

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 , varies dramatically across the Solar System, despite little variation on Earth. NASA's Genesis mission directly sampled the solar wind and confirmed that the Sun — and, by inference, the protosolar nebula from which the Solar System formed — is highly depleted in the heavier isotope compared with the reference nitrogen isotopic composition, that of Earth's atmosphere. In contrast, the inner planets, asteroids, and comets are enriched in ^{15}N by tens to hundreds of per cent; organic matter in primitive meteorites records the highest $^{15}\text{N}/^{14}\text{N}$ isotopic ratios. The measurements indicate that the protosolar nebula, inner Solar System, and cometary ices represent three distinct isotopic reservoirs, and that the ^{15}N enrichment generally increases with distance from the Sun. The ^{15}N enrichments were probably not inherited from presolar material, but instead resulted from nitrogen isotope fractionation processes that occurred early in Solar System history. Improvements in analytical techniques and spacecraft observations have made it possible to measure nitrogen isotopic variability in the Solar System at a level of accuracy that offers a window into the processing of early Solar System material, large-scale disk dynamics and planetary formation processes.

The Solar System formed when a fraction of a dense molecular cloud collapsed and a central star, the proto-Sun, started burning its nuclear fuel¹. 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 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 parts per million level for most elements of the periodic table². Relics of the initial heterogeneous mixture of stellar debris can only be found in nano- to micrometre-sized presolar grains that were thermally resistant enough to survive high-enthalpy processing³. However, the light elements hydrogen, carbon, nitrogen, and oxygen, show significant, sometimes extreme, isotope variations among Solar System objects and reservoirs, from a few per cent for C and O, up to several hundred per cent for H and N (ref. 4). These light elements, by far the most abundant ones in the PSN, were all present predominantly in the gaseous state (including H_2 , CO and N_2 , as well as 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^{4,6}. Thus, these isotope compositions convey a unique record of the processes that formed the Solar System.

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 $21 \pm 0.5 \times 10^{-6}$ (ref. 7) to D-rich 'hotspots' in meteorites, with values up to 720×10^{-6} (ref. 8). Inner Solar System objects (~ 150×10^{-6} ; ref. 7) and comets ($150\text{--}500 \times 10^{-6}$; refs 9–11) show intermediate values, and possibly indicate an increase of the D/H ratio with heliocentric distance. This suggests a scenario in which nebular H_2 (poor in deuterium) exchanged isotopically with H_2O at low temperature, resulting in a preferential D-enrichment of the water. Deuterium-rich water then froze out onto grain surfaces and exchanged isotopically with organics and silicates as a result of turbulent transport and aqueous alteration on forming planetesimals¹². Although this scenario is not without weaknesses and is still

a matter of debate, the D/H isotopic tracer offers the possibility of investigating 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 that of the terrestrial oceans¹⁰.

The relative proportion ^{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:

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

where $\delta^{15}\text{N}$ expresses the deviation of the sample ratio relative to a standard in parts per thousand (‰). The nitrogen standard is the isotope composition of atmospheric N_2 ($^{15}\text{N}/^{14}\text{N} = 3.676 \times 10^{-3}$; ref. 13). On Earth, most variations are of the order of 10 parts per thousand¹⁴. Because the range of extraterrestrial N isotope variations can be much larger than the ‰ level, cosmochemists use instead the absolute value of the $^{15}\text{N}/^{14}\text{N}$ ratio, following the stable isotope convention that the rare, heavy isotope is the numerator. To complicate matters further, astronomers and astrophysicists instead use the $^{14}\text{N}/^{15}\text{N}$ notation (272 for atmospheric N_2 ; despite using the D/H notation for hydrogen as cosmochemists do). Both notations are given here for the sake of understanding by both of 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. First, the initial $^{14}\text{N}/^{15}\text{N}$ ratio of the Solar System was unknown. Second, 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 from a distance by spectroscopic methods. The analysis of solar wind (SW) 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

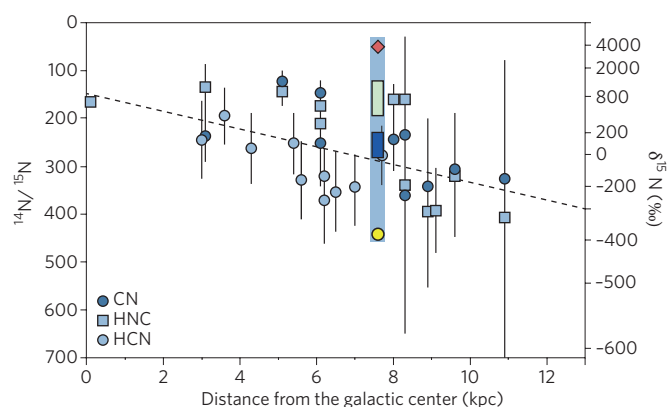


Figure 1 | Nitrogen isotope variation in molecular clouds from our galaxy as a function of distance from the galactic centre. Isotope compositions are given in both absolute $^{14}\text{N}/^{15}\text{N}$ ratios and $\delta^{15}\text{N}$ values (deviation from the atmospheric $^{15}\text{N}/^{14}\text{N}$ ratio). The observed correlation (dashed line) appears to be consistent with secondary ^{15}N production in massive stars. The total N isotope range within the Solar System (blue shading), defined by the most ^{15}N -rich hotspot in the Isheyevo meteorite²⁴ (red diamond) and the PSN (yellow circle) composition³¹, is comparable to that in our galaxy. The range for the inner Solar System and comets are shown by dark blue and green boxes, respectively. Error bars indicate 1σ uncertainties. Data from refs 17,18.

that are particularly relevant in the context of the measurements currently being made of Comet 67P/Churyumov-Gerasimenko by the Rosetta spacecraft instruments.

Nucleosynthesis of N isotopes and galactic evolution

The production paths of nitrogen isotopes and their corresponding rates are not fully understood^{15–17}. ^{14}N is produced during the cold CNO cycle in low to intermediate mass stars ($M_{\text{solar}} < M < 7 M_{\text{solar}}$), and is released to the ISM by dredge-up events during asymptotic giant branch (AGB) phases that terminate the lives of most stars (secondary production, where ^{14}N is 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). During the cold CNO cycle ^{15}N is destroyed, 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 secondary types of production. 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 galactic centre (Fig. 1; refs 17,18). Because stars in the galaxy centre tend to be more metal-rich (where metallicity is 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 billions years ago (Ga). However, a $^{14}\text{N}/^{15}\text{N}$ value of ≥ 400 has been proposed for the local ISM²³ 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 $\text{NH}_3\text{-NH}^+$ (refs 20–22) or in HCN (Fig. 2), suggest that the nitrile formation path (leading to HCN and CNH) drastically enriches ^{15}N compared with the amine path (NH compounds)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 meteorite²⁴ and the protosolar nebula

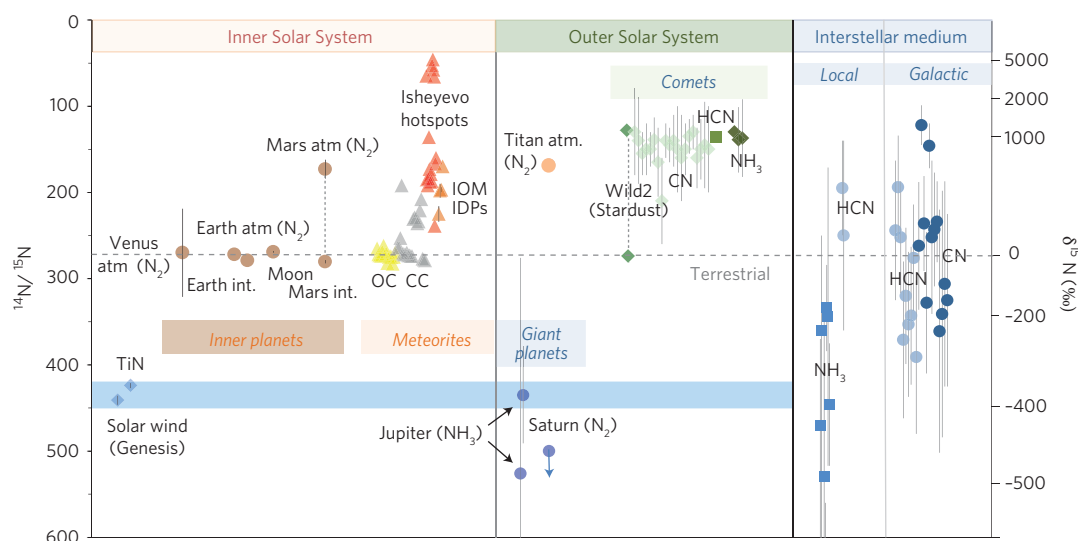


Figure 2 | Nitrogen isotope variations in Solar System objects and reservoirs. The value of the PSN (blue shading) is defined by the measurement of SW nitrogen collected by NASA's Genesis mission^{30,31}. Apart from the Sun, TiN (ref. 28), and the atmospheres of the giant planets^{26,27,43}, all Solar System objects and reservoirs are significantly enriched in ^{15}N compared with 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. Note the nonlinear positive scale for the right-hand y axis.

Box 1 | Analysis of nitrogen isotopes.

For geochemical applications, nitrogen isotopes have historically been measured using isotope ratio mass spectrometers operated in dynamic pumping mode⁸⁷. 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^{88,89}. In this method, nitrogen is extracted from the samples by various destructive techniques such as crushing, laser ablation, laser- or furnace-heating, and purified from interfering carbon compounds, and is analysed 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. The instrumental precision and reproducibility are 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 (at a scale as small as ≤ 10 μm) or a high depth resolution (≤ 10 nm; Fig. B1; ref. 41). While the isotope analysis of nitrogen by SIMS is challenging due to its low ionization efficiency, an intense CN^- signal forms in the presence of carbon when the sample surface is bombarded 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 diamonds⁹⁰. Furthermore, the nitrogen isotope composition of SW collected during NASA's Genesis mission was determined with high precision by SIMS³¹. Using a standard made of the same material as the sample, and with a known N abundance and isotope composition, is critical for accurate measurement by this technique, as the ionization rate depends on the sample matrix.

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 comets from the Oort cloud and Jupiter family. Notably, the Rosetta Orbiter

Spectrometer for Ion and Neutral Analysis (ROSINA) on board the Rosetta spacecraft has been able to determine the abundance of N_2 *in situ* in the coma of comet 67P/Churyumov-Gerasimenko⁹¹.

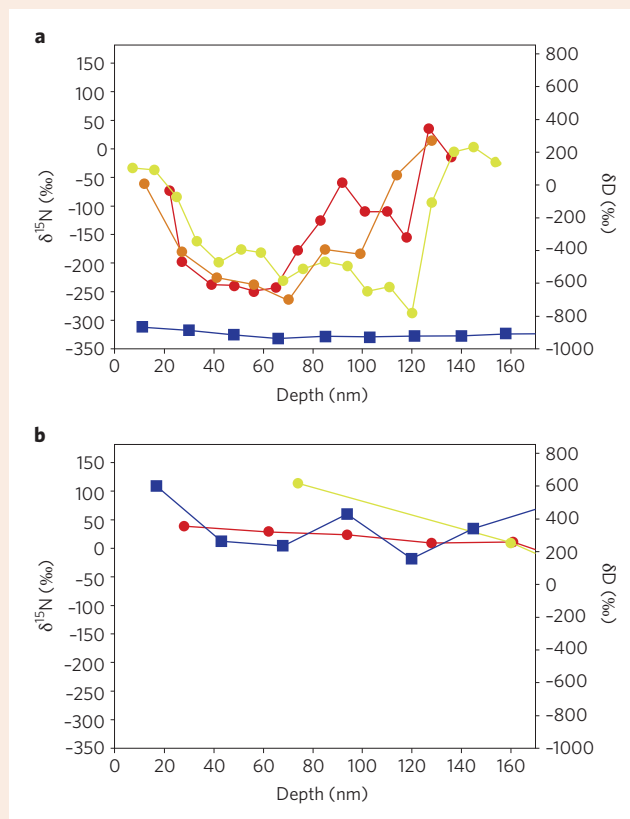


Figure B1 | Nitrogen and hydrogen isotope variations within single lunar grains. **a**, $\delta^{15}N$ values (measured at three different spots; circle symbols) as low as -250 ‰ together with very low δD values (blue squares) at depths ≤ 120 nm have been found in breccia 79035. The D-poor hydrogen component ($\delta D \approx -900$ ‰) 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 nitrogen. **b**, Ilmenite grain (soil 71501) containing non-solar N — associated with D-rich (planetary) hydrogen — which is enriched in ^{15}N to a similar level to meteoritic nitrogen. Data from ref. 41.

composition (Figs 1 and 2), 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, the element carbon, whose two stable isotopes ^{12}C and ^{13}C are also produced in different nucleosynthetic pathways and show a diversity of isotopic compositions among molecular clouds, displays a near-constant isotopic composition in the Solar System within $\sim 10\%$ (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 — for example, interactions with solar/stellar photons versus low-temperature isotope exchange — is still debated (Boxes 2 and 3).

The protosolar nebula

The N isotope analysis of Jupiter's atmosphere by spectroscopy ($^{14}N/^{15}N = 526^{+585}_{-169}$, $\delta^{15}N = -483^{+245}_{-272}$ ‰)²⁶ and by *in situ* mass spectrometry ($^{14}N/^{15}N = 435 \pm 60$; $\delta^{15}N = -375 \pm 80$ ‰)²⁷ suggested a ^{15}N -poor nebular nitrogen composition. Independently, a $^{14}N/^{15}N$ ratio of 428 ± 8 ($\delta^{15}N = -364 \pm 12$ ‰) 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 SW (the corpuscular emission of the Sun that 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

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 ISM with sufficient density, for example during the collapse of dense pre-stellar cores forming dark molecular clouds or in the cold regions of the disk surrounding the protostar. The possibility of ^{15}N fractionation has been established experimentally⁹². Elemental ^{15}N reacts with $^{14}\text{N}_2\text{H}^+$, which recombines to give ^{15}N -rich $^{14}\text{N}^{15}\text{N}$. He^+ releases additional $^{15}\text{NH}^+$, which is incorporated into NH_3 and NH_2 . These molecules freeze out onto dust grains to yield ^{15}N -rich ammonia ice⁷³. However, because nitrogen is continuously cycled between N and N_2 , backward reactions tend to limit ^{15}N enrichments to 30% or less⁷². To circumvent this problem, it has been proposed⁷³ that coupling between N and N_2 is removed when N_2 is deficient in the gas — for example, 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 System⁵. Different reaction paths could also account for the large fractionation between amines such as NH_3 and nitriles such as NH_2 (ref. 19). These possibilities are subject to discussion owing 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 $^{14}\text{N}^{14}\text{N}$ saturates with respect to that of $^{15}\text{N}^{14}\text{N}$, because the latter is much less abundant. Therefore, photons with wavelengths able to dissociate $^{14}\text{N}^{14}\text{N}$ get consumed at a

greater rate than those photodissociating $^{15}\text{N}^{14}\text{N}$. Dissociated N^+ recombines with surrounding atoms and ions such as 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 signatures⁹⁵. Another model based on quantum mechanics⁹⁶ is substantiated by photodissociation experiments with UV light from a synchrotron radiation source illuminating a N_2 – H_2 mixture⁷⁴. The produced NH_3 , which is frozen out onto a cold finger and analysed 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. Both cases rely on 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.

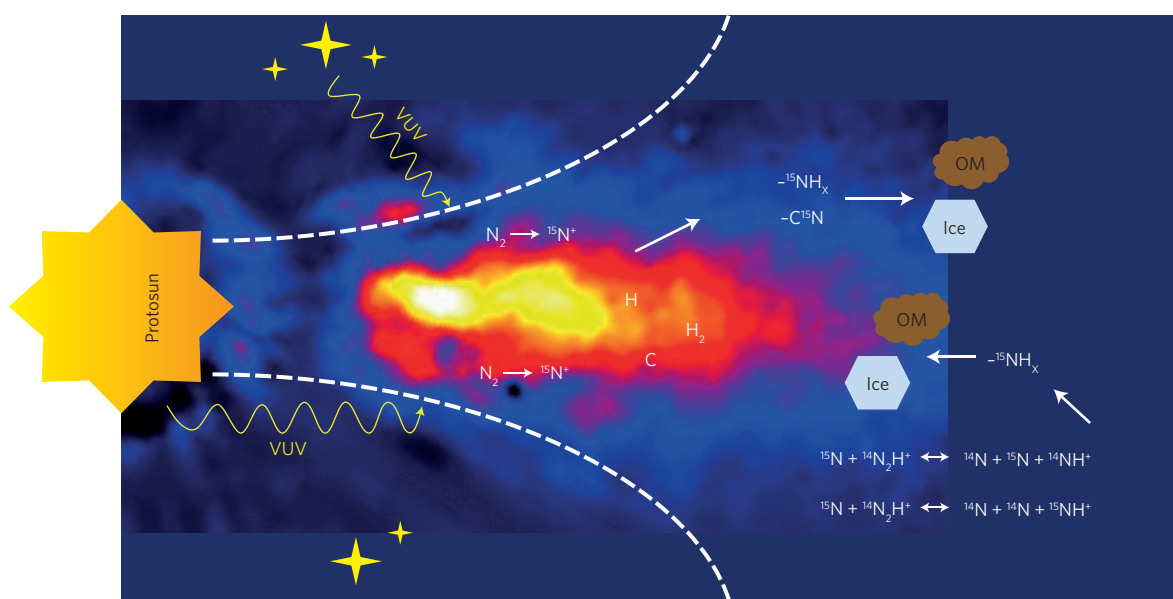


Figure B2 | Processes leading to a progressive ^{15}N enrichment in the Solar System. Schematic of the protoplanetary disk, made of gas and dust, with the proto-Sun at the centre. ^{15}N -enriched $^{15}\text{NH}_x$ (and C^{15}N) is produced by ion–molecule reactions in the cold regions of the disk^{72,73} or as a result of photodissociation of N_2 by vacuum ultra violet (VUV) light from the proto-Sun or from nearby stars⁷⁴ at the disk surface (indicated by the dashed white lines), and is removed from the gas by freezing out and/or trapping in organic matter. Image of Beta Pictoris courtesy of NASA.

for sampling. The nitrogen isotope composition of the modern SW was recently measured directly thanks to NASA's Genesis mission²⁹. The Genesis spacecraft sampled the SW for 27 months at the Lagrangian point L2 and returned SW-irradiated material for laboratory analysis in 2004. Despite a hard landing when the parachute

failed to open, the SW-implanted target material could be analysed by two different extraction techniques for N isotopes: laser ablation–static mass spectrometry³⁰ and ion probe analysis³¹. Both methods gave consistent results that permitted definition of the PSN nitrogen isotope composition: $^{14}\text{N}/^{15}\text{N} = 441 \pm 5$ ($\delta^{15}\text{N} = -383 \pm 8\text{‰}$; ref. 31),

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 ^{15}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 protostars⁷⁵. 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 light⁷⁴, or from self-shielding⁹⁵ (Box 2), and appears to have occurred within the first few tens to hundreds thousands of years after Solar System formation⁷¹. 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 photons⁹⁵. This process, which has been advocated to explain the oxygen isotope composition of refractory phases in meteorites, might also have been rapid (≤ 2 Myr), according to the chronology recorded by these refractory phases⁹⁷.

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 loss⁷⁸. The enrichment in both D and ^{15}N of the Martian atmosphere 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.

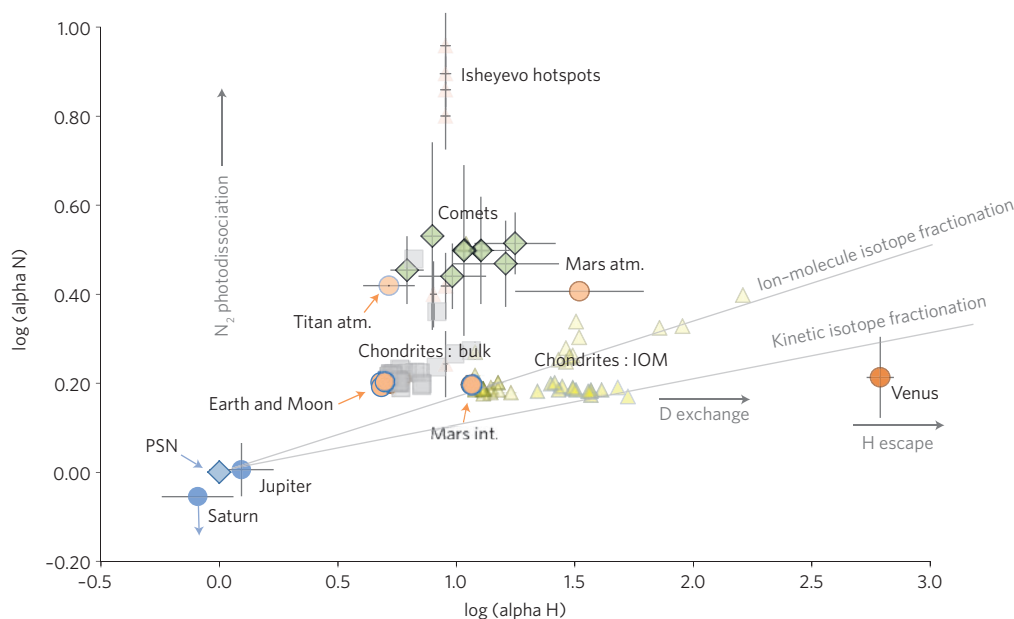


Figure B3 | Hydrogen and nitrogen isotope ratios of Solar System objects and isotope fractionation processes. Alpha H and alpha N are defined as the D/H and $^{15}\text{N}/^{14}\text{N}$ ratios normalized to the protosolar nebula values ($[2.1 \pm 0.5] \times 10^{-5}$ (ref. 7) and $[2.27 \times 0.03] \times 10^{-3}$ (ref. 31), respectively), as in ref. 76. 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 atmosphere⁸⁴; comets^{66,67,85,86}. The observed H–N isotope compositions require various isotope fractionation processes.

after moderate (24‰) correction for isotope fractionation in solar processing. Because the modern SW has a N isotope composition very close to that of Jupiter and osbornite, this comparison confirms that the Sun has neither synthesized N nor significantly fractionated N isotopes by more than about 3% from its birth to present-day. The PSN value constitutes the anchor value with which to compare other nitrogen isotope signatures of Solar System objects (Fig. 2).

The surface of the Moon

The Moon's surface lacks atmospheric shielding and full magnetic field protection, and has thus 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 scientific priority for the Apollo and Luna programmes. One of the most intriguing results of the lunar exploration was the discovery of N isotope variation in lunar soils and rocks^{32,33} of ~30%, one order of magnitude larger than that on Earth. Spallation by cosmic rays, which produces ^{15}N from ^{16}O , can account for some of the low $^{14}\text{N}/^{15}\text{N}$ 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 SW³⁴, so lunar nitrogen has been assumed to be solar as well. Thus, prior to the Genesis mission, the N isotope variations, which seemed to relate to the period of soil exposure, were attributed to secular changes in the

isotopic composition of the SW^{33,35}. However, no nucleosynthetic process within the Sun capable of changing the N isotope composition could be identified³⁶, 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 time³⁷, implied a negligible secular evolution of the SW. Finally, the development of coupled noble gas–nitrogen isotope analysis — together with the Genesis results — demonstrated that, contrary to noble gases, an additional, non-SW nitrogen component is present in lunar soils^{38–40}. The simultaneous 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 ¹⁵N-depleted SW-nitrogen (¹⁴N/¹⁵N > 340, $\delta^{15}\text{N} < -200\text{‰}$) is mixed to a variable extent with heavy (¹⁵N-rich) nitrogen. The N isotope signature of the non-solar end-member (¹⁴N/¹⁵N = 265 ± 5 ; $\delta^{15}\text{N} = 50\text{--}100\text{‰}$) 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 ¹⁵N-rich component is supplied by an ‘Earth wind’, a flux of terrestrial atmospheric nitrogen⁴². Early in the history of the Earth–Moon system, before the development of the terrestrial 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 far side. Future sampling may permit discrimination between an asteroidal or terrestrial origin of the ¹⁵N 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 during future lunar missions to investigate the origin of volatile elements in the inner Solar System.

Planets, asteroids and comets

The atmospheres of Jupiter^{26,27} and Saturn⁴³ are as ¹⁵N-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 bodies⁴⁴. The second possibility implies that these icy planetesimals had a solar-like N isotope composition and were not as ¹⁵N-rich as present-day comets.

In the inner Solar System, the Earth and Moon⁴⁵, as well as the interior of Mars⁴⁶ and the atmosphere of Venus⁴⁷, are richer in ¹⁵N 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 on 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 ¹⁵N by up to 25‰ (ref. 51), and a few meteorites defining the CB–CH group that present bulk ¹⁵N enrichments up to 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 with abundant ¹⁵N (refs 51,54). One member of this ¹⁵N-rich group, the Isheyevo meteorite, contains so-called ¹⁵N hotspots⁵⁵, measured on a micrometre scale by ion probe^{24,56}, characterized by the most extreme ¹⁵N enrichments found in the Solar System, up to about 450‰ (¹⁴N/¹⁵N ~ 50; $\delta^{15}\text{N} \sim 4,500\text{‰}$)²⁴. ¹⁵N-rich hotspots are typically found in IOM of primitive meteorites⁵⁷ and interplanetary dust particles⁵⁸ (small $\leq 50\text{ }\mu\text{m}$ volatile-rich grains snowing onto Earth’s surface, some of which are probably cometary), as well as in nano-sized globules of the Tagish Lake meteorite⁵⁹. As IOM shows systematically higher ¹⁵N contents than bulk meteorites and the inner planets, ¹⁵N-rich nitrogen hosted by organic molecules within dust grains must have been mixed with ¹⁵N-poor PSN N₂ to match bulk values^{30,31}.

Cometary matter was returned to Earth for analysis^{60,61} by NASA’s Stardust mission, which collected grains from a Jupiter-family comet named 81P/Wild2 in 2004, and returned to Earth two years later. As a result of the collection of grains at high-velocity, ices were lost during recovery, and only silicate and metal grains survived. Analyses have shown that the 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}. ¹⁵N/¹⁴N ratios are also comparable to the values found in meteorites, and excesses of ¹⁵N typical of cometary values are not observed in bulk analyses⁶³, probably because such excesses are hosted by cometary ice (CN, HCN, NH₃) that was lost during Stardust collection. On a smaller scale, ¹⁵N-rich hotspots with a maximum $\delta^{15}\text{N}$ value of $1300 \pm 400\text{‰}$ are observed, similar to the highest values found in IOM and IDPs⁶². Several presolar grains that have much larger C and N isotope variations (from +60 to +964‰ for $\delta^{13}\text{C}$, and from –518 to –350‰ for $\delta^{15}\text{N}$) have been identified⁶².

Additional cometary N isotope data are from radio and optical spectroscopic observations of CN, HCN, and NH₂ (the latter presumably derived from the photodissociation of NH₃)^{64–68}. Measurements are challenging due to spectroscopic interferences and low abundances of the analysed molecules, so those data have significant uncertainties compared with laboratory measurements (Box 1). All data collected so far indicate no systematic difference in the ¹⁴N/¹⁵N ratio between these different molecules within uncertainties: The mean ¹⁴N/¹⁵N ratios of CN (18 comets), HCN (1 comet), and NH₂ (3 comets) are 148 ± 6 ($\delta^{15}\text{N} = 840 \pm 75\text{‰}$), 139 ± 26 ($\delta^{15}\text{N} = 650 \pm 400\text{‰}$), and $\sim 140 \pm 40$ ($\delta^{15}\text{N} = 940 \pm 500\text{‰}$), 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, whose population is attributed to scattering of icy bodies originally located within the region of Uranus and Neptune^{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.

The available cometary data is inconsistent with a systematic N isotope variation with heliocentric distance beyond Jupiter. The observation that NH₂ 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 radicals¹⁹, 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 ¹⁵N-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 is studying comet 67P/Churyumov–Gerasimenko, will hopefully provide an *in situ* inventory of the ¹⁴N/¹⁵N ratios of different species degassed by the comet.

Towards a Solar System view

The picture emerges that there are at least three isotopic reservoirs in the Solar System (Fig. 2): the PSN, poor in ¹⁵N (¹⁴N/¹⁵N = 441 ± 5 ; $\delta^{15}\text{N} = -387 \pm 8\text{‰}$); the inner Solar System, where planets and bulk meteorites are enriched by a factor of 1.6 relative to the PSN (¹⁴N/¹⁵N = 272 ± 15 ; $\delta^{15}\text{N} = 0 \pm 50\text{‰}$); and cometary ices, enriched in ¹⁵N by a factor of 3 relative to the PSN (¹⁴N/¹⁵N = 147 ± 11 ; $\delta^{15}\text{N} = 850 \pm 150\text{‰}$). The distribution of N isotopes in the Solar System is roughly consistent with an increase of ¹⁵N enrichments with radial distance from the Sun, in qualitative agreement with the D/H ratio (Fig. B3). However, other isotopic systems such as carbon do not show similar variations, and evidence suggests that a homogeneous, ¹⁵N-poor isotope signature initially characterized the Solar System.

A mechanism is required to explain the progressive temporal and spatial evolution of nitrogen isotopes in the Solar System. The recent

detection of ^{15}N -enriched nitrogen in a CAI, which last interacted with the nebular gas ≤ 0.15 Ma as shown by the ^{26}Al – ^{26}Mg chronometer, suggests that at least some regions of the disk were driven toward isotopically heavy values within the first few hundred kyr after Solar System formation⁷¹. 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 versus $^{15}\text{N}/^{14}\text{N}$ 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 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 are responsible, such as 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 and dust grains from nearby stars.

All of these possibilities have profound astrophysical implications and can be tested using nitrogen isotopes from observation and dedicated modelling. Irrespective of the origin 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 mixing stands for the outer Solar System, since all cometary N analysed 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, as evidenced by the discovery of an ocean-like D/H ratio in a comet¹⁰. So far, all cometary measurements indicate a three-fold ^{15}N enrichment in comets compared with terrestrial N, suggesting that nitrogen isotopes represent a more powerful tracer than H isotopes for investigating the origins of planetary atmospheres. Thus, N isotopes are the tracer of choice to investigate the evolution of planetary atmospheres under the actions of thermal and non-thermal escape processes.

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References

1. Boss, A. P. & Goswami, J. N. in *Meteorites and the Early Solar System II* (eds Lauretta, D. S. & McSween, H. Y.) 171–186 (Univ. Arizona Press, 2006).
2. Warren, P. H. Stable-isotopic anomalies and the accretionary assemblage of the Earth and Mars: A subordinate role for carbonaceous chondrites. *Earth Planet. Sci. Lett.* **311**, 93–100 (2011).
3. Zinner, E. *et al.* NanoSIMS isotopic analysis of small presolar grains: Search for Si_3N_4 grains from AGB stars and Al and Ti isotopic compositions of rare presolar SiC grains. *Geochim. Cosmochim. Acta* **71**, 4786–4813 (2007).
4. Clayton, R. N. Isotopes: from Earth to the solar system. *Annu. Rev. Earth Planet. Sci.* **35**, 1–19 (2007).
5. Rodgers, S. D. & Charnley, S. B. Nitrogen superfractionation in dense cloud cores. *Mon. Not. R. Astron. Soc.* **385**, L48–L52 (2008).
6. Robert, F. The D/H ratio in chondrites. *Space Sci. Rev.* **106**, 87–101 (2003).
7. Robert, F., Gautier, D. & Dubrulle, B. The solar system D/H ratio: Observations and theories. *Sp. Sci. Rev.* **92**, 201–224 (2000).
8. Deloule, E., Robert, F. & Doukhan, J. C. Interstellar hydroxyl in meteoritic chondrules: Implications for the origin of water in the inner solar system. *Geochim. Cosmochim. Acta* **62**, 3367–3378 (1998).
9. Bockelée-Morvan, D., Crovisier, J., Mumma, M. J. & Weaver, H. A. in *Comets II* (Festou, M. C., Keller, H. U. & Weaver, H. A.) 391–423 (Univ. Arizona Press, 2004).
10. Hartogh, P. *et al.* Ocean-like water in the Jupiter-family comet 103P/Hartley 2. *Nature* **478**, 218–220 (2011).

11. Altwegg, K. *et al.* 67P/Churyumov-Gerasimenko, a Jupiter family comet with a high D/H ratio. *Science* **347**, 1261952 (2015).
12. Jacquet, E. & Robert, F. Water transport in protoplanetary disks and the hydrogen isotopic composition of chondrites. *Icarus* **223**, 722–732 (2013).
13. Nier, A. A. Redetermination of the relative abundances of the isotopes of carbon, nitrogen, oxygen, argon, and potassium. *Phys. Rev.* **77**, 789–793 (1950).
14. Cartigny, P. & Marty, B. Nitrogen isotopes and mantle geodynamics: the emergence of life and the atmosphere-crust-mantle connection. *Elements* **9**, 359–366 (2013).
15. Audouze, J., Lequeux, J. & Vigroux, L. Isotopes of carbon, nitrogen and oxygen as probes of nucleosynthesis, stellar mass losses and galactic evolution. *Astron. Astrophys.* **43**, 71–83 (1975).
16. Chin, Y., Henkel, C., Langer, N. & Mauersberger, R. The detection of extragalactic ^{15}N : consequences for nitrogen nucleosynthesis and chemical evolution. *Astrophys. J.* **512**, L143–L146 (1999).
17. Adande, G. R. & Ziurys, L. M. Millimeter-wave observations of CN and HNC and their ^{15}N isotopologues: a new evaluation of the $^{14}\text{N}/^{15}\text{N}$ ratio across the galaxy. *Astrophys. J.* **744**, 194 (2012).
18. Dahmen, G., Wilson, T. L. & Matteucci, F. The nitrogen isotope abundance in the Galaxy, I. The Galactic disk gradient. *Astron. Astrophys.* **295**, 194–198 (1995).
19. Hily-Blant, P., Bonal, L., Faure, A. & Quirico, E. The ^{15}N -enrichment in dark clouds and Solar System objects. *Icarus* **223**, 582–590 (2013).
20. Bizzocchi, L., Caselli, P. & Dore, L. Detection of N^{15}NH^+ in L1544. *Astron. Astrophys.* **510**, L5 (2010).
21. Gerin, M. *et al.* Detection of $^{15}\text{NH}_2\text{D}$ in dense cores: A new tool for measuring the $^{14}\text{N}/^{15}\text{N}$ ratio in the cold ISM. *Astron. Astrophys.* **498**, L9–L12 (2009).
22. Lis, D. C., Wootten, A., Gerin, M. & Roueff, E. Nitrogen isotopic fractionation in interstellar ammonia. *Astrophys. J. Lett.* **710**, L49–L52 (2010).
23. Wielen, R. & Wilson, T. L. The evolution of the C, N, and O isotope ratios from an improved comparison of the interstellar medium with the Sun. *Astron. Astrophys.* **142**, 139–142 (1997).
24. Briani, G. *et al.* Pristine extraterrestrial material with unprecedented nitrogen isotopic variation. *Proc. Natl Acad. Sci. USA* **106**, 10522–10527 (2009).
25. Hashizume, K., Chaussidon, M., Marty, B. & Terada, K. Protosolar carbon isotopic composition: implications for the origin of meteoritic organics. *Astrophys. J.* **600**, 480–484 (2004).
26. Fouchet, T. *et al.* ISO-SWS observations of Jupiter: measurement of the ammonia tropospheric profile and of the $^{15}\text{N}/^{14}\text{N}$ isotopic ratio. *Icarus* **143**, 223–243 (2000).
27. Owen, T., Mahaffy, P. R., Niemann, H. B., Atreya, S. & Wong, M. Protosolar nitrogen. *Astrophys. J.* **553**, L77–L79 (2001).
28. Meibom, A. *et al.* Nitrogen and carbon isotopic composition of the Sun inferred from a high-temperature solar nebular condensate. *Astrophys. J.* **656**, L33–L36 (2007).
29. Burnett, D. S. & Genesis Sci, T. Solar composition from the Genesis Discovery Mission. *Proc. Natl Acad. Sci. USA* **108**, 19147–19151 (2011).
30. Marty, B. *et al.* Nitrogen isotopes in the recent solar wind from the analysis of Genesis targets: Evidence for large scale isotope heterogeneity in the early solar system. *Geochim. Cosmochim. Acta* **74**, 340–355 (2010).
31. Marty, B., Chaussidon, M., Wiens, R. C., Jurewicz, A. J. G. & Burnett, D. S. A ^{15}N -poor isotopic composition for the solar system as shown by Genesis solar wind samples. *Science* **332**, 1533–1536 (2011).
32. Becker, R. H. & Clayton, R. N. Nitrogen abundances and isotopic compositions in lunar samples. *Proc. Lunar Sci. Conf. 6th* 2131–2149 (1975).
33. Kerridge, J. F. Solar nitrogen: Evidence for a secular change in the ratio of nitrogen-15 to nitrogen-14. *Science* **188**, 162–164 (1975).
34. Bogard, D. D., Nyquist, L., Hirsch, W. C. & Moore, D. Trapped solar and cosmogenic noble gas abundances in Apollo 15 and 16 deep drill samples. *Earth Planet. Sci. Lett.* **21**, 52–69 (1973).
35. Clayton, R. N. & Thieme, M. H. in *The Ancient Sun: Fossil Record in the Earth, Moon and Meteorites* (eds Pepin, R. O. *et al.*) 463–473 (Pergamon, 1980).
36. Geiss, J. & Bochsler, P. Nitrogen isotopes in the solar system. *Geochim. Cosmochim. Acta* **46**, 529–548 (1982).
37. Wieler, R. The solar noble gas record in lunar samples and meteorites. *Space Sci. Rev.* **85**, 303–314 (1998).
38. Wieler, R., Humbert, F. & Marty, B. Evidence for a predominantly non-solar origin of nitrogen in the lunar regolith revealed by single grain analyses. *Earth Planet. Sci. Lett.* **167**, 47–60 (1999).
39. Hashizume, K., Marty, B. & Wieler, R. Analyses of nitrogen and argon in single lunar grains: towards a quantification of the asteroidal contribution to planetary surfaces. *Earth Planet. Sci. Lett.* **202**, 201–216 (2002).
40. Furi, E., Marty, B. & Assonov, S. S. Constraints on the flux of meteoritic and cometary water on the Moon from volatile element (N-Ar) analyses of single lunar soil grains, Luna 24 core. *Icarus* **218**, 220–229 (2012).
41. Hashizume, K., Chaussidon, M., Marty, B. & Robert, F. Solar wind record on the Moon: deciphering presolar from planetary nitrogen. *Science* **290**, 1142–1145 (2000).
42. Ozima, M. *et al.* Terrestrial nitrogen and noble gases in lunar soils. *Nature* **436**, 655–659 (2005).

43. Fletcher, L. N. *et al.* The origin of nitrogen on Jupiter and Saturn from the $^{15}\text{N}/^{14}\text{N}$ ratio. *Icarus* **238**, 170–190 (2014).
44. Owen, T. *et al.* A low-temperature origin for the planetesimals that formed Jupiter. *Nature* **402**, 269–270 (1999).
45. Kerridge, J. F., Eugster, O., Kim, J. S. & Marti, K. Nitrogen isotopes in the 74001/74002 double-drive tube from Shorty Crater, Apollo 17. *Proc. 21st Lunar Planet. Sci. Conf.* **54**, 291–299 (1991).
46. Mathew, K. J. & Marti, K. Early evolution of Martian volatiles: Nitrogen and noble gas components in ALH84001 and Chassigny. *J. Geophys. Res.* **106**, 1401–1422 (2001).
47. Hoffman, J. H., Oyama, V. I. & von Zahn, U. Measurements of the Venus lower atmosphere composition: A comparison of results. *J. Geophys. Res.* **85**, 7871 (1980).
48. Alexander, C. M. O. *et al.* The origin of chondritic macromolecular organic matter: A carbon and nitrogen study. *Meteorit. Planet. Sci.* **33**, 603–622 (1998).
49. Robert, F. & Epstein, S. The concentration and isotopic composition of hydrogen, carbon and nitrogen in carbonaceous meteorites. *Geochim. Cosmochim. Acta* **46**, 81–95 (1982).
50. Kerridge, J. F. Carbon, hydrogen and nitrogen in carbonaceous chondrites: abundances and isotopic compositions in bulk samples. *Geochim. Cosmochim. Acta* **49**, 1707–1714 (1985).
51. Weisberg, M. *et al.* The CR chondrite clan. *Proc. NIPR Symp. Antart. Meteorites* **8**, 11–32 (1995).
52. Grady, M. M. & Pillinger, C. T. ALH 85085: nitrogen isotope analysis of a highly unusual primitive chondrite. *Earth Planet. Sci. Lett.* **97**, 29–40 (1990).
53. Prombo, C. A. & Clayton, R. N. A striking nitrogen isotope anomaly in the Bencubbin and Weatherford meteorites. *Science* **230**, 935–937 (1985).
54. Marty, B., Kelley, S. & Turner, G. Chronology and shock history of the Bencubbin meteorite: A nitrogen, noble gas, and Ar–Ar investigation of silicates, metal and fluid inclusions. *Geochim. Cosmochim. Acta* **74**, 6636–6653 (2010).
55. Ivanova, M. A. *et al.* The Isheyevo meteorite: Mineralogy, petrology, bulk chemistry, oxygen, nitrogen, carbon isotopic compositions, and ^{40}Ar – ^{39}Ar ages. *Meteorit. Planet. Sci.* **43**, 915–940 (2008).
56. Bonal, L. *et al.* Highly ^{15}N -enriched chondritic clasts in the CB/CH-like meteorite Isheyevo. *Geochim. Cosmochim. Acta* **74**, 6590–6609 (2010).
57. Busemann, H. *et al.* Interstellar chemistry recorded in organic matter from primitive meteorites. *Science* **312**, 727–730 (2006).
58. Aléon, J., Robert, F., Chaussidon, M. & Marty, B. Nitrogen isotopic composition of macromolecular organic matter in interplanetary dust particles. *Geochim. Cosmochim. Acta* **67**, 3773–3783 (2003).
59. Nakamura-Messenger, K., Messenger, S., Keller, L. P., Clemett, S. J. & Zolensky, M. E. Organic globules in the Tagish Lake meteorite: remnants of the protosolar disk. *Science* **314**, 1439–1442 (2006).
60. Brownlee, D. E. The Stardust mission: Analyzing samples from the edge of the solar system. *Annu. Rev. Earth Planet. Sci.* **42**, 179–205 (2014).
61. Brownlee, D. Comet 81P/Wild 2 under a microscope. *Science* **314**, 1711–1716 (2006).
62. McKeegan, K. D. *et al.* Isotopic compositions of cometary matter returned by Stardust. *Science* **314**, 1724–8 (2006).
63. Stadermann, F. J. *et al.* Stardust in Stardust—the C, N, and O isotopic compositions of Wild 2 cometary matter in Al foil impacts. *Meteor. Planet. Sci.* **313**, 299–313 (2008).
64. Arpigny, C. *et al.* Anomalous nitrogen isotope ratio in comets. *Science* **301**, 1522–1524 (2003).
65. Jehin, E., Manfroid, J., Hutsemékers, D., Arpigny, C. & Zucconi, J.-M. Isotopic ratios in comets: status and perspectives. *Earth. Moon Planets* **105**, 167–180 (2009).
66. Bockelée-Morvan, D. *et al.* Large excess of heavy nitrogen in both hydrogen cyanide and cyanogen from comet 17P/Holmes. *Astrophys. J.* **679**, L49–L52 (2008).
67. Rousselot, P. *et al.* Toward a unique nitrogen isotopic ratio in cometary ices. *Astrophys. J.* **780**, L17 (2014).
68. Shinnaka, Y., Kawakita, H., Kobayashi, H., Nagashima, M. & Boice, D. C. $^{14}\text{NH}_2/^{15}\text{NH}_2$ ratio in comet C/2012 S1 (Ison) observed during its outburst in 2013 November. *Astrophys. J.* **782**, L16 (2014).
69. Duncan, M. J. & Levison, H. F. A disk of scattered icy objects and the origin of Jupiter-family comets. *Science* **276**, 1670–1672 (1997).
70. Carusi, A., Kresák, L., Perozzi, E. & Valsecchi, G. B. High-order librations of Halley-type comets. *Astron. Astrophys.* **187**, 899–905 (1987).
71. Füri, E., Chaussidon, M. & Marty, B. Evidence for an early nitrogen isotopic evolution in the solar nebula from volatile analyses of a CAI from the CV3 chondrite NWA 8616. *Geochim. Cosmochim. Acta* **153**, 183–201 (2015).
72. Terzieva, R. & Herbst, E. The possibility of nitrogen isotopic fractionation in interstellar clouds. *Mon. Not. R. Astron. Soc.* **317**, 563–568 (2000).
73. Charnley, S. B. & Rodgers, S. D. The end of interstellar chemistry as the origin of nitrogen in comets and meteorites. *Astrophys. J. Lett.* **569**, L133–L137 (2002).
74. Chakraborty, S. *et al.* Massive isotopic effect in vacuum UV photodissociation of N_2 and implications for meteorite data. *Proc. Natl Acad. Sci. USA* **111**, 14704–14709 (2014).
75. Aléon, J. Multiple origins of nitrogen isotopic anomalies in meteorites and comets. *Astrophys. J.* **722**, 1342–1351 (2010).
76. Marty, B. The origins and concentrations of water, carbon, nitrogen and noble gases on Earth. *Earth Planet. Sci. Lett.* **313**–**314**, 56–66 (2012).
77. Füri, E., Deloué, E., Gurenko, A. & Marty, B. New evidence for chondritic lunar water from combined D/H and noble gas analyses of single Apollo 17 volcanic glasses. *Icarus* **229**, 109–120 (2014).
78. Grinspoon, D. H. Implications of the high D/H ratio for the sources of water in Venus' atmosphere. *Nature* **363**, 428–431 (1993).
79. Leshin, L. A. Insights into martian water reservoirs from analyses of martian meteorite QUE94201. *Geophys. Res. Lett.* **27**, 2017–2020 (2000).
80. Leshin, L. A. *et al.* Volatile, isotope, and organic analysis of martian fines with the Mars Curiosity rover. *Science* **341**, 1238937 (2013).
81. Alexander, C. M. O., Fogel, M., Yabuta, H. & Cody, G. D. The origin and evolution of chondrites recorded in the elemental and isotopic compositions of their macromolecular organic matter. *Geochim. Cosmochim. Acta* **71**, 4380–4403 (2007).
82. Macy, W. & Smith, W. H. Detection of HD on Saturn and Uranus, and the D/H ratio. *Astrophys. J.* **222**, L73 (1978).
83. Mahaffy, P. R., Donahue, T. M., Atreya, S. K., Owen, T. C. & Niemann, H. B. Galileo probe measurements of D/H and $^3\text{He}/^4\text{He}$ in Jupiter's atmosphere. *Space Sci. Rev.* **84**, 251–263 (1998).
84. Niemann, H. B. *et al.* Composition of Titan's lower atmosphere and simple surface volatiles as measured by the Cassini-Huygens probe gas chromatograph mass spectrometer experiment. *J. Geophys. Res.* **115**, E12006 (2010).
85. Ceccarelli, C. *et al.* in *Protostars and Planets VI: Part IV: Astrophysical conditions for life* (eds Beuther, H. *et al.*) 859–882 (University of Arizona Press, 2014).
86. Manfroid, J. *et al.* The CN isotopic ratios in comets. *Astron. Astrophys.* **503**, 613–624 (2009).
87. Javoy, M. & Pineau, F. The volatiles record of a “popping” rock from the Mid-Atlantic Ridge at 14°N : chemical and isotopic composition of gas trapped in the vesicles. *Earth Planet. Sci. Lett.* **107**, 598–611 (1991).
88. Hashizume, K. & Marty, B. in *Handbook of Stable Isotope Analytical Techniques* (ed. de Groot, P. A.) 361–375 (Elsevier Science, 2004).
89. Barry, P. H., Hilton, D. R., Halldórsson, S. A., Hahm, D. & Marti, K. High precision nitrogen isotope measurements in oceanic basalts using a static triple collection noble gas mass spectrometer. *Geochim. Geophys. Geosyst.* **13**, Q01019 (2012).
90. Hauri, E. H., Wang, J., Pearson, D. G. & Bulanova, G. P. Microanalysis of $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and N abundances in diamonds by secondary ion mass spectrometry. *Chem. Geol.* **185**, 149–163 (2002).
91. Rubin, M. *et al.* Molecular nitrogen in comet 67P/Churyumov–Gerasimenko indicates a low formation temperature. *Science* (2015).
92. Adams, N. G. & Smith, D. $^{14}\text{N}/^{15}\text{N}$ isotope fractionation in the reaction $\text{N}^+\text{H} + \text{N}_2$: Interstellar significance. *Astrophys. J.* **247**, L123–L125 (1981).
93. Geppert, W. D. *et al.* Dissociative recombination of N^+H^+ : evidence for fracture of the N–N Bond. *Astrophys. J.* **609**, 459–464 (2004).
94. Molek, C. D., McLain, J. L., Poterya, V. & Adams, N. G. A remeasurement of the products for electron recombination of N_2H^+ using a new technique: no significant $\text{NH} + \text{N}$ production. *J. Phys. Chem. A* **111**, 6760–6765 (2007).
95. Clayton, R. N. Self-shielding in the solar nebula. *Nature* **415**, 860–861 (2002).
96. Muskatel, B. H., Remacle, F., Thieme, M. H. & Levine, R. D. On the strong and selective isotope effect in the UV excitation of N_2 with implications toward the nebula and Martian atmosphere. *Proc. Natl Acad. Sci. USA* **108**, 6020–6025 (2011).
97. Davis, A. M. *et al.* in *Protostars and Planets VI* (eds Beuther, H. *et al.*) 809–831 (Univ. Arizona Press, 2015).
98. Alexander, C. M. O. *et al.* The provenances of asteroids, and their contributions to the volatile inventories of the terrestrial planets. *Science* **337**, 721–723 (2012).

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Competing financial interests

The authors declare no competing financial interests.