Earth Moon Planet (2009) 105:167–180
DOI 10.1007/s11038-009-9322-y

Isotopic Ratios in Comets: Status and Perspectives

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Received: 20 February 2009 / Accepted: 26 May 2009 / Published online: 13 June 2009
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Abstract Isotopic abundance ratios are excellently suited to probe the origin of solar system matter. We review the recent measurements of the isotopic ratios of the light elements (D/H, ^{12}C/^{13}C, ^{16}O/^{18}O, ^{14}N/^{15}N, ^{32}S/^{34}S) in cometary dust and gas and discuss briefly their implications. Special emphasis will be put on the determinations and progress performed in the field over the past years thanks to high resolution spectroscopy of cometary comae obtained with the ESO Very Large Telescope. Future perspectives from space missions and ground-based observations with new large and extremely large telescopes operating in the optical, infrared and submillimeter wavelengths will be presented.

Keywords Comets · Abundances · Isotopic ratios · Light elements ·
Large telescopes

1 Introduction

Determination of the abundance ratios of the stable isotopes of the light elements in different objects of the Solar System provides important clues to the study of its origin and early history. Comets formed 4.6 Gyr ago and, because they are small bodies, they were much less altered since their formation than the planets and their satellites. They are believed to have preserved unprocessed material of the solar nebula from the time of formation of the solar system.

Measuring isotopic abundance ratios in comets is a very difficult task. In situ measurements with a mass spectrometer onboard a spacecraft are most accurate (provided confusion between species can be avoided) but are very expensive and can only sample a

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small amount of material of a single comet within reach of a spacecraft (mainly ecliptic comets).

Isotopic ratios can be determined remotely by high-resolution spectroscopy of molecular bands. In this case several tons of volatile compounds of the coma are sampled through the slit of a spectrograph fed by a telescope. Many more targets are available. Such measurements are not an easy task at all, not merely because the emissions of the low-abundance species are very weak, but also, particularly for optical spectra, because of rather tight blends with lines from the normal species or from various other faint features which must be disentangled. Moreover the best contrast with the underlying scattered solar continuum must be obtained. Other specific problems occur in the case of near infrared spectroscopy like the need to remove the many telluric features while for radio observations it is difficult to get simultaneously both the rare and the abundant isotopes. All such measurements indeed require high signal-to-noise spectra of high spectral resolution, and until quite recently were feasible only on exceptional comets. The accuracy of the determinations also depends in this case on the models representing the emission by the various isotopologues, as well as by other species showing up in the same domain.

2 Status After the Passage of Great Comet C/Hale-Bopp

The paucity of isotopic data for comets is well illustrated by the fact that around year 2000, isotopic ratios—except for carbon—had only been measured in three active comets coming from the Oort cloud. After the breakthrough of the first measurements of D/H, $^{16}O/^{18}O$ and $^{32}S/^{34}S$ in comet 1P/Halley published ten years after the spectacular Giotto flyby (Balsiger et al. 1995; Eberhardt et al. 1995; Altwegg 1996), ten more years, and the great comets C/1996 B2 Hyakutake and C/1995 O1 Hale-Bopp, were needed to get new measurements of D/H (Bockelée-Morvan et al. 1998; Meier et al. 1998a, b, respectively), $^{32}S/^{34}S$ (Jewitt et al. 1997; Crovisier et al. 2004) and the first measurement of $^{14}N/^{15}N$ in a comet (Jewitt et al. 1997; Arpigny et al. 2000, 2003). An overview of these results is given in Altwegg and Bockelée-Morvan (2003), Bockelée-Morvan et al. (2004) and Table 1.

Below we highlight the new results since 2002 and show that most of them are coming from new facilities, opening for the first time the possibility of making those measurements in many comets.

3 $^{12}C/^{13}C$ and $^{14}N/^{15}N$: A Decade of Measurements in the CN Coma of Comets

The nitrogen isotopic ratio $^{14}N/^{15}N$ was measured for the first time in comet Hale-Bopp in 1997 in HCN as well as in the CN band. The $^{12}C/^{13}C$ ratio was determined simultaneously. The $^{12}C/^{13}C$ and $^{14}N/^{15}N$ values derived from the HCN emission at sub-millimetre range (111 ± 12 and 323 ± 46 respectively, Jewitt et al. 1997; 109 ± 22 and 330 ± 98, Ziurys et al. 1999), were consistent with the telluric value (89 and 272, respectively, Anders and Grevesse 1989), although uncertainties are rather large for nitrogen. The $^{12}C/^{13}C$ value derived from CN was terrestrial, but the nitrogen isotopic ratio ($^{14}N/^{15}N = 140 \pm 35$) was widely discordant (Arpigny et al. 2003).

The conflicting results and the evidence for an anomalous value of $^{14}N/^{15}N$ clearly demanded further measurements. An observing campaign was then initiated with the high-resolution UV-Visible Echelle Spectrograph (UVES) mounted on the 8 m telescope Kueyen of the ESO Very Large Telescope (Chile), in order to gather high quality data on

Table 1 Isotopic ratios in comets

	Species	Comets	Method (facility)	Reference
D/H (1.56×10^{-4})				
$(3.08 \pm 0.5) \times 10^{-4}$ $(3.06 \pm 0.34) \times 10^{-4}$	H_2DO^+	1P/Halley	Mass spectro (Giotto)	Balsiger et al. (1995), Eberhardt et al. (1995)*
$(3.3 \pm 0.8) \times 10^{-4}$	HDO	C/1995 O1 (Hale-Bopp)	Radio spectro (JCMT)	Meier et al. (1998a)
$(2.9 \pm 1.0) \times 10^{-4}$	HDO	C/1996 B2 (Hyakutake)	Radio spectro (CSO)	Bockelée-Morvan et al. (1998)
$(2.3 \pm 0.4) \times 10^{-3}$	DCN	C/1995 O1 (Hale-Bopp)	Radio spectro (JCMT)	Meier et al. (1998b)
$(4.6 \pm 1.4) \times 10^{-4}$	D	C/2001 Q4 (NEAT)	UV spectro (HST STIS)	Weaver et al. (2008)
$(2.5 \pm 0.7) \times 10^{-4}$	OD	C/2002 T7 (LINEAR)	Near UV spectro (VLT UVES)	Hutsemékers et al. (2008)
$(4.09 \pm 1.45) \times 10^{-4}$	HDO	8P/Tuttle	Near IR spectro (VLT CRIRES)	Villanueva et al. (2009)
$[10^{-4}–10^{-3}]$	D	81P/Wild2	Laboratory NanoSIMS (Stardust)	McKeegan et al. (2006)
$^{12}C/^{13}C$ (89)				
93 ± 10	$^{12}C^{13}C$	4 OCC	Optical spectro (Palomar Coudé, 2DC McDonald)	Wyckoff et al. (2000)
90 ± 10	^{13}CN	1P/Halley + 3 OCC	Optical spectro (1.9 m Mount Stromlo)	Kleine et al. (1995), Wyckoff et al. (2000)*
111 ± 12 109 ± 22	$H^{13}CN$	C/1995 O1 (Hale-Bopp)	Radio spectro (JCMT, 12 m NRAO)	Jewitt et al. (1997), Ziurys et al. (1999)*
90 ± 20	^{13}CN	C/1995 O1 (Hale-Bopp)	Optical spectro (SOFIN NOT, 2DC McDonald)	Arpigny et al. (2000, 2003), Manfroid et al. (2009)*
89.1 ± 4.2	^{13}CN	14 OCC	Optical spectro (VLT UVES + 2DC McDonald)	Arpigny et al. (2003), Jehin et al. (2004, 2006, 2008), Manfroid et al. (2005, 2009)*, Hutsemékers et al. (2005), Bockelée-Morvan et al. (2008a, b)

Table 1 continued

	Species	Comets	Method (facility)	Reference
97.2 ± 7.6	^{13}CN	4 JFC	Optical spectro (VLT UVES + 2DC McDonald)	Hutsemékers et al. (2005), Jehin et al. (2006, 2008), Bockelée-Morvan et al. (2008a), Manfroid et al. (2009)*
94 ± 8	H^{13}CN	C/1995 O1 (Hale-Bopp)	Radio spectro (JCMT)	Bockelée-Morvan et al. (2008a)
114 ± 26	H^{13}CN	17P/Holmes	Radio spectro (30 m IRAM)	Bockelée-Morvan et al. (2008a)
90 ± 20	^{13}CN	17P/Holmes	Optical spectro (2DC McDonald + HIRES KeckI)	Bockelée-Morvan et al. (2008a)
[90–94]	^{13}C^{-}	81P/Wild2	Laboratory NanoSIMS (Stardust)	McKeegan et al. (2006)
^{14}N/^{15}N (272)				
323 ± 46 330 ± 98	HC^{15}N	C/1995 O1 (Hale-Bopp)	Radio spectro (JCMT, 12 m NRAO)	Jewitt et al. (1997), Ziurys et al. (1999)*
150 ± 30	C^{15}N	C/1995 O1 (Hale-Bopp)	Optical spectro (SOFIN NOT, 2DC McDonald)	Arpigny et al. (2000, 2003), Manfroid et al. (2009)*
144.0 ± 6.5	C^{15}N	14 OCC	Optical spectro (VLT UVES + 2DC McDonald)	Arpigny et al. (2003), Jehin et al. (2004, 2006, 2008), Manfroid et al. (2005, 2009)*, Hutsemékers et al. (2005), Bockelée-Morvan et al. (2008a, b)
156.8 ± 12.2	C^{15}N	4 JFC	Optical spectro (VLT UVES + 2DC McDonald)	Hutsemékers et al. (2005), Jehin et al. (2006, 2008), Bockelée-Morvan et al. (2008a), Manfroid et al. (2009)*
205 ± 70	HC^{15}N	C/1995 O1 (Hale-Bopp)	Radio spectro (JCMT)	Bockelée-Morvan et al. (2008a)
139 ± 26	HC^{15}N	17P/Holmes	Radio spectro (30 m IRAM)	Bockelée-Morvan et al. (2008a)

Table 1 continued

	Species	Comets	Method (facility)	Reference
165 ± 40	$C^{15}N$	17P/Holmes	Optical spectro (2DC McDonald + HIRES KeckI)	Bockelée-Morvan et al. (2008a)
[118–270]	$C^{15}N^-$	81P/Wild2	Laboratory NanoSIMS (Stardust)	McKeegan et al. (2006)
$^{16}O/^{18}O$ (499)				
518 ± 45 470 ± 40	$H_2^{18}O$	1P/Halley	Mass spectro (Giotto)	Balsiger et al. (1995), Eberhardt et al. (1995)*
530 ± 50	$H_2^{18}O$	4 OCC	Radio spectro (Odin)	Lecacheux et al. (2003), Biver et al. (2007)*
425 ± 55	^{18}OH	C/2002 T7 (LINEAR)	Optical spectro (VLT UVES)	Hutsemékers et al. (2008)
[490–520]	Minerals	81P/Wild2	Laboratory NanoSIMS (Stardust)	McKeegan et al. (2006)
$^{32}S/^{34}S$ (23)				
23 ± 6	$^{34}S+$	1P/Halley	Mass spectro (Giotto)	Altwegg (1996)
27 ± 3	$C^{34}S$	C/1995 O1 (Hale-Bopp)	Radio spectro (JCMT)	Jewitt et al. (1997)
16 ± 3	$H_2^{34}S$	C/1995 O1 (Hale-Bopp)	Radio spectro (30 m IRAM)	Crovisier et al. (2004)
16 ± 3	$C^{34}S$	17P/Holmes	Radio spectro (30 m IRAM)	Biver et al. (2008)

JFC Jupiter family comets, *OCC* Oort cloud comets

The table with the individual measurements and other information is available at http://wela.astro.ulg.ac.be/themes/solar/Comets/pub_gen_e.html

The terrestrial value is indicated for each ratio

* When several references are available for one comet, the value quoted has been taken from the last paper

different comets presenting a variety of origins and physical conditions. The bright CN violet band $B^2\Sigma^+$–$X^2\Sigma^+$ (0,0) at 3880 Å, was the main target of these studies; it was analysed using the model developed by Zucconi and Festou (1985) and recently improved (Manfroid et al. 2009). For the Northern objects, observations were obtained with the HIRES and the 2DCoudé spectrographs mounted, respectively, on the Keck I telescope and the 2.7 m telescope of the McDonald Observatory. Thanks to all these efforts, measurements of both $^{12}C/^{13}C$ and $^{14}N/^{15}N$ in 18 comets were made over a period of about 10 years, thus increasing the statistics on those two isotopic ratios. A homogeneous reanalysis of a whole sample of 220 high resolution spectra of 22 comets is under way (Manfroid et al. 2009).

The carbon ratio had already been determined in 1975 in four bright comets using the C_2 Swan bands from photographic optical spectra [unfortunately the C_2 isotopic emissions are contaminated by NH_2 (Danks et al. 1974; Lambert and Danks 1983)], and in four Oort cloud comets using the CN violet band (Kleine et al. 1995; Wyckoff et al. 2000, and references therein). All the derived values agreed with the terrestrial value, although with large error bars in some cases. Figure 1 illustrates the huge improvement in data quality obtained with the ESO large telescope and the UVES spectrograph. It also shows that new data for carbon itself were needed.

The comets studied in the more recent investigations belong to different dynamical classes, comprising dynamically-new as well as long-period comets; for the first time they also include short-period and relatively low activity comets from the Halley- and Jupiter-Family (Hutsemékers et al. 2005). In some cases the comets could be observed at various heliocentric distances (Manfroid et al. 2005); for a couple of them the ratios could be obtained at different distances from the nucleus (Manfroid et al. 2009). All the values determined for the carbon and nitrogen isotopic ratios are consistent, within the error margin, irrespective of the type of comet or the heliocentric distance at which it was observed (Fig. 2). These studies lead to the following average ratios: $^{12}C/^{13}C = 91.0 \pm 3.6$ and $^{14}N/^{15}N = 147.8 \pm 5.7$, all comets being taken together (Manfroid et al. 2009), while no significant difference emerges between OCC and JFC (Fig. 2; Table 1). Some of those data were obtained after an important observing campaign dedicated to comet 9P/Tempel1 prior, during and after its impact with the Deep Impact NASA spacecraft. No change in the isotopic ratios, within the error bars, was observed suggesting that these ratios are the same on the surface and in the interior of the nucleus (Jehin et al. 2006), provided the impactor was able to release material from deep enough (A'Hearn et al. 2005; Meech et al. 2005). The invariability of the ratios in comets observed at heliocentric distances between 1 and 4 AU and in the inner coma close to the nucleus or ranging up to 50.000 km and 100.000 km in the case of comets C/2001 Q4 (NEAT) and C/2002 T7 (LINEAR), respectively, points to a unique carbon and a unique nitrogen ratio in the various possible parents of CN. This is reinforced by the fact that gas-rich comets like deVico or dust-rich comets like Hale-Bopp do not show any difference in the isotopic ratios.

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 outburst in October 2007 (Bockelée-Morvan et al. 2008a). The carbon and nitrogen isotopic ratios derived from the two techniques are indeed in agreement with each other and with the values found in other comets (Table 1). The reanalysis of the Hale-Bopp sub-millimeter data (Bockelée-Morvan et al. 2008a) 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. These

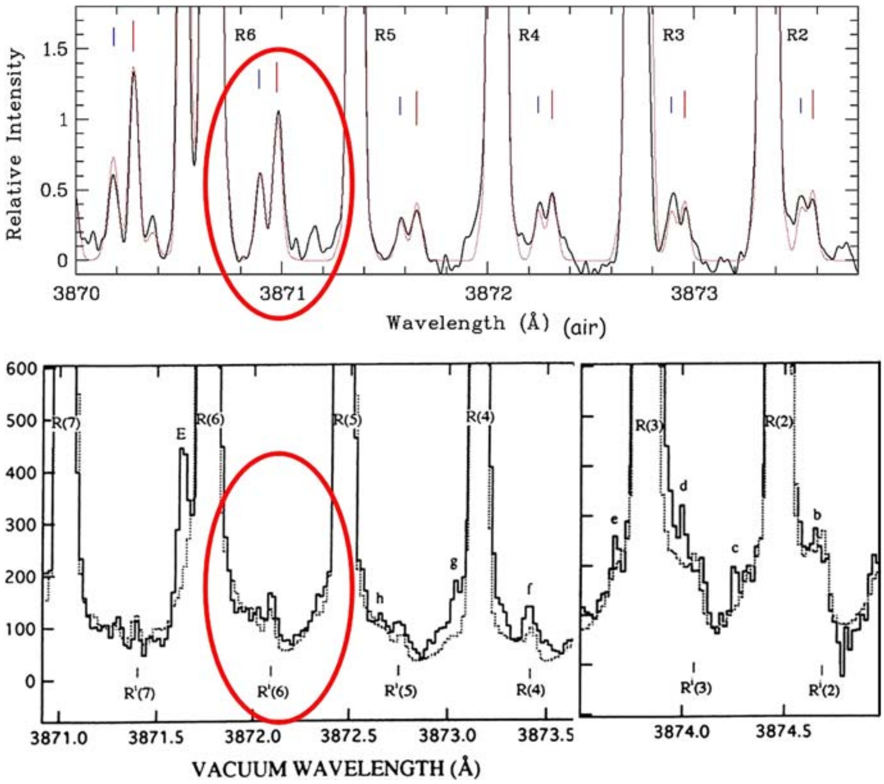

Fig. 1 *Top panel*. A section of the UVES spectrum of the CN (0,0) violet band in Jupiter Family comet 88P/Howell. Thick (*black*) line: mean observed spectrum (total of 12 h exposure time); thin (*red*) line: synthetic spectrum of $^{12}C^{14}N$, $^{12}C^{15}N$ and $^{13}C^{14}N$ with the adopted isotopic abundances. The lines of $^{12}C^{15}N$ are identified by the short ticks and those of $^{13}C^{14}N$ by the tall ticks. The quantum numbers of the R lines of $^{12}C^{14}N$ are also indicated (from Hutsemékers et al. 2005). *Bottom panel*. Same CN spectrum of 1P/Halley obtained with the 1.9 m telescope at Mount Stromlo Observatory (total of 4 h exposure time). Figure from Kleine et al. (1995). This spectrum was the best from which the carbon ratio was measured in a comet before the use of a very large telescope. This figure shows the huge improvement in data quality (resolution and line profile, signal-to-noise ratio) using new state of the art instrumentation even for a much less active comet (Howell had a heliocentric magnitude of ~9.0, Halley ~6.0). It is nevertheless interesting to point out that some of the "unidentified" features in the Halley spectrum correspond to the $C^{15}N$ lines: notably the features labelled "h" and "d", which correspond to R(5) and R(3), respectively, while "f" and "b" are blends between the $C^{15}N$ and ^{13}CN lines, at R(4) and R(2), respectively. More $C^{15}N$ are found in adjacent sections of the Halley spectrum. (Color figure online)

results are now compatible with HCN being an important parent of CN in cometary atmospheres.

In conclusion, whilst the value for the $^{12}C/^{13}C$ ratio, 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).

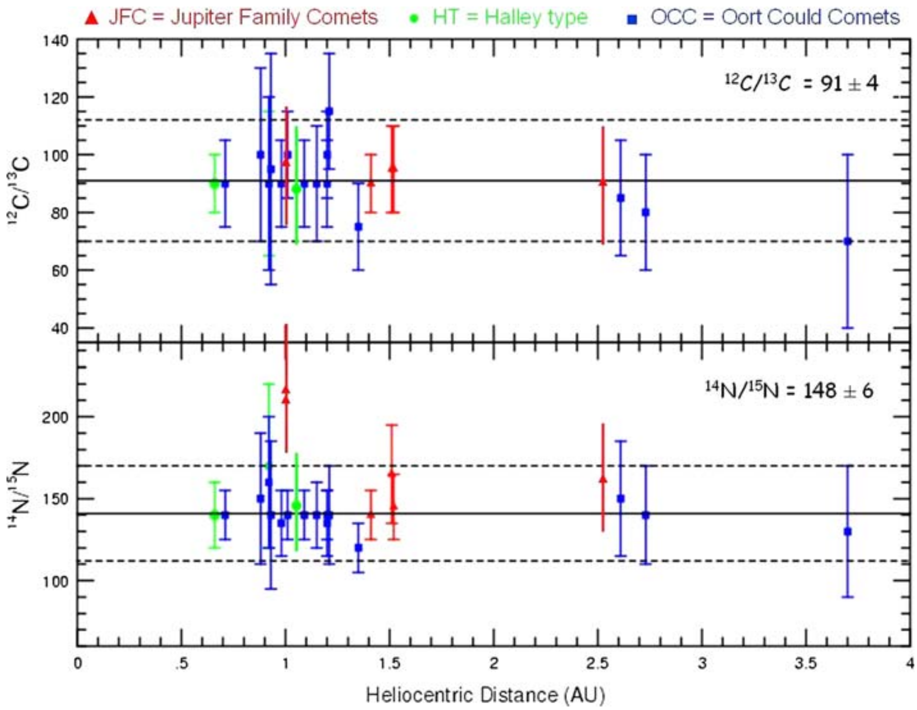

Fig. 2 $^{12}C/^{13}C$ and $^{14}N/^{15}N$ measurements from cometary CN in 18 comets of various types (11 OCC, 4 JFC, 3 HT) with respect to their heliocentric distance (24 measurements), from Manfroid et al. (2009)

New measurements of $^{12}C/^{13}C$ and $^{14}N/^{15}N$ in cometary dust have been obtained from the detailed laboratory analysis of the dust particules of the Jupiter family comet 81P/Wild 2. Those grains were collected in the coma by the NASA Stardust spacecraft during an encounter in January 2004 and brought back to Earth two years later (McKeegan et al. 2006). The results show that most of the dust grains (or what is left of them) have nitrogen and carbon isotopic ratios in agreement with the solar value and the bulk of meteorites (Table 1). As in primitive meteorites and IDPs (Floss et al. 2006) hotspots highly enriched in ^{15}N have been found that might have the same origin as species observed in the gaseous phase of the coma. All the particles have a solar $^{12}C/^{13}C$ and the dispersion (as in the case of the volatile component) is small when compared to the large variations that were observed in CHON grains of Halley (Jessberger and Kissel 1991). The homogeneity of the carbon ratio between comets, meteorites, the Sun, the Earth and other bodies of the solar system seems to indicate that little or no fractionation of carbon occurred in the protosolar cloud and in the solar nebula.

4 D/H

The deuterium versus hydrogen isotopic ratio is especially interesting because hydrogen is abundant in comets through water and because this ratio is particularly sensitive to the physical conditions that were prevailing when the cometary material formed. The determination of D/H is also crucial to understand the origin of water on Earth, a still open debate. However, only a few measurements of D/H in comets exist to date due to the extreme difficulty of detecting this rare isotope. Until recently this was only possible in exceptional comets visible only once in a decade, like Halley, Hale-Bopp and Hyakutake.

The in situ measurements from the neutral and ion mass spectrometers onboard the Giotto spacecraft were the first to provide a D/H value in a comet. They gave D/H = $(3.16 \pm 0.34) \times 10^{-4}$ for H_3O^+ in Halley (Eberhardt et al. 1995; Balsiger et al. 1995), a factor of two higher than the terrestrial value in the ocean [D/H (VSMOW[1]] = 1.56×10^{-4}). The advent of powerful sub-millimeter telescopes, namely the Caltech Submillimeter Observatory and the James Clerck Maxwell telescope located in Hawaii, allowed 10 years later the determination of the D/H ratio for two exceptionally bright comets. In comet Hyakutake, D/H was found equal to $(2.9 \pm 1.0) \times 10^{-4}$ in H_2O (Bockelée-Morvan et al. 1998), while in comet Hale-Bopp the ratios D/H = $(3.3 \pm 0.8) \times 10^{-4}$ in H_2O and D/H = $(2.3 \pm 0.4) \times 10^{-3}$ in HCN were measured (Meier et al. 1998a, b), confirming the high D/H value in comets. Both Hyakutake and Hale-Bopp are Oort-Cloud comets. More recently, bulk fragments of 81P/Wild 2 grains returned by Stardust indicated moderate D/H enhancements with respect to the terrestrial value. Although D/H in 81P/Wild 2 cannot be ascribed to water, the measured values overlap the range of water D/H ratios determined in the other comets (McKeegan et al. 2006).

Interestingly, after a very quiet period, three new determinations of D/H in three different new Oort cloud comets using three different techniques have been reported at the 10th Asteroids Comets and Meteors conference held in Baltimore, Maryland, USA in July 2008.

Using Hubble Space Telescope (HST) observations of C/2001 Q4 (NEAT) in April 2004, Weaver et al. (2008) discovered atomic D emission. The Space Telescope Imaging Spectrograph (STIS) spectra of Q4 (NEAT) show clear detections of the D Lyman-α line at 1215.34 Å on three different dates. Both D and H lines are observed simultaneously and are well separated from the terrestrial lines. They are used to derive the respective production rates, whose ratio is assumed to be identical to D/H. The preliminary value of $(4.6 \pm 1.4) \times 10^{-4}$ appears to be consistent within error bars with the values derived in other comets, though marginally higher.

Villanueva et al. (2008) report on the observations in early 2008 of the HDO transitions near 3.7 μm in the Halley-Family comet 8P/Tuttle using the new high resolution Cryogenic Infrared Echelle Spectrograph (CRIRES) of the ESO VLT. As no line could be identified individually, 23 lines were co-added to get the HDO production rate. The ratio to the derived production rate of H_2O, using lines in neighbouring wavelength regions taken a few days apart, gave a formal value of D/H of $(4.09 \pm 1.45) \times 10^{-4}$ (Villanueva et al. 2009). This method used for the first time might be one of the most straightforward ways to get the D/H ratio in H_2O in moderately active comets ($Q[H_2O] > 10^{29}$ s^{-1}).

In the best optical spectrum from the large collection of UVES spectra, namely C/2002 T7 (LINEAR) observed in May 2004 (see also below), OD lines in the bright ultraviolet OH $A\ ^2\Sigma^+ - X\ ^2\Pi_i$ system at 310 nm were looked for. The strength of the optical method for the measurements of isotopic ratios is that both normal and rare species have lines in the same spectral interval and are thus observed simultaneously, avoiding problems with the production rate determinations while the comet activity might be variable. Since no individual OD line could be detected, the 30 brightest OD lines (as predicted by the model) have been co-added. After removing a few of them, blended with other emissions, an average profile is built, after careful Doppler-shifting and weighting, using the best

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[1] Vienna Standard Mean Ocean Water.

observations carried out on May 6 and May 26, 2004. OD is detected as a faint emission feature on both dates. From the measurement of the line intensities OD/OH a mean D/H value of (2.5 ± 0.7) × 10^{-4} is obtained (Hutsemékers et al. 2008). This measurement is compatible with other values of D/H in cometary water and marginally higher than the terrestrial value.

5 $^{16}O/^{18}O$

Oxygen is the other constituent of water and the third most abundant element in the Universe. The first value of the oxygen ratio in a comet was again obtained by the in situ measurements aboard the Giotto spacecraft and gave $^{16}O/^{18}O = 495 \pm 37$ 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 $^{16}O/^{18}O = 530 \pm 60$, 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 [$^{16}O/^{18}O$ (VSMOW) = 499], although marginally higher.

The laboratory analyses of the silicate and oxide mineral grains from comet 81P/Wild 2 provided $^{16}O/^{18}O$ ratios also in excellent agreement with the terrestrial value. Only one refractory grain appeared marginally depleted in ^{18}O ($^{16}O/^{18}O = 576 \pm 78$) as observed in refractory inclusions in meteorites (McKeegan et al. 2006).

More recently, a new technique was used to derive the oxygen ratio. Among the spectra obtained with UVES at the VLT, the spectrum of C/2002 T7 (LINEAR) appeared good enough to detect a few ^{18}OH lines in the bright ultraviolet OH system at 310 nm allowing, for the first time, the determination of the $^{16}O/^{18}O$ ratio from ground-based observations (Fig. 3).

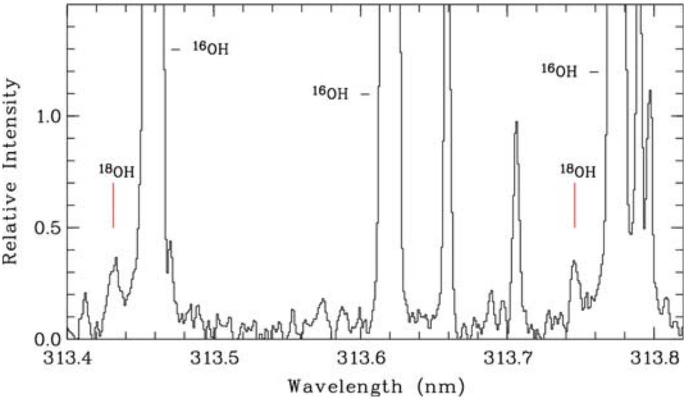

Fig. 3 A section of the UVES spectrum of the OH(1,1) band in comet C/2002 T7 (May 6, 2004) showing nicely the brightest expected ^{18}OH lines (Hutsemékers et al. 2008). Two other lines are also detected in the brighter OH(0,0) band but they are severely blended with the ~500 times stronger ^{16}OH line

From the ^{16}OH/^{18}OH ratio, ^{16}O/^{18}O = 425 ± 55 is derived, equal, within the uncertainties, to the terrestrial value and to the ratio measured in other comets, although marginally smaller (Hutsemékers et al. 2008). 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). New and more accurate measurements are clearly needed to decide if isotopic fractionation of oxygen occurs in cometary ices. The C/2002 T7 (LINEAR) data were not optimized for ^{16}OH/^{18}OH (or OD/OH) measurement, so that, with improved observing circumstances, this opens the possibility of measuring those ratios for moderately active comets that are visiting the inner solar system at a rate of about one per year.

6 ^{32}S/^{34}S

The only new measurement of this ratio (16 ± 3) has been obtained from sub-millimeter observations of CS at IRAM observatory during the outburst of comet 17P/Holmes (Biver et al. 2008). It agrees with the value (16 ± 3) determined from H_2S in Hale-Bopp by the same team (Crovisier et al. 2004), and it is marginally lower than the Earth value of 23 (Anders and Grevesse 1989) and the measurements in Halley by Giotto (23 ± 6, Altwegg 1996), as well as the value obtained from sub-millimeter observations of Hale-Bopp (27 ± 3) by Jewitt et al. (1997).

7 Challenges and Future Prospects

(1) The first challenge for the next 10 years is to continue to increase the number of isotopic measurements in comets of all families but especially in Jupiter Family comets (JFC). We should not forget that while more than 20 measurements are now available for some elements, like carbon and nitrogen, allowing rough statistical studies, the number of comets in the Solar System is estimated to be about 10^{12}. Moreover, important quantities like D/H and ^{16}O/^{18}O are still missing in JFC and clearly many more measurements are also needed for Oort cloud comets (OCC).

(2) At the same time it would be important to improve the accuracy of the determinations. Most often, D/H is only known within a factor of about two. So far no clear difference between comets of different origins could be detected. Even in the larger sample of about 20 comets for which ^{12}C/^{13}C and ^{14}N/^{15}N ratios were determined with about 10% and 20% accuracy at best, no trend can be observed (Fig. 2). Getting the uncertainties down to 5% will require (1) an important observational effort to improve the signal to noise ratio of the data, where larger telescopes will obviously help, and (2) better modelling, not only for the targeted species but also for the contaminating species. Reaching the real scatter for each isotope from comet to comet would provide invaluable information.

(3) The third challenge is to determine a given ratio from as many species as possible. Different species might have different sensitivities to local conditions, thus giving new information on their formation process. This has been done for D/H in comet Hale-Bopp using HDO and DCN lines (Meier et al. 1998a, b) which gave different D/H ratios. Also ^{14}N/^{15}N in comets Hale-Bopp and 17P/Holmes using C^{15}N and HC^{15}N lines (Bockelée-Morvan et al. 2008a, b) which finally gave similar values.

The measurement of $^{15}NH_2$ would be very important, as it is linked to ammonia, an important reservoir of nitrogen in comets and in the solar system (while CN is a trace species). Ammonia is linked to N_2 and the comparison with the ratio in the terrestrial atmospheric N_2 would then be more straightforward.

(4) To have a complete inventory of the isotopes in cometary material, they have to be measured simultaneously (in the same comet) within refractory and volatile species.

Thanks to the advent of large ground-based telescopes and space telescopes working in different wavelength ranges as well as complex spacecrafts, a lot of progress will be made for each of these goals within the next 10 years. Synergies will be welcome as each method can only give a limited part of the answers.

High resolution ($\lambda/\Delta\lambda \sim 10^5$) UV-Visible spectroscopy with instruments like UVES on the ESO VLT and HIRES on the Keck I telescope, give access for reasonable amount of telescope time to carbon and nitrogen ratios (via ^{13}CN, $C^{15}N$ and $^{12}C^{13}C$) for typical OCC's ($\sim$3/year) and bright JFC's ($\sim$1/year) and give also access to OD and ^{18}OH for bright OCC's ($\sim$1/year) as recently shown by Hutsemékers et al. (2008). They should also allow the detection of $^{15}NH_2$ for bright OCC's (work in progress); unfortunately, the isotopic shift for ^{15}NH with respect to ^{14}NH is too small to use the bright NH emission at 335 nm. A study of the C_2 Swan bands from the UVES spectra has been initiated to derive the carbon ratio (see first result by Rousselot et al. 2008). ND and ^{13}CH could be detected with UVES only for great comets (once in a decade).

We will have to wait until at least 2015 for an Extremely Large Telescope (ELT) like the 43 m European-ELT, with a collecting area 25× larger (allowing to go 3.5 mag fainter) and equipped with a spectrometer like CODEX (hopefully working also in the near UV range) to measure such rare species as OD, ^{18}OH, ND, $^{15}NH_2$, ^{13}CH in typical OCC's and bright JFC's, while it will allow routine measurements of ^{13}CN and $C^{15}N$, in typical JFC's and OCC's. With an ELT we could derive isotopic abundances for dozens of comets each year.

High resolution ($\lambda/\Delta\lambda \sim 10^5$) near-infrared (1–5 μm) spectroscopy with instruments like CRIRES at the ESO VLT and NIRSPEC at Keck II should be able to provide D/H from water (HDO lines) in bright OCC's ($\sim$1/yr) as shown by Villanueva et al. (2009). Depending on the level of enrichment in D, other deuterated species like CH_3D might also be detected in such comets (Kawakita and Kobayashi 2007). Those measurements will be possible for bright JFC's and typical OCC's only with an ELT.

Millimeter and submillimeter telescopes like the 30 m dish at IRAM, the 10 m Caltech Submillimeter Observatory (CSO) dish and the James Clerk Maxwell Telescope can detect $H^{13}CN$, $HC^{15}N$, $C^{34}S$ and HDO but only in exceptional comets. The situation will change after 2013 with the 64× 12-m submillimeters antennas (70–900 GHz) of the Atacama Large Millimeter Array (ALMA) project. Its huge collecting area on a unique dry observing site will give a tenfold improvement with respect to current radio facilities and allow to observe HDO and other deuterated molecules (DCN, HDCO, etc.) in typical OCC's and bright JFC's, while other isotopes (^{13}C,^{15}N, ^{34}S) will be detected in typical JFC's and OCC's. Mapping of D/H and other ratios will be possible in the brightest comets.

The first measurement of D/H in a JFC will most probably be done with Herschel, the 3.5 m European far IR (60–670 μm) space telescope and HIFI (Heterodyne Instrument for the Far Infrared), its very high resolution spectrometer (500–1250 GHz). By targeting the HDO (1_{10}–1_{01}) fundamental line at 509 GHz, D/H will be measured in the bright JFC, 103P/Hartley 2, in October 2010. $H_2^{18}O$ and $H_2^{17}O$ are also in the wavelength range of

Herschel and might also be obtained as well as D/H for a couple of bright OCC's during the expected 3 years of operations of the space observatory.

D/H ratios should be obtained for at least a dozen OCC's and half a dozen JFC's at the horizon of 2020, and several times more comets for the other isotopes. The use of many different facilities working in various wavelengths domains will help to get those ratios from various species.

The last challenge will be reached in 2015 by the ambitious ROSETTA space mission which will orbit the nucleus of low activity JFC 67P/Churyumov-Gerasimenko. The mass spectrometers of the orbiter, ROSINA and COSIMA, will, respectively, study in great detail the gas and dust (organic/inorganic) composition of the coma, while PTOLEMY MODULUS, the mass spectrometer of the PHILAE lander, will get all the light isotopes from different kind of surface material (dust, ices, organics, etc.) to at least 20 cm below the surface. We should note that the Microwave Instrument of the orbiter (MIRO) will also detect $H_2^{16}O$, $H_2^{17}O$ and $H_2^{18}O$ in the coma.

ROSETTA will then provide for the first time a detailed inventory of the light isotopes in refractory and volatile material of a comet. With the high precision of the data it should be possible to detect small variations of the isotopic ratios in the coma for instance from different jets coming from various active regions of the nucleus and trace the homogeneity of the material within the surface of the nucleus.

8 Conclusions

Even if comet 67P, the target of ROSETTA, is too weak for a study of the isotopes with ground-based telescopes, the comparison of the isotopic ratios measured in situ with those of other comets determined remotely will shed new light on the isotopic composition of comets in general. This is a good example of synergies between ground and space based observatories that will continue to bring important discoveries in the next 10 years. Will D/H in JFC's be the same as in OCC's? Space missions HERSCHEL and ROSETTA will be the first to make such measurements, but accurate measurements in a large sample of OCC's from ground-based telescopes, are also needed in order to get the best possible comparison. Will the $^{14}N/^{15}N$ ratios measured by ROSETTA from different species, located in the comet's coma (dust, gas) or in the nucleus (for instance organic compounds) be enriched the same way in ^{15}N as observed for the CN gaseous emission of other comets? or will they display an Earth (272 from atmospheric N_2) or Jupiter like value (435 ± 58 from NH_3, Owen et al. 2001)? This will have important consequences on the chemical history of the solar system and on the comet formation. Will $^{16}O/^{18}O$ and $^{32}S/^{34}S$ have isotopic anomalies in comet comae as some data might suggest? There are so far only few measurements and the error bars are large. Again, only large telescopes and comet rendezvous could help find the answers. All the data that will be collected in the next decade from different facilities targeting different species coming from different cometary material will offer a much better view of the isotopic composition of comets.

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