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PROTOSOLAR NITROGEN

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ABSTRACT

We have derived a value of $^{15}N/^{14}N = (2.3 \pm 0.3) \times 10^{-3}$ in the Jovian atmosphere using data from the *Galileo* Probe Mass Spectrometer. Adopting this as the average value for nitrogen in the solar nebula leads to a consistent interpretation of other measurements of nitrogen isotopes in the solar system, once nuclear evolution in the Galaxy and ion-molecule reactions in the interstellar medium are taken into account. The result confirms the assumption that atmospheric nitrogen on Earth was not delivered as N_2 but that N_2 was the dominant form of nitrogen in the solar nebula.

Subject headings: Earth — ISM: abundances — ISM: evolution — ISM: molecules — planets and satellites: individual (Jupiter) — solar system: formation

The sources and reservoirs of nitrogen in the solar system are presently poorly defined. One consequence of this is that the measurement of $^{15}N/^{14}N = 3.66 \times 10^{-3}$ in terrestrial atmospheric N_2 is commonly adopted as the solar system value of this important ratio (e.g., Anders & Grevesse 1989). The main difficulty in deriving a more fundamental value has been the absence of a definitive determination of $^{15}N/^{14}N$ in the Sun. The record of nitrogen trapped in lunar soils is sufficiently confusing that it has proved impossible to obtain an unambiguous solar wind isotope ratio from this source, although it appears that a reliable upper limit of 2.8×10^{-3} has finally been established (Hashizume et al. 2000). Yet the first direct measurement in the solar wind gave $^{15}N/^{14}N = 5^{+2}_{-1} \times 10^{-3}$, even higher than the atmospheric value (Kallenbach et al. 1998). In contrast, Fouchet et al. (2000) found $^{15}N/^{14}N = 1.9^{+0.9}_{-1.0} \times 10^{-3}$ at 400 mbar in the atmosphere of Jupiter from a study of NH_3 absorptions in the planet's disk-average IR spectrum, recorded with the *Infrared Space Observatory* (*ISO*). As Jupiter exhibits the same relative abundances of N, C, S, Ar, Kr, and Xe as the Sun (Owen et al. 1999; Mahaffy et al. 2000) while its hydrogen and helium define solar nebula isotopic ratios (Mahaffy et al. 1998), we expect Jupiter's nitrogen to exhibit the same isotope ratio as the Sun, just as other elements such as carbon and xenon do (Niemann et al. 1998; Mahaffy et al. 2000). Hence, the disagreement between the solar wind and Jovian measurements is surprising, although the error bars on each measurement are large (Fig. 1). Fouchet et al. (2000) suggested that some as yet unknown fractionation process associated with the formation of the ammonia clouds in Jupiter's atmosphere might enrich ^{14}N at the 400 mbar pressure level corresponding to their observation, thereby reducing or even eliminating this disagreement.

The ongoing analysis of *Galileo* Probe Mass Spectrometer (GPMS) measurements in Jupiter's atmosphere allows us to derive an independent value for this fundamental isotope ratio. Extraction of the Jovian atmospheric abundance of NH_3 from the GPMS data is complicated by the strong interaction of NH_3 with the vacuum surfaces of the mass spectrometer (Niemann et al. 1998), but these effects do not inhibit a measurement of $^{15}N/^{14}N$. The methods for both the abundance and isotope determinations will be presented in detail elsewhere (P. R. Mahaffy et al. 2001, in preparation); here we briefly describe the gas-processing sequences and spectral features that yield the Jovian $^{15}N/^{14}N$ ratio.

Nitrogen isotope measurements are difficult to obtain from the singly charged ratio of $^{15}NH_3^+/^{14}NH_3^+$ at 18 and 17 amu because the contribution of water to 18 amu cannot easily be independently constrained. Thus, the new measurement comes from a study of the doubly ionized ammonia (NH_3^{++}) signal in the GPMS data set; $^{15}NH_3^{++}$ produces a signal at 9 amu, while $^{14}NH_3^{++}$ produces a signal at 8.5 amu. The contribution of $^{14}NDH_2^{++}$ at 9 amu will be negligible, as will the signal from H_2O^{++}. Since the focus of the predetermined measurement sequence was on singly charged species and not on these doubly charged species, there is only one 8.5 amu measurement in this data set (at measurement step 5696) at a pressure of 17.2 bar. Nevertheless, the value of the 8.5 amu signal can be predicted at any point in the probe descent by determining the ammonia fractional contribution to 17 amu and using the NH_3^+/NH_3^{++} ratio established from both the flight data themselves and associated studies on the engineering unit presently operational in our laboratory. During direct atmospheric sampling through pressure reduction capillary leaks, the count rate at 9 amu is too low to provide an isotope determination. However, there is one measurement period where the GPMS analyzed an ammonia-enriched gas sample obtained from the Jovian atmosphere. Although gas was sampled for this measurement between 0.9 and 2.9 bar, the local ammonia profile inferred from attenuation of the probe radio signal (Folkner, Woo, & Nandi 1998) and from the Net Flux Radiometer experiment (Sromovsky et al. 1998) indicates that most of the ammonia we measure was introduced to our enrichment cell near the high-pressure end of this sampling period. The measured ammonia mixing ratio increases by more than 2 orders of magnitude between the 400 mbar level sampled by the *ISO* spectra of Fouchet et al. (2000) and our determination. Hence, any isotope fractionation that might exist above the ammonia clouds would not affect our measurement. Gas released from this en-

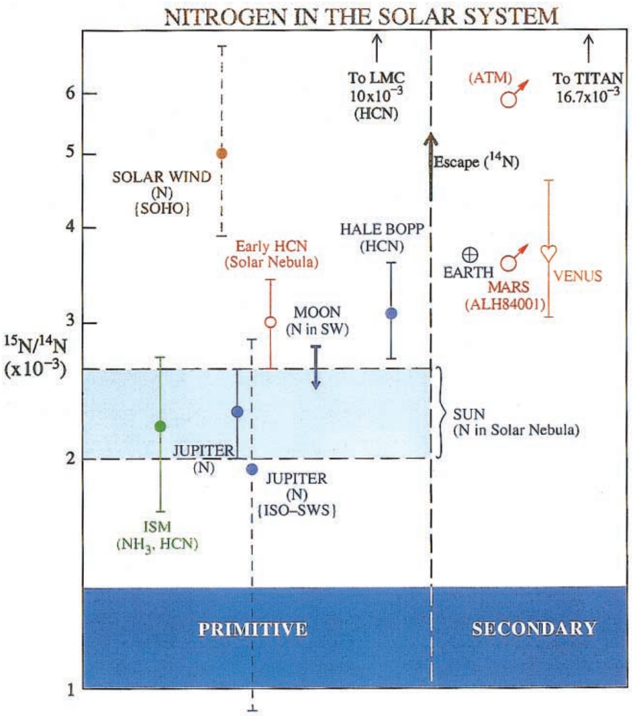

FIG. 1.—*Left-hand side*: Measurements of ^{15}N/^{14}N in primitive nitrogen-containing reservoirs: the local ISM (Dahmen et al. 1995), the Large Magellanic Cloud (LMC; Chin et al. 1999), the solar wind (SW) from the *Solar and Heliospheric Observatory* (*SOHO*; Kallenbach et al. 1998) plus an upper limit from lunar soils (Hashizume et al. 2000), comet Hale-Bopp (Jewitt et al. 1997), and two measurements in Jupiter, from the *ISO* Short-Wavelength Spectrometer (*ISO*-SWS; Fouchet et al. 2000) and the present work. Both Jupiter values refer to total planetary nitrogen, as the NH_3 observed by *ISO*/SWS is produced on the planet. The point labeled "Early HCN" is a value calculated from the present Jupiter value using the work of Terzieva & Herbst (2000). Note the good agreement between this calculated value and the observed ratio in comet Hale-Bopp. *Right-hand side*: Measured values of ^{15}N/^{14}N on Earth, Mars (Nier & McElroy 1977; Mathew & Marti 2001), Venus (Hoffman et al. 1980), and Titan (Marten et al. 1997). The arrow on the dividing line shows the direction of increase in ^{15}N/^{14}N resulting from preferential ^{14}N escape from planetary atmospheres.

richment cell produced enough ammonia in the ion source of the mass spectrometer to give statistically significant count rates at 9 amu, corresponding to the doubly charged ammonia molecule containing ^{15}N. It is from these three measurements with four points for the singly ionized ammonia that the value of $^{15}NH_3^{++}/^{14}NH_3^{++}$ is established, yielding $^{15}N/^{14}N = (2.3 \pm 0.3) \times 10^{-3}$ (Fig. 1).

To put this result in the proper context, we can use current information about interstellar nitrogen together with models for Galactic evolution to deduce the likely starting conditions in the solar nebula. The dominant (>90%) form of nitrogen in interstellar clouds is commonly deduced to be N_2 (Womack, Wyckoff, & Ziurys 1992; van Dishoeck et al. 1993). While this homonuclear molecule cannot be observed directly, Dahmen, Wilson, & Matteucci (1995) showed that $^{15}N/^{14}N = (2.2 \pm 0.5) \times 10^{-3}$ in interstellar HCN at the Sun's distance from the Galactic center at the present epoch. By studying HCN in the Large Magellanic Cloud, Chin et al. (1999) were able to demonstrate that ^{15}N/^{14}N should decrease with time in a galaxy's interstellar medium (ISM), as they found $^{15}N/^{14}N = 10^{-2}$ in this immature Galaxy. The decrease is attributed to early primary production of ^{15}N in massive stars with short lifetimes that become Type II supernovae. In contrast, it appears that ^{14}N is mainly produced by long-lived low- and intermediate-mass stars as a secondary element (Dahmen et al. 1995; Chin et al. 1999). ^{14}N thus builds up in the ISM over time as these stars shed their atmospheres, decreasing the interstellar value of ^{15}N/^{14}N. This interpretation is strengthened by the discovery that $^{15}N/^{14}N \sim 10^{-2}$ in the poststarburst galaxy NGC 4945 as well (Chin et al. 1999).

Thus, we would predict that the value of ^{15}N/^{14}N in interstellar molecules like NH_3 and HCN was higher 4.6 billion years ago in the fragment of an interstellar cloud that collapsed to form the solar nebula than it is in the local ISM today. Using the value of $^{15}N/^{14}N = 3.1^{+0.5}_{-0.4} \times 10^{-3}$ measured in HCN in comet Hale-Bopp (Jewitt et al. 1997) as representative of original solar nebula HCN, we see that this prediction is fulfilled (Fig. 1).

On Jupiter and the Sun, the nitrogen from compounds like HCN must have been overwhelmed by nitrogen from N_2 at the time these objects formed. Terzieva & Herbst (2000) have shown that ion-molecule reactions in interstellar clouds will enrich ^{15}N/^{14}N in HCN compared with the value in N_2 by a factor that varies according to temperature and formation time, reaching a maximum of 30%. As a result, the N_2-derived nitrogen on Jupiter should exhibit a lower value of ^{15}N/^{14}N than we find in the contemporaneous, but icily isolated, cometary HCN. The new measurement on Jupiter exhibits the maximum difference predicted by the Terzieva & Herbst calculations. We therefore feel reasonably secure in suggesting that the protosolar value of $^{15}N/^{14}N = (2.3 \pm 0.3) \times 10^{-3}$ (Fig. 1).

This result reciprocally supports our earlier suggestion that the nitrogen on Jupiter was delivered as N_2, not N compounds, and therefore should have a lower value of ^{15}N/^{14}N than the terrestrial atmosphere (Owen & Bar-Nun 1995). It similarly strengthens the widely held assumption that N_2 was the dominant form of nitrogen in the outer solar nebula and in the interstellar cloud that preceded it.

Returning to the nitrogen in our planet's atmosphere, we can evaluate meteorites and comets as potential sources. Meteorites exhibit a range of values for the nitrogen isotopes that bracket the terrestrial number. However, the meteorites we know would have delivered the wrong ratio of ^{84}Kr/^{132}Xe (by a factor of ~20) and thus seem unlikely to have been major carriers of terrestrial volatiles without major fractionation in the atmosphere, which would have affected the nitrogen isotopes as well. Choosing comets instead, we have only the single example of HCN in Hale-Bopp where the nitrogen isotopes have been measured (Jewitt et al. 1997). Assuming this comet is "typical"—and its value of D/H in H_2O suggests that it is (Meier & Owen 1999)—Earth may have lost some ^{14}N by escape to reach its present value of $^{15}N/^{14}N = 3.7 \times 10^{-3}$ from the cometary value of $3.1^{+0.5}_{-0.4} \times 10^{-3}$. On the other hand, HCN is a trace constituent in comets, and we may safely assume that the nitrogen isotope ratio will differ in different nitrogen compounds in cometary nuclei, just as D/H is different in H_2O and HCN (Meier & Owen 1999). We note that ^{15}N/^{14}N is almost uniformly larger than the terrestrial atmospheric value, ranging up to 5.4×10^{-3}, in the organic compounds in cluster interplanetary dust particles, which are commonly associated with comets (Messenger 2001). The *dominant* nitrogen carrier(s) in several comets will need to be identified and examined before the escape issue can be addressed. N_2 will not play a role here, as this molecule is notoriously deficient in comets, causing their overall underabundance of nitrogen.

Meanwhile, we can consider the interesting case of Mars, where we find that atmospheric nitrogen is highly enriched in

^{15}N as a result of nonthermal N escape (Nier & McElroy 1977), while an internal component has been identified in some of the Martian meteorites with $^{15}N/^{14}N$ close to the telluric value (Mathew & Marti 2001; Fig. 1). This dichotomy is also found in D/H in Martian water, which is enriched by a factor of 5.5 in the atmosphere but close to the cometary value of 2 times standard mean ocean water in Martian minerals (Owen & Bar-Nun 1998; Leshin 2000). The comparison between nitrogen and water on Mars tends to support cometary delivery of both species and suggests that the average value of $^{15}N/^{14}N$ in cometary nitrogen is indeed close to the telluric ratio.

On Titan, we know only that atmospheric nitrogen reveals evidence of massive early escape (Marten et al. 1997; Lunine, Yung, & Lorenz 1999; Lammer et al. 2000), while the data for Venus (Hoffman, Oyama, & von Zahn 1980) are not yet precise enough to allow what will ultimately be a highly informative comparison with Earth.

Turning to the Moon, the latest analysis of nitrogen in the outer rims of individual grains of lunar soil (Hashizume et al. 2000) suggests an upper limit on the value of solar wind $^{15}N/^{14}N \leq 2.8 \times 10^{-3}$. Unraveling the lunar record of implanted nitrogen isotopes is beyond the scope of this article. We simply suggest that the low protosolar value of $^{15}N/^{14}N$ we have established here strongly supports this new upper limit and the prior conclusion of Wieler, Humbert, & Marty (1999) that the dominant source of N on the Moon is not the solar wind.

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