NITROGEN ON THE MOON: WHAT DOES IT TELL US?

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Abstract. The lunar regolith contains gases that have been implanted in its grains by the solar wind. These gases include nitrogen, and measurements of $^{15}N/^{14}N$ in lunar soils have revealed puzzling temporal variations. These variations have frustrated attempts to determine the value of $^{15}N/^{14}N$ in proto-solar nitrogen. A new measurement of this important isotope ratio on Jupiter allows us to clarify the lunar problems and to establish relationships among nitrogen reservoirs in the solar system and the galaxy.

1. Introduction: Confusion on the Moon

Nitrogen is one of the six most abundant elements in the Universe. It is the major component of the air we breathe and it is an essential element for the chemistry that enables life as we know it. Despite its obvious importance, we have not had reliable proto-solar abundances for nitrogen's two stable isotopes, ^{14}N and ^{15}N, i.e., the values in the primordial solar nebula that produced the Sun and planets. As a result, it has become customary to adopt the atmospheric value of $^{15}N/^{14}N$ = 3.66×10^{-3} as the proto-solar standard (e.g., Anders and Grevesse, 1989). Yet there are excellent reasons to believe that the atmospheric value does not represent the average value in the original solar nebula. First, because the dominant reservoir of nitrogen in the nebula was probably N_2, whereas the nitrogen on Earth was most likely delivered as N compounds (Owen and Bar-Nun, 1995). Second, there is always the possibility that some ^{14}N escaped from the Earth's atmosphere over geologic time, increasing the value of $^{15}N/^{14}N$. Thus it is important to establish the average starting value of $^{15}N/^{14}N$ in the solar nebula in order to trace the processes that formed planetary atmospheres and to establish the relationship of the nebular gas to the interstellar medium, taking account of a possible evolutionary change in $^{15}N/^{14}N$ in the galaxy with time.

In principle, the nitrogen numbers should come from the abundances in the Sun itself. There has been insufficient mixing between the solar photosphere and the deep interior for the nuclear reactions in the latter to change the isotopic composition of photospheric nitrogen (Geiss and Bochsler, 1982). Unfortunately, the absorption lines of ^{15}N – either in atomic or molecular form (e.g., as CN) – have

Earth, Moon and Planets **85–86:** 343–350, 2001.

proved to be too weak or too overlapped by other absorptions to allow the solar spectrum to be used to make the measurement. Attention has therefore turned to the solar wind, specifically to its record on the lunar surface.

All the noble gases and nitrogen have been found in samples of lunar soil returned to Earth by the Apollo astronauts, apparent evidence of solar wind implantation. However, investigation of these samples revealed a surprising characteristic of the nitrogen they contained. Whereas the relative abundances and individual isotope ratios of the noble gases were essentially the same in all of the returned samples, the ratio $^{15}N/^{14}N$ was found to have increased by 30% over the last 1.7 billion years (Kerridge, 1975, 1993). The cause of this increase became a matter of dispute. Kerridge (1975, 1980, 1989) and Becker and Pepin (1989), maintained that it indicates a real change in the composition of the solar wind, reflecting as yet unidentified nucleosynthetic processes in the Sun. In contrast, Geiss and Bochsler (1982) suggested that the nitrogen measured on the Moon must be a mixture of a constant solar wind with a variable component of light nitrogen (low $^{15}N/^{14}N$), whose point of origin and means of delivery were not yet established. Possible sources suggested for this light nitrogen have included meteorites (Brilliant et al., 1992), nitrogen escaping from the interior of the Moon (Becker and Clayton, 1975) and nitrogen escaping from the Earth's exosphere (Geiss and Bochsler, 1991). There was a general consensus that the isotope ratio in the contemporary solar wind recorded by the Moon was close to $^{15}N/^{14}N = 4.3 \pm 0.3 \times 10^{-3}$.

The collection of lunar measurements published by Kerridge (1993) showed that the variation of $^{15}N/^{14}N$ on the Moon has not been a steady increase with time, but instead was sporadic. Earlier analyses had focussed on data going back only 2 billion years, whereas new measurements allowed an inspection of the last 3.5 billion years of lunar history. To the untutored eye, this data set seems relatively uniform with a large "spike" of light nitrogen about 1.7 billion years ago superimposed on smaller variations. It is the spike and the subsequent apparent increase in $^{15}N/^{14}N$ toward the present epoch that led to the original idea of a steady increase in ^{15}N on the Moon, as only this part of the record had been available.

Subsequent analyses of individual grains by Wieler et al. (1999) revealed that wide variations up to two orders of magnitude occurred in the ratio of $^{14}N/^{36}Ar$ from grain to grain, whereas the ratios of Ar/Kr and Kr/Xe remained remarkably constant. These authors therefore concluded that $\sim$90% of the nitrogen on the Moon was not delivered by the solar wind.

2. Non-Lunar Nitrogen

The confused state of the measurements on the Moon clearly invited determinations of nitrogen isotopes in other places in the solar system to provide perspective, if not resolution. Kallenbach et al. (1998) accomplished the first direct measurement of nitrogen in the solar wind using SOHO. They found $^{15}N/^{14}N = 5.0^{+2}/_{-1}$

$\times\ 10^{-3}$, a higher value than the one derived from the lunar samples, but with an uncertainty that overlapped the lunar value.

This should have settled the matter, but it didn't. Jewitt et al. (1997) had found that $^{15}N/^{14}N = 3.1^{+0.5}/_{-0.4} \times 10^{-3}$, in the HCN of Comet Hale–Bopp. This is evidently distinctly different from the ratio found in the solar wind, if one believes the error bars on both measurements. The disagreement is even worse than it first appears. The nitrogen in interstellar clouds is commonly assumed to be primarily (50 to 90%) in the form of N_2, which cannot be observed directly by radio telescopes because its rotational spectrum is forbidden (Womack et al., 1990; van Dishoeck et al., 1993). If this assumption is correct, the nitrogen in the Sun should also have been delivered primarily as N_2, with HCN only a minor constituent. Terzieva and Herbst (2000) have shown that ion-molecule reactions in the interstellar medium will tend to enrich ^{15}N in HCN relative to the value in N_2. Thus one would predict that $^{15}N/^{14}N$ in interstellar HCN should be larger than the value in N_2 in the same cloud. Forming the Sun and the comets from such ISM cloud material should then lead to the preservation of the higher value in the icily isolated cometary HCN compared to the value measured in the N_2 – dominated solar (or Jovian) nitrogen. The measurements reported by Jewitt et al. (1997) and Kallenbach et al. (1998) give exactly the opposite proportion (Figure 1).

Furthermore, the ratio of $^{15}N/^{14}N$ in the ISM should decrease with time. This follows from observations of HCN in the Large Magellanic Cloud by Chin et al. (1999) who found $^{15}N/^{14}N \approx 10^{-2}$ in massive star forming regions in this immature galaxy. They obtained the same result in the post-starburst galaxy NGC 4945. They attributed this high value of the ratio to the primary production of ^{15}N in Type II supernovae, whereas ^{14}N is a secondary product, coming from nucleosynthesis in low mass stars that shed their atmospheres in their dying phase (Wilson and Matteucci, 1992; Chin et al., 1999). It follows that the HCN in the local ISM today should have a lower value of $^{15}N/^{14}N$ than HCN observed in Comet Hale–Bopp, which was isolated from the ISM 4.6 By ago. Dahmen et al. (1993) have reported $^{15}N/^{14}N = 2.2^{+0.4}/_{-0.2} \times 10^{-3}$ in the local interstellar HCN, which is indeed lower than the cometary value (Figure 1). This agreement with expectation supports the validity of the cometary measurements, but leaves open the disagreement with the solar wind value.

Jupiter, like the Sun, should have obtained its nitrogen primarily in the form of N_2. Thus another surprise occurred when Fouchet et al. (2000) found $^{15}N/^{14}N = 1.9^{+0.9}/_{-1.5}$ from a study of NH_3 in Jupiter's infrared spectrum. One expects the Jovian and solar values of this ratio to be identical, as the carbon and xenon isotopes are (Niemann et al., 1998; Mahaffy et al., 2000). The large error bars on the Jovian determination and the possibility of some kind of fractionation effect above the ammonia ice clouds in the 400 mb region of Jupiter's atmosphere where the Jovian value was determined left open the possibility that Jovian and solar values might not be as disparate as they appeared. Nevertheless, the disagreement was disturbing.

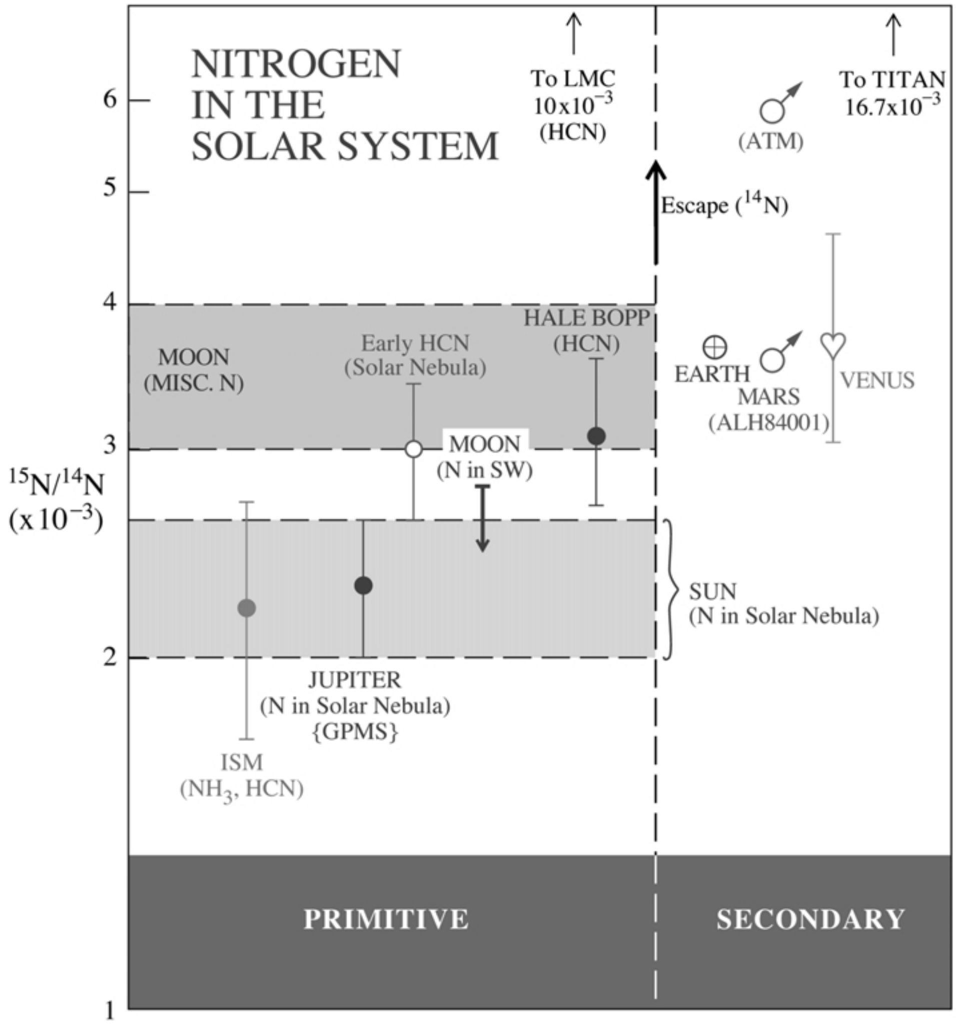

Figure 1. The left hand side of the figure shows measurements of ^{15}N/^{14}N in primitive nitrogen-containing reservoirs: the local interstellar medium (ISM) (Dahmen et al., 1995); the Large Magellanic Cloud (LMC) (Chinn et al., 1999); an upper limit on the Solar Wind (SW) from lunar soils (Hashizume et al. (2000); Comet Hale–Bopp (Jewitt et al., 1997); and the present work. The point labeled "Early HCN" is a value calculated from the present Jupiter value, using the work of Terzieva and Herbst (2000). Note the good agreement between this calculated value and the observed ratio in Comet Hale Bopp. The right-hand side of the chart shows measured values of ^{15}N/^{14}N on Earth, Mars, Venus and Titan. 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.

3. Solving the Lunar Riddle

The solar wind includes a high energy component, usually referred to as solar energetic particles. These can penetrate more deeply into lunar grains than the normal solar wind (SW) and exhibit different isotopic values. One must therefore be concerned about which component is being measured when extracting gas from lunar grains. This problem was finessed by Hashizume et al. (2000) who used an ion microprobe to study the radial gradient of implanted atoms in individual grains. They were able to distinguish grains that contained solar wind nitrogen in their outer layers from other grains that did not. Measuring the implanted solar wind with this technique, they found that $^{15}N/^{14}N$ in the nitrogen decreased as they probed more deeply into the grains, until it was overwhelmed by the background – other nitrogen that was present in their samples. In this way they established an upper limit for $^{15}N/^{14}N < 2.8 \times 10^{-3}$ in normal solar wind nitrogen, apparently supporting the general trend of the Fouchet et al. (2000) determination, as opposed to the direct measurement by Kallenbach et al. (1998).

Using Jupiter again as a surrogate for the Sun, there is the possibility of studying the nitrogen isotopes using the data obtained by the Galileo Probe Mass Spectrometer. It has not yet been possible to obtain an accurate mixing ratio of NH_3 on Jupiter from these measurements because of problems with enrichment of ammonia in the instrument. However, these difficulties do not prevent an evaluation of $^{15}N/^{14}N$ from measurements of the relative abundances of the corresponding NH_3 ions, in both singly and doubly ionized states. Following this approach led to a determination of $^{15}N/^{14}N = 2.3 \pm 0.3 \times 10^{-3}$ (Owen et al., 2001; Mahaffy et al., 2001) (Figure 1).

The probe result refers to ammonia collected during descent through the Jovian atmosphere between 0.9 to 2.9 bars. The ammonia mixing ratio in the Jovian atmosphere as measured by Net Flux Radiometer on the probe increased by a factor 20 over this range (Sromovsky et al., 1998; Atreya et al., 1999), so the mass spectrometer data used for this analysis were clearly biased toward the high pressure end of the collection interval. The isotope ratio derived from mass spectrometer measurements could therefore not have been affected by the hypothetical cloud-condensation-related fractionation postulated by Fouchet et al. (2000) as a possible explanation of the disagreement between their result and that of Kallenbach et al. (1998). (The nominal pressure level for ammonia cloud formation is $\sim$750 mb, while the Fouchet et al. disk-average observation corresponded to a level of $\sim$400 mb, with an NH_3 mixing ratio 150 times less than the value at 2.9 bars.) Indeed the required magnitude of their hypothetical fractionation made it an unlikely explanation to begin with, as Fouchet et al. (2000) themselves pointed out.

Falling well below the Hashizume et al. upper limit on $^{15}N/^{14}N$ in the solar wind on the Moon, the Jovian value must be a close approximation to the value of proto-solar nitrogen in the solar system. This conclusion gains force from its consistency with the astrophysical constraints: the Jovian (N_2) value is not only distinctly lower than the contemporaneous cometary (HCN) value, the ratio of these two measurements agrees with the prediction of the Terzieva and Herbst (2000) ion-molecule calculations, if one assumes that the HCN was formed at low temperature and sequestered at a relatively early time (Figure 1).

4. Conclusions

Given the consistency between galactic evolution models, the ion-molecule calculations and the two measurements of primordial nitrogen – as HCN and N_2 – in the solar system, it appears that our value of $^{15}N/^{14}N = 2.3 \pm 0.3 \times 10^{-3}$ is indeed the right number for protosolar N_2. We can therefore strongly endorse the new upper limit of $^{15}N/^{14}N < 2.8 \pm 10^{-3}$ established by Hashizume et al. (2000) for implanted solar wind nitrogen in lunar grains, and the prior conclusion of Wieler et al. (1999) that ~90% of the nitrogen implanted on the Moon is of non-solar origin.

So what is the source of this lunar nitrogen? This is clearly a difficult and complex problem. We can only suggest some likely possibilities, based on the recent results reviewed above. We need to identify a source of nitrogen that at least satisfies the following minimal criteria:

1. The ratio of $^{15}N/^{14}N$ must be able to vary by ~30% to account for the low $^{15}N/^{14}N$ spike in the lunar record 1.7 billion years ago.
2. The variation should be random.
3. The ratio of $^{14}N/^{36}Ar$ in this source must be much larger than the solar value.

As a working hypothesis, we propose that a mixture of cometary and meteoritic bombardment could satisfy these three edicts. The bombardment of comets in particular could create a temporary atmosphere that would become ionized, thereby allowing the solar wind magnetic field to drive atmospheric ions into the surface materials. Comets that had formed at temperatures near or below 30 K could trap N_2 in amounts that would lower their overall value of $^{15}N/^{14}N$ toward the 2.3×10^{-3} measured on Jupiter (Owen and Bar-Nun, 1995; Owen et al., 1999). Hence occasional impacts by such low temperature comets could provide a source of light nitrogen on the Moon. For example, such an impact would have been capable of producing the spike in the lunar record 1.7 billion years ago that is evident in the data presented by Kerridge (1993).

These conclusions can be tested by the next generation of space missions that will include several investigations of comets as well as new, direct measurements of the solar wind. Further measurements of lunar soils by ion microprobe will obviously help to unravel the history of nitrogen on the Moon. Simultaneous determinations of carbon and neon abundances and isotope ratios would be very helpful as a means of identifying possible nitrogen carriers. Finally, it would be very useful to send missions to both Mars and Venus that could improve existing measurements of nitrogen isotopes in the atmospheres of these planets. Such studies would help us understand the delivery and isotopic evolution of this vital element that dominates the blue skies of our beloved planet.

Acknowledgements

We thank Cesare Barbieri for including us in this remarkable, renaissance-like conference. John Kerridge provided valuable insights into the lunar nitrogen problem and Francesca Matteucci offered a helpful perspective on galactic evolution. This research was supported in part by NASA, which also provided the Galileo Mission.

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