NANOPHASE FE-OXIDE, FE-SULFIDE, AND ILMENITE IN HIGH-TI LUNAR SOIL. K. D. Burgess and R. M. Stroud, 1ASEE Postdoctoral Fellow, Naval Research Laboratory, Washington, DC 20375 (kate.burgess.ctr@nrl.navy.mil), 2Naval Research Laboratory, Washington, DC 20375.

Introduction: Space weathering on airless bodies includes a number of processes, such as micrometeorite impacts and solar wind bombardment, leading to a variety of alteration features, including vapor deposited layers and creation of nanophase opaque minerals [1-3]. Although space weathering on a planetary scale has important implications for remote sensing measurements [3], direct laboratory observation and analysis of the individual nano-scale features is necessary for determining which processes and reactions dominate on specific airless bodies. Transmission electron microscopy (TEM) is the most commonly employed method for such studies [2]. Recent improvements TEM and electron energy-loss spectroscopy (EELS) instrumentation and techniques provide significant increases in both the spatial and energy resolution, enabling better direct observation of nanophase iron oxides in mature lunar soil [4].

We report here results from an aberration-corrected scanning transmission microscope (STEM) study of the composition and oxidation state of soil grains from mature lunar soil 79221.

Methods: Samples were prepared using focused ion beam (FIB) microscopy. The grains were sputter-coated with a gold protective layer (~30 nm thick) and a thick carbon film (1-2 µm) before ion milling to prevent damage to the grain surface by the ion beam. Samples were moved directly from the FIB to the pre-bake vacuum chamber where they were heated to 140°C for six hours to drive off adsorbed water before insertion in the UHV system.

Equipment: Electron energy loss spectroscopy (EELS) and energy dispersive x-ray spectroscopy (EDS) data were collected with PRISM, the NION UltraSTEM200 at the Naval Research Laboratory, equipped with a Gatan Enfinium ER EEL spectrometer with and a Bruker SSD-EDS detector. The STEM was operated with at 200 kV, with a ~ 80pm, 0.1 to 0.2 probe. Spectra were collected as spectrum images (SI), with a spectrum collected for each pixel for mapping of possible variations in thickness, composition, and oxidation state. Each pixel has a short dwell time (0.01-0.5s). Fe L-edges in EEL spectra are caused by the excitation of inner shell (2p) electrons to the unoccupied 3d orbitals. EEL spectra of metallic Fe and Fe²⁺ and Fe³⁺ bearing minerals show distinct edge shapes and chemical shifts that depend on the oxidation state and the symmetry and coordination of the atom site.

Results: Three FIB sections from three different grains have been analyzed. Two grains are presented here, one predominantly composed of plagioclase, and the other is a glassy sphere (GS), partially devitrified and including plagioclase, pyroxene, olivine, ilmenite, and chromium-bearing ulvospinel. GS lacks an Fe-rich rim; Plag1 has a complex 100-200 nm thick rim with significant nanocrystals and compositional layering.

Glassy Sphere. The glassy sphere from which sample GS was removed is ~30 nm in diameter; smaller spheres and “splashes” cover the surface, a common feature of mature soils [5]. A glassy “splash” coats much of the surface of GS and contains significant nano- and micro-phase Fe⁰. The interior of the grain is largely devitrified; most sub-grains are larger than 500 nm. However a number of nanocrystals are also observed. Where they are far from other crystals, they are predominately Fe⁰, but where they are spatially associated with the pyroxene dendrites, Fe-sulfide and ilmenite are found.

Figure 1. HAADF images of GS showing ilmenite, olivine, pyroxene, and Fe-rich nanocrystals. EELS and EDS analysis shows the nanocrystals are Fe-sulfide and ilmenite, often in close spatial association. The EDS map of Fe, Ti, and S shows two such particles.

Plag1. The bulk of this sample is crystalline plagioclase. There is a vapor deposited rim composed of layers of several compositions and rich in Fe that are continuous for up to several microns. A likely splash melt of 100-500 nm covers another portion of the surface. The corner of the grain is amorphous and has a very different composition from the bulk of the grain, with significant nanophase Fe⁰ and Fe-oxides, but the transition is not abrupt as it is with the splash melt lay-
er. Large cracks and vesicles are present in the grain in and around this region.

**Figure 2.** HAADF image of amorphous corner of Plag1. Nanophase Fe (bright spots) are ubiquitous in the region. Black regions are vesicles.

Close analysis of some of the nanophase iron (npFe) shows variations in oxidation state, both in interior and rim particles.

**Figure 3.** False color RGB image and summed Fe L-edge spectra of two Fe-rich nanoparticles from indicated region in lunar soil 79221 (Fig. 2). The bottom rim of the lower nanoparticle (red) is clearly highly oxidized (plotted against Fe$^{3+}$-bearing basaltic glass), while the core of the lower nanoparticle is metallic Fe (gray). The upper nanoparticle (green) more closely resembles the wustite standard (black) with its narrower peaks.

**Figure 4.** Multiple layers of npFe with varying major element composition are present in the vapor deposited rim of Plag1, as seen in HAADF image and Fe and Al element maps. The bottom right image shows the relative contribution of the EELS signal for oxidized (red) and reduced (green) components. The nanoparticles furthest from the surface are oxidized while the more ordered layers are metallic Fe. The amorphous material between the particles (black) has less Fe, but both oxidized and reduced states are present. Beam damage likely affects the oxidation state in the amorphous regions; however, oxidation states in crystalline regions are less affected and do not change on repeated measurements.

**Conclusion:** As technique and instrument developments allow us to measure composition and oxidation state of space weathered materials at finer scales, new complexity in nanophase opaques can be observed. Processes leading to the oxidation of Fe, both in vapor deposited rims and grain interiors, need to be included in descriptions of lunar space weathering. Such processes could include loss of hydrogen during heating or movement of oxygen in the silicate matrix as new material is reduced. Additionally, optical measurements of nanophases other than metallic Fe may be needed to fully account for space weathering features seen in remote measurements.

**Acknowledgements:** This work was supported by the RISE node of NASA’s Solar System Exploration Research Virtual Institute.