IMPROVED CONSTRAINTS ON THE NITROGEN ISOTOPES IN THE PROTOSOLAR NEBULA: IMPLICATIONS FOR THE SOURCE OF THE EARTH'S NITROGEN.

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Introduction: We can trace the origin and evolution of the solar system through stable isotope ratio measurements. The D/H ratio in primordial water (e.g. cometary ice) is an established proxy for temperature conditions during formation of comets and other icy bodies. This ratio varies significantly and indicates complex thermal and chemical evolution of the protosolar nebula (PSN) during solar system formation. Nitrogen isotope ratios also vary significantly, and in a few cases correlate to D/H ratios. However, a lack of consistent correlation between D/H and $^{14}N/^{15}N$ suggests greater complexity in the variability of nitrogen ratios in the PSN [1]. Nitrogen in the PSN was primarily in the form of N_2 [2].

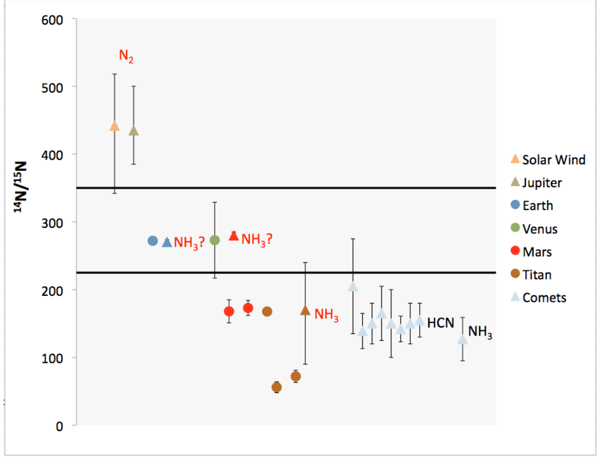

Figure 1: Measurements of $^{14}N/^{15}N$ throughout the solar system. Triangles are primordial values representing $^{14}N/^{15}N$ in the PSN. Circles are isotope ratios that have evolved over the 4.6 Billion year history of the solar system. The primordial value for Titan is inferred from models of atmospheric evolution. The primordial values for Earth and Mars are inferred from measurements in the mantle and meteorites, respectively. The composition of each primordial $^{14}N/^{15}N$ is provided as either the constituent that was measured (black) or inferred (red) based on current understanding of the evolution of the solar system.

Figure 1 illustrates measurements of $^{14}N/^{15}N$ throughout the solar system. The ratios are either primordial – a value that was obtained during solar system formation, or evolved – a ratio that has changed over the history of the solar system. The values of these measured ratios can be divided into three categories:

(1) The solar wind [2] and Jupiter [3] have the lightest ratios

(2) Earth, Venus and primordial Mars (based on meteorite ratios [4]) have moderately heavy ratios and

(3) Titan and HCN [5] and NH_3 [6] in comets and the atmosphere of Mars have the heaviest values.

Jupiter's nitrogen was measured in NH_3, but its source was N_2 in the PSN [2]. The agreement between $^{14}N/^{15}N$ in Jupiter's atmosphere and the solar wind gives a primordial ratio for N_2 in the PSN of ~435 [3]. Earth, Venus and primordial Mars appear to have a similar source of nitrogen, which is still under debate but is commonly thought to be primordial NH_3 ice [3]. The current ratio in Mars's atmosphere is heavier than its primordial value due to extensive atmospheric escape. HCN and NH_3 in comets are primordial, while Titan's ratio is very likely to have evolved over the history of the solar system.

Nitrogen at Titan: The $^{14}N/^{15}N$ in Titan's atmosphere has been measured in N_2 and HCN and are found to be much heavier than the $^{14}N/^{15}N$ for the Earth, Mars and Venus. This poses a potential problem because the source Titan's nitrogen is likely to be NH_3 ice [3], meaning a similar origin for Titan's and the terrestrial planet's nitrogen. One possible explanation of the difference in Titan's and the Earth's ratios is extensive atmospheric loss for Titan similar to what has occurred at Mars. We evaluated the evolution of $^{14}N/^{15}N$ in Titan's atmosphere previously [8], but revisit this based on improved understanding of hydrodynamic escape [9].

Sputtering and Chemistry. Currently nitrogen escapes from Titan at a small rate due to sputtering. This process is efficient at fractionating the isotopes due to diffusion. Efficiency is characterized by a fractionation factor, f. If $f < 1.0$ the lighter isotope is preferentially removed while the heavier isotope is preferentially removed when $f > 1.0$. For escape at Titan $f = 0.729$ [10]. Chemistry preferentially incorporates the heavy isotope from into HCN [8,11] with highly efficient fractionation: $f = 2.995$ and has a stronger overall influence on the nitrogen isotope ratio. However, photochemical fractionation requires methane to be present in Titan's atmosphere. Our previous modeling of evolution of methane found that the current inventory of methane has only been present in Titan's atmosphere for less than one billion years [10]. Inventories of surface organics give a time frame of ~730 million years (Myr) [12]. Figure 2 illustrates the nitrogen isotope ratio as a function of time for three conditions of methane presence. It is clear from this Figure that even if methane has only been present for 730 Myr, the initial ratio is heavier than the current ratio as a result of the strong influence that photochemical fractionation has over the evolution of Titan's atmosphere. The escape rate due to sputtering is so low that the lifetime of Titan is not long enough for sputtering to cause the ratio to evolve from the terrestrial value (272) to the current value in Titan's atmosphere (167.7).

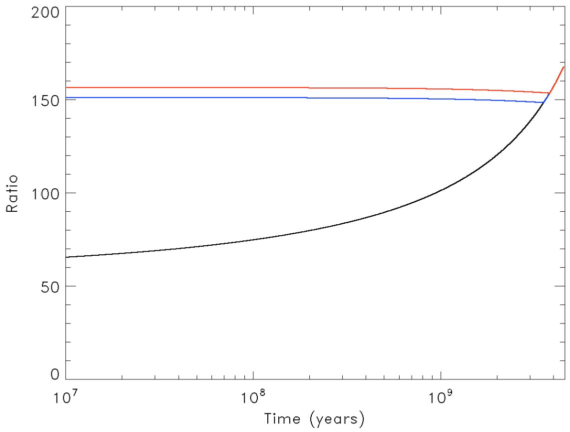

Figure 2: The $^{14}N/^{15}N$ as a function of time assuming that escape occurs only due to sputtering. Three cases of methane presence are evaluated: constant methane presence (black), methane present for the last billion years (blue) and methane present for the last 730 Myr (red). Chemistry clearly has a stronger effect on the isotopes than sputtering.

Thermal Escape. Hydrodynamic escape is suggested to have changed the $^{14}N/^{15}N$ at Titan from Earth's value to 167.7. We previously found that hydrodynamic escape at Titan could not account for this because the heavy isotope is dragged out of the atmosphere with the lighter isotope [8]. This is the case for a hydrogen atmosphere in the early solar system. Recent studies of hydrodynamic escape suggest mass-dependent fractionation [9] that we explore here. In hydrodynamic escape of nitrogen, fractionation is mass-dependent and $f = 0.966$. We use this to estimate the ratio of the initial mass of the atmosphere to the current mass, or n_0/n:

$$\frac{n_0}{n} = \left(\frac{R}{R_0}\right)^{\frac{1}{1-f}}$$

where R is the current ratio and R_0 is the initial ratio.

Figure 3 illustrates the initial atmospheric mass in terms of current atmospheres for a range of f. Hydrodynamic escape requires 10^{14} times the current mass of the atmosphere, which is too much mass to be lost even through hydrodynamic escape. Therefore, it is not possible for escape to change $^{14}N/^{15}N$ at Titan from 272 to 167.7 which means that the initial ratio is limited to 175±75.

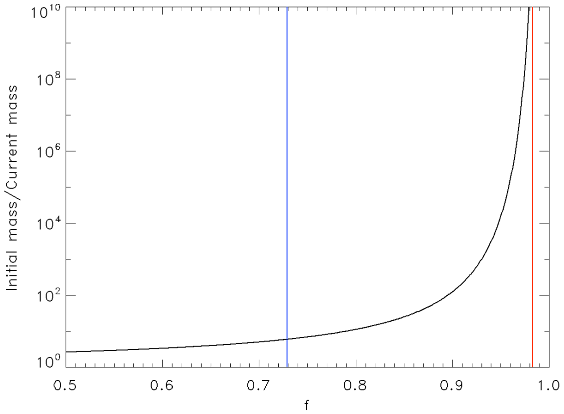

Figure 3: Initial atmospheric mass in terms of current atmospheres as a function of *f*. Hydrodynamic escape (red) requires an initial atmosphere more than 10^{14} times greater than the current atmosphere, while Sputtering requires only 6 times the current atmosphere. However, sputtering is too slow to change the ratio from 272 to 167.7.

Figure 1 summarizes $^{14}N/^{15}N$ in the solar system showing that $^{14}N/^{15}N$ in NH_3 in comets is likely to be similar to HCN and NH_3 giving two distinct nitrogen inventories in the PSN: N_2 with an isotope ratio of ~435 and HCN and NH_3 with an isotope ratio of ~150. The nitrogen delivered to the terrestrial planets is likely to have come partially from NH_3 ice and partially from a reservoir with a solar ratio.

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