

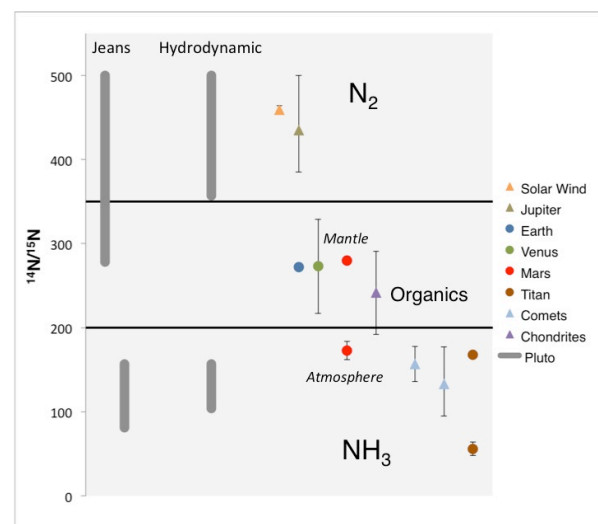
**ISOTOPE GEOCHEMISTRY FOR COMPARATIVE PLANETOLOGY OF EXOPLANETS.** K. E. Mandt<sup>1,2</sup>, S. Atreya<sup>3</sup>, A. Luspay-Kuti<sup>1</sup>, O. Mousis<sup>4</sup>, A. Simon<sup>5</sup> and M. D. Hofstadter<sup>6</sup>. <sup>1</sup>Southwest Research Institute (6220 Culebra Rd., San Antonio, TX 78238 [kmandt@swri.org](mailto:kmandt@swri.org)), <sup>2</sup>University of Texas at San Antonio (One UTSA Blvd, San Antonio, TX), <sup>3</sup>University of Michigan, Ann Arbor, MI, <sup>4</sup>Aix Marseille Université, CNRS, LAM (Laboratoire d'Astrophysique de Marseille) UMR 7326, 13388, Marseille, France, <sup>5</sup>Goddard Space Flight Center, Greenbelt, MD, <sup>6</sup>NASA Jet Propulsion Laboratory, Pasadena, CA.

**Introduction:** Isotope geochemistry has played a critical role in understanding processes at work in and the history of solar system bodies [see 1, and references therein]. Application of these techniques to exoplanets would be revolutionary and would allow comparative planetology with the formation and evolution of exoplanet systems. The roadmap for comparative planetology of the origins and workings of exoplanets involves isotopic geochemistry efforts in three areas: (1) technology development to expand observations of the isotopic composition of solar system bodies and expand observations to isotopic composition of exoplanet atmospheres; (2) theoretical modeling of how isotopes fractionate and the role they play in evolution of exoplanetary systems, atmospheres, surfaces and interiors; and (3) laboratory studies to constrain isotopic fractionation due to processes at work throughout the solar system.

**Example of Nitrogen:** Stable isotope ratio measurements combined with modeling of isotopic fractionation has played a critical role in understanding origins and workings throughout the solar system. This work has evaluated the origin of volatiles on Earth [e.g. 2], the history of Mars based on how its atmosphere evolved [e.g. 3, 4], the loss of water from Venus [e.g. 5], and the origin of nitrogen on Titan [6].

In the case of nitrogen, measurements from multiple solar system bodies have allowed us to begin to map out the origin and history of nitrogen in the solar system, as illustrated in Fig. 1 [from 7]. The nitrogen isotope ratio measured in the solar wind and the atmosphere of Jupiter are presumed to be representative of  $N_2$  in the protosolar nebula (PSN) because the most abundant form of nitrogen was  $N_2$ . Trace amounts of HCN and  $NH_3$  were present in the PSN, and isotope ratios for these constituents measured in comets are presumed to represent their primordial ratio. On the other hand, nitrogen isotope ratio measurements made in the atmospheres of the terrestrial planets and Titan are known to have evolved from their primordial ratio due to fractionation of the isotopes by escape and photochemistry. Modeling of how the ratio changes over time helps us to understand the origin of nitrogen in these bodies [2,3,4,6], but uncertainties remain. In particular, condensation and evaporation may play an important role in Titan's atmosphere, but little is known about the fractionation of isotopes due to these pro-

cesses. Furthermore, Fig. 1 emphasizes the limited number of nitrogen isotope measurements. This makes understanding the origin of volatiles in Pluto's atmosphere and on Kuiper Belt Objects (KBOs) in general difficult. Measurements of nitrogen isotopes in Pluto's or Triton's atmosphere combined with modeling of atmospheric evolution could help discern the conditions under which KBOs formed [7].



**Figure 1: Nitrogen isotope ratio measurements throughout the solar system [7]. Triangles are primordial values representing  $^{14}N/^{15}N$  in the protosolar nebula. Circles are isotope ratios that have evolved over the history of the solar system. A possible range of values was estimated for Pluto, based on the source of nitrogen and the type of escape.**

**The Roadmap to Exoplanet Origins and Workings:** Based on this example of what we have learned from isotope studies in our solar system, we can identify three areas where further development is needed to allow us to begin evaluating origins and workings in exoplanet systems.

**Observations:** Observations are the most critical aspect of any exoplanet origins and workings program, but significant technological development is required.

One of the most groundbreaking projects for understanding solar system origins was the Galileo Probe Mass Spectrometer (GPMS) [8]. GPMS not only provided the nitrogen isotope ratio illustrated in Fig. 1, but also the elemental abundances and other isotope ratios

in Jupiter's atmosphere. These measurements had significant implications for understanding the formation of Jupiter within the context of solar system formation. The roadmap for understanding the formation of giant planets should first include atmospheric probes sent to Saturn, Uranus and Neptune. These projects are certain to be equally groundbreaking in their impact as was GPMS. However, because sending a probe to a giant exoplanet is not realistic by 2050, it is critical to develop technology to obtain as many of these measurements as possible in the atmospheres of exoplanets through significant advances in remote sensing. These technology advancements should be tested on the giant planets in our solar system through observations that coincide with atmospheric probes that provide ground truth to remote observations. Therefore, part of the long-term roadmap to comparative planetology for the formation of giant planets in our solar system and exoplanets should include a long term program of atmospheric probes in support of a remote sensing development program.

A major limitation of isotopic geochemistry throughout the solar system is the limited number of observations available. Most of the isotope ratios illustrated in Fig. 1 are the result of a single or a statistically small number of measurements in an atmosphere or in the coma of a comet. However, both the Cassini and Rosetta missions have provided ongoing monitoring of isotopic composition of the atmosphere of Titan and of the coma of comet 67P/Churyumov-Gerasimenko (CG), respectively. For Titan, the Huygens Gas Chromatograph Mass Spectrometer (GCMS) [9] provided one-time measurements at the surface, while the Cassini Ion Neutral Mass Spectrometer (INMS) [10] and the Cassini Composite Infrared Spectrometer (CIRS) [11] measured isotopes in the upper and lower atmosphere, respectively over more than a decade. Although this combination of remote sensing and in situ efforts improved understanding of the dynamics of Titan's atmosphere [10], much more can be learned about the workings of Titan's atmosphere from further evaluations of this extensive dataset. The same can be said for the Rosetta dataset, for which the current analysis is limited to the D/H ratio measured early in the mission [12]. The roadmap for studying terrestrial exoplanet atmospheres should first include future missions within the solar system that involve long-term monitoring using a combination of in situ and remote measurements to evaluate temporal and spatial variations of isotopic composition. This will provide important context to isotopic measurements in terrestrial exoplanet atmospheres, for which technology development must also be a priority.

Finally, future efforts should also include in situ surface isotopic composition of icy moons, comets, Pluto and other Kuiper Belt Objects to understand the differences between atmospheric and surface measurements. These measurements will not only help us to better understand the origins of these bodies, but further understanding the influence of surface processes on fractionation of isotopes will provide critical context for exoplanet isotope measurements.

*Theoretical studies:* Measurements of isotope ratios in atmospheres have little value for planetary origins without an understanding of how they have evolved over time. Theoretical studies to evaluate origins require models that properly constrain the influence of processes such as escape [e.g. 5, 6], photochemistry [e.g. 13], condensation [e.g. 14] and sublimation on isotope ratios as well as models that put these fractionating processes into the context of evolution over time [3,4,5,6,7,10,11,15,16]. These capabilities must continue to be developed.

*Laboratory studies:* Finally, laboratory studies provide ground truth for understanding processes at work throughout the solar system. In the short term the processes of condensation, evaporation and sublimation [e.g. 16] would be of high value for understanding the origin and evolution of bodies like Titan and Pluto. However, improving laboratory capabilities is essential and must go beyond the technology currently available today if we hope to apply isotope geochemistry to exoplanets.

**Summary:** Isotope geochemistry has played a critical role in establishing our current understanding of the origin and evolution of solar system bodies and is essential for expanding research on origins and workings to exoplanet systems. Long term efforts should focus on measurements, modeling, and laboratory studies.

**References:** [1] Mandt K. E. et al. (2015a) *SSRv*, 197, 297–342. [2] Marty B. (2012) *EPSL*, 313–314, 56–66. [3] Jakosky B. M. (1991) *Icarus*, 94, 14–31. [4] Mandt K. E. et al., (2015b) *Icarus*, 254, 259–261. [5] Donahue T. M. (1999) *Icarus*, 141, 226–235. [6] Mandt K. E. et al., (2014) *ApJL*, 788, L24. [7] Mandt K. E. et al., (2016) *PSS*, 130, 104–109. [8] Niemann H. B. et al., (1999) *JGR*, 103, 22,831–22,845. [9] Niemann H. B. et al., (2010) *JGR*, 115, E12006. [10] Mandt K. E. et al., (2012) *ApJ*, 749, 160. [11] Nixon C. A. et al., (2016) *ApJ*, 749, 159. [12] Altwegg et al., (2015) *Science*, 347, 1261952. [13] Liang M.-C. et al., (2007) *ApJ*, 130, 104–109. [14] Kornblum, Z. C. & Ishida, T., (2005) *J. Chem. Phys.*, 122, 094317. [15] Mandt K. E. et al., (2009) *PSS*, 57, 1917–1930. [16] Luspay-Kuti A. et al., (2012) *GRL*, 39, L23203.