From Interstellar Material to Cometary Particles and Molecules

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The birthplace of stars, planets, and small bodies are molecular clouds consisting mainly of H and He gas as well as tiny amounts of solid particles. Dust and gas from such an interstellar cloud collapsed to form a central condensation that became the Sun, as well as a surrounding disk — the solar nebula. In this protoplanetary disk innumerable submicrometer particles — icy and refractory in nature — agglomerated to larger planetesimals and subsequently into planets. Comets were formed from remnant inner disk material that was not incorporated into planets. Comets assembled beyond the orbit of Jupiter and may therefore provide a record of some pristine material from the parent interstellar cloud. Our knowledge of the composition of comets is predominantly based on evaporation of volatile species and thermal emission from siliceous and carbonaceous dust when bright comets approach the Sun. The investigation of outgassing curves from bright comets has provided a general link with abundances of ices and gas phase molecules detected in dense interstellar clouds. Theoretical models indicate that bulk material in cometary nuclei is stratified in density, porosity, and composition and contains coexisting ice phases, possibly clathrates and trapped gases. It is therefore apparent that the outgassing of species from cometary nuclei will not essentially mimic that expected from pure sublimation of ices of interstellar composition. The current lack of astronomical data related to solar-type star-forming regions, and the statistically small sample of comets studied to date, are the major obstacles to be overcome before a coherent link between interstellar and solar system material can be established. This chapter attempts to compile the current knowledge on the connection between interstellar and cometary material, based on observations of interstellar dust and gas, observations of cometary volatiles, simulation experiments, and the analysis of extraterrestrial matter.

1. INTRODUCTION

In the 1950s comets were described by *Whipple* (1950) as "dirty snowballs" made up of water ice and small rock particles. Cometary observations and related investigations between then and now strongly improved our knowledge and view on these precious and most pristine solar system objects. For a historical perspective on comets the readers are referred to *Festou et al.* (1993a,b, 2004). The apparition of unusually bright comets in the last 2–3 decades and the observations using advanced instrumentation allowed us to get important insights into the coma chemistry (*Bockelée-Morvan et al.,* 2004; *Hanner and Bradley,* 2004) and their relation to the parent interstellar cloud (*Irvine and Lunine,* 2004).

The origin of comets and the content of pristine interstellar material incorporated in them are far from being understood. The assumption that cometary nuclei are aggregates of pristine interstellar ices and dust (*Greenberg,* 1982; *Li and Greenberg,* 1997) is clearly a gross simplification. Processing of infalling interstellar medium (ISM) material within the solar nebula must have occurred in one way or another. A pivotal epoch of processing is when interstellar material is first accreted. However, no detailed studies of the chemistry at the accretion shock exist (cf. *Neufeld and Hollenbach,* 1994). With this caveat, we can consider two limiting cases of processing. First, interstellar material entering far out in the nebula, where the accretion shock is weak (100 AU), should be largely unmodified when first incorporated. In this case, chemical reactions will proceed as this material is transported radially inward (*Aikawa et al.,* 1999; *Gail,* 2001). Second, accretion closer to the protosun will lead to complete dissociation and destruction of interstellar molecules. In this case, the molecules will subsequently form solely from nebular chemistry (e.g., *Fegley and Prinn,* 1989) and these can be radially mixed outward. Today results indicate that presolar material has been chemically and physically processed according to the distance from the protostar (*Chick and Cassen,* 1997; *Fegley,* 1999). Comets are therefore a mixture of interstellar and processed material and their initial composition will differ according to their place of formation.

The "long-period" comets probably formed across the giant planet formation region (5–40 AU) with the majority of them originating from the Uranus-Neptune region. For a detailed discussion of cometary reservoirs and cometary evolution the readers are referred to *Jewitt* (2004), *Dones et al.* (2004), and *Meech and Svoreň* (2004). Given the gradient in physical conditions expected across this region of the nebula, chemical diversity in this comet population is to be expected, as has been inferred for short-period comets (*A'Hearn et al.,* 1995). Processing and dynamical exchange of icy planetesimals in the comet-forming region could have contributed to chemical heterogeneity, or may have "homogenized" cometary nuclei before their ejection to the Oort cloud (*Weissman,* 1999), where they could have experienced further material processing and evolution (*Stern,* 2003). Remote infrared observations of parent volatiles in six Oort cloud comets (including Hyakutake and Hale-Bopp) showed that they have similar volatile organic compositions (*Mumma et al.,* 2003), appear to be more pristine, and display a reasonable similarity to interstellar cloud material.

The noble gas differentiation, deuterium enrichment, and low ortho-para ratio measured in water are all consistent with formation of precometary ices at ~30 K, similar to the conditions in the Uranus-Neptune region (*Bockelée-Morvan et al.,* 2004). Comet-forming material in the Jupiter-Saturn region (5–10 AU) experienced higher temperatures and may also have been exposed to a much higher degree of radiation processing before its assembly into comets. Extrapolating from the case of C/1999 S4 (LINEAR), there is some evidence that such comets should exhibit depletions and different abundance ratios compared to those formed at 30 AU and beyond (*Mumma et al.,* 2001a).

Comets are made of silicates (~25%), organic refractory material (~25%), small carbonaceous molecules (few percent), and ~50% water ice with small admixtures of other ice species (*Greenberg,* 1998). Molecular ices and the gases released upon sublimation, silicate dust, and solid-state carbonaceous materials are the major components of dusty cometary comae that can be studied by astronomical observations and through laboratory simulations (*Rodgers et al.,* 2004; *Hanner and Bradley,* 2004; *Colangeli et al.,* 2004). Studying these compounds in comets, in the ISM, and in meteoritic materials allows us to reveal which processes occurred in the ISM and which occurred during the formation of the solar nebula. For example, the appearance of Mg-rich crystalline silicates in some comets and the scarcity of crystalline silicates in the ISM [<5%, *Li and Greenberg* (1997), <0.5%, *Kemper et al.* (2004)] indicates cometary crystalline silicates are grains that condensed at high temperatures [~1400 K, *Grossman* (1972)] or were annealed from amorphous silicates at somewhat lower temperatures [>900 K, *Fabian et al.* (2000)] in the solar nebula. The origin of cometary solid-state carbonaceous materials is less clearly defined than the origin of the siliceous materials. The bulk of solid-state cosmic C in the interstellar medium is in an unknown form. There is strong evidence that amorphous C and similar macromolecular material takes up most of the

C in the interstellar medium (*Ehrenfreund and Charnley,* 2000; *Mennella et al.,* 1998). The same trend is observed in meteorites, where macromolecular material takes up more than 80% of the C (*Sephton et al.,* 2000; *Gardinier et al.,* 2000). The link between macromolecular C in the solar system and the interstellar macromolecular C is yet to be understood, but it is tempting to assume that such a material is also present in comets.

Cometary nuclei are a highly porous agglomeration of grains of ice and dust and they appear stratified in density, porosity, ice phases, and strength. For a detailed discussion on cometary structure and properties, the readers are referred to *Prialnik et al.* (2004) and *Weissman et al.* (2004). The nuclear ice component probably consists of different coexisting ice phases, including amorphous ice, crystalline ice, and clathrates, with gases trapped in bulk and clathrate hydrates (see Fig. 12 in *Prialnik et al.,* 2004). The structure of the nucleus and the internal processes lead to certain sublimation characteristics and outbursts of ice, dust, and gas when the nucleus approaches the Sun (*Meech and Svoreň,* 2004; *Prialnik et al.,* 2004; *Colangeli et al.,* 2004). Monitoring the sublimation pattern of cometary material provides a powerful tool to obtain more information on their composition. However, from observations it is not possible to achieve a direct correspondence between the heliocentric distance and the volatility of species as defined by their sublimation temperatures, e.g., as pure ices (*Capria,* 2002). The size distribution of grains in cometary bulk material extends over several orders of magnitude, including the pores in between.

The effect of pore size distribution seems to be important for the thermal conductivity. *Shoshany et al.* (2002) show in their models that the thermal conductivity is lowered by several orders of magnitude at high porosities. The physics of the processes responsible for driving sublimation and outbursts from the interior of cometary nuclei is described by *Prialnik et al.* (2004). Heat waves from the surface or internal radioactive heating provide the energy within the cometary nucleus for water ice crystallization, which releases latent heat. The trapped gaseous species, which are released during the crystallization process, move through the pores and carry along small, detached dust particles. Another source of gas in the interior can be sublimation of volatile ices from the pore walls. Once gas is released from the ice in the interior of the nucleus, its pressure will cause it to flow to the surface. Free gases present in the cometary interior are expected to affect the thermal and mechanical structure of the nucleus. The internal pressure may surpass the tensile strength of the fragile grainy configuration. This results in cracking of the porous matrix and subsequent outbursts of gas and dust (*Prialnik,* 2002). Internal pressure buildup by gas, thermal stress, and rotation may cause disruption of the fragile material. On the contrary, sintering (increase of contact area between grains — the Hertz factor — due to heating or compaction) and pore blocking due to larger grains as well as recondensation of volatiles may reconsolidate material. The complexity of internal processes may produce an individual pattern for each comet.

Large-scale groundbased simulation experiments (e.g., KOSI Kometen-Simulation) have been performed to study the evolution of cometary nuclei (*Kochan et al.,* 1998; *Colangeli et al.,* 2004). Sublimation experiments with ice-mineral mixtures showed the metamorphosis of ice, the reduction of volatiles in surface layers, and the formation of a porous low-density (0.1 g/cm^3) dust mantle (*Grün et al.,* 1993). The formation of a dust mantle on the surface and a system of ice layers below the mantle from the different admixed materials have been detected after the insolation of the artificial comet. Those experiments allowed for studies of the mechanisms for heat transfer between the comet surface and its interior, compositional structural and isotopic changes that occur near the comet's surface, and the mechanisms of the ejection of dust and ice grains from the surface (*Kochan et al.,* 1998; *Colangeli et al.,* 2004). In the following sections we will emphasize the discussion on the main components that provide insights into the interstellar–solar system connection and emphasize the processes that could contribute (or not) to modifying interstellar material as it becomes incorporated into comets.

2. TRACING INTERSTELLAR CLOUD MATERIAL IN COMETS

In cometary science, a central issue is elucidating and quantifying which aspects of their chemical composition and heterogeneity can be attributed to being either pristine or partially processed interstellar material, or material formed purely from nebular processes (*Irvine et al.,* 2000; *Irvine and Lunine,* 2004). Astronomical observations now allow us to follow in detail the chemical evolution of pristine interstellar material in a system analogous to that from which the protosolar nebula formed (*Mannings et al.,* 2000; *van Dishoeck and Blake,* 1998; *Ehrenfreund and Charnley,* 2000). The meteoritic record, interplanetary dust particles (IDPs), and asteroidal observations all indicate that some interstellar material underwent a very significant degree of processing in the protosolar nebula (e.g., *Ehrenfreund et al.,* 2002). Observations of a cometary volatile inventory that is largely consistent with the interstellar inventory, and dust grains indicative of nebular processing, are evidence for contributions from at least two sources. However, in many cases, it is not a simple matter to discern which source is responsible for a particular chemical or physical characteristic; a plausible theoretical argument can usually be made for each. Here we discuss several distinctive features of cometary composition. This is done in the context of the processes that may have acted to modify interstellar material incorporated in the protosolar nebula (see section 5.3 of *Wooden et al.,* 2004). We attempt to evaluate the likelihood of each feature being symptomatic of either interstellar origin or complete nebular reprocessing, or some intermediate between these extremes.

For comets we can only compare their volatile composition directly with that of interstellar ices. However, it appears that, in the dense core from which the protosun

formed, chemical conditions eventually evolved to the point where almost all the heavy volatile material had condensed as ice onto dust grains (*Brown et al.,* 1988; *Bergin et al.,* 2002). As cold interstellar gas and ice-mantled dust grains collapsed onto the protosolar nebula, they were heated by radiation and gas-grain drag (e.g., *Lunine,* 1989). Nonrotating collapse calculations indicate that infall timescales can become shorter than most chemical timescales. This results in material from the cool envelope collapsing onto the central protostar without significant chemical alteration (*Rodgers and Charnley,* 2003). However, because of rotation of the dense cloud core, infalling parcels of gas and dust far from the axis of rotation would have had sufficient angular momentum to move along ballistic trajectories and become incorporated in a disk, rather than fall directly into the protosun (*Cassen and Moosman,* 1981; *Terebey et al.,* 1984).

Infalling matter passes through the accretion shock where significant processing can occur. Far from the protosun, the lower nebular (preshock) densities and slower shock speeds meant less processing of interstellar material. In this case, processing may simply involve removal and postshock recondensation of the ices (e.g., *Lunine,* 1989). Approaching the protostar, higher postshock temperatures and enhanced UV fields led to increasingly hostile conditions for the survival of interstellar ices, volatile and refractory organics, and refractory dust grains (*Neufeld and Hollenbach,* 1994; *Chick and Cassen,* 1997).

Compositional and isotopic evidence from analysis of meteorites and IDPs suggests, however, that some volatile interstellar molecules may have entered the nebula relatively unscathed (*Messenger,* 2000; *Irvine et al.,* 2000). The phase of large-scale accretion of molecular cloud material lasted around a few hundred thousand years; most of this was consumed by the protosun (*Cameron,* 1995). Comets began to be assembled in the 5–100-AU region of the nebula toward the end of the stage of nebular disk dissipation (lasting about 50,000 years), when viscous effects dominated nebular evolution. During this stage, the interstellar mass accretion rate was probably about 10–100 times less than that occurring in the initial phase of accretion. Comet formation ended after a further 1–2 m.y., when solar accumulation almost finished and when giant planet formation (at 5–40 AU) was almost complete.

During disk dissipation, there was large-scale inward transport of most of the gas and dust and outward transport of most of the angular momentum (e.g., *Ruden and Pollack,* 1991). Turbulent motions, whether convective or magnetohydrodynamic in origin, produced an outward diffusion of material from the inner nebula (*Morfill and Volk,* 1984). This led to radial mixing of the products of two chemistries (*Irvine et al.,* 2000; *Markwick and Charnley,* 2004). The cold outer protosolar nebula, where accretion favors retention of ISM integrity, was in fact a chemically active region (e.g., *Aikawa and Herbst,* 1999a; *Aikawa et al.,* 1999). Cosmic rays (beyond about 10 AU) and other sources of ionization such as X-rays (*Glassgold et al.,* 1997), UV photons (*Willacy and Langer,* 2000), and radioactive decay [e.g.,

[26]Al and [60]Fe; *Finocchi and Gail* (1997)] can drive a non-equilibrium chemistry involving ion-molecule and neutral-neutral reactions. In the hot inner nebula (within about 1 AU), material can be completely destroyed and lose its interstellar integrity (*Fegley and Prinn,* 1989). The composition of this region is governed by a gas-grain chemistry in thermodynamic equilibrium. There is little direct chemical knowledge about the 5–40-AU regions of disks where comets are formed. Infrared observations of CO can probe the hot innermost regions of disks but these regions are not at present easily accessible to radioastronomical observations (*Dutrey et al.,* 2004).

Radial mixing offers a means of transporting crystalline silicates, be they condensates or annealed grains, outward from the inner nebula into the 5–40-AU region where they were incorporated into comets (*Gail,* 2001; *Bockelée-Morvan et al.,* 2002). However, nebular shocks at around 5–10 AU are another possible candidate (*Harker and Desch,* 2002) and, if correct, would place constraints on the efficiency of radial mixing and thermal convection in the nebula. Shocks in icy regions of the nebula have also been proposed as the origin of chondritic fine-grained phyllosilicates (*Ciesla et al.,* 2003). The detailed effects of such shocks on the volatile organic inventory are probably extensive, and need to be explored to coherently assess nebular processing of cometary materials. Inward transport of the products of "interstellar chemistry," or of similar chemistry in the cold disk, could account for the similarities between the volatile inventory of comets and these products. The key question is therefore how much radial mixing actually occurred (see *Lunine,* 1997; *Fegley, 1999,* 2000; *Lunine and Gautier,* 2004). For a detailed discussion on the physical and chemical processes of disks the readers are referred to *Dutrey et al.* (2004), *Boss* (2004), and *Lunine and Gauthier* (2004).

2.1. Is There Interstellar Cloud Material in Comets?

The gases observed in cometary comae originate from the nuclear ices and so offer insight into the nucleus composition. Coma molecules can either have a "native" source, and so have been sublimed directly from the nucleus itself, or they may appear throughout the coma from an "extended" source, probably due to the decomposition of large organic particles or molecules. For a detailed discussion on cometary volatiles and coma chemistry, the readers are referred to *Bockelée-Morvan et al.* (2004) and *Rodgers et al.* (2004). A comparison with the inventory of interstellar ices, as well as with the gases found in dark molecular clouds and in regions of massive and low-mass star formation, suggests a direct link. Apparent evidence for the retention of an interstellar origin are the facts that the major ice components, and many of the trace molecular species, are also found in cometary comae. However, as briefly discussed here, there are differences in the relative abundances of some cometary species when compared to their interstellar values. Thus, there is some circumstantial evidence for processing of the

precursor interstellar volatiles; the location, epoch, and source of this processing is largely to be determined.

Silicate and C-based micrometer-sized dust particles that are produced in the outflows of late-type stars provide a catalytic surface for a variety of reactions to occur when they are dispersed throughout the molecular cloud (*Ehrenfreund et al.,* 2003). In dense clouds, ices are stable and efficiently formed on the surface of such dust particles. The formation of interstellar ices has been discussed in *Wooden et al.* (2004). An extended inventory of interstellar ice species has only been established for bright high-mass star-forming regions (e.g., *Gibb et al.,* 2000). Whether those abundances are relevant for a comparison with cometary composition in low-mass systems is strongly questioned. There are only incomplete datasets available for solar-type stars. Most of them are characterized by a low flux and were therefore difficult to observe by satellites such as the Infrared Space Observatory (ISO). Groundbased observations allow us only to observe small wavelength regions in telluric windows (*Boogert et al.,* 2002). Table 1 lists solid state abundances measured in high- and low-mass (solar-type) star-forming regions in comparison with cometary volatiles.

As discussed by *Wooden et al.* (2004), the spectrum of interstellar clouds is very rich and shows some very strong bands that mask the signature of a number of other spe-

TABLE 1. Interstellar ice abundances measured toward high- and low-mass (solar-type) star-forming regions (*Gibb et al.,* 2000, *Nummelin et al.,* 2001, *Pontoppidan et al.,* 2003, *Taban et al.,* 2003) are compared to measured abundances of cometary volatiles in comet Halley, Hyakutake, Hale-Bopp, Lee, LINEAR and Ikeya-Zhang (see *Bockelée-Morvan et al.,* 2004, Table 1).

	High-mass Stars	Solar-type Stars	Comet Average
H_2O	100	100	100
CO	9–20	5–50	1.8–30
CO_2	12–20	12–37	3–6
CH_3OH	0–22	0–25	1.8–2.5
CH_4	1–2	<1	0.14–1.5
H_2CO	1.5–7	—	0.4–4
OCS	0–0.3	<0.08	0.1–0.4
NH_3	0–5	—	0.5–1.5
HCOOH	0.4–3	—	0.09
C_2H_6	<0.4	—	0.11–0.67
HCN	<3	—	0.1–0.3
C_2H_2	—	—	0.1–0.5

The strong diversity of abundances among the main species CO, CO_2, and CH_3OH, even within high- and low-mass star-forming regions, hampers the search for an interstellar/cometary link. The lack of data for the low flux solar-type stars adds to those uncertainties. In contrast to cometary observations, there is no evidence for the presence of C_2H_6, HCN, and C_2H_2 nor S-bearing species (apart from tiny abundances of OCS) in interstellar ices. H_2CO and HCOOH are only tentatively measured in interstellar ices and need a more firm abundance determination.

cies. After H_2O and CO (which may have multiple sources in comets), species such as CO_2, CH_3OH, OCS, NH_3, and CH_4 seem to be among the only molecules that could provide constraints on an interstellar/cometary link. Most of the other weak features may escape detection or their abundance remains poorly determined in the ISM. This applies to C_2H_2, C_2H_6, and HCN, of which none have been observed in the interstellar solid phase. The only molecules that show a similar abundance in comets and some low-mass star-forming regions [such as "Elias 29" (*Boogert et al.,* 2000)] are CH_4 and CH_3OH.

The ice phases within interstellar grain mantles will — when incorporated into comets — contribute to the outgassing properties, as do the structures of cometary nuclei that are stratified in temperature, porosity, density, and composition (*Prialnik et al.,* 2004). Interstellar icy grains are characterized by different ice phases, amorphous, crystalline, segregated boundary layers and possibly clathrates (*Ehrenfreund et al.,* 1999).

In particular, some CO, CO_2, and CH_3OH seem to be present in pure form [e.g., "apolar" CO layers in cold clouds or segregated boundary phases of CO_2 and CH_3OH in warmer cloud regions (*Ehrenfreund et al.,* 1999)], which would allow sublimation at a much lower temperature than when trapped in an H_2O ice matrix. Sublimation of such species at large heliocentric distances could provide evidence for such ice layers. No attempt has ever been made to correlate the outgassing pattern of cometary volatiles with the different ice phases present in interstellar grain mantles.

Carbon dioxide and CH_3OH are the most important ice species (after H_2O and CO) that can be used as a tracer for the interstellar/cometary link. ISO identified CO_2 ice as one of the major components in interstellar ice mantles with an average abundance of ~15–20% relative to water ice. Recently, CO_2 ice abundances of up to 37% (relative to water ice) have been measured toward low-mass protostars (*Nummelin et al.,* 2001). Whereas CO_2 ice is ubiquitous in the interstellar medium (every target measured has CO_2 abundances above 10% relative to water ice), the measured abundance of CH_3OH is highly variable and in fact is undetected toward many sources. Among high-mass and low-mass protostars, the CH_3OH abundance ranges from small upper limits to 25% relative to water ice (*Dartois et al.,* 1999; *Pontoppidan et al.,* 2003). The cometary abundance of methanol is appreciable but generally much smaller (~2%) when compared to interstellar ices (5–25%). Similarly, CO_2 appears to be much less abundant in comets than in molecular clouds (*Feldman et al.,* 2004). Both these observations suggest either partial degradation of the interstellar molecules or complete production of them in the solar nebula. If energetic processing of molecular ices is an efficient means of forming CO_2 (*Wooden et al.,* 2004), and given the more energetic environment of the protosolar nebula, it is surprising that CO_2 is not at least as abundant as in molecular clouds. This may rule out energetic processing of ices in the outer nebula as the source of these compounds. *Gail* (2002) has shown that radial mixing of oxidized C dust from

the inner nebula could not explain the cometary CH_3OH abundances. In this region an additional possible source of methanol is Fischer-Tropsch-type (FTT) synthesis (*Fegley and Prinn,* 1989). Perhaps the simplest explanation is that these molecules are interstellar but have had their original populations partially depleted in the nebula. For example, CO_2 (and H_2CO) are very susceptible to destruction by H atoms in warm gas (*Charnley and Kaufman,* 2000). This may point to CO_2 molecules being partially destroyed at the accretion shock or in nebular shock waves. The situation is less clear for CH_3OH since the direct detection of methanol in a protostellar disk [at <100 AU (*Goldsmith et al.,* 1999)] indicates a large fractional abundance of 3×10^{-7}, apparently at the disk surface, but a lower value deeper in the disk of 2×10^{-8}. This lower value may simply arise from depletion onto dust, in which case the abundance of methanol in any precometary ices could in fact be similar to that found in comets.

The current interstellar ammonia abundances, which are much lower than originally estimated (*Taban et al.,* 2003), are more compatible with cometary measurements (see Table 1). Both interstellar and nebular chemistries will produce N_2 efficiently (e.g., Owen et al., 2001). Thus perhaps one of the most perplexing problems in making a definite connection between the major interstellar volatiles and those in comets is widespread depletion/lack of N_2 as measured by N_2^+ observations of the latter (*Cochran et al.,* 2000; *Cochran,* 2002). This may simply be a volatility issue.

Molecular N may have been more readily evaporated relative to CO due to modest warming of precometary ices (e.g., *Irvine et al.,* 2000). A further possibility is that CO was selectively trapped during formation of clathrate hydrates, whereas N_2 was not (*Iro et al.,* 2003). Alternatively, this deficiency could have an origin in the prestellar phase (*Charnley and Rodgers,* 2002), in which case (and if production and/or mixing of N_2 in the nebula is inefficient) all comets may to some degree show this deficiency relative to the ISM value.

The problem in comparing the abundances of S-bearing compounds is that the cometary parents CS_2 and H_2S are not detected in interstellar ices; although gaseous H_2S is observed to be abundant in star-forming regions. CS_2 and S_2 are unknown in the ISM. The most abundant of the interstellar S-bearing compounds have all been detected in comets. However, some of them are photoproducts of other compounds (e.g., CS_2 and CS, SO and SO_2), or may have a distributed (polymeric?) source (e.g., CS, OCS). These considerations make it very unlikely that cometary sulfuretted species represent pristine interstellar material.

The simple hydrocarbons CH_4, C_2H_2, and C_2H_6 also present ambiguity. Methane is the only molecule among these three that is present in interstellar ices (~1% relative to water ice); acetylene has a cometary abundance similar to the interstellar gas (e.g., *Lahuis and van Dishoeck,* 2000). It is therefore tempting to identify them as being of interstellar origin where ethane forms by reduction of acetylene on cold (10 K) grains. Alternatively, these hydrocarbons could have an

origin in nebular chemistry, probably involving some form of gas-grain chemistry. For example, *Gail* (2002) showed that mixing of oxidized C dust could explain the abundances of CH_4 and C_2H_2 in comets, but not the presence of C_2H_6. If this particular nebular chemistry was the origin of these hydrocarbons, then it requires outward radial mixing of CH_4 and C_2H_2 and inward transport of C_2H_6 from the outer nebula, where it perhaps formed on grains. Alternatively, FTT synthesis would require that they all be transported outward (*Fegley and Prinn,* 1989). Unfortunately, it is difficult to detect C_2H_6 in the ISM and therefore to definitively decide on the origin of these compounds in cometary matter.

Apart from the most abundant species, some organic molecules found in molecular clouds have also been identified in the coma of Hale-Bopp (*Bockelée-Morvan et al.,* 2000, 2004). Simulations of interstellar ice analogs show increasing complexity on the molecular scale when energetic and thermal processing is applied (*Allamandola et al.,* 1997; *Moore and Hudson,* 1998; *Cottin et al.,* 2001a; *Colangeli et al.,* 2004). Those complex organics that have been observed in laboratory spectra of processed ice mixtures may or may not be present at small abundance in interstellar grain mantles. However, with current astronomical instrumentation they cannot be observed in the interstellar solid phase. Their signatures will in most cases be too weak relative to the continuum or they will be masked by the presence of other strong bands. Thus, there will never be definite proof for the presence of specific, large organic species in interstellar ice mantles; some indications may come from gas-phase measurements in hot cores that sample the material evaporating from icy particles.

For molecules whose formation involves gas-grain chemistry, we are generally comparing the abundances measured toward regions of massive star formation, so-called hot molecular cores. Such regions may also exist around low-mass cores (*Schoier et al.,* 2002) but these are generally less-well characterized.

The difficulties inherent in connecting observed cometary volatiles with interstellar molecular cloud material can be illustrated for the case of the HNC molecule. Cometary HNC was originally discovered in the coma of Hyakutake (*Irvine et al.,* 1996); the high HNC/HCN ratio provided strong evidence that this HNC was preserved interstellar material. Subsequent calculations showed that the HNC/HCN ratios in Hyakutake and Hale-Bopp could apparently be produced by chemical reactions in the coma (*Rodgers and Charnley,* 1998; *Irvine et al.,* 1998). Further measurements of HNC/HCN ratios in other comets, when confronted with these models, demonstrated that gas-phase chemistry cannot in general be the origin of HNC. The most likely source of HNC in the coma is the decomposition of a large organic, perhaps polymeric, compound (*Rodgers and Charnley,* 2001a; *Irvine et al.,* 2003).

The C chain radicals, C_2 and C_3, are widespread in comets and their abundances indicate a marked variation with the Tisserand parameter (*A'Hearn et al.,* 1995). Identification of their chemical parent(s) is an important problem

whose resolution should shed light on chemical differentiation and the place of origin of particular comets. *Helbert et al.* (2002) have shown that the abundances of these molecules could be derived from C_2H_2, CH_3CCH, and C_3H_8 in a coma chemistry driven by electron-impact dissociations. However, methylacetylene and propane have not yet been detected in comets. In this picture, the same uncertainties in distinguishing interstellar and nebular contributions to the hydrocarbons persist. Synthesis of long, unsaturated, C-chain molecules appears to be one signature of interstellar organic chemistry. There have been tentative detections of C_4H and its possible parent C_4H_2 in Halley and Ikeya-Zhang respectively (*Geiss et al.,* 1999; *Magee-Sauer et al.,* 2002). The detection of a large suite of long C-chain molecules in comets, similar to the large ones found in molecular clouds, would be strong evidence for an interstellar origin of these organics.

Of the many other small interstellar organics also found in comets, HNCO, NH_2CHO, CH_3CHO, and HCOOH are expected, along with H_2CO and CH_3OH, to be products of interstellar grain-surface chemistry (*Charnley,* 1997). Although there are differences between the interstellar and cometary abundances, the fact that these molecules are associated with ices does suggest that they are products of interstellar chemistry. As these surface reactions involve low-temperature H-atom additions, they cannot proceed efficiently on surfaces warmer than about 15 K since the H-atom residence time then becomes shorter than the timescales to migrate and react, as shown experimentally (*Watanabe et al.,* 2003). This does not represent a problem in 10-K molecular clouds, but greatly constrains the region of the nebula where such a chemistry could occur. Any differences between the interstellar and cometary abundances may then be due to selective processing in the nebula (see the discussion on methanol above).

The other simple cometary organics, CH_3CN, HC_3N and $HCOOCH_3$, cannot be formed in the coma, and current theories of their formation require gas-phase reactions (*Rodgers and Charnley,* 2001b). The cometary abundances of CH_3CN and HC_3N are consistent with them being either the products of interstellar chemistry or similar processes in the outer nebula. However, interstellar $HCOOCH_3$ is believed to form around protostars in an ion-molecule chemistry driven by evaporated ice mantles (*Blake et al.,* 1987). The methyl formate in comets may then have originated in a sequence involving the desorption of ices, an intervening period of ion-molecule chemistry, followed by recondensation. These conditions may have occurred upon the first accretion of interstellar material, or perhaps during alternating inward and outward radial mixing of interstellar material in the nebula.

In summary, volatile cometary material shows a general qualitative link with the interstellar ice phase and the inventory of identified interstellar molecules. It is unlikely that these similarities reflect the wholesale incorporation of unaltered interstellar ices into comets (cf. *Greenberg,* 1982). As infalling interstellar material is decelerated at the accretion shock, it experiences chemical alteration to varying

degrees, depending upon the epoch and position of entry into the nebula. These changes range from those associated with simple evaporation-recondensation of ices in the outer disk regions, to complete molecular dissociation in the inner ones. We may also expect that the (interstellar) chemical clock can be further reset during the assembly of cometesimals in the nebula. It is now realized that the chemistry occurring in the outer regions of protoplanetary disks closely resembles that of dense interstellar regions. Hence, the pristinity of interstellar matter accreted under even the most benign conditions can become further adulterated. Elucidating in detail how the pristine inventory of available interstellar volatiles can be corrupted will require careful modeling of nebular chemistry, subject to the constraints that will be provided by future observations of disk and comet composition.

2.2. Isotopic Fractionation: An Interstellar Signature in Comets?

In cold interstellar clouds, both gas-phase and grain-surface chemistries can lead to enhanced isotopic fractionation in molecules (*Wooden et al.,* 2004). In comets, several molecular isotopic ratios have been measured and these can, in principle, provide important cosmogenic information (Table 3 in *Bockelée-Morvan et al.,* 2004). It must, however, be stressed that conclusions drawn from such observations may be biased due to the limited data available.

Similar $^{18}O/^{16}O$ ratios, both close to the terrestrial value, were measured in Halley and Ikeya-Zhang (*Balsiger et al.,* 1995; *Lecacheux et al.,* 2003). The $^{13}C/^{12}C$ ratio has been measured in C_2, CN, and HCN for several comets and this is also apparently terrestrial (*Wyckoff et al.,* 2000). From this data, one may draw the conclusion that either the natal cloud was of solar composition, or these ratios were set in the protosolar nebula. However, the absolute interstellar fractionation expected in C and O isotopes is generally much less than in other isotopes (*Langer et al.,* 1984). Calculations demonstrate that C-isotopic fractionation by ion-molecule reactions selectively enhances ^{13}C in CO, whereas derived cometary $^{13}C/^{12}C$ ratios are not based on isotopes of CO.

Thus, it cannot be ruled out that other cometary molecules, perhaps derived from CO on dust, may possess higher $^{13}C/^{12}C$ ratios. The ^{13}C enhancements found in IDPs and carbonaceous chondrites may have an origin in these species (e.g., *Cronin and Chang,* 1993).

Enhanced D fractionation is observed in many interstellar molecules. The measured D/H ratios range from about 1×10^{-4} for water to 0.5 for formaldehyde (*Ceccarelli,* 2002). Recently, there has been growing evidence for "superdeuteration" in some molecules (H_2CO, NH_3), exhibited in high D/H ratios and the presence of multideuterated species: D_2CO, ND_3, CHD_2OH (*Loinard et al.,* 2000; *van der Tak et al.,* 2002; *Parise et al.,* 2002). Interestingly, this "superdeuteration" is observed in either low-mass prestellar cores, where CO depletion onto dust may be responsible (*van der Tak et al.,* 2002), or in cores where low-mass star formation has already occurred and the products of grain-surface

deuteration are in the gas phase, e.g., in IRAS 16293-2422 (*Loinard et al.,* 2000).

The fractionation ratio HDO/H_2O has only been measured in three comets (Halley, Hyakutake, and Hale-Bopp), where it was found to be around 3×10^{-4}. In Hale-Bopp, the DCN/HCN ratio was determined to be about 0.002. Coma chemistry models demonstrate that these ratios are truly those of the material residing in the nucleus (*Rodgers and Charnley,* 2002). Gas-phase water D/H ratios measured in massive star-forming regions are generally low, around 0.0003, and comparable with the cometary values. However, recent determinations of HDO/H_2O in Orion suggest it could be higher: ~0.004–0.011 (*Pardo et al.,* 2001). Searches for HDO ice in low-mass protostellar cores yield only an upper limit on HDO/H_2O of about 0.02 (*Parise et al.,* 2002). Surveys of low-mass protostellar cores consistently yield DCN/HCN ratios about a factor of 30 larger than the cometary ratio (*Roberts et al.,* 2002), the latter of which is comparable to the value found in massive cores like Orion (0.003).

Thus, it is difficult to elucidate the physical conditions under which cometary ices formed (and hence the probable location) by making analogies with interstellar sources, at least for these two molecules. The D/H ratios measured in massive cores appear to resemble cometary values best, but low-mass cores are more physically relevant to protoplanetary nebulae and thence, presumably, to comet formation. It is possible that high molecular D/H ratios existed in the protosolar natal cloud core and these were diluted by chemical reactions during accretion and within the nebular disk. Ideally, one would wish to compare D fractionation between the envelope and disk of a forming protostar. Thus far, the only detection of a deuterated molecule in a disk, DCO$^+$ in TW Hya, yields a D/H ratio of 0.035 (*van Dishoeck et al.,* 2003). This is comparable with that found in low-mass cores but larger than found in massive cores. However, one must be careful in drawing conclusions based on a molecular ion. This observation only provides information on the potential of disk chemistry to deuterate molecules (e.g., *Aikawa and Herbst,* 1999b) and gives no direct connection to the neutral molecules observed in cometary nuclei.

Thus, albeit based on just three measurements, comets appear to be less deuterated than the material from which the protosolar nebula probably formed. This conclusion comes with the important caveat that the interstellar molecules with the most distinctive D fractionation have not yet been measured in comets (i.e., isotopomers of formaldehyde, ammonia, and methanol).

There is some evidence that this may be the case since it has been suggested that there may be differentiation in the D/H ratios between nuclear HCN and the DCN and HCN released into the coma from outgassing grains (*Blake et al.,* 1999).

Furthermore, the carbonaceous component of some IDPs, probably of cometary origin, exhibit D/H ratios close to the interstellar range and higher than that found for HCN [D/H of 0.008 in "Dragonfly" (*Messenger,* 2000)]. Assuming that similarly lower cometary D/H ratios will be found in formal-

dehyde, ammonia, and methanol, the D/H ratios in comets could result from "erosion" of the pristine D/H ratios at the accretion shock or in nebular shocks. Ion-molecule chemistry in the outer nebula could also act to lower the original interstellar fractionation (*Aikawa and Herbst,* 1999b). Alternatively, it has been proposed that lowering of the water fractionation may proceed by neutral exchange processes in the nebula (*Drouart et al.,* 1999), however, the value of the solid HDO/H_2O ratio assumed in this model is at present controversial (*Texeira et al.,* 1999; *Dartois et al.,* 2003). Important goals for future observations should be to determine the D/H ratios of selected molecules, such as water and HCN, in disks, and also to measure D/H in cometary molecules whose interstellar counterparts are known to have large values (e.g., formaldehyde).

Radio observations of HCN in Hale-Bopp indicate a $^{14}N/^{15}N$ ratio of around 300 (e.g., *Jewitt et al.,* 1997; *Crovisier and Bockelée-Morvan,* 1999); as with C and O, this is consistent with a terrestrial value (270). Recent measurements of $C^{15}N$ and $C^{14}N$ in Comets Hale-Bopp and C/2000 WM1 (LINEAR) near perihelion by *Arpigny et al.* (2003) indicate that $C^{14}N/C^{15}N$ is about 130, and significantly different from that in HCN. For both molecules (HCN and CN) the $^{12}C/^{13}C$ ratios were found to be terrestrial. Some CN is certainly coming from photodissociation of HCN but the observations of *Arpigny et al.* (2003) indicate that there must also be another, probably polymeric, parent for CN that is much more highly fractionated in ^{15}N. Such low $^{14}N/^{15}N$ ratios are also detected in IDPs (*Messenger,* 2000) and can be explained by interstellar chemistry theories (*Charnley and Rodgers,* 2002). This emphasizes the crucial point for understanding the origin of cometary isotopic fractionation — one must attempt to measure isotopic ratios of several different molecules.

2.3. Silicates

Dust grains are entrained in the flow of escaping gases from the nucleus. Dust grains in the coma scatter and absorb sunlight, reemitting the absorbed energy in the thermal infrared. At 1 AU, the highly refractory silicate grains are warmed to radiative equilibrium temperatures well below their melting or annealing temperatures. Therefore, the properties of the silicate grain component of comae dust probe the mineralogy and crystallinity of the silicate dust in the nucleus. Cosmic-ray bombardment of surfaces of long-period comets while in the Oort cloud has the potential to alter the properties of the silicates on the nuclear surface. Collisional evolution of short-period comets in the Kuiper belt and UV irradiation during their many perihelion passages may also alter the grain properties. Comparing the dust properties in long- and short-period comets compares the effect of minimal vs. significant parent-body processing.

As discussed in *Hanner and Bradley* (2004), IR spectra of comets and laboratory studies of cometary interplanetary dust particles show that silicates in comets are dominated by two minerals — olivine and pyroxene or $(Mg_y,Fe_{(1-y)})_2SiO_4$ and $(Mg_x,Fe_{(1-x)})SiO_3$ — and are in two forms: amorphous and crystalline (*Colangeli et al.,* 2004).

Thermal emission models of Comet 19P/Borrelly, one of the few short-period comets with a silicate feature, fit either a grain population dominated by discrete amorphous pyroxene and amorphous C grains (*Hanner et al.,* 1996) or core-mantle aggregate particles consisting of amorphous olivine cores with amorphous C mantles (*Li and Greenberg,* 1998a). Amorphous pyroxene and olivine are found in long period comets in varying proportions (*Hanner et al.,* 1994; *Hanner and Bradley,* 2004). In the core-mantle aggregate model (*Hage and Greenberg,* 1990), long-period comets are fitted with organic refractory mantles (*Li and Greenberg,* 1998b), while short-period Comet Borrelly is better fitted with amorphous C mantles (*Li and Greenberg,* 1998a). These comparisons suggest that parent-body processing and UV irradiation do not change the silicate mineralogy while it may carbonize the organic grain component (*Li and Greenberg,* 1998a). In highly active long-period comets we can compare the grain properties of particles dredged up from deeper layers of the nucleus and entrained in jets with those particles released into the coma from the nuclear surface. In Comet Hale-Bopp, grain mineralogy as revealed through the shape of the 10-μm spectral resonances was uniform to within the measurement uncertainties at different positions in the coma at a given epoch (*Hayward et al.,* 2000), except for a drop in the crystalline pyroxene resonance in the sunward direction (*Harker et al.,* 2002). The grain temperatures and the optical and near-IR polarization were significantly enhanced in Hale-Bopp's jets (*Hadamcik and Levasseur-Regourd,* 2003), indicating a difference in grain morphology or size (*Levasseur-Regourd et al.,* 2002). Analysis of Hale-Bopp suggests that differences between surface and jet particles can be attributed to grain morphology but not silicate mineralogy. Studying the silicate mineralogy and crystallinity therefore probes interstellar and nebular processes affecting silicate dust grains prior to their incorporation into comets (*Hanner et al.,* 1996). The evidence, although not unanimous, forms a consensus that cometary amorphous silicates are of probable interstellar origin while crystalline silicates are of probable nebular origin (*Hanner and Bradley,* 2004; *Wooden,* 2002).

Amorphous silicates in comets probably are relic grains from the interstellar medium (cf. *Hanner and Bradley,* 2004). Formation of amorphous silicates requires very rapid cooling that is probable for an asymptotic giant branch (AGB) stellar outflow (*Wooden et al.,* 2004; *Tielens et al.,* 1997) but formation is unlikely under conditions in the solar nebula (*Yoneda and Grossman,* 1995). Amorphous or glassy forms of minerals are relatively rare in meteoritic materials compared to crystalline forms. Iron-bearing amorphous olivine is fitted to the interstellar 10-μm absorption feature and interstellar extinction curve (*Li and Greenberg,* 1997). Iron-bearing amorphous olivine and pyroxene in a 5 : 1 ratio are fitted to the absorption feature in the line-of-sight to the galactic center (*Kemper et al.,* 2004). By the relative

absence of amorphous silicates from highly processed solar nebula materials (chondrules) and their ubiquity in the ISM, amorphous silicates in comets are probably interstellar.

Further evidence of the interstellar source for cometary amorphous silicates arises from the laboratory studies of chondritic porous interplanetary dust particles (CP IDPs), which are of probable cometary origin (*Bradley,* 1988; *Hanner and Bradley,* 2004). Chondritic porous IDPs are aggregates of crystalline and amorphous silicates, the so-called "GEMS" (*Hanner and Bradley,* 2004), in a matrix of carbonaceous materials (see section 2.4). Irradiation of GEMS by high-energy particles during their residence time in the ISM has been invoked to explain radiation tracks, compositional gradients with GEMS' radii, and the presence of nanophase Fe (*Bradley,* 1994).

Laboratory experiments demonstrate that ion bombardment of 4-KeV He[+] ions at fluxes typical of the ISM shocks can amorphize crystalline olivine, increase porosity, reduce the Fe from its stoichiometric inclusion in the mineral to embedded nanophase particles, and damage the chemistry by reducing the O/Si and Mg/Si ratios, effectively increasing pyroxene at the expense of olivine (*Carrez et al.,* 2002). Ion bombardment by 50-KeV He[+] ions, characteristic of supernovae shocks, does amorphize the crystalline silicates but leaves the chemistry unaltered (*Jäger et al.,* 2003). Thus, ion bombardment can create the highly radiation damaged, Mg-rich GEMS with nanophase Fe inclusions (*Brownlee et al.,* 2000) in CP IDPs whose spectra are very similar to the amorphous silicates observed in cometary emission spectra (*Hanner and Bradley,* 2004; *Bradley et al.,* 1999a,b). Therefore, morphology and mineralogy indicates that the cometary amorphous silicates have an interstellar origin.

Halley's Fe/Mg ratio is 0.52 and the solar value is 0.84 (*Jessberger et al.,* 1988), so Halley's Fe content is close to solar. However, only 30% of the Fe is in silicates while 70% is in FeS and Fe grains. Halley's Fe grains are highly reduced, as there is <1% FeO. This is also characteristic of the iron within GEMS in CP IDPs where it exists as nanophase Fe or FeS and where the nanophase Fe has been attributed to ion bombardment in the interstellar medium.

The crystalline silicates in comets are of probable nebular origin**.** The existence of Mg-rich crystalline silicates in comets is revealed by the sharp resonances in cometary 10-μm spectra (*Hanner and Bradley,* 2004; *Harker et al.,* 2002; *Wooden,* 2002). Comet Hale-Bopp's observed 10-μm silicate feature is best-fitted by Mg-rich pyroxene "Cluster" (*Messenger,* 2000) CP IDPs (*Wooden et al.,* 2000). In fact, all crystalline silicates observed by the ISO short wavelength spectrometer (SWS) in comets, stellar outflows, and protoplanetary disks are Mg-rich (*Bouwman et al.,* 2001; *Molster et al.,* 2002a). Figure 1 presents from the ISO-SWS database the best comparison between a pre-main-sequence Herbig Ae star with a protoplanetary disk, an O-rich AGB star, and Comet Hale-Bopp. The clear contrast of strong crystalline peaks is seen in many but not all Herbig Ae stars (*Meeus et al.,* 2001). Crystalline silicates are preferably detected in binary AGB stars that possess disks (*Molster et al.,*
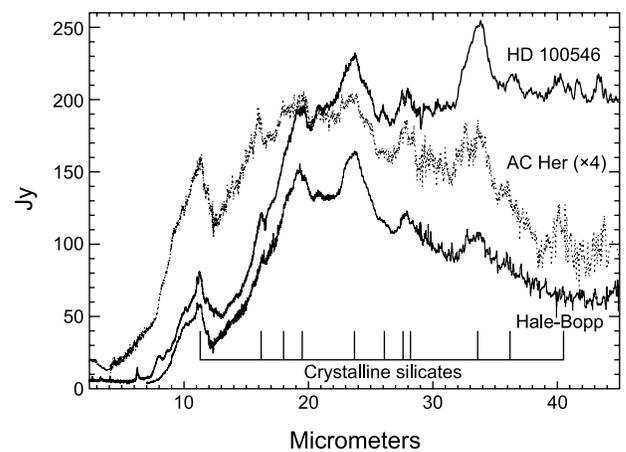
Fig. 1.   Infrared Space Observatory (ISO) short wavelength spectrometer (SWS) spectra of the pre-main-sequence Herbig Ae star HD 100546 (*Malfait et al.,* 1998), the O-rich post-AGB binary star AC Her (*Molster et al.,* 2002 a,b,c), and Comet Hale-Bopp (*Crovisier et al.,* 1997), showing the strong similarities in their spectral features. The Mg-rich crystalline silicate resonances are identified. Note the far-IR spectra are dominated by isolated crystalline silicate features of Mg-rich crystalline olivine with a few features of Mg-rich crystalline pyroxene.

2002a), where crystallization is attributed to a low-temperature mechanism that occurs over longer times in the spherical outflows of single AGB stars (*Molster et al.,* 1999).

In the solar system, only silicate crystals in CP IDPs and in Antarctic micrometeorites have such high Mg contents (*Bradley et al.,* 1999c) as deduced for cometary crystals. Comet Halley's silicates are also very Mg-rich compared to chondrules and meteoritic materials. The range of Fe contents in silicate crystals in chondrules is due to the rapid melting of grain aggregates at high temperatures followed by rapid cooling (*Delany,* 1995; *Kracher et al.,* 1984). Since cometary crystals have very little Fe, these crystals have not suffered chondrule-like postformation heating events in the nebula and represent primitive solar nebula materials (*Wooden et al.,* 2000).

The appearance of Mg-rich crystalline silicates in some comets indicates that cometary crystalline silicates are grains that condensed at high temperatures [~1400 K (*Grossman,* 1972; *Hanner and Bradley,* 2004)] or were annealed from amorphous silicates at somewhat lower temperatures [>900 K (*Hallenbeck et al.,* 1998, 2000; *Fabian et al.,* 2000; *Hanner and Bradley,* 2004)] in the solar nebula. If annealing processes occurred in the inner nebula (*Mousis et al.,* 2002; *Bockelée-Morvan et al.,* 2002), then such temperatures occurred early (<300,000 yr) and radial diffusion rapidly transported a uniform concentration of crystals to beyond the snow line where comets formed (5–40 AU) (*Bockelée-Morvan et al.,* 2002). Annealing also may have occurred in shocks in the nebula in the 5–10-AU region, producing

local enhancements in the crystalline concentration (*Harker and Desch*, 2002). Annealing temperatures are not reached in the accretion shock between outer disk surface and the prenatal cloud (*Chick and Cassen*, 1997; *Neufeld and Hollenbach*, 1994). Future observations may reveal differences in the crystalline-to-amorphous ratios between long- and short-period comets that will help to constrain solar nebula models. The detection of cometary crystals in long- and short-period comets, however, may not only depend on their concentration but also on grain properties such as grain size and porosity (*Hanner and Bradley*, 2004).

Challenges to the interpretation that cometary amorphous silicates are interstellar and cometary crystals are primitive solar nebula grains comes from recent discoveries using the nanoSIMS (secondary ion mass spectrometry). NanoSIMS is an ion microprobe, allowing elemental and isotopic analysis of small features of solid samples. Six out of more than 1000 subgrains in nine CP IDPs have anomalous $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios and clearly carry presolar isotopic signatures (*Messenger et al.*, 2003). Three of the six presolar grains are identified with mineral phases and have AGB isotopic ratios: one forsterite crystal and two GEMS. About 1% by mass of the CP IDPs have distinct presolar signatures. The detection of a presolar forsterite crystal (*Messenger*, 2000) contradicts the concept that Mg-rich cometary crystals are solar nebula grains. The mass fraction, however, is within the range estimated for the ISM [<0.5% (*Kemper et al.*, 2004)]. The measured mass fraction of presolar GEMS, however, is significantly less than the cometary high mass fraction of amorphous silicates of probable interstellar origin [*Hanner and Bradley* (2004); Hale-Bopp, *Harker et al.* (2002)]. At this time, the nanoSIMS instrument detects only the subgrains with large isotopic anomalies. Higher-precision measurements on CP IDPs are required to improve our understanding of the range of isotopic ratios that are considered to be interstellar and of the processes in the ISM that may alter the signatures of the origins of dust grains.

The presence of silicate crystals in comets implies mixing of high-temperature and low-temperature materials in the comet-forming zone. The presence of silicate crystals in comets implies that processed nebular materials were incorporated with volatile-rich icy material. This implies a significant degree of radial transport and/or mixing in the nebula. In CP IDPs of probable cometary origin, the close proximity of oxidized, reduced, and metallic mineral phases, i.e., mineral phases in contact with but far from equilibrium with each other, indicates that these micrometer-sized aggregates of submicrometer units suffered minimal alteration after the grains accreted their constituent parts. "The fact that (postaccretion) alteration of aggregate IDPs hardly reached thermodynamic equilibrium at sub-micrometer scales supports the view that energy for alteration was either scarce or unavailable for sufficiently long periods of time, or both" (*Rietmeijer*, 1998). Porosity distinguishes primitive but not necessarily presolar origin. The high porosity of cometary grains, including CP IDPs (*Rietmeijer*, 1998) and the high porosity deduced from thermal emission models of Hale-

Bopp (*Harker et al.*, 2002; *Li and Greenberg*, 1997), is similar to what is plausible for both interstellar material (*Iati et al.*, 2001; *Vaidya and Gupta*, 1999) and grain aggregates in the solar nebula (*Dominik and Tielens*, 1997). Thus, grains of probable cometary origin are aggregates of silicate and carbonaceous materials that have seen significantly different environments in the solar nebula prior to both their aggregation into a single porous particle and their incorporation into comets.

2.4. Carbonaceous Matter

Our knowledge on carbonaceous material of comets is rather limited. *In situ* measurements of a few nanograms of Halley's coma show C-rich grains that are apparently components of various types, including pure C particles, polycyclic aromatic hydrocarbons (PAHs), branched aliphatic hydrocarbons, C-O or C-N polymers, and more complex compounds containing all four C, H, O, and N atoms (*Fomenkova*, 1997). CHON organic compounds were first described as being similar to kerogens (*Jessberger et al.*, 1988). Heteropolymers or complex organic molecules also are proposed (*Kissel et al.*, 1997). Some of the species remain very speculative due to the limited resolution of the mass spectrometers that flew through Halley's coma.

The *in situ* measurements of Halley reveal that 25% by mass are siliceous-free CHON grains, 25% are carbonaceous-free silicate grains, and 50% are mixed carbonaceous and silicate grains. Mixed grains of greater mass exist in the innermost parts of the coma, while carbonaceous-free silicate grains are dominant further out in the coma (*Fomenkova*, 1999). This suggests that the organic material is the "glue" that holds the silicates together and that the organic material desorbs in the inner coma (*Boehnhardt et al.*, 1990; *Fomenkova*, 1997), freeing the isolated silicate mineral phases. This scenario is also proposed for Comet Hale-Bopp near perihelion (≤1.5 AU) when its amorphous grains showed an increase in porosity, a steeper size distribution (more smaller grains), and slightly higher relative mass fraction of crystalline silicates (*Harker et al.*, 2002). Furthermore, within this same heliocentric range (≤1.5 AU), Comet Hale-Bopp has a strong distributed source of CO, i.e., the CO spatial distribution is more radially extended than the distribution of the dust and other gas components; only 50% of the CO originated from the nucleus (*DiSanti et al.*, 2001).

The other 50% of the CO is deduced to arise from the desorption of an unknown organic component of the dust. A possible candidate for the distributed CO is polyoxymethylene (POM), which is a polymer of formaldehyde (*Boehnhardt et al.*, 1990). The desorption of POM first into formaldehyde followed by photodegradation into CO would, however, create far more formaldehyde (*Cottin et al.*, 2001b) than detected in Hale-Bopp's coma (*Bockelée-Morvan et al.*, 2000). Following the heliocentric dependence of both dust properties and distributed CO sources is currently one of the best observational strategies for studying the organic component of cometary dust.

Infrared observations of dusty comae ubiquitously detect a strong near-IR spectrally featureless thermal emission that is well-fitted by amorphous C. The spectroscopic detection of solid state CHON particles if they are made of kerogen-like material is difficult in the near- and mid-IR because kerogen is about 30 times less absorptive than Fe-bearing amorphous silicates, and even less absorptive than amorphous C; spectroscopic resonances are weak compared to the other grain species. Unidentified gas phase lines are seen in comets at very high spectral resolution in the near-IR (*Magee-Sauer et al.,* 2002; *Mumma et al.,* 2001b) and may be relevant to the mystery of the form of cometary organic gas-phase molecules. The detection of phenantrene ($C_{14}H_{10}$), a gas-phase PAH macromolecule, in Halley is suggested based on UV spectroscopic data (*Moreels et al.,* 1994). The emission band at 3.28 μm in a few comets suggests the presence of aromatics (*Bockelée-Morvan et al.,* 1995; *Colangeli et al.,* 2004); the unambiguous detection of the 3.28-μm feature in moderate resolution IR spectra requires the deconvolution of emission from gas species in the same spectral range. No PAHs have been detected in the ISO IR spectra of C/1995 O1 Hale-Bopp (*Crovisier et al.,* 1997, *Crovisier,* 1999), which may be due to the large heliocentric distance at the time of observation. Polycyclic aromatic hydrocarbons are very strong absorbers of UV radiation and emitters of IR photons, and as such, represent the observable "tip of the iceberg" of cometary organics.

Chondritic porous IDPs are cometary grains that contain both presolar and solar isotopic materials. [For in-depth discussions on the connection between properties of CP IDPs and comets, see *Hanner and Bradley* (2004), *Sykes et al.* (2004), *Wooden* (2002), and *Messenger and Walker* (1998).] Chondritic porous IDPs have high entrance velocities relative to asteroidal particle trajectories (into Earth's stratosphere where they are collected by high-flying aircraft), high porosity and fragility (indicative of minimal processing in the solar nebula), high Mg contents (in comparison with meteoritic materials), contain D-rich organic material (*Keller et al.,* 2000, 2002) and isotopic anomalies in N and C in the C phase (*Messenger,* 2000), and contain highly radiation damaged amorphous silicate spherules (GEMS) in a C-rich matrix (*Bradley et al.,* 1999a). In fact, most of the CP IDPs have remarkably high C abundances, typically several times higher than those of CI chondrites. Carbon is so abundant that it can be directly observed in ultramicrotome sections where it is often seen as regions of pure amorphous C covering areas as large as 1 μm across (*Brownlee et al.,* 2002). Infrared spectroscopy of the ~3.4-μm CH-stretching region in CP IDPs shows the presence of aliphatic hydrocarbons (*Brownlee et al.,* 2000; *Flynn et al.,* 2002). Recent laboratory data show that the abundant organic materials, specifically the aliphatic and aromatic materials, in the CP IDP "Dragonfly" are responsible for the extremely high D/H relative to terrestrial material and indicate a presolar origin (*Keller et al.,* 2002).

In this same "Dragonfly" particle, the CO carbonyl stretch is observed (*Flynn et al.,* 2002), indicating the possible presence of functional groups associated with aldehydes, ketones, and organic acids.

Amorphous C in comets and CP IDPs is likely of interstellar origin. *In situ* measurements of Comet Halley reveal both discrete and mixed mineral assemblages. Of the total grains, ~8–10% by mass is elemental C that is of AGB origin based on its $^{13}C/^{12}C$ ratio (*Fomenkova,* 1999). Amorphous C is invoked to fit the near-IR emission in comets (e.g., *Hanner et al.,* 1994; *Harker et al.,* 2002), although highly absorbing organic refractory mantles on silicate cores can also produce this observed emission in some comets (*Greenberg and Hage,* 1990; *Li and Greenberg,* 1998b). Of Halley's particles, the elemental C component best represents the amorphous C that is abundant in CP IDPs and that is invoked to produce the near-IR thermal emission from comets [20% by mass of the submicrometer grains in Hale-Bopp (*Harker et al.,* 2002)]. Models of the near-IR reflectance spectra of Centaurs and Kuiper belt objects utilize, by number, an amorphous C abundance of 1–20% (D. Cruikshank, personal communication, 2003). Elemental C is, however, ≪1% by mass in carbonaceous chondrites and 3–5% of aqueously altered primitive meteorites (*Brearley and Jones,* 1998). The depletion of amorphous C in inner solar system bodies relative to outer solar system bodies may be a result of the oxygenation of C into CO and CO_2 in the chondrule-formation process (*Ash et al.,* 1998; *Wooden,* 2002; *Cuzzi et al.,* 2003).

Comparing the soluble fraction of carbonaceous meteorites with cometary volatiles indicates that CI chondrites can be strongly related to comets. From the analyses of amino acids in different meteorites it was recently concluded that the formation of an extensive number of amino acids made through processes such as Strecker-Cyanohydrin synthesis and Michael addition, as observed in the Murchison meteorite, requires the presence of a number of aldehydes and ketones, as well as ammonia, water, HC_3N, and HCN (*Ehrenfreund et al.,* 2001). All the small molecules required to make amino acids are in the current inventory of cometary volatiles. However, no ketones and only formaldehyde and acetaldehyde (0.02%) are detected in comets (*Bockelée-Morvan et al.,* 2004). The low number of amino acids and peculiar abundance ratio in CI chondrites (such as Orgueil) is more compatible with cometary chemistry than with chemistry on asteroidal bodies (*Ehrenfreund et al.,* 2001).

In the ISM, the distribution of C is still an unsolved question. In dense molecular cloud material a reasonable fraction of C is incorporated into CO gas (20%) and a small percentage (~5%) is present in C-bearing ice species (discussed in section 2.1). Diffuse interstellar clouds are exposed to UV radiation and show very low levels of CO gas. In such environments about 15% of the cosmic C is attributed to PAHs. Polycyclic aromatic hydrocarbons seem to be prevalent in the diffuse interstellar medium and on the edges of molecular clouds but may or may not be present within molecular clouds. This leaves a large fraction (>50%) of the cosmic C unaccounted for in the interstellar medium.

Laboratory simulations in combination with interstellar observations argue that this missing C is incorporated into solid-state macromolecular C (cf. Fig. 17 of *Pendleton and Allamandola,* 2002) such as amorphous and hydrogenated amorphous C (see *Colangeli et al.,* 2004; *Ehrenfreund and Charnley,* 2000; *Mennella et al.,* 1998).

Though many different forms of C have been discussed, hydrogenated (and dehydrogenated) amorphous C provide currently the best fit to observations of the UV bump at 220 nm in the interstellar extinction curve and simultaneously the best quantitative solution for current dust models (*Mennella et al.,* 1998). Note that graphite has been popularly invoked in the past to explain the UV 220-nm bump (*Hoyle and Wickramasinghe,* 1999; *Li and Draine,* 2001); graphite does not comprise a significant mass fraction of CP IDPs (D. Brownlee, personal communication, 2003).

Carbonaceous chondrites are known to contain a substantial amount of C, up to 3% by weight, and exhibit a range of thermal and aqueous alteration believed to have occurred on their parent bodies. The major part of this C, namely up to 90%, corresponds to a macromolecular organic fraction (*Hayes,* 1967). Solid-state ^{13}C nuclear magnetic resonance (NMR) investigation of the macromolecular material reveals a high level of branching of the aliphatic chains and shows that the aromatic units are highly substituted, especially in the Murchison meteorite (*Gardinier et al.,* 2000). Given that macromolecular C is inferred to constitute more than half the C in the interstellar medium, constitutes ~ 80% of the C in meteorites, and is present in comets, there probably exists a lineage between these reservoirs. Many small (organic) molecules observed in cometary comae originate wholly or partially from the decomposition of much larger molecules/particles. There is at present, however, no direct or indirect evidence that large polymers similar to those possibly present in comets (e.g., POM, PACM, HCN-polymers) reside in the interstellar medium. Observations of interstellar organic compounds, laboratory simulations, and the analysis of extraterrestrial samples offer insights into the molecular forms of the cometary C. We await future *in situ* measurements and the return of cometary samples by the *Stardust* mission to give a more conclusive answer.

3.   CONCLUSIONS

The composition of comets provides important clues on the processes that occurred during the formation of our solar system. However, comets certainly evolve chemically and physically as they visit the inner solar system frequently and they are exposed to processing in their storage location. Any proposed similarities between interstellar and cometary material can be tested by astronomical observations, laboratory simulations, and the analysis of extraterrestrial samples, such as IDPs and carbonaceous chondrites. Comparison of interstellar ice abundances to cometary volatiles shows a possible link between them. The physical properties of ice,

the main component of comets, depend on the structural parameters of the material, such as porosity, grain size, material strength, and local density. Organic molecules may act as glue within ice-dust mixtures that also enhances material strength and thermal conductivity. Sublimation of material from cometary nuclei is triggered by a complex system of internal processes (*Prialnik et al.,* 2004) and, even if these molecular ices were present in the same relative proportions as interstellar ices, it is unlikely that the cometary outgassing pattern would accurately reflect this.

The infrared signatures of silicates in comets and in circumstellar regions, as well as analyses of isotopic ratios in IDP silicates, have greatly improved our knowledge of dust in the early solar system and its link to that of comets. The existence of crystalline silicates in comets, as revealed by cometary IR spectra and their apparent scarcity in the ISM, has been invoked as an argument for mixing of "high-temperature" and "low-temperature" materials in the comet-forming zone. In particular, the appearance of Mg-rich crystalline silicates in some comets indicates that these grains originally condensed at high temperatures or were annealed from amorphous silicates at somewhat lower temperatures in the solar nebula. This is proof that processed nebular materials were incorporated into comets.

The overall picture shows that comets are a mixture of interstellar and nebular components (see Fig. 2). Based on the molecular data available in sample comet populations, there is evidence both for chemical heterogeneity, as expected, and also for some degree of chemical homogeneity. Cometary comae are now known to contain many molecules identified in the interstellar medium; the majority of these species emanate from the nuclear materials. These facts are highly suggestive of cometary nuclei containing appreciable fractions of pristine or partially modified interstellar molecules, but are by no means definitive proof of a direct heritage. Compositional similarities do not provide sufficiently accurate constraints; differences may be more illuminating. Cometary nuclei contain at least two molecules not yet identified in molecular clouds: CS_2 and C_2H_6. It would be of interest to definitively rule out the presence of some common, relatively abundant, interstellar molecules. Current upper limits on possible candidates, such as dimethyl ether, are not stringent enough (*Bockelée-Morvan et al.,* 2004).

The molecular isotopic fractionation, measured in D and heavy N, both suggest an origin in chemistry at very low temperatures. Whether this occurred in cold molecular clouds or in the protosolar nebula cannot be decided based on the available data. It could be argued that the D/H ratios in water and hydrogen cyanide are not particularly strong discriminants of formation site. Detection of cometary molecules with D/H ratios above 10%, as well as evidence for multideuteration, would significantly favor a direct interstellar origin (*Ceccarelli,* 2002); however, the current upper limits on D/H in cometary formaldehyde and methanol (Table 3 of *Bockelée-Morvan et al.,* 2004), although meager,
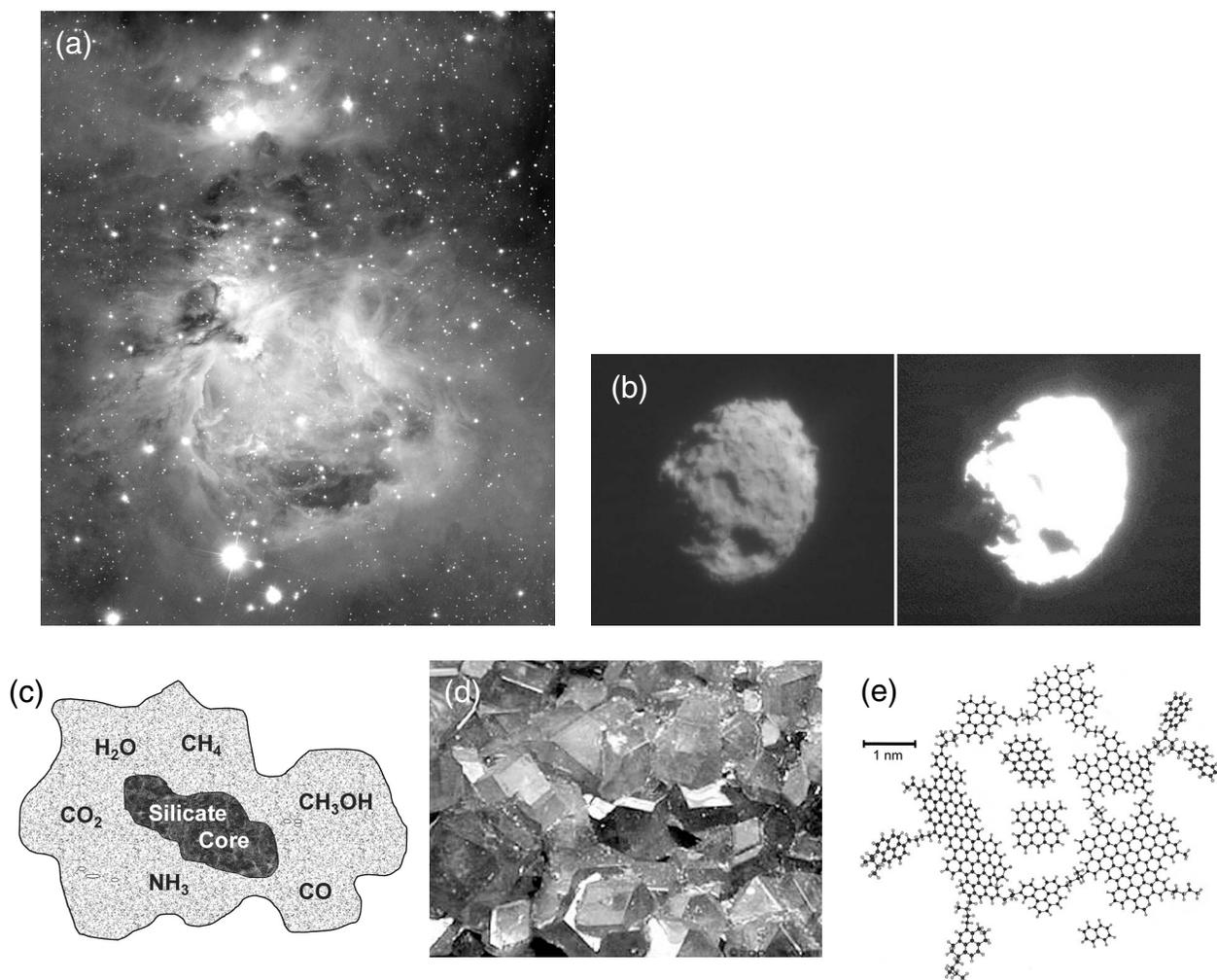
Fig. 2. Comets and their interstellar heritage. **(a)** Interstellar clouds collapse to form stars and protoplanetary disks from which planets, comets and asteroids form. Ices, amorphous silicates, and organics can be observed in dense and diffuse clouds. In protoplanetary disks the infalling material is modified according to the distance from the protostar. Ultraviolet radiation and cosmic rays, shocks, and turbulent mixing alter the original interstellar material before planetary and cometary formation. Image of Orion, courtesy of Robert Gendler. **(b)** Comets are a mixture of interstellar and nebular components; the degree of mixing may be individual for each comet. Their composition, as inferred from observations and the Comet Halley flyby missions, indicate ~50% ice (predominantly water), 25% silicates (amorphous and crystalline), and organic refractory material. Image of Comet Wild 2 Stardust encounter, courtesy of the Stardust Team, Jet Propulsion Laboratory/NASA. **(c)** Interstellar icy grains are characterized by different ice phases — amorphous, crystalline, segregated boundary layers, and possibly clathrates — and besides water, contain partly substantial amounts of CO_2, CO, and CH_3OH. Sublimation of material from cometary nuclei is triggered by a complex system of internal processes and, even if these molecular ices were present in the same relative proportions as interstellar ices, it is unlikely that the cometary outgassing pattern would accurately reflect this. **(d)** Cometary amorphous silicates are of probable interstellar origin while crystalline silicates condensed at high temperatures or were annealed from amorphous silicates at somewhat lower temperatures in the solar nebula. Image courtesy of S. Balm. **(e)** Macromolecular carbon is inferred to constitute more than half of the carbon in the interstellar medium and ~80% of the carbon in meteorites. A lineage between those reservoirs is expected, and such material should also exist in comets. Credit: *Pendleton and Allamandola* (2002).

suggest otherwise. It is therefore of considerable importance to know if low D/H fractionation ratios, of at most a few percent, are common in a statistically larger sample of comets.

Future scientific endeavors aimed at improving our knowledge of the interstellar/solar system connection will include ground- and spacebased telescopes using new and sensitive instrumentation. Such observations should focus on the isotopic ratios in comets, the detection of more cometary organics, and the compilation of detailed chemical inventories of solar-type star-forming regions and their corresponding disks. Theoretical models of the chemical processes associated with the accretion of molecular cloud material and radial mixing in the early solar nebula are vital for determining the starting material from which comets

formed. Theoretical models of comet nuclei should aim to reproduce the observed pattern in order to deduce internal properties of comet nuclei that are inaccessible to observations (*Prialnik et al., 2004,* and Fig. 13 therein). As emphasized by *Colangeli et al.* (2004), laboratory simulations on mixtures of refractory matter and ice will offer a new perspective in the interpretation of cometary observations.

The analysis of extraterrestrial materials (in particular carbonaceous chondrites) remains a crucial method to study refractory matter, including silicates and organics. Isotopic data remain the most important tool to establish a link between regions in interstellar clouds and small solar system bodies. Recent isotopic measurements have allowed the identification of presolar silicates in IDPs; their absence in meteorites indicates that they could not survive parent-body alteration (*Messenger et al.,* 2002). New sensitive techniques, such as the nanoSIMS ion microprobe, can probe isotopic ratios within tiny particles and will contribute significantly to our knowledge of presolar materials. Future observations of more comets will enable a broader consensus on cometary diversity to be established. The ultimate goal of understanding cometary physics and chemistry, and their relation to the parent interstellar cloud, will be attained by future space missions performing *in situ* experiments and possibly bringing a cometary sample back to Earth.

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