HYDROGEN AND NITROGEN COSMOCHEMISTRY: A REVIEW

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ABSTRACT

Hydrogen and nitrogen are both unique elements, showing substantial variation relative to each other and to their only secondary isotopes (deuterium and nitrogen-15). Yet compared to other elemental and isotopic systems—oxygen in particular—hydrogen and nitrogen are less-often examined in a comprehensive cosmochemical context. We review the cosmochemistry of these elements, starting with their cosmic and interstellar abundances, then the protosolar nebula and primitive (cometary and carbonaceous) bodies, and finally the planets of the solar system. We summarize the major observations which have thusfar provided key constraints on the cosmochemical evolution of H and N, and emphasize areas which would benefit from future investigation.

1. COSMIC ORIGINS AND ABUNDANCES

To first order, the universe consists primarily of hydrogen atoms formed during the Big Bang. Nucleosynthesis set a primordial isotopic ratio of $\sim$25 deuterium atoms (D = ^{2}H) per million ^{1}H atoms. A basic description of most interstellar material is the state of its hydrogen: either ionized (H^+), neutral atomic (H) or molecular (H_2).

Of the universe's next five most abundant elements—He, O, C, N and Ne—*nitrogen* is by far the most unique. With its seven-proton ($Z = 7$) nucleus, N is the most abundant odd-Z element (the next most common is Al with $Z = 13$). Its odd atomic number reflects the fact that N is not an end-product of *primary* stellar nucleosynthesis, which produces even-Z elements like He, O, C and Ne in concentric "fusion shells" in massive ($> 10 M_\odot$) stars. Nitrogen does *not* accumulate in such a fusion shell, though it is a common product of the CNO cycle, an example of *secondary* stellar nucleosynthesis which can occur even in less massive stars like our Sun (McSween and Huss 2010). Another source of nitrogen is nucleon-capture during supernovae (*e.g.*, Meyer and Bojazi 2011), but this process is not as well understood. Empirically, the observed cosmic ratio is $\sim$85 N atoms per million H atoms, with an isotopic ratio of $\sim$2300 ^{15}N atoms per million ^{14}N atoms.

The odd-Z nature of nitrogen—and its resulting valence electron configuration—has unique implications for its chemistry. Unlike noble gas elements (*e.g.*, He and Ne), nitrogen readily forms molecules, with itself and other abundant atoms like H, O and C. Unlike O and C, however, N does *not* commonly combine with rock-forming elements like Si, Mg and Fe. That is, there are far fewer *nitrides* in the universe than there are *oxides* and *carbides*. This is in part because N is a factor of 3–10 less abundant than O and C everywhere in the universe, and also because many gaseous molecular forms of N, like N_2 and HCN, have very stable triple bonds which are much more difficult to break than those of other common compounds like H_2O and CO.

Because of its preponderance in molecules (rather than neutral atomic or dust/ice phases), one might think that nitrogen abundance in the interstellar medium (ISM) should be relatively straightforward to measure (*e.g.*, from spectroscopic lines). However, neutral N_2—the long-assumed (and model-predicted) predominant form of nitrogen in the ISM (Herbst and Klemperer 1976)—is notoriously difficult to measure directly due to a lack of observable rotational and vibrational lines. The usual work-around is to observe N_2H^+ and infer the N_2 ratio from chemical modeling. However, recent analyses (Maret et al. 2006) have challenged the abundant-N_2-gas model in favor of atomic-N and icy-N (grain-based NH_3 and N_2 ices) in at least one cold molecular cloud (the B68 pre-stellar core).

The inferred gas-phase N/H ratio of the ISM in the line-of-sight toward ζ *Ophiucus* is markedly close to the bulk N/H of our solar system—the precise ISM/solar ratio being 0.93 (Palme and Jones 2005). By comparison, the O/H and C/H ratios in the gaseous ISM are depleted relative to our solar system, having ISM/solar ratios of 0.63 and 0.56, respectively. Again, the inference is that O and C are abundant in condensed (ice and dust grain) phases, whereas N is predominantly in gas form.

Ion-molecule reactions and grain-surface processes can give rise to substantial inhomogeneities in N/H, D/H and ^{15}N/^{14}N in the ISM (Ehrenfreund and Charnley 2000). Simple N-bearing ices like HCN and NH_3 may be partially disassembled and subsequently incorporated into more complex (often chain-like) organic molecules, such as CH_3C_3N and NH_2CHO. Heavy isotope enrichments—sometimes by factors of up to five relative to primordial—even for simple molecules like HDO/H_2O and $HC^{15}N/HC^{14}N$ can be commonplace, as measured in interplanetary dust particles (Messenger 2000; Floss et al. 2006).

2. PROTOSOLAR NEBULA

As mentioned above, the bulk N/H ratio in the solar system (by mass, overwhelmingly the Sun) is markedly close to that of the local gas-phase ISM. The solar photosphere's abundance is N/H $\approx 8.5 \times 10^{-5}$ (Holweger 2001), while the ISM's N/H ratio in the direction of ζ *Ophiucus* is $\sim$7% smaller (Savage and Sembach 1996). One might suppose that the larger solar value is the result of H-depletion from fusion in the Sun, though the reported errors on each value (30% and 15%, respectively) are sufficiently large that we can declare them effectively

equivalent.

Isotopically, the Sun's present D/H ratio is vanishingly small, since deuterium in the Sun is rapidly destroyed in the process of H-fusion. Hence, as will be discussed later, the initial bulk D/H of the protosolar nebula must be inferred from other solar system reservoirs, such as Jupiter. The protosolar value of ^{15}N/^{14}N $= (2.27 \pm 0.03) \times 10^{-3}$ was measured in the solar wind by the *Genesis* spacecraft (Marty et al. 2010), and is assumed to be representative of the bulk protosolar nebula. While CNO-cycle fusion reactions in the Sun's core have presumably altered the bulk nitrogen ratio somewhat, the surface abundances are not presumed to have changed much (McSween and Huss 2010).

Temporal and spatial variation in the ratios of N/H, D/H and ^{15}N/^{14}N are certain to have existed in the protosolar nebula. One probable driver of such inhomogeneities is gas-to-solid phase transition—the freezing-out of compounds in "snowlines". Given a model for gas pressure and temperature as a function of position in the disk, the phase diagram of a given compound dictates the partial pressure of the gas component relative to the solid (ice) phase. As the temperature drops, provided there are sites for nucleation (*e.g.*, dust grains), the condensed phase will be preferred for a given compound beyond a certain radius (*i.e.*, below a certain temperature) from the proto-Sun (Aikawa 2003; Aikawa and Nomura 2008).

Aside from H$_2$, two of the most abundant molecular species in the protosolar disk were H$_2$O and CO; these two compounds however had very different snowline locations (Brown 2012; Figure 1). Whereas the much more volatile CO condensed beyond $\sim$100 AU, water probably condensed in the vicinity of $\sim$3 AU. A multitude of carbon-bearing compounds had snowlines in the 10–20 AU region, but the only significant N-bearing ices—HCN and NH$_3$—condensed at 25–35 AU. The disk's density in the outermost regions, where N$_2$, CO and CH$_4$ ices were stable, was likely low enough, and the temperature cold enough (*i.e.*, equilibrative timescale long enough), to prevent the condensation of these species. Intense UV radiation from other nearby stars (Bergin et al. 2007) may also have prevented the condensation in these outermost regions.

Thus, to first order, one would expect the fraction of H in the gaseous part of the disk to drop most abruptly at $\sim$3 AU, and the fraction of N in the gas to drop most abruptly at $\sim$30 AU. If H$_2$ and N$_2$ gases are the most abundant forms of these elements, however, then the fractional changes in question may have been small. While condensation alone does not change the bulk (gas + solid) spatial distribution of these elements, the snowlines may have acted as cold-traps. That is, given suitable mixing across the snowline boundaries, molecules that entered the cold side would be sequestered in ice and not re-enter the warmer region, thereby driving a spatial inhomogeneity. Even if such cold-trapping did not occur, the inevitable loss/dissipation of the gaseous part of the disk to space would similarly create spatial discontinuities in the elemental ratios across the H and N snowlines.

Other complications to this story could have further altered the elemental distribution of H and N. As depicted in Figure 1, $\sim$1000-km scale and larger planetes-
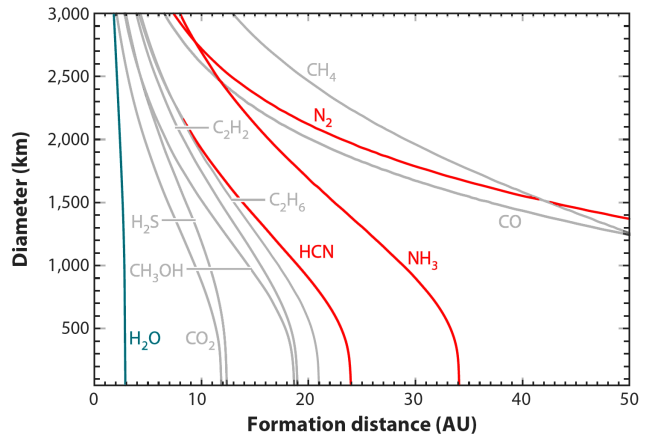

FIG. 1.— The surface chemistry of a planetesimal in the protosolar nebula is a function of both its orbital distance and its size. More volatile species condense out at greater heliocentric distances, but may be retained closer in if the body's gravity is sufficient to maintain an atmosphere. To first order, the solid-phase H abundance increases most abruptly at $\sim$3 AU, while the solid-phase N abundance increases most abruptly at $\sim$30 AU. Figure adapted from Brown (2012).

imals could retain N$_2$, HCN and NH$_3$ in atmospheres, even in warmer regions of the disk. Such atmospheres may have been transient however, and through Rayleigh distillation (see later discussions) may have severely fractionated the ratios N/H, D/H or ^{15}N/^{14}N. Trapping of N-containing molecules in H$_2$O-molecule "cages" (Iro et al. 2003)—*i.e.*, either amorphous ice or clathrates—could also alter these ratios, particularly if the abundant N$_2$ was among those trapped.

Snowline condensation may have been a source of *isotopic* fractionation as well, via zero-point energy (*i.e.*, non-kinetic) phase-exchange effects. Such equilibrium fractionation has long been known to be a function of temperature, both through theoretical (*e.g.*, Herzfeld and Teller 1938) and experimental (*e.g.*, Merlivat and Nief 1967) work. Hence, isotopic composition of the ices may have varied with radius in the protosolar disk, though the equilibrative timescales might not have been shorter than the gas disk's lifetime.

In the previous section we noted the anomalous H and N chemistry of ices and organics on interstellar grains. In certain regions of the protosolar nebula these grains may have been sufficiently heated to sublimate off and/or dissociate these compounds, thereby erasing the grain's local chemical inhomogeneity. In colder regions of the disk, however, these compounds may have been incorporated into planetesimals *without* reequilibration. We comment on this matter below in the context of particular solar system bodies, *e.g.*, comets.

Far-infrared water-emission-line data from the *Herschel Space Observatory* (Pilbratt et al. 2010; Hogerheijde et al. 2011; Zhang et al. in prep.) constitute the most direct observations of a protosolar H$_2$O snowline to date, in the nearby TW Hydrae system. Instruments are not currently capable of spatially resolving snowline boundaries, so line-inferred temperatures must be used as a proxy for orbital distance in the disk. Such modeling should be possible for species like HCN as well in the near future (G. Blake, personal communication). Clues
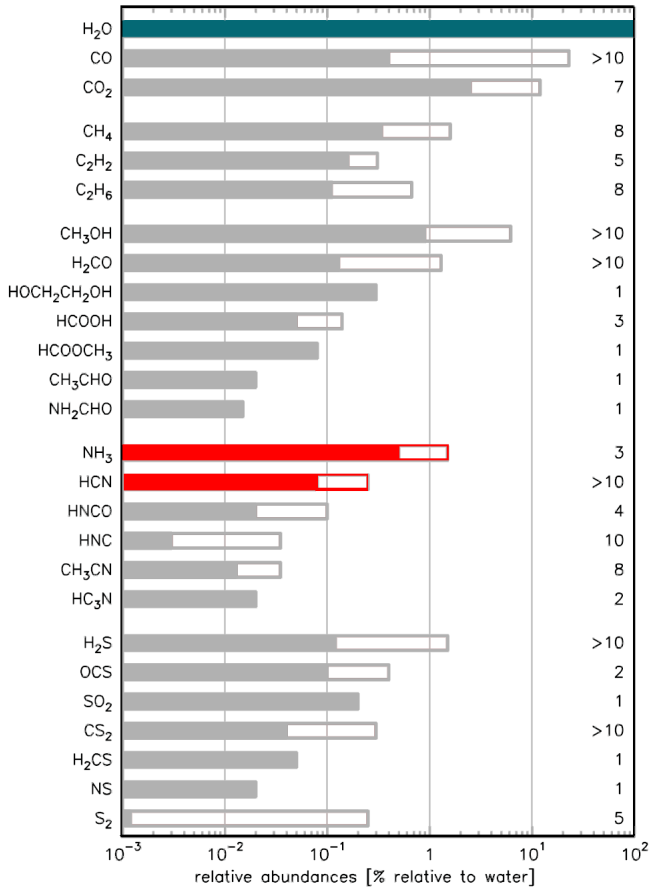
FIG. 2.— Observed chemical species in cometary comae. The numbers listed at the right of each entry are the number of comets in which the compound has been observed. The white bar at the right end of each bar represents the scatter in the abundance value. Figure adapted from Bockelée-Morvan (2011).
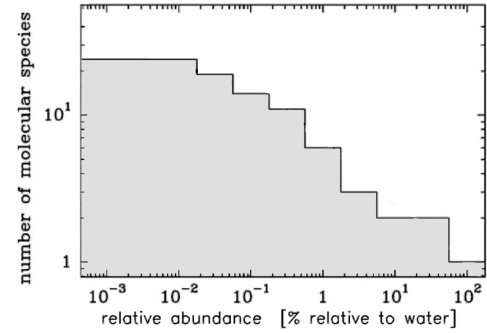

FIG. 3.— The number of organic species in comets grows with decreasing abundance, relative to water. The less abundant species also happen to be less volatile and larger (*e.g.* chain or ring structured). Figure adapted from Crovisier (2006).

is $\sim 6 \times 10^{-3}$. This is a factor ~ 70 greater than the cosmic N/H of $\sim 9 \times 10^{-5}$ (Section 1). The N/H ratio varies much less between comets than the C/H and O/H ratios, mostly because CO content varies by more than an order of magnitude between individual comets. Additionally, the C/H ratio resolves two distinct comets groups (Mumma and Charnley 2011)—"carbon-chain typical" (high C/H) versus "carbon-chain depleted" (low C/H)—whereas N/H variation is smaller and not capable of distinguishing these two comet types. Figure 3 shows that the number of organic species observed in comets at a given abundance is inversely proportional to the abundance. Hence, –OH, –NH$_2$ and –CN functional groups in more complex (but less abundant) species must be taken into account as well for more precise elemental characterization.

The two dynamical classes of comets—long-period comets (LPCs) and short-period comets (SPCs)—appear distinct in their D/H, at least on the basis of a handful of LPC measurements of $\sim 2\times$ terrestrial D/H (Jehin et al. 2009) and a single SPC measurement of terrestrial D/H (Hartogh et al. 2011). LPCs were at some early time gravitationally scattered (by encounters with the giant planets) out to the Oort Cloud: a spherical zone at $\sim 10,000$ AU from which they are occasionally perturbed inward on highly eccentric and isotropically-inclined orbits. One recent hypothesis (Levison et al. 2010) supposes that these Oort cloud comets were instead captured from nearby protoplanetary disks while the Sun was still in its birth cluster. The second dynamical type, SPCs, have less-energetic orbits, with lower inclinations and semi-major axes comparable to Jupiter (~ 5 AU, hence they are often called *Jupiter-family* comets). The connection between KBOs and SPCs has been evident since the discovery of a class of objects known as *centaurs* (Kowal 1978), which are orbitally intermediate (between KBOs and SPCs) comet-like objects, and from dynamical simulations (*e.g.*, Levison and Duncan 1997) that show continuous exchange of objects between the two populations.

The higher-than-terrestrial D/H of LPCs was first realized when the Giotto spacecraft performed in-situ mass-spectrometry of the coma of comet 1P/Halley (Eberhardt et al. 1987). In the subsequent decades, many authors (*e.g.*, Delsemme 1999; Robert 2006) have hypothesized on the origin of this D/H enrichment and its

to the primordial location of the H and N snowlines can also be found in the chemistries of solar system bodies today, as will be discussed in the following sections.

3. COMETS

Water is by far the most abundant gas observed in cometary comae (when ~ 1 AU from the Sun), representing on average $\sim 80\%$ by abundance of all molecules present (Figure 2). The most abundant N-bearing cometary gases are NH$_3$ and HCN, at about 1% and 0.1% abundances, respectively, relative to H$_2$O. As noted in the previous section, each of these three compounds (H$_2$O, NH$_3$ and HCN) likely experienced condensation within ~ 40 AU of the protosun (Figure 2), while N$_2$ had a much farther-out snowline. Their conspicuous lack of N$_2$ may suggest that the comets we observe today formed within the N$_2$ iceline (~ 100 AU) but exterior to the NH$_3$ and HCN icelines (~ 30 AU). A vast number of objects beyond the present-day orbit of Neptune (~ 30 AU)— namely Kuiper belt objects (KBOs)—presently occupy this region of the solar system in stable orbits. Hence the notion of comets forming there is quite plausible, and their relation to KBOs manifest.

Making the first-order assumption that all cometary H is in H$_2$O and all N is in NH$_3$ and HCN, then according to the abundances in Figure 2 the bulk cometary N/H
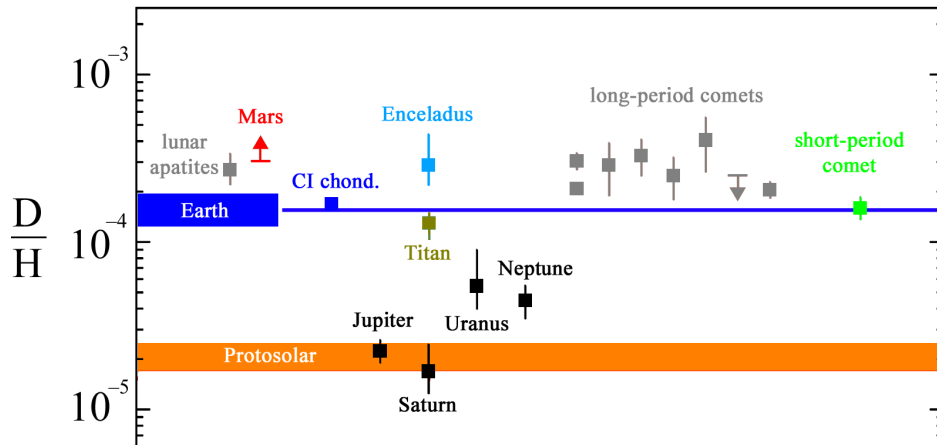
FIG. 4.— Summary of solar system objects with isotopic data for hydrogen, roughly ordered horizontally by increasing distance (semi-major axis) from the Sun. Figure adapted from Bockelée-Morvan et al. (2012), with additional data from Greenwood et al. (2011), Bézard et al. (2012), and Fisher (2007).

implications for the origin of Earth's and Mars' surface water reservoirs. Most arguments appeal to protosolar-nebular fractionation processes, like those discussed in Section 2. Two additional major observations were made since then: (1) as mentioned above, SPCS have a lower (terrestrial) D/H (Hartogh et al. 2011), as observed in comet 103P/Hartley 2 with far-infrared spectroscopy by the Herschel Space Observatory, and (2) SPCs contain dust grains which at some point experienced very hot (*i.e.* rock-melting) temperatures (Simon et al. 2008), as observed in comet 81P/Wild 2 via sample-collectors aboard the Stardust spacecraft.

To date, all cometary $^{15}N/^{14}N$ estimates derive from observation of either HCN (observable via submillimeter-band emission), or its daughter molecule CN (observable via ultraviolet-band emission). HCN is the most abundant and most volatile of the –CN-bearing species in cometary nuclei. However, $^{15}N/^{14}N$ measurements are typically made when a comet is brightest and most active (close to the Earth and Sun), and therefore subli-mating less volatile, more complex –CN-bearing species as well. The number of cometary organic species as a function of their abundance follows a linear trend in log-log space (Figure 3); hence these complex species may well be significant to the bulk cometary $^{15}N/^{14}N$, as discussed by Arpigny et al. (2003). However, Manfroid et al. (2009) shows no variation in the $^{15}N/^{14}N$ ratio as a function of heliocentric distance, out to ∼4 AU. The de-rived $^{15}N/^{14}N$ in both comet types is enriched by a factor of ∼2 relative to terrestrial and chondrites, the only ex-ception being 73P/Schwassmann-Wachmann 3, an SPC with a $^{15}N/^{14}N$ consistent (within error) with the chon-dritic value (Jehin et al. 2008)[1].

A major problem, already noted elsewhere (Owen 2008; Jehin et al. 2009), is that NH_3 is more abundant than HCN—often by an order of magnitude—in both LPCs and SPCs. Despite this, no $^{15}N/^{14}N$ data exists

for NH_3 or other –NH_2-bearing species. It is thus possible that bulk cometary nitrogen is in fact *always* consistent with the terrestrial $^{15}N/^{14}N$ value.

Another issue concerns how well the retrieved coma el-emental and isotopic abundances reflect the bulk chem-istry of a comet. Moores et al. (2012) for instance ar-gue from experimental work that the D/H ratio in water can *decrease* by a factor of up to ∼2.5 upon sublimation from dust grains, *i.e.*, a reverse isotope effect. Factor of ∼2 deviations (both enrichment and dilutions) from the mean terrestrial D/H value are seen even on Earth under extreme conditions (Hoefs 2009), *i.e.*, deviations of this magnitude are rather commonplace, and perhaps more so under the extreme conditions of space.

Finally, in addition to LPCs and SPCs, a third popu-lation of comets has been discovered in the last decade in the main asteroid belt. These *main-belt comets* (MBCs; Hsieh and Jewitt 2006) are dynamically stable, indicat-ing that could have resided in the main belt (at ∼3 AU) over the age of the solar system. Observationally, some of these MBCs show recurrent activity around perihe-lion, where the warmer temperatures are sufficient for the sublimation of subsurface ices. The rate of sublimation is sufficiently fast for the ice depths in these asteroids to re-treat to thermally-impenetrable depths after only a few thousand years (Schorghofer 2008), but collisions with smaller asteroids can replenish the near-surface ice reser-voir, allowing these MBCs to be observable today. Un-fortunately, the gas emission is sufficiently weak in these objects to make chemical analysis impossible. Given current instrumental sensitivities, the ultraviolet-band CN-emission line seen prominently in virtually all other comets is undetectable in MBCs (Licandro et al. 2011), and searches for far-infrared water emission lines have also proven futile (de Val-Borro et al. 2012). Hence, the possibility of a drastically different chemistry for MBCs (*e.g.*, N-poor if they formed interior to the HCN and NH_3 snowlines) is not ruled out.

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[1] This particular comet (73P) also showed distinctly anomalous ortho-to-para abundance ratios (Shinnaka et al. 2011), indicative of a formation temperature of ∼50 K (as compared to the ∼30 K derived for all other comets), and was observed while fragmenting violently (another unique occurrence).

4. CARBONACEOUS METEORITES

Primitive (type 1 and 2) carbonceous chondrites are typically quoted as containing bulk ∼20% abundance wa-ter and ∼3% abundance carbon (*e.g.*, Krot et al. 2005),
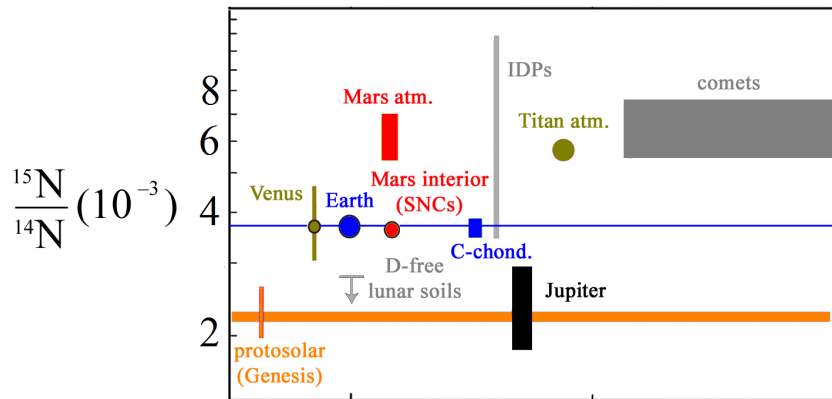
FIG. 5.— Summary of solar system objects with isotopic data for nitrogen, roughly ordered horizontally by increasing distance (semi-major axis) from the Sun. Figure adapted from Marty et al. (2010).

and a C/N ratio of ∼12 (Palme and Jones 2005). It follows that the N/H ratio of these meteorites is ∼10^{-2}, the same order of magnitude as that of comets. Indeed, complex organic material of an unidentified structure, known as "CHON", was observed in the dust of comet Halley (Kissel et al. 1986), and determined to be similar in some respects to the material in primitive carbonaceous chondrites and interplanetary dust particles (IDPs). One of the largest discrepancies was the C/H ratio, which was significantly enriched in the cometary dust relative to chondrites, while the comet dust's N/H ratio was closer to that of meteorites (Jessberger et al. 1988).

Organics in carbonaceous chondrites fall into two categories: soluble and insoluble. The less-common *soluble* compounds are extractable with some solvent and more easily lost from the sample. These include various acids (*e.g.*, amino, carboxylic, sulfonic) and both aliphatic and aromatic hydrocarbons (Pizzarello et al, 2006). The more common *insoluble* compounds consist of mostly sheeted (graphitic) carbon, which likely is an aggregate of smaller aromatic units (Cody et al. 2002). Locally, large (factors of ∼2–5) heavy-isotope enrichments in both D/H and ^{15}N/^{14}N are seen in both classes of organics, and likely originated from the ion-molecule reactions described earlier as occurring in the ISM. The bulk D/H of carbonaceous meteorites (mostly in –OH in hydrated mineral phases), however, is consistent with terrestrial (Robert 2006). Likewise, the bulk ^{15}N/^{14}N is consistent with terrestrial, with the anomalous ^{15}N-rich compounds concentrated in unhomogenized "hotspots" (Busemann et al. 2006).

5. GAS-GIANT PLANETS

According to the core-accretion model of gas-giant planet growth (Pollack et al. 1996), ice-rich planetesimals grow in the still gas-rich protosolar nebula exterior to the H_2O-snowline. These can combine to form a ∼$10M_{\oplus}$ body in ∼10^7 years, at which point runaway accretion of the surrounding gas occurs, producing a ∼$100M_{\oplus}$ planet of mostly solar (*i.e.*, H-rich) composition in less than 10^6 years.

The N/H, D/H and ^{15}N/^{14}N we measure at the surfaces of the Jupiter, Saturn, Uranus and Neptune today depend on the:

1. compositions of the initial solid core and the sub-

sequently accreted gaseous envelope

2. extent of mixing between the solid core and the gaseous envelope

3. amount of contamination from late impactors

Item 1 depends on the protosolar disk's chemistry and its spatial variation (as discussed in Section 2), the core's initial location in the disk, and the extent to which it migrates radially during accretion. Traditionally, radial migration through the disk is believed to occur only *after* the planet is fully formed and has opened a gap in the disk (Ward 1997)[2]. Given this assumption, differences in bulk chemistry between the gas giants might be indicative of their initial location in the disk. For example, as shown in Figure 4, the D/H ratios of Uranus and Neptune (measured by Feuchtgreuber et al. 1999) are factors of ∼2–3 higher than those of Jupiter and Saturn, which are essentially protosolar. This difference could reflect a primordial D/H gradient in H_2 gas in the disk's radial direction. Alternatively, the D-enrichment of Uranus and Neptune may be due to their accretion of a less-massive gaseous envelope (given that they are only ∼$15M_{\oplus}$ total) relative to their initial core—*i.e.*, even if the respective chemistries of their cores and gaseous envelopes were the same as those of Jupiter and Saturn, a mixing ratio discrepancy could account for the D/H (Owen and Encrenaz 2006). Finally, it is possible that Uranus and Neptune experienced more extensive D-distillation via atmospheric escape of H (see discussion in the following section regarding terrestrial planets).

The "Nice model" of late-stage planetary migration (Tsiganis et al. 2005) predicts that the gradual orbital evolution of our solar system's giant planets may have at one time caused an epoch of abrupt upheaval from orbital resonance. During this event, conservation of angular momentum and orbital energy resulted in substantial radial shuffling of objects: Uranus and Neptune may have "switched places", large amounts of Kuiper belt objects may have been scattered inward toward Jupiter, some of which may have impacted the planets and some of which may have been thrown out to the Oort cloud or trans-

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[2] However, one recent model (Levison in prep) radically challenges this view by supposing that gas accretion happens over the course of an outward core migration from ∼1 AU to ∼10–30 AU.
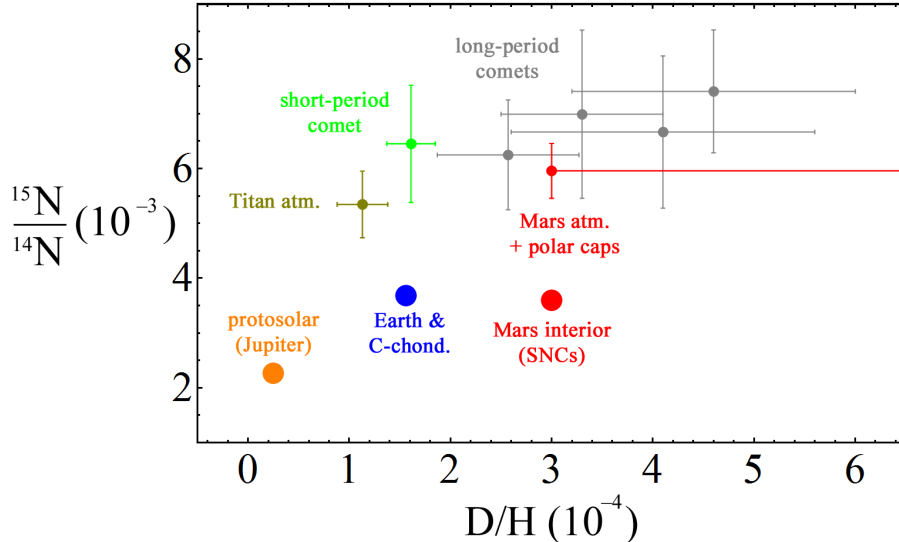
FIG. 6.— Summary of solar system objects with isotopic data for *both* H and N. References: *protosolar* (Jupiter H_2 and NH_3, solar wind N)—Fouchet et al. 2004, Marty 2012; *Mars interior* (SNCs, *i.e.*, Chassigny)—Bogard et al. 2001; *Titan atmosphere* (CH_4 and N_2 at surface)—Bézard et al. 2012; *short-period comet* (H_2O, HCN)—Hartogh et al. 2011, Meech et al. 2011; *long-period comets* (H_2O, HCN)—Jehin et al. 2009, Manfroid et al. 2009; *Mars atmosphere* (H_2O, N_2)—Owen et al. 1977, Fisher 2007.

Neptunian Scattered disk (Levison et al. 2008). The timing and severity of this event is difficult to constrain—some (*e.g.* Gomes et al. 2005) have linked it to the Late-Heavy Bombardment event seen in cratered bodies). In any case, its potential to have chaotically altered the architecture of the solar system clearly makes specifying the original location of the gas-giants difficult (uncertainty arises with respect even to their initial radial ordering).

Item 2 (extent of core-envelope mixing) can be assessed with thermodynamic modeling of planetary contraction/expansion and convection, while keeping track of the chemistry that results. Empirically, however, exchange between Jupiter's troposphere and interior seems to occur given its depletion in helium (Niemann et al. 1998) and the presence of CO and PH_3 (Bézard et al. 2002). Current surveys indicate a large population of Jupiter-mass exoplanets orbiting at ∼0.1 AU from their parent stars, and simulations show that our own solar system's Jupiter may have at some early time migrated inward to temporarily occupy such an extremely small orbit (Walsh et al. 2011). Were that to have occurred, Jupiter may temporarily have become a "hot Jupiter", *i.e.*, sufficiently turbulent and hot to become extensively chemically mixed.

Finally, Item 3 (contamination from late impactors) has been invoked as one explanation for the observed N/H ratio of Jupiter, which at 5×10^{-4} is a factor ∼5 higher than the protosolar N/H value. This value is based of data collected by the Galileo probe as it descended into Jupiter's atmosphere (Owen et al. 1999). As noted in previous sections, protosolar N/H is ∼9×10^{-5} and cometary N/H is ∼6×10^{-3}, given which a reasonable mixture of 93% protosolar with 7% cometary indeed gives Jupiter's observed N/H. Absent independent evidence for or against deep mixing, however, there is no way to distinguish this 7% from coming from the planet's initial core as opposed to externally in late impactors. Moreover, because comets and carbonaceous

chondrites have the same order of magnitude N/H, this hypothesis can equally substitute carbonaceous asteroids for the comets.

Complicating this simplistic explanation are the observations that the $^{15}N/^{14}N$ ratio of Jupiter agrees well with the protosolar value (while protosolar D/H is *defined* as Jupiter's, since D is destroyed in the Sun), and that the factor ∼5 enrichment in N/H is accompanied by a nearly equivalent enrichment in C/H. Yet, as discussed earlier, virtually all known comets have a twofold $^{15}N/^{14}N$ enrichment, and the C/N ratio of comets and carbonaceous chondrites is ∼10, while the protosolar C/N is less than ∼3 (Palme and Jones 2005).

In other words, the comets we observe today cannot be responsible for Jupiter's N/H enrichment, as they would have also enriched $^{15}N/^{14}N$ to greater than protosolar, and would have enriched C/H by factor greater than ∼5. This lead Owen et al. (1999) to posit the former existence of a different class of comets, called *solar composition icy planetesimals*, (SCIPs), which were objects having solar composition in all elements in all elements heavier than carbon. In Section 2 we discussed at least a few ways these SCIPS could have existed. One possibility is "bubble-rich" amorphous ice (or perhaps clathrates) containing abundant trapped CO and N_2 gases (but not H_2). Another possibility is that these objects had diameters greater than ∼1000 km (see Figure 1), and therefore could sustain CO and N_2 ice crusts (possibly even mantles) with bound atmospheres above.

6. TERRESTRIAL PLANETS

Despite predictions (*e.g.*, Cassen 1994) that the terrestrial planets (Mercury, Venus, Earth, and Mars and the Moon) formed in too hot a region of the protosolar disk to allow for the direct accretion or adsorption of volatile H- or N-bearing ices from the disk gas, each of them clearly shows extant or residual H and N surface reservoirs. Earth and Mars both have condensed H_2O covering significant portions of their surface, and N_2 gas as

one of their primary atmospheric constituents. Mercury and the Moon both have H- and N-rich volatile condensates in permanently-shadowed craters near their poles, discovered initially by radar (Slade et al. 1992; Nozette et al. 1996), and later confirmed by the MESSENGER and LCROSS spacecraft missions (Lawrence et al. in press; Schultz et al. 2010). Venus' surface pressure and temperature do not permit H_2O to exist in condensed form, though the extremely high D/H of what little does exist in its atmosphere suggests an initially vast reservoir (for reasons to be explained presently)—and as on Mars N_2 is the second most abundant gas (after CO_2).

In general, terrestrial planet formation may take ~ 10 times longer than gas-giant planet formation (Morbidelli et al. 2012), and occurs mostly after the gaseous part of the protosolar nebula has dissipated. The accretion of surface volatiles is often hypothesized to have occurred via impacts of primitive small bodies *after* the bulk (rocky component) of the terrestrial planets were fully formed. Testing this *late-veneer* origin for the H- and N-bearing volatiles of the terrestrial planets is complicated, but may be broken down into constituent processes.

One such process is *mixing*—if two impacting small body types (A and B) each have their own N/H, D/H and $^{15}N/^{14}N$, with a fraction $0 \leq x_A \leq 1$ of volatiles contributed from type A (and fraction $1 - x_A$ from type B), then mass-chemical balance defines the following system of equations:

$$\left(\frac{N}{H}\right)_{\text{planet}} = x_A \left(\frac{N}{H}\right)_A + (1 - x_A)\left(\frac{N}{H}\right)_B \quad (1)$$

$$\left(\frac{D}{H}\right)_{\text{planet}} = x_A \left(\frac{D}{H}\right)_A + (1 - x_A)\left(\frac{D}{H}\right)_B \quad (2)$$

$$\left(\frac{^{15}N}{^{14}N}\right)_{\text{planet}}\left(\frac{N}{H}\right)_{\text{planet}} = x_A \left(\frac{^{15}N}{^{14}N}\right)_A \left(\frac{N}{H}\right)_A$$
$$+ (1 - x_A)\left(\frac{^{15}N}{^{14}N}\right)_B \left(\frac{N}{H}\right)_B \quad (3)$$

In previous sections we identified at least four possible choices for A and B, each with a distinct elemental + isotopic composition: long-period comets (LPCs), short-period comets (SPCs), carbonaceous chondrites, and solar composition icy planetesimals (SCIPs).

A second process to model is *atmospheric escape*. Given a planet's mass (gravity) and atmospheric temperature (kinetic energy distribution), atomic and molecular species below a cutoff mass (above a cutoff velocity) have sufficient energy to escape the planet. Another heuristic explanation of atmospheric escape is that the mean-free-path (inter-collisional distance) of a species exceeds the scale height for that species (the *e*-folding height for its pressure and density). The instantaneous rate of escape depends on the species' mass and atmospheric concentration. Isotopes and isotopologues thus have slightly different escape rates, and the net effect is *distillation*.

Consider the planet Mars: most of its water ice is trapped in the polar caps, with only a very small amount in the atmosphere (and therefore capable of escaping). If

the polar cap periodically exchanges in full with the atmosphere during warmer epochs (*e.g.*, Fisher 2007), then we can assume that the ice caps will enrich in deuterium as well. Its nitrogen is presumably all in atmospheric N_2, and always subject to escape. The equations describing Mars' evolution are:

$$\left(\frac{N}{H}\right)_{\text{planet}} = \frac{N_{\text{esc}} + N_{\text{present}}^{\text{atm}}}{H_{\text{esc}} + H_{\text{present}}^{\text{ice}}} \quad (4)$$

$$\left(\frac{D}{H}\right)_{\text{planet}} = \left(1 + \frac{H_{\text{esc}}}{H_{\text{present}}^{\text{ice}}}\right)^{\alpha_H - 1} \left(\frac{D}{H}\right)_{\text{present}}^{\text{ice}} \quad (5)$$

$$\left(\frac{^{15}N}{^{14}N}\right)_{\text{planet}} = \left(1 + \frac{N_{\text{esc}}}{N_{\text{present}}^{\text{atm}}}\right)^{\alpha_N - 1} \left(\frac{^{15}N}{^{14}N}\right)_{\text{present}}^{\text{atm}} \quad (6)$$

Equations 5 and 6 assume the distillation process obeys *Rayleigh fractionation*. This means that if the D/H ratio of the atmosphere at time t is R, then the next increment of atmosphere removed (during time dt) has a ratio $\alpha_H R$, where α_H is the hydrogen fractionation factor. Note that there is no time dependence in these equations, since they are given in terms of the cumulative amounts of H and N that have escaped up to the present time.

Combining Equations 1–3 with Equations 4–6 (*i.e.*, removing dependence on the "planet"-subscripted terms) gives a system of three equations that can be used to solve for x_A and up to two other unknowns. Well-constrained quantities include $H_{\text{present}}^{\text{ice}} \approx 25$ meters H_2O global-equivalent layer (from radar sounding of the polar caps and mid-latitude glaciers, *e.g.*, Plaut et al. 2007; Phillips et al. 2008; Holt et al. 2008); the atmospheric $^{15}N/^{14}N$ and N_2 abundance as measured by the Viking lander (Owen et al. 1977); and the lower bound $H_{\text{esc}} \gtrsim H_{\text{present}}^{\text{ice}}$, from obvious geomorphic evidence of early abundant surface waters (*e.g.*, Carr 1987).

The factor α_H describes how preferentially retained D is relative to H. For the current Mars atmosphere this has been estimated as ~ 0.1 from photochemical modeling (*e.g.*, Cheng et al. 1999; Krasnopolsky and Feldman 2001), meaning H is ~ 10 times more efficiently lost than D. Water isotopologues are too heavy to escape Mars, while H_2-gas isotopologues *are* sufficiently light. The solar-radiation-driven reaction

$$HDO + H_2 \leftrightarrow H_2O + HD \quad (7)$$

thus dictates how D and H partition into hydrogen gas at Mars' surface before escaping. As mentioned in Section 2, isotopic fractionation factors are commonly a function of temperature, so that the distillation ratio may have been different during early Mars' warmer Noachian period.

The escape of N from Mars is less-well understood: dissociative recombination into N_2^+ in the upper atmosphere and subsequent solar-wind-stripping is one possibility, in which case models predict $\alpha_N \approx 0.9$ (McElroy et al. 1977; Fox and Haĉ 1997). Impact erosion (in which no fractionation would occur, *i.e.*, $\alpha_N = 1$) is another possibility (Melosh and Vickery 1989).

As shown in Figure 5, Mars' atmosphere today is enriched in $^{15}N/^{14}N$ to roughly the same extent as comets. The composition of the Martian mantle (or perhaps just trapped primordial atmosphere) can be inferred from SNC meteorites (*e.g.*, Chassigny), and is evidently enriched in D/H but not in $^{15}N/^{14}N$ (Bogard et al. 2001). The Mars atmospheric D/H has been measured as $\sim$5–6 times higher than terrestrial (Yung et al. 1988). However, because the fraction of water in the polar caps overwhelmingly dominates the planet's total water budget, this is by no means indicative of the planets bulk D/H, which is only really constrained by the lower limit of $\sim$2 times terrestrial, in accordance with the SNC value and modeling of polar cap exchange (Fisher 2007).

Other processes which could complicate this model are volcanic outgassing of H- and N-bearing species and sequestration of these species into crustal hydrated minerals (Mustard et al. 2012) and nitrates (Manning et al. 2009). The sequence and duration of each of these processes (delivery, escape, outgassing and sequestration) changes the outcome as well. Nonetheless, Mars is certainly simpler to model than Earth, which has ongoing tectonics and biological processes to modify its observable H and N chemistries. Venus' extremely high D/H indicates that it likely had at least an Earth-ocean's worth of water at one point. Even though N_2 only represents 3.5% of Venus' atmosphere, its partial pressure is roughly the same as that of the Earth, and its $^{15}N/^{14}N$ ratio is likewise terrestrial.

The permanently-shadowed polar volatiles of Mercury and the Moon require a similar kind of distillation model, as molecules "hop" randomly across their surface, often escaping but sometimes reaching the cold traps in these craters, where they accumulate. The elemental and isotopic fractionations occurring as a result of this process may be extreme. In the case of the Moon, spectra taken during the LCROSS impact plume experiment indicate a NH_3 abundance of $\sim$6% relative to H_2O (Colaprete et al. 2010)—a factor $\sim$6 enrichment in N/H relative to cometary and carbonaceous. As an even greater extreme, the ejecta plume had a $\sim$17% abundance of H_2S relative to H_2O—a factor $\sim$100 enrichment relative to cometary—but again, this is not surprising if sulfur's

substantial mass relative to oxygen is the cause for retention.

7. CONCLUSION

In this review, we present hydrogen and nitrogen cosmochemistry, from the ISM to evolved terrestrial planets, similarly (and alternatively) to how oxygen cosmochemistry has been treated (*e.g.*, Clayton 2003; Yurimoto et al. 2007). Although O-isotopes and C/O ratios are a more commonly explored topic in cosmochemistry— in part because the ^{16}O, ^{17}O, ^{18}O three-isotope system makes connections to physical fractionation processes more straightforward, and also because oxygen is a prominent constituent of all three phases of matter (gas, ice and rocks)—H and N systematics are sufficiently unique to merit their own discussion and application. Unlike oxygen, H and N are sufficiently volatile and low-mass to experience extreme fractionations, and unlike the noble gases they incorporate into a multitude of chemical species. Ultimately, the most information comes from simultaneously considering as many elemental and isotopic systems as possible, but the purpose of this review is to present the H and N separately as two complementary systems, and together as a single, self-contained and informative system.

In the course of this review we have identified many areas where future modeling or observations could prove valuable to our understanding of H and N cosmochemistry. Unambiguous determination of the most prominent N-bearing species in the ISM (N_2 gas, atomic N or N-ices) would further refine our cosmic inventory of this element. Direct imaging of water and N-bearing snowlines in protosolar disks would allow for better modeling of comet and planet formation zones. Abundance measurements of $^{15}NH_3$ in comets would provide more precise bulk $^{15}N/^{14}N$ values for comets. Chemical characterization of main-belt comets would test their hypothetically N-ice-poor formation environment at $\sim$3 AU. Better determination of N/H and isotopic ratios of the gas-giant planets would put further constraints on the putative solar-composition icy planetesimals. Lastly, isotopic measurements (particularly D/H) of the Martian polar ice caps, and Mercury's and the Moon's polar volatiles would further constrain the origin of these reservoirs.

REFERENCES

Aikawa, Y., 2003. Chemistry in protoplanetary disks. 25th meeting of the IAU, Joint Discussion 14.

Aikawa, Y., Nomura, H., 2008. Observations and modeling of gaseous protoplanetary disks. Phys. Scr. T130 014011.

Arpigny, C. et al., 2003. Anomalous nitrogen isotope ratio in comets. Science 301, 1522–1525.

Bergin, E.A., Aikawa,Y., Blake, G.A., van Dishoeck, E.F., 2007. The chemical evolution of protoplanetary disks. In: Protostars and Planets V, ed. B. Reipurth, D. Jewitt, K. Keil (Tucson, AZ: Univ. Arizona Press).

Bézard, B., Lellouch, E., Strobel, D., Maillard, J.P., Drossart, P., 2002. Carbon monoxide on Jupiter: Evidence for both internal and external sources. Icarus 159, 95–111.

Bézard, B., Yelle, R., Nixon, C.A., 2012. The composition of Titan's atmosphere. In: Titan—Surface, Atmosphere and Magnetosphere, Eds. I. Muller-Wodarg, C. Griffith, E. Lellouch and T. Cravens, Cambridge University Press.

Bockelée-Morvan, D., 2011. An overview of comet composition. Proc. IAU symp. 280, 261–274.

Bockelée-Morvan, D. et al., 2012. Herschel measurements of the D/H and $^{16}O/^{18}O$ ratios in water in the Oort-cloud comet C/2009 P1 Garrad. Astron. Astrophys. 544, L15.

Bogard, D.D., Clayton, R.N., Marti, K., Owen, T., Turner, G., 2001. Martian volatiles: Isotopic composition, origin, and evolution. Space Sci. Rev. 96, 425–458.

Brown, M.E., 2012. The compositions of Kuiper belt objects. Annu. Rev. Astron. Astrophys. 40, 467–494.

Busemann, H., Young, A.F., Alexander, C.M., Hoppe, P., Mukhopadhyay, S., Nittler, L.R., 2006. Interstellar chemistry recorded in organic matter from primitive meteorites. Science 312, 727–730.

Carr, M., 1987. Water on Mars: Its inventory, history and fate. Bull Am. Astron. Soc. 19, 815.

Cassen, P., 1994. Utilitarian models of the solar nebula. Icarus 112, 405–429.

Cheng, B.M. et al., 1999. Photo-induced fractionation of water isotopomers in the Martian atmosphere. Geophys. Res. Lett. 26, 3657–3660.

Clayton, R.N., 2003. Oxygen isotopes in the solar system. Space Sci. Rev. 106, 19–32.

Cody, G.D., Alexander, C.M., Tera, F., 2002. A chemical comparison of the organic solids from Orgueil, Murchison, and Tagish Lake. Meteorit. Planet. Sci. Supp. 37, A36.

Colaprete, A. et al., 2010. Detection of water in the LCROSS ejecta plume. Science 330, 463–468.

Crovisier, J., 2006. New trends in cometary chemistry. Faraday Discuss. 133, 375–385.

De Val-Borro, M. et al., 2012. An upper limit for the water outgassing rate of main-belt comet 176P/LINEAR observed with Herschel/HIFI. Astron. Astrophy. 546, L4.

Delsemme, A.H., 1999. The deuterium enrichment observed in recent comets is consistent with the cometary origin of seawater. Planet. Space Sci. 47, 125–131.

Eberhardt, P. et al., 1987. The D/H ratio in water from comet P/Halley. Astron. Astrophys. 187, 435–437.

Ehrenfreund, P., Charnley, S.B., 2000. Organic molecules in the interstellar medium, comets, and meteorites: A voyage from dark clouds to the early Earth. Annu. Rev. Astron. Astrophys. 38, 427–483.

Feuchtgreuber, H., Lellouch, E., Bézard, B., Encrenaz, T., de Graauw, T., Davis, G.R., 1999. Detection of HD in the atmospheres of Uranus and Neptune: A new determination of the D/H ratio. Astron. Astrophys. 341, L17–L21.

Fisher, D.A., 2007. Mars' isotope (D/H) history in the strata of the North Polar Cap: Inferences about the water cycle. Icarus 187, 430–441.

Floss, C. et al., 2006. Identification of isotopically primitive interplanetary dust particles: A NanoSIMS isotopic study. Geochim. Cosmochim. Acta 70, 2371–2399.

Fox, J.L., Hać, A., 1997. The $^{15}N/^{14}N$ isotope fractionation in dissociative recombination of N_2^+. J. Geophys. Res. 102, 9191–9204.

Gomes, R., Levison, H.F., Tsiganis, K., Morbidelli, A., 2005. Origin of the cataclysmic Late Heavy Bombardment period of the terrestrial planets. Nature 435, 466–469.

Greenwood, J.P., Itoh, S., Sakamoto, N., Warren, P., Taylor, L., Hisayoshi, Y., 2011. Hydrogen isotope ratios in lunar rocks indicate delivery of cometary water to the Moon. Nature Geoscience 4, 79–82.

Hartogh, P. et al., 2011. Ocean-like water in the Jupiter-family comet 103P/Hartley 2. Nature 478, 218–220.

Herbst, E., Klemperer, W., 1973. The formation and depletion of molecules in dense interstellar clouds. Astrophys. J. 185, 505–534.

Herzfeld, K.F., Teller, E., 1938. The vapor pressure of isotopes. Phys. Rev. 54, 912–915.

Hoefs, J., 2009. Stable isotope geochemistry. Springer-Verlag: Berlin Heidelberg, pp. 136–149.

Hogerheijde, M.R. et al., 2011. Detection of the water reservoir in a forming planetary system. Science 334, 338–340.

Holt, J.W. et al., 2008. Radar sounding evidence for buried glaciers in the southern mid-latitudes of Mars. Science 322, 1235.

Holweger, H., 2001. Photospheric abundances: Problems, updates, implications. In: Solar and Galactic composition (ed. R.F. Wimmer-Schweinsgruber). American Institute of Physics, pp. 23–30.

Hsieh, H.H., Jewitt, D.C., 2006. A population of comets in the main asteroid belt. Science 312, 561–563.

Iro, N., Gautier, D., Hersant, F., Bocklée-Morvan, D., Lunine, J.I., 2003. An interpretation of the nitrogen deficiency in comets. Icarus 161, 511–532.

Jehin, E. et al., 2008. Optical spectroscopy of the B and C fragments of comet 73P/Schwassmann-Wachmann 3 at the ESO VLT. LPSC Contribution No. 1405, paper id. 8319.

Jehin, E., Manfroid, J., Hutsemékers, D., Arpigny, C., Zucconi, J.M., 2009. Isotopic ratios in comets: Status and perspectives. Earth Moon Planet. 105, 167–180.

Jessberger, E.K., Christoforidis, A., Kissel, J., 1988. Aspects of the major element composition of Halley's dust. Nature 332, 691–695.

Kissel, J. et al., 1986. Composition of comet Halley dust particles from Giotto observations. Nature 321, 336–337.

Kowal, C.T., 1978. Surprise in the solar system. The Sciences 18, 12–15.

Krasnopolsky, V.A., Feldman, P.D., 2001. Detection of molecular hydrogen in the atmosphere of Mars. Science 294, 1914–1917.

Krot, A.N., Keil, K., Goodrich, C.A., Scott, E.R.D., Weisberg, M.K., 2005. Classification of meteorites. In: Meteorites, comets and planets: Treatise on Geochemistry, vol. 1. Elsevier, p. 83.

Lawrence, D.J. et al., in press. Evidence for water ice near Mercury's north pole from MESSENGER neutron spectrometer measurements. doi:10.1126/science.1229953.

Levison, H.F., Duncan, M.J., 1997. From the Kuiper belt to Jupiter-family comets: The spatial distribution of ecliptic comets. Icarus 127, 13–32.

Levison, H.F., Morbidelli, A., Van Laerhoven, C., Gomes, R., Tsiganis, K., 2008. Origin of the structure of the Kuiper belt during a dynamical instability in the orbits of Uranus and Neptune. Icarus 196, 258–273.

Levison, H.F., Duncan, M.J., Brasser, R., Kaufmann, D.E., 2010. Capture of the Sun's Oort cloud from stars in its birth cluster. Science 329, 190–193.

Licandro, J. et al., 2011. Testing the comet nature of main-belt comets: The spectra of 133P/Elst-Pizarro and 176P/LINEAR. Astron. Astrophys. 532, A65.

Manfroid, J. et al., 2009. The CN isotopic ratios in comets. Astron. Astrophys. 503, 613–624.

Manning, C.V., Zahnle, K.J., McKay, C.P., 2009. Impact processing of nitrogen on early Mars. Icarus 199, 273–285.

Maret, S., Bergin, E.A., Lada, C.J, 2006. A low fraction of nitrogen in molecular form in a dark cloud. Nature 442, 425.

Marty, B. et al., 2010. Nitrogen isotopes in the recent solar wind from the analysis of Genesis targets: Evidence for large scale isotope heterogeneity in the early solar system. Geochim. Cosmochim. Acta 74, 340–355.

McElroy, M.B., Kong, T.Y., Yung, Y.L., 1977. Photochemistry and evolution of the atmosphere of Mars: A Viking perspective. J. Geophys. Res. 82, 4379–4388.

McSween, H., Huss, G., 2010. Cosmochemistry. Cambridge University Press, Cambridge, pp. 54–84.

Melosh, H.J., Vickery, A.M., 1989. Impact erosion of the primordial atmosphere of Mars. Nature 338, 487–489.

Merlivat, L., Nief, G., 1967. Fractionnement isotopique lors des changements détat solide-vapeur et liquide-vapeur de l'eau à des températures inférieures à 0°C. Tellus 19, 122–127.

Messenger, S., 2000. Identification of molecular-cloud material in interplanetary dust particles. Nature 404, 968.

Meyer, B.S., Bojazi, M.J., 2011. Production of nitrogen-15 in explosive helium burning and supernova presolar grains. LPSC Contribution No. 1608, p.2376.

Moores, J.E., Brown, R.H., Lauretta, D.S., Smith, P.H., 2012. Experimental and theoretical simulation of sublimating dusty water ice with implications for D/H ratios of water ice on comets and Mars. Planetary Science 1, 2.

Morbidelli, A., Lunine, J.I., O'Brien, D.P., Raymond, S.N., Walsh, K.J., 2012. Building terrestrial planets. Annu. Rev. Earth Planet. Sci. 40, 251–275.

Mumma, M.J., Charnley, S.B., 2011. The chemical composition of comets—Emerging taxonomies and natal heritage. Annu. Rev. Astron. Astrophys. 49, 471–524.

Mustard, J.F., Poulet, F., Ehlmann, B.L., Miliken, R., Fraeman, A., 2012. Sequestration of volatiles in the Martian crust though hydrated minerals: A significant planetary reservoir of water. LPSC Contribution No. 1659, id.1539.

Niemann, H.B. et al., 1998. The composition of the Jovian atmosphere as determined by the Galileo probe mass spectrometer. J. Geophys. Res. 103 22831–22846.

Nozette, S. et al., 1996. The Clementine bistatic radar experiment. Science 274, 1495–1498.

Owen, T., 2008. The contributions of comets to planets, atmospheres, and life: Insights from Cassini-Huygens, Galileo, Giotto, and inner planet missions. Space Sci. Rev. 138, 301–316.

Owen, T., Encrenaz, T., 2006. Compositional constraints on giant planet formation. Planet. Space Sci. 54, 1188–1196.

Owen, T., Biemann, K., Biller, J.E., Lafleur, A.L., Rushneck, D.R., Howarth, D.W., 1977. The composition of the atmosphere at the surface of Mars. J. Geophys. Res. 82, 4635–4639.

Owen, T., Mahaffy, P., Niemann, H.B., Atreya, S., Donahue, T., Bar-Nun, A., de Pater, I., 1999. A low-temperature origin for the planetesimals that formed Jupiter. Nature 402, 269–270.

Palme, H., Jones, A., 2005. Solar system abundances of the elements. In: Meteorites, comets and planets: Treatise on Geochemistry, vol. 1. Elsevier, p. 41.

Phillips, R.J. et al., 2008. Mars north polar deposits: Stratigraphy, age, and geodynamical response. Science 320, 1182–1185.

Pilbratt, G.L. et al., 2010. Herschel Space Observatory. An ESA facility for far-infrared and submillimetre astronomy. Astron. Astrophys. 518, L1.

Pizzarello, S., Cooper, G.W., Flynn, G.J., 2006. The nature and distribution of organic material in carbonaceous chondrites and interplanetary dust particles. In: Meteorites and the Early Solar System II, D. S. Lauretta and H. Y. McSween Jr. (eds.), University of Arizona Press, Tucson, 943 pp., p.625–651.

Plaut, J.J. et al., 2007. Subsruface radar sounding of the south polar layered deposits of Mars. Science 316, 92.

Pollack, J.B., Hubickyj, O., Bodenheimer, P., Lissaur, J.J., Podolak, M., Greenzweig, Y., 1996. Formation of the giant planets by concurrent accretion of solids and gas. Icarus 124, 62–85.

Robert, F., 2006. Solar system deuterium/hydrogen ratio. In: Meteorites and the Early Solar System II, D. S. Lauretta and H. Y. McSween Jr. (eds.), University of Arizona Press, Tucson, 943 pp., p.341–351.

Robert, F., 2011. A distinct source for lunar water? Nature Geoscience 4, 74–75.

Savage, B.D., Sembach, K.R., 1996. Interstellar abundances from absorption-line observations with the Hubble Space Telescope. Annu. Rev. Astron. Astrophys. 34, 279–330.

Schorghofer, N., 2008. The lifetime of ice on main belt asteroids. Astrophys. J. 682, 697–705.

Schultz, P.H., Hermalyn, B., Colaprete, A., Ennico, K., Shirley, M., Marshall, W.S., 2010. The LCROSS cratering experiment. Science 330, 468–472.

Shinnaka, Y. et al., 2011. Ortho-to-para abundance ratio (OPR) of ammonia in 15 comets: OPRs of ammonia versus $^{14}N/^{15}N$ ratios in CN. Astrophys. J. 729, 81.

Simon, S.B. et al., 2008. A refractory inclusion returned by Stardust from comet 81P/Wild 2. Meteorit. Planet. Sci. 43, 1861–1877.

Slade, M.A., Butler, B.J., Muhleman, D.O., 1992. Mercury radar imaging: Evidence for polar ice. Science 258, 635–640.

Tsiganis, K., Gomes, R., Morbidelli, A., Levison, H.F., 2005. Origin of the orbital architecture of the giant planets of the solar system. Nature 435, 459–461.

Ward, W.R., 1997. Protoplanet migration by nebula tides. Icarus 126, 261–281.

Walsh, K.J., Morbidelli, A., Raymond, S.N., O'Brien, D.P., Mandell, A.M., 2011. A low mass for Mars from Jupiter's early gas-driven migration. Nature 475, 206–209.

Yung, Y.L., Wen, J., Pinto, J.P., Pierce, K.K., Allen, M., 1988. HDO in the Martian atmosphere: Implications for the abundance of crustal water. Icarus 76, 146–159.

Yurimoto, H., Kuramoto, K., Krot, A.N., Scott, E.R.D., Cuzzi, J.N., Thiemens, M.H., Lyons, J.R., 2007. Origin and evolution of oxygen isotopic compositions of the solar system. In: Protostars and Planets V, B. Reipurth, D. Jewitt, and K. Keil (eds.), University of Arizona Press, Tucson, pp.849–862