Asteroids, Comets, Meteors 2005
Proceedings IAU Symposium No. 229, 2005
D. Lazzaro, S. Ferraz-Mello & J.A. Fernández, eds.
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doi:10.1017/S174392130500671X

The molecular composition of comets and its interrelation with other small bodies of the Solar System

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Abstract. The present status of our knowledge of the composition of cometary nuclei is reviewed and compared with what we know on the composition of other Solar System minor bodies — interplanetary dust, meteorites, asteroids, trans-Neptunian objects. The current methods of investigations — by both in situ analysis and remote sensing — are described. Comets are active objects pouring their internal material to form a dusty atmosphere which can be investigated by remote sensing. This is not the case for minor planets and trans-Neptunian objects for which only the outer surface is accessible. Collected interplanetary dust particles and meteorites can be analysed at leisure in terrestrial laboratories, but we do not know for certain which are their parent bodies.

Considerable progresses have been made from spectroscopic observations of active comets, mainly at infrared and radio wavelengths. We probably know now most of the main components of cometary ices, but we still have a very partial view of the minor ones. The elemental composition of cometary dust particles is known from in situ investigations, but their chemical nature is only known for species like silicates which have observable spectral features. A crucial component, still ill-characterized, is the (semi-)refractory organic material of high molecular mass present in grains. This component is possibly responsible for distributed sources of molecules in the coma. A large diversity of composition from comet to comet is observed, so that no "typical comet" can be defined. No clear correlation between the composition and the region of formation of the comets and their subsequent dynamical history can yet be established.

Keywords. astrochemistry, comets, asteroids, Centaurs, trans-Neptunian objects, molecules, spectroscopy

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1. Introduction

Small bodies of the Solar System — comets, asteroids, trans-Neptunian objects (TNOs), even some planetary satellites — are interrelated in such a way that in many instances, transition objects have been identified and that a stringent separation between these different categories can no longer be made. Very small bodies — interplanetary dust particles (IDPs), meteors, meteorites —, which are mere decay products of these larger bodies, are also closely related. Even the line between *minor* and *major* planets is difficult to draw.

Indeed, all small bodies of the Solar System were presumably formed from the accretion of planetesimals, whose composition depends upon the epoch and the location of their formation in the primitive Solar Nebula. Therefore, the chemical compositions of all these minor bodies and the chemical processes governing their formation and evolution must be studied globally, in order to assess the interrelation between these objects and to achieve a general view of the Solar System formation and history.

In this context, I can only stress out the frustration of a cometary scientist who attempts to compare the clues to the rich and complex molecular content of comets with the

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Table 1. A synopsis of the means of investigation of the composition of comets and other small bodies of the Solar System.

Body[a]	remote sensing (from Earth or Earth orbit)	in situ (space mission)	sample return (lab. analysis)
Comets: nuclei	≈10[b]	*VEGA, Giotto* : 1P/Halley *Deep Space 1* : 19P/Borrelly *Stardust* : 81P/Wild 2 *Deep Impact* : 9P/Tempel 1 *Rosetta* : 67P/Churyumov-G.[c]	—
Comets: comae and tails	many	*ICE* : 21P/Giacobini-Zinner *VEGA, Giotto* : 1P/Halley *Giotto* : 26P/Grigg-Skjellerup *Deep Space 1* : 19P/Borrelly *Stardust* : 81P/Wild 2 *Deep Impact* : 9P/Tempel 1 *Rosetta* : 67P/Churyumov-G.[c]	*Stardust* : 81P/Wild 2[d]
Asteroids	many	*Galileo* : (951) Gaspra *Galileo* : (243) Ida + Dactyl *NEAR* : (253) Mathilde *NEAR* : (433) Eros *Deep Space 1* : (9969) Braille *Stardust* : (5535) Annefranck	*Hayabusa* : (25143) Itokawa[c]
TNOs	many	—	—
IDPs	zodiacal light	—	*Stardust*[d] stratospheric collect
Meteoroids	many	—	—
Meteorites	—	—	many

[a] Planetary satellites are not included.
[b] Comet nuclei with known albedo and colour.
[c] Pending success of mission.
[d] Pending return of sample.

sparse information available on the composition of asteroids and TNOs (Tables 1 & 2). Space missions have explored only six comets and seven asteroids so far, providing chemical information for only a few of them.

The present review relies on other, available reviews (e.g., in the *Comets II* and *Asteroids III* books) and concentrates on recent, new results. This study is not extended here to a comparison with protostellar objects and interstellar matter (this topic is covered in *Comets II* and the *Protostars and Planets* series of books).

Many related reviews are given in this Symposium. The most relevant ones are those by M.A. Barucci (surface properties of TNOs), J. Borovička (composition of meteoroids), C.R. Chapman (physical properties of small bodies), I. Mann (IDPs), R. Schulz (investigations of gas and dust in cometary comae), S.S. Sheppard (relations with irregular planetary satellites), and I. Toth (relations with asteroids).

2. Surfaces and nuclei: albedos, colours, reflectance spectra and densities

For inactive bodies, the only information on their composition available from remote sensing concerns their surface properties: albedo, colour, and reflectance spectrum.

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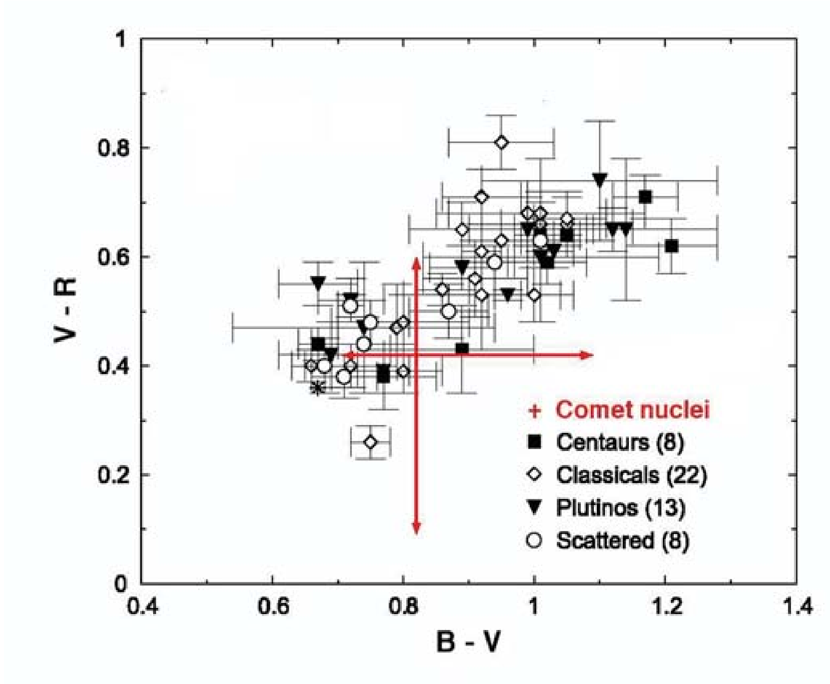

Figure 1. V–R vs B–V for TNOs and Centaurs (from Barucci et al. 2005) and for cometary nuclei. The cross with arrows indicates the mean value and range of variation from comet to comet (from Lamy *et al.* 2005). The star indicates the solar values.

Ironically, this information can only difficultly be obtained for comet nuclei, because at a distance, the nucleus signal cannot be easily separated from the strong signals of cometary dust and gas. Near-infrared spectroscopy, which is adequate for the identification of minerals and ice species, could only be performed from space by *Deep Space 1* on the nucleus of 19P/Borrelly, by *Deep Impact* on 9P/Tempel 1, and from the ground on a few comets (2P/Encke, 28P/Neujmin 1, 124P/Mrkos, 162P/Siding Spring and C/2001 OG_{108} (LONEOS)). As far as we know, bare comet nuclei do not show any sign of the molecular complexity of these bodies.

For all small bodies, the surface may be quite different from the inner material. This is due to the long-term chemical and physical processing by solar and cosmic radiation. For asteroids and TNOs, this process is know as *space weathering*. For comets, in addition to chemical processing due to irradiation, cometary activity itself leads to sublimation fractionation of the outer ice layers, and to the possible building up of a crust of dust particles too heavy to be dragged away by gas.

2.1. *Albedos and colours*

The albedos of comet nuclei (recently reviewed by Lamy *et al.* 2005) are found in a very narrow range, from 0.02 to 0.06 (except for 29P/Schwassmann-Wachmann 1 for which the albedo is possibly 0.13). TNOs and Centaurs have similar or higher values (when they are known). For instance, the two Centaurs Chiron and Asbolus have $A = 0.17$ and 0.12, respectively.

Some near-Earth asteroids (NEAs) could be disguised comets, as can be suggested by their low albedos (Stuart & Binzel 2004; Fernández *et al.* 2005). 15% of the NEAs could be dead comets.

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Table 2. Identified chemical compounds in Solar System small bodies.

Body	volatiles	semi-refractories	refractories
Comets	many (≈25)	indirect	some
TNOs and Centaurs	some (≈5)	indirect	?
Asteroids	—	?	yes
IDPs	—	yes	some
Meteorites (CC)	—	many	many

Figure 1 shows V–R vs B–V for TNOs, Centaurs and 14 comet nuclei. The colours of comet nuclei are not as red as some TNOs, and closer to the solar values. They do not show a diversity as large as that observed for TNOs.

2.2. *Reflectance spectroscopy*

Water ice has been detected at the surface of several Centaurs (2060 Chiron, 5145 Pholus, 10199 Chariklo) and trans-Neptunian objects (1996 TO_{66}, 1999 DE_9, 1999 DC_{36}, 50000 Quaoar, maybe 20000 Varuna). Pluto, Charon and Triton also show ice (de Bergh 2004). Several other ices have been also identified at the surface of these large bodies of the outer Solar System: CO, CO_2, CH_4, N_2, possibly NH_3 and CH_3OH (Cruikshank 2005).

Water ice was *not* detected at the surface of the nucleus of 19P/Borrelly in the 1.3–2.5 μm spectrum observed during its flyby by *Deep Space 1* (Soderblom *et al.* 2004; Fig. 2). The spectrum is featureless except for a puzzling, unidentified feature at 2.39 μm. A possibly related feature was observed by *Cassini/VIMS* at 2.41 μm on Saturn's retrograde satellite Phoebe (Clark *et al.* 2005; Fig. 2) and at 2.44 μm on Iapetus (Buratti *et al.* 2005), tentatively attributed to cyanides.

Other spectra of cometary nuclei are also featureless. So, there is exposed ice on the surface of TNOs and Centaurs, but apparently not on the surface of cometary nuclei. Cometary ice should be below the dust mantle.

2.3. *Densities*

An indirect clue to the composition of small bodies is their bulk density. A low density points to an icy and/or porous material, as expected for comet nuclei. Density evaluations are now available for many asteroids which are double or have satellites (some of them having densities just above 1000 kg m^{-3}), and for a single TNO (1999 TC_{36} which has a density of 550–800 kg m^{-3}; Stansberry *et al.* 2005). For comet nuclei, information is more sparse and present evaluations bear on the modelling of non-gravitational forces or on considerations on the rotation period and shape: they do not lead to stringent estimates (Weissman *et al.* 2005). A density ≈600 kg m^{-3} was derived from the kinematics of the ejecta of 9P/Tempel 1 following the *Deep Impact* experiment (A'Hearn *et al.* 2005b, 2006).

Some planetary satellites could be captured comets, Centaurs or TNOs. This should be the case for the irregular satellites with highly eccentric and/or highly inclined orbits of the giant planets (Jewitt & Sheppard 2005; Sheppard 2006). The case for Phoebe was noted above. Another interesting case is Jupiter's satellite Amalthea. Its density was measured by *Galileo* to be 857 ± 99 kg m^{-3}, suggesting porosity and a high abundance of water ice (Anderson *et al.* 2005).

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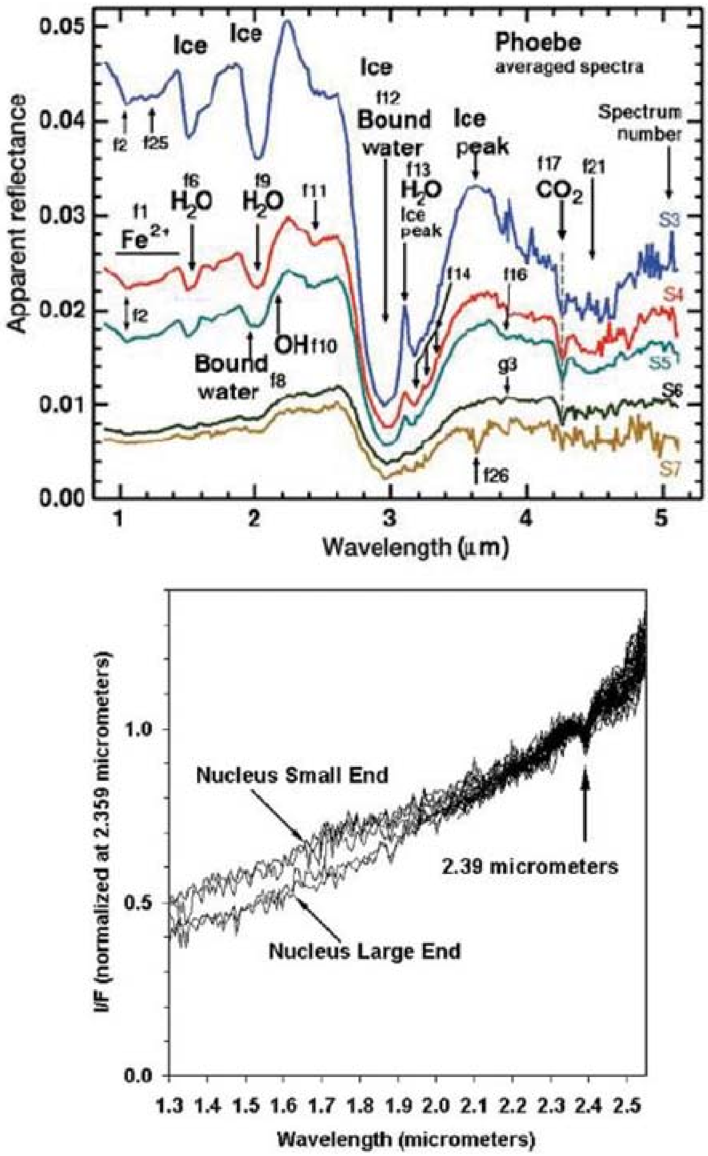

Figure 2. Surface spectroscopy of Saturn's retrograde satellite Phoebe (top) and of the nucleus of 19P/Borrelly (bottom). The satellite spectrum shows the features of several ices, in contrast to the comet spectrum which is almost featureless. Both spectra show a puzzling feature near 2.4 μm. (From Clark *et al.* 2005 and Soderblom *et al.* 2004.)

3. Spectroscopy of released material

For comets, we have the chance, as noted above, to observe material released from the surface or sub-surface of the nucleus. This contrasts with asteroids and TNOs which are inactive objects. Recent reviews on the spectroscopy of cometary comae were published by Bockelée-Morvan *et al.* (2005a), Despois *et al.* (2006) and Feldman *et al.* (2005). See also Crovisier (2004) and Schulz (2006).

Comet nuclei are composed of volatiles (ices, whose sublimation is the motor of cometary activity), refractories (yielding dust tails), and *semi-refractories*. The gross composition

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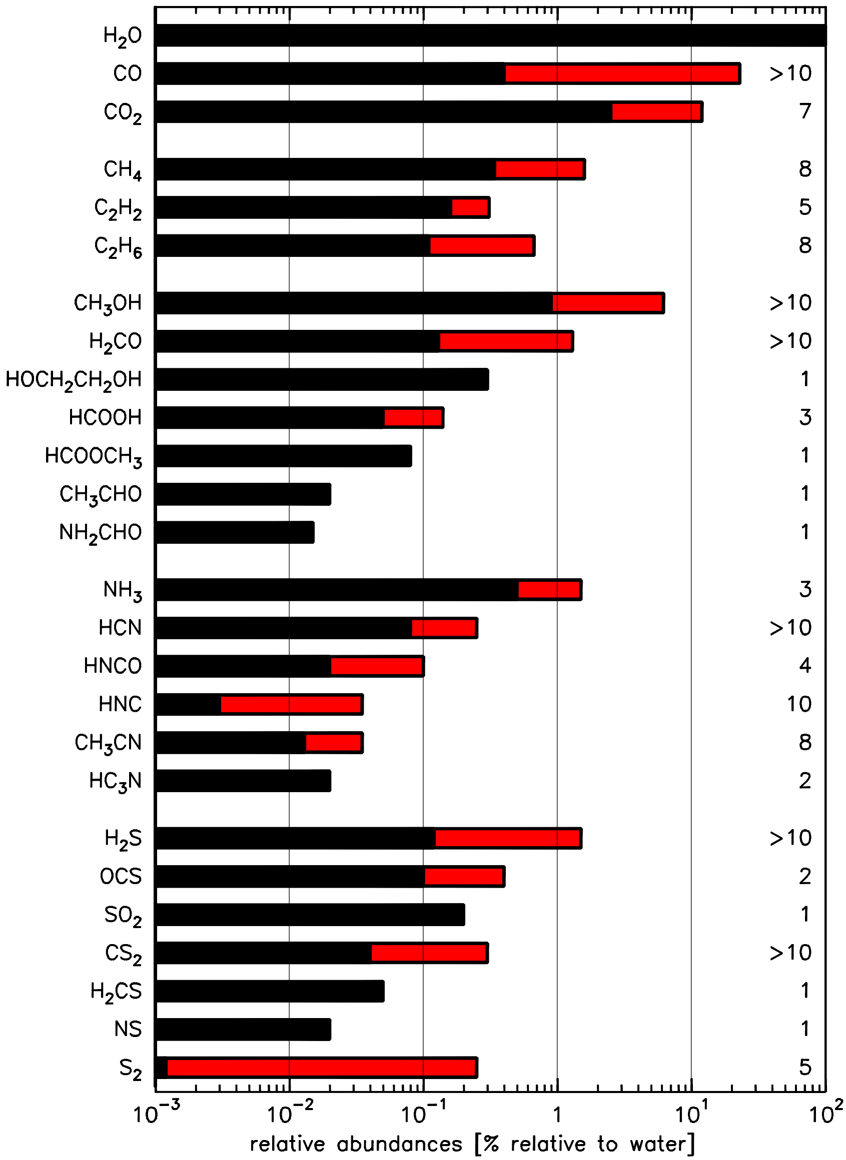

Figure 3. Relative production rates of cometary volatiles and their comet-to-comet variations. These rates are believed to trace the relative abundances in cometary ices. The grey part of each bar indicates the range of variation from comet to comet. On the right, the number of comets in which the species was detected is indicated. CO_2 data include direct infrared measurements as well as indirect measurements from CO prompt emission in the UV. CS_2 data include indirect determinations from UV and radio observations of the CS radical. Some species (e.g., H_2CO) are known to come (in part) from extended sources, not directly from the nucleus ices. The origins of NS and S_2 are ill-understood. (Updated from Bockelée-Morvan *et al.* 2005a.)

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Table 3. Upper limits on the relative abundances of selected species obtained in C/1995 O1 (Hale-Bopp). (Adapted from Crovisier *et al.* 2004.)

Molecule		$X/Q[H_2O]$ [a)]
Propyne	CH_3CCH	< 0.045
Ethanol	C_2H_5OH	< 0.10
Ketene	CH_2CO	< 0.032
Acetic acid	CH_3COOH	< 0.06
Dimethyl ether	CH_3OCH_3	< 0.45
Glycolaldehyde	CH_2OHCHO	< 0.04
Glycine I	NH_2CH_2COOH	< 0.15
Cyanodiacetylene	HC_5N	< 0.003
Methyl mercaptan	CH_3SH	< 0.05

[a)] For $Q[H_2O] = 100$

of volatiles is now fairly well known from the investigation of the gas coma that formed following their sublimation (see below). Refractories will also be discussed briefly below. *Semi-refractories* are only indirectly known. They are presumably high molecular-mass molecules, responsible for the *extended sources* that release simple molecules in the coma, following pyrolysis (thermal degradation) or UV photolysis. They are probably akin to the so-called *insoluble organic fraction* of meteorites (carbonaceous chondrites — Botta & Bada 2002) and to *tholins*, which are laboratory analogues of ices processed by radiation.

About 25 stable volatile molecules, likely to have sublimated from nucleus ices, are now known. Figure 3 shows a synopsis of the relative production rates of these molecules. Altogether, about 45 molecular species, radicals or molecular ions are identified in cometary atmospheres. This is to be compared with about 130 species (not counting isotopologues) which are known in the interstellar medium. But to be fair we must consider that all these interstellar molecules are not observed in the same classes of objects: some are specific to interstellar hot cores, or dark clouds, or circumstellar envelopes. Indeed, in protoplanetary discs, whose composition is directly relevant to comets, only a handful of molecules are observed in the gas phase (CO, HCN, HNC, CN, CS, H_2CO, HCO^+, C_2H...), because these small objects are difficult to investigate with present instrumentation and because most molecules are trapped as ices (Dutrey *et al.* 2005). On the other hand, many more complex organic molecules are identified from laboratory analyses of carbonaceous chondrites (Botta & Bada 2002).

Last news on detected species at radio wavelengths in comet Hale-Bopp, as well as upper limits on some rare species, may be found in Crovisier *et al.* (2004a, b). Limits obtained on a selection of species are listed in Table 3. Biver *et al.* (2005b, 2006) report detections of HC_3N and HCOOH, previously only observed in comet Hale-Bopp, in recent comets. High-resolution infrared cometary spectra are invaluable, especially for the observation of hydrocarbons (e.g., Mumma *et al.* 2003). However, they have not yet been fully exploited. For instance, the lines of ammonia, detected in at least two comets, have not been analysed yet, and upper limits on many species (e.g., C_2H_4) are still to be worked out.

As could be intuitively expected, the abundances of molecules are generally decreasing when the complexity is increasing. This is clear for homologous series of molecules (Table 4). However, some really complex molecules (as ethylene glycol discussed below) have unexpectedly high abundances.

The direct determination of water production rates in comets is now made easier by the observation of water hot bands in the infrared (e.g., Dello Russo *et al.* 2005) and

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Table 4. Homologous series of cometary molecules.

Alkanes	CH_4 methane	C_2H_6 ethane	C_3H_8 propane
Alcohols	CH_3OH methanol	C_2H_5OH ethanol	C_3H_7OH propanol
Aldehydes	H_2CO formaldehyde	CH_3CHO acetaldehyde	C_2H_5CHO propionaldehyde
Carboxylic acids	HCOOH formic acid	CH_3COOH acetic acid	C_2H_5COOH propionic acid
Cyanopolyynes	HCN hydrogen cyanide	HC_3N cyanoacetylene	HC_5N cyanodiacetylene

Molecules framed with a heavy line are those which are detected.
Molecules framed with a light line are those for which an upper limit is available.

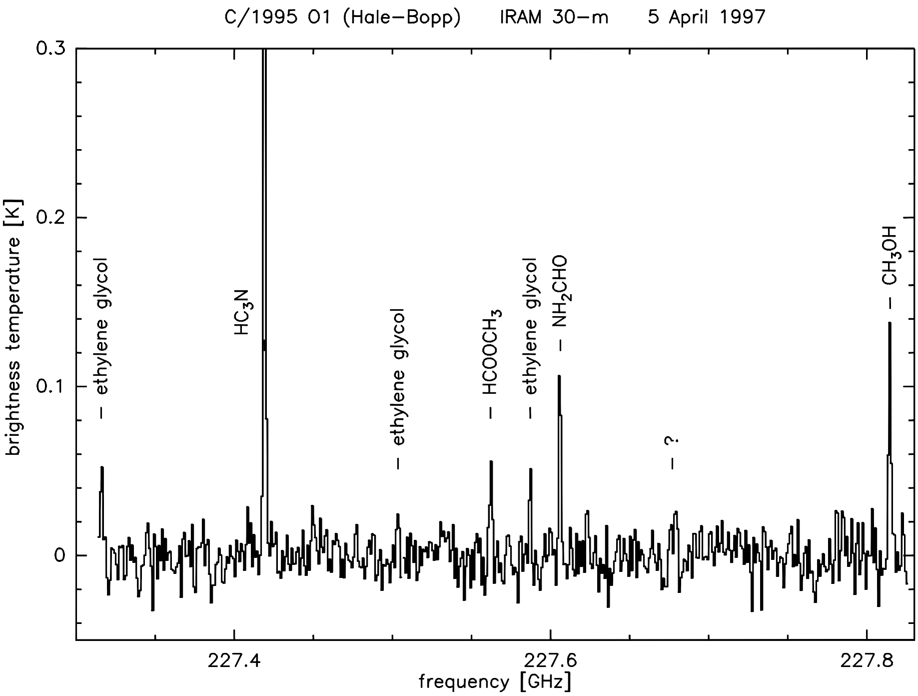

Figure 4. Detection of the radio lines of ethylene glycol and other complex organic species in C/1995 O1 (Hale-Bopp) with the *IRAM* 30-m telescope (Crovisier *et al.* 2004a).

of the submillimetric 557 GHz line with the orbital observatories *SWAS* (e.g., Bensch *et al.* 2004) and *Odin* (Lecacheux *et al.* 2003; Hjalmarson *et al.* 2005; Biver *et al.* 2005a; Fig. 5). The interpretation of these measurements, for which a radiative transfer treatment of optically thick lines is crucial, now benefits from new-generation modelling of the rotational lines of water (Bensch & Bergin 2004; Zakharov *et al.* 2005).

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3.1. *New species*

Acetaldehyde (CH_3CHO) was confirmed by the serendipitous presence of a line in a radio spectrum of comet Hale-Bopp secured with the IRAM interferometer (Crovisier *et al.* 2004b).

Ethylene glycol ($HOCH_2CH_2OH$) was identified through the presence of several lines in millimetric spectra of comet Hale-Bopp as soon as molecular data of this molecule were made available (Crovisier *et al.* 2004a; Fig. 4). Its production rate (≈0.25% that of water) makes it one of the most abundant organic molecules in cometary ices, despite its complexity. It is the third "CHO" molecule by order of abundance, after methanol and formaldehyde. Remarkably, this dialcohol is more abundant than ethanol (C_2H_5OH) or the related molecule glycolaldehyde (CH_2OHCHO), with could not be found with respective upper limits $< 0.10\%$ and $< 0.04\%$. In the interstellar medium, glycol aldehyde was recently observed in the Galactic Centre source Sgr B2 (Hollis *et al.* 2002), but its abundance relative to methanol and ethanol is quite smaller.

Molecular hydrogen (H_2) was observed by Feldman *et al.* (2002) in comet C/2001 A2 (LINEAR) with *FUSE*. However, this is not a pristine molecule coming from nucleus ices. It is rather a product of the photolysis of water and other molecules.

Carbon disulfide (CS_2) has been suspected for a long time to be the progenitor of the CS cometary radical. It was recently tentatively identified in the visible spectrum of comet 122P/de Vico (Jackson *et al.* 2004).

3.2. *Uncomfortable detections*

For a detection to be reliable, several of the following criteria should be met:

- a good signal-to-noise ratio;
- line shape and centre (when a good spectral resolution is available) as expected for the coma kinetics;
- several lines observed simultaneously, with relative intensities that make sense;
- observations at different times and/or in different comets, possibly by different telescopes and/or different teams.

This is not yet the case for some claimed molecular detections in comets, for which confirmation by further observation is needed:

- Thioformaldehyde (H_2CS): its detection relies on a single radio line with low signal-to-noise ratio (Woodney *et al.* 1999).
- NS radical: the detection of this unexpected radical relies on the observation of a couple of radio lines (Irvine *et al.* 2000). Neither H_2CS nor NS could be confirmed by Crovisier *et al.* (2004b).
- Acetaldehyde (CH_3CHO) has been observed in a single radio line with a decent signal-to-noise ratio, plus marginal lines (Crovisier *et al.* 2004b).
- For methyl formate ($HCOOCH_3$), a single radio line, which is a blend of several rotational transitions, has been observed with a low spectral resolution (Bockelée-Morvan *et al.* 2000).
- Diacetylene (C_4H_2), tentatively detected in the infrared spectrum of 153P/Ikeya-Zhang (Magee-Sauer *et al.* 2002), has not yet been confirmed in other comets.
- The detection of N_2^+ in the visible, on which relies the evidence of N_2 in cometary ices, appears to be highly controversial, since it could not be confirmed in high-resolution spectra of recent comets (Cochran *et al.* 2000; Cochran 2002). N_2 was not detected in *FUSE* spectra either (Feldman *et al.* 2004).
- For carbon disulfide (CS_2) tentatively identified in the visible (Jackson *et al.* 2004; see above), no quantitative analysis of the signal have yet been made, pending laboratory measurements of the band strengths.

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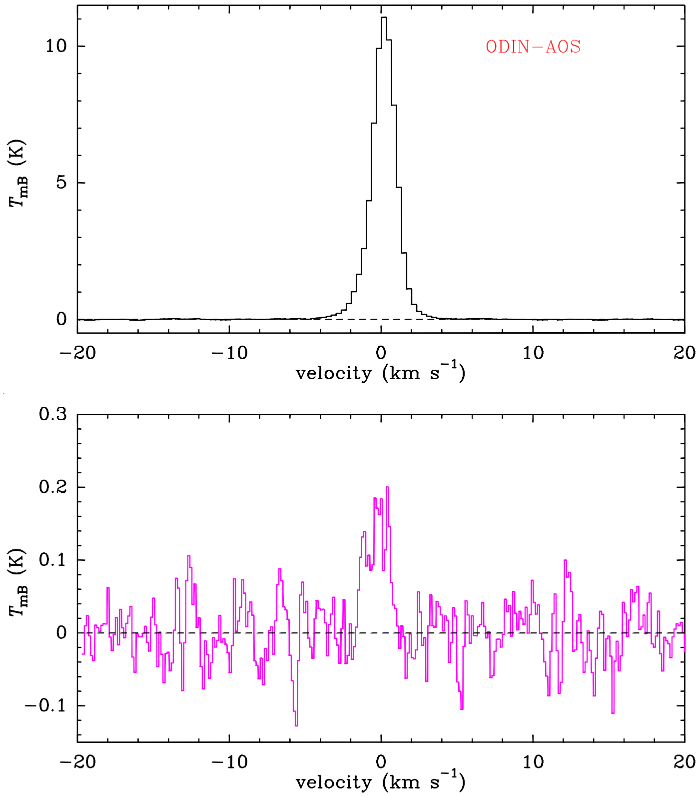

Figure 5. Spectra of the $H_2^{16}O$ (top) and $H_2^{18}O$ (bottom) 1_{10}–1_{01} millimetric lines observed by the *Odin* satellite in comet C/2001 Q4 (NEAT) from 26 April to 1 May 2004 (from Hjalmarson *et al.* 2005).

• Species only detected from mass spectroscopy — e.g., CH_2, C_2H_4, C_3H_2 (Altwegg *et al.* 1999) — are subject to mass ambiguity and to delicate modelling of ion chemistry in the cometary environment.

3.3. *Isotopes*

A detailed review on isotopic analyses of comets was published by Altwegg & Bockelée-Morvan (2003). See also Robert *et al.* (2000) for a discussion of the D/H ratio in the Solar System.

No recent progress has been made on the D/H ratio in cometary water despite sensitive attempts to detect HDO at infrared (Gibb *et al.* 2002) and radio wavelengths (Biver *et al.* 2005b, 2006; significant upper limits D/H < 0.00027 and < 0.00022 were obtained for 153P/Ikeya-Zhang and C/2004 Q2 (Machholz), respectively). Thus the D/H ratio is only precisely known for three comets — 1P/Halley, C/1996 B2 (Hyakutake) and C/1995 O1 (Hale-Bopp) —, all from the Oort cloud, all having D/H $\approx$0.0003. Further progress must await *Herschel*, *ALMA* and *Rosetta* or a really bright new comet. On the other hand, HDO was observed in the envelope of IRAS 16293–2422 and in the protoplanetary disc surrounding DM Tau, which are two solar-type protostars (Parise *et al.* 2005; Ceccarelli *et al.* 2005); D/H ratios 10–100 times higher than in cometary water are found.

For the first time in a comet, atomic deuterium was directly detected through its Lyman α line in C/2001 Q4 (NEAT) line with the *STIS* instrument of the *Hubble Space*

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Table 5. Spin temperatures observed in comets. Adapted from the compilation of Kawakita *et al.* (2004), and updated with recent results from Kawakita *et al.* (2005) and Dello Russo *et al.* (2005).

Comet	H_2O [K]	NH_3 [K]	CH_4 [K]	orbital period [yr]
1P/Halley	29 ± 2			76
C/1986 P1 (Wilson)	> 50			dynamically new
C/1995 O1 (Hale-Bopp)	28 ± 2	26^{+10}_{-4}		4 000
103P/Hartley 2	34 ± 3			6.4
C/1999 H1 (Lee)	30^{+15}_{-6}			dynamically new
C/1999 S4 (LINEAR)	$\geqslant 30$	27^{+3}_{-2}		dynamically new
C/2001 A2 (LINEAR)	23^{+4}_{-3}	25^{+1}_{-2}		40 000
153P/Ikeya-Zhang		32^{+5}_{-4}		365
C/2001 Q4 (NEAT)			33^{+3}_{-2}	dynamically new

Telescope (Weaver *et al.* 2004). The interpretation of this measurement, which is still in progress, could provide another determination of the D/H ratio in cometary water, provided the photolysis of deuterated water is well understood, and the contribution (expected to be minor) of other species to deuterium is evaluated.

New, sensitive limits on monodeuterated methane, for which a higher D/H ratio could be expected, were obtained by Kawakita (2005) and Kawakita *et al.* (2005). The limit $D/H > 0.01$ obtained for comet C/2001 Q4 (NEAT) suggests a methane formation at a temperature higher than 30 K.

Puzzling results were obtained for the $^{14}N/^{15}N$ ratio. Arpigny *et al.* (2003), Jehin *et al.* (2004), Manfroid *et al.* (2005) and Hutsemékers *et al.* (2005) have consistently observed $^{14}N/^{15}N \approx 150$ from high-resolution visible spectra of the CN radical in several comets, whereas $^{14}N/^{15}N$ was 300 (close to the terrestrial value) from a radio line of HCN observed in comet Hale-Bopp (Jewitt *et al.* 1998). In contrast, the $^{12}C/^{13}C$ ratio is found to be 90 ± 4 in CN for the whole sample, close to the terrestrial ratio. This points to an additional source of CN, other than HCN and heavily enriched in ^{15}N, which is still to be identified. High molecular weight organics such as polymerized cyanopolyynes were invoked. But surprisingly, the $^{14}N/^{15}N$ ratio does not vary from comet to comet, whereas these objects had strongly different dust-to-gas ratios. Other possible evidences of additional sources of CN are reviewed by Fray *et al.* (2005a).

The $^{16}O/^{18}O$ ratio in water was observed with the *Odin* satellite to be close to the terrestrial ratio (≈500) in four comets (Lecacheux *et al.* 2003; Biver *et al.* 2005c; Fig. 5). However, this ratio, which is evaluated from the comparison of a thin line and a heavily saturated line, is sensitive to modelling issues. This result could put constraints to some chemical models of protosolar nebulae which predict a significant enrichment of ^{18}O in cometary water (up to 20%), due to a self-shielding effect in the photolysis of CO (Qing-zhu Yin 2004).

3.4. *Spin species*

The ortho-to-para ratios (spin temperatures), now measured in three cometary molecules — water, ammonia, and methane —, are puzzling (see Kawakita *et al.* 2004 and Table 5 for a review on recent results; see also see Kawakita *et al.* 2005 for recent results on methane and Dello Russo *et al.* 2005 for further results on water spin temperatures). The observed spin temperatures are remarkably close to 30 K, whatever the molecule, the comet heliocentric distance or its dynamical history. What is the signification of this temperature? Although inter-spin conversions are strongly forbidden during non-destructive

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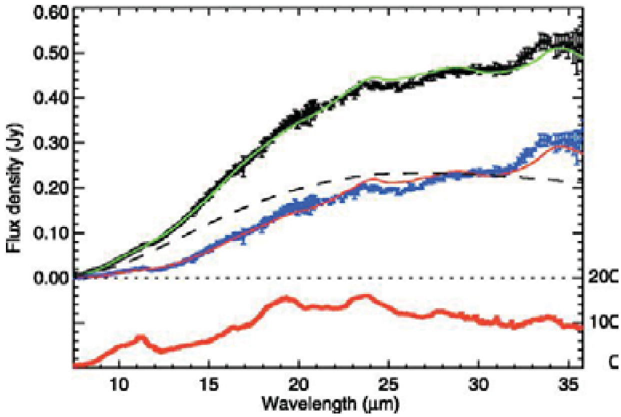

Figure 6. The infrared spectrum of 29P/Schwassmann-Wachmann 1 observed by *Spitzer*, with modelled spectra including forsterite and amorphous olivine. The *ISO* spectrum of comet Hale-Bopp is shown at the bottom for comparison. (From Stansberry *et al.* 2004.)

collisions or radiative transitions, preservation of the spin state over cosmological times is not universally accepted. This is still to be checked by laboratory simulations on analogs of cometary ices. Therefore, the present spin temperatures may not reflect the temperatures at the formation of the molecules. On the other hand, equilibration within the coma or at the comet surface would lead to spin temperatures depending on the heliocentric distance. A spin temperature in equilibrium with the internal temperature of the nucleus would depend upon the comet orbital history and differ between short-period and long-period comets.

3.5. *Unidentified spectral features*

Many unidentified spectral features have been spotted and catalogued in the UV (especially from recent observations by *FUSE*; Feldman *et al.* 2005) and in the visible (see, e.g., comprehensive atlases by Cochran & Cochran 2002, and Capria *et al.* 2005) spectra of comets: they are presumably coming from atoms, radicals and ions rather than from molecules. Identification should benefit from new, reliable databases of molecular lines. The NH_2 radical is still a good candidate for identifications. It has been noted (Wyckoff *et al.* 1999; Kawakita & Watanabe 2002) that some features are correlated with H_2O^+, and thus related to water ion chemistry.

In the infrared, several lines are reported consistently from comet to comet by the Mumma *et al.* group. Some of them could be due to radicals rather than simple small molecules. This is the case of of OH prompt emission, which is still to be fully understood (Bonev *et al.* 2004). Methanol is an important contributor to emission lines in the 3.3 μm region, but a comprehensive modelling of the fluorescence of this molecule is still to be done. No significant progress has been made on the emission of PAHs since the analysis of Bockelée-Morvan *et al.* (1995). (However, PAHs bands at 6–7 μm were observed in 9P/Tempel 1 with *Spitzer* following the *Deep Impact* event; Lisse *et al.* 2005a, 2005b.)

At radio wavelengths, some unidentified lines are still present, but with limited signal-to-noise ratios (Crovisier *et al.* 2004b).

3.6. *Dust*

Mid-infrared observations from space proved to be adequate for the identification of cometary dust silicates. The breakthrough performed by the identification of Mg-rich silicates (forsterite) from observations of the 2.5–45 μm spectrum of comet Hale-Bopp

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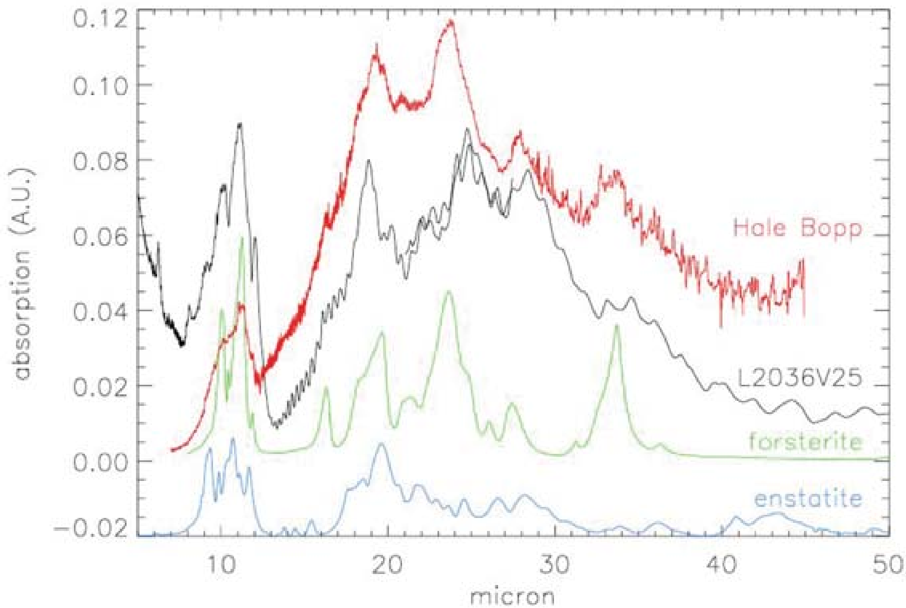

Figure 7. Comparative mid-IR spectra of C/1995 O1 (Hale-Bopp) observed with *ISO* (Crovisier *et al.* 1997) and of the IDP L2036V25 (Molster *et al.* 2003).

(Crovisier *et al.* 1997, 2000; Hanner *et al.* 2005) with the *Infrared Space Observatory* (*ISO*) is now supplemented by observations with the *Spitzer Space Telescope* (e.g., 29P/Schwassmann-Wachmann 1 by Stansberry *et al.* 2004, see Fig. 6; C/2004 Q2 (Machholz) by Wooden et al., *in preparation*; 9P/Tempel 1 by Lisse *et al.* 2005a, b). All these spectra show similar silicate emissions. *Spitzer* observations of Trojans also show similar silicate emissions (e.g., (624) Hektor; Emery *et al.* 2005). *ISO* observations of zodiacal light also revealed the signature of silicates at 10 μm (Reach *et al.* 2003).

Among recent analyses on the composition of cometary dust, one can note a study of the composition and size distribution of the dust of comet Hale-Bopp by Min *et al.* (2005); a comparison between cometary and circumstellar dust from observations of the dust around star HD 69830 by Beichman *et al.* (2005); a comparison of cometary dust and IDPs which emphasizes the similarity of their mid-infrared spectra (Molster *et al.* 2003; Fig. 7).

4. Extended sources of molecules in cometary comae

The case for a possible extended source of cometary carbon monoxide is a highly debated question. Interferometric radio observations of CO in comet Hale-Bopp did not show evidence of an extended source (Henry 2003; Bockelée-Morvan *et al.* 2005b and *in preparation*), in contrast with infrared observations (DiSanti *et al.* 2001). The existence of an extended source of CO in comet 29P/Schwassmann-Wachmann 1 advocated by Gunnarsson *et al.* (2002) is being revisited on the basis of observations obtained with the *HERA* mapping array at the *IRAM* 30-m telescope (Gunnarsson et al., *in preparation*).

The evidence of a distributed source of cometary formaldehyde is more firmly established. Cottin *et al.* (2004) and Fray *et al.* (2004, 2005b) have investigated in the laboratory the release of H_2CO from polyoxymethylene (POM) following UV photolysis or thermal degradation. They showed that this latter process could explain the *Giotto*

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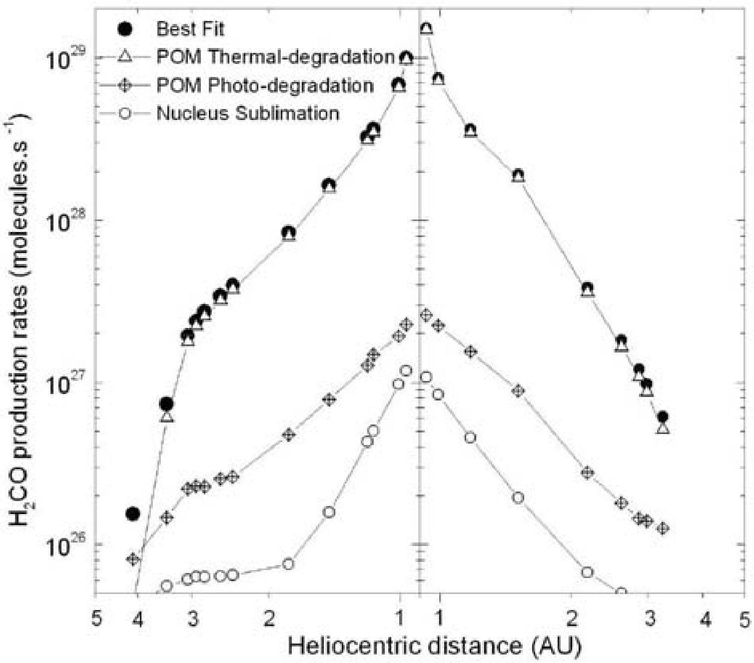

Figure 8. The contributions of various sources of formaldehyde as a function of heliocentric distance for C/1995 O1 (Hale-Bopp), according to the model of Fray *et al.* (2005b).

observations of formaldehyde in 1P/Halley, as well as the production of H_2CO in comet Hale-Bopp and its evolution with heliocentric distance (Fig. 8). Of course, this does not prove that POM is indeed the source of cometary formaldehyde, but it suggests that POM-like polymers might be present on cometary grains.

The case for hydrogen isocyanide HNC is still an open problem. Possible formation mechanisms involving ion–molecule reactions, isomerisation of HCN, or the degradation of cyanopolyyne polymers have been invoked (Rodgers & Charnley 1998; Fray *et al.* 2005a). This problem is discussed by Biver *et al.* 2005b and Bockelée-Morvan *et al.* 2005c), on the basis of observations of the HNC/HCN ratio as a function of heliocentric distance and of interferometric maps of HNC in C/1995 O1 (Hale-Bopp).

5. In situ investigations and sample returns

Direct chemical analyses can be made by in situ exploration or on returned samples.

5.1. *In situ analyses*

In situ analyses of the coma of 1P/Halley were performed by mass spectroscopy with *VEGA* and *Giotto* (e.g., Altwegg *et al.* 1999; Jessberger & Kissel 1991). They will be repeated with improved sensitivity and resolution with the *Rosetta* instrumentation. Much more information is expected on complex cometary molecules from in situ analyses after the landing on the nucleus of 67P/Churyumov-Gerasimenko of *Philae*, which is equipped with mass spectrometers and gas chromatographs.

On the other hand, *NEAR Shoemaker* measured the elemental composition of (433) Eros with its x-ray spectrometer. It was found to be similar to ordinary chondrites (Trombka *et al.* 2000), which was not unexpected, since most NEAs are believed to be

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related to ordinary chondrites. In the near future, *Hayabusa* will also investigate the composition of (25143) Itokawa.

5.2. *Sample returns*

Meteorites are samples naturally returned to Earth which can be submitted to detailed chemical analyses. Indeed, complex organic molecules, including many aliphatic hydrocarbons, PAHs and amino acids, have been identified in carbonaceous chondrites (Botta & Bada 2002). Could some meteorites (carbonaceous chondrites) be pieces of cometary nuclei? This is still an open question (Campins & Swindle 1998). One should note the relatively high density ($\approx$2000 kg m^{-3}; only a few measurements are available, however; Perron & Zanda 2005) of carbonaceous chondrites compared to the low density of cometary nuclei. This suggests that cometary nuclei may be too fragile to survive their entry in the Earth atmosphere.

IDPs are indeed collected in the stratosphere. Some of them are of cometary origin, but which ones? The sample return mission *Stardust* (Tsou *et al.* 2004), on its way back from 81P/Wild 2, should soon provide ground truth for the link between IDPs and cometary dust, despite the probable loss of all semi-refractory matter in the collect process.

6. Insight from the *Deep Impact* mission

Cometary molecular abundances derived from material released in the coma may greatly differ from real abundances within the nucleus because of sublimation fractionation effects (e.g., Prialnik 2005). How to get under the processed surface of cometary nuclei and verify if the matter released in cometary atmospheres is representative of the inner nucleus? Indeed, inner material is released during partial or total disruption of cometary nuclei, as was the case for D/1993 F2 Shoemaker-Levy 9 or C/1999 S4 (LINEAR), but such unpredictable events can difficultly be thoroughly observed.

Investigating inner nucleus cometary material using a controlled experiment was the goal of the *Deep Impact* mission to comet 9P/Tempel 1 (A'Hearn *et al.* 2005a, b, 2006). A high-energy impact was to excavate matter from $\approx$10–30 m under the nucleus surface. How does the molecular production of 9P/Tempel 1 compare with "standard" comets before and after the impact? The observations are still being analysed and it is premature to draw definite conclusions (Table 6). However, the surge of new gas-phase material following the impact — at least as seen by Earth-based telescopes with large fields of view — was only a small fraction of the quiescent coma (Meech *et al.* 2005, Küppers *et al.* 2005). It will not be easy to extract the contribution due to pristine material.

7. The diversity of comets

The molecular composition of a fairly large number of comets has now been investigated, at both radio and infrared wavelengths (especially from high-resolution IR spectroscopic observations from the group of Mumma et al.).

A first study of this diversity based upon radio spectroscopy was made by Biver *et al.* (2002). It is now updated by Biver *et al.* (2005b, 2006). The sample of comets now amounts to 33 objects. This diversity is shown in Figs 3 & 9.

This diversity can also be studied from the observations of daughter species, which are indirect, but give access to a larger sample of comets (see Schulz 2006).

Jupiter-family comets, which are weaker objects, are still ill-known, despite recent observations of 2P/Encke and 9P/Tempel 1.

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Table 6. The top-ten volatile compounds (plus hydrogen cyanide) observed in comets.

	C/1995 O1 (Hale-Bopp)	"standard comet" [a]	9P/Tempel 1 before impact [b,c]		9P/Tempel 1 after impact [c]	
			radio	IR	radio	IR
H_2O	100	100	100	100	100	100
CO	12–23	< 1.7–23				4.3
CO_2	6	—				
H_2CO	1.1	0.13–1.3				
CH_3OH	2.4	< 0.9–6.2	1.7–3.2	1.3	7.2	0.99
H_2S	1.5	0.12–1.5	0.44			
NH_3	0.7	—				
CH_4	1.5	0.2–1.5				0.54
C_2H_2	0.2	0.15–0.3				0.13
C_2H_6	0.6	0.12–0.8		0.19		0.35
HCN	0.25	0.08–0.25	0.08–0.13	0.18	0.17	0.21

[a] A "standard comet" cannot be defined. The range of values for comets observed to date is listed. Jupiter-family comets are only sparsely observed and ill-represented.
[b] A comprehensive characterization of the chemical composition of 9P/Tempel 1 in its quiet state before impact was difficult because this comet was weak, about 1000 times less productive than C/Hale-Bopp. As far as we know, it was a "normal" comet.
[c] Relative abundances from Earth-based observations are listed here. Radio: preliminary values from IRAM observations (Biver *et al.* 2005a); IR: from Keck/NIRSPEC observations (Mumma *et al.* 2005).

The next major step in our understanding of comets — and of the Solar System formation itself — will be to establish to which extent this diversity reflects the primordial chemical composition of comets, and how it relates to the formation sites of these bodies.

8. Conclusion

Some pending problems related to cometary molecules are listed below.

- The origin of molecules/radicals such as NS and S_2 is still unknown (Rodgers & Charnley 2005).
- Many progenitors of the C_2 radical are now known, especially hydrocarbons. Others may still have to be found. On the other hand, progenitors for C_3 are still to be found: HC_3N is not abundant enough, and propyne (CH_3CCH), which has been proposed, is not detected (Table 3). This topic has been recently discussed by Helbert *et al.* (2005).
- Are supervolatiles (N_2, noble gases) present among cometary ices? This would put stringent constraints to the formation temperature of comets.
- Clathrates versus adsorption on amorphous ice is a key issue to the formation of comets, as recently discussed by Gautier & Hersant (2005).
- What is the meaning of the spin temperatures retrieved from the ortho-to-para ratios of several cometary molecules? Why are they so similar?
- Why is the $^{14}N/^{15}N$ isotopic ratio different in HCN and in the CN radical? Have we really missed a significant source of CN? The $^{14}N/^{15}N$ ratio in HCN has only been measured in one comet and should be investigated in other objects.
- What is the D/H ratio in water for Jupiter-family comets? What is their contribution to Earth water?
- How is the comet composition related to their origins? Why do the chemical composition vary so much from comet to comet, whereas other parameters, such as the $^{14}N/^{15}N$ ratio, the D/H ratio and the spin temperatures, seem to be homogeneous?

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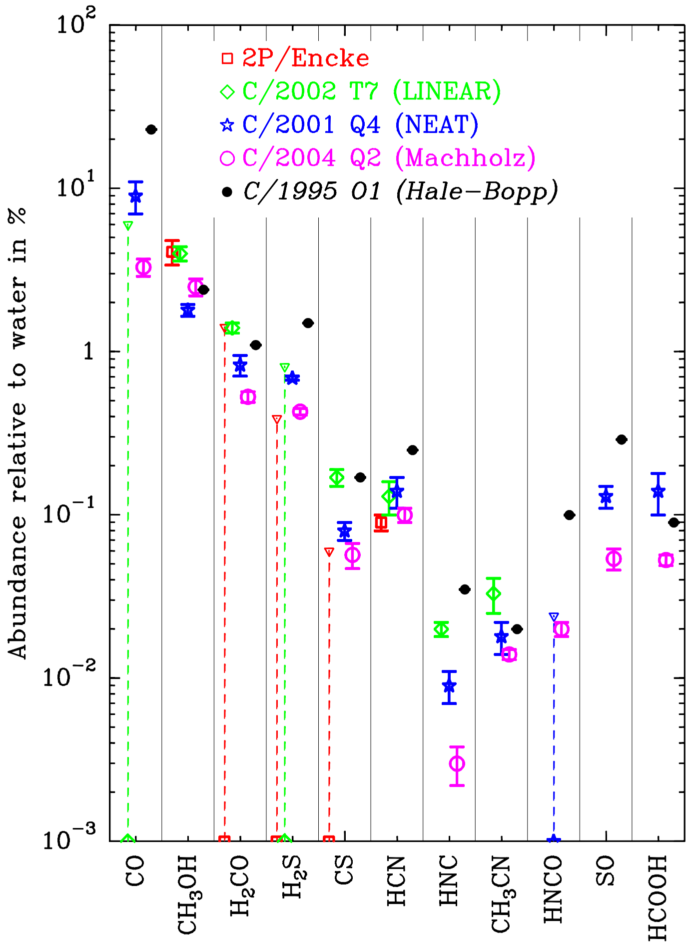

Figure 9. Relative abundances of selected molecules observed at radio wavelengths in a sample of recent comets, with comet Hale-bopp shown for comparison (from Biver *et al.* 2005b, 2006).

• Why are exposed ices obvious on the surface of TNOs and other distant small bodies, but inconspicuous on cometary nuclei?

These topics should be addressed in future observations, taking benefit of improved instrumentation and of space missions.

Acknowledgements

I thank all my colleagues for allowing me to report their results before publication.

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https://doi.org/10.1017/S174392130500671X Published online by Cambridge University Press