INFRARED SPECTROSCOPY OF INDIVIDUAL SUB-MICRON PRESOLAR AND EARLY SOLAR SYSTEM DUST GRAINS IN THE ELECTRON MICROSCOPE.

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Introduction: Although IR spectroscopy methods are widely used in planetary materials analyses, they are typically not suitable for invididual presolar and early solar system grains, due to the sub-diffraction-limited size of many of these grains. Vibrational electron energy loss spectroscopy (EELS) in the transmission electron microscope (TEM) is an emerging method for the probing the infrared (IR) features of nanoscale materials [1], in conjunction with the more routine TEM elemental and structural analyses of the individual sub-μm grains. We seek here to demonstrate the viability of the vibrational EELS method for the characterization of the IR properties of individual sub-μm astrosilicates. The eventual goal of these measurments is to relate the variation in the IR properties of the individual grains to variations in astronomical and remote sensing spectra, such as the "10-μm" Si-O strectch feature used to distinguish olivines and pyroxenes from amorphous silicates in circumstellar and cometary spectra.

Methods: San Carlos olivine was prepared for use as a standard, by hand grinding and drop casting onto lacey carbon film, Cu grid TEM supports. Individual isolated early solar system silicate grains were identified in focused ion beam lift-out sections of a C-rich clast in the matraix of LAP 02342 [2]. Presolar silicates in DOM 08006 were previously identified first by SIMS at the Carnegie Institution of Washington, and then extracted by focused ion beam lift-out at NRL [3]. Initial TEM characterization was performed with the JEOL 2200FS and Nion UltraSTEM 200-X microscopes at the Naval Research Laboratory. Vibrational EELS measurements were performed at Rutgers University with the monocrhomated Nion HERMES STEM, at an operating voltage of 60 kV, with a 1 Å, 10 pA, monochromated 0.01 eV probe.

Results: An example raw vibrational electron energy loss spectrum of a FIB section of a presolar polycrystalline olivine grain (Fo_{90}) is shown in Fig. 1. This spectrum was collected with the beam positioned in the center of the grain, to minimize the spectral contributions from surrounding grains. Figure 2 shows comparable spectra obtained from San Carlos olivine (Fo_{90}) particles. The dispersed particles allowed for spectra to be collected in two geometries, first with the STEM beam positioned off the edge of a thick particle, in the "Aloof" mode, and second with the STEM beam positioned on the sample. A transmission (on sample) geometry spectrum was also obtained from a thinner olivine particle (p2). The Si-O stretch mode and O-Si-O beand modes are visible in all three spectra, but the bend mode is most easily observed in the Aloof geometry measurement.

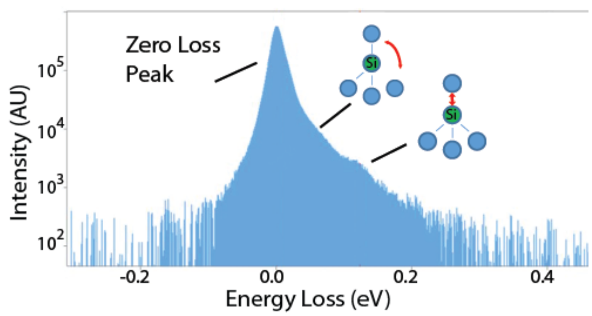

Fig. 1. Raw transmission geometry vibrational electron energy loss spectrum from a polycrystalline presolar olvine grain. Two vibrational modes are cleared detected, the "10-μm" Si-O stretch mode (130 meV) , and the "18-μm" O-Si-O bend mode (60 meV), superimposed on the tail of the zero loss peak.

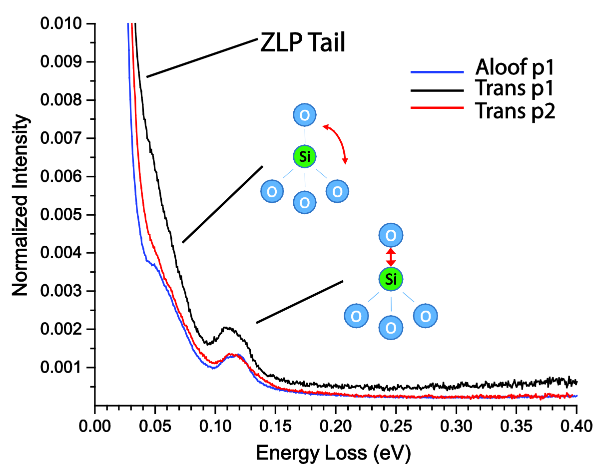

Fig. 2. Example vibrational electron energy loss spectra from two San Carlos Olivine particles (p1 and p2), normalized to the intensity of the zero loss peak (ZLP) For p1, spectra were collected with the STEM beam positioned adjacent to the sample (Aloof) and on the sample (Trans).

For more direct comparison with conventional IR measurements, it is necessary to substract the zero loss background from the spectrum and make a simple transformation from energy to wavelength scales. Figure 3 shows an example spectrum from a San Carlos olivine grain taken in Aloof mode, after background substraction and transformation. The "10-µm" and "18-µm" features are clearly observed, however the intensity of the "18-µm" feature is very sensitive to the details of the instrument condition and background subtraction, and may have excess intensity due to background uncertainty in the raw spectrum.

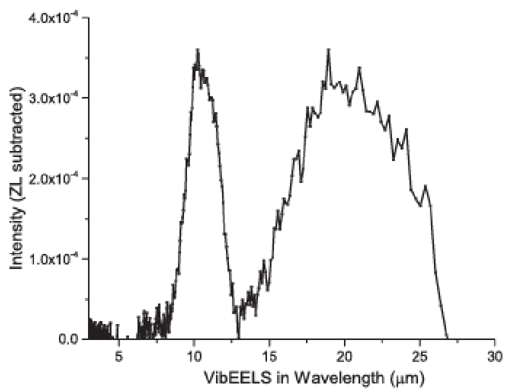

Fig. 3. Vibrational elelctron energy loss spectrum of San Carlos olivine (Aloof mode), after subtraction of zero loss peak, and transformation to wavelength scale.

Additional spectra from bona fide astrosilicates are shown in Fig. 4. These spectra were obtained from three grains an unusal C-rich clast in the LAP 02342 meteorite, prepared by focused ion beam lift-out. The measurements were made in transmission mode in order to maximize the fraction of the spectral signal from the target grains, and limit contributions from surrounding grains. Significant variations in the details of the 10-µm and 18-µm features are observed, which are qualitatively in agreement with expectations for amorphous silicates (GEMS) and olivine (Fo_{90}). Our highest spectral resolution olivine measurement (Fig. 4 1st) indicates a split in the 10-µm feature, whereas the amorphous silicates with higher Fe content show a broad 10-µm feature shifted to lower wavelength. A second measurement of the same olivine grain using longer collection times shows feaures similar to the amorphous grains.

Discussion: We have successfully demonstrated that the vibrational EELS method can be used to meaure IR absorption features of individual astrosilicates that are below the diffraction size limit, and thus too small for conventional IR spectroscopy. Although our preliminary measurements focused on anhydrous silicates, this method can easily be extended to higher energy loss (shorter wavelength) to examine features in the 3-µm range (0.4 to 0.5 eV) associated with hydrated silicates and organic matter. Lower energy loss (< 0.05 eV) features, corresponding to > 20 µm, are more difficult to measure, due to the steeply increasing background of the zero loss tail [4]. Use of the Aloof geometry is advantageous, because it appears to reduce the intensity of the zero loss tail (see Fig.2), in addition to limiting any beam damage to the sample. For individual meteorite matrix grains in lift–out sections, the use of Aloof mode would require "FIB surgery" to remove surrounding grains, which we did not perform for these experiments. However, even in transmission mode, feaures in the 10-µm range (0.10 eV -0.13 eV), are well above the zero loss tail. We plan additional measurements to establish reliable measurement and singal processing protocols for quantitative determination of the 3-µm and 10-µm features in individual astrosilicates.

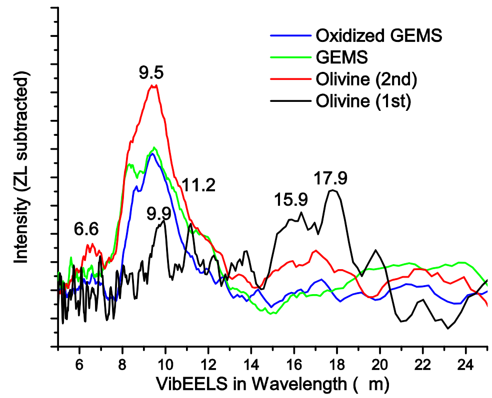

Fig. 4. Vibrational EELS measurments (transmitted mode) of glassy and crystalline silicate grains in a C-rich clast in the matrix of LAP 02342. The olivine (Fo90) grain was measured twice, at lower and higher dose conditions, and likley experienced some beam alteration.

References: [1] Krivanek O. et al. (2014) *Nature*, 514, 209-212. [2] Stroud R. M. et al. (2016) *Abstracts of the 79th Met. Soc. Meeting*, Abstract #1921. [3] Nittler L. R., et al. (2018). *GCA*, 226, 107-131. [4] Lagos M. and Batson P. E. (2018) *Nano Lett., 18*, 4556-4563.

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