Fe-redox changes in Itokawa space-weathered rims

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Abstract—Synchrotron Fe-K X-ray absorption spectroscopy and transmission electron microscopy have been used to investigate the mineralogy and Fe-redox variations in the space-weathered (SW) rims of asteroidal samples. This study focuses on the FIB lift-out sections from five Itokawa grains, returned by the Hayabusa spacecraft, including samples RB-QD04-0063, RB-QD04-0080, RB-CV-0011, RB-CV-0089, and RB-CV-0148. Each of the samples featured partially amorphized SW rims, caused by irradiation damage from implanted low mass solar wind ions, and the impacting of micrometeorites. Using bright-field and HAADF-STEM imaging, vesicular blistering and nanophase Fe metal (npFe0) particles were observed within grain rims, and solar flare tracks were observed in the substrate host grain, confirming the presence of SW zones. We use Fe-K XANES mapping to investigate Fe-redox changes between the host mineral and the SW zones. All SW zones measured show some increases in the ferric-ferrous ratio (Fe3+/ΣFe) relative to their respective host grains, likely the result of the implanted solar wind H+ ions reacting with the segregated ferrous Fe in the surface material.

INTRODUCTION

Launched in May 2003, the JAXA Hayabusa spacecraft reached the near-Earth asteroid 25143 Itokawa (original designation 1998 SF36) in September 2005. Itokawa measures 535 m × 294 m × 209 m, and has been termed a “rubble-pile” asteroid due to its low density (1.9 g cm−3) and high porosity, appearing to have a surface rich in boulders and smoother terrains, suggesting mass movement and resurfacing processes (Fujiwara et al. 2006). The Hayabusa spacecraft attempted two touchdowns, both in the Muses Sea smooth terrain of Itokawa, with an impact sampler for the collection of surface regolith. Neither touchdown collection functioned as planned, but an estimated total mass of <100 µg (Yoshikawa et al. 2015), in the form of over 1500 particles varying in size up to 180 µm in diameter (most under 10 µm), had drifted into the sample catcher before closing and returning to Earth (Yano et al. 2006).

The mineralogy of the returned Itokawa samples consists largely of olivine, low-Ca pyroxene, and plagioclase, and minor abundances of Ca-rich pyroxene, troilite, kamacite, taenite, chromite, and Ca-rich phosphates (Tsuchiyama et al. 2011). Prior to the Hayabusa mission, asteroid Itokawa had been identified as an S-type asteroid, revealed from the ground-based observed red-sloped S(IV)-type spectrum analogous to laboratory measurements of ordinary chondrite meteorites (Binzel et al. 2001). The distinctive reddening in Itokawa’s ground-based observed S(IV)-type spectrum and Hayabusa’s onboard near-infrared spectrometer data could be accounted for by fitting modeled nanophase reduced iron (npFe0) data to the spectral data of ordinary chondrites, suggesting the asteroid’s surface material consists of an estimated average 0.05% npFe0 (Binzel et al. 2001; Hiroi et al. 2006). This presence of npFe0, resulting in the surface spectral
reddening, has been proposed to be due to weathering effects from exposure to the space environment (Pieters et al. 2000).

Space weathering is largely the result of the implantation by the solar wind, micrometeorite impacts, and irradiation by cosmic rays upon airless bodies exposed to space (Keller and McCay 1997; Clark et al. 2002; Pieters and Noble 2016). Noguchi et al. (2011, 2014a) identified three “zones” investigating space-weathered rims on Itokawa grains. Zone I is a 2–3 nm thick amorphous redeposition layer of sputtered ions and/or condensation impact-generated vapors from neighboring mineral grains, and compositionally distinct from the substrate mineralogy. Zone II is a thicker (30–60 nm) layer, suggested to be formed by the solar wind implanted 4 keV He\(^{++}\) ions contributing to the segregation and partial amorphization of the host surface material (Takigawa et al. 2019). The Zone II composite rim may also be thicker due to the addition of vesicles (Matsumoto et al. 2015), measuring up to 20 × 50 nm oriented parallel to the grain surface, due to the implanted 1 keV H\(^+\) ions (Takigawa et al. 2019). Zones I and II are also rich in npFe\(^0\) particles (except in Zone II for non-ferromagnesian silicate host grains), measuring 1–2 nm in densely arranged layers (Noguchi et al. 2011; Keller and Berger 2014; Pieters and Noble 2016), reduced by the loss of oxygen during deposition and considered to be the cause of the surface spectral reddening of asteroid and lunar soil (Keller and McKay 1997; Hapke 2001). The various features of space weathering reported in Itokawa samples are also observed in Apollo lunar soil and regolith samples (Keller and McKay 1997; Pieters et al. 2000; Hapke 2001; Pieters and Noble 2016).

Zones I and II are underlain by Zone III, typically at depths of >100 nm consisting of the original well-crystalline substrate mineral (Noguchi et al. 2011, 2014a), untouched by space weathering effects except for tracks left by heavier ions from solar flares and cosmic rays (Keller and McKay 1997; Noguchi et al. 2014b). Counting the solar flare tracks allows a grain’s exposure age to be determined (Berger and Keller 2015), and Itokawa grains from the first touchdown site are less developed with a lower density of solar flare tracks than grains from the second touchdown, which has increased space weathering (Noguchi et al. 2014b), suggesting an exposure age difference between the two touchdown sites.

The aim of this investigation is to obtain further accurate mineralogical information relating to possible Fe-redox variations in the space-weathered (SW) surface material of asteroid Itokawa. The presence of SW rims on the Itokawa samples will be confirmed using transmission electron microscopy instruments, observing similar space weathering features to those previously investigated. In order to assess Fe-redox variations in the SW rims of Itokawa grains, the I14 Beamline at the Diamond Light Source synchrotron, Oxfordshire, UK, was used to perform Fe-K X-ray absorption spectroscopy (XAS). I14 is a hard X-ray nanoprobe beamline capable of beam spot sizes down to ~50 nm, although limited to a mechanical spatial resolution of ~100 nm, and produces XRF maps via raster scanning coverage of the sample. The beamline energy can range 5–23 keV, with an energy resolution down to 0.25 eV. Fe-K X-ray absorption near-edge structure (XANES) is a new technique for investigating the SW mineralogy of Itokawa. XANES mapping using the I14 beamline gives a high spatial resolution capable of analyzing the <100 nm thick SW zones. This will provide the opportunity to characterize potential oxidation and/or reduction in the ferromagnesian silicate mineralogy, and any metallic npFe\(^0\) that occurs in the SW surface of Itokawa, as well as other surfaces exposed to the space environment.

**SAMPLES AND METHODS**

Five Itokawa samples have been allocated for this investigation: RB-QD04-0063 (#0063), RB-QD04-0080 (#0080), RB-CV-0011 (#0011), RB-CV-0089 (#0089), and RB-CV-0148 (#0148). Each of these samples was recovered from the first Hayabusa touchdown site, captured in room B (RB) of the sample catcher. Despite samples from the second touchdown site apparently showing greater space weathering maturity (Noguchi et al. 2014b), samples from the first touchdown site were selected for investigation based on the availability of samples with grain sizes suitable for FIB lift-out section preparation.

Prior to preparation of the sections, the original grains were individually curated (Yada et al. 2018) and have diameters of: ~33 \(\mu\)m (#0063), ~35 \(\mu\)m (#0080), ~43.7 \(\mu\)m (#0011), ~86.16 \(\mu\)m (#0089), and ~21.2 \(\mu\)m (#0148). Each of the five grains is embedded in epoxy resin and ultra-micromotomed to produce ~100 nm thick sections, which were then examined using a JEOL JEM-ARM200F at the Ultramicroscopy Research Center, Kyushu University. The remainder of the original potted butts was again embedded in epoxy resin to prepare for polished samples 8 mm in diameter. From these embedded grains, focused ion beam (FIB) lift-out sections have been prepared using an FEI Quanta 200 3DS and Helios NanoLab 3G CX Focused Ion Beam at Kyoto University, for analysis with scanning transmission electron microscopy (STEM) and XAS. Each FIB lift-out section was attached to a 3 mm TEM Cu-grid, and thinned to <100 nm, suitable for STEM analysis and the I14 beamline.
X-Ray Absorption Spectroscopy

Using the Diamond I14 Beamline, the Itokawa grain FIB lift-out sections were analyzed for X-ray fluorescence (XRF) and Fe-K XAS, including the XANES and extended X-ray absorption fine structure (EXAFS) features. All data were obtained in fluorescence mode.

To produce Fe-K XANES maps, a series of XRF maps were obtained via raster scanning, with the sample moving across the beam at energies between 7000 and 7300 eV. The tunable monochromators allow for higher resolution increments down to 0.25 eV over the XANES region (~7100 to 7150 eV). With >100 XRF maps to collect and the instrument sample holder motors performing at the nanometer scale, some minor shifting of the sample between each XRF map is inevitable. Therefore, definable features in the sample are used for tracking during XANES mapping to ensure the sample is returned approximately to the same physical location between each XRF map. Such features can be mineralogical or artifacts of the FIB section and require an elemental composition observable in XRF maps with absorption edge energies lower than that of the XANES map energies (i.e., <7000 eV). Therefore, sample tracking between each map was achieved using the Pt-strip remnants from the FIB section preparation, observed in the Pt-M absorption edge XRF maps (2331 eV), on samples #0080 and #0063, and using the Ca-rich pyroxene inclusion in sample #0089 for tracking in the Ca-K absorption edge XRF maps (4038 eV). The tracking feature is also used to accurately align each of the XRF maps when compiling the XANES map data file. Any further necessary alignments can also be achieved when processing the XANES map in Mantis 2.3.02 (Lerotic et al. 2014), using the “Align stack” tool with either automatic or manual alignments. Using Mantis 2.3.02, each XRF map measured throughout the XANES map can be observed. The XANES maps can also be cropped to focus on a region of interest. XAS spectra can be obtained by manually selecting a region with the “Select ROI (Lasso)” tool or using the “Cluster Analysis” software feature. Each XAS spectrum data were then normalized using Demeter Athena 0.9.26 (Ravel and Newville 2005).

Fe-rich reference materials measured include Fe metals, Fe oxides, Fe sulfides, and ferromagnesian silicates—all of which have been found in Itokawa samples (Nakamura et al. 2011; Tsuchiyama et al. 2011). All reference minerals measured at the I14 beamline were in powder-pellet form, measured in fluorescence mode over a similar range of energies to the Itokawa samples, and processed via DAWN 2.10 (Basham et al. 2015) before normalizing in Athena.

Additional standard reference minerals have been measured for Fe-K XAS on the I18 Beamline at Diamond, including powder-pellet samples and thick/concentrated polished block samples, to complement the I14 measured reference materials and the ferric-ferrous ratio calibration. An Fe metal foil sample is used at Diamond Light Source beamlines I14 and I18 to define an absolute energy grid by calibrating the first derivative in the Fe metal to $E_0 = 7112$ eV, a value also used in other Fe-K XANES investigations (e.g., Cottrell et al. 2009), and thus, all XAS data measured are shifted in line with the measured Fe metal in Athena.

After normalizing XAS data in Athena, a spline function is fitted under the 1s → 3d pre-edge peaks. A filter was applied for noise reduction in the spectra to allow for ease of fitting the smooth background spline function. By subtracting the background baseline from the data, the centroid energy position was defined as the intensity-weighted average across the pre-edge peak. A “tight” curvature to the spline function reduces potential asymmetric weighting within the centroid (Berry et al. 2003).

A ferric-ferrous ratio calibrated using standard reference materials of known ferric ($\text{Fe}^{3+}$) content can be used to semiquantitatively estimate the unknown $\text{Fe}^{3+}$ content in other samples and determine redox changes within a sample (Dyar et al. 2001; Wilke et al. 2001, 2004; Berry et al. 2003; Cottrell et al. 2009; Hicks et al. 2014; Fiege et al. 2017). The Fe-K XANES pre-edge is associated with the 1s → 3d transition in iron and an increase in this pre-edge centroid energy position equates to an increase in $\text{Fe}^{3+}$ content. The ferric-ferrous ratio ($\text{Fe}^{3+}/\Sigma\text{Fe}$) is a best fit, assuming a linear correlation, between the centroid energy positions of standard reference ferrous and ferric endmembers. Additionally, the Fe-K absorption edge energy position (defined here as half normalized intensity, or 0.5 on the edge jump) was also considered, which is known to shift positively with increased $\text{Fe}^{3+}$ content too, but was not the focus of $\text{Fe}^{3+}/\Sigma\text{Fe}$ estimations due to the multiple scattering that can occur in the absorption edge region (Dyar et al. 2001). Several Fe-K XAS measurements and pre-edge centroid energy positions were obtained from minerals olivine, magnetite, nontronite, and hematite. Uncertainty in the pre-edge centroid energy position was estimated from the standard deviation in the difference between each measured centroid position and average position for each respective mineral group. Uncertainty in the $\text{Fe}^{3+}/\Sigma\text{Fe}$ values was estimated from the standard deviation in the difference between the experimental $\text{Fe}^{3+}/\Sigma\text{Fe}$ values (determined from the measured centroid energy position on the ferric-ferrous...
ratio) and the theoretical Fe$^{3+}/\Sigma$Fe values in a select sample of reference materials.

Crystallographic coordination geometry has been known to significantly influence the energy and intensity of the $1s \rightarrow 3d$ pre-edge peaks, as well as nonlinear correlations, resulting in estimated Fe$^{3+}/\Sigma$Fe ratio uncertainties of 5–15% (Dyar et al. 2001, 2002; Wilke et al. 2001). The crystallographic coordinates and orientation of the Itokawa samples are unknown relative to the X-ray beam. However, the Itokawa samples contain individual mineral grains, identifiable in TEM analyses, where the SW rims would have the same crystallographic coordination as the host mineral, albeit with partial amorphization. Therefore, the selected regions of the Itokawa samples to be investigated only include host grain material that is directly adjacent to the SW material for comparisons. Definitively quantifying the Fe$^{3+}/\Sigma$Fe ratio in an unknown Fe silicate Itokawa sample will be difficult, but in using a generic Fe$^{3+}/\Sigma$Fe calibration ratio line, established by the Fe silicate reference minerals, the Fe-redox variations ($\Delta$Fe$^{3+}/\Sigma$Fe) can be estimated reliably, thus overcoming any polarization issues in this investigation.

**Transmission Electron Microscopy**

Prior to XAS analysis at the I14 Beamline, initial HAADF-STEM imaging and TEM-EDX chemical composition measurements of the <100 nm thick samples were performed using a JEOL JEM 3200FSK at the Kyushu University Ultramicroscopy Research Center. This initial TEM imaging is done to confirm the presence and locations of space weathering on the samples.

Additional imaging of the samples was performed using a JEOL 2100 + TEM at the University of Nottingham. This provides an overview of each sample in bright-field (BF) and dark-field (DF) TEM images using the Gatan Digital Micrograph Camera, and the photomerge tool in Adobe Photoshop CC 2017. TEM-EDX measurements at an accelerating voltage of 200 kV were performed on each grain and various inclusions within each sample, from which their mineralogy was confirmed.

HR-TEM imaging was also obtained of the SW zones at the electron Physical Science Imaging Centre (ePSIC) facility at Diamond Light Source. A JEOL ARM200CF (E01) instrument at an accelerating voltage of 200 kV, and a JEOL ARM300CF (E02) with accelerating voltage 300 kV, and variable beam currents ranging ~25–330 pA. Imaging of the SW zones on samples #0063 and #0089 were performed using the ePSIC E01 instrument, but further analysis and measurements of lattice spacings in #0063 were obtained using the ePSIC E02 instrument.

**RESULTS**

**Samples and Transmission Electron Microscopy**

**Mineralogy**

Three of the five Itokawa samples in this study are olivine, including #0063, #0080, and #0148. Sample #0063 has two individually identified olivine grains in the ~100 nm thick section, along with <3 µm sized plagioclase inclusions, plus metallic Al contamination from the sample catcher on the edge of the sample grain. Sample #0011 is a low-Ca pyroxene, and sample #0089 contains both olivine and low-Ca pyroxene, with a small (<7 µm wide) Ca-rich pyroxene inclusion. A HAADF-STEM image of sample #0080 can be seen in Fig. 1, BF-TEM images of samples #0063 and #0089 in Figs. 2 and 3, and a HAADF-STEM image of #0011 in Fig. 4. TEM-EDX chemical composition measurements have also been performed on the substrate mineralogy of these FIB sections, the results of which are presented in Table 1.

**Space-Weathered Zones**

All five Itokawa grains feature space-weathered zones (irradiation-damaged rims) on their original surfaces. The change in appearance between the partially amorphized rims and the unaltered substrate mineralogy was easily identifiable in both BF and DF TEM imaging, with rims typically measuring 50–100 nm depth from the surface of each grain (Figs. 5a–c).

Vesicular blistering was observed in some regions of the space weathering zones of samples #0063 (Fig. 5b) and #0148. Where these features are present, the partially amorphized Zone II was typically thicker, up to depths of ~200 nm. The lenticular vesicles within this zone measure up to ~60 × 20 nm, with the long axis parallel to the external surfaces, similar to those observed in previously studied Itokawa samples (Noguchi et al. 2014a) and lunar samples (Keller and McKay 1997). It is thought that these blisters occur due to the segregation of low-mass $^4$He$^+$ and H$^+$ ions from the solar wind implanted in Zone II of the SW rims (Igarashi et al. 2002; Noguchi et al. 2014a; Matsumoto et al. 2015).

Nanoparticles were also observed within the partially amorphized Zone II of the SW rims, confirmed as nanophase iron (npFe$^0$) particles based on [110] lattice spacing measurements. Lattice spacing was typically observed in BF-STEM, measuring the lattice spacings from at least three particles, shown in Figs. 5d–f, averaging 0.203 nm from a range 0.199–0.209 nm. However, these npFe$^0$ features were most easily identified in HAADF-STEM (assumed to be npFe$^0$ particles based on previous studies of Itokawa...
samples (Noguchi et al. 2014a; Matsumoto et al. 2015) with similar chemical compositions), with images counting 10s–100s of small white particles no larger than ~2–3 nm in diameter (e.g., Fig. 5c).

Evidence of a Zone I feature is lacking in our HAADF-STEM and BF-STEM imaging. Because Zone I deposits are composed of sputter and/or impact vapor from neighboring mineral grains, it is most easily identified by the presence of elements not included in the substrate host mineral (e.g., S; Noguchi et al. 2014a). EDX and lattice spacing measurements showed the SW rims to be S-free, and not to have any significant chemical composition variations.

**Zone III—Substrate Grain**

Fractures and dislocations were observed throughout the substrate grain below the SW zones (Fig. 5a). Some smaller (<0.7 μm) dislocations appear straight and oriented roughly parallel to each other, although oriented irrespective of the grain surface, such as those seen in the #0080 olivine showing as white curves in HAADF-STEM imaging (Fig. 1). This is possibly indicative of planar fracturing and screw dislocations from shock and collisional fragmentation in the asteroid’s history, as previously observed in Itokawa samples and ordinary chondrites (Harries and Langenhorst 2014; Langenhorst et al. 2014). Sample #0089 also featured small (<0.3 μm) roughly parallel dislocations in the low-Ca pyroxene. However, a high abundance of randomly oriented curved fractures feature in samples #0011 (Fig. 4) and #0148, some measuring up to ~2 μm in length, although some shorter (<0.4 μm) dislocations appear roughly parallel to each other throughout the #0011 pyroxene grain.

Lattice spacing measurements confirmed the crystalline substrate mineral in #0063 as olivine (Fig. 5d), with spacings of 0.248 nm [112] and 0.280 nm [130]. Olivine compositions can vary between forsterite (Mg-rich) and fayalite (Fe-rich) with lattice spacings varying from ~0.246 nm [112] and ~0.277 nm [130] for forsterite to ~0.250 nm [112] and ~0.282 nm [130] for fayalite (Downs and Hall-Wallace 2003). The olivine in #0063 has spacings situated between the forsterite and fayalite endmembers, which is confirmed with its measured forsterite (Fo75) composition (Table 1) and similar compositions of Fo69-75 for other Itokawa host olivine grains in this study.

Solar flare tracks show up as fine lines in both BF and DF TEM imaging (Fig. 5a), left by heavy solar flare and cosmic ray ions impacting the grains. Typically, they were observed randomly distributed up to ~1.5 μm below the surface of the grains, but some samples such as #0080 and #0011 have an apparent higher density of solar flare tracks impacting the grains up to ~4 μm deep.

These observations confirm the presence of SW surfaces on the grains being investigated based on the similar observations of various features in previous
investigations of asteroid Itokawa and Apollo lunar samples (Noguchi et al. 2011; Keller and Berger 2014; Pieters and Noble 2016). These various features include the partially amorphized rims, npFe$^0$ particles, and solar flare tracks that would not be found throughout the core of the host grain material.

X-Ray Absorption Spectroscopy

With the available beamtime, three samples (#0080, #0063, and #0089) were prioritized and measured for XANES mapping analysis. XANES mapping for sample sections #0063 and #0080 included 152 XRF maps, at energies ranging 7050–7290 eV, with a higher energy increment resolution of 0.25 eV over the pre-edge region in the energy range 7100–7125 eV. The XANES map for sample section #0089 included 138 XRF maps, at energies ranging 7012–7238 eV, with the highest energy resolution of 0.5 eV over the energy range 7093–7136.5 eV.

The XANES maps for both #0080 and #0063 samples were collected with a pixel size of 0.15 µm. The #0080 map measures 63 × 84 pixels (9.45 × 12.6 µm) with an average time of 179 s to measure each XRF map, and the #0063 map measures 131 × 71 pixels (19.65 × 10.65 µm) with an average time of 259 s per XRF map. The #0089 XANES map was collected with a pixel size of 0.1 µm, measuring 288 × 135 pixels (28.8 × 13.5 µm) with an average time of 401 s per XRF map.

Figures 1–3 show a single XRF map for each sample corresponding to the TEM images. The selected XRF maps shown in Figs. 1–3 are the maps at the energy obtained closest to ~7120.7 eV (the average Fe-K absorption edge position from all Itokawa host sample results presented in Table 2). These are Fe-K XRF maps; hence, the Fe-poor plagioclase inclusions do not appear in the #0063 XRF image (Fig. 2).
Mantis—Cluster Analysis

The XANES maps were analyzed within Mantis 2.3.02 using the “Cluster Analysis” tool. Each selected region analyzed is highlighted in Figs. 1–3 as regions A–F, all featuring SW zones. All selected regions also include the substrate host grain mineral and the adjacent epoxy resin up to ~5 μm distance from the respective SW zone. Host minerals analyzed include all significant ferromagnesian mineralogy identified within each section that features space weathering. This includes one region from the #0080 olivine (A), one region from each of the two olivine grains in #0063 (B and C), the thin (~100 nm) region of olivine in #0089 (D), the #0089 Ca-rich pyroxene (E), and the low-Ca pyroxene (F). The Mantis “Cluster Analysis” tool was able to isolate the three defining features (SW zone, host grain, and epoxy) from each region to produce Fe-K XAS spectra from the counts measured throughout the range of XRF maps. The size of the areas (in μm²) that cover each of the host grain and SW zone regions is stated in Table 2.

Fe-K XAS spectra from the epoxy regions were assumed background scatter from the bulk of the sample section, rather than a direct measure of Fe in the epoxy resin itself, for TEM-EDX analyses of the epoxy resin revealed little to no traceable Fe content. Therefore, XAS measurements over the epoxy region suggest the absorption coefficient of the background scatter from the sample to have an edge jump (the edge step, or measured change in absorption) averaging ~11% that of the measured magnitude in edge jump for the host grain for all measured sample regions. An
example can be seen in Fig. 6 (left-inset) showing all three spectra (SW zone, olivine host, and epoxy) for sample #0080 (A), with the raw intensity of the background scatter over the epoxy region exhibiting an absorption coefficient edge jump of ∼7% that of the edge jump magnitude seen in the olivine host itself.

Table 1. Compositions of Itokawa grains, including the substrate host mineralogy and inclusions.

|                   | RB-QD04-0080   | RB-QD04-0063   | RB-CV-0089   | RB-CV-0011   | RB-CV-0148   |
|-------------------|----------------|----------------|-------------|------------|------------|
|                   | Olivine (A)    | Olivine (B)    | Olivine (C) | Plagioclase| Ca-rich pyroxene | Pyroxene (E) | Pyroxene (F) | Olivine (G) |
| SiO₂              | 37.0           | 40.7           | 39.1        | 68.7       | 40.3        | 55.9        | 57.3        | 57.3        | 39.0        |
| TiO₂              | –              | –              | –           | –          | –           | 0.4         | 0.2         | 0.6         | –           |
| Al₂O₃             | –              | –              | –           | 23.2       | –           | –           | –           | –           | –           |
| FeO               | 27.8           | 21.8           | 23.5        | 22.3       | 22.3        | 5.6         | 15.5        | 14.5        | 26.0        |
| Cr₂O₃             | –              | –              | –           | –          | 1.0         | –           | –           | –           | –           |
| MgO               | 35.2           | 37.5           | 37.4        | 37.5       | 14.8        | 26.0        | 26.9        | 35.0        | –           |
| MnO               | –              | –              | –           | –          | –           | –           | –           | –           | –           |
| CaO               | –              | –              | –           | –          | 2.4         | –           | –           | –           | –           |
| Na₂O              | –              | –              | –           | –          | 5.5         | –           | –           | –           | –           |
| K₂O               | –              | –              | –           | –          | 0.4         | –           | –           | –           | –           |
| SO₃               | –              | –              | –           | –          | –           | –           | –           | –           | –           |
| Total             | 100.0          | 100.0          | 100.0       | 100.0      | 100.0       | 100.0       | 100.0       | 100.0       | 100.0       |
| Fo₆₉              | Fo₇₃           | Fo₇₄           | Ab₇₆An₁₈    | Fo₇₅       | W₀₂₄En₄₄    | W₀₂₂En₇₃    | W₀₁En₇₆    | Fo₇₁        | –           |
When the epoxy and host spectra are normalized, so that the edge jump in both spectra is 1.0, they show very similar XAS structure and the Fe-K absorption edge has only minor shifting. This is also similar for all selected regions (A–F) with only minor (<0.25 eV) positive or negative shifts in the absorption edge between the substrate host grain and the epoxy background. The absorption edge shift for the SW zone is typically double or more that of the background positive shifts measured, suggesting that the Fe-K absorption edge variations observed for the SW zones are varying independently of the background and Fe-free epoxy.

The raw spectra for the SW zones also have a lower absorption coefficient, with edge jumps averaging ~54% that of the edge jump in the host grain for all regions (A–F). This may be due to the partially amorphous condition of the weathered rims, and the presence of vesicular blistering, reducing the density of the material relative to the crystalline host grain mineral, which has also been observed in experimentally weathered Fe-rich olivine by ion irradiation (Leroux et al. 2019). Absorption coefficient is dependent on the density of a material (Calvin 2013), and so consequently, a reduced material density in the weathered rim results in a smaller measured edge jump in the Fe-K XAS.

It is also important to note that the size of the regions selected using the Mantis software was also wider than the ~50–100 nm wide weathered rims, with some selected SW zone regions as wide as ~500 nm (e.g., see SW zone for #0089 [E] in Fig. 3). Therefore, the selected SW zone regions likely consist of significant and uneven measures of higher counts from over the host material, as well as low background scatter from
over the adjacent epoxy material. It is very likely that the resulting absorption coefficient for the space-weathered zones and estimations of the Fe-redox in the material are therefore affected by this “dilution” from non-SW material.

### Table 2. Fe-K XANES 1s → 3d pre-edge and absorption edge, with \( \Delta \text{Fe}^{3+}/\Sigma \text{Fe} \) estimations.

| Hayabusa samples Region | Sample feature | Measured area (µm²) | Pre-edge centroid (eV) | Absorption edge a (eV) | Host-SW zone energy shift (eV) b | \( \Delta \text{Fe}^{3+}/\Sigma \text{Fe} \) b |
|-------------------------|----------------|---------------------|------------------------|------------------------|----------------------------------|-----------------------------------------------|
| RB-QD04-0080 (A) SW zone | Olivine host | 2.55 | 7113.17 | 7121.50 | 0.24 | 0.14 ± 0.03 |
| RB-QD04-0063 (B) SW zone | Olivine host | 1.80 | 7113.07 | 7121.10 | 0.06 | 0.03 ± 0.03 |
| (C) SW zone | Olivine host | 6.97 | 7113.01 | 7120.70 | 0.07 | 0.04 ± 0.03 |
| RB-CV-0089 (D) SW zone | Olivine host | 1.43 | 7113.31 | 7121.20 | 0.07 | 0.04 ± 0.03 |
| (E) Ca-rich SW zone | Pyroxene host | 4.84 | 7113.24 | 7121.20 | 0.07 | 0.04 ± 0.03 |
| (F) SW zone | Pyroxene host | 7.57 | 7113.09 | 7120.60 | 0.12 | 0.07 ± 0.03 |

**Reference minerals**

| Mineral class | Mineral group | Pre-edge centroid (eV) | Absorption edge a (eV) | \( \text{Fe}^{3+}/\Sigma \text{Fe} \) a [Experiment] | \( \text{Fe}^{3+}/\Sigma \text{Fe} \) a [Theoretical] |
|---------------|---------------|------------------------|------------------------|-----------------------------------------------|-----------------------------------------------|
| Metal | Fe metal | - | 7119.70 | - | - |
| Olivine c,d | 7112.89 | 7120.15 | 0.00 | - | - |
| Olivine c,d | 7112.89 | 7120.45 | 0.00 | - | - |
| Nontronite d | 7114.69 | 7125.25 | 1.01 ± 0.015 | 1.00 | 0.00 |
| Oxide | Magnetite d | 7114.44 | 7122.15 | 0.66 ± 0.012 | 0.67 | 0.67 |
| Magnetite d | 7114.51 | 7121.90 | 0.68 ± 0.012 | 0.67 | 0.67 |
| Limonite d | 7115.17 | 7124.30 | - | - | - |
| Hematite d | 7115.35 | 7123.20 | 1.00 ± 0.012 | 1.00 | 0.00 |
| Goethite d | 7115.22 | 7124.25 | - | - | - |
| Cr oxide | Chromite d | 7113.11 | 7120.30 | - | - |
| Sulfd | Troilite d | 7113.21 | 7117.15 | - | - |
| Pyrrhotite d | 7113.42 | 7118.10 | - | - | - |
| Carbonate | Siderite d | 7113.92 | 7121.50 | - | - |
| Silicate | Olivine c,d | 7112.89 | 7120.35 | -0.01 ± 0.015 | 0.00 | 0.00 |
| Olivine e | 7112.93 | 7120.30 | 0.01 ± 0.015 | 0.00 | 0.00 |
| Nontronite d,f | 7114.62 | 7124.95 | 0.98 ± 0.015 | 1.00 | 1.00 |
| Nontronite d,f | 7114.62 | 7124.95 | 0.98 ± 0.015 | 1.00 | 1.00 |
| Augite e | 7113.63 | 7122.15 | - | - | - |
| Oxide | Magnetite d | 7114.44 | 7121.10 | 0.66 ± 0.012 | 0.67 | 0.67 |
| Magnetite e | 7114.49 | 7120.85 | 0.67 ± 0.012 | 0.67 | 0.67 |
| Hematite d | 7115.34 | 7122.30 | 0.99 ± 0.012 | 1.00 | 1.00 |
| Hematite e | 7115.40 | 7122.70 | 1.01 ± 0.012 | 1.00 | 1.00 |

To account for energy discrepancies among Diamond I14 and I18 beamtime sessions sp19138-1 (September 2018), sp19138-2 (December 2018), and sp19641-1 (January 2018), all data are aligned to an absolute energy grid by calibrating the first derivative in Fe metal to \( E_0 = 7112 \) eV.

aFe-K absorption edge is defined by the energy of the normalized spectra at an intensity of 0.5 (a.u.).
bFe-K pre-edge centroid shift and \( \text{Fe}^{3+}/\Sigma \text{Fe} \) difference between the SW zone and sample host grain mineral.
cSan Carlos olivine (Fournelle 2011).
dDilute powder pellet samples in kapton tape. Measured in transmission.
eAGAR Standard Mineral Reference purchased from AGAR—Micro-Analysis Consultants Ltd (AGAR Scientific Ltd 2017). Samples are thick/concentrated. Measured in fluorescence.
fNontronite (NAu-2) (The Clay Minerals Society 2019).

Fe-K 1s → 3d Pre-Edge Centroid Acquisition and Fe-Redox

All reference minerals measured are listed in Table 2, with ferric content stated (\( \text{Fe}^{3+}/\Sigma \text{Fe} \) Theoretical) only where the ferric-ferrous content is known for that
mineral sample. A selection of individual Fe-K XAS spectra from each of the mineral groups measured is presented in Fig. 7a, and the baseline-subtracted pre-edge centroids for silicates and oxides in Fig. 7b, for comparing and identifying samples of unknown mineralogy. The complementary I18 Fe-K XAS measurements of olivine (San Carlos) were used, where I14 measurements produced a significantly low signal-to-noise ratio in the spectra due to the low-Fe content (Fo90) in the mineral, providing the ferrous (Fe\(^{2+}/\Sigma Fe = 0.0\)) standard reference for the ferric-ferrous ratio calibration.

The ferromagnesian silicate standards olivine (San Carlos) and nontronite (NAu-2) measured in this study range from highly ferrous (Fe\(^{3+}/\Sigma Fe\)Theoretical = 0.0) to highly ferric (Fe\(^{3+}/\Sigma Fe\)Theoretical = 1.0), respectively. These Fe silicate reference minerals are measurements of dilute powder pellets, with multiple micron-scale grains in random crystallographic orientations relative to the beam, with the exception of a single olivine reference measurement from a thick/concentrated polished sample of unknown geometry. Using these known Fe silicate ferrous and ferric endmember ratios and the measured pre-edge centroid positions given in Table 2, an Fe\(^{3+}/\Sigma Fe\) ratio calibration line is plotted with 7112.91 ± 0.03 eV established at the pure ferrous position, shown in Fig. 7c labeled Fe\(^{3+}/\Sigma Fe\) ratio (silicates). Figure 7c also includes data for silicate glass, referenced from Berry et al. (2003), which vary in ferric content (determined by Mössbauer spectroscopy) and closely matches the Fe\(^{3+}/\Sigma Fe\) ratio line for silicates in this investigation. The pre-edge centroid positions for oxides magnetite and hematite, referenced in Berry et al. (2003), were aligned with the magnetite and hematite measured in this investigation (a difference of ~0.37 eV) to ensure that the silicate glass data were aligned with the energy grid defined in this investigation.

The Fe\(^{3+}/\Sigma Fe\) ratio (silicates) calibration line for this investigation equates to:

\[
\text{Centroid} = 1.7467 \times \text{Fe}^{3+}/\Sigma \text{Fe} + 7112.91 \pm 0.03. \quad (1)
\]

An Fe\(^{3+}/\Sigma Fe\) ratio in Fe oxides can also be estimated using reference minerals hematite (Fe\(^{3+}/\Sigma Fe\)Theoretical = 1.0) and magnetite (Fe\(^{3+}/\Sigma Fe\)Theoretical = 0.67). However, an Fe\(^{3+}/\Sigma Fe\) ratio for Fe oxides should be assessed independently of the Fe silicates due to significant component peaks within the pre-edge unrelated to the 1s → 3d transition, in particular hematite (Wilke et al. 2001).

The Fe\(^{3+}/\Sigma Fe\) ratio (silicates) calibration line establishes a generic gradient in which the 1s → 3d pre-edge centroid increases with an increased Fe\(^{3+}/\Sigma Fe\) ratio in the Fe silicate minerals. This gradient is used to estimate the Fe-redox variations (ΔFe\(^{3+}/\Sigma Fe\)) between host and SW material within an individual Itokawa mineral grain.
The Fe\(^{3+}/\Sigma\)Fe ratio calibration line is based on the pre-edge centroid energy position measured for mostly powder pellet reference minerals, with random crystallographic orientations, whereas the Itokawa samples are single crystal grains with unknown orientations. With unknown crystal geometry, uncertainty could be 5–15% (Dyar et al. 2001). However, this investigation focuses on the Fe-redox variations (\(\Delta FE^{3+}/\Sigma FE\)) within individual mineral grains, thus polarization effects may be discounted. Therefore, uncertainty in the calibration is based on the standard deviation between the known ferric-ferrous ratio (Fe\(^{3+}/\Sigma\)Fe\(^{3+}\)) of the reference minerals and their estimated ferric-ferrous ratio (Fe\(^{3+}/\Sigma\)Fe\(^{3+}\)) values as determined by the “Fe\(^{3+}/\Sigma\)Fe ratio” calibration lines. For Fe silicates and oxides, Fe\(^{3+}/\Sigma\)Fe uncertainty is determined to be ±0.015 and ±0.012, respectively. The uncertainty in the measured centroid energy positions is estimated to be ±0.03 eV for all I14 and I18 Fe silicates and oxides.

Figure 6 (left) and Fig. 8a show the full Fe-K XAS spectra for SW zones and their respective host grain measurement, revealing little variation overall between the two features for each of the samples (A–F), and no significant influence upon the spectra, if any, from other possible Fe-rich mineral groups such as those shown in Fig. 7a. The partially crystalline Fe silicate remains the dominant phase, despite npFe\(^{0}\) particles being present within the SW zone (see STEM results). Therefore, the Fe silicate Fe\(^{3+}/\Sigma\)Fe ratio calibration is solely used for estimating Fe-redox variations in the Itokawa samples between host and SW zone features.

Figure 6 (right) and Fig. 8b show the Fe-K XANES region for the Itokawa samples, including the 1\(s\)→3\(d\) pre-edge peaks and up to the absorption edge position at half-normalized intensity. Although not used for
analyzing $\text{Fe}^{3+}/\Sigma\text{Fe}$ values, assessment of the Fe-K XANES absorption edge presents a consistent trend of shifts to higher energy positions suggesting increases in $\text{Fe}^{3+}$ content. Measuring the Fe-K XANES pre-edge centroids, shown in Fig. 6 (right-inset) and Fig. 8c, gives a more accurate analysis for estimating variations in $\text{Fe}^{3+}$ content. The baseline-subtracted pre-edge centroids (Fig. 8c) and the differences between the host grain and SW zone reveal the two peaks within the pre-edge feature that are typically associated with $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ at approximate energy positions $\approx 7112.7$ and $\approx 7114.4$ eV, respectively. The centroid energy positions, defined as the intensity-weighted average, are presented in Table 2.

The centroid positions for SW zones range from 7113.03 to 7113.31 eV ($\pm 0.03$ eV), and the host grain centroid positions range 7112.91–7113.24 eV ($\pm 0.03$ eV). Using the ferric-ferrous ratio equation, a centroid energy position of 7112.91 $\pm 0.03$ eV equates to $\text{Fe}^{3+}/\Sigma\text{Fe} = 0.00 \pm 0.015$, which suggests some of the host grain mineralogy (e.g., #0063 [C]) with centroid positions up to 7113.24 $\pm 0.03$ eV may already feature a minor ferric content. The olivine of grain #0080 (A) and the Ca-rich pyroxene of #0089 (E) appear to remain nearly pure-ferrous with centroid positions of 7112.93 $\pm 0.03$ eV and 7112.91 $\pm 0.03$ eV, respectively.

Determining any potential Fe-redox changes in the Itokawa space-weathered rims was achieved by observing the $1s \rightarrow 3d$ pre-edge centroid energy shifts from the host grain to the space-weathered rim (Host-SW zone energy shift) for each measured sample region. Regardless of host ferric content, each sample region measured shows an increase in the Host-SW zone energy shift, suggesting an increased ferric content from the host grain mineralogy to the SW rims for each sample. The Host-SW zone energy shifts are shown in Fig. 8c, the shifts visually presented in Fig. 9 for each measured region, with the estimated Fe-redox change ($\Delta\text{Fe}^{3+}/\Sigma\text{Fe} \pm 0.03$), and all values stated in Table 2. The largest Fe-redox change from the host grain to SW zone is shown in the #0080 (A) olivine with a difference of up to $\Delta\text{Fe}^{3+}/\Sigma\text{Fe} = 0.14 \pm 0.03$. However, olivine sample regions #0063 (B) and #0089 (D) show a difference as low as $\Delta\text{Fe}^{3+}/\Sigma\text{Fe} = 0.03 \pm 0.02$ and $0.02 \pm 0.03$, respectively, revealing little to no difference within error.

**DISCUSSION**

Analysis of Fe-K XANES measurements at SW zones reveals some increase in ferric content relative to their respective host grains. Regardless of the small magnitude of the ferric contents, these results suggest a minor Fe-redox change in the SW zones. The $\approx 50$–$100$ nm thick surfaces of these ferromagnesian asteroidal grains have been partially amorphized, along with blistering and nanophase Fe metal particle formation (confirmed by STEM observations), but the dominant Fe silicate phase has also become oxidized via one process or another.

It is important not to neglect the possibility that the surface of Itokawa grains collected by Hayabusa may have been oxidized since entering Earth’s atmosphere. The sample container was opened under vacuum a week after landing (Yada et al. 2014), and the samples stored and protected from terrestrial atmospheric contamination in clean chambers under vacuum or pure N$_2$ gas. Before opening, the sample container seal may have been permeable to terrestrial atmospheric contamination (Okazaki et al. 2011), and the originally metallic npFe$^0$ particles oxidized (Noguchi et al. 2014a). Since then, the FIB lift-out sections of this investigation have also been exposed, from their extraction in June 2018 to the final XANES map measurement in December 2018. However, detectable quantities of such primary mineral modification can require up to a few decades of exposure for olivine and pyroxene (Velbel 2014). The grains have never been exposed to non-ambient fluids, heated water, etc., associated with more rapid hydrous alteration. Thus, it is assumed that any estimation of oxidation found in the samples is not a result of terrestrial contamination.

**Oxidation of Space-Weathered Zones**

**H$^+$ Solar Wind Implantation**

The npFe$^0$ particles, observed in the SW zones of Itokawa grains, also occur in the SW zones of Apollo lunar samples and are suggested to have formed due to reactions with the implanting solar wind H$^+$ ions (Hapke 2001; Thompson et al. 2016). As the impacting solar wind particles and/or micrometeorites liberate the various oxide molecule constituents from the crystal structure of their host mineral, the FeO oxide molecules react with the implanted H$^+$ to reduce the Fe to metal (i.e., $\text{Fe}^{2+}\text{O}(s/l)+2\text{H}^+\rightarrow\text{Fe}^0(s)+\text{H}_2\text{O}(l)$). A by-product of this reaction is water vapor, which may then react with the further FeO in the surrounding matrix. Thus, the implanted H$^+$ ions can be a catalyst for the iron charge disproportionation reaction, $3\text{Fe}^{2+}\rightarrow\text{Fe}^0+2\text{Fe}^{3+}$, via the following process:

$$3\text{Fe}^{2+}\text{O}(s)+2\text{H}^+\rightarrow\text{Fe}^0(s)+\text{H}_2\text{O}(g/l)+2\text{Fe}^{2+}\text{O}(s)\rightarrow\text{Fe}^0(s)+\text{Fe}_2^{2+}\text{O}_3(s)+\text{H}_2(g)$$

This reaction results not only in Fe$^0$ metal, which condenses into nanoparticles, but also ferric (Fe$^{3+}$) oxidized iron surrounded by the partially amorphized remnants of the host mineral in the SW zone.
Additionally, the resulting H$_2$ gas contributes to the observed low density and vesicular blisters.

The water vapor by-product may also react with the host mineralogy, whether olivine or pyroxene, via a process analogous to serpentinization (Oze and Sharma 2006; Holm et al. 2015). The anaerobic oxidation of ferrous fayalite with the water vapor leads to the formation of magnetite and silica, and H$_2$ gas as well (i.e., $3\text{Fe}^{2+}_2\text{SiO}_4+2\text{H}_2\text{O}\rightarrow2\text{Fe}^{3+}_2\text{Fe}^{2+}_2\text{O}_4+3\text{SiO}_2 + 2\text{H}_2$). The H$_2$ gas can also react further with surrounding Fe$^{3+}$/O, as explained above, producing more Fe metal.
The reduction of Fe from fayalite to metal is also possible via thermal reduction, as demonstrated in femtosecond laser experiments (Fazio et al. 2018). This is without the need for H+ ions, with by-products of quartz melt and SiO gas, as well as O2 gas possibly leading to oxidation. Buividus et al. (2014) performed Fe-L NEXAFS, also on femtosecond laser irradiated olivines, estimating considerable increases in Fe3+, and most likely Fe0 too.

Overall, the iron charge disproportionation reaction (3Fe2+ → Fe0 + 2Fe3+) suggests that where there is reduced iron due to space weathering, as in the form of npFe0 particles observed in this investigation as well as other Itokawa (Noguchi 2011, 2014a) and Apollo lunar samples (Keller and McKay 1997; Pieters et al. 2000; Hapke 2001; Pieters and Noble 2016), then there may also be oxidation of the ferromagnesian host mineralogy. This oxidized ferrous iron would be situated throughout the now partially amorphized “Zone II” of the SW surfaces of the grains.

Fe3+ in the Host Olivine and Pyroxene Grains

As already noted above, some of the ferromagnesian host grain minerals may have a minor ferric content, estimated from the Fe-K XANES analysis. At least two of the six measured grains, the #0080 (A) olivine and #0089 (E) Ca-rich pyroxene grain with centroid positions of 7112.93 and 7112.91 ± 0.03, respectively, equate to being near pure-ferrous. However, other host materials do not appear to be pure-ferrous, such as #0063 (C) olivine with a centroid position of 7113.24 ± 0.03 eV that equates to a Fe3+ / ΣFe value of ~0.19 ± 0.015.

Olivines can contain some Fe3+ ions, preferentially occupying the M2 lattice positions, and even exist in a highly ferric state as laihunite (Xu et al. 2014). Laihunite has been found in metamorphic and volcanic rocks and Martian meteorites (Noguchi et al. 2009; Martin et al. 2011). However, the olivines of this study have only minor ferric contents. Shock-induced dislocations of the mineral structure, which are observed in the host mineral grains of this study (Figs. 1 and 5a), can result in oxidation of Fe2+ to Fe3+, although an oxidizing environment or atmosphere may be required during the shock event (Bauer 1979). Similarly, pyroxene may also feature a ferric content, where Fe3+ occupies the M1 octahedron site (Deer et al. 2013).

Within the space-weathering rims, the Fe2+ is segregated to condense as npFe0, and the Fe3+ from the host grain mineral remains present among the silicate phase, and so the latter’s Fe3+/ΣFe ratio increases. Although partially amorphous, the resulting Fe-K XAS spectra resemble an Fe silicate with an increased Fe3+/ΣFe ratio, including positive shifts in the pre-edge centroid and absorption edge positions, thus an apparent Fe-redox change in the Fe silicate material. However, this does not explain the presence of Fe3+ in the SW zones of #0080 (A) and #0089 (E) where the host grains are near pure-ferrous and oxidation processes would be required in order for the SW rim to acquire Fe3+.

Fe3+ in the host mineral grain, raising the Fe3+/ΣFe ratio after the segregation of the Fe2+, may be possible but is not the only explanation for increased ferric content. The orientation of the Itokawa single grain crystalline samples within each measurement is an unknown factor. Dyar et al. (2001, 2002) found that definitively quantifying the Fe3+/ΣFe content of mineral samples could produce an error of ±0.05 to 0.15 primarily due to changes in the crystallographic coordination and orientation relative to the X-ray beam. Therefore, the apparently higher than expected Fe3+/ΣFe value of ~0.19 ± 0.015 for #0063 (C) may be due to polarization effects from the unknown crystallographic orientation of the Itokawa sample. The results in this investigation ignore polarization effects by instead analyzing direct comparisons between the host and its SW material for changes in Fe-redox (ΔFe3+/ΣFe) within an individual grain.

Fe3+ in Lunar Space Weathering

There have been various experiments involving Fe-K XAS analyses of Apollo lunar samples. Fe3+ valence states in lithic fragments of lunar soil, reported by Joy et al. (2015), found ferric ratios of Fe3+/ΣFe ~ 0.45 in magnetite grains suggested to have formed by desulfurization from surrounding troilite. McCanta et al. (2017, 2019) also assessed Fe-K XAS measurements in partially crystalline lunar picritic glass beads, estimating up to Fe3+/ΣFe < 0.6. This was interpreted as possible evidence of the oxidizing effect of H2O in the lunar interior. However, Fe-K XANES analyses for determining Fe-redox in the SW surfaces of Apollo lunar samples are notably lacking.

Thompson et al. (2016) have investigated Fe-redox variations, specifically in the npFe0 particles in the agglutinative glasses of the SW rims of lunar soil samples, using electron energy loss spectroscopy (EELS). By examining a range of lunar samples based on the SW maturity, Thompson et al. (2016) found Fe0 metal and mixed-valence Fe in the npFe particles correlating with sample maturity. In immature samples, where space weathering effects are present but minimal compared to other SW samples, 84% of npFe particles are pure Fe0 and the rest are mixed with minor Fe3+ content. In the more mature lunar SW samples, the npFe particles are Fe2+ and Fe3+, with ferric contents up to as much as...
Fe^{3+}/ΣFe ~ 0.56, and some mature samples contained no Fe^0. Thompson et al. (2016) suggest this correlation of oxidation state with maturity is explained by taking oxygen from the surrounding glassy matrix, but also from the H_2O vapor formed in the segregation by the implanted H^+ ions.

The increased oxidation state of npFe particles relative to sample SW maturity might also be found for other airless bodies, including asteroid Itokawa. However, the lattice spacings measured in the Fe nanoparticles of this study ranged 0.199–0.209 nm, averaging 0.203 nm, with a likely S-free composition, confirming the nanoparticles to be Fe-metal similar to previous Itokawa space weather investigations (Noguchi et al. 2011, 2014a). Based on d-spacing searches in the American Mineralogical Crystal Structure Database (Downs and Hall-Wallace 2003), iron metal typically has spacings averaging ~0.203 nm [110], whereas oxidized iron such as wustite (FeO) or magnetite (Fe_3O_4) feature larger spacings averaging ~0.215 nm [200] and ~0.253 nm [311], respectively. Thus, the results suggest little to no oxidation present in the npFe^0 particles observed in this study, and therefore a lack of weathering maturity in the samples.

Because of the low gravity and the movement of fine regolith on asteroid Itokawa, it is expected that the development of significantly mature space weathering may not be possible, with the most weathered regions appearing to be the boulder-rich areas (Abe et al. 2006; Pieters and Noble 2016), an area not sampled by Hayabusa. Of course, as shown in this study and others (Noguchi et al. 2011, 2014a), some space weathering does exist in the fine particles collected by Hayabusa and shows the same vapor deposits and solar wind irradiation effects as lunar regolith. Hayabusa collected from two touchdown sites, with SW rims on Itokawa grains from the first touchdown site observed to be less developed and have a lower density of solar flare tracks than grains from the second touchdown (Noguchi et al. 2014b). This may suggest a higher SW maturity at the second Hayabusa touchdown site.

Remote Characterization Studies of Space Weathering on Asteroid Itokawa

Asteroid Itokawa, an S-type asteroid, is spectrally similar to ordinary chondrite meteorites measured in laboratory experiments, except for a darkening of the spectra and a reddening that increases with increasing wavelength (Pieters et al. 2000; Binzel et al. 2001; Hiroi et al. 2006; Nakamura et al. 2011). This darkening and reddening of the spectra are similarly observed in lunar reflectance spectra (Keller and McKay 1997; Hapke 2001; Noble et al. 2005; Pieters and Noble 2016). Based on the laboratory experiments of irradiated analog samples of meteorites and lunar samples, the darkening is due to the presence of agglutinate glass and large (>40 nm) iron particles in the SW rims, and the reddening is due to the smaller npFe^0 particles.

Hiroi et al. (2006) compared the near-infrared reflectance spectra of two regions on Itokawa’s surface (not the two locations of Hayabusa’s touchdowns), using Hayabusa’s onboard NIRS instrument with a wavelength range of 0.76–2.10 μm. One region was dark and red, the other bright and blue. The spectra were consistent with LL5-6 chondrites, using the Alta’ameem LL5 meteorite as an analog and applying phase reddening via the model formula developed by Hapke (2001). Additionally, Hiroi et al. (2006) estimated the npFe^0 content to be 0.069 vol% in the dark and red region (assumed to be the more SW region of the two) and 0.031 vol% in the bright and blue region, which is consistent with the ground-based observed estimations of 0.05% (Binzel et al. 2001). However, discrepancies between the model and observed spectra occur throughout, in particular around 1.7 μm onward. A match to analog model data can differ due to surface roughness and incident angle variations, but also further mineralogical complexities, possibly including Fe^{3+}.

The Fe-K XANES mapping results for the SW zones in this study appear to be dominated by the ferromagnesian-silicate phase, shown in the Fe-K XAS for all six measured regions (A-F) in Figs. 6a and 8a, revealing little to no spectral structure variations between the host and SW zone that could be associated with the Fe-K XAS of Fe metal (Fig. 7a). The SW rims are partially amorphized, including some relict crystalline host mineralogy, showing that not all iron in the SW zone is segregated to form npFe^0 particles. STEM-EDX and TEM-EDX analyses here and by Noguchi et al. (2014a) found the SW zones, in particular the composite rims of Zone II, overall to have an elemental composition similar to the Zone III substrate host mineral; hence, the Fe-K XAS spectra remain very much the same between host and SW zone in all regions measured (Fig. 8a), except for the oxidation effects in the 1s → 3d pre-edge peaks. However, where there is npFe^0 formation, even in minor quantities of ~0.05% as suggested by Binzel et al. (2001) and Hiroi et al. (2006), then iron disproportionation suggests there will be Fe^{3+} formation too. The minor presence of both npFe^0 and Fe^{3+} confirmed in this study is surrounded by the mostly ferrous host mineral composition.

Spectral reflectance models by Thompson et al. (2016), involving lunar soil and the oxidation of npFe^0, found simulated spectra, in the range 0.5–1.5 μm, not only to reden and darken in the presence of Fe^0 but
also that Fe$^{3+}$ increases the reddening effect. This effect also brightens the SW surface significantly compared to Fe$^{2+}$- and Fe$^{0}$-rich zones. In these simulated spectra, the 1.0 absorption band associated with olivine, a feature observed on Itokawa (Abe et al. 2006), is also slightly reduced possibly suggesting a decrease in the presence of crystalline olivine in the weathered surface.

The consistent mineralogy and the space weathering features such as depths, partial amorphization, the presence of npFe$^{0}$ particles, and vesicular blistering, have previously been investigated in Hayabusa--Itokawa samples (Noguchi et al. 2011; Keller and Berger 2014; Pieters and Noble 2016). In addition, this study has shown that the SW surfaces of Itokawa grains contain a minor ferric presence in the ferromagnesian, amorphous silicate phase. Therefore, constraining spectral effects that may be attributed to the Fe$^{2+}$→Fe$^{3+}$ charge transfer in ferric silicates and oxides may be beneficial for future remote sensing investigations of space weathering on the surfaces of S-type asteroids and other airless bodies exposed to the space environment.

More constrained spectral models will also allow for accurate assessments of the complex mineralogy in other asteroids and airless bodies, including low-albedo C-type asteroids which typically have no apparent absorption bands indicative of space weathering (Pieters and Noble 2016). Early analysis of asteroid Ryugu spectral observations, by the JAXA Hayabusa2 spacecraft, suggests some regional darkening that may be related to space weathering (Sasaki et al. 2019). A reduction in the reddening may also be related to space weathering as laboratory ion irradiation experiments have determined a bleaching and brightening effect to the spectral slope for carbonaceous meteorites with hydrated materials (Lantz et al. 2017) and the reduction of the OH signature, similarly detected by the NIR3S instrument on Hayabusa2 (Kitazato et al. 2019). Investigating any space weathering effects in the mineralogical samples returned by Hayabusa2, some of which may be hydrated and possibly already feature a ferric content, will provide an important comparison to the SW Itokawa samples.

CONCLUSIONS

The irradiation-damaged SW rims of Itokawa asteroid grains have been studied using Fe-K XANES, TEM-EDX, and HAADF-STEM imaging.

1. FIB lift-out sections were prepared from all five samples. Between the five samples, at least eight distinct ferromagnesian silicate host grains were observed, including five olivines, two Ca-low pyroxenes, and a small Ca-rich inclusion. Each included an SW zone. The surface SW zones are partially amorphized, measuring 50–100 nm deep, with features such as vesicular blistering, from the implantation of low mass He and H ions, as well as small (<5 nm) nanophase Fe metal (npFe$^{0}$) particles. In the substrate host grains, fractures and dislocations (probably shock-induced) were observed along with solar flare tracks penetrating at least ~4 µm deep.

2. Three of the samples (#0080, #0063, and #0089) were measured using the Fe-K XANES mapping technique, which included six of the Fe silicate host grains and their SW zones. Using the 1$s$ → 3$d$ transition pre-edge peaks to estimate variation in ferric-ferrous ratios ($\Delta$Fe$^{3+}$/ΣFe), differences were found between the host mineral and the SW zones within individual grains. 1$s$ → 3$d$ pre-edge centroid energy positions in the host grain minerals range 7112.91–7113.24 eV (±0.03 eV), in the SW zones range 7113.03–7113.31 eV (±0.03 eV). The largest Fe-redox change is estimated to be $\Delta$Fe$^{3+}$/ΣFe = 0.14 ± 0.03 from the host grain to SW zone in the #0080 (A) olivine.

3. The presence of Fe$^{3+}$ is likely due to reactions resulting from implantation of solar wind H$^+$ ions on the ferrous surface material. The iron disproportionation reaction, $3$Fe$^{2+}$ → Fe$^{0}$ + 2Fe$^{3+}$ via the formation of water vapor, results in Fe metal condensates and an oxidized Fe silicate phase, as well as H$_2$ gas contributing to the vesicular blisters or further reactions with the remaining ferrous Fe.

4. The samples investigated in this study are all from the first Hayabusa touchdown site. Further investigation of the Fe-redox in SW zones in samples from both touchdown sites could highlight variations, in particular regarding maturity of space weathering on asteroid Itokawa. Additional samples in such an investigation could include Apollo lunar samples, and other future asteroid sample return. Techniques such as EELS may also provide additional results to constrain oxidation and Fe-redox variation in the silicate phase and npFe$^{0}$ particles. These variations could highlight spectral effects due to Fe$^{3+}$ in SW silicate materials, providing more accurate spectral fits for remote sensing data of airless bodies.

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SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article.

Material S1. Additional notes on data analysis.