Oxygen in Comets and Interplanetary Dust Particles

**Scott A. Sandford,[1] Scott Messenger,[2] Michael DiSanti,[3]
Lindsay Keller,[2] and Kathrin Altwegg[4]**

*[1]NASA Ames Res. Center, Astrophysics Branch, Moffett Field, California, 94035, U.S.A.
[2]NASA Johnson Space Center, Astromaterials Res. Office, Houston, Texas, 77058, U.S.A.
[3]NASA Goddard Space Flight Center, Greenbelt, Maryland, 20771, U.S.A.
[4]University of Bern, Physikalisches Institut, Bern Bern 3012, Switzerland
e-mail (corresponding author): ssandford@mail.arc.nasa.gov*

INTRODUCTION

Comets have enormous scientific significance because they represent samples from the most distant regions of the Solar System and probably best preserve the original starting materials. Comets are rich in volatiles and ices because they formed in cold regions of the solar nebula (Boss 1998), well beyond the "snow line" where water ice condensed. These objects derive from two distinct source regions: the Kuiper Belt—a flattened disk ($i < 30°$) of plutons and other small Solar System bodies beyond the orbit of Neptune (30-50 AU); and the Oort cloud—a spherically distributed population of bodies residing very far from the Sun (10^3-10^5 AU). Whereas Kuiper Belt objects (KBOs) are thought to have formed in place (Luu and Jewitt 2002), the Oort cloud comets are thought to have been gravitationally scattered from the neighborhood of the giant planets (Oort 1950). Owing to the large range in radial distances over which comets formed (5-50 AU), cometary materials have experienced correspondingly wide ranges of thermal histories, and may incorporate different proportions of presolar and Solar System components. Overall, comets are likely to preserve the most pristine material to be found in the Solar System, and thus represent the closest remaining link to the dense molecular cloud from which our Solar System formed. Comparison of cometary and asteroidal materials also provides insight into large-scale heterogeneity and transport of materials in the early solar nebula. The chemistry, mineralogy, and isotopic distributions of oxygen in cometary materials can provide unique insights into these issues. However, comets remain enigmatic objects and many of their basic properties are not well understood.

Our current knowledge of the chemical distribution and isotopic composition of oxygen in comets is based on several different lines of evidence, including: remote observation of comets using telescopes and spacecraft; direct laboratory analyses of interplanetary dust particles thought to come from comets; inferences from meteoritic materials; theoretical considerations and inferences from interstellar materials; and *in situ* measurements at comets.

It should be noted that, despite their uncertain provenance, studies of stratospherically collected interplanetary dust particles (IDPs) have provided some of the most detailed information so far on the distribution of O in the non-volatile fraction of cometary materials. Anhydrous IDPs have been linked to short-period comets by their unequilibrated mineralogy, fragile structure, fine grain size (50-1,000 nm), high volatile element and C content, and their high abundances of presolar materials (Bradley et al. 1988; Nier and Schlutter 1990, 1992; Thomas et al. 1993; Zolensky and Barrett 1994; Messenger and Walker 1997; Messenger 2000; Messenger et al. 2003). These IDPs have also been dynamically linked to comets from their inferred high atmospheric entry velocities that reflect eccentric orbits prior to Earth encounter (Joswiak et al. 2000). Owing to the stochastic nature of orbital evolution of interplanetary

dust particles (see, for example, Liou and Zook 1996, 1997), the origins of specific IDPs are uncertain, but it is highly likely that many, if not most, of the anhydrous IDPs have cometary origins. In the discussions that follow, we will therefore consider their chemical, mineralogical, and isotopic compositions to have bearing on the nature of cometary materials. It should be noted that samples recently returned to Earth from Comet 81P/Wild 2 by the Stardust Mission are generally consistent with this basic contention (Brownlee et al. 2006).

Each of the approaches described above provides unique insights into the nature of cometary materials and their oxygen carrier reservoirs. Each approach also suffers from different "selection effects" in terms of limitations as to what can be learned from them. A complete understanding of the nature of carriers of oxygen in comets requires a careful synthesis of evidence gathered from these different approaches.

Since comets are known to consist of mixtures of both volatile and refractory components (cf. Festou et al. 2004) and these two components are often amenable to study using very different techniques, the discussion is divided into sections that deal with these reservoirs of material somewhat independently. Our current understanding of the chemical forms of oxygen within both the volatile and refractory components of comets is considered first, followed by a review of what is known about the oxygen isotopic ratios in these different cometary components.

THE CHEMICAL FORM OF OXYGEN IN THE INTERSTELLAR MEDIUM, "COMETARY" INTERPLANETARY DUST PARTICLES, AND COMETS

Oxygen carried by carbonaceous materials in the interstellar medium, meteorites, cosmic dust, and cometary samples

The history of oxygen begins with its nucleosynthetic production in stars (D. Clayton 2003; Meyer 200X). Newly synthesized oxygen is ejected into interstellar space from asymptotic giant branch (AGB) stars, novae, and supernovae in mineral grains, free atoms, and gas phase molecules. The nature of the ejecta is dependent on a number of variables including gas density, temperature, and composition (cf. Gail and Sedlmayr 1987).

One of the most critical variables that defines the nature of stellar ejecta is the C/O ratio of the material in the outflow. If C/O > 1 in a local outflow region, then most of the O can be incorporated into the very stable CO molecule. This leaves the excess C free to become incorporated into SiC and other oxygen-free materials. If, however, C/O < 1 then most of the C is incorporated into CO and the excess O is free to form other materials, principally molecular oxides, silicates, and oxide minerals (Tsuji 1986; Tielens 1991). Thus, the principal O-bearing components that are injected into the diffuse interstellar medium (ISM) are CO gas and a variety of refractory oxygen-bearing minerals.

Once injected into the galaxy's diffuse interstellar medium, these materials are repeatedly cycled through a wide variety of environments (**Fig. 1**). These include the diffuse ISM, dense molecular clouds, and star-formation regions, from which most of the material is ultimately recycled back into the diffuse ISM, although some of the material is incorporated into newly formed stars and planetary systems. The conditions in these different environments vary over a wide range of temperatures, pressures, radiation fluxes, etc. Transitions between these environments can radically transform the state of the oxygen.

The diffuse interstellar medium. The diffuse ISM is filled with a high radiation field. This radiation is sufficient to destroy most gas phase molecules. In addition, shock waves from energetic events like supernova explosions frequently traverse the diffuse ISM. These shock waves can destroy dust particles by a variety of processes (sputtering, grain-grain collisions, etc.) (cf. Seab 1987; Shull and Draine 1987; McKee 1989; Jones et al. 1994). As a result of these destructive processes, the majority of O in the gas phase portion of the diffuse ISM is in
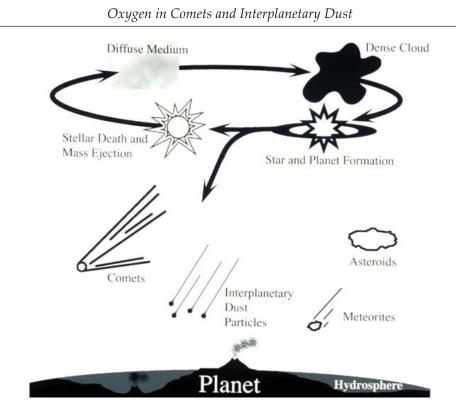
Figure 1. Materials in the galaxy are repeatedly cycled through a wide variety of environments, including the diffuse ISM, dense molecular clouds, and star-formation regions. Most of the material in star–formation regions is redistributed back into the general diffuse and dense ISM, but a small fraction ends up in stars and planets. Some of this material is returned to the ISM at the end of the stars' lifecycles. Comets are thought to be relatively pristine reservoirs of the material from which the Solar System formed.

the form of atomic O (Cartledge et al. 2001). The main carrier of O among solids in the diffuse ISM is silicates; infrared absorption spectra taken on lines of sight passing through the diffuse ISM suggest that the silicates are largely non-crystalline (Kemper et al. 2004).

The diffuse ISM also contains C-rich materials. The principal organic component of the gas phase consists of polycyclic aromatic hydrocarbons (PAHs) (Onaka et al. 1996), while the main organic component of the solid phase consists of C-rich grains that contain both aromatic and aliphatic structures (Sandford et al. 1991; Pendleton et al. 1994). Current infrared spectroscopic evidence, however, suggests that neither of these C-rich populations carry very much oxygen (Pendleton and Allamandola 2002).

Dense interstellar molecular clouds. Shocks and the radiation field of the diffuse ISM can penetrate the edges of dense molecular clouds, so it is perhaps not surprising that oxygen found in the edges of clouds is still largely present in the form of atomic O and amorphous silicates (cf. Whittet et al. 1996; Vastel et al. 2000). However, the greater density of gas and dust found deeper in dense interstellar clouds promotes the synthesis of a wide variety of new molecular materials. In addition, the interiors of these clouds have optical depths that are sufficient to absorb most of the radiation field present in the ambient diffuse ISM. This allows newly created molecular species to survive over appreciable time scales. These large optical depths also result in very low gas and grain temperatures (10 K < T < 50 K). Under these conditions, molecular species can be formed by a variety of different chemical processes *and* survive.

One of the principal chemical processes that occurs in the gas phase is ion-molecule reactions (cf. Herbst 1987; 2003). These reactions create a variety of O-bearing species (van Dishoeck and Blake 1998; Ehrenfreund and Charnley 2000). The resulting compounds are fairly simple and relatively volatile; these species are not particularly "meteoritic." Further chemical processing is required to "set" the oxygen into forms that can survive in meteoritic materials.

At the low temperatures that occur in dense clouds, however, most gas phase species will condense onto the first dust grain they collide with (Fig. 2). This results in additional gas-grain chemistry. In this case the H/H_2 ratio plays a critical role in determining what will be produced by gas-grain reactions (cf. Tielens and Hagen 1982; d'Hendecourt et al. 1985; Brown and Charnley 1990; Hasegawa et al. 1992; Charnley 1997). In environments where $H/H_2 > 1$, the principal chemical reactions add hydrogen to other atomic species on the ice surface, resulting in simple hydrides like H_2O, CH_3OH, NH_3, and CH_4. This results in highly polar ices dominated by H_2O. If, however, the local gas has $H/H_2 < 1$, gas-grain reactions yield ices dominated by less-polar molecules like CO, CO_2, O_2, and N_2. Infrared spectra of the ices in dense clouds support this basic concept (Sandford et al. 1988; Tielens et al. 1991). Provided they were not greatly warmed during their incorporation into comets during formation of the Solar System, it is possible that these icy materials could be directly preserved in comets. As with the products of gas phase ion-molecule reactions, however, these icy compounds would not have efficiently survived in meteoritic materials; further chemical processing was required to "set" the oxygen in these ices into the more refractory forms that survived in meteoritic materials.

One process that may play a role in generating more refractory materials is irradiation chemistry (Fig. 2). The ice mantles surrounding dust grains in dense clouds and the protosolar nebula can be further processed by cosmic rays, UV radiation from the attenuated diffuse ISM field, or UV produced by nearby stars and cosmic ray interactions (Norman and Silk 1980; Prasad and Tarafdar 1983). These forms of radiation can break bonds within molecules in the ice and generate ions and radicals that can subsequently react. This results in additional chemistry that forms a wide variety of more complex, largely C-rich, species.
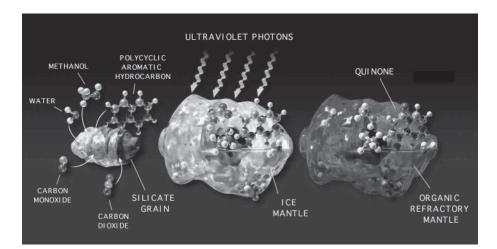

Figure 2. A large fraction of the volatile materials in dense interstellar clouds condense onto grain mantles. These ices are generally rich in oxygen in the form of molecules like H_2O, CH_3OH, CO, and CO_2. Cosmic rays and UV photons can break down these molecules into ions and radicals that can recombine to produce considerably more complex, and more refractory, O-bearing organic species.

Laboratory studies show that some of the species produced by charged particle and UV irradiation contain oxygen and resemble those found in meteoritic and cometary materials. These include molecular species like amphiphiles, amino acids, and aromatic ketones and alcohols (cf. Dworkin et al. 2001; Bernstein et al. 1999, 2002a, 2003). Of particular interest is the irradiation of PAHs in mixed molecular ices, since this results in the addition of excess H and a variety of chemical side groups (=O, -OH, -NH$_2$, -CN, -CH$_3$, -OCH$_3$, etc.) derived from other species in the ice (Bernstein et al. 2002b, 2003). As shown in Figure 3, in H$_2$O-rich ices, i.e., the ices seen to dominate most dense clouds, the principal additions to PAHS are =O and -OH groups linked to peripheral C atoms on the PAH, and bridging oxygen spanning "bay" regions (aromatic ethers) (Bernstein et al. 1999). Many of these species resemble those found in meteorites. For additional, more detailed discussion of oxygen in the interstellar medium, see the chapter by Jensen et al. (200X).

The oxygen in organics in meteorites, cosmic dust, and comet samples. Some of the oxygen in C-rich carriers in primitive meteorites resides in soluble species like amino acids, amphiphiles, carboxylic acids, etc. (cf. Cronin et al. 1988; Krishnamurthy et al. 1992; Huang et al. 2005). However, a major C-rich carrier of oxygen in meteorites is an insoluble macromolecular material ("kerogen") of uncertain origin (Cronin et al. 1988; Cody et al. 2002). In the Murchison carbonaceous chondrite, this material has relative abundances of C, O, and N of 100:18.3:3.8, respectively (Cody et al. 2002). The oxygen in this macromolecular material is found in both aromatic and aliphatic moieties (Gardinier et al. 2000; Cody et al. 2002). The meteoritic macromolecular material appears to be *much* more O-rich than the C-rich solid-state material seen in the diffuse ISM, but considerably less O-rich than the average of organics in collected IDPs (Flynn et al. 2006) and the organics seen in cometary grains returned from comet 81P/Wild 2 by the Stardust mission (Sandford et al. 2006).

Because of their small sizes, considerably less detail is available about the nature of the organics in IDPs. They contain abundant aromatic species (see, for example, Allamandola et al. 1987; Wopenka 1988; Quirico et al. 2005), and a variety of specific PAHs have been identified in them (Clemett et al. 1993; 1998). The total oxygen content of the organics in IDPs is generally much higher than that seen in the macromolecular material in meteorites (Flynn et al. 2006; Sandford et al. 2006), but the nature of the molecular carriers is still unclear. Given the abundance of aromatic species in these particles, aromatic ketones and alcohols may be possible carriers. Amino acids have been identified in larger Antarctic micrometeorites (Matrajt
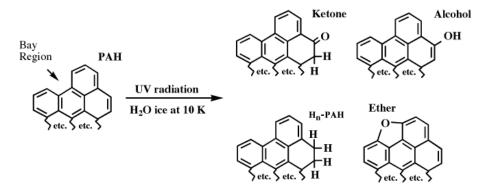

Figure 3. Polycyclic aromatic hydrocarbons (PAHs) are abundant in space. Their exterior carbon rings are easily functionalized with oxygen when they are irradiated in O-bearing ice mantles in dense interstellar clouds. The mix of functional groups depends somewhat on the composition of the ice, but =O, -OH, -O- (ether), and –O-CH$_3$ groups are commonly seen in laboratory simulations.

et al. 2004), but these are unlikely to be a major reservoir of the O found in IDPs since they are minor components in meteorites and micrometeorites. Furthermore, these amino acids may be products of aqueous processing (Strecker synthesis), and the parent bodies of anhydrous IDPs have not experienced hydrous alteration.

The organics returned from comet 81P/Wild 2 by the Stardust spacecraft are generally considerably richer in O than meteoritic organics, but are comparable, on average, to those of measured stratospheric IDPs (Sandford et al. 2006). X-ray Absorption Near Edge Spectroscopy (XANES) studies of these cometary samples demonstrate that the O is present in a wide variety of bonding states, including aldehydes, alcohols and esters. While the 81P/Wild 2 samples have O/C ratios somewhat similar to those seen in IDPs, it is clear that the two types of samples are not identical. The Wild 2 samples appear to contain a labile organic component that is missing from anhydrous IDPs (Sandford et al. 2006). If anhydrous IDPs have a cometary origin, this suggests that they may have lost a more labile fraction of their original organics during atmospheric entry or during their transit through interplanetary space from their parent body to Earth. Also, as noted above, the organics in IDPs are generally dominated by aromatic materials. In contrast, many Wild 2 samples contain little or no aromatic materials. The organics in these aromatic-poor grains contain large amounts of O, indicating that the O in Comet Wild 2 organics cannot be solely associated with aromatic species. In these particles, the carrier may be dominated by a "polymeric" material akin to polyoxymethylene or related "irregular" molecular structures similar to those made when mixed molecular ices are processed by high energy radiation (Schutte et al. 1993; Bernstein et al. 1995; Sandford et al. 2006).

The generally increasing O content of organics from the diffuse ISM, to meteorites, to IDPs and cometary samples suggests that meteoritic, IDP, and cometary organics do not simply consist of unaltered organics from the diffuse ISM, but must contain contributions from either dense cloud, protosolar nebula, and/or parent body processes. The fact that material in IDPs and from comet 81P/Wild 2 generally shows higher O contents than meteoritic organics further suggests that dense cloud and/or protosolar nebular processes (radiation processing, gas and gas-grain chemistry, etc.) must generally act to drive up the overall O content of organics more than do parent body processes (aqueous alteration, heating, etc.)

In summary, oxygen is seen in a variety of forms in stellar outflows, the diffuse ISM, and dense molecular clouds. Silicates and other oxides are the main carriers of solid-state oxygen in the diffuse ISM and are major carriers in dense clouds. Most of the gas phase O in the diffuse ISM is in the form of atomic O; very little oxygen seems to be associated with the C-rich materials seen in the diffuse ISM. Most of the non-mineral oxygen seen in the dense ISM is in relatively volatile, "non-meteoritic" forms, and much of it is in the form of ices. "Fixing" interstellar oxygen into C-rich forms that can survive incorporation into asteroidal and cometary parent bodies requires significant processing in dense cloud and protostellar nebular environments. These chemical processes result in organics that contain oxygen in a diverse set of molecules ranging from small, soluble species to macromolecular "kerogens." In the specific case of comets, the organics (at least for comet 81P/Wild 2) are extremely O-rich and the oxygen is present in a wide variety of bonding states.

Direct detection of oxygen-bearing volatiles in comets

Whipple (1951) was the first to recognize the importance of comets for the history of our Solar System. Late in the last century it was accepted that comets represent the best-preserved material from the early Solar System. Because they retain their volatiles, comets also appear to have retained their full complement of solar nebular oxygen (Fig. 4). Furthermore, since some molecules found in comets, e.g., C_4H (Geiss et al. 1999), can be traced back to the dark molecular cloud from which our Solar System formed, we can use cometary volatiles and their abundances to study the processes that led from the molecular cloud through accretion into the solar nebula, to the present constituents of cometary nuclei (e.g., Altwegg et al. 1999).
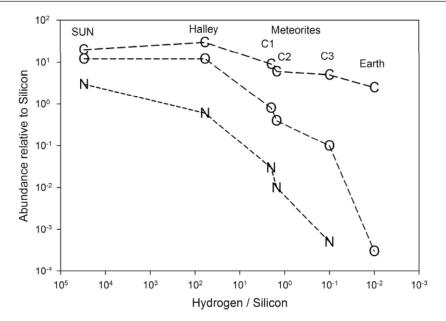
Figure 4. Elemental abundances of carbon (C), oxygen (O) and nitrogen (N) in different bodies of our Solar System as a function of hydrogen/silicon ratio (after Geiss 1988).

Until about 1980, it was assumed that comet nuclei primarily contained frozen H_2O, NH_3, and CH_4. However, models based on this assumption, even when supplemented with a few other minor species, failed to explain the radicals and ions identified in spectra of cometary comae. One of the first models to come close to explaining the observations was based on the assumption that cometary nuclei consisted of frozen interstellar molecules and grains (Biermann et al. 1982; Greenberg 1982). Since that time, considerable progress has been made in finding new molecular species in comets and in modeling and understanding their compositions in this context (e.g., Altwegg et al. 1999).

Figure 5 shows the abundances of cometary molecules compared with those of molecules in molecular clouds having C/O ratios near solar. Such data are becoming increasingly available (e.g., Ehrenfreund and Charnley 2000). The relative abundances of most cometary molecules measured so far are similar to those seen in interstellar dense clouds; the ranges of observed molecular abundances, relative to H_2O, generally overlap in these objects. This suggests that much of the volatile component in comets has been preserved from the preceding cold molecular cloud stage. However, the degree of processing experienced by their ices is a fundamental question in cometary science, and indeed this is the primary driver for building a new taxonomy of comets based on composition.

One of the defining characteristics of comets is their high abundance of volatiles (ices). As mixtures of nebular and interstellar ices, their compositions may be sensitive indicators of spatial and temporal variations in the nebular thermal environment. The dominant cometary ice phases (polar and apolar) are major reservoirs of primordial volatile oxygen. Measuring the compositions of cometary native ices (i.e., those contained in the nucleus) can therefore provide unique constraints on the origin and history of O-bearing icy materials in the Solar System. These data reflect the degree to which the composition of organic pre-cometary ices varied with distance from the young Sun (and with time) in the early solar nebula. Their structure and composition depend on local conditions (chemistry, temperature, degree of
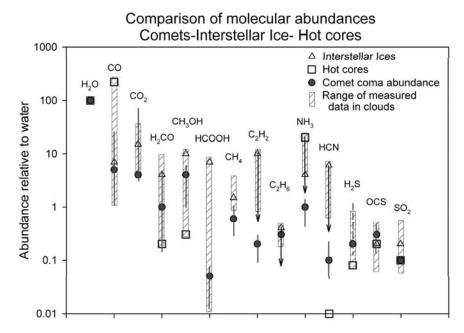
Figure 5. A comparison between the relative abundances of various molecular species in ices found in dense molecular clouds (triangles), in gases in "hot cores" within dense molecular clouds (squares), in the gas phase in cometary comae (circles), and the range of abundances found in gas phase molecules in dense molecular clouds (cross-hatched bars). All abundances are normalized to the abundance of H_2O, which has been assigned a value of 100. Arrows indicate upper limits. After Crovisier (1998).

radiation processing) prevalent when and where they formed (Mumma et al. 1993; Irvine et al. 2000; Bockelée-Morvan et al. 2004). Measured cometary ice compositions can be compared with interstellar ices, with laboratory-processed analogs, and with formation models of comets and the proto-solar nebula.

Oxygen plays a prominent role in the volatile composition of comets. Most of the volatile oxygen is in the form of H_2O, and since this is the most abundant ice in comets, it is generally used as the reference against which the abundances of other ices are measured. In terms of oxidized carbon, abundances of CO (relative to H_2O) are highly variable among comets, ranging from less than 1% to nearly 20%. Abundances of H_2CO and CH_3OH as high as ~3% and ~7%, respectively, have been reported (see, e.g., Fig. 12 of Bockelée-Morvan et al 2004). CO_2, although observed in only a few comets, appears to be present at levels of several percent. By contrast, hydrocarbon molecules (CH_4, C_2H_2, C_2H_6) provide an overall lower contribution to the total budget of volatile carbon. Abundances of the simplest fully reduced one-carbon molecule, CH_4, although variable among comets, are at most $CH_4/H_2O \sim 2\%$ (see Gibb et al. 2003), and C_2H_2 and C_2H_6 are even less abundant (e.g., $C_2H_6/H_2O \sim 0.6\%$ and $C_2H_2/H_2O \sim 0.2\%$ in most Oort cloud comets observed to date). This is surprising in view of the very hydrogen-rich composition of the solar nebula, in which comets formed. It is consistent, however, with material formed in an interstellar cloud or in a kinetically controlled solar nebula, where CO can either condense directly in polar (H_2O-rich) or apolar (H_2O-poor) ices (see below).

Cometary nuclei warm when approaching the Sun, causing their ices to sublime, releasing volatiles into their comae (i.e., atmospheres), where they can be sensed spectroscopically at infrared wavelengths (principally between 2.8 and 5.0 μm) and sub-millimeter wavelengths. A fundamental challenge for cometary observations is distinguishing direct release by the

nucleus (parent volatiles) from sources of extended release in the coma (e.g., by thermal degradation of grains or by chemistry). The spectral signature of volatiles consists of emission lines arising from fluorescent vibrational excitation by incident solar radiation. Although the presence of such lines in cometary spectra was predicted previously (Mumma 1982; Crovisier and Encrenaz 1983; Weaver and Mumma 1984; Bockelée-Morvan and Crovisier 1987), their detection required the development of astronomical spectrometers having sufficiently high sensitivity and spectral resolving power (e.g., $\lambda/\Delta\lambda \sim 2 \times 10^4$ or higher).

Modern IR spectrometers have small (sub-arc-second) pixels, and so are well-suited for measuring molecular abundances of volatiles in comets. They also provide spatial coverage of the sky, thereby permitting an accurate measure of the spatial distribution of emission in the coma. The emission intensity for direct release is highly peaked at the nucleus and decreases approximately as inverse projected distance from the nucleus, whereas distributed release gives rise to a flatter spatial profile of emission. This is particularly relevant to CO and H_2CO, for which significant, or even dominant, distributed source contributions have been observed in some comets (Eberhardt et al. 1987; Meier et al. 1993; Wink et al. 1997; Eberhardt 1999; DiSanti et al. 1999, 2003).

Advances in instrumentation over the past decade now enable the routine detection of multiple parent volatiles in comets, primarily through resonant (i.e., fundamental-band) ro-vibrational transitions occurring between excited and ground vibrational states. Detected molecules include CO (Fig. 6A), monomeric formaldehyde (H_2CO, Fig. 6B), and methyl alcohol (CH_3OH, Fig. 6C). Together with CO_2, these represent the principal reservoirs of volatile oxidized carbon in comets.

Ground-based detection of H_2O requires sensing non-resonant ("hot band") transitions (Figs. 6A, 6D) that occur between two excited vibrational states that are not significantly populated in the terrestrial atmosphere (Dello Russo et al. 2000). Prompt emission from OH was also proposed for sounding H_2O in comets (Mumma 1982; Bockelée-Morvan and Crovisier 1989; Mumma et al. 2001). In contrast to the relatively flat spatial distribution of emission from fluorescent OH, the spatial profile of OH prompt emission faithfully traces that of parent (H_2O). Through simultaneous measurement with H_2O, a method has been developed for using OH prompt emission lines to quantify H_2O production in comets (Bonev et al. 2004; Bonev 2005). These OH lines can therefore be used to establish both the spatial distribution and production rate of H_2O when emissions from H_2O itself are not available for observation within the band pass used.

The abundances (i.e., the production rates) of parent volatiles are determined by applying a quantum mechanical fluorescence model to the observable ro-vibrational lines. In most cases the analysis requires development of new (or extension of existing) fluorescence models appropriate to the low temperatures (20-150 K) typical of cometary comae. Such fluorescence models need to be formulated from high-resolution laboratory spectra, synthesized at the desired rotational temperature, and convolved to the instrumental resolution. Interpretation of infrared emission from H_2CO (Reuter et al. 1989; DiSanti et al. 2006), CH_3OH (Reuter 1992), and H_2O (Dello Russo et al. 2000, 2005) has been approached in this manner. Because CO is a linear molecule having a relatively simple spectral signature, its rotational temperature can be measured directly by comparing the flux (W m^{-2}) contained in lines spanning a range of rotational energies (Herzberg 1950; DiSanti et al. 2001). More recently, a general method has been developed for measuring rotational temperatures of any molecular species for which a fluorescence model exists over a range of temperatures (Dello Russo et al. 2005; DiSanti et al. 2006).

Besides H_2O, CO, CH_3OH, and H_2CO, the other main O-containing gas phase species in cometary comae is CO_2 (e.g., Feldman et al. 1986; Crovisier et al. 1997), which has typical abundances relative to H_2O of 1-10% (Bockelée-Morvan et al. 2004). A host of other O-
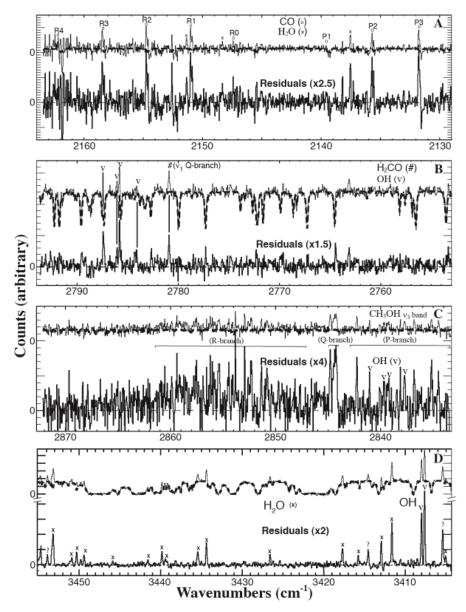
Figure 6. Spectra of oxygen-bearing molecules in comet C/2004 Q2 (Machholz) obtained with the Near IR Spectrometer (NIRSPEC) at the Keck Observatory. In each panel, the upper trace shows the extracted spectrum (solid) including dust continuum emission, and the superimposed modeled atmospheric transmittance (heavy dashed trace). The bottom trace shows residual cometary emission in excess of the continuum. **A**. Simultaneous measure of CO fundamental and H_2O hot band emission near $\lambda = 4.7$ μm. CO lines are labeled by their rotational designations, and are blue-shifted relative to their terrestrial counterparts due to the geocentric velocity of the comet (~ −20 km s^{-1}). **B**. Region of H_2CO emission near 3.6 μm, showing the ν_1 Q-branch plus four lines of OH prompt emission, used as a proxy for H_2O. **C**. CH_3OH ν_3 band emission, centered near 3.52 μm, with P-, Q-, and R-branches indicated. **D**. H_2O hot band emissions near 2.9 μm. Detailed treatment of these and other comet Q2 spectra can be found in Bonev (2005).

containing species have also been identified in comets, including HCOOH, HCOOCH$_3$, CH$_3$CHO, NH$_2$CHO, HNCO, OCS, and SO$_2$, but these species are generally present at abundances well below 1% that of H$_2$O (see Bockelée-Morvan et al. 2004 for a review).

The discovery of cometary CO during spacecraft ultraviolet observations of Comet West (1976 VI) (Feldman and Brune 1976; Feldman 1978) established this molecule as an important component in these primitive Solar System objects. Since then, CO has been observed extensively at UV (Festou et al. 1982; Feldman et al. 1997), IR (Mumma et al. 2003, and references therein), and radio (Biver et al. 2002) wavelengths, and it has become the cornerstone for studies of oxidized carbon in comets. Pure CO ice has the lowest sublimation temperature (~25 K) of any parent molecule, so fractionation of CO-rich, pre-cometary ices should depend strongly on local temperatures. Alternatively, if trapped in H$_2$O-rich ices, CO can be captured at higher temperatures (~50 K, or perhaps even to 150 K; Sandford and Allamandola 1988, 1990; Crovisier and Encrenaz 2000). In the IR, CO emission has been detected in all Oort cloud comets observed since 1996, and the large variation in its native abundance relative to H$_2$O (1–20%) suggests that pre-cometary ices experienced a range of temperatures (indeed, Oort cloud comets formed in the giant planets' region, ~5-30 AU from the Sun, over which local temperatures would have varied greatly). However, the abundances of CO and CH$_4$ (the next most volatile parent molecule in comets, after CO) are not correlated among the comets studied (Gibb et al. 2003), suggesting that thermal effects alone cannot explain volatile abundances in cometary nuclei.

A plausible means of converting CO to H$_2$CO and H$_2$CO to CH$_3$OH involves hydrogen atom addition reactions on the surfaces of pre-cometary grains. This process is analogous to the H-atom addition (e.g., to C$_2$H$_2$) proposed to explain the high abundance ratio of C$_2$H$_6$/CH$_4$ observed in C/1996 B2 (Hyakutake) (Mumma et al. 1996) and subsequent comets. The relative abundances of native CO, H$_2$CO, and CH$_3$OH to each other and to H$_2$O in comets provide a measure of the efficiency of hydrogenation of CO on grain surfaces. UV and proton irradiation of laboratory analogs of pre-cometary ice (mixed H$_2$O and CO) demonstrated the production of HCO, H$_2$CO, CH$_3$OH, and formic acid (Bernstein et al. 1995; Hudson and Moore 1999). Hydrogen-atom irradiation, both of polar (mixed H$_2$O, CO) ice and of apolar (pure CO) ice, showed the conversion efficiency to be highly dependent on temperature in the 10–25 K range and on the density of H atoms (Hiraoka et al. 2002; Watanabe and Kouchi 2002; Watanabe et al. 2004). Hydrogen-atom addition to CO proceeds through the highly-reactive formyl radical (HCO). This subsequently converts to formaldehyde polymers such as polyoxymethylene (POM) and related derivatives (Huebner et al. 1987; Meier et al. 1993; Schutte et al. 1993), and also to H$_2$CO and then to CH$_3$OH. The relative abundances of CO, H$_2$CO and CH$_3$OH test their inter-relationship in comets, and the laboratory yields provide a basis for comparison in assessing natal conditions.

The presence of formaldehyde and related compounds in comets may also have been important for the origin of life. For example, H$_2$CO has been proposed as the principal one-carbon molecule capable of generating complex organics of biological importance (Weber 2000; 2002). H$_2$CO may also have played a central role in the formation of amino acids in primitive meteorite parent bodies during aqueous alteration via Strecker-cyanohydrin synthesis. Alternative mechanisms for producing amino acids in pre-cometary ices without liquid water have also been identified (Bernstein et al. 2002a; Muñoz Caro et al. 2002). These studies either employ HCN, NH$_3$, and H$_2$CO directly, or generate them *in situ* (Moore and Hudson 2003). Cometary organic molecules may also have contributed to the formation of nucleobases (Oró 1960), sugars (Weber 2002), possible pre-RNA backbones (Nelson et al. 2000), and a host of biochemical intermediates (Oró et al. 1990) either on the icy body or after accretion to the early Earth.

The oxygen-bearing minerals in "cometary" IDPs and samples from comet 81P/Wild 2

The remote detection of oxygen-bearing minerals in comets. The presence of O-bearing minerals in comets can be detected at infrared wavelengths, primarily through the use of spectroscopy in the 8-13 μm region where the characteristic Si-O stretching vibrations of silicate minerals fall, but silicate features can sometimes be detected out to 40 μm. When small cometary grains are ejected from a cometary nucleus, they are heated by solar radiation. This energy is subsequently re-radiated in the infrared, resulting in a quasi-blackbody continuum upon which a superimposed silicate emission feature is sometimes seen. To produce a strong feature in emission, the emitting silicate particles must be smaller than 1 μm in radius; particles larger than this will, for the most part, only contribute to continuum emission, and their mineralogy is difficult to assess in this manner. The strength and profile of the emission features are therefore dependent on grain composition, size and albedo, and emission models must be used to interpret these features (see Hanner and Bradley 2004 for a review).

The infrared emission features of dust in cometary comae are generally interpreted to be largely dominated by olivine, pyroxene, and "glassy" silicates (e.g., Hanner et al. 1994; Wooden et al. 1999; Crovisier et al. 2000; Hanner and Bradley 2004). Models of the silicate emission feature suggest that only a minor fraction of the silicates (15-30%) are in crystalline form; the remainder of the silicates may be amorphous.

A unique opportunity to study cometary dust remotely occurred when the Deep Impact mission sent a 364 kg impactor into the nucleus of comet 9P/Tempel 1 at 10.2 km/sec. The impact produced large amounts of ejecta from the surface layers of the comet, and infrared spectra of the ejecta were collected by the Spitzer Space Telescope (Lisse et al. 2006). Emission signatures due to amorphous and crystalline silicates, amorphous carbon, carbonates, phyllosilicates, polycyclic aromatic hydrocarbons, H_2O gas and ice, and sulfides were reported. Many of these materials are seen in chondritic porous IDPs and samples from comet 81P/Wild 2 (see below), but others, for example phyllosilicates and carbonates, have yet to be confirmed in Wild 2 samples. The reason for these apparent differences has yet to be fully resolved.

Overall, the spectral features observed in cometary infrared emission spectra imply a fairly complex mineralogy that includes both amorphous and crystalline grains, with olivine and pyroxene being the dominant crystalline phases. The mineralogical mixture is largely consistent with the composition of chondritic porous IDPs and samples returned from comet 81P/Wild 2, although it is difficult to assess the abundance of glassy silicates in the Wild 2 samples (see the following two sections).

Oxygen-bearing minerals in "cometary" IDPs. Interplanetary dust particles are collected in the stratosphere at 20-25 km altitude and are typically 5-15 μm in diameter. There are two major types of IDPs: chondritic porous (CP) IDPs that are typically anhydrous; and chondritic smooth (CS) IDPs that have undergone aqueous alteration that formed clay minerals and carbonates. The CP IDPs have been linked to cometary sources from their inferred orbital characteristics (Brownlee et al. 1995), fine-grained mineralogy (Bradley and Brownlee 1986), infrared spectral properties (Sandford 1991), and high abundances of presolar materials (Messenger et al. 2003). These particles have escaped the thermal metamorphism and aqueous alteration that affected even the most primitive meteorites, and are characterized by high carbon and nitrogen abundances (Thomas et al. 1993; Keller et al. 2004; Flynn et al. 2006), unequilibrated mineralogy (Keller and Messenger 2005), and the presence of non-solar hydrogen and nitrogen isotopic signatures and abundant presolar silicates (Messenger et al. 2003). Typical CP IDPs are highly porous particles that consist of fine-grained crystalline silicates, GEMS (glass with embedded metal and sulfides, Bradley 1994) grains, and Fe-Ni sulfides, all bound together by an organic-rich carbonaceous matrix. The constituent grains in IDPs are much smaller (<1 μm) than typical meteorite matrix grains. The abundance of glassy grains (e.g., GEMS grains) is also much higher in IDPs than in meteorite matrices.

Crystalline silicates in CP IDPs are predominantly olivine and low-Ca pyroxene, with lesser high-Ca pyroxene, feldspar, and rare melilite. Multiple lines of evidence suggest a high-temperature, nebular condensation origin for most of the crystalline silicates in CP IDPs. The olivine and pyroxene grains are typically single crystals and have Mg-rich (atomic Mg/(Mg+Fe) ~ 0.9-1.0) and Mn-rich (Mn/(Mn+Mg+Fe) up to 0.05) compositions that are consistent with condensation at temperatures of around 1100-1200K (Wai and Wasson 1977; Klöck et al. 1989). Many of the enstatite grains and some of the forsterite crystals show unique whisker and platelet morphologies as well as characteristic defects (axial screw dislocations) that suggest growth from the vapor phase (Bradley et al. 1983). The crystalline silicates observed in CP IDPs also show marked similarities in terms of mineralogy, size, composition, and abundance to those inferred to exist around young stars and in comets through astronomical infrared (IR) spectroscopic measurements (Keller and Messenger 2005, and references therein). Additional evidence that the crystalline silicates are an early-formed component of CP IDPs comes from the presence of pre-accretionally irradiated rims on many of the crystalline grains, indicating that the grains were exposed as small objects prior to accretion into their parent bodies (Bradley et al. 1984). Enstatite and forsterite grains in IDPs typically contain up to 5 wt% Cr_2O_3 + MnO, and in many cases this total exceeds the FeO content. Low-Fe, Mn-rich forsterites were identified in IDPs by Klöck et al. (1989) and have also been observed in some primitive meteorites. These grains are believed to have formed via gas-solid condensation in the solar nebula, with forsterite forming at higher temperatures than enstatite (Klöck et al. 1989; Weisberg et al. 2004). It is not known whether the Cr in these silicates is di- or trivalent, but Na is not detected in the pyroxenes, so the charge-balanced substitution Na+Cr^{3+} for 2Mg does not appear to be operating. This suggests Cr^{2+} substitution for Mg, in both pyroxene and olivine. Minor diopside grains in anhydrous IDPs tend to be more Cr-rich than enstatite in the same particles.

Amorphous silicates (GEMS) are a major component of primitive CP IDPs, and they record variable oxidation states. GEMS grains are <0.5 μm in diameter, consisting of abundant 10 to 50 nm-sized kamacite and Fe-Ni sulfide grains dispersed in a Mg-Si-Al-Fe amorphous silicate matrix. To date, GEMS grains have not been found in any abundance in meteorite samples, although a possible case has been reported (Mostefaoui et al. 2004). Bradley et al. (1999) proposed that GEMS are preserved interstellar (IS) silicates, based on observed preaccretional irradiation effects and IR spectral properties that closely resemble IS dust. Oxygen isotopic measurements confirm that at least a small fraction (<5%) of GEMS are demonstrably presolar, while the remainder have oxygen isotopic compositions that are indistinguishable from solar values (Engrand et al. 1999; Messenger et al. 2003).

GEMS with solar oxygen isotopic compositions either had their isotopic compositions "homogenized" through processing in the interstellar medium (Tielens 1998), or formed in the early Solar System (Keller and Messenger 2004). Bulk elemental compositions of GEMS grains have been systematically measured, and results show that they have sub-chondritic S/Si, Mg/Si, Ca/Si, and Fe/Si ratios. For these ratios, the average GEMS compositions are ~60% of solar values, although the average Al/Si ratio in GEMS is indistinguishable from solar (Keller and Messenger 2004). The elemental and isotopic data for GEMS grains suggest that most formed in the early solar nebula either as shock melts or as direct, non-equilibrium condensates. In this model, the preaccretional irradiation effects observed in GEMS grains occurred in the solar nebula—this view is supported by the similar magnitude of irradiation effects experienced by GEMS grains and many of the crystalline silicates in CP IDPs. If most GEMS grains are condensates, then a mechanism has to exist to transport the GEMS grains (as well as forsterite and enstatite) to the comet-forming region, perhaps through bipolar outflows during the early accretion phase of the disk (Shu et al. 2001) or turbulent mixing within the nebular disk (Cuzzi et al. 2003).

Keller and Messenger (2004) proposed that most GEMS grains are non-equilibrium condensates that formed after high-temperature crystalline silicates (forsterite, enstatite, diopside) condensed, but prior to the main phase of sulfide formation/condensation. In this scenario, conditions during condensation were sufficiently reducing to keep Fe in the metallic state at least to temperatures below ~1000 K (the upper stability limit for the preservation of the amorphous silicate matrix before it anneals [Brownlee et al. 2005]), and Fe^{2+} only became abundant when sulfidization reactions began, at ~700 K. Individual GEMS grains can contain both nanophase kamacite and taenite; however, their compositions are not in equilibrium (Keller et al. 2005). X-ray mapping experiments have also revealed Fe- and Cr-rich grains within GEMS, but it has not been determined if these are nanophase metal or chromite grains (Keller et al. 2005). Mapping experiments also show that the amorphous silicate matrix of GEMS grains tends to be highly SiO_2-normative, with much of the Fe present as metal, although electron energy-loss spectroscopy measurements of Fe oxidation states in some FeS-free GEMS grains have documented a mixture of Fe metal and Fe^{2+} in the amorphous silicate matrix (Keller and Messenger 2004).

Sulfides, another major constituent of CP IDPs, are predominantly low-Ni pyrrhotites with a wide range of grain sizes (Zolensky and Thomas 1995; Dai and Bradley 2001). The pyrrhotite occurs as isolated single crystals as well as 10-50 nm-sized grains decorating the exterior of GEMS grains. The sulfides are believed to be the products of sulfidation of pre-existing FeNi metal in the early nebula (Lauretta et al. 1997).

Oxygen-bearing minerals in samples from comet 81P/Wild 2. The preliminary studies of samples returned from comet 81P/Wild 2 by the Stardust spacecraft have demonstrated that these materials contain a wide variety of O-bearing minerals (Brownlee et al. 2006; Keller et al. 2006; Zolensky et al. 2006). Dominant among these are olivine and pyroxene with wide composition ranges. Relatively refractory O-bearing phases, such as spinel and anorthite, have also been found (Zolensky et al. 2006), albeit in very low abundances. So far, the most refractory phases appear to be both compositionally and isotopically similar to phases found in some of the Ca-, Al-rich inclusions (CAIs) in carbonaceous chondrites (McKeegan et al. 2006; Zolensky et al. 2006). The presence of these mineral grains, particularly the phases found in CAIs, strongly suggests that a great deal of mixing occurred in the protosolar nebula and that comets contain substantial amounts of material that formed much closer to the Sun than did comets. As with IDPs, sulfides are also a major component of Wild 2 samples (Zolensky et al. 2006)

The issue as to whether the returned cometary grains contain oxygen carried in amorphous, glassy phases similar to the GEMS seen in IDPs currently remains unresolved. Glassy phases are seen associated with Stardust impact tracks, but it has proven difficult to unequivocally establish a cometary origin for these materials since the samples were collected in aerogel, which is itself an amorphous, glassy material (Zolensky et al. 2006).

OXYGEN ISOTOPES IN THE INTERSTELLAR MEDIUM, COMETS, COMETARY SAMPLES, AND "COMETARY" IDPS

Isotopic ratios can provide strong constraints on the nucleosynthetic, chemical, and physical formation processes and alteration histories of O-bearing materials. As with the composition of O-containing organics and minerals, the isotopic composition of oxygen in comets can be studied both remotely and *in situ,* as well as from collected samples.

Oxygen isotopes in interstellar materials

The largest O-isotopic anomalies in meteoritic materials occur in presolar grains, whose isotopic signatures reflect *nucleosynthetic* processes. These are discussed in a separate section below and in other chapters in this book, especially Meyer et al. (200X). Chemical processes

can also affect O-isotopic distributions. Chemical processes occurring in the interstellar medium have imprinted meteoritic materials with isotopic signatures in other light elements, most prominently in H and N. Several different interstellar chemical processes (ion-molecule reactions, gas-grain reactions, unimolecular photodissociation of PAHs, and ice irradiation) can produce significant D/H and $^{15}N/^{14}N$ fractionations (cf. Tielens 1997; Sandford et al. 2001; Charnley and Rodgers 2002), and isotopic anomalies in these elements are seen in the interstellar medium, comets (cf. Mauersberger et al. 1988; Loinard et al. 2000; Jehin et al. 2004) and in meteorites (cf. Zinner 1988, 1997; Krishnamurthy et al. 1992; Messenger 2000). These interstellar processes largely require that some fractionation occur initially in the gas phase.

O-isotopic fractionation has been observed in some interstellar molecular clouds. However, O in the gas phase in the ISM resides primarily in CO, O, and possibly O_2; theory suggests that very little ion-molecule fractionation in O-isotopic ratios should occur in these species or their reaction products (e.g., Langer et al. 1984; Langer and Graedel 1989). The observed O-isotopic fractionation in interstellar clouds may be better attributed to photochemical self-shielding of $C^{16}O$ isotopomers (Thiemans 1988; Lada et al. 1994; R. Clayton 2003; Lyons and Young 2005). Fractionations generated in this manner may explain the ^{16}O-rich components seen in some meteoritic materials (R. Clayton et al. 1985, and references therein). According to a recently proposed model, selective photodissociation of this sort could have resulted in substantial differences in the O-isotopic compositions of CO ($\delta^{18}O = -60$ to -450) and H_2O ($\delta^{18}O = +100$ to $+250$ ‰) molecules inherited by the Solar System (Yurimoto and Kuramoto 2004). This model predicts that the Sun is ^{16}O-rich, and raises the possibility that ices in Kuiper Belt objects have retained the pronounced O-isotopic anomalies. Presently, the O-isotopic composition of cometary ices (Balsiger et al. 1995) and the Sun (Hashizume and Chaussidon 2005; Ireland et al. 2006) are not well constrained, although results from the Genesis mission may soon better establish the isotopic composition of O in the Sun (Wiens et al. 2004; Davis et al. 200X).

No model has yet attempted to predict how, if at all, O-isotopic fractionation due to photochemical self shielding of CO might be passed on to interstellar or Solar System organics or minerals. So far oxygen isotopes, unlike hydrogen and nitrogen isotopes, have not proven to be useful markers of interstellar (as opposed to circumstellar) heritage. However, significant O-isotopic anomalies may have been preserved in cometary ices. Additionally, excess D or ^{15}N may still be useful as possible tracers for O-containing materials formed by interstellar processes.

In situ measurement of the oxygen isotopes in the volatile material of comet Halley

Isotopic ratios can provide clues to the physical conditions that prevailed during the formation of cometary volatiles. The reappearance of comet Halley in 1985 and the appearance of the two bright comets towards the end of the last century, Hyakutake and Hale-Bopp, triggered an enormous scientific interest in these small icy bodies and in their relationship with interstellar materials. However, after the multi-spacecraft visit at comet Halley in 1986, only a few missions have specifically targeted comets. These include Deep Impact (A'Hearn et al. 2005), Stardust (Brownlee et al. 2003, 2004), and Rosetta (Schwehm et al. 2006), the latter now on its long journey to comet 67P/Churyumov-Gerasimenko.

Oxygen isotopes in comets. The only *in situ* measurement of oxygen isotopes in a comet stems from the comet 1P/Halley flyby of the European spacecraft Giotto (**Fig. 7**, modified from Balsiger et al. 1995). The $^{16}O/^{18}O$ ratio measured in the coma in the hydronium ion was 518 ± 45 (Balsiger et al. 1995) and 470 ± 40 (Eberhardt et al. 1995) at distances of 1300 km and 8000 km from the nucleus, respectively, both within error of the terrestrial value, 499. These measurements cannot exclude the possibility that some isotopic fractionation occurs in the coma and that these values may not exactly represent the mean H_2O isotopic ratio in the nucleus. Possible, although weak, fractionation processes could include: mass dependence of flow field; mass dependence of ion-neutral reaction rates in reaction; isotope dependence of photo-
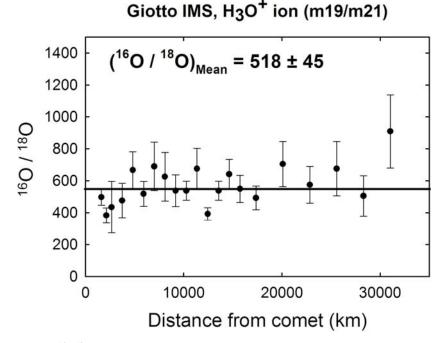
Giotto IMS, H_3O^+ ion (m19/m21)

Figure 7. The $^{16}O/^{18}O$ oxygen isotopic ratio in the hydronium ion in the coma of comet 1P/Halley measured by the ion mass spectrometer IMS (data from Balsiger et al. 1995). The $^{16}O/^{18}O$ ratio of Standard Mean Ocean Water (SMOW) is 498.7. Modified from Balsiger et al. (1995).

ionization rate in reaction; isotope dependence of photo-destruction rate or recombination rate; fractionation during sublimation; and fractionation within the nucleus.

The hydronium ion (H_3O^+) was the most abundant ion within 2×10^4 km of Halley's nucleus and is the product of the following chemical reactions in the cometary coma:

$$H_2O + h\nu \rightarrow H_2O^+ + e^-$$

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$$

The hydronium ion is mainly destroyed by electron recombination or by proton transfer to other species with a higher proton-affinity (e.g., to H_2CO).

No value is available for $^{16}O/^{17}O$ from the comet 1P/Halley flyby. This isotopic ratio cannot be measured by remote sensing due to the lack of unequivocal lines for the different isotopes. No oxygen isotopic ratios have yet been determined for other molecular species.

As discussed above, one model predicts that H_2O in the interior of molecular clouds (MC) is isotopically heavy ($\delta^{18}O_{MC}$= +100 to +250) and that CO is isotopically light ($\delta^{18}O_{MC}$= −60 to −450) as a result of photochemical self-shielding. Unfortunately, the uncertainties in the $\delta^{18}O$ values determined by Giotto at comet 1P/Halley are too large to resolve isotopic variations of this magnitude, but do exclude significantly larger fractionation effects. Higher precision measurements could be obtained by spacecraft measurements of neutral H_2O and CO molecules made closer to a cometary nucleus, or by laboratory analysis of a returned sample of cometary ices.

Oxygen isotopic compositions of meteorites, "cometary" IDPs and samples from comet 81P/Wild

Studies of meteoritic materials have shown O-isotopic heterogeneity from planetary to micrometer scales. At the planetary scale, the bulk O-isotopic compositions of several meteorite groups, the Earth, and Mars differ at sub-‰ levels, suggesting variable contributions from different O reservoirs. On the other extreme, microscopic presolar grains found scattered in meteorites and IDPs exhibit exotic O-isotopic compositions that vary by orders of magnitude. Refractory inclusions in primitive meteorites also commonly exhibit significant anomalies at the percent level, generally viewed as enrichments in ^{16}O, although the origin of this effect is still unsettled. Possibilities include nucleosynthetic production of ^{16}O-rich materials and O isotopic fractionation by self-shielding (see, for example, Thiemans 1988; R. Clayton 2003; Lyons and Young 2005, and references therein). Studies of the O-isotopic composition of cometary materials can thus provide important insights into first-order questions of the early history of the Solar System, such as: was the Solar System thoroughly homogenized isotopically; are comets composed of mostly pristine or mostly processed materials; and was there large-scale radial transport of material within the solar nebula? Answering these questions requires high-precision bulk isotopic measurements, searches for presolar dust grains in comets, and isotopic analysis of mineral grains in comets.

At the moment, relatively little information exists about the O-isotopic distribution in meteoritic or IDP organics. Halbout et al. (1990) found relatively normal oxygen (δ^{17}O = +3.3‰) and carbon (δ^{13}C ≤ −48‰) in the Orgueil macromolecule even though the same material contained large D-excesses (δD = +1360‰). Oxygen isotopic anomalies have been found associated with meteoritic organics in one case; the carrier of the anomalies, however, was found to be SiO_2 grains contained within the Murchison macromolecule (Aléon et al. 2005). These large oxygen isotopic anomalies could have a solar origin and are likely not associated with the processes that made the organics. While the O-isotopic compositions of meteoritic organics appear to be largely normal and do not correlate with D or ^{15}N enrichments, it should be noted that excess D or ^{15}N in organic materials might still be useful as a possible tracer for interstellar organic molecules that contain oxygen given that many of the same dense cloud processes thought to produce both D and ^{15}N enrichments are also expected to produce O-addition on organics.

Due to the small sizes of stratospheric IDPs (~10^{-9} g), O-isotopic measurements of these samples have so far only been possible by secondary ion mass spectrometry (SIMS). This technique offers superb spatial resolution and sensitivity, enabling *in situ* isotopic measurements at sub-μm scales. Early studies found the bulk O-isotopic compositions of IDPs to fall within the range of meteoritic materials (McKeegan 1987a,b; Stadermann 1990). However, the fine-grained, complex mineralogy of IDPs has limited these measurements to typically 5 to 10‰ precision. This precision is sufficient to show that refractory minerals in some IDPs are enriched in ^{16}O at levels comparable to those found in carbonaceous chondrites, with ^{16}O excesses of 16 to 38‰ (McKeegan 1987a,b). More recently, several IDPs containing large forsterite and enstatite grains were analyzed, enabling more accurate matrix corrections to be applied, resulting in analytical precision of ~1.5‰ (Engrand et al. 1999; Aléon et al. 2006). The O-isotopic compositions of the grains measured with high precision fell near the range of values displayed by those forsterite and enstatite from carbonaceous chondrites (e.g., Leshin et al. 1997). It has not yet been possible to determine the bulk O-isotopic compositions of IDPs with the necessary precision (< 1‰) to determine how they compare to the bulk O-isotopic compositions of known meteorite groups.

Oxygen isotopic measurements of mineral grains can provide a sensitive measure of what fraction of cometary material has a presolar origin. Because of the fine grain sizes (50 nm to 1.0 μm) of IDPs and cometary samples from 81P/Wild 2, addressing this question has

only recently become possible, following major advances in secondary ion mass spectrometry that now enable isotopic measurements on this scale. Long considered "missing," presolar silicates now appear to be the most abundant type of presolar mineral grain, other than perhaps nanodiamonds (most of which may not be presolar). Presolar silicates have now been identified in meteorites, micrometeorites, and IDPs by their anomalous O-isotopic compositions, primarily through enrichments in $^{17}O/^{16}O$. Presolar silicates are significantly more abundant in IDPs (450-5500 ppm; Messenger et al. 2003; Floss and Stadermann 2004) than in meteorites (<180 ppm; Nguyen and Zinner 2004; Nagashima et al. 2004; Mostefaoui and Hoppe 2004) and in most micrometeorites (50-130 ppm; Yada et al. 2006) studied thus far. One exceptional micrometeorite, having a high presolar silicate abundance (~900 ppm), is postulated to have a cometary origin (Yada et al. 2006).

The great majority (>95%) of crystalline silicates measured to date in both IDPs and meteorites however, are isotopically solar to within ~10%. For example, Messenger et al. (2003) examined 1031 grains found within nine different IDPs and only detected six silicate grains that had non-solar O-isotopic ratios. Of these six circumstellar grains, one was identified as a crystalline silicate (forsterite) and two were amorphous silicate "GEMS". Astronomical observations and nucleosynthetic models suggest that it is unlikely (but not impossible) that the more abundant grains with normal, solar oxygen isotopic compositions originated from evolved stars. Furthermore, although crystalline silicates are observed in evolved stellar outflows (Molster et al. 2002), they are quickly (~10 Ma) rendered amorphous or destroyed in the diffuse ISM (Tielens et al. 1994). Thus, observations of abundant, isotopically solar crystalline silicates in "cometary" IDPs support the idea of large-scale transport of material in the early solar nebula.

Initial O-isotopic measurements of the cometary samples returned from 81P/Wild 2 are largely consistent with the results from IDPs. Most of the samples analyzed so far have O-isotopic compositions that lie within the range of meteoritic materials, i.e., they have normal "solar" ratios (McKeegan et al. 2006). Initial results include targeted measurements of several forsterite grains and one refractory mineral assemblage. The latter particle, containing refractory minerals similar to those found in some CAIs in meteorites, was found to exhibit the same ^{16}O enrichments typical of meteoritic CAIs. So far, only one presolar grain has been observed, and it is not known whether it was a silicate or oxide grain (McKeegan et al. 2006). Given the limited number of measurements made to date, it is not yet possible to make any definitive statement about the abundance and mineralogy of presolar grains in Wild 2 samples, other than to note that presolar grains with O-isotopic anomalies clearly do not appear to be *more* abundant than seen in meteoritic materials.

FUTURE *IN SITU* MEASUREMENTS OF ISOTOPIC RATIOS IN COMETS

The International Rosetta Mission, launched by ESA, is anticipated to yield high quality *in situ* isotopic measurements of cometary materials. This spacecraft will rendezvous with comet 67P/Churyumov-Gerasimenko (C-G) in 2014, and it will study the nucleus of comet C-G and its environment in detail for a period of nearly two years.

Rosetta possesses several instruments that will perform isotopic measurements. The two sensors of ROSINA (Rosetta Orbiter Spectrometer for Ion and Neutral Analysis) (Balsiger et al. 2007) will determine the composition of the comet's atmosphere and ionosphere. ROSINA will measure the mass range from 1-300 amu at a mass resolution of m/Δm = 3000 at the 1% level, so it will be able to resolve CO from N_2 and ^{13}C from ^{12}CH), and also the oxygen isotopes in H_2O. The time-of-flight secondary ion mass spectrometer COSIMA (Kissel et al. 2007) will measure the abundances and isotopic compositions of key elements of cometary grains. The MIRO (Microwave Instrument for the Rosetta Orbiter; Gulkis et al. 2007) instrument

uses a submillimeter radiometer/spectrometer that is fixed and tuned to measure four volatile species - CO, CH_3OH, NH_3, and three isotopomers of water, $H_2^{16}O$, $H_2^{17}O$, and $H_2^{18}O$. These measurements will provide measures of surface temperature, gas production rates and relative abundances, and velocity and excitation temperature of each species, along with their spatial and temporal variability. PTOLEMY MODULUS (Wright et al. 2007), a gas analysis instrument capable of performing isotopic measurements on individual components from solid samples of the comet's surface, is carried by the Rosetta lander. MODULUS will measure H, C, N, and O isotopic ratios. Rosetta will be the first spacecraft capable of measuring all O isotopomers of molecules (e.g., H_2O, CO, CO_2) on a cometary surface and in the very near coma of the nucleus (1 km). By comparing isotopic ratios measured in the bulk of the coma and comparing it with isotopic ratios measured in jets, it can be determined whether the molecules in the nucleus are isotopically fractionated.

CONCLUSIONS

The chemical and isotopic state of oxygen in primitive Solar System materials is the result of a combination of nucleosynthetic, interstellar, protosolar, and parent body processes. As a result, the carriers of oxygen that formed comets cover a wide span of chemical and physical properties, ranging from volatile molecules, such as H_2O, CH_3OH, CO, CO_2, and H_2CO, to organic-rich materials, to refractory minerals, such as anorthite and forsterite). The volatiles show abundances that suggest that these materials have a close connection to the volatile materials in the original interstellar cloud from which the Solar System formed. The organic species in meteorites and comets appear to be considerably richer in oxygen than organics seen in the diffuse interstellar medium, suggesting that oxygen has been introduced to the organics by dense cloud, solar nebular, and/or parent body processing. Isotopic measurements demonstrate that a portion, albeit a small one, of the oxygen in meteoritic and cometary materials is derived from circumstellar grains that show clear evidence of their nucleosynthetic origins. Overall, oxygen-bearing compounds in comets, as characterized by remote-sensing data and from measurements of collected IDPs and Stardust samples, seem to have a largely solar composition, suggesting that the solar nebula as a whole was relatively well-mixed isotopically.

Overall, the samples from comet 81P/Wild 2 show a high degree of chemical and mineralogical heterogeneity. This implies that they are the repositories of material created in a wide variety of different environments, again suggesting there was a great deal of mixing in the solar nebula. Furthermore, the large degree of heterogeneity seen in Wild 2 samples indicates that the materials returned from comet 81P/Wild 2 did not undergo any major degree of parent body processing within the cometary nucleus. It should be noted, however, that Comet Wild 2 is a relatively "fresh" comet in the sense that it has likely made very few close passages to the Sun. Materials in short-period comets that have made larger numbers of perihelion passages may have experienced greater degrees of parent body processing.

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