Tracking Hydrothermal Alteration in Meteorites with Oxidation State Measurements by STXM-XANES and Aberration-Corrected STEM-EELS

De Gregorio, B.[1], Stroud, R.[1], Nittler, L.[2], Alexander, C.[2], Davidson, J.[2], Moyano-Cambero, C.[3] and Trigo-Rodriguez, J.[3]

[1] U.S. Naval Research Laboratory, United States, [2] Carnegie Institution of Washington, United States, [3] Institute of Space Sciences - Institut d'Estudis Espacials de Catalunya, Spain

Percolation of aqueous fluids into geological materials can cause significant geochemical alteration of organic and mineral components of the rock. Chemical reactions involving loss or addition of water have a homogenizing effect, and can be traced by changes in oxidation state of organic and inorganic components across the sample. This is particularly important for the study of primitive meteorites, which originally formed from dust, gas, and ice in the early Solar Nebula. These primordial components were combined into asteroids and comets. Accreted ices led to abundant aqueous fluids on asteroids, and large asteroids accumulated enough radioisotopes to drive hydrothermal circulation of these fluids. However, the extent of aqueous alteration has been shown to be variable in the least altered meteorites, particularly at the sub-m scale.

Here we apply these ideas to an ultra-carbonaceous xenolith trapped within the meteorite LAP02342 using aberration-corrected STEM and synchrotron-based STXM to measure variations in oxidation state of organic matter and Fe-bearing silicate minerals. This trapped xenolith shares affinities with cometary material, and is therefore likely to reveal how hydrothermal fluids have interacted with primitive Solar Nebula components. A series of FIB-extracted lamellae were prepared to compare organic and inorganic components in the xenolith, in the surrounding meteorite material, and along the contact boundary between the two. The lamellae were first characterized at STXM beamline 5.2.2 at the Advanced Light Source, Berkeley, CA USA. Next, the lamellae were characterized using the aberration-corrected Nion UltraSTEM200 at the U.S. Naval Research Laboratory, operated at 60 keV to minimize beam damage of organic matter. This microscope includes a Gatan Enfinium ER EEL spectrometer and a large solid angle (~0.6 sr), windowless, Bruker SDD X-ray spectrometer. Carbon *K*-edge EELS data acquired from the samples had a measured energy resolution of ~300 meV, comparable to the 100 meV energy resolution of the XANES data. Oxidation of organic matter was evaluated by comparing the relative intensity of pre-edge peaks from oxygen-bearing functional groups (ketone at 286.7 eV and carboxyl at 288.5 eV) with that of the aromatic carbon peak (285.0 eV). For silicate grains, oxidation state was estimated from $L_{2,3}$ peak splitting in Fe-XANES spectra, using relative peak areas to estimate $Fe^{3+}/\sum Fe$.

FIB lamellae extracted from the trapped xenolith contain abundant organic matter, and many of the silicate grains contain ultra-structures typical of early Solar Nebula material (Figure 1a-b), although some of these grains show evidence of partial re-equilibration and recrystallization. The surrounding meteorite material is distinct, consisting predominantly of intergrown silicate minerals with pockets of organic matter (Figure 1a). EELS and XANES spectra from xenolithic organic matter reveal a greater abundance of aromatic carbon bonding and a lower abundance of oxygen-bearing functional groups (Figure 1c-d). Maps of Fe valence state in Fe-bearing silicates also indicate that more reduced material is present within the xenolith (Figure 2). These observations suggest that the highly-oxidizing hydrothermal fluids from the surrounding meteorite did not penetrate into the xenolith, which was altered primarily by less-oxidizing fluids derived from primary ices within the xenolith.

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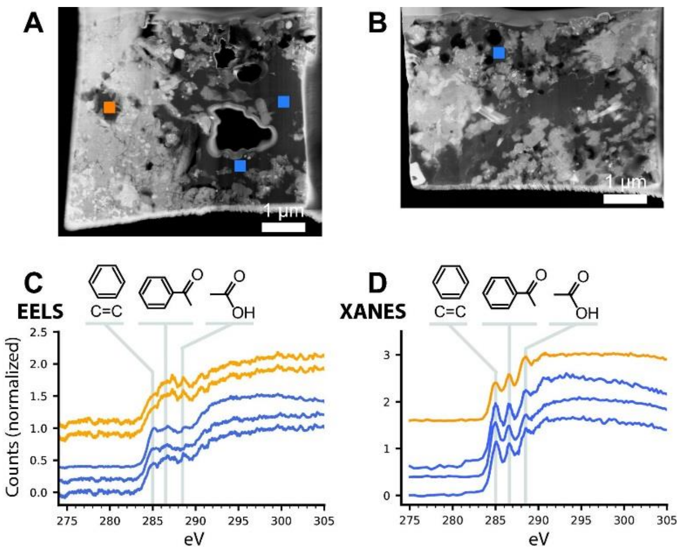

Figure 1. (a-b) High-angle annular dark field STEM images of two of the FIB lamellae from the micrometeorite xenolith trapped in LAP 02342. Lamella (a) was extracted from the edge of the xenolith, and the dichotomy between the surrounding fine-grained matrix (left side) and xenolith (right side) is visible. Lamella (b) was extracted from the xenolith. (c-d) Carbon STEM-EELS and STXM-XANES data from the same regions of the FIB lamellae. Blue spectra were acquired from xenolith organic matter from blue locations shown in (a-b), while orange spectra were acquired from matrix organic matter from the orange location show in (a).

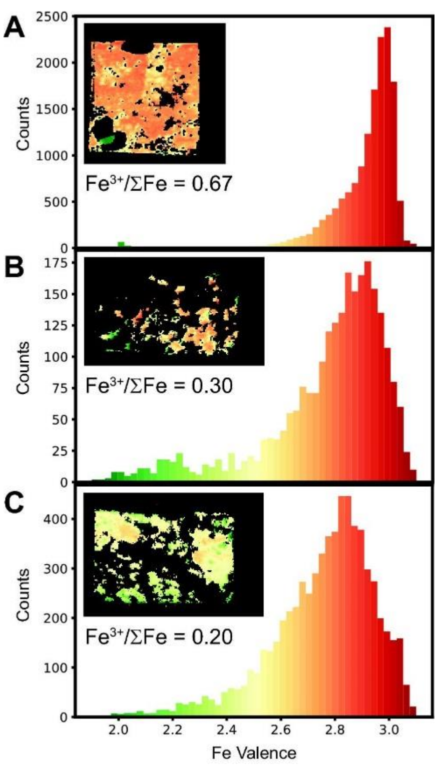

Figure 2. Distributions of Fe valence state for three FIB lamellae from LAP 02342 derived from Fe-XANES data: (a) surrounding fine-grained matrix, (b) border region of xenolith, and (c) xenolith lamella shown in Figure 1b. Insets show maps of Fe valence across each lamella.