

## NITROGEN ISOTOPIC FRACTIONATION IN HYDROCARBON PLASMA.

François Robert<sup>1</sup>, Adriana Gonzalez<sup>1</sup>, Rémi Duhamel<sup>1</sup>, Sylvie Derenne<sup>2</sup> <sup>(1)</sup> IMPMC - Muséum National d'Histoire Naturelle - 61 rue Buffon - 75231 Paris Cedex 05. France. ([francois.robert@mnhn.fr](mailto:francois.robert@mnhn.fr)). <sup>(2)</sup> METIS, CNRS/UPMC UMR 7618, Paris, France

**Introduction.** It is now well established that the variations of the nitrogen isotopic compositions (<sup>15</sup>N/<sup>14</sup>N) in the solar system exceeded by far the theoretical expectations of mass dependent fractionation during isotopic exchanges. Indeed, the solar gas is depleted in <sup>15</sup>N (with δ<sup>15</sup>N down to -400‰ [1]) while the planetary material is enriched in <sup>15</sup>N by several hundreds to thousands of ‰ [2]. The cause of such <sup>15</sup>N enrichments is actively debated. Experimentally, a huge nitrogen isotope effect was reported in an experiment where H<sub>2</sub> react with N atoms to form NH<sub>3</sub> (δ<sup>15</sup>N NH<sub>3</sub> ≈ 2000‰ [3]). The N atoms were produced by UV photolysis of N<sub>2</sub> using the synchrotron light. In another type of experiments, N atoms were produced in plasma discharges of mixture of N<sub>2</sub>-CH<sub>4</sub>-H<sub>2</sub>O [4] and yielded moderate <sup>15</sup>N/<sup>14</sup>N variations in the left-over gas products. Chemical reactions between organic radicals in hydrocarbon plasma produce a black deposit of insoluble organic matter containing hydrogen isotopic variations with δD up to +1500‰ [5].

In the same spirit, we have performed experiments aim at producing two types of radicals: (1) organic radicals produced by the dissociation of hexylamine (CH<sub>3</sub>-(CH<sub>2</sub>)<sub>4</sub>-CH<sub>2</sub>-NH<sub>2</sub>) or butyronitrile (C<sub>4</sub>H<sub>7</sub>N) and (2) N atoms produced by the dissociation of N<sub>2</sub>. In a theoretical treatment proposed to account for the ozone isotopic anomaly (6), the origin of the mass independent isotopic effect was attributed to the reactions involving two indistinguishable isotopes. We have therefore run two types of experiments: (1) one involving only the products of the dissociation of pure hexylamine (or butyronitrile) and (2) another one involving the mixing of N<sub>2</sub> and hexylamine. The aim of this experiment (2) was to produce reactions between N from N<sub>2</sub> and N from -CN.

**Experimental.** Irradiation experiments were performed in a high vacuum glass line (see ref.<sup>(5)</sup> for details). The flow of organic and N<sub>2</sub> gases was dynamically pumped and the pressure was maintained at 3 mbar, with a constant flow of the gases. The reaction setup, includes a removable U-shaped Pyrex tube where the synthesis takes place (1.2 cm diameter, 10 cm in length). An Evenson cavity was used to excite microwave discharges with 2450 MHz microwave generator (Ophos Instruments). After one hour of reaction, ≈10 mg of organic matter was deposited on walls. The synthesized material was extracted with a mixture of dichloromethane/methanol (2/1 v/v) by magnetic stirring at room temperature and the insoluble fraction (IOM) represented ≥90% of the total collected organic matter. The organic structure of this IOM was studied through GC-MS.

Elemental (for H, C, N, O and Si) and isotopic measurements (<sup>13</sup>C/<sup>12</sup>C and <sup>15</sup>N/<sup>14</sup>N) were performed with the Cameca NanoSIMS 50 at MNHN, Paris. Secondary ions were imaged for the <sup>15</sup>N/<sup>14</sup>N ratio, using a Cesium primary beam. The determination of the secondary ions intensity for <sup>12</sup>CH<sup>-</sup>, <sup>12</sup>C<sub>2</sub><sup>-</sup>, <sup>13</sup>C<sub>2</sub><sup>-</sup>, <sup>12</sup>C<sup>14</sup>N<sup>-</sup> and <sup>12</sup>C<sup>15</sup>N<sup>-</sup> was performed in the multicollection mode. The isotopic variations were studied at a spatial resolution of 25 μm<sup>2</sup> i.e. 5 μm x 5 μm.

**Results.** Isotopic variations are restricted to ±60‰ in the IOM produced from pure hexylamine or butyronitrile while their mixing with N<sub>2</sub> induces several hundred of per mil variations. Ion images of huge <sup>15</sup>N/<sup>14</sup>N variations were also recorded. A possible reaction responsible for these variations is the formation of the complex (CN<sub>2</sub>)\* resulting from the reaction N<sup>•</sup> + CN<sup>•</sup>.

**References:** [1] Marty B., et al. (2011) *Science* 332: 1533-1536. [2] Briani G., et al., (2009). *PNAS*, 106: 10522-10527. [3] Chakraborty S., et al., (2008). *Science*, 324, Issue 5894, pp. 1328-1331. [4] Kuga M., et al. (2015). *PNAS* vol. 112 no. 23, 7129-7134. [5] Robert F., et al. (2017). *PNAS*, vol. 114 no. 5, 870-874. [6] Reinhardt, P & Robert, F. *Earth and Planetary Science Letters* (2013). 368, 195-203.