



## Organic chemistry in a CO<sub>2</sub> rich early Earth atmosphere



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### ABSTRACT

The emergence of life on the Earth has required a prior organic chemistry leading to the formation of prebiotic molecules. The origin and the evolution of the organic matter on the early Earth is not yet firmly understood. Several hypothesis, possibly complementary, are considered. They can be divided in two categories: endogenous and exogenous sources. In this work we investigate the contribution of a specific endogenous source: the organic chemistry occurring in the ionosphere of the early Earth where the significant VUV contribution of the young Sun involved an efficient formation of reactive species. We address the issue whether this chemistry can lead to the formation of complex organic compounds with CO<sub>2</sub> as only source of carbon in an early atmosphere made of N<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>, by mimicking experimentally this type of chemistry using a low pressure plasma reactor. By analyzing the gaseous phase composition, we strictly identified the formation of H<sub>2</sub>O, NH<sub>3</sub>, N<sub>2</sub>O and C<sub>2</sub>N<sub>2</sub>. The formation of a solid organic phase is also observed, confirming the possibility to trigger organic chemistry in the upper atmosphere of the early Earth. The identification of Nitrogen-bearing chemical functions in the solid highlights the possibility for an efficient ionospheric chemistry to provide prebiotic material on the early Earth.

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### 1. Introduction

Life is supposed to have appeared on Earth before 3.5 Ga during the Archean and maybe before the Late Heavy Bombardment (LHB) during the Hadean (Nisbet and Sleep, 2001). The presence of liquid water and organic matter is now widely accepted as conditions for the apparition of life (Cottin et al., 2015). Understanding the origins of these organic molecules, which are implicated in the apparition of life is of prime interest for astrobiology. Different origins are proposed for the organic matter on the early Earth at this period: exogenous delivery by meteorites and comets, or endogenous formation in hydrothermal vents or in the primitive atmosphere (Chyba and Sagan, 1992).

Reduced atmospheres are known to be an important source of organic matter as pointed out by the observation of Titan the largest satellite of Saturn (Tomasko and West, 2010; Waite et al., 2010) or by experiments realized by Miller about the reactivity of the early Earth atmosphere (Miller, 1953). However, if the question of the degree of oxidation of the early Earth atmosphere and so its composition is not completely solved, there is evidence that

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the upper mantle of the Earth was at the present redox state since 3.9 Ga (Delano, 2001) and probably 4.4 Ga (Trail, 2011) resulting in a relatively oxidant primitive atmosphere dominated by molecular nitrogen N<sub>2</sub> and carbon dioxide CO<sub>2</sub> (Kasting, 1993). The composition of the early Earth's atmosphere is an important parameter to consider for the production of organic matter. Different experiments highlighting the fact that chemistry in oxidant atmospheres produces less organic compounds than in reduced atmospheres (Schlesinger and Miller, 1983b, 1983a).

Recent experimental works showed that organic aerosols can be produced in an atmosphere dominated by CO<sub>2</sub> with a minor amount of methane CH<sub>4</sub> (Trainer et al., 2006). But it remains uncertain whether CH<sub>4</sub> was present in the primitive atmosphere of the Earth. Indeed, today 70% of the methane emissions have biogenic sources and for an important part from ecosystems, which do not exist during the Hadean and the Archean eons (Denman et al., 2007). The two principal abiotic sources of methane considered for the early Earth are delivery by meteoritic and cometary impacts and production by serpentinization process (Kasting, 2005). These sources could be responsible for a methane amount of only few ppm<sub>v</sub> in the primitive atmosphere of the Earth (Emmanuel and Ague, 2007; Feulner, 2012; Guzmán-Marmolejo et al., 2013; Kasting, 2005), which is much lower than the amount considered in experimental simulations (Trainer et al., 2006) or climate model (Charnay et al., 2013). For these reasons, we have chosen to ex-

plore a potential organic chemistry in an early Earth's atmosphere with only CO<sub>2</sub> as source of carbon.

Moreover, if CH<sub>4</sub> concentration should be low in the early Earth's atmosphere, molecular hydrogen H<sub>2</sub> could be present in a larger amount. Indeed, assuming that the loss of hydrogen to space was limited by diffusion, a mixing ratio of 10<sup>-3</sup> has been established for the early Earth's atmosphere (Kasting, 1993). But, assuming a lower Jeans escape than today, Tian et al. (2005) has proposed that H<sub>2</sub> mixing ratio could be 100 times higher, reaching 10% and up to 30%. According to the authors, this lower efficiency of the Jeans escape for H<sub>2</sub> would be explained by a lower temperature of the exobase at this period. Indeed, in one hand the higher CO<sub>2</sub> concentration at this period would result to a higher radiations backed to space and in the other hand, the lower oxygen concentration in the atmosphere (O<sub>2</sub>) would result to a lower heating of the exobase by the atomic oxygen UV absorbance (Martin et al., 2006; Tian et al., 2005). This new calculation has been discussed since, notably because of the limited amount of CO<sub>2</sub> present in the atmosphere to cool the exobase (Catling, 2006; Tian et al., 2006). A more recent model has determined a hydrogen mixing ratio of 1% at the homopause. It results that the exact concentration of H<sub>2</sub> during the Hadean and the Archean remains difficult to determine but could be important. For this reason, the influence of H<sub>2</sub> on the primitive atmospheric reactivity needs to be studied.

We present in this paper an experimental study of the organic growth occurring in an early Earth's atmosphere made of N<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>. A first study performed in similar conditions highlighted an important formation of water vapor in the stratosphere and ionosphere of the early Earth (Fleury et al., 2015). We are now interested in investigating the concomitant formation of organic molecules, as both gaseous and solid products. The composition of the Earth atmosphere has evolved over geological time, notably CO<sub>2</sub> whose concentration during the Hadean and the Archean is not precisely known (Feulner, 2012). For this reason, we also take into account the influence of the CO<sub>2</sub> initial amount on the atmospheric chemistry of the early Earth simulated in our experiments.

## 2. Experimental setup and analytical protocols

### 2.1. Experimental simulation

We used here the PAMPRE experimental setup, which has been described in details in previous publication (Szopa et al., 2006). It is a Radio Frequency Capacitively Coupled Plasma (RF CCP) at low pressure. In this experiment, a discharge is generated between a polarized electrode and a cylindrical grid grounded electrode confining the plasma. Before each experiment, the reactor is heated and pumped down to  $2 \times 10^{-6}$  mbar. The gaseous flow is then injected continuously and pumped through a rotary vane vacuum pump. Three gas bottles are used in the experiments to generate the reactive gaseous mixture: one with high-purity of N<sub>2</sub> (99.999%), one containing a N<sub>2</sub>-H<sub>2</sub> mixture with 5% of H<sub>2</sub> and one with CO<sub>2</sub> (>99.995%).

The generator RF power is set to 30 W and the total gas flow rate to 55 sccm resulting in a 0.9 mbar pressure in the reactor. The modeling of the used plasma has been done in pure N<sub>2</sub> (Alves et al., 2012). The electrons energy distribution function (EEDF) presents a maximum at 2 eV and a relatively populated tail for electron energy above 4 eV and up to 14 eV mimicking the young solar spectrum, which presents a higher UV and X-ray emission flux and a lower visible and infrared emission flux than today (Claire et al., 2012). The electrons present in our plasma have sufficient energy to dissociate and ionize N<sub>2</sub> and activate nitrogen

chemistry as well as CO<sub>2</sub> and H<sub>2</sub>. The PAMPRE experiment can be so used to simulate the reactivity of the upper layers (above the troposphere) of the early Earth, where N<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub> can be dissociated and ionized.

The hydrogen mixing ratio is kept constant at 4% for all experiments. This concentration is chosen in agreement with recent modeling studies of the H<sub>2</sub> mixing ratio, giving an upper limit about 1% for the Archean atmosphere (Kuramoto et al., 2013) and up to 30% (Tian et al., 2005). The gas flow is adjusted among N<sub>2</sub> and CO<sub>2</sub> from an experiment to another to introduce CO<sub>2</sub> at different mixing ratios: 1%, 5% and 10%.

### 2.2. Cryogenic trapping

In order to detect and identify gas species produced in low quantity, we have trapped the volatile species and accumulated them by cooling the plasma box. For that, a part of the experiments presented below is performed with a continuous injection of liquid nitrogen (L<sub>N2</sub>) inside the stainless-steel block supporting the grounded electrode. The plasma box is cooled by thermal conduction. The temperature is fixed at 173 K to prevent N<sub>2</sub>, H<sub>2</sub> and CO<sub>2</sub> condensation. However, the trapping of CO<sub>2</sub> has been observed in the results presented in the section 3.3.2. The trapping of the reactants is discussed in the same section and has been taken into account for the interpretation of the results. Products are accumulated during 4 or 8 h of plasma duration. After plasma turning off, the reactor is pumped to eliminate N<sub>2</sub>, H<sub>2</sub> and CO<sub>2</sub>. The reactor is isolated and the plasma box is warmed up to room temperature. Trapped gases are released and analyzed by mass spectrometry, infrared spectroscopy and by Gas Chromatography coupled to Mass Spectrometry (GC-MS).

### 2.3. Mass spectrometry on gaseous phase

Measurements of the gas phase trapped during a part of the experiments, as described in section 2.2, are achieved with a Pfeiffer QME 200 quadrupole mass spectrometer (QMS). In the spectrometer, neutral species are ionized by electron impact at 70 eV. Gases are transferred to the spectrometer through a capillary tube, which is long enough to keep the pressure below 10<sup>-5</sup> mbar in the spectrometer when the pressure inside the reactor is 0.9 mbar. Its resolution is 100 at *m/z* 100 and it covers 1–100 *u* mass range. Gas trapped are analyzed with a long scanning acquisition of 1 s for each mass between *m/z* 1 and 60.

### 2.4. Infrared spectroscopy on gaseous phase

Trapped molecules are also analyzed with a Thermo Scientific Nicolet 6700 Fourier Transform Infrared (FTIR) spectrometer. A schema of the FTIR setup on the PAMPRE reactor, seen from above, is presented in Fig. 1. The infrared beam is emitted by the FTIR source and passes through the reactor via two KBr windows. Then, the beam is collected by a Mercury Cadmium Telluride (MCT) detector cooled by liquid nitrogen.

In the results presented below, IR spectra are recorded in the 650–4500 cm<sup>-1</sup> range with a resolution of 1 cm<sup>-1</sup> after a co-addition of 500 scans. With only one passage of the beam through the reactor, the corresponding path length is 50.8 ± 0.2 cm.

### 2.5. GC-MS analysis of the gaseous phase

To analyze the gaseous phase *ex situ* by GC-MS, we transfer the trapped gases in the reactor into another external cold trap. It is a cylindrical glass coil immersed in liquid nitrogen and connected to the reactor. Before transferring gases, the cold trap is pumped

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