IDENTIFICATION OF SOLAR WIND-SOURCED WATER IN THE SPACE WEATHERED RIMS OF LUNAR SOILS. A. M. Kling[1*], J. Greer[2,3], M. S. Thompson[1], P. R. Heck[2,3], [1]Department of Earth, Atmospheric, and Planetary Sciences, Purdue University, West Lafayette, IN, 47907 (*klinga@purdue.edu), [2]Chicago Center for Cosmochemistry, Dept. of the Geophysical Sciences, University of Chicago, Chicago, IL, 60637, [3]Robert A. Pritzker Center for Meteoritics and Polar Studies, Negaunee Integrative Research Center, Field Museum, Chicago, IL, 60605.

Introduction: The production of water (OH and/or H_2O) in soils due to the implantation of solar wind hydrogen ions into oxygen-bearing minerals on the lunar surface has previously been hypothesized on the basis of remote sensing datasets [1,2,3,4], ion irradiation experiments [5,6], and computer simulations [7,8]. Water produced through solar wind irradiation has already been identified in the rims of interplanetary dust particles [9] and grains returned from asteroid Itokawa [10] and has been predicted to exist in the space weathered rims of lunar soil particles. Solar wind water has also been identified within lunar agglutinate grain interiors [11] and within the rim of a space weathered lunar ilmenite grain [12]. However, our understanding of the relationship between microstructural space weathering characteristics and solar wind water in silicate minerals is still at a very early stage.

Space weathering processes are driven by solar wind irradiation and micrometeorite bombardment and alter the optical, chemical, and microstructural properties of grains on the surfaces of airless bodies [13]. Examples of microstructural changes in space weathered samples include the production of amorphous rims (<100 nm in thickness) due to solar wind irradiation, vesicles that may form from the coalescence of implanted solar wind H and He, and submicroscopic Fe-bearing particles called nanophase iron (npFe), present in both grain rims and agglutinate interiors [14].

In this work, we use a set of coordinated analytical techniques including transmission electron microscopy (TEM) and atom probe tomography (APT) to identify water sourced from the solar wind in space weathered rims of lunar soils, characterize the microstructural environments in which the water exists, and identify the concentrations of hydrogen species with depth.

Methods: Here we analyze grains from the Apollo 79221 regolith sample, a mature lunar mare soil. The sample was first sieved to a size fraction of >45 µm. Then, individual grains were transferred to an aluminum stub coated in carbon tape and the stub was sputter coated with Pt. We analyzed grains on the stub in the Hitachi TM 4000 Plus benchtop scanning electron microscope (SEM) equipped with Oxford energy dispersive x-ray (EDX) detectors at Purdue University. We targeted grains 100-200 µm in diameter that displayed vesicles or bubbles at their surface as evidence of solar wind irradiation. Grains of clinopyroxene, olivine, plagioclase, and ilmenite were identified for further analysis.

Focused Ion Beam sample preparation: A Helios G4 UX Dual Beam focused ion beam SEM (FIB-SEM) at Purdue University was used to prepare electron-transparent (<100 nm thick) cross sections of individual grains for analysis in the TEM. Adjacent FIB sections were also prepared for each grain for subsequent APT analyses using the TESCAN LYRA3 FIB-SEM at UChicago. The APT FIB sections were cut and annularly milled to produce 4-5 nanotips that were then sharpened via ion-milling to have a radius of ~30 nm at the apex.

Transmission Electron Microscopy: We acquired high-resolution TEM (HRTEM) images of the clinopyroxene FIB section to characterize space weathering features such as amorphous rims, vesicles, and nanophase iron particles (Fig. 1). Low-loss electron energy loss spectra (EELS) were collected using a Thermo Scientific Themis Z monochromated and aberration-corrected TEM equipped with a Gatan Quantum 965 EELS detector at Purdue. Spectra were collected as linescans across vesicles, within and outside amorphous rims, and around npFe to identify the presence of H and H_2O via the hydrogen core scattering edge (H-K), energy gap of water (EG), and ionizing threshold of water (IT) [9]. These measurements will be replicated on FIB sections from olivine, plagioclase, and ilmenite grains.

Atom Probe Tomography: The nanotips were analyzed with a CAMECA LEAP 5000XS tomograph at Northwestern University. A description of the methodology used for APT analyses is given in [15].

Results and discussion: HRTEM imaging of the clinopyroxene section shows the presence of an amorphous space weathered rim which includes vesicles and npFe particles (Fig. 1). One region of the space weathered rim exhibits a high density of vesicles and hollow npFe particles (Fig. 1b). EELS spectra collected from these hollow npFe indicate they have mixed oxidation states, like those seen in [16]. TEM imaging also showed the presence of Fe nanoparticle-rich veins present throughout the section (Fig. 1d). These veins are present above, below, and cross cutting the space weathered rim, and have no single orientation. The anticorrelation of FeO and H across these veins as revealed by APT [17] may indicate an oxidation process to form these structures.

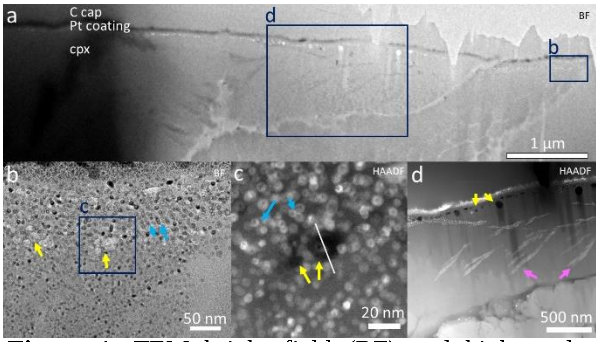

Figure 1. TEM bright field (BF) and high angle annular dark field (HAADF) images of the clinopyroxene grain and b) the region dense with vesicles (yellow arrows) and hollow npFe particles (light blue arrows), c) a vesicle analyzed with EELS, and d) the veins (pink arrows) in the section.

EELS spectra collected from a vesicle in the clinopyroxene grain include the H-K, IT, and EG features, indicating the presence of hydrogen and water within vesicles in the space weathered rim of the grain (Fig. 2). The edge positions of the features in spectra a and b in Figure 1 are IT (2.4 eV), EG (6.7 eV), and H-K (13.7 eV). The edge shapes and positions are similar to those from [9] and those known for water and H.

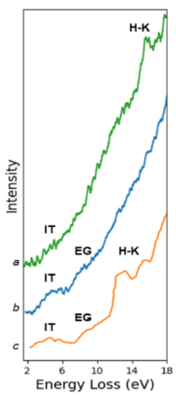

Figure 2. Low-loss electron energy loss spectra of a) a vesicle from the space weathered rim of a lunar clinopyroxene displaying a strong H-K and weak IT feature, b) another vesicle from the lunar clinopyroxene with EG and IT features, and c) a vesicle from the space weathered rim of an IDP from [9] which displays H-K, IT, and EG features.

APT analyses identified H, OH, and H_2O in the clinopyroxene and olivine samples analyzed thus far. The clinopyroxene sample exhibits an enrichment in the hydrogen species to a depth of ~100 nm. In the olivine sample, all three of these hydrogen species were present above background levels and exhibited a steady decline in concentration with depth in the APT tip, which extended to a maximum depth of 126 nm (Fig. 3). This concentration profile does not have a clear maximum concentration at ~40-60 nm as seen in a space weathered ilmenite grain from a submature mare sample [12] which may indicate that mature samples may redistribute these species through diffusion into vesicles and/or deeper into the sample. APT measurements also identified vesicles within the olivine and ilmenite samples and observed an increase in hydrogen and helium species upon intersecting one of the vesicles in the ilmenite sample [15]. The presence of water within the vesicles may serve as an oxidizing agent which may explain the spatial correlation between the hollow npFe and the high density of vesicles.

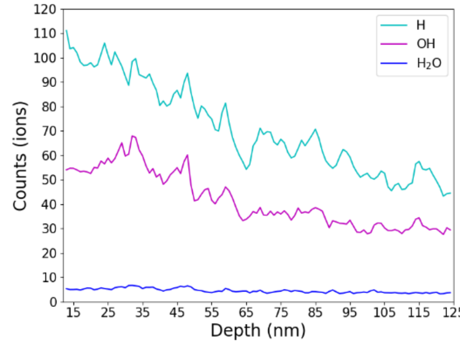

Figure 3. Depth profile of hydrogen species concentration obtained by APT on an olivine tip. The top 11 nm of data have been removed as this was the extent into the sample of adsorbed hydrogen species.

Conclusions: The presence of water in the space weathered rims of lunar soils grains provides evidence that solar wind implantation of hydrogen is a viable mechanism to form water on the lunar surface. This serves as a ground-truth for hydration detected on the lunar surface via remote sensing. The concentration of water we have observed within vesicles in these rims has implications relevant to how water is stored and its ability to diffuse in and out of grains over diurnal or longer timescales. SOFIA remote sensing detections of molecular water suggest that the water may reside somewhere within the interior of lunar grains to allow it to survive a lunation [18]. The water we have observed trapped within vesicles in the space weathered rims of lunar grains may be a source for these observations.

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