COLD-CURATION ENHANCED RETENTION OF SOLAR WIND VOLATILES IN LUNAR SOIL SILICATES. K. D. Burgess,[1] B. A. Cymes[2], R. M. Stroud[1*], and ANGSA Science Team[3]; [1]Materials Science and Technology Division, Code 6366, Naval Research Laboratory, 4555 Overlook Ave. SW, Washington, DC 20375, USA (kate.burgess@nrl.navy.mil); [2]NRC Postdoctoral Fellow, Materials Science and Technology Division, Code 6366, Naval Research Laboratory, 4555 Overlook Ave. SW, Washington, DC 20375, USA; [3]ANGSA Science Team list at https://www.lpi.usra.edu/ANGSA/teams/; *now at Arizona State University, Tempe, AZ 85287.

Introduction: The solar wind delivers significant amounts of hydrogen and helium to the surfaces of planetary bodies over time, a process that influences the composition of the surface and the atmosphere or exosphere, remote measurements, and resources available for current and future utilization. On airless bodies such as the Moon and asteroids, this solar wind irradiation is an important component in the formation of space weathering features such as nanophase metallic iron (npFe^0), amorphous rims, and vesicles within the top 100-200 nm of grain surfaces [1,2]. The remote sensing data from many instruments investigating the lunar surface show a clear hydration signal that varies based on latitude, temperature, time of day, and magnetic fields [3], all indicating a relationship with the solar wind. However, the form of this hydration (hydroxyl or molecular water) and how it is stored or trapped in surface material beyond a single lunar day has been a matter of significant discussion [3]. Recent results from returned samples from asteroid Itokawa show elevated H/OH/H_2O in space weathered rims [4], and the authors used this data to estimate the potential contribution of the solar wind to Earth's water. Vesicles in a space weathered rim of an interplanetary dust particle (IDP) were shown to contain water [5], confirming that water can be formed and retained in the rims of silicate grains. Helium has been measured in vesicles in Apollo lunar samples [6], but so far only in ilmenite and chromite, which are known to retain more He compared silicate phases.

We have investigated space weathered rims on the frozen soils 72320 and 76240 recently made available through the Apollo Next-Generation Sample Analysis (ANGSA) Program, as well as continued detailed examination of space weathered rims in traditionally-curated Apollo lunar samples in an effort to understand how and where solar wind volatiles are retained in soil particles and the role of curatorial differences in affecting what can be measured.

Methods: Soil grains from Apollo samples 79221, 72320/1, and 76240/1 were prepared for scanning transmission electron microscope (STEM) analysis using standard techniques in a FEI Helios G3 equipped with an Oxford 150 mm^2 SDD energy dispersive X-ray spectrometer (EDS). Soils 72321 and 76241 are the traditionally-curated counterparts to the frozen samples. All samples were prepared at least in part at ambient conditions, and frozen soil samples were at room temperature for up to 16-20 hours prior to their examination. A few samples were re-examined after a month at ambient conditions for comparison. STEM analyses included imaging, EDS to determine composition, and electron energy-loss spectroscopy (EELS), which is sensitive to composition, oxidation state, and structure of the material. EDS and EELS data were collected as spectrum images, with a spectrum collected for every pixel, to allow for mapping.

Results and Discussion: FIB sections from multiple olivine grains in soil 72320 have vesicular rims that were analyzed for the presence of hydrogen and/or helium, in addition to observation of other space weathering features. An olivine sample from 72321, also with a vesicular rim, provided direct comparison. Other phases, including phosphates and metal particles from 79221, were also examined in detail.

Frozen sample A and the non-frozen sample show the presence of small (3-5 nm) npFe^0 in a crystalline, vesicular rim with the same composition as the bulk material. The vesicles in the rims are elongate, 20-50 nm, parallel or sub-parallel to the surfaces of the grains, which in SEM appeared to possibly have blisters. Overall, the two rims are remarkably similar. EELS analysis of the vesicles and surrounding rim material, however, show peaks at ~8 eV, ~13 eV, and ~22 eV in some vesicles in the frozen sample that are not seen in the room temperature sample. These peaks are associated with the energy gap (EG) in water, H K-edge, and He K-edge, respectively [5]. The significant difference in vesicle contents between the two otherwise very similar grains from the same soil suggests that the cold curation (-20°C) for the past 50 years has made real differences in the amount of volatile loss from the special ANGSA samples.

Frozen sample B contains spherical vesicles between the olivine substrate and glassy silicate rim (Fig. 1). Several of these vesicles also show evidence of water. The strength of the signal is highly reliant on the amount of beam interaction with the sample, appearing or increasing with increased dwell time or decreased pixel size. Changes to the EELS signal based on these interactions is a known feature of vesicles that contain water [5], and could be material dependent. The frozen samples in general are highly reactive in the beam.

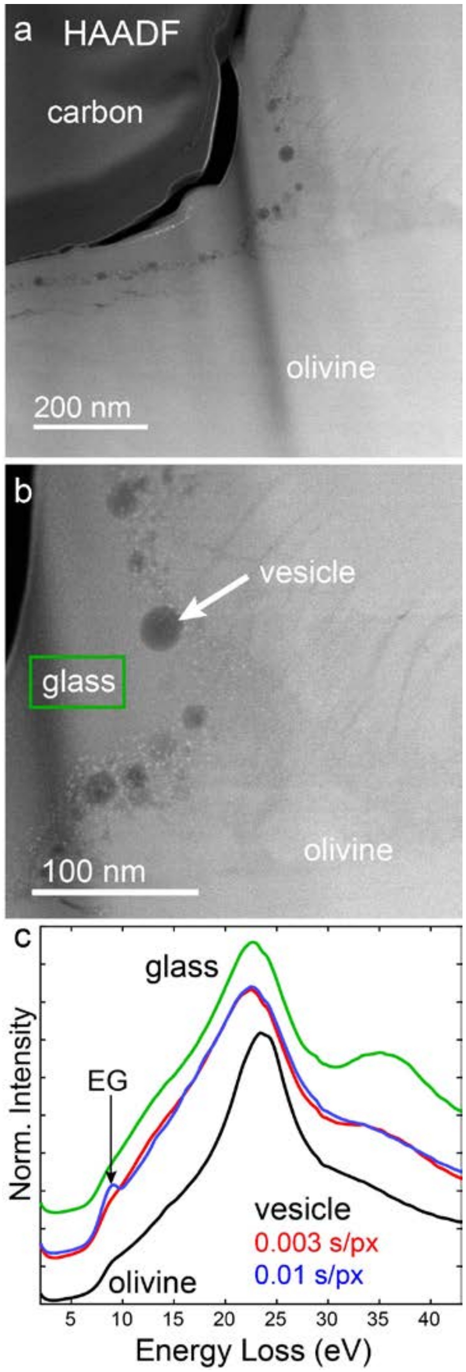

Figure 1. (a) HAADF image of an olivine rim with glassy coating from 72320. (b) Close-up image of rim, showing vesicles and npFe0 between the glassy rim and the unaltered olivine. (c) Low-loss EELS data extracted from several regions showing the olivine (black), glass (green), and region inside a vesicle (red and blue). The blue spectrum was acquired using longer dwell time and shows a distinct ~8.5 eV peak, associated with the energy gap of water (EG).

In addition to silicates, FIB-sectioned lunar apatite and Fe metal show extensive space weathering of these phases, including the formation of vesicular rims. The Fe metal grain, ~2 µm across, contains abundant He measured in its vesicles, as well as signals associated with water. The vesicles in rims of several small apatite grains show a very strong water signal in EELS, as well as indications of elevated water/OH in the rim generally compared to the bulk. These non-silicate phases are much less abundant on the Moon, but the greater volatile retention could mean they play a significant role in exospheric cycling and resources for exploration.

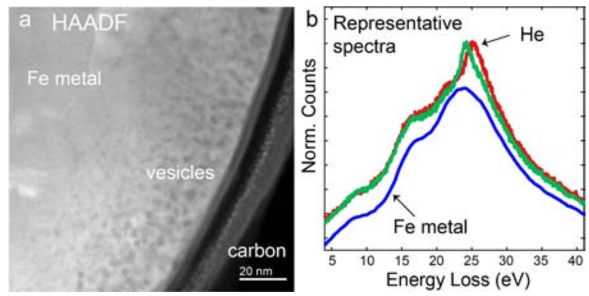

Figure 2. (a) HAADF image of a vesicular rim of an Fe metal particle from soil 79221. (b) Low-loss EELS data extracted from several vesicles showing a distinct He peak at ~22 eV.

Conclusion: The combination of STEM-EDS maps and EELS data provides a powerful way to interrogate the space weathered surfaces of lunar and other planetary samples and increase our understanding of the processes that alter the surfaces of airless bodies. The detection of H and He in silicates from the frozen ANGSA samples but not the room temperature samples suggests that curation plays an important role in retaining volatiles in planetary samples over decades. Additionally, non-silicates consistently show different response than the main silicate phases on the Moon and demonstrate that minor phases on the lunar surface could play important long-term roles in volatile retention and cycling.

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References: [1] Keller, L.P., and McKay, D.S. (1997) *Geochim Cosmochim Acta*, *61*, 2331. [2] Pieters, C.M., and Noble, S.K. (2016) *J Geophys Res*, *121*, 1865. [3] Lucey, P.G., et al. (2021) *Geochemistry*, 125858. [4] Daly, L., et al. (2021) *Nat Astron*, *5*, 1275. [5] Bradley, J.P., et al. (2014) *Proc Nat Acad Sci*, *111*, 1732. [6] Burgess, K.D., and Stroud, R.M. (2018) *Geochim Cosmochim Acta*, *224*, 64.