

SOLAR WIND-SOURCED WATER STORED IN NANOSCALE RESERVOIRS IN LUNAR SOIL GRAINS.

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Introduction: The widespread presence of water on the lunar surface measured by remote sensing spacecraft is likely the result of space weathering processes [1,2]. The primary space weathering mechanism that drives the production of this water on the lunar surface is solar wind irradiation. In this process, energetic H⁺ ions (~1 keV) from the solar wind are continually irradiating the lunar surface, where they are implanted up to ~100 nm deep into individual lunar soil grains. The implantation of ions results in microstructural changes including the formation of a disordered nanocrystalline or amorphous rim and the production of elongated defects and vesicles [3]. Defects present within the solar wind-irradiated rim are predicted to serve as trapping sites where implanted hydrogen ions may react to form OH and/or H₂O [4].

However, simulations of the thermal stability of the trapped hydrogen and water in these defects have suggested that these sites may not be able to store hydrogen or water over either diurnal or geologic timescales [5]. This has resulted in the hypothesis that the molecular water recently observed on the lunar surface must be trapped within impact glasses to be thermally stable and not diffuse out on diurnal timescales [6]. However, vesicles formed by space weathering have been shown to trap solar wind-sourced water in interplanetary dust particles [7] and may indicate that an impact event after solar wind hydrogen implantation may not be necessary to form and trap water. Here, we present the results of coordinated nano-scale imaging and analyses including scanning transmission electron microscopy (STEM), electron energy loss spectroscopy (EELS), and atom probe tomography (APT) to identify solar wind-sourced water stored in vesicles in space weathered lunar soil grains.

Methods: Here we analyze Apollo regolith sample 79221, a mature lunar mare soil. An olivine grain, an ilmenite grain, and an agglutinate grain were identified using scanning electron microscopy (SEM) and selected for further analyses. Two cross sections were extracted from each grain using focused ion beam-scanning electron microscopy (FIB-SEM). One FIB section was thinned to electron transparency for S/TEM analyses and the other was annularly milled to form four to five nanotips for subsequent APT analyses.

Electron energy loss spectra were collected in the low-loss energy region (0 to ~50 eV) using a Thermo

Fisher Scientific Themis Z monochromated and aberration-corrected TEMs equipped with Gatan Quantum 965 EELS detectors at Purdue University and Ohio State University. Spectra were collected as linescans and spectrum images across vesicles as well as within and outside amorphous rims to identify the presence of H and H₂O via the hydrogen core scattering edge (H-K), the energy gap of water (EG), and ionizing threshold of water (IT) [7].

The APT nanotips were analyzed with a CAMECA LEAP 5000XS tomograph at Northwestern University following the methodology in [8].

Results and Discussion: Transmission electron microscopy analyses of the olivine reveal a nanocrystalline rim that extends to a depth of ~150 nm overlying a crystalline interior that retains solar energetic particle (SEP) tracks. Energy dispersive x-ray spectroscopy (EDS) mapping show that the rim is compositionally similar to the grain interior, indicating that this rim is formed due to solar wind irradiation and not via impact or vapor melt deposition [9]. Vesicles, elongated defect structures, and chains of nano-vesicles were identified within the rim using Bright Field (BF) TEM and high resolution (HRTEM) imaging.

TEM analyses of the agglutinate grain surface reveal a glassy matrix rich in Mg, Ca, Al, Si, O, Fe, and Ti with embedded nanophase iron particles and vesicles present within ~100 nm of the grain surface. As the vesicles are constrained entirely to within the upper 100 nm of the agglutinate rim and are not observed elsewhere at depth into the grain, they are interpreted to have formed due to solar wind implantation after agglutinate formation and did not form concurrently with the agglutinate.

Low-loss EELS spectra from both the agglutinate rim and within vesicles display a feature of variable intensity peaking at ~8.6 eV which corresponds to the energy gap of water (Fig. 1). A small peak at ~13 eV was also identified in some vesicles in olivine corresponding to the H-K edge. Additionally, a peak at ~22 eV was identified within vesicles in the olivine which corresponds to the He-K edge (Fig. 1). While this He-K edge has been identified in lunar oxide minerals previously [10], this is its first identification within lunar silicate materials.

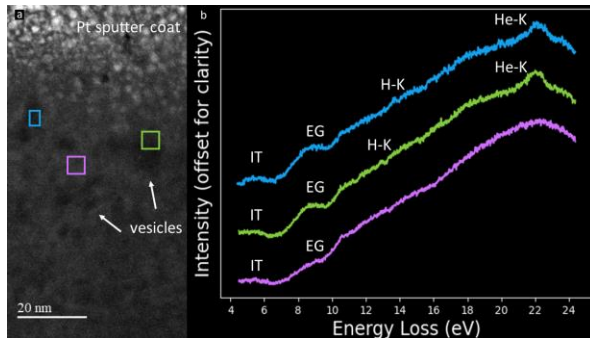


Figure 1. a) Annular dark-field STEM image of space weathered rim of lunar olivine. Darker areas denote the presence of vesicles. b) Low-loss electron energy loss spectra summed from areas within vesicles (blue and green) and rim material (pink). Identified features of interest include the IT, EG, H-K edge, and He-K edge.

Complete APT reconstructions were created for two olivine and two agglutinate nanotips. The two olivine nanotips sampled ~ 120 nm and ~ 85 nm deep into the grain from the surface, respectively. The two agglutinate nanotips sampled ~ 260 nm and ~ 130 nm deep into the grain from the surface, respectively. In all nanotips for which complete reconstructions were made, H, OH, and H_2O were identified by their respective mass-to-charge-state ratios.

The olivine nanotips show a steady decline in concentration of H, OH, and H_2O with depth from the grain surface (Fig. 2). In addition to the overall trend of declining H, OH, and H_2O concentration with depth, there are isolated peaks of increased concentration of these species throughout the depth of the tip (Fig. 2). These peaks of increased concentration are associated with areas of higher atomic density. We interpret these areas to be vesicles formed as space weathering products based on their sizes, shapes, and distribution throughout the solar wind-irradiated rim. The presence of H, OH, and H_2O throughout the depth of the solar wind irradiated rim as well as their increased concentrations in vesicles formed as products of space weathering leads us to believe that these detections are real, are inherent to the sample, and that these species are sourced from the solar wind.

Implications for Detecting Water on the Moon:

The identification of increased water content in vesicles by both APT and EELS analyses indicate that vesicles, and other complex microstructural features like defects, may be sites where water can be trapped and stored in higher concentrations. This directly supports the prediction that radiation-induced defects from the solar wind may act to trap implanted hydrogen and allow it to react to form OH and/or H_2O [4].

Our results also have important implications regarding the interpretation of remote sensing

observations of water on the lunar surface. Infrared and ultraviolet remote sensing observations of the lunar surface have indicated there may be a diurnal trend in water content on the lunar surface [2,11]. It has been suggested that the accumulation of defects due to solar wind irradiation, such as those observed in this study, may contribute to the observed diurnal water content variations on the lunar surface [12]. Additionally, infrared remote sensing detections of molecular water on the lunar surface suggest that the water retained in lunar regolith over the course of a lunar day may reside somewhere within the interior of lunar grains in order to not be lost via thermal escape [6]. The water we have observed trapped within vesicles and in the space weathered rims of lunar grains may be a source for these observations. These vesicles and other defects may serve as sites where water can be stored without diffusing out of host grains during the diurnal temperature cycles that occur on the Moon.

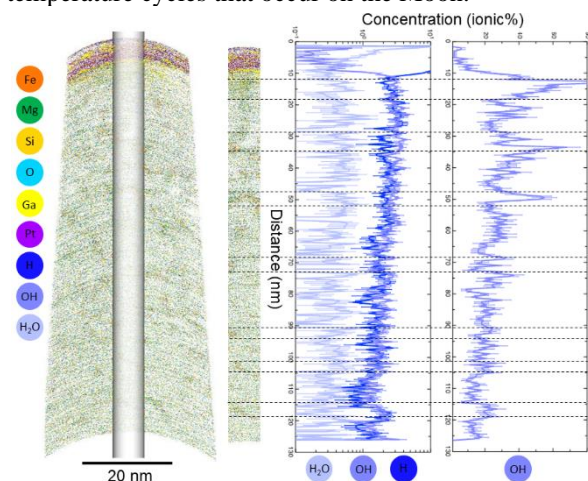


Figure 2. APT reconstruction of olivine tip B. Areas of increased atomic density indicate the presence of vesicles. Depth profiles of H, OH, and H_2O are plotted logarithmically and show a steady decrease in concentration with depth. OH is plotted again, linearly. The peaks in concentration correspond to vesicles and other defects identified in the reconstruction.

References: [1] McCord, T. et al. (2011) *JGR Plan.*, 116, E00G05. [2] Sunshine, J. M. et al. (2009) *Science*, 326(5952), 565–568. [3] Keller L. P. and McKay D. S. (1993) *Science*, 261(5126):1305-1307. [4] Farrell, W. M. et al. (2015) *Icarus*, 255, 116-126. [5] Tucker, O. J. et al. (2019) *JGR Plan.*, 124(2), 278-293. [6] Honniball, C. I. et al. (2021) *Nat. Astro.* 5, 121–127. [7] Bradley, J. P. et al. (2014) *PNAS*, 111, 1732–1735. [8] Greer, J. et al. (2022) *LPS LIII* #1508. [9] Keller, L. P. & McKay, D. S. (1997) *GCA*, 61, 2311–2341. [10] Burgess, K. D., and Stroud, R. M. (2018) *GCA*, 224, 64-79. [11] Hendrix, A.R. et al. (2019) *GRL*, 46, 2417-2424. [12] Morrissey, L.S. et al. (2022) *Icarus*, 379, 114979.