

COSPAR 2010

Exobiology

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[Fig. 1]



[Fig. 2]

The past two years have been the extension of the previous biennial period. Ground laboratory work on samples, observations and basic research preparing further missions were performed by scientific teams supported by grants from CNES.

Planetary missions

Missions like ExoMars and Cassini are gathering data on, respectively, Mars and the system of Saturn. Several papers on the habitability and the complex chemistry of Titan were published by the international team. These findings pointed out the rich photochemistry leading from simple compounds like ammonia, methane and carbon dioxide to organic molecules. One of the major outputs of these analysis is the demonstration of ethane lake enrichment on Titan by organic compounds compared with the atmospheric concentrations.

Stardust: the comet still has something to tell

The detailed work on comet grains gathered by the US mission Stardust is continuing at its pace, as an international team is refining the method to perform non-destructive analysis and nano-imaging, using the Synchrotron of the ESRF. The analysis of new samples in the perspective of astrobiology has already begun.

Experiments in low Earth orbit

Experiment STONE on the Russian capsule Foton delivered

its data. At the same time French and international teams prepared for the experiments Expose EuTEF and Expose-R. These two facilities were positioned outside the ISS. The samples from Expose-EuTEF were retrieved in August 2009, while those from Expose-R will be recovered by the end of 2010.

ExoMars: two missions in one

The NASA/ESA agreement, reshaping the mission in two successive launches and three different objects, did not slow down the development of the instruments planned for the analytical laboratory of the planned rover. The French teams involved in the European and international instrument teams were continuing the definition phase of the instruments which will now be launched in 2018. The development is encouraging, the technical readiness level is reaching a high score while the mission itself is still not well defined. Prototypes are on the verge of being tested and used on the ground in laboratories as well as field campaigns.

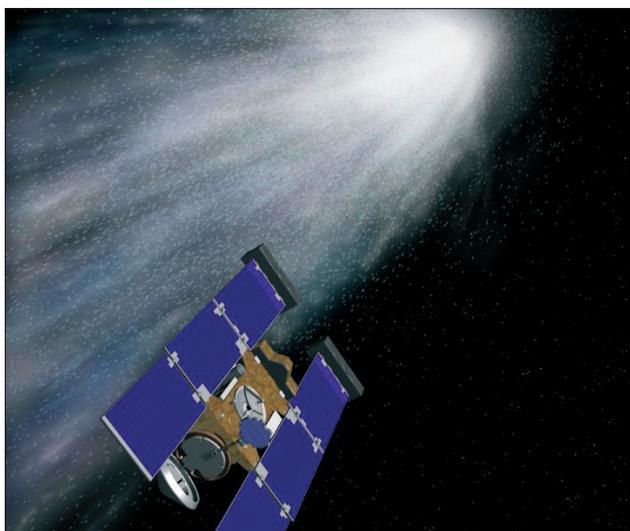
From space to the laboratory and vice versa

Supporting the analysis of the Cassini-Huygens mission, researchers from the LPCE performed measurements of the optical properties of levitating particles in microgravity during parabolic flights defining characteristics of those grains which could be detected by remote sensing measurements performed from the spacecraft. Researchers from the LPG managed the extensive analysis of the tholins produced



[Fig. 3]

in various conditions using very high resolution mass spectrometry. This validated the description of the Titan atmospheric chemistry and the variety of the compounds which has led to a new scientific field called Tholinomics! Chirality and the understanding of the enantiomeric excess which is found in some meteorites lead to numerous experiments using synthesis and destruction of compounds under UV polarised light as well as the study of the enrichment or depletion in the enantiomeric ratio when compounds condense or sublimate.



[Fig. 4]

In order to prepare the mission ExoMars, extensive field work was done to prepare a collection of terrestrial reference rocks within a European network.

New instruments

The agency supports work for future state-of-the-art instrumentation through the research and technology programme. The scientific teams focus on instruments with new analytical principles like para electronic resonance, improving the specificity and sensitivity of systems like biochips or gas chromatography (derivatisation and analysis of chiral molecules). Preliminary developments began to perform non-destructive analysis of samples under strict containment. These systems could be used for instance for the analysis of Martian samples under quarantine.

Outreach

Among other activities connected with universities, the agency supported the astrobiology course organised by the university of Bordeaux, dedicated to PhD students.

During the International Year of Astronomy 09, the agency supported and organised numerous public events around astrobiology and the exploration of the solar system. For the national science festival in 2009 an interactive public event combined with daily conferences was organized inside the CNES premises.

Fig. 1: Photochemical processing of amino acids and other organic compounds in Earth orbit.

Fig. 2: Expose-R.

Fig. 3: Expose-R is installed on the outside of the Russian segment of the ISS.

Fig. 4: Stardust comet Wild 2 encounter.

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The molecular structure of the insoluble organic matter in carbonaceous chondrites.

La structure moléculaire de la matière organique insoluble des chondrites carbonées.

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Abstract

The molecular structure of the insoluble organic matter of the Murchison and Orgueil meteorites was investigated using a combination of spectroscopic and microscopic tools along with chemical and thermal degradations. Eleven parameters were derived and a model of molecular structure was drawn so as to fit with these parameters. Several cosmochemical implications such as the timing and mechanism of formation of this macromolecule and the extent of parent body alteration can be deduced from this structure.

L'étude de la structure chimique de la matière organique insoluble des météorites Orgueil et Murchison par spectroscopies, microscopie et dégradations thermiques et chimiques a permis de déterminer onze paramètres à partir desquels un modèle de structure moléculaire est dessiné. Plusieurs implications cosmochimiques comme le mécanisme et le lieu de formation de cette matière organique macromoléculaire et le degré d'altération sur le corps parent peuvent être déduits de cette structure.

Carbonaceous chondrites are known to contain substantial amounts of organic matter, mainly occurring as Insoluble Organic Matter (IOM). A precise knowledge of the structure of this macromolecule contains key information to trace its mechanisms and conditions of formation. The molecular structure of the IOM from the Murchison and Orgueil meteorites has been investigated by our group using a large set of analytical methods including various spectroscopic techniques, electron microscopy and thermal and chemical degradations. Although each technique alone cannot provide definite information on the chemical structure of such a com-

plex material, the combination of the results can be used to reconstruct the IOM molecular structure.

H/C atomic ratio along with Fourier Transform InfraRed (FTIR) and solid state ¹³C Nuclear Magnetic Resonance (NMR) spectra indicated a strong aromaticity for these IOMs. High resolution transmission electron microscopy [1] and electron paramagnetic resonance [2][3] revealed that the IOM polyaromatic moieties are of rather small size (one to four ring large) and highly substituted, consistently with pyrolysis and oxidation studies[4][5]. FTIR and ¹³C NMR pointed to a high branching

level in the aliphatic chains [6]. Ruthenium tetroxide oxidation, an efficient technique to assess the nature of aliphatic chains in aromatic macromolecules, revealed the short length of the chains, <3 C atoms for side chains born by aromatic moieties and from 2 C to 7 C for aliphatic bridges between aromatic units, their high branching level [4] and the occurrence of aliphatic chains linking several aromatic units in agreement with the high degree of cross-linking evidenced by ^{13}C NMR. Besides C and H, O is the most abundant element of the IOM. Spectroscopic analyses revealed that O is mainly linked to O (as in ether or aliphatic alcohols) and involved in carboxylic groups (acids and/or esters). Pyrolysis in the presence of tetramethylammonium hydroxide, which acts as both a base and a methylating agent, showed the presence of ester linkages between aromatic moieties and RuO_4 oxidation indicated that ether and ester functional groups occur within aliphatic linkages. A number of S-containing products (thiophenes) are released upon pyrolysis of the IOMs in agreement with a substantial S content in the IOM. K-edge S XANES revealed that organic S is distributed amongst thiophenes and aliphatic sulphides in the IOMs, the relative amount of thiophenes being higher in Orgueil than in Murchison. N was also shown to occur in the IOM. ^{15}N NMR revealed that N is mainly involved in heterocyclic units such as pyrroles, and that amide/amine groups are virtually absent. A low contribution of nitrile groups can be put forward.

Taken together, these techniques provided a set of eleven parameters that was used to build a model of molecular structure of the IOM [7]. The resulting structure (Fig. 3) accounts for all the molecular units (atoms or functional groups) whose abundance is higher than 3%. As a result, rare molecular occurrences are ignored in order to limit the structure around ~200 C atoms. The present structure should be regarded as a statistical model and not as a unique solution that fits the measured parameters (Fig. 4). Note also that, because of its small size, this modelled structure cannot account for the large diversity of the products identified in pyrolysis and oxidation experiments.

Comparison with the soluble fraction indicates that the latter seems to be a mixture of products derived from different processes, at variance with what is commonly expected, *i.e.* a continuum from small soluble molecules to large insoluble ones. Soluble compounds might also be derived from a precursor which has now been totally converted into the products, the IOM being the leftover part of an initially more composite material.

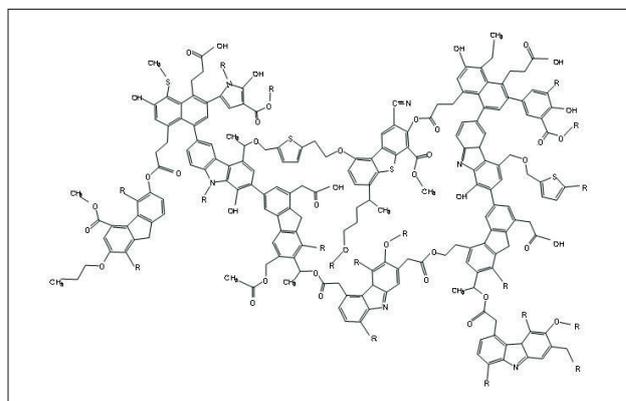
Several cosmochemical implications are derived from this structure. Based on the fact that aromatic moieties are highly substituted and aliphatic chains highly branched, it can be anticipated that the synthesis of this IOM occurred through successive additions of single C units in the gas phase ending by a spontaneous cyclization for chain length ≥ 7 C. The aromatic units in the IOMs are much smaller than interstellar PAHs, which has been interpreted as the result of a selective preservation of smaller PAHs in IOM prior to their destruction by UV-irradiation. The molecular speciation of O and S in chains can be regarded as the consequence of the alteration of the



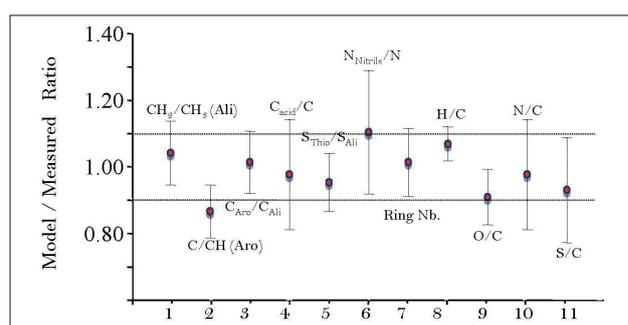
[Fig. 1]

[Fig. 2]

parent body, O being related to the aqueous alteration experienced by primitive carbonaceous chondrites and S speciation reflecting the extent of hydrothermal event. Several features of the IOM chemical structure are in favour of an organo-synthesis in the Solar T-Tauri disk. Indeed, D/H distribution at the molecular level and combined NanoSIMS and pulsed EPR studies showed a correlation between D/H and C-H bond energy [8][9] which led us to propose that the isotope exchange had taken place in a high density medium such as UV irradiated regions of the T-Tauri Solar disk [10] after the formation of the IOM. The occurrence of mechanically trapped noble gases between the lattices of the macromolecular layers of the IOM [11] also supports such a mechanism.



[Fig. 3]



[Fig. 4]

Fig. 1: Orgueil meteorite.

Fig. 2: Fragment of the Murchison meteorite (at right) and isolated individual particles (shown in the test tube).

Fig. 3: Model of molecular structure of the IOM of Murchison. R stands for an organic moiety.

Fig. 4: Ratio of the values for the parameters calculated from the modelled structure in Fig. 3 to those experimentally measured in the IOM of Murchison.

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Astrochemistry and astrobiology laboratories in Earth orbit.

Des laboratoires d'astrochimie et d'exobiologie en orbite terrestre.

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Abstract

Solar UV radiation is a major source of energy to initiate chemical evolution in the solar system. UVolution, PROCESS and Amino are three experiments selected by ESA to be flown in Earth orbit (Foton or ISS) to improve our knowledge of the chemical evolution of organic molecules involved in extraterrestrial environments. For the first time, gaseous mixtures have been exposed in space. Measurements in space have been compared to similar experiments implemented in the laboratory.

Le rayonnement UV solaire est la principale source d'énergie à l'origine de l'évolution chimique dans le système solaire. UVolution, Process et Amino sont trois expériences qui ont été sélectionnées par l'ESA pour être mises en orbite terrestre (Foton ou ISS) afin d'étudier l'évolution des molécules organiques dans les environnements extraterrestres. Les mesures en orbite ont systématiquement été comparées à des mesures similaires, réalisées en laboratoire.

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 are trapped by the geomagnetic field. On the other hand, the solar electromagnetic radiation above the Earth's atmosphere is composed of 45% of infrared radiation, 48% of visible light and only 7% of UV light [1]. The latter photons are, however, the most energetic and occur at sufficient levels to induce photochemical evolution.

Photochemistry indeed has a leading part in the chemical evolution of organic matter in the solar system and in the interstellar medium, specifically in the VUV domain (Vacuum Ultra Violet - $\lambda < 200$ nm). For this reason, laboratory studies of the photolysis of organic compounds related to astrophysical environments are common and different kinds of UV sources are used, e.g. monochromatic (e.g. H_2/He (122 nm)) or simulating a wider range of UV (e.g. high pressure Xenon lamps (190 nm - 400 nm)). However, it is not possible to simulate the whole range of wavelengths corresponding to the most energetic part of the solar radiation below 200 nm [2], therefore results obtained in the laboratory are extremely

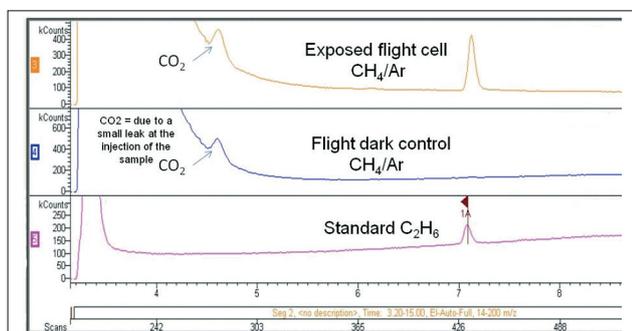
difficult to extrapolate to extraterrestrial environments. To do so, the absorption spectra in the VUV of each molecule should be measured, as well as the quantum yield of their destruction at each wavelength. This last measurement is especially difficult and requires monochromatic sources with well-constrained fluxes. Subsequently, both results have to be convoluted and scaled to the solar spectrum. On the other hand, UV light reaching low Earth orbit (at the altitude of the ISS) is unfiltered. Therefore, with experiments conducted in space, hundreds of samples can be exposed simultaneously, measurement is direct across the real solar UV spectrum, and the measurements can be easily extrapolated to various astrophysical environments.

Moreover, the simulation of cosmic particles in addition to UV photons requires additional tools (ion and electron guns) and increases the complexity of ground experiments. Therefore, space is a unique laboratory allowing the simultaneous exposure of samples to all space parameters as well as the irradiation of the samples under identical conditions.

Ground laboratory experiments are also implemented on the target compounds we have selected for this program for comparison.

Recently, two experiments were flown and returned safely to Earth: UVolution (Biopan on Foton M3 Russian automated capsule) and PROCESS (outside the European Columbus module of the ISS).

The UVolution experiment on Biopan-6 in 2007 (September 14 - September 26) successfully tested the exposition of gas mixtures in space in sealed cells simulating the atmosphere of Titan, and compared the kinetics of photolysis in space and in the laboratory for solid state samples related to comets ($\lambda > 115$ nm / cutoff with MgF_2 windows) and Mars ($\lambda > 190$ nm / cutoff with quartz windows). The results have shown that current extrapolation procedures of laboratory simulations to space conditions (typically by taking into account only the influence of the Lyman α line at 122 nm) are extremely hazardous and can lead to errors of a factor of 100 on the kinetics for photolysis in the VUV [3] (Fig. 3). The case of Martian simulations is more favorable, showing that the lamps simulating the UV flux reaching the surface of Mars ($\lambda > 190$ nm) are more acceptable than in the previous case. However, there still remains a factor of two to thirteen between space



[Fig. 1]

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and laboratory results depending on the molecule [4]. Interestingly, UVolution results have shown that the photolysis of organic molecules is activated by the presence of a mineral analogue of Martian soil.

For the first time, gaseous samples simulating the atmosphere of Titan were exposed in space and were analyzed by gas chromatography/mass spectrometry analysis. Fig. 1 shows an example of an analysis of a gaseous sample exposed during UVolution, by gaseous chromatography.

A second experiment, PROCESS, was part of the payload of Expose-E on the EuTEF facility and was returned to Earth in September 2009 after 1.5 yr in space. The analysis and processing of PROCESS results are still in progress.

Amino is a third experiment, part of the payload of Expose-R outside the Russian module Zvezda. Expose-R was installed outside the ISS in March 2009 and should return to Earth after 1.5 yr in space.

Biopan and Expose facilities are very valuable. However, these experiments suffer from significant limitations that adversely impact science output:

- the ratio of exposure times against total stay in space is relatively small (~10%),
- there is no ability to monitor samples *in situ* (real time IR and UV spectrometers on board): the only spectra available are measured before launch and after return to Earth,
- there is no ability to control the sample temperature, and no possibility to expose icy mixtures relevant to cometary nucleus, interstellar grains and icy satellite surfaces.

New projects are underway to address these issues and fly new improved instruments in the years to come.

Molecule	J_{space} ($\text{ph.cm}^{-2}\text{s}^{-1}$)	J_{lab} ($\text{ph.cm}^{-2}\text{s}^{-1}$)	$J_{\text{lab}}^{\text{Ly}\alpha}$ ($\text{ph.cm}^{-2}\text{s}^{-1}$)	$J_{\text{space}} / J_{\text{lab}}^{\text{Ly}\alpha}$	$J_{\text{lab}}^{115-220}$ ($\text{ph.cm}^{-2}\text{s}^{-1}$)	$J_{\text{space}} / J_{\text{lab}}^{115-220}$
Glycine	$1,0 \cdot 10^{-6}$	$8,6 \cdot 10^{-6}$	$5,9 \cdot 10^{-9}$	175	$1,0 \cdot 10^{-7}$	10
Adenine	$< 1,9 \cdot 10^{-7}$	$3,7 \cdot 10^{-7}$	$1,1 \cdot 10^{-9}$	≤ 169	$1,9 \cdot 10^{-8}$	≤ 9
Xanthine	$5,0 \cdot 10^{-7}$	$1,3 \cdot 10^{-6}$	$4,0 \cdot 10^{-9}$	123	$7,0 \cdot 10^{-8}$	7
PolyC3o2	$1,3 \cdot 10^{-6}$	$1,3 \cdot 10^{-5}$	$1,1 \cdot 10^{-8}$	115	$3,0 \cdot 10^{-7}$	7
PolyHCN	$8,0 \cdot 10^{-7}$	$2,0 \cdot 10^{-6}$	$1,8 \cdot 10^{-9}$	455	$3,0 \cdot 10^{-8}$	26

[Fig. 2]

Fig. 1: Analysis of a closed cell containing CH_4 and Ar exposed during UVolution in 2007 and its flight dark control (not exposed) by gas chromatography. The measurements show the formation of C_2H_6 by photochemistry.

Fig. 2: Comparisons between J measured in space (J_{space}) and in the laboratory (J_{lab}). Extrapolation of J measured in the laboratory to space and comparison with space measurements with the assumptions that photolysis occurs only at Lyman α or from 115 nm to 200 nm.