Organics in the samples returned from comet 81P/Wild 2 by the Stardust Spacecraft

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Abstract. The Stardust Mission collected samples from Comet 81P/Wild 2 on 2 Jan 2004 and returned these samples to Earth on 15 Jan 2006. After recovery, a six month preliminary examination was done on a portion of the samples. Studies of the organics in the samples were made by the Organics Preliminary Examination Team (PET) - a worldwide group of over 55 scientists. This paper provides a brief overview of the findings of the Organics PET. Organics in the samples were studied using a multitude of analytical techniques including spatial determination of C and heteroatom elemental abundances (STXM), functional group identification (micro-FTIR/Raman, C,N,O-XANES), and specific molecular identification of certain classes of organics (HPLC-LIF, L2MS, TOF-SIMS). Analyses were also made of spacecraft components and environmental samples collected near the recovered returned capsule to assess contamination issues. The distribution of organics (abundance, functionality, and relative elemental abundances of C,N,O) is heterogeneous both within and between particles. They are an unequilibrated reservoir that experienced little parent body processing after incorporation into the comet. Some organics look like those seen in IDPs (and to a lesser extent, meteorites), while new aromatic-poor and highly labile organics, not seen in meteoritic materials, are also present. The organics are O,N-rich compared to meteoritic organics. Some of the organics have an interstellar heritage, as evidenced by D and ^{15}N enrichments.

Keywords. Stardust Mission, comets, organics, dust, isotopes, astrochemistry, astrobiology

1. Introduction

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 (Mannings *et al.* 2000). The collapsing material formed a disk surrounding a central protostar. Much of the material was incorporated into the central protostar, which eventually became our Sun, some was ejected from the system by bipolar jets and gravitational interactions, and 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 (Bottke *et al.* 2002, Festou *et al.* 2004).

The importance of these small bodies outweighs their minor contribution to the mass of our Solar System because their materials have undergone less parent-body processing and they contain more pristine early nebular materials. We receive samples of these objects on Earth in the form of meteorites and interplanetary dust particles (IDPs), and these demonstrate that comets and asteroids do contain primitive materials (Kerridge & Matthews 1988, Lauretta & McSween 2006). Since comets are thought to have formed and resided in the outer Solar System, they probably contain a more representative portion of the volatile components of the original protoplanetary disk and have undergone less

parent-body processing since formation. Thus, cometary materials may represent the best samples of early nebular materials available for study and may provide insights into the formation of the entire Solar System, not just comets. The nature of cometary volatiles and organics is also of astrobiological importance since these materials may have delivered significant volatiles and organics to the early Earth's surface after it had cooled. Finally, because comets are thought to be the end result of a series of universal processes involving stellar, interstellar, and star-forming environments, they should be generally representative of the composition of these bodies in other stellar systems. 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 organics is the combined result of information gathered using many different techniques. These include telescopic remote-sensing techniques (Ehrenfreund *et al.* 2004, Bockelée-Morvan *et al.* 2004), laboratory simulations (Bernstein *et al.* 1999, Cottin *et al.* 2001, Dworkin *et al.* 2001, Bernstein *et al.* 2002), spacecraft flybys of individual comets (Reinhard 1986, Sagdeev *et al.* 1986, Brownlee *et al.* 2004, A'Hearn *et al.* 2005), the study of meteoritic materials found on Earth (Bradley *et al.* 1988, Lauretta & McSween 2006), and now the study of cometary samples from Comet 81P/Wild 2 (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). I concentrate here on what we have learned from the samples returned by Stardust.

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

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 (Brownlee *et al.* 2003, Tsou *et al.* 2003). Our understanding of cometary organics made a quantum leap forward with the 15 Jan 2006 return of samples from Comet 81P/Wild 2 (Sandford *et al.* 2006).

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

The Stardust spacecraft retrieved samples from Comet 81P/Wild 2, a comet currently in an orbit that approaches the orbits of both Jupiter and Mars. This roughly 4.5-km-diameter body has spent most of the past 4.5 billion years in the Kuiper Belt. Only recently did it wander into the inner Solar System, where it had a close encounter with Jupiter on 10 Sept 1974 that placed it in its current orbit.

Images taken during the Stardust flyby on 2 Jan 2004 showed the presence of over 20 dust jets coming from the nucleus (Sekanina *et al.* 2004). 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 when they impacted at 6.12 km s^{-1} into silica aerogel, a porous glass comprised of nm-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 tiles collected over a thousand 5-300 μm (and many smaller) comet particles. Onboard impact sensors indicate that most of the collected particles were associated with just a few specific dust jets (Tuzzolino *et al.* 2004).

Particle impacts into aerogel made tracks whose shapes depended on the nature of the impactor. Solid particles produced long, thin tracks. However, many tracks show bulbous

upper regions and multiple 'roots'. These tracks were produced by weak aggregate particles that broke apart on impact (Brownlee *et al.* 2006, Hörz *et al.* 2006). Upper parts of tracks are lined with melted aerogel containing dissolved projectile material; mid-regions contain less melt, more preserved projectile material, and compressed aerogel; and track ends contain largely unmelted terminal particles. The deepest penetrating particles are usually solid mineral grains or aggregates of larger grains. Approximately 15% of the Stardust collector surface was the aluminum frame and foils used to hold the aerogel. Impacts on these 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 Samples*

Approximately 200 investigators around the world participated in the Preliminary examination of the samples returned by Stardust. Their findings appeared in the 15 Dec 2006 issue of *Science*. These results were obtained using a wide variety of analytical techniques. Investigators paid 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 to be of low-enough abundance or were sufficiently well characterized that they can generally be distinguished from the cometary organics (Sandford *et al.* 2006). Most problematic was the aerogel collector medium itself; tiles can contain one-quarter to a few weight percent C. Nuclear magnetic resonance studies indicate that this C is largely in the form of Si-CH_3 groups easily distinguishable from the cometary organics described below. It should also be noted that not all the organics will be fully representative of the original cometary material because some may have been modified during impact. There is also evidence that at least some organic compounds were generated or altered by the impact heating of the aerogel itself (Sandford *et al.* 2006, Spencer & Zare 2007, Sandford & Brownlee 2007). Despite these difficulties, much has been learned about cometary organics and the origin of the Solar System from these samples.

Analytical techniques used during the preliminary examination of Wild 2 organics include laser desorption, laser ionization mass spectrometry (L2MS), liquid chromatography with UV fluorescence and time-of-flight mass spectrometry (LC-FD/TOF-MS), scanning transmission X-ray microscopy (STXM), X-ray absorption near edge spectroscopy (XANES), IR and Raman spectroscopy, ion chromatography (IC), secondary ion mass spectrometry (SIMS), and time-of-flight SIMS. A summary of the findings of these analyses is provided below. More complete discussions of the organics preliminary results can be found in Sandford *et al.* (2006) and its associated supporting online material, Sandford (2008), and in a soon-to-appear special issue of *Meteoritics and Planetary Science*.

Multiple experimental techniques demonstrate that the samples contain polycyclic aromatic hydrocarbons (PAHs). L2MS 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 (Sandford *et al.* 2006, Clemett *et al.* 2008, Spencer *et al.* 2008). 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 diffusely along track walls in the absence of larger PAHs. Such distributions are observed in high-laser-power L2MS measurements of Stardust aerogel tiles, suggesting many of the lower-mass PAHsmay originate from impact processing of C original to the aerogel (Spencer & Zare 2007, Sandford & Brownlee 2007). The second type of PAH population, associated with whole particles, shows complex distributions that strongly resemble those seen in some meteorites and IDPs. The similarity to IDPs extends to masses beyond 300 amu, although several

track spectra show mass envelopes extending up to 800 amu with both odd and even mass peaks. Such high-mass envelopes in IDPs have been attributed to polymerization of smaller aromatics by radiation processing during extended exposure to interplanetary space or heating during atmospheric entry (Clemett *et al.* 1993, Clemett *et al.* 2008). Similar polymerization of the original PAH population in the Stardust samples by impact heating may explain the higher-mass envelopes observed in them (Sandford *et al.* 2006). 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.

The presence of PAHs has also been confirmed by time-of-flight SIMS analyses. A steep decrease in PAH abundance with increasing number of C atoms is seen (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 two broad bands centered near 1360 Δcm^{-1} and 1580 Δcm^{-1}. These D and G bands, respectively, are characteristic of sp^2-bonded carbon in condensed carbon rings. The spectra are similar to those of many IDPs and primitive meteorites, and 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 samples or variable processing during impact. However, G bands with low frequencies and large widths indicate that at least some organics were captured with little alteration. Many Raman spectra of Wild 2 particles are characterized by high backgrounds that increase with increasing Δcm^{-1} position, indicating the samples may be rich in heteroatoms like N. In a few cases, aromatic materials were also identified by the detection of an aromatic CH stretching mode band using IR spectroscopy (Sandford *et al.* 2006, Rotundi *et al.* 2008, Bajt *et al.* 2008).

It was possible to extract individual particles from Stardust aerogel and microtome them into multiple slices thin enough for scanning transmission X-ray microscopy and C,N,O-XANES analyses. C-XANES spectra of these thin sections confirm the presence of aromatic bonds. Full C,N,O-XANES spectra showed $1s$-π^* transitions consistent with variable abundancesof aromatic, keto/aldehydic, and carboxyl moieties, as well as amides and nitriles (Figure 1a) (Sandford *et al.* 2006, Cody *et al.* 2008). 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 IDPs and meteorites. Some particles contain abundant C, none of which is aromatic (particle 1 in Figure 1a). XANES analyses also provided quantitative estimates of atomic O/C and N/C ratios present in the samples (Figure 1b). Overall, the Wild 2 organics were found to be considerably richer in 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 (Sandford *et al.* 2006, Cody *et al.* 2008). 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 (Sandford *et al.* 2006, Glavin *et al.* 2008). Stardust may have returned a 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, samples of non-track-bearing flight aerogel were searched for excess primary amines. Only methylamine (MA), ethylamine (EA), and glycine were detected above background levels. 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
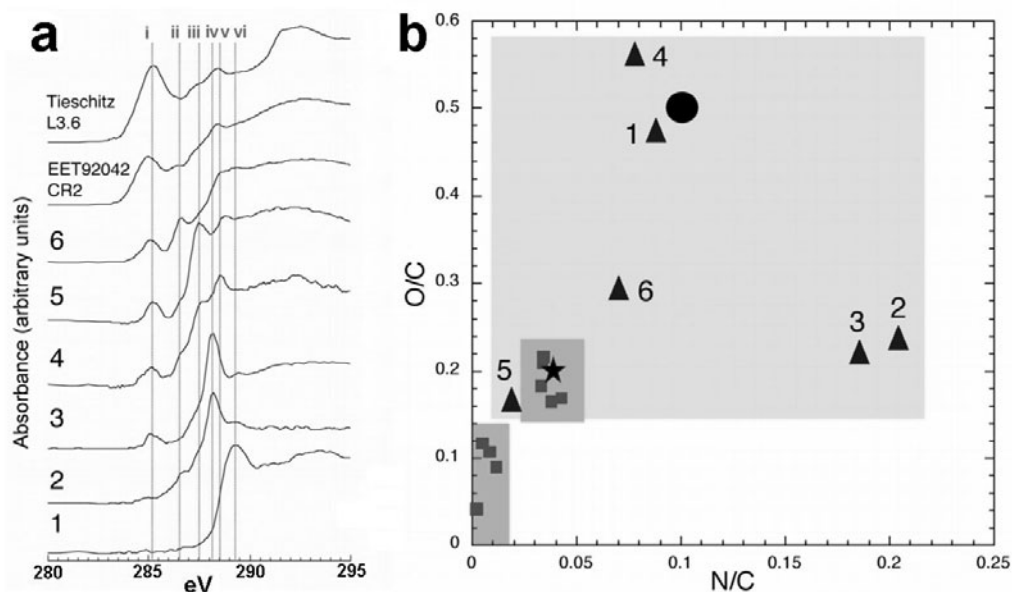
Figure 1. (a) C-XANES spectra of six samples from Comet Wild 2 samples (1 to 6) compared with organic matter from two primitive meteorites. Positions associated with specific organic functional groups are marked with dashed vertical lines: (i) C=C, (ii) C=C-O, (iii) C=O, (iv) N-C=O, (v) O-C=O, and (vi) C-O. Sample chemistry clearly varies enormously between samples. (b) Atomic O/C and N/C for the six samples in panel (a) (black triangles) compared with chondritic meteorite organic matter (gray squares in the dark gray shaded areas, 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 (black star) and stratospheric interplanetary dust particles (IDPs) (black circle). Figure adapted from Sandford *et al.* (2006).

a track were similar to those in aerogel not near a track, suggesting that these amines, if cometary, originate from submicrometer 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 the presence of both aromatic and nonaromatic functional groups (Keller *et al.* 2006, Sandford *et al.* 2006, Rotundi *et al.* 2008, Bajt *et al.* 2008). 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≡N stretching vibrations. 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$_2$-/-CH$_3$ band depth ratios in the returned samples are typically about 2.5, corresponding to a functional group ratio of about 3.7. This value is similar to that seen in the IR spectra of anhydrous IDPs, but considerably larger than seen in insoluble organics in primitive meteorites (1.1) and the diffuse ISM (1.1-1.25), suggesting that the aliphatic moieties in particles from Comet 81P/Wild 2 are longer, less branched, or contain more cyclic aliphatic structures. 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 (Sandford *et al.* 2006, Bajt *et al.* 2008). 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.

SIMS ion imaging has been used to make elemental maps of Wild 2 particle sections (Sandford *et al.* 2006). 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. SIMS was also used to make H, C, and N isotopic measurements of Wild 2 particles (McKeegan *et al.* 2006, Matrajt *et al.* 2008). D/H enrichments are observed within approximately half the particles. 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. Isotopic anomalies in N in the form of ^{15}N excesses are also seen (McKeegan *et al.* 2006). As with D, these anomalies are heterogeneously distributed and appear in the form of 'hot spots'. 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 (Messenger 2000, Sandford *et al.* 2001, Aléon & Robert 2004, Busemann *et al.* 2006).

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

Overall, the organics in the Wild 2 samples show many similarities with those seen in IDPs, and to a lesser extent with those in primitive meteorites. 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. These variations indicate that cometary organics represent a highly unequilibrated reservoir of materials. Wild 2 organics contain both aromatic and nonaromatic fractions. Compared to IDPs and meteorites, 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 nonaromatic fraction is more abundant relative to aromatics than seen in IDPs and meteorites. The labile materials may be absent from stratospheric IDPs because they are lost and/or modified during atmospheric entry or by radiation during transit from their parent body to Earth. The organics in Stardust samples appear to be 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 high ratios of -CH$_2$-/-CH$_3$ show 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 (Pendleton & Allamandola 2002). 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 that expected from radiation processing of astrophysical

ices in dense clouds and the polymerization of simple species such as HCO, H_2CO, and HCN (Schutte *et al.* 1993, Bernstein *et al.* 1995).

3. Conclusions

The successful return and study of Comet 81P/Wild 2 samples is a fresh example of the power of sample return studies. A 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.

Information resulting from studies of Wild 2 samples using a variety of analytical techniques suggests that comets (or at least this one) are rich in organic materials that come in a wide variety of forms spanning a large range in molecular structure, volatility, and molecular complexity. The distribution of organics is heterogeneous both within and between particles, i. e., they represent an unequilibrated reservoir of materials that experienced little parent body processing in the comet. The organic populations detected are distinct from those seen in primitive meteorites and IDPs, but some show similarities to both. A diverse set of both aromatic and non-aromatic functionalities are present. Some of the organics are qualitatively similar to the insoluble macromolecular material that dominates the organic fraction of primitive meteorites. However, the cometary material differs from its meteoritic counterparts by being richer in both O and N, much like IDPs. The cometary materials also appear to contain an organic fraction of intermediate volatility that has no clear meteoritic counterpart. The nature of this labile 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. On the whole, the organics appear to be more "primitive" than the bulk of organics in primitive meteorites and richer in non-aromatic materials. D and ^{15}N enrichments in many particles suggest a 'presolar' heritage.

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.

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Discussion

MUMMA: In your discussion of the chemical structure, you show the XANES spectra and I am struck by your identification of the aromatic peak corresponding to the C=C sp^2 bond. It is not clear to me why that must be aromatic. For example, the tetramer of HCN is actually such sp^2 carbon with side members of NH_2 and CN, and higher order HCN oligomers also have many C=C sp^2 bonds. So, how did you identify that this feature is caused by an aromatic chemical structure as opposed to another? I have always thought the term "aromatic" implies a ring structure, but you seem to be implying that an oligomer of HCN could have a ring structure.

CODY: If carbon is sp^2 bonded to nitrogen you will observe a 1.3 eV shift up from 285 eV. Distinguishing between C=C from C=N is not a problem. In the case of C-XANES the use of the word "aromatic" is sometimes used loosely, not in a strict organic chemical sense. Olefinic carbon absorbs at the same energy as benzene as also do polyenes and polynnes.

MUMMA: So the presence of this peak does not imply a ring structure?

CODY: Not necessarily.

SANDFORD: Of course we see the aromatic signature in the Raman spectra and in the L2MS spectra we clearly see ring structure. You are not going to get that kind of spectrum from olefinic material. It is not impossible that the particle that George measured had mostly olefinic carbon while the next particle analyzed by someone else measured carbon in aromatic rings. What would be safest to say is that rings or PAH must be present, but not every C=C has to be in a ring.

ZIURYS: My question is whether there is any evidence for phosphorus or you did not look for it?

FLYNN: There are definitely evidence for phosphorus in some particles, what we don't know is whether the phosphorus is spatially associated with organics.

IRVINE: Given how little I think we really know about interstellar grains, what do you mean when you say that this is not a collection of interstellar grains?

SANDFORD: Well, everything that ends up in the solar nebula was interstellar one time. However, when we went to this comet some people expected that we would find a thousand times more circumstellar grains than found in meteorites, but that's not what we see. The number of grains that show isotropic anomaly is modest. Obviously every atom in a comet was interstellar at some point so part of the issue is just how much they have been modified by some process and by the formation of the Solar System.

IRVINE: I wouldn't imagine that all interstellar grains are isotopically anomalous.

SANDFORD: Certainly there are processes that can mix things up in the interstellar medium. The main point I want to make is that some people thought these circumstellar isotropically anomalous grains might be very abundant in comets, but that is not the case.

Scott Sandford (photo by Dale Cruikshank).