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Influence of Frozen Curation on Volatile Retention in Pristine Apollo 17 Samples: Initial Results Using Aberration-Corrected STEM-EELS and EDS

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Solar wind irradiation delivers a significant amount of H and He to the surface of airless bodies such as the Moon, Mercury and asteroids. It is one of the major agents of space weathering, and induces physical and chemical changes to the planetary surface, which result in altered spectral properties visible using remote sensing techniques [1, 2]. These changes often manifest as thin (<200 nm), amorphous rims on the surfaces of individual soil grains that can contain vesicles, nanophase metallic iron particles (npFe^0), or a combination of these features [1-3].

How and when H and He became trapped within vesicles in space weathered rims is unresolved. To address these questions, we are analyzing pristine lunar soils from the Apollo collection that have been maintained at frozen temperatures since their return to Earth in 1972, and were recently released for study as part of the Apollo Next Generation Sample Analysis (ANGSA) initiative. The frozen samples will be analyzed using scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) to measure volatiles trapped within vesicles and defects. Additionally, energy dispersive spectroscopy (EDS) data will be acquired to determine composition and elemental distribution. These data will be compared to measurements of portions of equivalent samples stored at room temperature to evaluate volatile retention.

Lunar soil grain samples were prepared for STEM analysis by both ultramicrotome (UM) sectioning and by focused ion beam (FIB) microscopy. UM samples were prepared by embedding soil grains in epoxy and sectioning to ~100 nm using a diamond knife. The sections were then supported on 3 mm lacey-carbon-coated Cu grids. FIB samples were prepared by dispersing grains onto carbon tape; the sample was then coated with ~80 nm of amorphous carbon. Individual grains were identified and sectioned using a FEI Helios G3 Dual Beam FIB-SEM. Prior to lift-out, the grains were protected with ~1 µm of protective carbon and thinned to 1-2 µm using a 30 keV Ga$^+$ beam. The lamellae were then welded using Pt or W to Cu TEM half-grids and thinned to electron transparency (80-100 nm). The first samples prepared consisted of sub-45 µm fractions of Apollo 17 soils 72321 and 76241, which were stored under ultra-pure nitrogen at room temperature since their return. The frozen samples, 72320 and 76420, will be prepared similarly with UM and FIB with the exception that samples will be stored in a freezer in between preparation steps to minimize exposure to room temperature.

Prior to introduction into the UHV STEM environment, samples were held under vacuum at ~20 °C for 48 hours to drive off adsorbed water. STEM data were acquired with an aberration-corrected Nion UltraSTEM200-X at NRL operated at 200 keV and 40 pA with a ~0.1 nm probe. The STEM is equipped with a Gatan Enfinium ER Dual EELS spectrometer and a Bruker X-flash windowless SDD-EDS spectrometer. Images were acquired in HAADF mode, which is sensitive to sample density. EDS and EELS data were acquired as spectrum images (SI).

The primary mineral phases present in the lunar soils studied are anorthite, orthopyroxene, clinopyroxene, olivine, ilmenite, and glass of intermediate composition. In the room temperature samples, 72321 and 76241, we have not observed discrete H in these phases using EELS-SI; however, unequivocal TEM observations of H and H_2O trapped in space weathered rims of lunar minerals have been only very recently reported [4, 5], so its paucity is not unexpected. In contrast, we have measured He regularly within the lunar soils in specific phases including ilmenite and vesicular $npFe^0$.

Helium has a single excitation edge at ~22 eV and detecting the He K-edge in lunar minerals presents a significant challenge for two main reasons. First, the K-edge overlaps with both the silica plasmon at ~22 eV and also the ilmenite plasmon at ~25 eV and second, because He is present in low abundance compared to the bulk material. Therefore, a reliable method for locating He in lunar minerals has been to find dense accumulations of it where the edge is clearly superimposed over the plasmon where it can then be deconvoluted. We typically observe the edge onset vary ~22 eV to ~24 eV, which is associated with differing confinement pressure [6].

We have observed He within oxide phases, such as ilmenite ($FeTiO_3$) (Fig. 1) where it has been previously measured in other lunar samples [7] and we have also measured He within ~20-80 nm $npFe^0$ particles, where it occurs in void spaces [8]; helium has also been measured within chromite [7]. The lunar silicates, despite often having vesicular textures, lack He or H. The diffusion rate of helium in silicates such as augite and olivine are several orders of magnitude faster than through ilmenite and metallic iron, thus we suspect that the frozen samples may reveal H or He both in greater abundances in oxides and $npFe^0$ and also within silicate minerals and glass, given that cold storage likely slowed the rate at which implanted volatiles would be lost.

Detailed STEM-EELS and EDS analysis of room-temperature curated lunar samples 72321 and 76241 has shown where implanted solar wind ions persist in the lunar regolith, namely within oxides and vesicular $npFe^0$. By investigating equivalent frozen-curated samples 72320 and 76240 with STEM-EELS, we will be able to determine if helium occurs in larger quantities in similar phases to quantify nominal diffusion losses. Cold curation likely slowed volatile diffusion, therefore we aim to find both H and He within other lunar phases like glass and silicates. The results of this study aim to shed light on outstanding questions within the space weathering community, such as the individual and tandem influence of solar wind irradiation and micrometeorite bombardment, as well as inform our strategies for long-term sample curation in future sample return missions [9].

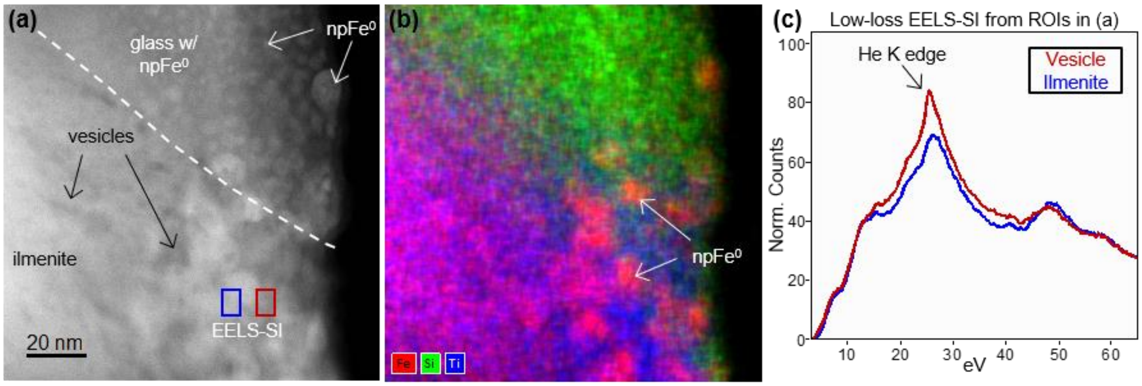

Figure 1. Space weathered rim of an ilmenite- ($FeTiO_3$) and glass-bearing grain. **(a)** HAADF-STEM image of vesicles and $npFe^0$ in ilmenite and $npFe^0$ in glass, dashed line represents the phase boundary. **(b)** Overlain EDS element maps of Fe, Si, and Ti showing the boundary between ilmenite and glass. **(c)** Low loss EELS spectra extracted from a spectrum image corresponding to the area in (a) showing the spectrum from an ilmenite vesicle where the helium K-edge is visible compared to a spectrum from adjacent 'bulk' ilmenite (red and blue boxes).

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