OXIDATION STATE STUDIES OF THE EFFECTS OF SIMULATED SPACE WEATHERING.

R. A. Colina-Ruiz[1], H. A. Ishii[2], J. J. Gillis-Davis[3], D. Sokaras[1], T. Kroll[1] and R. C. Walroth[1], [1]SLAC National Accelerator Laboratory (2575 Sand Hill Rd., Menlo Park, CA 94025), [2]Hawai‘i Institute of Geophysics and Planetology (1680 East-West Rd., POST Building, office 602, Honolulu, HI 96822), [3]Washington University in St. Louis (1 Brookings Dr., St. Louis, MO 63130).

Introduction: Space weathering is a comprehensive term for a set of processes that occur on the Moon and other airless bodies, primarily micrometeorite bombardment and charged particle irradiation. The effects of space weathering in lunar regolith include darkening and reddening of the spectral signature, and an increase in the abundance of certain elements (e.g. He, H) associated with solar wind bombardment. Inspection of returned samples has revealed the presence of agglutinates in the regolith, as well as nanophase Fe (npFe) which is believed to be the cause of spectral alterations [1, 2].

It has been previously established that there is an increase in ferromagnetism in returned samples associated with space weathering, commonly reported as the ratio of ferromagnetic resonance intensity (I_S) to the total Fe content (expressed as FeO, written as I_S/FeO). Analysis by electron energy loss spectroscopy (EELS) has revealed the presence of multiple Fe oxidation states, including Fe^0, Fe^{2+}, and Fe^{3+} [3]. The presence of oxidized Fe has been attributed to O atoms migrating to the rims of npFe particles, while others have indicated that this may be terrestrial oxidation [4,5]. While efforts have been made to catalog Fe oxidation states, other elements such as Ti have not been as extensively studied. In 2018, it was announced that NASA would make previously unopened samples from the Apollo missions available for new studies.

Herein, we report preliminary work done in preparation of extensive characterization of the oxidation states present within those pristine samples. Samples include a suite of standards, as well as minerals representative of lunar soils that have been subjected to laboratory simulations of space weathering events. Analytical methods include X-ray spectroscopy, EELS (results pending), and density functional theory (DFT).

X-ray Absorption Spectroscopy: Space weathering effects are expected to be most pronounced close to the surface of mineral grains (<200 nm). As soft X-ray methods are more surface sensitive, we selected edges in this region for analysis, O K-edge, and Fe $L_{2,3}$-edge.

O K-edge XAS: Pulsed laser irradiation of olivine and pyroxene measurements were performed to simulate the micrometeorite component of space weathering [6]. Spectra of weathered and unweatherd samples, as well as Fe and Ti oxide standards, were measured at beamline 10-1 at the Stanford Synchrotron Radiation Lightsource. Data were acquired using total electron yield (TEY), which is sensitive to the top 2 nm of a sample, as well as total fluorescence yield (TFY), which is sensitive to a depth of several hundred nm. Figure 1 shows O K-edge data for weathered and unweathered simulants. We note that the features in TFY data are not as pronounced, indicating that local electronic changes are likely close to the surface.

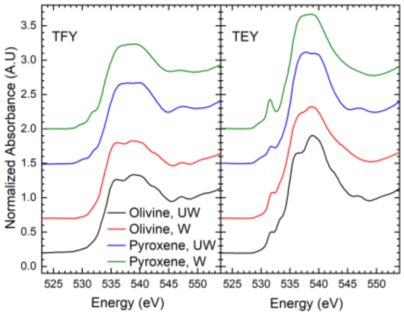

Figure 1. O K-edge XAS of unweathered (UW) and weathered (W) minerals, using TFY (left) and TEY (right) modes.

An increase in intensity around 532 eV is observed for both olivine and pyroxene after irradiation in the TEY data [7], as well as a more pronounced shoulder at 534 eV as is shown in Figure 2. These features are likely related to Si-O bonding and point to an increase in the unoccupied orbitals around O.

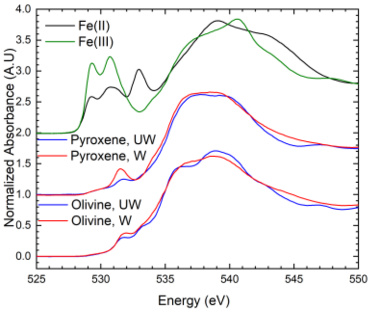

Figure 2. TEY O K-edge XAS of unweathered (UW) and weathered (W) minerals along with calibrants for Fe(II) and Fe(III).

Fe $L_{2,3}$-edge XAS: Weathered and unweathered pyroxene and olivine data, as well as Fe(II) ($FeCO_3$) and

Fe(III) (Fe_2O_3) standards spectra at Fe $L_{2,3}$-edge are shown in Figure 3. A shift to higher energy is observed for weathered respect to unweathered minerals. Peak position and line shape changes when the charge state and crystal field on Fe changes. The intensity of peak ~707 eV is relatively higher than peak ~709 eV, indicating t_{2g}/e_g is higher for weathered than unweathered minerals, a signature of a weaker crystal field interaction due to symmetry distortions around Fe or O vacancies [8,9].

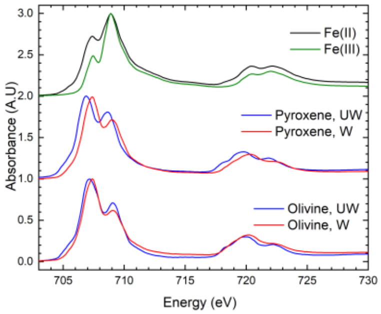

Figure 3. TEY Fe $L_{2,3}$-edge XAS of minerals unweathered (UW) and weathered (W) minerals along with calibrants for Fe(II) and Fe(III).

Density Functional Theory: In order to further understand the X-ray spectroscopy results, we simulated spectra by DFT. We were able to reproduce features in the X-ray absorption and emission spectra of standards, and further investigations are ongoing to simulate various potential species that could be present in the weathered material. Figure 4 shows a comparison of calculated and experimental XES spectra for SiO_2, showing that DFT can predict features with a high degree of fidelity.

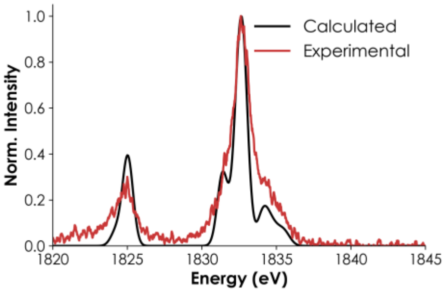

Figure 4. Comparison of calculated and experimental data for SiO_2 XES from Si Kβ.

Electron Energy Loss Spectroscopy: The mineral standards, laboratory-space-weathered olivine and pyroxene, and the synchrotron X-ray-exposed lab-weathered samples have also been prepared as electron transparent thin sections by focused ion beam (FIB) methods for analysis by transmission electron microscopy methods. EELS, like XAS/XES, is highly sensitive to the oxidation state. The mineral thin sections act as EELS oxidation state standards for Ti, Fe, and O for direct comparison with the XAS/XES bulk analyses. In space-weathered samples, non-uniform distribution of oxidation state may occur over small spatial scales. Using EELS mapping with nanometer-scale spatial resolution, the distribution of oxidation states will be extracted in the surface and near-surface regions of the lab-weathered samples before and after X-ray exposure to explore the degree of oxidation state variation and provide context for interpreting bulk XAS/XES results. Figure 5 shows Fe oxidation state mapping from an interplanetary dust particle. High-resolution EELS mapping can reveal nanoparticles of reduced iron as well as variations in Fe^{2+}/Fe^{3+} content. These analyses on mineral standards and laboratory analogs will provide a foundation for analyzing and interpreting the Apollo samples in the future.

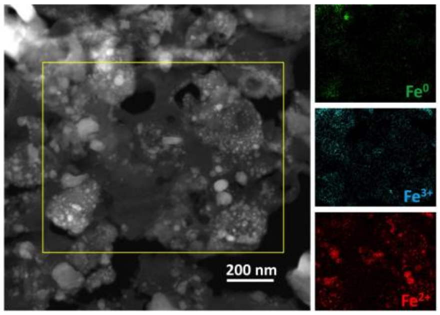

Figure 5. STEM HAADF image from an IDP U220GCA and maps of Fe^0, $Fe^{2+,}$ and Fe^{3+} extracted from EELS spectra mapping of the region indicated by the yellow box.

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