THE "AMINO" EXPERIMENT ON EXPOSE

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ABSTRACT

The "AMINO" experiment will take place, end of 2004, in the "EXPOSE" ESA device on the Columbus module outside the International Space Station (ISS). The objective of the "AMINO" experiment is mainly to study space chemistry in the solar system in relationship to the origin of life. The main goal is to support the hypothesis that extraterrestrial life-related compounds, ranging from bioorganic precursors to biological macromolecules, might have been delivered to the primitive Earth when associated with comets, meteorites or micrometeorites. Another aspect of organic chemistry in the solar system that one associated to Titan's environment. This domain is of primary interest for exobiology, due to the rich organic chemistry that occurs on Titan. The last interesting chemistry domain in the solar system concerns comets. Some cometary analogues and related compounds will be also studied.

1. INTRODUCTION

Among the different hypotheses put forward to explain the origin of the terrestrial life, delivery of exogenous organic molecules to the primitive Earth is now considered as the most promising theory. Space chemistry has revealed an unexpected complexity as shown by the growing number of molecules detected in the interstellar space [1]. More of 120 molecules were identified and most are organic and among them, all the expected precursors for the building blocks of life. Another example of the complexity of the space organic chemistry is carried out by the study of carbonaceous chondrites that contain up to 5% by weight of organic matter. The study of the Murchison meteorite, which formation is contemporary of that of the solar system, has revealed the presence of about 500 organic compounds, including nucleic bases and 80 amino acids, 8 of these being components of the contemporary proteins [2]. In 1997, an excess of about 9% of the L-form for isovaline and α-methyl-isoleucine, non-protein amino acids, which cannot result from biological contamination and cannot racemize easily, were found in the Murchison meteorite. On the other hand, norvaline and α-amino-n-butyric acid, their Cα-hydrogen analogs which can easily racemize, were found as racemic mixtures (equal mixture of L and D enantiomers) [3]. This supports a possible asymmetric synthesis in space followed by an 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 contribution on Earth could also have carry safely, organic molecules to the primitive Earth. The study of micrometeorites extracted from old Antarctica blue ice [4] show that about 80% of carbonaceous ones, in the 50 to 100 µm size range, remain unmelted after crossing the terrestrial atmosphere. Analyses of such micrometeorites [5] have shown traces of amino acids such as α-amino butyric acid. Recent sample exposition to space conditions, onboard MIR Station, have demonstrated that 5 µm thick film of meteorite powder was able to protect efficiently associated amino acids against solar radiation [6].

Comets also represent an important source of interstellar organic molecules delivered to the primitive Earth. The organic fraction, represents about 33% of the cometary dust, and contains many precursors of the biological monomers, such as hydrogen cyanide, formaldehyde, formic acid (HCOOH), acetaldehyde (CH_3CHO) or imidazole ($C_3H_4N_2$) [7] and more complex organic molecules such as hexamethyl-tetramine (HMT) or polyoxymethylene (POM, $(CH_2\text{-}O)_n$).

The molecules detected in the interstellar medium appear of lesser complexity than those found in meteorites or comets. However, it is assumed that chemical complexity can be reached if molecular concentrations are high enough, and if the produced compounds can be concentrated and protected against photolysis. The photoprocessing of the interstellar dust grains is known to produce a mantle of refractory organic molecules at their surface. During its lifetime, the grain mantle is subjected to ultraviolet radiation present in the interstellar medium which can lead to chemical complexity. Such evolution was recently reproduced during laboratory simulations to produce many complex organic molecules including up to 16

amino acids [8]. As the cometary nucleus is formed by aggregation of interstellar grains, it is important to understand the refractory core mantle chemistry during the grain lifetime and the final evolution of such produced organic molecules in the comets.
Another aspect of organic chemistry in the solar system may be studied in Titan's environment. This domain is of primary interest for exobiology, due to the rich organic chemistry that occurs in its atmosphere. The Cassini-Huyghens mission under way to Titan will provide more information from 2004 on. However, laboratory simulations and modelling will be always necessary to understand the chemical processes driving to the production and the evolution of organic molecules in Titan's atmosphere.
Recently, the panspermia theory was rejuvenated. Since bacteria and bacterial spores are able to resist to space conditions [9], their transfer between planets via meteorites seems possible if sufficiently protected from UV radiation. Another alternative to this theory is the transfer of informational macromolecules such as DNA in place of living organisms.
Before reaching the Earth, organic molecules are exposed to UV radiation in interstellar space and in the solar system. UV flux in diffuse interstellar medium is about 10^8 photons cm^{-2} s^{-1}. In Earth orbit, the corresponding solar flux is in the range of 10^{16} photons cm^{-2} s^{-1}. It means that a one week corresponds to a 275 000 year trip in the interstellar medium. Comparatively to ground experiments, space is an extended laboratory allowing to expose samples to all space parameters simultaneously and to irradiate many samples under strictly identical conditions.

2. GENERAL SCIENTIFIC AIMS

2.1 Amino acids, peptides and derivatives exposed to space conditions (CBM, Orléans)

The program will complete the previous short and medium-term space missions by a long term exposition. The goal of these experiments is to understand the chemical comportment of simple biological molecules when exposed to space conditions, mainly to vacuum and radiation. This should allow to understand in which conditions the biological building blocks could survive space exposition.
For these experiments, amino acids, peptides and derivatives will be studied in respect of their chemical reactivity as photolysis, polymerization or racemization. Samples will be exposed as dry films loaded on MgF_2 windows allowing irradiation in the vacuum UV (VUV). Samples will be either exposed inside vented cavities connected to spatial medium, either exposed inside isolated closed cells to allow by-products recovering for further identification. Mineral surfaces mimicking micro-meteorites will also be associated to the samples in order to study their protective effect and possible chemical activity.
Biological building blocks such amino acids could be also be synthesized from simple gaseous precursors during a long term exposition to solar radiation. This experiment could mimic the photochemistry occurring in gaseous phase in the interstellar space in the vicinity of icy dust grains.

2.2 Space chemistry of CHON materials: cometary and Titan's aerosol analogs (LISA, Créteil)

The organic chemistry on Earth is closely associated to the presence of water. However, another important spatial organic chemistry, without water, exists in the solar system, which can be studied in Titan's environment.
The laboratory aerosol analogs are now well accepted as representative of Titan's aerosols. The studies showed that aerosols represent an important sink for the atmospheric nitrogen, and that they cannot be dissolved in hypothetical hydrocarbon lakes at Titan's surface. As a consequence, the only way for this trapped nitrogen to be re-injected in the atmosphere is via the interaction of these deposited aerosols with lightening, volcanism or high energy particles like cosmic rays which can reach the surface.
The project is to give answers to these questions by exposing organic samples, representative of Titan's atmosphere, to space conditions and especially to vacuum and solar irradiation. Tholins are Titan's aerosols analogs synthesized in the laboratory from CH_4:N_2, or CH_4:N_2:H_2O:CO:CO_2 containing mixtures. The chemistry of such a mixture submitted to the whole solar spectrum may lead to solid residues containing tholins. Moreover, the study of tholins' evolution in space will be of primary importance to develop theoretical models.
Another important chemistry in the solar system is that related to comets. Laboratory simulation experiments have allowed to synthesize many complex organic molecules. HMT (Fig.1) was synthesized during irradiation on cometary ice analogs with UV or protons. This long-term exposition will allow to study its stability against solar UV and give informations on its possible actual presence on comets.

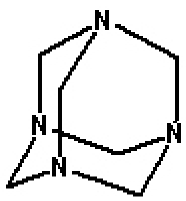

Figure 1: HMT

POM are other compounds produced from cometary ice analogs, when submitted to thermal processes. Two different POM structures will be studied.

2.3 Study of adenine and RNA resistance (University P. & M. Curie, Paris)

The aim of these experiments is to check the conservative or modified properties such as integrity

and aminoacylation of RNA strands after space exposition.
Salt is known to be abundant on numerous astral and planetary bodies such as Mars and Europa [10]. On the other hand, salt may stabilize and protect RNA against degradation. We have already shown the resistance of tRNA at 85˚C and that of selected RNA at 96˚C, both in the presence of high salt concentration. It therefore important to study and understand the influence of high salt concentration on nucleic bases and RNA resistance.
Bases, including adenine, nucleosides, and a GAAA RNA stem-loop (Fig.2) will be exposed during the mission, free, in the presence of clay, and in the presence of high salt concentration.

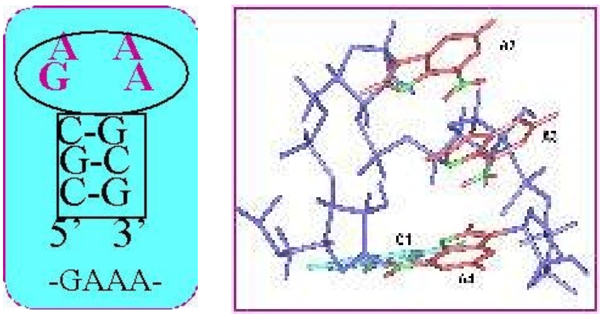

Figure 2: GAAA RNA stem-loop

The aim is to control, in situ, the putative modification of bases and nucleotides after space exposition with SERS (Surface Enhanced Raman Spectroscopy). This technic allows picomole detection of adenine and small RNA when adsorbed on montmorillonite.

2.4 Exobiology and DNA transfer (INRA, Versailles, Observatoire de Paris, Meudon)

The hypothesis that life exists or has existed elsewhere than on Earth is suggested by the finding of planets in the vicinity of other stars and the discovery of many of the chemical components of life outside the biosphere. Life on Earth probably originated from a single source, since the same genetic code is used by all organisms studied so far. It is therefore not inconceivable that life as we know it was imported from the outside, particularly given the resistance shown by known bacteria and bacterial spores to space.
Until life is demonstrated outside Earth, there is no way to directly test the panspermia hypothesis. It is possible, however, to accumulate circumstantial evidence by studying the effects of space conditions on life and its components. This is a extension of published research using spores of Bacillus subtilis, showing that of the numerous possible liabilities in space, UV light is probably the most destructive, the primary target being cellular DNA. Panspermia theory may be updated, preferring to consider DNA transfer as a current event. The goal is to consider the possibility that DNA could carry biological information over long distances and times. It is possible that DNA has been and still is the vehicle for the transfer of biological information from space to Earth and between different locations on Earth and among different organisms. For the exposition experiments, to better use the limited space available, we set out to define an experimental system consisting of multiple small samples (1 µL). MgF_2 or plastic microscope slides will be prefered for their hydrophobicity and that DNA samples stick well to them. The ability of such surface to retain DNA and release it after sample rehydration was tested.
DNA will be tested either alone or complexed with proteins as histones, polyamines and mineral powders. We will use a portion of the *nptII* gene, encoding resistance to kanamycin, in a marker rescue assay for the integrity of the biological information. The second technical improvement was to introduce a signature into the nucleotide sequence, through the construction of an nptII gene containing four regularly spaced base substitutions at the *NcoI* site, converting it into a *draII* site. This modified *nptII* is easily identified by restriction enzyme digestion and sequencing. It should allow to argue against the possibility of DNA contamination from outside sources, e.g. wild bacteria. (Fig.3).

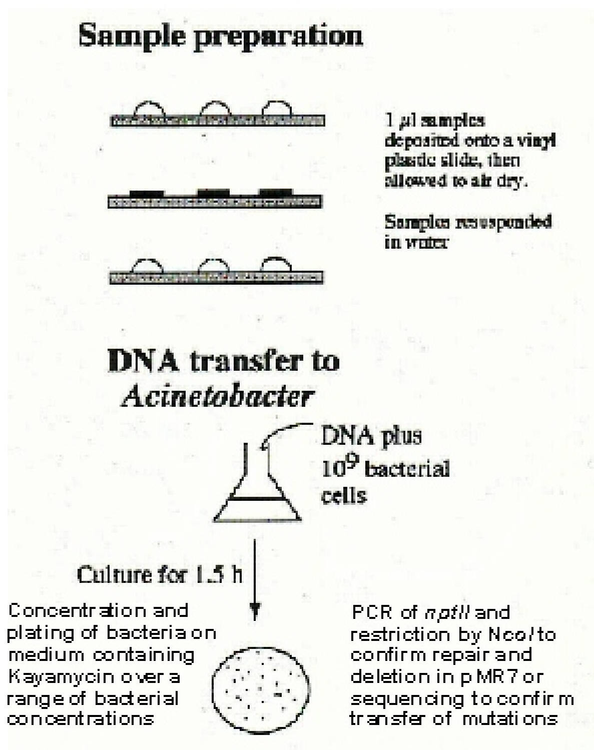

Figure 3: sample preparation

3. MATERIAL REQUIREMENTS

2.1 The cells

The “AMINO” experiment will use cavities capped by individual quartz or MgF_2 windows. For dry films exposition, cavities will be vented to allow pressure equilibration, and protected with 0.22 µm filters to prevent cross-contamination with outer Space (Fig.4a). These samples will be loaded in solution or in suspension, and then dried on the inner face of each sample-carrier window.

In order to recover gaseous by-products and to expose liquid or gaseous samples, closed cells will be required (Fig.4b)

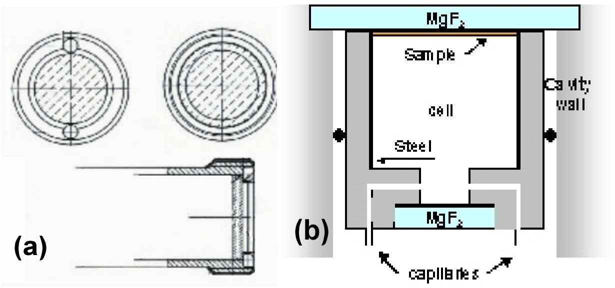

Figure 4: Cells for “AMINO” sample carrier: (a) Vented cell; (b) Close cell with an example of a sample exposed as dry film.

2.2 Temperature requirements

Temperature sensors need to be installed inside two opposing cavities to measure the temperature in both exposed and light protected cells. According to the previous missions, the temperature difference between exposed and dark control cavities is usually about 5 C. During the mission, temperature should be in the -10 C to +40 C range.

3.3 Windows requirements

For nucleic acids, which absorb around 254 nm, quartz windows, allowing irradiation down to 180 nm, will be used. For amino acids, peptides, and cometary and Titan’s analogs, vacuum UV irradiation is needed down to the intense Lyman α band of hydrogen at 121.6 nm. MgF_2 windows, 1-2 mm thick, which are transparent down to 110 nm (Fig.5), are then needed for a full UV irradiation of the samples.

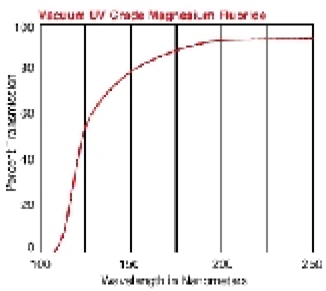

Figure5: Vacuum UV absorption spectrum of 1mm thick MgF_2

4. CONCLUSION

The “AMINO” program will explore the main aspects of the solar system chemistry, from the processing of simple organic molecules under UV radiation to the photo-resistance and the chemical evolution of biological molecules exposed to the space conditions. The“EXPOSE” mission offers a 1 to 3 years exposition time which is impossible to reproduce in laboratory simulations. This mission should provide enough data for a better understanding of the solar system chemistry and to provide more information about the space contribution to the origins of life on Earth. solar system chemistry and gain a extrapolate.

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