COMPARISON OF VOLATILE CONTENT IN LUNAR SOILS STORED AT -20 °C AND 20 °C MEASURED USING STEM-EELS.
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Introduction: A sub-set of the lunar regolith samples collected during the Apollo 17 mission were stored under unique conditions for future study following their return. The samples included an unopened core sample vacuum container (CSVC), regolith stored in a special environmental sample container (SESC) under a helium atmosphere, and regolith stored under ultra-pure nitrogen under freezing temperatures (-20 °C). As part of the Apollo Next Generation Sample Analysis (ANGSA) Program, which was tasked with studying these special lunar samples, we are analyzing the frozen regolith portions with scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS). We aim to understand how frozen storage affected the retention of volatile elements in the regolith, primarily H and He implanted by the solar wind. Additionally, outstanding questions remain in the space weathering community regarding the effects of solar wind irradiation and ion implantation on lunar soil components, including those regarding volatile production and cycling relevant to human exploration and in situ resource utilization [1]. The frozen ANGSA samples provide an excellent opportunity to address these points because they represent the most pristine lunar material currently on Earth likely to have retained volatiles for characterization.

Methods: We prepared soil grains of 72320 and 76240 for STEM-EELS analysis by ultramicrotome (UM) sectioning to 100 nm and by preparation of 80-100 nm thick lamellae in a FEI Helios G3 Dual Beam FIB-SEM. The samples were stored in a -20 °C freezer in between preparation steps to minimize exposure to elevated temperatures. We collected STEM data on the aberration-corrected Nion UltraSTEM200-X at NRL. The STEM is equipped with a Gatan Enfinium ER Dual EELS spectrometer and a Bruker X-flash windowless SDD-EDS X-ray energy dispersive spectrometer. The resulting data from the frozen samples are being compared to data collected from soils 72321 and 76241 which were prepared and analyzed by the same methods.

Results and Discussion: Volatile hydrogen and helium are expected to reside within vesicles present in space weathered rims – zones of alteration ~200 nm thick on the surface of individual soil grains. The presence of hydrogen in an EELS spectrum is measured via the ionization K-edge at 13.5 eV. Additionally, a peak at ~8 eV is known to appear which represents the energy gap features associated with hydrogen in the form of H_2O [2]. Helium is measured by the ionization K-edge at ~22 eV. Both samples 72321 and 76241 lack discrete hydrogen within vesicles within minerals in the samples analyzed (~10 TEM grids), which include silicates (orthopyroxene, clinopyroxene, anorthite, olivine), oxides (ilmenite), and glass. Helium has been detected within samples 72321 and 76241, but only in ilmenite and metallic iron nanoparticles, phases in which helium is expected to diffuse out from more slowly than from silicates. Preliminary measurements of sample 72320 show that hydrogen and helium are present within vesicles in multiple olivine grains (see Burgess et al., this meeting) and within vesicles in two glass grains in sample 76240. In the first glass grain, there is a population of nanophase metallic iron particles ($npFe^0$) that range in diameter from 2 to 30 nm present alongside vesicles which range in diameter from 10 to 120 nm. EELS spectrum image pixels were summed from two small vesicles toward the top of the image, vesicle 1 contains H and vesicle 2 contains both H and He (Fig. 1). In the second glass grain, H is measured within a single vesicle (Fig. 2). The grain also contains a population of $npFe^0$ ~5 nm in diameter and also a few larger $npFe^0$ ~15 nm in diameter.

Conclusion: Initial STEM-EELS data from the frozen ANGSA lunar soil samples suggest that cold curation enhances volatile retention in silicate and glass phases. Moving forward, in addition to measuring vesicles in other mineral phases (e.g. pyroxene, plagioclase) to constrain the presence of H and He within them to support the preliminary data, we aim to determine if larger quantities of He are retained in the frozen samples within ilmenite and $npFe^0$, which would also further support this conclusion.

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References: [1] Thompson, M., et al. (2021) *BAAS*, 53(4), 172. [2] Bradley, J.P., et al. (2014) *PNAS*, 111, 1732.

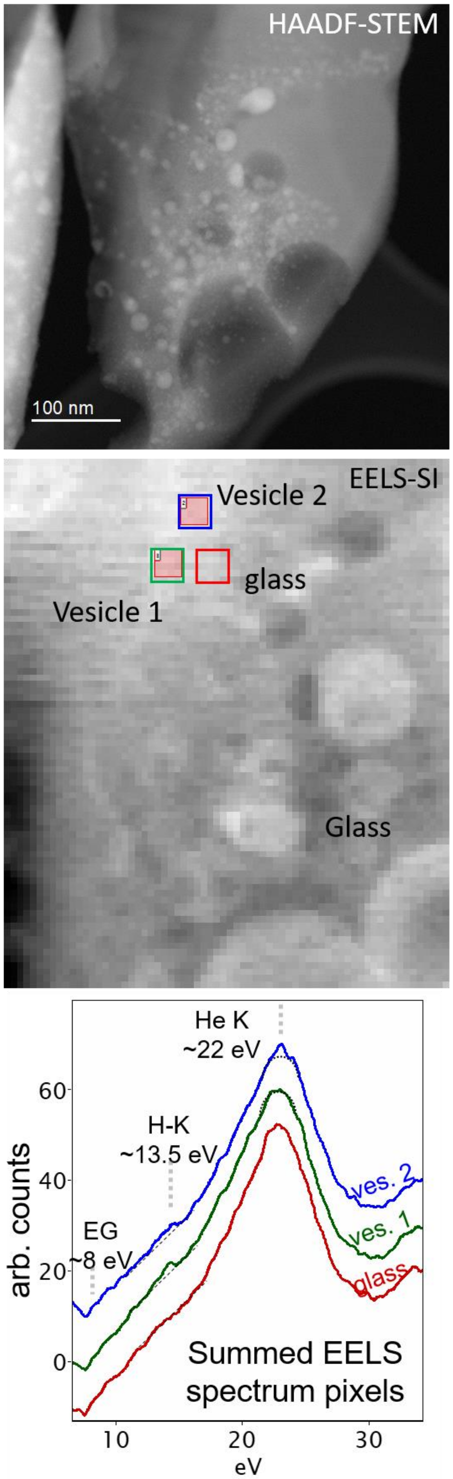

Figure 1. (a) HAADF-STEM image of glass grain from soil 76240 with nanophase metallic iron particles and vesicles. (b) EELS-SI image showing regions where spectra were summed. (c) EELS spectra from regions in (b) showing the presence of H and He within vesicles in the glass grain.

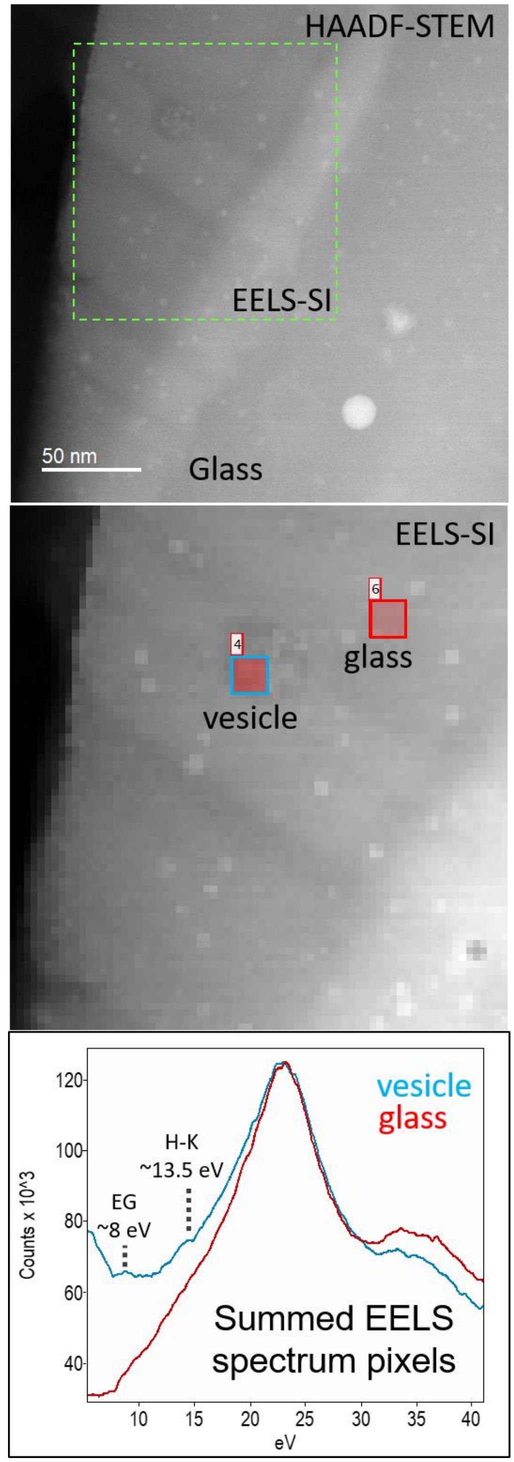

Figure 2. (a) HAADF-STEM image of the rim of a glass grain from soil 76240 containing small nanophase metallic iron particles and a single 20 nm vesicle. (b) EELS-SI image showing regions from where spectra were summed. (c) EELS spectra from regions in (b) showing the presence of H within the vesicle in the glass grain.