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Cometary Isotopic Measurements

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Abstract Isotopic ratios in comets provide keys for the understanding of the origin of cometary material, and the physical and chemical conditions in the early Solar Nebula. We review here measurements acquired on the D/H, $^{14}N/^{15}N$, $^{16}O/^{18}O$, $^{12}C/^{13}C$, and $^{32}S/^{34}S$ ratios in cometary grains and gases, and discuss their cosmogonic implications. The review includes analyses of potential cometary material available in collections on Earth, recent measurements achieved with the Herschel Space Observatory, large optical telescopes,

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and Rosetta, as well as recent results obtained from models of chemical-dynamical deuterium fractionation in the early solar nebula. Prospects for future measurements are presented.

Keywords Comets · Isotopes

1 Introduction

The solar system formed about 4.6 billion years ago from an infall of matter inside a molecular cloud. A wealth of processes happened, involving chemistry, and dynamics at all scales before the solar system reached its present state with its cortege of planets and small bodies (e.g. Ceccarelli et al. 2014; Mandt et al. 2015, this issue). The view that comets are among the most primitive materials in the solar system stems from their primitive element abundances, similar to that of the bulk solar system for most elements (as deduced from analyses of 1P/Halley and 81P/Wild 2 for rock forming elements), and their extraordinary composition richness in elements in the gas phase, which resembles that of interstellar clouds (Jessberger and Kissel 1991; Bockelée-Morvan et al. 2000; Cochran et al. 2015, this issue; Brownlee 2014). Comets formed in the outer skirts of the solar nebula and trapped volatile species formed either in the presolar cloud or in situ. However, the discovery that comets incorporated high-temperature components formed in the neighborhood of the forming Sun, points out to a large diversity of formation conditions for the comet material, which in turn provides constraints on mixing processes in the solar nebula (Brownlee et al. 2006; Bockelée-Morvan et al. 2002; Wooden 2008).

The isotopic abundances are key tracers for reconstructing the origin and history of cometary material. Indeed, isotopic fractionation is sensitive to environmental conditions, such as temperature, density, radiation, and composition. The strongest variations among volatile element isotope ratios are observed for hydrogen. Therefore deuterium fractionation is an Ariadne's thread for understanding the very first steps of solar system formation, starting with the pre-collapse phase to the formation of planetesimals (Ceccarelli et al. 2014). Key information can also be inferred from the large nitrogen isotopic variations observed among solar system objects, although they are still difficult to interpret.

In this chapter, we review isotopic measurements acquired so far on comets, including on dust particles collected by the Stardust mission (Brownlee 2014). Different lines of evidence indicate that samples from comets have been recovered on Earth. Such samples are of uttermost interest since they allow extremely precise elemental, mineralogical and isotopic analyses at different scales down to the nanometer. Hence this review also present isotopic properties of interplanetary dust particles (IDPs) and micrometeorites of probable cometary origin. To put the measurements into context, we summarize recent studies on interstellar deuterium and nitrogen fractionation, initiated by recent measurements in interstellar sources. Finally, we present prospectives for new isotopic measurements in comets, especially with instruments onboard the Rosetta/Philae space mission.

2 Isotopic Measurements in Cometary Volatiles

Because of the faint signatures of deuterated species, D/H ratios were only obtained in a handful of bright comets. Table 1 lists measurements of the D/H ratio in cometary water acquired so far. It is worth remembering that the D/H ratio is equal to half the HDO/H_2O ratio, because water contains two atoms of hydrogen.

Table 1 D/H ratios in cometary molecules

Species	Parent molecule	D/H ratio[a]	Comet	Reference
H_2DO^+	H_2O	$(3.08 \pm 0.5) \times 10^{-4}$	1P/Halley	Balsiger et al. (1995)
		$(3.06 \pm 0.34) \times 10^{-4}$	1P/Halley	Eberhardt et al. (1995)
		$(2.1 \pm 0.3) \times 10^{-4}$	1P/Halley	Brown et al. (2012)
HDO	H_2O	$(2.9 \pm 1.0) \times 10^{-4}$	C/1996 B2 (Hyakutake)	Bockelée-Morvan et al. (1998)
		$(3.3 \pm 0.8) \times 10^{-4}$	C/1995 O1 (Hale-Bopp)	Meier et al. (1998a)
		$(4.09 \pm 1.45) \times 10^{-4}$	8P/Tuttle	Villanueva et al. (2009)
		$(1.61 \pm 0.24) \times 10^{-4}$	103P/Hartley 2	Hartogh et al. (2011)
		$(2.06 \pm 0.22) \times 10^{-4}$	C/2009 P1 (Garradd)	Bockelée-Morvan et al. (2012)
		$(5.3 \pm 0.7) \times 10^{-4}$	67P/Churyumov-Gerasimenko	Altwegg et al. (2014)
		$< 2.5 \times 10^{-4}$[b]	153P/Ikeya-Zhang	Biver et al. (2006)
		$< 5.6 \times 10^{-4}$	C/2007 N3 (Lulin)	Gibb et al. (2012)
		$< 2 \times 10^{-4}$	45P/Honda-Mrkos-Pajdušáková	Lis et al. (2013)
OD	H_2O	$(2.5 \pm 0.7) \times 10^{-4}$	C/2002 T7 (LINEAR)	Hutsemékers et al. (2008)
D	H_2O	$(4.6 \pm 1.4) \times 10^{-4}$	C/2001 Q4 (NEAT)	Weaver et al. (2008)
DCN	HCN	$(2.3 \pm 0.4) \times 10^{-3}$	C/1995 O1 (Hale-Bopp)	Meier et al. (1998b)
		$(2.3 \pm 0.6) \times 10^{-3}$	C/1995 O1 (Hale-Bopp)	Crovisier et al. (2004)
		$< 1 \times 10^{-2}$	C/1996 B2 (Hyakutake)	Bockelée-Morvan et al. (1998)
		$< 1 \times 10^{-2}$	103P/Hartley 2	Gicquel et al. (2014)
HDCO	H_2CO	$< 2 \times 10^{-2}$	1P/Halley	Balsiger et al. (1995)
		$< 5 \times 10^{-2}$	C/1995 O1 (Hale-Bopp)	Crovisier et al. (2004)
CH_3D	CH_4	$< 1 \times 10^{-1}$	153P/2002 C1 (Ikeya-Zhang)	Kawakita et al. (2003)
		$< 1 \times 10^{-2}$	C/2001 Q4 (NEAT)	Kawakita et al. (2005)
		$< 5 \times 10^{-3}$	C/2004 Q2 (Machholz)	Bonev et al. (2009)
		$< 6.4 \times 10^{-3}$	C/2004 Q2 (Machholz)	Kawakita and Kobayashi (2009)
		$< 7.5 \times 10^{-3}$	C/2007 N3 (Lulin)	Gibb et al. (2012)
NH_2D	NH_3	$< 4 \times 10^{-2}$	C/1995 O1 (Hale-Bopp)	Crovisier et al. (2004)
ND	NH_3	$< 6 \times 10^{-3}$	C/1996 B2 (Hyakutake)	Meier et al. (1998c)
CH_3OD	CH_3OH	$< 1 \times 10^{-2}$	1P/Halley	Eberhardt et al. (1994)
		$< 3 \times 10^{-2}$	C/1995 O1 (Hale-Bopp)	Crovisier et al. (2004)
CH_2DOH	CH_3OH	$< 8 \times 10^{-3}$	C/1995 O1 (Hale-Bopp)	Crovisier et al. (2004)
HDS	H_2S	$< 2 \times 10^{-1}$	C/1995 O1 (Hale-Bopp)	Crovisier et al. (2004)
		$< 8 \times 10^{-3}$	17P/Holmes	Biver et al. (2008)
CD		$< 3 \times 10^{-2}$	C/1996 B2 (Hyakutake)	Meier et al. (1998c)

[a] Value for the parent molecule, except for ND and CD, where it refers to ND/NH, and CD/CH values

[b] Revised value using updated H_2O production rates from Biver et al. (2007)

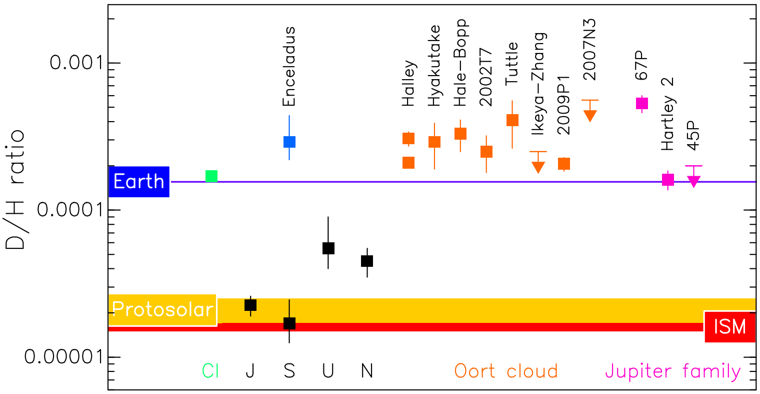

Fig. 1 D/H ratio in the water of comets compared to values in carbonaceous meteorites (CI), Earth's oceans (VSMOW), and Enceladus. Displayed data for planets, the interstellar medium, and the protosolar nebula refer to the value in H_2. Adapted from Lis et al. (2013)

2.1 Deuterium

2.1.1 Water

The first measurements of the D/H ratio in cometary H_2O were obtained in comet 1P/Halley from mass-resolved ion-spectra of H_3O^+ acquired with the Ion Mass Spectrometer (IMS) (Balsiger et al. 1995) and the Neutral Mass Spectrometer (NMS) (Eberhardt et al. 1995) instruments onboard the European Giotto spacecraft. These independent data provided a consistent D/H value of $\sim 3 \times 10^{-4}$, which corresponds to twice the Vienna Standard Mean Ocean Water VSMOW of 155.76 ± 0.1 ppm (Table 1, Balsiger et al. 1995; Eberhardt et al. 1995). However, Brown et al. (2012) reexamined the NMS measurements, reevaluating the D/H ratio in comet 1P/Halley to $(2.1 \pm 0.3) \times 10^{-4}$.

From observations undertaken with the Caltech Submillimeter Observatory and the James Clerk Maxwell telescope (JCMT), HDO was detected in the bright long-period comets C/1996 B2 (Hyakutake) and C/1995 O1 (Hale-Bopp) from its 1_{01}–0_{00} line at 464.925 GHz (Bockelée-Morvan et al. 1998; Meier et al. 1998a). The derived D/H values in these two comets are in agreement with the determinations in comet Halley (Table 1, Fig. 1). However, observations of the HDO 1_{10}–1_{01} transition at 509.292 GHz in the Halley-type comet 153P/Ikeya-Zhang yielded D/H $< 2.5 \times 10^{-4}$, suggesting for the first time an hydrogen isotopic diversity in the Oort-cloud population (Biver et al. 2006).

Using the new high resolution Cryogenic Infrared Echelle Spectrograph (CRIRES) of the Very Large Telescope (VLT), Villanueva et al. (2009) observed in early 2008 the HDO ro-vibrational transitions near 3.7 μm in the Halley-family comet 8P/Tuttle originating from the Oort cloud. Twenty three lines were co-added to get a marginal detection of HDO, from which a formal value of D/H of $(4.09 \pm 1.45) \times 10^{-4}$ was derived.

In cometary atmospheres, water photodissociates into mainly OH and H. The OD/OH ratio was measured to be $(2.5 \pm 0.7) \times 10^{-4}$ in the Oort-Cloud comet C/2002 T7 (LINEAR) through ground-based observations of the OH $A^2\Sigma^+$–$X^2\Pi_i$ ultraviolet bands at 310 nm obtained with the VLT feeding the Ultraviolet-Visual Echelle Spectrograph (UVES) (Hutsemékers et al. 2008). No individual OD line was detected, but a marginal 3σ detection of OD was obtained by co-adding the brightest lines. Atomic deuterium (D) emission was also discovered during ultraviolet observations of comet C/2001 Q4 (NEAT) in April 2004 using the Space Telescope Imaging Spectrograph (STIS) of the Hubble Space Telescope (Weaver et al. 2008). The Lyman-α emission from both D and atomic hydrogen were detected, from which a preliminary value $D/H = (4.6 \pm 1.4) \times 10^{-4}$ was derived, assuming that H_2O is the dominant source of the observed D and H, as it is likely the case. The strength of the optical method is that both normal and rare isotopologues have lines in the same spectral interval and are observed simultaneously, avoiding problems related to comet variable activity.

The most recent spectroscopic D/H measurements in cometary water were acquired using the ESA Herschel space observatory. The HDO 1_{10}–1_{01} transition at 509.292 GHz was observed using the Heterodyne Instrument for the Far-Infrared (HIFI) in the Jupiter-family comets 103P/Hartley 2 and 45P/Honda-Mrkos-Pajdušáková (Hartogh et al. 2011; Lis et al. 2013), and in the Oort-cloud comet C/2009 P1 (Garradd) (Bockelée-Morvan et al. 2012). Observations of HDO were interleaved with observations of the H_2O and $H_2^{18}O$ 1_{10}–1_{01} lines. Since the H_2O ground state rotational lines in comets are optically thick, optically thin lines of $H_2^{18}O$ provide, in principle, a more reliable reference for the D/H determination. The $HDO/H_2^{18}O$ was measured to be 0.161 ± 0.017 for comet Hartley 2, i.e., consistent with the VSMOW value for this ratio of 0.1554 ± 0.0001. The $HDO/H_2^{18}O$ value of 0.215 ± 0.023 for comet Garradd suggests a significant difference (3-σ) in deuterium content between the comet Garradd and Hartley 2. Hartogh et al. (2011) derived a D/H ratio of $(1.61 \pm 0.24) \times 10^{-4}$ for comet Hartley, assuming an $H_2^{16}O/H_2^{18}O$ ratio of 500 ± 50 which encompasses the VSMOW value and values measured in cometary water (Jehin et al. 2009, see Sect. 2.3). For comet Garradd, the derived D/H ratio is $(2.06 \pm 0.22) \times 10^{-4}$ based on the $HDO/H_2^{16}O$ production rate ratio, and $(2.15 \pm 0.32) \times 10^{-4}$, using the same method as Hartogh et al. (2011). Herschel observations in the Jupiter family comet 45P/Honda-Mrkos-Pajdušáková were unsuccessful in detecting the HDO 509 GHz line, but resulted in a 3σ upper limit for the D/H ratio of 2.0×10^{-4} which is consistent with the value measured in comet 103P/Hartley 2 and excludes the canonical pre-Herschel value measured in Oort-cloud comets of $\sim 3 \times 10^{-4}$ at the 4.5σ level (Lis et al. 2013).

Whereas the Herschel measurements were suggesting a Earth-like value for Jupiter family comets, the ROSINA mass-spectrometer onboard Rosetta (Balsiger et al. 2007) measured in comet 67P/Churymov-Gerasimenko a D/H value of $(5.3 \pm 0.7) \times 10^{-4}$, i.e., more than three times the VSMOW value (Altwegg et al. 2014).

2.1.2 *HCN*

The first detection of DCN (J:5-4; 362.046 GHz) was obtained by Meier et al. (1998b) in the bright Oort comet C/1995 O1 (Hale-Bopp) using the JCMT, where a D/H ratio of $(2.3 \pm 0.4) \times 10^{-3}$ was derived. Crovisier et al. (2004) obtained a marginal 3σ detection of DCN (J:2-1; 217.2385 GHz) with the IRAM 30m telescope toward the same comet and reported a D/H ratio consistent with Meier et al. (1998b). The deuterium enrichment in HCN is 7 times larger than that measured in H_2O in comet Hale-Bopp and most Oort cloud comets. (Sect. 2.1.1).

Bockelée-Morvan et al. (1998) derived a 3σ upper limit of DCN (J:5-4; 362.046 GHz) in the bright long-period comet C/1996 (Hyakutake) by using the 10.4m Leighton telescope of the Caltech Submillimeter Observatory (CSO). They obtained a $D/H < 1.0 \times 10^{-2}$. Gicquel et al. (2014) measured for the first time an upper limit for DCN (J:4-3; 362.0465 GHz) in a Jupiter-Family comet (103P/Hartley 2) using the JCMT. They concluded to a D/H ratio $< 1.0 \times 10^{-2}$. Blake et al. (1999) deduced a larger D/H ratio in jets from interferometric radio data, which might suggest variations in the coma. The $(D/H)_{HCN}$ ratios deduced from single-dish observations are summarized in Table 1.

By comparison, a range of (0.4–7.0) × 10^{-2} for the DCN/HCN ratio was determined in the interstellar medium (ISM) (Roberts et al. 2002; Jørgensen et al. 2004). The low DCN/HCN value in comets compared to the ISM can suggest some reprocessing in the Solar Nebula that occurred before the incorporation of these molecules into comets (Mousis et al. 2000), as it will be discussed in depth in Sect. 4.2. Alternatively, the D/H ratios in both water and HCN in comet Hale-Bopp may reflect an ion-chemistry at about 30–35 K which took place either in the presolar cloud or in the outer regions of the solar nebula (Meier et al. 1998b).

2.1.3 CH_4

Because methane has four identical H-atoms to be substituted with deuterium, the abundance ratio of singly deuterated methane (CH_3D) relative to CH_4 is enhanced, i.e., $D/H = 0.25 \times (CH_3D/CH_4)$.

Constraints on the D/H ratio in methane were obtained from observations of vibrational bands in the near-IR. The strongest vibrational band of CH_3D in cometary atmospheres is the ν_4 band around 3000 cm^{-1}, which is close to the ν_3 vibrational band of CH_4. They are close to each other and this situation allows us to measure emission lines of CH_4 and CH_3D simultaneously.

The first trial to detect CH_3D in comet 153P/Ikeya-Zhang provided a 2σ upper limit for the D/H ratio of 0.075 (Kawakita and Watanabe 2003). A more stringent upper limit of 0.01 was later reported in comet C/2001 Q4 (NEAT) (Kawakita et al. 2005). In comet C/2004 Q2 (Machholz), 3σ upper limits of 0.003 and 0.005 were reported by Kawakita and Kobayashi (2009) and Bonev et al. (2009), respectively. More recently, Gibb et al. (2012) derived $D/H < 0.007$ (3σ) in comet C/2007 N3 (Lulin).

Chemical network models for low temperature environments (e.g., Aikawa and Herbst 1999) predict large CH_3D/CH_4 abundance ratios, up to 0.1–0.2 at 10 K (i.e, D/H up to 0.025–0.05). Upper limits measured in comets cannot be explained by methane deuteration at such low temperatures.

2.1.4 Other Molecules

Some constraints on the level of deuteration in other cometary molecules have been obtained. Using Hale-Bopp data in the millimeter range, Crovisier et al. (2004) obtained D/H upper limits for NH_3, H_2CO, and CH_3OH (both CH_3OD, and CH_2DOH), which range typically from 0.01 to 0.05. An upper limit of $D/H < 0.008$ was obtained for H_2S in comet 17P/Holmes (Biver et al. 2008). Measurements for some of these molecules will be possible from Rosetta (see Sect. 5.1 and Table 6), or will need to await for a very bright comet observed with ALMA (see Sect. 5.2).

2.2 Nitrogen

Figure 2 summarizes nitrogen isotopic ratios measured in comets, and how they compare to values measured in other primitive Solar System materials.

2.2.1 HCN and CN

The nitrogen isotopic ratio $^{14}N/^{15}N$ was measured for the first time in comet C/1995 O1 (Hale-Bopp) in 1997 in HCN as well as in the CN violet band. The $^{14}N/^{15}N$ values derived from the HCN emission at sub-millimetre range (323 ± 46, Jewitt et al. 1997; 330 ± 98

Table 2 Isotopic ratios in comets: Carbon, oxygen, nitrogen and sulfur

Isotopic ratio	Species	Value	Comet	References
$^{12}C/^{13}C$	[C_2]	93 ± 10	4 comets	Wyckoff et al. (2000)
		85 ± 20	C/2002 T7	Rousselot et al. (2012)
		80 ± 20	C/2001 Q4	Rousselot et al. (2012)
		94 ± 33	C/2012 S1	Shinnaka et al. (2014a)
	[CN]	91 ± 4	21 comets	Manfroid et al. (2009)
		95 ± 15	103P/Hartley 2	Jehin et al. (2011)
		95 ± 25	C/2012 F6	Decock et al. (2014)
	[HCN]	111 ± 12	C/1995 O1	Jewitt et al. (1997)
		114 ± 26	17P/Holmes	Bockelée-Morvan et al. (2008)
$^{14}N/^{15}N$	[HCN]	205 ± 70	C/1995 O1	Bockelée-Morvan et al. (2008)
		139 ± 26	17P/Holmes	Bockelée-Morvan et al. (2008)
	[CN]	141 ± 29	21 comets	Manfroid et al. (2009)
		220 ± 40	73P (fragment C)	Manfroid et al. (2009)
		165 ± 40	17P/Holmes	Bockelée-Morvan et al. (2008)
		155 ± 25	103P/Hartley 2	Jehin et al. (2011)
	[NH_2]	90–190	12 comets	Rousselot et al. (2014)
		139 ± 38	C/2012 S1	Shinnaka et al. (2014b)
		140 ± 30	C/2012 F6	Decock et al. (2014)
$^{16}O/^{18}O$	[H_2O]	518 ± 45	1P/Halley	Balsiger et al. (1995)
		470 ± 40	1P/Halley	Eberhardt et al. (1995)
		530 ± 60	4 comets	Biver et al. (2007)
		425 ± 55	C/2002 T7	Hutsemékers et al. (2008)
		300 ± 150	C/2012 F6	Decock et al. (2014)
		523 ± 32	C/2009 P1	Bockelée-Morvan et al. (2012)
$^{32}S/^{34}S$	[CS]	27 ± 3	C/1995 O1	Jewitt et al. (1997)
	[CS]	16 ± 3	17P/Holmes	Biver et al. (2008)
	[S^+]	23 ± 6	1P/Halley	Altwegg (1996)
	[H_2S]	16 ± 3	C/1995 O1	Crovisier et al. (2004)

Ziurys et al. 1999), were consistent with the telluric value (272, Anders and Grevesse 1989) while the ratio derived from optical high resolution spectroscopy of CN (140 ± 35, Arpigny et al. 2003) was widely discordant. Subsequent observations of a dozen comets of various origins lead to $^{14}N/^{15}N = 147.8 \pm 5.7$ from CN (Jehin et al. 2009). The discrepancy between CN and HCN, a presumed parent, was eventually solved with the quasi simultaneous sub-millimeter and optical observations of HCN and CN in comet 17P/Holmes performed a couple of days after its huge and bright outburst in October 2007 (Bockelée-Morvan et al. 2008). The nitrogen isotopic ratios derived from the two techniques are found in agreement with each other and with the values found in other comets. The reanalysis of the Hale-Bopp sub-millimeter data (Bockelée-Morvan et al. 2008) also gave much lower values for the nitrogen ratio and established that HCN has most probably the same non-terrestrial nitrogen isotopic composition as CN. No other measurements in HCN have been made due to the difficulty of detection of the faint $HC^{15}N$ lines in the radio range but the CN bright violet band (0, 0) at 3880 Å was observed in about 20 comets since Hale-Bopp with high resolution optical spectrometers like the Ultraviolet and Visual Echelle Spectrograph (UVES) mounted at the ESO Very Large Telescope (VLT), the High Resolution Echelle Spectrometer

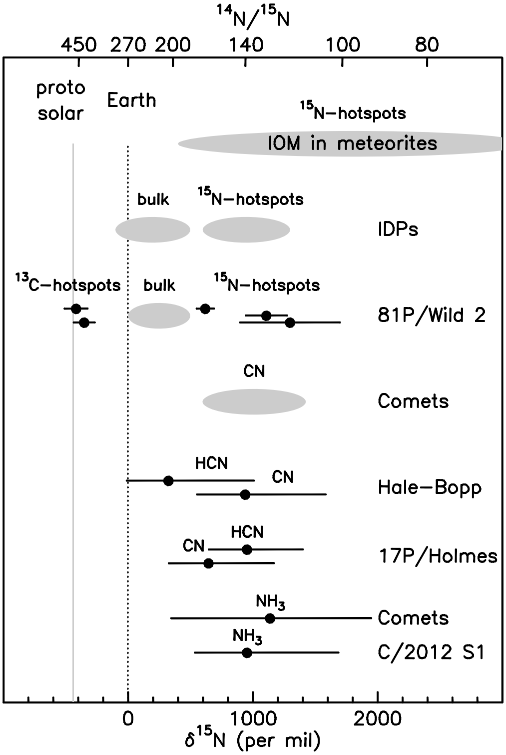

Fig. 2 N isotope measurements in primitive matter of the Solar System, given either as $^{14}N/^{15}N$ ratios or $\delta^{15}N$ values ($\delta^{15}N = (^{14}N/^{15}N)/(^{14}N/^{15}N)_{Earth} - 1$). Shown are the protosolar value measured by the Genesis mission (Marty et al. 2011), values in HCN and CN 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), in NH_3 from NH_2 observations (Rousselot et al. 2014; Shinnaka et al. 2014b), in dust particles of comet 81P/Wild 2 collected by the Stardust mission (McKeegan et al. 2006), in interplanetary dust particles IDPs (Floss et al. 2006), and in the 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 (2011)

(HIRES) at Keck, the High Dispersion Spectrograph (HDS) at Subaru and the 2D Coudé at the Harlan telescope at the McDonald Observatory (Table 2). They provided measurements of $^{14}N/^{15}N$ for comets of various origins (new Oort-cloud comets, Halley type comets, and Jupiter family comets), for comets at various heliocentric distances (from 0.6 AU to 3.7 AU), at different distances from the nucleus, during comet outbursts or splitting events (Jehin et al. 2004; Manfroid et al. 2005; Hutsemékers et al. 2005; Jehin et al. 2006, 2008, 2009; Manfroid et al. 2009; Jehin et al. 2011; Decock et al. 2014). All the measurements are providing the same value for the nitrogen ratio within the errors but one comet, the carbon poor and split comet 73P/Schwassmann-Wachmann 3 (Jehin et al. 2008; Shinnaka et al. 2011). Whilst the value for the $^{12}C/^{13}C$ ratio (see Sect. 2.3.1), derived from C_2, CN and HCN, is in very good agreement with the solar and terrestrial value of 89, the nitrogen isotopic ratio, derived from CN and HCN, is very different from the telluric value of 272. The large ^{15}N excess in cometary volatiles relative to the Earth atmospheric value indicates that N-bearing volatiles in the solar nebula underwent important nitrogen isotopic fractionation at some stage of the Solar System formation or earlier in the proto-solar cloud (Rodgers and Charnley 2008).

2.2.2 NH_3

Ammonia molecules represent typically a little bit less than about 1 % (relative to water) of the molecules observed in cometary coma (e.g. Biver et al. 2012), only about ten molecules have a similar or higher abundance. Photolysis of ammonia by solar UV radiation in the coma produces the NH_2 radical with 95 % efficiency (Huebner et al. 1992). This radical has a long lifetime against photodissociation and has many emission lines in the optical wavelength range.

Direct measurement of the $^{14}N/^{15}N$ isotopic ratio in ammonia, through inversion (in radio), rotational (submillimetre), or vibrational (near-infrared) transitions, are usually difficult due to a lack of sensitivity for the $^{15}NH_3$ detection at the available facilities. Indirect measurement of the $^{14}N/^{15}N$ isotopic ratio in ammonia, however, can be done by using NH_2 emission lines in the optical range because these lines have a strong intensity and are easy to observe in this spectral range. The main problem for doing such a measurement has been, for a long time, the lack of accurate wavelengths measurements. Up to recently only one paper had been published mentioning isotope shifts between $^{14}NH_2$ and $^{15}NH_2$ (Dressler and Ramsay 1959) but this shift was presented in a general plot that was by far not accurate enough for searching for the faint $^{15}NH_2$ emission lines.

To efficiently search for these lines it was necessary to perform new laboratory experiments. Such experiments have been conducted in the Advanced Infrared Line Exploited for Spectroscopy (AILES) of synchrotron SOLEIL (Source Optimisé de Lumière d'Energie Intermédiaire du LURE) and permitted us to establish a list of wavelengths for $^{15}NH_2$ emission lines accurate to about 0.01 Å for the $((0,10,0)–(0,0,0))$ and $((0,9,0)–(0,0,0))$ bands of the $\tilde{A}^2A_1 - \tilde{X}^2B_1$ system. These wavelengths led to the first clear detection of $^{15}NH_2$ in comets by Rousselot et al. (2014) made by combining spectra of 12 comets taken by the UVES spectrograph at the 8-m ESO Very Large Telescope ($\lambda/\Delta\lambda \simeq 80000$) located in Chile. The inferred $^{14}N/^{15}N$ ratio is 127 in ammonia (in the range 90–190 taking into account uncertainties).

This work assumed two reasonable assumptions: (i) a similar photodissociation efficiency for $^{14}NH_3$ and $^{15}NH_3$ to produce, respectively, $^{14}NH_2$ and $^{15}NH_2$ radicals, (ii) similar transition probabilities for both $^{14}NH_2$ and $^{15}NH_2$. For the second point the average of many spectra obtained at different heliocentric velocities, i.e. with different Doppler shifts with respect to the solar absorption lines, avoided the issue (in the absence of a complete fluorescence modelling) of being affected by the Swing effects and helped to provide a more robust measurement.

Immediately after the first report another measurement was published, based on a high-resolution ($\lambda/\Delta\lambda = 72000$) spectrum obtained on comet C/2012 S1 (ISON) with the 8-m SUBARU telescope and the High Dispersion Spectrograph (Shinnaka et al. 2014b). The measured value of $^{14}N/^{15}N = 139 \pm 38$ is consistent with the previous measurement, and confirms that ammonia in comets is highly fractionated in ^{15}N, comparably to CN and HCN.

2.3 Carbon, Oxygen, and Sulfur

2.3.1 Carbon

There are two stable carbon isotopes: ^{12}C and ^{13}C. The ratio $^{12}C/^{13}C$ has been measured in different solar system objects. The terrestrial value is 89 and is similar to the one detected in other solar system objects, such as the Sun, Venus, the Moon, Mars, Jupiter, Saturn, Titan, Neptune, meteorites or the IDPs (Woods and Willacy 2009). This ratio is larger than the value of ∼68 measured in the local interstellar medium, that may result from a ^{13}C enrichment since the formation of the Solar System (Milam et al. 2005).

For comets, historically the first ^{12}C/^{13}C ratio determinations were obtained from the ^{12}C^{13}C emission spectrum in the optical range for four bright comets: Ikeya 1963 I (Stawikowski and Greenstein 1964), Tago-Sato-Kosaka 1969 IX (Owen 1973), Kohoutek 1973 XII (Danks et al. 1974), and Kobayashi-Berger-Milon 1975 IX (unpublished data from Lambert and Danks mentioned by Lambert and Danks 1983; Vanysek 1977; Wyckoff et al. 2000). The emission lines used for theses measurements, that belong to the $(1,0)$ Swan bands, are strongly blended with NH_2 emission lines. For this reason the CN B-X $(0,0)$ band was later favored for measuring the ^{12}C/^{13}C ratio. It has been used for the first time for comet 1P/Halley (Wyckoff and Wehinger 1988; Wyckoff et al. 1989; Kleine et al. 1995). Since then the CN B-X (0,0) band has been used with success for measuring the ^{12}C/^{13}C ratio in many comets of different origins, with an average ratio of 91.0 ± 3.6 (Manfroid et al. 2009). Recently emission lines of the (2, 1) and $(1,0)$ bandheads of ^{12}C^{13}C have been used to measure the ^{12}C/^{13}C ratio in comets C/2002 T7 (LINEAR) and C/2001 Q4 (NEAT) (Rousselot et al. 2012).

Some other determinations of the ^{12}C/^{13}C ratio have been performed with radio spectroscopy of H^{13}CN. These measurements have been performed for comets C/1995 O1 (Hale-Bopp) (Jewitt et al. 1997; Ziurys et al. 1999; Bockelée-Morvan et al. 2008) and 17P/Holmes (Bockelée-Morvan et al. 2008). All determinations are consistent with the terrestrial value. Measurements made in the dust samples collected by the Stardust spacecraft are presented in Sect. 3.

2.3.2 *Oxygen*

The first value of the oxygen isotopic ratio in a comet was obtained by the in-situ measurements aboard the Giotto spacecraft and gave $^{16}\mathrm{O}/^{18}\mathrm{O} = 495 \pm 37$ for H_3O^+ in comet 1P/Halley (Eberhardt et al. 1995; Balsiger et al. 1995). Seventeen years after the Giotto flyby, a deep integration spectrum of the bright comet 153P/2002 C1 (Ikeya-Zhang) with the sub-millimeter satellite Odin led to the detection of the $H_2^{18}O$ line at 548 GHz (Lecacheux et al. 2003). Subsequent observations resulted in the determination of $^{16}\mathrm{O}/^{18}\mathrm{O} = 530 \pm 60$, 530 ± 60, 550 ± 75 and 508 ± 33 in the Oort cloud comets Ikeya-Zhang, C/2001 Q4, C/2002 T7 and C/2004 Q2 respectively (Biver et al. 2007). Within the error bars, all these measurements are consistent with Halley and the terrestrial value ($^{16}\mathrm{O}/^{18}\mathrm{O}_{\mathrm{VSMOW}} = 499$), although marginally higher.

A few ^{18}OH lines belonging to the ultraviolet OH system at 310 nm were detected in the spectra of the bright comets C/2002 T7 (LINEAR) and C/2012 F6 (Lemmon) with UVES at the ESO VLT and allowed for the first time the determination of the ^{16}O/^{18}O ratio from ground-based observations. From the ^{16}OH/^{18}OH ratio, $^{16}\mathrm{O}/^{18}\mathrm{O} = 425 \pm 55$ and 350 ± 150 were derived respectively (Hutsemékers et al. 2008; Decock et al. 2014). These values are equal, within the uncertainties, to the terrestrial value and to the ratio measured in other comets, although marginally smaller. An enrichment of ^{18}O in comets has been predicted by some models of the pre-solar nebula by CO self-shielding to explain the so-called"oxygen anomaly" i.e. the fact that oxygen isotope variations in meteorites cannot be explained in any easy way (Yurimoto and Kuramoto 2004). Recently H_2O, and $H_2^{18}O$ 1_{10}–1_{01} lines were observed with high signal-to-noise ratio in the Oort Cloud comet C/2009 P1 (Garradd) using the HIFI instrument onboard the IR Herschel space telescope (Bockelée-Morvan et al. 2012). The measured oxygen ratio of 523 ± 32 is consistent with the terrestrial value.

2.3.3 Sulfur

A few measurements have been acquired for the $^{32}S/^{34}S$ ratio in cometary gases. The first investigation was made in comet 1P/Halley through in situ mass spectrometry (S^+ ion, Altwegg 1996). Using millimetre spectroscopy, determinations were made for CS (Jewitt et al. 1997; Biver et al. 2008), a photo-dissociation product of CS_2, and for H_2S (Crovisier et al. 2004). Inferred values are given in Table 2. They are consistent within 2σ with the terrestrial value of 23.

3 Measurements in Cometary Dust and Analogs

Samples from comets have been identified on Earth. Dust particles directly sampled from comet 81P/Wild 2 have been collected by the Stardust mission and returned to laboratories in 2006. For others, a cometary origin is inferred from different lines of evidence. Such samples provide unique information since extremely precise elemental, mineralogical and isotopic analyses at different scales down to the nanometer permit direct comparison with asteroidal material delivered by meteorites. However, they do not allow access to the composition of ices, because these phases, if any, were lost during processing on parent bodies, during atmospheric entry, or during sampling in the case of Stardust grains.

At least three types of samples with certain to probable cometary origin are available in laboratories:

- The NASA Discovery Stardust mission collected micro-grains of cometary material in the tail of comet 81P/Wild 2 and returned this cometary matter to Earth for laboratory analysis (Brownlee et al. 2006; Brownlee 2014);
- Interplanetary dust particles (IDPs) are small grains collected in the Earth stratosphere by NASA, that have sizes typically below 50 µm (Sect. 3.2). Among these particles, a subset, the chondritic-porous anhydrous IDPs, are thought to have a cometary origin.
- Ultracarbonaceous Antartic Micrometeorites (UCAMMs) recovered in Antarctic snow show compositions and stable isotope signatures also consistent with derivation from a cometary reservoir (Sect. 3.3).

Besides these materials for which a cometary origin is beyond doubt or reasonably well constrained, other cosmochemical materials on Earth have been proposed to be cometary in origin, such as some of the volatile-rich carbonaceous chondrites, as first suggested by Anders (1975), and others (e.g. McSween and Weissman 1989; Campins and Swindle 1998; Gounelle et al. 2006; Weisberg and Connolly 2008; Haack et al. 2011). Recently, a piece of carbon-rich material found in Egypt and nicknamed Hypatia has been interpreted as originating from a comet that exploded over Africa 35 Myr ago and made the Lybian glass strewnfield (Kramers et al. 2013).

3.1 Stardust

In 2004, NASA Discovery's Stardust mission succeeded in collecting grains from a Jupiter-family comet (JFC) named 81P/Wild 2, and in returning them to Earth two years later for laboratory analyses (Brownlee et al. 2006; Brownlee 2014). JFCs, a sub-population of the Kuiper belt object (KBO) family, are thought to represent primitive material consisting of silicates, organics and ice that was assembled in the outer solar system and stored beyond the orbit of Neptune since 4.5 Gyr. Before 1974, comet 81P/Wild 2 was on a 43-year orbit that ranged from Jupiter to beyond Uranus. Since then it is on a 6-year orbit crossing the Earth's region. Comet Wild 2 is a particularly active comet with up to 24 jets identified and a water loss estimated at 20000 tons per day. The spacecraft flew within 236 km of the comet's 4.5 km diameter nucleus. Cometary grains were collected during a flyby encounter by passive implantation into aerogel, a low-density silica foam, and by impacting onto the aluminum frame (Brownlee et al. 2003, 2004). On January 15th, 2006, the Stardust sample container returned safely to Earth, delivering the first cometary samples for laboratory analysis (Brownlee et al. 2006; Brownlee 2014). Due to the high differential velocity of 6.1 km/s between the spacecraft and the comet, cometary grains suffered mass loss and fragmentation during the collection process, to various extents that depended on the nature and density of the grains. While the finest material was mostly severely heated and mixed with the collecting silica aerogel during capture, some of the coarsest grains did not heat up to the melting point, and detailed mineralogical and geochemical analyses down to the nanometer scale revealed the nature of this cometary matter.

Contrary to some expectations, grains collected by Stardust are not dominated by interstellar grains coated with radiation-processed organics. Most of the analyzed materials are isotopically close to chondritic material, and were likely formed by the same set of high temperature processes that led to the formation of constituents of primitive meteorites. As for chondrites, Wild 2 grains contain chondrules, calcium-aluminum rich inclusions, Mg-rich olivines and pyroxenes. In comet Wild 2, such a high temperature material has been assembled with ice, demonstrating that large scale lateral mixing took place in the forming solar system.

There are nevertheless significant differences between comet Wild 2 and volatile-rich meteorites, e.g. carbonaceous chondrites. Organics in Wild 2 material are scarce, and there is little evidence for the occurrence of hydrated material, contrary to hydrous carbonaceous chondrites for which parent body aqueous alteration resulted in the formation of clay minerals and carbonates. It is not clear whether these differences are due to the high speed collection of grains or not. Wild 2 material appears to contain a mix of material more diverse than that found in chondrites, which may also point to a different processing history of cometary bodies compared to asteroids. Below is a summary of the isotopic compositions measured in Stardust material (McKeegan et al. 2006, and references therein).

- Bulk material presents moderate excesses of D with D/H ratios up to a factor of three higher than terrestrial (VSMOW). No hydrated minerals have been identified in Stardust samples, so it is likely that the measured D/H values are related to the carbonaceous phases, and are not representative of the D/H ratio of water in comet 81P/Wild 2. Variations in δD ($\delta\mathrm{D} = [(\mathrm{D/H})/(\mathrm{D/H})_{\mathrm{VSMOW}} - 1] \times 1000$) within a particle are also observed with some "hotspots" having a δD up to 2200 ± 900 permil. Because of the association with carbon and the lack of evidence for any hydrated minerals in Wild 2 grains, it is unlikely that the D/H values are related to cometary water.
- Overall, the $^{13}\mathrm{C}/^{12}\mathrm{C}$ ratio (δ^{13}C from -20 to -50 permil relative to terrestrial standard) shows moderate variations.
- Likewise, most $^{15}\mathrm{N}/^{14}\mathrm{N}$ ratios cluster around the terrestrial value and are also consistent with values found in most meteorites (Stadermann et al. 2008). A few δ^{15}N values range from $+100$ to $+500$ permil. So far, excesses of ^{15}N typical of cometary values (around $+800$ to $+1000$ per mil, Sect. 2.2) are not observed in bulk analysis. On a smaller scale, ^{15}N-rich hotspots with a maximum of $\delta^{15}\mathrm{N} = 1300 \pm 400$ permil are observed, similar to the highest values found in refractory organic matter in interplanetary dust particles (IDPs, see Sect. 3.2) and in various types of carbonaceous chondrites (CR, CH-CB and

CM, Busemann et al. 2006; Briani et al. 2009). Several presolar grains have been identified showing much larger C and N isotope variations (from +60 to +964 permil for δ^{13}C, and from -518 to -350 permil for δ^{15}N), although these components appear to contribute little to the isotope variability due to their apparent scarcity (Floss et al. 2013). In summary, the Wild 2 grains display both low and high ^{15}N, indicating an unequilibrated mixture of a ^{15}N-poor material (perhaps protosolar N trapped in ice) component with a more refractory (high C/N) organic material and high δ^{15}N (McKeegan et al. 2006).

- The three oxygen isotopic compositions of silicate and oxide mineral grains from comet 81P/Wild 2 were measured using ion micro- and nanoprobe techniques. The average composition of olivine and pyroxene minerals, as well as of chondrule fragments, is consistent with average chondritic material (e.g. supplementary information in McKeegan et al. 2006; Nakamura et al. 2008; Bridges et al. 2012; Nakashima et al. 2012). In contrast, the O-isotope ratio of the refractory phase "Inti" exhibits a δ^{16}O enrichment plotting along the CCAM line with $\delta^{17}\mathrm{O} = -62 \pm 20$ permil and $\delta^{18}\mathrm{O} = -42 \pm 10$ permil (McKeegan et al. 2006, suppl. info). A detailed study of "Inti" subsequently performed by Simon et al. (2008) confirmed that Inti is indeed ^{16}O-rich, with $\delta^{18}\mathrm{O} \sim \delta^{17}\mathrm{O} \sim -40$ permil. The occurrence of silicates plotting close to the Terrestrial Fractionation (TF) line together with the ^{16}O-rich material (Ca-Al-rich inclusions) is in agreement with that observed in carbonaceous chondrites (McKeegan et al. 2006, suppl. info). These observations confirm that Wild 2 material contains oxides that were synthesized in the most inner regions of the solar system. Several presolar grains were identified in Stardust samples (at least 6). However, a large fraction of these tiny phases may have been destroyed during impact in the aerogel so that their initial abundance in Comet 81P/Wild 2 may have been higher than inferred from direct counting (Floss et al. 2013).
- Another interesting observation on Wild 2 material is the occurrence of CAIs as mentioned above. In the refractory minerals that were analyzed for Mg isotopes, no trace of the extinct ^{26}Al radioactivity ($T_{1/2} = 0.7$ Myr) could be found (Matzel et al. 2010; Ogliore et al. 2012; Nakashima et al. 2015), in contrast to the case of most of CAIs of primitive meteorites. The latter incorporated live ^{26}Al with an initial, "canonical" $^{26}\mathrm{Al}/^{27}\mathrm{Al}$ of 5×10^{-5}, indicating early and fast ($T < 1$ Myr) formation of these high temperature condensates. The lack of ^{26}Al in Wild 2 material could indicate that these CAIs formed before the injection of ^{26}Al in the solar nebula, or that they formed later than a few Myr when all the ^{26}Al was already transformed to ^{26}Mg. As these CAIs are not as refractory as those usually carrying ^{26}Al excesses in meteorites, the hypothesis of a late formation is favored. Late exchange of Mg isotopes through metamorphism or chemical alteration cannot either be excluded.
- Up to the Stardust sample return, noble gases had not been unambiguously identified in comets. This is unfortunate because these elements are chemically inert and have the potential to trace the physical conditions of comet formation such as the nature of ice, the formation, temperature, the composition of the ambient gas etc. Cometary light noble gases (He, Ne) have been found in Stardust aerogel (Marty et al. 2008). Gases are not located in the terminal grains implanted deeply in the foam (which were presumably dried up during the entry process). They appear to reside into the walls of the cavities formed when high velocity grains exploded during aerogel entry. The $^{3}\mathrm{He}/^{4}\mathrm{He}$ ratio (2.5×10^{-4}) is intermediate between that of the solar wind (post-D burning helium) and the protosolar nebula ratio, raising the possibility that cometary matter recorded the activity of the protoSun. By contrast, the neon isotopic composition is closer to that of Ne trapped in chondrites than to the solar composition, supporting the hypothesis of an asteroid-comet continuum and suggesting that this Ne component was trapped in dust and not in ice. Both

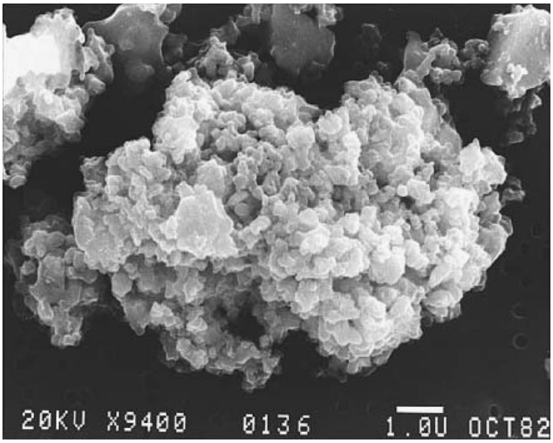

Fig. 3 Secondary electron micrograph of a chondritic porous (CP) anhydrous IDP. From Bradley (2005)

He and Ne from Stardust samples were released at high temperature indicating that their host is refractory (dust and/or organics) (Marty et al. 2008).

In summary, the collection of cometary grains from comet 81P/Wild 2 by the Stardust spacecraft and their analysis in the laboratory has demonstrated that a large fraction of dust trapped in this body is derived from precursors that share mineralogical and isotopic similarities with carbonaceous chondrites, that were thermally and chemically processed in the inner solar system, consistent with models advocating large scale radial mixing in the nascent solar system.

3.2 Interplanetary Dust Particles

Since 1981, NASA has been collecting interplanetary dust particles (IDPs) in the stratosphere, between 17–19 km altitude (Brownlee 1985). Due to their low densities, the fluffiest particles preferentially accumulate at such altitudes. Typical IDP sizes range from 1 to ~50 µm, most particles being in the ~2–15 µm size range. One class of IDPs, the chondritic porous anhydrous particles (CP-IDPs, Fig. 3) are thought to originate from comets. Such chondritic porous dust particles have also been identified from Antartic snow and ice collections (Noguchi et al. 2015).

CP-IDPs mainly consist of anhydrous crystalline phases (Mg-rich olivines, pyroxenes and low-Ni Fe sulfides Bradley 2005), as well as primitive glassy components called Glass Embedded with Metals and Sulfides (GEMS) that have a debated (solar vs. presolar) origin (Bradley 2013; Keller and Messenger 2013, and references therein). Early studies on the origin of IDPs used the helium and neon release temperature in IDPs to assess the temperature reached during atmospheric entry. This entry velocity may then be related to the asteroid vs. cometary origin (Nier and Schlutter 1993). This type of analyses first suggested a cometary origin for the CP-IDPs (Brownlee et al. 1995). They are usually rich in carbonaceous matter (from ~5 to ~45 wt%, (Keller et al. 1994), and their mineralogy is compatible with that of comets 1P/Halley and C/1995 O1 (Hale-Bopp) (e.g., Hanner and Zolensky 2010; Brunetto et al. 2011, and references therein). Some larger CP-IDPs are fragmented into several patches during impact in the collector, leading to the appellation of "cluster IDPs". It has been proposed that a large proportion (if not all) of CP- or cluster IDPs are of cometary origin (e.g., Bradley and Brownlee 1986; Ishii et al. 2008, and references therein). In addition, IDPs collected in April 2003 during a period predicted to show an increase in dust flux from comet 26P/Grigg-Skjellerup may originate from this Jupiter-family comet (Busemann et al. 2009).

The D/H ratios in CP- and cluster IDPs exhibit elevated values associated with the organic matter, typically ranging from $D/H \sim 10^{-4}$ to $\sim 8 \times 10^{-3}$, i.e. up to ∼ 50 times the terrestrial value in the case of one cluster IDP (Messenger 2000 and references therein). The D/H values of two IDPs possibly originating from the 26P/Grigg-Skjellerup collection (GSC-IDPs) also show high D/H values with ratios ranging from 5.4×10^{-4} to 1.5×10^{-3}.

In cluster IDPs, the nitrogen isotopes show substantial variations, with an average $^{14}N/^{15}N$ ratio around 236. The IDP organic matter exhibits ^{15}N-rich and ^{15}N-poor areas with $\delta^{15}N$ up to 1300 permil and $\delta^{15}N$ as low as -93 ± 4 permil (Messenger 2000; Floss et al. 2006). The two GSC-IDPs have bulk $^{14}N/^{15}N$ values varying from 238 ± 4 ($\delta^{15}N = 145 \pm 15$ permil) to 183 ± 6 ($\delta^{15}N = 485 \pm 35$ permil), with ^{15}N-rich hotspots showing $^{14}N/^{15}N$ values as low as 118 ± 18 ($\delta^{15}N = 1310 \pm 150$ permil) (Busemann et al. 2009).

The bulk carbon isotopes in normal and cluster IDPs are within the terrestrial range. In the GSC-IDPs, there are sub-regions showing carbon isotopic anomalies (^{12}C-rich, $\delta^{13}C = -280$ permil), suggesting the presence of primitive organic matter, or presolar grains (Busemann et al. 2009).

The bulk oxygen isotopic compositions of CP-IDPs are usually within the range of values observed for carbonaceous chondrites, although heavy oxygen isotopic compositions, with $\delta^{17}O$, $\delta^{18}O$ up to +80 to +200 permil, have been identified in one IDP (e.g., Starkey et al. 2014, and references therein). In the CP- and GSC-IDPs there are numerous localized isotopic anomalies suggesting an abundant content in presolar silicates, some of them possibly being GEMS (Messenger et al. 2003, 2005; Busemann et al. 2009; Keller and Messenger 2013, and references therein). The O isotopes are distinct in various solar system materials, and therefore provide a unique tool to trace genetic relationship between solar system reservoirs. The O isotopic composition of carbonaceous chondrites is related to that of chondritic porous IDPs, Stardust grains and UCAMMs (Sect. 3.3), and suggests a genetic continuum between carbonaceous chondrites and comets (Aléon 2010; Nakashima et al. 2012; Davidson et al. 2012; Starkey and Franchi 2013, and references therein).

3.3 Ultracarbonaceous Antarctic Micrometeorites

Micrometeorites dominated by organic matter were identified in the CONCORDIA collection (Duprat et al. 2010; Dobrică et al. 2011, 2012) and in a collection performed at Dome Fuji (Nakamura et al. 2005) (UCAMMs, for Ultracarbonaceous Antarctic Micrometeorites, Fig. 4). These particles contain more than 50 % of organic matter in volume, i.e. a carbon content up to ten times that of the most C-rich carbonaceous chondrites (e.g., Alexander et al. 2012). Such concentrations of carbonaceous matter are comparable with that of the most C-rich IDPs (Thomas et al. 1993; Keller et al. 2004), and compatible with CHON grains detected in comet Halley by the Giotto and VEGA space missions in 1986 (Kissel and Krueger 1987; Lawler and Brownlee 1992).

The hydrogen isotopic composition of UCAMMs exhibit extreme D enrichments over large areas ($> 100\ \mu m^2$), with D/H ratios up to 10–30 times the VSMOW value (Duprat et al. 2010; Dartois et al. 2013; Slodzian et al. 2013; Bardin et al. 2014). This isotopic composition is a signature of a primitive organic matter from cold and dense regions of the protosolar cloud or protoplanetary disk. Remarkably, the extreme D excesses observed in UCAMMs are not limited to hotspots of 1–2 µm in size like usually observed in IDPs or meteoritic insoluble organic matter (e.g., Remusat et al. 2010, and references therein). The

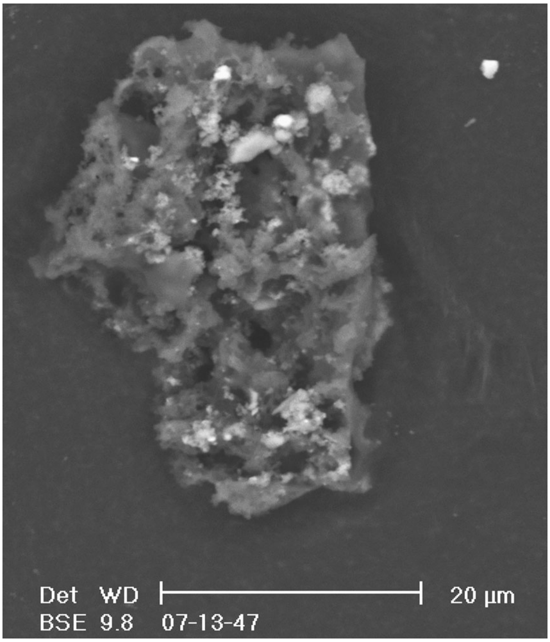

Fig. 4 Backscattered electron micrograph of a fragment of CONCORDIA Ultracarbonaceous Antarctic Micrometeorite (UCAMM). All *dark grey patches* are constituted of organic matter. *Light grey flakes* are silicates, and *bright spots* are Fe-Ni sulfides. From Duprat et al. (2010)

association in UCAMMs of primitive organic matter with mineral phases (including crystalline minerals) that show evidence of nebular processing (Dobrică et al. 2012), suggest that deuteration of the organic matter may have taken place in the outer regions of the protoplanetary disk rather than in the presolar molecular cloud core (Duprat et al. 2010). The organic matter itself is rich in N with concentrations of N/C ratios up to 0.15. The formation of such an N-rich organic matter can result from long term irradiation by non-attenuated galactic cosmic rays of N_2–CH_4 rich ices present at the surface of icy bodies in the external regions of the solar system (Dartois et al. 2013).

The nitrogen isotopic composition of UCAMMs is under investigation. It reveals a heterogeneous distribution of the $^{15}N/^{14}N$ ratios showing both ^{15}N-rich and ^{15}N-poor regions (Duprat et al. 2014).

The oxygen isotopic composition of UCAMMs is also currently under investigation. The bulk oxygen isotopic composition of two UCAMMs plots slightly above the terrestrial fractionation line with $\delta^{18}O \sim -5$ permil and $\delta^{17}O \sim 10$ permil (Kakazu et al. 2014).

3.4 Other Potential Cometary Samples on Earth

Some of the carbonaceous chondrites, especially those of the CI type (e.g., Orgueil), as well as CM or CR chondrites, may represent fragments of nuclei from extinct comets (Gounelle et al. 2006; Weisberg and Connolly 2008; Haack et al. 2011). Arguments for such an origin are: (i) ellipsoidal trajectories and high entry (18 km/s) velocities inferred from ground-based investigations, that point to a JFC origin; (ii) abundant organics (up to 5 % C) and hydrated minerals (equiv. 10–20 % water), leading to an estimated water/rock ratio of about 1, comparable to those of comets (e.g., comet 9P/Tempel 1); (iii) the similarity of oxygen isotope trends of Stardust oxides with those of carbonaceous chondrites (Sect. 3.1); (iv) elevated D/H or $^{15}N/^{14}N$ ratios; v) abundance of glassy phases. Their bulk D/H or N isotopic compositions are however not as elevated as those observed in comet water and CN, HCN and NH_3,respectively. If these meteorites represent cometary nuclei, this difference may be due to loss of ice-bearing D and ^{15}N for CCs. Elevated D/H ratios in hydrated phases in Semarkona (unequilibrated LL3 chondrite) were however recently measured (up to 1.8×10^{-3}). These phases could result for the local alteration of silicates using D-rich water (ice grain?) that could be the source of part of the water emitted by Oort cloud comets (Piani et al. 2015).

Recently, Kramers et al. (2013) claimed that a peculiar cm-sized stone found in Egypt and nicknamed Hypatia could be a comet fragment that would have exploded in the atmosphere over Northern Africa 26 Myr ago, resulting in a glass strewnfield in the Lybian desert. Altogether, the absence of an impact crater large enough to account for the extent of the Lybian tektite field, physical considerations raised long ago (Urey 1957), and the peculiar composition of Hypatia (Kramers et al. 2013) are in agreement with such an origin. The Hypatia stone has a $^{40}Ar/^{36}Ar$ ratio lower than that of air, demonstrating an extraterrestrial origin. It is rich in carbon in the cubic form and hosts abundant nano- to microdiamonds. Hypatia's C isotope composition also clearly indicate an extraterrestrial origin and noble gas isotope signatures suggest the occurrence of unequilibrated material containing dust from AGB stars winds. Further elemental and isotopic measurements are underway to explore this exciting possibility.

4 Discussion

One viewpoint for the origin of cometary materials is that they are pristine remnants of the interstellar material that collapsed to form the solar nebula Greenberg (1982). Alternatively, cometary molecules may have formed in the cold outer regions of the solar nebula regions. The analogy between cometary and interstellar ice-composition indeed suggests that those materials formed by similar processes, i.e., ion-molecule and grain-surface reactions at low temperatures (Bockelée-Morvan et al. 2000). However, the presence of crystalline silicates and other high temperature condensates in comets indicates that comets incorporated also materials formed in the hot innermost regions of the disk (Brownlee et al. 2006; Bockelée-Morvan et al. 2002; Wooden 2008), or which underwent processing through, e.g., nebular shocks (Harker and Desch 2002), or in the surface layers during protosolar luminosity outbursts (Ábrahám et al. 2009). In the latter two cases, where a purely nebular origin may be indicated, mixing of material radially outwards or vertically downwards to the midplane, would also lead to cometary ices having a composition derived from a chemistry radically different from that of the interstellar medium.

Isotopic ratios in comets can provide constraints to the different scenarios. The ISM-comet connection can be tested by comparing isotopic ratios in both kinds of material. Tables 4 and 5 provide respectively hydrogen and nitrogen isotopic ratios measured in molecular clouds, dark cores and protostars.

4.1 Interstellar Isotopic Fractionation

Cosmic rays drive an ion-molecule chemistry in dense interstellar clouds. At the cold temperatures of these environments ($\sim$ 10 K) the zero-point energy difference between isotopically-substituted molecules can become important in exothermic ion-molecule reactions. For example, although D isotope-exchange reactions of the form

$$XH^+ + HD \rightleftharpoons XD^+ + H_2 + \Delta E \qquad (1)$$

Table 3 Ion-molecule isotopic exchange reactions

No.	Reaction	$\Delta E/k$ (K)	Reference
R1	$H_3^+ + HD \rightleftharpoons H_2D^+ + H_2$	143.0	Giles et al. 1992
R2	$H_2D^+ + HD \rightleftharpoons HD_2^+ + H_2$	187.0	Giles et al. 1992
R3	$HD_2^+ + HD \rightleftharpoons D_3^+ + H_2$	234.0	Giles et al. 1992
R4	$CH_3^+ + HD \rightleftharpoons CH_2D^+ + H_2$	370.0	Millar et al. 1989
R5	$C_2H_2^+ + HD \rightleftharpoons C_2HD^+ + H_2$	550.0	Millar et al. 1989
R6	$^{13}C^+ + {}^{12}CO \rightleftharpoons {}^{12}C^+ + {}^{13}CO$	35.0	Watson et al. 1976
R7a	$^{14}N_2H^+ + {}^{14}N^{15}N \rightleftharpoons {}^{14}N^{15}NH^+ + {}^{14}N_2$	10.7	Adams and Smith 1981
R7b	$^{14}N_2H^+ + {}^{14}N^{15}N \rightleftharpoons {}^{15}N^{14}NH^+ + {}^{14}N_2$	2.3	Adams and Smith 1981
R8	$^{15}N^+ + {}^{14}N_2 \rightleftharpoons {}^{14}N^+ + {}^{14}N^{15}N$	28.3	Terzieva and Herbst 2000
R9	$^{15}N^+ + {}^{14}NO \rightleftharpoons {}^{14}N^+ + {}^{15}NO$	24.3	Terzieva and Herbst 2000
R10a	$^{15}N + {}^{14}N_2H^+ \rightleftharpoons {}^{14}N + {}^{14}N^{15}NH^+$	36.1	Terzieva and Herbst 2000
R10b	$^{15}N + {}^{14}N_2H^+ \rightleftharpoons {}^{14}N + {}^{15}N^{14}NH^+$	27.7	Terzieva and Herbst 2000
R11	$^{15}N + C^{14}NC^+ \rightleftharpoons {}^{14}N + C^{15}NC^+$	36.4	Terzieva and Herbst 2000
R12	$^{15}N + HC^{14}NH^+ \rightleftharpoons {}^{14}N + HC^{15}NH^+$	35.9	Terzieva and Herbst 2000

are exothermic in the forward direction (to the right) the higher abundance of H_2 relative to HD (H_2/HD $\sim 2 \times 10^{-5}$) means that the reverse reaction will dominate except at very low temperatures. Table 3 lists the major ion-molecule reactions leading to isotopic fractionation in low-temperature interstellar clouds. Although reaction (R1) has long been known to initiate D fractionation in molecular clouds (e.g., Millar et al. 1989), the enhanced depletion of CO onto dust and the low electron fractions found in high-density molecular cores both conspire to permit reactions (R2) and (R3) to play important roles (Roberts et al. 2003). The spin-state of the colliding H_2 molecules, whether *para* or the higher-energy *ortho* state, plays an important role in interstellar fractionation. The higher internal energy of *ortho*-H_2 can essentially quench ion-molecule deuteration when the ortho/para ratio (OPR) is high (Pagani et al. 2011). In such CO depletion cores, where protostars are about to form, gas-phase deuteration is enhanced and, as D_3^+ becomes the major ion, this leads to very high atomic D/H ratios. Atom addition reactions on dust, primarily starting from condensed CO, can lead to many organic compounds, such as formaldehyde, methanol, formic acid, acetaldehyde, isocyanic acid and formamide, molecules which are also identified in comets (e.g., Charnley and Rodgers 2008; Herbst and van Dishoeck 2009). High atomic D/H ratios in the condensing gas consequently leads to very high D/H ratios and the formation of many multiply-deuterated isotopologues for surface-formed molecules (Charnley et al. 1997); these latter species include D_2O, D_2CO, CHD_2OH, CD_3OH, NHD_2, ND_3 and D_2S (Parise et al. 2006; Ceccarelli et al. 2014). These characteristics are observed in the interstellar medium and Table 4 summarizes the range of D/H ratios found in cold dark clouds and in cores forming both low-mass and massive protostars. In the latter regions the highest D/H ratios are due to highly-fractionated ices being evaporated from warm dust grains (e.g., Charnley et al. 1997).

Reaction (R6) is the primary ion-molecule means of fractionating carbon in interstellar molecules. At low temperatures this has the effect that most ^{13}C nuclei become incorporated into ^{13}CO, leading to a relative depletion of ^{13}C in other interstellar molecules. This can have the secondary consequence that molecules formed on grains should have $^{12}C/^{13}C$ ratios similar to that of the accreted CO molecules in their carbonyl or carboxyl functional

Table 4 Interstellar deuterium fractionation ratios (%)

Molecule	Cold molecular clouds[1]	Low-mass protostars[2]	High-mass protostars[3]
HDO	–	0.04–8 0.03–18	0.03–2
NH_2D	5–13	7–10	0.7
DCN	1–7	0.4–7	0.05–2
DNC	1–13	2–6	0.06–12
CH_2DOH	10	37–65	0.06
CH_3DOD	1–3	1–5	0.05
HDCO	7–10	2–17	0.07–14
D_2CO	–	5–44	0.3
HDS	–	5–15	<2
DC_3N	2–13	–	1.5

[1] Ratios for L1544, TMC-1, L183: Howe et al. (1994), Turner (2001), Shah and Wootten (2001), Lis et al. (2008), Bizzocchi et al. (2014)

[2] Ratios from compilation of Taquet et al. (2014) for several protostars; exception is that DNC ratios are from Butner and Charnley (unpublished work). For HDO, values for the inner and outer regions of the protostellar envelope are given

[3] Ratios for various sub-components of Orion-KL (Hot Core, Compact Ridge, Extended Ridge), see for example Blake et al. (1987), Turner (1990), Minh et al. (1990), Mangum et al. (1991), Bergin et al. (2010), Esplugues et al. (2013), Neill et al. (2013). Entry for DNC is from the sample of Fontani et al. (2014)

groups, whereas other functional groups formed by addition of C atoms should be relatively depleted in ^{13}C (Charnley et al. 2004). Observations have confirmed this in the case of CO and methanol (Wirström et al. 2011). Isotope-selective photodissociation (Bally and Langer 1982) can also fractionate carbon in molecular clouds. In this case, the self-shielding of ^{12}CO molecules leads to regions where ^{13}CO is preferentially destroyed. However, most work has been focussed on understanding the concomitant fractionation resulting from isotope-selective photodissociation of $^{12}C^{18}O$ and $^{12}C^{17}O$ in the context of understanding the origin of the $^{16}O : {}^{17}O : {}^{18}O$ ratios measured in primitive meteoritic matter (Lee et al. 2008). Ion-molecule reactions involving oxygen isotopes produce negligible fractionation in interstellar clouds (Langer et al. 1984).

Significant isotopic enrichments in N-bearing interstellar molecules (relative to a putative $^{14}N/^{15}N$ elemental ratio of 440) can occur by the set of ion-molecule reactions listed in Table 3. Table 5 summarizes the $^{14}N/^{15}N$ ratios measured in molecular clouds and in the earliest phase of low-mass star formation (‘Class 0’).

Early chemical models of dense cores, in which nitrogen was assumed to be initially fully molecular, predicted that fractionation in amines is dependent on the level of CO depletion, as well as low temperatures. (Charnley and Rodgers 2002). Rodgers and Charnley (2008) showed that when N atoms are initially abundant, as one might expect since dense clouds form from diffuse gas, then reaction (R12) efficiently incorporates ^{15}N into $HC^{15}NH^+$. Electron dissociative recombination of $HC^{15}NH^+$ then produces $HC^{15}N$, $H^{15}NC$ and $C^{15}N$ and to ^{15}N enrichment in nitriles early in dense cloud evolution. These chemical models predict that nitriles should be more enriched than amines (Rodgers and Charnley 2008), as observed (Table 5). Thus, interstellar ^{15}N fractionation follows two distinct pathways, one rapid, involving N_2 and NH_3, and the other one much slower, involving atomic N, and responsible for the ^{15}N enrichment in HCN and other nitriles (Table 3). It is then possible that N_2 and

Table 5 Interstellar nitrogen isotope ratios

Source	Type	NH_3	N_2H^+	HCN	HNC	CN	Reference
L1544	dark core	>700	1000 ± 200	140–360	>27	500 ± 75	1, 2, 3, 4, 5
L1498	dark core	–	–	>75	>90	500 ± 75	4, 5
L1521E	dark core	–	–	151 ± 16	–	–	6
L1521F	dark core[§]	–	–	>51	24–31	–	4, 4
L183	dark core	$530\pm^{570}_{180}$	–	140–250	–	–	1, 3
NGC 1333-DCO$^+$	dark core	$360\pm^{260}_{110}$	–	–	–	–	1
NGC 1333-4A	Class 0 protostar	344 ± 173	–	–	–	–	7
Barnard 1	Class 0 protostar	$300\pm^{55}_{40}$	$400\pm^{100}_{65}$	$330\pm^{60}_{50}$	$225\pm^{75}_{45}$	$290\pm^{160}_{80}$	8
L1689N	Class 0 protostar	$810\pm^{600}_{250}$	–	–	–	–	4
Cha-MMS1	Class 0 protostar	–	–	–	135	–	9
IRAS 16293A	Class 0 protostar	–	–	163 ± 20	242 ± 32	–	10
R Cr A IRS7B	Class 0 protostar	–	–	287 ± 36	259 ± 34	–	10
OMC-3 MMS6	Class 0 protostar	–	–	366 ± 86	460 ± 65	–	10

References: (1) Gérin et al. (2009); (2) Bizzocchi et al. (2013); (3) Hily-Blant et al. (2013a); (4) Milam and Charnley (2012); (5) Hily-Blant et al. (2013b); (6) Ikeda et al. (2002); (7) Lis et al. (2010); (8) Daniel et al. (2013); (9) Tennekes et al. (2006); (10) Wampfler et al. (2014). For Barnard 1, the entry for the N_2H^+ ratios is that for $^{14}N^{15}NH^+$; a lower limit of 600 is obtained for the ratio derived from $^{15}N^{14}NH^+$

[§] L1521F does contain a very low luminosity object (VeLLO, Bourke et al. 2006)

NH_3 result from the separation of the nitrogen into at least two distinct reservoirs, with distinct ^{15}N enrichment, which never equilibrated. However, because of the small energy barrier for the first step of the ion-molecule reaction sequence

$$N^+ \xrightarrow{H_2} NH^+ \xrightarrow{H_2} NH_2^+ \xrightarrow{H_2} NH_3^+ \xrightarrow{H_2} NH_4^+ \xrightarrow{e^-} NH_3, NH_2 \qquad (2)$$

Ammonia formation also depends on the H_2 ortho/para spin ratio (OPR)—the higher energy ortho form can overcome the reaction barrier (Wirström et al. 2012). This can lead to reaction (R8) becoming important when the OPR is very small and to both enrichment and depletion of ^{15}N in NH_3 as the cloud core evolves.

The high $^{14}N_2/^{14}N^{15}N$ ratio measured in L1544 and Barnard 1 (Table 5) is a puzzle currently unresolved by existing models. The inefficiency of isotope-selective photodissociation of $^{14}N_2$ and $^{14}N^{15}N$ in molecular clouds (Heays et al. 2014) means that this process is excluded as a possible solution. The two existing measurements suggest a connection to the ammonia fractionation and measurements of these ratios in more sources is required.

The two existing measurements suggest a connection to the ammonia fractionation, and measurements of these ratios in more sources is now required. However, very recently, Roueff et al. (2015) published a study which re-assessed several of the ion-molecule fractionation pathways proposed by Terzieva and Herbst (2000), quantified some of the neutral-neutral reactions suggested by Rodgers and Charnley (2008), and considered new fractionation reactions for ^{13}C. Quantum-chemical calculations presented by Roueff et al. show that, in conflict with Terzieva and Herbst (2000), reactions (R9), (R10a), (R10b) and (R12) in Table 3 each possess activation energy barriers that will lead to negligible rates at around 10 K. Model calculations incorporating these new data indicate that, as expected, the calculated

$^{14}N/^{15}N$ ratios in HCN and HNC are much less enriched in ^{15}N than predicted in earlier models (e.g., Rodgers and Charnley 2008) and is observed (see Table 3). The calculations of Roueff et al. also predict that the ($^{14}N/^{15}N$ ratio in N_2H^+ should be close to elemental (≈ 400), in contrast to the depleted ratios observed in L1544 (~ 1000, Bizzocchi et al. 2013) and the enrichments predicted by previous theoretical models (e.g., Wirström et al. 2012). Thus, when compared to much of the published literature on interstellar ^{15}N fractionation, the work of Roueff et al. demonstrates that our current theoretical understanding of the underlying gaseous fractionation processes is far from complete.

4.2 Deuteration in the Solar Nebula

Cometary D/H values are lower than in most interstellar sources (Tables 1, 4). This low deuterium fractionation in comets can be interpreted by ion-molecule chemistry in gas phase at 25–35 K (Meier et al. 1998a, 1998b). Ion-molecule reactions in the outer solar nebula could also act to lower the interstellar fractionation (Aikawa and Herbst 1999). Alternatively, the low D-enrichment in H_2O might result from the mixing of D-rich water vapor originating from the pre-solar cloud or outer cold disk, and material reprocessed in the inner hot solar nebula (Hersant et al. 2001; Mousis et al. 2000; Kavelaars et al. 2011). Indeed, at high temperatures (>500 K), water molecules quickly exchange their deuterium with the main hydrogen reservoir H_2, so that the deuterium enrichment in water can not exceed the protosolar value of $0.21 \pm 0.04 \times 10^{-4}$ by more than a factor of 3 (Geiss and Gloeckler 1998) in high-T conditions. Transport mechanisms invoked so far include turbulent diffusion, which is also responsible for angular momentum transport in the solar nebula. Models are able to explain both the low, i.e. terrestrial, bulk deuterium enrichment measured in meteorites and the D/H ratio of $\sim 3 \times 10^{-4}$ measured in the water of Oort cloud comets, and Enceladus's plume (Hersant et al. 2001; Kavelaars et al. 2011; Waite et al. 2009). The higher deuterium enrichment in HCN measured in the Oort cloud comet Hale-Bopp (compared to the value in H_2O) might be explained by a lower efficiency of deuterium exchange between HCN and H_2 in the solar nebula (Mousis et al. 2000).

These models also 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. It was generally agreed that Oort-cloud comets formed closer to the Sun than Jupiter-family comets (Dones et al. 2004, and references therein). However, in the framework of the Nice model, the Oort-cloud and the Scattered Disk, which is the source of the Jupiter-family comets, formed together as a result of late planetary migration which dispersed the trans-neptunian disk (Brasser and Morbidelli 2013). Therefore, in this picture, Jupiter-family comets are expected to exhibit similar or larger D/H than the Oort-cloud comets. The high deuterium enrichment measured in comet 67P/Churyumov-Gerasimenko is in line with these models (Altwegg et al. 2014), whereas the ocean-like D/H value found in the water of the Jupiter-family comets 103P/Hartley 2 and 45P/Honda-Mrkos-Pajdušáková is not. More recent calculations of the D/H distribution in the solar nebula showed that it is possible to obtain a non-monotonic gradient of the D/H ratio if fresh material from the infalling outer envelope fed the solar nebula continuously (Yang et al. 2013). Jacquet and Robert (2013) suggest that deuterium-poor ice grains condensed at the snow line were transported outwards in the comet-formation region, via turbulent diffusion. This scenario could also explain the distribution of D/H in CCs.

Another possible solution is that the Jupiter-family comets 103P/Hartley 2 and 45P/Honda-Mrkos-Pajdušáková formed closer to the Sun than other comets. According to the Grand Tack scenario, when the giant planets were still embedded in the nebular gas disk, there was a general radial mixing of the distribution of comets and asteroids (Walsh et al. 2011) so that the Kuiper Belt was populated by objects formed in a large range of heliocentric distance. Both the similarity of the D/H ratio in comets 103P/Hartley 2 and 45P/Honda-Mrkos-Pajdušáková with that found in carbonaceous chondrites, and the isotopic diversity observed in the Oort-cloud and Jupiter-family populations of comets are in agreement with such a scenario.

It was generally admitted that the extreme D-enrichments observed in primitive meteorites and IDPs are reflecting those acquired in the presolar cloud. The discovery of large D enrichments over large areas ($> 100\ \mu\text{m}^2$) of carbonaceous matter in UCAMMs would then require a large degree of preservation of such D-rich matter. Alternatively, cold chemistry in the outer regions of the protoplanetary disk could be responsible for such enrichments. 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 also suggests that deuterium enrichments could have been acquired within the protoplanetary disk itself (Remusat et al. 2006). Whether this mechanism affected the D-fractionation observed in cometary HCN and H_2O has still to be investigated. Recent work by Cleeves et al. (2014) has demonstrated that, if cosmic-rays cannot penetrate the protosolar disk, then nebular chemistry alone cannot generate the D/H ratios measured in primitive materials such as comets and meteorites. In this case, all the D fractionation in the nebula must be directly inherited from the interstellar medium (Willacy et al. 2015).

4.3 Nitrogen Isotopes

In the solar system the $^{14}N/^{15}N$ ratio presents variations that remain difficult to interpret (Fig. 2). The analysis of Genesis solar wind samples (Marty et al. 2011), considered as representative of the protosolar nebula, provided a $^{14}N/^{15}N$ ratio of 441 ± 5. This value is in agreement with the in situ measurements made in the ammonia of Jupiter's atmosphere (Fouchet et al. 2004) which probably comes from primordial N_2 (Owen et al. 2001). These values differs from the terrestrial ratio measured in the atmospheric N_2 (272). The Earth's ratio is enriched in ^{15}N compared to the protosolar nebula and is similar to the bulk of ratios derived from the analysis of comet 81P/wild 2 grains (McKeegan et al. 2006). Nitrogen isotopic ratios have also been measured in Titan's atmosphere. This atmosphere is dominated by N_2 molecules and two in situ measurements, based on Cassini GCMS and INMS data (Niemann et al. 2010; Mandt et al. 2009) have been published: 167.7 ± 0.6 and 143. Because of the low abundance of primordial Ar observed by Cassini-Huygens, it is generally assumed that N_2 is of secondary origin in this atmosphere and was delivered in a less-volatile form, probably NH_3.

In comets, a similar ^{15}N enrichment is observed for both CN/HCN and ammonia (Fig. 2). This is in contrast with interstellar sources where molecules carrying the nitrile (–CN) functional group are more enriched in ^{15}N than the molecules carrying the amine (–NH) functional group (Table 5). As discussed in Sect. 4.1, the different studies of interstellar chemistry are able to explain the ^{15}N enrichment measured for cometary HCN but this is less clear for ammonia (Sect. 4.1).

Ion-molecule chemistry in dense interstellar and/or protostellar material could induce ^{15}N enrichment in the ammonia ice produced in such environments (Charnley and Rodgers 2002). Alternatively, the ^{15}N enrichment observed in cometary ices could result from isotopic fractionation processes that occurred in the late protosolar nebula (Aléon 2010).

A property of primitive solar system material, is that there is no strict correlation between deuterium and ^{15}N enrichments (Aléon 2010; Marty 2012, and references therein). Interestingly, Wirström et al. (2012) show that while the nitriles, HCN and HNC, have the greatest ^{15}N enrichment, this enrichment is not expected to correlate with extreme D enrichments.

Finally, models considering self-shielding of N_2 photodissociation can explain enrichment in ^{15}N for HCN, but for ammonia the enrichment in ^{15}N depends on the place in the nebula (Heays et al. 2014).

5 Prospects for the Future

5.1 Measurements from Rosetta

5.1.1 ROSINA

Mass spectrometry is a powerful tool to measure the isotopic ratios of the light volatiles in simple species of the coma. Mass spectrometers with high resolution (to resolve molecules on integer mass) and high dynamic range (to detect minor species) are required. On board the Rosetta orbiter is the Rosetta Orbiter Spectrometer for Ion and Neutral Analysis experiment (ROSINA). Its aim is to characterize *in situ* the volatiles in the coma of 67P/Churyumov-Gerasimenko (Balsiger et al. 2007). ROSINA consists of two complementary mass spectrometers, the Double Focusing Mass Spectrometer (DFMS) and the Reflectron Time of Flight mass spectrometer (RTOF), and a pressure sensor (COPS). DFMS has a mass per charge range of 12–150 amu/e and a mass resolution of 9000 at 50 % peak height at mass 28. It is optimized for very high mass resolution and large dynamic range and can resolve, e.g., CO and N_2 on mass/charge 28 amu/e, or ^{12}CH and ^{13}C on mass/charge 13 amu/e (Balsiger et al. 2007).

Since the first encounter at a comet by VEGA 1 on March 6, 1986, there have been several missions to comets, like Deep Space (19P/Borrelly), Stardust (81P/Wild 2), and Deep Impact (9P/Tempel 1). However, since Giotto none of them carried a mass spectrometer for *in situ* investigations of the gas coma. ROSINA will provide information about H_2O and other molecules in the coma (e.g., abundance of CO and N_2, Rubin et al. 2015, local abundances in the coma, extended sources, e.g., CN, etc.) and measure the isotopic composition of several species. In the following is a discussion of the capability of ROSINA to measure isotopic ratios.

For the light volatiles H, C, N, O, and S, DFMS is expected to measure at least the isotopic ratio in one molecule: for D/H in H_2O as it has been shown by Hässig et al. (2013), for $^{13}C/^{12}C$ in CH_4, CO_2, H_2CO, for $^{15}N/^{14}N$ directly in N, for $^{17}O/^{16}O$ in H_2O, for $^{18}O/^{16}O$ in H_2O, and for the sulfur isotopes directly in S and H_2S. There are three factors which influence whether an isotopologue can be detected or not:

- Mass resolution of DFMS, e.g., it is not possible to resolve the isotopologues of HCN.
- Abundance of main species and dynamic range: e.g., in order to determine the ratio of oxygen the peaks on mass 16 and 17 are needed since the signal for ^{17}O has to be separated from ^{16}OH, which might be much more abundant and thus hide the signal of ^{17}O. First results were derived already during the comet approach phase (see Sect. 2.1.1, Altwegg et al. 2014), and further results are expected in summer 2015 when 67P/Churyumov-Gerasimentko is at its perihelion.
- Some species are already present in the spacecraft background, e.g., CH_4 and HCN (for entire inventory see SchläPpi et al. 2010) and have to be accounted for.

An overview about the detection capabilities for isotopic ratios at comet 67P/Churyumov-Gerasimenko is given in Table 6.

Table 6 An overview on the detection capabilities of ROSINA for the light volatiles. The table is based on the current knowledge about abundances and isotopic ratios on comets (Bockelée-Morvan 2011; Jehin et al. 2009; Rousselot et al. 2014)

	Target species	Mass (amu)	Closest neighbour	Mass (amu)	Feasibility
D/H	HDO	19.0163	$H_2^{17}O$	19.0142	✓
	NH_2D	18.0323	$^{15}NH_3$	18.0230	(✓)
	CH_3D	17.0370	$^{13}CH_4$	17.0341	(✓)
	DCN	28.0166	CH_2N	28.0182	–
			$H^{13}CN$	28.0137	
$^{13}C/^{12}C$	$^{13}CH_3D$	18.0404	NDH_2	18.0323	(✓)
	^{13}C	13.0028	CH	13.0073	✓
	$^{13}CH_4$	17.0341	CH_3D	17.0370	✓
	$H^{13}CN$	28.0137	DCN	28.0166	–
			CH_2N	28.0182	
	^{13}CN	27.0059	HCN	27.0104	(✓)
	$^{13}CO_2$	44.9926	CHO_2	44.9971	✓
	$H_2^{13}CO$	31.0134	CH_3O	31.0178	✓
	^{13}CO	28.9977	CHO	29.0022	(✓)
$^{15}N/^{14}N$	$^{15}NH_3$	18.0230	NH_2D	18.0323	(✓)
	$HC^{15}N$	28.0074	N_2	28.0056	–
			$H^{13}CN$	28.0137	
	$C^{15}N$	26.9996	^{13}CN	27.0059	(✓)
	^{15}NN	29.0026	CO	27.9944	(✓)
			CHO	29.0022	(✓)
$^{17}O/^{16}O$	^{17}O	16.9986	OH	17.0022	?
	$H_2^{17}O$	19.0142	HDO	19.0163	✓
	$C^{17}O$	28.9986	^{13}CO	28.9977	-
	$CO^{17}O$	44.9935	$^{13}CO_2$	44.9926	(✓)
$^{18}O/^{16}O$	^{18}O	17.9986	H_2O	18.0100	✓
	$H_2^{18}O$	20.0143	HF	20.0057	✓
	$C^{18}O$	29.9986	NO	29.9974	?
	$CO^{18}O$	45.9935	NO_2	45.9924	?
$^{33}S/^{32}S$	^{33}S	32.9709	HO_2	32.9971	✓
	$H_2^{33}S$	34.9866	Cl	34.9683	✓
$^{34}S/^{32}S$	^{34}S	33.9673	H_2O_2	34.0049	✓
	$H_2^{34}S$	35.9830	HCl	35.9761	✓
			^{36}Ar	35.967	(✓)

✓: ROSINA will determine ratio, (✓): determination is dependent on abundance, ?: not enough data available to make predictions, (–): ROSINA will not be able to determine the isotopic ratio

5.1.2 Rosetta: COSAC and Ptolemy

The Philae Lander (Bibring et al. 2007b) has two Gas Chromatography (GC)—Mass Spectrometer instruments, COSAC (Goesmann et al. 2007) and Ptolemy (Wright et al. 2007).

The two instruments are complimentary in that COSAC aims to analyse the chemical composition of the organic compounds whereas Ptolemy aims to accurately measure the isotopic composition of the abundant chemical components, although there is some degree of overlap.

The Ptolemy mass spectrometer is an ion trap mass spectrometer (March and Todd 2005) with a mass range of 10 to 150 Da and unit mass resolution. With a low resolution mass spectrometer separation of isobaric interferences directly by mass spectrometry is not possible. However, Ptolemy uses various chemical and gas chromatographic methods to separate the molecular species of interest. Ptolemy includes a reference gas reservoir so that aliquots can be processed and analysed in the same procedure as the sample gas to give a direct comparison with known terrestrial values. Reference gases processed through the Ptolemy GC system have shown that the precision for $\delta^{13}C$, $\delta^{15}N$ and $\delta^{18}O$ of approximately 20 permil can be achieved.

Comet samples can be collected by the Philae Lander Sampler Drill and Distribution system (SD2), from depths of up to 30cm (Finzi et al. 2007). These samples will be transferred into one of either 10 High Temperature Ovens (HTO), which have a maximum temperature of $\sim 600\,^{\circ}C$, or 16 Medium Temperature Ovens (MTO), which have a maximum temperature of 180 °C. The MTOs incorporate a window so that observations can be made of the sample by the CIVA microscopes (Bibring et al. 2007a) before and after heating. Samples are then heated in controlled temperature steps to evolve volatiles into the Ptolemy chemistry system. These gases will then be processed for isotopic analysis. One of the high temperature ovens contains a trapping material that passively collects coma gas when positioned in an exposed, low temperature position on the Lander balcony. The collected gas is then released into the Ptolemy system by heating the oven to 200 °C. Evolved gas will then be processed and analyzed in a similar way to the drill samples. This will allow a direct comparison of the coma composition at the Lander site and the Orbiter.

Usually a small aliquot of evolved gas is analyzed directly to obtain a bulk compositional mass spectrum. The processing that the sample undergoes is dependent on the required isotopic analysis. The various sample processing schemes are:

1. Organic composition. Injection of the sample into GC column A (30 m CP-Sil 8CB) which separates organic molecules to obtain chemical composition of organic molecules.
2. Carbon and nitrogen isotopic analysis. Injection of the sample into GC column B (30 m CP-PoraPLOT Q) which separates CO and N_2 from CO_2. As the sample elutes from the column it passes through a Rhodium oxide reactor which oxidises the CO to CO_2. Isotopic exchange on the reactor gives the CO_2 a terrestrial oxygen isotopic signature thus allowing accurate carbon isotopic analysis (Santrock et al. 1985).
3. Oxygen and hydrogen isotopic analysis of water. The water is reduced to CO and H_2 by passing over a platinised carbon reactor which are then separated by GC column C (15 m 5 Angstroem molecular sieve MXT). Note that this is the only scheme which also gives a direct measurement of the $^{17}O/^{16}O$ ratio as well as the $^{18}O/^{16}O$ ratio.
4. Bulk hydrogen, carbon and nitrogen isotopic analysis. Combustion of the sample to H_2O, CO_2 and N_2. The carbon and nitrogen isotopes can then be analysed by either direct analysis or by using scheme (2) whilst water is analysed by scheme (3).
5. Noble gas analysis. Exposure of the sample to getters to remove all active gases to allow analysis of the noble gas concentrations and isotopic values.
6. Oxygen isotopic analysis of minerals. A reactor containing Asprey's salt (Asprey 1976) is heated to produce fluorine which is then used to liberate oxygen from the sample. Due to the reactive nature of this experiment this will be attempted near the end of the Lander mission.

Table 7 Ptolemy measurements of isotopic ratios

Species	Method	Isotope ratio	Requirements
Bulk C	Combustion of solid sample to CO_2	$^{13}C/^{12}C$	
Bulk N	Combustion of solid sample to N_2	$^{15}N/^{14}N$	
Bulk H	Combustion of solid sample to H_2O followed by reduction to CO and H_2	D/H	
H_2O	Reduction to CO and H_2 (channel C)	$^{18}O/^{16}O$ $^{17}O/^{16}O$ D/H	
CO_2	Direct analysis	$^{13}C/^{12}C$ $^{18}O/^{16}O$	(2)
	Channel B	$^{13}C/^{12}C$	
CO	Direct analysis	$^{13}C/^{12}C$ $^{18}O/^{16}O$	(1), (2)
	Channel B oxidation to CO_2	$^{13}C/^{12}C$	
CH_4	Removal CO and CO_2 by getters, combustion to CO_2, then direct analysis	$^{13}C/^{12}C$	
	Channel B, oxidation to CO_2	$^{13}C/^{12}C$	
N_2	Direct analysis		(2)
	Channel B, combustion to N_2	$^{15}N/^{14}N$	
NH_3	Channel B, combustion to N_2	$^{15}N/^{14}N$	
Noble gases	Removal of active gases by getters		
Minerals	Reaction with fluorine, direct analysis	$^{18}O/^{16}O$	

(1) $^{13}C/^{12}C$ measurement assumes $\delta^{17}O$—the terrestrial value within 200 permil

(2) Providing the CO/N_2 ratio is known

A summary of the various schemes and species targeted for isotopic analysis is shown in Table 7.

Ptolemy analysis of comet samples is a destructive technique that uses a relatively large amount of power and the target isotopic scheme has to be decided in advance and pre-programmed into the instrument. The planned First Science Sequence (FSS), which lasted from Lander touchdown until the non-rechargeable batteries were exhausted some 60 hours later, was to include the collection of 2 samples by SD2 from a depth of about 30cm from the comet surface. Both samples were to be delivered to HTOs, one for Ptolemy and the other for COSAC. The aim of the Ptolemy experiment was to heat a sample in a HTO in four temperature steps using the following schemes; −50 °C carbon and nitrogen isotopic analysis of CO and N_2, +100 °C oxygen and hydrogen isotopic analysis of water, +400 °C carbon and nitrogen isotopic analysis of CO, CO_2 and N_2, +600 °C bulk carbon and nitrogen isotopic analysis. This is then followed by a reference gas analysis.

Following a successful, but non-optimal landing, there was insufficient power for SD2 to collect a sample for Ptolemy. (SD2 did operate and attempted to collect a sample for COSAC, but it remains unknown whether or not a sample was delivered to the oven). The Ptolemy sequence was changed to a single isotopic analysis using the CASE oven in the hope that some material may have been collected during and after the landing. Although the sequence was successfully executed, the signal was too small to give meaningful isotope ratios.

The Long Term Science Sequence (LTS) was expected to start within a few weeks of the FSS where recharging of the Philae secondary batteries would allow intermittent operations for up to six months. In the current configuration it is hoped that the Lander will have sufficient power to begin operations in spring 2015. Ptolemy operation is severely restricted by power resources, however during the LTS the composition of the sample before analysis will be better characterized including ROLIS and CIVA imaging and ongoing observations from orbiter instruments e.g. ROSINA. The Ptolemy aim is to target particular abundant species for isotopic analysis, make coma observations using the adsorbent oven as the comet becomes more active and finally attempt a fluorination of the refractory residue from a High Temperature Oven.

5.1.3 MIRO

The main goals of the Microwave Instrument for the Rosetta Orbiter (MIRO) are to measure the thermal emission from nucleus sub-surface layers in two continuum channels (0.5 and 1.6 mm), and to characterize the outgassing of four fundamental molecules (H_2O, CO, NH_3, CH_3OH) from their lines near 0.5 mm (Gulkis et al. 2007). The fundamental rotational lines $1_{10} - 1_{01}$ of the three oxygen-related isotopologues of water ($H_2^{16}O$, $H_2^{18}O$, and $H_2^{17}O$) are observed simultaneously to determine the $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios.

5.2 Measurements from Ground-Based and Space-Based Facilities

The Atacama Large Millimeter/submillimeter Array is currently under construction in northern Chile's Atacama desert at an altitude of 5000 meters above sea level. The ALMA interferometer will initially be composed of 66 antennas working at millimeter and submillimeter wavelengths (Wootten 2008). ALMA signifies the beginning of a new era for cometary science, in which routine measurements of the three-dimensional distributions of molecular species are now possible for almost all comets, with visual magnitudes of 8 or brighter. For the brightest comets, it will be possible to detect molecules which have strong lines in the microwave range, such as HDO, DCN, $H^{13}CN$, $HC^{15}N$, $H^{15}NC$, $H_2^{34}S$, and $C^{34}S$, isotopes of CH_3OH, etc. Hence, it will be possible to probe the isotopic diversity in the comet population. The prospects for ALMA observations of comets are discussed by Biver (2005) and Bockelée-Morvan (2008).

The upcoming of 40-m class optical telescopes will ease the characterization of deuterium fraction in water and methane in comets. At the European Extremely Large telescope (E-ELT) built by the European Southern Observatory, high-resolution spectroscopy in the L and M near-IR bands will be offered by one of the first generation instruments ELT-MIR.

5.3 On the Analyses of Cometary Samples on Earth

Samples of Comet 81P/Wild 2 returned by the Stardust mission are continuously being analyzed. Indigenous organic compounds recovered from this samples may include potential prebiotic compounds like glycine (Elsila et al. 2009). Further improvement in laboratory techniques may enable the measurement of the isotopic compositions of these compounds in order to ascertain their indigenous origin. In the coming year, with the forthcoming return of samples from primitive asteroids (Hayabusa 2 and Osiris-Rex missions), more constraints will be available on the relationship between primitive asteroids and carbonaceous chondrites (CI, CM, CR) that are suspected of having a cometary origin. The origin of GEMS in CP-IDPs is still debated, as some of these glassy inclusions (the largest ones) show isotopic anomalies possibly related to a presolar heritage, although their collection in silicon oil may bias the analyses (Bradley 2013; Keller and Messenger 2013). By contrast, UCAMMs are collected in water and do not suffer such bias. Analyzing the oxygen isotopic composition of GEMS in UCAMMs should provide more clues on the origin of these phases that seem ubiquitous in cometary material. UCAMMs offer an opportunity to directly study the association of organics and minerals in primitive dust. Measuring both the hydrogen and nitrogen isotopic compositions of organic matter in UCAMMs will shed more light on the formation and evolution of organic matter in the solar system (e.g., Floss et al. 2012; Haenecour et al. 2014; Bardin et al. 2014; Duprat et al. 2014). Since UCAMMs did not endure substantial alteration at atmospheric entry or during their stay in the snow, their content in presolar grains should also provide a valuable constraint on the interstellar heritage in cometary solids.

6 Summary

In this chapter, we reviewed the isotopic composition of cometary volatiles and grains, as well as that of potential cometary material available in collections on Earth. We discussed the isotopic ratios in the light of processes governing interstellar fractionation. Comparing isotopic ratios in comets and planets can shed light to the origin of volatiles in planets, as discussed in Mandt et al. (2015, this issue).

Important progresses in our knowledge of comet composition will benefit from current or future space missions to comets (e.g., the Rosetta mission of ESA) and from telescopic observations with yet available or new instrumentation (e.g., 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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