

Heterogeneous solid/gas chemistry of organic compounds related to comets, meteorites, Titan, and Mars: Laboratory and in lower Earth orbit experiments

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Abstract

To understand the evolution of organic molecules involved in extraterrestrial environments and with exobiological implications, many experimental programs in the laboratory are devoted to photochemical studies in the gaseous phase as well as in the solid state. The validity of such studies and their applications to extraterrestrial environments can be questioned as long as experiments conducted in space conditions, with the full solar spectrum, especially in the short wavelength domain, have not been implemented. The experiments that are described here will be carried out on a FOTON capsule, using the BIOPAN facility, and on the International Space Station, using the EXPOSE facility. Vented and sealed exposition cells will be used, which will allow us to study the chemical evolution in the gaseous phase as well as heterogeneous processes, such as the degradation of solid compounds and the release of gaseous fragments.

Four kinds of experiments will be carried out. The first deal with comets and are related to the Rosetta mission, the second with Titan and are related to the Cassini–Huygens mission, the third with the search for life-related organic compounds on Mars and, finally, the fourth are a continuation of previous studies concerning the behavior of amino acids in space.

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1. Introduction

Solar UV radiation is a major source of energy to initiate chemical evolution towards complex organic structures, but it can also photodissociate the most elaborate molecules. Thus, Solar UV can erase the organic traces of past life on the surface of planets, such as Mars (Oro and

Holzer, 1979), destroy organic molecules present on meteorites (Barbier et al., 1998), influence the production of extended sources in comets¹ (Cottin et al., 2004), or initiate chemistry in Titan's atmosphere (Sagan and Thompson,

¹ The spatial distribution in the coma of some molecules is not compatible with an emission from the nucleus only or photolysis of a gaseous known parent compound. This supports the hypothesis that there is an (at least one) additional source which produces the observed molecule as it spreads outwards the nucleus. This is what is called an *extended source*.

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1984). AMINO, PROCESS, and UV-olution are three experiments selected to be flown on the EXPOSE facility on the International Space Station, or on the BIOPAN facility during the FOTON M3 space capsule mission. The goal of our experiments is to improve our knowledge of the chemical nature and evolution of organic molecules involved in extraterrestrial environments with astrobiological implications. Most of the previous experiments implemented in space so far were carried out in vented cells exposed to Solar UV radiation (Barbier et al., 1998, 2002b; Boillot et al., 2002). In such cases, solid organic samples are deposited behind a window transparent to UV, and exposed to the solar flux. If the studied molecule is sensitive to energetic photons, its photodestruction can be quantified after the experiment when sample are brought back to Earth for analysis. However, gaseous products resulting photolysis are lost in space. A first use of sealed cells is reported in Ehrenfreund et al. (2007). This allows studying chemical evolution in the gaseous phase as well as heterogeneous processes (degradation of solid compounds and release of gaseous fragments). In our case, both vented and sealed exposition cells will be used. Four kinds of experiments will be carried out. The first deal with comets and are related to the Rosetta mission; the second deal with Titan and are related to the Cassini–Huygens mission; the third are related to the search for organic compounds on Mars within the framework of the preparation of MSL 2009 instrument SAM (Cabane et al., 2004), while the fourth are a continuation of previous studies about the behavior of amino acids in space (Barbier et al., 1998).

2. Astrobiological relevance: organic molecules in the Solar System and the origins of life

These experiments, through the choice of the targeted Solar System environment and targeted compounds, are closely linked to the field of exo-astrobiology. Primitive terrestrial life emerged with the first aqueous chemical systems able to transfer their molecular information and to evolve. Unfortunately, the direct clues which may help chemists to identify the molecules that participated in the emergence of life on Earth about 4 billion years ago have been erased. It is generally believed that primitive life originated from the processing of organic molecules by liquid water. Oparin (1924) suggested that the small organic molecules needed for primitive life were formed in a primitive atmosphere dominated by methane. The idea was tested in the laboratory by Miller (1953) when he exposed a mixture of methane, ammonia, hydrogen, and water to electric discharges. In his initial experiment, he obtained a great diversity of organic molecules, some of which, like amino acids, are key ingredients to life as we know it on Earth. Miller's laboratory synthesis of amino acids occurs efficiently when a reducing gas mixture containing significant amounts of hydrogen is used. Similar results are observed if the same kinds of experiments are conducted under UV photolysis. However, the actual composition of the primitive Earth's

atmosphere is still unknown. Nowadays, most geochemists favor a neutral or weakly reducing atmosphere dominated by carbon dioxide (Kasting, 1993). Under such conditions, chemical evolution and the production of the building blocks of life appear to be very limited if only endogenous syntheses in primitive Earth atmosphere are considered (Schlesinger and Miller, 1983). Even if the H₂ content of early atmosphere is still under discussion and model dependent (Tian et al., 2005, 2006; Catling, 2006), other sources have to be investigated. Nowadays, the origin of the first ingredients in the recipe for life between exogenous delivery and endogenous syntheses is debated, and in both cases, photolysis plays a central part in initiating the first steps of chemical evolution.

Moreover, the question of the origin of life on Earth is tightly related to the possibility that life may also have arisen on our neighbor planet, Mars. It is now established that more than 4 billion years ago, Mars environment was similar to that of the early Earth (Bibring et al., 2006), with a dense atmosphere and liquid water. If life developed on Mars, independently of the Earth, this could mean that the jump from chemistry to biology is written in the laws of the “natural” evolution of organic matter each time the requirements “organic matter + liquid water” on a rocky planet are fulfilled. Therefore, the search for organic material at the Martian surface is critical. (Water and organic molecules are not enough – the silicates and other minerals are also important – providers of energy from chemical reactions going on at the surfaces; stable surfaces upon which organic molecules can achieve the necessary conformation; once life starts, providers of energy and carbon....)

2.1. Exogenous delivery

Among the hypotheses investigated to explain the origin of the biological building blocks, the seeding of the primitive Earth by molecules from outer space is of growing interest. Each year more and more molecules are detected in the interstellar medium (see for instance Ehrenfreund and Charnley (2000), for a review on this topic). Most of these compounds are based on C, H, O, N, and reveal a complex organic chemistry in molecular clouds, in contrast with the poor complexity of the chemical processes on the primitive Earth environment if the H₂ content of the atmosphere was low. Comets and primitive meteorites may have kept the memory of the composition of the organic rich interstellar medium or presolar nebula, which gave birth to our Solar System. The study of meteorites, particularly carbonaceous chondrites that contain up to 5% by weight of organic matter, has allowed a close examination of extraterrestrial organic material in the laboratory. Analysis of the Murchison meteorite, whose formation is contemporary with the birth of the Solar System, has revealed more than 500 organic compounds and among them, several nucleic bases and 74 amino acids, 8 of these being used by contemporary proteins (Cronin et al. (1988) or Botta

and Bada (2002), for a recent review). Comets are another source of interesting organics for the primitive Earth. To date, more than 20 gaseous molecules have been detected in the atmosphere (including H₂O, CO, CO₂, CH₃OH, H₂CO, HCN, NH₃) (Biver et al., 2002). However, until the in situ analysis of comet 67P/Churyumov–Gerasimenko in 2014 by the Rosetta mission, we have no direct information about the molecular composition of the nucleus, which is suspected to be extremely rich in organic compounds of high molecular weight. The presence of such complex refractory material is inferred from in situ analysis of cometary grains (Kissel and Krueger, 1987; Kissel et al., 2004), from the observation of the density distribution of molecules such as H₂CO, CN or CO, which can only be explained by the slow degradation of “unseen” complex refractory material (such a phenomenon is usually referred as an “extended source” (Cottin et al., 2004; Fray et al., 2006), and from laboratory simulation of cometary ice analogues (for reviews see Cottin et al. (1999); Despois and Cottin (2005)). The large range of chemicals observed or strongly suspected to be present in comets suggests that comets may have played a key role in the chemical evolution leading to the emergence of life on Earth (Oro and Cosmovici, 1997). Chemical evolution in comets and meteorites, production of extended sources, and the residual organic component that can be imported to planets, are strongly dependent of photochemical processes that need to be documented (Fig. 1).

2.2. Endogenous synthesis

Unlike the primitive Earth, the composition of Titan's atmosphere (N₂ and CH₄ at a few percent level) implies

that it is an extremely efficient “chemical factory”. The simplest molecules such as molecular nitrogen and methane, submitted to Solar UV photolysis and the impacts of electrons trapped in the magnetosphere of Saturn, evolves towards complex organic hazes hiding the surface of this satellite of Saturn (Sagan and Thompson, 1984). Most probably, the lack of liquid water on Titan prevents the chemical evolution towards life. However, this planet offers an unique opportunity to study endogenous syntheses of exobiological interest since it has been shown that the hydrolysis of laboratory analogues of Titan's organic haze (Tholins) release amino acids (Khare et al., 1986). Therefore, considering the lack of direct traces from Earth's primitive environment about 4 billions years ago or more, when prebiotic chemistry gave birth to the first living systems, it is of prime interest to study extraterrestrial environments in which prebiotic syntheses may occur. Titan's case will tell us how far chemical evolution can go with a chemically favorable atmospheric composition but in the absence of liquid water.

Moreover, recent data from the Cassini–Huygens space-craft, orbiting the Saturnian's system have raised new questions regarding the photochemistry of Titan's atmosphere: where in the atmosphere is the origin of this organic photochemistry located? In the stratosphere or in the ionosphere, where evidence of exceptional activity was revealed by Cassini–Huygens? What is the chemical nature of the solid end product of methane photochemistry? Is it a PAH-like material or high molecular weight polynes? What are the possible photoproducts of Titan's haze particles? Just as for comets, Solar UV driven photochemistry, plays a key role in the evolution of organic chemistry of Titan.

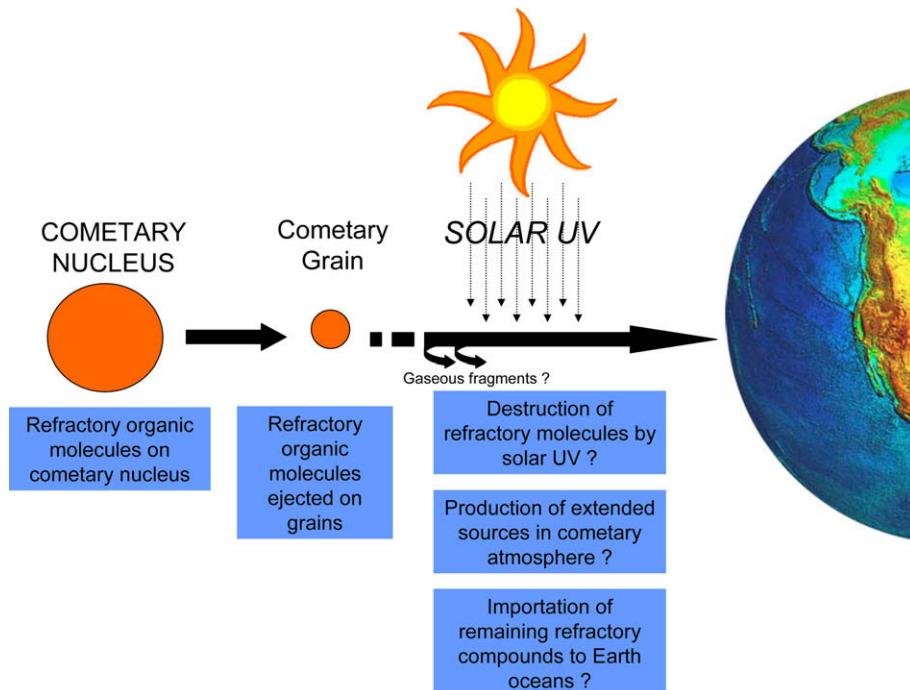


Fig. 1. History of a complex organic molecule from a cometary nucleus to potential importation to Earth on grains.

2.3. Life on another planet?

One of the main goals of astrobiology is the search for and the study of extraterrestrial life. This has important implications for our understanding of the origins of life on Earth which remains, so far, the only planetary body where we are sure that life is present.

Mars is certainly the best target in the Solar System to search for past and even for present extraterrestrial life. Indeed it is now more and more obvious that the red planet has seen liquid water for a long period of time and in particular more than 4 billion years ago (Bibring et al., 2006), when life was probably already present on the Earth, and when environments on both planets were very similar (Westall, 2005), contrary to what they are today.

Hence, it is reasonable to assume that the same processes of chemical evolution, which allowed the emergence of life on Earth, through prebiotic chemistry and the increasing complexity of organic matter in liquid water towards self-replicating systems, also occurred on Mars. Since the degradation of surface conditions on Mars (3.8–3.5 Ga), both planets have followed different evolutions and life may have disappeared from the red planet, or, if it has survived it may be now located in the subsurface of the planet, protected from the hostile surface.

However, in both cases, past or present biological activities should feed the Martian environment with many organic and inorganic compounds, including important and specific biomarkers. If life never arose on Mars, in spite of a noticeable prebiotic chemistry, there is a good probability that traces of the prebiotic processes should still be present after 4 billion years of evolution of the red planet, since the tectonic activity that has eliminated all rocks older than about 4 Gy on Earth was of extremely limited extent on Mars. Prebiotic signatures should therefore be detectable near the surface or in the surface rocks. In addition, since Mars is still experiencing a noticeable bombardment of meteoritic and cometary material, its surface should also include organic matter imported through these processes. To date, such compounds have never been detected on Mars. Photolysis of organic molecules at the surface of Mars is a key factor determining their evolution and interest to be searched for with the next Martian rovers.

3. Some basics of photochemistry in Earth laboratories and in Space

Earth orbit is subjected to intense radiation of both solar and galactic origin. Cosmic radiation entering the Solar System is composed of protons, electrons, α -particles and heavy ions. Solar particle radiation is emitted as solar wind during chromospheric eruptions. It is composed of up to 95% of protons, α -particles, and heavy ions. Protons and electrons do not reach the Earth because they are trapped by the geomagnetic field. On the other hand, the solar electromagnetic radiation above the Earth's atmosphere is composed of 45% infrared radiation, 48% visible light,

and only 7% UV light (Horneck et al., 2002). But the latter photons are the most energetic, and at sufficient levels can induce photochemical evolution.

Experiments to irradiate organic compounds can easily be implemented on Earth with specific sources, such as ion or electron guns, or UV lamps. However, it is very difficult to combine all the energetic sources occurring in space to their full extent. For example, in the laboratory, we can either choose to irradiate a molecule at 122 nm (H_2/He lamp – with MgF_2 window) or 147 nm (Xe lamp – with MgF_2 window) or 193 nm (CH_4/He lamp – with quartz window). Fig. 2 is a comparison of the spectrum of Solar UV emitted by the Sun between 100 and 200 nm, with typical spectra UV lamps used in the laboratory for photochemical studies in this UV domain.

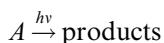
Our goal is to improve our knowledge of the chemical nature and evolution of organic molecules involved in extraterrestrial environments and/or with exobiological implications. Many experimental programs are devoted to photochemical studies of molecules in the gaseous phase as well as in the solid state. Ground laboratory experiments have been (or will be) implemented on the target compounds that we have selected for this program. However, the validity of such studies and their application to extraterrestrial environments can be questioned as long as experiments conducted in space conditions, with the full solar spectra especially in the short wavelength domain, have not been implemented.

Moreover, compared to ground experiments, space is a unique laboratory allowing the exposure of samples to all space parameters simultaneously and irradiating many samples simultaneously under strictly identical conditions.

Therefore, Earth orbit provides a unique opportunity to study the effects of UV radiation on organic molecules.

Solar energy is the main “engine” for chemical evolution in the Solar System.

The photodestruction of a molecule can be written:



with A being a molecule, and products the resulting fragments. This photochemical reaction is fully understood with the knowledge of the photodestruction rate of A , and the nature of the products. If $[A]$ is the number density of A (cm^{-3}), the photolysis rate is usually described by:

$$\frac{d[A]}{dt} = -J[A] \quad (1)$$

with $J = \int_{\lambda} \sigma_{\lambda} I_{\lambda} d\lambda$, σ_{λ} being the destruction cross-section of the molecule (cm^2), which is actually the product of the cross-section of the molecule and the quantum yield of the photolysis reaction, and I_{λ} is the UV flux (photons $\text{s}^{-1} \text{cm}^{-2}$). Both σ and I are a function of the wavelength λ .

The integrated form of Eq. (1) is:

$$[A](t) = [A]_0 \exp(-Jt). \quad (2)$$

J is then experimentally determined through the measurement of A from the slope of a plot of $\ln([A])$ vs. t :

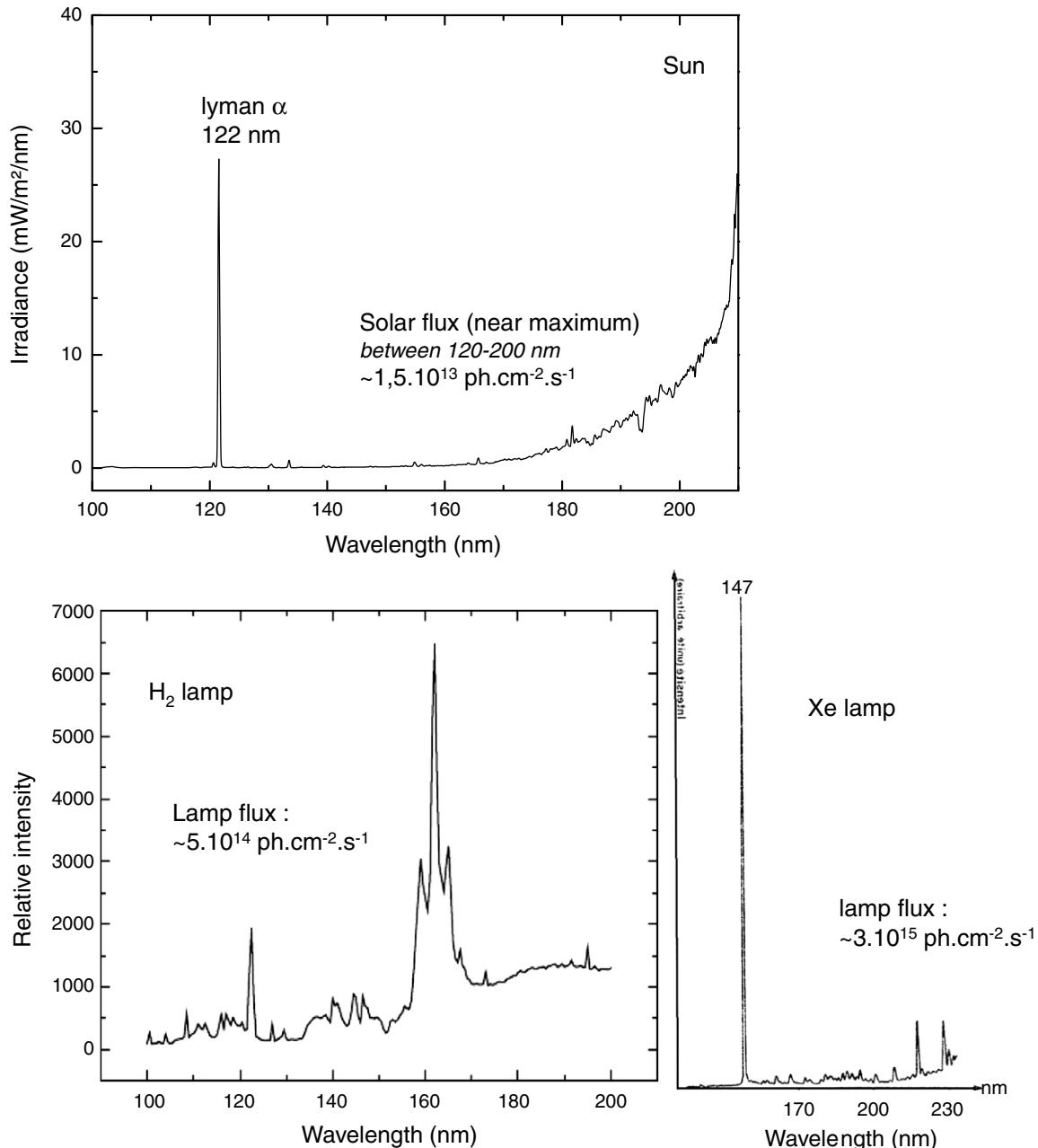


Fig. 2. Comparison of the solar spectrum between 100 and 200 nm (Thuillier et al., 2004) with two laboratory UV lamps (H₂ and Xe lamps) (Bossard, 1979; Cottin et al., 2003).

$$\ln([A]) = -Jt + \ln([A]_0). \quad (4)$$

Such a study is quite simple to implement in the laboratory, when in situ measurement of A is feasible, or if the experiment can be repeated for different times of photolysis (Gerakines et al., 1996; Cottin et al., 2003). Products can be analyzed with different analysis tools, such as infrared spectrometry, gas chromatography, etc.

However, for experiments conducted in space, only two points are available to plot Eq. (4): $t=0$ (preparation of sample before launch) and $t=\text{total time of exposition in orbit}$, which makes the estimation of J quite inaccurate.

Therefore, instead of plotting Eq. (4) as a function of time, J can be derived if several samples with different $[A]_0$ are exposed for the same duration, plotting $\ln[A]$ as a function of $\ln[A]_0$. Thus, for the same total time of exposition, with different initial abundances in several exposed samples, J can be measured as shown in Fig. 3.

4. Experimental procedure

4.1. Ground experiments

Experiments in space are associated with a ground support experimental program already in progress. At the

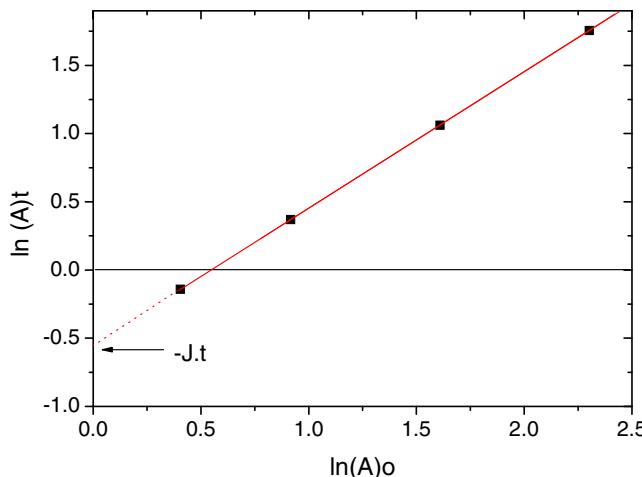


Fig. 3. Measurement of J in space experiments plotting $\ln[A]_t$ as a function of $\ln[A]_0$.

Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), Service d'Aéronomie (SA), and Centre de Biophysique Moléculaire (CBM) we have access to:

- a full potential for photolysis experiments at different wavelengths in far UV,
- synthesis facilities for tholins, and other non-commercial organic products,
- a large range of analysis tools: IRTF, UV, GC–MS, HPLC.

LISA has already developed the tools to study the effect of photolysis on gaseous mixtures or solid molecules. In the framework of cometary study, the SEMAPHORE cométaire experiment (Fig. 4) already yielded quantitative results concerning the photodegradation of polyoxymethylene: POM ($-(\text{CH}_2-\text{O})_n-$, polymer of formaldehyde) (Cottin et al., 2000), hexamethylenetetramine: HMT ($\text{C}_6\text{N}_4\text{H}_{12}$) (Cottin et al., 2002) and HCN polymers (Fray et al., 2004). As shown in Fig. 4, the compounds can be irradiated at different wavelengths. Destruction of the initial material can be studied, as well as, the simultaneous formation of gaseous photolysis products. Successful results have already been derived from laboratory work concerning POM, allowing one step further into understanding H_2CO extended source in comets (Cottin et al., 2004; Fray et al., 2006). It has been shown that a few percent of POM in mass on grains can explain the observed distribution of formaldehyde in comets P/Halley and Hale–Bopp (C/1995 O1). It is now crucial that such laboratory results be validated by space experiments. Concerning other cometary or meteoritic molecules, or Titan program with Tholins or gas mixtures, they can also be irradiated with the same setup.

But as already mentioned above, the full solar spectrum cannot be reproduced with such an apparatus. Therefore, we can only access wavelength dependant results with an extrapolation to other wavelengths, whose reliability is limited by the few UV lines we can access with the setup (122, 147, and 193 nm in our case).

A larger range in wavelengths (112–370 nm) is achieved in the CBM simulation chamber presented in Fig. 4b. However, with this chamber, the gaseous photoproducts cannot be analyzed during the photolysis.

Concerning organics on Mars, a new experimental device has been devised, MOMIE (Martian Organic Material Irradiation and Evolution) (Fig. 5). Its principle is relatively simple: to stimulate the evolution of target molecules either on their own or in a mineral matrix (Mars regolith analogues) under various forms of energy (UV lamp, laser...). Spectroscopic (in situ) and chemical (in situ or a posteriori) analyses allow qualification/quantification of the degradation of the target molecules. Since most of the energetic range of Solar UVs is filtered by the Martian atmosphere, in this case, a high pressure Xenon lamp provides a rather satisfactory simulation of the solar flux reaching the Martian soil, i.e. for wavelength above 190 nm (Fig. 6).

4.2. Space laboratories

The experiment series presented in this paper is built upon the results of a previous set of experiments already implemented in space. The latter were mainly devoted to the exposition of amino acids to space conditions (solar light, galactic cosmic rays (GCR), temperature, and vacuum).

DUST experiment on BIOPAN-1 in 1994: (Barbier et al., 1998).

DUST experiment on BIOPAN-2 in 1997: (Barbier et al., 2002b).

PERSEUS-EXOBIOLOGIE experiment on MIR in 1999: (Boillot et al., 2002).

These successful experiments have shown that amino acids are readily destroyed in space unless they are protected in a mineral matrix.

The new experiments are summarized in Table 1, and described in the next sections of this paper. International Space Station average altitude is about 340 km, and FOTON altitude ranges between 250 and 300 km.

For AMINO, PROCESS, and UV-olution, the procedure followed is:

For one molecule studied at a specific $[A]_0$, then two samples are exposed in space (influence of UV, GCR, and T), two samples are exposed as dark controls (influence of GCR and T), two ground controls are kept in the dark for the same duration as the space exposition and with a similar temperature history (influence of T), and two ground controls are kept in the dark at constant T (273 K).

4.2.1. AMINO (EXPOSE-R/International Space Station)

The AMINO experiment has been accepted to be part of the first wave of experiments that will be implemented on the EXPOSE-R facility (Fig. 7a) on the Russian module of the International Space Station. Along with amino

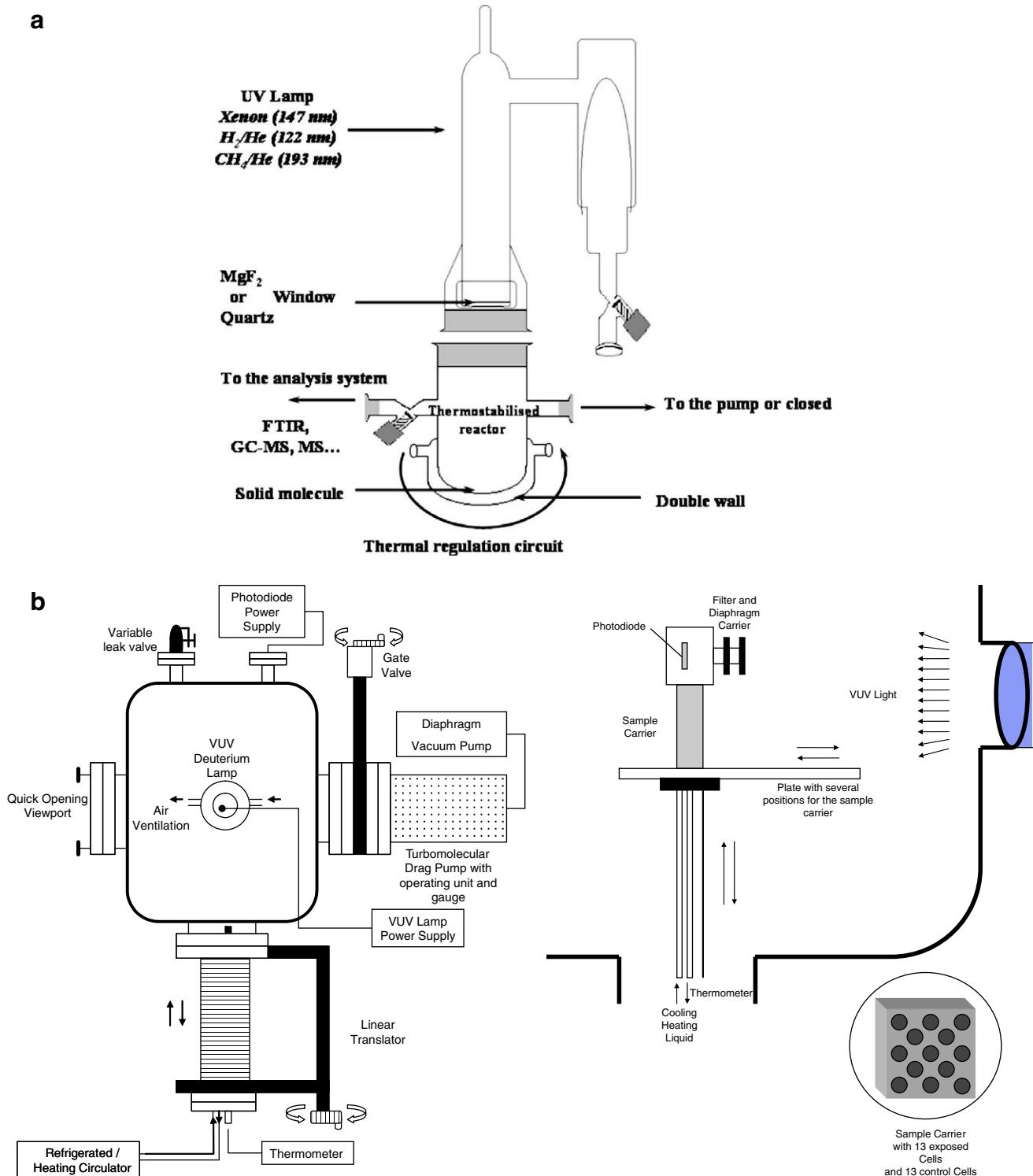


Fig. 4. (a) Experimental setup for laboratory experiments supporting space irradiation experiments. Solid molecules are deposited at the bottom of a Pyrex reactor and placed under vacuum. The solid compound can be photolyzed at different wavelengths and at a controlled temperature. The UV lamp is a Pyrex bulb filled with an appropriate gas or gas mixture according to the emitted wavelength: H₂ (2%) in He for a 122 nm emission (Lyman α), Xe for 147 nm, or CH₄ (1%) in He for 193 nm. Discharge in the lamp is initiated with a Tesla coil and the gas is excited by a microwave generator at 2450 MHz. (b) Left: Irradiation chamber at the Centre de Biophysique Moléculaire in Orléans (volume about 20 l, deuterium lamp irradiation: 112–370 nm, temperature range: -50°C to $+200^{\circ}\text{C}$). Right: Enlarged views of the sample holder inside the chamber.

acids, samples relevant to cometary or Titan's chemistry will be exposed, and for the first time gaseous mixtures will be submitted to photolysis in space thanks to closed cells

specifically designed for those new generation experiments. Other experiments, beyond the scope of this paper since they deal with biology, are also included in AMINO (Bar-

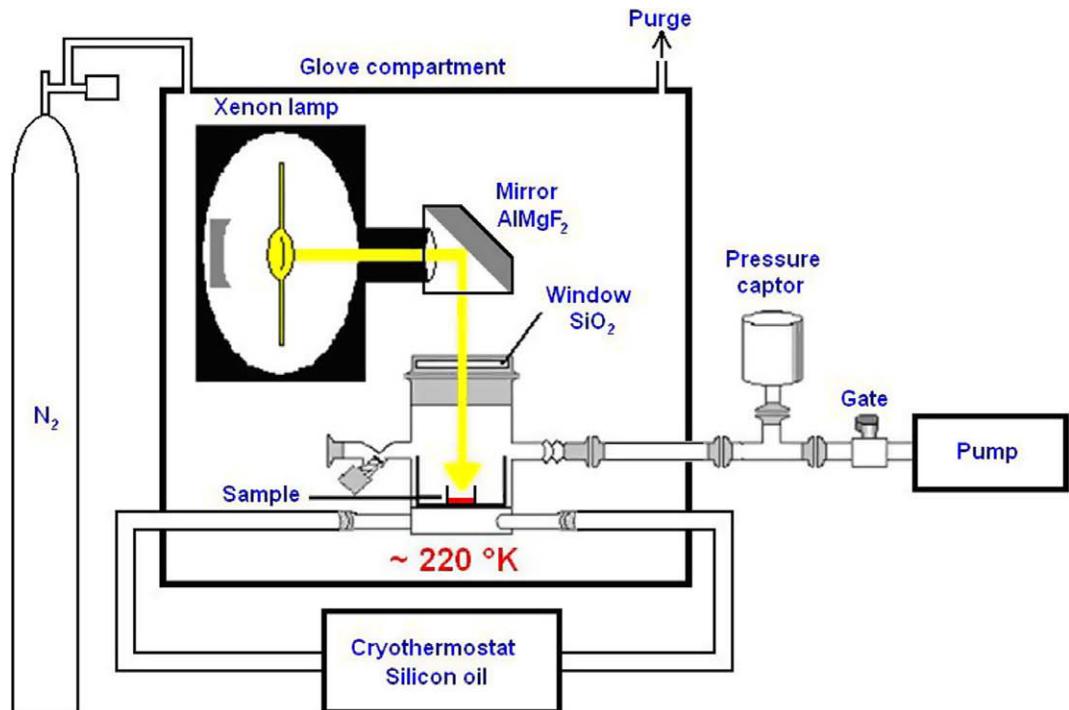


Fig. 5. The MOMIE experiment is composed of a glass reactor in which organic molecules are introduced. This reactor is pumped to vacuum ($\sim 10^{-2}$ mbar) and cooled down to a temperature of approximately -55°C with a cryothermostat (KRYOMAT RUL 80, LAUDA). The irradiation source is a Xenon lamp (Arc Source "Research" 50–200 W Xe and Hg(Xe), LOT ORIEL) (for more details see Stalport et al., 2008).

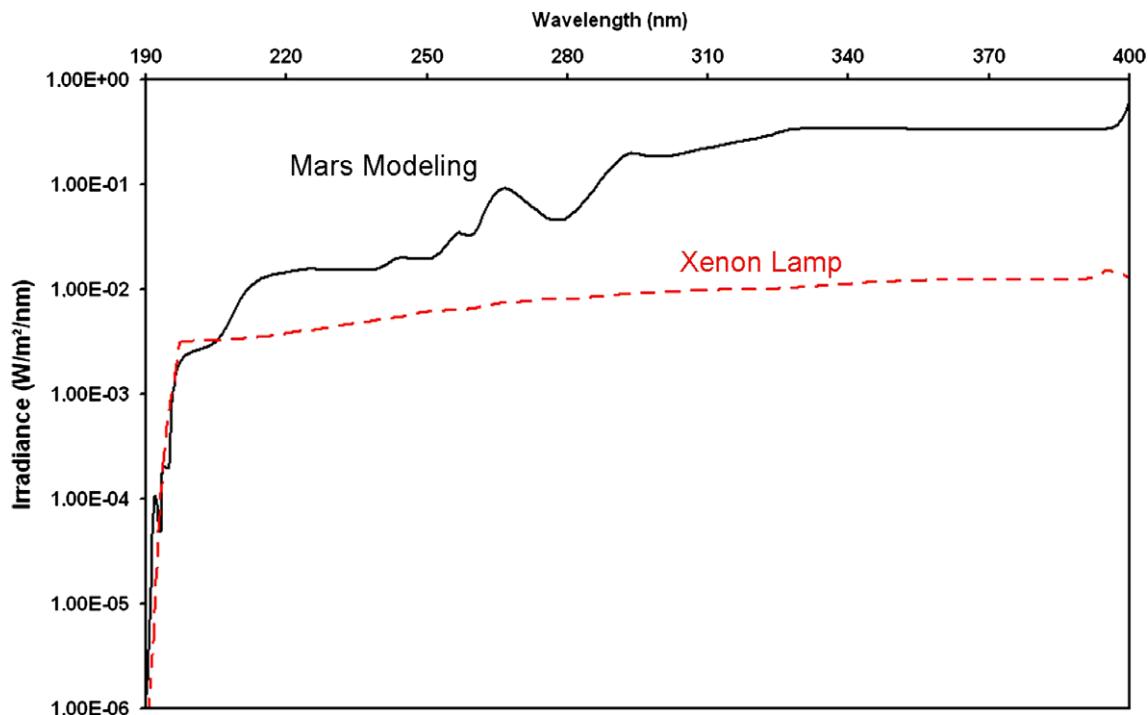


Fig. 6. Spectrum of the Xenon lamp (dotted line) in the MOMIE reactor compared to the Mars modelling spectrum (Patel et al., 2002). Both spectra are very close and cross each other at approximately 190 nm.

bier et al., 2002a). Two sample holders, similar to the one shown in Fig. 6b, are devoted to AMINO, with the following distribution of samples: 1/4 – amino acids, 1/4 – comet

related experiment, 1/8 – Titan related experiments, the remaining being biology related material. Each sample holder can receive 20 samples exposed to the Sun, and 20

Table 1

List of experiments dedicated to astrochemistry using the EXPOSE and BIOPAN facilities

Name	Space facility	Space vehicle	Launch	Duration	Principal investigator	Related solar system objects
AMINO	EXPOSE-R	ISS (Russian module)	2008 (1st semester)	1 year	A. BRACK (\rightarrow end of 2006) then H. COTTIN	Comets, Meteorites, Titan
PROCESS	EXPOSE-EuTEF	ISS (European module: Columbus)	2008 (1st semester)	1.5 year	H. COTTIN	Comets, Meteorites, Titan, Mars
UV-olution	BIOPAN	FOTON	September 14th, 2007	11.8 Days	H. COTTIN	Comets, Titan, Mars

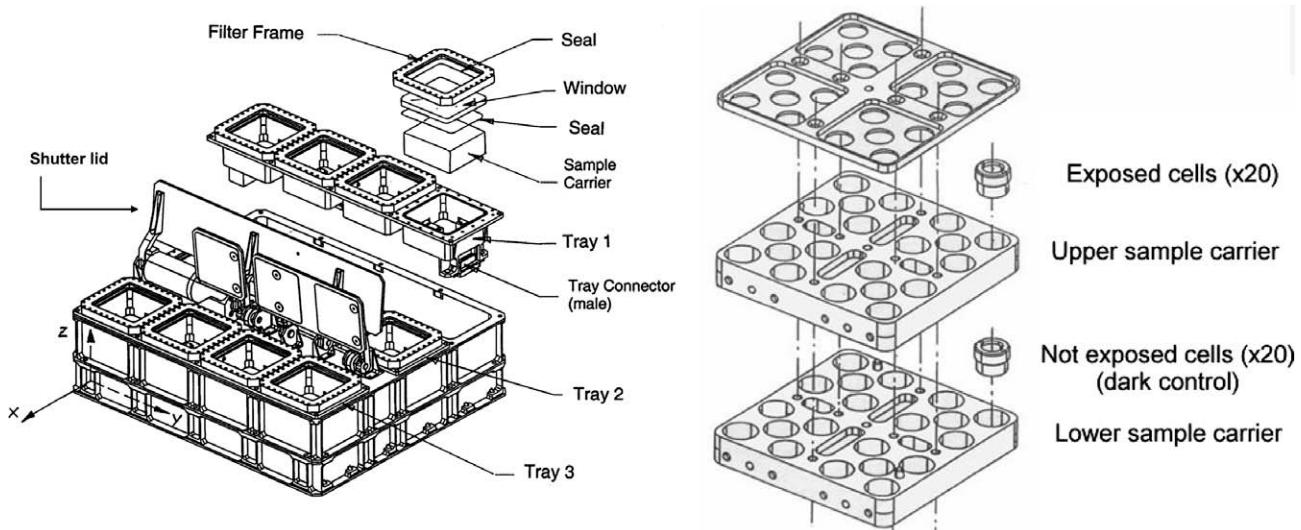


Fig. 7. The EXPOSE facility (480 × 520 × 327.5 mm) is made of three experiment trays into which four square sample carriers (77 × 77 × 26 mm) are fitted (left). For AMINO and PROCESS, each sample carrier is designed to receive up to 20 exposition cells (right). Shutter lids will be open during the whole flight. Pictures courtesy of Kayser-Threde GmbH.

dark in-flight controls. With the closed cells, AMINO allows us to study chemical evolution in the gaseous phase, and to collect the gaseous fragments produced when refractory compounds are irradiated. Those cells are presented in Section 4.2.4 of this paper. To date, the launch of the AMINO experiments is scheduled for the end of the first semester of 2008 for an exposition duration of one year. After exposition, the samples will be delivered back to Earth via a US Space Shuttle or a Russian PROGRESS capsule.

Due to the rotation of the International Space Station around the Earth and upon itself, it is important to note that for a duration of one year in space, the integrated time of full exposition of the cells to the Sun is only approximately 10 days.

André Brack (CBM, Orléans, France) was the PI of this experiment until the end of 2006. Hervé Cottin (LISA, Créteil, France), took charge of the experiment since then.

4.2.2. PROCESS (EXPOSE-EuTEF/International Space Station)

PROCESS is a second experiment, similar to AMINO, that will be set outside the European module Columbus on the International Space Station. A second EXPOSE

facility, called EXPOSE-EuTEF (European Technology Exposure Facility) will be flown on Columbus at the beginning of 2008. PROCESS is dedicated to the study of photochemical processes relevant to comets (1/4), meteorites (1/4), Mars (1/4), and Titan (1/4). Two sample holders (with a total of 40 exposed samples, and 40 in-flight dark controls) are attributed to PROCESS. The duration of the experiment in space is about 1.5 years, but may vary depending on future Space Station extravehicular activities. As for EXPOSE-R, after exposition, the samples will be delivered back to Earth via a US Space Shuttle or a Russian PROGRESS capsule.

Hervé Cottin (LISA, Créteil, France) is the PI of this experiment.

4.2.3. UV-olution (BIOPAN/FOTON M3)

BIOPAN is an ESA multi-user space exposure facility, designed for exobiology, radiation biology, radiation dosimetry, and material science investigations in space (Demets et al., 2005). It carries its payload experiments on the inner side of two 38 cm circular plates (one lid and one bottom plate) facing each other at launch and recovery. After orbit insertion, the lid is opened to expose the package to space conditions, until it is closed and sealed

before the recovery of the capsule. BIOPAN is attached to the outer shield of a FOTON Russian capsule. UV-olution will be flown on BIOPAN 6, on the capsule FOTON M3. Launch is scheduled on September 14th 2007, for an 11.8-day duration in orbit (Fig. 8).

UV-olution is split into two parts and fits onto the lid of BIOPAN (Fig. 9). A 140 cm² surface is allocated to the experiment, for a total surface area of 1080 cm² for all the BIOPAN experiments on the bottom plate and lid. The UV-olution surface allows the exposition of 60 cells (vented or closed). The sample holders have been designed by Didier Chaput (CNES) and manufactured by COMAT Aerospace (Toulouse, France).

Hervé Cottin (LISA, Créteil, France) is the PI of this experiment.

4.2.4. Experiment cells

Two kinds of cells are used in the three experimental programs: vented and sealed cells. In the vented cells, gaseous fragments resulting from the photolytic processes on the exposed samples are released into space and lost for analysis. In this case, those volatile molecules cannot further interact with the solid phase sample deposited on the window.

Vented cells are shown in Fig. 10. They are made of a cylindrical aluminum body onto which a 9 mm (diameter) by 1 mm (thickness) MgF₂ or quartz window is glued (epoxy glue). The walls of the cell are treated with Alodine®. The sample is deposited on the inner side of the window (see Section 4.3). The refractory sample can be analyzed before and after exposition via infrared measurements. After exposition, it can be recovered with a solvent for further analyses with HPLC or gas chromatography coupled to a mass spectrometer.

Sealed cells (Fig. 11) are made of two cylindrical aluminum bodies which can be screwed one into the other. An

O-ring (Viton®) prevents leaks between the two parts. The volume inside the cell is approximately 275 mm³. Sealed cells can be used to study the photolysis of a 100% gaseous starting mixture, or for the same kind of solid materials as those deposited in the vented cells. In this case, gaseous fragments resulting from photolytic processes on the solid exposed samples are kept inside the cell and can be analyzed after the recovery of the experiment. The walls of the two parts are treated with Alodine®. Two MgF₂ or quartz windows are glued at both ends of the cell, allowing (1) photolysis of the sample from the top window and (2) in situ UV or infrared analysis of the sample. However, infrared analysis inside the cell is limited by the infrared cutoff of the windows ($\sim 1000\text{ cm}^{-1}$ for MgF₂ and $\sim 3000\text{ cm}^{-1}$ for quartz). Moreover, the optical path length inside the cell is only 4.3 mm, limiting the sensitivity for spectroscopic detection. Analysis for lower wavelengths and with a larger path length is aided by the use of an analytical cell (see Section 4.2.5). The deposition of a solid sample can be done when the two parts are separated using the same procedure as that used for a vented cell. After the deposition of the solid sample, an inert gas (Ar) is introduced using the analytical cell. If the starting material inside the cell is made only of gaseous compounds, then the preparation of the cell proceeds only through the analytical cell. In each case, the total pressure inside the cell before launch is adjusted with Ar to 1.5 bar. This pressure allows avoiding contamination from Earth's atmosphere before launch. The sealed cells are conceived to leak at a maximum level of about $1 \times 10^{-9}\text{ mb s}^{-1}$ when placed in vacuum, which allows experiment durations of a few years.

4.2.5. Analytical cell

The analytical cell is shown in Figs. 12 and 13. Although called "analytical", it is used for both filling and sampling the sealed cells with gas, and for infrared analysis of the

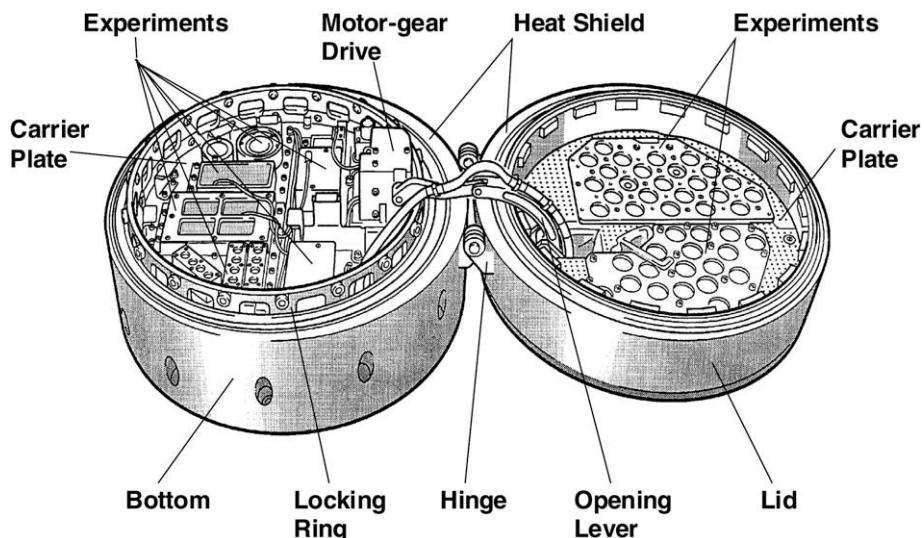


Fig. 8. The BIOPAN facility with the lid open. The bottom part is at left and the lid part, at right, can be opened and closed by telecommand from ground. The diameter of the facility is 38 cm. Picture courtesy of Kayser-Threde GmbH.

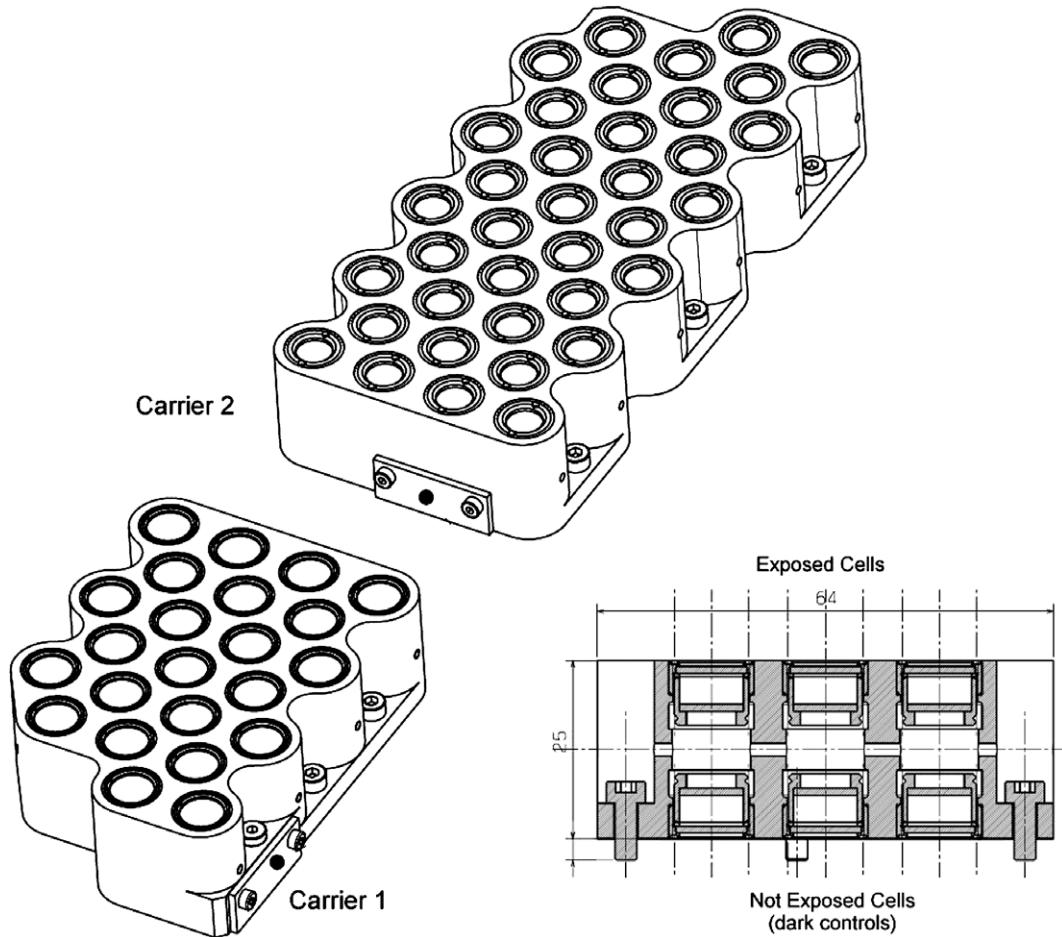


Fig. 9. UV-olution aluminum sample holders ($134 \times 64 \times 25$ mm and $88 \times 64 \times 25$ mm). The two carriers are designed to receive 33 and 27 exposed samples. In each case, both exposed cells and in-flight controls are screwed onto the sample holder. Picture courtesy of COMAT aerospace.

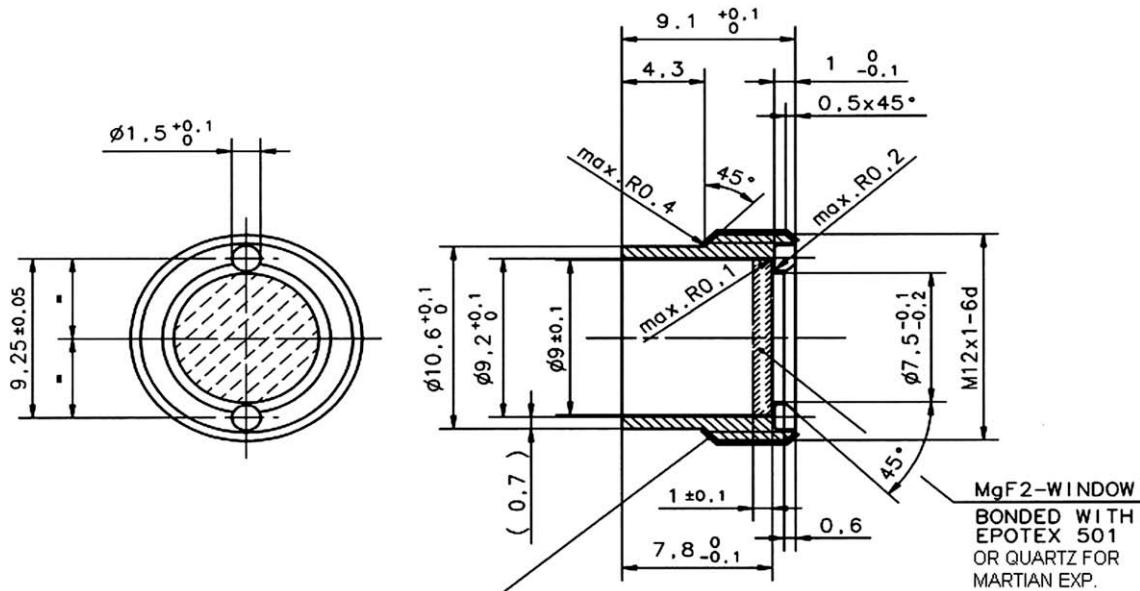


Fig. 10. Design of a vented cell made of an aluminium cylinder on top of which a MgF₂ or quartz window is glued. The organic molecule is deposited onto the inside face of the window. Picture courtesy of COMAT aerospace.

gaseous content of the sealed cells. It is basically made of two main Inox parts on the inside of which both parts of

a sealed cell are separately fitted. The two analytical cell parts are then adjusted and sealed with a Viton® O-ring.

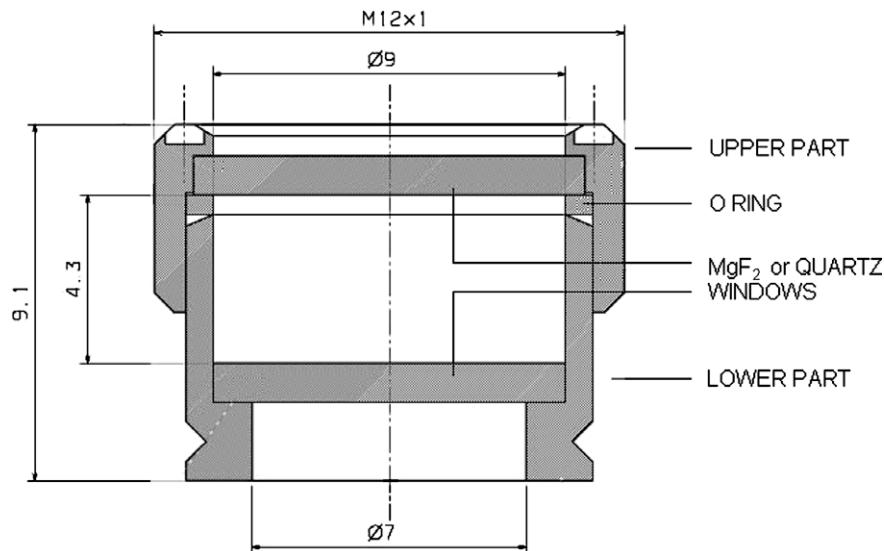


Fig. 11. Design of a sealed cell. Two aluminium cylinders are screwed into each other. Two MgF_2 or quartz windows at both ends allow the analysis of molecules inside the cell by spectroscopy. Sealing (relative to lab atmosphere or vacuum in space) is ensured by a Viton® O-ring. Picture courtesy of COMAT aerospace.

The gaseous component of the experiment can then be introduced inside the analytical cell before screwing the two parts of the sealed cell one into the other, using a screw connecting one part of the sealed cell to the outside of the analytical cell, enclosing the gases inside the sealed cell. The sealed cell can then be removed from the analytical cell and placed on a sample holder for the experiment in space.

After exposition in space, the content of the sealed cell can be analysed *in situ* by infrared spectroscopy, within the limitation of the wavelength range previously mentioned. Subsequently the two parts of the exposed cell can be unscrewed inside the analytical cell to release gases that will fill an infrared compartment embedded inside the analytical cell. KBr or CsI windows enable infrared analysis over a wider wavelength range (respectively, 400 and 200 cm^{-1}) with a 2-cm optical path length. Sampling of the gas in the analytical cell can also be made to perform gas chromatography/mass spectrometry analysis. When the two parts of the sealed cell are separated, and when the analysis of the gases has been made, study of the refractory component can be achieved in the same way as done for the open cells. Sealed and analytical cell have been designed and manufactured by COMAT Aerospace (Toulouse, France).

4.3. Deposition procedure

Films of organic samples can be obtained on the windows as described in Barbier et al. (2002b) and Boillot et al. (2002), as evaporation residues of a solution in which the molecules are previously solubilized, alone or with a suspension of minerals for organo-mineral mixtures. The thickness of the film is estimated from the initial concentration and molecular volume of each species loaded. Organic

films can also be obtained by sublimation of the compounds and condensation onto the cell window. The thickness of the film can be estimated *in situ* from interference measurements, previously calibrated with atomic force or confocal microscopy. A sublimation chamber similar to ours is presented in Ten Kate et al. (2005).

5. Target molecules

In this section, the molecules selected to be exposed during one (or more) of the space experiment and their astrochemical relevance are presented.

5.1. Comets

Laboratory experiments conducted on interstellar and cometary ice analogues have shown that high molecular weight organic molecules are synthesized from mixtures of simple compounds detected in the cometary atmosphere (see a review in Cottin et al. (1999)). Among those complex compounds, polyoxymethylene (POM: $-(\text{CH}_2-\text{O})_n-$ polymer of formaldehyde); hexamethylenetetramine (HMT: $\text{C}_6\text{N}_4\text{H}_{12}$), HCN polymers and carbon suboxide polymers ($(\text{C}_3\text{O}_2)_n$) are of prime interest (Schutte et al., 1993; Bernstein et al., 1995; Cottin et al., 2001; Gerakines and Moore, 2001), and their presence on the cometary nucleus could allow an interpretation of the extended source phenomena detected in the cometary atmosphere. As an example, the presence of polyoxymethylene at a mass level of a few percent is, to date, the best explanation for the origin of the puzzling occurrence of extended sources of formaldehyde in comet Halley (Cottin et al., 2004) and comet Hale–Bopp (Fray et al., 2006). On the other hand, HCN polymers could be a source for the

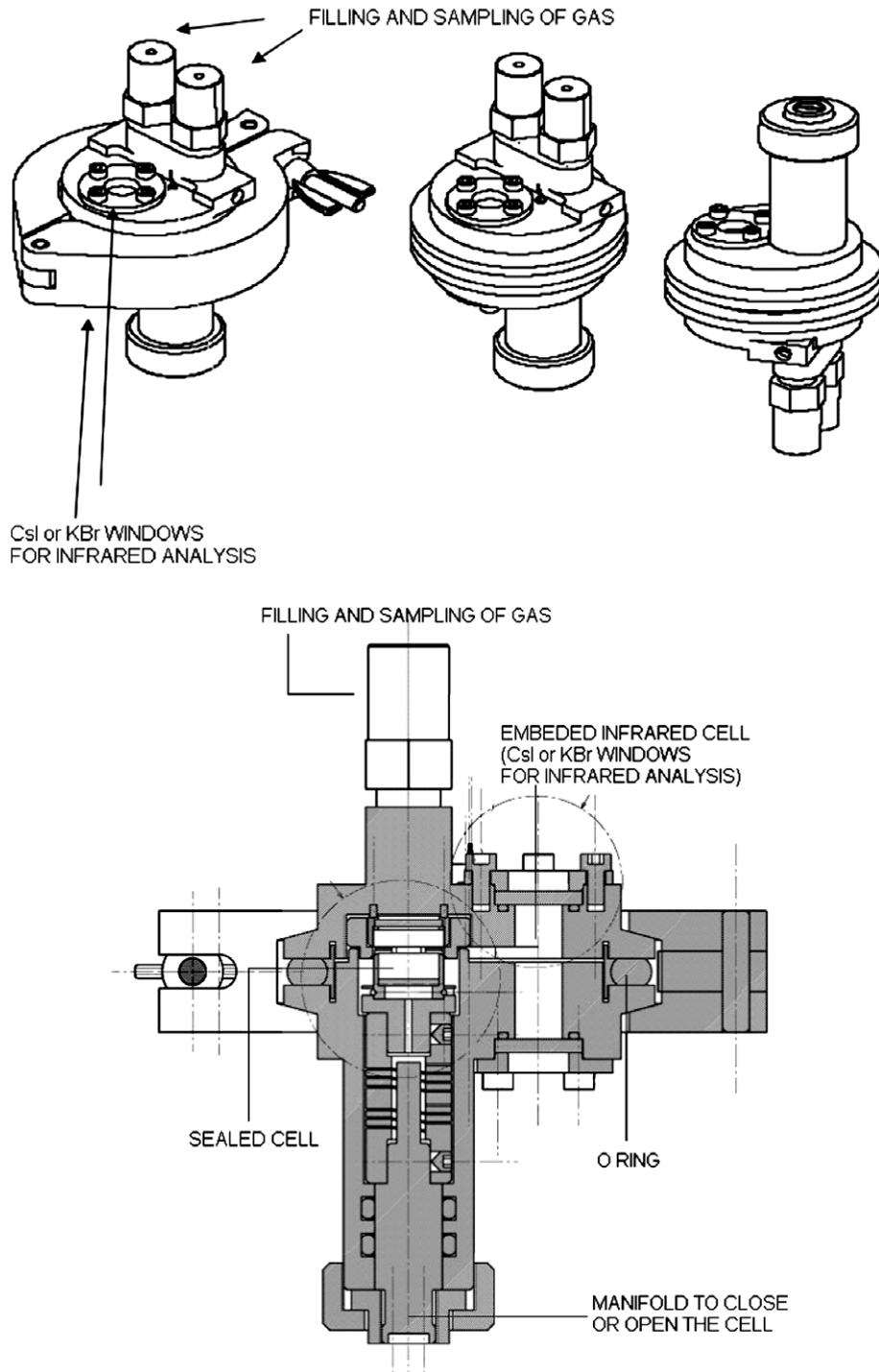


Fig. 12. Design of the analytical cell. It allows the filling or sampling of gases inside a sealed cell which can be fitted inside. An embedded infrared cell can be used for the analysis of gases in the infrared range. Picture courtesy of COMAT aerospace.

observed CN extended sources in comets (Fray et al., 2005) as it contains C–N bonds which can be released from the polymer by photolysis, whereas carbon suboxide polymers could explain the CO extended source (DiSanti et al., 1999, 2003). Moreover, these compounds may have strong exobiological implications. In Earth's primitive oceans, POM could have been a source of concentrated formaldehyde, a key compound involved in the synthesis

of sugars (Shapiro, 1988), although this is still debated. On the other hand, hydrolysis of HMT and HCN polymer releases amino acids (Matthews and Moser, 1967; Wolman et al., 1971). Therefore, experiments related to POM, HMT, HCN, and carbon suboxide polymers are scheduled for AMINO, PROCESS, and UV-olution. The photostability of these compounds will be studied if the molecules are exposed as pure deposits, or embedded

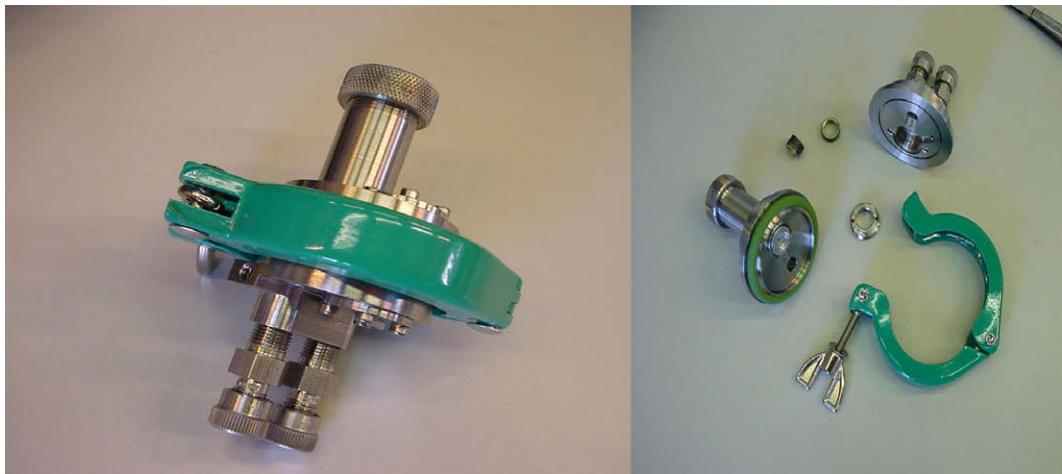


Fig. 13. Views of the analytical cell. It can be split in two for installation or to extract a sealed cell before or after closing.

in a mineral or organic matrix closely related to their actual space environment.

5.2. Meteorites

Another example of the complexity of organic chemistry occurring in space is documented by studies of carbonaceous chondrites that contain up to 5% by weight of organic matter. The Murchison meteorite has numerous organic compounds, including nucleic bases and amino acids. An excess of about 9% of the L-form for isovaline and α -methyl-isoleucine, non-protein C_α di-substituted amino acids, was found in the Murchison meteorite (Cronin and Pizzarello, 1997). These amino acids do not result from biological contamination and do not racemize easily. On the other hand, norvaline and α -amino-n-butyric acid, their C_α -monosubstituted analogues which can easily racemize, were found as racemic mixtures (equal mixture of L and D enantiomers) (Cronin and Pizzarello, 1997). This supports a possible asymmetric synthesis in space followed by a progressive racemization. This excess of left-handed amino acids could be an explanation for the emergence of a primitive one-handed life.

Micrometeorites (size < 1 mm), which represent more than 99% of the exogenous materials arriving on Earth (Maurette, 1998, 2006), could also have safely carried organic molecules to the primitive Earth. The study of micrometeorites extracted from old Antarctica blue ice shows that about 80% of the carbonaceous ones in the 50–100 μm size range are not melted after crossing the terrestrial atmosphere (Maurette, 1998, 2006). Analyses of such micrometeorites have shown traces of amino acids such as α -amino butyric acid (Brinton et al., 1998). Recent sample exposition to space conditions, onboard the MIR Station, has demonstrated that a 5 μm thick film of meteorite powder was able to efficiently protect associated amino acids against solar radiation (Boillot et al., 2002).

Experiments involving amino acids will therefore be implemented on AMINO and UV-olution, and will focus on degradation and racemization processes. They will be more specifically dedicated to the following materials: protein amino acids (glycine), non-protein amino acids (D-alanine, D-aspartic acid, α -amino isobutyric acid, D-amino butyric acid) and a small peptide (dileucine) to compare the chemical stability of proteinaceous and non-proteinaceous amino acids and peptide in space. Special attention will be devoted to decarboxylation reactions and racemization, i.e. the transformation of one enantiomer into its mirror image. All the amino acid related experiments will be implemented in vented cells. In some experiments, the organic material will be embedded in a mineral matrix (Allende meteorite powder).

5.3. Titan

Titan's aerosol analogues (Tholins) have been produced for years in laboratories with a wide range of experimental conditions (Coll et al., 1999). We plan to expose the main gaseous compounds of Titan's atmosphere ($\text{N}_2 + \text{CH}_4$) to the full solar spectrum, with known isotopic ratios in N or C. Indeed, in the case of nitrogen, Titan presents a $^{14}\text{N}/^{15}\text{N}$ value which is 1.5 times less than that for the primordial N, suggesting that the present mass of the atmosphere was lost several times (Niemann et al., 2005). It could also be interpreted as an isotopic fractionation during N integration in aerosols. If not, this implies that ^{14}N escapes preferentially into the Interplanetary Medium. A similar discussion can be developed for the $^{13}\text{C}/^{14}\text{C}$ ratio: its determination in the solid products can provide information on the chemical pathways involved in their synthesis (Nguyen et al., in press). We will also compare the products of our space experiments with the well characterized laboratory products (gaseous and solid) collected so far (Coll et al., 1999).

On the other hand, exposition to the solar spectrum of laboratory made, Titan aerosol analogues (Tholins) will

help us to understand the evolution and the degradation of such a chemical structure, and therefore understand the transformation of the aerosols during their sedimentation in the atmosphere of Titan. These results have direct application to the understanding of the nitrogen cycle on Titan. This is also important to predict the nature of molecules that can condense onto the aerosols, since the nature of the aerosols is of prime importance for the nucleation process (Guez et al., 1997).

5.4. Mars

Martian irradiance at the surface has a shape close to the solar spectrum except for wavelengths shorter than 190–200 nm. Indeed, the Martian CO₂ atmosphere stops these short wavelengths. Using a quartz window, an irradiance representative of the Martian surface condition is obtained inside. For each compound, we plan to distinguish the evolution of the molecule on its own as well as associated with an analogue of the Martian soil (Feldspar and Ti-magnetite, along with minor olivine, pyroxene, and glass), in order to predict which are the resulting products.

Although numerous experiments relating to the survival and evolution of different forms of bacteria at the Martian surface have been carried out (Green et al., 1971; Mancinelli and Rocco, 1989; Horneck, 1993; Mancinelli and Klovstad, 2000), few have studied the same phenomena in the case of organics (Oro and Holzer, 1979; Stoker and Bullock, 1997; Ten Kate et al., 2005, 2006).

As a reference, we plan to study the only organic molecule already studied in space (Stoker and Bullock, 1997): glycine. We also plan to study the evolution under solar irradiation of molecules of biotic origin that are very resistant in the terrestrial environment, which is much more aggressive than the Martian one (fluid circulation, tectonics, etc.): 2-methylhopane and 3-methylhopane (oldest hopane molecular fossils found on Earth = 2.7 Gy-old, Brocks et al., 1999). In addition, benzoic acid will be studied. It is proposed as a terminal molecule resulting from the potential oxidation of organics at Mars surface and presented as a molecule resistant to the surface conditions of Mars (Benner et al., 2000). This hypothesis has to be checked experimentally due to the fact that no benzoic acid has been yet detected on Mars.

Martian related experiments will be carried out in both vented and sealed samples. In sealed samples, experiments will be conducted under a CO₂ Martian analogous atmosphere.

6. Conclusions

The AMINO, PROCESS, and UV-olution experimental programs will address the main aspects of photochemistry related to astrobiology in the Solar System. However, even if these space laboratories offer an environment impossible

to accurately reproduce in the laboratory; ground experiments are still necessary in preparation and in support of these experiments.

With respect to comets, we may be able to answer the following questions: (1) What is the stability of refractory molecules once synthesized in cometary and/or interstellar ices, and what are the chances for their actual presence on comets and cometary dust, and subsequent importation to Earth's ocean? (2) What kinds of shielding effect can we expect from the mineral and organic matrix in which they are embedded? (3) What are the gaseous photodegradation products of the target molecules, and are they related to the extended sources?

With respect to meteorites: (1) What is the stability of amino acids and small peptides in space, and their history before being imported to Earth via meteorites and micrometeorites? (2) To what extent does Solar UV radiation affect any enantiomeric excess of compounds with an asymmetric carbon?

Regarding Titan: (1) Could the isotopic integration of C and N in Titan's aerosols explain the isotopic ratios in Titan's atmosphere measured by Cassini-Huygens? (2) In the case that no direct role can be demonstrated, what will be the implications of these results on Titan's environment: isotopic fractionation during the escape from Titan's atmosphere, internal source of methane? (3) Are aerosols a final sink for nitrogen, or is any nitrogen released from the aerosols when they are exposed to photons?

With respect to Mars: (1) Which molecules are formed as a result of the irradiation of the target molecules, in terms of gaseous molecules or solid products (degradation/evolution/reaction of the original solid products)? (2) Are they likely to be detectable in the next future missions to Mars (future in situ NASA/ESA missions...)?

Space laboratories such as BIOPAN and EXPOSE offer great opportunities to perform photochemistry experiments with a "perfect" UV source for astrochemistry: the Sun. In such experiments however, the total exposition time to photons is a key parameter if one wishes to extrapolate results over relevant astrophysical time scale. The duration of the effective exposition to Solar UVs is difficult to estimate before the mission. One of the issues for such calculation is uncertainty in what pointing mode the International Space Station will be in during the exposure period. Also, shadowing and reflections from the structure further complicate the issue. Therefore, the exact exposition time is measured during the actual experiment. Next generations for such experiments should address this issue, optimizing the photolysis time using a sun pointing device. Similar experiments could also be implemented at the surface of the Moon for extra-long exposure duration. Another flaw, addressed in this paper, is that it is not possible to acquire data during the experiment. In the future, onboard spectrometers and transmission of data to Earth could allow measuring the destruction of exposed compounds with their degradation products while the experiment is still in space.

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