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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. © 2007 COSPAR. Published by Elsevier Ltd. All rights reserved.

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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

* Corresponding author. E-mail address: cottin@lisa.univ-paris12.fr (H. Cottin). 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,

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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*.

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 dependant (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

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