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Investigation of ion beam techniques for the analysis and exposure of particles encapsulated by silica aerogel: Applicability for Stardust

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Abstract–In 2006, the Stardust spacecraft will return to Earth with cometary and perhaps interstellar dust particles embedded in silica aerogel collectors for analysis in terrestrial laboratories. These particles will be the first sample return from a solid planetary body since the Apollo missions. In preparation for the return, analogue particles were implanted into a keystone of silica aerogel that had been extracted from bulk silica aerogel using the optical technique described in Westphal et al. (2004). These particles were subsequently analyzed using analytical techniques associated with the use of a nuclear microprobe. The particles have been analyzed using: a) scanning transmission ion microscopy (STIM) that enables quantitative density imaging; b) proton elastic scattering analysis (PESA) and proton backscattering (PBS) for the detection of light elements including hydrogen; and c) proton-induced X-ray emission (PIXE) for elements with Z >11. These analytical techniques have enabled us to quantify the composition of the encapsulated particles. A significant observation from the study is the variable column density of the silica aerogel. We also observed organic contamination within the silica aerogel. The implanted particles were then subjected to focused ion beam (FIB) milling using a 30 keV gallium ion beam to ablate silica aerogel in site-specific areas to expose embedded particles. An ion polished flat surface of one of the particles was also prepared using the FIB. Here, we show that ion beam techniques have great potential in assisting with the analysis and exposure of Stardust particles.

INTRODUCTION

Analytical instrument developments over the past 10 years have enabled new levels of mineralogical and chemical investigations of interplanetary dust particles (IDPs) (e.g., Dai et al. 2002; Messenger et al. 2003). Despite the comparisons that can be drawn between the composition of IDPs and astronomical features (e.g., Keller et al. 2002), it is currently not possible to unambiguously identify IDPs with specific parent bodies. The successful capture of near-intact particles using silica aerogel, first in the laboratory and then in low-Earth orbit (Barrett et al. 1992; Brownlee et al. 1994; Tsou 1995), lead to the NASA Discovery class mission Stardust, the first cometary sample return (e.g., Brownlee et al. 1997). In January 2004, the Stardust flyby of comet Wild 2 was successful, and it is expected that a large number of cometary particles were captured in the dedicated silica aerogel collector (Brownlee et al. 2004). The scientific community must now wait until January 2006 when the sample return capsule lands back on Earth to harvest the bounty of cometary particles and contemporary interstellar grains. Instruments already suitable for the analysis of IDPs are also suitable to carry out the analysis of the unique particles captured by Stardust (e.g., Zolensky et al. 2000; Stephan 2001). Despite the availability of instrumentation, there are a number of technical challenges to be resolved before sample return. Perhaps the most significant challenges are technical rather than scientific because the identification, extraction, and handling of small captured hypervelocity particles from silica aerogel is not straightforward (Tsou

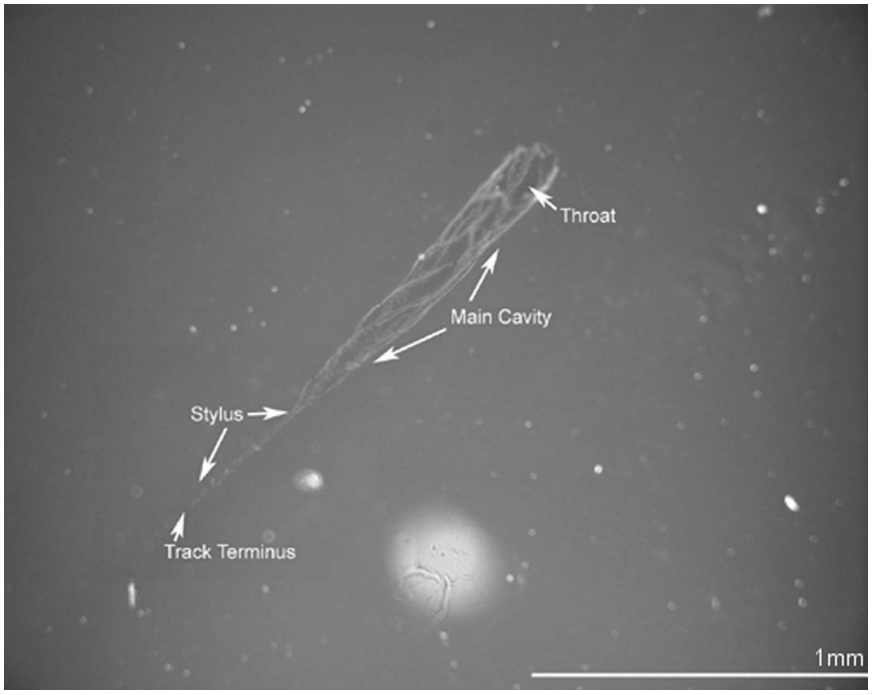

Fig. 1. Optical transmitted light micrograph of a hypervelocity impact track preserved in silica aerogel (density of 0.02 g/cm^3) from the NASA Orbital Debris Collector Experiment. The track terminology is taken from Hörz et al. (2000).

1995). Previous efforts at particulate extraction have included cleaving the aerogel apart using biological dissection razorblades to expose individual particles for extraction with a micromanipulator. Although extremely simple, this technique was used very successfully in the recovery of a number of particles (over 100) from the silica aerogel collector exposed on the Mir space station (Bernhard et al. 2000). However, this technique can lead to a catastrophic failure of the aerogel during the cleaving that results in the loss of particulate material (Stadermann and Floss 2000). Laser ablation extraction has also been used to recover particles accelerated into silica aerogel using a light-gas-gun (Graham et al. 2001). Westphal et al. (2002), using automated micromanipulators and glass micro-needles, extracted individual particles down to 3 μm in diameter and, more recently, keystones of silica aerogel containing entire impact tracks (Westphal et al. 2004). Beyond mechanical extractions, it is important to investigate emerging technologies that could be suitable for Stardust. Despite the range of extensive techniques available for small particle analysis (Zolensky et al. 2000), some of these techniques degrade volatile-rich materials, others produce contamination, and others require tailored specimen preparation. Therefore, it is important that application of the various analytical methods be hierarchical. Furthermore, since thousands of cometary particles may be captured, it is essential that analytical techniques capable of rapid and non-destructive in situ analysis be identified and evaluated. Synchrotron-based analytical techniques appear to be promising for making in situ measurements (e.g., Raynal et al. 2000; Flynn et al. 2001, 2003; Borg et al. 2002; Keller et al. 2003). Other small-scale laboratory-based techniques have been successfully applied to embedded particles, e.g., micro-Raman spectroscopy (Burchell et al. 2001; Kearsley et al. 2001; Graham et al. 2001). In this paper, which is the second in a series of research on extraction and analysis techniques relevant to Stardust carried out by BayPAC (Bay Area Particle Analysis Consortium), a consortium of Lawrence Livermore National Laboratory (LLNL), University of California at Berkeley, Ernest Orlando Lawrence Berkeley National Laboratory, and Stanford University, we discuss the applicability of ion beam techniques for the analysis of material embedded in silica aerogel using: i) a 3 MeV hydrogen ion beam; and ii) 30 keV focused gallium ion beam to expose embedded materials for subsequent detailed microanalysis.

PARTICLE CHARACTERIZATION USING A NUCLEAR MICROPROBE

The development of the extraction technique described in Westphal et al. (2002, 2004) is a significant milestone. However, it is only the first stage of the analytical strategy for Stardust particles. The initial scientific questions to be asked about the preserved particles will be very simple: what is their morphology, mineralogy, and bulk chemistry, and how do they compare to the current repository of IDPs?

When a particle is captured in silica aerogel as a result of a hypervelocity collision, a number of characteristic features

are generated (see Hörz et al. [2000] and Fig. 1). Silica aerogel experiments (e.g., NASA Orbital Debris Collector Experiment [ODC]) in low-Earth orbit (LEO) enable the investigation of "real" micro-particles captured in silica aerogel collectors; however, such impact events will have occurred over a range of velocities (typically >10 km/s). Therefore, these may not be representative of the features preserved in the Stardust collectors where the encounter velocity was approximately 6 km/s. The LEO-derived impact events tend to show a high degree of particle fragmentation on the micron and sub-micron scales (e.g., Hörz et al. 2000; Westphal et al. 2004). Therefore, it is reasonable to assume that if cometary particles are similar to fluffy anhydrous IDPs, they may exhibit similar behavior upon collision with the silica aerogel collectors, even at the lower velocity.

If the Stardust silica aerogel collectors return with a number of impact events showing fragmentation of the cometary debris, then one of the critical tasks will be to obtain a true representative composition. Therefore, any preliminary characterization will scan the entire impact event for cometary debris. Ideally, the applied technique will have limited or no detrimental effects on the encapsulated particles. The major and minor elemental compositions of IDPs have been successfully investigated using nuclear microprobe techniques (e.g., Arndt et al. 1996; Wies et al. 2002). However, the techniques have not been widely used in cosmic dust research despite being relatively non-destructive (Zolensky et al. 2000). Thus, nuclear microprobe analysis could be well-suited for characterizing captured particles due to the ability of the primary beam to penetrate the silica aerogel and the adequate signal that can be detected during sample-beam interactions (Morse et al. 1997). These interactions can be detected in a number of ways: a) scanning transmission ion microscopy (STIM) that enables quantitative density imaging; b) proton elastic scattering analysis (PESA) and proton backscattering (PBS) for the detection of light elements including hydrogen; and c) proton-induced X-ray Emission (PIXE) for elements with Z >11.

Sample Preparation

For the experimental work described here, 20 mg/cc silica aerogel manufactured at NASA/JPL by Dr. Steve Jones was used. Previous laboratory simulations that mimic the Stardust capture have used light-gas-guns, as these enable the acceleration of the projectiles at the mission encounter velocity of 6.1 km/s (e.g., Hörz et al. 1998; Burchell et al. 2001). However, because the initial purpose of the analysis described here was to investigate the suitability of the nuclear microprobe, specially selected particles were chosen that would test the analytical techniques. Therefore, hypervelocity acceleration of materials was not required. A glass micro-needle has been used to implant the following materials into the bulk aerogel at approximately 10 μm depth: a) a tungsten sphere (10 μm in diameter) because it has extremely high density compared to the silica aerogel and should, therefore, be easily detected using STIM, and since it is a high Z element, it should be easy to map using PIXE; b) a polystyrene sphere (7 μm in diameter) to evaluate the possibility of detecting organic species during the initial characterization using PESA and PBS; c) a fragment of the matrix material from the Orgueil meteorite to represent a complex unknown meteorite material, as it is possible that Stardust may return particle compositions that, as yet, have been routinely identified in IDPs (Fig. 2). While the manual embedding technique does not allow the investigation of impact effects such as shock and thermal alteration on the particles, it does enable a wide range of particles, including IDPs, to be embedded into silica aerogel. This allows the nuclear microprobe's ability to detect both inorganic and organic material in a wide range of particles to be tested. After implantation, a small wedge or the so-called "keystone" of aerogel containing the analogue particles was extracted from the bulk using the mechanical recovery techniques described in Westphal et al. (2004).

The silicon microforklifts that are used to extract the keystones from bulk silica aerogel have been designed to integrate with a number of instrument mounts including the nuclear microprobe. Therefore, the keystone did not need to be mounted on any support film that could cause contamination or limit the interpretation of the acquired data. The keystone was mounted within the microprobe target chamber with the largest dimension in the vertical axis. The top surface of the keystone was normal to the incident beam direction, and it was oriented so that the embedded particles were facing downstream from the incident beam.

Scanning Transmission Ion Microscopy (STIM)

For all analyses, an incident 3 MeV proton beam was focused onto the keystone. As STIM uses ~10^6 lower beam currents than PESA, PBS, and PIXE, the initial analysis was by STIM. Using STIM, it is possible to quantify the column density of the silica aerogel and the embedded particles by measuring the energy lost from the 0.5 μm focused incident beam as it traverses the sample (Lefevre et al. 1987). The simple physics involved in this ion energy loss mechanism, combined with available accurate databases, enable the ion energy losses to be readily converted into specimen-projected densities, which can be used to determine specimen mass (Lefevre et al. 1987; Lefevre et al. 1991; Bench et al. 1993). STIM has been used previously to determine the densities of thin material films of known density and composition (Bench 1991). Conversion of energy losses to densities using the known material composition established that the technique is quantitative, with ann accuracy >95% in determining sample densities, as demonstrated in Bench (1991). The keystone sample was subjected to an initial coarse STIM scan that was

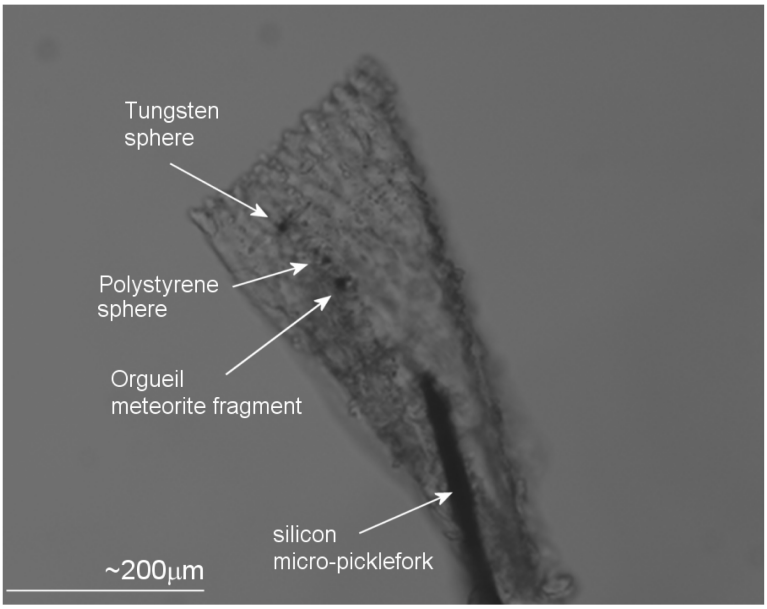

Fig. 2. Optical transmitted light micrograph of the silica aerogel keystone containing the embedded particles of tungsten, polystyrene, and Orgueil meteorite fragment. The keystone was extracted from bulk silica aerogel using the technique described in Westphal et al. (2004).

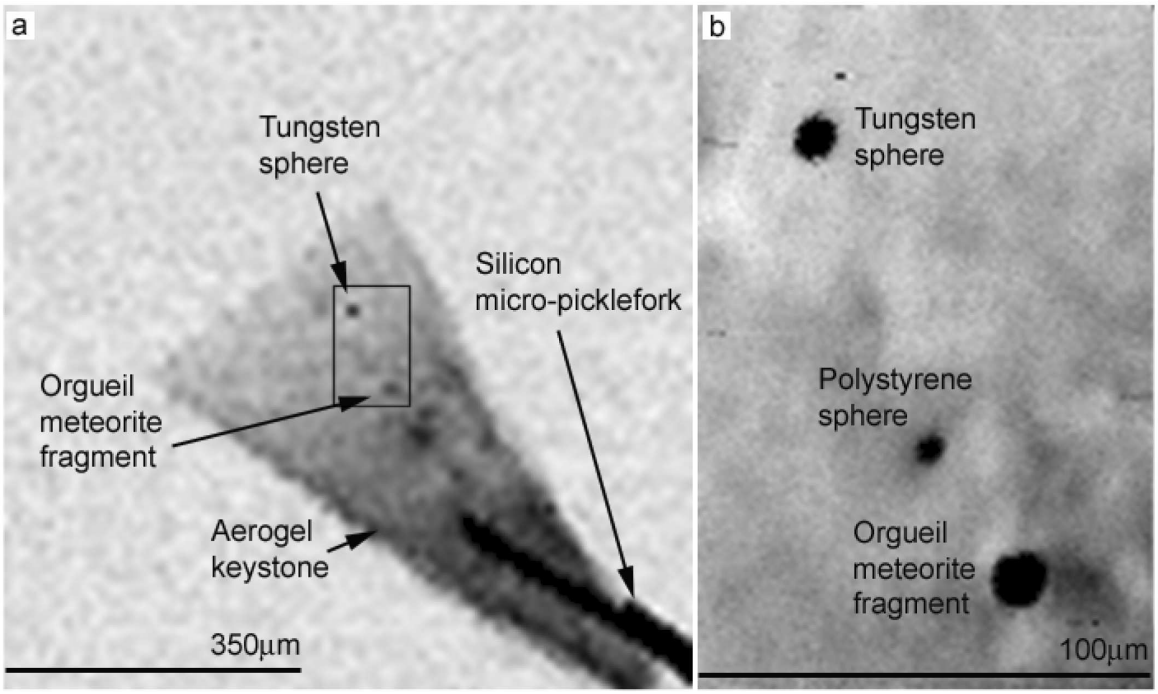

Fig. 3. a) STIM scan over the entire sample. In the image, it is clearly possible to see one of the supporting micro-forks. From the image, it is possible to see the variable column density of the silica aerogel; b) the high resolution scan of the region of interest highlighted in the coarse scan (black rectangular box) shows the particles of interest.

carried out over the entire sample (Fig. 3a) and then a high resolution scan over the area of interest containing the particles (Fig. 3b). From the STIM scans, it is noted that the silica aerogel has a variable density with an average density of 550 ± 40 μg/cm^2 (calculated from the high resolution scan). Despite the variation, the three embedded particles are clearly visible in the high resolution scan (Fig. 3b). Areal density (μg/cm^2) is converted to mass by integrating the areal density of the particle over the area of the region of interest exposed to the particle beam. The tungsten sphere has a measured mass of 9.0 ± 0.7 ng that compares well to the predicated mass of 10.1 ng. The measured mass for the polystyrene

sphere of 0.19 ± 0.02 ng agrees with its predicated mass of 0.19 ng. The Orgueil fragment has a measured mass of 2.6 ± 0.4 ng. Error estimates are made by the addition in quadrature of 1σ for counting statistics and error propagation of the following analysis parameters: pixel size, beam energy, energy loss equation, etc. The major advantage of STIM is that virtually every incident ion produces useful information in traversing the sample, i.e., the technique is nearly 100% efficient (Lefevre et al. 1991). Consequently, even with low beam currents, data acquisition is rapid. Therefore, a number of high resolution STIM scans could be used to locate fragmented debris; however, the experimental parameters used here do not allow for a complete assessment, and previous work has indicated that most material mass is lost during melting, a process that will occur during hypervelocity capture (Anderson and Ahrens 1994). It is also expected that Stardust will capture a wide range of materials from single crystal grains (e.g., forsterite) to complex heterogeneous particles similar to anhydrous IDPs. Even though the densities of these materials vary, it will be possible, with the current capabilities, to use STIM to rapidly select materials of immediate interest with a diameter of down to 0.5 μm. A complication to the application of STIM to "real" impact events is that the particles are typically coated with a condensed aerogel ablation shield that forms during the hypervelocity impact event (Hörz et al. 2000). This condensed material could lead to false STIM estimation of density; however, as we combine the STIM measurements with PIXE elemental analysis, it should be possible to discriminate between the ablation material and the particulate debris. Furthermore, any measurements acquired while the particles are still encapsulated must be viewed as only preliminary guidance to the composition and nature of the captured material.

By acquiring multiple STIM scans in multiple directions through a sample, it is also possible to carry out ion microtomography (IMT) (Pontau et al. 1989). Cross-sectional views and three-dimensional reconstructions can be acquired, both of which would be very useful in studying impact morphologies, as these are three-dimensional events.

Proton Elastic Scattering Analysis (PESA) and Proton Backscattering (PBS)

With PESA, protons with energies above 1 MeV that elastically scatter from target atoms into forward angles can be detected by a particle detector (Cahill et al. 1987). Some of the kinetic energy of the projectile ion is absorbed by the recoiling target atom because the recoil energy depends on the target mass. By measuring the energy of the scattered ions, it is possible to discriminate between ions scattered from H and ions scattered by other elements. Integrating the number of ions scattered from H gives a quantitative measure of the sample hydrogen content. This technique works best for samples with small column densities in which proton-slowing by ordinary electronic stopping is small.

To acquire an H distribution map for the embedded particles (Fig. 4), the 3 MeV proton beam was focused to a 2 μm spot size as it was scanned across the region of interest within the keystone. A beam current of approximately 0.9 nA and a charge of 1.5 μC were deposited over the scanned region. The PESA data were recorded in list mode along with coincident beam spatial coordinates arising from scanning. The data was subsequently processed off-line using the in-house ion microanalysis package (IMAP) developed by Lawrence Livermore National Laboratory/Sandia National Laboratories (Morse et al. 1999). To measure the H content of the polystyrene sphere and the Orgueil meteorite fragment, it was first necessary to calculate the H content of the silica aerogel background. The PESA data suggests that the silica aerogel has a variable H content that was averaged for the scanned region to be 0.29 ± 0.02 μg/cm^2. The H content for the polystyrene sphere was measured to be 10.2 ± 1.5 pg (the predicated mass is 14.6 pg), and the Orgueil fragment was 2.4 ± 0.9 pg.

Coupled with the ability to detect H enrichments in situ, further identification of light elements (C, N, and O) is possible by measuring the energies of the backscattered particles from the incident 3 MeV proton beam that have collided elastically with the sample (Cookson 1987; Fraser 1995). The acquired proton backscattered spectrum will retain high-energy edges corresponding to the backscattering from atoms with different masses within the sample, thus making elemental detection possible (Fraser 1995). For proton backscattering analysis of the keystone, the detection is accomplished with a 100 mm^2 silicon surface barrier particle detector. The detector is located 55 mm from the sample and subtended a mean scattering angle of 1600. The particles were recorded in list mode along with coincident beam spatial coordinates arising from electrostatically scanning the 2 μm in diameter beam spot. Data were reduced off-line, and spectra from features of interest within scanned regions were extracted and analyzed using IMAP (Morse et al. 1999) (Fig. 5). The spectrum acquired for the silica aerogel (Fig. 5a) detected, not surprisingly, Si and O, but it also detected trace levels of C (2 ± 1 μg/cm^2). It is not possible to state the nature of the C in terms of inorganic or organic components. However, identification of both H and C within the silica aerogel could indicate indigenous organic relics from the silica aerogel-forming process or background terrestrial contamination. Previous analyses of silica aerogels have indicated both of these to be the case (Hartmetz et al. 1990, Barrett et al. 1992, Wright et al. 1994). This indigenous organic material may be a problem for Stardust analysis because if, as expected, the cometary particles are similar to chondritic anhydrous IDPs, they are likely to be carbon-rich. Therefore, it could be impossible to unambiguously state the origin of organic material identified by in situ measurements.

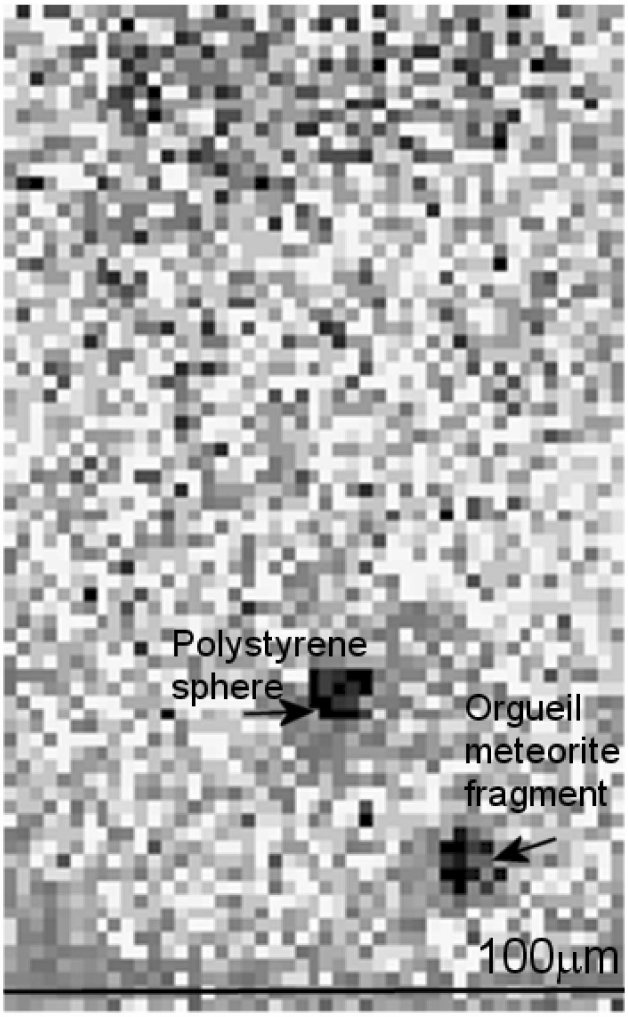

Fig. 4. Distribution of H acquired using PESA for the region of interest within the "keystone" that contains the embedded particles.

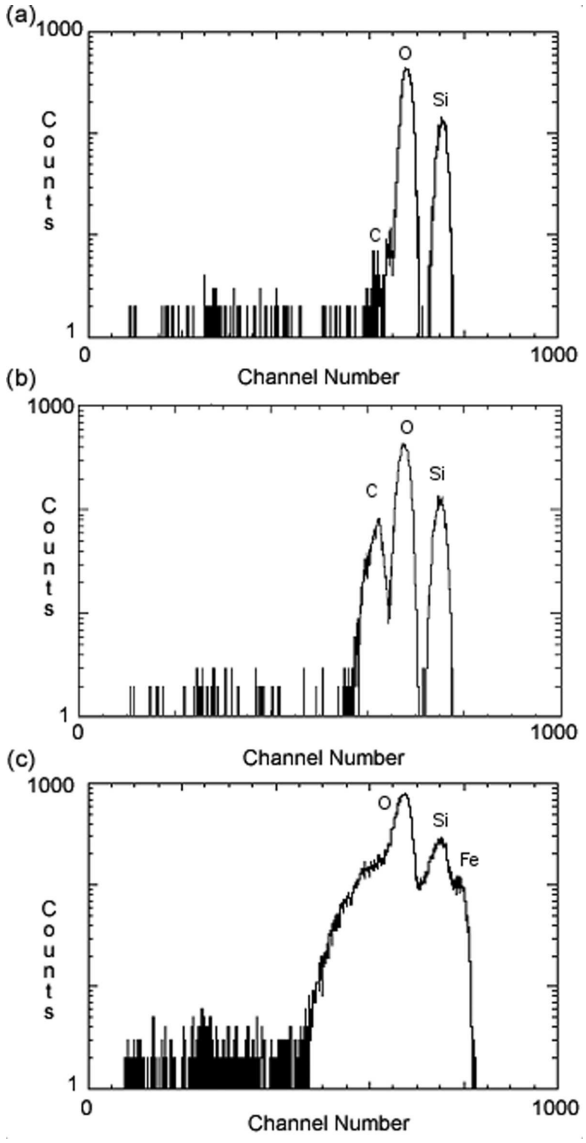

Fig. 5. a) Proton backscattered spectra acquired for the silica aerogel substrate; b) polystyrene sphere; c) Orgueil fragment. The spectra were obtained for a total beam charge of 1 μC.

Detailed characterization of the Stardust flight-grade silica aerogel similar to the work carried out by Hartmetz et al. (1990) and Wright et al. (1994) before the return should enable a great degree of confidence in potential levels of organic contamination.

The PBS spectrum for the polystyrene (Fig. 5b) detected C and O with Si from the silica aerogel. The C content was measured as 150 ± 20 pg, a level that compared favorably with the predicated C content of 174 pg. The PBS spectrum for the Orgueil fragment (Fig. 5c) was considerably different to the silica aerogel and the polystyrene sphere. No significant C was detected, and both the Si and O signals were background-corrected for the silica aerogel contributions. The analysis also detected Fe that could be associated with silicate or metallic phases within the fragment. The high Fe content of the particle and the overall size and geometry of the fragment in relation to the detector prevented the identification of the C (minimum detectable limit of approximately 200–300 pg) and the accurate quantification of the O content (approximately 800 ± 400 pg).

While advances in instrumentation have lead to a new level of understanding the nature and origin of organic material in meteorites (e.g., Sephton 2002; Cody et al. 2002), the characterization of organic material in IDPs has been a much harder task due to the small sample size/concentration levels and it requires highly specialized analysis, e.g., tagging a sample using specific fluorescent molecular probe or C-XANES analysis (Clemett et al. 2002; Flynn et al. 2003). Such analysis of the Stardust particles would certainly require that they are free from the silica aerogel. Notwithstanding the potential contamination problem, the combined analysis of PESA and PBS would enable a preliminary identification and

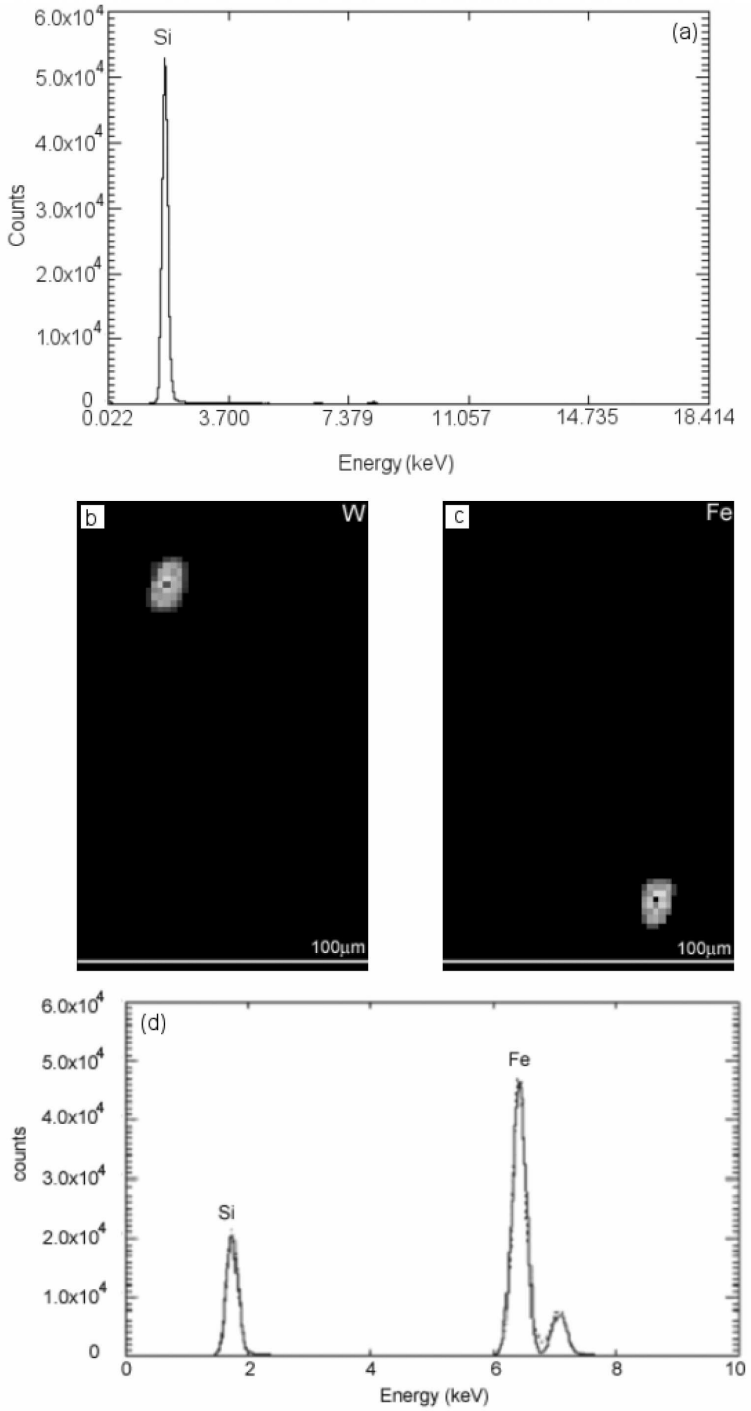

Fig. 6. a) PIXE spectrum acquired from the background aerogel; b) PIXE elemental map for W; c) PIXE elemental map acquired for distribution of Fe in the Orgueil meteorite fragment; d) PIXE X-ray spectrum acquired for the Orgueil fragment after processing.

screening for the C-rich particulates preserved in the silica aerogel, so these particulates could then be extracted and analyzed in further detail.

Proton-Induced X-Ray Emission (PIXE)

Of all the analytical techniques associated with nuclear microprobe analysis, PIXE is the most common and is used in material, geological, and planetary sciences (e.g., Fraser 1990; Arndt et al. 1996; Wies et al. 2002). PIXE uses a high-energy (MeV) proton beam that interacts primarily with atomic electrons within the sample to create vacancies in inner shell orbitals. When an outer shell electron fills a vacancy, the excess energy resulting from the transition can be released as

an X-ray photon, the energy of which is characteristic of the emitting atom. The proton-induced X-rays produced from the interaction between the 2 μm focused 3 MeV proton beam and the keystone were detected with an energy dispersive Iglet-X X-ray detector, manufactured by Ortec, that subtended a solid angle of ~200 milli-steradians to the specimen. The detector is located at an angle of 135° with respect to the incident beam. As the beam is scanned across the region of interest within the keystone, X-ray energy spectra are stored for each beam location. The total charge deposited over the scanned area was approximately 1 μC. After data acquisition, maps of element concentrations and X-ray spectra from beam locations corresponding to embedded particles were generated using IMAP (Morse et al. 1999) (Fig. 6).

The data acquired from the silica aerogel did not identify any elements with a Z of 12 or below (Fig. 6a). These may well be present, but the current configuration of the energy-dispersive X-ray detector inhibits the detection of low energy X-rays due to the Be window used to protect it from moisture and backscattered protons. The analysis indicated that the density of Si was variable, with an average density for the scanned region of 284 ± 30 μg/cm^2. This value compares well with the calculated Si density measured by STIM of 260 ± 20 μg/cm^2 (assuming that the silica aerogel was composed solely of Si and O). PIXE is not particularly well-suited for light element detection, so no significant measurements were recorded for the polystyrene sphere. The main elemental data acquired from the PIXE analysis was for the tungsten sphere (Fig. 6b) and the Orgueil fragment (Figs. 6c–6d). From the PIXE data, the mass of the embedded tungsten sphere was measured to be 9.8 ± 0.5 ng and was in agreement with the measured STIM mass (9.0 ± 0.7 ng) and the calculated mass (10.1 ng). As the Orgueil fragment was extracted from the matrix of the meteorite, which is heterogeneous on the μm-scale, it represented a more realistic analogue to the material that might be encountered by Stardust. The data acquired from the Orgueil fragment was background-corrected for the contribution of Si from the silica aerogel; the major elemental component identified was Fe (Figs. 6c–6d). The other detected elements are given in Table 1. At present, it is not possible to detect Mg at low levels, so we could not determine if the Fe was associated with a silicate or simply a metallic phase (oxide or metal). Later characterization by X-ray diffraction at the Natural History Museum in London found the major mineralogical composition to be magnetite (Fe_3O_4).

Using PIXE, we have successfully imaged and quantitatively analyzed elements with Z >11 in the embedded particles. However, it has been highlighted in this work and by previous researchers (Zolensky et al. 2000) that there are significant detection limits with light elements that are beyond the quantitative capabilities of the current Ortec Iglet-X X-ray detector used. The analytical range of the microprobe for the sensitive quantitative analysis could be extended to include elements from C to Na and to increase the sensitivity for the detection of Mg and Al by using a windowless detector.

Table 1. Elemental data acquired from the embedded Orgueil meteorite fragment with a mass of 2.6 ± 0.4 ng (from the acquired STIM data) using analysis techniques associated with the nuclear microprobe at LLNL.

Technique	Element	Content (pg)	Wt% of STIM mass
PESA	H	2.4 ± 0.9	0.1
PIXE	Al	10 ± 3	0.4
PIXE	Si	83 ± 24	3.2
PIXE	S	36 ± 6	1.4
PIXE	Ca	5 ± 2	0.2
PIXE	Cr	2.6 ± 0.3	0.1
PIXE	Mn	2.4 ± 0.4	0.1
PIXE	Fe	1330 ± 140	51.9
PIXE	Ni	16 ± 2	0.6
PBS	O	800 ± 400	31
Sum of STIM mass wt%			89.0

Disadvantages of Nuclear Microprobe Analysis

There are several limitations in using the nuclear microprobe for in situ analysis. First, it has already been shown that, with the current Be window and energy dispersive detectors, there is a limit in the detection of light elements. Second, while STIM is essentially non-destructive because the technique uses million-fold lower beam currents than the other techniques (PESA, PBS, and PIXE), which are generally assumed to be only partially non-destructive, as there is potential for sample damage from the higher beam currents employed. Previous researchers have studied the alteration of stoichiometry in a sample due to the loss of H and O during repeated PESA analysis (Delto et al. 2002). However, it is possible to limit the potential beam damage by reducing the overall total charge deposited on the sample during the analysis. Furthermore, collecting PESA, PBS, and PIXE concurrently can reduce the acquisition time for data collection.

FOCUSED ION BEAM MICROMACHINING OF SILICA AEROGEL

When developing a strategy for the characterization of the cometary particles to be returned by Stardust, it is important to have analytical techniques that can be employed in the preliminary stages for the post-flight program to study aerogel encapsulated cometary material. However, detailed mineralogical and chemical investigations will need sample preparation and almost certainly will require the particulate fragments to be free of silica aerogel. Westphal et al. (2002) showed that individual particles as small as 3 μm in diameter could be extracted intact from silica aerogel. However, it is

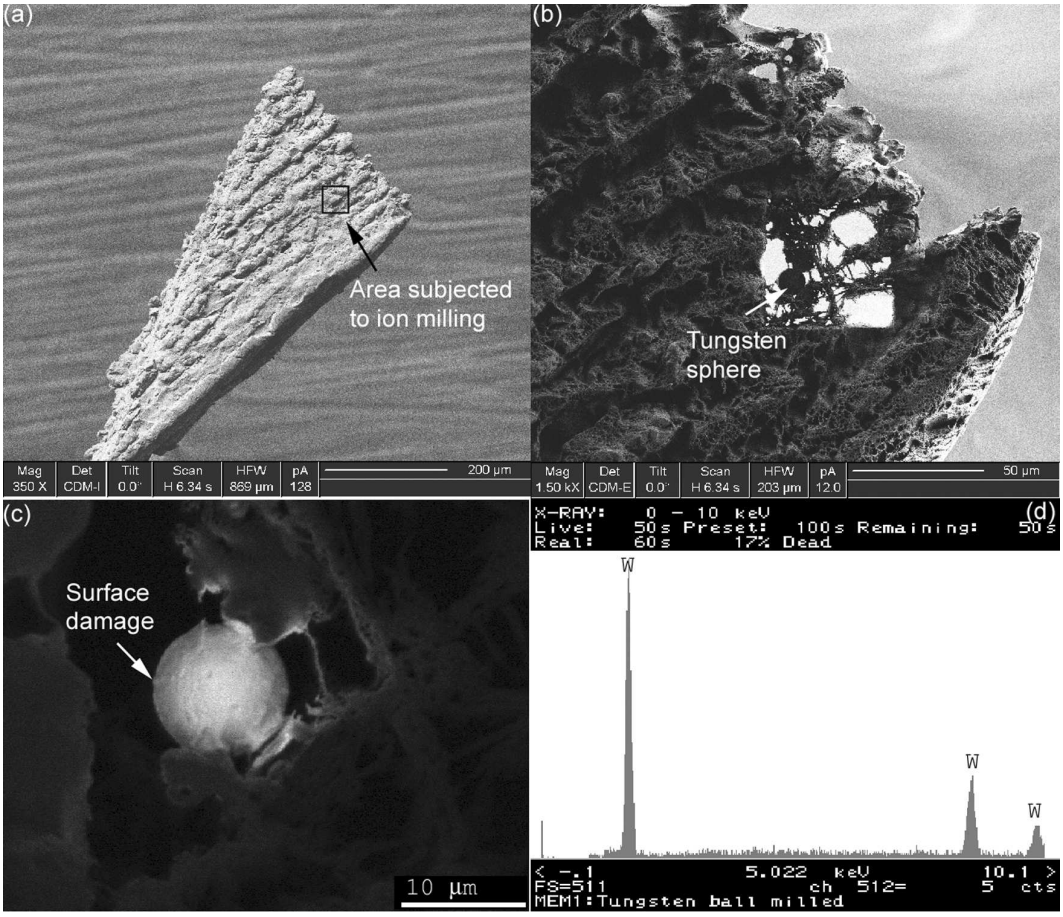

Fig. 7. a) Ion micrograph of the intact silica aerogel keystone; b) secondary electron micrograph of the keystone after the encapsulating silica aerogel has been removed by rastering the Ga^+ ion beam across the selected 50 µm × 45 µm rectangular area. The tungsten sphere is clearly visible in the center of the image; c) backscattered electron micrograph of the tungsten sphere. The white arrow locates the slight surface damage sustained by the tungsten sphere by the Ga^+ ions; d) the X-ray energy dispersive spectrum acquired for the tungsten sphere.

unlikely that the same technique could be employed on sub-µm-sized fragments.

Ion beam techniques can be used for analysis and can also be employed to micromachine or microfabricate materials. Focused ion beam (FIB) microscopy was principally used in the semiconductor industry, as it enabled the in situ manipulation and machining of materials on the sub-micron scale (e.g., De Veirman and Weaver 1999; Lábár and Egerton 1999). FIB microscopy uses a focused beam of Ga ions to ablate volumes of material from precise locations and at carefully controlled rates (see Phaneuf [1999] for a detailed discussion on design and operation of the FIB microscope). The significant benefit of the technique is that the sample can be imaged with nm-scale resolution during the ion milling using both ion and secondary electron imaging. The technique has been used in both geological and planetary sciences to prepare electron-transparent thin sections of materials (Heaney et al. 2001; Stroud et al. 2002; Stroud 2003; Lee et al. 2003). Apart from this more traditional use of FIB, it has also been shown that the technique can be used to remove the silica aerogel film that coats the surface of particles that have been laboratory impacted and subsequently recovered from silica aerogel (e.g., Graham et al. 2002). This suggested that FIB could be used to expose particulates in the silica aerogel.

Using an FEI 200TEM workstation, the tungsten sphere and the Orgueil fragment have been subjected to site-specific ion milling to remove the silica aerogel covering them. From the initial ion image of the keystone, it was not possible to locate the particles. However, it was possible to match topographic features from the optical transmitted light micrograph of the keystone (Fig. 2) or the STIM image (Fig. 3) and the ion image (Fig. 7a) to indicate the approximate location of the tungsten sphere. An 50 µm × 45 µm area was selected around this region of interest, and the silica aerogel was subsequently removed by rastering the 400 nm spot-sized gallium ion beam at 30 kV with a 20 nA beam current until the tungsten sphere was exposed (Fig. 7b). During the milling that took approximately 7 min, the entire process was monitored by collecting secondary electron images. Despite the monitoring, the silica aerogel was ablated at such a rapid rate that the top surface of the

tungsten sphere was also subjected to slight ion milling (Fig. 7c). It is also clear from the acquired images that the ion beam can have detrimental effects on the supporting silica aerogel. This is evident because there is a distinct difference in the edge of the silica aerogel between the initial ion image and the secondary electron image acquired after the milling, as some material has been lost. Additional imaging and microanalysis of the tungsten sphere were carried out using a conventional JEOL 840 scanning electron microscope (Figs. 7c–7d). It would be expected that, after in situ characterization, exposed particles would be removed from the supporting silica aerogel using a micromanipulator.

If the observations from particles captured on LEO exposed silica aerogel collectors provide an accurate analogue to how the Stardust particles will be preserved, then it is entirely possible that some fragments may be on a scale that prohibits intact extraction. Therefore, this material would have to be analyzed in situ. As has already been discussed, there are limitations to such analysis particularly because of backgrounds due to contamination in the silica aerogel. However, FIB can be used to remove the encapsulating silica aerogel and also to prepare a polished section of sample while it is still surrounded by silica aerogel. The Orgueil fragment was subjected to an initial milling procedure (i.e., ion beam focused to 400 nm with a 20 nA beam current) similar to that of the tungsten sphere to remove the silica aerogel. The entire sample was then tilted to 45°, and the Orgueil grain was subjected to further ion milling at initially high beam currents to remove the outer surface of the grain but then at progressively lower currents of 10000, 7000, and then 5000 pA to clean up the milled surface (Fig. 8a). After the sample is orientated back to a normal 0° of tilt, the top surface of the grain has now been polished flat (Fig. 8b), and the sample can be analyzed using a number of electron and ion beam techniques (Fig 8c). By preparing the sample this way, any contaminating silica aerogel is removed.

There are a number of disadvantages to using FIB for particle extraction. First, compared to an optical system, the instrumentation is very expensive (a typically system costs around $1 million). Second, during the ion milling process, it is possible to generate imaging artifacts at the high beam currents, although these are typically removed by the final "cleaning" stages of the milling procedure that are carried out at lower beam currents (Fig. 8b). Third, it is possible to deposit an amorphous film (nanometer thick) on the surface that has been milled during the higher beam current stages. Again, this can be nearly completely removed by the final stages of the sample preparation (Lee et al. 2003). Perhaps one of the most significant disadvantages is that older FIB microscopes use the ion beam to mill and image the sample. It would appear that prolonged exposure of the silica aerogel under the ion beam could cause it to disintegrate. This potential problem can also be resolved by the fact that modern

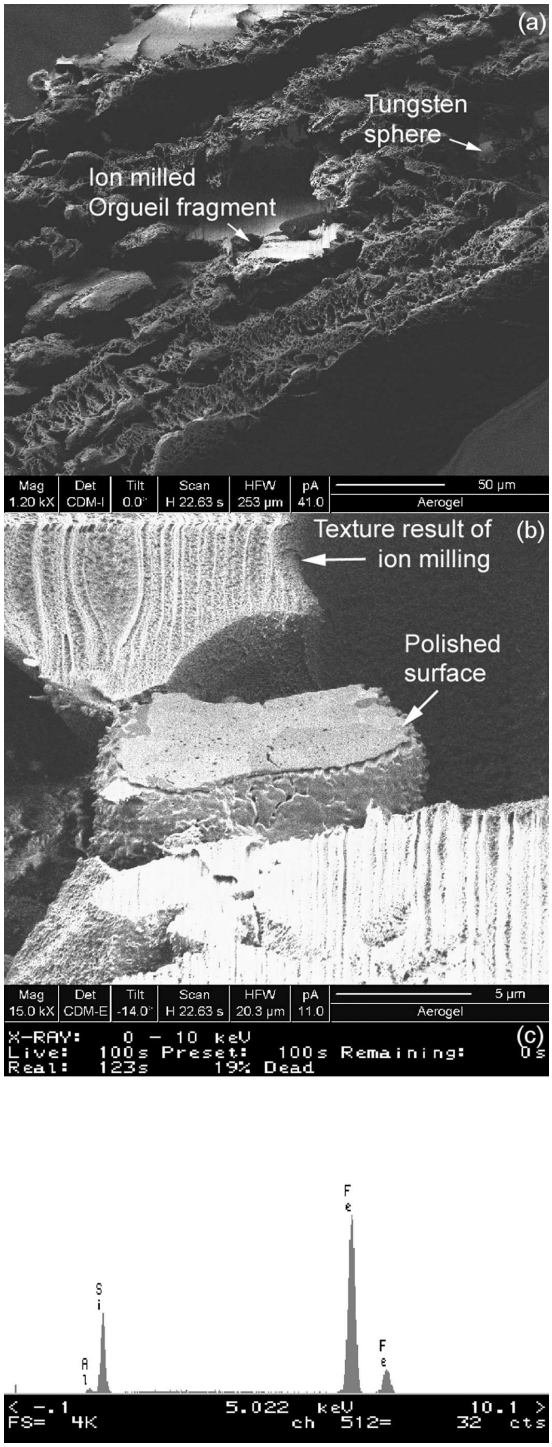

Fig. 8. a) Secondary electron micrograph of the embedded Orgueil meteorite after the top surface of aerogel has been removed by the ion milling; b) secondary electron micrograph of the fragment after the ion beam has been used to produce a polished flat surface. The polished surface appears to show some structural or crystallographic phase information. The surface structure observed on the surrounding silica aerogel (indicated by a white arrow) is an artifact of the milling process; c) the X-ray energy dispersive spectrum acquired for the fragment.

fully equipped FIB systems use dual beam technologies: all the imaging is carried out using the electron beam, while the ion beam is used for the milling. Furthermore, these newer instruments now typically include a scanning transmission electron microscopy detector (for high resolution imaging), electron backscattered diffraction detection (for crystallographic analysis), and energy-dispersive X-ray detection (for elemental analysis).

Since there are multiple potential benefits from using an "all-in-one" instrument to prepare and chemically analyze samples at the initial stages of particle characterization, it is clear that FIB microscopy will play a significant role in the characterization of Stardust materials.

SUMMARY

The observation that micrometeoroids captured in LEO fragment upon impact suggests that the cometary particles captured by Stardust will also have fragmented. Therefore, it is important to develop techniques capable of analyzing embedded materials. The nuclear microprobe at Lawrence Livermore National Laboratory has been successfully used to characterize embedded particles in low-density silica aerogel using STIM, PESA, PBS, and PIXE. The combination of these techniques allows for the detection of both inorganic and organic components within a particle, while still encapsulated in silica aerogel.

While it is important to have the capability of acquiring measurements from embedded particles, further investigations of mineralogy and chemistry will require the particles to be extracted from the silica aerogel. This was originally shown to be possible using a mechanical recovery technique (Westphal et al. 2002, 2004). It has now been shown that FIB microscopy can be used to rapidly ablate the silica aerogel encapsulating embedded particles, leaving the particles exposed and in a configuration suitable for further detailed characterization while still in the silica aerogel or after extraction using micromanipulators. We will now employ these techniques on micrometeoroids captured in collectors that have previously been exposed in LEO.

By applying and learning from these techniques now, we will be ready for the return of the precious Stardust particles in 2006.

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