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Benjamin Fleury, Ludovic Vettier, Nathalie Carrasco

To cite this version:

HAL Id: insu-01208323
https://hal-insu.archives-ouvertes.fr/insu-01208323
Submitted on 2 Oct 2015

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Organic chemistry in the ionosphere of the early Earth

B. Fleury (1), L. Vettier (1), and N. Carrasco (1)
(1) Université Versailles St-Quentin ; Sorbonne Universités, UPMC Univ. Paris 06 ; CNRS/INSU, LATMOS-IPSL, 11 Boulevard d’Alembert, 78280 Guyancourt, France (nathalie.carrasco@latmos.ipsl.fr)

Abstract
The emergence of life on the Early Earth during the Archean has required a prior complex organic chemistry providing the prerequisite bricks of life. The origin of the organic matter and its evolution on the early Earth is far from being understood. Several hypotheses are investigated, possibly complementary, which can be divided in two main categories: the endogenous and the exogenous sources. In this work we have been interested in the contribution of a specific endogenous source: the organic chemistry occurring in the ionosphere of the early Earth. At these high altitudes, the VUV contribution of the young sun was important, involving an efficient production of reactive species. Here we address the issue whether this chemistry can lead to the production of larger molecules with a prebiotic interest in spite of the competitive lysing effect of the harsh irradiation at these altitudes.

1. Introduction
1.1 Main composition of the early Earth
Recent geological studies inform us on the composition of the primitive atmosphere of the Earth during the Hadean and the Archean epochs, before the rise of oxygen 2.5 Gyr ago [1]. The atmosphere is now known to have been mainly composed of molecular nitrogen N₂, carbon dioxide CO₂ and water vapor H₂O. Molecular hydrogen H₂ is moreover suggested as having been additionally outgassed from the mantle [2]. As the upper atmosphere is expected to be dry due to the cryogenic trapping in the troposphere, our study has been based on an atmosphere mainly made of N₂ and a few percents of CO₂ and H₂.

1.2 Experimental simulation
To reproduce the organic chemistry which as been initiated by solar VUV photons in the ionosphere of the early Earth, we have used a plasma experiment. This is a Radio-Frequency Capacitively Coupled Plasma (RF CCP) at low pressure [3][4]. The characterization of the plasma discharge has been previously modeled and shows a maximum of the energy distribution at 600 nm and a tail with wavelengths down to 70 nm [5]. This similarity with the young Sun spectrum enables to simulate in the laboratory the energy deposition on the top of the early Earth atmosphere. The products are accumulated during the discharge by cryogenic trapping and are further analyzed by in situ mass spectrometry and mid-infrared absorption spectroscopy.

3. Results
CO₂ is found to be efficiently dissociated, with consumptions larger than 20%. It must be noted that CO₂ is the only source of carbon for organic chemistry in the present case. Hydrogen and nitrogen are also partially dissociated in the discharge even if in lower amounts than CO₂. The main product is carbon monoxide CO. However a strong coupling between the reactive species is observed through the productions of water H₂O, ammonia NH₃, HCN and methanimine, CH₂=NH₂. Larger molecules are also detected in the gas products trapped and their identifications are in progress (Figure 1). Solid organic aerosols are finally collected showing that an efficiently organic growth is actually occurring in the discharge.
4. Summary and Conclusions

In the present experimental study we have simulated the chemistry occurring in the partially ionized ionosphere of the early Earth. We have chosen the extreme scenario of an oxidative atmosphere where carbon is only supported by carbon dioxide (no methane). The result is that we have not only observed prebiotic small bricks in the gas phase such as ammonia, methylamine and hydrogen cyanide, but also in the solid phase with the production of solid organic aerosols. This study confirms that the ionosphere could be an important source of prebiotic material, with a global scale on the early Earth. It would be responsible for the production of molecules with a prebiotic interest directly from the main atmospheric constituents, and their destruction under solar VUV irradiation would be prevented by the continuous conversion into solid organic aerosols.

Acknowledgements

We thank the Région Ile-de-France for their financial support (DIM ACAV thesis grant).

References


