Terrestrial Analysis of the Organic Component of Comet Dust*

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Key Words

comets, organics, astrochemistry, spectroscopy, ices, astrobiology, meteorites, interplanetary dust particles

Abstract

The nature of cometary organics is of great interest, both because these materials are thought to represent a reservoir of the original carbon-containing materials from which everything else in our solar system was made and because these materials may have played key roles in the origin of life on Earth. Because these organic materials are the products of a series of universal chemical processes expected to operate in the interstellar media and star-formation regions of all galaxies, the nature of cometary organics also provides information on the composition of organics in other planetary systems and, by extension, provides insights into the possible abundance of life elsewhere in the universe. Our current understanding of cometary organics represents a synthesis of information from telescopic and spacecraft observations of individual comets, the study of meteoritic materials, laboratory simulations, and, now, the study of samples collected directly from a comet, Comet P81/Wild 2.

1. INTRODUCTION

IDP: interplanetary dust particle

It is now understood that our Solar System formed from the collapse of a portion of a dense interstellar molecular cloud of gas, ice, and dust (1). The collapsing material formed a disk surrounding a central protostar. The material in this disk ultimately suffered one of several different fates. Much of the material was incorporated into the central protostar, which eventually became our Sun. A portion of the material was also ejected from the system by bipolar jets and gravitational interactions in the disk. Most of the remaining material was incorporated into small bodies, called planetesimals, which subsequently accreted to form the planets. However, some of these planetesimals escaped ejection from the system or incorporation into larger bodies and survived in the form of asteroids and comets (2, 3).

The importance of these small bodies far outweighs their minor contribution to the mass of our Solar System. All the material that ended up in the Sun and planets has been thoroughly reprocessed in the more than 4.5 billion years since these bodies formed. Other than clues about the bulk elemental abundances of the original materials from which they formed, these large bodies cannot provide many insights into the nature of the raw starting materials from which they were made.

The material in smaller bodies such as asteroids and comets has undergone considerably less parent-body processing and contains more pristine samples than planets. Fortunately, we can study cometary and asteroidal materials by a number of means. We receive samples of these objects on Earth in the form of meteorites and interplanetary dust particles (IDPs), and these samples generally demonstrate that comets and asteroids, indeed, comprise primitive materials (4, 5). In the case of meteorites, this is evidenced by their great ages (the clustering of meteorite ages around 4.56×10^9 years is taken to represent the formation time of our Solar System).

However, the study of meteorites has also demonstrated that they are not completely pristine samples of the original material from which everything else was made. Meteorites show evidence of varying degrees of thermal processing and aqueous alteration, most of which is thought to have occurred shortly after their parent asteroids formed (6). Also, most meteorites are from asteroids that formed in the region between Mars and Jupiter, a region warm enough that these bodies did not incorporate a full share of the more volatile components in the protosolar disk. Thus, meteorites provide insights into the nature of protosolar materials, but they have some limitations.

Comets are thought to have formed and been stored much further out in the Solar System. Comets probably contain a more representative portion of the volatile components of the original protoplanetary disk and have undergone less parent-body processing since formation (3). Thus, cometary materials may represent the best samples of pristine early solar system materials presently available for study and may provide powerful insights into the formation of the entire Solar System, not just comets.

The nature of cometary volatiles and organics is also of great astrobiological importance. The accretionary processes that made Earth are expected to have formed a molten body that destroyed any molecular complexity of the original starting materials and at least partially devolatilized the planet. Making Earth habitable may therefore have required the delivery of additional volatiles and organics to its surface after it had cooled. Although the collision of entire asteroids and comets should have delivered organics to the early Earth, this is likely to have been a relatively inefficient process. The large temperatures and pressures resulting from the hypervelocity impact of such large objects with the Earth probably destroyed much of the incoming material (7, 8). However, these same small bodies, particularly comets, also eject much of their mass into the interplanetary medium in the form of very small grains. These small grains can survive collision with the Earth's atmosphere while undergoing considerably less alteration (see Section 3.2). Thus, comets probably delivered organic materials to the early Earth both directly as large bodies and indirectly via small dust grains, with the latter probably supplying the main source of surviving organics.

Investigators have frequently discussed the idea that comets and asteroids delivered key volatiles and organics to the early cooling Earth that may have played a role in the origin and evolution of life (9–13), and it represents a focal point in the field of astrobiology. Thus, understanding the nature of cometary materials is important both because it provides information about the materials that formed the Solar System and because it may provide insights into the origin of life on Earth.

Because the composition of comets is thought to be the end result of a series of universal processes involving stellar, interstellar, and star-forming environments, it should be generally representative of the composition of these bodies in other stellar and planetary systems. Thus, insofar as comets have played a role in the formation of life on Earth, we expect them to be available to play a similar role in other planetary systems containing appropriate conditions for the origin of life (whatever those may be). Understanding comets in this context may therefore provide insights into the frequency of life elsewhere in the universe.

Our current understanding of comets and their constituent organics is the combined result of information gathered using a number of different techniques. These include the use of telescopic remote-sensing (largely spectroscopic) techniques, laboratory simulations, spacecraft flybys of individual comets, the study of meteoritic materials found on Earth, and the study of cometary samples returned to Earth from Comet 81P/Wild 2 by the Stardust spacecraft.

Here I concentrate on laboratory studies of actual samples, particularly on stratospheric IDPs thought to come from comets and samples from Comet 81P/Wild 2. I also restrict myself primarily to discussions of cometary organics and, to a lesser extent, cometary volatiles. Cometary minerals are only briefly mentioned, and then only when they bear on the discussion of associated organics. Those interested in pursuing the subject of cometary mineralogy can find a good introduction to the relevant literature elsewhere (14–17).

There are numerous advantages to sample return for the study and understanding of our Solar System. Having actual samples on hand in terrestrial laboratories allows for the use of state-of-the-art analytical techniques and equipment, providing for the ultimate current precision, sensitivity, resolution, and reliability. In contrast, spacecraft instruments making in situ measurements are, of necessity, not state of the art. Sample returns also avoid limitations associated with cost, power, mass, and reliability that are imposed on spacecraft instruments (some of the terrestrial analytical devices used to study Stardust samples were not only more massive than the Stardust spacecraft, they were more massive than Stardust's launch pad!). In addition, returned samples are a resource for current and future studies by a broad international community that can use many different analytical techniques in an iterative and fully adaptive fashion not limited by instrument designs or ideas current at the time of the spacecraft's launch. Also, the samples reside in terrestrial laboratories, so researchers can replicate and verify analyses using multiple, fully calibrated techniques and instruments. Finally, because the actual analyses are done on Earth, sample return takes advantage of a tremendous resource not fully available to nonreturn missions, namely the expertise of the world's analytical chemists, physicists, and meteoriticists.

The study of samples of this sort represents a significant analytical challenge. Both stratospheric IDPs and the Wild 2 comet samples consist of particles that are typically smaller than 25 μm in diameter and contain less than 1 ng of total material. To further complicate matters, these particles generally consist of highly heterogeneous aggregates of subgrains in the micrometer and submicrometer size range (see Sections 3.2 and 4.1). Despite the difficulty in measuring complex subnanogram samples, we have learned a surprising amount from these samples. Furthermore, if the past is any indication, there is every reason to expect that the challenge represented by these samples will be met by continued improvements in analytical techniques, leading to new revelations about the nature of our Solar System and its formation.

2. EVIDENCE FOR COMETARY ORGANICS FROM NONLABORATORY STUDIES

Although this review focuses on what we have learned about comets on the basis of laboratory studies of cometary samples, it is worth touching briefly on what we know about comets based on a number of other approaches. These are summarized in the subsections that follow.

2.1. Evidence for Cometary Volatiles and Organics from Telescopic Observations

Comets formed and have since spent most of their time in the outer Solar System, where they are difficult to reach by spacecraft or detect telescopically. As a result, much of what we know about comets comes from the small population of comets that have been perturbed into orbits that bring them close to the Sun. The telescopic imaging of comets was sufficient to suggest a model, first described by Whipple (18), of comets as "dirty snowballs" (i.e., they consist of a mixture of dust grains and volatile ices). These materials are inert when comets reside in the cold outer Solar System, but in the inner Solar System, the ices sublime and produce outgassing that forms the cometary dust and gas comae and tails associated with visible comets (19–21).

Telescopic studies of the composition of comets rely heavily on the use of spectroscopic detection of the molecules in cometary comae. The list of gas-phase species identified in cometary comae using telescopic ultraviolet (UV), infrared (IR), and submillimeter spectroscopy is dominated by simple, volatile molecules, the dominant species being H_2O followed by CO, CO_2, CH_3OH, CH_4, H_2CO, and NH_3. Their relative abundances are similar to the ices seen in dense interstellar clouds (22), consistent with the idea that comets contain relatively unprocessed nebular materials. However, molecules released from the comet are immediately exposed to solar radiation and are subject to photodissociation and fast ion-neutral reactions (19). Some species (e.g., H_2O) show spatial distributions that suggest they are primary ice components (i.e., they were released directly from the comet nucleus). Others, such as CN and H_2CO, show distributions suggesting injection in an extended volume around the nucleus, either through the delayed sublimation of ejected ice grains or through the sequential photolysis of more complex molecular species (23–25).

ISM: interstellar medium

CHON particle: particle rich in the elements C, H, O, and N

The presence of more complex organics is inferred from species showing extended coma distributions that suggest they are photofragments of more complex organic parent molecules (26). Also, the surfaces of comets are observed to have very low albedos, inconsistent with surfaces dominated by ice, but suggestive of the presence of complex organics (27–31). We can also infer the presence of complex organics from the identification of an IR emission feature centered near 2950 cm^{-1} thought to result from C-H stretching vibrations in organic dust grains being heated by the Sun following ejection from the nucleus (32–36). Finally, we see a variety of complex organics in various environments in the interstellar medium (ISM) (37–40), and one would expect some of these materials to survive incorporation into comets.

2.2. Evidence for Cometary Organics from Laboratory Simulations

As mentioned above, the ices in comets appear to have similar compositions to the ices seen in interstellar clouds. Extensive laboratory simulations of mixed-molecular ices having interstellar cloud compositions have demonstrated that UV and charged-particle irradiation of such materials results in the production of a host of more complex organic materials (41–47), many of which are of astrobiological interest (amino acids, amphiphiles, quinones, etc.). Thus, the radiation processing of cometary ices and their interstellar precursors is expected to have resulted in cometary volatiles containing a variety of more complex organics.

2.3. Evidence for Cometary Organics from Spacecraft Flybys

A small number of comets have been studied using spacecraft flybys. These include the Giotto and two Vega spacecraft flybys of Comet Halley (48, 49), the Deep Space 1 flyby of Comet Borrelly (50), the Stardust spacecraft flyby of Comet Wild 2 (28), and the Deep Impact spacecraft flyby of Comet Tempel 1 (31). Researchers have studied the organics in these comets using both IR spectroscopy and mass spectrometry. The IR spectra obtained by spacecraft are largely consistent with data obtained from more remote telescopes (32, 33).

Mass spectra taken by the Giotto and Vega spacecraft showed that the Comet Halley dust grains consisted of mineral grains, CHON particles (particles dominated

CC: carbonaceous chondrite

IOM: insoluble organic macromolecular material

PAH: polycyclic aromatic hydrocarbon

by C, H, O, and N), and mixtures of the two (51–55). The CHON particles appeared to be rich in O and N relative to C compared to normal meteoritic materials. The Stardust spacecraft was also equipped with a mass spectrometer (56), which obtained limited spectra that confirmed cometary particles contain organics and suggested they were rich in nitrogen (57). Further measurements of this type are expected from a high-resolution time-of-flight secondary ion mass spectrometer on the Rosetta spacecraft, currently on its way to a 2014 rendezvous with Comet 67 P/Churyumov-Gerasimenko (58).

3. EVIDENCE FOR COMETARY ORGANICS FROM ORPHANED SAMPLES: METEORITES AND STRATOSPHERIC DUST PARTICLES

3.1. Organics in Meteorites

Most meteorites probably come from asteroids, not comets. However, meteorites still represent materials that have undergone considerably less processing than planetary materials. Thus, organics found in the least processed meteorites might be expected to have similarities with cometary organics. The most appropriate meteorites for comparison are the carbonaceous chondrites (CCs), which are thought to be among the least processed meteorites (59).

CCs contain a complex population of organics (60, 61) that includes both soluble and insoluble phases. The vast majority of the carbon is present in an insoluble organic macromolecular material (IOM) (**Figure 1**). This insoluble material contains more than 90% of the carbon in CCs and can survive exposure to water and aqueous acids. IOM is highly aromatic and consists of disorganized aromatic, heteroaromatic, and hydroaromatic ring domains cross-linked by a wide variety of short methylene chains, biphenyl groups, ethers, sulfides, etc. (60, 62, 63). The fraction of C in aromatic domains within the CC Murchison IOM is between 0.61 and 0.66, and only ~30% of this C is bonded to H, indicating the aromatics are highly substituted (63). The abundance of N, O, and S in IOM varies between meteorites, but the IOM in Murchison ($C_{100}H_{71}N_{1.2}O_{12}S_2$) is representative. Oxygen is present in a wide range of functionalities, and nuclear magnetic resonance studies suggest that O-containing functional groups in the Murchison IOM are highly linked (63). The formation history of meteoritic IOM is currently poorly understood. Possibilities include formation in the ISM, the protosolar nebula, the meteoritic parent bodies, or some combination of these.

CCs also contain soluble organics. These have been more widely examined than the IOM because they are amenable to study by traditional wet-chemistry analytical techniques (60). Extractable organics that have been identified include amino acids, amines, and amides (61, 64, 65); aliphatic hydrocarbons (66, 67); polycyclic aromatic hydrocarbons (PAHs) (62, 68, 69); carboxylic, dicarboxylic, and hydrocarboxylic acids (64, 70, 71); amphiphiles (72, 73); quinones (70); nitrogen heterocycles (67); and sugars (74). Many of these species play important biochemical roles in life on Earth, particularly the amino acids, amphiphiles, and quinones (75, 76). This is one

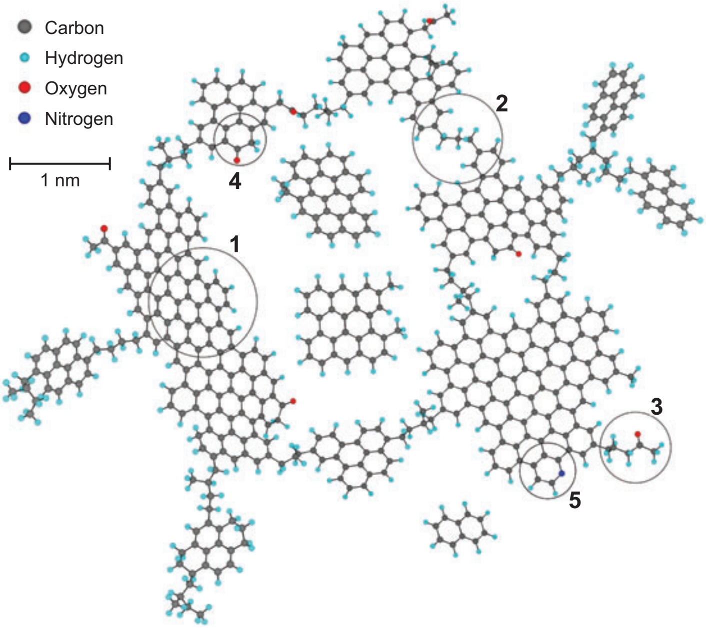


Figure 1

The carrier of the bulk of the solid carbon in the diffuse interstellar medium is thought to consist of a network of aromatic structures (such as that in circle 1) interlinked by short aliphatic bridges (circle 2) and containing aliphatic carbonyl groups (circle 3), aromatic carbonyl groups (circle 4), and aromatic nitrogen (circle 5), similar to the structures shown here. This structure is similar to that of the insoluble organic macromolecular material that composes the majority of the organics in primitive meteorites, although the meteoritic material appears to be considerably richer in oxygen. Figure adapted from Reference 40.

of the prime motivations for considering the possibility that accreted extraterrestrial materials may have played key roles in the origin of life.

One indication that meteoritic organics represent relatively unprocessed materials is the presence of nonterrestrial enrichments in D and ^{15}N in them (64, 71, 77). As discussed in more detail in Section 5, these enrichments suggest the presence of molecules produced in the ISM that have never fully equilibrated with normal solar system materials. Given that cometary materials have experienced even less parent-body processing than asteroidal materials (i.e., meteorites), one would anticipate that such isotopic anomalies might also be common in cometary samples.

3.2. Organics in Stratospheric Interplanetary Dust Particles

Dust particles ejected from comets and asteroids enter solar orbits that evolve under the influence of nongravitational forces (78–81), and some of these particles ultimately collide with Earth. Many particles vaporize as they enter Earth's atmosphere (shooting stars), but particles under a few hundreds of micrometers in diameter can survive deceleration high in Earth's atmosphere, where gas densities are low, without melting (82). These particles can be collected in the stratosphere using high-altitude aircraft (83–86). Typical collected stratospheric IDPs have diameters of <25 μm and masses on the order of 1 ng. This precludes the use of many analytical techniques. Nonetheless, over the past 25 years or so, investigators have successfully studied these particles using a variety of microanalytical techniques.

Studies have demonstrated that these particles are indeed extraterrestrial and can be separated into several different classes (85). Particles in one of these classes, referred to as anhydrous porous IDPs, are likely cometary dust grains (87–89). These IDPs consist of unequilibrated mixtures of anhydrous minerals (predominantly olivines, pyroxenes, and iron-rich sulfides) residing in porous aggregate structures (88–90) and are generally rich in C. Meteorites typically contain a few percent C by weight, but the average weight percentage of C in a suite of 19 IDPs was $12.5 \pm 5.7\%$, and values as high as 24% were seen (88).

Organics in these particles have been studied using several analytical techniques. Two-step laser-desorption laser-ionization mass spectrometry (L^2MS) studies have shown that these particles contain variable and rich spectra of alkylated and unalkylated PAHs (91, 92). In some cases, the distribution of PAHs looks similar to CCs, but some IDPs show richer PAH populations that extend to higher masses (93, 94). Raman spectra of these PAHs confirm the presence of poorly ordered aromatic materials (95–97). Both aromatics and aliphatic $-CH_3$ and $-CH_2-$ groups have been detected in some particles based on the presence of their characteristic C-H stretching bands in the 3100–2800 cm^{-1} IR region (98, 99). These spectra generally show $-CH_2-/-CH_3$ band area ratios of >2, a considerably larger ratio than seen in IOM in primitive CCs ($\sim$1.1) and in the diffuse ISM (1.1–1.25) (38, 40). The higher $-CH_2-/-CH_3$ implies IDPs contain longer or less branched aliphatic chains.

Finally, carbon X-ray absorption near-edge spectroscopy (C-XANES) measurements of IDPs demonstrate that organics are present that have a variety of C-bonding states (98, 100, 101). They confirm the presence of abundant aromatic materials and show that IDP organics typically have higher O/C and N/C ratios than meteorites. In many cases, the organic matter appears to be the glue that holds subgrains in the IDP together. Overall, the IDP results indicate that most of the organics are inconsistent with formation by aqueous processing, but they already existed at the time that primitive, anhydrous dust was being assembled (98, 101). This implies the organics likely formed in either the solar nebula or in an interstellar environment.

In summary, the organics seen in stratospheric IDPs, many of which are thought to come from comets, appear to have many similarities to the materials seen in CCs. In particular, both appear to be dominated by aromatic materials. However, there are some distinct differences: The IDPs sometimes show more complex populations of PAHs, and the overall organic population in the anhydrous stratospheric IDPs has considerably higher O/C and N/C ratios than found in meteorites. The nature of the organics suggests the bulk of the material has interstellar or protosolar nebula origins rather than parent-body origins.

4. ORGANICS FROM COMET 81P/WILD 2: THE STARDUST COMET SAMPLE RETURN MISSION

Our understanding of cometary organics made a quantum leap forward with the January 15, 2006, return of samples from Comet 81P/Wild 2 by the Stardust spacecraft (102). One of the scientific goals of Stardust was to establish whether comets contained complex organic materials and to establish the abundance, chemical, and isotopic nature of any organics present (102–104). Such information provides insights into the formation and evolution of comets and places constraints on the environments and processes by which they were made. Characterization of these organics also allows for comparison of cometary materials with other extraterrestrial materials (meteorites, IDPs, and ISM organics).

4.1. The Collection of Material from Comet 81P/Wild 2

Stardust was the first mission in history to return solid samples from an astronomical body beyond the Earth-Moon system. The mission retrieved samples from Comet 81P/Wild 2, a comet currently in an orbit that approaches the orbits of both Jupiter and Mars. This ~4.5-km-diameter body was formed and spent most of the past 4.5 or so billion years in the Kuiper belt outside the orbit of Neptune. Only recently did it wander into the inner Solar System, where it had a close encounter with Jupiter on September 10, 1974, that placed it in its current orbit. The comet has an expected dynamical lifetime of $\sim 10^4$ years before it hits a larger object or is ejected from the Solar System (105). In its current orbit Comet 81P/Wild 2 approaches the Sun close enough that solar heating causes classic cometary activity near perihelion.

During the Stardust flyby on January 2, 2004, the comet was active, and images showed the presence of at least 20 dust jets coming from the nucleus (28, 106) (**Figure 2*a***). Stardust approached to within 234 km of Wild 2's surface, and the encounter occurred at a solar distance of 1.86 AU. Particles ejected from the comet were exposed to space for only a few hours before collection, but solar heating probably vaporized most ices during transit from Wild 2 to Stardust. Particles were collected for return when they impacted at 6.12 km s^{-1} into silica aerogel, a porous glass comprised of nanometer-sized silica filaments with bulk density that varied from <0.01 g cm^{-3} at the impact surface to 0.05 g cm^{-3} at 3-cm depth. Stardust aerogel tiles collected over a thousand 5–300-μm (and many more smaller) comet particles. Onboard impact sensors indicate that most of the collected particles were associated with just a few specific dust jets (107).

Particle impacts into aerogel produced tracks whose shapes depended on the nature of the impacting particle (**Figure 2*b***). Nonfragmenting particles produced carrot-shaped tracks with length/diameter ratios of >25. However, many tracks show bulbous upper regions and sometimes multiple roots. These tracks were produced by weakly bound aggregate particles that broke apart on impact with the aerogel (102, 108). The upper parts of tracks are lined with melted aerogel that contains dissolved projectile material; the mid-regions contain less melt and more preserved projectile material and compressed aerogel; and the track ends contain largely

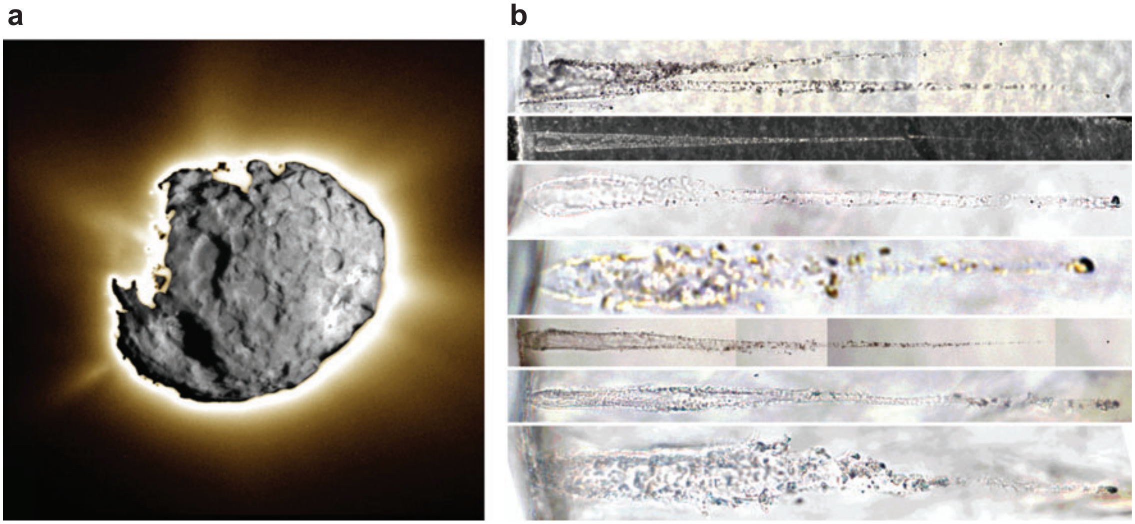


Figure 2

(*a*) A composite image of Comet 81P/Wild 2 consisting of a 10-ms exposure image (to capture the surface of the cometary nucleus) overlain on a 100-ms exposure image (to capture the large number of dust jets emerging from the nucleus). The nucleus is a very dark (albedo of ∼0.03) ∼5 km-diameter oblate spheroid covered with unique topographical structures. (*b*) Optical images of seven tracks produced by Wild 2 particles that impacted Stardust aerogel collector material. Solid particles left thin carrot tracks (see fifth track from top), but most impacting particles consisted of weakly bound aggregates of smaller grains that produced more bulbous tracks, often with multiple roots. Figure adapted from Reference 102.

unmelted materials (terminal particles). In most cases, the deepest penetrating particles are solid mineral grains or aggregates comprised of micrometer-size or larger grains. In addition to aerogel, approximately 15% of the Stardust collector surface was the aluminum frame and aluminum foils used to hold the aerogel. Impacts on the frame produced bowl-shaped craters lined with melted, and in some cases unmelted, projectile residues (108).

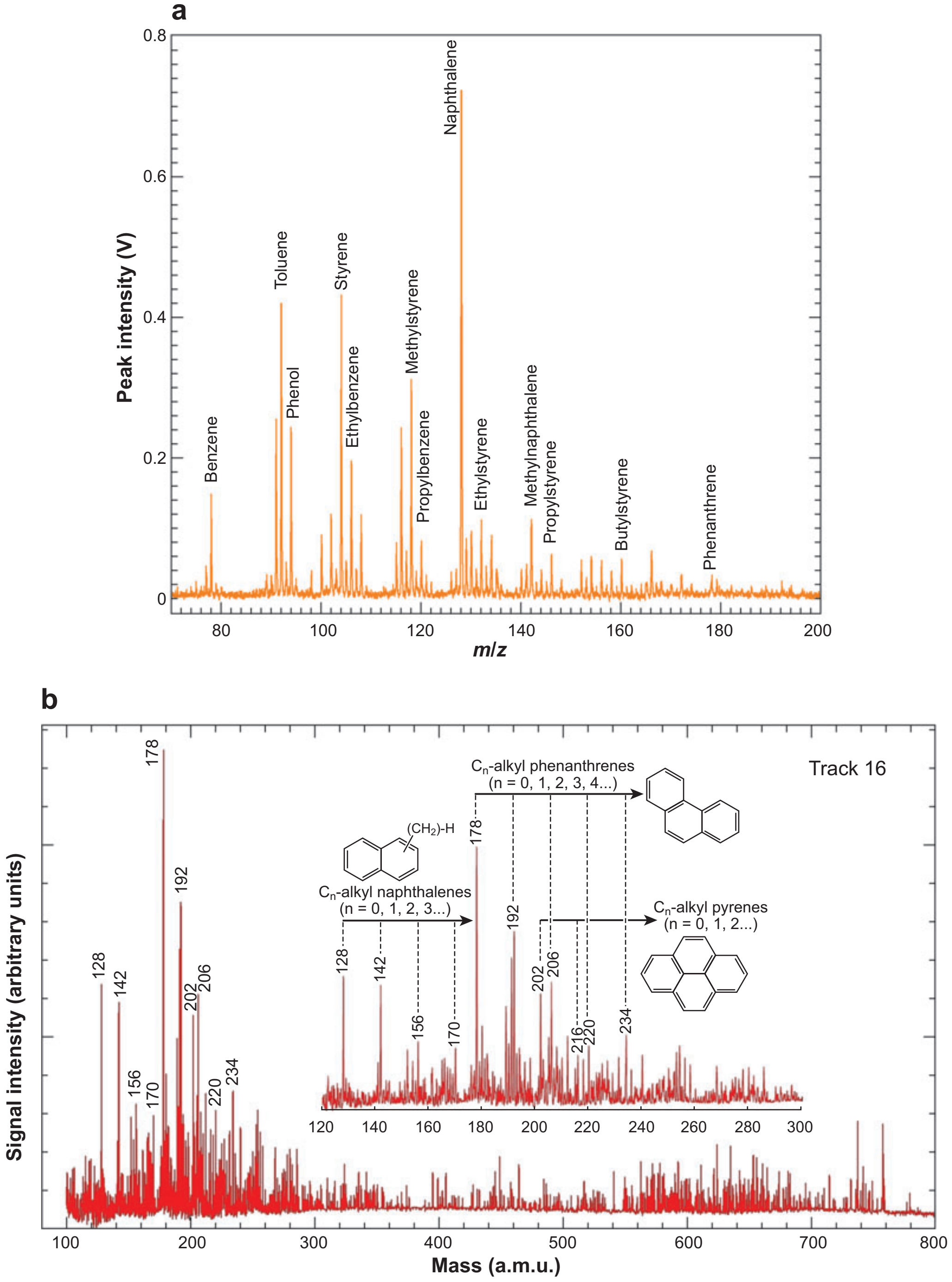
4.2. Measurement of Wild 2 Organics in the Returned Samples

Approximately 200 investigators around the world participated in the preliminary examination of the samples returned by Stardust, and their findings appeared in a special issue of *Science* (16, 17, 102, 108–111). The results presented in these studies were obtained using an enormous variety of analytical techniques, some of which did not exist when Stardust was launched.

As mentioned above, the analysis of the Wild 2 samples was a challenging prospect because the samples were complex, nanogram-sized aggregates that broke up into smaller particles and were distributed along the entire length of aerogel tracks. For organics analyses, investigators had to pay additional attention to the possibility of contaminants associated with the aerogel collector medium, flight of the spacecraft, and return and recovery of the sample return capsule. Fortunately, contaminants were found generally to be of low-enough abundance or were sufficiently well characterized that they can be distinguished from the cometary organics (111). Most problematic was the aerogel collector medium itself. Stardust aerogel consists primarily of amorphous SiO_2 but contains from one-quarter to a few weight percent C. Nuclear magnetic resonance studies indicate that this C is largely in the form of simple $Si{-}CH_3$ groups easily distinguishable from the cometary organics described below. It should be noted that not all the organics in the samples will be fully representative of the original cometary material because some may have been modified during aerogel impact. There is also evidence that at least some organic compounds were generated or altered by the impact heating of the aerogel itself (111–113) (see below). Despite these difficulties, we have learned a great deal about cometary organics and the origin of the Solar System from these samples.

Analytical techniques used during the preliminary examination of organics in the Wild 2 samples include L^2MS, liquid chromatography with UV fluorescence detection and time-of-flight mass spectrometry (LC-FD/TOF-MS), scanning transmission X-ray microscopy (STXM), XANES, IR and Raman spectroscopy, ion chromatography with conductivity detection (IC), secondary ion mass spectrometry (SIMS), and time-of-flight SIMS. A summary of the combined findings of these analyses is provided below. More complete discussions of the organics preliminary examination results can be found in Sandford et al. (111) and its associated supporting online material, and in a forthcoming special issue of *Meteoritics and Planetary Science*.

Multiple experimental techniques demonstrate that the samples contain PAHs. L^2MS mass spectra obtained from individual particles and on aerogel surfaces along impact tracks show PAHs and their alkylated derivatives, with two distinct types of PAH distributions distinguishable from low-aerogel backgrounds (111, 114, 115) (**Figure 3**). In some cases, PAH populations dominated by benzene and naphthalene (one- to two-ring PAHs), including alkylation out to several CH_3 additions, are observed in the absence of larger PAHs (**Figure 3*a***). Such distributions resemble pyrolysis products of meteoritic IOM and are observed in high-laser-power L^2MS measurements of Stardust aerogel tiles, suggesting many of the lower-mass PAHs may originate from impact processing of C original to the aerogel (112, 113). The second type of PAH population shows complex distributions that strongly resemble those seen in some meteorites and IDPs (**Figure 3*b***). The similarity to IDPs extends to masses beyond 300 a.m.u., although several track spectra show mass envelopes extending up to 800 a.m.u. with both odd and even mass peaks. Such high-mass envelopes in IDPs have been attributed to the polymerization of smaller aromatics within the samples by radiation processing during their extended exposure to interplanetary space or heating during atmospheric entry (91, 115). Similar polymerization of the original PAH population in the Stardust samples by impact heating may explain the higher-mass envelopes observed in them (111). The more complex comet mass spectra also include additional mass peaks not observed in meteorite mass spectra, but seen in some IDP spectra, that suggest the presence of O- and N-substituted aromatic species having heterofunctionality external to the aromatic structure.


a
Peak intensity (V)
0
0.2
0.4
0.6
0.8
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100
120
140
160
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Benzene
Toluene
Phenol
Styrene
Ethylbenzene
Methylstyrene
Propylbenzene
Naphthalene
Ethylstyrene
Methylnaphthalene
Propylstyrene
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Phenanthrene
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Signal intensity (arbitrary units)
Mass (a.m.u.)
100
200
300
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Track 16
128
142
156
170
178
192
202
206
220
234
(CH2)-H
Cn-alkyl naphthalenes
(n = 0, 1, 2, 3...)
Cn-alkyl phenanthrenes
(n = 0, 1, 2, 3, 4...)
Cn-alkyl pyrenes
(n = 0, 1, 2...)
128
142
156
170
178
192
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The presence of PAHs has also been confirmed by time-of-flight SIMS analyses of terminal particles extracted from aerogel tracks, a dissected aerogel keystone with a particle track split down the middle, and residues found in a crater in aluminum foil. The mass distribution shows a steep decrease in PAH abundances with an increasing number of C atoms (111, 116, 117). Raman spectra acquired from 12 Stardust particles also confirm the presence of aromatic materials (111, 118). All the Raman spectra are dominated by two broad bands centered at $\sim$1360 Δcm^{-1} and $\sim$1580 Δcm^{-1}. These D and G bands, respectively, are characteristic of graphite-like sp^2-bonded carbon in condensed carbon rings. The Raman spectra are similar to those of many IDPs and primitive meteorites, and the G band position and width parameters span the entire range observed in IDPs and meteorites. It is not clear whether this variation reflects heterogeneity in the cometary samples or variable processing during aerogel impact. However, the presence of G bands with low frequencies and large widths indicates that at least some organics were captured with relatively little alteration. Many Raman spectra of Stardust particles are characterized by very high backgrounds that increase with increasing Δcm^{-1} position, indicating that the samples may be rich in noncarbon heteroatoms such as N. In a few cases, aromatic materials were also identified by the detection of an aromatic CH stretching mode band using IR spectroscopy (111, 118, 119).

It was possible to extract many individual cometary particles from Stardust aerogel and microtome them into multiple slices thin enough to make them amenable to scanning transmission X-ray microscopy and C,N,O-XANES analyses. C-XANES spectra of many of these thin sections confirmed the presence of aromatic bonds. Full C,N,O-XANES spectra showed $1s$-π^* transitions consistent with variable abundances of aromatic, keto/aldehydic, and carboxyl moieties, as well as amides and nitriles (**Figure 4*a***) (111, 120). Although confirming aromatics are present, the XANES data suggest that considerably less olefinic and aromatic material is present in Comet Wild 2 samples than seen in CCs and IDPs. Some particles contain abundant C, none of which is aromatic (particle 1 in **Figure 4*a***).

XANES analyses also provided quantitative estimates of atomic O/C and N/C ratios present in the various functional groups identified (**Figure 4*b***). Overall, the

Figure 3

(*a*) Polycyclic aromatic hydrocarbons (PAHs) found along the walls of tracks are dominated by simple distributions of one- and two-ring PAHs and their alkylated variants. These PAHs may result (all or in part) from the impact alteration of C in the original aerogel collector material. (*b*) The PAH populations found in extracted particles can show a much richer distribution of higher-mass species. Observed species include naphthalene ($C_{10}H_8$, two rings, 128 a.m.u.), phenanthrene ($C_{14}H_{10}$, three rings, 178 a.m.u.), and pyrene ($C_{16}H_{10}$, four rings, 202 a.m.u.), along with their alkylated homologs extending up to at least C_4-alkyl. Peaks at 101, 112, 155, and 167 a.m.u. (not shown), inconsistent with simple PAHs, were observed when an attenuated laser photoionization pulse was used to minimize photofragmentation. These peaks could result from O- and N-substituted aromatic species having heterofunctionality external to the aromatic structure (i.e., not N or O heterocyclics). Similar mass peaks have been observed in several interplanetary dust particles (9). Figure adapted from supporting online material associated with Reference 111.

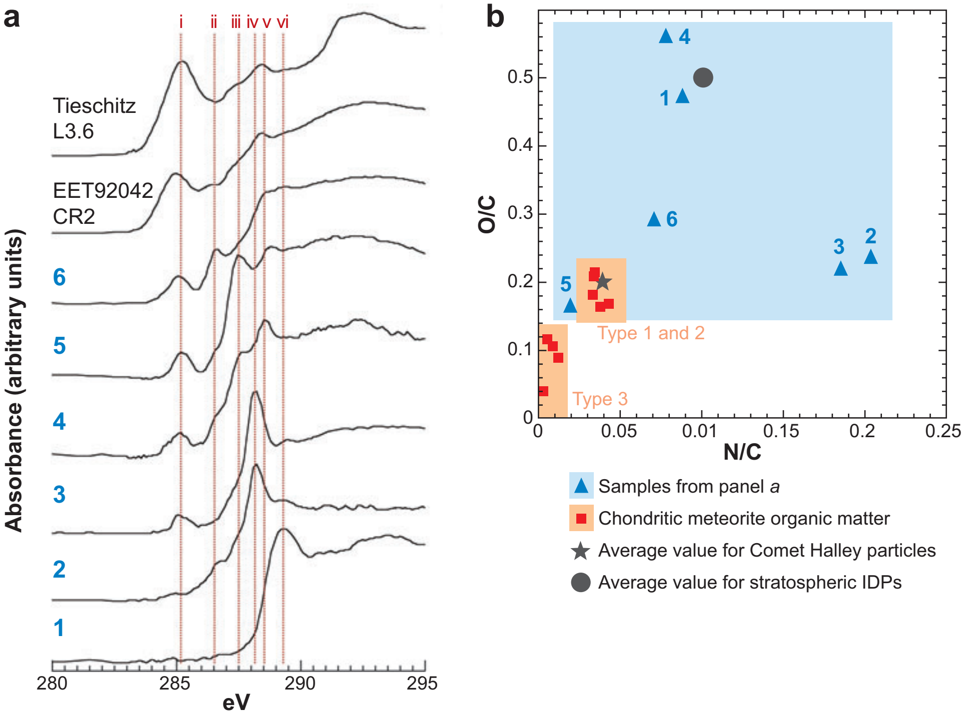

Figure 4

(*a*) C X-ray absorption near-edge spectroscopy spectra of six samples from Comet Wild 2 samples (*1 to 6*) compared with organic matter from two primitive meteorites. Positions associated with specific organic functional groups are marked with dashed vertical lines (i, C=C; ii, C=C–O; iii, C=O; iv, N–C=O; v, O–C=O; and vi, C–O). Sample chemistry clearly varies enormously between samples. (*b*) Atomic O/C and N/C for the six samples in panel *a* (*blue triangles*) compared with chondritic meteorite organic matter (*red squares*, in which the higher values correspond to petrologic type 1 and 2, and the lower values are type 3) and the average values for Comet Halley particles (*star*) and stratospheric interplanetary dust particles (IDPs) (*circle*). Figure adapted from Reference 111.

Wild 2 organics were found to be considerably richer in the heteroatoms O and N relative to both meteoritic organic matter and the average composition of Comet Halley particles measured by Giotto, but qualitatively similar to the average O/C and N/C reported for stratospheric IDPs (111, 120). Both the O and N exist in a wide variety of bonding states. Particles particularly rich in N exhibit abundant amide C in their XANES spectra.

The presence of N-containing compounds is further suggested by studies of collector aerogel using LC-FD/TOF-MS (111, 121). Stardust may have returned a diffuse sample of gas-phase molecules that struck the aerogel directly from the cometary coma or that diffused away from grains after impact. To test this possibility, investigators carried samples of flight aerogel through a hot-water extraction and acid hydrolysis procedure to determine if excess primary amine compounds were present in the aerogels. Only methylamine (MA), ethylamine (EA), and glycine were detected above background levels, and the absence of MA and EA in a flown aerogel witness coupon suggests that these amines are cometary in origin. The concentrations of MA and EA in aerogel adjacent to a track were similar to those present in aerogel not located near a track, suggesting that these amines, if cometary, originate from submicrometer particles or gas that directly impacted the collector. The presence of excess glycine may indicate a cometary origin for this amino acid as well. No MA, EA, or glycine was detected in non-acid-hydrolyzed aerogel extracts, suggesting that they are present in an acid-soluble bound form, rather than as a free primary amine. Compound specific isotope measurements will be necessary to constrain the origin of these amines.

IR spectra taken from tracks and individual extracted particles show the presence of both aromatic and nonaromatic chemical functional groups (16, 111, 118, 119). IR spectra of particles and tracks often contain absorption features at 3322 cm^{-1} (–OH), 3065 cm^{-1} (aromatic CH), 2968 cm^{-1} ($-CH_3$), 2923 cm^{-1} ($-CH_2-$), 2855 cm^{-1} ($-CH_3$ and $-CH_2-$), and 1706 cm^{-1} (C=O). One particle also showed a weak 2232 cm^{-1} band consistent with $-C{\equiv}N$ stretching vibrations. Combined, the IR data indicate the presence of aromatic, aliphatic, carboxylic, and N-containing functional groups, consistent with the results of other analytical techniques. The observed $-CH_2-$ (2923 cm^{-1})/$-CH_3$ (2968 cm^{-1}) band depth ratios in the returned samples are typically ~2.5, corresponding to a functional group ratio of $-CH_2-/-CH_3 \sim 3.7$ in these cometary samples, assuming typical intrinsic band strengths for these features. This value is similar to that seen in the IR spectra of anhydrous IDPs, but considerably larger than seen in IOM in primitive CCs (~1.1) and the diffuse ISM (1.1–1.25), suggesting that the aliphatic moieties in particles from Comet 81P/Wild 2 are longer or less branched than those in meteorites and the diffuse ISM. The ratio of aromatic to aliphatic C–H is quite variable in the IR spectra, consistent with the variations implied by XANES data.

In several cases it was possible to make IR spectral maps of entire impact tracks and their surrounding aerogel. The organic components that produce the –OH, $-CH_3$, $-CH_2-$, and C=O IR absorption bands sometimes extend well beyond the visible track edge (**Figure 5**) (111, 119). This implies that the particles contained organics that volatilized and diffused into the surrounding aerogel during impact. Because similar length tracks are also seen in the same aerogels that show no IR-detectable organics beyond those seen in the original aerogel, this material is unlikely to result from impact-altered aerogel carbon.

Researchers using SIMS ion imaging have made elemental maps of Wild 2 particle sections (111). These maps demonstrated that N and S are associated with organic molecules and show that Wild 2 samples contain highly heterogeneous N distributions, with N/C ratios ranging from 0.005 to almost 1. Some particles exhibit the entire range of values, whereas others fall more uniformly at the high N/C end of the range. However, there are regions with high C content that are not rich in N. Sulfur is typically associated with C and N, but is also distributed in small hot spots presumably owing to sulfides, which are common in the samples (17).

SIMS was also used to make H, C, and N isotopic measurements of Wild 2 particles (110, 122). D/H enrichments up to approximately three times the terrestrial value are observed within approximately half the particles. D enrichments are seen

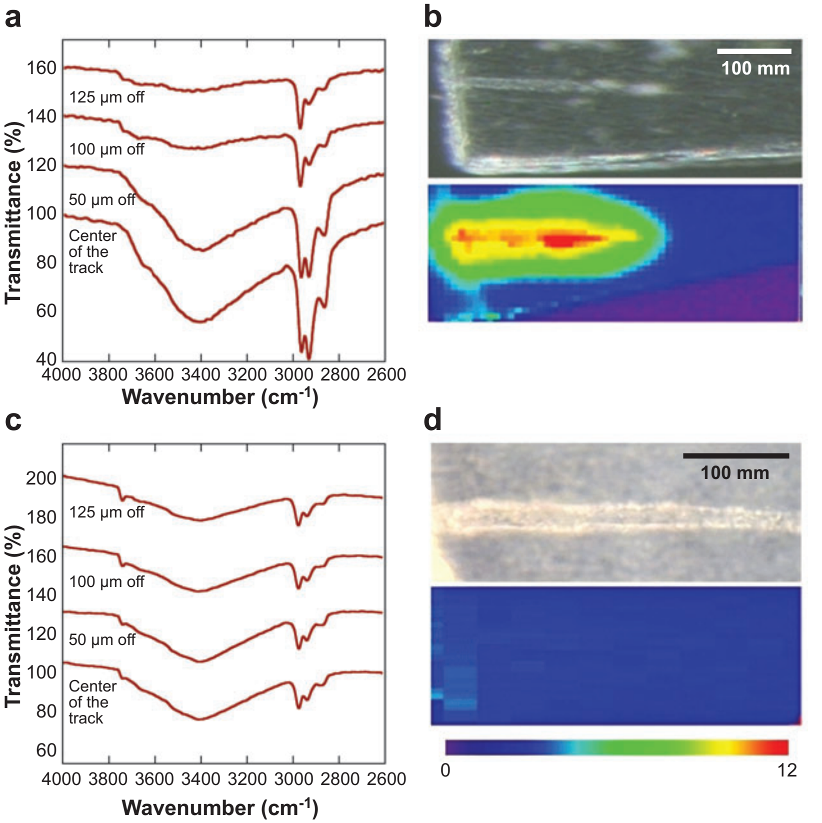

Figure 5

Infrared transmittance spectra and maps obtained from two particle tracks in Stardust aerogel. (*a*) Spectra taken along a line perpendicular to cometary impact track 59. In addition to aerogel features, the spectra across track 59 display peaks at 3322 (broad), 2968, 2923, 2855, and 1706 cm^{-1} (not shown), both inside the track and extending outward into the aerogel. (*b*) An optical image of track 59 (*top panel*) and a corresponding map showing the intensity distribution of the 2923 cm^{-1} peak due to excess cometary $-CH_2-$ (*bottom panel*). (*c*) Spectra taken along a line perpendicular to cometary impact track 61. Unlike track 59, these spectra show no evidence for extended excess $-CH_2-$, but only show the features due to aerogel. (*d*) An optical image of track 61 (*top panel*) and a corresponding 2923 cm^{-1} peak map showing that no excess $-CH_2-$ is present (*bottom panel*). The false-color image scale shown at the bottom is used in both maps (*b*, *d*). In both cases, the entrance of the cometary particle is from the left side. Figure adapted from Reference 111.

in meteorites and IDPs and are thought to result from materials with an interstellar/protostellar chemical heritage (123–126). The D enrichment in Wild 2 samples is heterogeneously distributed and associated with C, indicating the carrier is probably organic. The elevated D/H ratios are comparable with those of many IDP and meteorite samples, although none of the comet samples examined to date has shown ratios as extreme as the most anomalous IDPs and meteorites. Investigators also observed isotopic anomalies in N in the form of ^{15}N excesses (110). As with D, these anomalies are heterogeneously distributed and appear in the form of hot spots that differ from the surrounding material. When observed, the D and ^{15}N enhancements provide clear evidence of a cometary origin for the organics and suggest that cometary organics contain materials with an interstellar/protostellar chemical heritage.

4.3. An Overview of the Nature of Organics from Comet 81P/Wild 2

Overall, the organics in the Wild 2 cometary samples show many similarities with those seen in IDPs, and to a lesser extent with those in primitive CCs. However, there are some distinct differences; some of the cometary material appears to represent a new class of organics not previously seen in other extraterrestrial samples. These differences make the returned comet samples unique among currently available extraterrestrial samples.

Raman, XANES, and SIMS data all demonstrate that the distribution of organics (overall abundance, functionality, and relative elemental abundances of C, N, and O) is remarkably heterogeneous both within particles and between particles. The observed variations indicate that cometary organics represent a highly unequilibrated reservoir of materials. Similar to meteoritic organic matter, Wild 2 organics contain both aromatic and nonaromatic fractions. However, the Stardust samples exhibit a greater range of compositions (higher O and N concentrations) and include an abundant organic component that is poor in aromatics and a more labile fraction (possibly the same material). The nonaromatic fraction appears to be far more abundant relative to aromatics than in meteorites. The labile materials may be absent from stratospheric IDPs because they are lost and/or modified during atmospheric entry heating or by radiation during the IDPs' transit from their parent body to Earth. Given the O- and N-rich nature of the Stardust materials, these labile organics could represent a class of materials that have been suggested as parent molecules to explain the extended coma sources of some molecular fragments such as CN (23, 24). In general terms, the organics in Stardust samples appear to be even more primitive than those in meteorites and IDPs, at least in terms of being highly heterogeneous and unequilibrated.

The presence of high O and N contents and the high ratios of $-CH_2-/-CH_3$ seen in the IR data indicate that the Stardust organics are not identical to the organics seen in the diffuse ISM, which look more like the insoluble macromolecular material seen in primitive meteorites but with even lower O/C ratios (40). This implies that cometary organics are not the direct result of stellar ejecta or diffuse ISM processes, but rather the ultimate result of dense cloud and/or protosolar nebular processes. The overall composition is qualitatively consistent with what is expected from radiation processing of astrophysical ices in dense clouds and the polymerization of simple species such as HCO, H_2CO, and HCN (42, 127).

5. H, C, N, AND O ISOTOPES AND THE ORIGIN OF COMETARY ORGANICS

To understand the nature of cometary organics, we need to establish their isotopic systematics. This is important for both practical and scientific reasons. Practically speaking, the detection of nonterrestrial isotopic ratios in returned samples provides clear proof that the samples are extraterrestrial and not contamination. The D and ^{15}N enrichments seen in stratospheric IDPs and samples from Comet Wild 2 provide clear proof that they have an extraterrestrial origin. Scientifically, the identification of isotopic anomalies, and their carriers, in cometary organics provides important insights into the processes and environments responsible for their creation.

A number of interstellar chemical processes and environments can fractionate H, N, C, and O isotopes, and some of these environments are expected to leave characteristic isotopic fingerprints in their products. There are at least four different interstellar processes that can lead to D-enriched organics (124), largely at the expense of D loss from molecular H_2. These are gas-phase ion-molecule reactions (128, 129), gas-grain reactions (129–131), unimolecular photodissociation of species such as PAHs (37), and UV photolysis of D-enriched ices (132). The first three of these produce isotopic fractionations resulting from the zero-point energy differences of H and D bonds, whereas the fourth takes simple, previously enriched molecules and passes the enrichments on to more complex species. Each process involves different environments or compositional components of the ISM, and each leaves a distinct D signature in the resultant organic population (124). For example, in the case of PAHs, each process places excess D in different populations of PAHs and/or on different molecular sites on the enriched PAHs. Thus, the molecular identity of carriers of excess D, and the molecular positions of the excess D, can provide important clues about the carrier's natal environment.

Some of these interstellar processes can also drive isotopic fractionation involving C, N, and O. However, isotopic zero-point energy differences are significantly smaller for these elements, and their fractionations are expected to be smaller (129). Gas-phase ion-molecule reactions can enrich ^{15}N relative to ^{14}N in many molecules in cold interstellar clouds at the expense of N_2 and NH_3 (133, 134). Expectations for C and O are less clear, however. In the case of C, ion-molecule reactions and proton transfer reactions (135, 136) compete with isotope-selective photodissociation reactions (129) that produce the opposite $^{13}C/^{12}C$ fractionations. As a result, overall C isotope fractionation in the gas phase depends on the relative importance of different processes, an issue that is not fully understood. Oxygen in the gas phase resides primarily in CO, O, and O_2, and theoretical calculations suggest that little $^{16}O/^{18}O$ fractionation should occur in these species or their products via ion-molecule reactions (135). However, CO photolytic self-shielding could produce significant mass-independent fractionation of ^{16}O relative to both ^{17}O and ^{18}O in some environments (137, 138).

In summary, one would expect many organic molecules having interstellar origins to show enrichments in D and ^{15}N, and possibly ^{16}O. In the case of C, the existence of multiple reaction schemes that cause opposite fractionations suggests that C isotopes should not correlate with D fractionations in any simple way. Isotopic analyses of stratospheric IDPs and Wild 2 samples appear to be qualitatively consistent with these expectations. Significant enrichments are seen in both D and ^{15}N in both types of samples (92, 100, 110, 123, 139). In contrast, C isotopes show only minor variations (139), and O-isotopes are generally found to have solar abundances [although oxide minerals in a few particles have been seen to be enriched in ^{16}O (139, 140)].

The heterogeneous distribution of the observed D and ^{15}N anomalies in these samples suggests that materials having an interstellar heritage were mixed with solar nebular materials during the formation of the Solar System but that they were not exposed to significant processing after the component subgrains were assembled, either within the protosolar nebula or in the particle's parent body.

6. ANALYTICAL CHALLENGES FOR FUTURE STUDIES OF EXTRATERRESTRIAL SAMPLES

The successful return of samples from Comet 81P/Wild 2 is a fresh example of the power of sample return studies and reiterates the value of such samples as already demonstrated by NASA's lunar, cosmic dust, solar wind, and meteorite collections. The astrophysical community's appreciation of the value of such missions is evidenced by the large number of scientists who participated in the preliminary examination of these samples and the significant number of future sample return missions currently being considered by NASA. Given that currently available samples will continue to be studied for decades to come, and that new samples will almost certainly be coming from additional solar system objects, it is worth considering what analytical challenges are likely to be important for the study of extraterrestrial samples in the future.

6.1. Ever Smaller Samples

Certainly one challenge is the continued pursuit of the ability to study ever smaller samples. Typical Stardust particles had original diameters of <25 μm and total masses of ~ 1 ng, and had their component subgrains smeared out along millimeter-long tracks. Of this material, only a fraction was organic, and some of this material was further dispersed by being vaporized and redeposited in the surrounding aerogel. Clearly the ability to measure very small samples is a necessity. Many of the analytical techniques used on the Stardust samples did not exist or were immature when the spacecraft originally launched in 1999. Improving technologies allowed the samples returned in 2006 to be studied in a number of ways that were completely unanticipated by the mission's original co-investigators. Despite these successes, there are multiple future improvements in the study of small particles that are desirable. First, of course, there will undoubtedly be areas in which technological advances will allow for the use of whole new analytical techniques that have been previously restricted only to larger samples. Each of these will open a new window onto the study of these samples.

Continued improvements in sensitivity will also be helpful. However, for extraterrestrial samples, true sensitivity is not so much a measure of how little of an individual organic molecule can be detected, but whether that molecule can be detected and identified in the midst of a complex mixture of other organics. When pursuing possible analytical techniques that could be applied to IDPs and Stardust samples, I have more than once been disappointed to find that a technique advertised to be able to detect subnanogram samples actually needs the sample to be a pure compound or needs 1 g of material in a sample chamber to generate the nanogram that is measured, and so on. In the case of samples such as those from Comet 81P/Wild 2, techniques are needed that can study subnanogram samples that are compositionally complex and for which the nanogram of mixed material is all there is, which is indeed an analytical challenge.

6.2. Wedding Isotopic Analyses to Molecular Analyses

Understanding the H, N, C, and O isotopic ratios of extraterrestrial organics is important, both because the detection of anomalous ratios proves the materials are extraterrestrial and because the magnitude and molecular locations of the excesses provide important insights into the carrier's formation environment. Of particular interest are enrichments of D and ^{15}N.

To date, most studies of D and ^{15}N excesses in extraterrestrial materials have been restricted to identifying their presence, the magnitude of the anomaly, and, in some cases, mapping the distribution of the anomalous material within the overall sample. These anomalies are often associated with C, and the carriers are inferred to be organic in nature. In many cases, separate analytical studies of these same samples have shown that a variety of organic materials is indeed present. However, these independent observations neither prove the anomalous D and ^{15}N carriers are organics nor tell us about the molecular nature of the actual carriers. To realize the full potential of these materials for establishing the astrophysical environments in which these carriers were formed and evolved, we need the ability not only to detect D and ^{15}N enrichments, but also to establish (*a*) what specific molecular species are carrying the anomalies and (*b*) where the D and ^{15}N are sited on the carrier molecules. Wedding these two types of information from small samples that contain complex mixtures of organics is clearly an analytical challenge of the first order, but it is one that represents the frontier for our next leap forward for understanding how complex organics form and evolve in space.

7. CONCLUSIONS

Our understanding of cometary organics is based on information gathered from telescopic observations, comet flybys by spacecraft, the study of meteorites and IDPs, laboratory simulations, and the study of samples returned from Comet 81P/Wild 2 by Stardust. Our understanding of these materials is incomplete, although considerable progress has been made in recent years. Because one major advantage of sample return missions is that the samples continue to be available for further study, additional major progress can be expected as Wild 2 samples continue to be studied and analytical techniques improve.

When combined, the information gathered by these various approaches suggests that comets are rich in organic materials that come in a wide variety of forms, spanning a large range in volatility and molecular complexity. At one extreme are cometary ices that contain a variety of simple volatile molecules. The delivery of these volatiles (particularly H_2O) could have played a key role in making the early Earth habitable. These same volatiles may have played critical roles in the production of more complex organic materials via radiation processing. At the opposite extreme, comets also appear to contain organic materials that are qualitatively similar to the insoluble macromolecular material that dominates the organic fraction of primitive carbonaceous chondritic meteorites. Both materials are rich in interlinked aromatic domains. However, the cometary material differs from its meteoritic counterparts by being richer in both O and N, suggesting cometary materials have experienced less thermal processing. Comets also appear to contain an organic fraction of intermediate volatility that has no clear meteoritic counterpart. The nature of this material is currently poorly constrained, but its composition appears to be qualitatively consistent with the kinds of organics expected to be produced by radiation processing of mixed-molecular ices.

Because the processes that led to life on Earth are poorly understood, it is difficult to assess the importance cometary organics may have had for the origin of life. However, it is becoming increasingly clear that comets contain a complex population of organic materials. This population appears to include a wider range of organics than is found in primitive meteorites, which themselves contain many species of astrobiological interest (amino acids, quinones, amphiphiles, etc.). Clearly comets contain a unique population of components that have much to tell us about the nature of interstellar and protostellar chemistry, and insights already gathered from the recent studies of cometary samples returned by the Stardust spacecraft suggest exciting progress will continue in this field in the coming years.

SUMMARY POINTS

1. Comets appear to contain abundant organic materials.
2. Cometary organics represent a complex mixture of unequilibrated species.
3. Cometary organics must represent a variety of formation processes and environments.
4. Organics from Comet 81P/Wild 2 appear to have experienced little processing while residing in the comet parent body.
5. Cometary organics include both volatile and refractory species in a wide variety of bonding states.
6. Cometary organics are richer in O and N relative to C than is typical for meteorites.
7. The presence of D and ^{15}N enrichments in cometary materials indicates that at least some of the organics in these bodies have an interstellar chemical heritage.

FUTURE ISSUES

1. What are the molecular carriers and bonding sites of D and ^{15}N isotopic enrichments in primitive extraterrestrial organic samples?
2. What do these molecular carriers and bonding sites tell us about the processes and environments in which they were made?

DISCLOSURE STATEMENT

The author is not aware of any biases that might be perceived as affecting the objectivity of this review.

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