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Isotopic constraints on the source of Pluto's nitrogen and the history of atmospheric escape

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ABSTRACT

The origin and evolution of nitrogen in solar system bodies is an important question for understanding processes that took place during the formation of the planets and solar system bodies. Pluto has an atmosphere that is 99% molecular nitrogen, but it is unclear if this nitrogen is primordial or derived from ammonia in the protosolar nebula. The nitrogen isotope ratio is an important tracer of the origin of nitrogen on solar system bodies, and can be used at Pluto to determine the origin of its nitrogen. After evaluating the potential impact of escape and photochemistry on Pluto's nitrogen isotope ratio ($^{14}N/^{15}N$), we find that if Pluto's nitrogen originated as N_2 the current ratio in Pluto's atmosphere would be greater than 324 while it would be less than 157 if the source of Pluto's nitrogen were NH_3. The *New Horizons* spacecraft successfully visited the Pluto system in July 2015 providing a potential opportunity to measure $^{14}N/^{15}N$ in N_2.

1. Introduction

The *New Horizons* mission (Stern, 2008a) arrived in the Pluto system in July 2015 and made unprecedented observations of Pluto's surface and atmosphere. These observations could provide clues to the origin and evolution of Pluto's atmosphere as well as further constraints on the role of nitrogen in the formation and evolution of the solar system. A key measurement will be the $^{14}N/^{15}N$ in N_2, the primary constituent of Pluto's atmosphere (Jessup et al., 2013), which could help to constrain the origin of nitrogen on Pluto and the dominant escape process in Pluto's atmosphere.

Pluto is likely to have formed in the outer solar system (Brown, 2002) and is thought to owe its present orbit to the migration of the giant planets (Levison et al., 2007). Its mass density indicates that Pluto is severely depleted in water ice relative to its rock abundance, which is between 50% and 80% (McKinnon and Mueller, 1988; Olkin et al., 2003). This high rock abundance suggests formation in a CO-rich and ice-poor region of the protosolar nebula (PSN), loss of volatiles by the impact formation of Charon, or a combination of these two factors (McKinnon and Mueller, 1988). The surface of Pluto consists of a spatially heterogeneous mixture of N_2, CH_4, CO and C_2H_6 ices (Cruikshank et al., 2014). The most abundant ice on the surface is N_2 and is presumed to be the primary constituent in Pluto's tenuous atmosphere (Owen et al., 1993).

Determining what was the source of Pluto's nitrogen can provide important information about the temperature and composition of the region of the PSN in which Pluto formed. The most likely source of Pluto's nitrogen was either N_2 or NH_3 that were trapped in ices in the PSN. However, it is important to note that significant amounts of nitrogen in the PSN were also bound in refractory organic molecules. As the formation process for these organics is poorly understood, we focus on N_2 and NH_3 for the sake of this study.

N_2 is believed to have been ~10 times greater in the PSN than NH_3 (Lewis and Prinn, 1980), but requires much colder temperatures to be trapped in water ices, whether the ices are amorphous (Bar-Nun et al., 1985, 1988) or crystalline (Mousis et al., 2012, 2014). Pluto would have accreted N_2 ice in greater abundance than NH_3 ice if its formation temperature was less than ~40 K, which may have been possible in the outer solar system. However, comets also formed in the outer solar system and are believed to be deficient in N_2 relative to NH_3 suggesting either that temperature conditions could have been too warm for N_2 to be trapped in icy grains (Iro et al., 2003) or that comets did not retain N_2 i) beyond their first pass through the solar system (Owen et al., 1993) or ii) due to internal radiogenic heating at early epochs after formation (Mousis et al., 2012). The recent detection of N_2 in comet 67P/Churyumov–Gerasimenko (hereafter 67P/CG) by Rosetta shows that the abundance of N_2 relative to CO is a factor of

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25.4 lower than the protosolar value (Rubin et al., 2015). This measurement puts a constraint on the formation temperature of 67P/CG of 32–70 K (Lectez et al., 2015). If the composition of 67P/CG, which is believed to be a Kuiper Belt comet, is indicative of the general composition of Kuiper Belt objects, then Pluto could have formed in a similar temperature range and may have retained some N_2 from the PSN. As the relative abundance of N_2 to NH_3 in 67P/CG is not yet known, it is unclear if these results suggest greater retention of NH_3 over N_2 for Pluto.

It appears, based on the above results, that there is a large uncertainty in the source of nitrogen for Pluto. If temperatures were low enough during formation, the source of Pluto's nitrogen could have been N_2, but if temperatures were above the limits described above (typically 70–80 K for enabling ammonia hydrate formation in the PSN), the source of nitrogen for Pluto's surface and atmosphere would have been NH_3 that was later converted to N_2, as was the case for Titan (Mandt et al., 2014).

Stable isotope ratios that are presumed to be primordial, or representative of conditions in the PSN, can help constrain the role of nitrogen in the formation and evolution of the solar system. Measurements of comets, meteorites and giant planet atmospheres are presumed to represent primordial conditions, while the terrestrial planets, Pluto, Saturn's moon Titan and Neptune's moon Triton have atmospheres that have evolved over the history of the solar system.

Fig. 1 illustrates $^{14}N/^{15}N$ measurements throughout the solar system. They are identified as either primordial (triangles), or evolved (circles). The primordial ratios provide constraints for $^{14}N/^{15}N$ in N_2, NH_3, HCN and organics in the PSN. The solar wind (Marty et al., 2011) and Jupiter (Owen et al., 2001) have the lightest ratios, with values in the range of ~440, and represent primordial $^{14}N/^{15}N$ in N_2. HCN (Bockelée-Morvan et al., 2008) and NH_3 (Rousselot et al., 2014; Shinnaka et al., 2014) in comets give a primordial $^{14}N/^{15}N$ in HCN and NH_3 of ~160 and ~133, respectively. The bulk $^{14}N/^{15}N$ of organic material found in Ordinary and Carbonaceous Chondrites (Alexander et al., 2012) is intermediate to N_2 and HCN and NH_3 in the PSN.

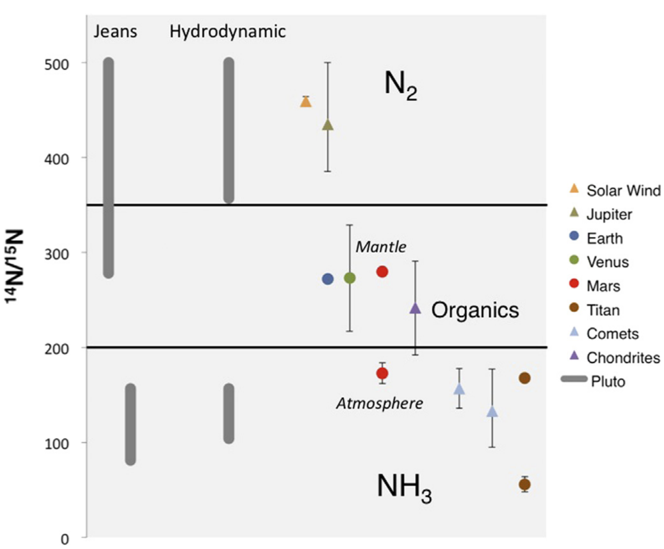

Fig. 1. Measurements of nitrogen isotope ratios, or $^{14}N/^{15}N$, in the solar wind, comets and the atmospheres of Jupiter, terrestrial planets and Titan. Triangles are primordial values representing $^{14}N/^{15}N$ in the PSN. Circles are isotope ratios that have evolved over the 4.6 billion year history of the solar system. $^{14}N/^{15}N$ in the atmosphere of Mars is much lower than in the mantle, although it is unclear if the mantle measurement can be considered as primordial. The primordial value for Titan is inferred from models of atmospheric evolution. Since $^{14}N/^{15}N$ has not yet been measured for Pluto, we provide a range of values based on the source of the nitrogen and the type of escape as described in Section 3.

Mars, Titan, Venus and the Earth have ratios that are presumed to have evolved over time. The atmosphere of Mars has a much lower $^{14}N/^{15}N$ (Nier and McElroy, 1977; Wong et al., 2013) than the mantle based on SNC meteorite ratios (Mathew and Marti, 2001) because of extreme fractionation by escape processes that preferentially remove the lighter isotope from the atmosphere (e.g. Fox and Dalgarno, 1983). However, we recently demonstrated (Mandt et al., 2014) that escape could not significantly fractionate the $^{14}N/^{15}N$ in N_2 in Titan's atmosphere from its current value of 167.7 ± 0.7 (Niemann et al., 2010), which provides a primordial ratio for Titan that is similar to NH_3 and HCN in comets. The $^{14}N/^{15}N$ in HCN in Titan's atmosphere is ~65 (Vinatier et al., 2007), which results from strong photochemical fractionation by self-shielding of N_2 (Liang et al., 2007). Although Earth and Venus are not expected to have experienced much fractionation due to escape, the source of nitrogen for Earth, Venus and Mars is poorly understood (e.g. Hutsemèkers et al., 2009; Alexander et al., 2012) and their ratios are designated as evolved in Fig. 1.

$^{14}N/^{15}N$ in Pluto's atmosphere has not yet been measured, and the primordial $^{14}N/^{15}N$ ratio for Pluto it is not presently known. The bulk of the atmosphere ($>99\%$) is expected to be N_2, with trace amounts of CH_4, CO and HCN (e.g. Young et al., 1997; Lellouch et al., 2011; Krasnopolsky and Cruikshank, 1999).

At Pluto, several poorly constrained processes could fractionate $^{14}N/^{15}N$: sublimation, condensation, escape and photochemistry. It is unknown if, or by how much, sublimation and condensation would fractionate $^{14}N/^{15}N$ because, to the best of our knowledge, this has never been measured in the laboratory for N_2. We therefore assume that the sublimation process releases N_2 with a $^{14}N/^{15}N$ value reflective of the surface ice ratio, and that condensation temporarily removes N_2 from the atmosphere, stores it on the surface, and re-releases it without any additional fractionation. The condensed N_2 is, therefore, assumed to have a ratio reflective of atmospheric N_2 at the time of condensation. We do know that escape preferentially removes the lighter isotope while photochemistry will preferentially remove the heavier isotope due to self-shielding (Liang et al., 2007; Mandt et al., 2009). Of the two known fractionating processes, the dominant process will be escape because it is estimated to have rates as much as three orders of magnitude greater than photochemical loss rates for N_2 (Krasnopolsky and Cruikshank, 1999).

The Alice Ultraviolet spectrometer on *New Horizons* (Stern et al., 2008b) is expected to be able to measure $^{14}N/^{15}N$ in N_2 in Pluto's atmosphere if the value is ≤ 330 (Jessup et al., 2013). We provide here interpretations for measurements within several ranges of values for $^{14}N/^{15}N$ based on the source of nitrogen and the type of escape relying on the very limited amount of information presently available for Pluto's atmosphere.

2. The history of Pluto's atmosphere

2.1. Current state of knowledge

Because of Pluto's small size and large distance from the Sun, its atmosphere is difficult to observe from Earth. Observations show that Pluto currently has a tenuous atmosphere with a surface pressure of 6–24 μbar that is composed primarily of N_2 (e.g. Young et al., 1997; Lellouch et al., 2011). Pluto's very high obliquity of 102–126° (Dobrovolskis and Harris, 1983), and eccentric orbit will result in extreme seasonal effects that are poorly understood because Pluto's atmosphere was first detected in 1988 (Hubbard et al., 1988) and observations of the atmosphere have only covered ~10% of a Pluto year. Model predictions suggest that surface pressures could vary over a Pluto year by as little as a factor of four (Young, 2013; Olkin et al., 2014) or as much as four orders of magnitude (Young, 2013; Hansen et al., 2014).

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