

## COMETS: A LINK BETWEEN INTERSTELLAR AND NEBULAR CHEMISTRY

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The chemical and isotopic composition of comets is reviewed, with emphasis on results obtained since the *Protostars and Planets III* conference. Observations from the apparitions of comets Hyakutake (C/1996 B2) and Hale-Bopp (C/1995 O1) have almost tripled the number of known cometary parent molecules, including nonpolar hydrocarbons observed in the infrared. Large D/H fractionation has been observed for water and HCN, whereas the carbon, nitrogen, and sulfur isotopic ratios appear to be solar. Cometary dust has been shown to include both crystalline and amorphous silicates, including both olivines and pyroxenes. The dust thus appears similar to that observed in some interplanetary dust particles (IDPs) and to some circumstellar grains. The chemistry of potential cometary volatiles in the solar nebula is reviewed and is contrasted with that expected for preserved interstellar matter. We conclude that cometary nuclei likely contain interstellar material that has been partially processed in the nebula and partially diluted with nebular condensates. The chapter concludes with recommendations for future observational, laboratory, and theoretical work that could clarify the origin of cometary matter.

### I. INTRODUCTION

The structure and chemical composition of comets clearly provide key data on the processes and conditions in the outer solar system at the time of its formation and potentially in the interstellar molecular cloud from which the solar nebula condensed (the “natal cloud”). Cometary nuclei are the most volatile-rich, and hence the least thermally processed, material that

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enters the inner solar system. This does not mean that comets are pristine samples of the ancient solar system. Numerous processes over the last 4.5 Gyr can affect their nature: cosmic rays; the interstellar radiation field; heating pulses from passing stars and from supernovae while the nuclei are in the Oort Cloud or Edgeworth-Kuiper Belt; and, of course, solar irradiation as the comets approach the Sun. Nonetheless, the record that comets preserve should be substantially easier to read than that in the planets, satellites, asteroids, and meteorites, which have been chemically differentiated or at least volatile depleted relative to the nebula as a whole.

Of crucial importance to many issues concerning the formation of solar-type stars and planetary systems is the question of whether or not comets contain relatively unprocessed interstellar molecular material. In the classical view of planetesimal formation, the solar nebula began in a sufficiently hot state that any preexisting matter was vaporized to its atomic constituents and was well mixed. Subsequently, as the nebula cooled, solids condensed in accordance with thermochemical equilibrium, resulting in a gradient in composition with respect to distance from the Sun that reflected the corresponding temperature and density gradients (Lewis 1972). In the outer portions of the nebula the cold temperature led to efficient condensation of volatiles, producing the nuclei of the comets (and other icy objects). However, as noted long ago by Urey (1953), "at lower temperatures [in the solar nebula] thermodynamic equilibrium may not be reached even in periods of time that are long compared to the age of the universe, and at these temperatures the kinetics of thermal reactions or of photochemical reactions become important." Lewis and Prinn (1980) subsequently showed that the conversion of the dominant high-temperature equilibrium species, CO and N<sub>2</sub>, to methane and ammonia is so slow that only minor amounts of NH<sub>3</sub> and CH<sub>4</sub> should be present in the solar nebula itself. However, in the higher-density subnebulae around the forming jovian planets, these conversions can proceed rapidly, so CH<sub>4</sub> and NH<sub>3</sub> are expected to be the dominant carbon- and nitrogen-bearing gases in those environments (Prinn and Fegley 1981, 1989).

In contrast, Greenberg (1982, 1998) has long argued that comets are fundamentally aggregates of ice-mantled interstellar grains that survived the formation of the nebula. If this view is correct, it has profound implications for the character of the processes by which matter accreted into the outer nebula, requiring that passage through any accretion shock be a rather gentle process. Moreover, it would mean that comets were direct probes of the nature of the natal cloud and of the interstellar medium (ISM) in a more general sense. It is now generally accepted that meteorites contain refractory presolar grains such as SiC, diamond, graphite, and Si<sub>3</sub>N<sub>4</sub> (Zinner 1997), and isotopic data also strongly suggest that organic material in carbonaceous chondrites contains interstellar molecules or their immediate derivatives (Cronin and Chang 1993; Cronin et al. 1995; Messenger

and Walker 1997). If the latter view is indeed correct, then it would seem hard to avoid the conclusion that even more interstellar material is preserved in comets. The striking similarities in the composition of cometary and interstellar ices point in this direction, as will be discussed in this review, but the alternative possibility (that such similarities simply reflect general properties of low-temperature, disequilibrium chemistry in solar-composition material) must be borne in mind.

Since there have been as yet no *in situ* analyses of cometary nuclei, and only one set of close spacecraft encounters with a comet (Halley), deducing the nature of comets remains a matter of interpreting the complex and interlinked physics and chemistry of the processes that produce the coma and tail as the nucleus approaches the Sun. Much progress has been made in recent years as advances in instrumentation have allowed the detection of "parent" molecules, which presumably have sublimated from the nucleus, in addition to their photodissociation and photoionization products ("daughter" molecules) traditionally observed at optical and ultraviolet wavelengths. However, many questions remain concerning chemistry in the coma, fractionation during the complex sublimation process, release of molecules from solid grains, and other processes that influence the interpretation of coma observations. Some of these will be discussed below. It remains clear, however, that space missions that actually sample cometary nuclear material are extremely important.

The period since *Protostars and Planets III* has produced extremely important results for our understanding of comets. In part this has been due to the fortuitous apparitions of two very bright comets: C/1996 B2 (Hyakutake), a moderately active comet that passed very close to the Earth, and C/1995 O1 (Hale-Bopp), a very active comet. The impact of D/1993 F2 (Shoemaker-Levy 9) with Jupiter provided a unique opportunity to study the internal strength of a comet as well as other phenomena associated with this encounter (Noll et al. 1996). These and other observations were facilitated by new astronomical instrumentation, including spacecraft, and have resulted in major discoveries in the composition and nature of comets. Among these results has been the discovery of a whole new set of solar system objects in the Kuiper Belt that are certainly related to comets (see chapters by Jewitt and Luu, Farinella et al., and Malhotra et al., this volume), as well as the unexpected detection of X-ray emission from comets, which, however, is probably more related to the solar wind or to the solar UV spectrum than to the nature of comets themselves (e.g., Lisse et al. 1996, 1998; Mumma et al. 1997*b*; Dennerl et al. 1997; Cravens 1997; Krasnopolsky 1997; Krasnopolsky et al. 1997).

Although no single review can cover all aspects of comets, that at *Protostars and Planets III* by Mumma et al. (1993) was very comprehensive. Consequently, the present paper will focus on recent results rather than seeking great breadth. We do point out the following other recent

reviews concerning comets: A'Hearn (1998), A'Hearn et al. (1998), Eberhardt (1999), Campins (1998), Sekanina et al. (1998), and the references that begin section III.A.

## II. INTERSTELLAR GRAINS

In considering the question of whether comets consist of or contain interstellar molecular material, it is obviously crucial to investigate the nature of interstellar solids. The latter include quite refractory material such as silicates and silicon carbide, both refractory and more volatile organic matter, and ices. There has been significant progress toward understanding the nature of interstellar grains in the last several years, in part because of the success of the *Infrared Space Observatory* (ISO), but very fundamental questions remain.

Direct investigation of the interstellar grains can be carried out by infrared spectroscopy as well as by the traditional studies of the interstellar extinction and polarization in the ultraviolet, visible, and near infrared. In addition, it remains possible that some of the Diffuse Interstellar Bands (DIBs) may originate in the grains, and DIBs as well as other phenomena strongly suggest the presence of interstellar polycyclic aromatic hydrocarbon molecules (PAHs), which may simply be the small end of a continuous spectrum of grain sizes (e.g., Salama 1996; Snow 1997). Moreover, because there is certainly interchange of material between the gas and solid phases in dense interstellar clouds, the composition of the gas provides clues to that of the grains in various environments; this is very important, because the gas can be observed at high spectral resolution and sensitivity at millimeter and submillimeter wavelengths.

The precise nature of the bulk of the organic matter in interstellar grains remains unknown, however (cf. Tielens et al. 1996). This is perhaps not surprising, given the difficulty in characterizing the organic matter in the comet Halley CHON particles (e.g., Fomenkova 1997), in the matrix of carbonaceous chondrites (Cronin and Chang 1993), and in terrestrial kerogens, in spite of the analytical tools that can be brought to bear on these samples. The apparent preservation of interstellar organic molecules in carbonaceous chondrites and the mass spectroscopy of the CHON particles suggest, however, that comets contain complex, heteropolymeric organic matter, some of which may include the corresponding portion of interstellar grains.

Knowledge of interstellar and circumstellar silicates has grown significantly over the last few years with the ability of ISO to obtain complete infrared spectra over the range  $2.4 \leq \lambda \leq 45 \mu\text{m}$  (and, at lower resolution,  $43 \leq \lambda \leq 196 \mu\text{m}$ ). Circumstellar silicates are seen to include both amorphous and crystalline material, including both olivines  $[(\text{Mg,Fe})_2\text{SiO}_4]$  and pyroxenes  $[(\text{Mg,Fe,Ca})\text{SiO}_3]$  (Waelkens et al. 1998;

Malfait et al. 1998). Curiously, in the interstellar environment (away from circumstellar envelopes and disks), crystalline silicates have not been identified. The greater similarity of the Hale-Bopp silicates to those in circumstellar as opposed to interstellar environments is puzzling (see section III.B).

The volatile content of comets provides the most stringent constraints on their origin, so the comparison with interstellar ices is particularly interesting. Here two sources of new data are especially important: (i) ISO and ground-based spectra of icy grain mantles in molecular clouds and (ii) millimeter/submillimeter observations of gas-phase molecules in “hot cores”: regions of high-mass star formation in molecular clouds where the grain mantles have been sublimated and/or sputtered from grains. These topics are reviewed in van Dishoeck and Blake (1998) and in the chapter by Langer et al., this volume. A definite similarity exists between interstellar ices and comets in both chemical composition and deuterium/hydrogen fractionation. However, several limitations in such comparisons should be borne in mind.

1. The sensitivity of the infrared spectra limits the identifiable ice constituents to those with abundances  $\geq 0.5\%$  relative to the principal component,  $\text{H}_2\text{O}$ .
2. The gas in hot cores includes the products of prestellar, cold, predominantly ion-molecule chemistry; molecules synthesized on the grains and subsequently released to the gas phase; and products of further chemical processing of the first two components in the gas heated by the young stars. Distinguishing among these components is not easy (e.g., it is unclear whether ethanol is synthesized on the grains or by high-temperature gas-phase reactions; Millar and Hatchell 1998), so the deduced composition of the icy grain mantles is model dependent.
3. Moreover, the hot core environment itself, representing a region of high-mass star formation, differs in unclear ways from that in regions of low-mass star formation, which may be more similar to that in which the solar nebula formed.

Isotopic abundances provide a particularly useful probe of chemical processes. The large deviations from terrestrial isotopic ratios for several elements in portions of meteoritic material provide the principal argument for the preservation of interstellar matter in these objects (e.g., Cronin and Chang 1993; Cronin et al. 1995). In comparing differences in isotopic ratios between the interstellar medium and comets, it is important to differentiate between overall nuclear isotope abundances (e.g.,  $^{12}\text{C}/^{13}\text{C}$ ), which are the result of ongoing nucleosynthesis in stars and typically show gradients with respect to both galactocentric distance and time, and chemical fractionation, which concentrates a particular isotope in specific molecular species under certain physical conditions. The Sun formed about 4.5 Gyr ago and, it is now believed, about 2 kiloparsecs closer to the

center of the Galaxy than its current location (Wielen et al. 1996), so the most relevant comparisons for solar system objects are with conditions at that position at that time, not with the local ISM today. Although there is considerable scatter in the data, perhaps as a result of local star formation history, the trends vs. galactocentric distance agree with current models for the relative abundances of the isotopes of C, N, and O (cf. Wielen and Wilson 1997, and references therein); the observed gradients for sulfur isotopes may require modifications to current theories (Chin et al. 1996). Estimates of the temporal evolution, in contrast, are based primarily on comparisons with current solar system values for all these elements.

Superimposed on these general trends of galactic isotopic evolution are chemical fractionation among and within clouds, due to variations in factors such as the UV field, electron density, kinetic temperature, overall density, and stochastic fluctuations such as might result from recent nearby supernovae. The very large D/H fractionation observed for many interstellar molecular species (up to 4 orders of magnitude) is reasonably well understood to be the result of both gas-phase and grain surface processes at low temperatures (e.g., Rodgers and Millar 1996; Irvine and Knacke 1989; Tielens 1983). The effects are much smaller for heavier atoms, but carbon isotope fractionation (up to a factor of a few) in particular sources (e.g., Langer et al. 1984; Taylor and Dickman 1989), and even differential  $^{13}\text{C}/^{12}\text{C}$  fractionation among the carbons at different positions in  $\text{HC}_3\text{N}$  in a given cloud (Takano et al. 1998), are observed. Chemical fractionation of oxygen is not thought to be significant under most conditions in the ISM (Langer et al. 1984); in addition, it would be difficult to separate from carbon isotopic fractionation, because the principal observed gas-phase reservoir for both C and O is CO. Although some fractionation might in principle occur at very low temperatures for nitrogen, the large  $^{14}\text{N}/^{15}\text{N}$  ratio would make it very difficult to measure (Guélin and Lequeux 1980). Fractionation is also expected to be small for sulfur, although there are some theoretical and observational suggestions that cold, dark clouds may be enhanced in  $^{34}\text{S}$  relative to  $^{32}\text{S}$  (Chin et al. 1996; Pratap et al. 1997) compared to warmer sources, perhaps by of order 40%. Comparisons to isotope ratios observed in comets are described below. It is unfortunate that the difficulty in observing through the terrestrial atmosphere has thus far precluded measurement of the  $\text{HDO}/\text{H}_2\text{O}$  fractionation in regions of low-mass star formation.

Likewise, the interesting results on the ortho-to-para abundance ratio for water in several recent comets (see below) cannot yet be compared to interstellar values, although such ratios have been measured for other molecular species in cold interstellar clouds (e.g.,  $\text{H}_2\text{CO}$ ,  $\text{H}_2\text{CCO}$ ,  $\text{H}_2\text{CS}$ ,  $\text{C}_3\text{H}_2$ ; Irvine 1992; Minh et al. 1995). Interestingly, a difference in the ratio for formaldehyde may exist between cold cloud cores with and without embedded young low-mass stars (Dickens 1998).

### III. THE COMPOSITION OF COMETS

#### A. The Composition of Cometary Volatiles

The composition of comets, as it was known at the time of the previous *Protostars and Planets* conference, was reviewed by Mumma et al. (1993), Festou et al. (1993), and Crovisier (1994). More recent results, including those from comets Hyakutake and Hale-Bopp, are described by Bockelée-Morvan (1997), Mumma (1997), Eberhardt (1998), Rauer (1999), and Bockelée-Morvan and Crovisier (1998); see also Crovisier (1998*a,b*; 1999) and Despois (1998). The improvement coming from the observations of these last two comets is really significant, because it increased the number of known *parent* molecules from about 8 to about 22. Our present knowledge of the composition of cometary volatiles is summarized in Table I. A sample spectrum is shown in Fig. 1.

Most of these new molecules have been detected through their rotational lines at radio wavelengths. This technique is very sensitive even to minor species, provided they are polar molecules. In addition to the previously known HCN, important new cyanide-containing molecules have been identified: HNC, an isomeric form of HCN (Irvine et al. 1996; see discussion in section V.B); and CH<sub>3</sub>CN and HC<sub>3</sub>N, pointing to the possible existence of carbon chain molecules such as those found in interstellar clouds (Bockelée-Morvan et al. 1998*b*). Ammonia has been firmly identified for the first time through its centimetric lines (Bird et al. 1997; Palmer et al. 1996).

Several new sulfur-bearing molecules have been identified to complement the already known H<sub>2</sub>S and CS<sub>2</sub> (the probable parent of CS). Surprisingly, SO and SO<sub>2</sub> were observed with a significant abundance, much higher than the upper limits previously inferred from UV data (Kim and A'Hearn 1991), which indicates that the UV excitation of these molecules has perhaps not been understood (Bockelée-Morvan et al. 1998*b*; Lis et al. 1998). OCS and H<sub>2</sub>CS were observed for the first time as minor constituents (Woodney et al. 1997, 1998; Dello Russo et al. 1998*a*). The mysterious S<sub>2</sub>, previously observed only in C/1983 H1 (IRAS-Araki-Alcock), was observed again in the near UV in comet Hyakutake (Weaver et al. 1996), the detection of this short-lived molecule benefiting in these two cases from the close approach of the comet to the Earth. Interferometric observations of Hale-Bopp suggest that SO may be in part a daughter radical produced from SO<sub>2</sub> photolysis in the coma (Wink et al. 1998).

Several CHON (organic) species have been detected with minor abundances relative to the previously known methanol and formaldehyde: formic acid (HCOOH), isocyanic acid (HNCO), methyl formate (HCOOCH<sub>3</sub>), and formamide (NH<sub>2</sub>CHO); see Bockelée-Morvan et al. (1998*b*) and Lis et al. (1997, 1998). In addition, significant upper

**TABLE I**  
Abundances of Cometary Volatiles

Molecule	Abundance <sup>a</sup>		Method <sup>b</sup>	N <sup>c</sup>	Comments
	Hale-Bopp	Other Comets			
H <sub>2</sub> O	= 100	= 100	IR	6	Also indirect (from OH, O, H)
CO	20	1–20	UV, radio, IR	>5	Extended source?
CO <sub>2</sub>	20 <sup>d</sup>	3–10	IR	3	
H <sub>2</sub> CO	0.1–1	0.1–1	Radio, IR	>5	Extended source
CH <sub>3</sub> OH	2	1–7	Radio, IR	>5	
HCOOH	~0.05		Radio	1	
HNCO	0.1		Radio	2	
NH <sub>2</sub> CHO	~0.01		Radio	1	
HCOOCH <sub>3</sub>	~0.05		Radio	1	
CH <sub>4</sub>	~0.6		IR	2	
C <sub>2</sub> H <sub>2</sub>	~0.1		IR	2	
C <sub>2</sub> H <sub>6</sub>	~0.3		IR	2	
NH <sub>3</sub>	0.6		Radio, IR	3	
HCN	0.2	0.05–0.2	Radio, IR	>5	
HNC	0.04		Radio	2	Extended source?
CH <sub>3</sub> CN	0.02		Radio	2	
HC <sub>3</sub> N	0.03		Radio	1	
H <sub>2</sub> S	1.5	0.2–1.5	Radio	>5	
H <sub>2</sub> CS	~0.02		Radio	1	
CS	0.2	0.2	UV, radio	>5	From CS <sub>2</sub> ?
OCS	0.5		Radio, IR	2	Extended source?
SO	~0.5		Radio	1	From SO <sub>2</sub> ?
SO <sub>2</sub>	~0.1		Radio	1	
S <sub>2</sub>		0.005	UV	2	

<sup>a</sup> Abundance relative to water. See text for references. All abundances were measured at  $r_h \sim 1$  AU except for CO<sub>2</sub> in Hale-Bopp. Listed abundances may be uncertain by a factor of 2 or more for some species and may not pertain to nucleus production for “extended sources.”

<sup>b</sup> Method of observation.

<sup>c</sup> Number of comets in which this species was reliably and directly observed.

<sup>d</sup> Measured at  $r_h = 2.9$  AU.



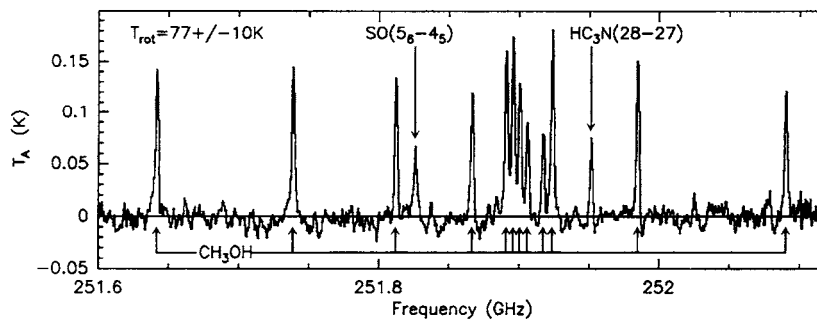


Figure 1. A spectrum of comet Hale-Bopp observed at the Caltech Submillimeter Observatory (CSO) on February 21, 1997, showing a series of lines of methanol and the corresponding rotational temperature, and the first observations of SO and HC<sub>3</sub>N in a comet (Lis et al. 1998). Such data illustrate the power of millimeter and submillimeter-wavelength observations for cometary studies.

limits have been obtained for molecules such as methylenimine (CH<sub>2</sub>NH), ethanol (C<sub>2</sub>H<sub>5</sub>OH), ketene (CH<sub>2</sub>CO), and many others.

The infrared is a unique domain for observing nonpolar species that do not have allowed rotational transitions as well as for obtaining new information on molecules also observed at radio wavelengths. Identifications of hydrocarbons in comets Hyakutake and Hale-Bopp from new ground-based observations (Mumma et al. 1996; Brooke et al. 1996; Weaver et al. 1998) include C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, and CH<sub>4</sub> (Fig. 2). Numerous other parent volatiles were detected at infrared wavelengths (e.g., CO, CH<sub>3</sub>OH, HCN, H<sub>2</sub>CO, OCS, NH<sub>3</sub>), and sensitive searches were performed for other species (e.g., C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, O<sub>3</sub>), although actual upper limits are not yet available.

Water has been detected from ground-based observatories only at infrared wavelengths. The approach of hot-band fluorescence developed for earlier comets was applied to comet Hyakutake (Mumma et al. 1996) and for Hale-Bopp was used to obtain production rates for various heliocentric distances (Dello Russo et al. 1999; Weaver et al. 1998). Observations of water in Hale-Bopp and 103P/Hartley 2 from space (with ISO) provided production rates and the ortho-para ratio, which agree well with those obtained for 1P/Halley (see section III.D).

The high spatial resolution afforded by long-slit spectrometers permits detailed study of the distribution of molecular emissions about the nucleus. These can discriminate nuclear from extended sources of "parent" volatiles. CO was studied in this way; similarly to comet 1P/Halley, when comet Hale-Bopp was at a heliocentric distance of approximately 1 AU, up to 50% of the CO was found to be produced from an extended source (DiSanti et al. 1999; Weaver et al. 1998). Water and HCN,

## C/1996 B2 Hyakutake, UT March 24.5, 1996

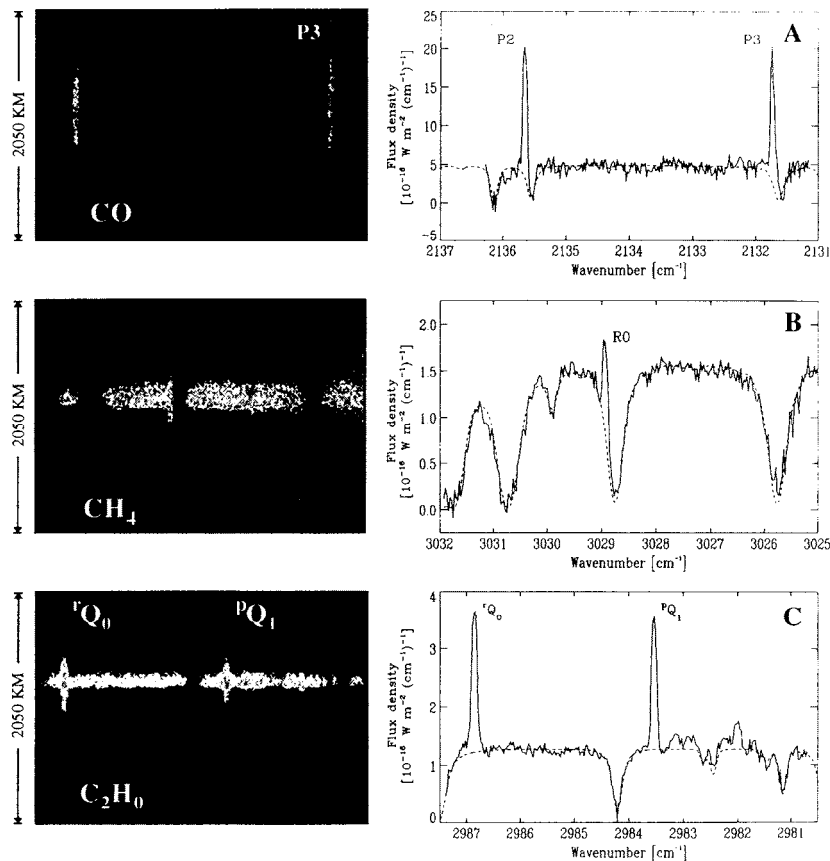


Figure 2. High-dispersion ( $R = 20,000$ ), long-slit spectra ( $0.2$  arcsec per pixel) of comet Hyakutake, showing emission from parent volatiles and dust. Full spectral-spatial frames are shown at left, and corresponding spectra extracted for seven rows centered on the nucleus are shown at right. Telluric lines are seen in absorption against the cometary continuum, and their cometary counterparts are Doppler-shifted to higher frequencies by the comet's motion. (*top*) The P2 and P3 lines of the carbon monoxide 1–0 vibrational band near  $4.69 \mu\text{m}$ ; (*middle*) the R0 line of the methane  $\nu_3$  band near  $3.30 \mu\text{m}$ ; (*bottom*) The  $rQ_0$  and  $pQ_1$  branches of the ethane  $\nu_7$  band near  $3.351 \mu\text{m}$ . These are the discovery spectra for saturated hydrocarbons in comets (Mumma et al. 1996).

however, appear to be released directly from the nucleus (Dello Russo et al. 1999, Magee-Sauer et al. 1998; Weaver et al. 1998). A comparison of the spatial distribution for OCS relative to those of water and dust in Hale-Bopp provided evidence that most OCS was produced from an extended source (Dello Russo et al. 1998a). The rotational temperature measured

for CO and HCN in Hale-Bopp revealed changes in the coma temperature with distance from the nucleus, similar to those predicted by models of photolytic heating (DiSanti et al. 1999; Magee-Sauer et al. 1998; Bockelée-Morvan and Crovisier 1987). The ability to distinguish direct and extended sources for “parent” volatiles is key to understanding the composition of cometary ices.

The ISO provided the second direct observation of CO<sub>2</sub> in a comet (Crovisier et al. 1996, 1997*b*) through its  $\nu_3$  band at 4.25  $\mu\text{m}$ . CO<sub>2</sub> can also be traced following its photodissociation from the CO Cameron system in the UV (e.g., Weaver et al. 1997). The direct detection is important; CO<sub>2</sub> production rates cannot be reliably derived from the UV observations because the rates of the relevant mechanisms are still poorly known.

Some words of caution are necessary concerning the relationship between reported “production rates” of cometary volatiles observed in the coma (as listed in Table I) and the actual molecular abundances in cometary ices:

1. *Sublimation fractionation* affects all production rates, depending on the heliocentric distance. This is now clearly shown by the evolution of production rates observed over the range of distance 1–7 AU in comet Hale-Bopp, which show significant variations relative to water for several species (Biver et al. 1997, 1998).
2. *Chemical reactions* in the coma may be able to synthesize some species of minor abundance in highly productive comets where the coma density could be high. This was evident from the [HNC]/[HCN] ratio varying with the heliocentric distance in Hale-Bopp (see the discussion in section V.B). Thus, one might question the significance of the abundances of some of the minor species detected in comet Hale-Bopp near its perihelion.
3. The existence of *extended sources* within the coma has been demonstrated for molecules such as CO, H<sub>2</sub>CO, OCS, and perhaps others. The sources of such molecules are poorly known. They might be grains with CHON mantles, but the desorption mechanism of molecules is still uncertain (see, e.g., Crovisier 1998*a*; Greenberg and Li 1998). For these molecules the production rates may not pertain to sublimation from the nucleus and thus may not be relevant to nuclear ice abundances.

## B. The Composition of Cometary Dust

In addition to the *in situ* analysis of P/Halley’s dust particles by mass spectroscopy (recently reanalyzed by Schulze et al. 1997 and Eberhardt 1999), which revealed the *elemental* rather than the *chemical* composition, the composition of cometary dust can be investigated by spectroscopy in the thermal infrared. Until recently, most of the clues came from the

analysis of the intricate band around 10  $\mu\text{m}$ . It revealed the presence of silicates, part of them being crystalline in some comets (e.g., Hanner et al. 1994).

ISO gave us, for the first time, access to the full infrared spectrum of a comet, from 2.4 to 196  $\mu\text{m}$ , covering thermal emission of cometary dust. In addition to the already well-known silicate bands around 10 and 20  $\mu\text{m}$ , the observations of comet Hale-Bopp revealed peaks at 16, 23.5, 27.5, and 33.5  $\mu\text{m}$  (Crovisier et al. 1997*a,b*). These were identified with Mg-rich olivine (forsterite,  $\text{Mg}_2\text{SiO}_4$ ). The Hale-Bopp spectrum appears strikingly similar to those of circumstellar dust around Vega-type stars (e.g., that of HD 100546, a Herbig Ae star; Waelkens et al. 1996; Malfait et al. 1998). Quantitative fits of the ISO spectra (with still preliminary calibration) with laboratory spectra of terrestrial and IDP (interplanetary dust particles) analogs reveal that, in addition to forsterite, amorphous silicates as well as a featureless component (such as amorphous carbon) are necessary to reproduce the spectra (Hanner et al. 1998; Brucato et al. 1999; Wooden et al. 1999).

ISO could observe comet Hale-Bopp only at heliocentric distances greater than 2.9 AU. In ground-based spectra in the 8–13  $\mu\text{m}$  window, features characteristic of pyroxene (at 9.3 and 10.0  $\mu\text{m}$ ) appeared at smaller heliocentric distances, implying the existence of two crystalline grain components with different temperatures: the hotter including olivines, the cooler, pyroxenes (Wooden et al. 1999). The dust of comet Hale-Bopp, with Mg-rich pyroxenes and olivines, thus seems to have a composition comparable with that of IDPs (Bradley et al. 1988, 1997). This composition is also compatible with that predicted for the first Mg silicates to condense from a solar-composition gas (Grossman and Larimer 1974).

Do Jupiter-family comets, presumed to have formed in the Edgeworth-Kuiper Belt, have the same composition as Oort Cloud comets? The former are fainter and more difficult to observe. Until recently, silicate bands were undetected or gave inconclusive results in the few Jupiter-family comets that were observed (e.g., Hanner et al. 1996). However, observations of 103/P Hartley 2 with ISO have now revealed the 11.3  $\mu\text{m}$  feature characteristic of crystalline olivine (Crovisier et al. 1999).

### C. Isotopic Abundances

Isotopic abundances (and especially the [D]/[H] ratio in water) in comet Halley from the *Giotto* mass spectrometers have now been refined (Balsiger et al. 1995; Eberhardt et al. 1995). In addition, new results were obtained from radio spectroscopic observations of comets Hyakutake and Hale-Bopp, resulting in determinations of the [D]/[H] ratios in water (Bockelée-Morvan et al. 1998*a*; Meier et al. 1998*b*) and HCN (Lis et al. 1998; Meier et al. 1998*a*), and of C, N, and S isotopic ratios in HCN and CS (Jewitt et al. 1997). All these results are summarized in Table II. A

**TABLE II**  
Isotopic Ratios in Comets

Isotopes	Molecule	Comet	Method	Cosmic Value	Comet Value	Reference
[D]/[H]	H <sub>3</sub> O <sup>+</sup>	Halley	Mass spect.	$1.5 \times 10^{-5}$	$3.08 \pm 0.53 \times 10^{-4}$	Balsiger et al. (1995)
	H <sub>2</sub> O	Hyakutake	Radio		$3.02 \pm 0.22 \times 10^{-4}$	Eberhardt et al. (1995)
		Hale-Bopp	Radio		$2.9 \pm 1.0 \times 10^{-4}$	Bockelée-Morvan et al. 1998a
	HCN	Hale-Bopp	Radio		$3.3 \pm 0.8 \times 10^{-4}$	Meier et al. (1998b)
	CH <sub>3</sub> OH <sup>a</sup>	Halley	Mass spect.		$2.3 \pm 0.4 \times 10^{-3}$	Meier et al. (1998a)
[ <sup>18</sup> O]/[ <sup>16</sup> O]	H <sub>3</sub> O <sup>+</sup>	Halley	Mass spect.	$2.0 \times 10^{-3}$	$< 1 \times 10^{-2}$	Eberhardt et al. (1994)
	CN	Halley	Visible		$1.93 \pm 0.12 \times 10^{-3}$	Balsiger et al. (1995)
	HCN	Hyakutake	Radio	$1.1 \times 10^{-2}$	$2.13 \pm 0.18 \times 10^{-3}$	Eberhardt et al. (1995)
		Hale-Bopp	Radio		$1.05 \pm 0.13 \times 10^{-2}$	Kleine et al. (1995)
					$2.9 \pm 1.0 \times 10^{-2}$	Lis et al. (1997)
					$1.11 \pm 0.18 \times 10^{-2}$	Lis et al. (1998)
					$0.90 \pm 0.09 \times 10^{-2}$	Jewitt et al. (1997)
[ <sup>15</sup> N]/[ <sup>14</sup> N]	CN	Halley	Visible	$3.6 \times 10^{-3}$	$< 3.6 \times 10^{-3}$	Kleine et al. (1995)
	HCN	Hale-Bopp	Radio		$3.1 \pm 0.4 \times 10^{-3}$	Jewitt et al. (1997)
[ <sup>34</sup> S]/[ <sup>32</sup> S]	Atomic S	Halley	Mass spect.	$4.2 \times 10^{-2}$	$4.5 \pm 1.0 \times 10^{-2}$	Krankowsky et al. (1986)
	CS	Hale-Bopp	Radio		$3.7 \pm 0.4 \times 10^{-2}$	Jewitt et al. (1997)

<sup>a</sup> [CH<sub>3</sub>OD + CDH<sub>2</sub>OH]/[CH<sub>3</sub>OH].

detailed discussion of the significance of the [D]/[H] ratio in comets is given in section IV.A below; cf. also Mumma (1997) and Bockelée-Morvan et al. (1998a).

The mean C, N, and S isotopic ratios are not significantly different from the solar values. This confirms, with an improved accuracy, previous determinations for volatiles from optical spectra and mass spectroscopy. Some individual grains measured *in situ* by the *Giotto* and *Vega* spacecraft did, however, show anomalous [<sup>12</sup>C]/[<sup>13</sup>C] ratios. Whereas the low (“heavy”) values might represent interference from <sup>12</sup>CH<sup>+</sup>, the high ratios (up to 5000) are similar to some values seen for micron-sized SiC grains in carbonaceous meteorites and are taken as evidence for the preservation of essentially unaltered presolar organic material (Eberhardt 1998, although there is no evidence for SiC in Halley from the high-fidelity mass spectra obtained with the PUMA-1 instrument; Schulze et al. 1997).

The three comets in which the [D]/[H] ratio has been determined are Oort Cloud comets. One could wonder what this ratio might be in Jupiter-family comets, perhaps formed at larger heliocentric distances; the answer might come from future cometary missions toward short-period comets.

#### D. The Spin Temperature of Cometary Water

As reviewed by Mumma et al. (1993), the ortho/para ratio (OPR) of cometary water is characterized by the spin temperature of this species. This parameter is believed to be of primordial character, because conversions between the ortho (hydrogen nuclear spins parallel) and para (spins opposite) states through collisions or radiative transitions are strictly forbidden. The real meaning of the spin temperature is not understood, however; it could be the temperature of water at the moment of its chemical formation, or it may reflect re-equilibration with the internal temperature of the nucleus.

The initial observations gave  $OPR = 2.5 \pm 0.1$  in 1P/Halley, corresponding to  $T_{\text{spin}} \approx 29$  K, and  $OPR = 3.2 \pm 0.2$  in C/1986 P1 (Wilson), consistent with  $T_{\text{spin}} > 50$  K (Mumma et al. 1993). However, these determinations are hampered by the difficulty in modeling opacity effects and because only part of the  $\nu_3$  vibrational band of water was observed.

ISO observed the  $\nu_3$  band of water in comets C/1995 O1 (Hale-Bopp) and 103P/Hartley 2 (Crovisier et al., 1997*b*, 1999). The full band was observed with a spectral resolution allowing resolution of the rotational structure, and the opacity was found to be moderate; see Fig. 3. Values of  $OPR = 2.45 \pm 0.10$  and  $2.70 \pm 0.10$ , corresponding to  $T_{\text{spin}} \approx 25$  and 35 K, were determined for Hale-Bopp and Hartley 2, respectively. Thus, the existence of OPR values significantly lower than the high-temperature limit of 3 is confirmed in both an Oort Cloud (Hale-Bopp) and a Jupiter-family comet. The issue is discussed further near the end of section IV.A.

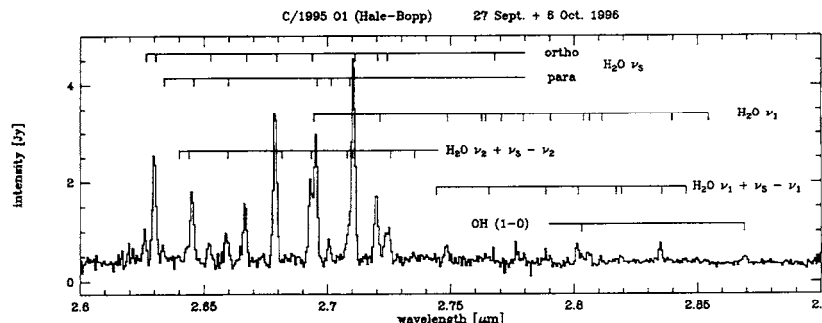
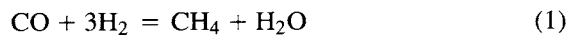


Figure 3. The region of the  $\nu_3$  band of water observed in the comet Hale-Bopp with the short-wavelength spectrometer of ISO (average of observations on September 26 and October 6, 1996, when the comet was at 2.9 AU from the Sun). The resolution of the rotation structure permits an evaluation of the rotational temperature (28 K) and of the ortho-to-para ratio ( $2.45 \pm 0.10$ , corresponding to a spin temperature  $\sim 25$  K; Crovisier et al. 1997*a,b*).

#### IV. NEBULAR CHEMISTRY OF COMETARY VOLATILES

##### A. Water

Because water is the dominant volatile in those comets for which its abundance has been determined, its origin is of prime importance for assessing how much comets represent pristine presolar material and how much presolar material reprocessed to a greater or lesser extent in the solar nebula. (We use the term “presolar” rather than “interstellar” to emphasize that some of this material may have been formed in circumstellar shells, while other portions may have been formed or modified in interstellar space.) As noted by Fegley (1993), water ice in comets could be pristine presolar ice, presolar water that was vaporized and recondensed in the solar nebula, or water synthesized in jovian protoplanetary subnebulae via thermochemical reactions such as



Even if all water in comets resulted from equation (1), which is not being advocated, this does not imply that  $\text{CH}_4$  and  $\text{H}_2\text{O}$  would be retained in a 1:1 ratio in comets, because of the greater volatility of  $\text{CH}_4$ ; the consequences of equation (1) for the  $[\text{D}]/[\text{H}]$  ratio of cometary water, and the production of intermediates such as  $\text{H}_2\text{CO}$  and  $\text{CH}_3\text{OH}$ , will be discussed below. In fact, the water in comets could be a mixture, with different comets having different proportions of pristine presolar water and reprocessed nebular water (cf. Fegley 1993; Mumma 1997).

Until *unaltered* samples of comet nuclei are accessible to chemical and physical measurements by spacecraft experiments or by laboratory

analyses of returned samples, the source of cometary water has to be inferred primarily from its hydrogen and oxygen isotopic composition. The available data are given in Tables II and III. The measured  $[D]/[H]$  ratios in Halley, Hyakutake, and Hale-Bopp cluster around  $30 \times 10^{-5}$ . This  $[D]/[H]$  ratio is about 20 times larger than the (present-day)  $[D]/[H]$  ratio in the local interstellar medium (Pisunov et al. 1997) and about twice as large as in terrestrial SMOW (Standard Mean Ocean Water), thus challenging the hypothesis that terrestrial water is derived primarily from cometary bombardments. What do the  $[D]/[H]$  ratios in Halley, Hyakutake, and Hale-Bopp tell us about the origin of water in these three comets?

One possible interpretation is that the water in these three comets is pristine interstellar water that was incorporated into the comets. The  $[D]/[H]$  ratios in cometary water are similar to the  $[D]/[H]$  ratios reported for water in the hot cores of molecular clouds, where massive stars are forming. For example, radio observations of HDO and  $H_2^{18}O$  by Jacq et al. (1990), Gensheimer et al. (1996), and Helmich et al. (1996) gave  $[D]/[H]$  ratios of order  $(20-60) \times 10^{-5}$  for hot core regions. This water vapor is thought to preserve the fractionation in the ice mantles of grains present in the cores before they were heated by the embedded young stars (Rodgers and Millar 1996). The accretion of unaltered water-bearing interstellar grains into comets may also explain the observed ortho/para ratios of cometary water vapor (discussed later in this section).

An important implication of the unmodified-interstellar-grain scenario is that other interstellar molecules will also be accreted unaltered into comets. For example, hydrogen cyanide with a  $[D]/[H]$  ratio of  $(230 \pm 40) \times 10^{-5}$  was observed in Hale-Bopp by Meier et al. (1998a), which is in the range reported in hot cores by Hatchell et al. (1998). Meier et al. (1998a) note that the  $[DCN]/[HCN]$  ratio is consistent with the  $[HDO]/[H_2O]$  ratio within the context of interstellar ion-molecule chemistry, provided that the chemistry has reached steady state and the temperature is of order 30–40 K (Millar et al. 1989). It should be noted, however, both that the interstellar hot cores are quite young, so steady-state models may not be applicable, and that the observed HCN ratio in the gas may have been diluted from an originally higher value on the presumed icy grain mantles (Hatchell et al. 1998).

Methanol ( $CH_3OH$ ) is also observed in comets (including Hale-Bopp, Hyakutake, and Halley), and it is present in hot cores, with  $[CH_3OD]/[CH_3OH]$  ratios of 0.01–0.06 (Mauersberger et al. 1988), while the  $[CH_2DOH]/[CH_3OD]$  ratio is of order unity (Jacq et al. 1993; Charnley et al. 1997). However, Eberhardt et al. (1994) reported a [deuterated  $CH_3OH$ ]/ $[CH_3OH]$  ratio  $< 0.01$  for Halley, where deuterated  $CH_3OH$  includes both  $CH_3OD$  and  $CDH_2OH$ , which could not be distinguished by the mass spectrometry. The cometary results thus seem to disagree with the deuterium fractionation for the hot cores. There are no reports of



**TABLE III**  
**[D]/[H] Ratios in Comets, the Solar System, and Interstellar Space**

Object or Species	D/H Ratio ( $\times 10^5$ ) <sup>a</sup>	$\delta D$ (%) <sup>a</sup>	Enrichment <sup>b</sup>	Reference
Present-day local ISM	$1.6 \pm 0.12$	-900	1	Mahaffy et al. (1998)
Solar wind	$2.1 \pm 0.5$	-865	1.3	Geiss and Gloeckler (1998)
Orion hot core: HDO/H <sub>2</sub> O	100-400	$(5.4-24.7) \times 10^3$	60-250	van Dishoeck et al. (1993)
Several hot cores: HDO/H <sub>2</sub> O	30	925	19	Gensheimer et al. (1996)
Several hot cores: DCN/HCN	90-400	$(5-25) \times 10^3$	56-250	Hatchell et al. (1998)
TMC-1: C <sub>3</sub> HD/C <sub>3</sub> H <sub>2</sub>	$(8-16) \times 10^3$	$(5-10) \times 10^6$	$(5-10) \times 10^3$	van Dishoeck et al. (1993)
TMC-1: CH <sub>2</sub> DC <sub>2</sub> H/CH <sub>3</sub> C <sub>2</sub> H	6000	385,000	3750	van Dishoeck et al. (1993)
TMC-1: DCN/HCN	2300	146,600	1440	van Dishoeck et al. (1993)
TMC-1: DC <sub>3</sub> N/HC <sub>3</sub> N	1500	95,280	940	van Dishoeck et al. (1993)
Halley: HDO/H <sub>2</sub> O	$31.6 \pm 3.4$	1030	20	Eberhardt et al. (1995)
Hyakutake: HDO/H <sub>2</sub> O	$29 \pm 10$	860	18	Bockelée-Morvan et al. (1998)
Hale-Bopp: HDO/H <sub>2</sub> O	$33 \pm 8$	1120	21	Meier et al. (1998a)
Hale-Bopp: DCN/HCN	$230 \pm 40$	13,760	144	Meier et al. (1998b)
IDPs (maximum value) <sup>c</sup>	400-800	24,800-50,000	250-500	Messenger and Walker (1997)
Venus: atm. H <sub>2</sub> O	$2200 \pm 300$	140,200	1400	Donahue (1995)
Mars: atm. H <sub>2</sub> O	$81 \pm 3$	4200	51	Donahue (1995)
Earth: SMOW	15.58	0	9.7	Lodders and Fegley (1998)
Jupiter: CH <sub>3</sub> D/CH <sub>4</sub>	$2.6 \pm 1.0$	-830	1.6	Fegley and Prinn (1988)
Jupiter: HD/H <sub>2</sub>	$2.6 \pm 0.7$	-830	1.6	Mahaffy et al. (1998)
Saturn: HD/H <sub>2</sub>	$2.5 \pm 1.0$	-840	0.9-2.2	Lodders and Fegley (1998) <sup>d</sup>
Titan: CH <sub>3</sub> D/CH <sub>4</sub>	$\sim 7.5$	$\sim -519$	$\sim 5$	Coustonis et al. (1998)
Neptune: HD/H <sub>2</sub>	$6.5 (-1.5, +2.5)$	$\sim -580$	$\sim 4$	Feuchtgruber et al. (1999)
Uranus: HD/H <sub>2</sub>	$5.5 (-1.5, +3.5)$	$\sim -650$	$\sim 3.4$	Feuchtgruber et al. (1999)
Chondrites: Semarkona (LL3)	$75 \pm 12$	$3815 \pm 170$		Delouile and Robert (1995)
phyllsilicates				
Renazzo (CR) phyllosilicates	$> 31$	$> 990$		Delouile and Robert (1995)
Chondrules (LL3, CR)	12-23	-230 to 480		Delouile and Robert (1995)
Orgueil (CI) kerogen	36.6	1360		Halbout et al. (1990)

<sup>a</sup> The delta notation is defined as  $\delta D$  (%) =  $[(D/H)_{\text{sample}}/(D/H)_{\text{SMOW}} - 1] \times 1000$  where SMOW is Standard Mean Ocean Water.

<sup>b</sup> The enrichment factor is defined as  $(D/H)_{\text{sample}}/(D/H)_{\text{ISM}}$ , taking  $(D/H)_{\text{ISM}} = (1.6 \pm 0.12) \times 10^{-5}$  as the average present day local ISM value. Measurements of the local ISM D/H ratio fall in the range of  $(1.4-2.2) \times 10^{-5}$  (Pisumkov et al. 1997).

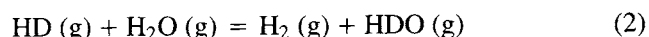
<sup>c</sup> Lower value for a particular "cluster" interplanetary dust particle, higher value for a "hotspot" on that particle.

<sup>d</sup> Griffin et al. (1996) give 2.3 (-0.8, +1.2).

deuterated  $\text{CH}_3\text{OH}$  in Hale-Bopp or Hyakutake. Finally, for formaldehyde both HDCO and  $\text{D}_2\text{CO}$  have been observed in hot cores (Sutton et al. 1995; Turner 1990; see also Rodgers and Millar 1996), whereas  $[\text{D}]/[\text{H}]$  ratios for  $\text{H}_2\text{CO}$  in comets have not been reported. Because the unmodified-interstellar-grain model implies high  $[\text{D}]/[\text{H}]$  ratios for formaldehyde in comets, it is important to see whether an upper limit for  $[\text{HDCO}]/[\text{H}_2\text{CO}]$  can be derived from the mass spectrometer data for Halley or from remote sensing observations of other  $\text{H}_2\text{CO}$ -bearing comets.

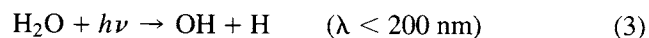
Another implication of the unmodified-interstellar-grain model is that infalling interstellar grains do not lose their volatiles during incorporation into the solar nebula. In other words, ices on infalling grains either are not vaporized or, if vaporized, do not undergo significant chemical or isotopic alteration before recondensing onto grain surfaces. In contrast, recent calculations (Chick and Cassen 1997; Cassen and Chick 1997; Engel et al. 1990; Lunine et al. 1991) indicate that a significant fraction of infalling icy grains may have been vaporized during incorporation into the solar nebula. For example, Chick and Cassen (1997) predict that the water ice vaporization distance lies between 2 and 30 AU, and Lunine et al. (1991) predict that  $\sim 90\%$  of water ice grains are vaporized at 30 AU and  $< 10\%$  of water ice grains are vaporized beyond 100 AU. While the computational results are somewhat dependent on how the solar nebula is modeled, including such poorly constrained parameters as the area/mass ratio for the infalling grains, it would seem that the vaporization of infalling icy grains may pose a hurdle for the unmodified-interstellar-grain model of cometary volatiles. These theoretical considerations and the possible lack of consistent D enrichments in cometary species such as methanol lead us to consider the alternative: that the D/H ratio of cometary water was produced either by fractionation within the solar nebula itself or by partial reprocessing of presolar water in the solar nebula.

In principle, deuterium isotopic exchange in the solar nebula between hydrogen and water (or other hydrides) via net reactions such as



leads to more HDO (or more  $\text{CH}_3\text{D}$ ,  $\text{NH}_2\text{D}$ , HDS) with decreasing temperature. Values of the D/H fractionation as a function of temperature are given for water in Fig. 11 of Prinn and Fegley (1989); comparison with the observed values in comets Hyakutake, Halley, and Hale-Bopp (Table III) indicates temperatures of order 140 K, close to the calculated water ice condensation temperatures in the solar nebula (where pressures are much higher than in the ISM). Although the correspondence with the nebular snowline is suggestive of the cometary water having been reprocessed in the solar nebula, isotope exchange kinetics at low temperatures are probably too slow for reaction (2) to have enriched water vapor in D within the lifetime of the solar nebula (Grinspoon and Lewis 1987; Fegley and Prinn 1989; Lecluse and Robert 1994).

As noted by Fegley (1993, 1997), it may be more realistic to consider the deuterium exchange process as a back reaction in which D-rich presolar water is losing deuterium to the surrounding H<sub>2</sub>-rich nebular gas. The derived D/H exchange temperatures would then be the maximum temperatures at which the water in Hyakutake, Halley, and Hale-Bopp last exchanged deuterium with nebular H<sub>2</sub>. This could occur, for example, via reactions such as



driven by scattered solar UV and the interstellar UV radiation field in optically thin regions (e.g., the outer skin) of the solar nebula. This is essentially the reverse of the scheme proposed by Yung et al. (1988) and is also supported by recent calculations (Gladstone and Fegley 1997) that indicate that photochemistry was an important disequilibrating process in the outer solar nebula. Ion-molecule reactions driven by galactic cosmic rays in the outer skin of the solar nebula (e.g., see the suggestions of Yung et al. 1988; Deloule and Robert 1995; Aikawa et al. 1998) might also drive the back reactions, but ion-molecule chemistry may only be significant in very low-density regions of the nebula. Grain-catalyzed thermochemistry, e.g., in the subnebulae surrounding the gas giant planets during their formation, probably also played a role both by facilitating the back reaction and also by producing D-poor water [via reaction (1)] which then diluted D-rich presolar water evaporated from presolar ice grains. As discussed later, the giant protoplanetary subnebulae may also have been the sources for the CH<sub>4</sub> and NH<sub>3</sub> in comets.

In principle, the oxygen isotopic composition of cometary water can also be used to constrain its origin (Table II). The [<sup>18</sup>O]/[<sup>16</sup>O] ratio for water in Halley was measured by the *Giotto* NMS and is the same within error as the [<sup>18</sup>O]/[<sup>16</sup>O] ratio for terrestrial SMOW. More precise measurements, however, would be needed to show that water in Halley and other comets has the same oxygen isotopic composition as water on Earth. Extensive measurements of the 16–17–18 oxygen isotope ratios in meteorites by Clayton and colleagues (Clayton 1993) show that different types of meteorites have oxygen isotopic compositions that differ from each other and from the oxygen isotopic composition of the Earth-Moon system. The SNC meteorites, which are widely believed to come from Mars, and the eucrite meteorites, which are widely believed to come from 4 Vesta, also have different oxygen isotopic compositions than the Earth and Moon or than other types of meteorites. The observed differences are not due to

mass-dependent isotopic fractionations and can be very small, on the order of parts per thousand or less. The origin of the oxygen isotope differences is controversial.

It is very important to measure the bulk 16–17–18 oxygen isotopic composition of comets to see where comets plot on the oxygen isotope composition diagram. However, the required measurements are extremely difficult and may be possible only with *in situ* spacecraft experiments or by laboratory analyses of returned samples from comet nuclei. Measurements on individual cometary grains or on mineralogical entities within grains would be particularly revealing, as would isotopic ratios for individual volatile species.

Finally, we consider some implications of the measured ortho/para ratios in cometary water. As discussed earlier, spin temperatures derived from the OPR are 25–35 K for Halley, Hale-Bopp, and Hartley 2, and > 50 K for Wilson. Mumma et al. (1993) argued that the OPR reflected the formation (or condensation) temperature of cometary water. Alternatively, if some process is able to equilibrate the OPR for water inside the cometary nucleus, the observed ratio may refer to this low temperature (Mumma et al. 1993). However, the orbital periods for Hale-Bopp, Halley, and Hartley 2 span the range from 4000 to 6 years, so it seems very unlikely that all three would have internal temperatures near 30 K; for Wilson, the only dynamically new comet in this sample, it was argued that the OPR in its outermost layer was reset to the high temperature limit of 3 by radiation damage while the comet was in the Oort Cloud. In either case, the OPR values for Halley and Hale-Bopp give temperatures that are significantly lower than those derived from the [D]/[H] ratios assuming reprocessing of interstellar water in the solar nebula. How can the apparent discrepancy be explained within the scenario that some reprocessing occurs in the nebula?

One possibility is that the OPR of cometary water was retained during back reaction of the D-rich cometary water with D-poor H<sub>2</sub> in the solar nebula. This scenario is supported by studies of ortho/para exchange and D/H exchange in hydrogen (e.g., Farkas 1935), but the large difference in energy between the lowest para and the lowest ortho state for H<sub>2</sub> compared with the corresponding difference for H<sub>2</sub>O would suggest that preserving the OPR in water would be much more difficult. Further experimental studies of the ortho/para conversion kinetics for water vapor and ice are needed to test this suggestion. Another possibility is that in the solar nebula the cometary water was physically diluted by nebular water having a lower [D]/[H] ratio but a similar OPR. This scenario requires temperatures < 50 K in the comet-formation zone of the outer solar nebula to preserve an OPR < 3 and is consistent with the low temperatures needed to condense CO and N<sub>2</sub> on outer solar system bodies such as Triton and Pluto. Alternatively, the possibility that the cometary OPR might be reset in the coma, where near-nucleus temperatures drop to ~30 K and proton transfer can occur with H<sup>+</sup> and H<sub>3</sub>O<sup>+</sup>, needs to be investigated.

To summarize, the observed  $[D]/[H]$  and ortho/para ratios in cometary water may be consistent either with unmodified interstellar water or with some physical mixing and limited reprocessing of interstellar water in the solar nebula. The upper limit on  $[D]/[H]$  in methanol from comet Halley may also be consistent with some physical mixing and limited reprocessing of interstellar methanol. However, the preservation of unmodified interstellar ices may be difficult, because water ice grains are calculated to have been partially or totally vaporized during infall into the solar nebula (Lunine et al. 1991; Cassen and Chick 1997), although the efficiency of this process might well be different for, and hence distinguish between, Oort Cloud and Jupiter-family (Edgeworth-Kuiper Belt) comets. Keeping interstellar water ice separate from nebular water ice also seems difficult. It is clear to us that laboratory studies of both  $[D]/[H]$  and ortho/para exchange under conditions relevant to comets are essential to the correct interpretation of the observational results.

At present the  $[^{18}O]/[^{16}O]$  ratio of cometary water, which agrees with terrestrial SMOW within large errors, does not provide strong constraints on its origin. High-resolution measurements of the  $^{16-17-18}O$  isotopic ratios in comets (and their constituent volatile and involatile components) will be very useful for constraining their origin and to see if comets are isotopically linked to the volatile-rich CI and CM2 chondrites.

## B. Carbon Compounds

As discussed earlier in this chapter, a diverse suite of carbon compounds has been observed in comets. Observations from the *Giotto* spacecraft indicate that P/Halley has about the solar  $[C]/[O]$  ratio (e.g., Schulze et al. 1997; Anders and Grevesse 1989) and that  $\sim 75\%$  of all carbon is sequestered in the CHON grains, with the other  $\sim 25\%$  present as volatile species (Delsemme 1988). However, these conclusions and the published bulk compositions for P/Halley depend upon several assumptions about the analysis of the PUMA and PIA data and the applicability of observed gas/dust ratios and dust chemistry to the larger particles not measured by the *Giotto* instruments (e.g., see McDonnell et al. 1997; Schulze et al. 1997; and references therein).

The volatile carbon compounds in comets are generally dominated by oxidized carbon species such as CO, CO<sub>2</sub>, H<sub>2</sub>CO, CH<sub>3</sub>OH, with smaller amounts of CH<sub>4</sub> and other hydrocarbons. If extended sources are considered, CO is generally the most abundant carbon gas, and the  $[CO]/[H_2O]$  ratio reaches several tens of percent. However, present observations show  $[CO]/[H_2O]$  ratios  $< 7\%$  for nuclear sources of CO. The  $[H_2CO]/[H_2O]$  ratio reached 7% in Halley when the extended source was considered but is typically much less when only nuclear production is considered (Eberhardt 1998). CH<sub>3</sub>OH seems to be more important than H<sub>2</sub>CO as a volatile present in cometary ices (Table I). Based on the data for nuclear sources of cometary volatiles compiled by Eberhardt (1998), ratios of the

oxidized carbon gases are  $\sim 0.3$  to  $> 3$  for  $[\text{CO}_2]/[\text{CO}]$ ,  $\sim 0.004$  to  $0.08$  for  $[\text{H}_2\text{CO}]/[\text{CO}]$ , and  $\sim 0.1$  to  $2.4$  for  $[\text{CH}_3\text{OH}]/[\text{CO}]$ .

Reduced carbon species are generally less abundant than oxidized carbon species in comets, but they are potentially very important for constraining the origin of cometary carbon volatiles. The  $\text{CH}_4$  abundance in Halley is somewhat controversial, but a recent reanalysis of the *Giotto* ion mass spectrometer data by Altwegg et al. (1994) reports an upper limit of  $0.01$  for the  $[\text{CH}_4]/[\text{H}_2\text{O}]$  ratio. The  $[\text{CO}]/[\text{H}_2\text{O}]$  ratio of  $0.035$  for Halley (Eberhardt 1998) then gives an upper limit of  $< 0.3$  for the  $[\text{CH}_4]/[\text{CO}]$  ratio in Halley, consistent with the  $[\text{CH}_4]/[\text{CO}]$  ratio of about  $0.1$  in Hyakutake, the first comet in which  $\text{CH}_4$  was definitely observed (Mumma et al. 1996). Acetylene and  $\text{C}_2\text{H}_6$  were also observed in Hyakutake, and their ratios relative to CO are  $\sim 0.05$ – $0.15$  and  $\sim 0.07$ , respectively (Brooke et al. 1996; Mumma et al. 1996). These three species were also detected in Hale-Bopp, with similar relative abundances (Mumma et al. 1997a; Weaver et al. 1998); the reductions are still preliminary, but only about 50% of the total CO comes from the nuclear source (DiSanti et al. 1999).

The approximate 3:1 ratio of refractory to volatile carbon species in Halley (Delsemme 1988) is the same as the 3:1 ratio for graphite to carbon gases ( $\text{CO} \sim \text{CO}_2 \sim \text{CH}_4$ ) inside the graphite stability field at  $T < 470$  K and  $P < 10^{-7.6}$  bar (Lewis et al. 1979). This similarity was noted by Fegley (1993), who suggested that Fe-grain-catalyzed chemistry, such as Fischer-Tropsch type (FTT) reactions, may be responsible for the carbon inventory in Halley, because  $\text{CH}_4$ ,  $\text{CO}_2$ , other oxidized carbon compounds, and volatile and involatile hydrocarbons can all be produced from mixtures of  $\text{CO} + \text{H}_2$  by FTT reactions. It is probably difficult to precipitate graphite from a solar gas at the low temperatures and pressures where Lewis et al. (1979) calculated that graphite is stable, and organic matter, such as the CHON particles in Halley, may be formed instead.

Recent experimental work by Fegley and Hong (1998) demonstrates that CO reduction to  $\text{CH}_4$  in  $\text{H}_2$ -rich gas is indeed catalyzed by Fe metal and alloys. They studied reduction of CO in an approximately solar-composition gas and found that high-purity Fe metal, Fe meteorite metal, and ordinary chondrite meteorite powder all catalyzed the production of large amounts of  $\text{CH}_4$ , with efficiencies up to 40% of the equilibrium values. The experiments with the ordinary chondrite meteorite powder were important because chondritic meteorites contain sulfides, which are potential catalyst poisons. Although the catalytic efficiency was less than that for high-purity Fe metal or iron meteorite metal, the powdered chondritic meteorite was still catalytically active and reduced CO to methane. The experimental work was done at 500–1000 K and ambient atmospheric pressure; it is relevant to giant protoplanetary subnebulae where  $\text{CH}_4$  production is predicted in the outer solar nebula (Prinn and Fegley 1989; Fegley and Prinn 1989; Fegley 1993).

A separate set of experiments by Llorca and Casanova (1998) is also relevant. They heated a CO-H<sub>2</sub> gas mixture containing 4000 ppmv CO with a catalyst (Fe-Ni particles supported on silica) in a sealed vessel for 1000 hr (~42 d) at 473 K and  $5 \times 10^{-4}$  bars total pressure. They found that carbonaceous material and (Fe,Ni)<sub>2</sub>C were formed on the catalyst and that CH<sub>4</sub> (90%), C<sub>2</sub>H<sub>6</sub> (~5%), C<sub>2</sub>H<sub>4</sub> (~2%), C<sub>3</sub>H<sub>8</sub> (~2%), C<sub>3</sub>H<sub>6</sub> (0.5%), and C<sub>4</sub>H<sub>10</sub> (0.4%) were formed in the gas phase.

These two studies show that Fe-grain-catalyzed chemistry is capable of producing CH<sub>4</sub>, higher hydrocarbons, and carbonaceous material under conditions relevant to the solar nebula and giant protoplanetary subnebulae (i.e., low [CO]/[H<sub>2</sub>] ratios, moderate *T*, low *P* to ~1 bar). Further experimental work needs to be done to see whether the 3:1 ratio of refractory to volatile carbon and the relative abundances of oxidized and reduced carbon gases observed in comets can be produced by Fe-grain-catalyzed chemistry. Further theoretical work is also needed to quantify the efficiency of mixing between the giant protoplanetary subnebulae and the surrounding solar nebula and the efficiency of radial mixing from the inner to outer solar nebula. It is also important to extend studies of grain-catalyzed chemistry to the even lower temperatures characterizing the outer nebula and to include determinations of possible deuterium fractionation.

Alternatively, the carbon chemistry of comets may reflect the carbon chemistry of unmodified interstellar grains (e.g., Greenberg 1993). All the molecular species found in comets (Table I) except the nonpolar ethane are detected in interstellar clouds, and observable ethane derivatives such as ethyl cyanide are widespread (e.g., Irvine 1998). Furthermore, the relative abundances for the organic molecules found in both comets and interstellar icy grain mantles are quite similar (within an order of magnitude if cometary HNCO, CH<sub>3</sub>CN, and HCN are combined for comparison with interstellar "XCN"; see the chapter by Langer et al., this volume); an exception is HCOOH, but this assignment in the case of the grain mantles may be tentative.

However, CO and CH<sub>4</sub> are highly volatile and may be vaporized from infalling interstellar grains during their accretion by the solar nebula, even at radial distances where water ice can be preserved. Moreover, although the production of CH<sub>4</sub> and other hydrides by laboratory UV irradiation of simulated interstellar ices (e.g., Greenberg 1993) has been used to argue for an interstellar origin of the carbon gases in Halley, the recent calculations by Gladstone and Fegley (1997) show that UV photochemistry is also important in the outer solar nebula. The relatively low D/H ratio in methane on Titan (see Table III) suggests that it may be possible to use D/H ratios to distinguish nebular from interstellar hydrides in comets.

To summarize, the carbon chemistry of Halley and other comets is dominated by refractory carbon species with smaller amounts of volatile carbon compounds. The volatiles are mainly oxidized carbon compounds (CO, CH<sub>3</sub>OH, H<sub>2</sub>CO) with smaller amounts of reduced carbon gases

(CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>). Production of refractory and volatile carbon species by Fe-grain-catalyzed FTT reactions is supported by experimental studies done at low [CO]/[H<sub>2</sub>] ratios, moderate temperatures, and low *P* to ~1 bar. However, the Fe-grain-catalyzed reactions have not reproduced all features of cometary carbon chemistry, and the efficiency of mass transport between possible FTT reaction sites (giant protoplanetary subnebulae, the inner solar nebula) and cometary formation sites (presumably in the Uranus-Neptune region of the outer solar nebula) is unknown. Conversely, the carbon chemistry of cometary ices is rather similar to the chemistry of interstellar ices. However, calculations of presolar grain heating during solar nebula accretion suggest that the preservation of (unmodified) volatile carbon compounds in interstellar grains during their infall into the solar nebula may be difficult.

### C. Nitrogen Compounds

The recent observations of Hale-Bopp and Hyakutake have greatly expanded the number of nitrogen compounds observed in comets. Several of these (HCN, CH<sub>3</sub>CN, HC<sub>3</sub>N, HNCO, NH<sub>2</sub>CHO) must be products of disequilibrium chemistry, such as UV-driven photochemistry and ion-molecule chemistry, although whether this processing occurred in interstellar space or in optically thin and low-density regions of the outer solar nebula is still unknown (Gladstone and Fegley 1997; Aikawa et al. 1998). Other compounds (N<sub>2</sub>, NH<sub>3</sub>) may be nebular products. At least part of the observed HNC is probably due to chemical processing in the cometary coma (Rodgers and Charnley 1998; Irvine et al. 1998*a,b*), raising the possibility that other trace constituents may also be influenced by coma chemistry.

Considering NH<sub>3</sub> and N<sub>2</sub> first, several lines of evidence summarized by Eberhardt (1998) show that the [NH<sub>3</sub>]/[H<sub>2</sub>O] ratio in Halley is ~1%, whereas the radio detections of NH<sub>3</sub> in Hyakutake and Hale-Bopp yield about 0.6% (Table I). The [N<sub>2</sub>]/[H<sub>2</sub>O] ratio in Halley is less well constrained, but observations of N<sub>2</sub><sup>+</sup> by Wyckoff et al. (1991) give [N<sub>2</sub>]/[H<sub>2</sub>O] ~ 0.02%. The derived [NH<sub>3</sub>]/[N<sub>2</sub>] ratio of ~30–50 is intermediate between the predicted [NH<sub>3</sub>]/[N<sub>2</sub>] ratios of ~200 in giant protoplanetary subnebulae and ~0.01 in the solar nebula. Prinn and Fegley (1989) argued that the intermediate ratio indicated a mixture of solar nebula and giant protoplanetary subnebula condensates in Halley, whereas Lunine (1989) and Engel et al. (1990) suggested an interstellar source for the NH<sub>3</sub> in Halley. The two alternatives (nebular versus interstellar) can probably be tested by measuring the D/H ratio in cometary NH<sub>3</sub>, because the interstellar source should give a significantly higher D/H ratio than the nebular sources. Experimental tests of NH<sub>3</sub> production by Fe-grain-catalyzed chemistry may also be useful in distinguishing between the two sources.

Nebular and interstellar sources have also been proposed for the origin of cometary HCN. Meier et al. (1998*a*) measured the [DCN]/[HCN]



ratio in Hale-Bopp and argued that the D/H ratio of  $\sim (230 \pm 40) \times 10^{-5}$  in the HCN is consistent with a low-temperature interstellar source and the [HDO]/[H<sub>2</sub>O] ratio in the same comet. Moreover, the high [DCN]/[HCN] ratio is inconsistent with the lightning shock chemistry source proposed by Prinn and Fegley (1989) and Fegley and Prinn (1989). It is very important to measure (or set upper limits on) the D/H ratio in HCN in other comets to see whether interstellar or nebular sources are implied. Methyl cyanide, but not HC<sub>3</sub>N, HNCO, or NH<sub>2</sub>CHO, were included in prior nebular chemistry modeling. However, the CH<sub>3</sub>CN abundances from disequilibrium chemistry in the nebula (quenched thermochemistry or lightning chemistry) are very much less than the [CH<sub>3</sub>CN]/[HCN] ratio of  $\sim 0.1$  in Hale-Bopp. Thus, other disequilibrium processes (UV photochemistry or ion-molecule chemistry) appear necessary to produce these species, either in the interstellar medium or in the nebula. All of these nitrogen-containing species observed in comet Hale-Bopp are also found in the dense cores of interstellar dark clouds, except NH<sub>2</sub>CHO, which is found in hot cores (Irvine 1999; Ohishi et al. 1992).

#### D. Sulfur Compounds

Here we focus on the sulfur compounds H<sub>2</sub>S, H<sub>2</sub>CS, CS<sub>2</sub>, S<sub>2</sub>, OCS, and SO<sub>2</sub> that are presumably parent (or primary) species emitted from comet nuclei. Sulfur monoxide (SO) is also observed in comets, but, as noted in section III.A, its source (nuclear emission vs. coma production) is not yet certain.

The [H<sub>2</sub>S]/[H<sub>2</sub>O] ratio in several comets ranges from  $\sim 0.2$  to 1.6% (this chapter, Eberhardt 1998). This is smaller than the solar S/O ratio, which corresponds to [H<sub>2</sub>S]/[H<sub>2</sub>O]  $\sim 2.5\%$ , but the total S-gas/[H<sub>2</sub>O] ratio in Hale-Bopp is  $\sim 2.8\%$ . The other major sulfur species are OCS and CS<sub>2</sub>, with SO<sub>2</sub>, H<sub>2</sub>CS, and S<sub>2</sub> being less abundant. However, this listing reflects the relative abundances of these compounds in only a few comets and may not be representative. Taken at face value, it appears that reduced sulfur compounds are more abundant than oxidized sulfur compounds, which is also true for nitrogen compounds but the opposite of the situation for volatile carbon compounds.

Fegley (1993) proposed that H<sub>2</sub>S and NH<sub>3</sub> in Halley formed by the decomposition of solid NH<sub>4</sub>SH. Ammonium hydrosulfide is a volatile solid that can be formed in the solar nebula at 134 K if rapid (i.e., heterogeneous) accretion isolates Fe metal from H<sub>2</sub>S gas (Fegley and Lewis 1980). The similar NH<sub>3</sub> and H<sub>2</sub>S abundances (Table I) are generally consistent with this idea. Ultraviolet photolysis of NH<sub>4</sub>SH also leads to disequilibrium sulfur chemistry (Lebofsky and Fegley 1976), but further work is needed to see how much S<sub>2</sub> can be produced. Two tests which may distinguish between interstellar H<sub>2</sub>S ice or nebular NH<sub>4</sub>SH as sources of cometary H<sub>2</sub>S are (1) the D/H ratio in H<sub>2</sub>S and (2) the presence of an extended source (NH<sub>4</sub>SH grains) vs. a point source (H<sub>2</sub>S ice).

With the exception of  $\text{H}_2\text{S}$ , the major sulfur gas over a wide  $P$ - $T$  range in a solar-composition gas, the sulfur species in comets ( $\text{H}_2\text{CS}$ ,  $\text{CS}_2$ ,  $\text{S}_2$ ,  $\text{OCS}$ , and  $\text{SO}_2$ ) appear to be products of disequilibrium chemistry. The sources of this disequilibrium are less certain. The relative abundances in Hale-Bopp of the polar sulfur-containing species ( $\text{H}_2\text{S}$ ,  $\text{H}_2\text{CS}$ ,  $\text{OCS}$ ,  $\text{SO}_2$ ,  $\text{SO}$ ), which can be observed in interstellar clouds, are quite similar to those measured in the region of low-mass star formation IRAS 16293–2422 (Blake et al. 1994), with one exception: The relative  $\text{H}_2\text{S}$  abundance is an order of magnitude larger in the comet. In warmer cores the  $\text{H}_2\text{S}$  abundance increases, and the relative composition is also quite similar to that in Hale-Bopp, except that the hot cores tend to have higher (and quite variable)  $\text{SO}_2$  and  $\text{SO}$  abundances (van Dishoeck and Blake 1998; Helmich and van Dishoeck 1997). It should be noted, however, that the  $\text{H}_2\text{S}$  abundance in these regions is typically not well constrained, because of the paucity of observable lines (cf. Minh et al. 1990). Likewise, the fraction of cometary  $\text{SO}$  corresponding to parent molecules in the nucleus, rather than daughter molecules produced in the coma, is unclear.

Equilibrium chemistry in the solar nebula is unable to produce  $\text{H}_2\text{CS}$ ,  $\text{CS}_2$ ,  $\text{S}_2$ ,  $\text{OCS}$ , and  $\text{SO}_2$  in the amounts observed in Hale-Bopp. However, Zahnle et al. (1995) showed that high-temperature shock chemistry during the impacts of fragments of Shoemaker-Levy 9 on Jupiter produced  $\text{CS}_2$ ,  $\text{CS}$ , and  $\text{S}_2$  from  $\text{H}_2\text{O}$ -poor jovian gas above the cloud tops. Oxidized sulfur gases, including  $\text{SO}$  and  $\text{SO}_2$ , were calculated to form from impact-induced shock chemistry of  $\text{H}_2\text{O}$ -bearing jovian gas. These results raise the possibility of producing some of the disequilibrium sulfur gases via lightning-induced shock chemistry in the outer solar nebula, but further work is needed to quantify this suggestion.

## V. FROM NUCLEUS TO COMA: MODELS AND RELATIONS

To infer the composition of the cometary nucleus from observations of the coma, the nature of the nucleus, the complexities of sublimation, and the degree of chemical processing in the coma must all be understood. Some recent research on these topics is described in this section (see also Rauer 1999).

### A. Nuclear Models, Fragmentation, and Activity

Because no macroscopic cometary samples have been studied in the laboratory, the nature of the nucleus must still be inferred from remote observations. Many very fundamental questions remain in this regard, including the density, structure, and degree of heterogeneity of the nucleus and the intrinsic similarities or differences among comets.

Potentially significant new information on the nature of at least one cometary nucleus has been provided by comet Shoemaker-Levy 9 (D/1993 F2), both in its close approach to Jupiter and consequent fragmentation

in 1992 and in its subsequent impact on that planet in 1994 (Noll et al. 1996). Models of the tidal breakup (Asphaug and Benz 1996) reproduced the observed fragmentation by starting with a nucleus that has zero strength: that is, a nucleus consisting of hundreds of pieces with dimensions of order 100 m each, that are bound together only gravitationally. Olson and Mumma (1994) obtained similar results for slightly smaller pieces. Interestingly enough, this is the size range found for the typical structural elements of cometary nuclei in a numerical simulation of cometesimal growth by Weidenschilling (1997). Such a model also seems to fit the prominent crater chains observed on Callisto and Ganymede, if the chains are the results of impacts from tidally disrupted comets (Schenk et al. 1996). There is not universal agreement on such a strengthless, "rubble pile" model of the nucleus, however. Sekanina (1996), for example, favors a cohesive nucleus that can fragment along weak points or cracks. A mechanism for forming deep cracks at low nuclear temperatures has been proposed by Jenniskens and Blake (1996), based on laboratory demonstration of a phase change in ice between two amorphous forms. The competing models for the structure of Shoemaker-Levy 9 are discussed in a recent review by A'Hearn (1998). Note that although detailed spectroscopic studies of the impacts with Jupiter were carried out, they do not unambiguously provide information on the chemical composition of Shoemaker-Levy 9 because of the interaction with jovian material (see Crovisier 1996 and Lellouch 1996).

References for various earlier models of the structure of cometary nuclei are given by Mumma et al. (1993). Since that time, in addition to the work on Shoemaker-Levy 9 described above, the structure and composition of the nucleus has been considered theoretically, by Bockelée-Morvan and Rickman (1998), Prialnik (1997), Enzian et al. (1998), Møhlmann (1996), Hughes (1996), and Greenberg (1998), among others. Laboratory work on the evolution of structure due to radiative heating in near surface layers has demonstrated the formation of compositional and structural stratification in comet analogs (e.g., Kossacki et al. 1997).

### **B. Chemistry in the Coma**

Chemistry in cometary comae has traditionally been assumed to involve (a) the sublimation of volatiles ("parent molecules") as the nuclear ices are heated by solar radiation and phase transitions and (b) the subsequent photolysis of these species to produce the radicals and ions ("daughter molecules") observed in visible wavelength spectra. It has been recognized that gas-phase reactions (ion-neutral and neutral-neutral) would occur in the coma of an active comet (e.g., Schmidt et al. 1988), but there had been little direct evidence for such processes, apart from the detection of mass spectrometry peaks in the spacecraft flyby of comet Halley that probably correspond to such protonated species as  $\text{H}_3\text{O}^+$  and  $\text{HCO}_2^+$  (Huebner et al. 1991).

This situation has changed significantly with the apparition of comet Hale-Bopp. The first unambiguous identification of  $\text{H}_3\text{O}^+$  was made from submillimeter observations (Lis et al. 1998). The first cometary detection of the  $\text{HCO}^+$  ion, a classic indicator of ion-molecule chemistry (Herbst and Klemperer 1973), was followed by maps that showed an emission pattern and intensity that could be understood in terms of gas-phase chemistry in the coma and interaction with the solar wind (Lovell et al. 1998*a,b*; Wright et al. 1998).

The origin of cometary HNC, first detected in comet Hyakutake (Irvine et al. 1996), raised the question: Was this neutral but “unstable” molecule produced by chemistry in the coma, or was it present in the nuclear ices? Observations of comet Hale-Bopp showed that the  $[\text{HNC}]/[\text{HCN}]$  ratio in the coma varied with heliocentric distance in a manner that could be explained if HNC were produced by the same gas-phase chemistry model that matched the  $\text{HCO}^+$  observations, but not if the HNC were intrinsic to the nucleus or if it were a simple photodissociation product of a larger parent molecule (Irvine et al. 1998*a,b*). Curiously, though, the coma chemistry models have been unable to reproduce the HNC abundance measured in comet Hyakutake, for which the gas production and hence density in the coma were very much less than in comet Hale-Bopp, with a correspondingly drastically reduced efficiency for gas-phase chemistry (cf. Rodgers and Charnley 1998).

### C. Nuclear Ices: Phase and Sublimation

Because the principal volatile constituent of comets is water, the phase or phases of  $\text{H}_2\text{O}$  ice present in the nucleus, its rate of sublimation, and the degree to which the sublimation of other volatiles is controlled by that of water are all key questions that must be solved to infer the nature of the nucleus correctly from observations of the coma. These issues have often been oversimplified in the past, such as by using equilibrium condensation theory for pure substances. In reality, all these problems involve the complex microphysics of inhomogeneous, poorly characterized solid mixtures.

For example, it is often assumed that the phase of  $\text{H}_2\text{O}$  ice formed by deposition of water vapor onto substrates at low temperature is determined solely by the temperature, with amorphous ice forming below 130 K, crystalline cubic ice for  $130 < T < 170$  K, and hexagonal ice for  $T > 170$  K. However, both theoretical and laboratory results indicate that the kinetics of the deposition and crystallization may control the crystallinity of ices in astrophysical situations. Thus, Kouchi et al. (1994) conclude that if interstellar icy grain mantles are preserved during the formation of the solar nebula, comets formed from these grains would contain amorphous water ice. In contrast, if such mantles were sublimed and then recondensed as the solar nebula cooled, the  $\text{H}_2\text{O}$  ice would be crystalline. The situation is even more complex, with the discoveries that more than one amorphous phase

of water ice exist (Jenniskens et al. 1995) and that the phase of deposited ice can be affected by the morphology (microstructure) of the underlying substrate (Trakhtenberg et al. 1997).

The sublimation of the volatiles in a cometary nucleus as it approaches the Sun is likewise a very complex process. Laboratory experiments for a water matrix deposited at low temperatures have demonstrated, for example, that the percentage of trace constituents in the sublimate depends on ice temperature, ice phase, and whether the release is primarily from the surface rather than the interior of a porous layer (Notesco and Bar-Nun 1997). The radical change in the composition of the subliming gas as comet Hale-Bopp approached the Sun was demonstrated by the  $[\text{CO}]/[\text{H}_2\text{O}]$  ratio, which varied from  $> 5$  to  $< \frac{1}{5}$  for heliocentric distances  $> 4.5$  and  $< 2.8$  AU, respectively (Biver et al. 1997, 1998). An interesting result reported by Jenniskens et al. (1997) is the presence of a viscous phase of liquid water that coexists with cubic crystalline ice for  $120 < T < 210$  K when a thin layer of amorphous ice is warmed above 120 K. The presence of liquid water in cometary nuclei might have interesting and significant chemical effects.

In comparing abundances in interstellar clouds to those in comets, it must be remembered that chemical fractionation occurs not only during sublimation, but also during the initial trapping of gases as ice particles form. For example, laboratory experiments show that condensation can enhance the abundance of CO relative to  $\text{N}_2$  and of  $\text{C}_2\text{H}_6$  relative to  $\text{CH}_4$ , compared to the initial gas phase (Notesco and Bar-Nun 1996; Notesco et al. 1997). The measured fractionation at a temperature of 50–60 K seems to match abundance ratios observed in comets Halley and Hyakutake, although this match involves assumptions about the composition of the initial gas. This temperature is significantly higher than the water spin temperature (OPR) reported for comet Halley.

## VI. SUMMARY

Comets are clearly chemically disequilibrium assemblages, which cannot be understood in terms of equilibrium models. On the one hand, the very few comets that have been observed in detail resemble interstellar material in several ways, both in their composition and their isotopic fractionation. On the other hand, accretion models suggest that the preservation of pristine interstellar material in the nebula may be difficult. Moreover, there must have been a variety of disequilibrium processes at work in the outer regions of the solar nebula where comets formed.

There has been considerable discussion in the literature concerning the ortho/para ratio measured for water in several comets, as discussed above in sections III.D and IV.A. The low spin temperatures that characterize this ratio in several comets, 25–35 K, are usually considered to represent the temperature of the cometary ices at the time of their

formation, which might provide constraints on the formation site. As noted by Mumma et al. (1993), however, there exists relatively little data on ortho/para conversion for water, so that it is unclear how the OPR will be affected by the condensation of water vapor onto grains, by storage in the Oort Cloud or Edgeworth-Kuiper Belt for 4.5 Gyr, by the warming of the ices prior to and during sublimation, and by possible processing in the coma. We do note that fractionation of the water OPR during condensation on various matrixes has been reported by Konyukhov et al. (1988).

We have discussed the compositional similarity between comets and interstellar volatiles at several points in this chapter. This applies to both the composition of icy grain mantles and to the gas-phase molecules that may have sublimated from the mantles in hot cores (compare Table I with the interstellar abundances in the chapter by Langer et al., this volume, and in van Dishoeck and Blake 1998). There are several caveats in such comparisons, however. As noted in section III.A, the observed composition of the coma differs in subtle ways from the composition of the nucleus. One might wonder, for example, whether some of the minor species detected in Hale-Bopp (perhaps  $\text{NH}_2\text{CHO}$ ,  $\text{HCOOCH}_3$ ) might not be produced by chemical processes in the coma. Likewise, the composition of hot cores certainly includes products of gas-phase chemistry in a warm environment, as well as the former constituents of grain mantles.

Isotopic fractionations are generally regarded as good tracers of the origin and evolution of cometary matter. Even here, though, questions arise. What is the significance of the agreement of the  $[\text{HDO}]/[\text{H}_2\text{O}]$  and  $[\text{DCN}]/[\text{HCN}]$  ratios between comets and hot cores if, as has been suggested, the interstellar  $[\text{DCN}]/[\text{HCN}]$  ratio no longer reflects the probable solid-phase value (Hatchell et al. 1998)? In other words, if comets preserve interstellar HCN, why is the D/H fractionation so *low* compared with that in cold clouds such as TMC-1? Likewise, is the failure to date to detect cometary HDCO and  $\text{CH}_3\text{OD}$  significant? Could the cometary isotopic ratios reflect nonequilibrium processes carried out in the cold, low-density regions of the nebula rather than in the interstellar environment?

We believe that the answers to these questions are not yet clear but that developments over the next several years should help to remedy this situation. In Table IV we list some recommendations for future observations, laboratory studies, and theoretical modeling that will significantly clarify the nature of comets. Thus, measurement of the D/H fractionation in additional species (including  $\text{H}_2\text{CO}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{S}$ ) and in Edgeworth-Kuiper Belt as well as in Oort Cloud comets may distinguish among possible sources for cometary volatiles. Both ground-based and spacecraft studies can help to discriminate between nuclear and extended sources of molecules such as CO, OCS,  $\text{H}_2\text{S}$ , and  $\text{H}_2\text{CO}$ , and returned samples should eventually provide an unbiased inventory of cometary composition and allow for the comparison of accurate isotopic ratios with

**TABLE IV**  
Recommendations

Measurement	Goal
<i>Earth-based remote sensing</i>	
D/H ratios in H <sub>2</sub> O from more comets	Constrain source of cometary water
O-P ratios in H <sub>2</sub> O from more comets	Constrain source of cometary water
<i>Spacecraft or Earth-based experiments</i>	
D/H ratios in CH <sub>3</sub> OH, H <sub>2</sub> CO for comets	Constrain source of cometary volatiles
D/H ratios in NH <sub>3</sub> and H <sub>2</sub> S	Constrain nitrogen and sulfur chemistry
Mapping of volatile emission	Resolve nuclear vs. extended sources (CO, H <sub>2</sub> CO, etc.)
<i>In situ</i> analyses of volatiles and grains	
Return cold (< 20 K) nuclei samples	Constrain origin of cometary material Composition and structure of nucleus Unbiased inventory of cometary volatiles
<i>Laboratory studies of returned comet samples</i>	
Study presolar grains in rock	Nature and abundance of presolar grains
<sup>16–17–18</sup> O isotopic ratios of rock	Plot comets on Clayton's 3 O isotope diagram Pristine presolar rock or nebular condensate?
<sup>16–17–18</sup> O isotopic ratios of water	Determine if comets provided Earth's oceans
Ti isotopic analyses of rock	See if comets are related to C chondrites; pristine presolar rock or nebular condensate?
<sup>26</sup> Al and other extinct radionuclides in rock	High presolar values or nebularlike values?
Radiometric dating of rock	Look for ages > age of solar system
<i>Experimental studies for data analysis</i>	
Conversion kinetics of ortho/para water	Interpret observed <i>o-p</i> ratios of cometary H <sub>2</sub> O
D/H exchange kinetics (H <sub>2</sub> O, CH <sub>4</sub> , NH <sub>3</sub> )	Interpret observed D/H ratios of cometary volatiles
Grain-catalyzed CO → organics reaction	Nebular vs. interstellar origin of organic molecules
Grain-catalyzed N <sub>2</sub> → NH <sub>3</sub> reaction	Nebular vs. interstellar origin of ammonia
<i>Theoretical modeling for data analysis</i>	
UV, X-ray photochemistry of gas and grains in outer solar nebula at and beyond snowline	Steady-state abundances of volatile carbon species (CO <sub>2</sub> , CH <sub>3</sub> OH, H <sub>2</sub> CO, HCOOH, etc.)
Ion-molecule chemistry in outer solar nebula	Compare composition and isotopic ratios with interstellar values

terrestrial values (e.g., for  $^{16-17-18}\text{O}$ ). Laboratory study is urgently needed of D/H exchange kinetics for cometary volatiles, of ortho/para conversion for water, and of low-temperature, grain-catalyzed reactions for the reduction of CO and  $\text{N}_2$  to organics and  $\text{NH}_3$ . Finally, realistic theoretical modeling of nonequilibrium chemistry in the outer solar nebula is needed to evaluate the extent to which such processes could mimic those that occur in interstellar clouds, accompanied by correspondingly detailed analyses of coma chemistry. Fortunately, such work is beginning (e.g., Aikawa et al. 1998; Willacy et al. 1998).

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