

# The Chemical Composition of Comets—Emerging Taxonomies and Natal Heritage

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## Keywords

astrochemistry, cometary molecules, interstellar molecules, nuclear spin temperatures, ortho-para ratios, primary volatiles

## Abstract

Cometary nuclei contain the least modified material from the formative epoch of our planetary system, and their compositions reflect a range of processes experienced by material prior to its incorporation in the cometary nucleus. Dynamical models suggest that icy bodies in the main cometary reservoirs (Kuiper Belt, Oort Cloud) formed in a range of environments in the protoplanetary disk, and (for the Oort Cloud) even in disks surrounding neighboring stars of the Sun's birth cluster. Photometric and spectroscopic surveys of more than 100 comets have enabled taxonomic groupings based on free radical species and on crystallinity of rocky grains. Since 1985, new surveys have provided emerging taxonomies based on the abundance ratios of primary volatiles. More than 20 primary chemical species are now detected in bright comets. Measurements of nuclear spin ratios (in water, ammonia, and methane) and of isotopic ratios (D/H in water and HCN; <sup>14</sup>N/<sup>15</sup>N in CN and HCN) have provided critical insights on factors affecting formation of the primary species. The identification of an abundant product species (HNC) has provided clear evidence of chemical production in the inner coma. Parallel advances have occurred in astrochemistry of hot corinos, circumstellar disks, and dense cloud cores. In this review, we address the current state of cometary taxonomy and compare it with current astrochemical insights.

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**Primary volatile:**

a chemical species stored as ice in the cometary nucleus and released as gas into the coma

**Cometary nucleus:**

a massive body composed of ices and rocky materials, formed in the protoplanetary disk

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## 1. INTRODUCTION

In his pioneering study of comet Encke, Fred Whipple proposed that escaping gases impose reaction forces on a solid body (the nucleus) at the core of a cometary coma, causing the comet to return to perihelion slightly earlier than expected. He envisioned the nucleus as an “icy conglomerate” composed of refractory (meteoritic) dust and native (primary) ices, whose sublimation upon warming created the visible coma and tails so familiar to ground-based observers (Whipple 1950). In so doing, Whipple adopted and extended Pol Swings’ suggestion that the nucleus of comet Encke contained polyatomic molecular ices, whose release and dissociation produced the free radical species observed at optical wavelengths (Swings 1948a,b). Whipple further proposed that water ice was dominant, with ices of methane, ammonia, and other species present in smaller amounts. Whipple and Swings suggested that the polyatomic molecules stored in the nucleus were of interstellar origin and, thus, of primary importance for understanding planetary origins.

This proposal triggered a decades-long race to detect the proposed primary (parent) volatiles through astrophysical spectroscopy, leading in 1985 to definitive detections of hydrogen cyanide and water vapor in the coma of comet 1P/Halley (Despois et al. 1986, Mumma et al. 1986, Schloerb et al. 1986, Weaver et al. 1986). In 1986, in situ measurements by a fleet of spacecraft confirmed these discoveries, added ten more species to the suite of known primary volatiles, and acquired images of a cometary nucleus for the first time (Praderie & Grewing 1987, Eberhardt 1999). The combined results decisively confirmed the Whipple-Swings model of the icy conglomerate nucleus.

Today, we recognize that the composition and structure of cometary nuclei are keys to understanding the formation and evolution of matter in the early Solar System (Mumma, Weissman & Stern 1993; Irvine et al. 2000; Bockelée-Morvan et al. 2004). Compared with dust, the ices are more sensitive to changes induced by thermal and radiation processing, so their identities and abundances can provide central clues to those aspects of planetary heritage.

Since 1986, ground-based capabilities have expanded rapidly; today, many primary volatile species are measured routinely in a moderately active comet. Improvements in sensitivity now permit measurement of primary volatiles at abundances as small as 100 ppm (relative to H<sub>2</sub>O). To date, more than 20 comets have been characterized in this way, and we now can build an emerging taxonomy based on cosmogonic parameters such as composition, isotopic fractionation, and nuclear spin temperatures of primary volatiles, along with dust signatures such as crystallinity and mineralogy. This taxonomy is crucial for extrapolating in-depth analytical information obtained from the few comets sampled directly to the many sampled only remotely. Relating those few comets to the various populations of icy planetesimals is a critical step for testing models of the evolution of material from the natal interstellar cloud core through entry into the protoplanetary disk, possible processing in the disk, formation of the final icy bodies, and injection into their cosmic reservoirs. With the aid of dynamical models, the new taxonomy will also help to establish the significance of each cometary class for exogenous delivery of organics and water to terrestrial planets.

In this review, we briefly compare groupings based on primary volatiles with groupings inferred from measurements of free radical species and show that the former approach provides additional key parameters that further test the taxonomic classification and its relationship to cometary origins. We discuss the emerging taxonomy obtained from primary volatiles in the context of early ejection from the giant planets’ feeding zones and of later disruption of an outer disk of icy planetesimals (17–30 AU) triggered by giant-planet migration.

We then introduce other extracted molecular parameters such as the nuclear spin temperature and isotopic enrichment factors, and show how formation temperatures indicated by these parameters can relate to the organic class and to formation distance from the young Sun. The relationship

to interstellar ices is mentioned as a means of identifying chemical changes in pre-cometary ices during the journey from the natal interstellar cloud core. We next address the delivery of water and organics to the terrestrial planets' region by comets, marrying the dynamical dispersion of icy planetesimals formed in diverse regions of the protoplanetary disk with the emerging taxonomy. Together they provide crucial insights into the delivery of water and prebiotic organics to early Earth.

Finally, we mention key contextual insights obtained from recent visits to three short-period comets. Relatively few comets can be visited directly, but those visits can provide a wealth of information through in situ investigations and return of authentic samples for detailed analysis in terrestrial laboratories. Insights gained from the controlled excavation of 9P/Tempel 1 by *Deep Impact*, by analysis of samples returned from 81P/Wild 2 by *Stardust*, and by the space- and Earth-based investigations of 103P/Hartley 2 demonstrate the value and importance of such missions and emphasize the promise of the coming *Rosetta* rendezvous with comet 67P/Churyumov-Gerasimenko along with the importance of future returns of cometary material. The fundamental advances gained from studies of these few comets provide critically important ground truth for interpreting and expanding the taxonomies derived from the much larger general cometary populations.

## 2. FORMATIVE REGIONS OF KUIPER BELT AND OORT CLOUD COMETS

Cometary nuclei today reside in (at least) two distinct reservoirs, the Oort Cloud (OC) and the Kuiper Belt (KB) (divided into the classical KB, the scattered disk, and the detached or extended disk populations) (Morbidelli, Levison & Gomes 2008). The detection of apparently active bodies in the main asteroid belt has provided evidence for a possible third reservoir for icy bodies, but little is known about their compositions or even their proposed volatile activity. Once injected into the inner planetary system, comets are classified dynamically as nearly isotropic [long-period comet (LPC) or Halley-type comet (HTC)] or ecliptic [Centaur-type, Encke-type, or Jupiter-family comet (JFC)]. The Tisserand parameter ( $T_j$ ) of its current orbit identifies the storage reservoir from whence a given comet came, revealing that ecliptic comets come from the scattered KB reservoir, whereas the storage reservoir for nearly isotropic comets (NICs) is the OC (Levison 1996; see also Horner et al. 2003).

### 2.1. From Formative Regions of Constituents and Cometary Nuclei to Reservoirs

Until recently, it was thought that most JFCs formed in the KB region ( $R_h > 30$  AU), whereas OC comets formed in the giant planets' region (5–30 AU). If so, the expected strong radial variations in temperature and other conditions in the protoplanetary disk should appear as distinct compositions for comets in these two populations, and each reservoir should be distinct (Mumma, Weissman & Stern 1993; Boss 1998). However, a new paradigm emerged in 2005, the Nice model (Gomes et al. 2005, Morbidelli et al. 2005). In this model, the migration of Saturn into 1:2 orbital resonance with Jupiter may have triggered disruption of an outer disk of icy planetesimals (15–35 AU) and of a massive primordial asteroid belt (Tsiganis et al. 2005; O'Brien, Morbidelli & Bottke 2006).

The Nice model predicts that comets ejected from the outer disk (beyond  $R_h \sim 15$  AU) later entered both the OC and the Kuiper Belt, though likely in different proportions [Crovisier 2007; see also A. Morbidelli, unpublished (astro-ph/0512256)]. Comets that formed in (and were ejected from) the giant-planet feeding zones (5–14 AU) probably entered the OC and the outer disk (Dones et al. 2004a,b). Subsequent disruption of the outer disk contributed some of the mass

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**Short-period comet:** a comet whose orbital period is less than ~200 years

**Kuiper Belt (KB):** a trans-Neptunian flattened disk of inactive comet nuclei at heliocentric distances ranging from ~30 AU to ~100 AU.

**Oort Cloud (OC):** a distant reservoir of inactive comet nuclei at heliocentric distances ranging from ~10,000 AU to ~50,000 AU

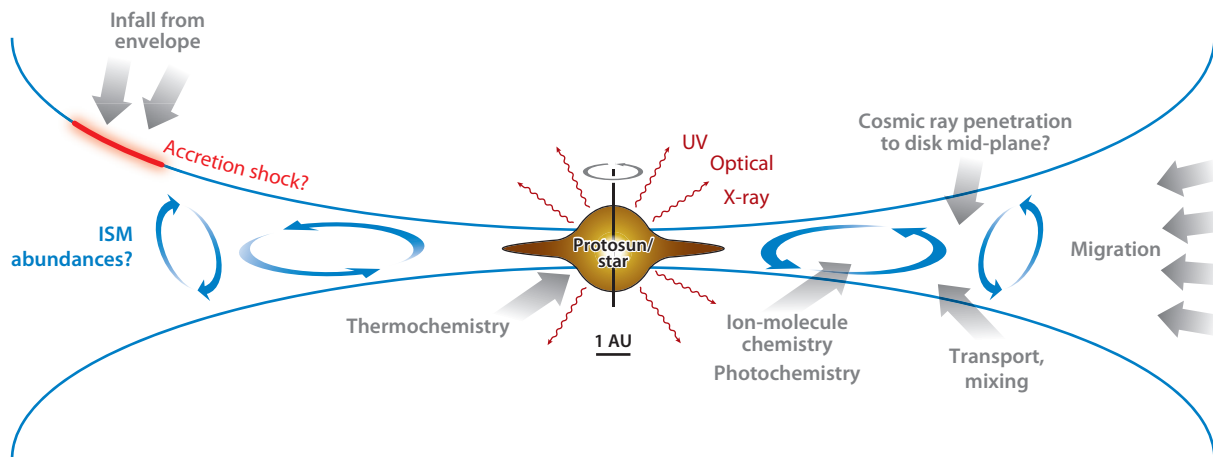
**Long-period comet (LPC):** a comet whose orbital period greatly exceeds ~200 years

**Jupiter-family comet (JFC):** a comet whose orbit is strongly influenced by Jupiter's gravitation

**Tisserand parameter ( $T_j$ ):** an approximation to the Jacobi constant, which is an exact integral of motion in the circular restricted 3-body problem; comets with  $2 < T_j < 3$  belong to Jupiter's dynamical family, whereas those with  $-2 < T_j < 2$  are NICs

**Ecliptic comet:** a short-period comet whose orbit is inclined by less than  $35^\circ$  from the ecliptic plane, and whose Tisserand parameter is greater than 2

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**Figure 1**

Processes affecting material in the protoplanetary nebula during planetary system formation (NASA and M.J. Mumma 2004). Major advances since 2000 include the introduction of new models for dynamical dispersion in the protoplanetary disk, confirmation of large-scale radial transport of rocky material from the near-solar region to the comet-forming region, and the development of new models for enhanced ion-molecule chemistry through X-ray ionization of nebular  $H_2$ .

impacting Earth during the Late Heavy Bombardment and could have contributed a portion of Earth's oceans (Gomes et al. 2005). A key issue is whether the composition of icy planetesimals in the outer disk (15–35 AU) differed from those formed in the inner disk (5–15 AU) prior to formation of the giant planets. In 2010, another new dynamical model appeared, suggesting that up to 90% of comets in the OC may have been captured from sibling stars in the Sun's birth cluster (Levison et al. 2010). If so, such comets may contain strong signatures of this natal heritage.

Knowledge of interstellar volatiles (gaseous and condensed) has advanced greatly in recent years through enhanced theoretical models, study of laboratory analogs, and astrophysical observations (Ehrenfreund et al. 1999, Charnley & Rodgers 2008, Herbst & van Dishoeck 2009). Laboratory studies of interplanetary dust particles (IDPs) suggest that some comets do contain interstellar mineral moieties, but samples returned (*Stardust*) from 81P/Wild 2 contain minerals processed strongly near the Sun, and many other comets reveal spectral signatures of crystalline silicates that seem to require high-temperature processing. Cometary ices also show strong differences—ices in some comets mimic interstellar ice chemistry, whereas others show strong evidence of processing in the Solar Nebula (Irvine et al. 2000). Aspects of such processing are illustrated in **Figure 1**.

Constraining the place of origin of precometary materials and the processes that attended their formation and subsequent evolution requires knowledge of the comet's native composition (elemental, chemical, isotopic) and cosmogonic parameters (nuclear spin species, mineralogy, crystallinity, etc.). By comparing the compositions of ecliptic comets and NICs—as well as both of these with aspects of interstellar volatiles—the emerging taxonomies may provide useful tests of these models for cometary origin.

## 2.2. Ground Truth for Cometary Taxonomies: 1P/Halley, 81P/Wild 2, and 103P/Hartley 2

In recent decades, it has become increasingly evident that certain types of asteroids and the (even more primitive) comets are rich in diverse classes of organic compounds. An improved

### Nearly isotropic comet (NIC):

a member of a population of comets deriving from the Oort Cloud, whose orbits are nearly randomly inclined to the ecliptic and whose periods greatly exceed ~200 years

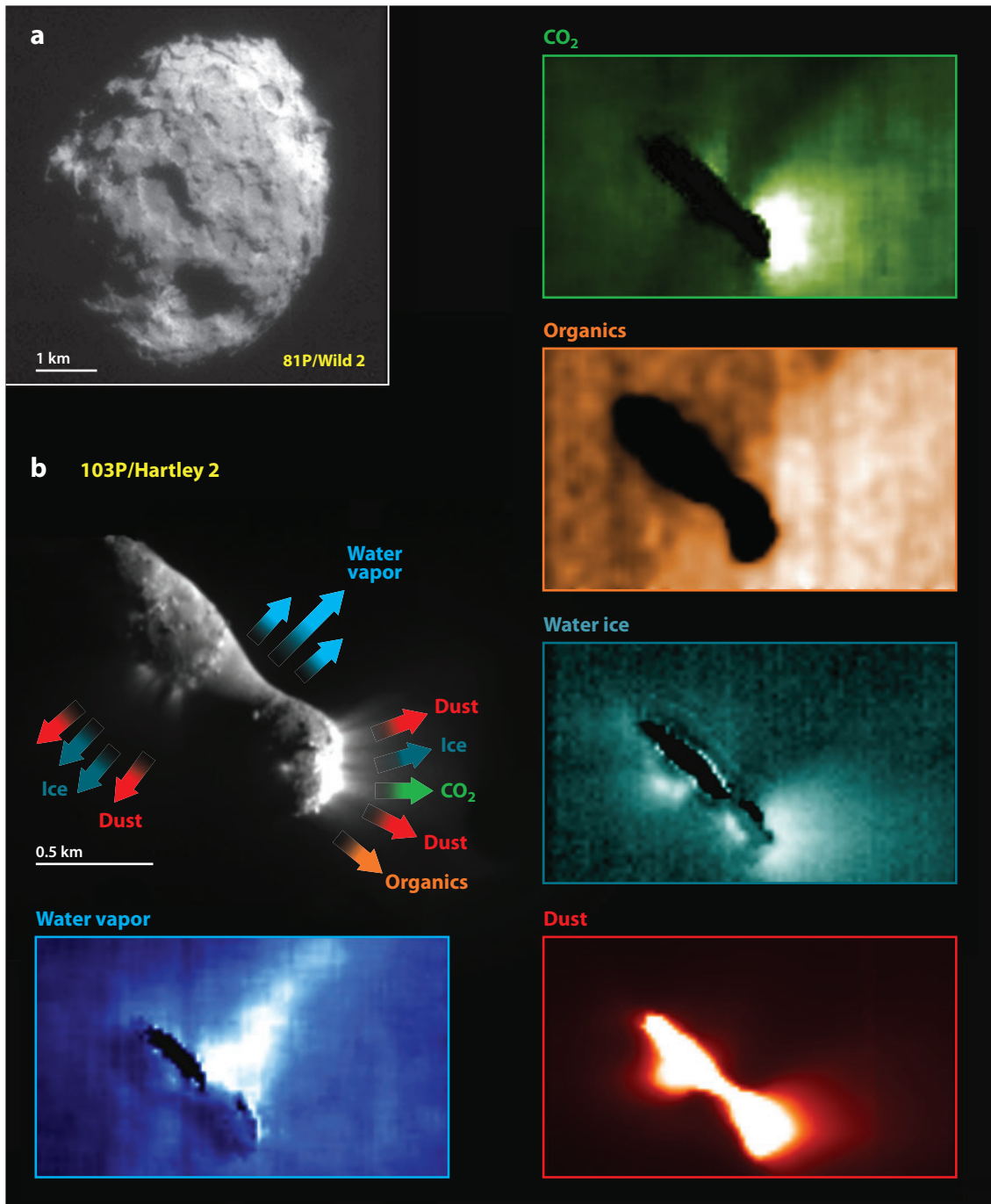
understanding of the organic composition of (and chemistry in) certain asteroid types is derived from increasingly detailed characterization of the carbonaceous meteorites that are believed to originate in the 2- to 4-AU region of the asteroid belt (Cronin 1998, Gilmour 2003). The rapid increase in our knowledge of comets has come from flyby missions to comet 1P/Halley in the mid-1980s (Praderie & Grewing 1987), improved remote sensing observations of comets from the mid-1990s onward (Mumma et al. 2003, Bockelée-Morvan et al. 2004, Crovisier 2006, DiSanti & Mumma 2008), the controlled excavation of 9P/Tempel 1 (*Deep Impact*, 2005; see A'Hearn et al. 2005; A'Hearn & Combi 2007a,b), the collection and return of dust grains from comet 81P/Wild 2 by *Stardust* (Brownlee et al. 2006), and the flyby of 103P/Hartley 2 during the EPOXI mission (A'Hearn et al. 2011, Meech et al. 2011).

Wild 2 was injected into its present orbit by a close encounter with Jupiter in 1974. Its surface morphology is highly unusual among imaged comets in showing extreme surface relief and unusual circular features (**Figure 2a**). Laboratory analyses of mineral grains returned from comet Wild 2 provided clear evidence of their processing near the young Sun, but little information was gained on the volatile fraction of this comet—frustrating its use as a witness sample for the emerging cometary taxonomy based on volatile composition. A remarkable exception is the evidence for glycine, the simplest amino acid and an important building block for terrestrial life (Elsila, Glavin & Dworkin 2009). In addition, methyl and ethyl cyanide were recovered from returned *Stardust* foils exposed to cometary gas, in ratios that mimic the methane/ethane ratios in many comets (Glavin, Dworkin & Sandford 2008).

The coordinated flyby of 103P/Hartley 2 during the EPOXI mission and the world-wide observing campaign during its recent near-Earth approach have provided remarkable images of the nucleus at radar (Harmon et al. 2011) and optical wavelengths (**Figure 2b**, and the companion article, A'Hearn 2011), along with much new information on the composition and heterogeneity of this Jupiter-family comet. That Hartley 2 was enriched in CO<sub>2</sub> (~10–20% relative to H<sub>2</sub>O) was known since its 1997 apparition (Colangeli et al. 1999, Crovisier et al. 1999)—EPOXI results confirm the larger value (near ~20%, however, optical depth effects are still being addressed, L.M. Feaga, private communication). By contrast, CO was unusually sparse (~0.15–0.45%; Weaver et al. 2011). Spectral maps of gaseous water and carbon dioxide, and of water ice, identified large differences in the spatial properties of their release from the nucleus (**Figure 2b**) and revealed that CO<sub>2</sub> sublimation controlled the release of large chunks of water ice from the small end of the nucleus. The production rate of water varied by a factor of two in accord with nucleus rotation; but CO<sub>2</sub> seemingly varied by a smaller factor, and this difference suggests compositional heterogeneity of the nucleus.

In ground-based data, the production rates of other primary volatiles (H<sub>2</sub>O, C<sub>2</sub>H<sub>6</sub>, HCN, CH<sub>3</sub>OH) also varied strongly with rotational phase (Dello Russo et al. 2011, Drahus et al. 2011, Mumma et al. 2011), but their abundance ratios remained constant over the three-month interval encompassing the EPOXI flyby (Mumma et al. 2011). The spatial profiles of individual volatile species (e.g., H<sub>2</sub>O and C<sub>2</sub>H<sub>6</sub>) differed substantially, suggesting the presence of two separate ice phases (polar and apolar) or even three (two being apolar) if CO<sub>2</sub> and ethane are not comingled in the nucleus (Mumma et al. 2011).

ISO observations of Hartley 2 in 1997 returned ortho-para abundance ratio (OPR) for H<sub>2</sub>O of  $2.76 \pm 0.08$  and  $2.63 \pm 0.18$ , and  $T_{\text{spin}}$  of  $34 \pm 3$  K (Crovisier et al. 1999). In 2010, Mumma et al. (2011) obtained an OPR in H<sub>2</sub>O of  $2.85 \pm 0.20$  (1 $\sigma$ )—the upper bound (3.05) is consistent with statistical equilibrium ( $T_{\text{spin}} > \sim 55$  K); the lower bound (2.65) defines  $T_{\text{spin}} > 32$  K (see Section 4). Dello Russo et al. (2011) reported OPR =  $3.4 \pm 0.3$  (1 $\sigma$ ). In H<sub>2</sub>O<sup>+</sup> and NH<sub>2</sub>, OPRs provided spin temperatures of  $>25$  K and  $33 \pm 3$  K, respectively (E. Jehin, private communication, as reported by Meech et al. 2011). This data set also provided isotopic ratios for <sup>12</sup>C/<sup>13</sup>C ( $95 \pm 15$ )



and  $^{14}\text{N}/^{15}\text{N}$  ( $155 \pm 25$ ) in CN that were consistent with the mean values reported for other comets (see Section 5.2).

The ratio of D/H in  $\text{H}_2\text{O}$ ,  $(16.1 \pm 2.4) \times 10^{-5}$ , agrees with Vienna Standard Mean Ocean Water (VSMOW) (Hartogh et al. 2011), the first determination for a comet from the Kuiper Belt (Section 5.1). This value is consistent with models for radial transport of precometary material from the inner Solar System outward to the comet-forming region. Spectral lines of  $\text{H}_2^{16}\text{O}$  are optically thick; and radial and azimuthal variations in density and temperature are expected, making optical depth corrections for them difficult to constrain uniquely. To avoid this difficulty, lines of HDO were compared with those of  $\text{H}_2^{18}\text{O}$  (in VSMOW, the two isotopologues appear in the abundance ratio  $\text{H}_2^{18}\text{O}/\text{HDO} = 6.4368$ ). If lines of both isotopologues are optically thin in Hartley 2, these measurements should return the true ratio ( $\text{H}_2^{18}\text{O}/\text{HDO}$ ) in Hartley 2. Assuming  $^{18}\text{O}/^{16}\text{O}$  to be the same as in VSMOW (Section 5.1), the D/H enrichment factor in Hartley 2 follows directly. The estimates for cometary delivery of Earth's water will need to be re-examined in light of this result.

The combined results permit a tentative placement of Hartley 2 within the emerging taxonomy based on volatile composition (Sections 3–5), but the full picture has yet to be viewed.

The coming decade should provide much more detailed chemical and organic characterization of these primitive bodies, through in-depth analyses of authentic samples, as well as continued studies of IDPs and various meteorite classes. Continued ground- and space-based observations will greatly extend the composition-based cometary taxonomy discussed herein and also will expand the known compositional diversity of asteroids and trans-Neptunian objects (Cruikshank et al. 2007). The recent discovery of apparently icy bodies in the main asteroid belt has stimulated considerable interest, though as yet the volatile fraction in them is poorly characterized.

When coupled with new views of chemical processing during the nebular phase (**Figure 1**) and of dynamical evolution during the first billion years of Solar System history, these advances present an opportunity to construct an integrated (and testable) model for the origins and delivery of organics and water to terrestrial planets.

### 3. PRIMARY AND PRODUCT VOLATILES IN COMETS

Active comets have long been grouped according to their orbital properties, and this has proven useful for identifying the reservoir from which a given comet emerged (OC, KB) (Levison 1996). However, it is now clear that icy bodies were scattered into each reservoir from a range of nebular distances and the populations in today's reservoirs thus share origins that are (in part) common. Moreover, Levison et al. 2010 suggest that a large fraction of the comets now in the OC may have been captured from stars in the Sun's birth cluster, before clearing of gas in the natal interstellar cloud; if so, a fraction of OC comets should reflect that origin and history.

Being the least modified bodies in the Solar System, the composition of comets should provide useful tests of the current theories and establish observational constraints that future models must

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#### Figure 2

The nuclei of two ecliptic comets. (a) The nucleus of comet 81P/Wild 2, imaged by *Stardust* (credit: NASA, JPL, and *Stardust* Team). Wild 2 was injected into its current orbit only recently, and its shape and morphology show few erosional effects. The circular areas and extreme vertical relief are not smoothed, and extreme spires are seen at the limb (Brownlee et al. 2004). (b) The nucleus of 103P/Hartley 2 imaged by *Deep Impact* (NASA, University of Maryland, and EPOXI Team). Hartley 2 is remarkably smooth on large scales, suggesting extensive erosional smoothing through mass wasting over many perihelion passages. Spectral maps reveal chemical heterogeneity in the gaseous release of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Water ice is associated with  $\text{CO}_2$  release, but not with the  $\text{H}_2\text{O}$  vapor released from the waist region. Adapted from A'Hearn et al. 2011.

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**Product volatile:**

a chemical species produced in the coma by destruction of a precursor or by chemical reactions

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satisfy. For that reason, increasing emphasis has been placed on classifying comets according to the composition of native ices and dust (rather than orbital dynamics). In recent years, surveys based on abundance measurements of product volatiles have been augmented by those based on abundance measurements of primary volatiles (native to the cometary nucleus) along with their nuclear spin temperatures (e.g., for  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{CH}_4$ ) and isotopic ratios (e.g.,  $\text{HDO}/\text{H}_2\text{O}$ ,  $\text{HC}^{14}\text{N}/\text{HC}^{15}\text{N}$ , and  $\text{C}^{14}\text{N}/\text{C}^{15}\text{N}$ ). Surveys based on dust properties are also underway, especially using the crystalline silicates as a signature of radial transport outward from the terrestrial planets region.

### 3.1. Taxonomies Based on Product Volatiles

The most complete compositional surveys are those based on product species. Free radical species [e.g.,  $\text{O}(^1\text{D})$ ,  $\text{CN}$ ,  $\text{C}_2$ ,  $\text{C}_3$ ,  $\text{OH}$ ,  $\text{NH}$ , and  $\text{NH}_2$ ] are produced in the cometary coma, from often uncertain precursors. Principal production mechanisms include photolysis and/or photoionization of gaseous precursors, chemical reactions among coma gases (neutral-neutral or ion-neutral collisions), and destruction of refractory organics on grains. (For a general review, see Feldman, Cochran & Combi 2004.) The species produced are termed product species in this review, because terms such as daughter or granddaughter imply a known functional derivation from an identified precursor, whereas the term secondary could imply a known generational relationship.

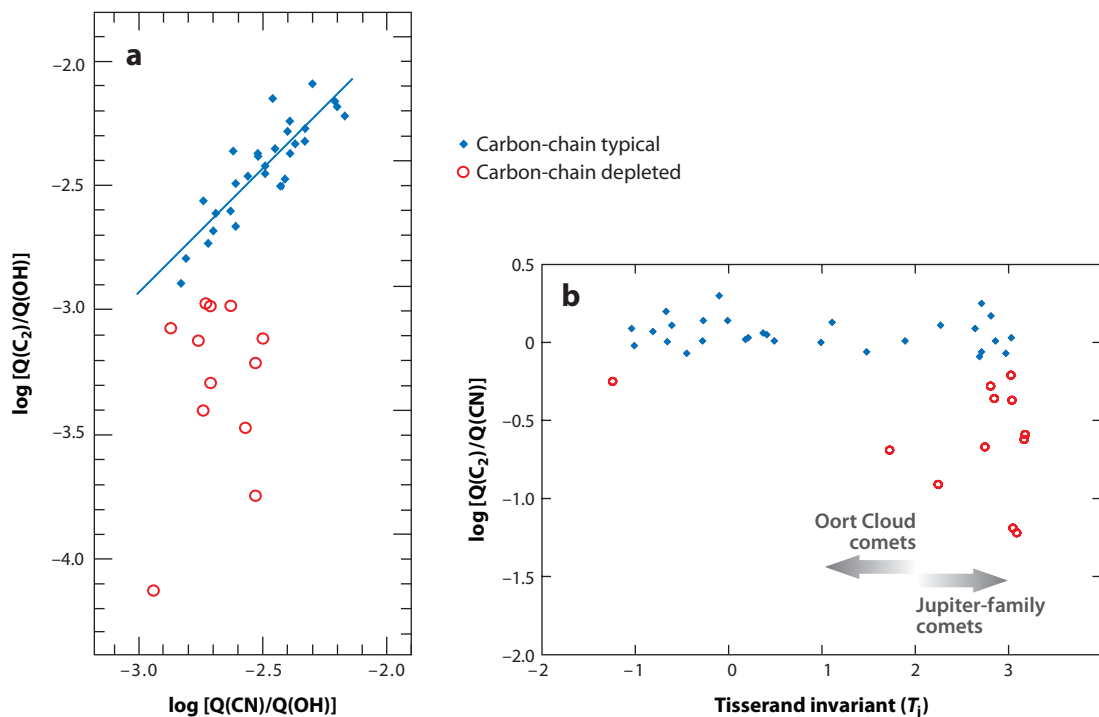
The  $\text{O}(^1\text{D})$  radical is produced by photolysis of  $\text{H}_2\text{O}$  (and by photolysis of  $\text{CO}$  and  $\text{CO}_2$ , to a lesser degree), and it emits a photon within minutes of its formation. This (prompt) emission traces the spatial distribution of its precursor molecule(s) (mainly water) in the coma, because optical pumping of the oxygen atom to  $(^1\text{D})$  from its ground electronic state  $(^3\text{P})$  is strongly forbidden. The other product species ( $\text{CN}$ ,  $\text{C}_2$ ,  $\text{NH}_2$ , etc.) are seen in solar pumped fluorescence, and complex models are used to constrain their production rates and possible precursors.

Combinations of these product species have been targeted by extensive compositional surveys at optical wavelengths (Newburn & Spinrad 1989, Cochran et al. 1992, A'Hearn et al. 1995, Fink & Hicks 1996, Fink 2009, Langland-Shula & Smith 2011), leading to taxonomic classifications by Fink (2009), A'Hearn et al. (1995), and Langland-Shula & Smith 2011. Four product species are also targeted individually for their intrinsic cosmogonic parameters, i.e., nuclear spin properties in  $\text{NH}_2$  and  $\text{H}_2\text{O}^+$  (see Section 4) and isotopic signatures of  $\text{D}/\text{H}$  in  $\text{OH}$  (Section 5.1) and  $^{14}\text{N}/^{15}\text{N}$  in  $\text{CN}$  (Section 5.2).

The compositional surveys produced massive databases of production rates for gases and dust, and they allowed identification of diversities and similarities in coma composition and gas-to-dust ratio among comets. Data exist for about two-thirds of the 246 currently known (numbered) periodic comets and for more than 60 unnumbered ones (mainly NICs). For ecliptic comets (mainly of the Jupiter family), data are often available for multiple apparitions. The individual surveys have not been combined into a single database, as common agreement would be needed on which procedure and which parameters to apply when calculating gas production rates from photometric fluxes.

A'Hearn et al. (1995) conducted a photometric survey of 85 comets, of which 41 were sufficiently well studied to form a restricted set for taxonomic classification. Based on filter photometry of five product species ( $\text{OH}$ ,  $\text{CN}$ ,  $\text{C}_2$ ,  $\text{C}_3$ , and  $\text{NH}$ ) and continuum (dust), this survey offers good coverage of the principal product species observed in the wavelength range 300–700 nm.  $\text{OH}$  serves as a proxy for water, but this is fluorescence from quiescent  $\text{OH}$  and not the prompt emission observed at IR wavelengths (denoted  $\text{OH}^*$ ) or the prompt  $\text{O}(^1\text{D})$  sampled by Fink (see below). The latter two prompt emissions follow the spatial distribution of the primary  $\text{H}_2\text{O}$  species, whereas the fluorescent  $\text{OH}$  follows the general distribution of quiescent  $\text{OH}$  in the coma and is thus less





**Figure 3**

Relative production rates for C<sub>2</sub>, CN, and OH in comets. (a) Identification of two distinct groups based on the C<sub>2</sub>/CN ratio. The solid line has a slope of unity. (b) The fraction of comets that are carbon-chain depleted (*open circles*) is greater among ecliptic comets ( $2 < T_j < 3$ ) than among nearly isotropic comets ( $T_j < 2$ ). Adapted from A’Hearn et al. 1995.

direct and its interpretation is more dependent on coma models. This survey led to the major discovery that a significant number of comets (most are ecliptic comets of the Jupiter family) are depleted in carbon-chain molecules, best recognized in the C<sub>2</sub>/CN production rate ratio (**Figure 3**). The term carbon-chain must not be taken too literally because only HCN and HC<sub>3</sub>N have been detected in comets, whereas true chains with up to 11 carbon atoms (e.g., cyanopolyynes, HC<sub>2n+1</sub>N,  $n = 1, 2, \dots$ ) are known in the ISM and have an identified causal link amongst members. Although correlated in abundance, the causal relation (if any) of C<sub>2</sub> and C<sub>3</sub> in comets is unknown—they may originate from different chemical pathways.

A’Hearn et al. suggested a taxonomy distinguishing comets with typical versus depleted carbon-chain abundance (based mainly on the C<sub>2</sub>/CN ratio), a distinction that has proven to be reasonable and useful. The number of objects sampled provides statistics adequate to conclude that the fraction of depleted comets is higher among ecliptic comets than among NICs (**Figure 3b**). However, the survey found that the origins of these product species varied, with most CN and some C<sub>2</sub> (but virtually no NH) produced from dust grains rather than from nuclear ices. Moreover, the production rates of C<sub>2</sub> and CN are known to vary along a comet’s orbit, and most comets were observed over a rather limited range of heliocentric distances.

Today, this survey has been extended to more than 165 comets of which 101 are adequately sampled for inclusion in a taxonomic study (Schleicher & Bair 2010). Cluster and principle component analyses reveal about 8–10 compositional groupings, several of which are subgroups of the original carbon-chain-depleted class defined by A’Hearn et al. (1995). All evidence continues

to indicate that the carbon-chain depleted class is primordial in nature and not associated with evolution. Unexpectedly, 4 comets are identified as being depleted in ammonia (the likely primary antecedent of NH) but not depleted in carbon-chain molecules. A complete description of these results is being prepared (D. Schleicher, private communication).

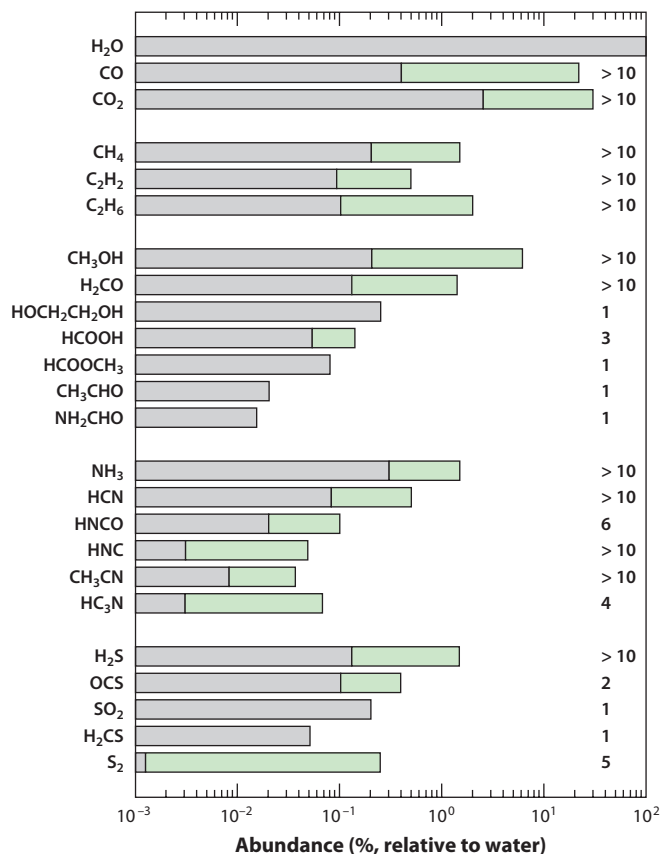
Spectroscopic surveys include those of Newburn & Spinrad (1989), Cochran et al. (1992), Fink (2009), and Langland-Shula & Smith (2011). A survey of 92 comets (Fink 2009, Fink & Hicks 1996) sampled O(<sup>1</sup>D), CN, C<sub>2</sub>, NH<sub>2</sub>, and dust through CCD spectroscopy (520–1,040 nm). Of those, 50 comets returned good emissions from product volatiles, and Fink (2009) organized them into four distinct taxonomic groups with 35, 11, 3, and 1 members, respectively. No new emission features were found in this sample. The latter two sets are distinguished from the first two sets by their NH<sub>2</sub> abundance. Alternatively, 13 of the 92 comets also appear in the restricted set (41 comets) of A’Hearn et al. (1995), and a detailed and careful comparison demonstrated that results from the two surveys are in reasonable agreement for them (Fink 2009). A’Hearn et al. sampled NH but not its likely parent, NH<sub>2</sub>. Cochran et al. (1992) surveyed 19 comets (in CN, C<sub>2</sub>, C<sub>3</sub>, CH, NH<sub>2</sub>, and dust), whereas Newburn & Spinrad (1989) surveyed 25 comets [in O(<sup>1</sup>D), CN, C<sub>2</sub>, C<sub>3</sub>, and dust]. Neither survey identified distinct taxonomic groups. Cochran’s survey has since been expanded to more than 95 comets, and a full description of the sampled comets is in preparation (A. Cochran, private communication). In a spectroscopic study of 26 comets (CN, C<sub>2</sub>, C<sub>3</sub>, OH, NH, and NH<sub>2</sub>) Langland-Shula & Smith (2011) confirmed the findings of earlier surveys, including the depletion of carbon-chain volatiles in some comets.

Although the diversities seen by A’Hearn et al. (1995) and Fink (2009) are in agreement, the product species observed can be produced from multiple precursors and even from different states of matter (condensed phase, vapor phase, etc.), obscuring the cause of this diversity along with its possible interpretation and, thus, its underlying significance.

### 3.2. Taxonomies Based on Primary Volatiles

Surveys of cometary primary volatiles are underway at IR and radio wavelengths. **Figure 4** provides an overview of primary volatiles detected in the two surveys, the number of comets in which a given species was detected, and the range of abundance ratios found among comets (Bockelée-Morvan et al. 2004, Crovisier 2006). The relationship among taxonomies based on product species and those based on primary volatiles is now being tested, and they are not always in agreement. For example, comet 8P/Tuttle is typical in the optical survey but is peculiar in the primary volatile composition surveyed at IR wavelengths (A’Hearn et al. 1995, Schleicher 2007, Bonev et al. 2008b). This difference is expected because many product species can be produced both from primary volatiles and from dust, but it is difficult to separately identify the contribution of each class of precursor (dust or gas). Moreover, some species (e.g., HNC, see below) may be produced by reactive chemistry in the coma. Quantifying the possible primary volatile species can help to identify the need for solitary versus multiple precursors for the product species.

**3.2.1. Radio surveys.** Radio techniques offer two major advantages for detection and characterization of primary volatiles. First, the spectra of complex volatiles are more easily modeled in pure rotational transitions than in their vibrational bands, making radio searches relatively more productive than IR for large polyatomics. This is a major strength of radio spectroscopy, and the detection of ethylene glycol (HOCH<sub>2</sub>CH<sub>2</sub>OH) provides a prime example. Second, very high spectral resolution is easily obtained, often approaching velocity resolution of 50 m s<sup>-1</sup> or even smaller. This enables measurement of spectral line shapes and Doppler shifts in the cometary coma and provides a measure of the line-of-sight motion of escaping gases relative to the cometary



**Figure 4**

Cometary volatiles detected in spectroscopic surveys. Most listed species are regarded as primary, except for HNC, which is in large part a product species. Others may be both primary and product in origin (e.g., H<sub>2</sub>CO, CO). For each molecular species, the number of comets in which it has been detected is shown on the right margin, and the range of values found among those detections is shown as a color bar (*light green*). The six species designated “1” on the right margin were detected only in comet Hale-Bopp, the brightest comet of the past several decades. Adapted from Crovisier (2006), with updates for CO<sub>2</sub> and NH<sub>3</sub>. See also Bockelée-Morvan et al. (2004).

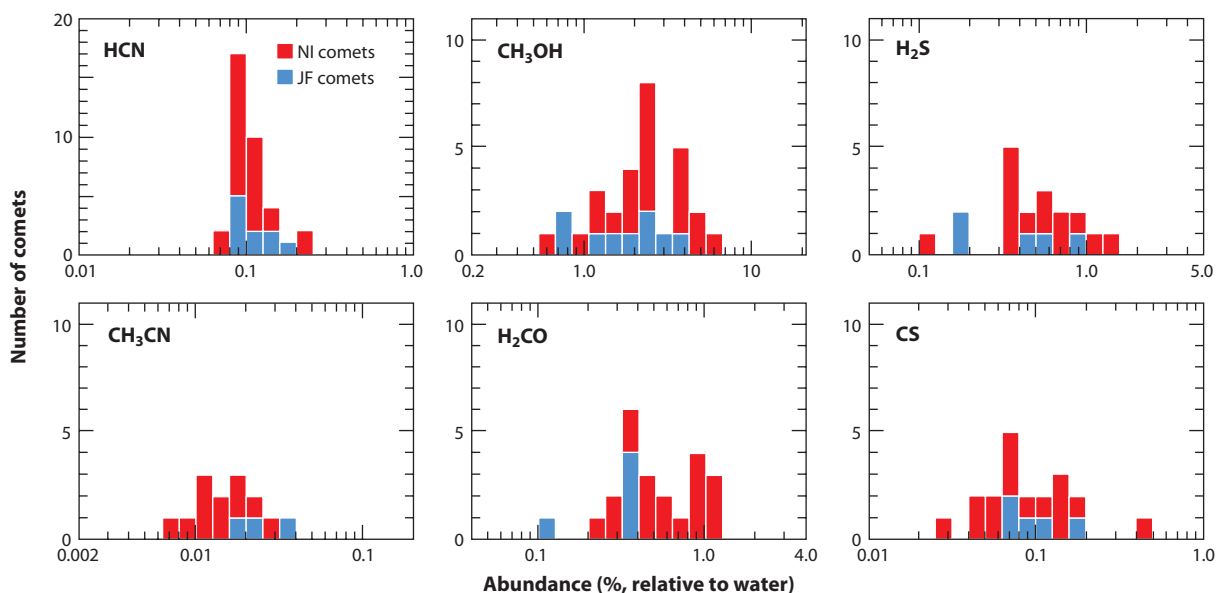
nucleus. When combined with 2D spatial mapping (via single-aperture stepping or multi-aperture interferometry), a 3D map of the species is obtained. One major shortcoming is that simultaneous measurement of multiple species is usually not possible. The spectral lines of some species (e.g., CO, H<sub>2</sub>CO) often require separate instrument settings and even entirely separate facilities. The dominant cometary volatile (water) is not directly accessible from the ground at radio wavelengths, so HCN has been used as its proxy for developing a database of compositional diversity.

**3.2.1.1 Cometary diversity as revealed at radio wavelengths.** Ten primary volatiles (CO, H<sub>2</sub>CO, CH<sub>3</sub>OH, HCOOH, HCN, HNCO, CH<sub>3</sub>CN, HC<sub>3</sub>N, NH<sub>3</sub>, and H<sub>2</sub>S), several product species (OH, CS, and NS), and HNC (a likely coma product) form the core results in the radio survey of more than 40 comets (Biver et al. 2002, Crovisier et al. 2009b). Two (CO, H<sub>2</sub>CO) can be both primary and product species.

Six more primary volatile species (labeled “1” in the right margin of **Figure 4**) were detected in comet Hale-Bopp (the brightest comet seen in recent decades), and sensitive upper limits were reported for many other primary and product species (Crovisier et al. 2004a). Perhaps the most remarkable of these detections was that of ethylene glycol. Its identification as a major irradiation product in methanol-rich ices (Hudson & Moore 2000) triggered a search for and identification of this molecule in Sagittarius B2 (Hollis et al. 2002). Thereafter, it was sought in archival spectra of comet Hale-Bopp and found at an unexpectedly high abundance (0.25%) (Crovisier et al. 2004b). Yet with ten atoms, the ro-vibrational structure of its vibrational bands has never been analyzed, and no quantum band models exist.

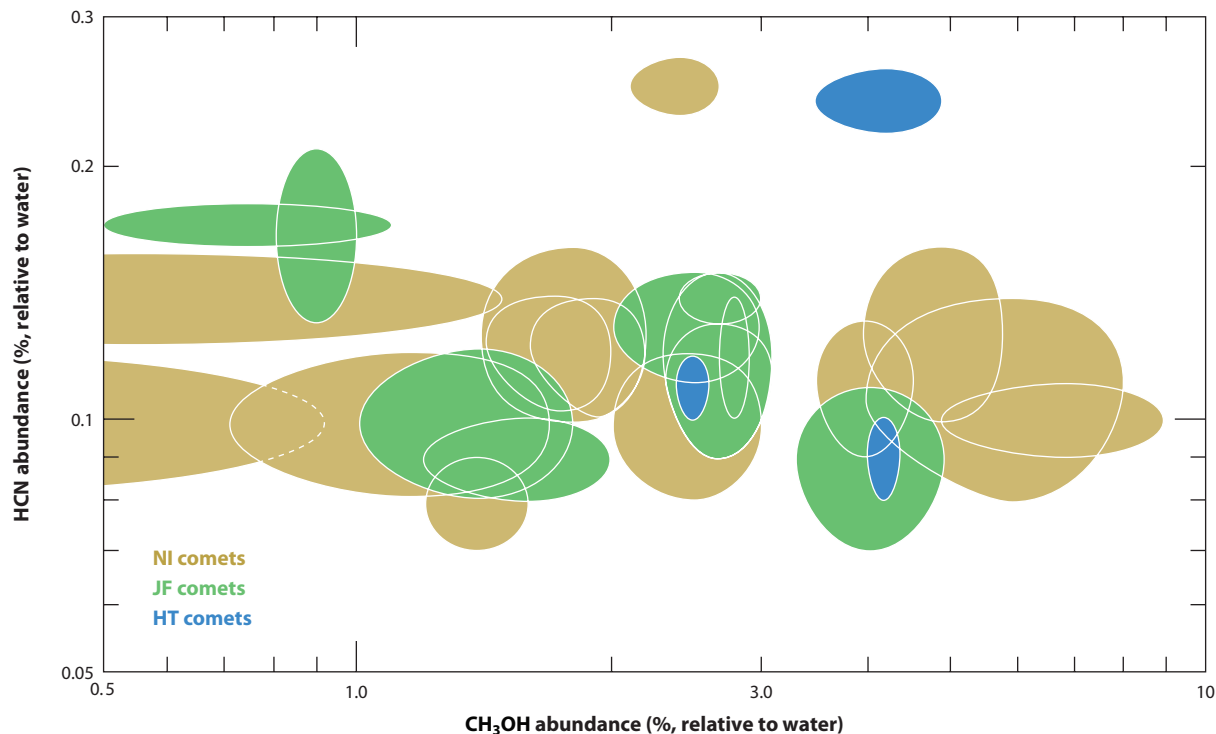
Water production rates have been inferred in more than 35 comets from radio observations of its product volatile (quiescent) OH, through its masering transitions near 18 cm. In a bright comet, OH often is measured at daily intervals for many months, providing a highly valuable database for comparison to other primary and product species (Crovisier et al. 2002, 2008). Radio OH measurements sample most of the coma and, thus, are relatively insensitive to short term (<1 day) variations in water production, such as were prominent in 103P/Hartley 2. For that reason, HCN is often used as a proxy for cometary water in studies of cometary diversity. Since 2000, H<sub>2</sub>O production rates have been measured at submillimeter wavelengths (e.g., 557 GHz) from space, e.g., using the *Submillimeter Wave Astronomy Satellite* (SWAS) (Neufeld et al. 2000), *Odin* (12 comets; Lecacheux et al. 2003, Biver et al. 2007), and *Herschel* (Bockelée-Morvan et al. 2010, Hartogh et al. 2010).

The compositional diversity among comets in the radio survey is demonstrated in **Figure 5** (Crovisier et al. 2009a). A comparison of HCN and CH<sub>3</sub>OH among comets appears in **Figure 6** (Crovisier et al. 2009b). No obvious trend appears in either figure (the bubble sizes



**Figure 5**

Histograms of molecular abundances relative to water based on radio observations of comets. HCN is detected in 36 comets. The blue shading pertains to the subsample of ecliptic (Jupiter family, JF) comets, the red shading to nearly isotropic (NI) comets (long-period and Halley-type). There is no obvious difference between JF and NI dynamical groups. Adapted from Crovisier et al. 2009a.



**Figure 6**

Comparison of HCN and  $\text{CH}_3\text{OH}$  abundance ratios (relative to water) as seen at radio wavelengths. The sizes of the ellipses represent the errors of the measurements. Note that the spread in abundance is much larger for methanol than for HCN. The two volatile species are not correlated. There is no obvious difference between Jupiter family (JF) and nearly isotropic (NI) dynamical groups. Adapted from Crovisier et al. 2009b.

in **Figure 5** represent the error estimates for each measurement). However, two factors must be considered when evaluating these comparisons.

First, HCN is a trace volatile that is assumed to be primary, and its production rate (**Figure 6**) is taken to be a proxy for water. However, its abundance relative to water shows a wide range of values (see **Figure 5**, and discussion below). Water production obtained from measurements at Nançay encompass quiescent OH integrated over a much larger fraction of the coma than is used for other species (e.g., HCN at Institut de Radio Astronomie Millimétrique). Thus, the HCN and water production rates refer to different mean production times, and the spread in HCN/ $\text{H}_2\text{O}$  ratios may represent (in part) temporal variations in production of HCN relative to water (compare Hartley 2; see Section 2.2). A similar spread may apply to other primary species measured in this way, and the spread for each species could depend on the sampling details (e.g., mean phase within a rotation period, binned fraction of a rotation period, etc.). In **Figure 5**, the values for HCN spread by a factor of 5 ( $\sim 1.5$ , if only the central two bins are considered), but other primary species ( $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{CN}$ , or  $\text{H}_2\text{S}$ , for example) exhibit spreads by a factor of 10 (radio  $\text{H}_2\text{CO}$  is often a product species, as is CS, so both are omitted from this discussion). HCN is known to be a product species (see Section 3.2.1.2). If HCN too is a product species (in part or in whole), it would not be a faithful proxy for the dominant primary volatile ( $\text{H}_2\text{O}$ ), and taxonomies based on comparisons to HCN would be biased.

Second, most radio measurements of volatiles are taken individually (by species) rather than simultaneously. Of the five comet nuclei imaged to date, three are strongly elongated of which 1P/Halley and 103P/Hartley 2 both show strong temporal variations in product and primary species associated with nucleus rotation (Millis & Schleicher 1986, Mumma & Reuter 1989, Biver et al. 2011, Mumma et al. 2011). Astronomical observations sample the production averaged over times related to the beam size (diameter at the comet), which varies with telescope aperture and wavelength (Section 3.2.3). Nucleus rotation then introduces uncertainty regarding the relationship among production rates measured at different rotational phases. Regardless, it is clear that the other three primary species in **Figure 5** vary by a greater factor among the sampled comets than does HCN. See also Section 3.2.3.

**3.2.1.2 The HNC problem.** Irvine et al. (1996) first detected HNC in C/1996 B2 (Hyakutake) with an abundance of 0.06 relative to its more stable isomer (HCN) and suggested that HNC could be primordial interstellar material. However, in Hale-Bopp the HNC/HCN ratio varied with heliocentric distance ( $R_h$ ), from  $< 0.02$  (at  $R_h > 2.5$  AU) to  $\sim 0.2$  at perihelion, demonstrating that HNC must be produced in the coma (Biver et al. 1997, Irvine et al. 1998). HNC has since been seen in almost a dozen comets, with HNC/HCN ratios ranging from  $\sim 0.03$  to 0.3 (Lis et al. 2008).

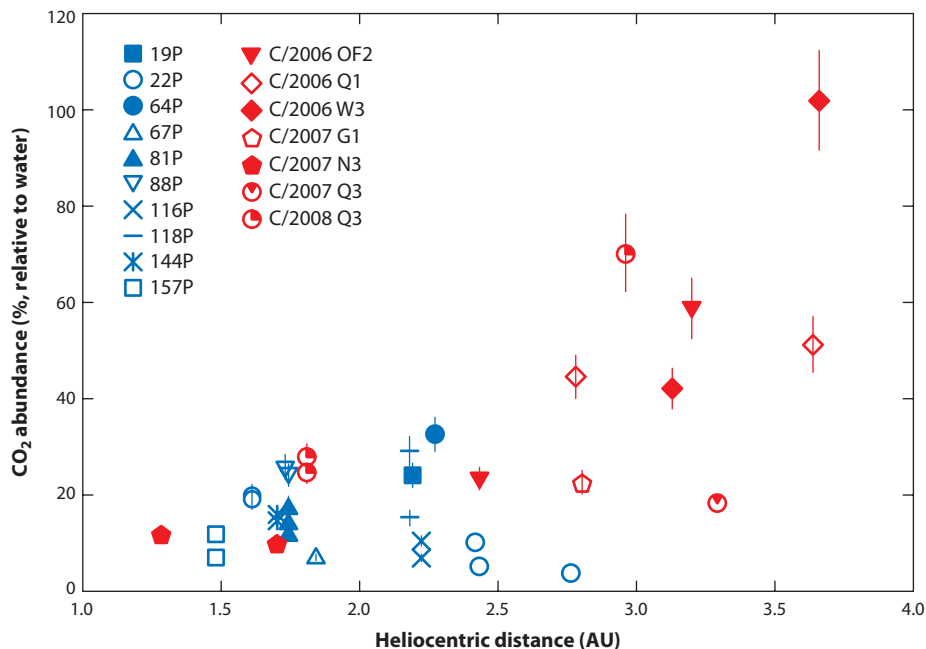
Lis et al. (2008) showed that the HNC/HCN ratio is insensitive to the comet's water production rate, but is strongly dependent on the heliocentric distance, with the largest ratios observed in comets with  $R_h < 0.8$  AU. This  $R_h$  dependence could plausibly be explained by thermal destruction of polymeric material, because only at small  $R_h$  will the dust be hot enough to drive this process. However, interferometric mapping of HNC in Hale-Bopp revealed a scale-length of  $< 2,000$  km (D. Bockelée-Morvan, private communication). Blake et al. (1999) reported compact HNC emission in Hale-Bopp, although there was also evidence for a more extended component related to dust.

Initial model calculations showed that HNC could potentially be formed in the coma by chemical reactions (Irvine et al. 1998, Rodgers & Charnley 1998). However, modeling of coma chemistry in comets less active than Hale-Bopp clearly showed that neither ion-neutral chemistry nor isomerization reactions (driven by suprathermal H atoms) could produce the observed levels of HNC (Rodgers & Charnley 2001a), and it was suggested that HNC is produced from the thermal degradation of organic dust grains, such as some variant of polymerized HCN (Rodgers et al. 2003).

Very recently, the outburst of 17P/Holmes allowed the instantaneous HNC/HCN ratio to be measured at 2.4 AU (Boissier et al. 2008). The derived value of 0.06 (Bockelée-Morvan et al. 2011) is larger than in Hale-Bopp (at this heliocentric distance) by a factor of  $\sim 1.5$ –2 (Biver et al. 1997, Irvine et al. 1998). Thermal degradation of dust is less efficient at 2.4 AU, strongly suggesting that HNC is in fact formed by (as yet unidentified) chemical reactions in the inner coma. It also questions whether HCN can be both a primary and product species.

**3.2.2. Infrared surveys.** At IR wavelengths (3–5  $\mu\text{m}$ ), trace volatiles (primary and product) are sampled simultaneously with  $\text{H}_2\text{O}$  (the dominant primary volatile) or its direct proxy (OH prompt emission, denoted  $\text{OH}^*$ ). The detection of  $\text{H}_2\text{O}$  in 1P/Halley in 1985 from NASA's Kuiper Airborne Observatory was the first direct detection of water in comets, and it marked the advent of IR remote sensing of primary volatiles (Mumma et al. 1986, Weaver et al. 1986).

Today, ten or more primary volatiles are detected simultaneously with cross-dispersed echelle spectrometers, including  $\text{H}_2\text{O}$ , CO,  $\text{H}_2\text{CO}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_6$ , HCN,  $\text{NH}_3$ , and OCS (Mumma et al. 2003, Bockelée-Morvan et al. 2004, DiSanti & Mumma 2008). Product volatiles



**Figure 7**

CO<sub>2</sub> and H<sub>2</sub>O in seventeen comets, surveyed with the *Akari* space observatory. For 7 of 14 comets seen at heliocentric distance less than 2.5 AU, the CO<sub>2</sub> abundance ratio exceeds 20%. There is no perceptible difference between Jupiter-family and nearly isotropic dynamical groups. The abundance ratios are artificially enhanced beyond 2.7 AU because of the decreasing volatility of water ice. After Ootsubo et al. (manuscript in preparation); H. Kawakita, personal communication.

(NH<sub>2</sub>, OH\*, and CN) are also detected. Symmetric species (CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>N<sub>2</sub>, etc.) lack a permanent dipole moment and so are not active in pure rotational emission (radio, submillimeter), and their excited electronic states are usually predissociated. Thus, they are uniquely sensed through their vibrational emissions at IR wavelengths, usually excited by solar fluorescence. At this writing, 26 comets have been characterized.

CO<sub>2</sub> can be detected only from space, and its vibrational fundamental band at 4.3 μm is one of the strongest emission features in near-IR spectra of comets. It was detected first in 1P/Halley with IKS on *Vega-1* (Combes et al. 1988), later with the *Infrared Space Observatory* (ISO) in C/1995 O1 (Hale-Bopp) (Crovisier et al. 1996, 1997) and in 103P/Hartley 2 (Colangeli et al. 1999, Crovisier et al. 1999), then with the *Deep Impact* spacecraft in 9P/Tempel 1 (A’Hearn et al. 2005, Feaga et al. 2007) and 103P/Hartley 2 (A’Hearn et al. 2011). Recently, CO<sub>2</sub>, CO, and H<sub>2</sub>O were targeted in C/2007 N3 (Lulin) and 16 other comets (10 JFC and 7 OC) with the *Akari* space observatory (Hamada et al. 2010, Ootsubo et al. 2010), providing the first survey in these key species. In preliminary results, CO<sub>2</sub> varies from ~3% to ~30% (relative to water) for 14 comets within 2.5 AU of the Sun, and comets from the Kuiper Belt and OC are indistinguishable (Ootsubo et al., manuscript in preparation; H. Kawakita, personal communication). Water ice is less volatile beyond ~2.7 AU, so the apparent CO<sub>2</sub> and CO abundance ratios are enhanced artificially at greater heliocentric distances (**Figure 7**).

Emission in the CO Cameron bands ( $a^3\Pi-X^1\Sigma^+$ ) has been used as a prompt emission proxy for CO<sub>2</sub>, but this system can also be excited by electron impact on CO (Weaver et al. 1994, Feldman

et al. 1997, but see Bhardwaj & Raghuram 2011). Feldman et al. (2009) extended this approach to far-UV emissions of CO, deriving H<sub>2</sub>CO and CO abundance in four comets from the CO ( $C^1\Sigma^+-X^1\Sigma^+$ ) and ( $B^1\Sigma^+-X^1\Sigma^+$ ) systems, respectively. A rotationally hot ( $\sim 500$  K) component of CO ( $C^1\Sigma^+-X^1\Sigma^+$ ) was argued to derive from dissociative excitation of CO<sub>2</sub> (consistent with laboratory results of Mumma, Stone & Zipf 1975).

IR spectroscopy with long-slit high-dispersion cryogenic grating spectrometers (e.g., the Near-InfraRed SPECTrograph (NIRSPEC) on Keck-2 and InfraRed Camera and Spectrograph (IRCS) on Subaru) is the approach preferred for the ground-based IR surveys, and the prime spectral region is 2.9–5.1  $\mu\text{m}$ . The long slit samples fluorescent emission from coma species at multiple points about the nucleus, and the nucleus-centered pencil beam is heavily weighted toward molecules within the collision-dominated zone of the inner coma. In this zone, the excitation of rotational states in a primary volatile is characterized by a rotational temperature, which permits extrapolation of the entire vibrational band intensity from the sampled lines (often the entire band is not sampled). Advanced line-by-line fluorescence models that permit extraction of rotational temperatures have been developed for many species, including H<sub>2</sub>O, HDO, CO, HCN, CH<sub>4</sub>, CH<sub>3</sub>D, H<sub>2</sub>CO, C<sub>2</sub>H<sub>6</sub>, NH<sub>3</sub>, NH<sub>2</sub>, and so on. Indeed, spectral lines of many H<sub>2</sub>O hot bands are sampled near 2.9  $\mu\text{m}$ , and a single rotational temperature (of the ground vibrational state) is found to satisfy the observed line intensities (Dello Russo et al. 2004, Bonev et al. 2008a). (For models of CH<sub>4</sub>, see Gibb et al. 2003; for CH<sub>3</sub>D, Kawakita & Watanabe 2003; for H<sub>2</sub>CO, DiSanti et al. 2006; for C<sub>2</sub>H<sub>6</sub>, Radeva et al. 2011 and Villanueva et al. 2011a; for NH<sub>3</sub> and NH<sub>2</sub>, Kawakita & Mumma 2011).

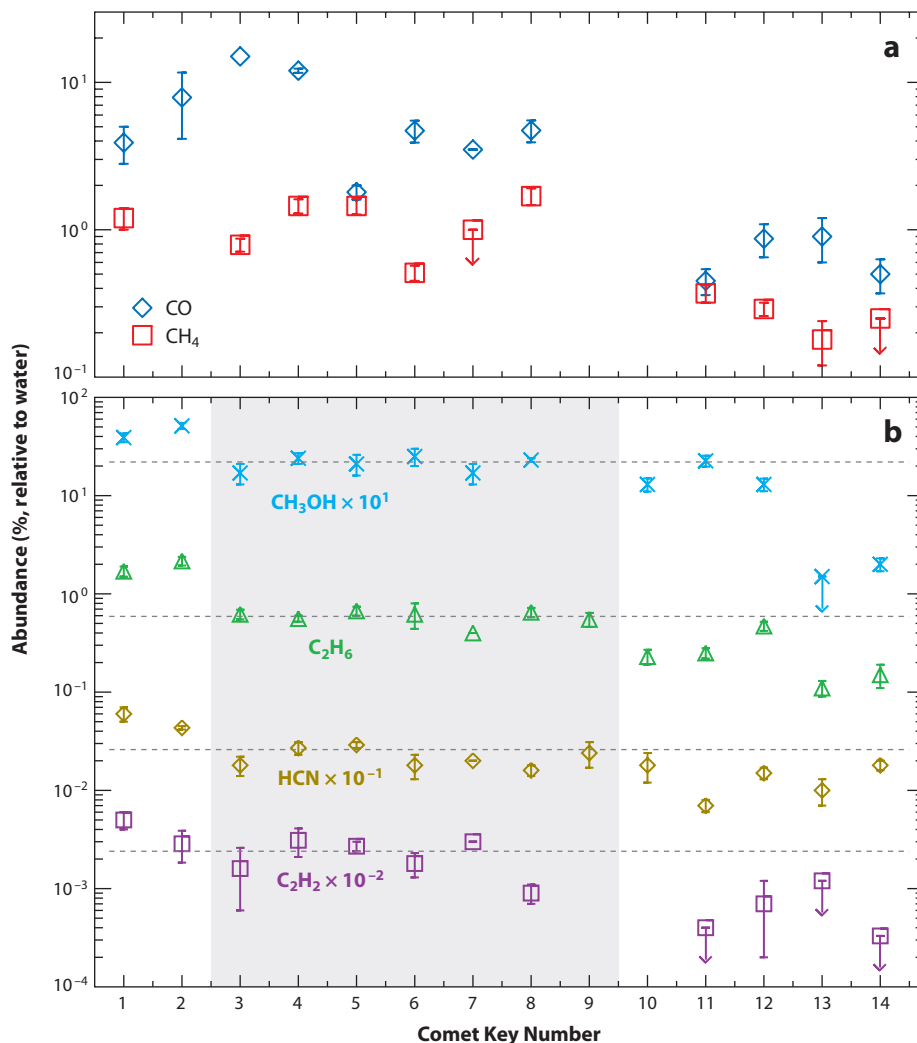
Cross-dispersed spectrometers permit simultaneous sampling of H<sub>2</sub>O or its direct proxy OH\* (Bonev et al. 2006) with other targeted species throughout the key 2.9–4.0 and 4.5–5.1- $\mu\text{m}$  spectral windows. Methods for guiding and correction of slit losses are robust, and the combined instrumental and modeling factors provide excellent control of systematic uncertainties that otherwise can affect measurement of production rates, abundance ratios, and related phenomena.

Abundance ratios of 6 primary volatiles for 12 comets in this IR survey are compared with those of comet 1P/Halley in **Figure 8** (and see **Table 1** for a legend of the comets in this figure). Histograms comparing abundance ratios for C<sub>2</sub>H<sub>6</sub> and CH<sub>3</sub>OH for these 13 comets are shown in **Figure 9**, along with a correlation diagram for these two primary volatiles.

This sample of 13 comets suggests the presence of three distinct groupings, based on organic composition. The hypervolatiles CO and CH<sub>4</sub> each exhibit a large range of abundances, but with no clear correlation between them (**Figure 8a**). However, abundances of four primary volatiles (C<sub>2</sub>H<sub>6</sub>, CH<sub>3</sub>OH, HCN, and C<sub>2</sub>H<sub>2</sub>) cluster tightly in 6 OC comets, and these comets form the dominant group (#3–8, **Figure 8b**).

Two comets exhibit enriched abundances (#1 and #2, **Figure 8b**)—#1 is from the OC and #2 is from the KB (**Table 1**)—both underwent disruption events—C/2001 A2 split several times, and 17P/Holmes experienced a major outburst. C/2007 W1 (Boattini) is also organics-enriched (data not shown), but did not experience an obvious disruption event (Villanueva et al. 2011b). Similarly, severely organics-depleted comets (#13 and 14, **Figure 8b**) also draw from both dynamical reservoirs; both organics-depleted comets suffered catastrophic disruption. C/1999 S4 disintegrated completely several weeks after its composition was characterized at IR wavelengths (Mumma et al. 2001). 73P/SW3 broke into multiple fragments in 1995 (Boehnhardt et al. 1995) and appeared to suffer continued fragmentation on apparitions in 2001 and 2006 (Boehnhardt et al. 2002, Weaver et al. 2006). In 2006, its brightest fragments, B (which experienced multiple outbursts due to continued fragmentation in 2006) and C (the relatively more stable fragment), showed similar organic composition and OPR (see also Sections 4 and 5.2), suggesting that its organics-depleted chemistry is primordial rather than resulting from thermal processing over





**Figure 8**

Results from a compositional survey of primary volatiles in comets, obtained with IR spectroscopy. Abundance ratios relative to water in 12 comets are compared with those of 1P/Halley (#7) taken in situ by mass spectroscopy. The abundance ratios of  $\text{CH}_3\text{OH}$ , HCN, and  $\text{C}_2\text{H}_2$  are scaled by factors of 10, 0.1, and 0.01, respectively, to ease comparison. (a) The hypervolatile species  $\text{CH}_4$  and CO are only coarsely correlated among these comets, with 8 comets (#1–8) having higher values in methane and CO compared to the remaining 4 comets (#11–14). (b) The light gray background embraces comets whose abundance ratios for an individual species are tightly grouped about a common mean value. Ethane and methanol are especially noteworthy, with 7 comets (#3–9) belonging to the normal group, whereas 2 are enriched (#1 and 2) and 2 are severely depleted (#13 and 14); three comets (#10–12) are transitional. The relationship of methanol and ethane is shown in greater detail in **Figure 9**. See also **Table 1** for a legend of the comets in this figure. After Mumma et al. 2011.

**Table 1** Legend for comets in Figure 8

No.	Name	Orbit <sup>a</sup>	Ref <sup>b</sup>
1	C/2001 A2 (LINEAR)	LPC (OC)	Gibb et al. 2007, Magee-Sauer et al. 2008
2	17P/Holmes	JFC (KB)	Mumma et al. 2011
3	C/1996 B2 (Hyakutake)	LPC (OC)	Biver et al. 2002 (CH <sub>3</sub> OH), Mumma et al. 2003
4	C/1995 O1 (Hale-Bopp)	LPC (OC)	Biver et al. 2002 (CH <sub>3</sub> OH), Mumma et al. 2003
5	C/1999 H1 (Lee)	LPC (OC)	Mumma et al. 2003
6	153P/Ikeya-Zhang	HTC (OC)	Mumma et al. 2003
7	1P/Halley	HTC (OC)	Eberhardt et al. 1994, Eberhardt 1999 (CH <sub>3</sub> OH)
8	C/2004 Q2 (Machholz)	LPC (OC)	Bonev et al. 2009
9	9P/Tempel1 (ejecta) <sup>c</sup>	JFC (KB)	Mumma et al. 2005, DiSanti et al. 2007a
10	9P/Tempel1 (ambient) <sup>c</sup>	JFC (KB)	Mumma et al. 2005
11	8P/Tuttle	HTC (OC)	Boehnhardt et al. 2008, Bonev et al. 2008b
12	C/2001 WM <sub>1</sub> (LINEAR)	LPC (OC)	Radeva et al. 2010
13	C/1999 S4 (LINEAR)	LPC (OC)	Mumma et al. 2001
14	73P/SW3-B and -C <sup>d</sup>	JFC (KB)	Villanueva et al. 2006, Dello Russo et al. 2007, DiSanti et al. 2007b, Kobayashi et al. 2007)

<sup>a</sup>Present orbital classification and likely dynamical reservoir. Abbreviations: HTC, Halley-type comet; JFC, Jupiter Family Comet; KB, Kuiper Belt; LPC, long-period comet; OC, Oort Cloud.

<sup>b</sup>Citations are general unless a specific molecule is listed.

<sup>c</sup>Ejecta, *Deep Impact* ejecta; ambient, quiescent coma.

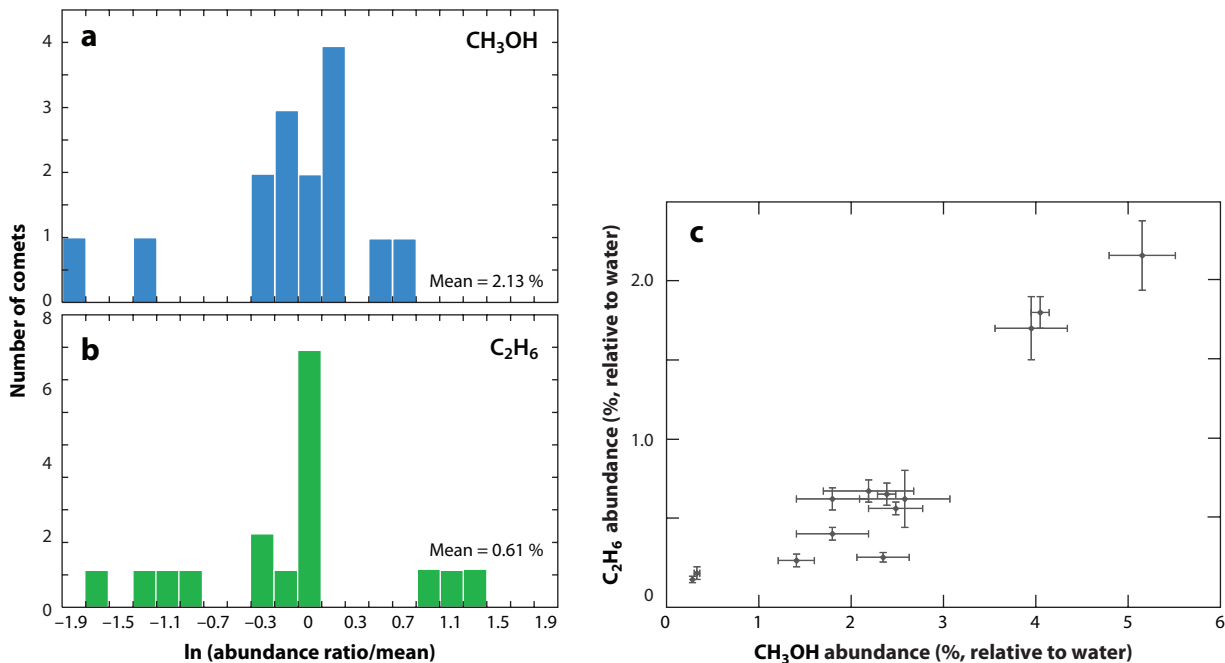
<sup>d</sup>The two brightest fragments, B and C, had essentially identical compositions.

the course of repeated perihelion passages (Villanueva et al. 2006, Dello Russo et al. 2007). The methanol-poor OC comet C/1996 Q1 (Tabur) (data not shown) also disintegrated (Biver et al. 2002). These depleted comets may have formed in the Jupiter-Saturn region of the protoplanetary disk, with later ejection to dissimilar reservoirs (OC and KB, respectively) (Mumma et al. 2001).

The three groups appear more clearly in histograms of the abundance ratios found for ethane and methanol, the putative products of hydrogenating C<sub>2</sub>H<sub>2</sub> and CO, respectively (**Figure 9a,b**). The abundance ratios for ethane and methanol vary together, but are not described by a simple proportional relation (**Figure 9c**). Although suggestive, the sampling of comets in each group is very far from being statistically adequate, and many more bodies must be characterized before the classes can be regarded as firmly established.

Although this comparison suggests three compositional groups, close inspection reveals minor differences within each group. In the dominant group, five OC comets (#3–7, including 1P/Halley) revealed similar abundances (relative to H<sub>2</sub>O) of HCN, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, and CH<sub>3</sub>OH, but a sixth [#8, C/2004 Q2 (Machholz)] showed somewhat lower C<sub>2</sub>H<sub>2</sub> (and perhaps slightly lower HCN). JFC 9P/Tempel 1 is included (#8) due to its normal abundance of C<sub>2</sub>H<sub>6</sub> and HCN in the ejecta expelled by the *Deep Impact* experiment (A'Hearn et al. 2005, Mumma et al. 2005, DiSanti et al. 2007a); however, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>2</sub>, and CH<sub>3</sub>OH were depleted (relative to normal) in the pre-impact release, so Tempel 1 also appears as somewhat depleted (#9).

Since 2006, the unexpected appearance of 2006 M4 (Swan) and campaigns on OC comets C/2006 W3 (Christensen), C/2007 W1 (Boattini), and C/2007 N3 (Lulin), and on JFCs 6P/d'Arrest and 103P/Hartley 2 added significantly to efforts to build a taxonomic classification for comets based on primary volatiles. With these in hand, the database now contains 26 comets. C/2007 W1 (Boattini) is organics-enriched (Villanueva et al. 2011b), 103P/Hartley 2 is organics-normal (Mumma et al. 2011), and 6P/d'Arrest is normal in CH<sub>3</sub>OH and NH<sub>3</sub> but



**Figure 9**

Diversity among comets, as seen in methanol and ethane. Histograms of abundance ratios relative to water are displayed for (a) methanol and (b) ethane. A correlation diagram (c) shows that their abundance ratios vary together, i.e., both are depleted, both are enriched etc. However, the data do not support a single mixing line joining two end members. After Mumma et al. 2011.

somewhat depleted in C<sub>2</sub>H<sub>6</sub> and severely depleted in C<sub>2</sub>H<sub>2</sub> and HCN (Dello Russo et al. 2009). The latter finding for 6P/d'Arrest emphasizes the risk of using HCN as a proxy for water (see Sections 3.2.1.1 and 3.2.1.2). A comparison of IR and optical results for d'Arrest demonstrates that NH<sub>3</sub> can be the principal source of NH<sub>2</sub> and NH, but HCN cannot be the sole (or even principal) source of CN, nor can C<sub>2</sub>H<sub>2</sub> be the principal source of C<sub>2</sub> in that comet (Dello Russo et al. 2009).

Three principal compositional groups (organics-normal, organics-enriched, and organics-depleted) are emerging, and members of each group are found in both ecliptic and NIC populations, i.e., in the OC and KB (Mumma et al. 2011). Although crudely consistent with the Nice dynamical model, numerical predictions are lacking. These groups may have different fractional representations in the two reservoirs, but improved statistics are needed—only 26 comets have been sampled to date. Congruence of the IR and optical surveys is mixed—3 comets are organics-enriched in the IR survey of primary volatiles, whereas not one is enriched in surveys of product species.

**3.2.3. Temporal and spatial variations in volatile production.** The degree of simultaneity when measuring primary volatiles also enters into consideration of the correlations presented in Figures 6 and 7.

Spacecraft images taken during flyby have revealed many active regions on the nuclei of 1P/Halley, 9P/Tempel 1, and 103P/Hartley 2. Jets of CO<sub>2</sub> and of H<sub>2</sub>O were identified in Tempel 1 and Hartley 2, consistent with compositional heterogeneity of constituent cometesimals expected

from formation models. Temporal modulation of chemical release should occur as diverse vents are periodically activated, on timescales related to the rotation period (typically greater than six hours). In a few cases, temporal monitoring has revealed important short-term periodicities in production rates, probably associated with nucleus rotation, e.g., of  $\text{H}_2\text{O}$  in C/2001 Q4 (Biver et al. 2009) and of  $\text{HCN}$  in 103P/Hartley 2 (Section 2.2). But, it is difficult to distinguish the signature of internal heterogeneity from that of changing overall activity, when primary species are measured sequentially. The association with nucleus rotation is unambiguous for Hartley 2 (see Section 2.2).

Simultaneous sampling of multiple primary species can test variations caused by differences in active area and in intrinsic abundance ratios; for example, short-term periodic variations of  $\text{H}_2\text{O}$ ,  $\text{HCN}$ ,  $\text{C}_2\text{H}_6$ , and  $\text{CH}_3\text{OH}$  were measured in 103P/Hartley 2 (Mumma et al. 2011) and of  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{H}_2\text{CO}$ , and  $\text{CH}_3\text{OH}$  in C/2002 T7 (Anderson 2010). In both comets, the production rates varied with time, but the abundance ratios remained invariant over multiple nucleus rotations—probably because the mean composition represented many individual active regions.

It is clear that serial spectroscopy is a powerful tool for testing temporal changes in volatile production and can be used to characterize the degree of internal heterogeneity if multiple primary volatiles are sampled simultaneously. However, major differences in apparent abundance ratios can result if quite different fields of view (FOV) are used to measure individual volatile species and, for extreme differences in FOV, the ability to detect heterogeneity by comparing production rates may be erased entirely.

The possibilities depend greatly on details of the observational geometry. For a circular field of view centered on a nucleus with steady production rate, a fraction  $2/\pi$  of the total beam content is located within the inscribed sphere (radius,  $R$  km) centered on the nucleus, and (neglecting destruction) it contains all volatiles released within a prior time ( $R/v$  sec, where  $v$  is outflow velocity in kilometers per second). Assuming  $1\text{-km s}^{-1}$  outflow velocity and  $5,000\text{-km}$  nucleocentric radius, the inscribed sphere contains the total production over the prior  $5,000$  s, while with  $50\text{-km}$  radius the total production over the prior  $50$  s is measured, and so on. The diffraction-limited telescopic field of view scales as wavelength/diameter, so a ten-meter telescope at  $3\text{-}\mu\text{m}$  wavelength has a  $1,000\text{-fold}$  smaller FOV than a radio telescope of similar size at  $3\text{ mm}$  wavelength. Differences in aperture size, atmospheric turbulence, and wavelength reduce this advantage to about 100, the ratio used above to compare temporal sensitivities.

Spatial measurements can augment temporal variations in powerful ways. Single-aperture spectroscopy provides line-of-sight (LOS) velocity profiles that can provide 3D steric information if outflow models are applied to stepped (2D) observations. Radio interferometers can map a detected volatile species in three dimensions (two transverse to the LOS and one along it as inferred from velocity profiles). Such interferometric maps have proven useful for examining spatial relations among primary volatiles to test heterogeneity in the coma (and nucleus), e.g., by revealing jets in individual primary species (Blake et al. 1999, Boissier et al. 2007, Bockelée-Morvan et al. 2009a, Hogerheidje et al. 2009). ALMA is expected to enable major advances in this area.

#### 4. NUCLEAR SPIN ISOMERS AND SPIN TEMPERATURES

Composition-based surveys of primary volatiles are augmented by surveys that target ratios of nuclear spin isomers and the inferred nuclear spin temperatures. The hydrogen atom carries a nuclear spin angular momentum, and molecules that contain two or more H-atoms in symmetrical locations (e.g.,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CH}_4$ ) form discrete quantized subspecies according to the total spin angular momentum (for  $\text{H}_2\text{O}$ , 0 and 1;  $\text{NH}_3$ ,  $1/2$  and  $3/2$ ; for  $\text{CH}_4$ , 0, 1 and 2, labeled ortho, para, meta, and so on).

The rotational energy levels for each spin species form a discrete ladder, and the lowest-lying levels for the various ladders differ slightly in energy. The relative populations among ladders can be expressed either as a numerical ratio (e.g., OPR) or as a spin temperature ( $T_{\text{spin}}$ ) related to the energy defect between ladders. Conversion of one spin species to another is strongly forbidden under quantum mechanical selection rules, leading to very long persistence times, so  $T_{\text{spin}}$  is considered to measure the formation temperature of the species (Mumma, Weaver & Larson 1987; Mumma, Weissman & Stern 1993; Bockelée-Morvan et al. 2004; Kawakita et al. 2006; Bonev et al. 2007). Although the OPRs for individual primary volatiles often show different values in a given comet, the spin temperatures derived from these ratios agree within confidence limits. Thus, the measured species reveal a common spin temperature. The underlying meaning of that temperature, however, is uncertain.

An OPR and spin temperature for H<sub>2</sub>O was first measured in NICs 1P/Halley (Mumma, Weaver & Larson 1987) and C/1986 P1 (Wilson) (Mumma, Weissman & Stern 1993; see also Bockelée-Morvan et al. 2004). By 2006, 9 comets had been quantified (Bonev et al. 2007), and today the number stands above 16—most from ground-based observatories. *Spitzer* measured OPR and  $T_{\text{spin}}$  in comets C/2003 K4 (LINEAR) and C/2004 B1 (LINEAR) (Woodward et al. 2007, Bockelée-Morvan et al. 2009b) (see below). The spin temperature is conveniently determined by locating the measured OPR on a theoretical curve relating the two parameters, as shown in **Figure 10a** for H<sub>2</sub>O (see Mumma, Weaver & Larson 1987). Other molecular species (NH<sub>2</sub>, NH<sub>3</sub>, CH<sub>4</sub>, H<sub>2</sub>CO, etc.) have different energy defects and spin states, and thus unique theoretical relations. Although population inversions are theoretically possible, none have been observed.

Until recently, all OPRs for H<sub>2</sub>O were extracted from spectra measured at wavelengths near 2.7  $\mu\text{m}$ , where water has two strong fundamental vibrational bands ( $\nu_1$ ,  $\nu_3$ ) along with numerous hot bands ( $\nu_1 + \nu_3 - \nu_1$ ,  $\nu_2 + \nu_3 - \nu_2$ , etc.). The methodology was extended to the H<sub>2</sub>O bending mode ( $\nu_2$ ) at longer wavelengths (6.27  $\mu\text{m}$ ) using the *Spitzer Space Telescope*. In C/2003 K4 (LINEAR), Woodward et al. (2007) found the water rotational temperature to be  $30.7 \pm 3.2$  K, whereas the OPR was measured to be  $2.47 \pm 0.27$  ( $T_{\text{spin}}$  of  $28.5 + 6.5/-3.5$  K) (**Figure 10b**). In C/2004 B1 LINEAR (preperihelion), the water rotational temperature was  $13.6 \pm 3.1$  K, whereas the OPR was measured to be  $2.31 \pm 0.18$  ( $T_{\text{spin}}$  of  $26 + 3/-2$  K) (Bockelée-Morvan et al. 2009b). This is the first example of a spin temperature higher than the rotational temperature in a comet. Additional comets have been quantified with *Spitzer*.

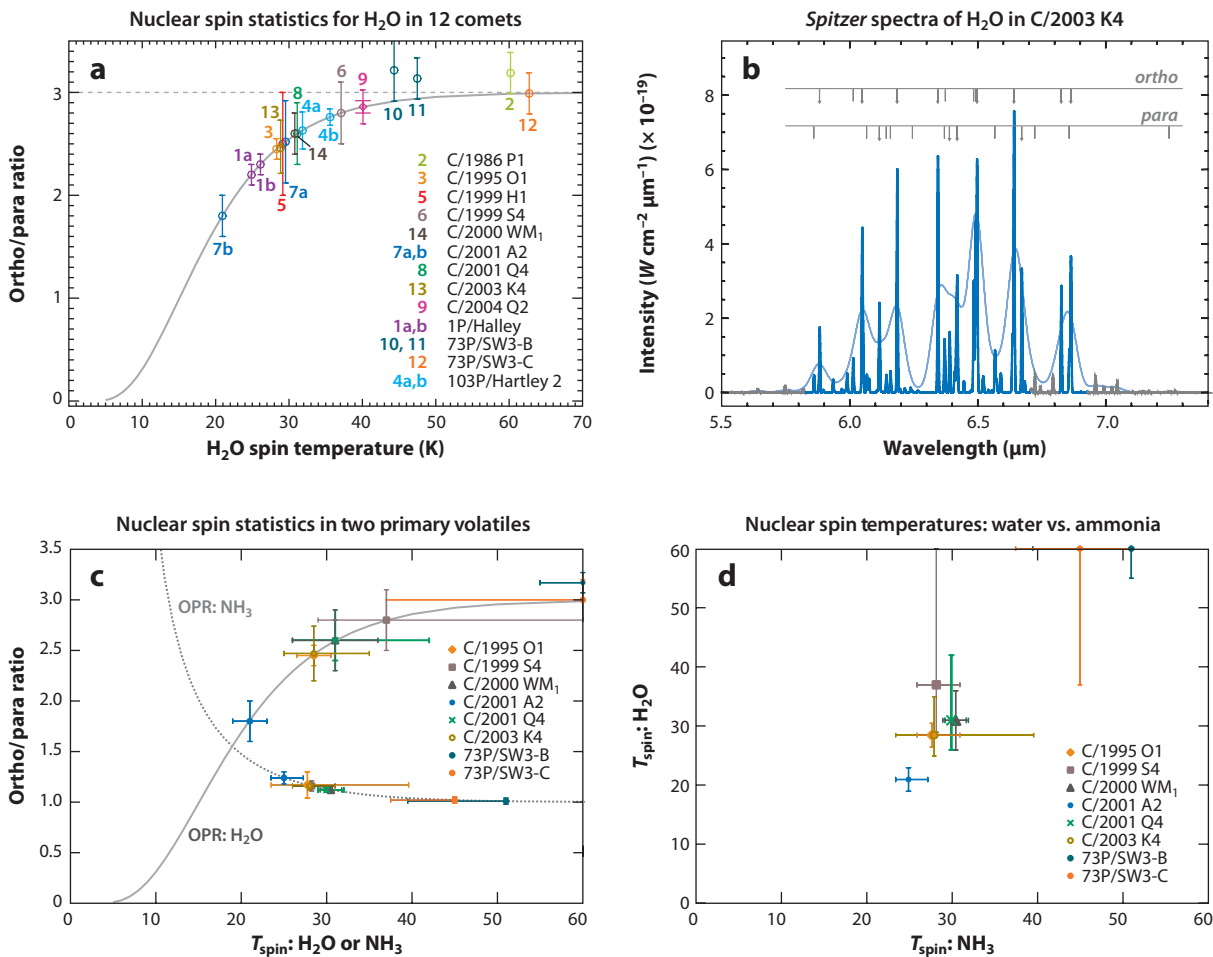
In C/2004 Q2 and 73P/SW3, the OPR was found to remain constant with increasing distance from the nucleus, although the rotational temperature decreased rapidly (Bonev et al. 2007, 2008a). Although all spin temperatures have exceeded  $\sim 20$  K to date, a wide range is seen, extending from 20 K in C/2001 A2 (LINEAR) to  $>50$  K for comet Wilson (a dynamically new comet). High values of  $T_{\text{spin}}$  ( $>40$ – $50$  K) are found in both NIC and ecliptic populations (**Figure 10a**) (Bonev et al. 2007, Woodward et al. 2007).

The principal dissociation channel of NH<sub>3</sub> produces NH<sub>2</sub> and H, and the spin isomeric ratios in NH<sub>3</sub> can be obtained from those of NH<sub>2</sub> by invoking selection rules presented by Quack (1977). Kawakita et al. (2001) obtained the first measurements of OPR and  $T_{\text{spin}}$  for cometary NH<sub>2</sub> in C/1999 S4 (LINEAR), invoking Quack's rules to infer the spin ratios in NH<sub>3</sub> (assuming NH<sub>3</sub> to be the sole precursor of NH<sub>2</sub>, see below). Kawakita et al. (2006) compared 7 comets and found that the spin temperatures for NH<sub>3</sub> and H<sub>2</sub>O in this group agree within error. Shinnaka et al. (2010) revised the fluorescence model and applied it to NH<sub>2</sub> in C2001 Q4 (NEAT, Near Earth Asteroid Tracking), resulting in more accurate spin temperatures. Shinnaka et al. (2011) applied the improved model to all 15 comets in their database, extracting OPR and  $T_{\text{spin}}$  for NH<sub>2</sub> (NH<sub>3</sub>), and comparing their results with the <sup>14</sup>N/<sup>15</sup>N ratios in CN, considered to be another cosmogonic

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**Dynamically new:** a comet making its first journey into the inner Solar System from the Oort Cloud

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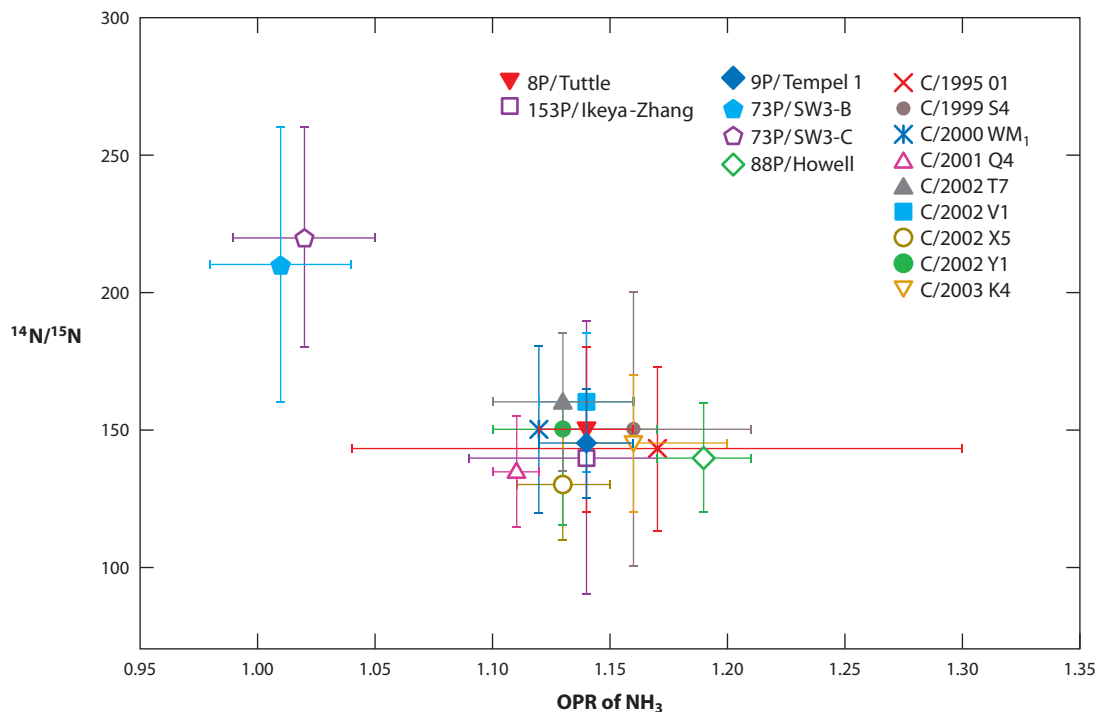


**Figure 10**

Ortho-para ratios (OPRs) and nuclear spin temperatures ( $T_{\text{spin}}$ ) for H<sub>2</sub>O and NH<sub>3</sub> in comets. (a) OPR for H<sub>2</sub>O (Bonev et al. 2007, Dello Russo et al. 2007, Woodward et al. 2007, Bonev et al. 2008a). The measured values are placed on a theoretical curve that connects them to the corresponding nuclear spin temperature (Mumma, Weaver & Larson 1987). For original sources, see Bonev et al. 2007 (#1–9), Dello Russo et al. 2007 (#11, 12), Woodward et al. 2007 (#13), Bonev et al. 2008a (#10). (b) The 6.5- $\mu\text{m}$  H<sub>2</sub>O band in C/2003 K4, both fully resolved and also convolved to the resolution of *Spitzer* (Woodward et al. 2007). Ortho and para lines are indicated. (c) OPRs and spin temperatures for NH<sub>3</sub> and H<sub>2</sub>O in eight comets (H<sub>2</sub>O from references cited in panel a, NH<sub>3</sub> measurements from Shinnaka et al. 2011). (d) A comparison of  $T_{\text{spin}}$  for NH<sub>3</sub> and H<sub>2</sub>O in the eight comets of panel c. The spin temperatures for these primary volatiles agree within a given comet. Six Oort Cloud comets show relaxed spin temperatures near 29 K. However, OPRs in two fragments of a Jupiter-family comet (73P/SW3) are consistent with statistical equilibrium (panel c). The lower bounds to their spin temperatures are shown as 95% confidence limits (panel d). Similar measurements are beginning to emerge for methane. The spin temperature measured for CH<sub>4</sub> in C/2001 Q4 (33K +2/-1) agrees with that found for NH<sub>3</sub> and H<sub>2</sub>O in that comet (Kawakita et al. 2006).

parameter (see Section 5.2). Fourteen comets agree with one another in both parameters, but 73P/SW3-B and -C stand apart (see Section 5.2).

OPRs for NH<sub>3</sub> and H<sub>2</sub>O in 8 comets are compared in **Figure 10c**, and the derived spin temperatures are compared in **Figure 10d**. The measured spin temperatures for six NICs agree within their respective confidence limits and cluster near 30 K, while the NIC C/2001 A2 (LINEAR)



**Figure 11**

The relationship of the  $^{14}\text{N}/^{15}\text{N}$  ratio in CN and the  $\text{NH}_3$  ortho-para ratio (OPR) (Shinnaka et al. 2011). Thirteen comets share a common OPR for  $\text{NH}_3$  and a common enrichment factor for  $^{15}\text{N}$  in CN. 73P/SW3-B and -C differ greatly, in both parameters (see Sections 4 and 5.2).



falls near 22K. The two fragments (B and C) of the ecliptic comet 73P/SW3 display OPRs that represent statistical equilibrium, and thus spin temperatures that are quite high—in distinct contrast with the other 7 comets.

The ortho-para-meta spin isomers of  $\text{CH}_4$  were measured in NICs C/2001 Q4 (NEAT) (Kawakita et al. 2005) and C/2004 Q2 (Machholz) (Bonev et al. 2009). Spin isomers in methane can be sampled from the ground (rarely) for comets with very large Doppler shift, but were inconclusive in a sample of 10 comets, excepting C/2001 Q4 for which  $T_{\text{spin}}$  for  $\text{CH}_4$  ( $33 \pm 2/-1$  K) agrees with values for  $\text{NH}_3$  ( $31 \pm 4/-2$  K), and  $\text{H}_2\text{O}$  ( $31 \pm 11/-4$  K) (Kawakita et al. 2006). A single measurement of methanol spin states in a comet (Hale-Bopp) has placed a lower limit on the spin temperature of  $>15$ –18 K (Pardanaud et al. 2007). Buntkowsky et al. (2008) proposed that sublimation phenomena may control the OPR of  $\text{H}_2\text{O}$ , but similar arguments have not been examined for  $\text{NH}_3$  or  $\text{CH}_4$ . It is difficult to imagine a mechanism (other than formation) that can produce such dissimilar OPR values for three primary species, yet produce the same spin temperature.

The comparison of  $\text{NH}_2$  spin ratios with the  $^{14}\text{N}/^{15}\text{N}$  ratio in CN (Shinnaka et al. 2011) demonstrates that 13 of 15 comets share a common OPR for  $\text{NH}_3$  and a common enrichment of  $^{15}\text{N}$  in CN (73P/SW3-B and -C differ greatly, in both parameters) (Figure 11, and Section 5.2). This sameness raises additional issues, because CN has both primary (e.g., HCN,  $\text{CH}_3\text{CN}$ , etc.) and unknown precursors in some comets (see the review by Fray et al. 2005). The dominant primary nitrile (HCN) is regularly quantified with radio and IR spectroscopy, and its production rate is sometimes much smaller than that of CN. The correlation of jets seen in CN and continuum

is suggestive of CN production from organic material on or within grains (A'Hearn et al. 1986, Klavetter & A'Hearn 1994). One candidate material is the tetramer of HCN (diaminomaleonitrile), which is technically an oligomer rather than an addition polymer.

Diaminomaleonitrile is composed of a C<sub>2</sub> backbone with two amine (NH<sub>2</sub>) and two nitrile (CN) side groups. It is a solid at room temperature with a melting point of 178°C. Being less volatile than both the HCN monomer and HCN addition polymers, this oligomer could reside on the surface of a comet nucleus for long intervals (Matthews & Ludicky 1992) and be carried by grains far into the coma before dissociating. It could provide a distributed source of NH<sub>2</sub>, C<sub>2</sub>, and CN (Huebner, Boice & Korth 1989; Magee-Sauer et al. 1999), but not of HCN itself. The <sup>14</sup>N/<sup>15</sup>N ratio in CN and HCN provides an interesting test of this hypothesis, because the isotopic ratio should be the same in the HCN monomer and in CN derived from the tetramer. This sameness was observed in comets 17P/Holmes and C/1995 O1 (Hale-Bopp) (see Section 5.2). Hale-Bopp had the highest dust-to-gas ratio of any comet, whereas 17P underwent a massive outburst and ejected relatively pristine dust in large amounts. The spin temperature in NH<sub>2</sub> might then vary according to its precursors (e.g., monomeric NH<sub>3</sub> versus the tetramer of HCN). A study of NH<sub>2</sub> in archival spectra of 17P/Holmes seems warranted.

## 5. ISOTOPOLOGUES IN COMETS

The isotopic ratios in primary volatiles are regarded as immutable signatures of formation processes. General reviews are given by Jehin et al. (2009), Bockelée-Morvan et al. (2004), and Altwegg & Bockelée-Morvan (2003). Here, we emphasize isotopologues of hydrogen (D/H) in primary volatiles of nitrogen (<sup>14</sup>N/<sup>15</sup>N) in CN and HCN, and of carbon (<sup>12</sup>C/<sup>13</sup>C) in CN, for which recent progress has been substantial (see Section 5.1, 5.2). Isotopic ratios of oxygen and sulfur (<sup>16</sup>O/<sup>18</sup>O, <sup>32</sup>S/<sup>34</sup>S) are mentioned briefly (see Section 5.3).

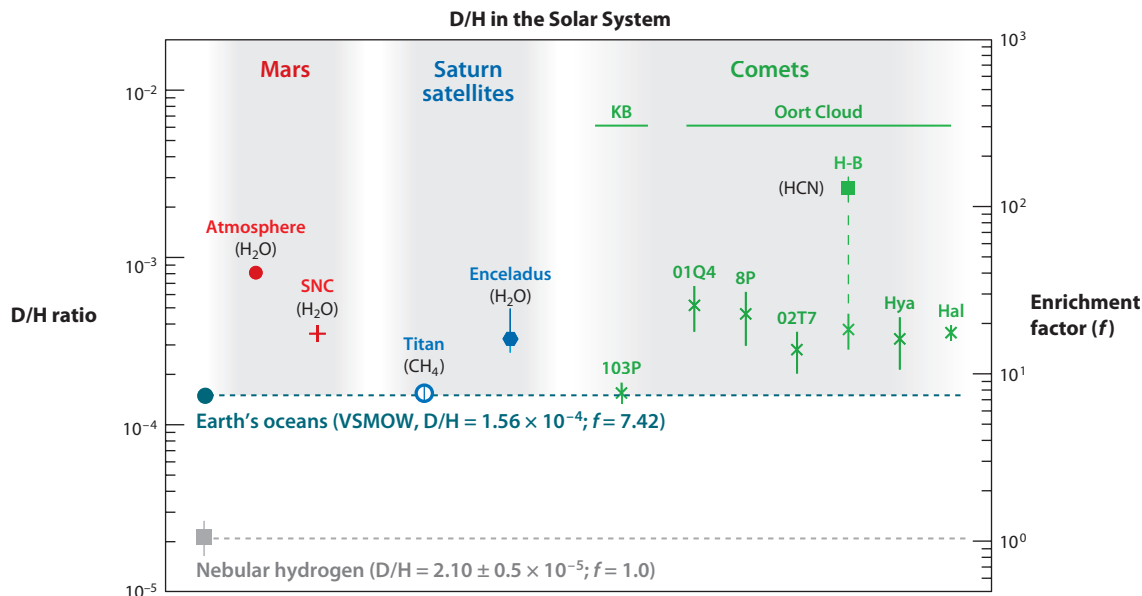
### 5.1. The D/H Ratio

Before 2010, the D/H ratio in cometary water had been measured in six comets, and all were from the Oort Cloud reservoir. The *Herschel* measurement of Hartley 2 added a seventh comet—the first from the Kuiper Disk (Hartogh et al. 2011) (see Section 2.2). The current status of D/H in the primary volatiles H<sub>2</sub>O and HCN is shown in **Figure 12**, along with values in VSMOW and the protosolar nebula. VSMOW is of interest mainly for assessing exogenous delivery of Earth's water.

Although the exact VSMOW value is known with high accuracy (D/H = 15.576 ± 0.01 × 10<sup>-5</sup>), its relevance to the bulk Earth is much less certain owing to the difficulty in estimating fractionation and abundance of water-equivalent hydrogen in the mantle and core. Hydrogen gas (H<sub>2</sub>, HD) was the principal hydrogen reservoir in the Solar Nebula, and Solar, Jovian, and Saturnian isotopic ratios are used to infer the protosolar (nebular) D/H ratio (solar wind, Geiss & Gloeckler 2003; Jupiter and Saturn, Lellouch et al. 2001 (ISO); Jupiter, Mahaffy et al. 1998 (Galileo/GCMS). On Neptune, D/H in H<sub>2</sub> is somewhat enriched at (4.5 ± 1) × 10<sup>-5</sup> (Lellouch et al. 2010). Following Lellouch et al. (2001), we here adopt the value 2.1 ± 0.4 × 10<sup>-5</sup> for protosolar D/H.

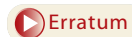
The first measurements of the D/H ratio in a comet were inferred from mass-resolved ion-spectra of H<sub>3</sub>O<sup>+</sup> and H<sub>2</sub>DO<sup>+</sup> in 1P/Halley, acquired by the Ion Mass Spectrometer (IMS) and Neutral Mass Spectrometer (NMS) instruments onboard *Giotto* (IMS, Balsiger, Altwegg & Geiss 1995; NMS, Eberhardt et al. 1995). Eberhardt et al. applied correction factors to the D/H ratio in hydronium ion in both investigations and obtained an improved value for the ratio of D/H in H<sub>2</sub>O (3.16 ± 0.34 × 10<sup>-4</sup>), one that was about twice higher than VSMOW and about a factor of 15 larger than the protosolar value. HDO was detected next in comets C/1996 B2 (Hyakutake) and C/1995 O1 (Hale-Bopp) through its 1<sub>01</sub>-0<sub>00</sub> rotational line at 465 GHz





**Figure 12**

The abundance ratio (D/H) of heavy (D) and light hydrogen (H) in selected Solar System objects is compared with the protosolar value ( $2.1 \pm 0.5 \times 10^{-5}$ ) (Lellouch et al. 2001). Absolute values of D/H are shown on the left, and their ratio to the protosolar value ( $f$ ) on the right. Earth's oceans (Vienna Standard Mean Ocean Water, VSMOW) are enriched relative to the protosolar value by a factor of  $\sim 7.4$  ( $D/H = 1.56 \times 10^{-4}$ ), whereas the mean of six Oort Cloud comets is enriched by a factor of  $\sim 15$ . Saturn's satellite Enceladus and SNC (shergottite, nakhlite, and chassigny) meteorites (early Mars) show enrichments similar to Oort Cloud comets, whereas Titan's atmosphere is less enriched and is consistent with VSMOW (Abbas et al. 2010). The high enrichment in Mars's atmosphere is due to escape of H over time. All comets sampled before 2010 are from the Oort Cloud reservoir, whereas Hartley 2 is from the Kuiper Belt. D/H in water from Hartley 2 is consistent with VSMOW (Hartogh et al. 2011). HCN in C1995 O1 (Hale-Bopp) is enriched in deuterium by a factor of  $\sim 100$  relative to the protosolar value—the combined enrichments in H<sub>2</sub>O and HCN are consistent with ion-molecule processing at  $\sim 30$  K. See also Sections 2.2 and 5.1. Comet key: 01Q4, C/2001 Q4 (NEAT); 8P, 8P/Tuttle; 02T7, C/2002 T7 (LINEAR); H-B, C/1995 O1 (Hale-Bopp); Hya, C/1996 B2 (Hyakutake); Hal, 1P/Halley; 103P, 103P/Hartley 2 ( $1.61 \pm 0.24 \times 10^{-4}$ ).



(Bockelée-Morvan et al. 1998, Meier et al. 1998b). The derived D/H values are in agreement with the determinations in 1P/Halley.

The D/H ratio in cometary water was also inferred from optical spectra of OD and OH, UV spectra of H and D, and IR spectra of H<sub>2</sub>O and HDO. Hutsemékers et al. (2008) report the detection of OD from ground-based spectra of the A-X band at 309 nm in comet C/2002 T7 (LINEAR) using the Ultraviolet and Visual Echelle Spectrograph (UVES) at ESO's Very Large Telescope (VLT). The Lyman- $\alpha$  lines of atomic D and H were detected in the Space Telescope Imaging Spectrograph (STIS) spectrum of C/2001 Q4 (NEAT) acquired from the *Hubble Space Telescope* (Weaver et al. 2008). High-resolution spectroscopy of the 3.7- $\mu$ m HDO  $\nu_1$  band, along with many lines of H<sub>2</sub>O hot-bands near 2.9  $\mu$ m, provided a measurement of D/H in 8P/Tuttle (an HTC) using the Cryogenic High Resolution IR Echelle Spectrometer (CRIRES) at the VLT (Villanueva et al. 2009). Within uncertainties, these new D/H retrievals are consistent with previous measurements.

However, the upper limits for HDO in comets C/2004 Q2 (Machholz) ( $< 2.3 \times 10^{-4}$   $3\sigma$ , Crovisier et al. 2005) and 153P/Ikeya-Zhang ( $< 2.8 \pm 0.3 \times 10^{-4}$ , Biver et al. 2006) suggest that the D/H ratio in these OC comets is lower than that in the six comets for which positive

detections were achieved. At the 95% confidence limit, the value for D/H in C/2004 Q2 Machholz is consistent with VSMOW. In 2010, *Herschel* achieved the first measurement of D/H in an ecliptic comet—the resulting D/H ratio for water in 103P/Hartley 2 ( $1.61 \pm 0.24 \times 10^{-4}$ ) is consistent with VSMOW (Hartogh et al. 2011, see Section 2.2).

As deuterium fractionation cannot occur in the coma (Rodgers & Charnley 2002), the value of D/H in molecules other than H<sub>2</sub>O can also provide unique insights into the formation temperature of precometary primary volatiles. The D/H ratio in HCN from comet Hale-Bopp ( $2.3 \pm 0.4 \times 10^{-3}$ , Meier et al. 1998a) demonstrated a higher deuterium enrichment in this organic molecule than in water (**Figure 12**)—the two enrichment factors in Hale-Bopp are consistent with formation by ion-molecule reactions at a temperature of  $\sim 30$  K, and this temperature is consistent with the spin temperature derived for water (Crovisier et al. 1997). Upper limits were also obtained for several monodeuterated primary species in Hale-Bopp (formaldehyde, ammonia, and two isotopologues of methanol (Crovisier et al. 2004a).

Deuterium fractionation in other volatile species is expected, and the abundance ratios of isotopologues are enhanced for molecules having multiple sites for deuterium substitution. Examples include C<sub>2</sub>H<sub>5</sub>D, NH<sub>2</sub>D, and CH<sub>3</sub>D with six, three, and four equivalent sites. CH<sub>3</sub>D has been targeted in comets, but not yet detected. Taking  $D/H = 0.25 \times (CH_3D/CH_4)$ , upper limits ( $2\sigma$ ) to the D/H ratios in methane were 0.075 and 0.01 in 153P/Ikeya-Zhang and C/2001 Q4 (NEAT), respectively (Kawakita et al. 2003, 2005). In C/2004 Q2 (Machholz), the upper limits ( $2\sigma$ ) were 0.0064 and 0.0033 (Boney et al. 2009 and Kawakita & Kobayashi 2009, respectively). The achieved sensitivities are as yet not sufficient to test alternative models for methane production and fractionation.

Detection prospects for deuterated isotopologues depend on molecular production rates, isotopic fractions, and the specific observing geometry (geocentric and heliocentric distances). Improved astronomical sensitivity (CRIRES/VLT, *Herschel*, ALMA) will permit routine measurement of D/H in water and hydrocarbons, and other isotopologues, tying each organic class to a place of origin in the protoplanetary disk (Encrenaz et al. 2005).

Chemical models of isotopic exchange with H<sub>2</sub> in a turbulent nebula predict a strong dependence of the D/H ratio on heliocentric distance (Horner, Mousis & Hersant 2007; Horner et al. 2008). Comets formed close to the orbit of Jupiter are expected to have lower D/H ratios, perhaps even lower than VSMOW. Comets formed outside the turbulent Solar Nebula (beyond 17 AU) should exhibit higher D/H ratios, as expected for unprocessed material of natal cloud origin. Values at Saturn's orbital position in the protoplanetary disk should have been intermediate [however, Lellouch et al. (2001) discuss weak evidence for a smaller D/H enrichment on Saturn]. A recent determination of D/H in methane (CH<sub>3</sub>D/CH<sub>4</sub>) in the atmosphere of Titan (Saturn's satellite) returned a value ( $D/H = 1.58 \pm 0.16 \times 10^{-4}$ ) consistent with VSMOW (Abbas et al. 2010) (**Figure 12**). However, the D/H ratio measured in an Enceladus plume (D/H in water,  $2.9 (+1.5/-0.7) \times 10^{-4}$ ) is about twice as large (Waite et al. 2009).

Dynamical models predict that icy planetesimals from the giant planet's feeding zones entered both principal reservoirs (KB, OC). If Titan's deuterium-enriched CH<sub>4</sub> was derived from icy planetesimals involved in its formation, we can expect that some fraction of comets will today retain that formation signature (VSMOW), whether now from the KB or the OC. 103P/Hartley 2 would seem to be the first such comet detected (see above, and Section 2.2). Measurements of the D/H ratio in a larger sample of comets, should provide further constraints for Solar Nebula models and for the origin of cometary (and perhaps terrestrial) water.

The similar D/H ratios measured in six OC comets might indicate that these comets accreted at similar distances from the Sun or that the radial distribution of the D/H ratio in Solar Nebula ices was almost uniform over the range of heliocentric distances where most OC comets accreted.

The proposed capture of OC comets from nearby stars in the Sun's birth cluster (Levison et al. 2010) may require revision of this picture.

## 5.2. Isotopes of Nitrogen and Carbon

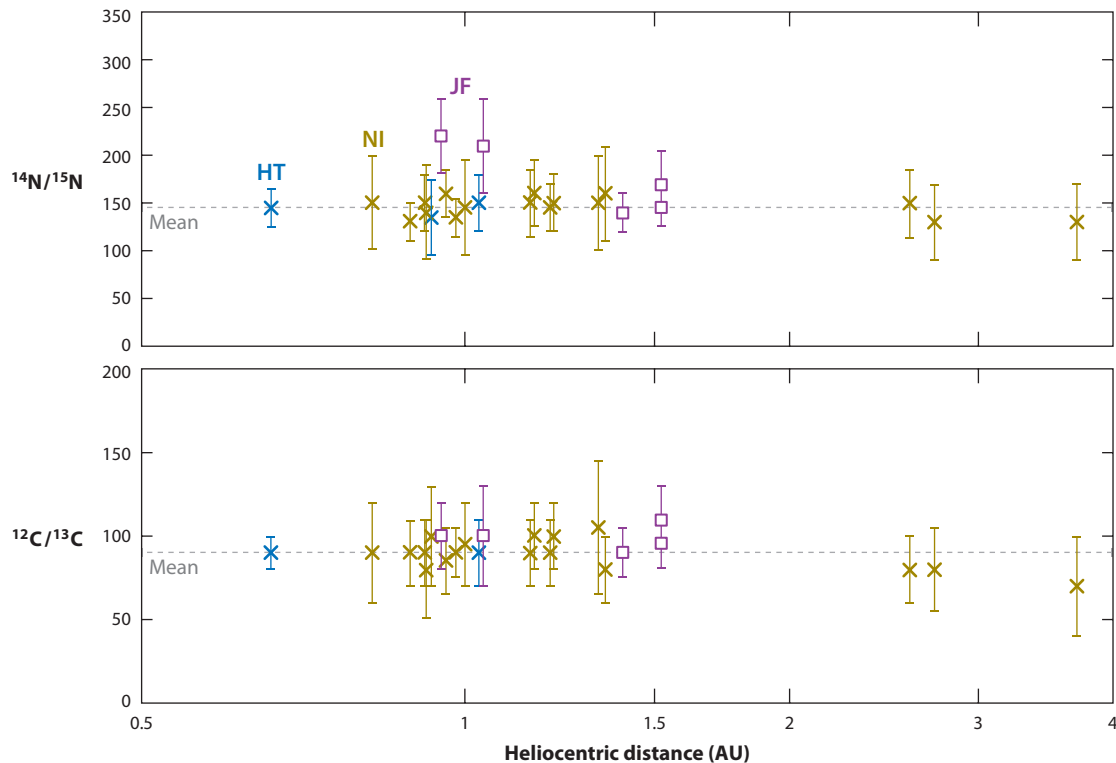
Arpigny et al. (2003) first reported a surprising twofold enrichment of heavy nitrogen in cometary CN, relative to the terrestrial value. Their measurements of C/1995 O1 (Hale-Bopp) and C/2000 WM<sub>1</sub> (LINEAR) were made at a heliocentric distance range (0.9–1.3 AU), where CN can have multiple precursors. They argued that a second precursor with much higher enrichment was needed because the reported <sup>14</sup>N/<sup>15</sup>N ratio in HCN was lower than the terrestrial value (Jewitt et al. 1997, Ziurys et al. 1999). In an attempt to isolate HCN as a sole precursor, Manfroid et al. (2005) extended this study to distances beyond ~2.7 AU but found no change in the C<sup>14</sup>N/C<sup>15</sup>N ratio.

Manfroid et al. (2009) extended the study to 23 comets from ecliptic and NI orbital groups. In 18 comets, isotopic ratios of carbon (<sup>12</sup>C/<sup>13</sup>C) and nitrogen (<sup>14</sup>N/<sup>15</sup>N) were determined from high-resolution spectroscopy of C<sub>2</sub> and CN emission in the visible spectrum, using mainly the CN (0–0) band. In 5 more comets, lower bounds were obtained. For some targets, isotopic ratios were measured at multiple heliocentric distances. Excepting the disrupted comet 73P/Schwassman-Wachmann 3, all individual values determined for the <sup>12</sup>C/<sup>13</sup>C and <sup>14</sup>N/<sup>15</sup>N isotopic ratios are consistent (within error) with the mean value obtained for all comets, irrespective of the type of orbit, the heliocentric distance at which the comet was observed, and (for carbon) the species (C<sub>2</sub> or CN) from which the ratio was determined. The average value for the <sup>12</sup>C/<sup>13</sup>C ratio is 91.0 ± 3.6 and the average value for the <sup>14</sup>N/<sup>15</sup>N ratio is 147.8 ± 5.7. The carbon isotopic ratio is consistent with the telluric value (88.99), but the nitrogen isotopic ratio is almost a factor of two smaller than the telluric value (273.72). The <sup>12</sup>C/<sup>13</sup>C and <sup>14</sup>N/<sup>15</sup>N ratios determined in this way are depicted in **Figure 13** (Manfroid et al. 2009).

The unexpected outburst of 17P/Holmes on October 24, 2007 enabled a new measurement of the HC<sup>14</sup>N/HC<sup>15</sup>N ratio, this time in an ecliptic (JF) comet. The derived isotopic ratios of <sup>12</sup>C/<sup>13</sup>C (114 ± 26) and <sup>14</sup>N/<sup>15</sup>N (139 ± 26) were consistent with the values measured almost simultaneously in the CN radical (Bockelée-Morvan et al. 2008). These researchers also reanalyzed the HCN data in comet Hale-Bopp and suggested that the <sup>14</sup>N/<sup>15</sup>N ratio had been overestimated in the previous studies conducted by Jewitt et al. (1997) and Ziurys et al. (1999). The new determination suggests a similar nitrogen isotopic composition for HCN and CN in comet Hale-Bopp, though the large uncertainty in their retrieval does not exclude HCN being less <sup>15</sup>N-rich than CN (**Figure 14**).

The surprising enrichment of heavy nitrogen in CN can be used to test both the possible precursors of CN, and their relation to interstellar chemistry. The principal photolysis channel for HCN produces CN, and their cometary populations must bear the same isotopic signature if HCN is the sole precursor of CN. In some comets, the production rates of HCN and CN are similar. At R<sub>h</sub> beyond ~3 AU in Hale-Bopp, the two production rates were equal and the parent scale length of CN agreed with the predicted photodissociation scale length of HCN, leading Rauer et al. (2003) to conclude that HCN was the sole precursor of CN at those distances. Based on measurements in comets Hale-Bopp, C/2001 Q4 (Neat), and C/2003 K4 (LINEAR), Manfroid et al. (2005) suggested that the <sup>14</sup>N/<sup>15</sup>N ratio in CN was equally low from 0.9 AU to 3.7 AU and argued that HCN was not the sole precursor of CN over this range. However, their data are also consistent with the view that all precursors of CN have the same <sup>14</sup>N/<sup>15</sup>N ratio.

In some comets, the production rate of CN is greater than that of HCN (a dramatic example is 6P/d'Arrest, see Section 3.2.2), showing that additional sources of CN are needed. Indeed, optical surveys found that dust is a principal source of CN in many comets (Section 3.1). In reviewing the

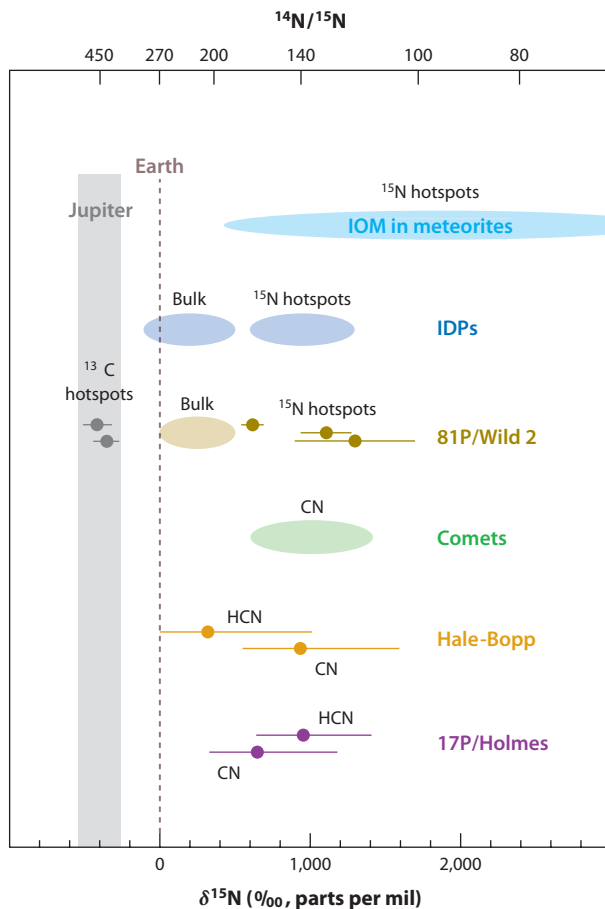


**Figure 13**

The  $^{12}\text{C}/^{13}\text{C}$  and the  $^{14}\text{N}/^{15}\text{N}$  isotopic ratios in CN (or  $\text{C}_2$ ) are shown versus heliocentric distance for comets of ecliptic and nearly isotropic (NI) dynamical classes. Ecliptic comets are further subdivided into Halley Type (HT) and Jupiter Family (JF) groups, whereas the NI group contains both long-period and dynamically new comets with  $T_J < 2$  (for consistency, we use the classification of Levison 1996; here, we group the external comet 153P/Ikeya-Zhang with the HT comets for convenience). Individual values for  $^{12}\text{C}/^{13}\text{C}$  and  $^{14}\text{N}/^{15}\text{N}$  are distributed around the mean values ( $91.0 \pm 3.6$  and  $147.8 \pm 5.7$ , respectively, shown as *horizontal dashed gray lines*). Neither ratio appears to depend on the dynamical class of the comet or on the heliocentric distance when measured. Adapted from Manfroid et al. (2009), who used the slightly different classification scheme of Horner et al (2003). See also Section 5.2.

origin of CN in comets, Fray et al. (2005) identified three principal lines of evidence that support the presence of multiple sources of CN in cometary atmospheres: (a) CN is often found in jets, (b) the radial distribution of CN is generally less extended than expected from HCN photodissociation alone, and (c) the CN/HCN production rate ratio exceeds unity in some comets (8P/Tuttle is a second recent example, see Bonev et al. 2008b). Possible additional sources of CN include the photolysis of acetonitrile ( $\text{CH}_3\text{CN}$ ), cyanoacetylene ( $\text{HC}_3\text{N}$ ), and  $\text{C}_2\text{N}_2$  (although not yet detected, dicyanogen is an expected primary volatile), and the thermal degradation of ( $^{15}\text{N}$ -rich) refractory organics present in dust grains (Fray et al. 2005).

Comets from the OC and from the KB possibly all exhibit a similar anomalous N isotopic composition in HCN. Abundance measurements strongly argue for the presence of other CN precursors (dust or gas-phase species) in cometary atmospheres. If correct, those additional precursors should share the same low  $^{14}\text{N}/^{15}\text{N}$  isotopic ratio to explain the consistent  $^{14}\text{N}/^{15}\text{N}$  values among the 18 comets now sampled, implying that a twofold  $^{15}\text{N}$  enrichment with respect to the telluric value is perhaps a general property of CN-bearing compounds in comets. If the HCN tetramer (diaminomaleonitrile) is an important precursor of CN, some  $\text{NH}_2$  radicals should also



**Figure 14**

Nitrogen isotopic measurements in primitive matter of the Solar System. Shown are values measured in Jupiter (Fouchet et al. 2004), comet 17P/Holmes (Bockelée-Morvan et al. 2008), comet Hale-Bopp (Arpigny et al. 2003; Bockelée-Morvan et al. 2008), and other comets (Arpigny et al. 2003; Hutsemékers et al. 2005; Manfroid et al. 2005, 2009), dust particles of comet 81P/Wild 2 collected by the *Stardust* mission (McKeegan et al. 2006), interplanetary dust particles (IDPs) (Floss et al. 2006), and insoluble organic matter (IOM) in carbonaceous meteorites (Busemann et al. 2006). So-called hotspots in meteorites are regions that present strong isotopic enrichments relative to the surrounding material. Points with error bars correspond to single measurements. When many measurements are available, ellipses encompassing the range of measured values are drawn. After Bockelée-Morvan (2010). See also Section 5.2.

be enriched in  $^{15}\text{N}$ . The  $^{14}\text{N}/^{15}\text{N}$  value in coma  $\text{NH}_2$  could then reflect the relative contributions of HCN tetramer,  $\text{NH}_3$ , and other nitrile precursors. If so, the OPRs observed for  $\text{NH}_2$  would require reinterpretation (Section 5.2). The possible relationship of nitrogen fractionation to interstellar origin is discussed in Section 7.2.

### 5.3. Isotopes of Oxygen and Sulfur

Measuring the  $^{16}\text{O}/^{18}\text{O}$  isotope ratio in cometary volatiles is of paramount importance to disentangling the diverse scenarios proposed to explain the oxygen isotopic anomaly in meteorites. Several measurements have been performed in cometary water either directly from the

**Table 2** Isotopic ratios in comets<sup>a</sup>

Isotopic ratio	Species	Value	Comet	Reference
D/H	H <sub>2</sub> O	$(3.06 \pm 0.34) 10^{-4}$	1P/Halley	Eberhardt et al. (1995)
		$(3.08 + 0.38 / - 0.53) 10^{-4}$	1P/Halley	Balsiger, Altwegg & Geiss (1995)
		$(2.9 \pm 1.0) 10^{-4}$	C/1996 B2 (Hyakutake)	Bockelée-Morvan et al. (1998)
		$(3.3 \pm 0.8) 10^{-4}$	C/1995 O1(Hale-Bopp)	Meier et al. (1998b)
		$(2.5 \pm 0.7) 10^{-4}$	C/2002 T7 (LINEAR)	Hutsemékers et al. (2008)
		$(4.6 \pm 1.4) 10^{-4}$	C/2001 Q4 (NEAT)	Weaver et al. (2008)
	HCN	$(4.0 \pm 1.4) 10^{-4}$	8P/Tuttle	Villanueva et al. (2009)
		$(2.3 \pm 0.4) 10^{-3}$	C/1995 O1(Hale-Bopp)	Meier et al. (1998a)
<sup>14</sup> N/ <sup>15</sup> N	CN	147.8 ± 5.7	18 comets	Manfroid et al. (2009)
	HCN	205 ± 70	C/1995 O1(Hale-Bopp)	Bockelée-Morvan et al. (2008)
	HCN	139 ± 26	17P/Holmes	Bockelée-Morvan et al. (2008)
<sup>12</sup> C/ <sup>13</sup> C	C <sub>2</sub>	93 ± 10	4 OC comets	Wyckoff et al. (2000)
	CN	91.0 ± 3.6	18 comets	Manfroid et al. 2009
	HCN	111 ± 12	C/1995 O1(Hale-Bopp)	Jewitt et al. (1997)
	HCN	114 ± 26	17P/Holmes	Bockelée-Morvan et al. (2008)
<sup>16</sup> O/ <sup>18</sup> O	H <sub>2</sub> O	518 ± 45	1P/Halley	Balsiger, Altwegg & Geiss (1995)
		470 ± 40	1P/Halley	Eberhardt et al. (1995)
		520 ± 25	4 OC comets	Biver et al. (2007)
	OH	425 ± 55	C/2002 T7 (LINEAR)	Hutsemékers et al. (2008)
<sup>32</sup> S/ <sup>34</sup> S	S <sup>+</sup>	23 ± 6	1P/Halley	Altwegg (1996)
	CS	27 ± 3	C/1995 O1(Hale-Bopp)	Jewitt et al. (1997)
	H <sub>2</sub> S	17 ± 4	C/1995 O1(Hale-Bopp)	Crovisier et al. (2004a)

<sup>a</sup>After Jehin et al. (2009).

observations of H<sub>2</sub>O and H<sub>2</sub><sup>18</sup>O or from observations of OH, H<sub>3</sub>O<sup>+</sup>, and their <sup>18</sup>O counterparts (Table 2). Uncertainties in the measured <sup>16</sup>O/<sup>18</sup>O values (typically 10%) are too large for enlightening significant deviations from the VSMOW value of 498.7, though marginal <sup>18</sup>O depletions or enrichments are suggested for some comets. The protosolar <sup>16</sup>O/<sup>18</sup>O value, as determined from the oxygen isotopic composition of calcium-rich inclusions, is ~530. The values measured in cometary water point to none to significant <sup>18</sup>O enrichment with respect to the protosolar value. However, more precise <sup>16</sup>O/<sup>18</sup>O measurements are needed.

A few measurements of the <sup>32</sup>S/<sup>34</sup>S isotopic ratio in different molecules have been obtained (Table 2). Most are consistent with the terrestrial value <sup>32</sup>S/<sup>34</sup>S = 22.2, except for H<sub>2</sub>S for which a marginal <sup>34</sup>S enrichment is suggested. Such enrichment would be important to confirm. Primitive matter contained in IDPs and carbonaceous meteorites presents much smaller anomalies in sulfur isotopic composition (Busemann et al. 2006, Floss et al. 2006).

## 6. TAXONOMY BASED ON GRAIN STRUCTURE AND MINERALOGY

Ices and rocky material (dust grains) are present in comet nuclei in roughly equal amounts. Although this review has so far addressed the volatile fraction of comets, much profound information about the high-temperature processing of precometary material is locked in the composition and structure of refractory grains. This information is key to understanding the varied processes experienced by this material prior to its incorporation into the cometary nucleus. Our

existing knowledge concerning the refractory organic material in comets is based on analysis of dust on space missions to 1P/Halley (e.g., Fomenkova 1999) and on analysis in terrestrial laboratories of samples returned from 81P/Wild 2 (e.g., Sandford et al. 2006). Since Hale-Bopp, IR spectral studies of cometary dust have provided detailed and increasingly rich information—both compositional and structural in nature—on mineral assemblages in comets.

### 6.1. Refractory Organic Grains

Prior to the spacecraft investigations of comet Halley, cometary dust grains were thought to be composed entirely of silicate material. It was also recognized that the amount of carbon stored in the nuclear ices could account for at most  $\sim 1/3$  of total carbon if bulk carbon was present in cosmic abundance relative to oxygen, and thus that about  $2/3$  of cometary carbon was missing. The discovery of refractory organic grains by the PUMA/PIA dust analyzers on the *Vega* and *Giotto* spacecraft (Kissel et al. 1986a,b) revealed a new component of the cometary nucleus, and its composition resolved the issue of missing carbon (Jessberger, Crostforidis & Kissel 1988). Known initially as CHON grains for their carbon, hydrogen, oxygen, and nitrogen content, they now are sometimes called CHON-PS in recognition of the phosphorus and sulfur in them.

The first detailed laboratory examination of cometary organo-silicate grains was enabled by samples of dust returned by the *Stardust* mission. The *Stardust* samples contain an organic component that is aromatic-poor but enriched in nitrogen and oxygen relative to meteoritic insoluble organic matter (IOM) (Sandford et al. 2006, Clemett et al. 2010). The aromatic component that is present is N-rich, with the nitrogen predominately incorporated in nitrile functional groups. However, a significant quantity of the organic nitrogen appears to be contained in aliphatic hydrocarbons, with methylamine and ethylamine identified as major carriers (Glavin, Dworkin & Sandford 2008). Overall, the *Stardust* refractory organic component is more closely related to that of IDPs than to that of carbonaceous chondrites (Clemett et al. 2010).

Several claims were advanced for detections of polycyclic aromatic hydrocarbon (PAH) molecules in cometary comae, specifically for phenanthrene (Moreels et al. 1994), pyrene, and anthracene (Clairemidi et al. 2004, 2008) in comet 1P/Halley. Lisse et al. (2006) observed Tempel 1 with *Spitzer* and identified PAHs and many mineralogical dust features in the postimpact spectra. A subsequent reanalysis of the ISO spectra of comet Hale-Bopp led Lisse et al. (2007) to conclude that PAHs were also present in that comet. However, the presence of PAHs in these spectra has been challenged, and so the question as to their presence in cometary comae is unresolved (Crovisier & Bockelée-Morvan 2008, Lisse 2008). Nevertheless, the presence of PAHs in comets is confirmed by analyses of the *Stardust* samples (Sandford et al. 2006, Keller et al. 2006, Clemett et al. 2010).

The RPA-1 electron analyzer on the *Giotto* spacecraft detected negative ions (i.e., anions) in the inner coma of comet 1P/Halley:  $O^-$ ,  $OH^-$ ,  $C^-$ ,  $CH^-$ , and  $CN^-$  (Chaizy et al. 1991). This was an important and unexpected discovery. These ions were determined to be of cometary origin and additional unidentified heavy, presumably organic, anions were also detected within the 22–65 and 85–110 amu mass regions, leading Chaizy et al. to conclude that these were the negatively charged versions of the complex CHON organics detected in Halley's coma (e.g., Altwegg, Balsiger & Geiss 1999). Regardless, the presence of abundant anions opens the prospect of a new channel for chemical processing in the inner coma via dissociative attachment (see Section 7). Ion-molecule reactions had previously been confined to cations reacting with neutral molecules.

### 6.2. Silicate Grains

Because silicates in the diffuse ISM are amorphous, the finding that silicate particles in some comets are largely crystalline was a great surprise (see reviews by Wooden 2008, Burchell & Kearsley 2009,

Kelley & Wooden 2009). Possible origins of these crystalline grains include direct condensation at high temperature in the inner Solar Nebula, or annealing in nebular shocks near Jupiter. Once these crystals are formed, they must be transported outward to the comet-forming zones to be incorporated into comet nuclei. Crystalline silicates were identified first from IR spectra of comet Halley (Bregman et al. 1987, Campins & Ryan 1989) and from spectra of many comets since then. Observations of Comet Hale-Bopp with ISO provided the first complete IR spectral survey of dust (5–40  $\mu\text{m}$ ), from which both amorphous and crystalline silicates were identified (Leech et al. 1997, Crovisier et al. 2000). A systematic IR survey of grain properties is underway with *Spitzer*, and many comets have been surveyed to date (cf. Kelley et al. 2006, Kelley & Wooden 2009).

Amorphous silicates are also found in comets (Harker et al. 2002) and cometary IDPs [as so-called Glass with Embedded Metal and Sulfides (GEMS), Hanner & Bradley 2004], where they can be the major reservoir (as high as 80%) of isotopically anomalous material (Keller, Nakamura-Messenger & Messenger 2009). IDPs recently collected from the dust stream of 26P/Grigg-Skjellerup contain abundant amorphous silicate and presolar grains, typical of the highly porous IDPs that historically have been discussed as cometary in origin (Nguyen, Busemann & Nittler 2007) and which may indicate a tentative interstellar origin for these particles (Busemann et al. 2008). However, the *Stardust* samples from comet 81P/Wild 2 are composed of predominately crystalline silicate material (>50%; Zolensky et al. 2008, Westphal et al. 2009), and anhydrous IDPs can contain crystalline grains with very high magnesium content (e.g., Wooden 2008). Such characteristics appear to be more representative of grains formed in the inner Solar System than of the ISM or outer disk (Westphal et al. 2009).

Grain properties thus provide key insights into the origin and evolution of cometary material. When coupled with evidence obtained from primary volatiles and related cosmogonic invariants (isotopic ratios, nuclear spin temperatures, etc.), powerful insights on processes affecting the origin and evolution of cometary material are gained (see Section 7). As yet, published results from grain surveys are too sparse for general comparison with surveys of primary volatiles and other properties in comets.

## 7. LINKS TO THE INTERSTELLAR MEDIUM

All cometary matter, in some form or other, was once in the ISM. The central issue is how much of this matter survived initial incorporation into the protosolar nebula and (later) the travails of a hot, energetic nebular chemistry. Understanding the similarities and differences between interstellar and cometary composition should shed light on the physics and chemistry of these processes.

Interstellar cloud material can first undergo chemical modification during the infall and accretion phase of protostellar evolution. Depending upon where and when this material enters the disk, any interstellar signatures may be completely lost or largely retained (Neufeld & Hollenbach 1994; Aikawa et al. 2008; Lee, Bergin & Lyons 2008; Charnley & Rodgers 2009; Visser et al. 2009; Visser & Dullemond 2010). Once in the nebula, any surviving interstellar signatures are subject to modification or obliteration. Indeed, chemistries similar to that in molecular clouds may have occurred in the outer regions of the protosolar nebula, making it possible that some of the chemical characteristics found in primitive material were actually set there. Recent reviews of the chemistry of protoplanetary disks and the protosolar nebula have been conducted by Ciesla & Charnley (2006), Bergin et al. (2007), Apai & Lauretta (2010), Bergin (2011), and Semenov (2011). Disk isotopic chemistry (D and  $^{13}\text{C}$ ) has been modeled recently by Willacy (2007) and by Woods & Willacy (2009).

Models of disk chemistry cannot be as well constrained as those of interstellar clouds, owing to the present difficulty in measuring chemical abundances (particularly isotopic ratios) of many



**Table 3** Representative ranges of molecular abundances in cometary and interstellar ices<sup>a</sup>

Molecule	Comets	Quiescent dense clouds	Low-mass protostars	Massive protostars
CO	0.4–30	9–36	0–100	3–50
CO <sub>2</sub>	2–30	15–44	2–68 <sup>b</sup>	4–23
CH <sub>4</sub>	0.4–1.6	<3	2–8	0.4–1.9
CH <sub>3</sub> OH	0.2–7	5–12	1–30	5–30
H <sub>2</sub> CO	0.11–1	...	~6	1–3
HCOOH	0.06–0.14	~2	1–9	3–7
NH <sub>3</sub>	0.2–1.4	<6–9	2–15	5–15
<sup>13</sup> C <sup>18</sup> HNCO	0.02–0.1	<2	<0.9	0.3–6
H <sub>2</sub> S	0.12–1.4	<1–4	...	<0.3–1
OCS	0.1–0.4	<0.2	...	0.04–0.2

<sup>a</sup>Abundances are expressed in percent relative to water. Relative abundances for native ices in the nucleus are taken to be the same as relative production rates for primary volatiles observed in cometary comae (**Table 4**). Interstellar entries are taken from Bergin et al. (2005), Boogert et al. (1996, 2004, 2008), Bottinelli et al. (2010), Dartois (2005), Dartois et al. (1999), Gerakines et al. (1999), Gibb et al. (2000, 2004), Knez et al. (2005), Oberg et al. (2008), Palumbo et al. (1997), Pontoppidan et al. (2008), Schutte et al. (1996), Smith (1991), van Broekhuizen et al. (2004).

<sup>b</sup>For most sources, the range is 20–30% (Pontoppidan et al. 2008)

<sup>c</sup>Assumes isocyanic acid ice is directly connected to the presence of OCN<sup>-</sup>, the proposed carrier of the 4.62- $\mu$ m absorption feature (e.g., Pontoppidan et al. 2003, van Broekhuizen et al. 2004).

species in protoplanetary disks. We therefore focus on the connection between comets and the known chemical composition of molecular clouds, and we now review the evidence for relatively unprocessed interstellar material in comets.

## 7.1. Candidate Interstellar Molecules

The known cometary molecules comprise a subset of those identified in the ISM (excepting, for example, C<sub>2</sub>H<sub>6</sub> and S<sub>2</sub>). We now consider the possibility that the molecular inventory of comets is the product of interstellar chemistry.

**7.1.1. Possible interstellar precursors of primary volatiles in cometary ices.** The composition of the cometary ice is qualitatively and, in many cases, quantitatively consistent with that determined for the major components of astronomical ices as measured by IR spectroscopy toward embedded protostars and background stars (**Table 3**): H<sub>2</sub>O, CO, CO<sub>2</sub>, CH<sub>4</sub>, CH<sub>3</sub>OH, H<sub>2</sub>CO, NH<sub>3</sub>, and HCOOH (van Dishoeck 2004, Gibb et al. 2004, Whittet et al. 2007, Boogert et al. 2011). Other molecules present at trace abundances in comets, including more complex molecules, are also detected in the gas phase of various interstellar sources (**Table 4**). Evaporation of these icy mantles in the immediate environs of massive and low-mass protostars gives rise, respectively, to so-called hot cores and hot corinos (Herbst & van Dishoeck 2009). This allows molecules that are only present in trace amounts within the ice matrix to be unambiguously identified with the much greater sensitivity of rotational gas-phase spectroscopy (Herbst & van Dishoeck 2009). **Table 4** displays quantitative comparisons of the relative abundance ratios of five comets and three interstellar sources: a hot core [Sgr B2(N)], a hot corino (IRAS16293-2422), and a cold dark cloud (L134N).

The interstellar ice mantles formed on dust grains in cold molecular clouds grow by the accretion of atoms and molecules from the gas. The simple hydrides are understood to form by H atom additions to heavy atoms (e.g., Watson 1976), although recent experiments indicate that

**Table 4** Representative abundances of molecules observed in comets and interstellar sources<sup>a</sup>

Molecule	Comets <sup>b</sup>					Interstellar Sources		
	Halley	Hyakutake	Hale-Bopp	2001 A2	73P/SW3	L134N <sup>c</sup>	IRAS 16293 <sup>d</sup>	Sgr B2(N) <sup>e</sup>
CO	3.5–11	14–30	12–23	4	0.5	26,400	8,000	1,000
CO <sub>2</sub>	3–4	...	6	...	...	...	...	...
CH <sub>4</sub>	<0.8	0.8	1.5	1.2	< 0.25	...	...	...
C <sub>2</sub> H <sub>2</sub>	0.3	0.2–0.5	0.1–0.3	0.5	<0.04	...	...	...
C <sub>2</sub> H <sub>6</sub>	0.4	0.6	0.6	1.7	0.14	...	...	...
CH <sub>3</sub> OH	1.8	2	2.4	2.8–3.9	0.22	1	10	3–200
H <sub>2</sub> CO	4	1	1.1	0.24	0.14	6.6	2	0.5
HCOOH	...	...	0.09	...	...	0.1	<0.03	0.1
HCOOCH <sub>3</sub>	...	...	0.08	...	...	...	0.09	1
CH <sub>3</sub> CHO	...	...	0.02	...	...	0.2	<0.07	0.2
(CH <sub>2</sub> OH) <sub>2</sub>	...	...	0.25	...	...	...	...	0.1
CH <sub>3</sub> OCH <sub>3</sub>	...	...	<0.5	...	...	...	0.16	0.3
NH <sub>2</sub> CHO	...	...	0.015	...	...	...	<0.001	0.2
NH <sub>3</sub>	1.5	0.5	0.7	...	<0.3	0.08	6	...
HCN	0.1	0.1–0.2	0.25	0.1–0.6	0.25	1.3	0.2	0.4
HNCO	...	0.07	0.1	...	...	...	0.3	0.6
HNC	...	0.01	0.04	0.0066	<0.0013	2.0	0.01	0.1
CH <sub>3</sub> CN	...	0.01	0.02	0.028	0.030	...	0.25	30
HC <sub>3</sub> N	...	...	0.02	...	...	0.06	0.03	5
H <sub>2</sub> S	0.4	0.8	1.5	1.15	0.25	0.3	3	...
CS	...	0.1	0.1	0.07	0.11	0.3	0.6	...
OCS	...	0.1	0.4	...	...	0.7	8	2
SO	...	...	0.3	...	...	6.6	8	...
SO <sub>2</sub>	...	...	0.2	...	...	0.1	3	30
CS <sub>2</sub>	0.2	0.1	0.2	...	...	...	...	...
H <sub>2</sub> CS	...	...	0.02	...	...	0.2	0.02	20
NS	...	...	0.02	...	...	...	0.02	...
S <sub>2</sub>	...	0.005	...	...	...	...	...	...

<sup>a</sup>Abundances are expressed in percent relative to water. (Data updated from Charnley & Rodgers 2008, Bockelée-Morvan et al. 2004, Charnley et al. 2002, and Ehrenfreund & Charnley 2000).

<sup>b</sup>Full comet designations are: 1P/Halley, C/1996 B2 (Hyakutake), C1995 O1 (Hale-Bopp), C/2001 A2 (LINEAR), 73P/Schwassman-Wachmann 3. Compared to Halley, Hyakutake, and Hale-Bopp, C/2001 A2 is enriched in organics, whereas 73P is depleted. For molecular abundances in C/2001 A2, see Biver et al. 2006, Gibb et al. 2007, Magee-Sauer et al. 2008; for 73P, see summary in DiSanti & Mumma 2008, and also Lis et al. 2008, Biver et al. 2008, Dello Russo et al. 2009. See Section 3.2.

<sup>c</sup>Lynds 134 North (L134N) is a cold dark interstellar cloud. Shown is the lower limit, as H<sub>2</sub>O is not detected in this source. Molecular abundances are from Ohishi, Irvine & Kaifu (1992), and the water abundance limit H<sub>2</sub>O/H<sub>2</sub> < 3 × 10<sup>-7</sup> is from Snell et al. (2000), assuming an H<sub>2</sub> column density of 1 × 10<sup>22</sup> cm<sup>-2</sup>.

<sup>d</sup>IRAS 16293-2422 is a binary solar-type protostar. Inner envelope abundances are from Schöier et al. (2002). For HCN, HNC, CS, and CO, entries are for the cooler envelope. Water abundances are from Parise et al. (2005), and additional hot core data for HCOOCH<sub>3</sub>, CH<sub>3</sub>OCH<sub>3</sub>, and NS are from Kuan et al. (2004), Huang et al. (2005a), and Chandler et al. 2005.

<sup>e</sup>Sagittarius B2 North [Sgr B2(N)] is a hot prestellar core. Shown is the upper limit, as the H<sub>2</sub>O abundance is not well constrained.

water ice could form from hydrogenation of both atomic and molecular oxygen (Ioppolo et al. 2008, Miyauchi et al. 2008, Dulieu et al. 2010). Oxidation and hydrogenation of condensed CO molecules produces  $\text{CO}_2$ ,  $\text{H}_2\text{CO}$ , and  $\text{CH}_3\text{OH}$ . Extension of these mechanisms to addition of C, O, and N atoms shows that, even at 10 K, a rich chemistry is possible in which various multiply bonded molecules are formed and can be subsequently hydrogenated (Charnley et al. 2001; Herbst & van Dishoeck 2009).

Recent observational studies provide strong support for such a surface chemistry (Bisschop et al. 2007b, 2008; Oberg et al. 2010), and many laboratory studies have confirmed the viability of solid-phase hydrogenation reactions (Hiraoka et al. 2005; Nagaoka, Watanabe & Kouchi 2005; Bisschop et al. 2007a; Watanabe & Kouchi 2008; Fuchs et al. 2009; Hidaka et al. 2009). Thus, in addition to formaldehyde and methanol, these processes could account for the presence of  $\text{HCOOH}$ ,  $\text{HNCO}$ , and  $\text{NH}_2\text{CHO}$  in comets. Ethane could be formed by analogous H additions to acetylene (Hiraoka et al. 2001), and the expectation that ethanol should also be present in comets is supported by the fact that hydrogenation of  $\text{CH}_3\text{CHO}$  has been demonstrated in the laboratory (Bisschop et al. 2007a). As hydrogenation of glycolaldehyde may produce ethylene glycol on interstellar dust (Charnley 2001, Charnley & Rodgers 2009), we might also expect the former molecule to be present in comets.

Observations by the *Herschel* satellite demonstrate that the dusty environment of young protostars receives large doses of UV and EUV radiation (Benz et al. 2010), and even in dark clouds, a weak flux of UV photons will exist (Prasad & Tarafdar 1983). Thus, in addition to chemical reactions on the ice surface, driven by accretion of reactive species, ices can also undergo secondary processing due to damage caused by photons and energetic cosmic ray particles (Bernstein et al. 1995, Moore & Hudson 1998, Bennett et al. 2005).

The fact that interstellar methyl formate ( $\text{HCOOCH}_3$ ) cannot be formed via atom addition reactions on dust (Charnley 1997) or in gas-phase ion-molecule chemistry involving methanol and formaldehyde (Blake et al. 1987, Karpas & Mautner 1989, Horn et al. 2004) led Garrod & Herbst (2006) to consider  $\text{HCOOCH}_3$  production during the hot core warm-up phase by reactions involving radical intermediates produced from photolysis of methanol and other ice molecules. In this case, radicals such as  $\text{HCO}$ ,  $\text{CH}_2\text{OH}$ ,  $\text{OH}$ ,  $\text{CH}_3$ , and  $\text{COOH}$  and  $\text{CH}_3\text{O}$  can associate in radical-radical reactions on/in grain mantles to produce more complex organics (e.g., Belloche et al. 2009, Kisiel et al. 2009). Recent experiments have confirmed the formation of  $\text{HCOOCH}_3$  and other organic molecules, including ethylene glycol ( $\text{HOCH}_2\text{CH}_2\text{OH}$ ), by the UV photolysis of interstellar ice analogs (Oberg et al. 2009).

No laboratory photolysis experiment has been able to produce large methanol abundances by UV irradiation (e.g., of  $\text{H}_2\text{O}/\text{CH}_4$  mixtures, d'Hendecourt et al. 1986). Hence, as interstellar organic synthesis by photolysis requires that the methanol be present *ab initio* (Bernstein et al. 1995, Oberg et al. 2009), cold atom additions to CO and other multiply bonded molecules should be regarded as the more fundamental grain processes.

Note, however, if no radical recombination occurs during the evaporation of molecular ices in a hotcore/corino or inner nebula environment, then a post-evaporation chemistry (e.g., Charnley, Tielens & Millar 1992) may still produce  $\text{HCOOCH}_3$ . For the case that the evaporated interstellar ices contain abundant methanol and formic acid, ion-molecule reactions of protonated methanol with  $\text{HCOOH}_3^+$  could produce gaseous  $\text{HCOOCH}_3$  that could subsequently freeze-out on dust grains (Charnley 1997). Earlier calculations demonstrated that these reactions would not be viable in cometary comae (Rodgers & Charnley 2001b), but recent model calculations (Laas et al. 2011) tend to support this scenario for the interstellar case. In summary, the volatile ices in comets are consistent with the chemistry associated with the formation and processing of interstellar ices.

**7.1.2. Other candidate interstellar precursors inferred from cometary data.** A signature of interstellar chemistry in cold dense gas is the efficient synthesis of long carbon-chain molecules—polyynes, cyanopolyynes, carbenes, cumulenes, and bare carbon chains (Ehrenfreund & Charnley 2000). Based on the known compositional synergy between interstellar and comet chemistry, it has been suggested that the unidentified *Giotto* organic anion mass peaks (see Section 6.1) could be attributed to known interstellar carbon-chain molecules or their decomposition products, e.g.,  $\text{HC}_3\text{N}$ ,  $\text{HC}_5\text{N}$ ,  $\text{H}_2\text{C}_3\text{O}$  (for  $\text{CCO}$  and  $\text{CCCO}$ ),  $\text{CH}_3\text{C}_3\text{N}$ ,  $\text{CH}_3\text{C}_4\text{H}$ , and  $\text{CH}_3\text{CCH}$  (Geiss et al. 1991, Mitchell et al. 1992; Altwegg, Balsiger & Geiss 1999; Ehrenfreund & Charnley 2000; Bockelée-Morvan et al. 2004; Feldman, Cochran & Combi 2004; Schleicher & Farnham 2004).

A recent development in astrochemistry has been the detection of the anionic forms of the carbon chains  $\text{C}_4\text{H}$ ,  $\text{C}_6\text{H}$ , and  $\text{C}_8\text{H}$  in interstellar clouds and in the circumstellar envelope of the AGB star IRC+10216 (McCarthy et al. 2006, Cernicharo et al. 2007, Remijan et al. 2007, Gupta et al. 2009, Cordiner et al. 2011). Detailed chemical models predict that more massive anions should be present, up to  $\text{C}_{10}\text{H}^-$ , as well as bare carbon chain anions  $\text{C}_n^-$  ( $n = 5\text{--}10$ ) (Millar et al. 2007, Harada & Herbst 2008, Cordiner & Millar 2009). The emission line profiles in IRC+10216 indicate that the anions are forming in the region of the outflow where the interstellar UV radiation field is driving the chemistry. This is analogous to the physical-chemical flow in cometary comae (Rodgers et al. 2004) and tentatively supports the view that long carbon chains and their fragmentation products, perhaps including the molecular radicals  $\text{C}_2$  and  $\text{C}_3$  (see Section 3.1), are present in the Halley data.

Other known interstellar molecules could act as parents of  $\text{C}_2$  and  $\text{C}_3$ . Jackson (1976) proposed that the main formation pathways for these species involved two-step photoprocesses starting, respectively, with acetylene ( $\text{C}_2\text{H}_2$ ) and propyne ( $\text{CH}_3\text{CCH}$ ). Krasnopolsky (1991) argued that allene ( $\text{H}_2\text{CCCH}_2$ , an isomer of propyne) and propynal ( $\text{HCCCHO}$ ) are the parents of the  $\text{C}_3$  radical, with a smaller contribution due to propyne. Structurally, the only observed cometary molecule with a  $\text{C}_3$  backbone is  $\text{HC}_3\text{N}$ , but this is unlikely to fragment to  $\text{C}_3$  due to the strength of the nitrile bond. Larger carbon chains could contribute, and analysis of mass spectrometer data from *Giotto* led to the suggestion that  $\text{C}_4\text{H}$  could be a parent for  $\text{C}_3$  (Geiss et al. 1999). The cyclic form of  $\text{C}_3\text{H}_2$  ( $c\text{-C}_3\text{H}_2$ , cyclopropenylidene) is the likely parent of the  $\text{C}_3\text{H}_3^+$  and  $\text{C}_3\text{H}^+$  detected in comet Halley (Korth et al. 1989; Marconi et al. 1989; Altwegg, Balsiger & Geiss 1999), and, because it is ubiquitous in astrochemistry, its photolysis (van Hemert & van Dishoeck 2008) could contribute to  $\text{C}_3$  in comets. Even if the  $\text{C}_3\text{H}_2$  isomers are not present in nuclear ices (which is indeed unlikely for the linear carbene form,  $\text{H}_2\text{CCC}$ ), they may be present in comae due to the destruction of organic dust or macromolecules (see below). Coma chemistry (beyond simple photolytic decomposition) has been proposed by Helbert and colleagues as the origin of  $\text{C}_2$  and  $\text{C}_3$  in comet Hale-Bopp at large heliocentric distances ( $\sim 3$  AU) (Helbert et al. 2005). They found that photolysis of  $\text{C}_2\text{H}_2$  and  $\text{C}_3\text{H}_4$  (a generic species for both allene and propyne) could produce the observed abundances. However, recent observations of  $\text{C}_2$  and  $\text{C}_2\text{H}_2$  in comet 8P/Tuttle at a heliocentric distance,  $R_h$ , of 1.15 AU demonstrated that acetylene photolysis could not be the primary source of dicarbon in this comet (Boney et al. 2008b).

In summary, circumstantial evidence suggests that other molecules known in the ISM are present in comets, although not yet identified by spectroscopy. Almost all cometary comae contain the molecular radicals  $\text{C}_2$  and  $\text{C}_3$ , which may be the fragments of unsaturated carbon-chain molecules. The positive identification of long carbon chains in comets would strengthen the view that the nuclear ices contain pristine interstellar molecules.

## 7.2. Refractory Organic Material

The IOM found in various classes of carbonaceous chondrites and IDPs derives from asteroids and comets. It contains aliphatic hydrocarbons, PAHs, fullerenes, and heteropolymers (Becker, Poreda & Bunch 2000; Pizzarello, Cooper & Flynn 2006). The first three classes of compounds are also present and abundant in interstellar and circumstellar environments (Tielens 2008, Cami et al. 2010), and so it is natural to inquire as to what extent they could have been incorporated unaltered into the protosolar nebula and subsequently into comets. PAHs are thought to take up about 10–20% of the Galactic carbon, and ISM dust contains various forms of amorphous carbon, for example, hydrogenated amorphous carbon (HAC), as well as graphite (e.g., Draine 2003). Although the spectral energy distributions of comets at IR wavelengths can be fitted by radiative transfer models that include dust grains containing amorphous carbon (Hanner et al. 1996), ascertaining the precise composition and structure of the refractory carbonaceous dust by remote observations is even more challenging than for the ISM. Due to their highly favorable stability properties, interstellar PAHs (and fullerenes) have been considered as good candidates for survival and incorporation into Solar System bodies (e.g., Li 2009).

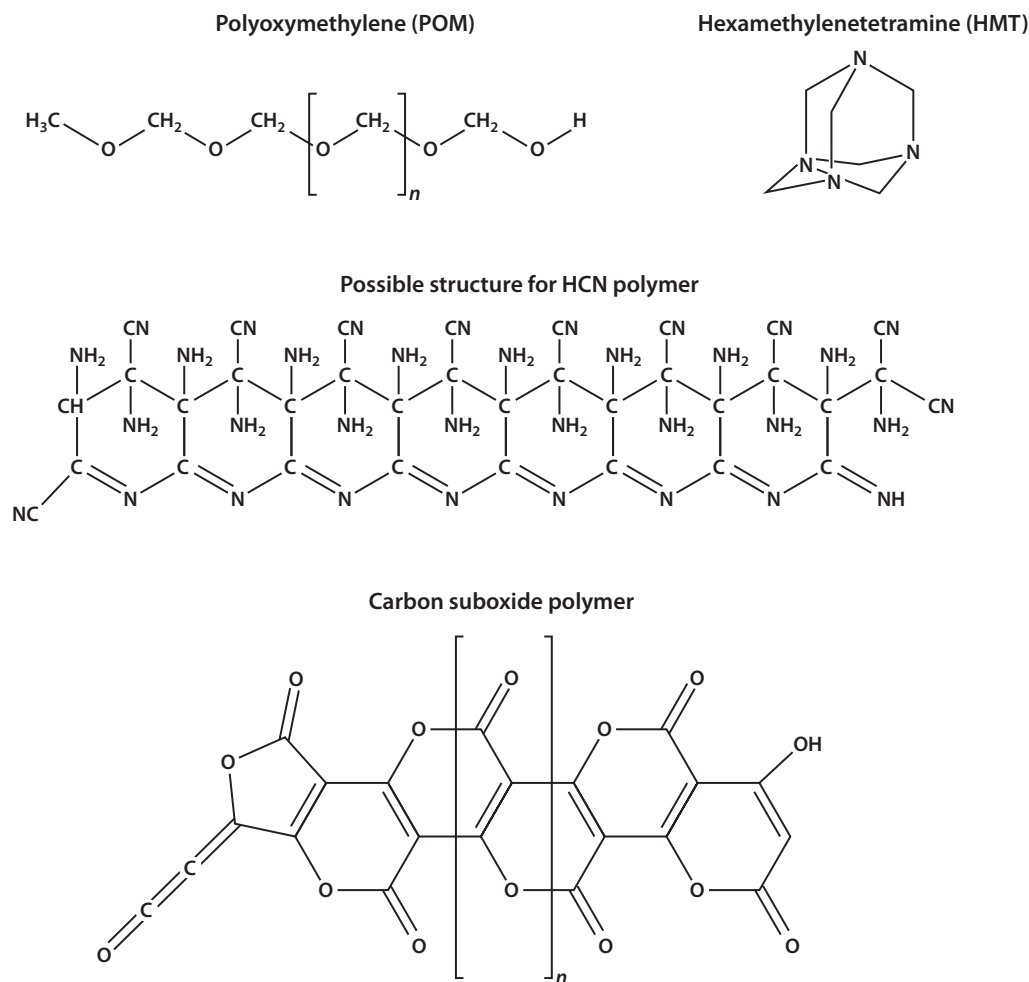
It appears that anhydrous IDPs are the most primitive type of IDP and are most likely samples of cometary dust (Sykes et al. 2004). These IDPs can contain up to 90% carbon by volume, mostly in organic form, and there are strong similarities between this material and the IOM found in meteorites (Flynn et al. 2000, 2004). For example, they contain aromatic, aliphatic, carbonyl and PAH structures (Clemett et al. 1993; Flynn et al. 2000, 2008; Matrajt et al. 2005). What is the evidence that the refractory organic material in anhydrous IDPs and the *Stardust* samples, and (by association) other comets, contains relatively unaltered interstellar matter? A case has been made for the existence of a common, primitive, molecular precursor for both cometary IDP and meteoritic IOM: complex sugars derived from interstellar formaldehyde and glycolaldehyde (Cody et al. 2008). Although it is difficult to account for the presence of methylamine and glycine in the *Stardust* organic samples (Glavin, Dworkin & Sandford 2008; Elsila, Glavin & Dworkin 2009) as pristine interstellar molecules, it is worth noting that they are also found in molecular clouds (Kaifu et al. 1974, Kuan et al. 2003; but see Snyder et al. 2005).

The similarity between interstellar and meteoritic IR absorption spectra in the 3–4  $\mu\text{m}$  C–H stretch region is suggestive of refractory material from the diffuse ISM having been incorporated into primitive matter (Pendleton & Allamandola 2002). Further evidence is the constant nanodiamond/IOM ratios that are consistently measured in presolar grains. Additionally, the fact that chemical reactions in the nebula simply cannot make sufficient amounts of IOM (by mass) strongly suggests that it was inherited from the ISM prior to undergoing varying degrees of chemical processing through irradiation and heating. On the negative side, a problem is that the aliphatic chain lengths inferred for anhydrous IDPs are longer than those measured in the ISM (Pendleton & Allamandola 2002, Flynn et al. 2008). The structure of the IOM suggests a network of aromatic rings linked by aliphatic groups, similar to the structure derived for dust in the diffuse ISM (Pendleton & Allamandola 2002). However, the large PAH structures proposed for the ISM population (>50 C atoms) are not found in meteoritic organic matter at the abundance expected (Cody et al. 2008).

The *Stardust* aromatic compounds, in particular, represent a lower fraction of the total organic material than we would expect from comparison with the interstellar organic inventory (Clemett et al. 2010). It has been suggested that interstellar PAHs were subjected to more severe radiation processing upon incorporation into the nebula and that this could account for the absence of large PAH molecules in IOM. However, based on the shorter chain lengths of interstellar aliphatic organics (see above), it has also been suggested that the more severe processing actually occurred

in the ISM (Flynn et al. 2008). These explanations are therefore mutually exclusive. An additional argument against interstellar PAHs lies in the fact that the PAHs in IOM are consistently found to exhibit  $^{12}\text{C}/^{13}\text{C}$  ratios that are solar. A wide distribution would be expected if they were injected into the ISM by stellar winds from many AGB stars with different  $^{12}\text{C}/^{13}\text{C}$  ratios (Alexander et al. 2008). Similarly, AGB stars are depleted in  $^{15}\text{N}$ , whereas IOM is known to contain  $^{15}\text{N}$  enrichments associated with the aromatic material (Keller et al. 2004). Overall, this makes the proposition that the PAH component of IDPs and meteoritic IOM was directly inherited from the ISM somewhat problematic (Alexander et al. 2008).

Several coma species are observed to have an extended or distributed source, including CO,  $\text{H}_2\text{CO}$ , CN,  $\text{C}_2$ ,  $\text{C}_3$  and several sulfur-bearing species (see Cottin & Fray 2008 for a detailed review). In all cases, the nature of the extended source is unknown but several specific macromolecular structures have been proposed (Figure 15), including polyoxymethylene (POM; the



**Figure 15**

Several macromolecular structures proposed to be present in comets (Cottin & Fray 2008). The structure shown for the HCN polymer is one possibility among others (see Minard et al. 1998 for more structures). Ballauff et al. (2004) proposed the structure shown for carbon suboxide polymers.

-CH<sub>2</sub>O- polymer; Huebner 1987), hexamethylenetetramine (HMT, C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>; Bernstein et al. 1995), and polyaminocynoacetylene and diaminomaleonitrile (PACM and DAMN; HCN-polymer; Rettig et al. 1992, Rodgers & Charnley 2001a). Fray et al. (2006) showed that POM is a possible source for formaldehyde if it accounts for a few percent (by mass) of the organic CHON dust material detected in Halley (e.g., Fomenkova 1999). Milam et al. (2006) observed H<sub>2</sub>CO in three comets and showed that an extended dust source is necessary to replicate the observational data; but they also argued that POM is not a viable source of formaldehyde and suggested instead that trapped H<sub>2</sub>CO monomers are released when organic material is vaporized. These large organic molecules are unknown in the ISM, but POM and HMT have been synthesized in interstellar ice analog irradiation and heating experiments (Schutte, Allamandola & Sandford 1993; Bernstein et al. 1995) and so could be present on interstellar dust grains. However, it is unclear whether or not they could possess the photolytic and thermal decomposition properties required to explain the distributed coma sources and yet be incorporated unaltered into the protosolar nebula/cometary dust.

### 7.3. Silicate Dust

Studies of cometary silicate dust grains clearly indicate that distinct similarities and differences indicate binary origins: 1. some grains retain signatures of interstellar origin, and 2. others reveal high-temperature formation and processing in the hot inner nebula (e.g., Wooden 2002; Alexander et al. 2007; Wooden et al. 2007). Remote IR sensing of comet dust grains shows that crystalline, Mg-rich silicates (mostly pyroxene and olivine) are present in both Jupiter-family and Oort Cloud comets. The latter exhibit a very large range (from 0% to ~70%) in the fraction of their silicates that are crystalline (e.g., Harker et al. 2002, 2004). By contrast, crystalline silicates are not detected in the diffuse ISM, where the dust population is almost completely composed of Fe/Mg-containing amorphous silicates (less than 2.2% crystalline; Kemper, Vriend & Tielens 2004, 2005).

Although the winds from late-type stars inject crystalline silicate dust (i.e., stardust) into the ISM, supernova shock waves may later efficiently destroy some stardust, with new grains reforming subsequently in the diffuse or dense ISM (Molster & Kemper 2005, Draine 2009). Another possible explanation is that irradiation by cosmic ray particles amorphizes crystalline stardust (cf. Demyk et al. 2001, Branga et al. 2007). It is estimated that only 4% of ISM dust is stardust (Draine 2009); however, these particles do appear in primitive matter as isotopically anomalous presolar grains (Clayton & Nittler 2004).

In summary, comets contain amorphous silicate dust that was likely inherited from the ISM. They do, however, also contain a large population of Mg-rich crystalline silicate grains. These grains are not annealed interstellar dust but were actually formed in the hot inner nebula and transported radially outward to the cooler regions where comets were assembled (Wooden et al. 2007).

### 7.4. Isotopic Fractionation

When compared to reference standards such as the local ISM, the Sun, or terrestrial matter, cometary fractionation ratios can, in principle, provide important information on the origin of cometary materials (Bockelée-Morvan et al. 2004; Ehrenfreund, Charnley & Wooden 2004). Chemical reactions in gas and on dust grains at low temperatures, such as are found in interstellar clouds and expected in the outer regions of the protosolar nebula, are very efficient at producing isotopically heavy molecules (e.g., Wooden, Charnley & Ehrenfreund 2004), and so measuring specific isotopic ratios in comets is a particularly useful technique for probing the ISM-comet connection.

**7.4.1. Hydrogen.** Deuterium fractionation ratios have been measured for two cometary molecules: water and hydrogen cyanide (**Figure 12**); upper limits exist for several others: monodeuterated methane, HDCO, ammonia, and two isotopologues of methanol (Crovisier et al. 2004a, Kawakita et al. 2005). Observationally, the DCN/HCN measurements are well below the ratios measured for gas around low-mass protostars (Roberts et al. 2002) but similar to that of hot cores near massive protostars (Hatchell, Millar & Rodgers 1998). In Hale-Bopp, the measured D/H ratios in water and HCN are compatible with ion-molecule chemistry in interstellar gas at about 25–35 K (Millar, Bennett & Herbst 1989), followed presumably by freeze-out on to dust grains. Water in other OC comets bears similar D/H ratios (see Section 5.1 and **Figure 12**), but the ratio is much smaller in the ecliptic comet 103P/Hartley 2 (Section 2.2), which is suggestive of different processing.

The D/H ratios in cometary water are also consistent with such ion-molecule chemistry and with some D/H measurements in the hot cores close to massive protostars (Jacq et al. 1990). However, recent *Herschel* observations of water deuteration in the Orion hot core yield an HDO/H<sub>2</sub>O ratio of about 0.02, a value probably more representative of an origin in grain-surface fractionation (Bergin et al. 2010). Recent observations of low-mass protostars also show similarly higher HDO/H<sub>2</sub>O ratios. In IRAS 16293-2422, the ratio is about 0.03 (Parise et al. 2005), and it is between 0.1–0.18 in the envelope of NGC 1333-IRAS2A (Liu et al. 2010). Although these new measurements begin to present a severe challenge to an ISM origin for cometary water, they place a similar strain on an origin in nebular chemistry. In this regard, Thi, Woitke & Kamp (2010) have constructed a model of water deuteration in the hot inner regions of protoplanetary disks in which HDO/H<sub>2</sub>O can be greater than 0.01 in the inner disk, with an average value of  $4.6 \times 10^{-3}$ . However, Jorgensen & van Dishoeck (2010) have placed a limit of HDO/H<sub>2</sub>O  $< 6 \times 10^{-4}$  in the warm inner disk of NGC 1333-IRAS4B.

The upper limits on monodeuterated ammonia, formaldehyde, and methanol in comet Hale-Bopp do not rule out their presence at interstellar deuteration levels, but the limit on CH<sub>2</sub>DOH is significantly below the ISM value (Crovisier et al. 2004a). In dense cloud cores, reactions on cold dust grains lead to very high D/H ratios and multiple deuterations in these interstellar molecules (e.g., Ceccarelli et al. 2007). Thus, their absence in comet Hale-Bopp is surprising if this comet contained pristine interstellar ices, especially in light of the recent interstellar measurements of ND/NH  $\sim 0.3$ –1.0 and D<sub>2</sub>CO/H<sub>2</sub>CO  $\sim 1.34$  (Bacmann et al. 2010, Bergman et al. 2011). However, isotopic measurements of deuteration in some IDPs show that primitive organic matter associated with comets does possess D/H ratios comparable to those of cold molecular clouds (Messenger 2000, Aléon et al. 2003, McKeegan et al. 2006).

The possibility of deuteration in the dense Solar Nebula must also be considered. The D enrichment measured in cometary H<sub>2</sub>O and HCN cannot be explained by isotopic exchanges with HD (the main deuterium reservoir). Calculations show that, starting from a D/H value in H<sub>2</sub>O equal to the protosolar value, only a moderate enrichment, by a factor of three at most, can be obtained. Therefore, the D enrichments measured in comets reflect (at least partly) fractionation effects that took place through ion-molecule and/or grain-surface reactions, either in the presolar cloud or in outer regions of the protosolar disk where the temperature was low enough and the ionization fraction high enough to permit efficient deuterium fractionation. This fractionation could have occurred in the cool outer disk, perhaps retaining some remnant interstellar signature, and been subsequently modified by radial transport into and out of the hotter inner disk.

Interestingly, the distributions of the OPRs measured in cometary H<sub>2</sub>O and NH<sub>3</sub> peak at a value corresponding to a spin temperature of about 30 K (see Section 4). Whether these two temperature indicators are linked causally is an open question; the answer requires still-missing information on the conditions permitting nuclear spin conservation in the interior of comet nuclei



during their residence time in the comet reservoirs and during sublimation. The high apparent formation temperature (of  $\sim 30$  K) argues against a solely interstellar origin for cometary HCN and H<sub>2</sub>O. Moreover, the observed D enrichments (with respect to the protosolar or interstellar values in H<sub>2</sub>) are comparable to those measured in molecular hot cores, but smaller than those found in dark clouds and in low-mass protostars. This agrees with models of deuterium chemistry in disks (e.g., Aikawa & Herbst 1999, 2001; Aikawa et al. 2002, Willacy 2007), which show that extensive chemical processing can occur, resulting in D/H ratios that can differ greatly from the values set in the parent molecular cloud, depending on the molecule.

The low cometary D/H values may also indicate that comets are mixing highly D-enriched molecules representative of interstellar-like chemistry with D-poor molecules reprocessed in the hot inner Solar Nebula, as proposed by Drouart et al. (1999), Mousis et al. (2000), and Hersant, Gautier & Huré (2001). Indeed, the presence of crystalline silicates and other high-T minerals in cometary grains (e.g., McKeegan et al. 2006) suggests that large-scale radial mixing occurred in the Solar Nebula, transporting material formed in the inner regions to the formation region of comets. These researchers investigate isotopic exchanges between H<sub>2</sub>O and H<sub>2</sub> in an evolving turbulent Solar Nebula fed by highly D-enriched water ices. For kinetic reasons, the isotopic exchange could have been substantial only in the inner warmer parts of the Solar Nebula, where it can equilibrate the D/H value in water to the protosolar value. These models predict that icy bodies formed at different radii from the Sun mix processed and unprocessed water in different proportions and should have different D/H ratios. The predicted D/H enrichments are consistent with a range of meteoritic and cometary values.

Mousis et al. (2000) and Hersant, Gautier & Huré et al. (2001) showed that models fitting D/H in H<sub>2</sub>O can also fit the D/H ratio in cometary HCN, providing HCN in ices falling into the turbulent part of the Solar Nebula were moderately deuterium-enriched. Interestingly, Bockelée-Morvan et al. 2002 showed that it is possible to explain both the D/H value in water and the silicate crystalline mass fraction by the same turbulent model of the Solar Nebula, assuming that crystalline silicates are formed by thermal annealing of interstellar amorphous silicates.

**7.4.2. Nitrogen.** Nitriles detected in cometary comae (CN and HCN) are significantly enriched in <sup>15</sup>N when compared to nebular and terrestrial <sup>14</sup>N/<sup>15</sup>N ratios (see Section 5.2 and **Figure 14**). Correspondingly low <sup>14</sup>N/<sup>15</sup>N ratios are also detected in carbonaceous IDPs and meteorites (Messenger 2000, Floss et al. 2004). Keller et al. (2004) concluded that the major carriers of D were aliphatic hydrocarbon groups on macromolecular material, and that the <sup>15</sup>N-rich phases are in the form of –NH<sub>2</sub> side groups, probably attached to aromatic material. However, Busemann et al. (2006) found that nitrile groups carried the <sup>15</sup>N enrichment.

The enrichment of <sup>15</sup>N in HCN (by a factor of  $\sim 3$  with respect to the protosolar value) (450 +138/–85) Fouchet et al. 2004, Meibom et al. 2007) is not as compelling as is the enrichment factor of deuterium (DCN/HCN), because there is only limited evidence for N isotopic fractionation in the ISM (Ikeda, Hirota & Yamamoto 2002; Lis et al. 2010b). Predicted <sup>15</sup>N enhancements in HCN via ion-molecule exchange reactions are modest (Terziewa & Herbst 2000). Highly fractionated NH<sub>3</sub> ice could have formed in the dense presolar core when CO was depleted onto grains, whereas N<sub>2</sub> remained in the gas phase (Rodgers & Charnley 2002, 2008a). Large <sup>15</sup>N enhancements can be generated in HCN and other nitriles, if CN reactions with atomic N are ineffective at low temperature (Charnley & Rodgers 2002, Rodgers & Charnley 2008b). Alternative mechanisms include a nucleosynthetic origin and photochemical self-shielding in the Solar Nebula (Clayton 2002a), similar to the mechanism proposed for explaining the oxygen isotope anomalies in meteorites (Clayton 2002b). Irrespective of the mechanism, protosolar HCN never

isotopically equilibrated with nebular  $N_2$  during the later phases of the evolution of the Solar System.

The large enrichments can be explained by interstellar chemistry theories involving ion-molecule  $^{15}N$  fractionation at 10 K (Charnley & Rodgers 2002, 2008), occurring in the dense central regions of starless cores (Bergin & Tafalla 2007) that exhibit selective depletion of CO molecules onto dust, relative to  $N_2$  (e.g., Bergin et al. 2002). Charnley & Rodgers (2002) demonstrated that this phenomenon could permit large isotopic fractionation effects and that condensation of the gaseous products on dust grains leads to ices with bulk enhancements in ammonia comparable to those of IDPs and peak monolayer enhancements comparable to those of their  $^{15}N$  hotspots (Rodgers & Charnley 2008a). In these models, most of the  $^{15}N$  enrichment was present in ammonia and  $N_2$  ices, and so a secondary level of processing was deemed necessary to incorporate it into organic material (i.e., the nitrile parent of CN).

The fact that cometary HCN is also enriched in  $^{15}N$  (Bockelée-Morvan et al. 2008) suggests that, to maintain the feasibility of an ISM origin, there should be a mechanism for fractionating HCN in dense cores. Motivated by the recent detection of CN and HCN in the CO depletion cores L1544 and L183 (Hily-Blant et al. 2008), Rodgers & Charnley (2008b) were able to show that there are in fact two  $^{15}N$ -fractionating pathways, which can occur as molecules are depleted: slow for ammonia ( $\sim 10^6$  years) and more rapid for HCN ( $\sim 10^5$  years). These theoretical models can explain the entire range of  $^{14}N/^{15}N$  ratios found in the laboratory analyses of primitive matter and also that measured in comets (Bonal et al. 2010).

Astronomical observations of starless cores have begun recently and could usefully constrain the models. Toward the Class 0 protostars Barnard 1 and NGC 1333, Lis et al. (2010b) measured  $^{14}NH_3/^{15}NH_3 \sim 334$ , and Gerin et al. (2009) found  $350 < ^{14}NH_2D/^{15}NH_2D < 850$ . Bizzocchi, Caselli & Dore (2010) measured  $^{14}N_2H^+/^{14}N^{15}NH^+ \sim 446$  in the starless core L1544. In all, these fractionation ratios are indicative of modest enrichment at best. A general problem for seeking large isotopic enrichments through  $NH_3$  and  $N_2$  is that these cores probably have lifetimes of  $\sim 2-7 \times 10^5$  years (Hatchell et al. 2007, Enoch et al. 2008) and so may not persist long enough to establish this chemistry. The shorter timescales for fractionation of HCN, HNC, and CN (Rodgers & Charnley 2008b) may allow large  $^{15}N$  enrichments to develop in dark molecular clouds. In this case, the nitrile fractionation data is fragmentary. The L1544 data of Hily-Blant et al. (2010) imply  $HC^{14}N/HC^{15}N \sim 261$  if  $^{12}C/^{13}C = 60$  is assumed. Earlier studies by Ikeda, Hirota & Yamamoto (2002) found  $HC^{14}N/HC^{15}N \sim 151$  in L1521E and  $> 813$  in L1498, whereas Tennekes et al. (2006) found  $H^{14}NC/H^{15}NC \sim 135$  in the environment of the Class 0 protostar ChAMMS1. Although these measurements are interesting, the derived ratios are subject to considerable uncertainty.

In summary, observations have now constrained cometary  $^{14}N/^{15}N$  ratios to within a restricted range of values. Both ecliptic comets and NICs are enriched to approximately the same degree, about twice the terrestrial value (Arpigny et al. 2003, Hutsemékers et al. 2005, Jehin et al. 2009, Manfroid et al. 2009). This fact, and the similarity of the  $^{14}N/^{15}N$  ratios found in IDPs, strengthens a putative link to interstellar chemistry as the origin of isotopically anomalous organic particles in comets. Pizzarello & Holmes (2009) have sketched a possible evolutionary sequence for interstellar nitrogen chemistry and fractionation in the protosolar natal cloud core that could be consistent with the isotopic trend they found in meteorites.

An understanding of the origin of the nitrogen isotopic anomalies in volatile Solar System material clearly demands more rigorous astronomical ground-truths (e.g., Aléon 2010). Hence, the measurement of key  $^{14}N/^{15}N$  isotopic ratios in molecular clouds is necessary, particularly in those highly depleted cores that are just about to form low-mass protostars (e.g., Bergin & Tafalla 2007) and are therefore putative analogs of the natal protosolar core. Only an extensive

multiple-transition survey of such cores can expect to locate and accurately measure the relevant isotopic fractionation ratios and allow comparison with the cometary values.

**7.4.3. Oxygen and Carbon.** The  $\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O}$  ratios have been measured in several comets and found to be close to the terrestrial value of 499 (Balsiger, Altwegg & Geiss 1995; Lecacheux et al. 2003; Biver et al. 2007); however, hydroxyl in comet C/2002 T7 does show an apparent enrichment in  $^{18}\text{O}$  (425, Hutsemékers et al. 2008). Oxygen isotopic anomalies are measured in primitive matter, such as chondrules and CAIs (Clayton & Nittler 2004). As interstellar ion-molecule chemistry is expected to lead to little fractionation in oxygen-bearing molecules (Langer et al. 1984), isotope-selective self-shielding of CO against photodissociation (e.g., van Dishoeck & Black 1988), in both nebular CO and interstellar environments, has been considered as a possible explanation for the meteoritic data (Yurimoto & Kuramoto 2004, Lyons & Young 2005, Yurimoto et al. 2007). Astrochemical models of protostellar core evolution that incorporate CO self-shielding suggest that cometary water could possess significant  $^{18}\text{O}$  enrichments (Lee, Bergin & Lyons 2008; Charnley & Rodgers 2009).

As measured in  $\text{C}_2$ , CN, and HCN, comets possess a solar  $^{12}\text{C}/^{13}\text{C}$  ratio (89). Langer et al. (1984) showed that there could be potentially large differences in the  $^{12}\text{C}/^{13}\text{C}$  ratios between CO and other molecules and so, as the  $^{12}\text{CO}/^{13}\text{CO}$  ratio in comets has not been measured, it is not known if volatile cometary carbon displays this trend. Circumstantial evidence comes from measurements of the isotope ratios in individual meteoritic organics, where formic acid and higher monocarboxylic acids are significantly enriched in D and in  $^{13}\text{C}$ . Both characteristics are expected if the  $\text{HCOOH}$  was formed from CO in interstellar ices (Ioppolo et al. 2011), leading Huang et al. (2005b) to conclude that the fractionation may have occurred in a molecular cloud.

In summary, large  $^{12}\text{C}/^{13}\text{C}$  variations can occur among interstellar molecules but are not evident in comets. This presents an issue that needs to be addressed by detailed CO isotope observations. However, perhaps the greatest challenge for tracing cometary origins through isotopes resides in the fact that in cometary CN, and presumably also in HCN, the  $^{12}\text{C}/^{13}\text{C}$  ratio is solar/terrestrial but the  $^{14}\text{N}/^{15}\text{N}$  is almost always enriched. The simplest explanation would be that the carbon ratio also reflects that of the protosolar core.

## 7.5. Ortho-Para Spin Ratios

The OPRs measured for cometary water and ammonia (**Figure 10c**), and that derived from methane, suggest molecule formation temperatures of  $\sim 25\text{--}35$  K, similar to the range inferred from the D/H ratios.

*Herschel* observations now permit the OPR in interstellar water to be measured directly. In regions of massive star formation, Melnick et al. (2010) find the OPR in  $\text{H}_2^{18}\text{O}$  to be 3, the high temperature limit, in all the major subregions of Orion-KL. Similarly, Lis et al. (2010a) find the  $\text{H}_2\text{O}$  OPR to be 2.8 in Sgr B2(M), but also identify a dynamical component in which it is about 2.35, corresponding to a spin temperature of 27 K. Vastel et al. (2010) derive an upper limit of 2.6 for the  $\text{D}_2\text{O}$  OPR in the core of the low-mass binary system IRAS 16293–2422, which (within the stated errors) corresponds to a lower limit of 13 K on the spin temperature. Although these interstellar water OPR measurements are only the first of many that will be made by *Herschel*, it is interesting that they already span the range found in comets.

The OPR of interstellar  $\text{CH}_3\text{OH}$  has been measured for relatively low-temperature clouds (Friberg et al. 1988, Menten et al. 1988), as well as in the cool envelopes of massive protostars (Wirström 2009), and found to lie in the range of 10–14 K. This temperature range is consistent with that required experimentally for methanol (and formaldehyde) production by hydrogenation

of CO ice on dust grains (e.g., Watanabe & Kouchi 2008). The lower limit of  $>15$  K suggested by the cometary data (Pardanaud et al. 2007), if accurate, presents a serious challenge to cometary methanol and formaldehyde being of interstellar origin because this is the temperature above which H atoms cannot remain physisorbed on the ice surface long enough to react efficiently with CO molecules (Watanabe, Shiraki & Kouchi 2003). The  $\text{H}_2\text{CO}$  OPR is unknown in comets but has been studied in detail in interstellar clouds (e.g., Dickens & Irvine 1999). These measurements indicate  $\text{H}_2\text{CO}$  formation on grains at temperatures of about 10–15 K in regions of low-mass star formation. In quiescent, starless clouds, however, the  $\text{H}_2\text{CO}$  OPR is at the high-temperature limit, which suggests that exothermic gas phase reactions are dominant. It would therefore be very useful to measure the  $\text{H}_2\text{CO}$  and  $\text{CH}_3\text{OH}$  OPRs in future comets. This would allow comparison of the OPR of these molecules with other cometary OPRs (particularly that of methane), and with the interstellar values.

## 8. SYNOPSIS

The chemical diversity found among comets demonstrates that a chemical record of early organics survives today. The discovery of comets with drastically depleted organic volatiles (Mumma et al. 2001, Villanueva et al. 2006, Dello Russo et al. 2007) argues that icy planetesimals from the Jupiter-Saturn region of the protoplanetary disk form a distinct population. This is important because that region contained far more initial material than did the Uranus-Neptune region, and potentially most of the icy planetesimals that impacted Earth were formed there. The question of gradients in isotope chemistry in the 5–40 AU nebular range is a key issue when considering cometary delivery of water to terrestrial planets.

The finding of organics-depleted comets in both OC (Mumma et al. 2001) and KB (Villanueva et al. 2006) reservoirs (though likely with different fractional representation) may be a signature of dynamical disruption of an outer disk (15–35 AU), as predicted by the Nice model. Thus, the issue of delivery of water and prebiotic organic compounds depends on a detailed understanding of the mass delivered from distinct nebular zones and at different times. Detailed studies of chemical composition are critically important, both to establish the taxonomy of comets based on their chemical composition and to quantify the diversity of asteroids and trans-Neptunian objects.

In comets, remote sensing can establish the gross taxonomic classes of icy planetesimals by measuring the volatile organic chemistry at abundances down to 100 ppm (relative to  $\text{H}_2\text{O}$ ). This is sufficient to quantify their gross isotopic chemistry and other cosmogonic parameters (e.g., nuclear spin ratios of molecules). For at least a few representative comets, more detailed compositional information is needed, at the parts-per-billion level, especially for the less-volatile organics. At this level, a wide variety of organic compounds have been isolated from the various carbonaceous meteorites (Botta & Bada 2002). For comets, *Stardust* samples can provide this information for refractory organics but not for volatiles. The coming rendezvous of the *Rosetta* spacecraft with comet 67P/Churyumov-Gerasimenko can test the volatile fraction as well, while returned samples (such as the proposed missions *Don Quixote* and OSIRIS-REX) could provide this information for asteroids.

Remote sensing of many comets provides the taxonomic context for extrapolating the in-depth analytical information obtained for the few comets visited by spacecraft. Tying those few comets to the general population of icy planetesimals will establish the significance of each taxonomic class for exogenous delivery of organics to Earth. In this way, the significance of exogenous organics for astrobiology can be assessed.

In making a tentative connection with the ISM, we have compared the measured chemical composition of comets to that of dense interstellar clouds and to regions of low-mass and

massive star formation (i.e., hot corinos and hot cores). In the first two cases, the comparisons have involved relatively isolated dense globules and protostellar cores, despite the fact that most stars actually form in clusters. Indeed, the presence of short-lived radioisotopes in the young protosolar nebula (e.g.,  $^{26}\text{Al}$ ), as inferred from the meteoritic record, strongly suggests that they were injected following the supernova explosion of a nearby massive star (e.g., Wadhwa et al. 2007). Consideration of the required nucleosynthetic yield, through the supernova progenitor mass, and the relative proximity of the protosolar nebula to the explosion, leads to the suggestion that the Sun formed in a large stellar cluster (e.g., Adams 2010). Thus, it may be more appropriate to consider comparison of cometary composition with the chemistry of dense interstellar clouds that are forming stellar clusters and massive stars.

Observations of IR dark clouds, understood to be the birth sites of massive stars (e.g., Battersby et al. 2010), indicate a chemistry that is reminiscent of that seen in clouds in which low-mass star formation is occurring (Vasyunina et al. 2011), although in general they appear to be chemically more evolved (Sakai et al. 2008). Recent molecular observations of a cloud with a site of clustered low-mass star formation (Friesen et al. 2009, 2010a,b) show anomalous D fractionation that may indicate a higher ionization rate for the cluster gas. Future detailed chemical studies of these environments may provide new insights into the connection between interstellar matter and cometary chemistry.

## DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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