Using X-ray Microfocus Spectroscopy to determine Cometary and Asteroidal Parent-Body Processes

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Since the *Stardust* and *Hayabusa* missions, we have investigated a selection of these returned cometary and asteroidal samples using Beamline I-18 at the *Diamond Light Source* synchrotron in UK, measuring Fe-K X-ray Absorption Spectroscopy (XAS) and transmission X-ray Diffraction (XRD). Such techniques are essential to determine the origin and evolution of fine grained planetary materials, and in particular we have identified evidence for water-rock reaction on the Wild2 parent body.

I-18 X-ray microfocus spectroscopy

Beamline I-18 has an energy range 2.0-20.7 keV and a spot size reduced to ~2.5 µm. X-ray Fluorescence (XRF) can provide chemical compositions, with XRF maps providing the opportunity to accurately locate features of interest at the micron-scale. Fe-K XAS measurements typically range 6900-7500 eV at variable energy resolutions 1.0-10 eV, with higher resolution steps of 0.1 eV focused over the XAS near-edge (XANES) region 7090-7150 eV necessary to accurately determine minor shifts and variations in the $1s \rightarrow 3d$ transition pre-edge peak structure and absorption edge. The $1s \rightarrow 3d$ centroid position is estimated from the intensity-weighted average energy position over the pre-edge peaks, and the absorption edge position is the energy at which intensity is 0.5 of the normalized spectra. Comparisons are made to reference materials, in particular the ferric content of silicates are estimated by comparing pre-edge centroids with the ferrous-ferric energy shift in standards [1]. Combined with XRF mapping, producing XANES maps can reveal any variations in the ferric content. Additionally, in-situ measurements of transmission-XRD are acquired at 13 keV, with observable 2θ ranging 5.5°-38.4°, corresponding to *d*-spacings 9-1.5 Å.

Identifying magnetite in Comet Wild 2 samples

Initial investigations of Comet Wild 2 samples returned by *Stardust* identified mostly high temperature ferromagnesian silicates [2], but additional constituents have included CAI's and chondrule-like fragments, suggesting links between carbonaceous chondrites and the Wild 2 material [3].

Hicks et al. (2017) [4] investigated the terminal grains of eight *Stardust* aerogel tracks, which include terminal grains identified as near pure magnetite Fe_3O_4. *Stardust* track C2045,4,178,0,0 (#178) featured a magnetite terminal grain measuring 10 µm in diameter, and a 5 µm magnetite terminal grain in track C2065,4,187,0,0 (#187), both visibly identified via XAS structure (Figure 1). In particular, absorption edge positions at 7121.5 and 7121.0 eV, and $1s \rightarrow 3d$ centroid positions estimated at 7113.1 and 7113.5 eV, closely resemble that of a magnetite powder standard with edge and centroid positions at 7120.8 eV and 7113.2 eV respectively. A small positive shift of up to ~0.5 eV in the Wild 2 grains, compared to the magnetite standard, could be due to a minor Ni^{2+} content identified with XRF, which replaces some Fe^{2+}, resulting in a higher $Fe^{3+}/\Sigma Fe$ content, thus a positive shift in the energy of the Fe-K XAS spectra.

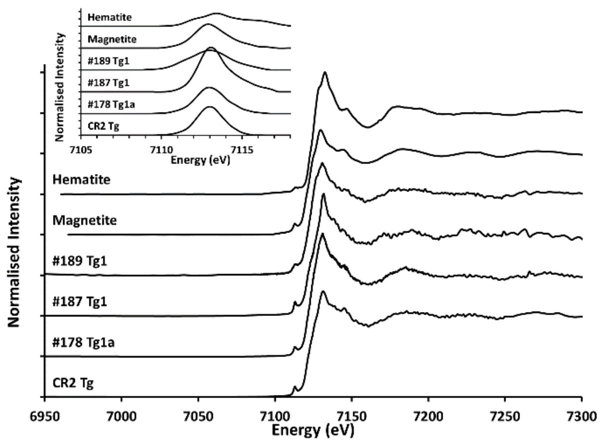

Figure 1. The Fe-K XAS and pre-edge centroid (inset) of terminal grains in tracks #178 (Tg1a), #187 (Tg1), and #189 (Tg1), and an analogue CR2 terminal grain (Tg) shot into aerogel, compared to powdered magnetite and hematite standard reference material.

In-situ transmission XRD analyses also identified magnetite with 2θ peaks at *d*-spacings 1.48 Å, 1.61 Å, 1.71 Å, 2.10 Å, 2.42 Å, 2.53 Å, and 2.96 Å for the cometary #178 (Tg1a and Tg2) and #187 (Tg1), closely matching the 2θ peaks a magnetite reference material. However, with unit cell dimensions ranging 8.355-8.370 Å for the cometary grains being slightly lower than that of a pure magnetite at 8.387 Å, this shift also suggests a Ni-bearing magnetite. Raman analyses performed at University of Kent also confirmed a Ni-bearing magnetite. Material in other *Stardust* tracks, identified via XAS analyses on I-18 at *Diamond*, include olivine (#177, #178, #187), pyroxene (#189, #190), Fe,Ni-metal (#170, #176), and Fe,Ni-sulfide (#187, #188) [4].

Magnetite grains are prominent in carbonaceous chondrites, if they have been oxidised and aqueously altered [5], thus the presence of magnetite in the Wild 2 mineral assemblage suggests further affinities to carbonaceous chondrites, probably resulting from hydrothermal alteration of the co-existing FeNi and ferromagnesian silicates in the cometary parent-body. Exploring this hypothesis further, powdered NWA 10256 CR2 chondrite material was shot into aerogel at 6.1 kms^{-1}, using a light gas gun [6], simulating the conditions of the *Stardust* collection. Fe-K XAS identified CR2 magnetite terminal grains (Figure 1) establishing the likelihood of preserving magnetite during capture in silica aerogel.

Itokawa ferromagnesian silicates and LL5 chondrite

Initial analyses of the Itokawa asteroid particles returned by *Hayabusa* had already found mineralogical, petrological, and oxygen isotopic affinities to LL5-6 chondrites [7,8,9]. We used Fe-K XAS to investigate the relative abundance of Fe^{3+} and Fe^{2+} ions in the ferromagnesian silicates of the Itokawa grains, comparing them to the Tuxtuac LL5 chondrite meteorite.

Noguchi et al. (2014) [10] investigated four samples from the first *Hayabusa* touch-down location: RB-QD04-0008; RB-QD04-0011; RB-QD04-0015; and RBQD04-0024. These samples, each embedded in epoxy resin, featured olivine with trace amounts of opaque minerals (0011 and 0015), olivine and high-Ca pyroxene (0008), and low-Ca pyroxene with plagioclase and small (<2 μm) opaque minerals (0024).

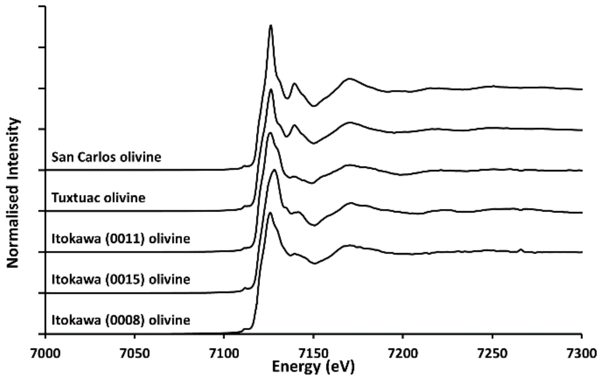

Figure 2. The Fe-K XAS for olivine in three Itokawa particles, the Tuxtuac LL5 chondrite, and a terrestrial olivine (San Carlos).

Fe-K XAS for the olivines (Figure 2) estimated absorption edges and $1s \rightarrow 3d$ centroids at 7119.5-7119.8 eV and 7112.5-7112.6 eV respectively, indistinguishable from those estimated for the Tuxtuac olivine and in terrestrial olivine. Edges and centroids for the low-Ca Itokawa pyroxene (7119.7 eV and 7112.6 eV), and the high-Ca Itokawa pyroxene (7119.4 eV and 7112.6 eV), are also indistinguishable from Tuxtuac and from Fe^{2+} in terrestrial augite. EXAFS analyses of the high-Ca Itokawa pyroxene suggested a disordered structure which may be partial equilibration or shock. A Ni-bearing phase associated with that high-Ca Itokawa pyroxene (0008) was also measured for Ni-K XAS, finding similarities to taenite in the LL5 Tuxtuac.

The Fe-K XAS analyses suggested a negligible abundance of Fe^{3+} ions in Itokawa and the LL5 ferromagnesian silicates, consistent with the initial analyses [7,8,9]. However, the EPMA analyses of the four Itokawa grains, that followed the Fe-K XAS analysis, suggested a wide range of thermal metamorphism corresponding to petrologic chondrite types LL4 to LL6.

Future XAS investigations of Planetary Sample Returns

As we continue to investigate planetary materials further, and as missions such as *Hayabusa 2* and *OSIRIS-REx* return samples to Earth, more advanced techniques will be essential to analyse micron-sized material, furthering our understanding of planetary formation. Offering similar techniques to I-18, but with higher spatial resolution down to ~50 nm, the new I-14 hard X-ray nanoprobe beamline at *Diamond* offers nanoscale microscopy with an energy range 5-23 keV, capable of XAS, XANES mapping, and XRD. Additionally, the I-08 Scanning X-ray Microscope (SXM) beamline performs XRF and XANES, but in the soft X-ray energy range 0.25-4.4 keV, including Si-K XANES, with a spatial resolution down to ~200 nm.

References

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