Microbeam Analyses of the Most Challenging Extraterrestrial Samples Ever Returned

Frans J.M. Rietmeijer
University of New Mexico, Albuquerque, NM
fransjmr@unm.edu

The NASA STARDUST Mission

This mission flew by Comet 81P/Wild 2 where it collected more than 10,000 particles, ranging from tens of nanometers to hundreds of microns, and carried them to Earth for a safe landing in the Utah desert on January 15, 2006. So what? The answer depends on one's interest. Technically, it was a perfect DISCOVERY-class mission from launch to soft-landing (Figure 1). Scientifically, it delivered some of the 4.6 Gyrs-old particles that went into making the planets of our solar system and for the first time ever we have samples from a known comet.

Many challenges lie ahead. First, the grains must be extracted from the capture cells, and prepared for mineralogical and chemical analyses, including stable isotopes and organic phases. Second, the NASA/JSC Stardust Curatorial Facility has to prepare and keep track of each sample allocation. Third, data collected in many laboratories around the globe will need to be synchronized for publication.

Figure 1: *After successful deceleration from 12.8 km/s, the STARDUST capsule made its final turn ending its journey. The now blackened heat shield preformed as expected and, but for a light 'sugar' coating of desert soil, the integrity of its cargo was maintained.* **Photo credit NASA JSC**

Supposedly, comet dust should be amorphous silicate-like materials, and small Mg-olivine (forsterite, Mg_2SiO_4), Mg-pyroxene (enstatite, $MgSiO_3$), and some Fe-Ni-sulfide grains. Comet Wild 2 is a 'garbage bag' with an unanticipated wide variety of minerals with some verging on the bizarre. In current models of solar system formation, the minerals condensed from a solar nebula gas, where the possibility exists that many of the minerals were thermally processed by approaching the sun, and then transported to their original formation zones by a combination of turbulent transport, expulsion in the sun's bipolar outflows, and eventual migration back to the solar nebula mid-plane. We have learned that our solar system is not unique. Infrared observations of young stars, such as Beta Pictoris (Figure 2), in different stages of evolution showed how cometesimals orbiting the star maintain a dusty disk. Grains in these disks include amorphous magnesiosilica grains, Mg-silicates, FeS, calcite ($CaCO_3$), dolomite [$CaMg(CO_3)_2$], spinel ($MgAl_2O_4$) and corundum (Al_2O_3) grains.The microscopic properties of the Wild 2 dust will link directly to the astronomical observations of comets.

The collector was an Au-foil covered aluminum frame that holds silica aerogel tiles. The low density, micro-porous (10-nm) aerogel was a rigid three-dimensional network of nanometer-sized SiO_2 clusters linked together forming chains. It has a high surface area (1000 m^2/g), very low thermal conductivity (~0.02 W/mK), and was designed for intact capture of particles impacting at 6.1 km/s (Figure 3). Initial inspection of the collector showed that all tiles were intact and literally riddled with tracks caused by impacting comet particles (Figure 4), but intact capture didn't happen. It was also not expected. Hypervelocity impact experiments using mineral or composite-mineral projectiles showed that they survived encapsulated in aerogel or fractured with aerogel penetrating along fractures. The grains in aerogel show survival as a function of grain size from fracturing of large grains to complete melting and dispersal in silica glass of small grains. Comet particles that impacted the aluminum frame produced craters that often contained a melt residue with preserved nanometer grains.

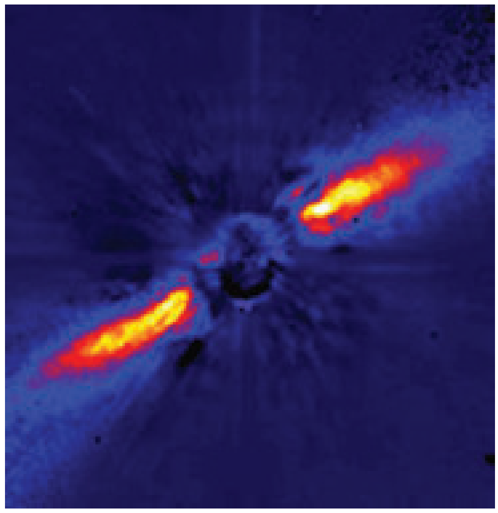

Figure 2: *Infrared image of the star Beta Pictoris (blocked by an occulting disk) and its circumstellar dust disk with wings extending to ~700 Astronomical Units (AU) compared to ~400 AU for the Kuiper Belt in our solar system. Taken in the early nineteen-eighties, it was the first glimpse of how the early solar system would have looked. Space-based telescopes have since seen many more disks in all stages of evolution including bi-polar outflows.* **Image: IRAS/ESO**

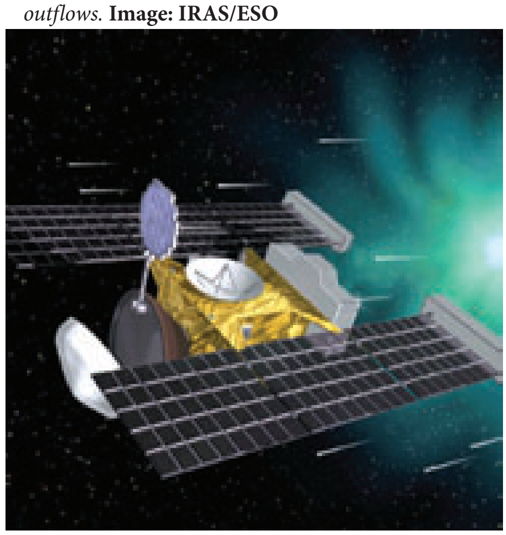

Figure 3: *An artist impression of the STARDUST craft approaching the comet and its ejected dust. It shows two solar panels with Whipple-shields. The particles impacted the collector of the extended 'tennis racket' that was then folded, and hermetically sealed by the white cone of the heat shield of the container that returned to Earth.* **Copyright © 2006 NASA/JPL**

Deceleration tracks in silica aerogel

Particles that impacted the aerogel carved their individual tracks. Track morphology is a first-order indicator of the physical property of the comet particle [1,2]. A thin, slender track indicates a particle that was a compact mineral grain with few fragments. In general, particle fragmentation led to substantial lateral tracks off the main track. Most tracks have a bulbous cavity with, or without (rare), a single stylus (Figure 5) or two bifurcating stylii. This cavity is caused by the sudden release of copious volatiles from a volatile-rich particle.

The track features suggested that most comet particles were weakly constructed mixtures of nanometer-size grains with occasional grains, ~1 to ~10µm, and terminal grains up to 20 µm in size at the end of a stylus. Track lengths range from 50 µm to 1 cm measured from the penetration hole to the end of the stylus; most track lengths are in the

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Figure 4: *Scientist in the Stardust receiving laboratory at NAA/JSC huddled over the array of tiles (bluish sheen) with comet particles. Already visible to the naked eye were many tracks with the anticipated shapes of hypervelocity-impacted particles.* **Photo credit NASA JSC**

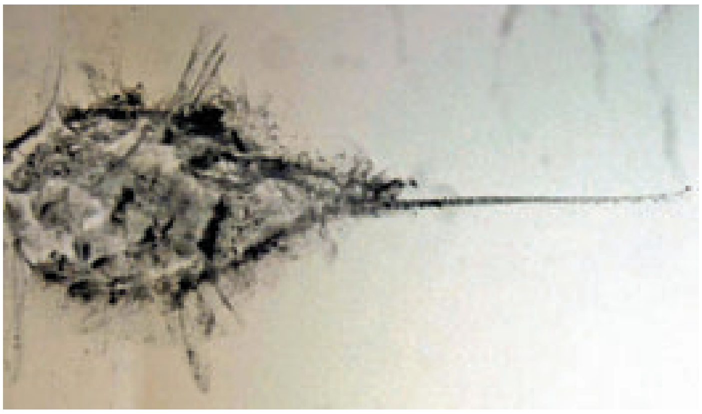

Figure 5: *Track 35 in aerogel cell C2054 with multiple grains <40 µm; over 50 grains were removed from the track during the Preliminary Examination Team phase. The particle entered from the left and while traveling (to the right) lost volatiles and stripped off its grains. It is a bulbous type track with multiple stylii, including the narrow stylus off to the right and the lateral features extending from the cavity. The track is ~1.7 mm long. Each black spot is a grain that will be extracted. Lateral forces also pushed grains into the track wall*. **Photo credit NASA JSC**

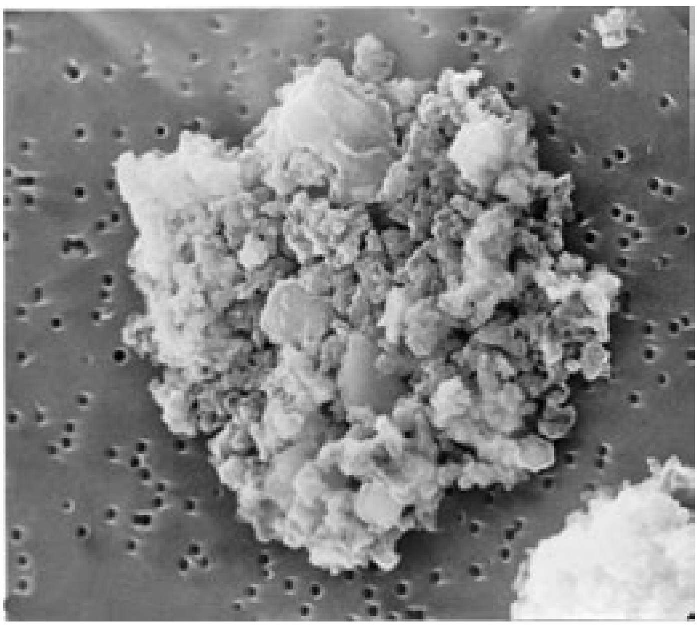

Figure 6: *Scanning electron microscope image of porous chondritic aggregate IDP W7029B13 (NASA number S-82-27575) that is 12 µm across on a nucleopore-filter (background) with platy silicate grains in a matrix of partially fused nanometer grains. Such IDPs have been collected in the Earth's lower stratosphere for almost three decades [4].* **Photo credit NASA JSC**

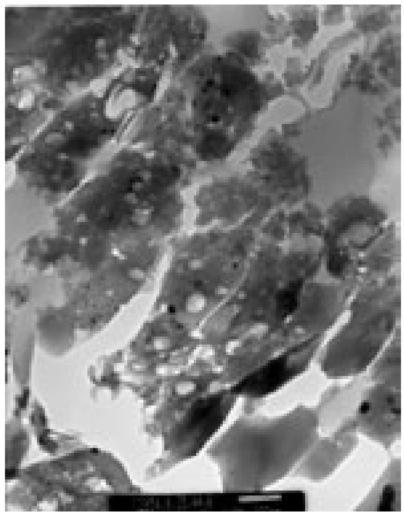

Figure 7: *TEM image of an ultramicrotome slice (70-nm thick) of typical, vesicular, silica-rich (>90-95 wt% SiO_2) glass (track 35, tile C2053) with opaque low-Ni Fe-S and Fe,Ni metal inclusions ranging from a few nanometers up to 100 nm [6]. The quenched-liquid inclusions form because sulfide melts cannot be assimilated in silica melts. The shard-like appearance became expressed during sample preparation. In the top right-hand corner the embedding material is visible (smooth gray), the scale bar is 200 nm.* **Image Frans Rietmeijer/UNM/NASA**

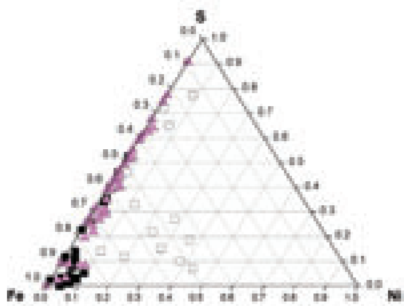

Figure 8: *Compositions of Fe-Ni-S inclusions (at%) in small portions of the silica-rich glass matrix in two different tracks: C2004,1,44 (filled squares), two different locations in C2054,0,35 (open squares and filled triangles). There are clear differences among and within tracks [6].* **Figure by Frans Rietmeijer/UNM/NASA**

millimeter range. In a typical track most grains of the comet particle were deposited near the entry hole, but with hundreds of grains also along the entire track including the stylus (Figure 5).

Morphology and chemical properties of Wild particles

The loose bonding of the comet aggregates suggests intact preservation in comet ice since accretion 4.56 Gyrs ago. Much stronger, up to 0.15 MPa, cometary meteors [3] continuously delivered aggregate interplanetary dust particles (IDPs) (Figure 6). Some aggregate IDPs are undoubtedly from comets but we don't know which ones [4]. The mechanically stronger IDPs (~5 to ~300 µm) were probably modified during ~10,000 years of space sojourn. It is unlikely that their Mg-Fe-Ca silicates and Fe-Ni sulfides (about 50 nm to ~10 µm) grains were altered substantially. These aggregate IDPs and the larger cluster IDPs could serve as a reference when investigating Wild 2 particles and grains. These IDPs have a chondritic bulk composition, *i.e.* their element abundances are similar to those in the solar photosphere and primitive CI ('I' stands for the Ivuna meteorite) carbonaceous chondrites. Albeit variable, the bulk composition of Wild 2 particles is CI-like for Mg, Si, Ca, Ti, Mn, Fe and Ni. Volatile elements (Cu, Zn and Ga) are present in >CI values [5]. The bulk sulfur content is <CI, but CI values for sulfur are found locally on a micron scale. Was sulfur lost during hypervelocity impact, or is comet Wild 2 simply low in sulfur? When trying to unravel the information arising from the comets particles, it is important to distinguish two repositories: (1) silica glass and (2) track walls and the stylus.

Dust and minerals in aerogel

Early results indicated that impact-induced temperatures reached ~1500°C but temperatures up to 10,000°C were theoretically possible with steep micron-scale gradients. At these temperatures, silica aerogel melts. In the high-resolution transmission electron microscope (HR-TEM) the original porous but somewhat compressed aerogel is readily recognizable. It is in contact with but not mixed with Si-rich glass that is quenched aerogel melt. The glass is a matrix for hundreds of randomly scattered opaque inclusions (Figure 7) that were derived from Fe-Ni-S

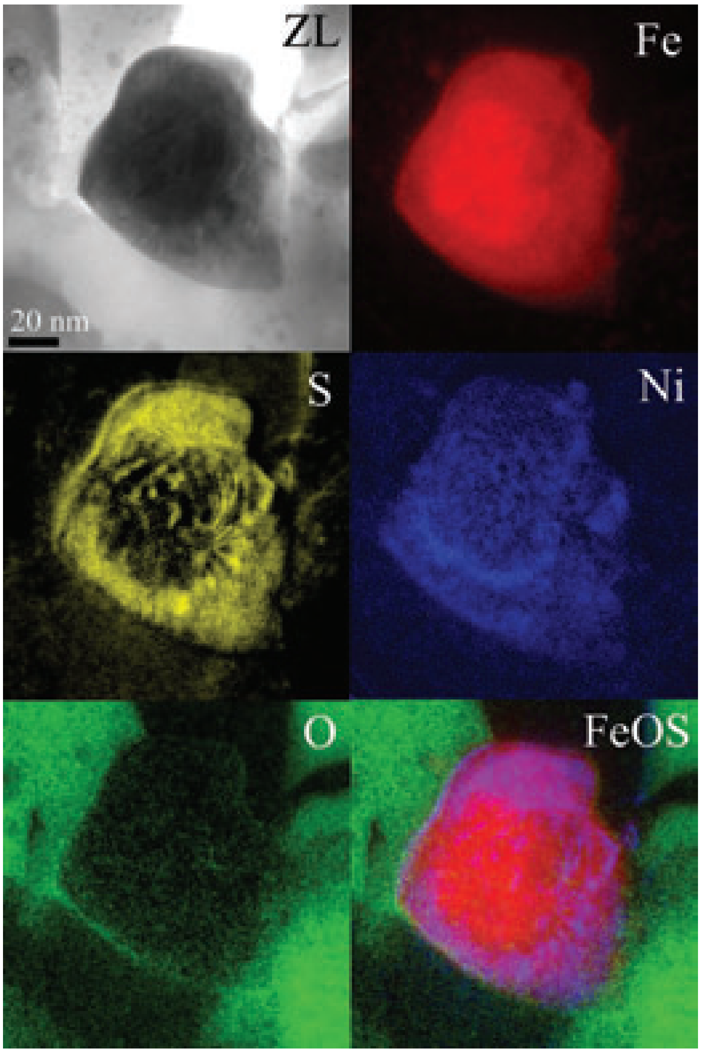

Figure 9: *Energy filtered TEM maps of a subhedral Fe-Ni-S nanograin (ZL: zero-loss image) embedded in the Si-rich glass matrix in track C2054,0,35. The Fe (red) and S (yellow) maps show typical zoning of a Fe-metal core and a FeS-like rim. The Ni (blue) map indicates a uniformly low distribution, which is common to many Fe-Ni-S grains in the Si-rich glass matrix (see Figure 8). The O-map (green) shows the sharp interface with the silica glass. The Fe-O-S maps indicate the complete absence of chemical interactions in this case. In other parts of the same track Fe-silicides formed when the low-Ni FeS and/or Fe-metal comet grains reacted with silica.* **Image by Adrian Brearley/UNM/NASA**

nanometer grains in the comet that melted during collection. The inclusion compositions covered the entire range from pyrrhotite [$(Fe,Ni)_{1-x}S$] and troilite (FeS) to Fe-Ni metal (Figure 8). The range between Fe and FeS (50 at%) could reflect continuous sulfur loss from melting grains. Many inclusions have a core-rim structure. The cores had low sulfur compositions. The rims contained more sulfur, generally FeS-like, but some grains with very high sulfur content were found (Figure 8). The rim can be only a few or several nanometers wide. The morphology of thicker rims suggests drag in a fluid medium but this notion and its implications, and the question of sulfur loss or re-distribution, are still poorly explored at this time. Other, subhedral, Fe-Ni-S inclusions have a Fe-rich metal core and a FeS-like rim (Figure 9). Both core and rim have low-Ni contents and in this grain Ni is somewhat enriched at the core-rim boundary. The EFTEM composite is a very visual reminder of the chemical and mineral complexity in the captured comet nanograins. What was indigenous to the comet, and which features were thermally induced? Obviously, more systematic analyses will be required.

Everywhere one looks, the glass matrix showed trace amounts of Mg, Ca, Al and K, with local concentrations up to 5-wt%, which came most likely from melted comet silicate nanograins that were assimilated in silica melt, *e.g.* amorphous K-rich aluminosilica grains. There were well-preserved Mg-rich olivine and low-Ca Mg-pyroxene crystals (~500nm) with a partial rim of highly compressed pure-SiO_2 aerogel. Other partial rims were silica-rich glass but without opaque inclusions, and yet other rims were Si-rich glass with opaque inclusions (Figure 10). The boundaries between crystal, rim and silica glass showed no evidence of chemical interactions. Whatever processes produced these rims, their formation preserved the comet grains. Typically, small grained comet particles, with sizes <500nm, experienced the most severe interactions with the aerogel. Larger comet grains escaped severe interactions with the impact-generated silica melt.

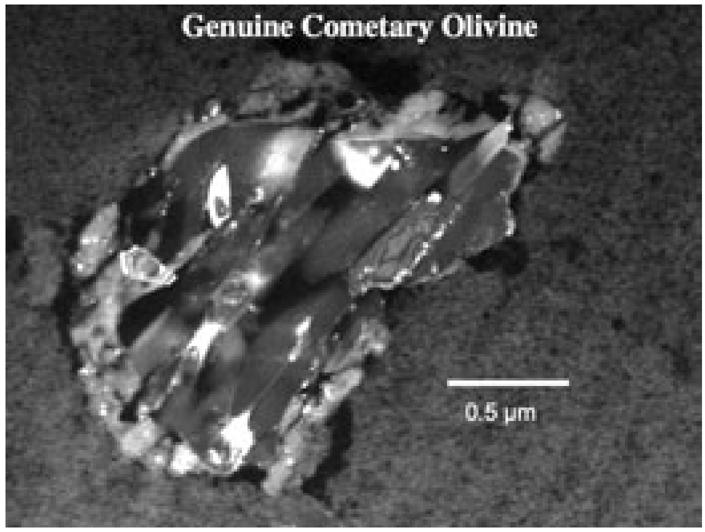

Figure 10: *HRTEM image of an olive crystal extracted from aerogel showing the common pervasive shattering of captured minerals. The narrow rim is S-rich glass with Fe-Ni-S inclusions. Silica glass could penetrate along fractures but when it occurred, it was recognizable. The background is an embedding medium.* **Photo credit NASA JSC**

Grains in tracks and terminal grains

A typical scenario for a comet particle with one or a few large (>5 µm) grains is that the particle gradually loses its numerous micron to nanometer sized subgrains during deceleration—depositing them along the entire track wall and the stylii (Figures 5 & 12). An entire track can be excavated intact from an aerogel tile to produce a keystone (Figure 11). In this way, with minimal interference by aerogel, measurements of grains along an entire track and other intact features were made, *e.g.* light-optical tomography, and a variety of chemical analyses [1,5,6]. Individual grains were extracted for analyses by Synchrotron XRD and XRF techniques, FTIR and Raman spectroscopy and HRTEM. A sample for HRTEM analysis had several serial ultramicrotome sections on a standard TEM grid prepared in an ultra-clean room at the NASA/JSC Curatorial Facility, thereby minimizing contamination of comet samples.

Minerals similar to comet grains occur in aggregate and cluster IDPs where they are well ordered, except when iron-oxidation had occurred. The abundance of beautiful, well-ordered, stoichiometric minerals in comet Wild 2 was truly amazing. The terminal grains were (1) Mg-rich olivine (Figure 10), with MnO and Cr_2O_3 each up to 1-wt%, (2) Mg-rich, low-Ca-pyroxene, (3) composite grains of about equal amounts of these minerals, and (4) mainly Fe,Ni-sulfide grains (Figure 13) [1,6]. The latter included an 8 µm grain identified as a large FeS crystal with a smaller low-Ca pyroxene crystal plus a fine-grained aggregate with a chondritic composition [1] that might be an example of surviving nanometer grains.

While the above-listed minerals are common, some terminal grains were amazing assemblages. For example, one composite refrac-

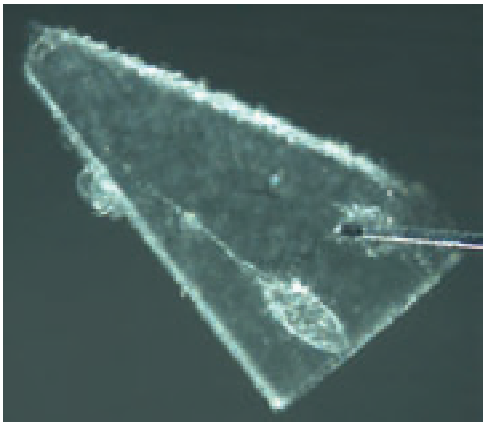

Figure 11: *A keystone with an intact bulbous track and a single stylus excavated from an aerogel tile using a specially developed technique for Stardust sample analyses [1,5,6]. The tack is several millimeters long. The blade on the right held the keystone during extraction.* **Photo by Hope Ishii/LLNL**

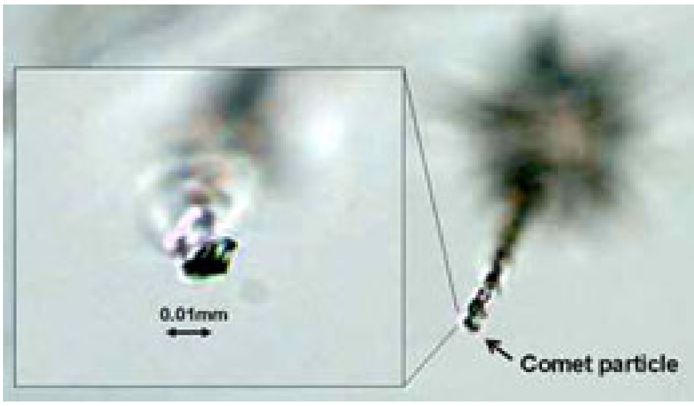

Figure 12: *This light-optical image shows a birefringent terminal grain (inset) looking up a track towards the penetration hole shown in the main image.* **Photo credit NASA JSC**

tory grain [1,6] was made up of high-temperature minerals (Figure 14). Such Ca-Al-Ti-rich minerals were previously found only in Ca-Al-rich inclusions in CV3 and CM2 carbonaceous chondrite meteorites and rare IDPs. Transport models predict that after formation near the sun, these minerals left the solar nebula via the sun's bipolar outflows, and were then transported to the Kuiper Belt to mingle with the dust from which comet Wild 2 accreted. Long-range transport models were now confirmed. Another terminal grain (track 56) was a sub- to micron grain sized composite of roedderite [$(Na,K)_2(Mg,Fe)_5Si_{12}O_{30}$], richterite (an amphibole mineral but no -OH yet reported), Na- and K-bearing silica glass, Mg-pyroxene, plus FeS [6]. It is extremely unusual to find such alkali-rich silicates in a comet. They are reminiscent of rare hyper-alkaline chondrules found in ordinary chondrite meteorites that make up about 85% of all meteorites. Chondrules are quenched-liquid droplets of uncertain origin but most certainly involved thermal processing of solar nebula dust and modification in asteroids. This bizarre terminal grain then also supports long distance dust transport.

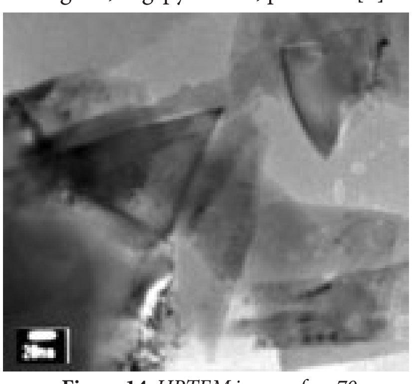

Figure 14: *HRTEM image of a ~70 nm euhedral spinel crystal (triangular on the left) found in the ~11 x 7 μm terminal grain of track 25. The geometric gray shapes are other comet grains. This composite grain is an assemblage of anorthite ($CaAl_2Si_2O_8$), gehlenite ($Ca_2Al_2SiO_7$), Ca-, Al, Ti-rich clinopyroxene, spinel, corundum, osbornite [(Ti,V)N] and perovskite ($CaTiO_3$) [6].* **Photo credit LLNL/JPL/NASA JSC**

Summary and future analyses

The STARDUST Preliminary Examination Team consisted of several sub-teams. I discussed HRTEM results from the Mineralogy/Petrology sub-team [6]. I invite the reader to peruse the papers and supplements in the special section of Science Magazine, 314, December 15, 2006. The captured grains are complex nanomaterials that pose a challenge to complete characterization using state-of-the-art techniques. Comet Wild 2 was a surprising mineralogical 'garbage bag'. Fortunately, the dark specter of hopeless contamination of the comet grains with silica did not happen and grain preservation is remarkably high. Excellent data will be forthcoming along with an understanding of all the implications. Our solar system is in the good mineralogical company of other young stars. The first olivine found settled the question: "are there Mg-silicate minerals in comet nuclei?" Models for long-range dust transport and dust aging are now an almost respectable new paradigm. Not a bad result after just one and a half year of scratching the tip of the iceberg. ■

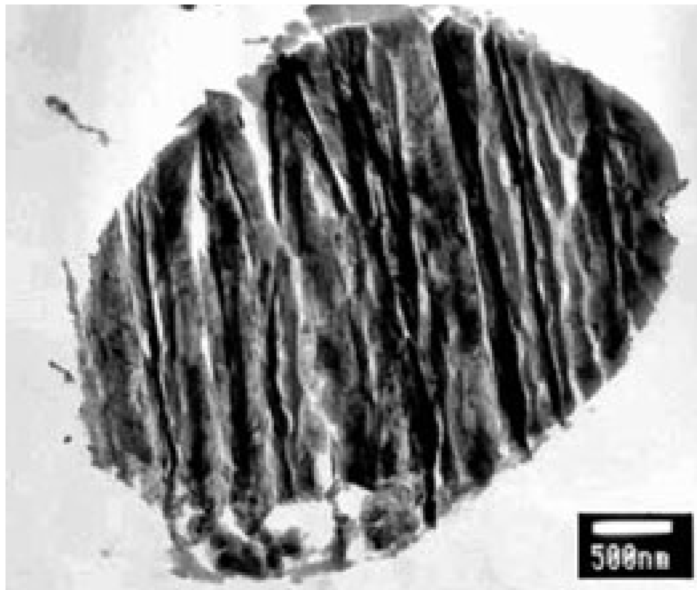

Figure 13: *HRTEM image showing a huge pyrrhotite terminal grain. The shattered appearance was caused during ultramicrotome section preparation. Similar artifacts were observed in pyrrhotite IDPs that experienced flash-heating and rapid cooling during deceleration in the atmosphere.* **Photo credit LLNL/JPL/NASA JSC**

Acknowledgments:

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References:

[1] D.E. Brownlee et al. Comet 81P/Wild 2 under a microscope. *Science* 314, 1711-1716 (2006).

[2] F. Hörz et al. Impact features on Stardust: Implications for comet 81P/Wild 2 dust. *Science* 314, 1716-1719 (2006).

[3] J. Borovička Physical and chemical properties of meteoroids as deduced from observations In *Asteroids, Comets, and Meteors* (eds. D. Lazzaro, S. Ferraz-Mello, J.A. Fernandez), Cambridge Univ. Press. Proc. IAU Symposium 229, pp. 249–271 (2006).

[4] F.J.M. Rietmeijer Interplanetary dust particles. In *Planetary Materials, Revs Mineral*., 36 (J.J. Papike, ed.), 2-1 – 2-95, Mineralogical Society of America, Chantilly, Virginia (1998).

[5] G.J. Flynn et al. Elemental compositions of comet 81P/Wild 2 samples collected by Stardust. *Science* 314, 1731-1735 (2006).

[6] M.E. Zolensky et al. Mineralogy and petrology of comet 81P/Wild 2 nucleus samples. *Science* 314, 1735-1739 (2006).

[7] D.J. Joswiak et al. A roedderite-bearing terminal particle from Stardust track 56: Comparison with rare chondrules in ordinary chondrites (abstract), *Lunar Planet. Sci*., 38, CD-Rom #2142, Lunar and Planetary Institute, Houston, Texas (2007); Other STARDUST papers delivered at this meeting can be found at http://www.lpi.usra.edu/meetings/lpsc2007/pdf/program.pdf

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