OXIDATION PROCESSES RECORDED IN SPACE WEATHERED APOLLO LUNAR GRAINS AND HAYABUSA ITOKAWA GRAINS. L. J. Hicks¹, J. C. Bridges¹, T. Noguchi², J. D. Piercy¹, and S. Neumann³, ¹School of Physics and Astronomy, University of Leicester, LE1 7RH, UK (ljh47@leicester.ac.uk), ²Kyushu University, Japan.

Introduction: Space weathering is largely the result of the bombardment by electrons and protons from the solar wind upon the exposed surface. The lunar surface shows these effects as an apparent darkening and reddening of the affected surfaces [1]. The surface soil samples returned by the Apollo lunar landings have featured space weathered rims [1,2]. The partially amorphized rims contain nanoparticle Fe metal (npFe⁰) particles suggested to have formed due to reactions with the implanting solar wind H+ ions, reducing the Fe oxides of the host mineralogy to form Fe metal [2,3]. The Fe particles have also been shown to become oxidized, with a correlation suggested between oxidation state and the maturity of the lunar soils [3].

In this study, we investigate the Fe-redox changes observed in the dominant silicate phase and the nanograins of the space weathered rims of lunar surface soil samples, using TEM and X-ray nanoprobe Fe-K XANES. The results of which will be compared to similar investigations of Hayabusa returned samples from asteroid 25143 Itokawa [4,5,6].

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 the Apollo 17 lunar landing [7]. Most of the sample grains provided for this investigation featured space weathering, indicated by the abundance of blisters on their surfaces. FIB-SEM lift-out sections were extracted successfully from at least three of the sample grains, depositing W on top of the grain surface during lift-out preparation.

Two of the lunar grains were augite pyroxene, En₁₈Fs₃₆ (#A17-3) and En₉₃Fs₅₁ (#A17-5), and one olivine Fa₃⁹ (#A17-6). All three sections have partially amorphised space weathered rims measuring up to ~100 nm thick (see Figure 1a), observed using a JEOL JEM-ARM300CF at ePSIC in the Diamond Light Source synchrotron facility.

The three lunar grains have been analysed using the I-14 X-ray Nanoprobe Beamline at Diamond, similarly to previously investigated Itokawa asteroid samples [4,5,6]. In order to analyse any Fe-redox changes in the space weathered rim from host mineralogy, Fe-K XAS spectra are obtained from a series of XRF maps over the region, typically measuring between 7000 and 7300 eV, with a higher resolution range of energy increments over the XANES features (~7100-7150 eV).

Results: The partially amorphised space weathered (SW) zones were successfully identified in HAADF-STEM imaging (Figure 1). Nano-grains measuring ~2-3 nm in diameter (see Figure 1c) could not be confirmed to have a Fe metal chemical composition using EDX at such high resolution. However, measuring lattice fringe spacings of ~2.06 Å (as observed in #A17-3, Figure 1) and others measuring up to ~2.10 Å confirmed Fe metal, similar to previous studies of Itokawa samples [8].

The XANES maps were processed using Mantis 2.3.02 [9], successfully isolating spectra for the SW zone and the grain substrate host mineralogy. All measured spectra were normalized in Athena 0.8.056 [10]. The 1s→3d pre-edge centroid positions is defined by the intensity-weighted average across baseline subtracted peaks, and the Fe-K absorption edge position defined here as half-normalised intensity, or 0.5 on the edge jump.

All three samples show positive shifts in the 1s→3d centroid position, up to ~0.09 eV increase compared to the substrate host mineralogy of augite or olivine. Figure 2 shows a centroid shift of +0.08 eV compared to

Figure 1. Space weathered rim of lunar augite sample (#A17-3). (a) HAADF image of ~80 nm thick space weathered rim, with crystalline substrate host augite below, and the W-dep above from FIB lift-out preparation. (b) HAADF image of space weathered rim revealing partially amorphized material and ~2-3 nm npFe⁰ particles. (c) Bright-Field image of npFe⁰ particle, observing lattice fringe spacings measuring 2.06 Å.
the pure ferrous (Fe^{2+}) olivine of sample #A17-6. Based on a ferric-ferrous ratio (Fe^{3+}/ΣFe), defined by standard reference minerals, the centroid results suggest increases in ferric content in the SW zones, up to Fe^{3+}/ΣFe ~0.05 ±0.03, compared to the substrate host mineral. Positive shifts in the absorption edge positions for SW zones also support these results.

![Figure 2](image1.png)

**Figure 2.** Normalised Fe-K XANES, showing 1s→3d pre-edge peak and absorption edge for sample #A17-6 olivine. The ‘SW Zone’ has an increased energy shift in the edge position compared to the substrate Olivine. (Inset) Baseline-subtracted 1s→3d pre-edge centroids showing a shift in the ‘SW Zone’ centroid position by +0.08 eV, suggesting an increased ferric content of Fe^{3+}/ΣFe = 0.05 ±0.03.

**Discussion:** The results of this investigation show a small increase in the oxidation state up to Fe^{3+}/ΣFe ~0.05 ±0.03. Similar results were also observed in the space weathered rims of asteroid Itokawa grains which featured increased oxidation states ranging from 0.02 to 0.14 (±0.03) [4,5,6], as shown in Figure 3. The Fe-K XAS spectra for the SW zones differed very little from their respective Fe-silicate host mineral, with no influence in the XAS from Fe metal, showing the silicate-composed partially amorphized rims to be the dominant phase.

Previous studies of the npFe^{0} particles in space weathered lunar regolith have shown evidence of oxidation [3]. However, the lattice fringe measurements in our samples show the nano-grains to have remained mostly metal, similar to npFe^{0} particles observed in other Itokawa grains [7].

The minor increase in oxidation state likely results from the implantation of solar wind H^{+} on the ferrous mineral grain surfaces, segregating the Fe to form Fe metal condensates and water vapour which then oxidises the remaining Fe in the partially amorphized rims.

Further investigations in to airless body samples and the oxidation of the weathered surfaces could reveal spectral effects due to Fe^{3+} in space weathered silicate materials. New samples could include material from asteroid 162173 Ryugu, to be returned by the Hayabusa 2 spacecraft in late-2020, or from 101955 Bennu returned by OSIRIS-REx.

**Conclusions:** The three FIB lift-out sections from Apollo lunar surface grains reveal space weathering to depths of up to ~100 nm, observed using TEM. The weathered rims feature non-oxidised npFe^{0} particles with measured lattice fringe spacings of ~2.06-2.10 Å. However, Fe-K XANES analyses suggest minor oxidation (Fe^{3+}/ΣFe ~0.05 ±0.03) occurring in the dominant silicate phase of the space weathered rims, likely resulting from the implantation of solar wind H^{+}. These results are consistent with previously analysed space weathered asteroid Itokawa samples, suggesting that minor oxidation of silicate material exposed on the surfaces of airless bodies in the space environment may be a key part of space weathering effects.