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Semi-Inverted Sample Preparation of Meteorites for High Resolution Analytical Electron Microscopy Using Correlative Raman Spectroscopy and Xe Plasma FIB

Suzy Vitale[1*], Andrew Steele[1], Liane G. Benning[2], and Richard Wirth[2]

[1.] Carnegie Institution for Science, Geophysical Laboratory, Washington, DC, USA.
[2.] German Research Center for Geosciences, GFZ, Potsdam Germany.
* Corresponding author: svitale@carnegiescience.edu

Many materials have regions of interest (ROIs) that are beneath the surface. A focused ion beam (FIB) is used to remove material at the microscale in order to expose these subsurface ROIs for analysis [1]. When the ROI is to be analyzed using high-resolution analytical electron microscopy, the sample must be very thin (>100 nm) in order to allow transmission of electrons through the sample. The FIB is used not only for ROI extraction but also for thinning the sample to electron transparency [2]. However, when the ROI is more than a few microns beneath the surface and is surrounded by a mineralogically heterogeneous matrix, as is the case for most meteorites, it can be challenging to uniformly thin the ROI to >100 nm.

Subsurface analytical techniques are critical for the study of abiotic organic macromolecular carbon (MMC) found within Martian meteorites. Only subsurface MMC can be studied because only subsurface MMC can be free of any potential Earth carbon contamination. This subsurface MMC, the study of which is fundamental to discerning the habitability of Mars, is found near titano-magnetite [3, 4] and mills much faster than the titano-magnetite. In these samples, both the titano-magnetite and MMC must be the same final thickness so that we can accurately study the electrochemical relationship between the titano-magnetite and MMC at transmission electron microscopy (TEM) resolutions. Here, we demonstrate a technique unique to Xe plasma FIB (PFIB) (due to length scale) that will allow ROIs as far as 50 um beneath the surface to be extracted and uniformly thinned to electron transparency.

First, a 250 um wide by 50 um deep trench was milled into the meteorite's surface using an FEI Helios G4 PFIB UXe in ten minutes (Figure 1). The sample was then removed from the PFIB, and Raman spectra and images were collected using a Witec α-Scanning Near-Field Optical Microscope that has been customized to incorporate confocal Raman spectroscopic imaging. MMC signatures were found in the cross section (Figure 2). The sample was then returned to the PFIB. The ROI was removed from the cross section using standard in-situ lift out steps [5], however once the sample was clear of the trench, the micromanipulator was rotated 180 degrees. The sample was then moved and attached to the FIB grid. The ROI was located with respect to the new top of the sample. Material was cut from the top of the sample in order to bring the ROI as close to the surface as possible, and without damaging the ROI. Tungsten was deposited on to top of the sample to create a new protective cap. Then the sample was thinned to approximately 70 nm using the ion beam. The sample was analyzed using scanning transmission electron microscopy (STEM) imaging and energy dispersive x-ray spectroscopy (EDS). Figure 3 shows a uniformly thinned region containing both titano-magnetite and the MMC.

These techniques improve our sample preparation process in several ways. Using a large cross section allows us to more accurately find the subsurface ROI using confocal Raman imaging spectroscopy. Strategic removal techniques allow us to position the ROI to the top of the sample for final FIB thinning. Placing the ROI at the top of the sample allows for ultra-thin lamellae despite differential milling issues.

The end result is the repeatable creation of high quality TEM samples of mineralogically heterogenous materials for research in the earth and planetary sciences.

References:

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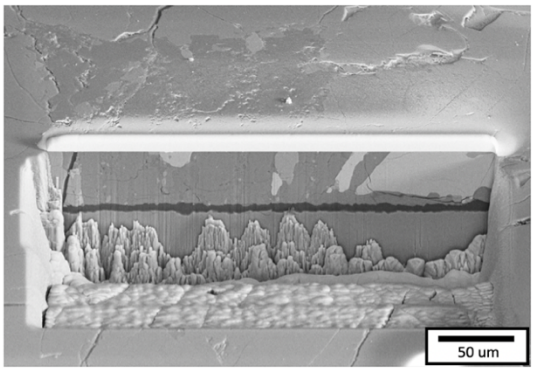

Figure 1. 250 um wide, 50 um deep trench milled into the meteorite's surface

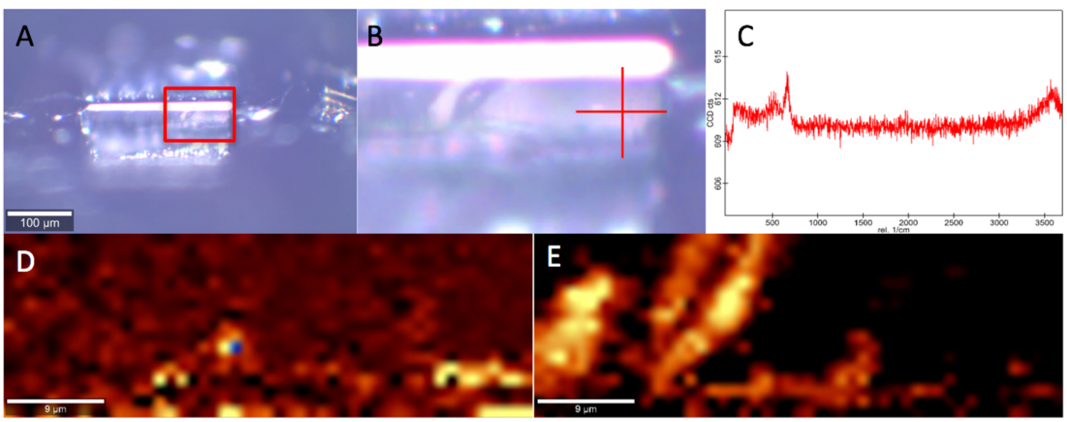

Figure 2. A, B) Optical images of cross section. C) Magnetite spectrum shown at cross in B. D) Map of macromolecular carbon. E) Feldspar map

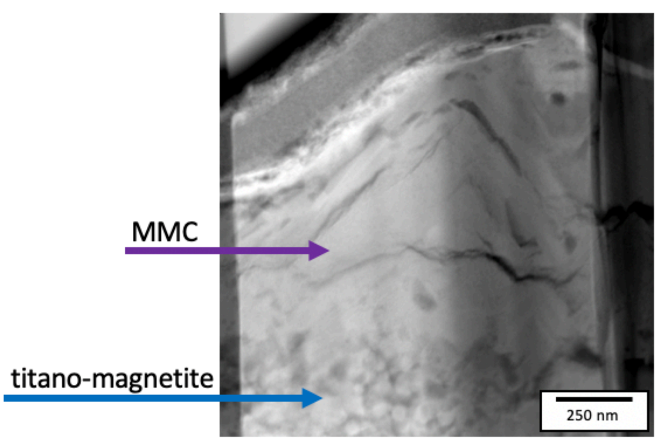

Figure 3. High-angle annular dark field (HAADF) STEM image showing uniformly thinned MMC and titano-magnetite

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