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## Organic chemistry in the ionosphere of the early Earth

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### 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 eons, before the rise of oxygen 2.5 Gyrs ago [1]. The atmosphere is now known to have been mainly composed of molecular nitrogen  $N_2$ , carbon dioxide  $CO_2$  and water vapor  $H_2O$ . Molecular hydrogen  $H_2$  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  $N_2$  and a few percents of  $CO_2$  and  $H_2$ .

#### 1.2 Experimental simulation

To reproduce the organic chemistry which has 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

$CO_2$  is found to be efficiently dissociated, with consumptions larger than 20%. It must be noted that  $CO_2$  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  $CO_2$ .

The main product is carbon monoxide CO. However a strong coupling between the reactive species is observed through the productions of water  $H_2O$ , ammonia  $NH_3$ , HCN and methanimine,  $CH_2=NH_2$ . 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.

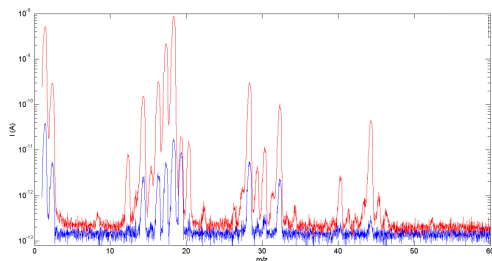


Figure 1: In blue, blank mass spectrum of the reactor. In red, mass spectrum of the products after 4 hrs of cryogenic trapping.  $M/z$  signatures are observed up to 60 u.

#### 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.

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