

**MULTIPLE ORIGINS OF NITROGEN ISOTOPIC ANOMALIES IN METEORITES AND COMETS.** J. Aléon<sup>1</sup>, <sup>1</sup>Centre de Spectrométrie Nucléaire et de Spectrométrie de Masse, Bat 104, Orsay Campus 91405, France ([Jerome.Aleon@csnsm.in2p3.fr](mailto:Jerome.Aleon@csnsm.in2p3.fr)).

**Introduction:** Having  $^{14}\text{N}/^{15}\text{N}$  ratios  $\geq 300$  [e.g. 1], interstellar molecules in our galaxy are systematically depleted in  $^{15}\text{N}$  relative to the terrestrial atmosphere ( $^{14}\text{N}/^{15}\text{N}_{\text{AIR}} = 272$ ), which is broadly understood in terms of stellar nucleosynthesis. The bulk  $^{14}\text{N}/^{15}\text{N}$  ratio of the protosolar nebula (PSN) determined from the atmosphere of Jupiter [e.g. 2], from TiN in a Ca-Al-rich inclusion [3] and more recently from the solar wind collected by the Genesis mission [4] agrees with these interstellar values ( $^{14}\text{N}/^{15}\text{N}_{\text{PSN}} \sim 400\text{-}450$ ). By contrast, organic molecules in primitive solar system objects such as comets and carbonaceous chondrites show variable and relatively large excesses of  $^{15}\text{N}$ . Notably, N isotopic ratios cluster around 140 in cometary HCN and CN [5] and reach  $\sim 50$  [6] in meteoritic macromolecular organic matter (acid insoluble residues, IOM, and micron-sized regions termed “hotspots” in IOM and interplanetary dust particles, IDPs). The origin of these  $^{15}\text{N}$  excesses is still poorly understood. Because of their association with organic molecules commonly enriched in D, an interstellar origin due to cold cloud chemistry has been repeatedly proposed [e.g. 7] despite classical ion-molecule reaction models fail to produce such enhancements [8] or require highly specific conditions [e.g. 9]. Moreover, systematic D and  $^{15}\text{N}$  isotopic mapping show that D-excesses and  $^{15}\text{N}$ -excesses are not directly correlated [e.g. 6-7], which led to suggestions that other processes such as isotope selective photodissociation of  $\text{N}_2$  upon self-shielding [10] or spallation by energetic particles could produce the observed  $^{15}\text{N}$ -excesses. In order to investigate the respective role of ion-molecule reactions and other possible processes, I report calculations of isotopic fractionation relative to the early PSN gas together with mass balance mixing calculations compared with a review of published coupled H and N isotopic composition of organic molecules from primitive chondrites, interplanetary dust particles and comets C/1995 O1 (Hale-Bopp) and 81P/Wild2 [11].

**Results and discussion:** In an H-N isotopic fractionation diagram (Fig. 1), three groups of isotopic compositions can be distinguished. (1) Bulk IOMs from carbonaceous chondrites (CCs), the most D-rich hotspots in IDPs and Hale-Bopp HCN plot along a straight line going through origin (hereafter fractionation line, F-line) indicating correlated H and N isotopic fractionation by a single process. (2) Nanoglobules in CCs and comet Wild2 and numerous hotspots in the IOM of CCs and in IDPs exhibit significant  $^{15}\text{N}$  ex-

cesses relative to the F-line, which are maximal in organic clasts from the Isheyevu CH/CB chondrite. (3) Bulk IOM in unequilibrated ordinary chondrites (UOCs) show large D-excesses starting from the F-line, which are not associated to  $^{15}\text{N}$ -excesses. None of these groups can be attributed to a mixing between a pure  $^{15}\text{N}$ -rich component and a pure D-rich component.

*Production of correlated D and  $^{15}\text{N}$  excesses by ion-molecule reactions.* The fractionation line defined by CC IOMs, D-rich hotspots in IDPs and Hale-Bopp HCN is correctly fitted by equilibrium isotopic fractionation using a pair of reaction exothermicities (220 K, 36 K) for H and N isotope fractionation, respectively. These exothermicities correspond exactly to those of the ion-molecule reaction between  $\text{H}_3^+$  and HD to produce  $\text{H}_2\text{D}^+$ , which is mostly efficient below 25 K [e.g. 12] and to the most  $^{15}\text{N}$  fractionating ion-molecule reactions [8], respectively. A striking feature is that these ion-molecule reactions must have occurred in close-to-equilibrium conditions, which is unexpected in the interstellar medium because of rapid competing reactions such as dissociative recombination with free electrons, or reactions with neutrals such as CO. To match the meteoritic and cometary record, the isotopic fractionation must thus have occurred in an extremely dense, cold medium with strong molecular depletions. Such conditions are potentially achieved in the last evolutionary stages of prestellar dense cores or in the outer midplanes of low mass star protoplanetary disks (PPD) [e.g. 9,13-14]. Interestingly, the slope of the fractionation line indicates that production of  $\text{H}_2\text{D}^+$  is the source of the deuteration but temperatures deduced from the amplitude of the deuteration correspond to 50-100 K, a range at which other ion-molecule reactions are significant sources of D [e.g. 12]. This discrepancy is best resolved by advocating a late isotopic exchange between a D-poor IOM and  $\text{H}_2\text{D}^+$  [15]: bulk IOM dominated by little exchangeable aromatic and aliphatic H would have lower D excesses, whereas hotspots rich in highly exchangeable H, possibly carried by radicals [15] would be more D-rich. Cometary HCN, by contrast, is likely to have directly recorded the transfer of D from  $\text{H}_2\text{D}^+$  via chemical networks at  $\sim 40\text{-}50$  K, possibly in a warmer layer of a PPD. The correlation between H and N isotopic fractionations support a similar exchange for N isotopes. Altogether, the last observations favour ion-molecule reactions in the dense outer midplane of the solar PPD rather than an interstellar origin.

*Late addition of a protosolar  $^{15}\text{N}$ -rich component in carbonaceous chondrites.* All data having  $^{15}\text{N}$ -excesses relative to the ion-molecule fractionation line can be matched by the mixing of a dominant component formed by ion-molecule reactions with a  $^{15}\text{N}$ -rich component best preserved in the hotspots of the Isheyevo CH/CB chondrite. In this component, H and N isotopes are roughly equally fractionated relative to the PSN gas ( $\sim 9$ ) suggesting that N-only fractionating processes such as  $\text{N}_2$  self-shielding or spallation may not provide the best explanation. Note that a pure N fractionation cannot be completely ruled out so that such processes remain possible even if a chemical origin is preferred. The abundance of  $^{15}\text{N}$ -rich hotspots in CR chondrites [7] suggests an increasing abundance of this component in the following order : CV/CI/CM < CR < CH/CB chondrites. This abundance pattern is qualitatively correlated with the age of chondrules in the corresponding meteorites, with chondrules in CV chondrites being older than those in CR chondrites by 1-2 Myr, themselves older than those in CB chondrites by 1-2 Myr [16-17]. This correlation is also visible in bulk and suggests that the  $^{15}\text{N}$ -rich component is increasingly produced as the solar PPD ages. Again this is at odd with the predictions of the self-shielding hypothesis, for which preliminary calculations indicate an early origin [10]. As a whole, the largest  $^{15}\text{N}$ -excesses in CCs and comet Wild2 likely result from the presence of a late protosolar component, possibly formed more and more efficiently in optically thin regions as the protosolar disk clears.

*Interstellar organic matter in ordinary chondrites.* By contrast with CCs and comets, H and N isotopes in UOCs are adequately explained by mixing between a dominant component akin to the IOM in CV chondrites and a component akin to observed interstellar molecules rich in D but depleted in  $^{15}\text{N}$  [1]. This suggests that UOCs do indeed contain interstellar organic matter, at most at the 1 atom % level. This interpretation is in good agreement with the large D-excesses observed in hydroxyls in UOCs and attributed to alteration by D-rich interstellar water [18]. An interesting paradox is that only UOCs seem to contain interstellar organic matter/water despite they are thought to come from a restricted number of inner main belt asteroids [19]. In that respect, CCs, chondritic IDPs, and both the long- and short-period comets Hale-Bopp and Wild2 appear to belong to the same family of primitive objects, which does not include UOCs as already suggested by O isotopes in silicates [20].

**Conclusions :** At least three components are required to explain the distribution of H and N isotopes in organic matter of primitive chondrites and comets, two of which probably originated in the solar PPD,

whereas only ordinary chondrites contain an interstellar component. H and N isotopic anomalies in CCs and comets thus appear to be excellent tracers of the physico-chemical conditions in the solar PPD. Detailed chemical models are now required to obtain quantitative information on the physics and chemistry of the solar protoplanetary disk.

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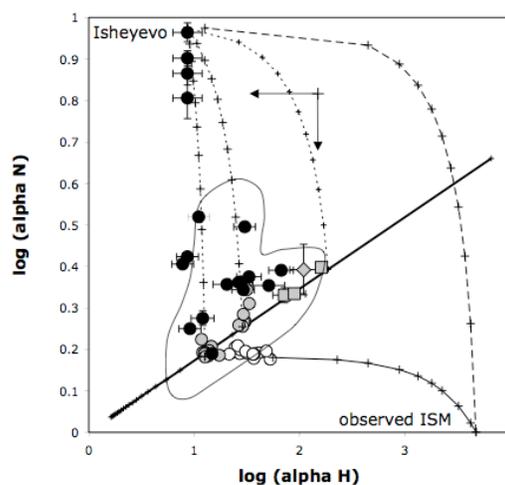


Fig. 1. Isotopic fractionation between organic matter and the PSN gas. Grey dots – bulk CC IOMs ; grey squares – D-rich hotspots in IDPs ; grey diamond – Hale-Bopp HCN ; black dots – nanoglobules and hotspots in CCs, IDPs and comet Wild2 ; white dots – bulk UOC IOMs ; plain contour – range for hotspots in the Grigg-Skjellerup IDPs ; thick line – fractionation line ; dotted curves – mixing curves between the F-line and the Isheyevo endmember ; plain curve – mixing curve between the F-line and the observed ISM ; dashed line – mixing line between the Isheyevo endmember and the observed ISM ; arrows – maximum compositions in CC IOM hotspots. Mixing lines shown for similar H/N ratios.