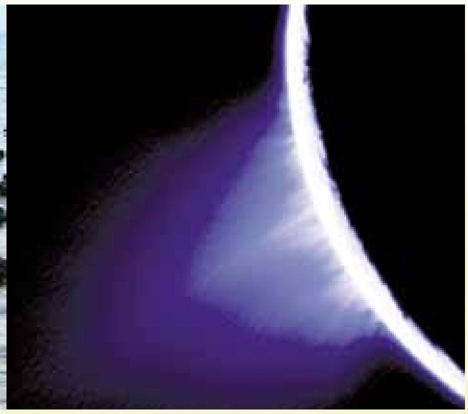
AUTHOR: M. Viso

# Exobiology

[Fig. 1]

[Fig. 2]



The French space agency CNES (Centre National d'Études Spatiales) provides funding to teams of astrobiologists for experiments regarding space exploration or to prepare future missions.

## Planetary missions

The joint US and Italian Cassini mission has been extended to 2017. Prof. François Raulin, Astrobiology Interdisciplinary Scientist, is developing new hypotheses with an international team about prebiotic chemistry while observing the complex chemistry of Titan [1][2][3]. These reviews are based on former demonstrations that the rich photochemistry contributes to the transformation of simple compounds like ammonia and carbon dioxide into complex organic molecules.

The Exomars programme has been radically reorganised several times in the past few years. While the details of a possible new partnership with Russia are being worked out, the French laboratories involved in the teams are continuing the advanced definition phase of the instruments. Although the mission itself is still not yet well defined, technical readiness levels are achieving high scores. Several prototypes and models are being tested in laboratories or used in field campaigns.

While awaiting the completion of missions to study the geological features in situ and possibly collect samples for later return to Earth, an international team led by Frances Westall in Orleans has developed the International Space Analogue Rockstore (ISAR) [4]. This collection of well-characterised rocks is available for testing and calibrating instruments to be flown on space missions. The initial collection includes basalts, either natural or artificial [5], sediments and other minerals whose characteristics are described in the database.

## Experiments in low earth orbit

The EXPOSE-R experiment was retrieved from its slot on the outside of Zvezda on 21 January 2011, after almost two years of exposure to the open space environment. Exposed samples were returned to Earth on STS-133, which landed on 9 March 2011. The samples were distributed a few weeks later. The French participating laboratories are now analysing the samples as well as the controls that remained peacefully in the original laboratories, or the ones processed at DLR, simulating space exposure. Several papers have been submitted for publication. Teams are preparing the next experiments which were selected in 2009 for flight.
EXPOSE R2 is now slated for launch to the ISS, by ESA, at the end of 2013 or early 2014.

## From space to the laboratory and back again

The ICAPS (Interactions in Cosmic and Atmospheric Particle Systems) project is under development at ESA to fly on board the ISS. The scientific team led by M. J. Blum (Braunschweig, Germany) is permanently upgrading the science case. The French team (A.-C. Levasseur-Regourd and J.-B. Renard) is performing measurements in parabolic flights to narrow the selection of the future flight samples. These preliminary experiments are performed using PROGRA2 during parabolic flights with the A300 Zero g sponsored by CNES and ESA.

Ground simulations of the chemistry found in interstellar ice, dust grains and comets also prepare the interpretation of the data from Rosetta. Hydantoin has been identified in the organic residues of photochemistry acting on ices [6]. This molecule is able to catalyse the polymerisation of peptides in water. It could have played a major role in the early organic chemistry on Earth.

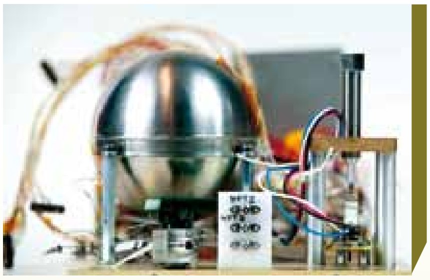
A science team in Marseille [7] obtained the synthesis of Hexamethylenetetramine (HMT) within an analogue of cometary ice without ultra-violet radiations, relying on temperature as the sole source of energy. Finally, using cutting-edge analytical systems, a team led by Louis le Sergeant d'Hendecourt demonstrated that under specific UV sources, the chemistry in simulated cometary ice produces up to 26 amino acids, some displaying two amino functions in a single molecule [8].
French planetologists and astrobiologists actively participate in international workshops shaping the future of planetary exploration [9].

## New instruments

The agency supports work for future state-of-the-art instrumentation through the research and technology programme. New analytical principles like Para-Electronic Resonance are strong candidates for space missions. Improvements in the specificity and sensitivity of systems like Biochips or Gas Chromatography (derivatisation and analysis of chiral molecules) are on their way. Containers dedicated to the analysis of Martian samples using a Synchrotron have been designed and a prototype is under test. Containment with three air-tight layers does not preclude the 3D scanning of the samples. The team is now optimising the design of the workstation to enable the container to be filled under appropriate conditions.

[Fig. 3]

[Fig. 4]



Scientists involved in cosmochemistry also gathered under the auspices of the agency to prepare the future of experiments from the laboratory up to space stations. As a first result it appears that further exposure of compounds in space will require active experiments and continuous measurements while exposed. This will lead to preliminary studies for a new generation of instruments.

## Outreach

Among other activities connected with the universities, the agency supported the now annual astrobiology course organised by Dr Muriel Gargaud and the University of Bordeaux, dedicated to PhD students (RED, *Rencontres d'Exobiologie pour Doctorants)*.
Finally, with the support of the agency as well as of several other institutions in Europe and Canada, the scientific community completed the publication of the 'Encyclopedia of Astrobiology' [10].

***[Fig. 1]***
***Stromatolites in the marine natural reserve of Hamelin Pool (Shark Bay, Australia). © GFDL/P. Harrisson***

***[Fig. 2]***
***Cassini imaging scientists used views like this one to help them identify the source locations for individual jets spurting ice particles, water vapor and trace organic compounds from the surface of Saturn's moon Enceladus. © NASA/JPL/Space Science Institute/2007***

***[Fig. 3]***
***EXPOSE-R outside the International Space Station. This experiment was retrieved from its slot on the January 21st 2011, after almost 2 years of exposure to the open space environment. © NASA***

***[Fig. 4]***
***A prototype of gas chromatograph for GC-MOMA space instrument onboard the Exomars mission. © N. Grand LISA/LATMOS***

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AUTHORS: O. Poch [1] - C. Brassé [1] - P. Coll [1] - F. Raulin [1]

# Exobiology

Laboratory contribution

## *Chemical evolution of organic aerosols on Titan's surface*

## Evolution chimique des aérosols à la surface de Titan

[1] LISA, Université Paris Est-Créteil, CNRS/ Université Paris Diderot/ IPSL, 61 Avenue Général de Gaulle, 94000 Créteil, France - contact : francois.raulin@lisa.u-pec.fr.

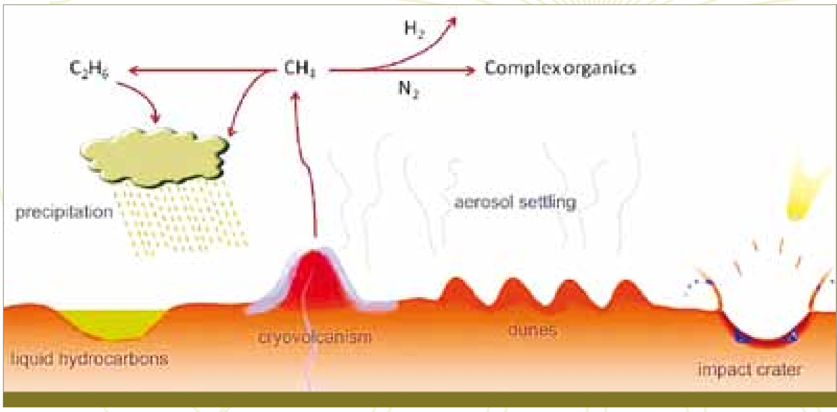
## Abstract

*The possible evolution of organic aerosols on Titan surface has been mimicked in the laboratory using Titan's tholins. Those were placed in pure water and in water-ammonia solutions during ten weeks at low temperature. The resulting products were quantitatively analyzed using chemical derivatization-GC–MS analysis. The main product is urea. Several amino acids, and potentially two nucleobases are also produced. The production yields have been determined for the first time.*

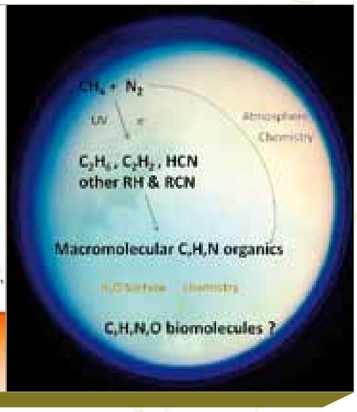
## Résumé

L'évolution possible des aérosols organiques à la surface de Titan a été simulée expérimentalement à l'aide de tholins. Ces analogues de laboratoire ont été mis dans l'eau pure ou ammoniaquée pendant 10 semaines à basse température. Les produits obtenus ont été analysés par dérivatisation chimique-CPG-SM.
Le principal produit est l'urée. Plusieurs acides aminés et –à confirmer– deux nucléobases sont aussi produits.
Les rendements de production sont déterminés pour la première fois.

[Fig. 1]




[Fig. 2]




**The largest satellite of Saturn** is one of the key planetary bodies in the solar system for astrobiological studies and in particular for organic cosmochemistry [1] [2]. Titan looks like an evolving planet, geologically active, with a complex organic chemistry occurring in the ionosphere where high molecular weight ions are present. These are likely to be involved in the formation of aerosols analysed in the lower atmosphere. Cassini-Huygens has demonstrated that the chemical composition of Titan's aerosols is similar to that of laboratory Titan's tholins. Many laboratory works have been carried out on Titan tholins [3] to study their physical and chemical properties.

The plasma tholins produced at LISA can release large amounts of HCN and $NH_3$ when pyrolyzed at 600°C, similarly to Titan's aerosols. These plasma tholins can thus be considered as good laboratory analogues of Titan's aerosols and can be used to study in Earth laboratory the properties of Titan's atmospheric particles.
Cassini–Huygens data has revealed a highly diversified solid surface on Titan with features that suggest aeolian, tectonic, fluvial processes, dunes, channels, lakes, impact craters and possible cryovolcanic structures (Fig. 1). Moreover, the existence of an internal liquid water ocean, containing a few percent ammonia has been proposed [1].

[Fig. 3]

| Product of biological interest | Yield (w/w) in % | | |
|---|---|---|---|
| | Tholins 1 - 279 K in water | Tholins 2 - 279 K in water/ammonia | Tholins 2 - 253 K in water/ammonia |
| Adenine | 0 | $1 - 2 \times 10^{-2}$ | 0 |
| Alanine | No data | $2 - 3 \times 10^{-2}$ | 0 |
| Aspartic acid | $1.6 – 2 \times 10^{-3}$ | $3 – 4 \times 10^{-3}$ | $0 – 3 \times 10^{-4}$ |
| Glycine | $4 - 6 \times 10^{-2}$ | $3 – 4 \times 10^{-1}$ | $0 – 4 \times 10^{-3}$ |
| Urea | 0 - 3 | 6 - 12 | 0 - 2 |
| Uracil | 0 | $6 – 9 \times 10^{-4}$ | 0 |

*[Fig. 1] - Methane cycle and variety of surface features able to participate in surface chemistry (adapted from [6]. © 2012, with permission from Elsevier).*

*[Fig. 2] - Titan, the largest satellite of Saturn, with its unique organics-rich atmosphere is an active prebiotic-like reactor at the planetary scale. © From [1] adapted from a NASA/JPL image; reproduced by permission of the Royal Society of Chemistry.*

*[Fig. 3] - Production yields (w/w) of amino acids, nucleobases and urea produced from hydrolysis of tholins after 10 weeks in water–ammonia solutions at different temperatures.*

This model of Titan's interior has recently been supported by Cassini-Huygens observations. It has also been proposed that ammonia–water mixtures can erupt from the putative subsurface ocean leading to cryovolcanism. Titan's aerosols, once on the surface, may chemically evolve in spite of the low surface temperature (94–92 K) if they are in contact with water or water–ammonia mixtures. Big impacts on Titan's surface may episodically melt the ice crust and form liquid water oases that could stay in the liquid state for up to several thousands of years (Fig. 1). This could favor a chemical evolution of the organic components of atmospheric aerosols that settled down to the surface. Otherwise, these organics may also evolve at much slower chemical rates in the absence of violent-impact episodes.

Several experimental works have already been performed to study the low temperature hydrolysis of the macromolecular organics of the aerosols [4] [5] [1]. The high temperature acidic hydrolysis of plasma-generated tholins produces a large variety of amino acids and other organics. The production of amino acids is still observed, when hydrolysis is performed with liquid water at neutral pH. Similar results are obtained from alkaline solutions, using water–ammonia mixtures. However, questions still remain. Could laboratory-synthesized tholins and by extrapolation Titan's aerosols, allow the production of biologically interesting compounds such as amino acids in the presence of low temperature water–ammonia mixtures? What could be the molecular nature of the products and their yields? What could be the chemical pathways that form these biologically interesting compounds?

To answer these questions we synthesized laboratory analogues of Titan's aerosols from a $N_2$:$CH_4$ (98:2) gas mixture irradiated in a low-temperature continuous-flow regime by a DC cold plasma discharge. The analogues were recovered, partitioned in several 10.0 mg samples and placed in aqueous ammonia solutions at low temperature for 10 weeks [6] [1]. After a chemical derivatization process performed on the refractory phase of the aerosol analogues, with MTBSTFA in DMF, some alkaline hydrolysis products were identified and quantified by gas chromatography coupled to mass spectrometry. The results show (Fig. 3) that Tholins are very reactive toward an oxygen source. Urea is identified as the main product of Titan's tholins hydrolysis in ammonia–water solutions, with a production yield in mass, ranging from 6% to 12% at 279 K after 10 weeks. Several amino acids —alanine, glycine and aspartic acid— and tentatively uracil and adenine nucleobases are also produced with yields from 0.001% to 0.4%. The determination of production yields carried out by the present study is a major step into the characterization of potential aerosols evolution on Titan (Fig. 2). Extrapolation of the obtained quantitative data can allow to estimate the possible concentration of these compounds in a Titan little pond, dissolved or in suspension (whatever the liquid is). With a flux of aerosols to Titan's surface of ~ $2 \times 10^{-14}$ $g.cm^{-2}.s^{-1}$, if 0.1% of the particle is transformed in amino acids, within 1000 years this gives ~ 1 mg amino acids per $cm^2$. In a 10 m deep little pond, this corresponds to ~ 10 $nmole.L^{-1}$. This range of concentration is compatible with the capability of analytical techniques for in situ space instrumentation.

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AUTHORS: L. Le Sergeant d'Hendecourt [1], U. Meierhenrich [2], C; Meinert [2], P. de Marcellus [1], L. Nahon [3]

# Exobiology

Laboratory contribution

## *Photochemistry of analogues of interstellar ices using circularly polarized light*

## Photochimie d'analogues de glaces interstellaires en lumière circulairement polarisée

[1] Institut d'Astrophysique Spatiale, CNRS – UPS, UMR 8617, Campus d'Orsay, Orsay, cedex, France, ldh@ias.u-psud.fr.
[2] Laboratoire de Chimie des Molécules Bioactives et des Arômes, UMR 6001, 9 Université de Nice-Sophia Antipolis, 06108 Nice, France.
[3] Synchrotron SOLEIL, 91192 Gif-sur-Yvette, France.

### *Abstract*

*Ices are very abundant in molecular clouds and their composition is well known. Photochemistry of interstellar ice analogues lead to the formation of an organic residue which, if hydrolyzed, show the presence of numerous amino-acids. The same experiment, performed using circularly polarized light has produced an enantiomeric excess in one amino acid, comparable to what is observed in some meteoritic organic samples suggesting a possible origin for this material on the surface of planets.*

### Résumé

Les glaces sont très abondantes dans les nuages moléculaires et leur composition chimique est bien connue. La photochimie d'analogues en laboratoire produit un résidu organique complexe dont l'hydrolyse permet d'isoler de nombreux acides aminés. La même expérience, réalisée avec du rayonnement circulairement polarisé, a permis de vérifier la possible production de ceux-ci avec un léger excès énantiomérique, analogue à celui observé sur certains acides aminés présents dans les météorites.

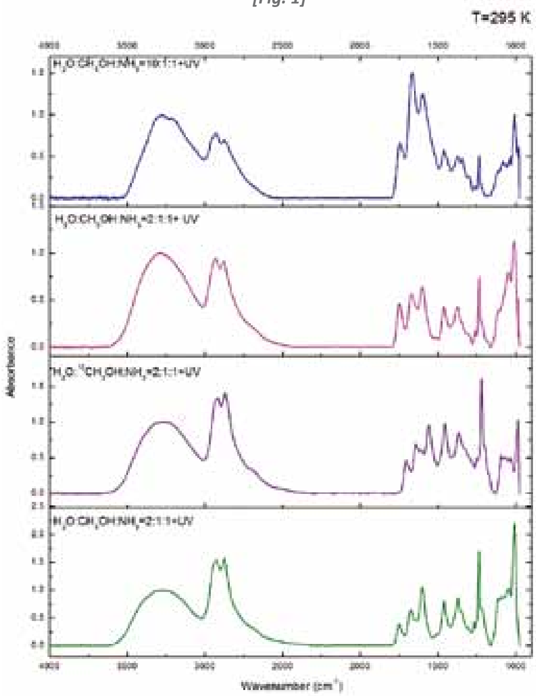
**Interstellar ices** are known to be very abundant in molecular clouds where stars, planets and debris such as comets and asteroids will form. The composition of these ices is quite well known, thanks to observations from satellites such as ISO in the late nineties and large ground based telescopes. They are principally made of water, methanol, ammonia, carbon monoxide and dioxide. This composition and their physical structure can be studied in the laboratory using simulations that mimic some interstellar processes.

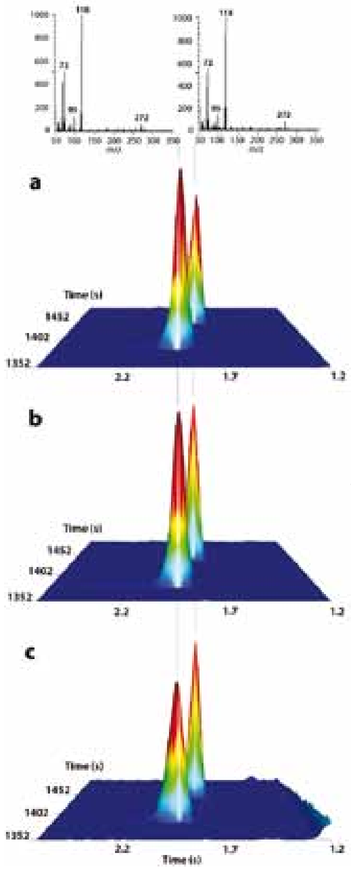
Many experiments have been performed to study the evolution of these ices upon energetic processing (ultraviolet photons, fast protons). These experiments always lead to the formation of organic residues that are the subject of chemical analyses. The infrared spectrum of a typical residue is shown on Fig. 1. Such a spectrum reveals the presence of numerous chemical functions such as carboxylic acids, alcohols, esters, ketones, hydrocarbons… This residue is thought to be made out of large macromolecules that remain fully hydro soluble because of the presence of hydrophilic functions. This property of solubility makes this material very attractive in the context of prebiotic chemistry.

Acid hydrolysis treatment of the residue, a classical procedure to study the composition of organic matter in meteoritic samples, has shown the presence of numerous amino acids which confirms the interest of such materials as a plausible candidate for the origin of exogeneous organic matter on the surface of telluric planets where, in the presence of liquid water, a much more complex and really prebiotic chemistry may then develop.

As well known, proteins from living organisms are composed of 20 amino acids that are (all but one) chiral molecules, bearing at least one asymmetric carbon. Chiral molecules may exist in two forms called enantiomers, R and L (for right and left), one being the image of the other in a mirror and thus not superimposable. In abiotic synthesis, amino acids are known to be strictly racemic meaning that the L and R forms are exactly equal in proportion. However, in living matter, amino acids are known to be only composed of the L enantiomer and this property is called homochirality. The origin of this reason is unknown. What is postulated however is that the induction of a small level of asymmetry in organic species can then lead quickly to homochirality via various amplification mechanisms.

[Fig. 1]




[Fig. 2]

To test this hypothesis, an experiment has been performed using the ultraviolet circularly polarized light from the synchrotron SOLEIL on the DESIRS beamline. The experiment is exactly the one described above and involves the photochemistry of interstellar ice analogues, made of water, methanol and ammonia. Again, at the end of the experiment, a residue is produced. This residue has been then hydrolyzed to provide amino acids. In this last experiment, a sensitive technique has been used, multidimensional gas chromatography coupled to mass spectrometry, that allows to separate enantiomers on one amino acid, alanine, a proteic amino acid, actually the most abundant one after glycine in the sample [1]. The result on alanine has shown significant excesses (up to 1.34%) in one enantiomeric form over the other. It has also been shown that this excess is roughly proportional to the number of chiral photons per molecule deposited to form the ice in the experiment where UV-CPL is simultaneously acting. The change in the helicity sign of the CPL changes the excess to the other enantiomer, as expected. Finally, measuring correctly so small excesses is possible with the use of labeled $^{13}C$ carbon atoms in the initial ice so that contamination can be easily avoided and the measurement remains thus significant.

A final test has shown, in the same experimental configuration that the use of linearly polarized light has produced, as expected, alanine in racemic proportion. Note that, measuring such a small excess (around 1%) is possible and meaningful since the carbon atoms of the initial ices are

*[Fig. 1] - Infrared spectra of a typical organic residues produced by the photochemistry of analogues of interstellar ices. Positions of the bands are given in cm$^{-1}$ and correspond to chemical molecular subgroups on macromolecular entities (P. Modica, PhD Thesis, 2013).*

*[Fig. 2] - Multi-dimensional gas chromatograms of $^{13}C$-alanine enantiomers for the three polarization regimes. Amino acids L-alanine (left signals) and D-alanine were produced by the 6.64-eV UV photo-irradiation with (a) left-handed circularly polarized light (L-CPL), (b) linearly polarized light (LPL), and (c) right-handed circularly polarized light (R-CPL). The alanine produced by irradiation with L- CPL shows an enantiomeric excess for the first eluting enantiomer, i.e., L-alanine, whereas the irradiation with R-CPL results in an enantiomeric excess of the second eluting enantiomer, i.e., D-alanine. Mass spectra for both enantiomers, given on the top of the figure, are identical.*

labeled in the isotope $^{13}C$ so that biological contamination can be safely avoided and the result can be trusted. The quality of the result is shown on Fig. 2.

CPL is observed in the Orion-KL nebula with the same helicity on very large scales, much larger than our solar system, in environments where ices do exist. It is thus proposed, that chiral asymmetry of the light may have been transferred to the chiral molecules that form this organic material. Such a slight asymmetry has indeed been detected in primitive materials from meteorites. It should be possible to establish a connection between photochemistry of interstellar ices and the abiotic organic matter found in meteorites. This asymmetry may be then amplified by a mechanism that remains to be elucidated so as to reach homochirality. This makes these organic residues possible candidates to investigate their possible role in prebiotic chemistry, leading further to the origin of life.

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