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Nitrogen isotope variations in the solar system

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

14

15 The solar system formed when a fraction of a dense molecular cloud collapsed and a
16 central star, the proto-Sun, started burning its nuclear fuel¹. The surrounding disk made of gas
17 and dust, the protosolar nebula (PSN), was thoroughly stirred and homogenized due to large-
18 scale heating and mixing driven by loss of the angular momentum, the energy delivered by the
19 proto-Sun, and magneto-rotational turbulence. The efficiency of these processes is evident in
20 primitive ("carbonaceous") meteorites, which show a remarkable homogeneity in the isotopic
21 compositions of their constituents down to the part per million level for most elements of the

22 periodic table². Relics of the initial heterogeneous mixture of stellar debris can only be found in
23 nano-to-micron-sized presolar grains that were thermally resistant enough to survive high
24 enthalpy processing³. However, the light elements hydrogen, carbon, nitrogen, and oxygen,
25 show significant, sometimes extreme, isotope variations among solar system objects and
26 reservoirs, from a few percents for C and O, to tens or even hundreds of percents for H and N
27 (ref. 4). These light elements, by far the most abundant ones in the PSN, share the property to
28 have been predominantly in the gaseous state (H₂, CO, N₂, etc., and their ionized derivatives) in
29 the presolar cloud and in the disk. Consequently, they were prone to efficient isotope exchange
30 and interactions with stellar photons and cosmic rays, either in the interstellar medium (ISM)⁵,
31 or in the presolar cloud or the PSN (e.g., refs. 4,6). Thus, these isotope compositions convey a
32 unique record of solar system forming processes.

33 The largest isotope variations are observed for hydrogen and nitrogen. The
34 deuterium/hydrogen (D/H) ratio varies by a factor of ~35, from the PSN value of $21 \pm 0.5 \times 10^{-6}$
35 (ref. 7) to D-rich "hotspots" in meteorites with values up to 720×10^{-6} (ref. 8). Inner solar
36 system objects ($\sim 150 \times 10^{-6}$; ref. 7) and comets ($150\text{-}500 \times 10^{-6}$; refs. 9–11) show intermediate
37 values, and possibly define an increase of the D/H ratio with heliocentric distance. A consistent
38 scheme emerges in which nebular H₂ poor in deuterium exchanged isotopically with H₂O at
39 low temperature, resulting in a preferential D-enrichment of the latter. Deuterium-rich water
40 then froze out onto icy grains and exchanged isotopically with organics and silicates as a result
41 of turbulent transport and aqueous alteration on forming planetesimals¹². Although this
42 scenario is not without weaknesses and is still a matter of debate, the D/H isotopic tracer
43 offers the possibility to investigate the relationships between the different solar system
44 reservoirs. In particular, it is central in the debate on the origin of water (cometary or
45 asteroidal) in the inner solar system including the oceans¹⁰.

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

49
$$\delta^{15}\text{N} = [({}^{15}\text{N}/{}^{14}\text{N})_{\text{sample}}/({}^{15}\text{N}/{}^{14}\text{N})_{\text{standard}} - 1] \times 1,000$$

50 where $\delta^{15}\text{N}$ expresses the deviation of the sample ratio relative to a standard in parts per
51 mil (‰). The nitrogen standard is the isotope composition of atmospheric N_2 (${}^{15}\text{N}/{}^{14}\text{N} = 3.676$
52 $\times 10^{-3}$; ref. 13). On Earth, most variations are of the order of a few to tens of permil (e.g., ref.
53 14). Because the range of extraterrestrial N isotope variations can be much larger than the
54 permil level, cosmochemists use instead the absolute value of the ${}^{15}\text{N}/{}^{14}\text{N}$ ratio, following the
55 stable isotope convention that the rare, heavy isotope is the numerator. To complicate matters
56 further, astronomers and astrophysicists use instead the ${}^{14}\text{N}/{}^{15}\text{N}$ notation (272 for air)
57 (despite using the D/H notation for hydrogen as do cosmochemists). Both notations are given
58 here for the sake of better understanding by these communities.

59 On Earth, the N isotope composition varies by no more than 2 %, but variations can reach
60 500 % on a solar system scale (Figs. 1 and 2). Until recently, the causes of this variability were
61 not understood, for two main reasons. Firstly, the solar system initial ${}^{14}\text{N}/{}^{15}\text{N}$ ratio was
62 unknown. Secondly, nitrogen isotopes are more difficult to quantify than hydrogen isotopes
63 because they are generally less abundant in cosmochemical material, and because they are
64 difficult to measure at distance by spectroscopic methods. The analysis of solar wind ions
65 returned to Earth by the Genesis mission – together with advances in high-spatial-resolution,
66 high-sensitivity isotope analysis in the laboratory as well as in high-resolution UV
67 spectroscopy (Box 1) – have permitted major leaps of understanding in the cosmochemistry of
68 this element. Here, we review recent advances in the domain that are particularly relevant in
69 the context of the measurements currently carried out on Comet 67P/Churyumov-
70 Gerasimenko by the Rosetta spacecraft instruments.

71

72 **Nucleosynthesis of N isotopes and galactic evolution**

73 The production paths and rates of nitrogen isotopes are not fully understood¹⁵⁻¹⁷. ¹⁴N is
74 produced during the cold CNO cycle in low to intermediate mass stars ($M_{\text{solar}} < M < 7 M_{\text{solar}}$) and
75 is released to the interstellar medium by dredge-up events during asymptotic giant branch
76 (AGB) phases that terminate the lives of most stars ("secondary" production, i.e., not produced
77 directly from H and He nuclei). This isotope is also produced in the so-called hot CNO cycle that
78 takes place in massive stars turning into AGBs during dredge-up from the carbon layer
79 ("primary" production from 3 alpha particles and two protons). ¹⁵N is destroyed in the cold
80 CNO cycle, requiring other mechanisms such as ¹⁵N production during the hot CNO cycle in
81 novae and, possibly, neutrino spallation on ¹⁶O in type II supernovae, both productions being
82 "secondary". Consequently, a nucleosynthetic isotope composition cannot be predicted from
83 theory, and estimates for the N isotope production in the galaxy rely on (limited) observations.

84 In molecular clouds, the N isotope composition is mainly measured in CN, HCN, HNC, and,
85 more recently, in NHD⁺ molecules¹⁷⁻²². For molecular N₂, the signal-to-noise ratio is too low for
86 a spectroscopic measurement. The data seem to define an isotope gradient with a decrease of
87 ¹⁵N relative to ¹⁴N with increasing distance from the galaxy center (Fig. 1; refs. 17,18). Because
88 stars in the galaxy center tend to be more metal-rich (metallicity being here the proportion of
89 elements heavier than helium), secondary production of ¹⁵N that presumably takes place in
90 novae and supernovae should decrease more rapidly with galactocentric distance than the
91 primary component of ¹⁴N production, in qualitative agreement with the observation (Fig. 1).
92 Strikingly, the solar system, represented by the PSN value (see next subsection), does not fit
93 the correlation. The observed offset could result from a localized N isotope evolution since the
94 solar system isolated nitrogen from the local ISM 4.56 Ga ago. However, a ¹⁴N/¹⁵N value of \sim
95 ≥ 400 has been proposed for the local ISM²³ where the Sun was born, consistent with the solar
96 ratio and implying little N isotope evolution with time. Alternatively, the apparent anomaly
97 may be explained by the uncertainty in the data defining the correlation depicted in Fig. 1. CN

98 or HCN, the molecules for which the nitrogen isotopic compositions are measured in dense
99 cores, could have been isotopically fractionated with respect to the source composition, and
100 may not be representative of the local ISM values. Indeed, measurements of the N isotope
101 compositions in three starless dense cores of the local ISM, either in $\text{NH}_3\text{-NH}^+$ (refs. 20–22) or
102 in HCN, suggest that the nitrile formation path (leading to HCN and CNH) drastically enriches
103 ^{15}N compared to the amine path (NH compounds) (Fig. 2; ref. 19).

104 Remarkably, the order of magnitude variation of the nitrogen isotope composition in the
105 solar system, defined by the most ^{15}N -rich portion of the Isheyev meteorite²⁴ and the
106 protosolar nebula composition (Figs. 1 and 2; see subsection below), is comparable to the
107 range of values measured in galactic molecular clouds all over the galaxy (Fig. 1). A
108 straightforward interpretation would be that the solar system contains isotopically
109 heterogeneous, nucleosynthetic nitrogen components inherited from ISM. However, other
110 isotope systems do not show correlated isotope variations. For example, nitrogen's "brother"
111 element carbon, whose two stable isotopes ^{12}C and ^{13}C are produced in different
112 nucleosynthetic pathways as well and also show a diversity of isotopic compositions among
113 molecular clouds, displays a near-constant isotopic composition in the solar system within ~ 10
114 % (ref. 25). The isotope variations of nitrogen in the solar system are therefore unlikely to
115 represent remnants of nucleosynthetic heterogeneities, and are instead attributed to isotope
116 fractionation. The nature of the fractionating processes (e.g., interactions with solar/stellar
117 photons vs. low temperature isotope exchange) are still debated (Boxes 2 and 3).

118

119 **The protosolar nebula**

120 The N isotope analysis of Jupiter's atmosphere by spectroscopy ($^{14}\text{N}/^{15}\text{N} = 526_{-169}^{+585}$, $\delta^{15}\text{N} = -$
121 483_{-272}^{+245} ‰; ref. 26) and by in-situ mass spectrometry ($^{14}\text{N}/^{15}\text{N} = 435 \pm 60$, $\delta^{15}\text{N} = -375 \pm 80$ ‰;
122 ref. 27) suggested a ^{15}N -poor solar nitrogen composition. Independently, a $^{14}\text{N}/^{15}\text{N}$ ratio of
123 428 ± 8 ($\delta^{15}\text{N} = -364 \pm 12$ ‰) has been obtained for a rare TiN (osbornite) phase within a

124 calcium-aluminum-rich inclusion (CAI) (ref. 28). Because osbornite was presumably the first
125 solid N-bearing phase to condense from the PSN, this value was concluded to correspond to the
126 PSN signature at the time of solid condensation.

127 At present, the isotopic composition of the PSN is best represented by that of the Sun,
128 which concentrates more than 99 % of the mass of the solar system. For the isotope analysis of
129 the Sun, only the solar wind (SW; the corpuscular emission of the Sun which consists of matter
130 from the solar convective zone, ionized in the photosphere and accelerated along open lines of
131 the Sun's magnetic field) is available for sampling. The nitrogen isotope composition of the
132 modern solar wind was recently measured directly thanks to NASA's Genesis mission
133 (Discovery Program)²⁹. The Genesis spacecraft sampled the SW during 27 months at the
134 Lagrangian point L2 and returned SW-irradiated material for laboratory analysis in 2004.
135 Despite a hard landing (the parachute failed to open), the SW-implanted target material could
136 be analyzed by two different extraction techniques for N isotopes (laser ablation-static mass
137 spectrometry³⁰ and ion probe³¹). Both methods gave consistent results that permitted to define
138 the PSN nitrogen isotope composition of $^{14}\text{N}/^{15}\text{N} = 441 \pm 5$ ($\delta^{15}\text{N} = -383 \pm 8 \text{‰}$; ref. 31), after
139 moderate (24 ‰) correction for isotope fractionation in solar processing. Because the modern
140 solar wind has a N isotope composition very close to that of Jupiter and osbornite, this
141 comparison confirms that the Sun did neither synthesize N nor significantly fractionate N
142 isotopes by more than about 3 % from its birth to present-day. The PSN value constitutes the
143 anchor value to which to compare other nitrogen isotope signatures of solar system objects
144 (Fig. 2).

145

146 **The surface of the Moon**

147 The surface of the Moon, which lacks atmospheric shielding and full magnetic field
148 protection, has accumulated SW ions for hundreds of millions of years. The analysis of SW,
149 either implanted into aluminum foils during the visits by the Apollo astronauts or in the lunar

150 soils that were recovered, was a science priority of the Apollo and Luna programs. One of the
151 most intriguing results of the lunar exploration was the discovery of a ~30 % N isotope
152 variation in lunar soils and rocks^{32,33}, one order of magnitude larger than that on Earth.
153 Spallation by cosmic rays that produces ¹⁵N from ¹⁶O can account for some of the low ¹⁴N/¹⁵N
154 values but fails to explain the occurrence of light (¹⁵N-poor) nitrogen on the Moon. Noble gases
155 in lunar soils are mostly derived from SW³⁴, so that lunar nitrogen was assumed to be solar as
156 well. Thus, prior to the Genesis mission, the N isotope variations, which seemed to relate to the
157 epoch of soil exposure, were attributed to secular changes in the isotopic composition of the
158 SW^{33,35}. This possibility, however, faced serious difficulties: no nucleosynthetic process within
159 the Sun capable of changing the N isotope composition could be identified³⁶, and comparison
160 with carbon (whose isotope composition in lunar samples varies much less than that of
161 nitrogen; ref. 25) and helium (whose isotope composition in lunar soils appears constant over
162 time; ref. 37) implied a negligible secular evolution of the SW. Finally, the development of
163 coupled noble gas-nitrogen isotope analysis - together with the Genesis findings -
164 demonstrated that, contrary to noble gases, an additional, non-SW nitrogen component is
165 present in lunar soils³⁸⁻⁴⁰. The conjoint measurement of H and N isotope variations through the
166 outer skin of lunar soil grains with an ion probe (Box 1; ref. 41) revealed that ¹⁵N-depleted SW-
167 N (¹⁴N/¹⁵N > 340, δ¹⁵N < -200‰) is mixed to a variable extent with "heavy" (¹⁵N-rich) nitrogen.
168 The N isotope signature of the non-solar end-member (¹⁴N/¹⁵N = 265±5; δ¹⁵N = 50-100‰) is
169 consistent with delivery of asteroidal, rather than cometary, material to the lunar surface, with
170 a flux comparable to that of interplanetary dust and micrometeorites on Earth, after scaling to
171 different gravitational focusing and surface areas of the two planetary bodies^{39,40}. An
172 alternative interpretation is that the ¹⁵N-rich component is supplied by an "Earth wind" flux of
173 terrestrial atmospheric nitrogen⁴². Early in the history of the Earth-Moon system, before the
174 development of the global geomagnetic field, interaction of the SW with Earth's upper
175 atmosphere may have resulted in a significant N⁺ escape flux. However, since the Moon is

176 tidally locked to Earth, the Earth wind contribution is expected to be absent on the lunar
177 farside. Future sampling may permit to distinguish between an asteroidal or terrestrial origin
178 of the ^{15}N enrichment. Hence, the lunar surface constitutes a superb opportunity to investigate
179 the nature and flux of matter and ions delivered to planetary surfaces through time, and will
180 certainly deserve further attention in future lunar missions aimed at investigating the origin of
181 volatile elements (e.g., water) in the inner solar system.

182

183 **Planets, asteroids and comets**

184 The atmospheres of Jupiter^{26,27} and Saturn⁴³ are as ^{15}N -depleted as the PSN. Thus, they
185 may represent remnants of the PSN gas, either trapped gravitationally during planetary growth
186 or inherited from accretion of icy bodies⁴⁴. The second possibility implies that these icy
187 planetesimals had a solar-like N isotope composition and were not as ^{15}N -rich as are present-
188 day comets (see below).

189 The inner planets – Earth and Moon⁴⁵, as well as the interior of Mars⁴⁶ and the atmosphere
190 of Venus⁴⁷ – are richer in ^{15}N than solar N by approximately 60 %, and have comparable N
191 isotope compositions on the scale of solar system variations (Fig. 2). In primitive meteorites,
192 nitrogen is mostly hosted in organics, particularly in insoluble organic matter (IOM) and, under
193 reducing conditions, in nitrides. Carbonaceous chondrites, which are rich in volatile elements
194 as their name implies, contain of the order of 1,000 ppm N, with bulk N isotope compositions
195 within 5 % of the terrestrial value⁴⁸⁻⁵⁰. An exception is the CR carbonaceous chondrite clan,
196 whose members are richer in ^{15}N by up to 25 % (e.g., ref. 51), and a few meteorites defining the
197 CB-CH group that present bulk ^{15}N enrichments up to 100-150 % (refs. 52,53). The causes of
198 these enrichments are unclear and could be related to impacts between asteroidal bodies and
199 volatile- and/or organic-rich objects rich in ^{15}N (refs. 51,54). One member of this ^{15}N -rich
200 group, the Isheyevo meteorite, presents so-called " ^{15}N hotspots" (ref. 55), measured on a
201 micron scale by ion probe^{24,56}, characterized by the most extreme ^{15}N enrichments found in the

202 solar system, up to about 450 ‰ ($^{14}\text{N}/^{15}\text{N} \sim 50$; $\delta^{15}\text{N} \sim 4,500$ ‰; ref. 24). ^{15}N -rich hotspots are
203 typically found in IOM of primitive meteorites⁵⁷ and interplanetary dust particles⁵⁸ (which are
204 small [$\leq 50\mu\text{m}$] volatile-rich grains snowing onto Earth's surface, and some of which are
205 probably cometary), as well as in nano-sized globules of the Tagish Lake meteorite⁵⁹. Since IOM
206 shows systematically higher ^{15}N contents than bulk meteorites and inner planets, ^{15}N -rich
207 nitrogen hosted by organic molecules within dust grains must have been mixed with ^{15}N -poor
208 PSN N_2 to match bulk values^{30,31}.

209 Cometary matter was analyzed on Earth thanks to NASA's Stardust mission (Discovery
210 program), which succeeded in collecting grains from a Jupiter family comet (JFC) named
211 81P/Wild2 in 2004, and in returning them to Earth two years later for laboratory analyses^{60,61}.
212 As a result of the high velocity collection, ices were lost during recovery, and only
213 silicate/metal grains survived. Analyses showed that cometary dust is derived from precursors
214 that share mineralogical and isotopic similarities with carbonaceous chondrites, consistent
215 with models advocating large-scale radial mixing in the nascent solar system⁶⁰⁻⁶². $^{15}\text{N}/^{14}\text{N}$
216 ratios are also comparable to the values found in meteorites, and excesses of ^{15}N typical of
217 cometary values (see below) are not observed in bulk analyses⁶³, probably because such
218 excesses are hosted by cometary ice (CN, HCN, NH_3) that was lost during Stardust collection.
219 On a smaller scale, ^{15}N -rich hotspots with a maximum $\delta^{15}\text{N}$ value of 1300 ± 400 ‰ are
220 observed, similar to the highest values found in IOM and IDPs⁶². Several presolar grains have
221 been identified showing much larger C and N isotope variations (from +60 to +964 ‰ for $\delta^{13}\text{C}$,
222 and from -518 to -350 ‰ for $\delta^{15}\text{N}$; ref. 62).

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

228 $^{14}\text{N}/^{15}\text{N}$ ratio between these different molecules within uncertainties: The mean $^{14}\text{N}/^{15}\text{N}$ ratios
229 of CN (18 comets), HCN (1 comet), and NH_2 (3 comets) are 148 ± 6 ($\delta^{15}\text{N} = 840\pm 75\text{‰}$), 139 ± 26
230 ($\delta^{15}\text{N} = 650\pm 400\text{‰}$), and $\sim 140\pm 40$ ($\delta^{15}\text{N} = 940\pm 500\text{‰}$), respectively (Fig. 2). Furthermore,
231 short- and long-period comets seem to have comparable N isotope compositions. Long-period
232 comets are thought to come from the Oort Cloud (OC comets), whose population is attributed
233 to scattering of icy bodies originally located within the Uranus-Neptune region^{69,70}. Short-
234 period comets are proposed to originate from the Kuiper belt reservoir, which is beyond the
235 present-day orbit of Neptune, and/or from the external edge of the disk. Due to gravitational
236 instabilities, some of these icy objects would then have been scattered and injected into the
237 Jupiter region, becoming isotropic (Jupiter Family comets - JFCs). Thus, the available cometary
238 data is inconsistent with a systematic N isotope variation with heliocentric distance beyond
239 Jupiter. The observation that NH_2 on one hand, and CN-HCN on the other hand, show similar N
240 isotope signatures is at odds with the prediction of significant nitrogen isotope fractionation
241 between amine and nitrile radicals¹⁹, unless isotope exchange subsequently erased this effect.
242 It should be emphasized, however, that our knowledge of nitrogen isotopes in cometary
243 material is limited. Depending on the thermal history of these bodies, it is possible that ^{15}N -
244 poor dinitrogen from the PSN is trapped in ices, and that the bulk N isotopic composition of
245 comets is de facto unknown. The ROSETTA space mission, which has just started to study
246 comet 67P/Churyumov-Gerasimenko, will hopefully provide for the first time an in-situ
247 inventory of the $^{14}\text{N}/^{15}\text{N}$ ratios of different species degassed by the comet.

248

249 **Conclusions and prospects**

250 The picture that emerges is that there are at least three isotopic reservoirs in the solar
251 system (Fig. 2): i) the PSN, poor in ^{15}N ($^{14}\text{N}/^{15}\text{N} = 441\pm 5$; $\delta^{15}\text{N} = -387\pm 8\text{‰}$), ii) the inner solar
252 system, where planets and bulk meteorites are enriched by a factor of 1.6 relative to the PSN
253 ($^{14}\text{N}/^{15}\text{N} = 272\pm 15$; $\delta^{15}\text{N} = 0\pm 50\text{‰}$), and iii) cometary ices, enriched in ^{15}N by a factor of 3

254 relative to the PSN ($^{14}\text{N}/^{15}\text{N} = 147 \pm 11$; $\delta^{15}\text{N} = 850 \pm 150$ ‰). Thus, the distribution of N
255 isotopes in the solar system is roughly consistent with an increase of ^{15}N enrichments with
256 radial distance from the Sun, in qualitative agreement with the D/H ratio (Fig. B3). However,
257 several lines of evidence demonstrate that a homogeneous, ^{15}N -poor isotope signature initially
258 characterized the solar system, thus requiring a mechanism for the progressive temporal and
259 spatial isotopic evolution. The recent detection of ^{15}N -enriched nitrogen in a CAI, which last
260 interacted with the nebular gas ≤ 0.15 Ma ago as shown by the ^{26}Al - ^{26}Mg chronometer, suggests
261 that at least some regions of the disk were driven toward isotopically heavy values very early
262 in solar system history, within the first few tens to hundreds thousands of years after solar
263 system formation⁷¹. The nature of the fractionating processes is still a matter of debate and
264 several processes might have played a role (Boxes 2 and 3). While some of the D/H vs. $^{15}\text{N}/^{14}\text{N}$
265 co-variations are consistent with either kinetic isotope fractionation or ion-molecule reactions,
266 many ^{15}N excesses are not correlated with enrichments in D, and thus require nitrogen-specific
267 isotope fractionation (Fig. B3). Furthermore, the increase of ^{15}N enrichments with radial
268 distance from the Sun could have resulted from different types of processes. The interaction
269 rate between the PSN gas and UV photons could have varied with heliocentric distance, with
270 enhanced ^{15}N fractionation occurring in the outer solar system, where the lower gas density
271 would have allowed deeper photon penetration and/or more efficient freezing out of
272 synthesized molecules than in the denser, hotter inner solar system. It is also possible that
273 several processes were involved: photodissociation by solar photons in the inner solar system,
274 and contribution of ^{15}N -rich ices formed early in the outer solar system by illumination of
275 ice/dust grains from nearby stars. All these possibilities have profound astrophysical
276 implications and can be tested using nitrogen isotopes, from observation and/or dedicated
277 modeling. Irrespective of the origin(s) of the ^{15}N -enrichment, large-scale turbulence and
278 mixing eventually regionally homogenized material available for planetary accretion, resulting
279 in the isotopic similarity seen for the Earth and most chondritic groups. The same requirement

280 of efficient isotope fractionation and mixing stands for the outer solar system since all
281 cometary N analyzed so far is enriched in ^{15}N by a factor of ~ 3 relative to inner planets (Fig. 2).

282 A particularly important question that remains to be addressed with nitrogen isotopes
283 concerns the origin and evolution of the terrestrial atmosphere and oceans. The isotopes of
284 hydrogen do not seem to provide an unambiguous tool for distinguishing between a cometary
285 versus asteroidal origin ever since the discovery of an ocean-like D/H ratio in a comet¹⁰. So far,
286 all cometary measurements indicate a 3-fold ^{15}N enrichment in comets compared to terrestrial
287 N, suggesting that nitrogen isotopes represent a more powerful tracer than H isotopes for
288 investigating the origin(s) of planetary atmospheres. Thus, N isotopes are the tracer of choice
289 to investigate the evolution of planetary atmospheres through time upon thermal and non-
290 thermal escape processes.

291

292 **Figure Legends**

293

294 **Figure 1: Nitrogen isotope variation in molecular clouds from our galaxy as a function of**
295 **distance from the galactic center.** Adapted from refs. 17,18. Isotope compositions are given
296 in both absolute $^{14}\text{N}/^{15}\text{N}$ ratios and $\delta^{15}\text{N}$ values (deviation in permil from the atmospheric
297 $^{15}\text{N}/^{14}\text{N}$ ratio). The observed correlation (dashed line; ref. 17) appears consistent with
298 secondary ^{15}N production in massive stars. The total N isotope range within the solar system,
299 defined by the most ^{15}N -rich "hotspot" in the Isheyevo meteorite²⁴ and the protosolar nebula
300 (PSN) composition³¹, is comparable to that in our galaxy. Error bars indicate 1σ
301 uncertainties¹⁷.

302

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

306 giant planets^{26,27,43}, all solar system objects and reservoirs are significantly enriched in ¹⁵N
307 compared to the PSN. Values determined for various N species in local and galactic molecular
308 clouds¹⁷⁻²² are shown for comparison. Uncertainties of spectroscopic measurements are shown
309 at the 1 σ level.

310

311 **Figure B1: Nitrogen and hydrogen isotope variations within single lunar grains.** a)
312 Silicate grain (breccia 79035) showing $\delta^{15}\text{N}$ values (circles) as low as -250‰ together with
313 very low δD values (blue squares) at depths ≤ 120 nm. The D-poor hydrogen component (i.e. δD
314 ≈ -900 ‰) represents implanted SW, highly depleted in deuterium due to D-burning in the Sun.
315 Thus, the low $\delta^{15}\text{N}$ values give a first-order estimate of the isotopic signature of SW-N. b)
316 Ilmenite grain (soil 71501) containing non-solar N – associated with D-rich (planetary)
317 hydrogen –, which is enriched in ¹⁵N to a similar extent as meteoritic nitrogen. Data from ref.
318 41.

319

320 **Figure B2: Processes leading to a progressive ¹⁵N-enrichment in the solar system.**
321 Schematic diagram of the protoplanetary disk made of gas and dust with the proto-Sun at the
322 centre. ¹⁵N-enriched ¹⁵NH_x (and C¹⁵N) is produced by ion-molecule reactions in the cold
323 regions of the disk^{72,73} or as a result of photodissociation of N₂ by UV light from the proto-Sun
324 or from nearby stars⁷⁴, and is removed from the gas by freezing out and/or trapping in organic
325 matter. (Image of Beta Pictoris; courtesy of NASA).

326

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

332 Isheyevo hotspots^{24,56}; Saturn^{43,82}; Jupiter^{27,83}; Titan atmosphere⁸⁴; comets ^{66,67,85,86}. The
333 observed H-N isotope compositions require various isotope fractionation processes.

334

335 **Box 1: Analysis of nitrogen isotopes**

336 For geochemical applications, nitrogen isotopes have historically been measured using isotope
337 ratio mass spectrometers operated in dynamic pumping mode (e.g., ref. 87). However, since this
338 technique is not suitable for the analysis of low nitrogen abundances, higher-sensitivity noble gas mass
339 spectrometers operated under static vacuum conditions are now the standard method to determine the
340 nitrogen isotopic composition of N-poor and/or small-sized (≤ 5 mg) terrestrial and extraterrestrial
341 samples (e.g., ref. 88,89). In this method, nitrogen – extracted from the samples by various destructive
342 techniques such as crushing, laser ablation, laser-, or furnace-heating, and purified from interfering
343 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
344 mono- or multi-collection mode. Measured peak heights and isotope ratios must be corrected for
345 isobaric mass interferences from CO, N_2H , and hydrocarbons (C_2H_x), which are ubiquitously present in
346 the mass spectrometer system, and the instrumental precision and reproducibility is monitored by
347 repeat analysis of atmospheric N_2 .

348 Secondary ionization mass spectrometry (SIMS) analysis represents a non-destructive means to
349 determine N isotope variations with a high lateral resolution (i.e., at a scale as small as ≤ 10 μm) or a
350 high depth resolution (i.e., ≤ 10 nm; Fig. B1; ref. 39). While the isotope analysis of nitrogen by SIMS is
351 challenging due to its low ionization efficiency, an intense CN^- signal is formed in the presence of carbon
352 by bombardment of the sample surface with a Cs^+ ion beam, and nitrogen isotope ratios have
353 successfully been determined in the form of $^{12}C^{15}N^- / ^{12}C^{14}N^-$ in various extraterrestrial
354 samples^{24,28,41,56,57,75} as well as in terrestrial diamonds⁹⁰. Furthermore, the nitrogen isotope composition
355 of solar wind collected during NASA's Genesis mission was determined with high precision by SIMS³¹.
356 Notably, since the ionization rate depends on the sample matrix, using a standard made of the same
357 material as the sample and with a known N abundance and isotope composition is critical for an
358 accurate measurement by this technique.

359 High-resolution radio and optical spectroscopy represents the only analytical means to
360 remotely determine the isotopic composition of cometary (atmospheric) nitrogen. Cometary emissions
361 are produced by absorption of solar light by the various molecules followed by re-emission of lines of
362 specific wavelengths, a process called resonance-fluorescence. Isotope ratios ($^{14}N/^{15}N$) are determined
363 by comparing the observed molecular spectra with synthetic spectra of the same species. Such
364 measurements require high signal-to-noise spectra together with a high spectral resolution, and have
365 so far only been feasible for nitrogen in the form of CN, HCN, and NH_3 for a limited number of Oort cloud
366 and Jupiter family comets. Notably, the Rosetta Orbiter Spectrometer for Ion and Neutral Analysis
367 (ROSINA) on board the Rosetta spacecraft has been able to determine, for the first time, the abundance
368 of N_2 *in-situ* in the coma of comet 67P/Churyumov-Gerasimenko⁹¹.

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 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 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 less⁷². 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 system⁵. 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 $^{14}\text{N}^{14}\text{N}$ saturates with respect to that of $^{15}\text{N}^{14}\text{N}$, because the latter is much less abundant, and, 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 (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 signatures⁹⁵. Another model based on quantum mechanics⁹⁶ is substantiated by photodissociation experiments with UV light from a synchrotron radiation source illuminating a $\text{N}_2\text{-H}_2$ mixture⁷⁴. 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.

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

409 Various isotope fractionation processes have been invoked to explain the hydrogen and
410 nitrogen isotope co-variations recorded by the different solar system objects and reservoirs. The kinetic
411 isotope fractionation line shown in Fig. B3 is an example of mass-dependent fractionation, proportional
412 to the square root of mass; however, different mass dependencies would lead to distinct slopes. The
413 ion-molecule isotope fractionation trend (from ref. 75) illustrates the effect of low temperature isotope
414 exchange between organics and the protosolar gas. The D-enrichment of ordinary chondrite IOM with
415 only slight or no concomitant ^{14}N enrichment (yellow triangles) has been proposed to reflect isotope
416 exchange of the molecular host with a D-rich component similar to gas phase molecules observed in
417 dense clouds, pre-stellar cores and class 0 protostars⁷⁵. In contrast, the ^{15}N enrichments above the
418 kinetic isotope fractionation line require preferential N isotope fractionation compared to D/H. This
419 could result from photodissociation of protosolar N_2 by UV light⁷⁴, or from self-shielding⁹⁵ (Box 2), and
420 appears to have occurred within the first few tens to hundreds thousands of years after solar system
421 formation⁷¹. Similarly, the enrichment in the heavy isotopes of oxygen (^{17}O and ^{18}O) relative to the
422 major, light isotope (^{16}O) recorded by solar system solids compared to the protosolar oxygen isotope
423 composition may be the result of illumination of the PSN gas by solar/stellar photons (e.g., ref. 95). This
424 process, which has been advocated to explain the oxygen isotope composition of refractory phases in
425 meteorites, might also have been rapid ($\leq 2\text{Ma}$), according to the chronology recorded by these
426 refractory phases (e.g., ref. 97).

427 Earth shares H and N isotope signatures with bulk chondrites (Fig. B3), whereas most comets
428 are richer in D and ^{15}N . These observations suggest an asteroidal, rather than cometary, origin for
429 terrestrial volatiles^{76,98}. While coupled H-N systematics provide a powerful means to trace the origin of
430 volatiles in the inner solar system, secondary fractionation processes that lead to a preferential loss of
431 light isotopes modified the H and N isotope signature of several solar system objects (Figs. 2 and B3).
432 The Venusian atmosphere is extremely depleted in water and rich in D as a consequence of
433 photodissociation of H_2O and subsequent H loss⁷⁸. The enrichment in both D and ^{15}N of the Martian
434 atmosphere^{79,80} is attributed to atmospheric escape processes. In contrast, Titan is rich in ^{15}N but not in
435 D (ref. 84), suggesting a source effect for nitrogen rather than isotope fractionation.

436
437 **References**

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664 **Additional information**

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