COMPARING ASTEROID ITOKAWA SAMPLES TO THE TUXTUAC LL5 CHONDRITE WITH X-RAY ABSORPTION SPECTROSCOPY. T. Noguchi[1], L. J. Hicks[2], J. C. Bridges[2], S. J. Gurman[2], and M. Kimura[1] College of Science, Ibaraki University (2-1-1 Bunkyo, Mito, Ibaraki 310-8512, Japan), [2]Dept. of Physics and Astronomy, University of Leicester, LE1 7RH, UK.

Introduction: The grains of Itokawa returned by the JAXA Hayabusa mission in 2010 showed mineralogical and isotopic affinities to LL5-6 chondrites [1,2,3]. If so, the redox state experienced by the grains in their parent body should be almost identical to that in LL5-6 chondrites. We measured the relative abundance of Fe^{3+} and Fe^{2+} ions in ferromagnesian silicates, which reflects the redox states, in grains from Itokawa and an LL chondrite. X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) are an X-ray Absorption Spectroscopy (XAS) spectroscopic technique which we use to compare Itokawa to chondrite meteorite samples.

Samples: Four samples collected during the first touch-down were allocated to our group. The optical photomicrographs before ultramicrotomy are presented in Figure 1. RB-QD04-0008 is a ~40 μm wide composite grain composed of olivine and high-Ca pyroxene crystals. It contains a small amount of opaque grains (<2 μm diameter). Both RB-QD04-0011 and RB-QD04-0015 are composed only of olivine including small amounts of opaque minerals (<2 μm in diameter). They are 35 μm and 46 μm wide, respectively. RB-QD04-0024 is a flat and thin ~50 μm wide grain composed of low-Ca pyroxene and plagioclase containing abundant small (<2 μm in diameter) opaque minerals. Because their sizes (~35 to ~50 μm) are comparable to the smallest grains investigated during the initial analysis (whole size range: ~30 to ~180 μm) [1], the mineralogy of the former is simpler than that of the latter.

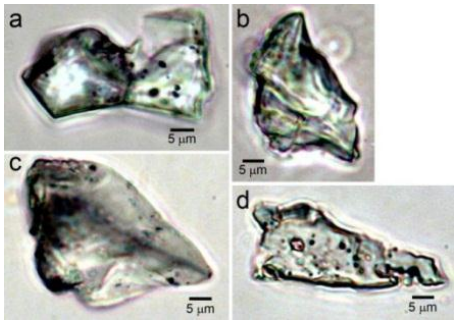

Figure 1. Optical images of the allocated grains embedded in epoxy resin. a) RB-QD04-0008, b) RB-QD04-0011, c) RB-QD04-0015, d) RB-QD04-0024.

A polished thin section of Tuxtuac LL5 was prepared and analysed by XAS and SEM-EDX for comparison with the four Itokawa particles.

Methods: All the samples were embedded in epoxy resin by using a N_2 purge glove box at the curation facility, JAXA/ISAS. Dew-point temperature was below -40 ^oC during embedding and curing. They were transferred to Ibaraki University in a N_2 gas filled aluminum laminated plastic bag. The bag was then opened and the samples stored in a vacuum desiccator prior to ultramicrotomy. They were ultramicrotomed into 90 nm thick sections by Reichert Ultracut-N for scanning transmission electron microscopy. After ultramicrotomy, ultrathin sections were quickly put back into in the vacuum desiccator. Then, they were carbon coated and observed by scanning electron microscopy (JEOL JIB-4501).

For comparison, we prepared a polished thin section of the Tuxtuac LL5 fall. Although low-Ca pyroxene in this meteorite was reported as untwinned [4], we found that many low-Ca pyroxene grains in the thin section exhibit twinning.

These samples were analysed using the Beamline I18 X-ray microfocus spectroscopy beamline at the Diamond Light Source, Oxfordshire, UK. Diamond is a 3 GeV synchrotron with ring currents of approximately 250 mA. Energy selection with fractional energy resolutions of 10^{-4}-10^{-5}, respectively are achieved with a Si (1 1 1) and (3 1 1) double crystal monochromator. A Si drift Vortex detector was used to measure the X-ray fluorescence and absorbance of elements with Z >40. Fe K edge X-ray XAS was performed on ~2.5 μm spots and also with a mapping routine over ~20 x 20 μm areas. Typical experimental conditions used for XAS were 1 s integration at each 0.2–0.4 eV energy step up to ~7100 eV, followed by a higher resolution of 0.1 eV energy steps over the XANES features up to 7150 eV, and continuing over the EXAFS region with steps of 2-4 eV up to 7660 eV.

After the XAS, chemical compositions of silicates in the Itokawa grains were measured by field-emission electron microprobe (FE-EPMA) at JEOL. Acceleration voltage and proble current are 15 kV and 9 nA.

Results:

Fe-K XANES of olivine. The Fe-K XANES plots of olivine in three Itokawa grains show a clear absorption pre-edge feature, which is common to olivine in the Tuxtuac LL5 and terrestrial olivine (San Carlos) (Fig. 2). Their edge positions and the pre-edge centroid positions of olivine in the three Itokawa particles are 7119.5-7119.8 eV and 7112.5-7112.6 eV, respectively.

These values are indistinguishable from those in terrestrial olivine and olivine in Tuxtuac.

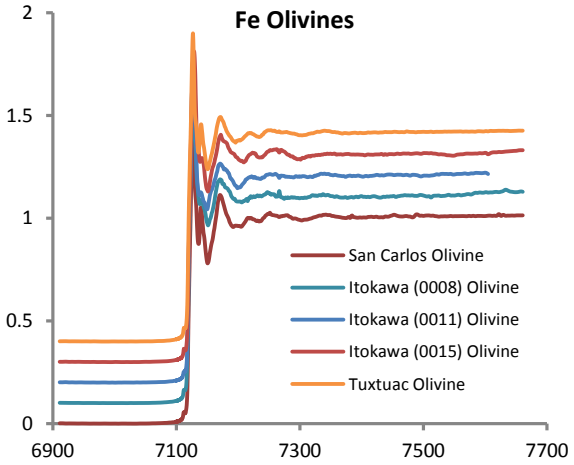

Figure 2. X-ray absorption spectra (normalized intensity vs. energy eV) around the Fe-K absorption edge for olivine and pyroxenes. Olivine in three Itokawa particles and Tuxtuac LL5 chondrite, and a terrestrial olivine (San Carlos).

Fe-K XANES and EXAFS of pyroxene. The edge position and the pre-edge centroid position of low-Ca pyroxene in the Itokawa grain 0024 are 7119.7 eV and 7112.6 eV, respectively. These values are indistinguishable from those of low-Ca pyroxene in Tuxtuac LL 5 chondrite: 7119.8-8 eV and 7112.6-8 eV, respectively. In the case of high-Ca pyroxene in Itokawa, the Fe-K absorption spectrum of a mixture of high-Ca pyroxene and an Fe- and Ni-bearing phase was obtained because the latter exists just below the high-Ca pyroxene in the Itokawa particle 0008. Nevertheless, the edge position and the pre-edge centroid position of the mixture of high-Ca pyroxene and Fe- and Ni-bearing phase are 7119.4 eV and 7112.6 eV, which are indistinguishable from the pre-edge peak derived from Fe^{2+} of terrestrial augite, 7119.3 eV and 7112.0 eV, respectively. The EXAFS suggested that the high-Ca pyroxene in 0008 is disordered and the low-Ca pyroxene in 0024 is ordered.

Fe-K and Ni-K XANES and EXAFS of metal and sulfides. To estimate the Fe- and Ni-bearing phase beneath high-Ca pyroxene crystal in the Itokawa grain 0008, Fe-K and Ni-K X-ray absorption spectra were obtained. Ni-K absorption spectrum of the Ni-bearing area in 0008 is more similar to taenite in Tuxtuac and metallic Ni than those of pentlandaite in Tuxtuac. This result is consistent with the Ni-K EXAFS data of these phases.

Chemical compositions of olivine and pyroxenes. Average and standard deviation of Fo mol% of olivine in RB-QD04-0008, 0011, and 0015 are 69.5 ± 0.6 (n=3), 70.3 ± 0.3 (n=3), and 69.0 ± 0.7 (n=2), respectively. Average and standard deviation of En and Wo mol% of low-Ca pyroxene in 0024 are 74.3 ± 0.3 and 2.2 ± 0.02 (n=3), repsectively. En and Wo mol% of high-Ca pyroxene in 0008 are 46.1 and 41.9, respectively. We could not measure plagioclase due to its small size.

Discussion: The Fe-K edge positions and the Fe-K pre-edge centroid positions of olivine, low-Ca pyroxene, and high-Ca pyroxene in the four Itokawa grains are indisutinguishable from those in Tuxtuac LL5 chondrite. These data indicate a negligible abundance of Fe^{3+} ions in ferromagnesian silicates in both the Itokawa grains and Tuxtuac, which is consistent with the mineralogical, petrological, and oxygen isotopic data of the Itokawa grains investigated in the initial analyses [1,2,3]. The four Itokawa grains do not contain small pentlandite inlcusions, which is consistent with the low abundance of pentlandite in LL chondrites (<<1%) [4,5].

Olivine and low-Ca pyroxene in the four Itokawa grains are homogeneous and their Mg/(Mg+Fe) ratios are within the range of those in the equilibrated grains investigated during the initial analysis [1]. However, Wo mol% of low-Ca pyroxene is higher than those in the equilibrated grains ($Wo_{1.4}$ [1]) and within the range of LL6 chondrites [6]. En and Wo mol% of high-Ca pyroxne in RB-QD04-0008 are within the range of poorly equilibrated grains in the initial analysis [1]. The disordered structure of high-Ca pyroxene indicated by the Fe-K EXAFS data might be related to partial equilibration or shock. However, it does not show mechanical twinning. Olivine attaching to the high-Ca pyroxene does not show undulatory extinction. Therefore, partial equilibration is more plausible than shock as a cause of its disordered structure, which is consistent with its chemical composition.

The Fe-K XANES and EXAFS data together with EPMA data of the four Itokawa grains suggest that the redox state experienced by the Itokawa grains are similar to those of LL chondrites. However, the four Itokawa grains represent a wide range of thermal metamorphism corresponding to petrologic types 4 to 6.

References: [1] Nakamura T. et al. (2011) *Science*, 333, 1113-1116. [2] Yurimoto H. et al. (2011) *Science* 333, 1116-1119. [3] Nakamura E. et al. (2012) *Proc. Nat. Acad. Sci.*, 109, 4031-4032. [4] Graham, A. M. et al. (1988) *Meteoritics*, 23, 321-323. [5] Jamsja, N. and Ruzicka, A. (2010) *MAPS*, 45, 828-849. [6] Scott, E. R. D. (1986) *Proc. 17th LPSC, Pt. 1, JGR*, 91, E115-E123.

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