Nitrogen isotope variations in the solar system

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The relative proportion of the two isotopes of nitrogen (^{14}N and ^{15}N) shows dramatic variations among the different solar system objects and reservoirs. NASA's Genesis mission, which provided the first direct sample of the solar wind, confirmed that the Sun, and by inference the protosolar nebula, is highly depleted in the heavy ^{15}N isotope. The inner planets, asteroids, and comets are enriched in ^{15}N by tens to hundreds of percent, with organic matter in primitive meteorites recording the most extreme ^{15}N/^{14}N ratios. Several lines of evidence suggest that these ^{15}N enrichments were not inherited from presolar material but are, instead, the result of N isotope fractionation processes that occurred early in solar system history. Together, these observations indicate that N isotopes are a powerful tool to investigate early material processing and large-scale disk dynamics as well as planetary formation processes. In addition, N isotopes are the tracer of choice to investigate the origin and evolution of planetary atmospheres.

The solar system formed when a fraction of a dense molecular cloud collapsed and a central star, the proto-Sun, started burning its nuclear fuel[1]. The surrounding disk made of gas and dust, the protosolar nebula (PSN), was thoroughly stirred and homogenized due to large-scale heating and mixing driven by loss of the angular momentum, the energy delivered by the proto-Sun, and magneto-rotational turbulence. The efficiency of these processes is evident in primitive ("carbonaceous") meteorites, which show a remarkable homogeneity in the isotopic compositions of their constituents down to the part per million level for most elements of the periodic table[2]. Relics of the initial heterogeneous mixture of stellar debris can only be found in nano-to-micron-sized presolar grains that were thermally resistant enough to survive high enthalpy processing[3]. However, the light elements hydrogen, carbon, nitrogen, and oxygen, show significant, sometimes extreme, isotope variations among solar system objects and reservoirs, from a few percents for C and O, to tens or even hundreds of percents for H and N (ref. 4). These light elements, by far the most abundant ones in the PSN, share the property to have been predominantly in the gaseous state (H_2, CO, N_2, etc., and their ionized derivatives) in the presolar cloud and in the disk. Consequently, they were prone to efficient isotope exchange and interactions with stellar photons and cosmic rays, either in the interstellar medium (ISM)[5], or in the presolar cloud or the PSN (e.g., refs. 4,6). Thus, these isotope compositions convey a unique record of solar system forming processes.

The largest isotope variations are observed for hydrogen and nitrogen. The deuterium/hydrogen (D/H) ratio varies by a factor of ~35, from the PSN value of $21\pm0.5\times10^{-6}$ (ref. 7) to D-rich "hotspots" in meteorites with values up to 720×10^{-6} (ref. 8). Inner solar system objects ($\sim150\times10^{-6}$; ref. 7) and comets ($150\text{-}500\times10^{-6}$; refs. 9–11) show intermediate values, and possibly define an increase of the D/H ratio with heliocentric distance. A consistent scheme emerges in which nebular H_2 poor in deuterium exchanged isotopically with H_2O at low temperature, resulting in a preferential D-enrichment of the latter. Deuterium-rich water then froze out onto icy grains and exchanged isotopically with organics and silicates as a result of turbulent transport and aqueous alteration on forming planetesimals[12]. Although this scenario is not without weaknesses and is still a matter of debate, the D/H isotopic tracer offers the possibility to investigate the relationships between the different solar system reservoirs. In particular, it is central in the debate on the origin of water (cometary or asteroidal) in the inner solar system including the oceans[10].

The relative proportion of the two stable isotopes of nitrogen, ^{14}N and ^{15}N, also shows outstanding variability in the solar system. For expressing the N isotope composition, geochemists and cosmochemists use the stable isotope delta notation:

$$\delta^{15}N = [(^{15}N/^{14}N)_{sample}/(^{15}N/^{14}N)_{standard} - 1] \times 1{,}000$$

where $\delta^{15}N$ expresses the deviation of the sample ratio relative to a standard in parts per mil (‰). The nitrogen standard is the isotope composition of atmospheric N_2 ($^{15}N/^{14}N = 3.676 \times 10^{-3}$; ref. 13). On Earth, most variations are of the order of a few to tens of permil (e.g., ref. 14). Because the range of extraterrestrial N isotope variations can be much larger than the permil level, cosmochemists use instead the absolute value of the $^{15}N/^{14}N$ ratio, following the stable isotope convention that the rare, heavy isotope is the numerator. To complicate matters further, astronomers and astrophysicists use instead the $^{14}N/^{15}N$ notation (272 for air) (despite using the D/H notation for hydrogen as do cosmochemists). Both notations are given here for the sake of better understanding by these communities.

On Earth, the N isotope composition varies by no more than 2 %, but variations can reach 500 % on a solar system scale (Figs. 1 and 2). Until recently, the causes of this variability were not understood, for two main reasons. Firstly, the solar system initial $^{14}N/^{15}N$ ratio was unknown. Secondly, nitrogen isotopes are more difficult to quantify than hydrogen isotopes because they are generally less abundant in cosmochemical material, and because they are difficult to measure at distance by spectroscopic methods. The analysis of solar wind ions returned to Earth by the Genesis mission – together with advances in high-spatial-resolution, high-sensitivity isotope analysis in the laboratory as well as in high-resolution UV spectroscopy (Box 1) – have permitted major leaps of understanding in the cosmochemistry of this element. Here, we review recent advances in the domain that are particularly relevant in the context of the measurements currently carried out on Comet 67P/Churyumov-Gerasimenko by the Rosetta spacecraft instruments.

Nucleosynthesis of N isotopes and galactic evolution

The production paths and rates of nitrogen isotopes are not fully understood[15–17]. ^{14}N is produced during the cold CNO cycle in low to intermediate mass stars (M_{solar}<M<7 M_{solar}) and is released to the interstellar medium by dredge-up events during asymptotic giant branch (AGB) phases that terminate the lives of most stars ("secondary" production, i.e., not produced directly from H and He nuclei). This isotope is also produced in the so-called hot CNO cycle that takes place in massive stars turning into AGBs during dredge-up from the carbon layer ("primary" production from 3 alpha particles and two protons). ^{15}N is destroyed in the cold CNO cycle, requiring other mechanisms such as ^{15}N production during the hot CNO cycle in novae and, possibly, neutrino spallation on ^{16}O in type II supernovae, both productions being "secondary". Consequently, a nucleosynthetic isotope composition cannot be predicted from theory, and estimates for the N isotope production in the galaxy rely on (limited) observations.

In molecular clouds, the N isotope composition is mainly measured in CN, HCN, HNC, and, more recently, in NHD^+ molecules[17–22]. For molecular N_2, the signal-to-noise ratio is too low for a spectroscopic measurement. The data seem to define an isotope gradient with a decrease of ^{15}N relative to ^{14}N with increasing distance from the galaxy center (Fig. 1; refs. 17,18). Because stars in the galaxy center tend to be more metal-rich (metallicity being here the proportion of elements heavier than helium), secondary production of ^{15}N that presumably takes place in novae and supernovae should decrease more rapidly with galactocentric distance than the primary component of ^{14}N production, in qualitative agreement with the observation (Fig. 1). Strikingly, the solar system, represented by the PSN value (see next subsection), does not fit the correlation. The observed offset could result from a localized N isotope evolution since the solar system isolated nitrogen from the local ISM 4.56 Ga ago. However, a $^{14}N/^{15}N$ value of ∼ ≥400 has been proposed for the local ISM[23] where the Sun was born, consistent with the solar ratio and implying little N isotope evolution with time. Alternatively, the apparent anomaly may be explained by the uncertainty in the data defining the correlation depicted in Fig. 1. CN or HCN, the molecules for which the nitrogen isotopic compositions are measured in dense cores, could have been isotopically fractionated with respect to the source composition, and may not be representative of the local ISM values. Indeed, measurements of the N isotope compositions in three starless dense cores of the local ISM, either in NH_3-NH^+ (refs. 20–22) or in HCN, suggest that the nitrile formation path (leading to HCN and CNH) drastically enriches ^{15}N compared to the amine path (NH compounds) (Fig. 2; ref. 19).

Remarkably, the order of magnitude variation of the nitrogen isotope composition in the solar system, defined by the most ^{15}N-rich portion of the Isheyevo meteorite[24] and the protosolar nebula composition (Figs. 1 and 2; see subsection below), is comparable to the range of values measured in galactic molecular clouds all over the galaxy (Fig. 1). A straightforward interpretation would be that the solar system contains isotopically heterogeneous, nucleosynthetic nitrogen components inherited from ISM. However, other isotope systems do not show correlated isotope variations. For example, nitrogen's "brother" element carbon, whose two stable isotopes ^{12}C and ^{13}C are produced in different nucleosynthetic pathways as well and also show a diversity of isotopic compositions among molecular clouds, displays a near-constant isotopic composition in the solar system within ~10 % (ref. 25). The isotope variations of nitrogen in the solar system are therefore unlikely to represent remnants of nucleosynthetic heterogeneities, and are instead attributed to isotope fractionation. The nature of the fractionating processes (e.g., interactions with solar/stellar photons vs. low temperature isotope exchange) are still debated (Boxes 2 and 3).

The protosolar nebula

The N isotope analysis of Jupiter's atmosphere by spectroscopy ($^{14}N/^{15}N = 526^{+585}_{-169}$, $\delta^{15}N = -483^{+245}_{-272}$ ‰; ref. 26) and by in-situ mass spectrometry ($^{14}N/^{15}N = 435\pm60$, $\delta^{15}N = -375\pm80$ ‰; ref. 27) suggested a ^{15}N-poor solar nitrogen composition. Independently, a $^{14}N/^{15}N$ ratio of 428±8 ($\delta^{15}N = -364\pm12$ ‰) has been obtained for a rare TiN (osbornite) phase within a calcium-aluminum-rich inclusion (CAI) (ref. 28). Because osbornite was presumably the first solid N-bearing phase to condense from the PSN, this value was concluded to correspond to the PSN signature at the time of solid condensation.

At present, the isotopic composition of the PSN is best represented by that of the Sun, which concentrates more than 99 % of the mass of the solar system. For the isotope analysis of the Sun, only the solar wind (SW; the corpuscular emission of the Sun which consists of matter from the solar convective zone, ionized in the photosphere and accelerated along open lines of the Sun's magnetic field) is available for sampling. The nitrogen isotope composition of the modern solar wind was recently measured directly thanks to NASA's Genesis mission (Discovery Program)[29]. The Genesis spacecraft sampled the SW during 27 months at the Lagrangian point L2 and returned SW-irradiated material for laboratory analysis in 2004. Despite a hard landing (the parachute failed to open), the SW-implanted target material could be analyzed by two different extraction techniques for N isotopes (laser ablation-static mass spectrometry[30] and ion probe[31]). Both methods gave consistent results that permitted to define the PSN nitrogen isotope composition of $^{14}N/^{15}N = 441\pm5$ ($\delta^{15}N = -383\pm8$ ‰; ref. 31), after moderate (24 ‰) correction for isotope fractionation in solar processing. Because the modern solar wind has a N isotope composition very close to that of Jupiter and osbornite, this comparison confirms that the Sun did neither synthezise N nor significantly fractionate N isotopes by more than about 3 % from its birth to present-day. The PSN value constitutes the anchor value to which to compare other nitrogen isotope signatures of solar system objects (Fig. 2).

The surface of the Moon

The surface of the Moon, which lacks atmospheric shielding and full magnetic field protection, has accumulated SW ions for hundreds of millions of years. The analysis of SW, either implanted into aluminum foils during the visits by the Apollo astronauts or in the lunar soils that were recovered, was a science priority of the Apollo and Luna programs. One of the most intriguing results of the lunar exploration was the discovery of a ~30 % N isotope variation in lunar soils and rocks[32,33], one order of magnitude larger than that on Earth. Spallation by cosmic rays that produces ^{15}N from ^{16}O can account for some of the low $^{14}N/^{15}N$ values but fails to explain the occurrence of light (^{15}N-poor) nitrogen on the Moon. Noble gases in lunar soils are mostly derived from SW[34], so that lunar nitrogen was assumed to be solar as well. Thus, prior to the Genesis mission, the N isotope variations, which seemed to relate to the epoch of soil exposure, were attributed to secular changes in the isotopic composition of the SW[33,35]. This possibility, however, faced serious difficulties: no nucleosynthetic process within the Sun capable of changing the N isotope composition could be identified[36], and comparison with carbon (whose isotope composition in lunar samples varies much less than that of nitrogen; ref. 25) and helium (whose isotope composition in lunar soils appears constant over time; ref. 37) implied a negligible secular evolution of the SW. Finally, the development of coupled noble gas-nitrogen isotope analysis – together with the Genesis findings – demonstrated that, contrary to noble gases, an additional, non-SW nitrogen component is present in lunar soils[38–40]. The conjoint measurement of H and N isotope variations through the outer skin of lunar soil grains with an ion probe (Box 1; ref. 41) revealed that ^{15}N-depleted SW-N ($^{14}N/^{15}N > 340$, $\delta^{15}N < -200‰$) is mixed to a variable extent with "heavy" (^{15}N-rich) nitrogen. The N isotope signature of the non-solar end-member ($^{14}N/^{15}N = 265 \pm 5$; $\delta^{15}N = 50\text{-}100‰$) is consistent with delivery of asteroidal, rather than cometary, material to the lunar surface, with a flux comparable to that of interplanetary dust and micrometeorites on Earth, after scaling to different gravitational focusing and surface areas of the two planetary bodies[39,40]. An alternative interpretation is that the ^{15}N-rich component is supplied by an “Earth wind” flux of terrestrial atmospheric nitrogen[42]. Early in the history of the Earth-Moon system, before the development of the global geomagnetic field, interaction of the SW with Earth’s upper atmosphere may have resulted in a significant N^+ escape flux. However, since the Moon is tidally locked to Earth, the Earth wind contribution is expected to be absent on the lunar farside. Future sampling may permit to distinguish between an asteroidal or terrestrial origin of the ^{15}N enrichment. Hence, the lunar surface constitutes a superb opportunity to investigate the nature and flux of matter and ions delivered to planetary surfaces through time, and will certainly deserve further attention in future lunar missions aimed at investigating the origin of volatile elements (e.g., water) in the inner solar system.

Planets, asteroids and comets

The atmospheres of Jupiter[26,27] and Saturn[43] are as ^{15}N-depleted as the PSN. Thus, they may represent remnants of the PSN gas, either trapped gravitationally during planetary growth or inherited from accretion of icy bodies[44]. The second possibility implies that these icy planetesimals had a solar-like N isotope composition and were not as ^{15}N-rich as are present-day comets (see below).

The inner planets – Earth and Moon[45], as well as the interior of Mars[46] and the atmosphere of Venus[47] – are richer in ^{15}N than solar N by approximately 60 %, and have comparable N isotope compositions on the scale of solar system variations (Fig. 2). In primitive meteorites, nitrogen is mostly hosted in organics, particularly in insoluble organic matter (IOM) and, under reducing conditions, in nitrides. Carbonaceous chondrites, which are rich in volatile elements as their name implies, contain of the order of 1,000 ppm N, with bulk N isotope compositions within 5 % of the terrestrial value[48-50]. An exception is the CR carbonaceous chondrite clan, whose members are richer in ^{15}N by up to 25 % (e.g., ref. 51), and a few meteorites defining the CB-CH group that present bulk ^{15}N enrichments up to 100-150 % (refs. 52,53). The causes of these enrichments are unclear and could be related to impacts between asteroidal bodies and volatile- and/or organic-rich objects rich in ^{15}N (refs. 51,54). One member of this ^{15}N-rich group, the Isheyevo meteorite, presents so-called "^{15}N hotspots" (ref. 55), measured on a micron scale by ion probe[24,56], characterized by the most extreme ^{15}N enrichments found in the solar system, up to about 450 % ($^{14}N/^{15}N \sim 50$; $\delta^{15}N \sim 4{,}500$ ‰; ref. 24). ^{15}N-rich hotspots are typically found in IOM of primitive meteorites[57] and interplanetary dust particles[58] (which are small [≤50μm] volatile-rich grains snowing onto Earth's surface, and some of which are probably cometary), as well as in nano-sized globules of the Tagish Lake meteorite[59]. Since IOM shows systematically higher ^{15}N contents than bulk meteorites and inner planets, ^{15}N-rich nitrogen hosted by organic molecules within dust grains must have been mixed with ^{15}N-poor PSN N_2 to match bulk values[30,31].

Cometary matter was analyzed on Earth thanks to NASA's Stardust mission (Discovery program), which succeeded in collecting grains from a Jupiter family comet (JFC) named 81P/Wild2 in 2004, and in returning them to Earth two years later for laboratory analyses[60,61]. As a result of the high velocity collection, ices were lost during recovery, and only silicate/metal grains survived. Analyses showed that cometary dust is derived from precursors that share mineralogical and isotopic similarities with carbonaceous chondrites, consistent with models advocating large-scale radial mixing in the nascent solar system[60–62]. $^{15}N/^{14}N$ ratios are also comparable to the values found in meteorites, and excesses of ^{15}N typical of cometary values (see below) are not observed in bulk analyses[63], probably because such excesses are hosted by cometary ice (CN, HCN, NH_3) that was lost during Stardust collection. On a smaller scale, ^{15}N-rich hotspots with a maximum $\delta^{15}N$ value of 1300±400 ‰ are observed, similar to the highest values found in IOM and IDPs[62]. Several presolar grains have been identified showing much larger C and N isotope variations (from +60 to +964 ‰ for $\delta^{13}C$, and from -518 to -350 ‰ for $\delta^{15}N$; ref. 62).

Additional cometary N isotope data are from radio and optical spectroscopic observations of CN, HCN, and NH_2 (the latter presumably derived from the photodissociation of NH_3)[64–68]. Measurements are challenging due to spectroscopic interferences and low abundances of the analyzed molecules, so that data have significant uncertainties compared to laboratory measurements (Box 1). All data collected to date indicate no systematic difference in the

$^{14}N/^{15}N$ ratio between these different molecules within uncertainties: The mean $^{14}N/^{15}N$ ratios of CN (18 comets), HCN (1 comet), and NH_2 (3 comets) are 148±6 ($\delta^{15}N$ = 840±75 ‰), 139±26 ($\delta^{15}N$ = 650±400 ‰), and ~140±40 ($\delta^{15}N$ = 940±500 ‰), respectively (Fig. 2). Furthermore, short- and long-period comets seem to have comparable N isotope compositions. Long-period comets are thought to come from the Oort Cloud (OC comets), whose population is attributed to scattering of icy bodies originally located within the Uranus-Neptune region[69,70]. Short-period comets are proposed to originate from the Kuiper belt reservoir, which is beyond the present-day orbit of Neptune, and/or from the external edge of the disk. Due to gravitational instabilities, some of these icy objects would then have been scattered and injected into the Jupiter region, becoming isotropic (Jupiter Family comets - JFCs). Thus, the available cometary data is inconsistent with a systematic N isotope variation with heliocentric distance beyond Jupiter. The observation that NH_2 on one hand, and CN-HCN on the other hand, show similar N isotope signatures is at odds with the prediction of significant nitrogen isotope fractionation between amine and nitrile radicals[19], unless isotope exchange subsequently erased this effect. It should be emphasized, however, that our knowledge of nitrogen isotopes in cometary material is limited. Depending on the thermal history of these bodies, it is possible that ^{15}N-poor dinitrogen from the PSN is trapped in ices, and that the bulk N isotopic composition of comets is de facto unknown. The ROSETTA space mission, which has just started to study comet 67P/Churyumov-Gerasimenko, will hopefully provide for the first time an in-situ inventory of the $^{14}N/^{15}N$ ratios of different species degassed by the comet.

Conclusions and prospects

The picture that emerges is that there are at least three isotopic reservoirs in the solar system (Fig. 2): i) the PSN, poor in ^{15}N ($^{14}N/^{15}N$ = 441±5; $\delta^{15}N$ = -387±8 ‰), ii) the inner solar system, where planets and bulk meteorites are enriched by a factor of 1.6 relative to the PSN ($^{14}N/^{15}N$ = 272±15; $\delta^{15}N$ = 0±50 ‰), and iii) cometary ices, enriched in ^{15}N by a factor of 3 relative to the PSN ($^{14}N/^{15}N$ = 147±11; $\delta^{15}N$ = 850±150 ‰). Thus, the distribution of N isotopes in the solar system is roughly consistent with an increase of ^{15}N enrichments with radial distance from the Sun, in qualitative agreement with the D/H ratio (Fig. B3). However, several lines of evidence demonstrate that a homogeneous, ^{15}N-poor isotope signature initially characterized the solar system, thus requiring a mechanism for the progressive temporal and spatial isotopic evolution. The recent detection of ^{15}N-enriched nitrogen in a CAI, which last interacted with the nebular gas ≤0.15 Ma ago as show by the ^{26}Al-^{26}Mg chronometer, suggests that at least some regions of the disk were driven toward isotopically heavy values very early in solar system history, within the first few tens to hundreds thousands of years after solar system formation[71]. The nature of the fractionating processes is still a matter of debate and several processes might have played a role (Boxes 2 and 3). While some of the D/H vs. $^{15}N/^{14}N$ co-variations are consistent with either kinetic isotope fractionation or ion-molecule reactions, many ^{15}N excesses are not correlated with enrichments in D, and thus require nitrogen-specific isotope fractionation (Fig. B3). Furthermore, the increase of ^{15}N enrichments with radial distance from the Sun could have resulted from different types of processes. The interaction rate between the PSN gas and UV photons could have varied with heliocentric distance, with enhanced ^{15}N fractionation occurring in the outer solar system, where the lower gas density would have allowed deeper photon penetration and/or more efficient freezing out of synthesized molecules than in the denser, hotter inner solar system. It is also possible that several processes were involved: photodissociation by solar photons in the inner solar system, and contribution of ^{15}N-rich ices formed early in the outer solar system by illumination of ice/dust grains from nearby stars. All these possibilities have profound astrophysical implications and can be tested using nitrogen isotopes, from observation and/or dedicated modeling. Irrespective of the origin(s) of the ^{15}N-enrichment, large-scale turbulence and mixing eventually regionally homogenized material available for planetary accretion, resulting in the isotopic similarity seen for the Earth and most chondritic groups. The same requirement of efficient isotope fractionation and mixing stands for the outer solar system since all cometary N analyzed so far is enriched in ^{15}N by a factor of ~3 relative to inner planets (Fig. 2).

A particularly important question that remains to be addressed with nitrogen isotopes concerns the origin and evolution of the terrestrial atmosphere and oceans. The isotopes of hydrogen do not seem to provide an unambiguous tool for distinguishing between a cometary versus asteroidal origin ever since the discovery of an ocean-like D/H ratio in a comet[10]. So far, all cometary measurements indicate a 3-fold ^{15}N enrichment in comets compared to terrestrial N, suggesting that nitrogen isotopes represent a more powerful tracer than H isotopes for investigating the origin(s) of planetary atmospheres. Thus, N isotopes are the tracer of choice to investigate the evolution of planetary atmospheres through time upon thermal and non-thermal escape processes.

Figure Legends

Figure 1: **Nitrogen isotope variation in molecular clouds from our galaxy as a function of distance from the galactic center**. Adapted from refs. 17,18. Isotope compositions are given in both absolute $^{14}N/^{15}N$ ratios and $\delta^{15}N$ values (deviation in permil from the atmospheric $^{15}N/^{14}N$ ratio). The observed correlation (dashed line; ref. 17) appears consistent with secondary ^{15}N production in massive stars. The total N isotope range within the solar system, defined by the most ^{15}N-rich "hotspot" in the Isheyevo meteorite[24] and the protosolar nebula (PSN) composition[31], is comparable to that in our galaxy. Error bars indicate 1σ uncertainties[17].

Figure 2: **Nitrogen isotope variations in solar system objects and reservoirs.** The value of the protosolar nebula (PSN) is defined by the measurement of solar wind nitrogen collected by NASA's Genesis mission[30,31]. Except for the Sun, osbornite (TiN)[28], and the atmospheres of the

giant planets[26,27,43], all solar system objects and reservoirs are significantly enriched in ^{15}N compared to the PSN. Values determined for various N species in local and galactic molecular clouds[17–22] are shown for comparison. Uncertainties of spectroscopic measurements are shown at the 1σ level.

Figure B1: Nitrogen and hydrogen isotope variations within single lunar grains. a) Silicate grain (breccia 79035) showing $\delta^{15}N$ values (circles) as low as -250‰ together with very low δD values (blue squares) at depths ≤120 nm. The D-poor hydrogen component (i.e, δD ≈ -900‰) represents implanted SW, highly depleted in deuterium due to D-burning in the Sun. Thus, the low $\delta^{15}N$ values give a first-order estimate of the isotopic signature of SW-N. b) Ilmenite grain (soil 71501) containing non-solar N – associated with D-rich (planetary) hydrogen –, which is enriched in ^{15}N to a similar extent as meteoritic nitrogen. Data from ref. 41.

Figure B2: Processes leading to a progressive ^{15}N-enrichment in the solar system. Schematic diagram of the protoplanetary disk made of gas and dust with the proto-Sun at the centre. ^{15}N-enriched $^{15}NH_x$ (and $C^{15}N$) is produced by ion-molecule reactions in the cold regions of the disk[72,73] or as a result of photodissociation of N_2 by UV light from the proto-Sun or from nearby stars[74], and is removed from the gas by freezing out and/or trapping in organic matter. (Image of Beta Pictoris; courtesy of NASA).

Figure B3: Hydrogen and nitrogen isotope ratios of solar system objects and isotope fractionation processes. Adapted from refs. 75,76. Alpha H and alpha N are defined as the D/H and $^{15}N/^{14}N$ ratios normalized to the protosolar nebula values ($[2.1 \pm 0.5] \times 10^{-5}$ (ref. 7) and $[2.27 \times 0.03] \times 10^{-3}$ (ref. 31), respectively). Data and corresponding uncertainties for Moon[45,77]; Venus[47,78]; Mars atmosphere[79,80]; chondrites, bulk[6,8,50]; chondrites, IOM[75,81];

Isheyevo hotspots[24,56]; Saturn[43,82]; Jupiter[27,83]; Titan atmosphere[84]; comets [66,67,85,86]. The observed H-N isotope compositions require various isotope fractionation processes.

Box 1: Analysis of nitrogen isotopes

For geochemical applications, nitrogen isotopes have historically been measured using isotope ratio mass spectrometers operated in dynamic pumping mode (e.g., ref. 87). However, since this technique is not suitable for the analysis of low nitrogen abundances, higher-sensitivity noble gas mass spectrometers operated under static vacuum conditions are now the standard method to determine the nitrogen isotopic composition of N-poor and/or small-sized (≤5 mg) terrestrial and extraterrestrial samples (e.g., ref. 88,89). In this method, nitrogen – extracted from the samples by various destructive techniques such as crushing, laser ablation, laser-, or furnace-heating, and purified from interfering carbon compounds – is analyzed in the form of N_2 at masses 28 ($^{14}N^{14}N$), 29 ($^{14}N^{15}N$) and 30 ($^{15}N^{15}N$) in mono- or multi-collection mode. Measured peak heights and isotope ratios must be corrected for isobaric mass interferences from CO, N_2H, and hydrocarbons (C_2H_x), which are ubiquitously present in the mass spectrometer system, and the instrumental precision and reproducibility is monitored by repeat analysis of atmospheric N_2.

Secondary ionization mass spectrometry (SIMS) analysis represents a non-destructive means to determine N isotope variations with a high lateral resolution (i.e., at a scale as small as ≤10 μm) or a high depth resolution (i.e., ≤10 nm; Fig. B1; ref. 39). While the isotope analysis of nitrogen by SIMS is challenging due to its low ionization efficiency, an intense CN^- signal is formed in the presence of carbon by bombardment of the sample surface with a Cs^+ ion beam, and nitrogen isotope ratios have successfully been determined in the form of $^{12}C^{15}N^-/^{12}C^{14}N^-$ in various extraterrestrial samples[24,28,41,56,57,75] as well as in terrestrial diamonds[90]. Furthermore, the nitrogen isotope composition of solar wind collected during NASA's Genesis mission was determined with high precision by SIMS[31]. Notably, since the ionization rate depends on the sample matrix, using a standard made of the same material as the sample and with a known N abundance and isotope composition is critical for an accurate measurement by this technique.

High-resolution radio and optical spectroscopy represents the only analytical means to remotely determine the isotopic composition of cometary (atmospheric) nitrogen. Cometary emissions are produced by absorption of solar light by the various molecules followed by re-emission of lines of specific wavelengths, a process called resonance-fluorescence. Isotope ratios ($^{14}N/^{15}N$) are determined by comparing the observed molecular spectra with synthetic spectra of the same species. Such measurements require high signal-to-noise spectra together with a high spectral resolution, and have so far only been feasible for nitrogen in the form of CN, HCN, and NH_3 for a limited number of Oort cloud and Jupiter family comets. Notably, the Rosetta Orbiter Spectrometer for Ion and Neutral Analysis (ROSINA) on board the Rosetta spacecraft has been able to determine, for the first time, the abundance of N_2 *in-situ* in the coma of comet 67P/Churyumov-Gerasimenko[91].

Box 2: Possible origin(s) of the ^{15}N-enrichment in solar system material

Two different processes are advocated to explain the ^{15}N enrichment in solar system material. In the first model, ^{15}N enrichment takes place during ion-molecule reactions in the interstellar medium with sufficient density, for example during the collapse of dense pre-stellar cores forming dark molecular clouds, and/or in the cold regions of the disk surrounding the protostar. The possibility of ^{15}N fractionation has been established experimentally[92]. Elemental ^{15}N reacts with $^{14}N_2H^+$, which recombines to give ^{15}N-rich $^{14}N^{15}N$. He^+ releases additional $^{15}NH^+$, which is incorporated into NH_3 and NH_2. These molecules freeze out onto dust grains to yield ammonia ice rich in ^{15}N (ref. 73). However, because nitrogen is continuously cycled between N and N_2, backward reactions tend to limit ^{15}N enrichments to 30 % or less[72]. To circumvent this problem, it has been proposed (ref. 73) that coupling between N and N_2 is removed when N_2 is deficient in the gas, e.g., frozen out with CO at very low temperature in dense cores, so that the extent of ^{15}N fractionation is no longer limited and can account for the extreme ^{15}N enrichments seen in the solar system[5]. Different reaction paths could also account for the large fractionation between amines (e.g., NH_3) and nitriles (e.g., NH_2)[19]. These possibilities are subject to discussion due to uncertainties in relevant chemical rates and branching ratios[93,94].

Other types of models advocate photodissociation of N_2 by UV light from the proto-Sun or from nearby stars. In one model, the photodissociation of $^{14}N^{14}N$ saturates with respect to that of $^{15}N^{14}N$, because the latter is much less abundant, and, therefore, photons with wavelengths able to dissociate $^{14}N^{14}N$ get consumed at a greater rate than those photodissociating $^{15}N^{14}N$. Dissociated N^+ recombines with surrounding atoms and ions (e.g., H and C) to form amines and nitriles, which can then be removed from the gas by freezing out. This process, which is called self-shielding and is known to occur in dense cores, is postulated to take place in the solar nebula, and not only accounts for ^{15}N fractionation but also for mass-independent oxygen isotope signatures[95]. Another model based on quantum mechanics[96] is substantiated by photodissociation experiments with UV light from a synchrotron radiation source illuminating a N_2-H_2 mixture[74]. The produced NH_3, which is frozen out onto a cold finger and analyzed for N isotopes, shows dramatic ^{15}N excesses up to 12,000 ‰. Although it is not clear if these excesses are the result of a peculiar quantum effect or are due to self-shielding in the experimental reactor, this straightforward and illuminating measurement provides a quantitative case of extreme ^{15}N enrichments in ice formed during interactions between dinitrogen and UV light in a manner reminiscent of the conditions that prevailed during early solar system evolution. In both cases, the key ingredient of the recipe is photons illuminating the PSN gas, indicating that specific environments are required in which the PSN is transparent enough to allow photons to react with gaseous molecules. Possibilities include the surfaces of the disk illuminated by the proto-Sun (Fig. B2) or by other young stars, or the outer regions of the disk illuminated by nearby stars. Once formed, amines and nitriles would then be decoupled from the gas and eventually be transported to regions where they can react with further radicals to yield ^{15}N-rich ices or organics.

Box 3. H-N isotope co-variations in the solar system and constraints on the origin of terrestrial volatiles

Various isotope fractionation processes have been invoked to explain the hydrogen and nitrogen isotope co-variations recorded by the different solar system objects and reservoirs. The kinetic isotope fractionation line shown in Fig. B3 is an example of mass-dependent fractionation, proportional to the square root of mass; however, different mass dependencies would lead to distinct slopes. The ion-molecule isotope fractionation trend (from ref. 75) illustrates the effect of low temperature isotope exchange between organics and the protosolar gas. The D-enrichment of ordinary chondrite IOM with only slight or no concomitant ^{14}N enrichment (yellow triangles) has been proposed to reflect isotope exchange of the molecular host with a D-rich component similar to gas phase molecules observed in dense clouds, pre-stellar cores and class 0 protostars[75]. In contrast, the ^{15}N enrichments above the kinetic isotope fractionation line require preferential N isotope fractionation compared to D/H. This could result from photodissociation of protosolar N_2 by UV light[74], or from self-shielding[95] (Box 2), and appears to have occurred within the first few tens to hundreds thousands of years after solar system formation[71]. Similarly, the enrichment in the heavy isotopes of oxygen (^{17}O and ^{18}O) relative to the major, light isotope (^{16}O) recorded by solar system solids compared to the protosolar oxygen isotope composition may be the result of illumination of the PSN gas by solar/stellar photons (e.g., ref. 95). This process, which has been advocated to explain the oxygen isotope composition of refractory phases in meteorites, might also have been rapid ($\leq$ 2Ma), according to the chronology recorded by these refractory phases (e.g., ref. 97).

Earth shares H and N isotope signatures with bulk chondrites (Fig. B3), whereas most comets are richer in D and ^{15}N. These observations suggest an asteroidal, rather than cometary, origin for terrestrial volatiles[76,98]. While coupled H-N systematics provide a powerful means to trace the origin of volatiles in the inner solar system, secondary fractionation processes that lead to a preferential loss of light isotopes modified the H and N isotope signature of several solar system objects (Figs. 2 and B3). The Venusian atmosphere is extremely depleted in water and rich in D as a consequence of photodissociation of H_2O and subsequent H loss[78]. The enrichment in both D and ^{15}N of the Martian atmosphere[79,80] is attributed to atmospheric escape processes. In contrast, Titan is rich in ^{15}N but not in D (ref. 84), suggesting a source effect for nitrogen rather than isotope fractionation.

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Additional information

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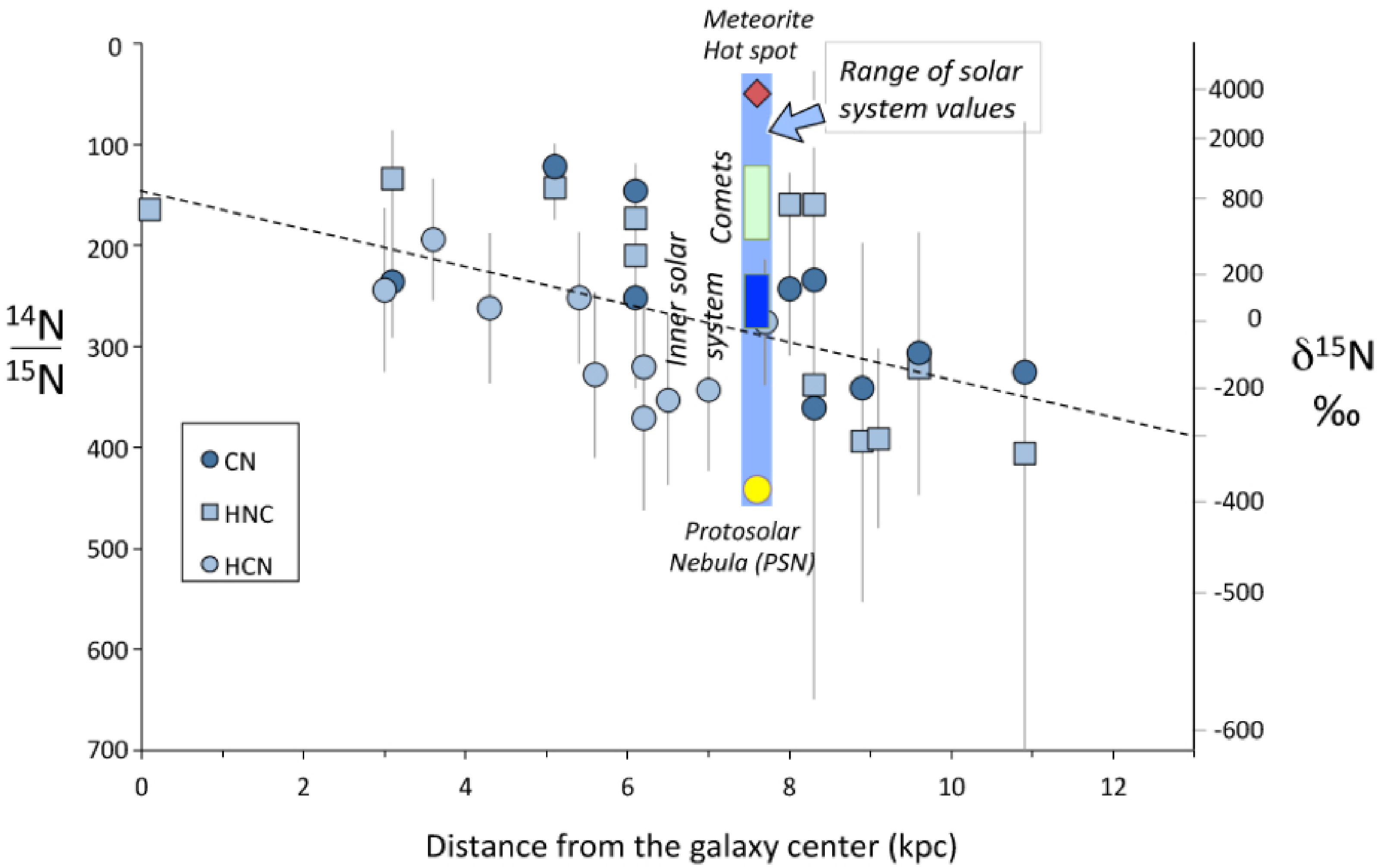

Meteorite
Hot spot
Range of solar
system values
Comets
Inner solar
system
Protosolar
Nebula (PSN)
CN
HNC
HCN
$\frac{^{14}N}{^{15}N}$
$\delta^{15}N$
‰
0
100
200
300
400
500
600
700
4000
2000
800
200
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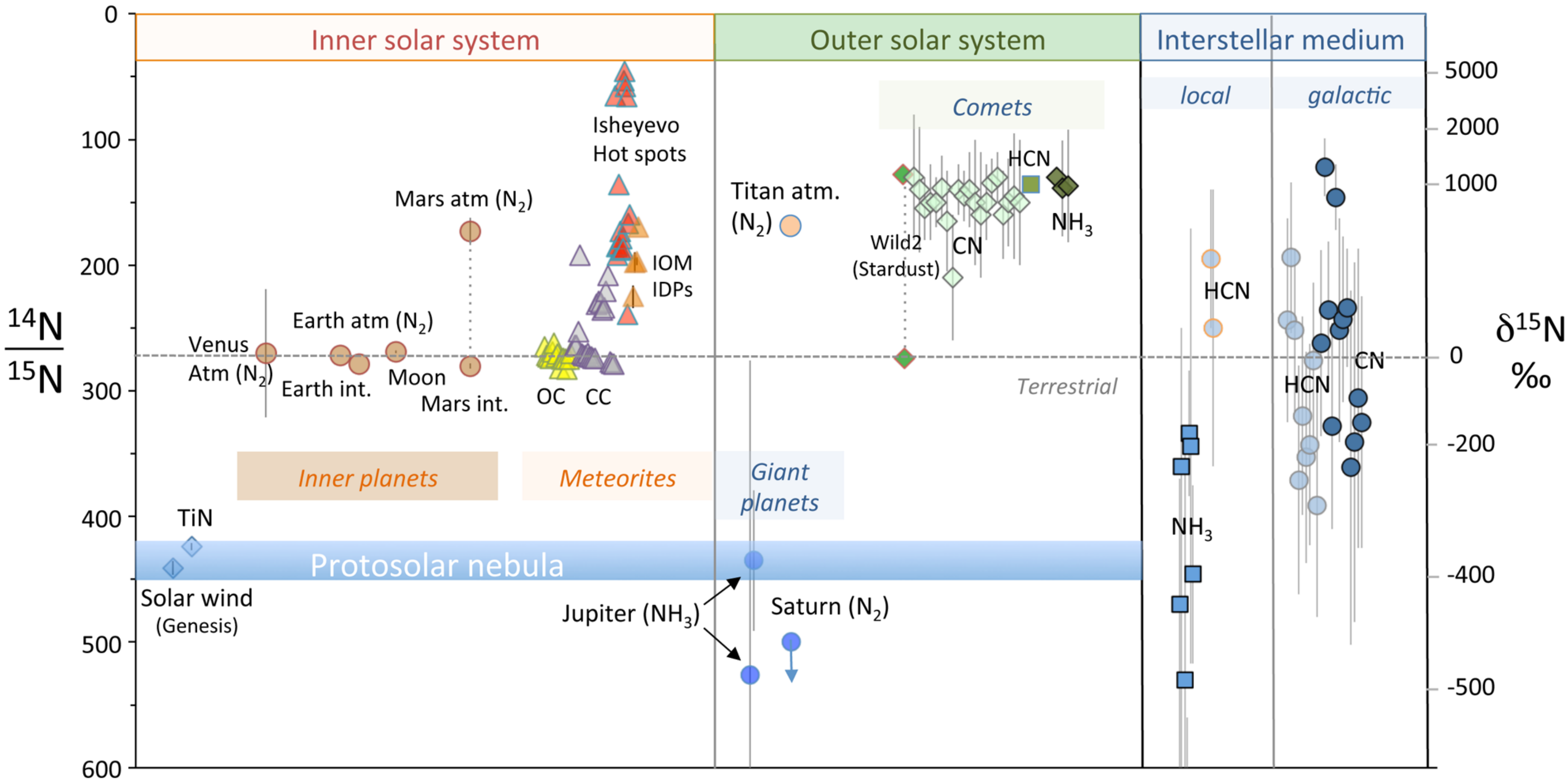
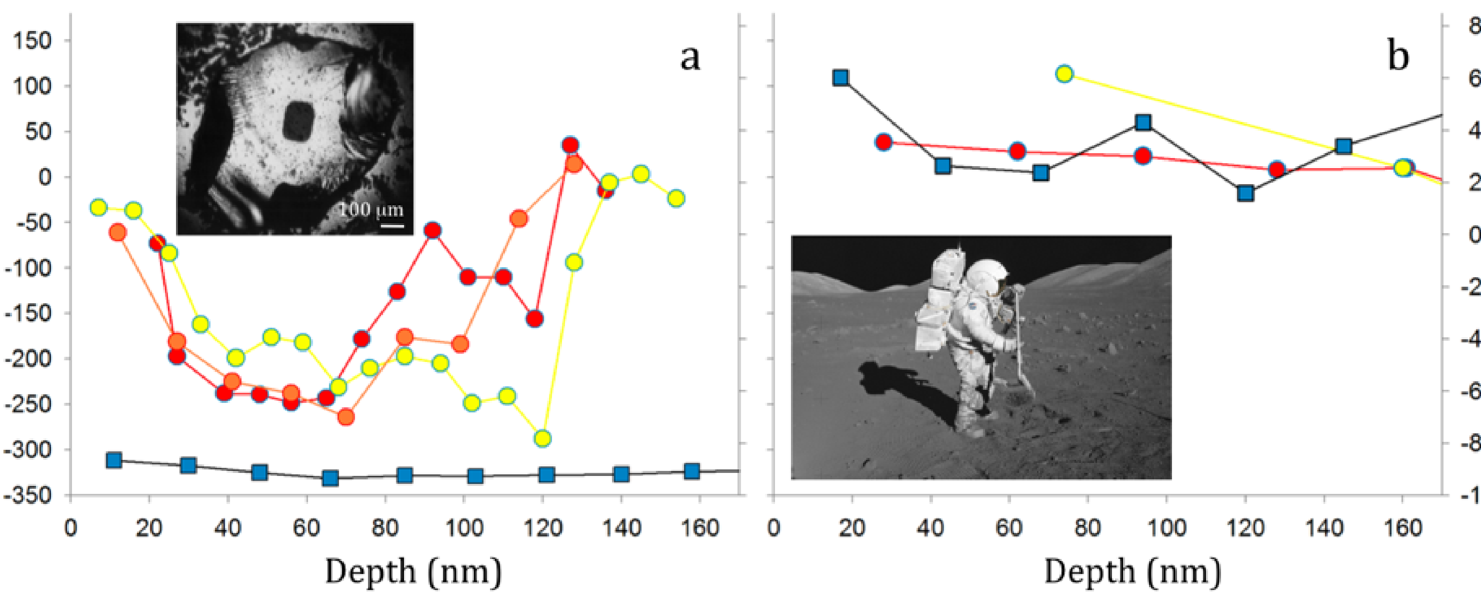
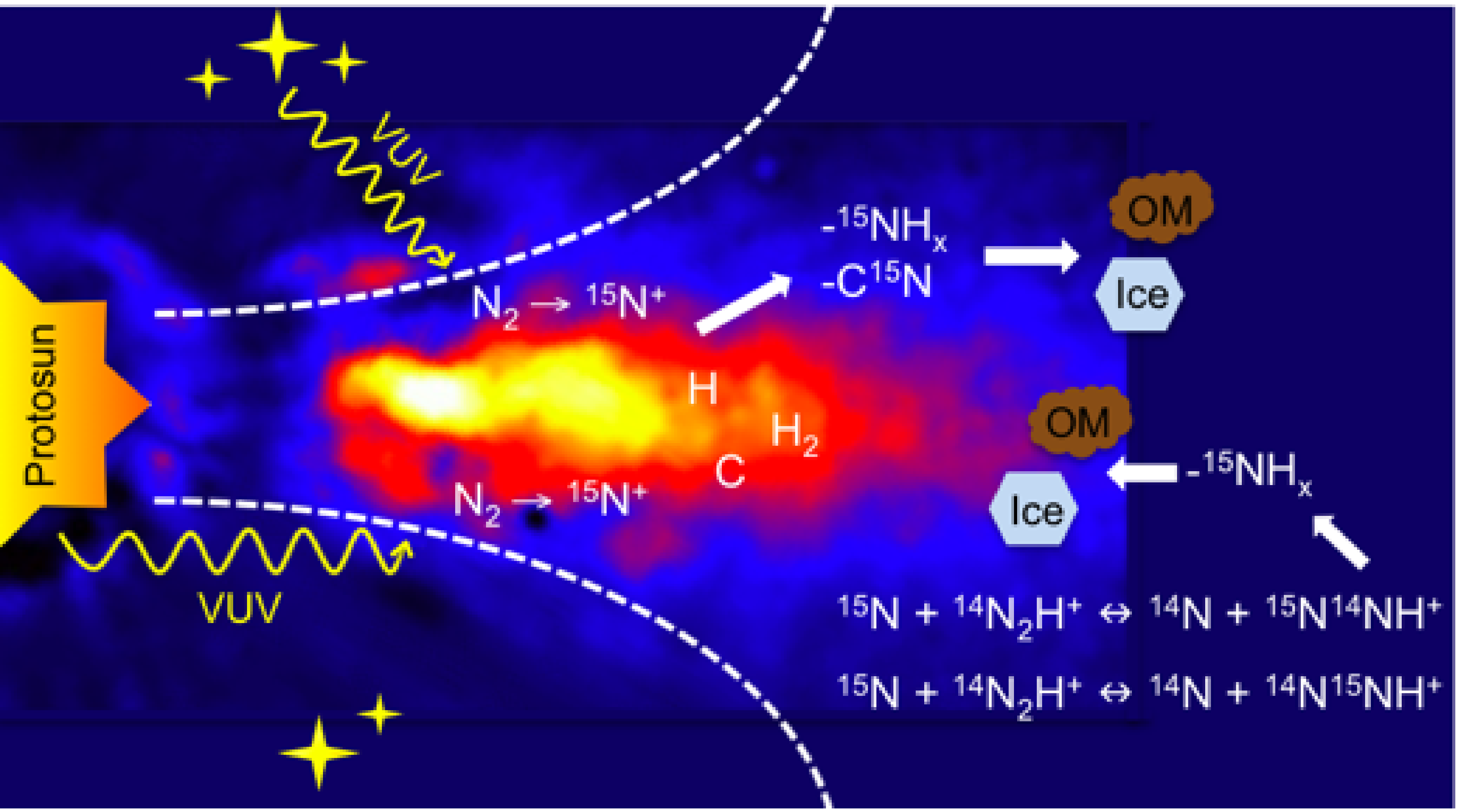
-200
-400
-500
-600
0
2
4
6
8
10
12
Distance from the galaxy center (kpc)



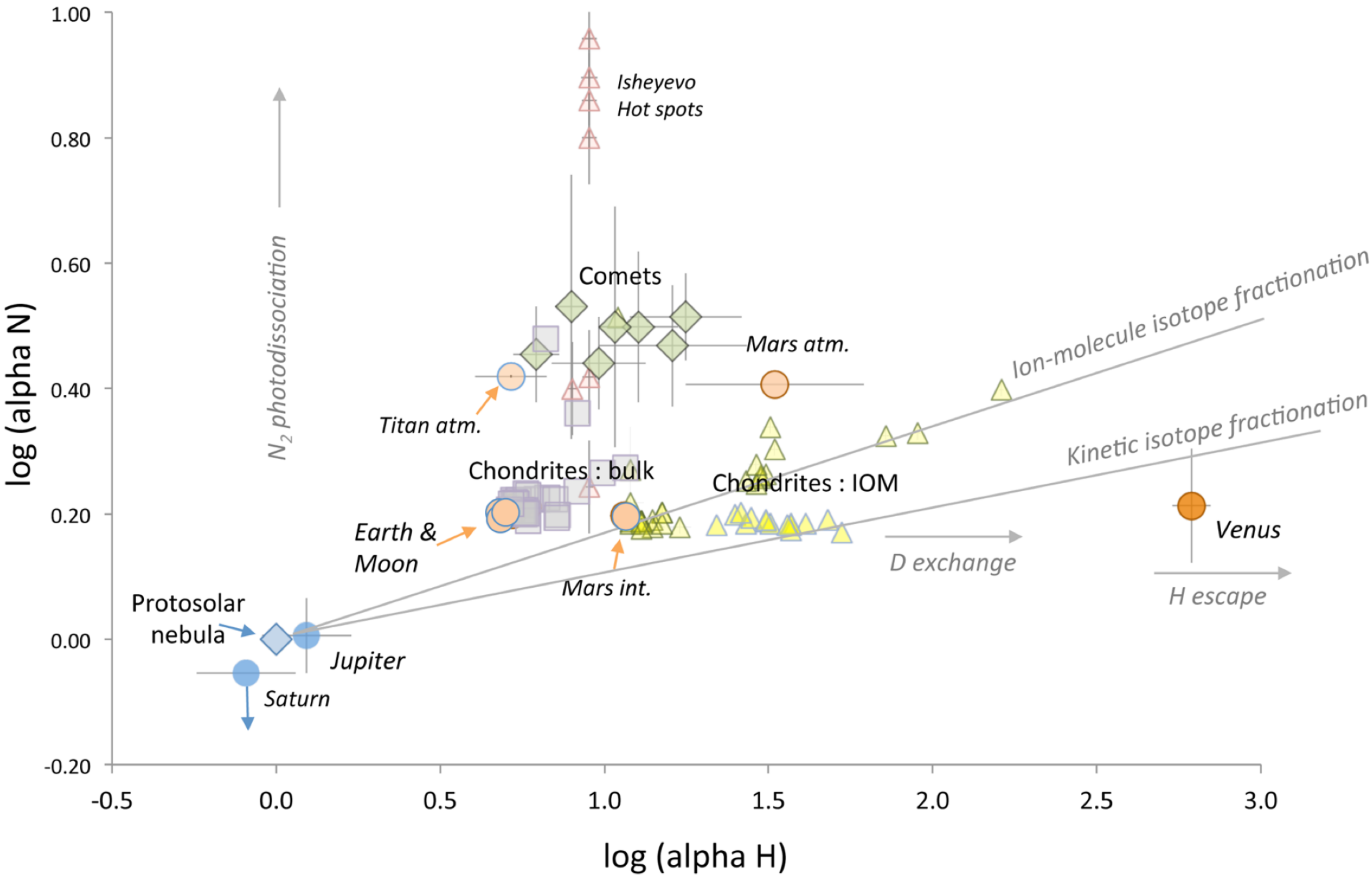
Inner solar system
Outer solar system
Interstellar medium
local
galactic
Comets
Isheyevo
Hot spots
Mars atm (N_2)
IOM
IDPs
Titan atm.
(N_2)
HCN
NH_3
Wild2
(Stardust)
CN
Earth atm (N_2)
Venus
Atm (N_2)
Earth int.
Moon
Mars int.
OC
CC
Terrestrial
HCN
CN
Inner planets
Meteorites
Giant planets
TiN
Protosolar nebula
Solar wind
(Genesis)
Jupiter (NH_3)
Saturn (N_2)
$\frac{^{14}N}{^{15}N}$
$\delta^{15}N$ ‰
0
100
200
300
400
500
600
5000
2000
1000
-200
-400
-500



a
b
100 μm
δ15N (‰)
δD (‰)
Depth (nm)
Depth (nm)
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
800
600
400
200
0
-200
-400
-600
-800
-1000
0
20
40
60
80
100
120
140
160



VUV
$-^{15}NH_x$
$-C^{15}N$
OM
Ice
$N_2 \rightarrow {}^{15}N^+$
Protosun
H
H_2
C
OM
$-^{15}NH_x$
Ice
$N_2 \rightarrow {}^{15}N^+$
VUV
$^{15}N + {}^{14}N_2H^+ \leftrightarrow {}^{14}N + {}^{15}N^{14}NH^+$
$^{15}N + {}^{14}N_2H^+ \leftrightarrow {}^{14}N + {}^{14}N^{15}NH^+$



log (alpha N)
log (alpha H)
1.00
0.80
0.60
0.40
0.20
0.00
-0.20
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Isheyevo
Hot spots
Comets
Mars atm.
Titan atm.
Chondrites : bulk
Chondrites : IOM
Earth &
Moon
Mars int.
Venus
Protosolar
nebula
Jupiter
Saturn
N2 photodissociation
Ion-molecule isotope fractionation
Kinetic isotope fractionation
D exchange
H escape