Revealing Histories of Nanoscale Components in Primitive Planetary Materials with High-Resolution Electron and X-ray Microscopies. B. T. De Gregorio1 and R. M. Stroud1,1 U.S. Naval Research Laboratory (4555 Overlook Avenue SW, Washington, DC 20375, e-mail: bradley.degregorio@nrl.navy.mil).

Introduction: Fine-grained material is ubiquitous in primitive chondrite meteorites, interplanetary dust, and comet samples. This material can include a wide variety of mineral and carbonaceous phases that existed during the initial phases of the nebular disk (e.g., interstellar grains), condensation phases that formed during disk cooling (e.g., calcium-aluminum inclusions), and exotic phases injected into the solar nebula from extrasolar sources (e.g., presolar grains). Determining the histories of these various materials is complicated by the fact that many of the phases can form via multiple mechanisms. For example, amorphous silicates, which are abundant in the fine-grained matrices of the most unaltered chondrites, have been argued to be an interstellar component or to have formed by nebular condensation (e.g., [1]). Similarly, some nanodiamonds in primitive chondrites contain signatures of a supernova origin [2], yet some researchers have argued that many nanodiamonds may have an interstellar or nebular origin [3, 4].

Petrographic context can be key to unraveling the various histories of these primordial components. High resolution microscopy methods are valuable due to the small grain sizes of these components (typically less than 1 μm), particularly techniques that can also provide compositional or chemical information, such as electron energy-loss spectroscopy (EELS) in a scanning-transmission electron microscope (STEM) or X-ray absorption near-edge structure spectroscopy (XANES) in a scanning-transmission X-ray microscope (STXM). Here we highlight recent work using these methods to unravel the complex histories of primitive fine-grained phases in planetary materials.

Methods and Instrumentation: STEM imaging and EELS was performed with an aberration-corrected Nion UltraSTEM 200 at NRL, operated at an electron beam energy of 60 keV to reduce the amount of knock-on damage and H loss in organic samples. The microscope also includes a large angle (0.7 sr) windowless energy dispersive spectroscopy (EDS) detector for measuring sample composition. EELS spectral resolution, as measured by the full-width half-maximum of the zero loss peak, is typically 350-400 meV, providing sufficient resolution to resolve fine structure at the C core-loss edge.

XANES was performed with the STXM instrument at beamline 5.3.2.2 at the Advanced Light Source, Lawrence Berkeley National Laboratory. This microscope uses Fresnel zone plate optics to produce a beam spot around 35 nm, and includes a monochromator grating to select X-ray energies with a precision of 100 meV.

Results: Mapping Aqueous Alteration Microenvironments. The primitive CR chondrite La Paz Icefield (LAP) 02342 contains a C-rich clast with compositional and isotopic affinities to ultracarbonaceous Antarctic micrometeorites [5]. To assess the level of parent body aqueous alteration experienced by this clast, we performed Fe-XANES and C-XANES mapping of focused ion beam (FIB) lamellae extracted from the clast, from the edge of the clast, and from nearby fine-grained matrix [Figure 1]. The Fe L-edge contains split peaks that can be used to estimate the ratio of Fe2+/Fe3+ in Fe-bearing silicates [e.g., 6]. After XANES mapping of the sample, the valence ratio of Fe was quantified using peak fitting and a linear calibration curve between Fe2+ and Fe3+ endmembers. Fe-bearing materials within the clast were found to contain 20-30% Fe3+, while similar phases in the surrounding matrix contained 60-70% Fe3+ (as estimated previously [6]). In addition, the range of oxidation state in clast phases was much broader than that of matrix phases.

Figure 1. (a) STXM image of a FIB-extracted lamella from the LAP 02342 C-rich clast, showing the locations of two fine-grained polyphase particles. (b) Fe-XANES of the two silicate grains in (a). Fe valence mapping of the (c) matrix and (d, e) clast lamellae, along with the distribution of Fe valence.
In addition, both C-XANES and C-EELS data reveal that the organic matter within the C-rich clast contained a lower abundance of oxygen-bearing functional groups than that observed in matrix organics.

Together, the XANES and EELS data provide a picture of isolated aqueous microenvironments. The homogenously oxidized matrix material is typical of parent body aqueous alteration. However, the clast appears to have been relatively isolated from parent body aqueous fluids, possibly due to the high abundance of organic matter coating mineral phases.

**Locating Nanodiamonds In Situ.** As mentioned above, presolar nanodiamonds with demonstrable supernovae heritage may be rare within the entire nanodiamond population in chondrites. While individual nanodiamonds may be too small to measure their isotopic composition, if we can identify nanodiamonds in situ, then we may still be able to infer their origins based on the isotopic composition of their host organic matter. To that end, we used C-EELS mapping to identify in insoluble organic matter (IOM) from the Murchison, Elephant Moraine (EET) 92042, and Bells chondrites. The core loss C edge of diamond is distinct from that of other carbonaceous phases, lacking an aromatic absorption at 285 eV and containing a second band gap at 302 eV [7,8]. In addition, the low energy plasmon peak is shifted from 25 eV to 33 eV. Because the plasmon peaks are significantly more intense than the core-loss peaks, high resolution low-loss EELS maps, containing several tens of nanodiamonds or nanodiamond clusters, were obtained from 1 µm² regions in 10-20 minutes [9].

In all three IOM samples, nanodiamonds were only observed within porous IOM, and were absent in dense, non-porous IOM or in globular IOM. Porous IOM represents diffuse organic matter dispersed in chondritic fine-grained matrix, while dense and globular IOM are found as larger carbonaceous particles and veins. Therefore, future in situ work looking for nanodiamonds should target diffuse IOM in FIB lamellae and crushed samples.

**Discussion:** STEM-EELS and synchrotron-based XANES work together to provide geochemical and petrographic information of primordial planetary materials at the nanoscale. While STXM-XANES can map out an entire FIB lamella, it cannot achieve the sub-nm spatial resolution of an aberration-corrected STEM. Thus, STXM is often necessary for large scale mapping, with STEM providing higher resolution mapping of sub-regions of the sample. However, if low-loss EELS can provide the same information as core-loss XANES (as in the case for locating meteoritic nanodiamonds), then the entire experiment can be performed using STEM. In most cases, STEM-EELS has sufficient spectral resolution to observe chemical features seen in XANES spectra, although beam damage is a known issue for STEM work.

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**Figure 2.** HAADF image of Bells IOM and low-loss EELS generated map of nanodiamonds. The orange and blue boxes show the locations of the EELS spectra shown in the upper right. The spatial resolution of this map is 2 nm.