THE OXIDATION STATE OF TI IN SYNTHETIC AND METEORITIC HIBONITE, WITH APPLICATION TO EARLY SOLAR NEBULA PROCESSES

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Introduction: Hibonite ($CaAl_{12}O_{19}$) is a Ti-bearing mineral found in calcium aluminium inclusions (CAIs) and is thought to be the second mineral to condense from a solar composition gas [1]. As such, the crystal chemistry of hibonite could provide insight into the conditions of the early Solar System. Ti may occur as Ti^{3+} under reducing conditions, with up to 23% of the Ti in meteoritic hibonite previously reported as Ti^{3+} [2].

We have used X-ray absorption near edge structure (XANES) spectroscopy and X-ray photo-emission electron microscopy (XPEEM) to determine Ti^{3+}/Ti^{4+} ratios for a range of meteoritic hibonites, with spatial resolutions between 3 µm and 100 nm. We aim to use this information to investigate if hibonite grains record temporal variations in oxygen fugacity in the early solar nebula.

Results and discussion: Ti-bearing hibonite samples were prepared at 1400 °C under oxidising and reducing atmospheres using a CO-CO_2 gas mixing furnace in order to produce a sample series with 0-100% $Ti^{3+}/\Sigma Ti$ (where $\Sigma Ti = Ti^{3+}+Ti^{4+}$). Rietveld refinement of neutron powder diffraction data was used to determine the site occupancy of Ti^{3+} and Ti^{4+} in the synthetic hibonite samples. XPEEM images were collected on the synthetic and meteoritic hibonites (e.g. Figure 1). Ti K- and L-edge spectra were recorded for the sample suite, and spectral features that vary as a function of Ti^{3+}/Ti^{4+} in the synthetic hibonite series were identified (e.g. Figure 2).

The resulting calibration curve was used to determine Ti^{3+}/Ti^{4+} ratios for the meteoritic hibonite grains. The results show that blue hibonite from CAIs in the unique Acfer094 meteorite and greeny-blue hibonite from a CAI in the CR2 El Djouf001 meteorite have up to 10% $Ti^{3+}/\Sigma Ti$, and colourless hibonite grains from the R3-6 Hughes030 and R3 NWA2446 meteorites have less than 3% $Ti^{3+}/\Sigma Ti$. These results suggest that CAIs from a wide range of meteorite types initially formed under very reducing conditions. Additionally, there is evidence that there may be a degree of core-to-rim variation in the nature of Ti within some hibonite grains.

References: [1] Lodders (2003) *Astrophys. J* **591**, 1220-1247; [2] Beckett *et al.* (1988) *GCA* **52**, 1479-1495.

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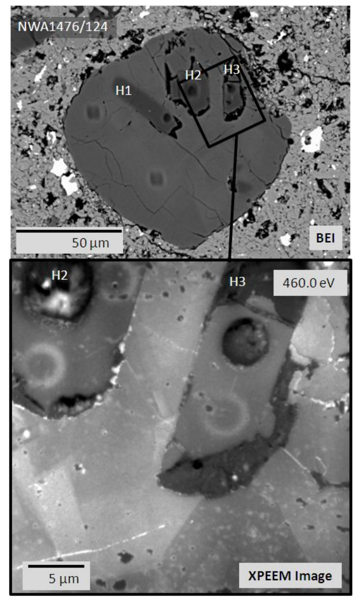

Figure 1: A backscatter electron image (BEI) collected using a scanning electron microscope is compared to a raw, single energy XPEEM image of two hibonite grains (H2, H3) and a Ti-rich pyroxene groundmass. Features are observed in the XPEEM images that are not evident in the BEI.

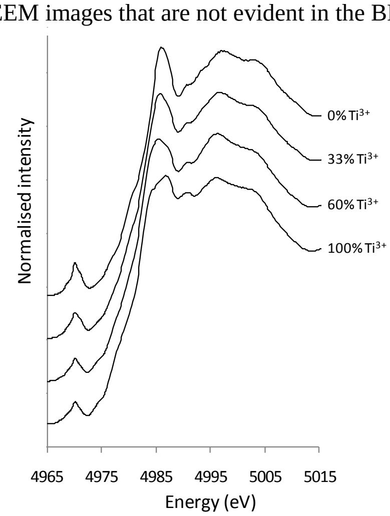

Figure 2: Ti K-edge XANES spectra from the synthetic hibonite sample series showing systematic variation in the spectra as a function of Ti^{3+}.