XANES AND EELS IDENTIFICATION OF FE-REDOX VARIATION IN SPACE WEATHERED APOLLO 17 LUNAR SURFACE SOIL. L. J. Hicks[1], J. C. Bridges[1], T. Noguchi[2], H. Hidaka[3], J. D. Piercy[1], and J. F. B. Kerr[1], [1]School of Physics and Astronomy, University of Leicester, UK (ljh47@leicester.ac.uk), [2]Kyushu University, Japan. [3]Nagoya University, Japan.

Introduction: Airless planetary bodies with surfaces exposed to the space environment are bombarded by electrons and protons from the solar wind and cosmic rays, as well as micrometeorites, resulting in space weathering [1].

Nanoprobe Fe-K X-ray absorption near-edge spectroscopy (XANES) mapping has previously been used by us to investigate the space weathered surfaces of returned asteroid Itokawa sample grains, revealing an increased ferric-ferrous ratio ($Fe^{3+}/\Sigma Fe$) relative to their respective host grain mineralogy. This is likely the result of the implanted solar wind H^+ ions reacting with the segregated ferrous Fe in the surface material [2].

Lunar surface soil samples returned by the Apollo missions also show space weathering, featuring partially amorphised rims containing nanophase Fe metal ($npFe^0$) particles [1,3]. Using electron energy loss spectroscopy (EELS), these npFe particles have been shown to become oxidized, with a correlation suggested between oxidation state and the maturity of the lunar soils [4]. This oxidation is suggested to be due to oxygen in the surrounding glassy matrix, and also H_2O vapour formed in the segregation by the implanted H^+ ions.

In this study, we investigate the Fe-redox variations observed in the dominant silicate phase and the nano-grains of the space weathered rims of lunar surface soil samples, using Fe-K XANES and EELS, with high-resolution STEM imaging. This work will also provide useful insight for further investigating of sample return, such as asteroid Ryugu samples returned by Hayabusa2.

Samples and Methods: The lunar sample number is 78481,29 - a surface sample collected from the top 1 cm of trench soils at Station 8 of Apollo 17 [5]. Three FIB lift-out sections have been extracted successfully.

The lunar grain lift-out sections have been analysed using the I-14 X-ray Nanoprobe Beamline at Diamond. Fe-Kα XAS spectra are obtained from a series of XRF maps over the samples, with energies typically in the range 7000-7300 eV, with a higher energy resolution range over the XANES features (~7100-7150 eV). The XANES maps are processed using *Mantis 2.3.02* [6], and isolated spectra normalized in *Athena 0.8.056* [7]. Similarly to the previously investigated Itokawa asteroid samples [2], increased Fe-redox variations from the host mineralogy to the space weathered zones are estimated by observing increased energy shifts in the $1s \rightarrow 3d$ pre-edge peak centroid positions, and comparing to standard reference minerals of known ferric-ferrous ratio ($Fe^{3+}/\Sigma Fe$).

EELS analyses are performed using the JEOL ARM200CF instrument at ePSIC in the Diamond Light Source synchrotron facility, using an accelerating voltage of 200 keV, current 15 µA, and measuring 0.25eV/ch with a 5 mm EELS aperture. This analysis provides verification of the Fe-redox variation by observing the shifts in the Fe-Lα peaks. Additional high-resolution STEM imaging are also performed at ePSIC using the JEOL JEM-ARM300CF instrument.

Results: Two of the lunar grains were augite pyroxene, $En_{81}Fs_{16}$ (#A17-3) and $En_{85}Fs_{12}$ (#A17-5), and one olivine Fa_{39} (#A17-6). Space weathering was identified in all three lunar samples (e.g. #A17-3 in Figure 1), with partially amorphised host grain material, protected under a deposition of W during the lift-out preparation. Particles measuring ~2-3 nm in diameter (Figure 1B), with lattice fringe spacings of ~2.06 Å, and others measuring up to ~2.10 Å, confirmed to be $npFe^0$, similar to previous studies of Itokawa samples [2,8].

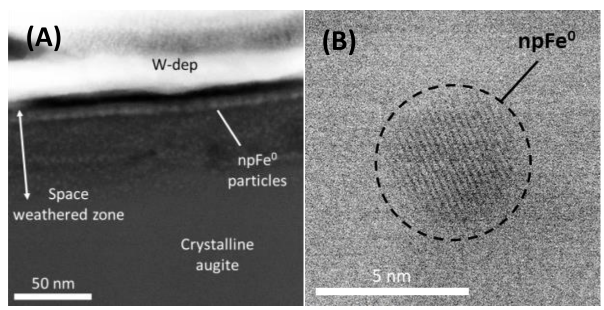

Figure 1. The space weathered surface of lunar augite sample (#A17-3). (A) HAADF image of ~80 nm thick space weathered zone, with crystalline substrate host augite below, and the W-dep above from FIB lift-out preparation. (B) Bright-Field image of $npFe^0$ particle, observing lattice fringe spacings measuring 2.06 Å.

Fe-K X-ray Absorption Spectroscopy (XAS)

There is a consistent positive shifting in the $1s \rightarrow 3d$ pre-edge centroid energy positions observed in all three lunar samples (Figure 2), with increases of up to ~0.23 eV in the space weathered (SW) zone compared to the substrate host mineralogy of augite or olivine.

Based on a ferric-ferrous ratio ($Fe^{3+}/\Sigma Fe$), defined by standard reference minerals, the centroid results suggest increases in ferric content in the SW zones, up to $\Delta Fe^{3+}/\Sigma Fe$ ~0.14 ±0.03, compared to the substrate host mineralogy. Positive shifts in the absorption edge positions for SW zones also support these results.

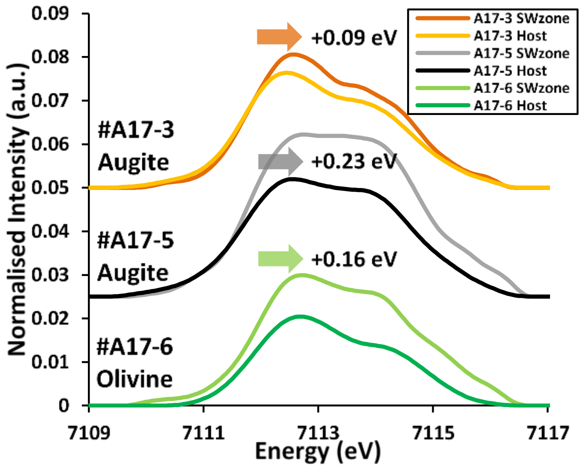

Figure 2. Normalised Fe-K XANES, showing baseline-subtracted 1*s*→3*d* pre-edge peak centroids for SW zone and Host mineral for each of the three lunar grains. The selected 1*s*→3*d* pre-edge centroids show shifts of up to +0.23 ±0.06 eV in the SW zone from their respective Host, suggesting an increased ferric content of up to $\Delta Fe^{3+}/\Sigma Fe$ = 0.14 ±0.03.

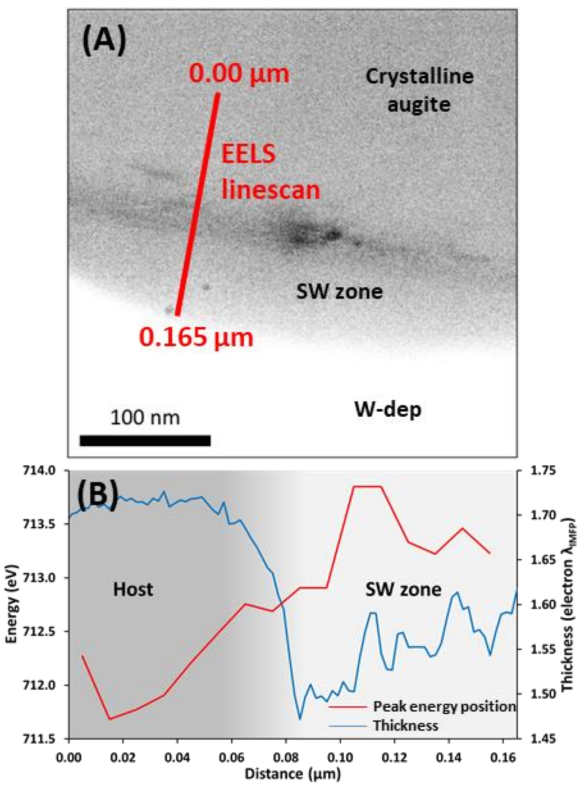

Figure 3. (A) HAADF image of space weathered zone in #A17-3, showing the location of the EELS linescan (red-line) from 0.00 µm to 0.165 µm. (B) EELS Fe-L peak energy position (red line) in eV, and sample thickness (blue line) in units of electron inelastic mean free path, λ, as measured along the linescan in (A).

Electron Energy Loss Spectroscopy (EELS)

A total of 18 EELS linescans were measured from the grain host to the space weathered (SW) zone in each of the three lunar grains.

Sample thickness is determined by the log-ratio of zero-loss electrons to the total transmitted intensity in the EELS spectrum, and shows the relative density to decrease along the linescan from the grain host mineral to the SW zone (Figure 3). This is expected due to the partial amorphisation and increased porosity in the space weathering, revealing the boundary between host and SW zone. For #A17-3 (Figure 3), the EELS Fe-L peak shifts in energy from an average of ~712.1 eV in the host to ~713.5 eV in the SW zone. This is typically consistent throughout all of the linescan measurements made for the three lunar samples, showing a positive shift in the peak from host to SW zone.

Similarly to Fe-K XANES pre-edge peaks, a positive shift in the EELS Fe-L peak position is indicative of increased ferric content, as shown by standard reference minerals measured, examples include Fe-rich olivine ($Fe^{3+}/\Sigma Fe$ = 0.00) and magnetite ($Fe^{3+}/\Sigma Fe$ = 0.67) with average EELS Fe-L peak positions of ~712.1 eV and ~713.6 eV respectively.

Discussion and Conclusion: Fe-redox variations have been analysed using Fe-K XANES and EELS measurements with consistent results that suggest increased oxidation in the space weathered surfaces. Fe-K XANES analyses suggest minor oxidation increases of up to $\Delta Fe^{3+}/\Sigma Fe$ ~0.14 ±0.03 occurring in the dominant silicate phase of the space weathered rims. These results are consistent with previously analysed space weathered asteroid Itokawa samples, which had shown increased ferric contents ranging $\Delta Fe^{3+}/\Sigma Fe$ ~0.02-0.14 ±0.03 [2].

Isolating an Fe metal spectrum in the Fe-K XANES measurements, and further investigation of oxidation within individual npFe particles, are future aims of this work. However, current results suggests that oxidation of silicate material exposed on the surfaces of airless bodies in the space environment is a key part of space weathering effects [1], and will be a significant feature to study in future samples returned by the Hayabusa2 and OSIRIS-REx spacecrafts.

References: [1] Pieters C. A. and Noble S. K. (2016) *JGR: Planets*, 121, 1865-1884. [2] Hicks L. J. et al. (in press) *Meteorit. Planet. Sci.*. [3] Hapke B. (2001) *JGR*, 106, 10039-10073. [4] Thompson M. S. et al. (2016) *Meteorit. Planet. Sci.*, 51, 1082-1095. [5] Butler P. (1973) *MSC 03211 Curator's Catalog*. pp 447. [6] Lerotic M. et al. (2014) *J. Synchrotron Radiat.*, *21*, 1206–1212. [7] Ravel B. and Newville M. (2005) *J. Synchrotron Radiat.*, 12, 537–541. [8] Noguchi T. et al. (2014) *Meteorit. Planet. Sci.*, 49, 188–214.