

## Organics in the Samples Returned by the Stardust Spacecraft from Comet 81P/Wild 2

S. A. Sandford

*NASA-Ames Research Center, Astrophysics Branch, Moffett Field, CA  
94035*

**Abstract.** Cometary organics are of great interest because these materials represent a reservoir of the original carbon-containing materials from which everything else in our Solar System was made and that may have played key roles in the origin of life on Earth. These organics are products of a series of universal chemical processes expected to operate in all galaxies, so they also provide insights into the abundance of Life elsewhere in the universe. Our understanding of cometary organics has made a quantum leap forward due to the recent availability of samples collected from Comet P81/Wild 2 and returned to the Earth by the Stardust mission.

### 1. Introduction

Most of the material in the protosolar disk from which our Solar System was made was incorporated into the Sun, was ejected from the system, or ended up in planets. However, minor amounts of material were incorporated into planetesimals that survived as asteroids and comets. The material in asteroids and comets have undergone considerably less parent body processing than planetary materials and therefore likely contain more pristine examples of the raw starting materials of the Solar System. However, the study of meteorites has demonstrated that they are not completely pristine samples, but show evidence of varying degrees of thermal processing and aqueous alteration (Kerridge & Matthews 1988; Lauretta & McSween 2006). Also, most meteorites are likely from asteroids that formed in the inner Solar System and did not incorporate a full share of the more volatile components in the original protosolar disk. In contrast, comets are thought to have formed in the outer Solar System, probably contain a larger portion of the volatile components of the original disk, and have likely undergone less parent body processing since formation. Thus, cometary materials may represent the best samples of pristine early Solar System materials available for study and they may provide powerful insights into the formation of the entire Solar System, not just comets. The nature of cometary volatiles and organics are also of great astrobiological importance since comets may have delivered key volatiles and organics to the early Earth (Oró et al. 1980; Thomas et al. 1996). Finally, since comets are thought to be the end result of a series of universal processes involving stellar, interstellar, and star-forming environments, their compositions should be generally representative of the compositions of these bodies in other planetary systems. Thus, insofar as comets have played a role in the formation of life on Earth, they would be expected to be available to play a similar role in other planetary systems containing ap-

propriate conditions for the origin of life (whatever those are!). Understanding comets in this context may therefore provide insights into the frequency of life elsewhere in the universe.

Our current understanding of comets has made a significant leap forward due to the study of cometary samples recently returned to the Earth from Comet 81P/Wild 2 by the Stardust spacecraft (Brownlee et al. 2006). One of the central scientific goals of the Stardust Discovery Mission was to establish whether comets contained complex organic materials and to establish the abundance, chemical, and isotopic nature of any organics present (Brownlee et al. 2003). The study of samples from Wild 2 represents a significant analytical challenge. The Wild 2 cometary particles that hit the Stardust collector were typically smaller than 25  $\mu\text{m}$  in diameter and contained less than a nanogram of material (Brownlee et al. 2006). To further complicate matters, most of these particles consisted of heterogeneous aggregates of subgrains in the  $\mu\text{m}$  and sub- $\mu\text{m}$  size range that broke upon impact (Brownlee et al. 2006; Hörz et al. 2006; Matrajt et al. 2008). Finally, only a portion of the material in the samples is organic. Despite these challenges, a surprising amount has been learned from these samples and more will be learned in the future.

## 2. Organics from Comet 81P/Wild 2: The Stardust Comet Sample Return Mission

### 2.1. The Collection of Material from Comet 81P/Wild

Stardust was the first mission in history to return solid samples from beyond the Earth-Moon system. The mission retrieved samples from Comet 81P/Wild 2, an  $\sim 4.5$  km diameter body currently in an orbit between Jupiter and Mars. Wild 2 entered this orbit on 10 September 1974 after a close encounter with Jupiter. During Stardust's flyby of Wild 2 on 2 January 2004, the comet showed evidence of at least 20 dust jets coming from the nucleus (Brownlee et al. 2004; Sekanina et al. 2004). Stardust approached to within 234 km of the comet's surface and cometary particles were collected as they impacted at 6.12 km/sec into silica aerogel. 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 the Stardust spacecraft. The aerogel collector medium consists of a porous glass having bulk densities that varied from  $< 0.01 \text{ g/cm}^3$  at the impact surface to  $0.05 \text{ g/cm}^3$  at 3 cm depth. Stardust aerogel tiles collected over a thousand 5–300  $\mu\text{m}$  (and many more smaller) comet particles. Onboard impact sensors indicate that the collected particles were largely associated with two specific dust jets (Tuzzolino et al. 2004).

Particle impacts into aerogel produced tracks whose shapes depended on the nature of the impacting particle. Non-fragmenting particles produced carrot-shaped tracks, but many tracks show bulbous upper regions and sometimes multiple 'roots'. These tracks were produced by weakly bound aggregate particles that broke apart upon impact with the aerogel (Brownlee et al. 2006; Hörz et al. 2006). In addition to aerogel,  $\sim 15\%$  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 (Hörz et al. 2006).

## 2.2. Measurement of Wild 2 Organics in the Returned Stardust Samples

Approximately 200 investigators around the world participated in the preliminary examination (PE) of the samples returned by Stardust and their findings appeared in a special issue of Science (Brownlee et al. 2006; Flynn et al. 2006; Hörz et al. 2006; Keller et al. 2006; McKeegan et al. 2006; Sandford et al. 2006; Zolensky et al. 2006). The analysis of the samples was challenging because the samples were complex, nanogram-sized aggregates that broke up into smaller particles and were distributed along the entire lengths of aerogel tracks. For organics analyses, additional attention had to be paid to the possibility of contaminants associated with the collector, spacecraft flight, and return and recovery of the sample return capsule (SRC). Fortunately, contaminants are found to be of low enough abundance or were sufficiently well characterized that they can usually be distinguished from the cometary organics (Sandford et al. 2006). Most problematic was the aerogel collector medium itself, which contained up to a few wt% C. This C is largely in the form of Si-CH<sub>3</sub> groups easily distinguishable from the cometary organics described below. There is evidence that at least some organic compounds were generated or altered by impact heating of the aerogel itself (Sandford et al. 2006; Sandford & Brownlee 2007; Spencer & Zare 2007). Despite these difficulties, a great deal has been learned about cometary organics and the origin of the Solar System from these samples.

Analytical techniques used during the preliminary examination (PE) of organics in the Wild 2 samples include two-step laser desorption ionization mass spectrometry (*L<sup>2</sup>MS*), Liquid Chromatography with UV Fluorescence Detection and Time of Flight Mass Spectrometry (LC-FD/TOF-MS), Scanning Transmission X-ray Microscopy (STXM), X-ray Absorption Near Edge Spectroscopy (XANES), infrared and Raman spectroscopy, Ion Chromatography with conductivity detection (IC), Secondary Ion Mass Spectrometry (SIMS), and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). A brief summary of the combined findings of these analyses is provided below. More complete discussions of the Organics PE results can be found in Sandford et al. (2006), its associated Supporting Online Material, and in an upcoming special issue of Meteoritics and Planetary Science.

Multiple experimental techniques demonstrate that the samples contain polycyclic aromatic hydrocarbons (PAHs). *L<sup>2</sup>MS* mass spectra obtained from individual particles and along impact tracks show PAHs and their alkylated derivatives. Two distinct types of PAH distributions are seen (Sandford et al. 2006; Clemett et al. 2009; Spencer et al. 2009). In some cases, PAH populations dominated by benzene and naphthalene (1–2 ring PAHs), including alkylation out to several -CH<sub>3</sub> additions, are observed in the absence of larger PAHs along track surfaces. Many of these lower mass PAHs may originate from impact processing of C original to the aerogel (Sandford & Brownlee 2007; Spencer & Zare 2007). The second population of PAHs shows complex distributions that resemble those seen in some meteorites and IDPs. 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 O- and N-substituted aromatic species having hetero-functionality external to the aromatic structure.

The presence of PAHs is confirmed by TOF-SIMS analyses of terminal particles extracted from aerogel tracks and residues found in a crater in aluminum foil. PAH abundances decrease sharply with increasing number of C atoms (Sandford et al. 2006; Stephan et al. 2008a,b). Raman spectra also confirm the presence of aromatic materials (Sandford et al. 2006; Rotundi et al. 2008). All the Raman spectra are dominated by broad bands centered at  $\sim 1360 \text{ cm}^{-1}$  and  $\sim 1580 \text{ cm}^{-1}$  that are characteristic of graphitic  $sp^2$ -bonded C in condensed rings. The profiles and positions of these bands indicate that at least some organics were captured with relatively little alteration. Many Raman spectra of Wild 2 particles also contain very high backgrounds that suggest they may be rich in heteroatoms such as N. In a few cases, aromatic materials were also identified by detection of an aromatic CH stretching mode band using infrared spectroscopy (Sandford et al. 2006; Rotundi et al. 2008; Bajt et al. 2009).

Individual particles extracted from Stardust aerogel were also microtomed into slices thin enough to be amenable to STXM and C,N,O-XANES analyses. C-XANES spectra of many of these thin sections confirmed the presence of aromatics. Full C,N,O-XANES spectra show variable abundances of aromatic, keto/aldehydic, and carboxyl moieties, as well as amides and nitriles (Sandford et al. 2006; Cody et al. 2007). While XANES data confirm aromatics are present, they also show the particles contain abundant non-aromatic C. XANES analyses also show that Wild 2 organics are considerably richer in O and N relative to both meteoritic organic matter and the average composition of Comet Halley particles measured by Giotto, but have O/C and N/C ratios similar to the average of IDPs (Sandford et al. 2006; Cody et al. 2007). Both the O and N exist in a wide variety of bonding states; particles rich in N exhibit abundant amide C in their XANES spectra.

To test whether Stardust may have returned a ‘diffuse’ sample of molecules that struck the aerogel directly from the cometary coma or that diffused away from grains after impact, a search was made for excess primary amines in flight aerogel using LC-FD/TOF-MS. Methylamine (MA), ethylamine (EA), and glycine were detected above background and control sample levels, suggesting they may have a cometary origin (Sandford et al. 2006; Glavin et al. 2008). MA and EA concentrations were similar in aerogels near and not near impact tracks, suggesting that these amines, if cometary, originate from sub- $\mu\text{m}$  particles or gas that directly impacted the collector. 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.

IR spectra taken from tracks and individual extracted particles show both aromatic and non-aromatic chemical functional groups are present (Keller et al. 2006; Sandford et al. 2006; Rotundi et al. 2008; Bajt et al. 2009). Infrared spectra of particles and tracks often contain absorption features at  $3322 \text{ cm}^{-1}$  ( $-\text{OH}$ ),  $3065 \text{ cm}^{-1}$  (aromatic CH),  $2968 \text{ cm}^{-1}$  ( $-\text{CH}_3$ ),  $2923 \text{ cm}^{-1}$  ( $-\text{CH}_2-$ ),  $2855 \text{ cm}^{-1}$  ( $-\text{CH}_3$  and  $-\text{CH}_2-$ ), and  $1706 \text{ cm}^{-1}$  ( $\text{C=O}$ ). One particle also showed a weak  $2232 \text{ cm}^{-1}$  band consistent with  $-\text{C}\equiv\text{N}$  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  $-\text{CH}_2-/-\text{CH}_3$  band depth ratios in the samples is typically  $\sim 2.5$ , a value similar to that seen from anhydrous IDPs, but considerably larger than seen in carbonaceous chondrites ( $\sim 1.1$ ) and the diffuse ISM (1.1–1.25). This

indicates that the aliphatics in Wild-2 samples 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 seen in the XANES data. IR spectral maps of entire impact tracks and their surrounding aerogel show that the organics that produce the -OH, -CH<sub>3</sub>, -CH<sub>2</sub>-, and C=O IR absorption bands sometimes extend well beyond the visible track edge (Sandford et al. 2006). This implies that some particles contained organics that volatilized and diffused into the surrounding aerogel during impact. Since similar length tracks are also seen in the same aerogels that show no excess IR-detectable organics, this material is unlikely to be due to impact-altered aerogel carbon.

SIMS ion imaging elemental maps of Wild 2 particle sections show that N and S are associated with organic molecules and that the N is very heterogeneously distributed with N/C ratios ranging from 0.005 to almost 1 (Sandford et al. 2006; Matrajt et al. 2008). Some particles exhibit the entire range of values, while others fall more uniformly at the high N/C end of the range. Sulfur is often associated with C and N. SIMS H/D isotopic measurements of Wild 2 particles show D enrichments up to about three times the terrestrial value within about half of the particles (McKeegan et al. 2006; Matrajt et al. 2008). The D enrichments are heterogeneously distributed and associated with C, indicating the carrier is probably organic. Isotopic anomalies were also observed in N (McKeegan et al. 2006). As with D, the anomalies are often heterogeneously distributed within the particles. These D and <sup>15</sup>N enrichments are likely due to materials with an interstellar/protostellar chemical heritage (Messenger 2000; Sandford et al. 2001; Aléon & Robert 2004) and provide clear evidence of a cometary origin for the organics. A number of interstellar chemical processes and environments can fractionate H and N isotopes. These processes are expected to leave characteristic isotopic 'fingerprints' in their products (Sandford et al. 2001) that can provide important clues about the carriers' natal environments. One would expect many organic molecules having interstellar origins to show enrichments in D and <sup>15</sup>N. Isotopic analyses of the Wild 2 samples appear to be qualitatively consistent with these expectations. The heterogeneous distribution of D and <sup>15</sup>N excesses in these samples suggests that materials having an interstellar heritage were mixed with solar nebular materials during Solar System formation, but that they were not exposed to significant processing after the component subgrains were assembled, either within the protosolar nebula or in the cometary parent body.

### 3. Summary and Conclusions

Overall, the organics in the Comet Wild 2 samples show many similarities with those in IDPs, and to a lesser extend, with those in primitive meteorites, but there are some very distinct differences. Like meteoritic organics, Wild 2 organics contain both aromatic and non-aromatic fractions. However, the Stardust samples exhibit a greater range of compositions (higher O and N concentrations), include an abundant organic component that is poor in aromatics, and a more labile fraction (possibly the same material). The non-aromatic fraction appears to be far more abundant relative to aromatics than in meteorites. Some

of the cometary material represents a new class of organics not previously seen in other extraterrestrial samples, making these samples unique among currently available extraterrestrial samples.

The distribution of organics (overall abundance, functionality, and relative elemental abundances of C, N, and O) is remarkably heterogeneous both between particles and within individual particles. Cometary organics clearly represent a highly unequilibrated reservoir of materials. This indicates that these materials did not undergo much parent body processing. 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 un-equilibrated. The presence of organics with high O and N contents and high ratios of  $-\text{CH}_2-$ / $-\text{CH}_3$  indicate that the Stardust organics are not identical to the organics seen in the diffuse ISM. 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.

Since the processes that led to life on Earth are poorly understood, it is difficult to assess the importance these cometary organics may have had for the origin of life. However, it is 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. Clearly comets contain unique organics that have much to tell us about the nature of interstellar and protostellar chemistry and the roles they may play in the origin of life.

**Acknowledgments.** This work was supported by NASA grants from the Origins of Solar System, Exobiology, Cosmochemistry, and Discovery Mission Programs. The author is grateful to the many, many people who made the Stardust Mission both a reality and a joy to work on.

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