NEAR-FIELD INFRARED SPECTROSCOPY AS A TOOL FOR ANALYSIS OF CHONDritic RETURRED SAMPLES. Timothy D. Glotch¹, Jordan M. Young¹, Ziheng Yao¹², Hans A. Bechtel², Victoria E. Hamilton³, Philip R. Christensen⁴, and Dante S. Lauretta⁵. ¹Stony Brook University (timothy.glotch@stonybrook.edu), ²Advanced Light Source, Lawrence Berkeley National Laboratory, ³Southwest Research Institute, ⁴Arizona State University, ⁵Lunar and Planetary Laboratory, University of Arizona.

Introduction: The relationships between organic and mineral components in meteorites have been a topic of extensive study [e.g., 1-3]. It will be especially important to understand these relationships in pristine carbonaceous chondrite samples returned by the Hayabusa2 and OSIRIS-REx missions. Our previous work has focused on using the Raman spectral properties of the disordered and graphitic (D and G) bands of polycyclic aromatic hydrocarbons (PAHs) to constrain the peak metamorphic temperatures experienced by a range of ordinary chondrite samples [4]. We found two populations of organic carbon in these samples that appear to reflect different thermal histories. We are currently working to further investigate this intriguing result using scattering-type scanning near field infrared spectroscopy and imaging (s-SNOM or nano-FTIR). This work describes imaging and spectroscopy of organic/silicate boundaries in H5 ordinary chondrite Allan Hills (ALH) 77012 at ~20 nm spatial scales, but also serves as a proof of concept for analyses of returned carbonaceous samples.

Methods: We acquired nano-FTIR spectra and images at the Synchrotron Infrared Nano Spectroscopy (SINS) beamline at the Advanced Light Source at Lawrence Berkeley National Laboratory. Images and spectra were collected on a standard petrographic thin section. For spectroscopy, the synchrotron infrared beam was focused onto a conductive atomic force microscope (AFM) tip in a neaspec neasNOM near-field system. Phase and amplitude spectra referenced to a gold standard were collected at harmonics of the AFM tip tapping frequency to remove the far-field signal. The spatial resolution of point spectroscopy measurements is controlled by the radius of curvature of the AFM tip, which is < 20 nm. Spectra were collected with a spectral sampling of ~2 cm⁻¹.

For imaging, a tunable laser centered at ~6 μm was used to illuminate the sample tip as the sample was rastered underneath it. The image was acquired with a spatial sampling of 53 nm/pixel. As with the spectroscopic measurements, near-field infrared phase and amplitude data were collected at harmonics of the tapping frequency.

Results and Discussion: Using Raman maps collected by [4] at Stony Brook University as guides, we focused our nano-IR measurements on organic/silicate boundaries in the H5 ordinary chondrite ALH 77012. Figure 1 shows a 6-μm nano-IR map of one of these boundaries. From the multiple datatypes that were collected simultaneously, we constructed an overlay of colorized optical amplitude (O3A) at a wavelength of 6 μm over the mechanical phase (M1P). The map shows a clear boundary trending from lower left to upper right. The upper portion of the image (yellow/white) has weak or absent spectral features between ~700 and 1200 cm⁻¹ (Figure 2). Based on the amplitude spectrum and the high reflectance of the material in reflected light micrographs, we interpret this phase to be a metal sulfide or oxide.

We collected multiple spectra on the Raman-identified organic material (displayed as red/orange in the lower right portion of the image in Figure 1). Multiple diagnostic features are present, in both the phase and amplitude spectra, although there is some variation from point to point. Major peaks in the phase spectra occur at ~880, 974, 1010, 1074, 1120, and 1290 cm⁻¹. Corresponding peaks in the amplitude
spectra occur at ~860, 950, 1009, 1054, 1114 cm\(^{-1}\), and 1280 cm\(^{-1}\). Most of these features correspond to pyroxene Si-O stretching and bending modes, although the shortest wavelength (highest wavenumber) feature is absent from spectra of pyroxene standards, and may correspond to weak features documented in some PAH spectra [5].

**Comparison to OTES Spectra of Bennu:** Direct comparison of nano-IR spectra with traditional far-field (e.g., reflectance, emissivity, absorbance) spectra remains challenging due to the strong interaction of the AFM tip with the sample, which can cause substantial shifts in band shape and position for strong vibrational modes. Nevertheless, we will work to acquire spectra of finely and poorly crystalline phases in Bennu- and Ryugu-relevant CI and CM meteorites to provide additional standards for analysis of OTES data. Several models exist to calculate the complex refractive indices of minerals from nano-IR data, and from these, standard reflectance models can be used to calculate far-field spectra from nano-IR measurements [6-8]. We are actively working to improve these models to provide direct links between meteorites and/or returned samples and remotely sensed data.

**Additional Work:** We will refine band identifications and pursue investigations of additional mineral and organic features in ALH 77012 and initial analyses of CI and CM chondrite meteorites relevant to the samples to be returned from Ryugu and Bennu.

At present, our imaging capability is limited to the ~6 micron region due to the laser available at the ALS SINS beamline. Imaging at wavelengths more relevant to chondritic silicates and organics would be enabled by modern tunable lasers or a multiple laser setup easily incorporated into the neaSNOM system. At the time of sample return, instruments with hyperspectral imaging capability from ~3-20 μm are likely to exist at multiple laboratory facilities.

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![Figure 2. Nano-IR amplitude (top) and phase (bottom) spectra acquired from ALH 770012. The colors of the curves correspond to the colors of the points in Figure 1. The spot size for each spectrum is ~20 nm.](image-url)