



Nitrogen isotopic fractionation during abiotic synthesis of organic solid particles



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ABSTRACT

The formation of organic compounds is generally assumed to result from abiotic processes in the Solar System, with the exception of biogenic organics on Earth. Nitrogen-bearing organics are of particular interest, notably for prebiotic perspectives but also for overall comprehension of organic formation in the young Solar System and in planetary atmospheres. We have investigated abiotic synthesis of organics upon plasma discharge, with special attention to N isotope fractionation. Organic aerosols were synthesized from N₂-CH₄ and N₂-CO gaseous mixtures using low-pressure plasma discharge experiments, aimed at simulating chemistry occurring in Titan's atmosphere and in the protosolar nebula, respectively. The nitrogen content, the N speciation and the N isotopic composition were analyzed in the resulting organic aerosols. Nitrogen is efficiently incorporated into the synthesized solids, independently of the oxidation degree, of the N₂ content of the starting gas mixture, and of the nitrogen speciation in the aerosols. The aerosols are depleted in ¹⁵N by 15–25‰ relative to the initial N₂ gas, whatever the experimental setup is. Such an isotopic fractionation is attributed to mass-dependent kinetic effect(s). Nitrogen isotope fractionation upon electric discharge cannot account for the large N isotope variations observed among Solar System objects and reservoirs. Extreme N isotope signatures in the Solar System are more likely the result of self-shielding during N₂ photodissociation, exotic effect during photodissociation of N₂ and/or low temperature ion-molecule isotope exchange. Kinetic N isotope fractionation may play a significant role in the Titan's atmosphere. On the Titan's night side, ¹⁵N-depletion resulting from electron driven reactions may counterbalance photo-induced ¹⁵N enrichments occurring on the day's side. We also suggest that the low δ¹⁵N values of Archaean organic matter (Beaumont and Robert, 1999) are partly the result of abiotic synthesis of organics that occurred at that time, and that the subsequent development of the biosphere resulted in shifts of δ¹⁵N towards higher values.

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1. Introduction

Organic compounds are widely distributed in the Solar System, from very simple to more complex molecules. In contrast to what happen on Earth where organic matter has been mostly synthesized by life since the Archaean, and possibly, the Hadean, eon(s), the formation of organic compounds is generally assumed to result from abiotic processes in the Solar System. Extraterrestrial organics are found mostly as amino-acids and kerogen-like material in

primitive meteorites and as organic haze in planetary atmospheres such as Titan's. Among such organic molecules, the nitrogen-bearing ones are of particular prebiotic interest, as nitrogen is a key element of proteins and nucleic acids. Furthermore, nitrogen seems to play a pivotal role during the production of organic aerosols in the N₂-rich atmosphere of Titan (Israël et al., 2005; Carrasco et al., 2013).

Nitrogen has two stable isotopes, ¹⁴N and ¹⁵N. The ¹⁵N/¹⁴N ratio (3.676×10^{-3} for the terrestrial atmospheric N₂) is often expressed in permil deviation to terrestrial atmospheric N₂ isotope composition (AIR) as $\delta^{15}\text{N} = [(^{15}\text{N}/\text{N})_{\text{sample}} / (^{15}\text{N}/^{14}\text{N})_{\text{AIR}} - 1] \times 1000$ (in ‰). Relative abundances of ¹⁴N and ¹⁵N fractionate upon physical, chemical and biological transformations of N-bearing

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compounds. Remarkably, the isotopic composition of nitrogen presents dramatic variations among Solar System objects and reservoirs, which are not fully understood. N₂ was probably the main N-bearing species in the protosolar nebula (PSN, Grossman, 1972) and was ¹⁵N-poor (¹⁵N/¹⁴N = 2.27 ± 0.03 × 10⁻³, that is, δ¹⁵N = -383 ± 8‰; Marty et al., 2011) whereas all other objects and reservoirs of the Solar System (with the exception of a few like Jupiter's atmosphere) are richer in ¹⁵N by several hundreds to thousands of permil. Most meteorite families and the inner planetary bodies including the Earth have comparable δ¹⁵N values within a few tens of ‰ whereas cometary CN and HCN are enriched in ¹⁵N by a factor of 3 relative to the PSN value (Bockelée-Morvan et al., 2008). ¹⁵N enrichments can be dramatic at the micron scale in meteoritic organics, with δ¹⁵N values up to 5000‰ (Briani et al., 2009). Some of these enrichments may be related to atmospheric processing, as proposed for the atmosphere of Mars (δ¹⁵N_{N2} = +660‰, Owen et al., 1977), but in other cases these ¹⁵N enrichments relative to the PSN nitrogen require other types of extensive isotope fractionation that are poorly understood.

Exothermic ion-molecule reactions at low temperature might have led to extensive N isotope fractionation under specific cold yet dense environments (e.g., dense cores, outer Solar System, Terzieva and Herbst, 2000; Rodgers and Charnley, 2008; Aleon, 2010; Hily-Blant et al., 2013). Alternatively, photodissociation of N₂ associated or not to self-shielding (Clayton, 2002; Lyons et al., 2009; Chakraborty et al., 2013), might have led to ¹⁵N-rich radicals prone to incorporation into forming organics. Such a photochemical induced fractionation has been invoked to address the ¹⁵N-rich HCN relative to N₂ in Titan's atmosphere (Vinatier et al., 2007; Liang et al., 2007; Croteau et al., 2011). However, those theoretical studies have focused on the isotopic composition of very simple gaseous N-bearing compounds, and the propagation and conservation of such a large N isotopic fractionation upon polymerization of organic solids has not yet been fully investigated.

Several experimental works have simulated the synthesis of gaseous and solid organic compounds in gas mixtures similar to Titan's atmosphere (see Coll et al., 2013, for a review) early Earth's atmosphere (Miller, 1953; Chang et al., 1983) or the PSN (Dzizczkiewicz and Lumkin, 1981; Kerridge et al., 1989), either by UV photons or by electron energy deposition. However, only a few of them have focused on the nitrogen incorporation into refractory organics from N₂ dissociation (Trainer et al., 2012; Gautier, 2013), and the extent of related N isotope fractionation is essentially undocumented.

Whatever the original mechanism of isotope selection, N₂ dissociation and nitrogen compound ionization are believed to play an important yet not fully understood role. Plasmas were used in the present study because of the strong covalent bond of N₂, which needs energies above 9.8 eV (<120 nm) to break. Recent experimental simulations have used VUV photons as incident energy but production of aerosols was not reported (Imanaka and Smith, 2010; Peng et al., 2013). So far, electron energy deposition stays the easiest energy source to simulate aerosol productions from irradiated gas mixtures. Here, we investigate the isotopic fractionation of nitrogen during synthesis of solid organics by plasma discharge using N₂-CH₄ and N₂-CO gaseous mixtures as proxies of Titan's atmosphere and the PSN, respectively.

2. Experimental methods

2.1. Aerosols production setups

Two experimental plasma setups were used for this study in order to produce nitrogen-rich aerosols: (i) the PAMPRE experiment (LATMOS, Guyancourt, France), designed to investigate Titan's ionosphere processes; and (ii) the Nebulotron experiment (CRPG,

Table 1

Qualitative comparison of the two plasma setups used in this study.

	PAMPRE	Nebulotron
Gas mixture	N ₂ (90–99%)–CH ₄	N ₂ (20%)–CO
Type of electric discharge	RF (13.56 MHz)	microwave (2.45 GHz)
Size of the reactor (height * diameter)	40 * 30 cm	10 * 0.8 cm
Volume of the plasma (cm ³)	740	2.5
Injected power (W)	30	30
W/cm ³	0.04	12
Pressure (mbar)	0.9	~1
Neutral temperature	300–350 K ^a	≥1000 K (estimated ^{c,d})
Electron density (cm ⁻³)	2 × 10 ^{8a}	5 × 10 ^{10–1} × 10 ¹¹ (estimated ^d)
Average electron energy	2 eV ^b	2 eV (estimated ^d)

^a Alcouffe et al. (2010).

^b Alves et al. (2012).

^c Es-Sebbar et al. (2009).

^d Gries et al. (2009).

Nancy, France), dedicated to simulate young solar nebula processes. Main experimental conditions and plasma characteristics are described below and in Table 1.

2.1.1. The PAMPRE experiment

The PAMPRE (for *Production d'Aérosols en Microgravité par Plasma REactif*) experiment consists of a stainless steel reaction chamber, where a radiofrequency discharge (RF, 13.56 MHz) is generated between two electrodes in a metallic cage confining the plasma (Sciamma-O'Brien et al., 2010; Szopa et al., 2006, Fig. 1a).

A gas mixture of high purity N₂ and CH₄ is flowed continuously through the plasma discharge in which electrons dissociate and ionize N₂ and CH₄. This initiates chemical reactions and molecular growth that results in the production of hydrocarbons and N-bearing molecules that eventually end up forming solid particles. These solid particles grow up in suspension in the plasma and fall in a glass vessel surrounding the metallic cage. After typical runs of 8 h, the produced solid particles, orange to brown in color, are collected for ex-situ analysis.

In this work, experiments were performed with a continuous 55 sccm (standard cubic centimeter per minute) N₂-CH₄ gas flow, containing 1%, 2%, 5% and 10% CH₄ in N₂. These gas proportions are representative of the composition of Titan's atmosphere (Niemann et al., 2005; Waite et al., 2005). For all experimental conditions, the injected RF power was fixed to 30 W, the pressure in the reactor was 0.9 mbar and the neutral gas temperature, measured by Alcouffe et al. (2010), ranged from 310 to 340 K depending on experimental conditions (Tables 1 and 2).

2.1.2. The Nebulotron experiment

The second experimental setup used in this study, the Nebulotron (CRPG-CNRS), consists of a vacuum glass line in which adjustable gas mixtures can be flowed through a microwave (2.45 GHz) plasma discharge (Robert et al., 2011). The aim of this setup is to simulate processes occurring in a CO-N₂ atmosphere. CO and N₂ are believed to have been the main gaseous species hosting C and N in the protosolar nebula (Grossman, 1972). The experimental setup consists of a quartz reactor (Fig. 1b) where a gas mixture of CO (purity 99.5%) and N₂ (purity 99.995%) is flowed continuously through the plasma discharge at a pressure of 1 mbar. As for the PAMPRE experiment, electrons dissociate and ionize N₂ and CO. In this setup however, organic aerosols grow up on the quartz tube surfaces that are cooled down by compressed air. After a typical 6 hours-long experiment, the plasma is turned off and the glass line is pumped out for 12 hours before opening the reactor to atmospheric pressure. The orange to dark solids are then recovered by gently scratching the quartz tube and stored in microvials for

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