A Hybrid Ultramicrotomy-FIB Technique for Preparing Serial Electron Transparent Thin Sections from Particulate Samples

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Introduction

Successful analyses of small particulate samples using multiple micro- and nano-beam analytical techniques depends critically on how the samples are prepared. Our focus is on coordinated analyses by transmission electron microscopy (TEM), synchrotron-based X-ray techniques, infrared spectroscopy, and ion microprobe methods, all of which require thin, continuous cross sections of particulate samples. Traditionally, particulate samples have been prepared using microtomy techniques [1]. However, for hard mineral particles ≳20 µm, microtome thin sections are compromised by severe chatter and sample loss. For these difficult samples, a hybrid technique was developed that combines traditional ultramicrotomy with focused ion beam scanning electron microscope (FIB-SEM) techniques, allowing for the *in situ* investigation of grain surfaces and interiors. Using this method, the number of FIB-SEM prepared sections that can be recovered from a particle with dimensions on the order of tens of micrometers is substantially increased, say from 1 or 2 sections to 10–15. These sections can be subsequently analyzed using a variety of electron beam techniques. Our purpose in developing this technique was to optimize preparation of electron transparent specimens from precious extraterrestrial particles.

Recent sample return missions, such as NASA's Stardust mission to comet 81P/Wild 2 and the Japan Aerospace Exploration Agency's (JAXA's) Hayabusa mission to asteroid 25143 Itokawa, have returned particulate samples (typically ~5–50 µm) that pose tremendous challenges to coordinated analysis using a variety of analytical techniques. In light of the rarity of these samples, the ability to glean maximal information from individual particles has become increasingly important. This also holds true for other extraterrestrial materials, including interplanetary dust particles, micrometeorites, and lunar regolith grains. The Itokawa grains provide our first direct insights into space weathering processes on asteroid surfaces. These particles record microstructural and chemical evidence of their exposure to the space environment. Surface exposure to the solar wind results in radiation damaged rims, whereas impact processes produce adhering

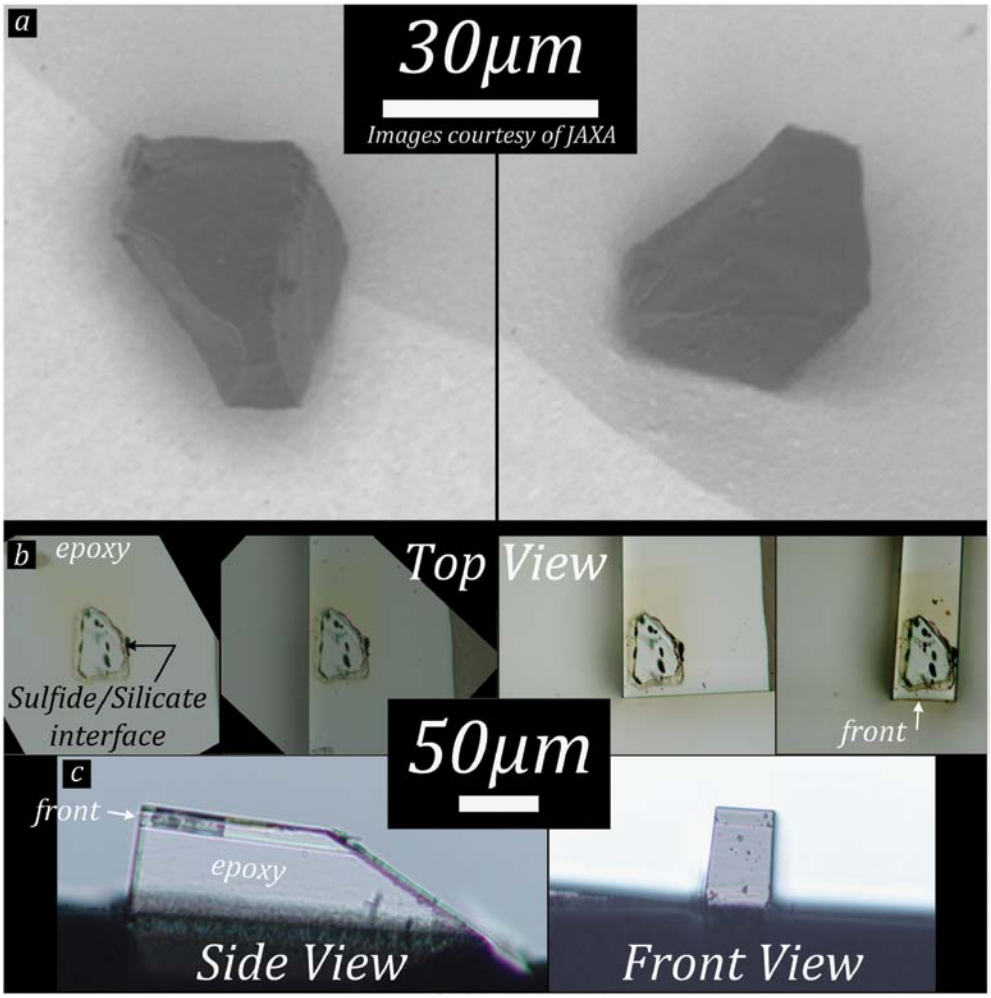
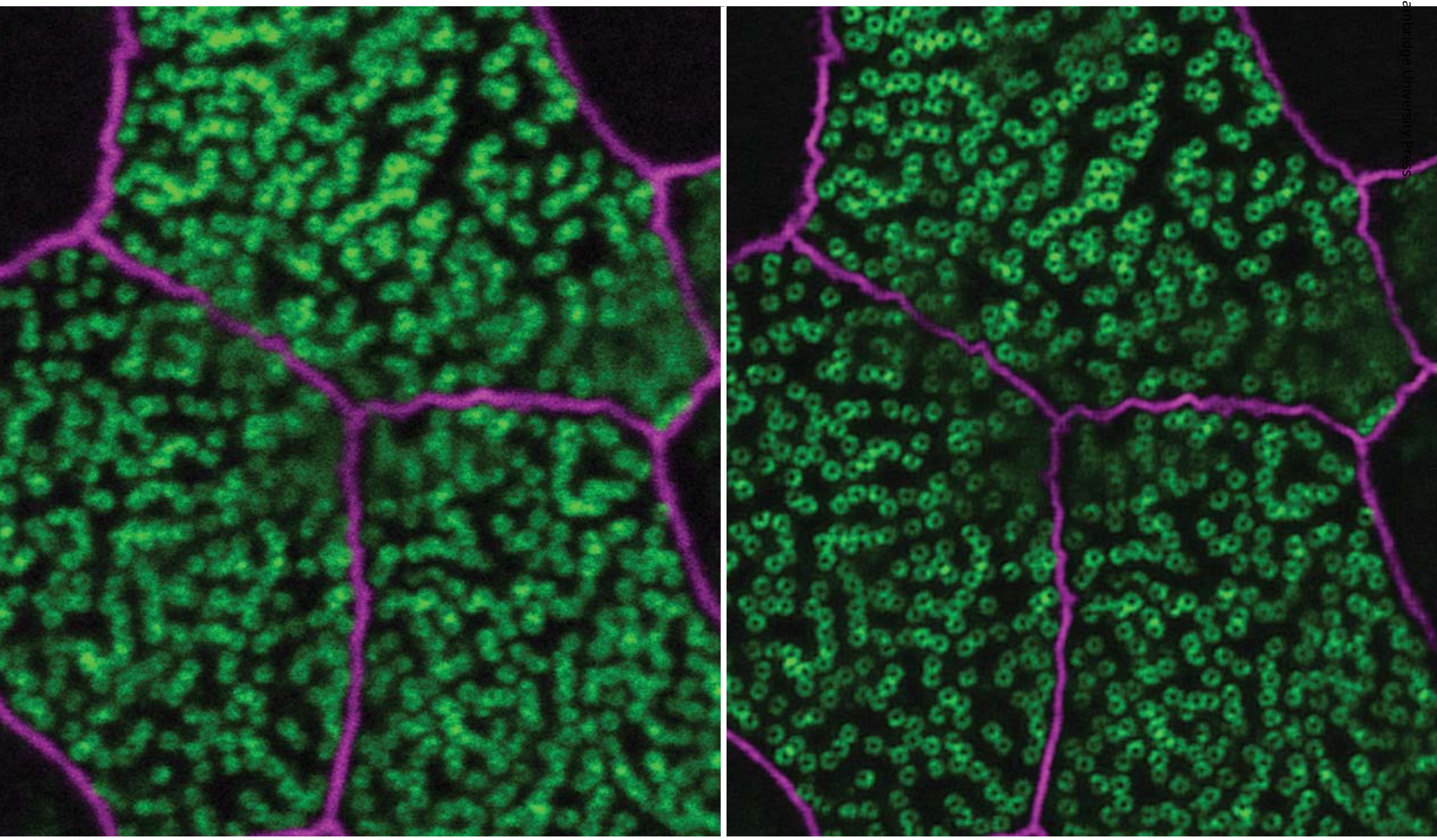


Figure 1: (a) Light microscopy images of Hayabusa particle RA-QD02-0211 prior to any sample preparation (these two images are courtesy of JAXA). (b) Sample was embedded in epoxy and sectioned using traditional microtome techniques. Material surrounding the grain was removed on three sides (shown in the top view images). The sulfide/silicate interface is indicated by the arrow in the first panel (the same interface is visible and labeled in Figure 2a). (c) Sample at the end of an exposed rectangular box sitting above the bulk of the epoxy (side and front view images).



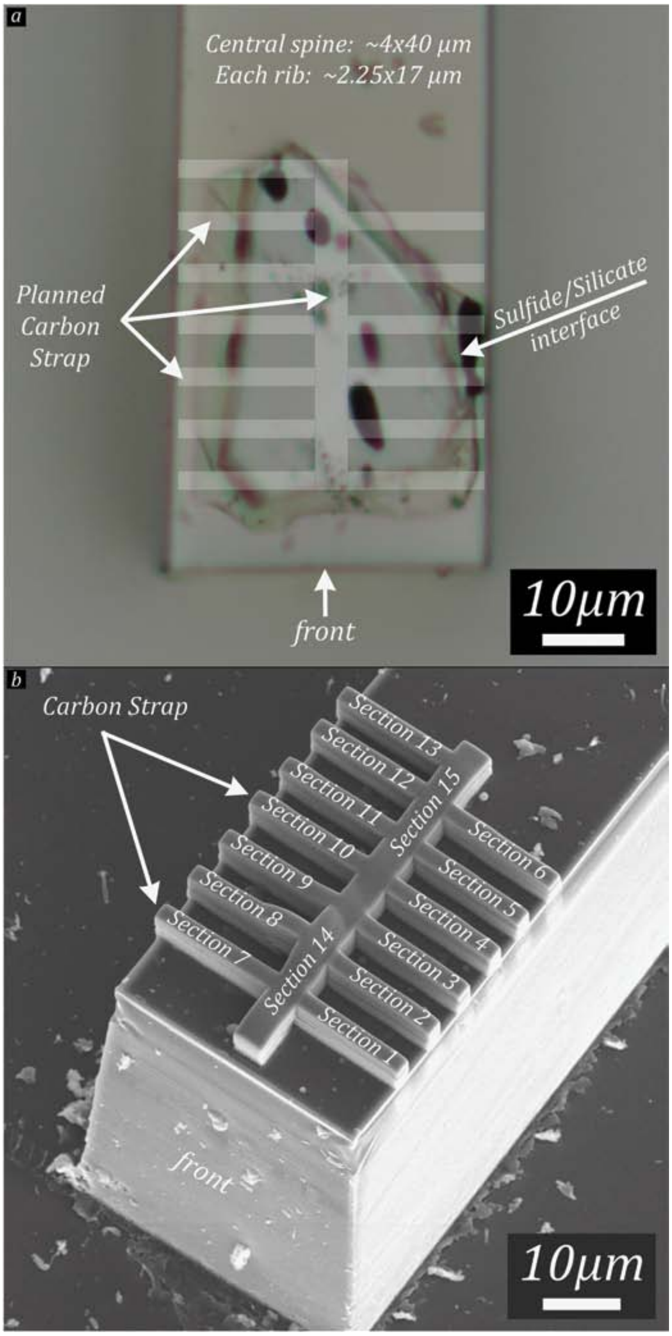


Figure 2: (a) Transmitted light petrographic image (top view) of the grain. The plan for the protective carbon strap is shown in white overlay. The central spine (running north/south) in this image contains the material for two FIB sections, while each of the ribs (running east/west off of the spine) delineates the location of an individual FIB section. On the right side of the grain, below the surface, is a sulfide intersecting two FIB sections. (b) Secondary electron image of the assembly after the protective carbon strap was applied. Sections 3 and 4 contain the sulfide/silicate interface.

particles and vapor-deposited or sputter-deposited material. Solar flare particle tracks in mineral grains speak to the duration and type of exposure these grains have experienced [2]. A process is needed for preparing these particles that conserves both interior and edge features and allows for preservation of as much of the grain as possible. This article describes a hybrid sample preparation technique for particles and its use on a particle returned by the Hayabusa mission.

Materials and Methods

Hayabusa particle RA-QD02-0211, a ~40 × 40 × 20 µm particle from asteroid Itokawa containing olivine and iron sulfides, was allocated by JAXA for analysis in our lab. It was imaged using a Nikon Eclipse ME600 petrographic microscope and embedded in a low-viscosity epoxy (Embed-812, from Electron Microscopy Sciences). Microtomed thin sections (~50–70 nm thick) suitable for light microscopy were prepared on a Leica EM UC6 ultramicrotome with a diamond knife. Additional electron-transparent thin sections were prepared using an FEI Quanta 600 3D dual beam FIB-SEM. A JEOL 2500SE field-emission scanning transmission electron microscope (STEM) was used for TEM analyses. The instruments are housed at NASA Johnson Space Center.

Microtomy. After embedding in epoxy, particle RA-QD02-0211 was partly sectioned to a depth of ~10 µm; 70 µm-thick sections were placed on carbon-coated Cu grids for TEM analyses. At this stage the potted butt was available for SEM, electron microprobe, and other analyses.

With the sample surface partly exposed, the bottom of the epoxy bullet was trimmed away, so that the total height was ~5 mm. This was done to produce dimensions suitable for FIB work. Next, using a diamond trim knife, the epoxy surrounding the grain was removed on 3 sides (to within a few micrometers of the grain). The depth of material removed extends well below the bottom of the particle, leaving the sample at the end of a rectangular box sitting above the surface of the bulk of the epoxy (Figure 1). The trimmed bullet was then attached to an SEM pin mount using carbon tape. The sides of the epoxy bullet were coated with conductive paint (coming close to, but not touching, the sample) and the entire assembly was coated with ~40 nm of carbon to eliminate sample charging during FIB work. Prior to coating the assembly with conductive material, petrographic microscope images were taken to define the bottom edge of the particle (Figure 1c).

FIB-SEM and STEM analysis. Based on the geometry of the exposed, microtomed grain, fifteen FIB sections were planned. For this particular grain, in addition to the space-weathering and edge effects, the interface between the sulfide and silicate was of interest, so the sections were spaced to include that feature (see Figure 2a). A continuous protective carbon strap was placed over the planned sections (see Figure 2b). The central "spine" of the planned FIB-milled specimen runs perpendicular to the front of the sample, and the "ribs" protruding from either side run parallel to the front. Each rib indicates the location of a planned FIB section, and the spine contains the final two planned sections (Figure 2b). The milled result has a 2 µm-wide spine and 2 µm-wide ribs (ribs are spaced a minimum of 3.5 µms apart, as narrower cuts result in too much re-deposition of material inside the trenches).

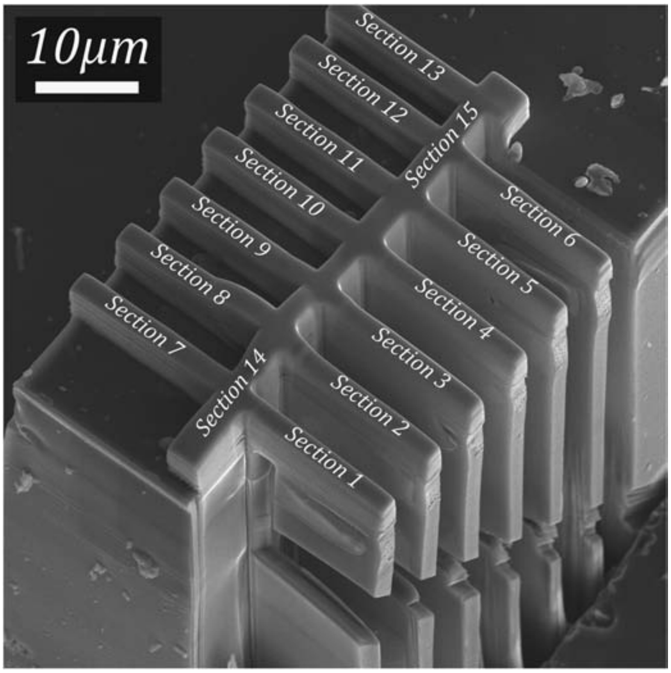


Figure 3: Secondary electron image showing that the material between Sections 1 through 6 has been milled away. The 2 µm-thick sections were undercut, and the medial material of each section was milled away along a 7° tilt. These sections, now attached only by an interior tab, are ready for lift-out.

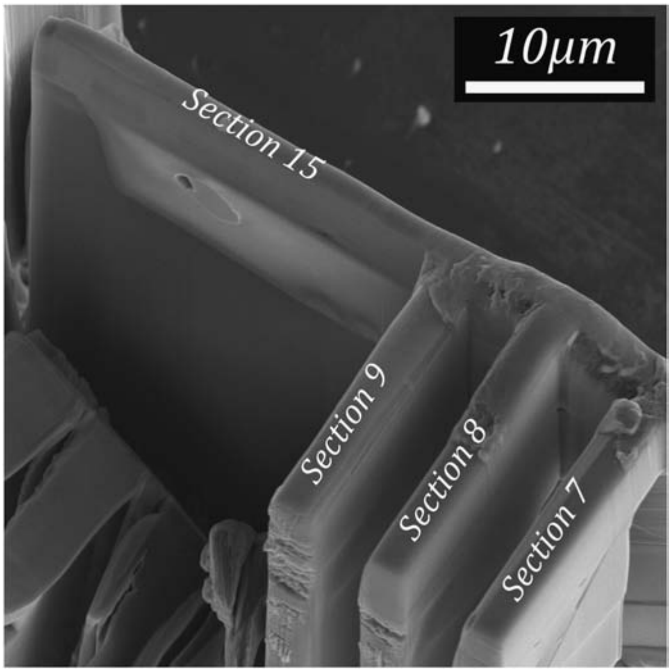


Figure 4: Secondary electron image taken after all the sections from side one had been removed, along with Sections 10 though 13 on side two. Section 15, located on the central spine, contains a multi-phase inclusion (see Figures 6b and 6c for more detail). This section will be removed using the same L-cut process as used on each of the spines.

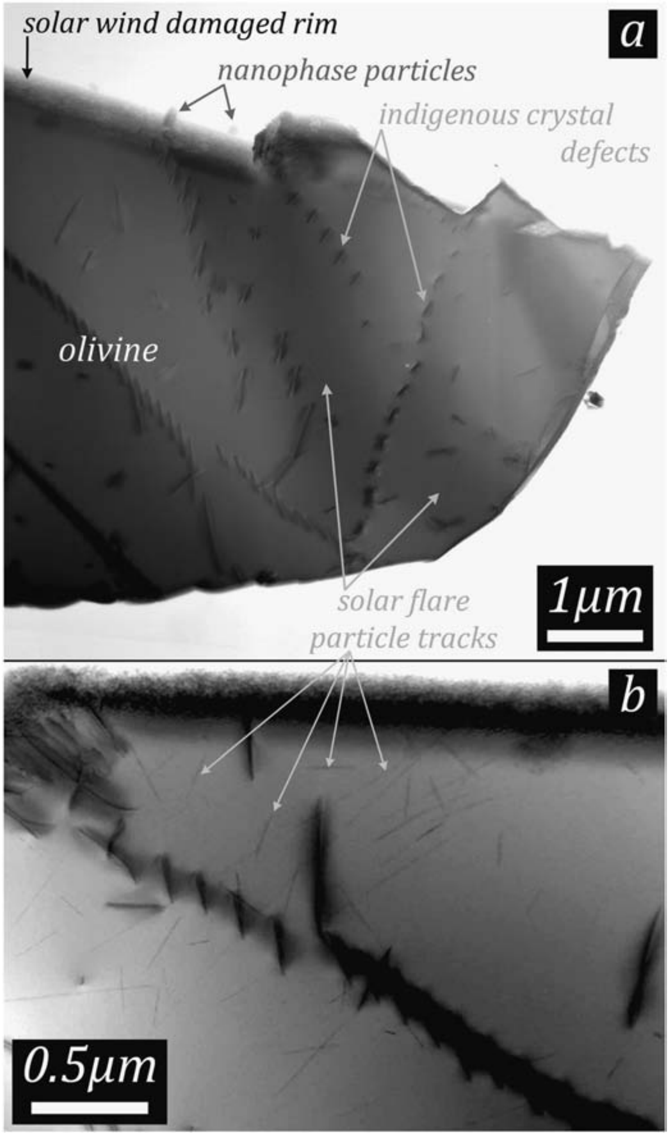


Figure 5: (a) Bright-field STEM image of Section 1, which is mainly olivine. Many space-weathering features can be seen in this image, including a radiation-damaged rim, adhering particles, and solar flare particle tracks (not easily visible at lower magnifications). (b) Higher-magnification image of solar flare particle tracks from Section 1 (arrow).

Using a 30 kV, 3 nA Ga ion beam, the front surface of the grain was exposed, and the trenches between sections were milled on one side of the central spine. Figure 3 shows an oblique view of side 1 after ion-milling. Rather than using the typical C-cut to prepare the sample for lift-out, an L-cut was used. The L-cuts were made through all the sections at a 7° tilt, leaving each section connected by an interior tab. As can be seen in Figure 3, with a 7° tilt, the cuts descend to greater depths in each section (moving from front to back). While milling the L-cut around Section 1, material surrounding the subsequent sections was also removed. In this case, the Hayabusa particle had a relatively constant depth, so the L-cut was placed just below the exposed grain in Section 1 (see Figure 3). For a particle with variable depths, the first cut should be planned so that the L-cuts do not transect the deepest portions of the grain. Prior to lift-out, each section's L-cut was cleaned up; that is, excess epoxy was removed from below the grain and the interior tab was thinned. Section 1, at the front of the assemblage, was lifted out first, attached to a TEM grid, and thinned

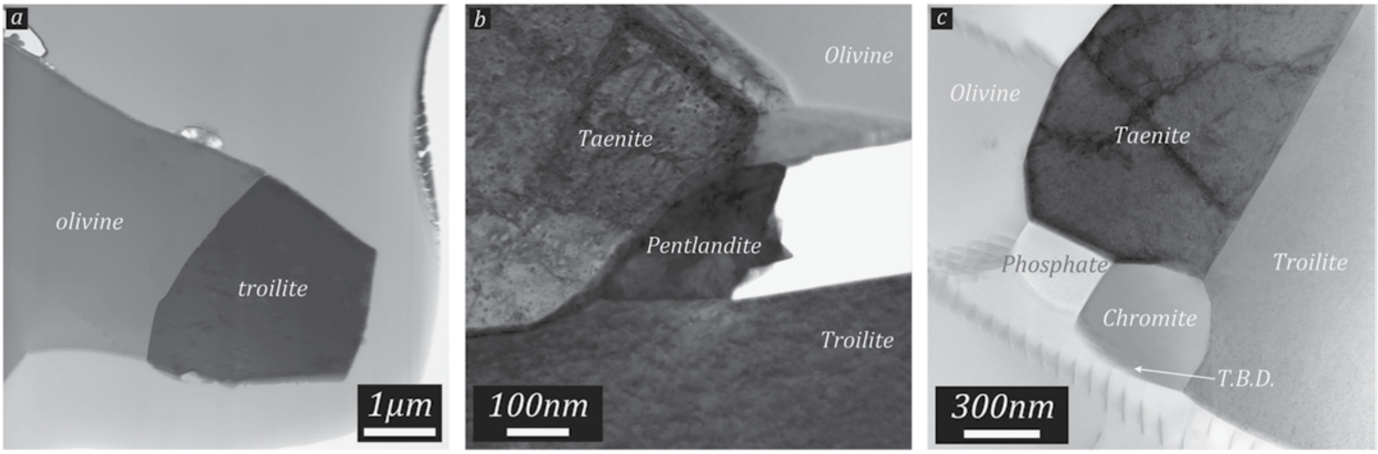


Figure 6: (a) Bright-field STEM image of Section 4, one of the two sections that contain the silicate/sulfide (olivine/troilite) interface indicated in Figures 1b and 2a. (b) and (c) Bright-field TEM and STEM images showing details of the inclusion from Section 15 (see Figure 4). While the bulk of Section 15 is olivine, the inclusion contains Ca-phosphate, chromite, taenite, troilite, pentlandite, and an as-yet unidentified Fe- and Cr-bearing phase (marked as T.B.D.). The pentlandite and troilite are crystallographically oriented, as are the olivine, chromite, taenite, and unidentified phase.

to electron transparency using traditional FIB techniques (for example, see [3]). Each subsequent section on side one underwent the same process. The procedure was repeated on the left side of the grain, starting with Section 13. As the ribs were removed from either side, the central portion of the particle becomes visible along the spine (Figure 4). Twelve of the fifteen planned sections were successful; three were deemed unsuccessful because little or none of the particle was present below the surface at those locations (Sections 7, 12, and 13 were mostly epoxy).

Results

Once thinned to ~100–200 nm, the sections were analyzed using TEM techniques in STEM and TEM modes. The sections each contain a slice of the particle surrounded by epoxy; edge features were conserved. For example, Figure 5a shows a bright-field image of Section 1; the preserved interior and edge features are easily discerned (solar-wind damaged rims, adhering particles, solar-flare particle tracks, and indigenous crystal defects). Figure 6 shows two sections that captured sulfide/silicate interfaces. This technique also unearthed two inclusions, which would likely not have been preserved had this grain been prepared using traditional techniques. The first inclusion was in Section 2. The second inclusion, seen in Figure 4 within Section 15, also shown in Figures 6b and 6c, contains six phases in addition to the bulk olivine in the exposed central spine: Ca-phosphate, chromite, taenite, troilite, pentlandite, and an as-yet unidentified phase (marked T.B.D.) containing Fe and Cr. These phases were identified using a combination of EDS analyses and measurements from selected area electron diffraction patterns.

Discussion

If this Hayabusa particle (Figures 6b and 6c) had been prepared using traditional techniques, chatter from the microtome process may plausibly have broken the inclusion into its component parts, thus the orientations of these minerals and details of their intergrowths may have been lost. Moreover, by producing 15 FIB sections, rather than 1 or 2, the odds of preserving such interesting interior features on one or more sections are significantly increased. These interior features reveal details about the histories of these grains. For example, the density of solar flare particle tracks can be used to infer the length of times the particle was at the regolith surface (that is, its exposure age). Preliminary results from studies of Hayabusa grains show that they have shorter exposure ages compared to typical lunar soils [4].

Conclusion

This hybrid technique, employing both microtomy and FIB, preserves both interior and edge features, including delicate features such as amorphous silicate rims and solar flare tracks, and allows for a more thorough characterization of μm-scale particles than either FIB or ultramicrotomy would afford alone. Analyses by TEM/STEM show the details of the preserved features, including surface modifications from exposure to the space environment, such as damaged rims that form in response to solar wind implantation effects and adhering grains. In addition, the FIB sections provide larger areas that are free of fractures and chatter effects in comparison to the microtome thin sections, thus enabling more accurate measurements of solar flare particle track densities, which are used to determine the surface exposure age of the particles.

Acknowledgements

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References

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BioWave Pro
PELCO


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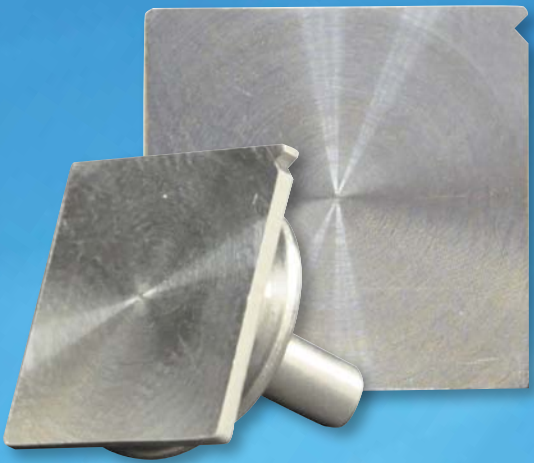

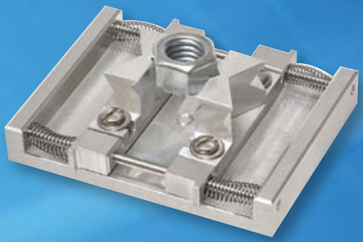

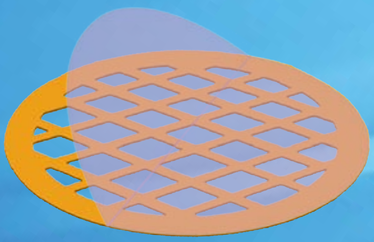

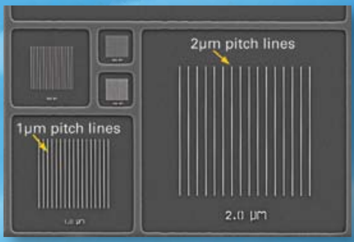
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