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An Overview of Comet Composition

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Abstract. Comets are made of ices, organics and minerals that record the chemistry of the outer regions of the primitive solar nebula where they agglomerated 4.6 Gyr ago. Compositional analyses of comets can provide important clues on the chemical and physical processes that occurred in the early phases of Solar System formation, and possibly in the natal molecular cloud that predated the formation of the solar nebula. This paper presents a short review of our present knowledge of the composition of comets. Implications for the origin of cometary materials are discussed.

Keywords. comets : general, astrochemistry, Solar System: formation

1. Introduction

Comets are remnants of the planetesimals that formed the outer planets. Formed at large distances from the primordial Sun, they have remained for most of their lifetime outside of the orbit of Pluto, either in the trans-Neptunian scattered disk (associated to the Kuiper Belt) or in the Oort cloud. These two dynamically instable comet reservoirs are supplying the ecliptic short-period (also called Jupiter family comets, JFC) and long-period dynamical classes of comets observed in the inner Solar System. Though a variety of subtle evolutionary mechanisms operated for cometary nuclei during their long storage in the Oort cloud and Kuiper belt (Stern 2003) and, for short-period comets, during their many passages close to the Sun, the bulk composition of cometary nuclei is still regarded to be in large part pristine, except possibly for the most volatile ices. Thus, observing comets today provides a window through which we can view an earlier time when the planets were forming. Their composition provides a record of the chemistry of the primitive solar nebula, in the region and at the time of their formation.

Comets have been studied by a number of in situ investigations from spacecraft encounters (Keller *et al.* 2005), the most recent ones being the Deep Impact and EPOXI missions towards 9P/Tempel 1 and 103P/Hartley 2, respectively (A'Hearn *et al.* 2005, 2011) and the Stardust mission which collected and returned dust samples of comet 81P/Wild 2 to Earth for laboratory analyses (Brownlee *et al.* 2006). Although the in situ measurements have provided important new findings concerning comet composition, the majority of results on the icy component of cometary nuclei have been derived from remote spectroscopic observations of gas phase species in the atmosphere. This paper presents a short review of our present knowledge of the molecular and isotopic composition of comets, focussing on volatiles. Detailed reviews have been published by Bockelée-Morvan *et al.* (2005), Mumma & Charnley (2011). Implications on the origin of cometary materials are discussed in Section 6. More detailed discussions are presented in Rodgers & Charnley (2008), Ehrenfreund *et al.* (2005) and Irvine *et al.* (2000).

2. Molecular composition of Comets

2.1. *Molecular inventory of cometary volatiles*

Our present knowledge of the composition of cometary nuclear ices is essentially based on investigations of the coma that develops when comets are approaching the Sun and ices sublimate. Indeed, direct investigations of the nucleus surface (only possible from a spacecraft) only showed the near-infrared spectral signature of water ice on the nucleus of 9P/Tempel 1 (Sunshine *et al.* 2007), and a still unidentified feature at 2.39 μm on that of 19P/Borrelly observed from the Deep Space 1 spacecraft (Soderblom *et al.* 2002).

About two dozens molecules (not including isotopologues, molecular ions, atoms and radicals) have now been identified in cometary atmospheres (Fig. 1). These identifications were obtained through millimetre, submillimetre and infrared spectroscopy, mass spectrometry aboard the Giotto and Vega spacecraft, and, at a lesser extent, using ultraviolet spectroscopy (see the review of spectroscopic identifications of Bockelée-Morvan *et al.* 2005). Most identifications were obtained in the exceptionally bright comets C/1995 O1 (Hale-Bopp) and C/1996 B2 (Hyakutake). Observations in the visible wavelength range sample signatures of radicals, atoms and ions that are photolysis and chemical products of parent molecules released from the nuclear ices.

The main components of cometary nuclear ices are water (about 80 % by number) followed by CO, CO_2, CH_3OH, CH_4, H_2S and NH_3 (Fig. 1). A recent investigation of the CO_2 abundance in 17 comets using the AKARI space telescope shows that CO_2 dominates over CO in most comets (Ootsubo *et al.* 2010; Hamada *et al.* 2010). Abundances of detected cometary parent molecules range from less than 0.01 % to 20 % relative to water, and generally decrease with increasing complexity, except for hydrocarbons. Complex species, such as methyl formate and ethylene glycol, are detected. The cumulative histogram of the number of detected species, N, as a function of their abundance, X, suggests that observational biases affect the detection of species with abundances $< 10^{-3}$ and that a large number of molecules remains to be identified in cometary atmospheres (Crovisier *et al.* 2004).

2.2. *Chemical diversity*

According to current theories, comet formation in the solar nebula extended over a wide range of heliocentric distances for both Oort cloud comets, and Jupiter family comets issued from the trans-neptunian scattered disk. The current vue is that the Uranus-Neptune zone is the main source region of Oort cloud comets, with some contribution from the Jupiter-Saturn region, while Jupiter family comets formed beyond Neptune. If comets originated from distinct regions of the solar nebula, they could display diversity in their chemical composition depending on the local temperature and nebular composition where they formed. If there was significant mixing of nebular material across large ranges in heliocentric distance, even individual cometary nuclei could exhibit chemical inhomogeneity.

Chemical diversity among comets is indeed observed for both parent volatiles and daughter species. From a study of radicals (OH, CN, C_2, C_3, NH) in 85 comets, A'Hearn *et al.* (1995) proposed the existence of two classes of comets, depending on their C_2 and C_3 abundances: "typical" comets and "carbon-depleted" comets. They found that about one-half of the Jupiter-family comets are C_2 and C_3-depleted, but the fraction of carbon-depleted Oort cloud comets is much smaller. An update of this study confirming these two compositional classes is presented by Schleicher (2008). Note that the parent of C_2 radical is likely C_2H_2 (via C_2H), but the origin of C_3 remains unclear (Helbert *et al.* 2005).

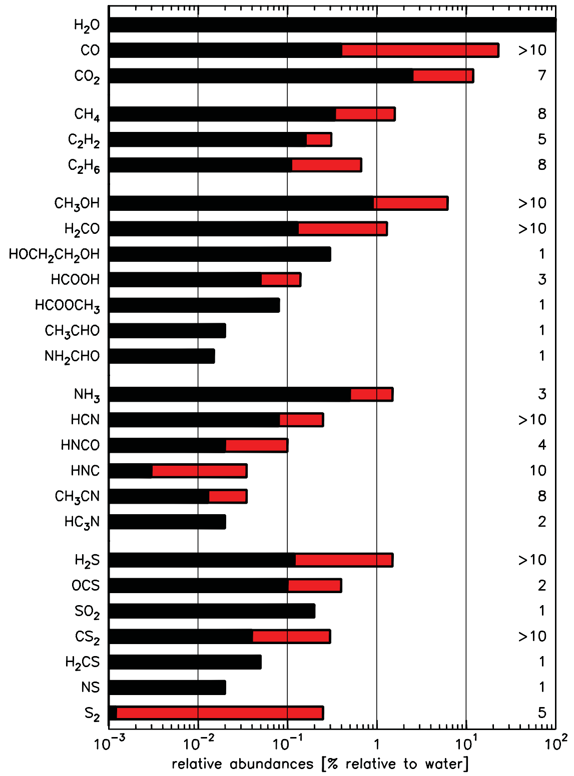

Figure 1. Abundances relative to water of cometary parent molecules. The range of measured values is shown in the gray (red in the color version) portion. The number of comets in which the molecule has been detected is given in the right (adapted from Bockelée-Morvan *et al.* (2005), courtesy J. Crovisier).

Surveys of parent volatile abundances show strong evidence for chemical diversity among comets. Depending on the molecule, abundances vary by a factor of a few to several tens (for CO) among comets (Fig. 1,2). Diversity is observed both within the population of Oort cloud comets and Jupiter family comets (Fig. 2). No obvious correlation is observed between the abundances of the hypervolatile species and the dynamical class. No trend between volatility and comet-to-comet variability is observed either (Biver *et al.* 2002; Gibb *et al.* 2003; Disanti & Mumma 2008). Three compositional classes, based on the organic composition (HCN, C_2H_2, C_2H_6 and CH_3OH), are possibly emerging (Mumma *et al.* 2008). Enriched and severely organic-depleted comets are present in both reservoirs (Mumma *et al.* 2008).

So far, Jupiter family comets have been still poorly investigated, because of their relatively low level of activity. A number of molecules have only been detected in comet C/1995 O1 (Hale-Bopp) or in a small number of comets.

Questions arise whether the molecular abundances measured in the coma are representative of those inside the nucleus, and to which extent the nucleus composition has been altered since comet formation. The chemistry could have evolved both during the long storage within the Oort cloud or Kuiper belt as well as during close passages to the Sun after removal from these reservoirs. Evolutionary effects are most important in the outer layers of a comet while the interior of the nucleus should be in large part

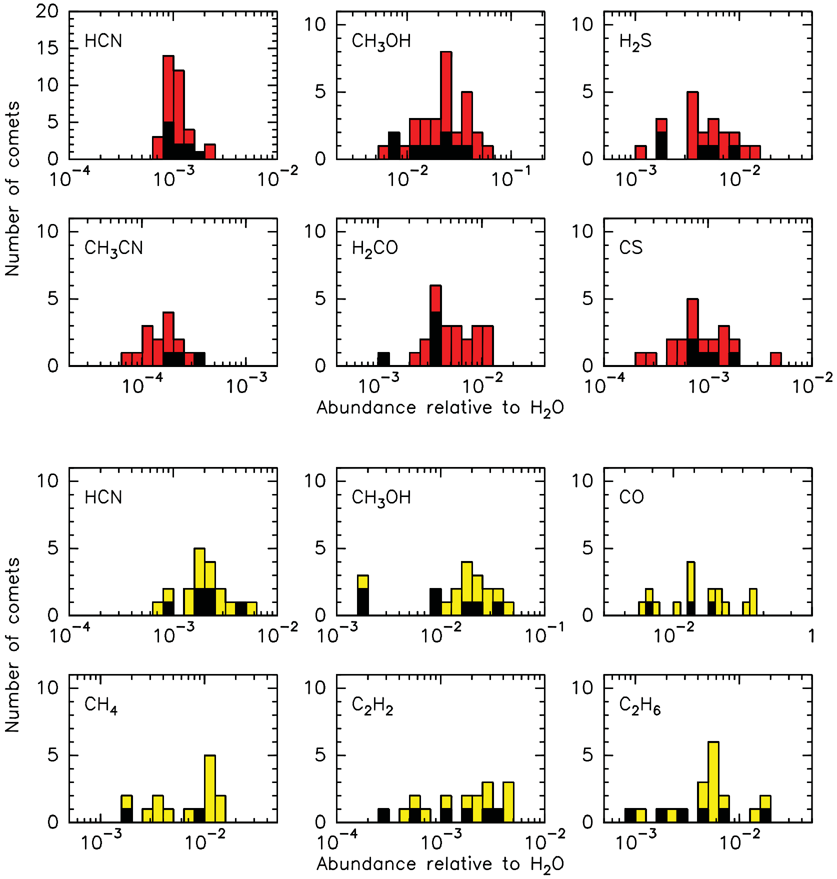

Figure 2. Histogram of molecular abundances relative to water from radio observations (top, Crovisier *et al.* 2009) and IR observations (bottom). The histogram for Jupiter family comets is in black.

pristine except for perhaps the most volatile species. The consistency of the volatile composition of 73P/Schwassmann-Wachmann 3 as a function of date and in its individual fragments suggests that evolutionary effects are small (Dello Russo *et al.* 2007). This might be related to the very low thermal conductivity of surface layers (Groussin *et al.* 2007; Gortsas *et al.* 2011). The fact that short-period and long-period comets display similar composition diversity, even in highly volatile species (the exception being CO, which is found abundant only in long-period comets) argues for the composition diversity to be largely pristine.

3. Isotopic composition of volatiles

Isotopic ratios are important diagnostics of how cometary materials formed because isotopic fractionation is very sensitive to chemical and physical conditions. So far, only a few isotopic ratios have been measured in cometary gases as summarized in Table 1 (see Jehin *et al.* 2009, for an extended review).

HDO has been observed from submillimetre spectroscopy in the bright comets Hale-Bopp and C/1996 B2 (Hyakutake), from which a D/H ratio of 3×10^{-4} consistent with

Table 1. Isotopic abundances in cometary volatiles

Isotopic ratio	Species	Value	Comet	References
D/H	[H_2O]	$(3.06\pm0.34)\times 10^{-4}$	1P/Halley	[1] [2]
		$(2.9\pm1.0)\times10^{-4}$	C/1996 B2 (Hyakutake)	[3]
		$(3.3\pm0.8)\times10^{-4}$	C/1995 O1 (Hale-Bopp)	[4]
		$(2.5\pm0.7)\times10^{-4}$	C/2002 T7 (LINEAR)	[5]
		$(4.1\pm1.5)\times10^{-4}$	8P/Tuttle	[6]
		$(4.6\pm1.4)\times10^{-4}$	C/2001 Q4 (NEAT)	[7]
		$< 2.5\times10^{-4}$	153P/Ikeya-Zhang	[8]
		$(1.61\pm0.24)\times10^{-4}$	103P/Hartley 2	[9]
	[HCN]	$(2.3\pm0.4)\times10^{-3}$	C/1995 O1 (Hale-Bopp)	[10]
$^{12}C/^{13}C$	[C_2]	93 ± 10	4 comets	[11]
	[CN]	91 ± 4	21 comets	[12]
	[HCN]	111 ± 12	C/1995 O1 (Hale-Bopp)	[13]
		114 ± 26	17P/Holmes	[14]
$^{14}N/^{15}N$	[HCN]	205 ± 70	C/1995 O1 (Hale-Bopp)	[14]
		139 ± 26	17P/Holmes	[14]
	[CN]	141 ± 29	21 comets	[12]
		220 ± 40	73P (fragment C)	[12]
$^{16}O/^{18}O$	[H_2O]	518 ± 45	1P/Halley	[2]
		470 ± 40	1P/Halley	[1]
		530 ± 60	4 comets	[15]
		425 ± 55	C/2002 T7 (LINEAR)	[5]
$^{32}S/^{34}S$	[CS]	27 ± 3	C/1995 O1 (Hale-Bopp)	[13]
	[CS]	16 ± 3	17P/Holmes	[16]
	[S^+]	23 ± 6	1P/Halley	[17]
	[H_2S]	16 ± 3	C/1995 O1 (Hale-Bopp)	[18]

[1] Eberhardt *et al.* (1995); [2] Balsiger *et al.* (1995); [3] Bockelée-Morvan *et al.* (1998); [4] Meier *et al.* (1998a); [5] Weaver *et al.* (2011); [6] Villanueva *et al.* (2009); [7] Hutsemékers *et al.* (2008); [8] Biver *et al.* (2006); [9] Hartogh *et al.* (2011); [10] Meier *et al.* (1998b); [11] Wyckoff *et al.* (2000); [12] Manfroid *et al.* (2009); [13] Jewitt *et al.* (1997); [14] Bockelée-Morvan *et al.* (2008); for Hale-Bopp, revised value from the data set of Jewitt *et al.* (1997) and Ziurys *et al.* (1999); [15] Biver *et al.* (2007); [16] Biver *et al.* (2008); [17] Altwegg (1996); [18] Crovisier *et al.* (2004); .

Giotto measurements in comet 1P/Halley has been derived (Table 1). More recently, similar values were obtained in other Oort cloud comets from observations of D, OD, and HDO in the UV, near UV, and near infrared, respectively. This is about twice higher than the D/H value in terrestrial water, and approximately one order of magnitude larger than the protosolar value in H_2 ($\sim 2\times10^{-5}$) (Fig. 3). The upper limit of 2.5×10^{-4} measured in comet 153P/Ikeya-Zhang might suggest that the D/H ratio is variable among comets (Biver *et al.* 2006). DCN has been detected in comet Hale-Bopp, yielding a D/H ratio in HCN seven times higher than that measured in cometary water (Table 1). Measurements of deuteration in other molecules have been attempted (Crovisier *et al.* 2004). An upper limit of 5×10^{-3} was derived for the D/H in CH_4 (Bonev *et al.* 2009; Kawakita and Kobayashi 2009). Deuterium enrichments are characteristic of interstellar or protosolar chemistry, and result from ion-molecule or grain-surface reactions at low temperature (Ehrenfreund *et al.* 2005).

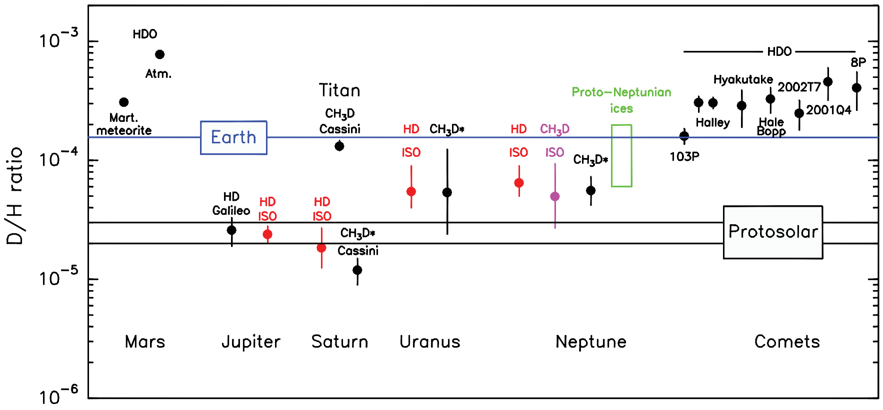

Figure 3. D/H in the Solar System.

The detection of deuterated molecules in the atmospheres of Jupiter family comets is difficult because of their faintness. HDO was detected in the JFC 103P/Hartley 2 with Herschel, from which a D/H value equal to the Earth value was derived (Hartogh *et al.* 2011). Hence, all comets do not share the same D/H.

Measurements have been obtained for the $^{12}C/^{13}C$ ratio in C_2, CN and HCN, for the $^{32}S/^{34}S$ ratio in CS, S^+, H_2S, and for the $^{16}O/^{18}O$ ratio in water: in first approximation they are consistent with terrestrial values ($^{12}C/^{13}C = 89$; $^{32}S/^{34}S = 23$; $^{16}O/^{18}O = 499$). Some measurements suggest an excess in ^{18}O and ^{34}S (Table 1).

The $^{14}N/^{15}N$ ratio has been measured in the CN radical in ~20 comets (Arpigny *et al.* 2003; Hutsemékers *et al.* 2005; Manfroid *et al.* 2005; Jehin *et al.* 2004; Manfroid *et al.* 2009). The average value is $^{14}N/^{15}N = 148 \pm 6$, with no significant differences emerging between Oort cloud and Jupiter family comets. Only comet 73P/Schwassmann-Wachmann 3 presents a value which is out of the typical range (210±50 and 220±40, for fragment B and C, respectively, Manfroid *et al.* 2009). The average value corresponds to a factor of two enrichment in ^{15}N with respect to the Earth atmospheric value $^{14}N/^{15}N = 272$. The $^{14}N/^{15}N$ ratio was measured in HCN in comets C/1995 O1 (Hale-Bopp) and 17P/Holmes, belonging to the Oort cloud and JFC classes, respectively. For comet Hale-Bopp, an $HC^{14}N/HC^{15}N$ ratio marginally higher than the terrestrial value was reported (Jewitt *et al.* 1997; Ziurys *et al.* 1999), but a reanalysis of the data suggests instead a value consistent with the value in CN (Bockelée-Morvan *et al.* 2008). The $HC^{14}N/HC^{15}N$ ratio measured in comet 17P/Holmes is also consistent with the value measured in CN (Table 1)(Bockelée-Morvan *et al.* 2008). There is some observational evidence that HCN photolysis is not the sole production mechanism of CN radicals. Indeed, for some comets, the CN production rate exceeds the HCN production rate (Fray *et al.* 2005). CN radicals are also produced by HC_3N and CH_3CN but those species are minor constituents of cometary atmospheres (Fig. 1). This led to the hypothesis that significant amounts of CN radicals could be produced by the thermal degradation of refractory organics present in dust grains. The similar isotopic properties of CN and HCN point to HCN being the prime parent of CN in cometary atmospheres, or imply that refractory organics producing CN radicals are equally enriched in ^{15}N.

^{15}N excesses observed in CN and HCN are similar to values measured in carbonaceous meteorites and Interplanetary Dust Particles (IDPs) (Floss *et al.* 2006; Busemann *et al.*

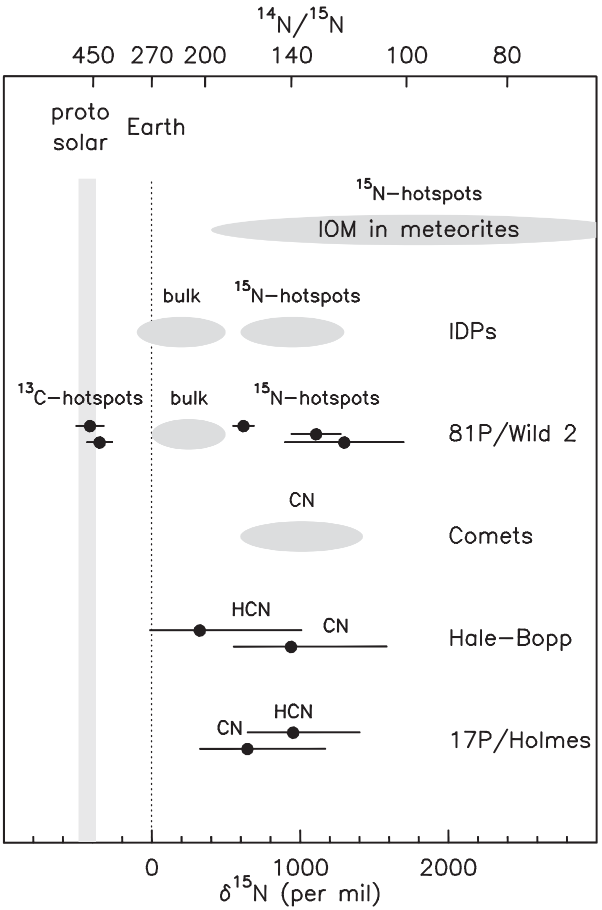

Figure 4. N isotope measurements in primitive matter of the Solar System, given either as $^{14}N/^{15}N$ ratios or $\delta^{15}N$ values ($\delta^{15}N$ = $(^{14}N/^{15}N)$ /$(^{14}N/^{15}N)_{Earth}$-1). Shown are the protosolar value measured by the Genesis mission (Marty *et al.* 2011), values for comet 17P/Holmes (Bockelée-Morvan *et al.* 2008), comet Hale-Bopp (Arpigny *et al.* 2003; Bockelée-Morvan *et al.* 2008) and other comets (Jehin *et al.* 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 are regions that present strong isotopic enrichments relative to the surrounding material.^{13}C hotspots refer to 81P/Wild 2 submicrometre grains enriched in ^{13}C with respect to the terrestrial $^{12}C/^{13}C$ ratio and depleted in ^{15}N. Points with error bars correspond to single measurements. When many measurements are available, ellipses encompassing the range of measured values are drawn. Adapted from Bockelée-Morvan *et al.* (2010).

2006)(Fig. 4). ^{15}N excesses are also present at the submicrometre scale in the dust particles collected by the Stardust mission in comet 81P/Wild 2 (McKeegan *et al.* 2006). Altogether, it indicates that N-bearing volatiles in the solar nebula underwent important N isotopic fractionation at some stage of Solar System formation.

4. Ortho-to-para ratios

Molecules with H atoms at symmetrical positions may exist in different nuclear-spin species, e.g. ortho and para species for molecules with two H atoms. The ortho/para

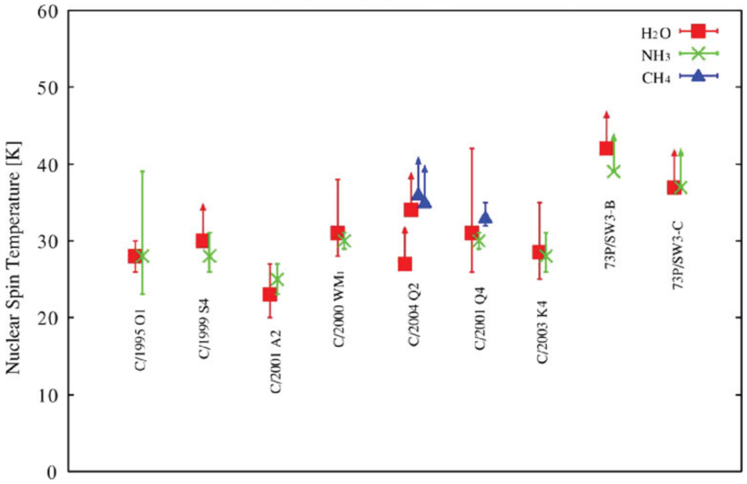

Figure 5. Comparison of nuclear spin temperatures of H_2O, NH_3 and CH_4 observed in comets. From Shinnaka *et al.* (2011).

ratio (OPR) in water and ammonia has been measured in a number of comets (see e.g., Kawakita *et al.* 2004, Bonev *et al.* 2007, Shinnaka *et al.* 2011). Measurements are also available for CH_4 (Kawakita *et al.* 2004) and CH_3OH (Pardanaud *et al.* 2007). Most measurements indicate a spin temperature within 25–35 K, though some comets exhibit higher spin temperatures, corresponding to equilibrated OPR. Interestingly, water, ammonia and methane shares the same nuclear spin temperature (Fig. 5). No relationship was found between the spin temperature and the comet dynamical origin, or with the heliocentric distance at which the comets were observed, and their volatile composition. However, there may be some link between the $^{14}N/^{15}N$ in CN and the spin temperature of NH_3 to be confirmed in the future: fragments B and C of comet 73P/Schwassmann-Wachmann 3 displays a $^{14}N/^{15}N$ ratio distinct from the average value (Sect. 3) and an equilibrated OPR in NH_3.

It is often argued in the literature that un-equilibrated spin temperatures have a meaning related to the temperature environment of the species in the nucleus or even before, i.e., they could indicate that molecules formed at ~30 K or were last processed at about 30 K (e.g., Shinnaka *et al.* 2011). However the real signification of the spin temperature is debated (Crovisier 2007). Buntkowsky *et al.* (2008) show, by quantum mechanics calculations, that the inter-conversion between para and ortho H_2O states is very fast inside the ice, and argue that the actual spin temperatures measured in cometary atmospheres depend both on the ice temperature and of the evaporation history of the ice. Thermal desorption is more efficient for para-water than for ortho-water: Dulieu *et al.* (2011) have estimated to ~ 2.4 ($T_{spin} \sim 28$ K) the OPR in water set by this process. Further work (both experiments and models) is needed to validate those interpretations with the constraint that the similarity in the spin temperatures of H_2O, NH_3 and CH_4 should be explained.

5. Dust composition

First insights on the composition of the refractory component of cometary nuclei were obtained from in situ measurements in comet 1P/Halley. Mass spectrometry analysis of cometary dust revealed the presence of both rocky (Mg, Si, Fe, Ca) and organic refractory particles, the so-called CHON organic grains (Jessberger *et al.* 1988). Amorphous carbon grains were also identified. Altogether, the dust grains of 1P/Halley were found to have a chondritic CI-like elemental composition for the most refractory elements, whereas enrichments are observed for the light elements C, H, N (Jessberger *et al.* 1988). The concentrations of C, H, O and N could not be determined in the dust grains of comet 81P/Wild 2 collected by Stardust but most other elements were also found to be in chondritic abundance (Flynn *et al.* 2006). A notable exception is sulfur, which was found to be depleted. Whether this depletion is real or reflects capture heating is debated (Zolensky *et al.* 2006).

The mid and far-IR spectra of comets show that silicates in comets are dominated by Mg-rich olivines and pyroxenes and are in two forms : amorphous and crystalline (Hanner *et al.* 2005). Crystalline silicates are grains that condense at high temperatures or can be formed from the annealing of amorphous silicates at somewhat lower temperature. The scarcity of the crystalline silicates in the interstellar medium indicates that these compounds formed in the inner hot regions of the solar nebula. Other high-temperature minerals are present in comet Wild 2 Stardust samples, such as Calcium Aluminium-rich inclusions (CAIs) or iron sulfides (Zolensky *et al.* 2006). Amorphous silicates are presumably relics of the presolar cloud and analogous to the glassy silicates grains (GEMS) found in IDPs. GEMS-like material is found in Stardust but was possibly created during capture (Ishii *et al.* 2008).

Our knowledge of the nature of the refractory organic matter is rather limited. Based on the mass spectra recorded by the Giotto and Vega spacecraft, a number of compounds have been hypothesized (see the review of Cottin *et al.* 1999). The presence of formaldehyde polymers is proposed to explain the extended distribution of formaldehyde in cometary atmospheres (Cottin *et al.* 2004). Spectroscopic studies of the 3.4 μm C-H signature of Stardust samples indicate that the aliphatic chains of the organics are longer than in carbonaceous meteorites, and in the diffuse interstellar medium. They are also significantly longer than in IDPs (Keller *et al.* 2006). The aromatic fraction of the total organic matter is small, but is rich in both oxygen and nitrogen compared with meteoritic insoluble organic matter (Sandford *et al.* 2006; Clemett *et al.* 2010). Glycine and PAHs have been identified in Stardust samples (Elsila, Glavin, & Dworkin 2009; Clemett *et al.* 2010).

6. Implications for the origin of cometary material

The identification of interstellar-like organic and other exotic gases sublimated from cometary nuclei gives the definite impression that comets preserve a record of the interstellar composition characteristic of the presolar cloud, or that cometary and interstellar molecules formed by similar processes (Irvine *et al.* 2000; Bockelée-Morvan *et al.* 2000; Ehrenfreund *et al.* 2005). The gas phase composition in the interstellar medium depends on many variables, but almost every parent species observed in comets has also been detected in the interstellar medium, either in cold dark molecular clouds or in dense cloud cores where star formation is taking place. The molecular composition of comets, interstellar ices, hot cores and hot corinos are all characterized by the presence of large quantities of saturated/hydrogenated species (e.g. H_2O, CH_4, CH_3OH, NH_3, H_2S), coexisting with oxidized molecules (as CO, CO_2 and SO_2). For interstellar ices, it is believed that this composition traces primarily a combination of ion-molecule and grain-surface processes at low temperature. Complex organic species can then form through energetic processing by UV photons and cosmic rays. Complex species are not abundant enough

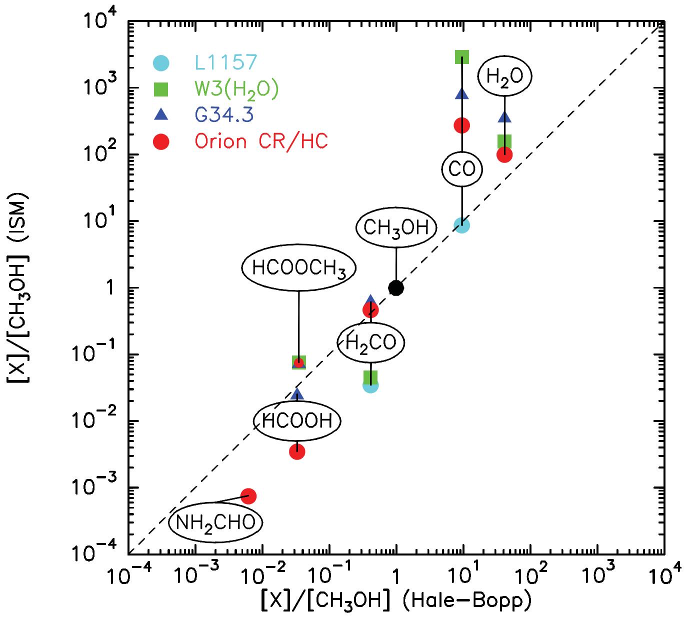

Figure 6. Molecular abundances in comet Hale-Bopp (CHO-bearing species) compared to those in the bipolar flow L1157 and several hot molecular core. From Bockelée-Morvan *et al.* (2000).

to be detected in interstellar ices, but are found in the hot cores containing massive protostars, or in the 'hot corinos' around low-mass protostars, where the hot environment allows the icy grain mantles to be evaporated. Figure 6 illustrates a quantitative similarity between interstellar and cometary volatile material. Discrepancies do exist. For example, the cometary abundance of ethylene glycol relative to methanol is much larger than measured in the hot core Sgr (B2) (Crovisier *et al.* 2004). The cometary abundance of methanol is generally much smaller when compared to interstellar ices (Ehrenfreund *et al.* 2005).

Another indicator of interstellar-like chemistry is the D/H ratio, as already discussed in Sect.3. However there is evidence that cometary D/H values are lower than in most interstellar sources, in particular around protostars where extreme deuteration is observed (Ceccarelli *et al.* 2007; Bergin *et al.* 2010). This low deuterium fractionation in comets is interpreted by ion-molecule chemistry in gas phase at relatively high temperature (25–35 K, Meier *et al.* 1998a, 1998b) or, alternatively, by mixing of D-enriched material with material reprocessed in the inner solar nebula (Hersant, Gautier, & Huré 2001). Ion-molecule reactions in the outer solar nebula could also act to lower the interstellar fractionation (Aikawa and Herbst 1999). Extreme D-enrichments are observed in primitive meteorites and IDPs. It was previously thought that these enrichments were reflecting those acquired in the presolar cloud. The negative correlation between the D/H ratios of the CH bonds and their binding energy in the Insoluble Organic Matter of Orgueil carbonaceous meteorite suggests that deuterium enrichments were acquired at the surface of the protosolar disk through intense UV irradiation from the proto-Sun (Remusat *et al.* 2006). Whether this mechanism affected the D-fractionation observed in cometary HCN and H_2O has still to be investigated. It is interesting to note that the cometary dust particles collected by Stardust are also less D-enriched than carbonaceous meteorites and IDPs (McKeegan *et al.* 2006).

The lower D/H value found in the water of the Jupiter family comet 103P/Hartley 2 with respect to Oort cloud comets was not anticipated by models which consider isotopic exchanges in the solar nebula (Hersant, Gautier, & Huré 2001; Kavelaars *et al.* 2011). Indeed, these models predict that comets formed at higher distances from the Sun should exhibit higher D/H ratios as they incorporated less processed material from the inner solar nebula. Further measurements of the D/H ratio in the two dynamical families are required to investigate whether a dichotomy is present, or whether the two families display an isotopic diversity. The current understanding of deuteration in different solar system reservoirs is clearly incomplete.

The isotopic composition of the main carrier of nitrogen in the solar nebula (N_2) has been recently evaluated to $^{14}N/^{15}N = 441 \pm 6$ from the study of solar wind ions sampled by the Genesis mission (Marty *et al.* 2011), a value close to measurements in the atmosphere of Jupiter (Fouchet *et al.* 2004). The interpretation of the ^{15}N enrichment in cometary HCN and CN (a factor of 3 with respect to the protosolar value) is not as compelling as for deuterium. There is indeed still little evidence for N isotopic fractionation in the interstellar medium (Ikeda *et al.* 2002; Gerin *et al.* 2009; Lis *et al.* 2010), though recent assessments of the N isotopic fractionation for starless and prestellar cores at various stages of evolution are promising (Milam & Charnley al. 2011). Rodgers & Charnley (2008) showed that interstellar chemistry can potentially produce ^{15}N enrichments in both nitrile and amine groups. On the other hand predicted ^{15}N enhancements in HCN for exchange reactions in the solar nebula involving the main nitrogen reservoir N_2 are modest (Terzieva & Herbst 2000). Alternative mechanisms include a nucleosynthetic origin and photochemical self-shielding in the solar nebula, as proposed for explaining the oxygen isotope anomalies in meteorites. Irrespective of the mechanism, protosolar HCN never isotopically equilibrated with nebular gas at later phases of Solar System evolution.

The molecular and isotopic compositions of cometary volatiles suggest an origin in chemistry at low temperature. Whether this occurred in the cold molecular cloud that predated the Solar System or in the outer regions of the solar nebula cannot be decided based on the available data. However, the composition of cometary dust shows that cometary nuclei also incorporated nebular products formed in the hot inner regions of the solar nebula, revisiting previous views according to which comets could be pure interstellar condensates (Greenberg 1982). By some process (e.g., turbulence, see Bockelée-Morvan *et al.* 2002, Ciesla 2007) high-T temperature materials were transported out to the region of formation of comets before their agglomeration, indicating that the solar nebula underwent large-scale radial mixing at early times. Surprisingly, the most recognizable characteristics of presolar material were found to be rare in Stardust samples compared to their occurrence in chondritic porous IDPs, believed to be of cometary origin (Ishii *et al.* 2008). Only a very few numbers of presolar grains identified by non-solar isotopic compositions have been found (McKeegan *et al.* 2006). Altogether, the mineralogical and isotopic composition of comet Wild 2 grains suggests that its refractory material more closely resembles an inner Solar System asteroid than an outer solar system comet with primitive unaltered dust. Likely, comet Wild 2 is not representative of the whole population of comets. Cometary nuclei may present a large diversity in their refractory composition, as observed for their icy composition, relevant to the place and time of their formation in the solar nebula.

Progresses in our knowledge of comet composition will benefit from future space missions to comets (e.g., the Rosetta mission of ESA) and from telescopic observations with yet available or new instrumentation (e.g., the Herschel space observatory, ALMA). Our understanding of comet composition in the context of the origin and evolution of our Solar System will greatly benefit from theoretical models of chemical and physical processes in the solar nebula, and from upcoming new results on the composition of protostellar sources and protoplanetary disks at different stages of evolution.

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