hydrocarbons detected on Mars with the SAM experiment onboard Curiosity

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1. Introduction

1.1 Interest of exploration on Mars

Organic molecules have been at the origin of the prebiotic chemistry that led to the emergence of life on Earth. Therefore, they are one of the key ingredients required to assess the habitability in environments of the solar system. On Mars, no endogenous organics were found until very recently (1) whereas they are expected to be present in the soil, either because they were kept safe in rocks since the early history of the planet, or because they are still brought to the Mars surface by exogenous sources. Because of their importance for astrobiology, efforts are still ongoing to search for these species in the Gale crater by the Curiosity rover, and especially the SAM experiment on its board.

1.2 Structure and aim of SAM

Sample Analysis at Mars (SAM) is one of the instruments of the MSL mission. It is devoted to characterize the composition in volatile species of the atmosphere and the soil samples collected by Curiosity, and more particularly the organic molecules. Three analytical devices are onboard SAM: the Tunable Laser Spectrometer (TLS), the Gas Chromatography (GC) and the Mass Spectrometer (MS) (2).

Solid sample preparation: To adapt the nature of a sample to the analytical devices used, a sample preparation and gas processing system implemented with (a) a pyrolysis system, (b) wet chemistry: MTBSTFA and TMAH (c) the hydrocarbon trap (silica beads, Tenax® TA and Carbosieve G) which is employed to concentrate

volatiles released from the sample prior to GC-MS analysis.

1.3 Detection of chlorinated hydrocarbons

Viking landers (1976): The origin of chloromethane and dichloromethane was explained at the time by terrestrial contamination from the instruments (3). In a recent paper from Navarro-González (4), these results have been reinterpreted and chlorinated compounds could have been the product of the reaction of perchlorates identified by Phoenix (5) with organic materials in the sample.

MSL (2011): Abundant chlorinated hydrocarbons have been detected with the SAM experiment when analyzing samples collected in several sites explored by the Curiosity rover (Table 1). Most of these chlorohydrocarbons are produced during the pyrolysis of the solid sample by the reaction of Martian oxychlorine compounds present in the soil with organic carbon from a derivatization agent (MTBSTFA) used in SAM (6, 7). Chlorobenzene cannot be formed by the direct reaction of MTBSTFA with perchlorates (6) and two other reaction pathways for chlorobenzene were therefore proposed : (I) reactions between the volatile thermal degradation products of perchlorates (e.g. O₂, Cl₂ and

| Viking | MSL | | |
|---------------------------------|----------------------------------|----------------------------------|----------------------------------|
| | RN | JK | CB |
| CH ₃ Cl | CH ₃ Cl | CH ₃ Cl | CH ₃ Cl |
| CH ₂ Cl ₂ | CH ₂ Cl ₂ | CH ₂ Cl ₂ | CH ₂ Cl ₂ |
| nd | CHCl ₃ | CHCl ₃ | CHCl ₃ |
| nd | CCl ₄ | CCl ₄ | CCl ₄ |
| nd | nd | nd | C ₃ H ₆ Cl |
| nd | C ₄ H ₇ Cl | nd | nd |
| nd | C ₆ H ₅ Cl | C ₆ H ₅ Cl | C ₆ H ₅ Cl |

Table 1: chlorinated hydrocarbon molecules detected during Viking and MSL missions (nd: Non Detected)

HCl) and Tenax® and (2) the interaction of perchlorates (T>200°C) with OM from Mars's soil such as benzenecarboxylates (8, 9).

1.4 Objectives

This study aims at evaluating the potential of several chemical pathways to form chlorinated hydrocarbons by specifically looking for: (a) all the organic products coming from the interaction of Tenax® and perchlorates, (b) also between some soil samples and perchlorates and (c) sources of chlorinated hydrocarbon precursors. This study should allow to improve the discrimination between chlorohydrocarbons formed with SAM internal organics and those produced with organics present in the soil samples analyzed.

2 Experiments and methods

To answer some of our remaining questions, laboratory experiments have been done in several solid matrixes which have been brought into direct contact with perchlorates and heated.

2.1 Solid matrix

Three solid matrixes have been analyzed.

Fused silica: It is used as a free organic sample.

Tenax®GR: This polymer absorbent can release organic compounds under high temperature (11).

JSC-Mars1: JSC-1 is Martian regolith simulant collected in volcanic active area in Hawaii (12).

2.2 GC-MS analysis

In this work, we have performed a (A, Table 2) direct (i.e. solid matrix and perchlorates are mixed together in the injector) and (B, Table 2) indirect (i.e.

| Composition of sample | | |
|-----------------------|---|-------------------|
| Direct contact (A) | | |
| A1 | 25mg Fused silica + 24 mg CaClO ₄ | |
| A2 | 25mg Tenax® GR + Various amount of CaClO ₄ | |
| A3 | 132mg JSC-Mars1 + CaClO ₄ (9 wt%) | |
| Indirect Contact (B) | | |
| | Reactor | Injector |
| B1 | 24mg CaClO ₄ | 25mg Fused silica |
| B2 | Various amount of CaClO ₄ | 24mg Tenax®GR |

Table 2: Samples use in GC-MS studies

perchlorate is in the reactor which is upstream from the injector where the solid samples are placed). The abundances of Ca-perchlorate used in these experiments are much higher than SAM perchlorate abundance estimates of 0.3-0.5 wt% at Rocknest (6). The GC-MS is a Thermo Trace GC Ultra with a Restek Rtx-5 Sil-MS column (30m×0.25mm×0.25µm), coupled to the MS (Thermo DSQII). The helium flow was maintained constant at 1mL/min (split 10mL/min). The temperature of the column was started at 35 °C maintained 8min then increased at 7 °C/min to a final temperature of 300 °C for another 2 min.

3 Results and discussions

Martian origin Once the OM and perchlorates raise a higher temperature than 400°C; chlorinated compounds are produced including linear (chlorinated alkane derivatives) and aromatic compounds (chlorinated phenyl derivatives). Among these aromatic compounds we have detected chlorobenzene (Table 1) which has already been detected with no ambiguity at the Mars surface by SAM. Then precursors of chlorinated hydrocarbons might be preserved on the surface of Mars notably by the phyllosilicates.

4 Conclusion

Chlorinated compounds highlighted by SAM on Mars could have several origins: from perchlorate and/or MTBSTFA oxidation, from Tenax® degradation with or without presence of perchlorate and/or Martian organics. We have established a list of all the compounds likely to be produced by SAM contamination and compared it with all the compounds detected by SAM.

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Enantiomeric derivatization on the Mars Organic Molecule Analyzer (MOMA) experiment aboard ExoMars 2018: how to unravel martian chirality

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1. Introduction

The origin of homochirality in life on Earth remains unknown. The answer to this question lies in the study of chirality elsewhere in the Solar System. The Sample Analysis at Mars (SAM) experiment aboard Curiosity established the presence of organic molecules indigenous to a clay-rich sample on Mars [1]. However, SAM does not have the ability to separate between the enantiomers of potential medium- or high- molecular weight organic molecules. One of the wet chemistry experiments to be used in the MOMA instrument of the Exomars mission is designed for the extraction and identification of refractory organic chemical components in solid samples using gas chromatography-mass spectrometry (GCMS), while keeping the chiral center of the molecules intact [2]. This derivatization technique, using dimethylformamide dimethylacetal (DMF-DMA) as a reagent, will allow MOMA to separate the enantiomers of molecules of interest for astrobiology, such as amino acids, sugars or carboxylic acids. We present here the results of laboratory experiments which display the feasibility and limitations of the detection of an enantiomeric excess of complex organic molecules in various analog samples, depending on the mineralogy of the Mars analog solid sample.

2. Discussion

DMF-DMA can react with a broad range of molecules containing a labile hydrogen such as alcohols, primary and secondary amines, carboxylic acids and amino acids in the free form. The methylated products of these molecules are typically much more volatile than the original non-derivatized molecule, which enables the transfer of the DMF-

DMA derivatives for GCMS analysis. Moreover, derivatization with DMF-DMA keeps the chiral center of the molecules intact, which allows for an enantiomeric separation on a chiral GC column downstream (Figure 1).

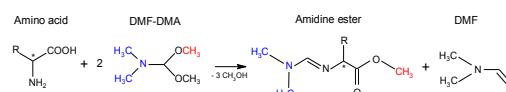


Figure 1: example of DMF-DMA derivatization on a chiral amino-acid. The derivatization preserves the chiral center of the molecule. Both derivatives' enantiomers can further be separated on a chiral GC column.

Racemisation (interconversion between L- and R-enantiomers) of chiral compounds can occur, especially when the molecules are heated or reside in wet conditions. The conditions of analysis during a derivatization experiment can thus interfere with the pristine enantiomeric state of the molecules present in the sample. Laboratory experiments on various analogs are thus necessary to establish the influence of the mineralogy in the racemization process of the organic molecules, under the conditions used for MOMA DMF-DMA derivatization. As an example, the water released from clay minerals may enhance the racemization, while organics preserved in sulfate samples would be more resistant to racemization. The laboratory studies are essential to pin down windows of preservation of organic molecules, and preservation of their enantiomeric state.

Moreover, MOMA will perform a new one-pot/one-step extraction and derivatization of the molecules from the solid sample. Because of the additional constraints imposed by such a process, a similar experiment using the MOMA capsules

containing the derivatizing reagent was performed in the laboratory, using a range of analog samples representing mineralogies likely to be encountered at Mars. The interactions between the molecules and the minerals is strongly dependant on the mineralogy of the sample, as is their extraction. The preliminary results show that even if more optimization is needed to have an optimal yield of recovery of organic molecules from the sample, we were able to detect a range of organics structures and also to separate and quantify their enantiomers in MOMA-like laboratory analyses.

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Collisional Induced Absorption (CIA) bands of CO₂ and H₂ measured in the IR spectral range

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Abstract

In this paper we present the results on the Collisional Induced Absorption (CIA) bands of CO₂ and H₂ measured employing two different experimental setup. Each of them allows us to reproduce typical planetary conditions, at a pressure and temperature from 1 up to 50 bar and from 298 up to 500 K respectively. A detailed study on the temperature dependence of the CO₂ CIA absorption bands will be presented.

1. Introduction

Linear symmetric molecules such as CO₂ and homonuclear such as H₂ possess no dipole moment, and in principle should not absorb light in the infrared, but exhibit collisional induced absorption bands even at a pressure of few bars. This absorption results from a short-time collisional interaction between molecules. The band integrated intensity shows a quadratic dependence versus density opposed to the absorption by isolated molecules, which follows the Beer's law [1]. This implies that absorption is due to the interaction of two molecules than by individual isolated molecules. These processes are very relevant in the relatively dense planetary atmospheres, such as those of planets, like Venus and Jupiter. More recently in extrasolar planets have been found to own very dense atmospheres which in principle may exhibit significant CIA. A detailed knowledge of these contributions can be very important to include this effect in the radiative transfer calculations.

2. Experimental setup

The experimental set-up is based on a Fourier Transform InfraRed (FT-ITIR) interferometer operating in a wide spectral range, from 350 to 25000 cm⁻¹ (0.4 to 29 μm) with a relatively high spectral resolution, from 10 to 0.07 cm⁻¹. Two dedicated gas cells have been integrated with the FT-IR. An High Pressure High Temperature (HPHT) absorption gas cell, shown in figure 1a, is characterized by an optical path of 2 cm and can sustain pressures up to 300 bar, temperatures up to 597 K. Another one, represented in figure 1b, is a Multi-Pass absorption cell (MP), designed to have a variable optical path, from 2.5 to 30 m, can be heated up to 300 K and work with pressures up to 10 bar.

2.1 Results and discussions

The CO₂ has been inserted into the HP-HT varying the pressure from 1 up to 50 bar and the temperature from 298 up to 600 K. The results are shown in figure 2a). The data are in agreement to [2] and the bands observed in the spectral range 1200-1400 cm⁻¹, are due to the strong Fermi- couplet doublet (ν₁, 2ν₂). The peak intensity of the CIA bands increases with the pressure and decreases with the temperature. The bands integrated intensities show a quadratic dependence vs density as reported in figure 2b, suggesting an absorption by pairs of molecules. Inserting the H₂ into the MP gas cell and maintaining the temperature @ 294K, the pressure has been varied from 1 up to 5 bar. In order to record the small absorption band, we fixed the optical path @ 15 m and, each absorption coefficient has been recorded with a resolution of 2 cm⁻¹. The spectra obtained in the spectral range of interest are shown in figure 2c). A preliminary comparison shows a good agreement with the results obtained by Borysow et al. [3].

3. Figures



Figure 1: experimental setup used to measure the CIA bands.

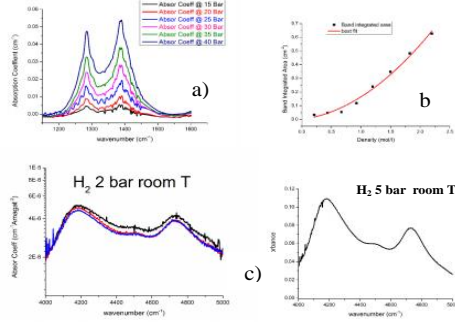


Figure 2: Absorption coefficients recorded using our experimental setups.

6. Summary and Conclusions

The CO₂ spectra have been measured for a wide range of temperatures, pressures and for a large spectral range. The quadratic component measured varying the pressure from 1 up to 50 bar is in good agreement with analyses performed by [4] on the band shape of the carbon dioxide in the region of the Fermi doublet. For what concerns the temperature dependence, the band integrated area seems not to have a strong dependence but future investigations are planned. The preliminary H₂ spectra recorded at different pressures are in good agreement with the model of Borysow [3].

Acknowledgements

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Photostability of glycine and nitrogen basis in cometary grains : application to the transport of organic matter within the primitive Earth

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1. Introduction :

The study of photochemistry in the solar system is of prime importance to assess complex organic chemistry in any extraterrestrial environment. Among those environments, comets and grains ejected from their nuclei are of particular interest in the context of astrobiology as they could have brought organic matter on the primitive Earth, and hence contribute to the emergence of life. Furthermore, they can provide precious information on the physico-chemical parameters prevailing in the primitive solar nebula during its formation.

In this context, we are studying the extent to which organic matter within grains may survive to solar radiation and the fraction of these organic molecules destroyed when it is subjected to sunlight.

2. Methodology and results :

Our work deals with the study of photochemical degradation of three nitrogenous bases (adenine, guanine and uracil) and one amino acid (glycine) in the solid phase subjected to VUV/UV energetically radiations ($\lambda < 300$ nm). The absorption cross sections of these molecules have been measured in the 115-300 nm range [1] (figure 1). These new data are then incorporated in a model which simulates the photodestruction kinetics of a pure organic film. The comparison between this model and experimental data collected with samples irradiated in low earth orbit [3, 4] as well as in the laboratory, allow to estimate accurately the photochemical lifetimes at different heliocentric distances. These lifetimes can be compared to the grains travel time, ie submitted to irradiation, once they are ejected from comet nucleus until a hypothetical arrival on Earth, and this, from different heliocentric distances of ejection. We will also describe the extent

to which organic molecules can be protected from UV radiation by the minerals composing cometary grains.

The results can lead to better understand the contribution of cometary grains in the establishment of an organic reservoir on primitive Earth. It can also be relevant to the interpretation of measurements by the Rosetta spacecraft in the environment of comet 67P.

Results show that glycine, adenine and guanine, potentially existing inside the cometary grains, would be entirely destroyed between the ejection of the grains and the arrival on earth if they exist at the surface. Below the surface, they are at the contrary very stable, thanks the effective protection of the mineral constitutive of the grain against solar radiations.

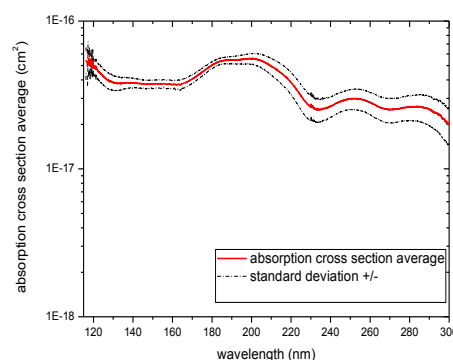


Figure 1 : Absorption cross section (cm²) of guanine solid sample (from 115 to 300 nm).

Acknowledgements:

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Petrographic/thermodynamic study of mineral assemblages of the H₂O-MgSO₄-CO₂ system

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Abstract

We investigate some petrographic and thermodynamic characteristics occurring during formation of clathrate hydrates from salty solutions. It is already suggested that the salting out effect has a great influence in the structure and composition of the icy satellites [1]. Here we show the textural evolution of the mineral assemblages formed when the H₂O-MgSO₄-CO₂ fluid is cooled under pressure and temperature conditions of Europa. Mineral formation/dissociation is recorded during pressure and temperature trajectories in order to determine how salting-out operates on the distribution of materials in icy crust of the icy moons. Detailed characterization of the involved mineral phases is carried out by Raman spectroscopy.

1. Introduction

Clathrate hydrates may have a starring role in planetary science due to their ability to act as efficient reservoirs of gases like CH₄ or CO₂. Some clathrate-forming volatiles, hydrated salts and water ice have been already detected on Europa's surface by remote spectroscopy [2, 3]. The formation of CO₂ clathrates is feasible under the conditions of Europa's internal ocean [4]. The presence of salts in the aqueous solutions affects clathrate hydrate stability by lowering the dissociation temperature [1]. However, under certain conditions, the gas exhibits more favoured interactions with water molecules than salts removing those from the system in order to form clathrates. When this process takes place, salinity increases in the remnant solution, which is known as salting-out phenomenon. We uphold that salting-out might has high impact on the icy moon geology and habitability.

Combining textural and thermodynamic characterization of the forming minerals, we should find signatures useful for the interpretation of some ambiguous remote data regarding endogenous processes and materials.

2. Methodology

Methods of experimental petrography are applied here to investigate the geochemistry and phase relationship of the interior of icy moons.

We run a salting-out experiment in a thermostated high pressure chamber equipped with a sapphire window ($\varnothing=2.5$ cm), which allows both, optical examination and Raman spectroscopy analysis. We evaluate mineral transformations and record thermodynamic changes of the system H₂O-MgSO₄-CO₂ using a personalized Labview program. The initial composition of the aqueous solution is 17 wt% MgSO₄, saturated with CO₂. All relevant processes and phases that occur during the variation of pressure and temperature are monitored, photographed and filmed.

3. Results

The experiment starts at room temperature and around 30 bar. At these conditions, the sample is shaken in order to force the formation of CO₂-clathrates.

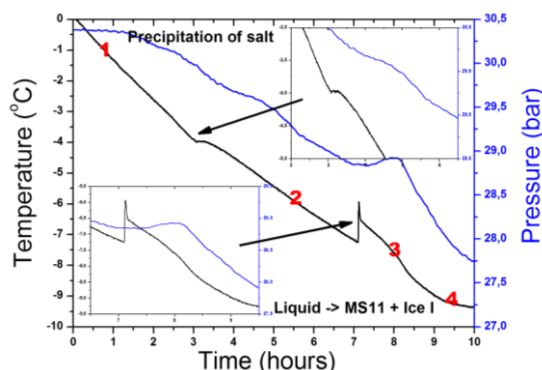


Figure 1: P-T-time diagram registered during cooling. Numbers indicate stages where some textural changes of the process occurred.

Figure 1 shows some phase changes when the temperature is decreasing. Upon cooling at 1°C/h, two main exothermic transformations are registered

in the T curve. The first one takes place as an inflexion at -4°C , in which some salt precipitates because of the salting-out. The second positive peak in temperature corresponds to salt formation after crossing the eutectic. Crystallization of meridianite (MS11) + ice I presents a significant ΔV , which is observed with an abrupt change in pressure [4].

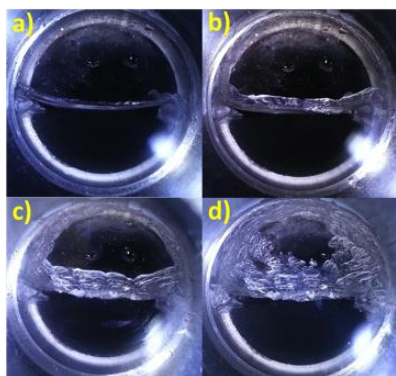


Figure 2: CO_2 -clathrates formation during the primary laminar growth at 2°C and 32 bar.

Some interesting macroscopic features are observed during the T-P evolution. In Figure 2, the laminar growth of clathrate hydrates before cooling is observed. The formation of these primary clathrates occurs between the fluids interface and in contact with the cold surface of the chamber walls and window. They present a significant grain size and are rather transparent. After that, when clathrates occupy all the room left by the liquid, they progressively recrystallize to form a massive texture until the original layering disappear (Fig. 3a and 3b).

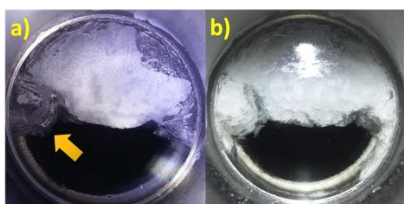


Figure 3: Changes in the crystal texture after primary clathrates crystallization. Note that the original layering pointed by the arrow (a), disappears (b).

Since the experiment starts with a CO_2 -supersaturated solution, some bubbles of CO_2 (g) appear in the liquid (Fig. 4-1) [5]. As mentioned before, clathrates crystallize taking advantage of available interfaces, like the bubbles' surface (Fig. 4-2), producing a spherical clathrate coating.

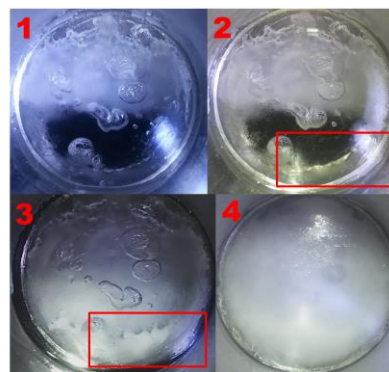


Figure 4: Observations at different points labeled in figure 1. Sulfates potentially crystallizing as consequence of the salting-out are in the red box.

4. Summary

Petrographic and thermodynamic information are used here to follow the evolution of salt-gas-rich fluids during cooling. Several features are observed, e.g. crystal layering and bubble coating, which are associated with change processes in the system. Some of these processes may be expressed on the surface as geological structures, which will be explored by future space missions to the icy moons.

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HPLC-Orbitrap analysis for identification of organic molecules in complex material

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Abstract

We performed High Performance Liquid Chromatography (HPLC) coupled to Orbitrap High Resolution Mass Spectrometry (OHR MS) analysis of Titan's tholins. This analysis allowed us to determine the exact composition and structure of some of the major components of tholins.

1. Introduction

Influx of solar photons and heavy charged particles from Saturn's magnetosphere on Titan's atmosphere - mainly comprised of methane and nitrogen - induce an intense organic photochemistry, which leads to the formation of a large amount of aerosols in suspension in the atmosphere [1]. The exact composition of these aerosols still remains unknown. A fruitful proxy to investigate these aerosols is the use of laboratory experiments that allow producing and studying laboratory analogs of Titan aerosol, so called tholins. We propose here an analysis of tholins with HPLC-OHRMS to unveil the isomeric ambiguity on some of the major compounds among the ~15,000 molecular peaks detected in tholins by high resolution mass spectrometry [3].

2. Methods

Tholins analyzed were produced with the PAMPRE [2] experimental platform at LATMOS, France, and prepared following the protocol detailed in Gautier et al. 2014 [3]. For strict identification of the compounds, chromatograms of tholins were compared to those of high purity standards corresponding to the possible isomers of the most intense molecules detected in tholins OHR mass spectrum [3].

Both tholins and standard compounds were analyzed by HPLC-OHRMS. HPLC was performed on a HPLC Ultimate 3000 system (Dionex) coupled with a LTQ-Orbitrap (ThermoScientific) equipped with an Electrospray Ionization Source (ESI). Analyses were performed in positive ionization mode. We tested three different chromatographic columns to get complementary separation on the compounds tested (octadecyl, cyano and aminopropyl columns).

3. Results

We tested 13 different standard compounds representing possible isomeric composition of 8 of the major molecules detected within tholins using OHRMS. Figure 1 presents a typical chromatogram for a comparison between our tholins sample with a mix of standard at m/z 84.056 on the aminopropyl column.

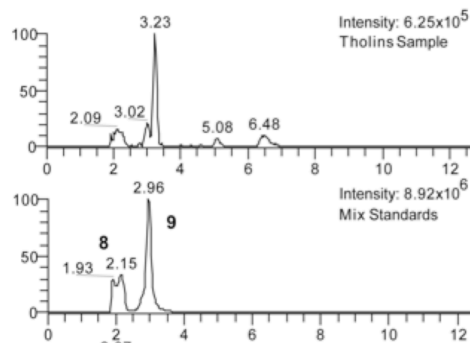


Figure 1: Comparative chromatogram at m/z 84.056 of tholins (top) and a mix of 3-aminopyrazole and 1-methyl-1,2,4-triazole.

Among the compounds tested we were able to strictly identify 6 compounds to be present in tholins. We also determined that 5 of the compounds tested were not present in significant amount, including Hexamethylenetetramine.

All the compounds confirmed has a high content in nitrogen with a ratio N/C comprised between 1.25 and 2, and most of these compounds include heterocycles.

4. Conclusion

Even though N-bearing compounds do not form the entire material (some pure hydrocarbon compounds are detected by OHRMS), it is clear that N-bearing aromatics constitute a significant part of tholins material.

Our work also confirms the importance of having chromatographic separation in the case of such complex material comprising thousands of different molecules, such as Titan tholins, to identify the structure of the molecules detected by OHR-MS. We also point out that, at the very least, two columns are needed to identify compounds due to the high number of possible isomers for a given molecular peak detected in high resolution mass spectrometry.

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Study of high pressure carbon dioxide clathrates hydrates on Ganymede

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Abstract

We present a combined experimental and theoretical investigation of carbon dioxide clathrate hydrates at high pressure. Experimental studies are carried out using several high pressure chambers reaching pressures up to 1 GPa. Using finite cluster and periodic models, we perform computer simulations under the density functional theory approximation that complement and provide a microscopic interpretation of these experiments, thus improving our knowledge of icy satellites such as Ganymede.

1. Introduction

Gas clathrate hydrates are thought to be relevant in the geological evolution and activity of several Solar System bodies where the appropriate conditions of high pressure and low temperature are achieved. Relevant examples of these bodies are the icy moons of the giant planets, in which gas hydrates have been proposed as significant constituents of their icy crusts and water rich reservoirs [1].

Carbon dioxide ice has been detected in the surface of the icy moons of Jupiter, and is supposedly originated by internal degasification. [2-5] Inside of these moons pressure can rise up to 1.3 GPa, as in the case of Ganymede. [6] Prompted by the limited available data and the current interest on the behavior of CO₂ hydrates at high pressure, a combination of new experiments and simulations of this system at different thermodynamic conditions is proposed.

2. Gas clathrate structures

There are several gas clathrate crystallographic structures. All of them have in common that they are composed by a network of water molecules connected via hydrogen bonds following the ice

rules, and usually enclosing nonpolar gas molecules showing guest-host van der Waals interactions.

Among all the possible structures, we will focus on the ones commonly related with the carbon dioxide clathrate hydrates. These are of two types: (i) with cages or polyhedral as in the cubic sI and sII, and in the hexagonal sH structures, and (ii) with channels instead of cages, as in the orthorhombic Filled Ice Structure (FIS). The polyhedra forming these clathrates are labeled as following: 5¹², which are present in the sI, sII and sH structures; 6²5¹², which are in the sI structure; 6⁴5¹², in the sII structure; and 6⁸5¹² and 4³5⁶6³, both in the sH structure. In this notation, A^b means that b faces of A vertices can be found in the surface of the cage.

A common reference on the behavior of gas clathrate hydrates at high pressure is the review of Loveday and Nelmes. [7] Unfortunately, information on carbon dioxide clathrates is not included in that work. The reason might be the lack of interesting results on this system at the time when the review was written. More recently, several studies have appeared, helping to understand a little more the behavior of carbon dioxide-water mixtures at high pressure using XRD and Raman spectroscopy. [8-11] These studies inform of a phase transition from the sI clathrate phase to the FIS structure at 0.7 GPa followed by decomposition of this new phase above 1.0 GPa.

3. Methodology

3.1 Experimental

High pressure experiments are carried out in a new design chamber, called VHPPC (very high pressure planetological chamber). It is able to reach 1 GPa, and temperatures down to 180 K. This chamber has a sapphire window that allows monitoring the system via Raman spectroscopy. A specific Raman head probe is built for spectroscopy analysis inside

VHPPC. The chamber is attached to a high pressure pump that uses a pressure intensifier to reach the required high pressures of Ganymede's interior. To control the temperature we employ a thermostatic bath introducing silicon oil as thermostating liquid. Pressure is measured directly *in situ* inside the chamber using a high pressure manometer, while temperature is measured indirectly as close as possible to the sample (See Figure 1). In addition to these experiments, Sapphire Anvil Cell (SAC) experiments are being also designed.

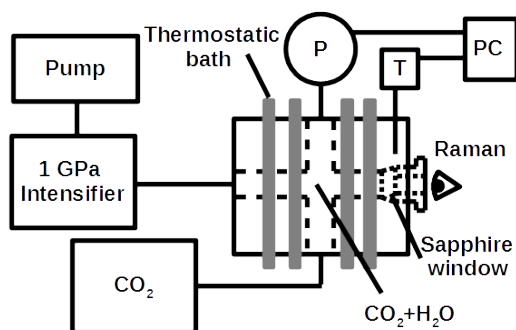


Figure 1: Scheme of experimental setup.

We start forming sI CO₂ clathrates from liquid water saturated with CO₂ gas. Once they form, the system is pressurized up to 1 GPa.

3.2 Theoretical

Density functional theory (DFT) first-principles calculations are also performed to describe the structures and behavior of the carbon dioxide-water system under hydrostatic pressure conditions. Obtaining the equation of state (EOS), energetic stability and infrared and Raman spectrum are the main objectives of these calculations. These properties help to analyze the experimental results. A detailed study of guest-host interactions is also underway. Quantum Espresso, [12] Gibbs2 [13] and Gaussian09 [14] are the main codes used to obtain these properties.

4. Summary

High pressure behavior of carbon dioxide-water mixtures, at 180-280 K and 0-1 GPa conditions, is studied combining both experimental and theoretical approaches using a new VHPPC that can reach the GPa regime for experiments and first-principles DFT finite and periodic simulations.

Acknowledgements

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Lipid biomarker preservation under extreme and prolonged dryness in the Atacama Desert, Chile and implications for Mars

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Abstract

Lipid biomarkers were analyzed from soils collected in the Yungay hyperarid core of the Atacama Desert. This region has experienced extreme and prolonged (>2 Ma) hyperaridity, thereby greatly limiting biologic activity over that timescale. Total lipid extracts reveal a remarkable degree of preservation in the diversity of lipid biomarkers despite the age of the soils, indicating that typical diagenetic processes influencing lipid destruction are very depressed in the Atacama.

1. Introduction

Molecular fossils or biomarkers [1] are the most direct biosignatures of early life on Earth and a key target in the search for life elsewhere [2]. The geologically short-lived nature of the majority of molecular biomarkers presents a challenge for reconstructing potential past biologic activity on Mars. Lipid biomarkers, which have a refractory hydrocarbon backbone, are known to survive oxidative degradation and are robust indicators of microbial presence and activity in extant ecosystems and in past environments recorded billions of years ago [3]. Prior to lithification, the environmental conditions and the biotic and abiotic processes that impact initial biomolecular preservation are key to establishing a geologically significant biomarker record.

The hyperarid core of the Atacama Desert in northern Chile offers a unique natural laboratory to investigate biomarker taphonomy under prolonged hyper-aridity. This region has been arid to semi-arid since the late Jurassic (150 Ma) and has experienced prolonged and largely continuous hyperaridity for at least the last ~2 Ma, possibly up to 15 Ma [4,5,6]. This extreme aridity has dictated the pedogenesis [7], lack of

habitation by plants or lichens, a sparse microbial population, and an inventory of organic carbon in the soils lower than elsewhere on Earth [8,9,10,11].

This work focuses on understanding the accumulation on degree of preservation of lipids in million-year-old hyperarid soils where primarily abiotic conditions influence their taphonomy.

2. Methods

2.1 Sampling

Due to the low biomass content in the soils, samples were collected by scientists wearing cleanroom suits, masks, glasses, and gloves to minimize contamination during sampling. Soils were collected with solvent cleaned tools, placed into ashed glass jars, and kept frozen until returned to NASA Goddard Space Flight Center for storage at -20 C°.

Samples were collected in September 2014 with depth in a ~2 m deep soil pit in the Yungay hyperarid core of the Atacama Desert, which experiences << 2 mm of precipitation per year. Surface soils were also collected in a slightly less hyperarid region near Chañaral which experiences ~12 mm of precipitation per year.

2.2 Laboratory Analysis

For each unique sample, approximately 100 g of soil was pulverized with a mortar and pestle. Soils were extracted three times using a modified Bligh Dyer [12] extraction protocol in which a slurry was created using a monophasic mixture of geo-clean water, methanol, dichloromethane, and soil. This mixture was separated and then resultant lipid fraction was collected and evaporated to near dryness. Medium acid methanolysis [13] and derivatization with Bis-

(trimethylsilyl) trifluoroacetamide (BSTFA) was performed on the concentrated lipid fraction to ensure detection of both free fatty acids and membrane-bound fatty acids. Extracts were run on GC-MS and LC-MS. Peak areas were quantified by comparison to an internal standard.

Additionally, evolved gas analysis (EGA) was performed on approximately 20 mg of pulverized soil. EGA parameters were similar to that of the Sample Analysis at Mars (SAM) instrument aboard the Mars Science Laboratory.

3. Preliminary Results

3.1 Total Lipid Extracts

A number of classes of lipids were identified in the total lipid extracts of soils including fatty acid methyl esters (FAMES), free fatty acids, primary fatty alcohols, monoalkylglycerol ethers, steranes, plant waxes, mid-molecular weight organic acids, and glycerol dialkyl glycerol tetraethers.

Despite the age of the deposits, the lipid content resembled that of a modern microbial population because the labile (fragile) lipids such as ester-linked membrane fatty acids were not degraded. Additionally, there was high relative concentration of free fatty acids (FFAs) and mid-molecular weight organic acids. FFAs are generated when cells die and their cellular membranes break down. These compounds are a rich food source for other microbes, and typically do not persist in the environment. The detection of FFAs in Yungay soils indicate a lack of microbial degradative activity, which supports the growing body of evidence that typical diagenetic processes influencing lipid destruction are very depressed in the Atacama.

Significant trends were observant in the abundance and diversity of lipids between surface and subsurface samples, and as a function of rainfall (Figure 1). The diversity and abundance of lipids at depth points to a remarkable degree of preservation under prolonged and extreme hyperaridity and in the absence of significant biological activity.

3.2 SAM-like Evolved Gas Analysis

Surface soils across a precipitation gradient transect from Yungay to Chañaral had very similar EGA

signals, dominated by H₂O and CO₂. O₂ and HCl traces were relatively featureless and two to three orders of magnitude less abundant than H₂O. The SO₂ signal was quite complex, with four major peaks. In soil pit samples known to contain more organic material than surface soils, masses consistent with cholorobenzene were present in the EGA signal.

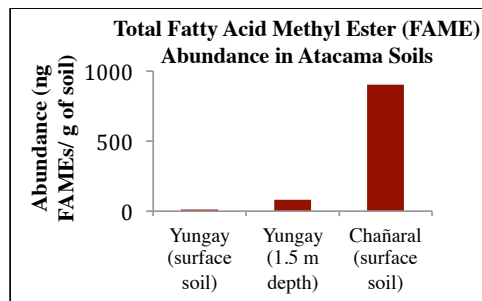


Figure 1: Membrane-bound fatty acid content of soils from the Atacama Desert.

Acknowledgements

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