MEASUREMENT OF HELIUM IN NANOPHASE IRON IN LUNAR SOILS TO TEST PROTOCOLS FOR ANALYSIS OF PRESERVED VOLATILES IN ANGSA FROZEN SAMPLES. K. D. Burgess, R. M. Stroud; U.S. Naval Research Laboratory, Washington, DC 20375 (kate.burgess@nrl.navy.mil).

Introduction: The Apollo Next-Generation Sample Analysis (ANGSA) special samples include two soils that were collected from within the shadows of boulders on the lunar surface and subsequently stored in a freezer shortly after their return to Earth (72320 and 76240). These samples are uniquely suited to the study the retention of solar wind volatiles in the space weathered surfaces of individual grains due to both their cold storage by curation and their cold collection location on the Moon. We will use Scanning transmission electron microscopy (STEM) with electron energy loss spectroscopy (EELS) to detect and quantify the hydrogen and helium potentially trapped in vesicles in the space weathered rims [1,2].

One of the first requirements of these studies is to ensure minimal loss of volatiles during sample preparation. The standard operating procedure for preparation of samples for analysis with the Nion UltraSTEM-X includes an overnight bake at 140°C under vacuum. However, the degree to which this bake could lead to the loss of volatiles from the sample is not well constrained. In order to test for this effect and still ensure our samples will not contaminate in the ultra-high vacuum (UHV) microscope, we have prepared a focused ion beam (FIB) sample likely to have some retained volatiles, and observed the sample both after a 2 ½-day, room-temperature vacuum-only “pump out” and a standard bake.

Methods: Grains from lunar soil sample 79221 were mounted on an SEM stub using carbon tape, then coated by 60 µm of evaporated carbon to reduce charging and provide added protection of the surface during the ion beam deposition and milling. SEM imaging and FIB sample preparation were done using an FEI Nova 600 equipped with an Oxford 80 mm^2 SDD energy dispersive X-ray spectrometer (EDS). After imaging, protective straps of C were deposited on the region selected for FIB milling. The sample was prepared using a 30 kV Ga^+ beam.

In order to help remove adsorbed water and to fix hydrocarbons prior to first loading in the STEM, the sample was held under vacuum for 65 hours at room temperature An analysis of the volatiles present in representative portions of the rim of the sample was performed with EELS and EDS. The sample was subsequently removed from the microscope and baked under vacuum at 140°C for 10 hours, according to our standard procedure for removing water and hydrocarbon contamination. The sample was again analyzed for retained volatile contents, both in regions previously examined and in new representative regions, to ensure patterns in volatile loss or retention were not due to beam damage effects. STEM analysis was carried out with the Nion UltraSTEM-X at NRL, operated at 200 kV. This microscope is equipped with a Gatan Enfinium ER spectrometer for EELS and a windowless, 0.7 sr Bruker SDD-EDS detector.

Results and Discussion: Our test-case lunar soil 79221 grain is a fragment of basaltic glass with a number of adhered grains and apparent blisters in the region selected for the FIB section (Fig. 1). Space weathered surfaces of the grain show abundant vesicles and nanophase iron inclusions ($npFe^0$) (Fig. 2). There is no obvious compositional rim other than slightly enhanced Fe around most of the grain. The $npFe^0$ are present in two populations: ubiquitous 1-4 nm inclusions within ~80 nm of the surface and 30-80 nm inclusions spread throughout the grain with only a few located near the grain surface.

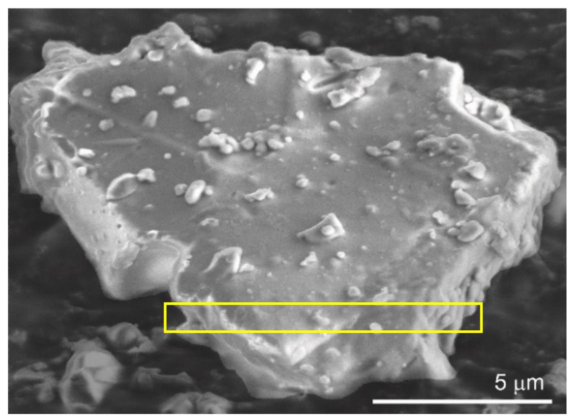

Figure 1. SEM image of glassy grain from mature soil 79221. Sample is tilted 52°. Yellow box indicates approximate location of FIB section.

The larger $npFe^0$ present within ~80 nm of the grain surface have a mottled or corroded appearance [3]. One inclusion, shown in Fig. 3, is corroded where it is closest to the rim but lacks the porous texture beyond this depth. EELS data from selected regions within the inclusion show the presence of He in some of the open pores near the surface. The sharp peak at 23 eV due to He is directly on top of the Fe metal plasmon peak but has a very different shape. The broad hump ~8-18 eV suggests either stress in the lattice or another species being present in the pore. Although clearly altered, the inclusion itself is metallic throughout with no difference with depth from the surface. In several of the $npFe^0$, the energy of the He peak shifts slightly between pores, indicating they are not connected.

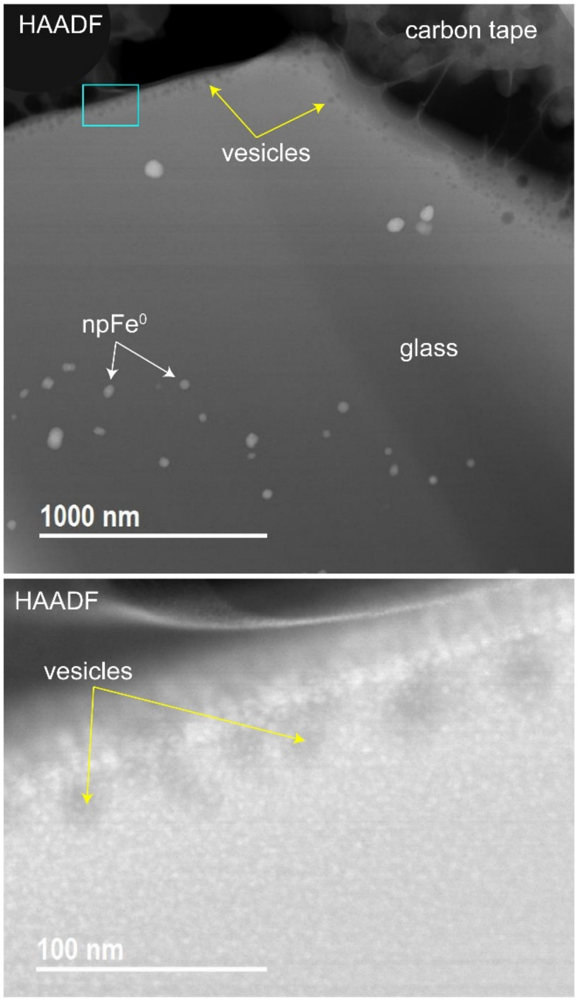

Figure 2. HAADF images of the grain show 30-80 nm npFe^0 throughout and vesicles and small npFe^0 (1-4 nm) in the rim. Vesicles are seen along significant portions of the grain rim.

The STEM analyses show that there are no differences in the grain before and after the bake. Where He was measured in pores in npFe^0, it is the same before and after. In addition, all vesicles measured in the glass are empty in both cases, which is not unexpected due to the long-term, room-temperature storage of the samples. Furthermore, the bake does not affect npFe^0 or vesicle size or the oxidation state of any portion of the sample, which provides further confirmation of previous results from our lab. Importantly, the unbaked sample is equally well-behaved in the microscope and does not show evidence of contamination or affect the vacuum system.

Conclusion: We compared the effects of the standard overnight vacuum bake at 140°C to an extended vacuum pump out on volatile content, vesicle and nanoparticle morphologies in a mature lunar soil grain. While the mature lunar soil sample examined here was stored at room temperature since its return from the Moon, it still retained some volatiles that were measureable using STEM-EELS. Use of the vacuum-only pump out procedure requires significantly more time than the standard overnight bake but reduces the risk of any volatile loss or other alteration to the sample without introducing contamination issues. Further testing of cryo-FIB preparation techniques to reduce the amount of time samples spend at room temperature prior to analysis is planned. This work will enable us to make the best use of the limited frozen sample.

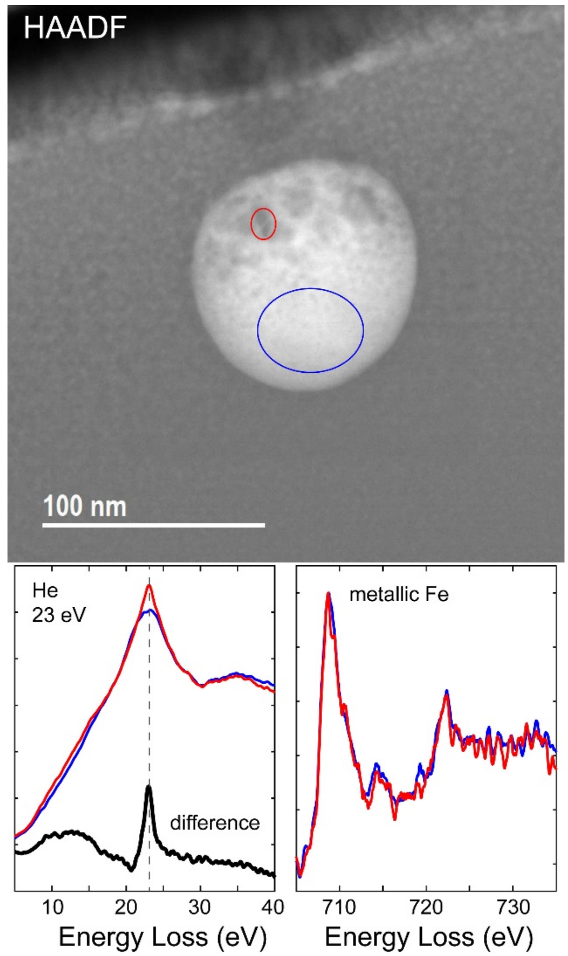

Figure 3. (a) HAADF image of npFe^0 near surface of lunar grain. (b) EELS from selected regions within the inclusion show the presence of He in holes formed in the inclusion where it is <80 nm from the surface. (c) Analysis of the Fe-L edge shows the particle is fully metallic and not oxidized.

Acknowledgements: This work was supported by the NASA ANGSA program.

References: [1] Bradley, J.P., et al. (2014) *PNAS*, *111*, 1732. [2] Burgess, K.D., and R.M. Stroud (2018) *GCA*, *224*, 64. [3] Burgess, K.D., and R.M. Stroud (2018) *JGR*, *123*, 2022.