NANOPROBE XANES ANALYSIS OF SPACE WEATHERED ITOKAWA GRAINS.

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Introduction: Space weathering on Asteroid 25143 Itokawa is largely the result of the bombardment by electrons and protons from the solar wind. Its effects are manifested by the apparent darkening and reddening of the affected surfaces [1].

Previous studies of Itokawa samples returned by the JAXA *Hayabusa* mission have identified three zones related to space weathering [2]. The outermost Zone I is an amorphous redeposition rim of vapor material, derived from dust impacts of neighboring minerals. Zone II below is a partially amorphised composite rim of the original grain mineralogy, featuring nanophase Fe^0 (npFe) particles, and occurs due to solar flare ion irradiation. Zone III is the original crystalline substrate mineral, untouched by space weathering effects typically at depths of >100 nm. Space weathering rims on Itokawa grains from the first touchdown site are less developed and have a lower density of solar flare tracks than grains from the second touchdown [2].

Samples and Methods: Five Itokawa grains from the first touchdown site have been allocated to this study: RB-QD04-0063; RB-QD04-0080; RB-CV-0089; RB-CV-0011; and RB-CV-0148. Each were embedded in epoxy resin and ultramicrotomed for ~100 nm thick sections which were observed using a JEOL JEM-ARM200F at the Ultramicroscopy Research Center, Kyushu University. The original potted butts were embedded again in epoxy resin to prepare polished samples 8 mm in diameter. From these embedded grains, FIB-SEM sections were obtained for TEM analyses and X-ray synchrotron nanoprobe analyses.

TEM-EDS chemical composition measurements have been performed on the FIB sections using a JEOL JEM-3200 FSK. Four of the five Itokawa grains are olivines, The olivine grain #0063 (shown in Figure 1 A-B) also features plagioclase inclusions. All of the FIB sections have space weathering rims measuring up

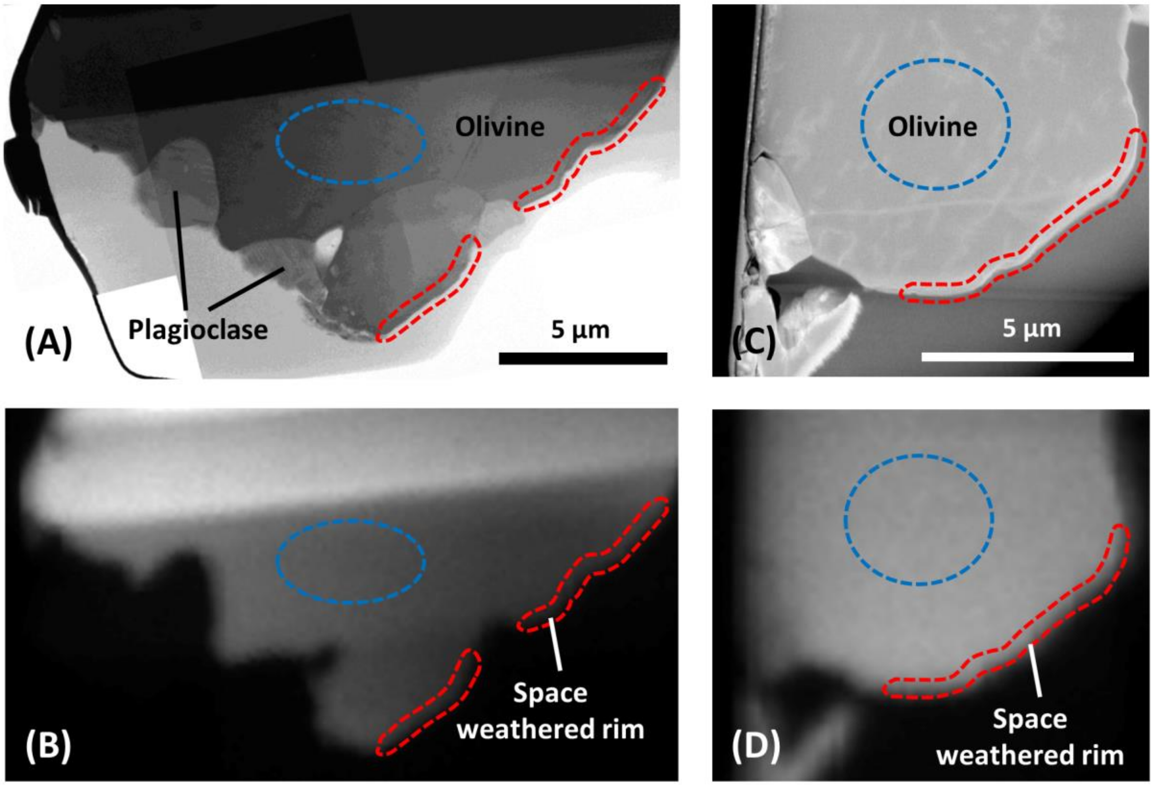

Figure 1. (A) HAADF-STEM image of RB-QD04-0063 olivine section, featuring plagioclase inclusions. (B) Fe-K XANES map of RB-QD04-0063 section at 7122.5 eV. (C) HAADF-STEM image of RB-QD04-0080 olivine section. (D) Fe-K XANES map of RB-QD04-0080 section at 7123.0 eV. Dotted lines show selected regions of interest for XANES spectra (see Figure 2) including the space weathered rims (red) and the substrate olivine mineral (blue).

to 100 nm thick.

Two of the Itokawa grains (#0063 and #0080) have been analysed using the I-14 X-ray Nanoprobe Beamline at the Diamond Light Source synchrotron. With a spatial resolution of 50 nm, and raster scanning to produce XRF maps, Fe-K X-ray Absorption Spectroscopy (XAS) has been obtained by producing high resolution XRF/XANES maps. A typical Fe-K XAS spectra, for analysing the Fe redox, measures between 7000 and 7300 eV with a higher resolution range of energy increments over the XANES features (~7100-7150 eV). The raw XAS and XANES map data is then processed using *Athena 0.8.056* and *DAWN 2.10* [3], and *Mantis 2.3.02* [4].

Results: Figure 2 compares the Fe-K absorption edge position between the space weathered rims and the substrate olivine mineral of the two grains. Any variation between the two spectra for each grain is very small, however a minor positive shift of up to ~0.5 eV (±0.25 eV) is observed in the Fe-K edge position for the weathered rims in both #0063 and #0080 compared to the respected substrate olivine mineralogy.

A positive shift in the Fe-K edge position can be deduced semi-quantitatively as an increase in the oxidation state from ferrous (Fe^{2+}) to ferric (Fe^{3+}), based on comparisons between reference materials of known ferrous-ferric content, similarly to previous studies of Itokawa, Comet Wild 2, and martian meteorite samples [2,5,6,7].

Therefore our results suggest there may be an increased oxidation state ($Fe^{3+}/\Sigma Fe > 0.11 \pm 0.05$) on the surface rims of the Itokawa olivine grains.

Discussion: Thompson et al. [8] had observed an increased Fe-oxidation state as a result of space weathering effects in Apollo lunar soils using EELS. The npFe particles in immature lunar soil are composed primarily of metallic Fe^0, but mature lunar soil contains oxidised Fe as Fe^{2+} and even components of Fe^{3+}, with an increasing ferrous and ferric content with increased maturity. Thompson et al. [8] hypothesised that the O in the surrounding silicate glass matrix may be the source of the npFe oxidation.

In early studies of Itokawa samples, npFe particles (1-2 nm) have been observed in the Zone II regions, where solar wind and ion implantation may have amorphised and reduced the Fe^{2+} in the silicates to form the metallic npFe particles [9]. However, the presence of npFe particles in our samples has not been determined using the I-14 nanoprobe.

Our Fe-K XAS spectra show the amorphous space weathered rims have retained their predominantly olivine composition (see Figure 2). An increased oxidation state of $Fe^{3+}/\Sigma Fe > 0.11$ (± 0.05), as suggested by our results, is small but reveals the possible breakdown and oxidation of the olivine into its amorphous state. The development of npFe particles may also have occurred, and any consequential oxidation of those particles, but they are clearly not the dominant phase detected in our Fe-K XAS measurements.

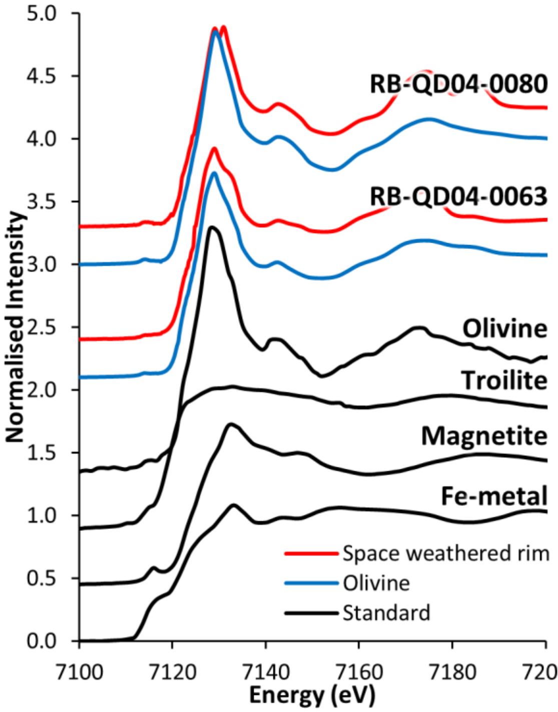

Figure 2. Fe-K XAS of Itokawa olivine grains #0063 and #0080 (blue) compared to their space weathered rims (red). San Carlos olivine, troilite, magnetite, and Fe-metal are also shown.

Due to our X-ray nanoprobe analyses of Itokawa samples, revealing insights into potential redox changes associated with space weathering, further similar studies are being considered for more Itokawa grains and lunar samples. These experiments will also inform studies of other airless Solar System bodies such as the returned samples of asteroids Ryugu and Bennu from the JAXA *Hayabusa 2* and NASA *OSIRIS-REx* missions.

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