PRESERVATION OF VOLATILES IN FROZEN LUNAR SAMPLES: ELECTRON MICROSCOPY OF ANGSA SAMPLES PREPARED BY ULTRAMICROTOMY.

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Introduction: A number of special regolith samples returned during the Apollo Program were stored under unique conditions – including cores sealed on the lunar surface, frozen samples, and samples stored in helium – for future study. One of the goals of the Apollo Next Generation Sample Analysis (ANGSA) initiative is to examine these special samples to provide new insight into lunar volatile reservoirs. Solar wind irradiation delivers a significant amount of volatile hydrogen and helium to the surfaces of airless bodies such as the Moon as part of a larger process called space weathering. The precise timing and mechanism of volatile entrapment within vesicles in thin patinas on individual soil grains during space weathering remain unresolved. We are analyzing the space weathered rims of frozen lunar soil grains with electron microscopy and microanalytical approaches to further understand the products of solar wind irradiation. The results will be compared to data collected on portions of equivalent samples stored at room temperature to evaluate the effects of curation conditions on volatile preservation.

Methods: We prepared soil grains of frozen samples 76240 and 72320 for analysis in the scanning transmission electron microscope (STEM) by ultramicrotome (UM) sectioning. UM sectioning is an efficient method to analyze many different grains on a single TEM grid. Additional targeted samples were also prepared by focused ion beam (FIB) – see Burgess et al. 2022, this conference. The samples were stored in a freezer between preparation steps to minimize exposure to elevated temperatures. The frozen samples were compared to 72321 and 76241, which have been stored under ultra-pure nitrogen at room temperature since their return. The STEM data were acquired with the aberration-corrected Nion UltraSTEM200-X at NRL. The dedicated STEM is equipped with Gatan Enfinium ER Dual EELS and Bruker X-flash windowless SDD-EDS spectrometers for electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy, respectively.

Results and Discussion: The lunar soils are comprised of the minerals anorthite, orthopyroxene, clinopyroxene, olivine, ilmenite, and glass of intermediate composition. The room temperature samples, 72321 and 76241, are lacking in discrete hydrogen in the vesicles identified within these phases. If retained at above the EELS detection limit, hydrogen would be visible in an EELS spectrum by the K edge at ~13.5 eV, and if present as H_2O or OH typically will also have the energy gap feature at ~8 eV, and potentially a weak ionization threshold feature at ~4.5 eV (e.g. [1]). In constrast, we have measured helium routinely within the 73221 and 76241 lunar soils (indicated by the He K-edge at ~22 eV), but only within more refractory phases, including ilmenite and vesicular nanophase iron particles, in which He diffuses more slowly. We anticipate the samples stored in frozen curation conditions may contain detectable levels of He, even in the silicate phases.

Preliminary data from the UM frozen samples have indeed revealed the presence of water within vesicles in a glass grain in 76240. We also observe an overall increase sample reactivity under the electron beam, potentially related to volatile evolution and degassing. Additionally, we have continued to identify helium within ilmenite and also nanophase metallic iron particles as we observed in the room temperature samples. On this point the aim is to determine if larger quanities of helium are retained in the frozen samples within these phases compared to the room temperature samples. We will continue to analyze additional material from the frozen samples to constrain the presence of hydrogen and helium in them to support these preliminary data; however, locating water within silicate glass vesicles is a very promising initial result suggesting that frozen storage made a meaningful impact on volatile retention.

References: [1] Bradley, J. P., Ishii, H. A., Gillis-Davis, J. J., Ciston, J., Nielson, M. H., Bechtel, H. A., and Martin, M. C. (2014) *PNAS* 111(5), 1732-1735.