New Integrated Analytical Capability at the University of Hawai'i

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The benefits of integrating instruments to enhance science yield were demonstrated during the Stardust preliminary examination [1-3]. We are implementing this approach at the University of Hawai'i (UH). Existing electron microprobe capabilities in the Department of Geology and Geophysics and ion microprobe, SEM and Raman capabilities in the W. M. Keck Cosmochemistry Lab are now augmented with the new **Advanced Electron Microscopy Center (AEMC)**, which hosts a 60-300 keV monochromated and dual spherical (Cs) aberration-corrected Titan TEM/STEM and our newest addition, a Helios NanoLab 660 dual-beam focused ion beam (FIB) instrument. The Titan has a high-angle annular dark field (HAADF) detector, Tridiem Gatan imaging filter (GIF) for imaging and spectroscopy, and an EDAX Genesis 4000 Si(Li) energy dispersive x-ray spectrometer. The FIB is equipped with an Oxford Instruments Xmax N80 SD detector for x-ray spectroscopy and mapping, retractable back-scatter and STEM detectors, EasyLift *in-situ* manipulator and C, Pt and W gas chemistries. These capabilities permit us to integrate TEM data with isotope data from the UH Cameca IMS 1280 ion microprobe, which provides <1 µm resolution or, with SCAPS, direct ion imaging, as well as with Raman spectroscopy from the Witec Confocal Raman Scanning System. Titan analyses can be performed at UH or from Lunar and Planetary Institute (LPI) in Tucson via commercial fiber optic network and a remote Titan control platform (PI T. Zega).

(left) Lean Teodoro, Hawaii Space Grant Consortium Fellow, working on the University of Hawaii-funded dual beam FIB in the Advanced Electron Microscopy Center (AEMC).

(right) Hope Ishii, AEMC Director, showing the NASA-funded, monochromated and dual-aberration corrected Titan (S)TEM to visitors Tim McCoy and Cari Corrigan.

Titan (S)TEM Capability Examples

Dual aberration correction combined with (optional) monochromated incident beam define the state-of-the-art in analytical STEM. These allow analysis of inorganic and organic extraterrestrial materials by a variety of methods in extreme detail.

Key Titan capabilities result from the Cs aberration correction and energy dispersive x-ray spectroscopy: The sub-Å electron probe enables single atom imaging, shown in Figure 5, and the little-explored realm of nano-petrography where low-electron-dose mapping with spatial resolution of 1-2 nm is achievable in suitably thin specimens.

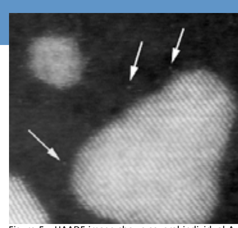

Figure 5: HAADF image shows several individual Au atoms (arrowed) teased off the edge of a gold nanoparticle using the sub-Å electron probe (300 keV Titan STEM image).

Figure 6 shows an example applied to FeNi sulfides, the most abundant crystalline phase in IDPs. Hexagonal 2C pyrrhotite is the predominant polytype. The relative distributions of S, Fe and Ni in the maps provide evidence of low temperature thermal alteration consistent with previous work [5]. For example, the S and Fe distributions correlate in the FeNi-sulfide grain "1" but Ni and Fe are decoupled. Other grains are Ni-enriched and S-depleted to varying degrees ("2" and "3"). Grain "4" shows a S-enriched rim with a corresponding S-depleted interior of a GEMS grain. These S-enriched rims have been interpreted as a primordial property that show GEMS formed in the solar nebula [6], but *in-situ* experiments using a TEM heating stage implicate atmospheric entry heating as the origin of S-enriched rims [7].

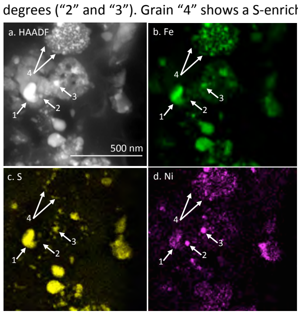

Figure 6: HAADF image and S, Fe and Ni maps of a thin section of a CP IDP (1-2 nm spatial resolution).

Figure 7 shows carbon-K edges from organic carbon in a chondritic IDP measured using a 80 keV monochromated electron energy-loss spectroscopy (MEELS) with 0.18 eV energy resolution. MEELS enables interrogation of molecular functionalities at the single nanometer scale.

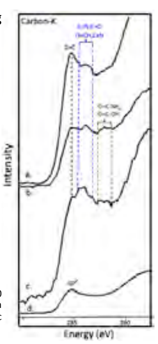

Figure 7: Monochromated 80 keV EELS from organic carbon in an IDP (a-c) and inorganic carbon film (d).

Helios FIB & Integrated Capability Examples

The Helios dual-beam FIB permits electron and ion beam imaging, highly-localized ion beam milling, and beam-induced deposition of C, Pt and W from organometallic gas precursors. Figure 1 shows an ion-beam milled pattern on a deposited pad of Pt. FIB milling and deposition in conjunction with *in situ* micromanipulation are used to prepare electron transparent thin sections of specific locations in samples for TEM analysis (Figure 2). The Helios dual-beam FIB and Titan aberration-corrected (S)TEM are the first of their kind in the State of Hawaii. It is anticipated that AMEC will become a facility for users throughout Hawaii and beyond.

Figure 1: Logo milled into a 25 micron wide Pt pad by FIB. The entire Pt pad is about 1/4th of the width of a human hair.

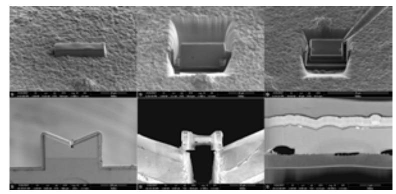

Figure 2: Secondary and backscattered electron images of FIB sample preparation of an electron transparent section of a chalcogenide multilayer solar cell deposited by a novel deposition process for subsequent TEM analysis (sample provided N. Gaillard, Hawaii Natural Energy Institute (HNEI)).

One of the key capabilities of the FIB for integrated analysis is to reconfigure a tiny TEM specimen like a thin section of a ~10 µm IDP into a SIMS-compatible specimen. Using the FIB, a Pt support strap and platform can be deposited on the underside of the carbon support film (Fig. 3a). Without this platform, the lifetime of the specimen in the ion beam is too short to reliably measure its isotopic compositions (Fig. 3c-f).

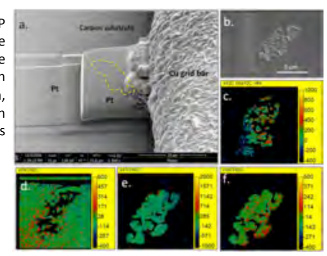

Figure 3: (a) Secondary electron (SE) image of the underside side of a carbon support film TEM grid after FIB deposition of a Pt support substrate. Dashed outline shows the position of a thin section of an IDP on the opposite side of the grid. (b) SE image of the thin section on the top side. (c-f) Maps of isotope ratios in delta notation (parts per 1000 relative to terrestrial standards): (c) $\delta(^{12}C^{15}N/^{12}C^{14}N)$, (d) $\delta(^{13}C/^{12}C)$, (e) $\delta(^{17}O/^{16}O)$, and (f) $\delta(^{18}O/^{16}O)$ isotope maps.

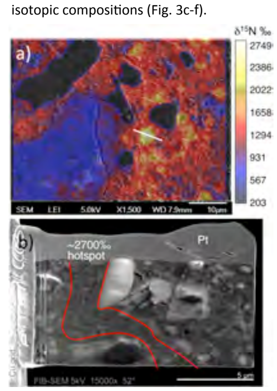

Figure 4: Lithic clasts in the Isheyevo meteorite show the highest ^{15}N anomalies ever measured. a) ims 1280 δ15N isotope map overlaid on SEM image of lithic clast from Isheyevo (CH/CB). White line indicates location from which FIB section was extracted. (b) FIB-SEM image of FIB section through ^{15}N-rich hotspot corresponds to vein of altered material rich in organics prior to final thinning [4].

Conversely, an isotopic "hot spot" in a thick-flat SIMS specimen can be harvested and recon-figured into an electron transparent TEM specimen. Figure 4 is an example of extraction of an extreme ^{15}N anomaly for TEM analysis [4].

Conclusions

Integration of new sample preparations and analytical capabilities at UH, the Titan TEM/STEM and Helios dual beam FIB, with existing capabilities, Cameca ims1280 ion microprobe, JEOL LV SEM and Witec Confocal Raman Scanning System, will enable assessment of fundamental properties of extraterrestrial materials with improved resolution and fidelity. Of particular interest are those fine-grained components, minimally explored thus far, and features that can now provide distinctions between primordial and secondary alteration effects.

References: [1] Graham G. et al. (2008) *Meteoritics & Planetary Science* 43, 561-569. [2] Ishii H. A. et al. (2010) *Lunar and Planetary Science Conference* 41, Abs. 2317. [3] Matzel J. et al. (2010) *Science* 328, 483-486. [4] Bonal L. et al. (20110) *Geochimica et Cosmochimica Acta* 74, 6590-6609. [5] Dai Z. R. and Bradley J. P. (2001) *Geochimica et Cosmochimica Acta* 61, 3601-3612. [6] Keller L. P. and Messenger S. (2011) *Geochimica et Cosmochimica Acta* 75, 5336-5365. [7]Bradley J. P. et al. (2014) *Lunar and Planetary Science Conference* 45, Abs. 1777.

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background image: low-angle grain boundary in $SrTiO_3$