THE SEARCH FOR WATER IN LUNAR SOILS THROUGH COORDINATED ANALYSIS OF SPACE WEATHERING CHARACTERISTICS IN AN APOLLO 17 SAMPLE

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Introduction: Space weathering processes affect the optical, chemical, and microstructural properties of grains on the surfaces of airless planetary bodies such as the Moon [1]. Examples of microstructural changes in space weathered samples include amorphous rims (upper 100 nm) that may contain nanoparticles of predominantly reduced Fe, called nanophase iron (npFe), and vesicles that may form from the coalescence of solar wind H and He [2,3]. npFe in space weathered rims average 3 nm in size in mature lunar soils [4]. Some nanophase iron particles previously identified in Apollo 17 soil sample 79221 exhibit a unique hollow structure, with oxidized iron rims and void space in their cores [4,5]. One proposed mechanism for forming these hollow nanoparticles is the progressive oxidation of particle rims which drives the outward diffusion of Fe metal nanoparticle interiors, leaving central void space [4]. Such oxidation of nanoparticle rims may be driven by the presence of water in the lunar soil grain itself. The formation of water in lunar soils through space weathering processes has been proposed to occur via the combination of implanted solar wind hydrogen and matrix oxygen. Water has been previously measured within vesicles in the space weathered rims of interplanetary dust particles [6] and has been proposed to be present within vesicles found in the space weathered rims of lunar soils. Here, we present findings of a high density of hollow npFe particles in the presence of vesicle-rich regions of space weathered rims and discuss their possible connection to the presence of water.

Methods: Apollo sample 79221 is a mature lunar mare soil. The regolith sample was first sieved to a >45 µm size fraction then grains were individually transferred to a carbon tape coated scanning electron microscopy (SEM) stub and sputter-coated with Pt. Electron-transparent focused ion beam (FIB) sections were extracted from individual grains for transmission electron microscopy (TEM) analyses using a Helios G4 UX Dual Beam SEM at Purdue University. We acquired high-resolution (HRTEM) images of the rim to characterize evidence of space weathering. such as amorphous rims, nanoparticles, and vesicles using a 200 keV Tecnai T20 TEM at Purdue. Low-loss electron energy loss spectra (EELS) are being collected to identify the presence of H, He, and H_2O in the vesicles using a Thermo Scientific Themis Z monochromated and aberration-corrected TEM equipped with a Gatan Quantum 965 EELS detector at Purdue. Core-loss EELS are being collected to determine the oxidation state of the npFe particles. Quantitative energy dispersive X-ray spectroscopy (EDX) was performed using a Super X EDX detector on the Themis Z. We also plan to extract atom probe tomography (APT) tips from regions of the grain adjacent to the TEM FIB sections and analyze them using the LEAP 5000XS tomograph at Northwestern University. APT will be used to quantify the amount of water in the grain rims and create a depth profile of the concentration of water [7].

Results and Discussion: HRTEM images show the presence of vesicles, npFe, and an amorphous rim in the grain with a clinopyroxene composition. Of particular note is the presence of hollow nanoparticles in regions of the rim with a high density of vesicles, with solid nanoparticles extending deeper into the sample below the vesicles. The hollow nanoparticles are ~6-8 nm in diameter and the vesicles range from 5-20 nm in diameter. The maximum depth of the hollow nanoparticles in the rim seems to be the same as that of the vesicles and varies between 20-100 nm.

HRTEM, EDX, and high-angle annular dark field (HAADF) imaging also show the presence of nanoparticle-rich veins present throughout the FIB section. These veins are Fe-enriched and Si-depleted relative to the rest of the grain and have compositions of O, Ca, and Mg consistent with the surrounding material. These veins do not have any single orientation and are present below the rim, in the rim, and crossing the rim-interior boundary. Their thicknesses are ~20-50 nm across and can span 100's of nm across the section. The existence of these veins below the ~100 nm depth of features associated with solar wind irradiation leads us to believe that this grain may exhibit a compound-type rim.

Preliminary low-loss EELS measurements have shown a possible detection of H within a vesicle in the rim based on the peak associated with the hydrogen K-edge. The possibility of the presence of water within the vesicles may explain the hollow nanoparticles that are spatially correlated with vesicles as the water may act as an oxidizing agent that drives the outward diffusion of the Fe nanoparticle interiors. Correlation of TEM and APT measurements may be able explain relationship between the vesicles and the hollow nanoparticles.

References: [1] Pieters C. M. and Noble S. K. (2016) *Journal of Geophysical Research: Planets* 121(10):1865–1884. [2] Keller L. P. and McKay D. S. (1993) *Science* 261(5126):1305-1307. [3] Keller L. P. and McKay D. S. (1997) *Geochimica et Cosmochimica Acta* 61:2311-2341. [4] Thompson M. S. et al. (2016). *Meteoritics & Planetary Science* 51(6):1082-1095. [5] Burgess K. D. and Stroud R. M. (2017) *Microscopy Today* 25(3): 32-39. [6] Bradley J. P. et al. (2014) *Proceedings of the National Academy of Sciences of the United States of America* 111(5):1732-1735. [7] Greer J. et al. (2020) *Meteoritics and Planetary Science* 55(2):426-440.