
Ti substitution mechanisms in hibonite
and the determination of
 $\text{Ti}^{3+}/\text{Ti}^{4+}$ by X-ray absorption spectroscopy
for use as an oxybarometer with
application to early Solar System processes

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Declaration

The work presented herein is the original work of the author,
unless specific reference is made to other sources.
No portion of this work has previously been submitted for a
degree at this, or any other university or institute of learning.

Patricia Mary Doyle
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For my Father

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ABSTRACT

Quantitative determination of element species is crucial for understanding geological processes, particularly changing redox conditions. As Ti^{3+} is stable under very reducing conditions, $\text{Ti}^{3+}/\text{Ti}^{4+}$ oxybarometers are suitable for investigating early Solar System processes. The systematics of $\text{Ti}^{3+}/\text{Ti}^{4+}$ in Ti-bearing $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ (Ti-CMAS) glasses and both synthetic and meteoritic hibonite ($\text{Ca}(\text{Al,Ti,Mg})_{12}\text{O}_{19}$) were investigated using X-ray absorption spectromicroscopy techniques. For this purpose suites of synthetic samples with 0-100% $\text{Ti}^{3+}/\Sigma\text{Ti}$ (where $\Sigma\text{Ti} = \text{Ti}^{3+} + \text{Ti}^{4+}$) were prepared in a 1 atm gas mixing furnace. The samples were characterised by electron microscopy, and when relevant, by X-ray diffraction and neutron powder diffraction (NPD).

The crystal structure of hibonite has five distinct Al sites onto which Ti may substitute. Structural refinements of NPD data using the Rietveld refinement method were used to determine Ti^{3+} and Ti^{4+} site occupancy in hibonite. Ti^{3+} was found to occupy the M4 octahedral site, whereas Ti^{4+} partitions between the M2 trigonal bipyramidal site and the M4 octahedral site. For hibonite with <1 Ti per formula unit Ti^{4+} partitions between the M2 and M4 site in a roughly constant ratio of 1:4.3, irrespective of the Ti^{3+} content.

Ti K-edge X-ray absorption near edge structure (XANES) spectra were collected from Ti-CMAS glasses and both synthetic and meteoritic hibonite. $\text{Ti}^{3+}/\text{Ti}^{4+}$ oxybarometers were developed using the synthetic samples, and the $\text{Ti}^{3+}/\text{Ti}^{4+}$ K-edge oxybarometer was used to quantify $\text{Ti}^{3+}/\Sigma\text{Ti}$ within hibonite from six different meteorites. Ti^{3+} hibonite was found in CAIs from the Acfer094 (unique), El Djouf001 (CR2), Murchison (CM2) and NWA1476 (R3) meteorites, whereas hibonite within CAIs from the NWA2446 (R3) and Hughes030 (R3-6) meteorites were Ti^{3+} poor. Furthermore, the $\text{Ti}^{3+}/\Sigma\text{Ti}$ varied within hibonite grains in CAIs from Acfer094 and El Djouf001. The presence of Ti^{3+} within hibonite in CAIs with no alteration minerals, or those that only experienced low temperature alteration, suggests they formed and/or were reprocessed under very reducing conditions ($<IW-2.7$). Hibonite within CAIs that had undergone extensive secondary alteration were Ti^{3+} -poor. It appears that the $\text{Ti}^{3+}/\Sigma\text{Ti}$ of the Ti^{3+} -poor CAIs re-equilibrated under oxidising conditions during a high temperature thermal metamorphic process.

X-ray photo-emission electron microscopy (XPEEM) images were collected from synthetic and meteoritic hibonites, from which Ti L-edge X-ray absorption spectra were extracted. A preliminary L-edge $\text{Ti}^{3+}/\text{Ti}^{4+}$ oxybarometer is presented. Core-to-rim zoning at the 200 nm scale was observed in two meteoritic hibonite samples, which suggests these grains record dynamically changing temperature and $f\text{O}_2$ conditions during the CAI forming process. Protocols are described under which the nm scale spatial resolution and spectroscopic capability in XPEEM can be utilised for the non-destructive study of meteorite mineralogy at the sub-micron level.

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Acronyms

Technical acronyms - techniques

EDS – Energy dispersive spectrometry
EELS - Electron energy loss spectroscopy
EPR – Electron paramagnetic resonance
ESR – Electron spin resonance
NPD – Neutron powder diffraction
WDS – Wavelength dispersive spectrometry
XANES – X-ray absorption near edge structure
XAS – X-ray absorption spectroscopy
XPEEM – X-ray photo-emission electron microscopy
XRD – X-ray diffraction

Technical acronyms - other

ADP – Atomic displacement parameter
BEI – Back scattered electron image
CAI – Calcium aluminium inclusion
CCR – Closed cycle refrigerator
CMAS – CaO-MgO-Al₂O₃-SiO₂
EMP – Electron microprobe
 fO_2 – Oxygen fugacity
FOV – Field of view
GSAS – General Structural Analysis System
HRPD – High resolution powder diffractometer
pfu – Per formula unit
ppl – Plane polarised light
PSD – Position sensitive detector
REE – Rare earth elements
sccm – standard cubic centimetre per minute
SEI – Secondary electron image
SEM – Scanning electron microscope
TOF – Time-of-flight
UHV – Ultra high vacuum
UIISO – (or U_{iso}) – the isotropic temperature factor in GSAS
xpl – Cross polarised light
XRF – X-ray fluorescence

Institutional acronyms

ALS – Advanced Light Source, Berkeley, USA

ANU – Australian National University, Canberra, Australia

DLS – Diamond Light Source, Oxfordshire, UK

IC – Imperial College, London, UK

NHM – Natural History Museum, London, UK

Quick-reference tables

Table 0-1 Molar mass of elements used in the study

Ordered by atomic number (Z)	
Symbol (Z)	Molar Mass (g/mol)
C (6)	12.010
O (8)	15.999
Mg (12)	24.312
Al (13)	26.982
Si (14)	28.085
Ca (20)	40.078
Ti (22)	47.867
Fe (26)	55.847
Rh (45)	102.90
Pd (46)	106.42
Re (75)	186.20
Au (79)	196.96

Table 0-2 $\log f_{\text{O}_2}$ to buffer curve conversion table

$\log f_{\text{O}_2}$ at 1400 °C	Relative to	
	IW	QFM
-3	$\Delta\text{IW}+6.5$	$\Delta\text{QFM}+3.3$
-9.4	$\Delta\text{IW}+0.1$	$\Delta\text{QFM}-3.1$
-11	$\Delta\text{IW}-1.5$	$\Delta\text{QFM}-4.7$
-12	$\Delta\text{IW}-2.5$	$\Delta\text{QFM}-5.7$
-13	$\Delta\text{IW}-3.5$	$\Delta\text{QFM}-6.7$
-13.5	$\Delta\text{IW}-4$	$\Delta\text{QFM}-7.2$
-14	$\Delta\text{IW}-4.5$	$\Delta\text{QFM}-7.7$
-16	$\Delta\text{IW}-5.5$	$\Delta\text{QFM}-9.7$
-18	$\Delta\text{IW}-7.5$	$\Delta\text{QFM}-11.7$
-20	$\Delta\text{IW}-9.5$	$\Delta\text{QFM}-13.7$

Notes: Buffer curves calculated using Myer and Eugster (1983).

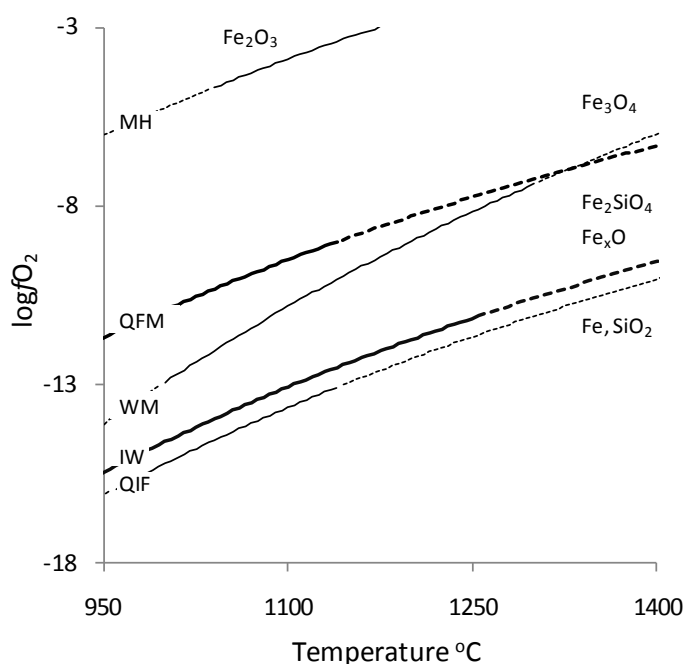


Figure 0-1 $\log f_{\text{O}_2}$ as a function of temperature showing mineral buffer curves: magnetite-hematite (MH), quartz-fayalite-magnetite (QFM), wüstite-magnetite (WM), iron wüstite (IW) and quartz-iron-fayalite (QIF). Buffer curves calculated using Myer and Eugster (1983). Dashed lines indicate extrapolation beyond the experimental datasets.

1 Thesis outline

1.1 Determining early Solar System processes

Analogues for early Solar System processes are sought through astronomical observations. Such observations and their associated hypotheses are “ground truthed” using meteorites and material returned from space missions (Russell, 2007). In recent years great strides have been made in understanding early solar nebula processes (Davis, 2003), aided in part by improvements in scientific capabilities that allow investigators to observe deeper into space and to study material on the sub-micron scale.

The oldest materials in the Solar System are refractory inclusions called calcium aluminium inclusions (CAIs), which are found in undifferentiated chondritic meteorites (Amelin *et al.*, 2002). Investigation of the mineralogy, texture, composition and isotopic characteristics of CAIs and other meteoritic components allows researchers to propose formation and subsequent reprocessing mechanisms (Krot *et al.*, 2003). Indeed, the CAI mineral assemblages observed are similar to those modelled to be the first to condense from a solar composition gas (Grossman, 1972). The evolution of the Solar System was, however, complex and models to describe this are constantly being modified as new information becomes available. For example, the isotopic composition of some CAI minerals indicates the solar nebula may have been cooler and less homogeneous than previously thought, as argued by Clayton (1978).

Oxygen fugacity (fO_2) indicates the potential for O_2 to be available and for redox variable elements to occur in their respective oxidation states (Fudali, 1965; Frost, 1991). The speciation of redox-variable elements in extraterrestrial materials therefore potentially provides information about oxygen-related processes in the early Solar System. Indeed, the mineral stability fields modelled by Grossman (1972), Wood and Hashimoto (1993), Yoneda and Grossman (1995) and Lodders (2003) indicate that minerals that form from a solar composition gas are strongly dependent on temperature and fO_2 . The fO_2 in the early solar nebula was affected by the abundance of dust, carbonaceous material and ice (Wood and Hashimoto, 1993; Grossmann *et al.* 2008). The presence of dust and the vaporisation of water ice would have resulted in oxidising conditions in the dust-rich mid-plane of the proto-planetary disk or localised round <100 km sized water-ice bodies that cross the water-ice thermal boundary on route to the proto-Sun (Grossmann *et al.*, 2008). The presence of carbonaceous material and the removal of water vapour would have produced reducing conditions. These

conditions would be prevalent within a small thermal stability field during which both dust and carbonaceous material are stable (Wood and Hashimoto, 1993), or caused by the loss of water vapour from the inner solar nebula either due to centrifugal action from the spinning disk, or by the formation of water ice (Grossmann *et al.*, 2008).

1.2 fO_2 s of a solar composition gas and extraterrestrial material

A gas of solar composition is thought to be more than 10^3 times enriched in H relative to the other elements, with He, C and O being the next most abundant elements (Lodders, 2003). CO, H₂O and SiO₂ were the major O-bearing gasses, and as the abundance of Si was lower than that of C and H, the H₂O/H₂ ratio (5.0×10^{-4}) or the C/O ratio (0.5) are thought to approximate the fO_2 of a solar composition gas (Lodders, 2003). At 1509 K the fO_2 of a solar composition gas is reported to be $\log fO_2 = -18.1$ (Grossman *et al.*, 2008), which is 6.8 log fO_2 units below the iron-wüstite buffer ($\Delta IW = 6.8$) and 10.2 log fO_2 units below the quartz-fayalite-magnetite buffer ($\Delta QFM = 10.2$).

The fO_2 s under which meteoritic components equilibrated and the methods used to determine these fO_2 s were succinctly summarised by Kozul *et al.* (1988). These include measuring the “intrinsic” fO_2 s of crushed samples in a high temperature furnace (e.g. Sato *et al.*, 1973), quantifying the fO_2 -dependant solubility of elements in another phase (e.g. Jurewicz *et al.*, 1995), or by determining the fO_2 using mineral equilibria that involve redox-variable elements (e.g. Simon *et al.*, 2005; Grossman *et al.*, 2008).

Many extraterrestrial materials equilibrated 6-7 log fO_2 units above a solar composition gas, plotting close to the iron-wüstite (IW) buffer curve. Figure 1-1a shows a summary of the fO_2 s determined for ordinary and carbonaceous chondrites (Brett & Sato, 1984), an achondrite (Brett *et al.*, 1977), a phosphate-bearing iron meteorite (Olsen and Fuchs, 1967) and lunar basalts (Sato *et al.*, 1973). As shown in Figure 1-1b, the fO_2 s determined for CAIs from the CV3 Allende chondrite plot just above the IW buffer curve, but it should be noted that these measurements were made on samples that had undergone secondary alteration (Kozul *et al.*, 1988). Similarly, metal nuggets found in CAIs have Nb, Ti and Zr contents consistent with formation, or re-equilibration, under conditions close to the IW buffer curve (Jurewicz *et al.*, 1995).

In contrast, phosphate-free iron meteorites may have equilibrated under “extremely” reducing conditions (Olsen and Fuchs, 1967). Enstatite chondrites equilibrated at fO_2 s that were 2.7 log units below the IW buffer (Brett & Sato, 1984), although the presence of minerals such as sinoite (Si₂N₂O), oldhamite (CaS) and graphite in these meteorites (Keil and Andersen, 1965) suggest the fO_2 under which they formed may have been lower, perhaps even more reducing than that under which CAIs formed (Guan *et al.*, 2000). Components within CAIs such as hibonite and Ti-augite (fassaite) equilibrated under conditions as reducing (Ihinger and Stolper, 1986; Beckett *et al.*, 1988), or more reducing (Simon *et al.*, 2005; Grossmann *et al.*, 2008) than a solar composition gas.

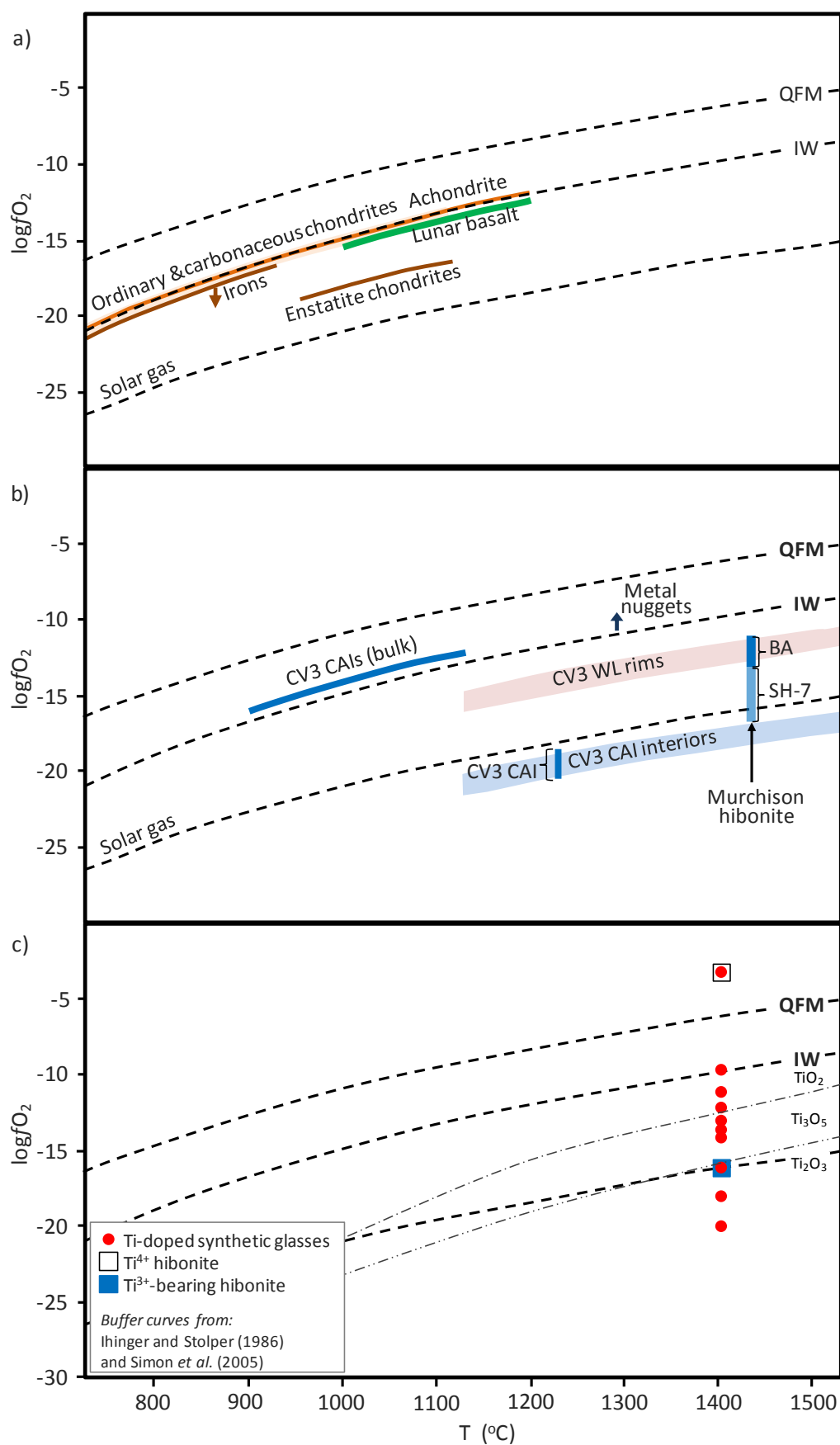


Figure 1-1 $\log f_{O_2}$ of extraterrestrial and synthetic material as a function of temperature for (a) different meteorite types and lunar basalt; (b) CAI components; and (c) synthetic samples in this study. The f_{O_2} of a solar composition gas and the iron-wüstite (IW), quartz-fayalite-magnetite (QFM) and Ti-oxide buffer curves are shown. See text for detail.

As is evident from Figure 1-1b, the fO_2 conditions of the early solar nebula changed over time. The mechanism and timescale for this change is, as yet, undetermined. CAIs are rimmed by sequences of mineral assemblages (Wark and Lovering, 1977) that are geochemically different from the core CAI (e.g. Rout *et al.*, 2009; Haggerty, 1978), based on which Simon *et al.* (2005) and Dyl *et al.* (2011) envisage rapidly changing fO_2 conditions in the early solar nebula. Of particular importance to the current study is the possibility that variable fO_2 conditions may also be recorded in hibonite as core to rim colour changes were reported for a hibonite grain from the R-type Hughes030 meteorite (Rout and Bischoff, 2008).

1.3 Ti-bearing hibonite

Ti-bearing meteoritic hibonite ($(Ca(Al,Ti,Mg)_{12}O_{19})$) varies in colour from colourless, to orange and blue (e.g. Rout and Bischoff, 2008), with the blue colour attributed to the presence of Ti^{3+} and indicative of formation under very reducing conditions (Ihinger and Stolper, 1986). Hibonite is modelled to be the second mineral to condense from a solar composition gas (Lodders, 2003) and may structurally accommodate up to a few wt% Ti and Mg, and trace amounts of rare earth elements (REEs) (MacPherson, 2003). Incorporation of Ti in hibonite can be achieved for both Ti^{3+} and Ti^{4+} , with Ti^{3+} substituting directly for Al^{3+} and Ti^{4+} undergoing a coupled substitution with Mg^{2+} for two Al^{3+} . Being one of the most refractory minerals in the Solar System, hibonite is likely to preserve the earliest fO_2 conditions and has the potential to record variation in fO_2 conditions.

Terrestrial hibonite is a fairly uncommon mineral, reported in medium- to high-grade metamorphic regions in Madagascar, Myanmar, Kenya, Mozambique, Tanzania, India and Siberia (Hainschwang *et al.*, 2010, Ulianov *et al.*, 2005; Rakotondrazafy *et al.*, 1996). The conditions of formation of terrestrial hibonite are very different to that of meteoritic hibonite (Rakotondrazafy *et al.*, 1996). Numerous element substitutions occur, including up to a few wt% REEs, Th, Ti^{4+} , Fe^{2+} and Fe^{3+} (Bermanec *et al.*, 1996; Rakotondrazafy *et al.*, 1996). Due to the occurrence of multiple element substitutions and the presence of Ti only in one oxidation state, terrestrial hibonites are not good analogues for meteoritic hibonite (e.g. Hofmeister *et al.*, 2004), whereas synthetic hibonites can be better tailored for this purpose.

1.4 Aims of this study

The principle aims of this study are three fold:

- 1) To determine the Ti substitution mechanisms in hibonite. In preparation for this study a suite of hibonites that contained Ti^{3+} , Ti^{4+} or mixed-valent Ti were synthesized in a 1 atm gas mixing furnace. These samples were then structurally characterised using Rietveld refinement of high resolution neutron powder diffraction data and the Ti site occupancy determined.

2) To use an integrated approach to develop reliable $\text{Ti}^{3+}/\Sigma\text{Ti}$ calibration curves using X-ray absorption spectroscopy techniques that provide 100 nm to μm scale spatial resolution. To this end, in addition to the synthetic hibonite samples, five suites of Ti-bearing glass compositions were synthesised under a range of $f\text{O}_2$ conditions (Figure 1-1c). The glasses and synthetic hibonites were analysed using microfocus X-ray absorption near edge structure (XANES) spectroscopy and X-ray photo-emission electron microscopy (XPEEM). Spectral features that varied as a function of synthesis conditions were used to develop $\text{Ti}^{3+}/\text{Ti}^{4+}$ oxybarometers.

3) To investigate whether hibonite records changes in the $f\text{O}_2$ of the early solar nebula. For this purpose hibonites from a range of different meteorite types with different evolutionary paths were characterised and then analysed by XANES and XPEEM. $\text{Ti}^{3+}/\Sigma\text{Ti}$ in the meteoritic hibonites was determined using the $\text{Ti}^{3+}/\text{Ti}^{4+}$ in hibonite oxybarometer, which is followed by a brief discussion of early solar nebula processes.

1.5 Structure of the thesis

Figure 1-2 summarises the structure and main findings in the study. Chapter 2 presents an overview of the techniques used. Chapters 3 and 4 include background information on sample synthesis and CAIs, together with the characterisation of the synthetic and meteoritic samples. The results chapters are introduced by a brief review of relevant literature and are structured according to technique: Chapter 5 covering the neutron powder diffraction study of synthetic Ti-bearing hibonite, and Chapters 6 and 7 the XANES and XPEEM studies (respectively). The results and main conclusions are summarised in Chapter 8, and the study is concluded with ideas for future work.

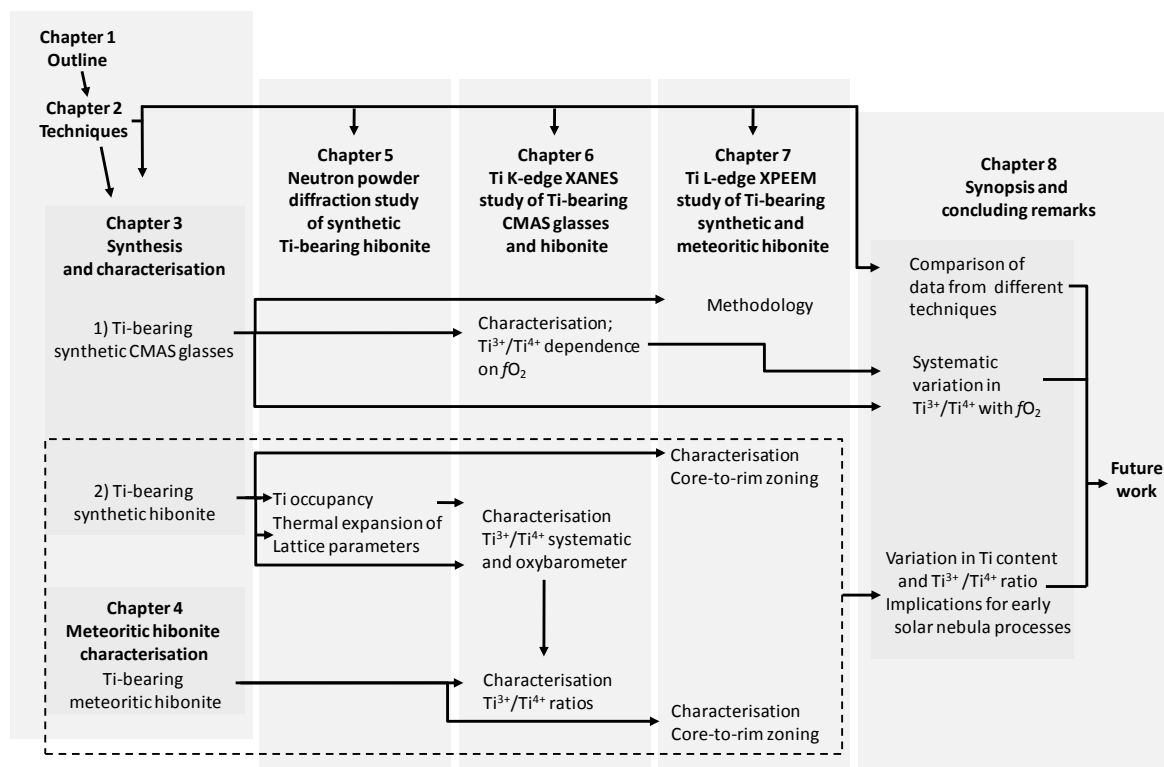


Figure 1-2 A schematic of the thesis structure – included are a summary of the main subject or findings of each chapter.

2 Instrumentation and Techniques

2.1 Synopsis

This study uses complementary analytical techniques to investigate the systematics of $\text{Ti}^{3+}/\text{Ti}^{4+}$ in hibonite and synthetic glasses. For this purpose samples were synthesised under known conditions and, along with meteoritic samples, were characterised using techniques such as X-ray powder diffraction and electron microscopy. Neutron powder diffraction was used to investigate the Ti substitution mechanism in hibonite. $\text{Ti}^{3+}/\text{Ti}^{4+}$ oxybarometers were developed for the synthetic glasses and hibonite using X-ray absorption near edge structure (XANES) spectroscopy, and X-ray photo-emission electron microscopy (XPEEM) was used to image and quantify $\text{Ti}^{3+}/\text{Ti}^{4+}$ within meteoritic hibonite. This chapter outlines the techniques used: from sample synthesis and characterisation to the spectromicroscopy.

2.2 Sample synthesis

2.2.1 1 atm gas mixing furnace configuration

In order to study the systematics of $\text{Ti}^{3+}/\text{Ti}^{4+}$ in amorphous and crystalline material, suites of synthetic samples were prepared under a range of oxygen fugacities ($f\text{O}_2$ s) in a 1 atm top-loading vertical gas-mixing furnace. The GERO 75242 furnace was customised with a bottom-opening valve for sample quenching. As shown in Figure 2-1, gas flowed in from below, past a sample within a ceramic-lined chamber, and was extracted to a fume hood above. A FCU-4 mass flow controller regulated the gas mixtures in the inner tube, ensuring a positive over-pressure in the furnace. The temperature was controlled by a Eurotherm 2416 proportional–integral–derivative (PID) set-point programmer. The samples were mounted either on metal loops (Pt or Re), which were attached to a chandelier, or within a Pt crucible or graphite mounts depending on the synthesis conditions. The sample mounts were fastened to a fixed length ceramic rod and top loaded such that the samples were as close to the hotspot as possible (Figure 2-2).

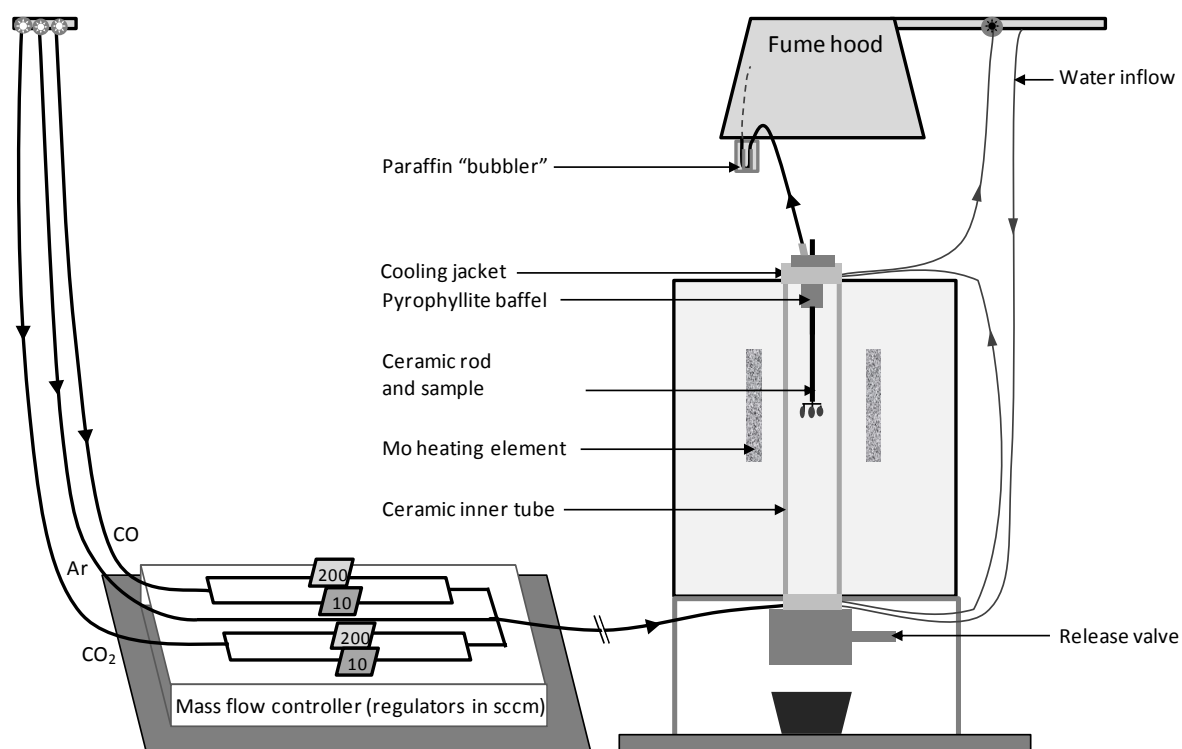


Figure 2-1 Schematic diagram of the main gas-mixing furnace components, including the mass flow controller.

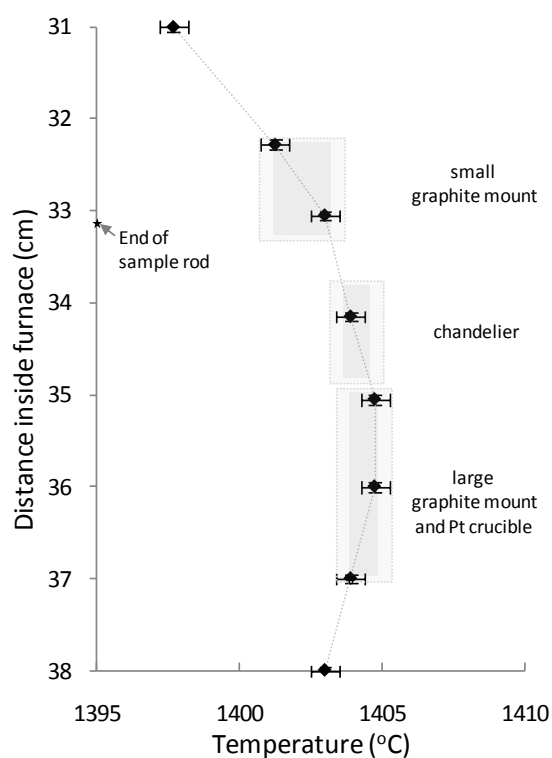


Figure 2-2 A vertical temperature profile for syntheses at 1400 °C showing the position of the sample mounts used relative to the hotspot, with the shaded areas representing the temperature ranges experienced by the samples (uncertainty indicated in lighter shading).

2.2.2 Thermal profile and temperature calibration

The thermal profile within a furnace is dependent on furnace design, gas composition, gas flow and temperature. Within a CO-CO₂ gas mixing furnace at 1400 °C the thermal profile may be expected to be symmetrical (Huebner, 1975). The thermal profile of the furnace was determined, and the temperature calibrated, as described below. The results of these experiments are presented in Figures 2-3 and 2-4, and the data is tabulated in Appendix A.1.

The hotspot position was initially determined by moving a Type B thermocouple (Pt-30%Rh vs. Pt-6%Rh) incrementally through a vertical profile in the furnace. A peak temperature of 1386 °C was located 36 cm into the furnace when using a set point of 1400 °C and no gas flowing. To investigate the offset between the hotspot temperature (T_H) and the programmed temperature (T_P), the thermocouple was positioned 36 cm into the furnace and the temperature recorded at 100 °C intervals between 1100 and 1500 °C with no gas flowing. A linear correlation was found, defined by the following relationship: $T_P = 1.067T_H - 82.385 (\pm 3 \text{ } ^\circ\text{C})$.

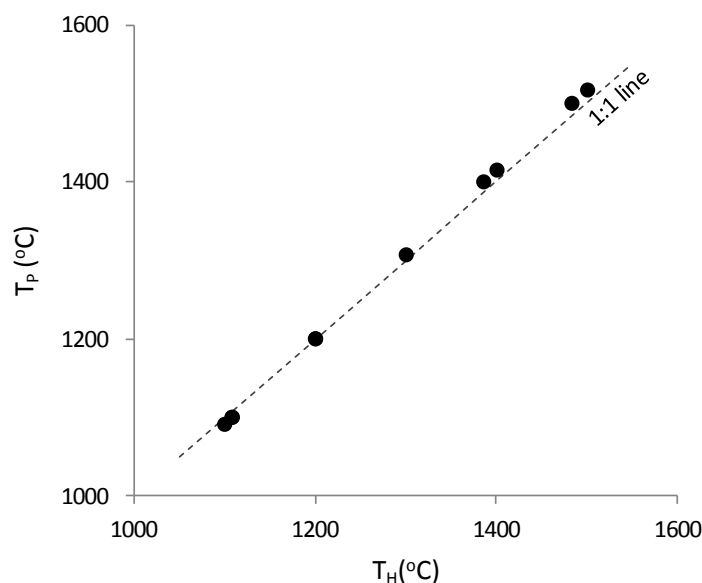


Figure 2-3 Programmed temperature (T_P) as a function of the hotspot temperature (T_H) with a 1:1 line shown.

The thermal profile was then more accurately determined at 1250 °C and 1400 °C using a Type B thermocouple with a gas flow of 100 sccm (standard cubic centimetres per minute) CO₂ to simulate synthesis conditions. The thermal profiles at both temperatures were symmetrical, and the hotspot region was 6 cm wide, the centre of which was 0.5 cm higher at 1400 °C than 1250 °C. The temperature at the hotspot (36 cm into the furnace) was then measured with gas flows representing the upper and lower limits used in the experiments (80 sccm and 200 sccm) to ascertain if gas flow modified the synthesis conditions, and no variation in hotspot temperature was observed as a function of gas flow.

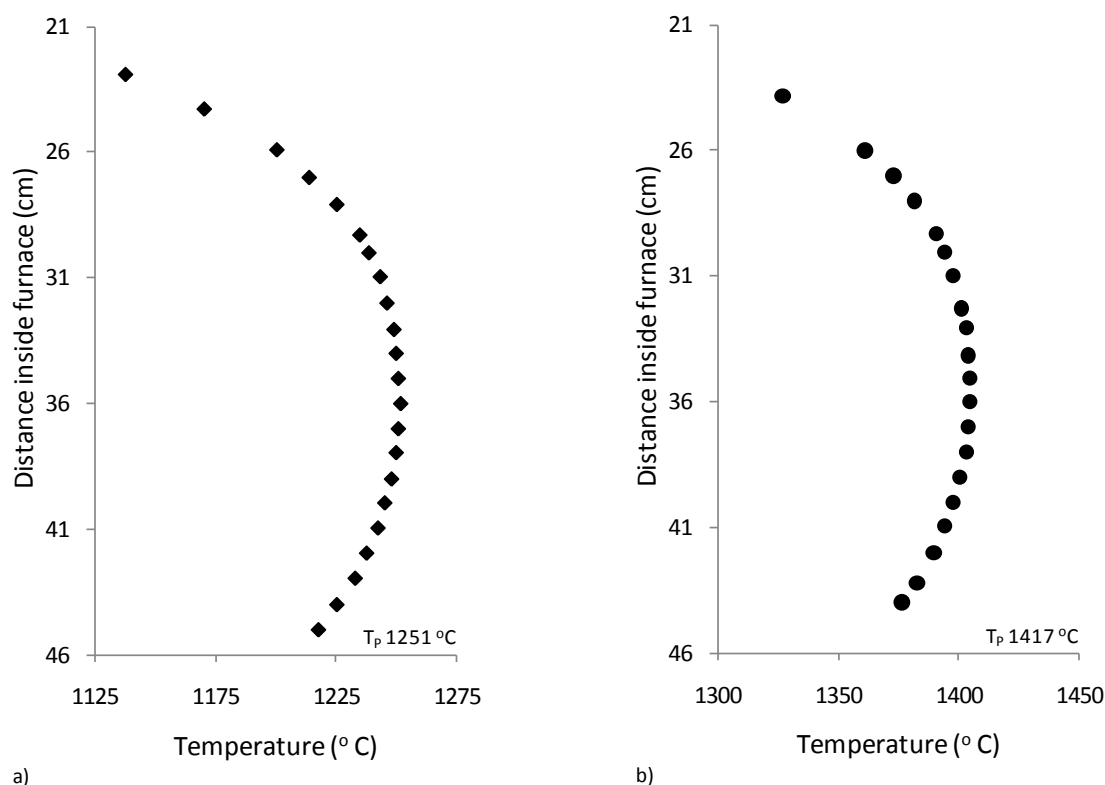


Figure 2-4 Hotspot profiles for the 1 atm CO-CO₂ gas mixing furnace for synthesis temperatures of (a) 1250 °C and (b) 1400 °C, with 100 sccm gas flowing. T_p = programmed temperature.

2.2.3 Oxygen fugacity calibration

The fO_2 within the furnace was varied by mixing different proportions of Ar, CO and CO₂ regulated by mass flow controllers. The gas flow mixtures used in the study are detailed in Appendix A.2. The CO-CO₂ mixtures used are equivalent to those defined by Deines *et al.* (1974). Above 1200 °C the fO_2 in a 1 atm CO-CO₂ gas mixing furnace may be expected to be equivalent to the actual CO-CO₂ mixture used and to be homogeneous throughout the furnace (Huebner, 1975). Nevertheless, the fO_2 of the hotspot was verified using the fO_2 -dependant solubility of Fe in a melt with an anorthite (CaAl₂Si₂O₈) and diopside (CaMgSi₂O₆) eutectic composition (AD), as defined by Holzheid *et al.* (1997).

In this calibration experiment, an AD composition powder was mixed with hydrated polyethylene oxide to make a slurry. This was then mounted on Fe loops 2 mm wide fashioned from Fe-foil and suspended on a chandelier mount. These samples were equilibrated under five fO_2 conditions between ΔIW -1.5 and ΔIW -4.5. The glass compositions were determined using electron microscopy techniques as detailed in Appendix A.2.2. The fO_2 of the hotspot was determined using Equation 2-1, which is derived from Holzheid *et al.* (1997) and the results are fully tabulated in Appendix A.2.2.

$$\log f_{\text{O}_2} = 2(\log \gamma_{\text{FeO}} + \log X_{\text{FeO}} - \log K^{\text{Fe-FeO(l)}})$$

Equation 2-1

Where:

 f_{O_2} = oxygen fugacity at 1404 °C (T_H) γ_{FeO} = 1.367 (from O'Neill and Eggins, 2002) X_{FeO} = the mole fraction of FeO in the anorthite-diopside (AD) melt $K^{\text{Fe-FeO(l)}}$ = the equilibrium co-efficient of the reaction: $\text{Fe(s)} + \frac{1}{2}\text{O}_2 = \text{FeO(s)} = \text{FeO(l)}$
= $e^{\Delta G/(-RT)}$ Where: ΔG = $-244118 + 115.559T - 8.474T \times \ln T$ R = $8.314472(15) \text{ JK}^{-1}\text{mol}^{-1}$ T = temperature (K)

The calculated f_{O_2} was linearly correlated with the flow-controlled f_{O_2} as defined by the CO-CO₂ gas mixtures used (Figure 2-5). Minor deviations from a 1:1 line were observed, with up to 0.15 log units in f_{O_2} difference at ΔIW -1.5.

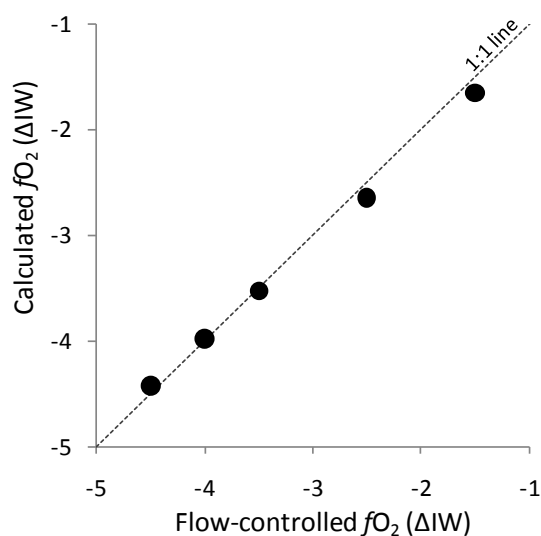


Figure 2-5 Calculated f_{O_2} using the f_{O_2} -dependant solubility of Fe in AD melts as a function of the flow-controlled f_{O_2} , showing a good correlation along a 1:1 line.

2.3 Electron microscopy

Synthetic and meteoritic samples were characterised using scanning electron microscopes (SEMs) and/or electron microprobes (EMPs). Within these microprobes an electron beam is generated by passing a current through a tungsten filament, after which the beam is focused by a series of lenses (Figure 2-6). Characteristic X-rays are emitted from the sample, and detected by energy dispersive (ED) and wavelength dispersive (WD) spectrometers, and the intensities of these X-rays are measured. ED spectrometers simultaneously collect the emitted X-rays as a function of energy, whereas WD spectrometers sequentially collect X-rays of a particular wavelength by using analysing crystals. Quantitative element analysis is made by comparing the intensity of specific X-rays with those from well characterised standards that are similar in composition to the phases being analysed.

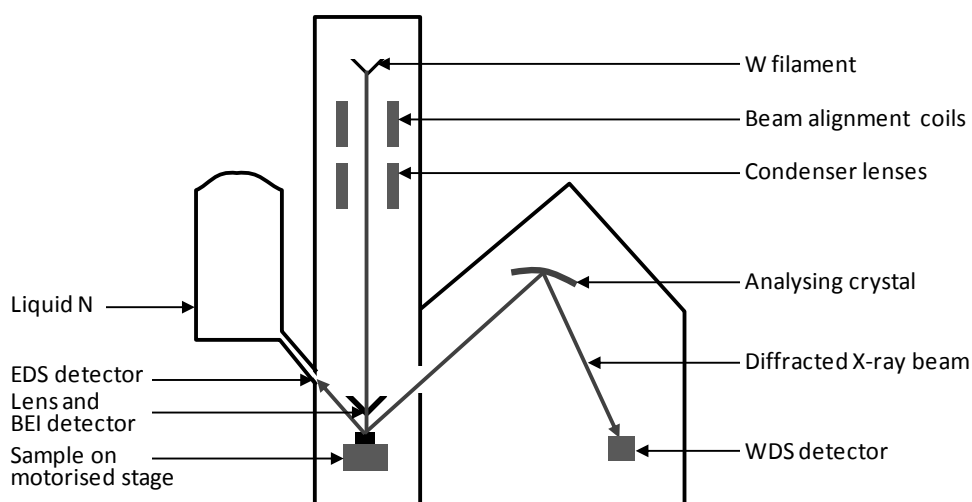


Figure 2-6 Schematic diagram of an electron microscope to which ED and WD spectrometers have been fitted (diagram after Watt, 1985).

2.4 Diffraction techniques

2.4.1 X-ray powder diffraction (XRD)

X-ray diffraction (XRD) was used for phase identification and initial crystal structure refinement of the synthetic hibonite samples. XRD data were collected from powdered samples using a Nonius PDS 120 powder diffraction system fitted with an Inel curved position sensitive detector (PSD) in a static beam-sample-detector geometry (Figure 2-7). The PSD simultaneously collects diffracted X-ray intensities over $120^\circ 2\theta$ (Schofield *et al.*, 2002), and thus a complete diffraction pattern is collected simultaneously, increasing counting statistics and reducing counting time.

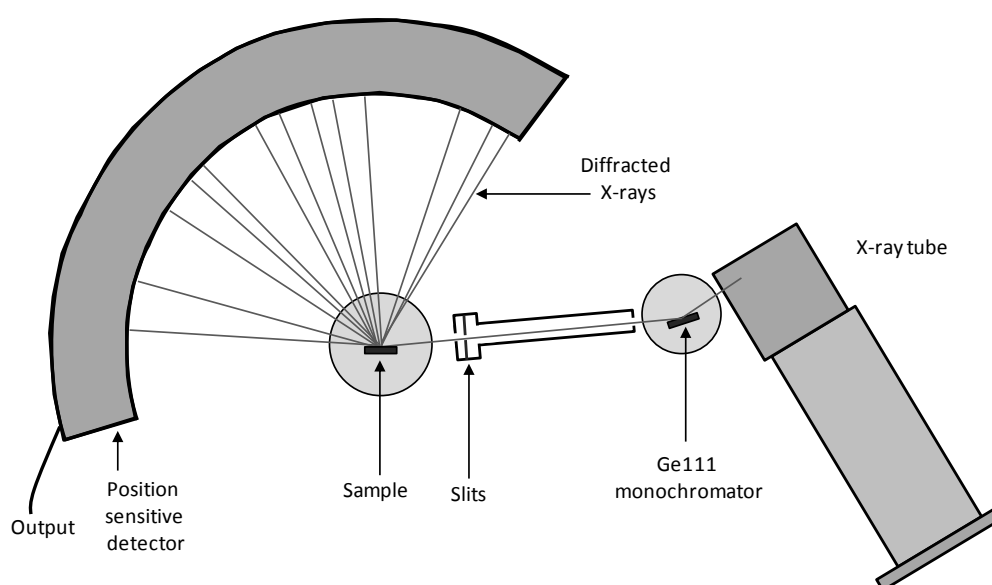


Figure 2-7 Schematic diagram of the Nonius PDS 120 powder diffraction system fitted with a position sensitive detector (PSD) that simultaneously collects diffracted X-rays over $120^\circ 2\theta$ (diagram after G. Cressey).

XRD is used for the characterisation of samples, including phase identification, phase quantification in polyphase mixtures and detailed structural analysis. The diffraction of an incident X-ray beam by an atomic plane within a crystal is described by the Bragg equation (Equation 2-2).

$$n\lambda = 2d\sin\theta$$

Equation 2-2

Where:

n	= an integer
λ	= wavelength (Å)
d	= inter-atomic spacing (Å)
θ	= angle of incidence (°)

In a monochromatic experiment the position of a measured diffraction peak relates to the atomic spacing (d), whereas the intensity of that peak is strongly influenced by the number and type of atoms that comprise the atomic plane. The position and intensity of diffraction peaks are thus unique to that material. As such, the XRD pattern is well suited for phase identification, with the understanding that variation in composition within a sample may modify peak positions and intensities. Phase identification is achieved through the comparison of the collected diffraction pattern with those from well characterised structures within crystallographic databases.

It is important to note that the atomic X-ray scattering factor (a measure of the ability of an element to scatter an X-ray beam) is directly proportional to the number of electrons, and hence the atomic number (Z) of an element (Figure 2-8). Consequently, when trying to refine crystal structures light elements can be difficult to locate precisely using XRD, particularly in systems containing elements with large atomic numbers, and distinguishing between elements of similar atomic number can also be challenging.

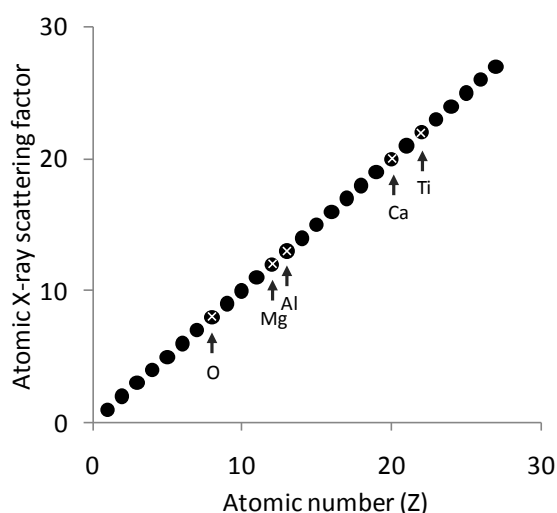


Figure 2-8 Atomic X-ray scattering factors at $0^\circ 2\theta$ showing a regular increase in the atomic scattering factor with atomic number. The elements present in Ti-bearing synthetic hibonite are highlighted with "x" (diagram after Parise, 2006).

2.4.2 Neutron powder diffraction

Neutron powder diffraction (NPD) data were collected at the ISIS neutron spallation source (Oxfordshire, UK) using the high resolution powder diffractometer (HRPD) for crystal structure refinements of a series of Ti^{3+} , Ti^{4+} and mixed-valent synthetic hibonite samples. In addition, variations in the lattice parameters of two synthetic Ti-bearing hibonite samples were investigated over the temperature range $7 \leq T \leq 275$ K.

ISIS is a pulsed, time-of-flight (TOF) neutron spallation source in which the neutron beam is created by bombarding a Ta target with proton pulses generated by a 0.8 GeV synchrotron (Wilson, 1995; Schofield *et al.*, 2003). The neutron energy is moderated by interaction with methane at 100 K before entering the HRPD beamline. A reflective glass conduit with a 36 km radius of curvature channels the neutron beam to the HRPD beamline which is located 100 m away from the target (Figure 2-9), resulting in increased peak resolution. As a consequence of such design features for the HRPD beamline, the peak resolution ($\Delta d/d$) of this diffractometer is currently unmatched by any other neutron powder diffractometers in the world (Ibberson, 2009). The long travel path, however, may result in fast neutrons from one pulse overlapping with slower neutrons from a former pulse. To prevent this occurring, the rotation speeds of disk choppers located at 6 and 9 m from the moderator (Figure 2-10) are set to ensure that only one pulse reaches the detector banks at a time (Ibberson *et al.*, 1992).

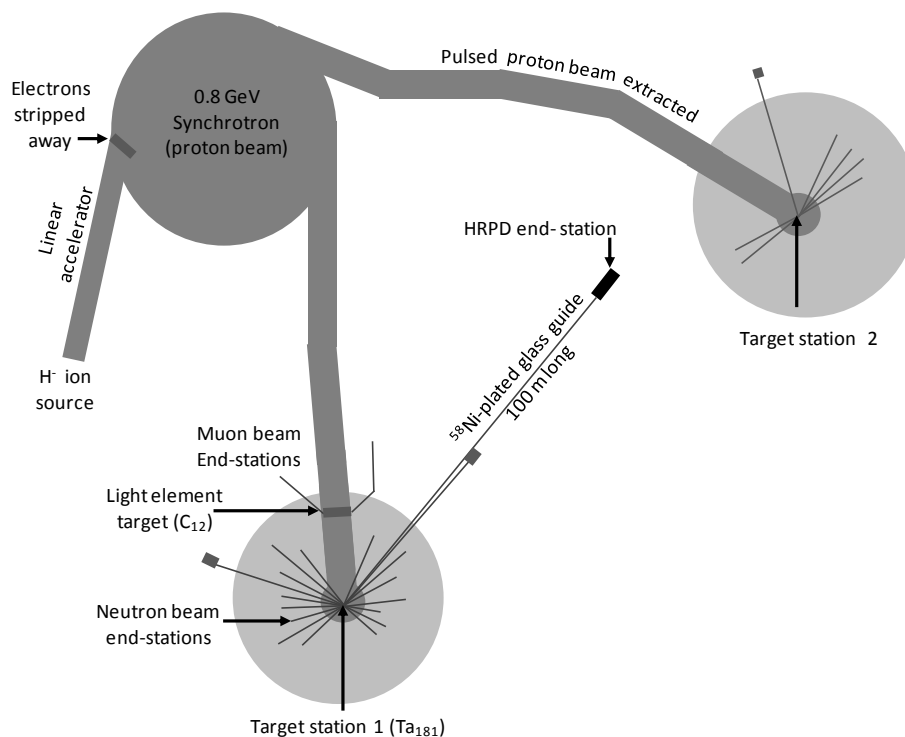


Figure 2-9 Schematic diagram of the ISIS pulsed neutron source showing the location of the HRPD end-station relative to the target (diagram after Hall, 2009).

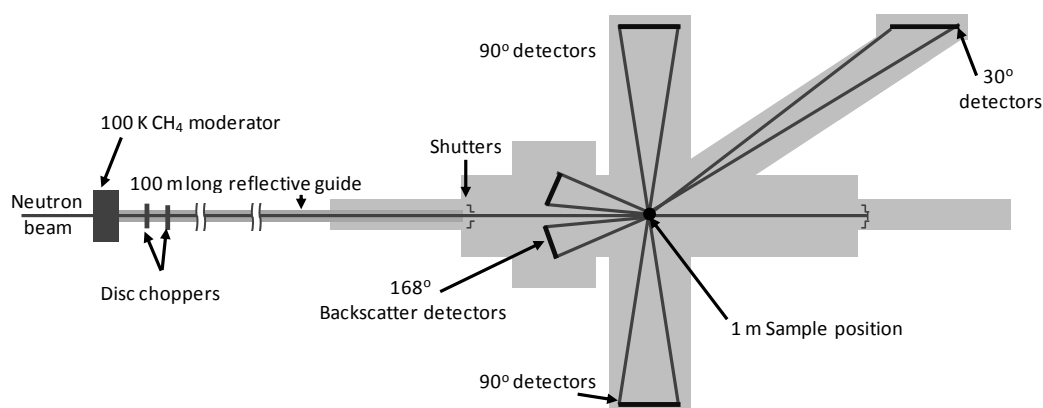


Figure 2-10 Schematic diagram of the HRPD neutron powder diffraction beamline at the ISIS pulsed neutron source showing the fixed source-sample-detector geometry (diagram after Ibberson *et al.*, 1992).

The diffractometer on HRPD comprises a fixed source-sample-detector geometry with mean 2Θ angles for the detector banks of 30° , 90° and 168° (Figure 2-10). The detector banks themselves are composed of an array of detectors with $28^\circ < 2\Theta < 32^\circ$, $87^\circ < 2\Theta < 93^\circ$, $160^\circ < 2\Theta < 176^\circ$ (Ibberson *et al.*, 1992). The detectors measure the arrival time of the neutrons, and due to the polychromatic nature of each neutron pulse, a full diffraction pattern is collected for each neutron pulse. By continually combining the TOF data from each pulse, a diffraction pattern is collected in which the counting statistics improve as a function of time. The data from the individual detectors are focused to the effective 2Θ angle of the detector bank by making a time correction for each dataset (Schofield *et al.*, 2003). In this way the count statistics are maximised and the data collection time is minimised.

The TOF of the individual neutrons are related to their wavelength by the de Broglie relationship (Equation 2-3). Furthermore, the TOF is directly proportional to the neutron wavelength as the mass of the neutron, Planck's constant and the length of the flight path are constant.

$$\lambda = h/mv = (h/mL)t \quad \text{Equation 2-3}$$

Where:

λ	= incident neutron wavelength (m)
h	= Planck's constant = $6.626068 \times 10^{-40} \text{ m}^2\text{kg}/\mu\text{s}$
m	= mass of a neutron = $1.675 \times 10^{-27} \text{ kg}$ (Parise, 2006)
v	= velocity of neutron (m. μs)
t	= time-of-flight of the neutron (μs)
L	= length of the flight path (m)

As described by Schofield *et al.* (2003) and Parise (2006), by combining the de Broglie relationship (Equation 2-3) with the Bragg equation (Equation 2-2), the neutron TOF is related to the d spacing of a crystal according to Equation 2-4.

$$d = (h/2mL\sin\Theta)t = (1.978 \times 10^{-3} / L\sin\Theta)t \quad \text{Equation 2-4}$$

Where:

d	= inter-atomic spacing ($\text{\AA}$) = $1.0 \times 10^{-10} \text{ m}$
h	= Planck's constant = $6.626068 \times 10^{-40} \text{ m}^2\text{kg}/\mu\text{s}$
m	= mass of neutron = $1.675 \times 10^{-27} \text{ kg}$ (Parise, 2006)
L	= length of the flight path (m)
Θ	= angle of incidence ($^\circ$)
t	= time-of-flight of the neutron (μs)

In contrast to the atomic X-ray scattering factors, the neutron scattering lengths do not increase systematically as a function of atomic number (Figure 2-11). This characteristic has two main advantages for a structural analysis of Ti-bearing hibonite ($\text{CaAl}_{12-x-2y}\text{Ti}_x^{3+}\text{Ti}_y^{4+}\text{Mg}_y\text{O}_{19}$) using NPD. Firstly, the position of the O-atoms may be well constrained as the coherent scattering from O is intense and not overshadowed by that of heavier elements. Secondly, due to the scattering lengths of Al, Ti and Mg (+3.45, -3.44 and +5.38 respectively; Sears, 1992), Ti and Mg occupancy within Al-sites may be quantifiably modelled.

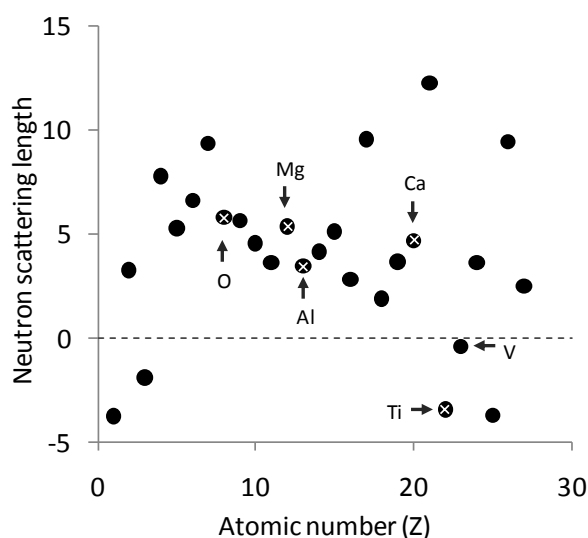


Figure 2-11 Neutron scattering lengths (Sears, 1992) as a function of atomic number showing the variability of the scattering lengths for the bulk element (isotopic variation is not shown). The elements present in Ti-bearing synthetic hibonite are highlighted with "x" (diagram after Parise, 2006).

2.5 X-ray absorption spectroscopy (XAS)

2.5.1 Quantitative determination of redox-variable element pairs

The speciation of redox-variable elements in geological materials provides an indication of the redox conditions under which they equilibrated (e.g. Frost, 1991). Traditionally, wet chemistry was used to determine the oxidation state of redox variable elements, but the determination of $\text{Ti}^{3+}/\text{Ti}^{4+}$ in Fe-bearing minerals has been shown to be erroneous (Whipple, 1979). Indirect information about oxidation states may be obtained using standard microanalytical techniques such as electron microprobe analysis (EMPA) or laser ablation inductively coupled mass spectrometry (LA-ICP-MS). The calculations of elemental oxidation states using these techniques are, however, based on stoichiometry and are therefore subject to a number of uncertainties, including structural vacancies and the presence of other polyvalent elements.

Some spectroscopic techniques directly measure the electronic structure of elements, from which their oxidation state may be determined (Henderson *et al.*, 1995; Schofield *et al.*, 1995; Cressey *et al.*, 1993). Additionally, a few of these techniques, such as electron energy loss spectroscopy (EELS) and X-ray absorption spectroscopy (XAS), provide nm to μm spatial resolution (e.g. Browning *et al.*,

2006; Berry *et al.*, 2008; Smith *et al.*, 2003), whereas Mössbauer, optical absorption and electron spin resonance (ESR) spectroscopies require larger volumes of sample. Moreover, some spectroscopies such as Mössbauer and ESR are restricted to particular elements, whereas EELS and XAS are both element specific and can be applied to the majority of elements (Malitesta *et al.*, 1995). Spectromicroscopy techniques such as X-ray absorption near edge structure (XANES) spectroscopy and X-ray photo-emission electron microscopy (XPEEM) are especially advantageous when working with museum specimens, samples from personal collections or unique material such as meteorites, as these methods are non-destructive (Schofield *et al.*, 2010). Therefore in this thesis, quantitative measurement of Ti oxidation states has been performed using XANES, and core-to-rim zoning of Ti content within mineral grains has been imaged using XPEEM.

2.5.2 X-ray Absorption Near Edge Structure (XANES) spectroscopy

Ti K-edge XANES spectra were recorded at beamline i18 of the Diamond Light Source (DLS), Oxfordshire (UK) from synthetic glasses, synthetic hibonite and meteoritic hibonite using a microfocused X-ray beam. The DLS is a third generation synchrotron source with a storage ring that is 561.6 m in circumference and that operates at a ring-energy of 3 GeV.

Using an in-vacuum undulator insertion device (Figure 2-12), X-rays sourced from the storage ring are directed through a complex set of beamline optics (Figure 2-13) and collimated, resulting in a high brightness, microfocused beam. A double crystal Si111 scanning monochromator is used to select the photon energy. Full details of this beamline are given by Mosselmans *et al.* (2009).

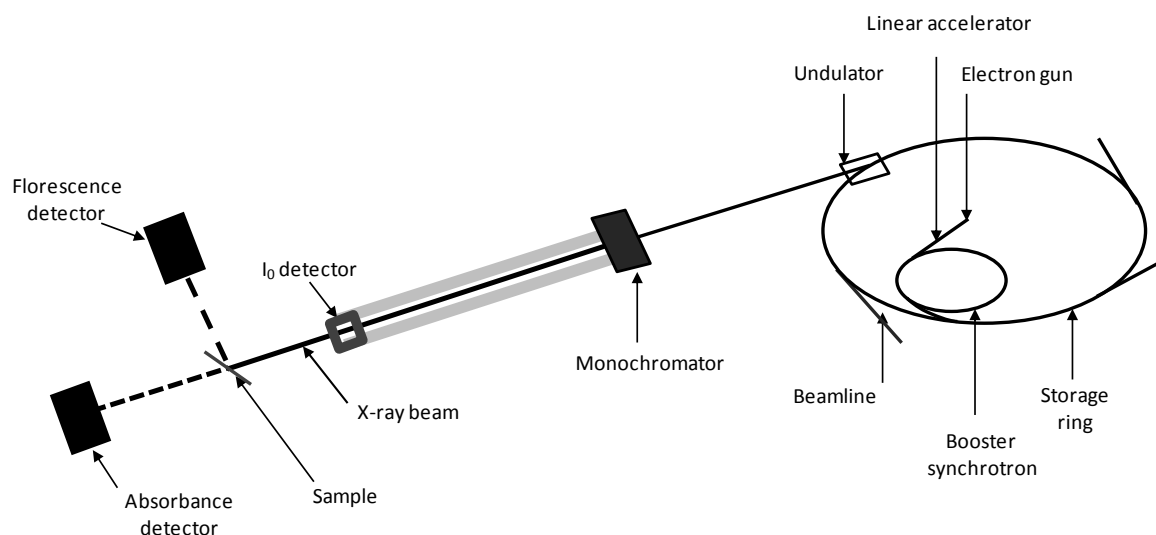


Figure 2-12 Schematic diagram of the i18 beamline at the DLS showing the synchrotron generated X-ray beam irradiating a sample mounted in air with an I_0 and absorbance detector orientated in line with the beam (90° to the sample surface, not shown) and a fluorescence detector orientated 90° to the beam (45° to the sample surface).

The x-y coordinates of samples were measured using an offline optical microscope, before the sample was attached to a kinematic sample mount and loaded onto a Newport-Microcontrol sample

stage. X-ray absorption is measured using a gas-filled I_0 detector, positioned between the exit slits and the sample, and an XSPRESS-2 detector for transmission experiments, whereas fluorescence is measured using an Ortec nine-element monolithic germanium detector set at 90° to the incident beam and 45° to the sample surface, as shown in Figure 2-12.

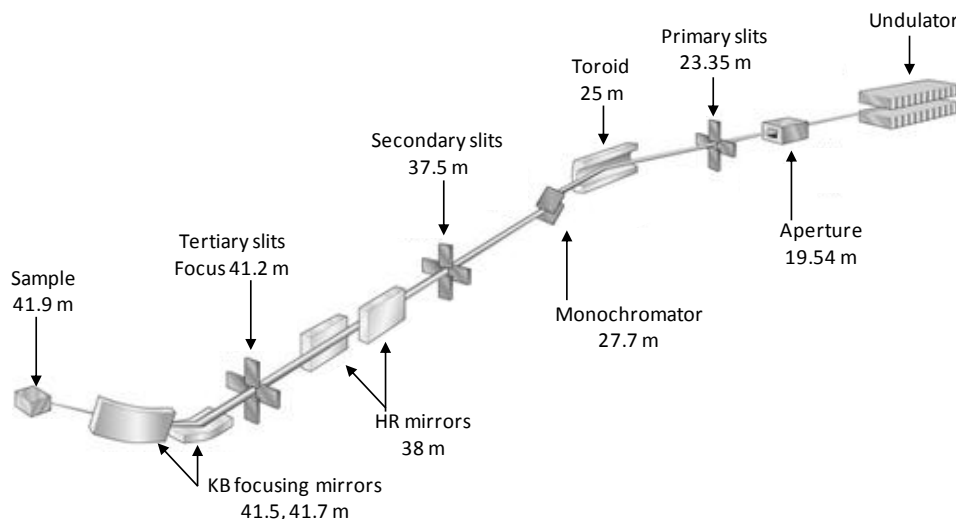
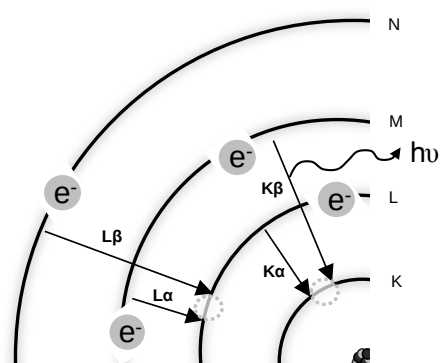


Figure 2-13 Schematic diagram of the i18 beamline optics at the DLS (Mosselmans *et al.*, 2009).

As the energy of the incident monochromatic X-ray beam equals (and just exceeds) the binding energy of an electron, it is absorbed by the sample by exciting an electron from an inner orbital either to an outer orbital or by expelling it beyond the bound state, both of which result in a core-hole in an inner orbital. The system returns to the ground state by an electron infilling the core-hole and the consequential emission of either a photon (as shown in Figure 2-14) or an electron (Calas and Hawthorne, 1988). As a consequence, X-ray absorption may be measured either directly or indirectly, with the latter measured as either X-ray fluorescence or photo-electron flux (Brown *et al.*, 1988).



$$E_{\text{photon}} = h\nu \quad \text{Equation 2-5a}$$

$$= 12406/\lambda \quad \text{Equation 2-5b}$$

Where:

E_{photon} = Energy of photon (eV)

h = Plank's constant = 6.63×10^{-34} J.s

ν = frequency (1 s^{-1}) = c/λ

c = speed of light $\approx 3.00 \times 10^{18}$ Å.s $^{-1}$

λ = wavelength (Å)

Figure 2-14 Schematic diagram of the release of an X-ray photon as an atom returns to the ground state by an electron dropping from an outer orbital to an inner orbital. The main transitions are named. (Diagram after Watt, 1985).

XANES spectra may be divided into three main regions, namely the pre-edge region, edge and post-crest region (Figure 2-15). The pre-edge is usually a weak feature <10 eV below the absorption

edge and is caused by electron transitions to empty or partially filled bound states. In theory the K-edge $1s \rightarrow 3d$ electronic transition for the first row transition elements is forbidden by dipole selection rules, however, the transition is allowed due to mixing of the metal d -orbitals with the ligand p -orbitals (Brown *et al.*, 1988). The pre-edge feature is consequently sensitive to d -orbital configuration and useful for oxidation state studies. The edge feature corresponds to the energy at which an electron is excited beyond the bound state. As core electrons are bound more tightly in higher oxidation states, the edge energy is strongly influenced by the oxidation state of the target element (Brown *et al.*, 1988). The post-crest region extends approximately 50 eV beyond the absorption edge. The structure in this region is a result of the resonance of multi-scattering processes from the interaction of non-bound electrons and is therefore influenced by the next-nearest neighbours of the target element (Brown *et al.*, 1988; Romano *et al.*, 2000).

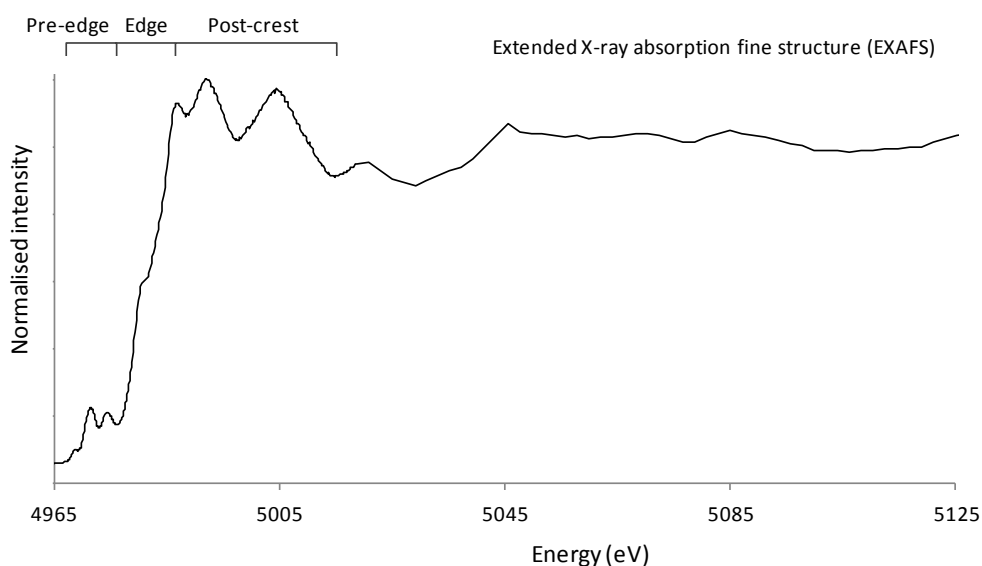


Figure 2-15 Ti K-edge spectrum collected from TiO_2 showing the XANES region with the three main regions therein marked, along with the EXAFS region.

2.5.3 X-ray Photo-Emission Electron Microscopy (XPEEM)

XPEEM images were successfully collected using the PEEM3 microscope at beamline 11.0.1 of the Advanced Light Source (ALS), Berkeley, California (USA). The ALS is a third generation synchrotron with a storage ring that is 196.8 m in circumference and that operates at a ring-energy of 1.9 GeV. XPEEM images over the Ti L-edge were captured for synthetic glasses, synthetic hibonite and meteoritic hibonite, after which Ti L-edge XAS spectra were extracted.

Synchrotron-derived X-rays from an undulator source obliquely illuminate a sample, while the monochromator is scanned in energy over the Ti L absorption edge. Photo-electrons are generated as a result of X-ray absorption processes as the energy of the incident X-ray beam reaches and exceeds the energy needed to induce a $2p \rightarrow 3d$ bound-state electronic transition in the target atom. The

resulting photo-electrons are collected under ultra high vacuum (UHV) on the order of 10^{-10} torr by a detector array within the PEEM including a phosphorescent plate and CCD camera, as shown in Figure 2-16. The photon-electron yield is projected onto a phosphor screen and the image is captured by a charge-coupled device (CCD) camera and recorded. This process is described in detail by Smith *et al.* (2004).

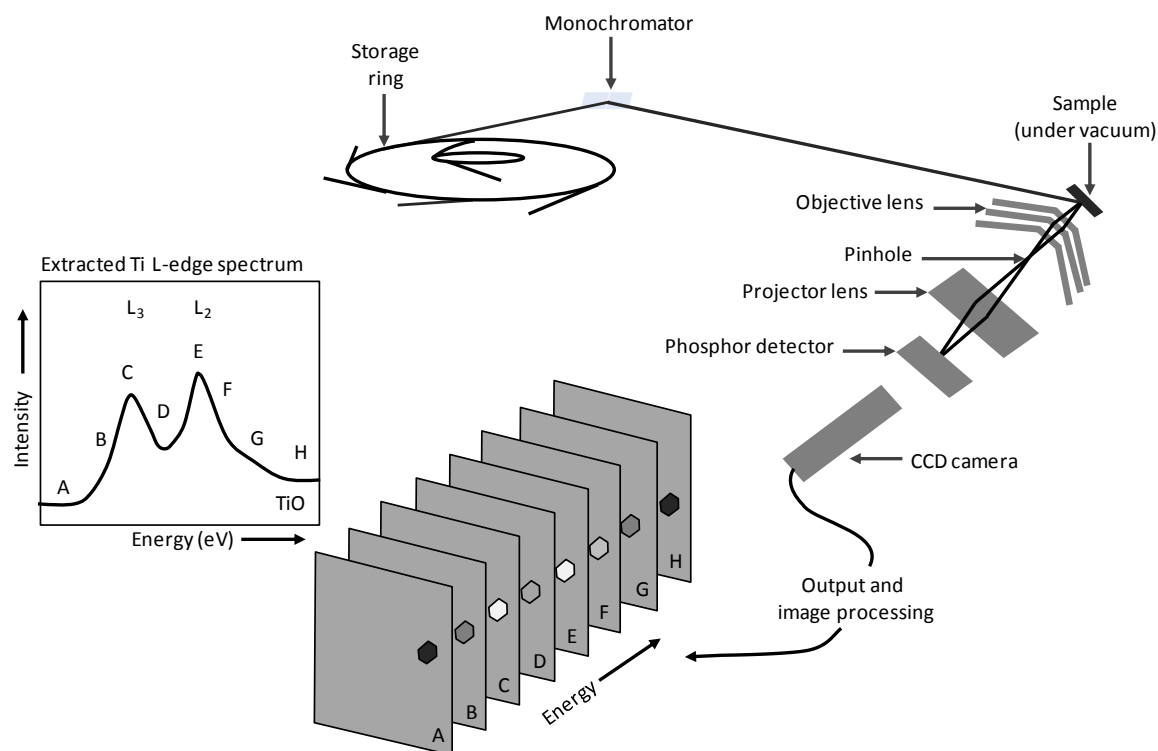


Figure 2-16 Schematic of the XPEEM image data collection and processing. X-rays from a synchrotron source obliquely illuminate a sample. The detector and image-capturing instruments are orientated 90° to the sample. An image stack and an extracted X-ray absorption spectrum are shown (after Smith *et al.*, 2004).

A shift in the absorption energy of the target element in different oxidation states occurs due to changes in the binding energy of electrons. Areas dominated by an element in different oxidation states may therefore be imaged using XPEEM, and contrast within the image due to different photo-electron yields relating to the distribution and concentration of specific elemental spacing. XPEEM images may be stacked using software such as PEEMVision (Scholl, 2010), as shown in Figure 2-16. In this way, L-edge XAS spectra may be extracted from regions 100×100 nm in size from geological samples (Smith *et al.*, 2003, 2004). The L-edge peaks are associated with $2p \rightarrow 3d$ transitions (Figure 2-17), which are allowed by dipole selection rules and are therefore more intense than the K-edge XANES pre-edge features which are also due to bound state electronic transitions (Cressey *et al.*, 1993). In addition, the core-hole lifetime of the Ti L_3 and L_2 edges (0.22 and 0.24 eV respectively; Krause and Oliver, 1979) are approximately 4 times smaller than that of the Ti K-edge (0.94 eV; Krause and Oliver, 1979). The spectral features within the L-edge XAS spectra are therefore very detailed, a characteristic useful for the determination of oxidation states of elements (Cressey *et al.*, 1993).

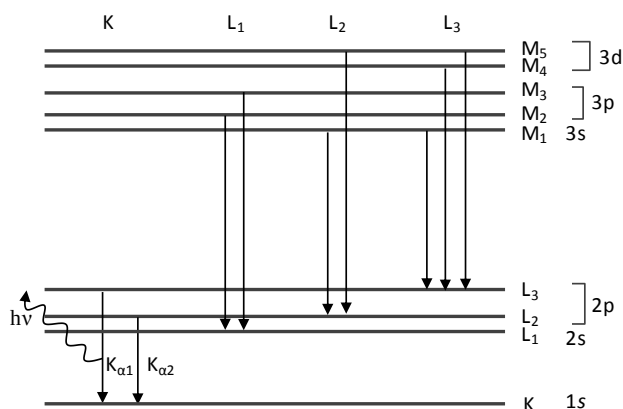


Figure 2-17 Schematic of the electronic transitions as an excited atom returns to the ground state with the emission of an X-ray photon ($h\nu$) shown for the $K_{\alpha 1}$ electronic transition. K-M electronic transitions are not shown (after Whitaker, 1999).

The complexity of an XPEEM experiment is enhanced as photo-electrons are only emitted from the top 2 - 20 nm of the sample (Frazer *et al.*, 2003) and because a consequence the analyses are made under ultrahigh vacuum (10^{-10} torr) in order to maximise photo-electron yield on the phosphorescent detector by avoiding diffraction or absorption of the photo-electrons by atmospheric molecules. Moreover, it is crucial to develop surface preparation protocols such that spectra extracted from XPEEM images reflect the oxidation state of the bulk sample. Additionally, spectroscopy using XPEEM is particularly difficult for geological samples as the samples are, in general, non-conductive. To overcome this issue, a conductive coating is therefore applied to the sample surface. This coating needs to be thick enough that the image is stable, but sufficiently thin for photo-electrons of the target atom to be transmitted through it. Surface preparation involving ion etching may introduce an additional complication if it enhances minor topography within the sample, as often encountered for geological materials with mixed mineralogy. Such topography may result in distortions in the photo-electron yield (Smith *et al.*, 2003, 2004) and subsequent degradation of the XPEEM images and the spectroscopic data. The potential benefit of increased spatial and spectral resolution associated with XPEEM, however, provides impetus to overcome any complexities associated with this technique.

3 Synthesis and Characterisation

3.1 Synopsis

Well characterised Ti^{3+} - and Ti^{4+} -bearing samples of known composition were required to better interpret spectral variations in $\text{Ti}^{3+}/\Sigma\text{Ti}$ (where $\Sigma\text{Ti} = \text{Ti}^{3+} + \text{Ti}^{4+}$) in Ti K-edge X-ray absorption near edge structure (XANES) and Ti L-edge X-ray photo-emission electron microscopy (XPEEM) data. For this purpose five Ti-bearing $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ (Ti-CMAS) glass compositions were produced over a range of 17 log units in $f\text{O}_2$ within a vertical gas-mixing furnace. In addition, a series of hibonite compositions were made to investigate Ti saturation and substitution mechanism in hibonite. Thereafter nine large-volume Ti-bearing hibonite samples were prepared, namely: Ti-rich and Ti-poor Ti^{3+} and Ti^{4+} hibonites, three mixed-valent hibonite samples ranging from 25 to 60% $\text{Ti}^{3+}/\Sigma\text{Ti}$, one sample approaching the upper limits of Ti^{3+} and Ti^{4+} saturation (respectively), and an analogue of a Ti^{3+} -rich meteoritic hibonite. X-ray powder diffraction and/or electron microprobe analysis were used to characterise the hibonite samples.

The glasses equilibrated under oxidising conditions were colourless, and with more reducing conditions the colour of the glasses deepened from light pink to purple. The Ti^{4+} hibonites were white in colour, whereas the Ti^{3+} -bearing hibonite samples were blue $\pm$ grey in colour. Of the nine large-volume hibonite samples produced, six samples were compositionally well defined and distinct from one another. The three remaining samples had TiO_2 contents lying on, or trending toward, a 1Mg:1Ti composition line.

3.2 Introduction

3.2.1 Previous oxidation state studies using glasses

Synthetic samples of set composition, produced under known temperature and oxygen fugacity ($f\text{O}_2$) conditions were reported to be “the key” to understanding V valence and $f\text{O}_2$ correlation in basaltic glasses (Sutton *et al.*, 2005). Systematic studies of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Cr}^{2+}/\text{Cr}^{3+}$ ratios in Ti-CMAS glasses were made using XANES spectroscopy by Berry *et al.* (2003) and Berry and O'Neill (2004) respectively. The compositions were based on the eutectic composition of anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) and

diopside ($\text{CaMgSi}_2\text{O}_6$) in which the element of interest was the only redox-variable ion over the $f\text{O}_2$ range investigated. Based on a suite of six Cr-doped Ti-CMAS compositions, Berry *et al.* (2006) showed $\text{Cr}^{2+}/\text{Cr}^{3+}$ ratios in glasses were also dependant on composition, with CaO- and MgO-rich compositions stabilising the more highly charged ion.

Ti-CMAS glasses with $<5\%$ $\text{Ti}^{3+}/\Sigma\text{Ti}$ were prepared by Schreiber *et al.* (1978), and the systematics of $\text{Ti}^{3+}/\text{Ti}^{4+}$ in CaO-SiO₂-TiO₂ slags with up to 40% $\text{Ti}^{3+}/\Sigma\text{Ti}$ were studied by Tranell *et al.* (2002). These studies showed that $\text{Ti}^{3+}/\text{Ti}^{4+}$ ratios were both temperature and composition dependant. This study aims to extend this knowledge by producing Ti-CMAS glasses with 0 – 100% $\text{Ti}^{3+}/\Sigma\text{Ti}$ by preparing the samples over a 17 log units in $f\text{O}_2$ range from $\Delta\text{IW}+6.5$ to $\Delta\text{IW}-10.5$ (where $\Delta\text{IW} = \log f\text{O}_{2(\text{Sample})} - \log f\text{O}_{2(\text{IW})}$). Five Ti-CMAS glass compositions were prepared in order to further investigate the compositional dependence of $\text{Ti}^{3+}/\Sigma\text{Ti}$. Understanding $\text{Ti}^{3+}/\Sigma\text{Ti}$ variation in glasses would augment our understanding of the first row transition elements and provide a framework for a spectroscopic study of $\text{Ti}^{3+}/\Sigma\text{Ti}$ in hibonite.

3.2.2 Previous hibonite studies

Hibonite (ideally $\text{CaAl}_{12}\text{O}_{19}$) has been previously synthesised to gain a better understanding of cosmochemical processes (e.g. Geiger *et al.*, 1988, Hofmeister *et al.*, 2004). Single hibonite crystals have been grown by heating mixtures of $\text{Al}_2\text{O}_3 + \text{CaAl}_4\text{O}_7$, or $\text{Al}_2\text{O}_3 + \text{CaO}$ using a laser (Hofmeister *et al.*, 2004) or by using a solvent and seed-crystal method (Utsunomiya *et al.*, 1988). Numerous syntheses at 1100 – 1300 °C have been developed by the ceramics industry (e.g. Callender and Barron, 2000; Singh *et al.*, 2002; Altay *et al.*, 2009). Hibonite has, however, most often been produced by sintering elemental oxides in stoichiometric proportions at temperatures ranging from 1300 to 1750 °C (e.g. Geiger *et al.*, 1988; Domínguez *et al.*, 2001; Du and Stebbins, 2004). In addition, syntheses have been attempted by sintering elemental oxides at high pressure (Geiger *et al.*, 1988) and under a range of $f\text{O}_2$ conditions with transition metal-doped elemental oxides (Ihinger and Stolper, 1986; Holtstam, 1996). Ti-bearing synthetic hibonites formed under reducing conditions were blue in colour, whereas those produced under oxidising conditions were colourless to orange in colour, and the colour change was correlated with the oxidation state of Ti (Ihinger and Stolper, 1986).

The highest recorded TiO₂ content in terrestrial and meteoritic hibonite is 9.7 and 8.7 wt% TiO₂ respectively (Rakotondrazafy *et al.*, 1996; Ireland, 1990). Up to 23% of the total Ti in a meteoritic hibonite was present as Ti^{3+} , which is calculated to be 1.1 wt% Ti₂O₃ (Beckett *et al.*, 1996).

The current study sought to investigate the Ti^{3+} and Ti^{4+} saturation level in hibonite, and thereafter produce Ti^{3+} , Ti^{4+} and mixed-valent hibonites in order to study the systematics of $\text{Ti}^{3+}/\text{Ti}^{4+}$ in hibonite using X-ray absorption spectroscopy. The samples were powdered and then structurally characterised by X-ray diffraction (XRD) and neutron powder diffraction (NPD), as will be discussed in this chapter and Chapter 5.

3.3 Methodology and experimental techniques

3.3.1 Sample synthesis

3.3.1.1 Ti-bearing glasses

Five Ti-CMAS compositions (Table 3-1) were selected in which Ti was the only redox variable element over the range of fO_2 s investigated. The compositions are based on the eutectic composition of anorthite and diopside (AD). To investigate the effect of composition on $Ti^{3+}/\Sigma Ti$, the maximum amount of enstatite ($MgSiO_3$), forsterite (Mg_2SiO_4), quartz (SiO_2) and wollastonite ($CaSiO_3$) soluble at 1400 °C were added (e.g. Berry and O'Neill, 2004).

Table 3-1 The ideal composition of the Ti-CMAS glass series and the calculated optical basicity

Series	Composition	SiO ₂	Al ₂ O ₃	CaO	MgO	Calculated optical basicity
AD	100% AD	49.83	15.24	23.25	10.68	0.596
AD+En	60% AD + 40% En (Enstatite, $MgSiO_3$)	53.60	9.14	13.95	22.31	0.581
AD+Fo	85% AD + 15% Fo (Forsterite, Mg_2SiO_4)	48.70	12.95	19.76	17.59	0.596
AD+Qtz	60% AD + 40% Qtz (Quartz, SiO_2)	69.50	9.14	13.95	6.41	0.547
AD+Wo	40% AD + 60% Wo (Wollastonite, $CaSiO_3$)	50.65	6.10	37.98	4.27	0.624

Note: AD = 42% Anorthite ($CaAl_2Si_2O_8$) + 58% Diopside ($CaMgSi_2O_6$). The 100 wt% total includes 1 wt% TiO_2

Ti-bearing glasses were prepared for three experiments as follows: 1) five Ti-CMAS compositions were prepared over 17 log units in fO_2 for XANES analysis; 2) AD+Fo glasses were prepared under five fO_2 conditions over 13 log units in fO_2 for XPEEM analysis; and 3) AD glasses were prepared over 17 log units in fO_2 for electron paramagnetic resonance (EPR) analysis.

Pre-dried SpecPure and technical grade elemental oxide powders (Appendix B.1.1) were weighed in stoichiometric ratios and ground by hand under acetone in a 132 mm diameter agate mortar, with 5 – 7 repeat grinds per composition. The respective powders were made into a slurry with hydrated polyethylene oxide (20% powder:80% H_2O) and attached to Pt loops (for $\geq \Delta IW-2.5$) or Re loops (for $\Delta IW+0.1$ to $\Delta IW-4.5$). The loaded loops were attached to either a Pt chandelier ($\geq \Delta IW-2.5$) or a ceramic chandelier ($\Delta IW-2.5$ to $\Delta IW-4.5$) with up to five compositions $\pm$ a Fe-loop sample (Chapter 2) mounted at a time. Samples to be prepared at $\leq \Delta IW-6.5$ were pressed into pellets and mounted in graphite holders. Mixtures of CO-CO₂ and CO-Ar were used to control the fO_2 ($\Delta IW+6.5$ to $\Delta IW-10.5$) in the vertical gas-mixing furnace, as detailed in Appendix A.2. In general the glasses were equilibrated at temperature (1404 ± 1 °C) for ~20 hours. The XANES and EPR samples were quenched into water, whereas the XPEEM samples were quenched at the bottom of the furnace in order to produce non-fractured samples from which a smooth polished surface may be prepared. The synthesis details for these experiments are tabulated in Appendix B.1.2.

3.3.1.2 Ti-bearing hibonite

Five to eight grams of pre-dried SpecPure and technical grade oxide powders (Appendix B.1.1) were ground by hand under acetone in an agate mortar, with 5-7 repetitions per composition (Table 3-2). Hibonite compositions were prepared for both Ti saturation experiments and for analysis by NPD. The latter required the preparation of large sample volumes ($>2 \text{ cm}^3$).

3.3.1.2.1 Saturation series experiments

In order to determine the appropriate stoichiometry for a series of Ti^{3+} , Ti^{4+} and mixed-valent hibonites, a series of hibonite samples were produced with a range in Ti contents. This saturation series was prepared for both Ti^{3+} and Ti^{4+} hibonite, having up to 14 and 28 wt% TiO_2 respectively.

There are five sites onto which Ti may substitute: one trigonal bipyramidal site (M2), one tetrahedral site (M3) and three octahedral sites (M1, M4, M5), the site multiplicity of which may be summarised as $^{[12]}\text{Ca}^{[6]}\text{M1}^{[5]}\text{M2}^{[4]}\text{M3}_2^{[6]}\text{M4}_2^{[6]}\text{M5}_6\text{O}_{19}$ (where the multiplicity is given by the subscript and coordination number in parentheses; after Bermanec *et al.*, 1996). Ti^{3+} may substitute directly for Al^{3+} , whereas Ti^{4+} undergoes a coupled substitution with Mg^{2+} in order to maintain charge balance (Allen *et al.*, 1978). The saturation series was based on the preferred site occupancy published at the time: Ti^{3+} on the M2 site (Beckett *et al.*, 1988) and Ti^{4+} on the M4 site (Bermanec *et al.*, 1996).

The following compositions were prepared for the Ti-saturation series: a 0Ti-hibonite ($\text{CaAl}_{12}\text{O}_{19}$), five Ti^{3+} -bearing hibonite compositions ($\text{CaAl}_{12-x}\text{Ti}_x\text{O}_{19}$, where $x < 1.25$ Ti per formula unit (pfu)) and five Ti^{4+} -bearing hibonite compositions ($\text{CaAl}_{12-2x}\text{Ti}_x\text{Mg}_x\text{O}_{19}$, $x < 2.50$ Ti pfu). The compositions are detailed in Table 3-2. The sample nomenclature used is a combination of the mixture number (Hib#) and the ratio of Ti:Mg cations ($\times 100$), or the ideal cation ratio in the case of the saturation series compositions.

The powders were pressed into 4 mm diameter pellets using a SPECAC press. The Ti^{4+} hibonite compositions were suspended in a CO-CO₂ vertical gas-mixing furnace in Pt baskets hanging from a Pt chandelier. The Ti^{3+} -bearing hibonite compositions were mounted in a 6-pellet graphite holder.

A summary of the experiments are shown in Table 3-2 and detailed in Appendix B.1.2. Most of the samples were sintered at $1404 \pm 2^\circ\text{C}$. This was within the temperature range in which hibonite was modelled to be stable within a nebular gas ($1372\text{--}1468^\circ\text{C}$, Yoneda and Grossman, 1995) and well below the experimentally determined incongruent melting temperature of hibonite ($1850 \pm 10^\circ\text{C}$ in the $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ system; De Aza *et al.*, 2000; Vázquez *et al.*, 2003). Different temperature and $f\text{O}_2$ conditions were tested for 0Ti and Ti-rich hibonite compositions in order to investigate if changing the synthesis procedures returned samples of different chemistry. For example, the product of one experiment was quenched in water, rather than in air, and other samples were powdered and re-sintered – up to four times for a Ti^{4+} saturation series experiment.

Table 3-2 The ideal stoichiometry of the synthetic hibonite samples and a summary of the synthesis experiments

Series	Composition based on ideal-site saturation	Ideal Stoichiometry (where Ca _{1.00} and O _{19.00})	Ideal %Ti ³⁺ /ΣTi [‡]	Hibonite mixture	Run numbers *	Sample Nomenclature*
OTi hibonite	N/A	CaAl _{12.00} O ₁₉	N/A	Hib1, HibA	B19/04/08; IC12/3/09 (air), IC23/3/09 (air); IC27/3/09 (air), IC24/7/09 IC4/8/09; IC7/8/09 (2-sinter, ΔIW+6.5); IC14/9/09 (ΔIW+6.6; 1300 °C) IC31/8/09 (ΔIW-6.5); IC12/9/09 (ΔIW-2.5)	Hib1(0), HibA(0)
Ti ⁴⁺ hibonite	25%SatM4	CaAl _{11.00} Ti _{0.50} Mg _{0.50} O ₁₉	0	Hib9	IC12/3/09 (air), IC23/3/09 (air); IC27/3/09 (air), IC24/7/09; IC12/8/09 (1 st sinter); IC27/8/09 (2 nd sinter)	Hib9(44,43)
	50%SatM4	CaAl _{10.00} Ti _{1.00} Mg _{1.00} O ₁₉	0	Hib4; HibB, HibE	B19/04/08; IC12/3/09 (air), IC23/3/09 (air); IC27/3/09 (air), IC24/7/09; IC9/8/09; IC24/8/09 (1 st sinter); IC1/9/09 (2 nd sinter)	HibE(98,91)
	75%SatM4	CaAl _{9.00} Ti _{1.50} Mg _{1.50} O ₁₉	0	Hib10	IC12/3/09 (air), IC23/3/09 (air); IC27/3/09 (air), IC24/7/09; IC14/9/09 (ΔIW+6.6; 1300 °C)	Hib10(150x2)
	Sat M4 (2Ti pfu)	CaAl _{8.00} Ti _{2.00} Mg _{2.00} O ₁₉	0	Hib3	B19/04/08; IC12/3/09 (air), IC23/3/09 (air); IC27/3/09 (air), IC24/7/09	Hib3(200x2)
	125% Sat M4	CaAl _{7.00} Ti _{2.50} Mg _{2.50} O ₁₉	0	Hib11	IC12/3/09 (air), IC23/3/09 (air); IC27/3/09 (air), IC24/7/09	Hib11(250x2)
Ti ³⁺ hibonite	25%SatM2	CaAl _{11.75} Ti _{0.25} O ₁₉	100	HibF	IC31/8/09; IC29/8/09	HibF(20,0)
	50%Sat M2	CaAl _{11.50} Ti _{0.50} O ₁₉	100	Hib5, HibD	B15/04/08; IC16/8/09, IC21/8/09 and IC23/8/09 (combined)	Hib5D(33,0)
	75% Sat M2	CaAl _{11.25} Ti _{0.75} O ₁₉	100	HibG	IC31/8/09; IC12/9/09 (ΔIW-2.5); IC16/9/09 (ΔIW-7.4; 1300 °C)	HibG(75,0)
	Sat M2 (1Ti pfu)	CaAl _{11.00} Ti _{1.00} O ₁₉	100	Hib7	B15/04/08; IC14/8/09; IC12/9/09 (ΔIW-2.5); IC19/9/09 (ΔIW-7.4; 1300 °C)	Hib7(100,0)
	125% Sat M2	CaAl _{10.75} Ti _{1.25} O ₁₉	100	HibH	IC31/8/09	HibH(125,0)
Mixed-valent hibonite	25%SatM2;75%SatM4	CaAl _{10.37} Ti _{0.88} Mg _{0.75} O ₁₉	14.7	HibJ	IC31/8/09; IC7/9/09	HibJ(82,60)
	50%SatM2;50%SatM4	CaAl _{10.75} Ti _{0.75} Mg _{0.50} O ₁₉	33.3	Hib8, HibC	B15/04/08; IC31/7/09 (1 st sinter) IC1/8/09(2nd sinter), IC13/8/09 and IC18/8/09 (combined)	Hib8C(73,49)
	75%SatM2;25%SatM4	CaAl _{11.12} Ti _{0.63} Mg _{0.25} O ₁₉	59.7	HibK	IC31/8/09; IC3/9/09	HibK(62,24)
	60%SatM2;45%SatM4	CaAl _{9.60} Ti _{1.50} Mg _{0.90} O ₁₉	40.0	HibT	IC6/9/09	HibT(137,83)
	10-43 Natural analogue 7%SatTi ³⁺ 48%SatTi ⁴⁺	CaAl _{10.97} Ti _{0.55} Mg _{0.48} O ₁₉	12.7	HibN	IC9/9/09	HibN(46,40)

Notes: On average samples were at temperature for 33 hours, although individual experiment periods ranged between 12 and 71 hours. See Appendix B.1 for detail. Unless otherwise stated, the Ti³⁺-bearing samples were produced at ΔIW-6.5, and the Ti⁴⁺ hibonite samples at ΔIW+6.5. *f*O₂ of “air” sinter calculated to be ΔIW+8.8. Hib5, HibD, Hib8 and HibC were mounted in small graphite mounts, the compositions compared by XRD analysis, and then combined. All other samples prepared at ΔIW-6.5 were prepared in a large graphite mount.

‡ “Ideal %Ti³⁺/ΣTi”=100Ti³⁺/(Ti³⁺+Ti⁴⁺), where Ti⁴⁺ was calculated using 1Ti⁴⁺:1Mg²⁺, with the remaining Ti cations = Ti³⁺.

* The sample nomenclature used is a combination of the mixture number (Hib#) and the ratio of Ti:Mg cations (x100). The ratio detailed is either the ideal cation ratio (for the saturation series compositions), or that determined by SEM (for the large-volume samples). Unless specified in the text (Chapter 3), the samples reported in this study were produced in the large-volume sinters (in **bold**).

3.3.1.2.2 Large-volume sample preparation

Two hibonite compositions were produced for both Ti^{3+} and Ti^{4+} : one Ti-rich and the other Ti-poor (Table 3-3). The Ti-rich compositions ideally have 0.5 Ti^{3+} pfu and 1 Ti^{4+} pfu, with these Ti pfu contents based upon the results of the saturation series experiments. Mixed-valent hibonite stoichiometries having 15%, 33% and 60% $\text{Ti}^{3+}/\Sigma\text{Ti}$ were then prepared. In addition, the composition of a Ti^{3+} -rich meteoritic hibonite (CAI#10-43) on loan for this study (12.7% $\text{Ti}^{3+}/\Sigma\text{Ti}$) and a >1 Ti per formula unit (pfu) hibonite (40% $\text{Ti}^{3+}/\Sigma\text{Ti}$) were produced. The latter was modelled such that the number of Ti^{3+} and Ti^{4+} cations were just below the upper limit of Ti-saturation of the respective sites, with the ideal composition having 0.60 Ti^{3+} and 0.9 Ti^{4+} pfu.

Table 3-3 Stoichiometric mixtures for the large-volume hibonite sample series

Series	Sample name	Ideal wt%				
		CaO	Al_2O_3	TiO_2	MgO	Total
Ti^{3+} hibonite	HibF(20,0)	8.36	89.26	2.98	N/A	100.60
	Hib5D(33,0)	8.27	86.43	5.89	N/A	100.59
Mixed-valent hibonite	HibK(62,24)	8.25	83.37	7.34	1.48	100.44
	Hib8C(73,49)	8.22	80.34	8.78	2.95	100.29
	HibJ(80,62)	8.20	77.31	4.42	10.22	100.15
	HibT(137,83)	8.00	69.82	17.09	5.17	100.09
	HibN(46,40)	8.27	82.49	6.45	2.86	100.07
Ti^{4+} hibonite	Hib9(44,43)	8.29	82.84	5.90	2.98	100.00
	HibE(98,91)	8.18	74.31	11.64	5.87	100.00

Note: See Table 3-2 for the ideal stoichiometry and % Ti^{3+} , and see Appendix B.2.1 for the ideal elemental wt%.

The powders were pressed into either 4 mm or 13 mm diameter pellets using a SPECAC press. Ti^{4+} hibonite compositions were suspended in a vertical gas-mixing furnace in a Pt crucible and the Ti^{3+} -bearing hibonite compositions were mounted in either a 6-pellet graphite mount or a specially designed large-volume graphite holder which could accommodate up to 3.6 cm³ sized pellets.

The Ti^{4+} hibonite samples were twice-sintered in CO_2 ($\Delta\text{IW}+6.5$), and the Ti^{3+} -bearing compositions were sintered in CO ($\Delta\text{IW}-6.5$). The samples were prepared at 1404 ± 2 °C and were, on average, at temperature for 36 hours. Individual sinters ranging between 12 and 71 hours, as detailed in Appendix B.1.2. The samples were extracted from the furnace when it reached ~ 600 °C, which was approximately two hours after ending the experimental conditions.

3.3.2 Sample characterisation and instrumental parameters

3.3.2.1 Ti-bearing glasses

The glass samples were mounted in epoxy resin for electron microscopy and spectroscopic analysis. The products of two experiments were laid parallel to one another in a rectangular epoxy mount for XANES analysis. AD+Fo glasses for XPEEM analysis were stuck to carbon tape within an 8 x 8 mm square in the centre of an Al-disk and set in epoxy. Fragments of the EPR sample series

were mounted in a circular epoxy mount. The epoxy resin discs were prepared, polished and coated with 15 nm carbon.

Chemical compositions were determined for the XANES and XPEEM samples using the Jeol 5900LV EDS SEM at the Natural History Museum (NHM). Analyses were made in high vacuum (HV) mode (20 kV, 2 nA, working distance 10 mm) using the following standards: Ca on CaSiO₃ (WOL), Al on Al₂O₃ (COR), Ti on TiO₂ (RUT), Mg on Mg₂SiO₄ (FOR), Si on Mg_{1.6}Fe_{0.4}SiO₄ (EAG), S on ZnS (ZNS). Further analyses were obtained using the Cameca SX100 WD EMP at the NHM (20 keV, 20 nA), with counting times of 15 s for all elements apart from Ca (20 s) and Fe (60 s). The analysing crystals employed were: Ca on PET (Sp1), Mg, Al and Si on LTAP (Sp2), Ti, Cr and S on LPET (Sp3), Fe on LLIF (Sp5), and the calibration made using: Mg on Mg₂SiO₄ (FOR), Al on Al₂O₃ (COR4), Si and Ca on CaSiO₃ (WOL4), S on BaSO₄ (BAR2), Ti on TiO₂ (RUT), Fe on Fe₂SiO₄ (FAY), and Cr on FeCr₂O₄ (CRO2). After identifying the presence of S within samples prepared at $\Delta IW < 6.5$, an X-ray fluorescence scan over the S K-edge showed that the S occurs as S²⁻ in these samples. The XANES glasses prepared at these fO_2 s were re-analysed by WDS EMP, along with the EPR samples. The following protocol was used on the Cameca SX100 WD EMP at the NHM (20 keV, 20 nA): Ca on PET (Sp1), Mg, Al and Si on LTAP (Sp2), Ti, Cr and S on LPET (Sp3), Fe on LLIF (Sp5). The calibrations were made using: Mg on Mg₂SiO₄ (FOR), Al on Al₂O₃ (COR2), Ca on CaSiO₃ (WOL4), S on ZnS (ZNS2), Ti on TiO₂ (RUT), Si and Fe on Fe₂SiO₄ (FAY), with counting times: Mg, Al, Si and S (20 s), Ca and Ti (20 s) and Fe (60 s).

Representative lower limits of detection for the microprobes are detailed in Appendix B.2.1. Matrix corrections to account for density, atomic number, absorbance and secondary fluorescence were made for EDS SEM analyses using the XPP routine and for the WDS EMP analyses using the PAP routine (Oxford Instruments). The results are shown in Tables 3-4 to 3-8.

EPR spectra were recorded in order to confirm the presence of Ti³⁺. In preparation for this analysis up to four glass beads from each fO_2 in the EPR sample series were ground to a homogenous grain size under acetone in an agate pestle and mortar. EPR measurements were made by A Burnham on a Bruker EPR spectrometer using the following operating conditions: 9.5 GHz X-band, 2600-4400 G field, 20 dB, 20 ms time constant and 40 ms conversion times. Details regarding the scan sequence are provided in Appendix B.2.2. As far as possible constant sample weights were used. Spectra represent the first derivative of the absorption, as described in a review by Beckett *et al.* (1988). No background correction was made as the signal intensity between 3400 and 3550 G for the sample produced at $\Delta IW + 6.5$ (intensity of 8730) was less than the standard deviations on the peak intensities of other analyses at 3438 G. The average peak intensity data are shown in Figure 3-4 and tabulated in Appendix B.2.2.

Ratios of redox variable elements show a dependence on composition (e.g. Schreiber *et al.*, 1978). Optical basicity is a useful composition-index for such studies, with Fe²⁺/Fe³⁺ and Cr²⁺/Cr³⁺ ratios being correlated with calculated optical basicity (Duffy, 1993; Berry *et al.*, 2006). Optical

basicity is quantitatively related to electronegativity and may simplistically be considered to be a measure of the electron density round the O in a metal-oxide pair (Duffy, 1993). The concentration of electrons round the oxygen atom in basic compositions stabilises the higher charged ion in a redox pair to lower fO_2 s (see Berry *et al.*, 2006).

Optical basicity of individual oxides within element-doped Tl^+ - or Pb^{2+} -bearing glasses were experimentally determined by Duffy (1993) using optical spectroscopy. From these values theoretical optical basicity (Λ) values of a melt composition may be calculated (Equation 3-1). The theoretical optical basicity of the glass samples were accordingly calculated, the results of which are shown in Table 3-6.

$$\Lambda_{comp} = \frac{1(prop\ MgO)\ \Lambda_{MgO}}{\#O} + \frac{1(prop\ CaO)\ \Lambda_{CaO}}{\#O} + \frac{2(prop\ SiO_2)\ \Lambda_{SiO_2}}{\#O} + \frac{1(prop\ Al_2O_3)\ \Lambda_{Al_2O_3}}{\#O} \quad \text{Equation 3-1 (after Duffy, 1993)}$$

Where:

$$prop\ oxide = \frac{wt\% \ oxide}{100}$$

Λ_{oxide} = Oxide optical basicity (values from Duffy, 1993)

$$\#O = 1(prop\ MgO) + 1(prop\ CaO) + 2(prop\ SiO_2) + 3(prop\ Al_2O_3)$$

3.3.2.2 Ti-bearing hibonite

The sintered pellets were broken into fragments with a metal hammer, crushed using a SPECAC press and then powdered under acetone in a 132 mm hand-held agate pestle and mortar. Where possible, a few small chips were preserved for microprobe analysis.

Powder XRD data were collected using an Inel curved position sensitive detector (PSD), with the X-ray tube operating at 35 mA and 40 kV. A Ge(111) monochromator was used to select Cu $K\alpha$ radiation. The beam was constrained to be 0.14 mm high and 5 mm wide by the vertical and horizontal slits (respectively). The powdered sample was mounted on a quartz substrate and the stage tilted $\sim 4^\circ$ with respect to the incident beam. During data collection the stage rotated parallel to the sample surface. NIST Si powder (SRM640) and Ag-Behenate ($C_{22}H_{43}AgO_2$) were used as an external 2θ calibration, and the 2θ linearization was made using a least squares cubic spline function. Phase identification was made using STOE Win XPOW (v2.08) interfaced with the Joint Committee on Powder Diffraction Standards (JCPDS) database of the International Centre for Diffraction Data (ICDD).

The pellet-chips were mounted in epoxy, coated with ~ 15 nm carbon and analysed by the Jeol 5900LV EDS SEM at the NHM in HV mode. Due to the small grain size and platy nature of the samples ($< 2 \times 5 \times 14\ \mu m$), the instrument was calibrated at 10 kV (2 nA) to excite a smaller volume close to the sample surface. The standards were calibrated to the respective K-lines of: Ca on $CaSiO_3$ (WOL), Al on Al_2O_3 (COR), Ti on TiO_2 (RUT), Mg and Si on $Mg_{1.6}Fe_{0.4}SiO_4$ (EAG), and Na (at 20 kV) on $NaAlSi_2O_6$ (JAD). Matrix corrections were made using the XPP routine (Oxford Instruments). Follow-up analyses were made on the SX100 Cameca WDS EMP analysis at NHM (10 keV, 20 nA).

Data reported herein were calibrated as follows: Na on NaAlSi₂O₆ (JAD, LTAP, Sp2, 10 s), and Si on Mg₂SiO₄ (FOR, TAP, Sp4, 20 s). The average compositions are detailed in Table 3-9, and the individual analyses are contained in Appendix B.2.1.

3.4 Results

3.4.1 Ti-bearing synthetic glass

3.4.1.1 XANES sample series

The glasses equilibrated at $\Delta IW+6.5$ were colourless. A light pink hue was detected for samples equilibrated at $\Delta IW+0.1$, with the colour deepening to pinky-purple as the conditions became more reducing. Distributed throughout AD+Qtz were $<30\ \mu\text{m}$ sub- to euhedral crystals of quartz (7 ± 1 modal%). Forsterite (Fo) crystals (MgSi₂O₄) with sub- to euhedral hexagonal form ($<30\ \mu\text{m}$) and containing $<0.07\ \text{wt}\%$ TiO₂ (see note in Table 3-5) were noted on the edges of some AD+En samples (4 ± 2 modal%).

The bulk compositions of the glasses prepared for XANES analysis were akin the composition of the ideal mixture, apart from AD+Qtz (Table 3-6). The samples were homogeneous apart from rare patches of slightly different composition in some AD and AD+Fo samples. These patches were $<250\ \mu\text{m}$ and normally adjacent to fractures or the sample rim, and they did not affect the bulk composition. The precipitation of quartz resulted in $\sim 5\ \text{wt}\%$ less SiO₂ in AD+Qtz than the ideal mixture. The TiO₂ content of the AD, AD+Wo and AD+Fo glasses were $1.03\ \text{wt}\%$, and for the AD+En and AD+Qtz glasses crystal precipitation raised the TiO₂ content to 1.06 and $1.12\ \text{wt}\%$ TiO₂ respectively.

The glasses mounted on Pt at $\Delta IW-1.5$ and $\Delta IW-2.5$ were TiO₂-poor (Table 3-4). This is in agreement with the study by Jurewicz *et al.* (1995) which showed that Ti solubility in Pt metal is fO_2 dependant, with Ti becoming soluble below $\Delta IW-1.5$ at $1404\ ^\circ\text{C}$ ($\log fO_2-10.9$). An equivalent set of glass compositions were mounted on Re and prepared under the same conditions, and the TiO₂ contents of these glasses were as expected (Table 3-4) and they were therefore used for the spectroscopic study.

Table 3-4 TiO₂ contents in the AD glass composition as a function of mount and fO_2 conditions

fO_2	Mount	Run number (ICdate)	wt% TiO ₂
$\Delta IW+0.1$	Pt	IC21/1/11	1.02 (0.01)
	Re	IC21/1/11	1.03 (0.01)
$\Delta IW-1.5$	Pt	IC11/8/09	0.8 (0.1)
	Re	IC15/2/10	1.02 (0.02)
$\Delta IW-2.5$	Pt	IC25/8/09	0.6 (0.1)
	Re	IC17/2/10	1.03 (0.02)

Note: The 2009 experimental products were analysed by EDS SEM, whereas the 2010 and 2011 experimental products were analysed by WDS EMP (standard deviation in parentheses). Further composition detail in Appendix B.2.1.2.

Table 3-5 Compositions of the five suites of Ti-CMAS glasses prepared over a range of fO_2 conditions, constituting the XANES sample series

ΔIW	Sample	SiO ₂	Al ₂ O ₃	CaO	MgO	TiO ₂	S	FeO	Total	#
+6.5	AD	49.72 (0.30)	15.66 (0.05)	23.03 (0.13)	10.79 (0.03)	1.04 (0.02)	<lld	<lld	100.24 (0.41)	12
	AD+En †	53.23 (0.48)	9.66 (0.02)	14.26 (0.11)	21.77 (0.07)	1.08 (0.02)	<lld	<lld	100.01 (0.63)	12
	AD+Fo	48.63 (0.47)	13.29 (0.06)	19.62 (0.12)	17.68 (0.11)	1.04 (0.02)	<lld	<lld	100.27 (0.66)	14
	AD+Qtz ‡	66.13 (0.60)	10.07 (0.08)	15.15 (0.08)	6.96 (0.05)	1.11 (0.02)	<lld	<lld	99.45 (0.70)	11
	AD+Wo	51.40 (0.37)	6.29 (0.03)	36.86 (0.11)	4.24 (0.03)	1.02 (0.02)	<lld	<lld	99.83 (0.47)	13
+0.1	AD	49.87 (0.21)	15.29 (0.07)	23.36 (0.11)	10.57 (0.06)	1.04 (0.02)	<lld	<lld	100.16 (0.28)	15
	AD+En	54.82 (0.34)	9.37 (0.08)	14.08 (0.04)	22.16 (0.09)	1.04 (0.02)	<lld	<lld	101.49 (0.44)	10
	AD+Fo	49.34 (0.25)	13.17 (0.07)	19.83 (0.09)	17.63 (0.07)	1.04 (0.02)	<lld	<lld	101.03 (0.34)	11
	AD+Qtz ‡	65.44 (0.42)	9.91 (0.08)	15.39 (0.09)	6.95 (0.05)	1.12 (0.02)	<lld	<lld	98.84 (0.54)	12
	AD+Wo	51.84 (0.34)	6.19 (0.08)	37.62 (0.16)	4.27 (0.04)	1.00 (0.02)	<lld	<lld	100.95 (0.44)	11
-1.5	AD	49.02 (0.22)	15.33 (0.05)	22.71 (0.14)	10.56 (0.04)	1.03 (0.02)	<lld	<lld	98.68 (0.33)	9
	AD+En	52.93 (0.49)	9.41 (0.10)	13.67 (0.07)	21.99 (0.12)	1.05 (0.02)	<lld	<lld	99.08 (0.69)	9
	AD+Fo	48.10 (0.61)	13.20 (0.10)	19.24 (0.12)	17.46 (0.13)	1.03 (0.02)	<lld	<lld	99.07 (0.91)	9
	AD+Qtz ‡	65.18 (0.17)	9.96 (0.07)	15.44 (0.07)	6.92 (0.04)	1.13 (0.02)	<lld	<lld	98.66 (0.27)	14
	AD+Wo	51.42 (0.35)	6.20 (0.03)	36.91 (0.17)	4.22 (0.02)	1.03 (0.02)	<lld	<lld	99.82 (0.49)	12
-2.5	AD	50.51 (0.15)	15.27 (0.07)	23.27 (0.07)	10.53 (0.05)	1.02 (0.02)	<lld	0.05 (0.00)	100.64 (0.28)	12
	AD+En †	54.41 (0.21)	9.26 (0.05)	14.14 (0.08)	21.96 (0.08)	1.03 (0.02)	<lld	<lld	100.86 (0.36)	12
	AD+Fo	49.63 (0.19)	13.06 (0.09)	19.93 (0.08)	17.44 (0.04)	1.03 (0.01)	<lld	0.05 (0.01)	101.15 (0.29)	12
	AD+Qtz ‡	65.73 (0.15)	10.10 (0.06)	15.47 (0.07)	7.03 (0.03)	1.15 (0.02)	<lld	0.06 (0.01)	99.54 (0.24)	12
	AD+Wo	51.07 (0.53)	6.16 (0.08)	37.58 (0.21)	4.25 (0.04)	1.00 (0.03)	<lld	0.04 (0.00)	100.11 (0.80)	16
-3.5	AD	50.16 (0.30)	15.25 (0.13)	23.09 (0.08)	10.54 (0.07)	1.02 (0.02)	<lld	0.45 (0.01)	100.52 (0.46)	9
	AD+En	54.35 (0.15)	9.33 (0.04)	14.15 (0.05)	21.58 (0.06)	1.05 (0.02)	<lld	0.43 (0.01)	100.89 (0.25)	10
	AD+Fo	49.31 (0.22)	13.10 (0.08)	19.73 (0.07)	17.36 (0.05)	1.03 (0.02)	<lld	0.28 (0.01)	100.81 (0.32)	9
	AD+Qtz ‡	66.20 (0.14)	9.71 (0.05)	14.88 (0.08)	6.83 (0.05)	1.09 (0.02)	<lld	0.28 (0.01)	98.99 (0.13)	7
	AD+Wo	51.79 (0.18)	6.18 (0.03)	37.14 (0.14)	4.24 (0.02)	1.02 (0.01)	<lld	0.28 (0.01)	100.64 (0.25)	10
-4	AD	50.21 (0.28)	15.36 (0.10)	23.25 (0.09)	10.57 (0.09)	1.03 (0.01)	<lld	0.25 (0.01)	100.67 (0.46)	12
	AD+En †	54.30 (0.27)	9.41 (0.05)	14.22 (0.05)	21.81 (0.06)	1.05 (0.02)	<lld	0.31 (0.01)	101.11 (0.31)	20
	AD+Fo	49.59 (0.19)	13.04 (0.10)	19.72 (0.16)	17.25 (0.07)	1.03 (0.02)	<lld	0.26 (0.01)	100.91 (0.30)	13
	AD+Qtz ‡	65.58 (0.14)	9.67 (0.06)	14.85 (0.09)	6.84 (0.04)	1.10 (0.02)	<lld	0.49 (0.03)	98.54 (0.23)	12
	AD+Wo	51.84 (0.19)	6.20 (0.02)	37.03 (0.14)	4.24 (0.02)	1.02 (0.02)	<lld	0.39 (0.01)	100.73 (0.23)	13
-4.5	AD	50.64 (0.09)	15.46 (0.06)	23.08 (0.12)	10.48 (0.05)	1.02 (0.01)	<lld	0.19 (0.01)	100.87 (0.18)	9
	AD+En †	54.06 (0.77)	9.53 (0.05)	14.18 (0.11)	21.95 (0.08)	1.06 (0.02)	<lld	0.22 (0.01)	100.99 (0.93)	28
	AD+Fo	50.03 (0.13)	13.16 (0.05)	19.65 (0.08)	17.13 (0.05)	1.05 (0.02)	<lld	0.23 (0.01)	101.26 (0.23)	13
	AD+Qtz ‡	66.24 (0.28)	9.77 (0.03)	14.91 (0.06)	6.90 (0.06)	1.12 (0.02)	<lld	0.29 (0.01)	99.24 (0.26)	9
	AD+Wo	52.29 (0.34)	6.26 (0.08)	37.23 (0.06)	4.34 (0.03)	1.01 (0.02)	<lld	0.18 (0.01)	101.31 (0.47)	13

Continued...

Table 3-5 continued...

ΔIW	Sample	SiO_2		Al_2O_3		CaO		MgO		TiO_2		S		FeO	Total		Less O equiv of S		Corrected total		#
-6.5	AD	49.43	(0.47)	15.50	(0.16)	23.63	(0.06)	10.54	(0.05)	1.04	(0.01)	0.05	(0.01)	<lld	100.20	(0.68)	0.02	(0.01)	100.18	(0.68)	9
	AD+En †	53.76	(0.55)	9.89	(0.13)	14.86	(0.11)	20.97	(0.21)	1.11	(0.02)	0.03	(0.01)	<lld	100.64	(0.68)	0.01	(0.01)	100.62	(0.68)	10
	AD+Fo	48.58	(0.62)	13.16	(0.14)	20.17	(0.11)	17.14	(0.10)	1.05	(0.01)	0.04	(0.01)	<lld	100.15	(0.87)	0.02	(0.01)	100.13	(0.86)	11
	AD+Qtz ‡	65.87	(0.29)	10.42	(0.09)	15.50	(0.09)	6.98	(0.05)	1.15	(0.02)	0.03	(0.01)	<lld	99.96	(0.38)	0.01	(0.01)	99.95	(0.38)	10
	AD+Wo	51.05	(0.18)	6.32	(0.03)	37.76	(0.10)	4.34	(0.02)	1.04	(0.01)	0.07	(0.01)	<lld	100.59	(0.31)	0.04	(0.01)	100.55	(0.31)	10
-8.5	AD	50.16	(0.10)	15.67	(0.09)	23.57	(0.08)	10.70	(0.02)	1.05	(0.02)	0.11	(0.02)	<lld	101.28	(0.22)	0.06	(0.01)	101.23	(0.21)	9
	AD+En †	54.74	(0.09)	9.73	(0.05)	14.70	(0.06)	21.12	(0.08)	1.09	(0.01)	0.09	(0.02)	<lld	101.48	(0.22)	0.04	(0.01)	101.44	(0.22)	13
	AD+Fo	49.39	(0.18)	13.40	(0.08)	20.22	(0.05)	17.46	(0.06)	1.07	(0.01)	0.11	(0.01)	<lld	101.65	(0.30)	0.06	(0.01)	101.60	(0.30)	9
	AD+Qtz ‡	66.05	(0.14)	10.37	(0.04)	15.77	(0.05)	7.23	(0.06)	1.16	(0.01)	0.04	(0.01)	<lld	100.61	(0.19)	0.02	(0.01)	100.59	(0.19)	9
	AD+Wo	51.25	(0.09)	6.39	(0.04)	37.96	(0.11)	4.33	(0.03)	1.06	(0.01)	0.13	(0.01)	<lld	101.13	(0.24)	0.06	(0.01)	101.06	(0.23)	9
-10.5	AD	49.88	(0.26)	15.65	(0.12)	23.67	(0.05)	10.62	(0.07)	1.05	(0.01)	0.26	(0.01)	<lld	101.15	(0.45)	0.13	(0.01)	101.01	(0.44)	9
	AD+En †	54.33	(0.22)	9.74	(0.09)	14.81	(0.05)	21.26	(0.08)	1.09	(0.01)	0.21	(0.01)	<lld	101.45	(0.37)	0.11	(0.01)	101.34	(0.37)	10
	AD+Fo	48.89	(0.29)	13.35	(0.10)	20.21	(0.06)	17.53	(0.08)	1.06	(0.01)	0.29	(0.01)	<lld	101.34	(0.49)	0.15	(0.01)	101.20	(0.49)	10
	AD+Qtz ‡	66.16	(0.23)	10.32	(0.06)	15.64	(0.13)	7.14	(0.03)	1.15	(0.01)	0.08	(0.03)	<lld	100.50	(0.21)	0.04	(0.01)	100.46	(0.20)	10
	AD+Wo	50.93	(0.13)	6.33	(0.04)	38.22	(0.13)	4.24	(0.03)	1.04	(0.01)	0.37	(0.01)	<lld	101.12	(0.14)	0.18	(0.01)	100.94	(0.14)	10

Notes: Analysis by WDS EMP (standard deviation in parentheses). # = number of analyses. Experiment number and sample mounting: $\Delta IW +6.5$ (IC5/8/09, Pt mount); $\Delta IW +0.1$ (IC12/2/10, Re mount); $\Delta IW -1.5$ (IC15/2/10, Re mount); $\Delta IW -2.5$ (IC17/2/10, Re mount); $\Delta IW -3.5$ (IC15/8/09, Re mount with Fe-loop); $\Delta IW -4$ (IC26/8/09, Re mount with Fe-loop); $\Delta IW -4.5$ (IC6/8/09, Re mount with Fe-loop); $\Delta IW -6.5$ (IC19/2/10, graphite mount); $\Delta IW -8.5$ (IC19/8/09, graphite mount); $\Delta IW -10.5$ (IC20/8/09, graphite mount)

† **Composition of the crystals in AD+Qtz samples:** (EDS SEM) 100.3 ± 0.3 wt% SiO_2 , 0.3 ± 0.1 wt% CaO and 0.4 ± 0.1 wt% Al_2O_3 , 100.9 ± 0.2 wt% total (i.e. SiO_2)

The analysis above is based on the crystals in AD+Qtz in IC25/8/09 and is representative of the series. The CaO and Al_2O_3 are presumed to be contamination from the adjacent glass.

‡ **Composition of the crystals in AD+En samples:** (WDS EMP) 42.46 ± 0.54 wt% SiO_2 , 57.69 ± 0.36 wt% MgO, 0.39 ± 0.02 wt% CaO, 0.05 ± 0.03 wt% TiO_2 , 100.71 ± 0.94 wt% total (i.e. Mg_2SiO_4)

The analysis above is the average of the forsterite crystals in AD+En produced under the following conditions: $\Delta IW -2.5$; -7.2, -7.7, -9.7, -11.7, and -13.7 (Appendix B.2.1.2.)

Table 3-6 Average compositions of the XANES glass sample series and the calculated optical basicity

Sample	SiO ₂		Al ₂ O ₃		CaO		MgO		TiO ₂		Total		Number of analyses	Calculated optical basicity	
AD	49.96	(0.49)	15.44	(0.17)	23.27	(0.30)	10.59	(0.09)	1.03	(0.01)	100.44	(0.73)	105	0.596	(0.013)
AD+En	54.09	(0.62)	9.53	(0.21)	14.31	(0.37)	21.66	(0.41)	1.06	(0.03)	100.80	(0.75)	134	0.581	(0.007)
AD+Fo	49.15	(0.59)	13.19	(0.12)	19.83	(0.31)	17.41	(0.19)	1.04	(0.01)	100.76	(0.75)	111	0.596	(0.014)
AD+Qtz	65.86	(0.36)	10.03	(0.27)	15.30	(0.33)	6.98	(0.13)	1.13	(0.02)	99.43	(0.39)	106	0.554	(0.022)
AD+Wo	51.49	(0.44)	6.25	(0.08)	37.43	(0.46)	4.27	(0.05)	1.02	(0.02)	100.62	(0.54)	117	0.621	(0.017)

Note: Analysis by WDS EMP (standard deviation in parentheses), with calculated optical basicity (standard deviation of the propagated error in parentheses).

A phase ($<2\ \mu\text{m}$) with a high backscatter co-efficient was observed in samples mounted on Pt or Re ($\geq\Delta\text{IW-4.5}$). These “specks” were attributed to the presence of Pt or Re blebs from the mount. A few such “specks” were observed in samples mounted in graphite ($\leq\Delta\text{IW-6.5}$). These are believed to be minor Fe impurities from the pellet press, although it is possible that a Ti^0 , Ti-C or Ti-S phase is present.

Trace quantities of Fe ($<0.50\ \text{wt}\% \text{FeO}$) were found in samples produced between $\Delta\text{IW-3.5}$ and $\Delta\text{IW-4.5}$. Samples loaded alongside a Fe-loop experiment sample were consistently more Fe-enriched than those mounted 20-30 mm away.

Sulphur was detected in samples mounted in graphite ($<\Delta\text{IW-6.5}$). The S-content increased as the conditions became more reducing and was independent of the equilibration time. Indeed, the samples produced at $\Delta\text{IW-6.5}$ were at temperature for longer than those prepared at more reducing conditions. The solubility of S in the Ti-CMAS glasses therefore appears to be $f\text{O}_2$ dependant. In addition, the S content is dependent on the glass composition. Indeed, Figure 3-1 shows the S-content is directly proportional to the calculated optical basicity of the glasses, with both parameters ordered as follows: $\text{AD+Qtz} < \text{AD+En} < \text{AD} \sim \text{AD+Fo} < \text{AD+Wo}$. This finding is in agreement with previous investigations of Fe-free Ti-CMAS glasses which showed that sulphur solubility was $f\text{O}_2$ dependant, with S becoming more soluble under more reducing conditions (O'Neill and Mavrogenes, 2002). Although the compositions used were not equivalent to those in this study, it was also found that the CaO-rich composition in their study was more S-rich than the other compositions, whereas the SiO_2 -rich composition had the lowest S concentration.

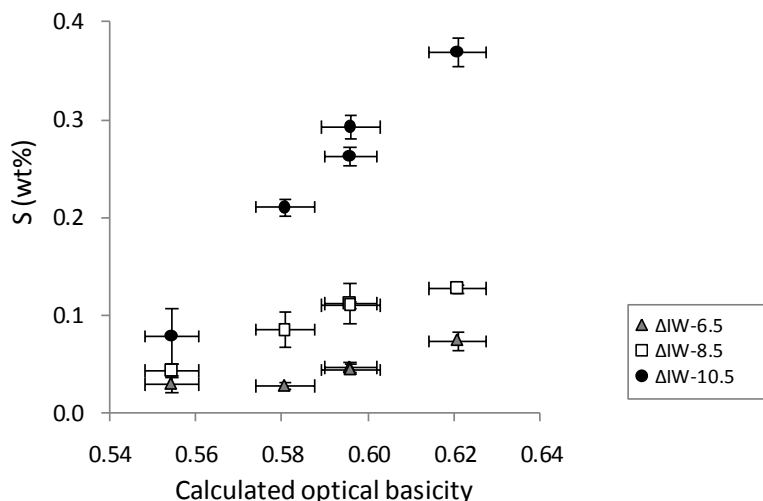


Figure 3-1 S-content as a function of calculated optical basicity showing a direct correlation and an increase in S content with lower $f\text{O}_2$ conditions.

3.4.1.2 XPEEM sample series

The average glass compositions of the AD+Fo series prepared under five $f\text{O}_2$ conditions for XPEEM are presented in Table 3-7. The low TiO_2 content of the $\Delta\text{IW-2.5}$ sample was due to Ti

solubility in the Ti-CMAS glasses under these fO_2 conditions. As for the XANES sample suite, a phase with a high backscatter co-efficient was noted in the samples prepared at ΔIW -2.5 and ΔIW -4.5. These are thought to originate from the metal mount, supported by textural evidence and EDS SEM analyses.

Table 3-7 Compositions of the AD+Fo XPEEM glass sample series prepared at five fO_2 conditions

ΔIW	SiO ₂	Al ₂ O ₃	CaO	MgO	TiO ₂	FeO	Total	#
+6.5	49.8 (0.6)	12.5 (0.2)	20.2 (0.2)	17.5 (0.2)	1.1 (0.1)	<lld	101.2 (0.9)	4
-2.5	49.5 (0.5)	12.5 (0.2)	20.2 (0.2)	17.5 (0.2)	0.4 (0.0)	<lld	100.1 (0.8)	6
-3.5	49.6 (0.2)	12.4 (0.1)	20.1 (0.1)	17.0 (0.2)	1.0 (0.1)	0.5 (0.1)	100.5 (0.5)	4
-4.5	49.9 (0.5)	12.6 (0.2)	20.0 (0.2)	16.6 (0.3)	1.0 (0.1)	<lld	100.2 (0.9)	4
-6.5	48.5 (0.4)	12.6 (0.1)	20.3 (0.3)	17.4 (0.3)	1.1 (0.1)	<lld	100.0 (0.8)	7

Notes: EDS SEM analysis (standard deviation in parentheses). # = number of analyses. Samples synthesised at 1404 °C, all quenched to the bottom of the furnace. Experiment number and sample mounting: ΔIW +6.5 (IC20/10/09, Pt); ΔIW -2.5 (IC21/10/09, Pt); ΔIW -3.5 (IC23/10/09, Re); ΔIW -4.5 (IC24/10/09, Re); ΔIW -6.5 (IC26/10/09, Graphite).

3.4.1.3 EPR sample series

The glasses equilibrated at ΔIW +6.5 were colourless. A light pink hue was detected for samples equilibrated at ΔIW +0.1, with the colour deepening to pinky-purple as the conditions became more reducing. Optically the EPR glasses differed from the glasses prepared in the XANES sample series. Evenly spaced sub-circular vesicles (~50 μm diameter) were observed in all the glass samples, irrespective of the mounting medium. In addition, the graphite-mounted samples contained numerous high backscatter co-efficient “specks” (Figure 3-2), more than observed in the Pt and Re mounted samples.

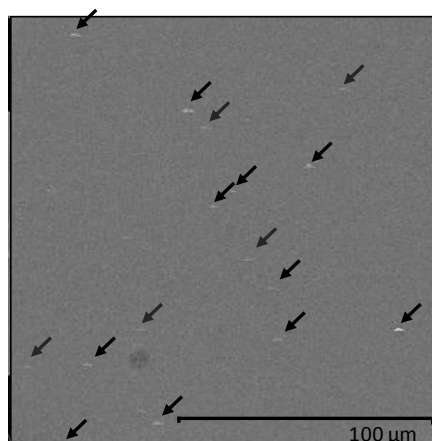


Figure 3-2 Backscatter electron image (BEI) of AD glass prepared at ΔIW -10.5 as part of the EPR series showing a large number of high backscatter co-efficient phases (positions indicated by arrows).

The major element composition and the TiO₂ content of the EPR samples (Table 3-8) were close to the ideal AD composition and to that of the XANES series AD samples. The S content of the EPR samples prepared at ΔIW -10.5 were, however, lower than that of the XANES sample prepared under the same conditions. It is possible that the original S content in the graphite mounts has been reduced

Table 3-8 Composition of EPR sample series

ΔIW	SiO_2		Al_2O_3		CaO		MgO		TiO_2		S		FeO		Total [†]		#
+6.5	50.11	(0.26)	15.46	(0.11)	23.51	(0.08)	10.67	(0.06)	1.04	(0.01)	<lld		<lld		100.81	(0.40)	10
+0.1	50.04	(0.38)	15.37	(0.10)	23.55	(0.04)	10.64	(0.06)	1.03	(0.01)	<lld		<lld		100.65	(0.54)	14
-1.5	50.63	(0.16)	15.59	(0.08)	23.42	(0.05)	10.71	(0.06)	1.04	(0.01)	<lld		0.07	(0.01)	101.45	(0.25)	11
-2.5	50.72	(0.21)	15.60	(0.06)	23.27	(0.04)	10.66	(0.10)	1.05	(0.01)	<lld		0.29	(0.01)	101.57	(0.35)	4
-3.5	50.24	(0.16)	15.42	(0.09)	23.40	(0.04)	10.60	(0.05)	1.04	(0.01)	<lld		0.32	(0.01)	101.01	(0.30)	12
-4	50.54	(0.27)	15.37	(0.12)	23.27	(0.10)	10.56	(0.07)	1.04	(0.01)	<lld		0.22	(0.01)	100.99	(0.51)	11
-4.5	50.54	(0.20)	15.43	(0.10)	23.38	(0.07)	10.58	(0.07)	1.05	(0.01)	<lld		0.13	(0.01)	101.12	(0.41)	11
-6.5	50.14	(0.19)	15.62	(0.08)	23.66	(0.09)	10.63	(0.06)	1.05	(0.01)	0.04	(0.01)	<lld		101.14	(0.34)	37
-8.5	50.12	(0.18)	15.71	(0.11)	23.77	(0.05)	10.74	(0.06)	1.05	(0.01)	0.08	(0.01)	<lld		101.48	(0.30)	28
-																	
10.5	50.11	(0.30)	15.65	(0.11)	23.67	(0.07)	10.69	(0.08)	1.05	(0.01)	0.07	(0.01)	<lld		101.26	(0.48)	42

Notes: WDS EMP data (standard deviation in parentheses). # = number of analyses. † The corrected total wt% for the S^{2-} bearing samples resulted in the totals decreasing by $\leq 0.04(0.01)$ wt%. Experiment number and sample mounting: $\Delta IW+6.5$ (IC13/1/11, Pt); $\Delta IW+0.1$ (IC21/1/11, Re); $\Delta IW-1.5$ (IC17/1/11, Re); $\Delta IW-2.5$ (IC16/1/11, Re); $\Delta IW-3.5$ (IC15/1/11, Re); $\Delta IW-4$ (IC18/1/11, Re); $\Delta IW-4.5$ (IC20/1/11, RE); $\Delta IW-6.5$ (IC12/1/11, graphite); $\Delta IW-8.5$ (IC10/1/11, graphite); $\Delta IW-10.5$ (IC11/1/11, graphite).

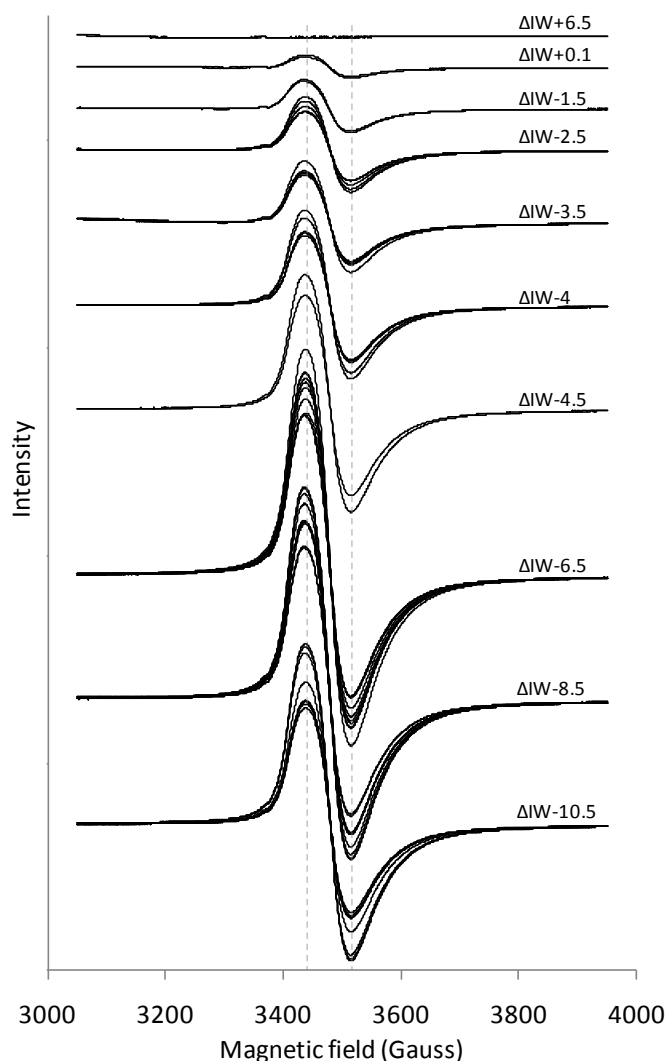


Figure 3-3 EPR spectra as a function of magnetic field strength for the AD composition prepared over 17 log units in fO_2 . The maxima (3437 ± 1 G) and minima (3514 ± 1 G) are marked by a dashed line and repeat analyses shown. Data are offset vertically for clarity.

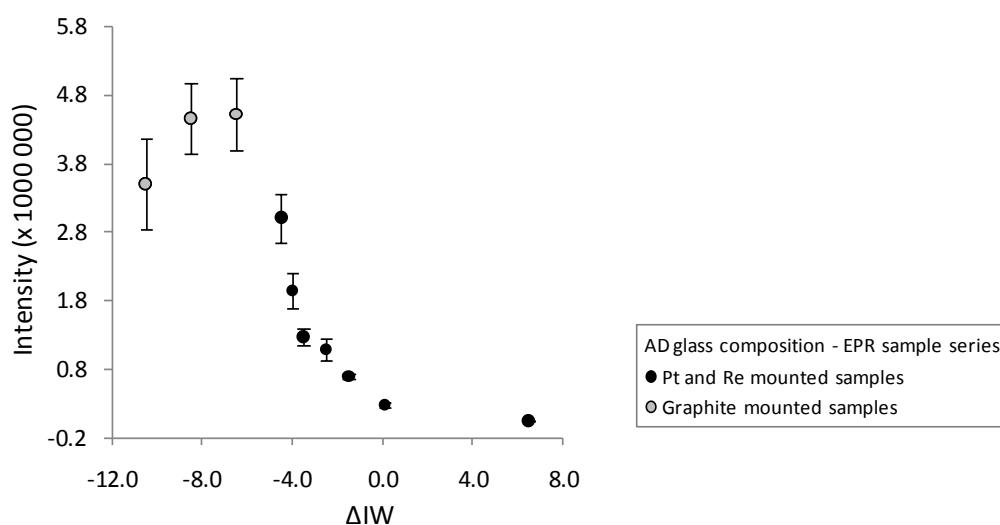


Figure 3-4 Average EPR intensities at 3438 ± 1 G for the AD EPR glass series as a function of fO_2 showing an increase in intensity $< \Delta IW - 6.5$, followed by a drop in intensity under more reducing conditions. The intensity of the samples mounted in graphite ($\leq \Delta IW - 6.5$) is more variable than for samples mounted on Pt or Re.

as a function of usage between the time the XANES and EPR samples were prepared. The FeO in the EPR samples is due to degradation of the inner tube of the furnace with increased use.

As shown in Figure 3-3, the EPR signal at 3437 ± 1 G increased as a function of fO_2 between $\Delta IW + 6.5$ and $\Delta IW - 6.5$. The EPR signal intensities of samples produced under fO_2 values $\leq \Delta IW - 6.5$ decreased in samples prepared under progressively lower fO_2 conditions, and showed more variability than for other samples.

Figure 3-4 shows a gradual increase in the EPR signal intensity with reduction in fO_2 for the Pt and Re mounted glass samples prepared at $\geq \Delta IW - 3.5$. Below $IW - 3.5$ the EPR signal intensity increases dramatically, giving the signal intensity an asymptotal form as a function of fO_2 at high fO_2 . This is consistent with an increase in the Ti^{3+} content as the conditions become more reducing, and is observed in other transition element redox studies (Berry and O'Neill, 2004).

Ideally, if all the Ti is present as Ti^{3+} , as expected for the glasses prepared at the lowest fO_2 values, the signal should saturate. Below $\Delta IW - 8$, however, the EPR signal intensity decreases as the conditions become more reducing. This suggests the presence of non-paramagnetic Ti. As the samples were mounted in S-bearing graphite and Ti is known to complex with both S and C (e.g. Bandi and Krapf, 1979) Ti-C or Ti-S compounds may have formed, which may account for the numerous specks in these samples. As the S-content in the EPR series samples is relatively low compared to the XANES glass samples, it is also possible that Ti^0 or Ti^{2+} may have formed under the extremely reducing conditions used to produce the EPR series samples.

3.4.1.4 Possible implications of minor impurities for XANES and XPEEM analyses

The Fe and S trace impurities in the bulk glasses would not directly affect the Ti spectra. The FeO and S contents were low (< 0.45 wt% FeO and < 0.27 wt% S) and neither the Fe K- and L-edges (7112 eV; 708-846 eV; Bearden and Burr, 1967), nor the S K- or L-edges (2472 eV; 164-229 eV; Bearden and Burr, 1967) would interfere with that of Ti (4966 eV; 455-563 eV; Bearden and Burr, 1967).

The high backscatter co-efficient “specks” observed in the glasses prepared under $\geq \Delta IW - 6.5$ may be expected to be Ti-free and would therefore not affect Ti spectroscopy. Numerous “specks” were observed in the graphite-mounted EPR samples which had lower EPR signal intensities than expected, suggesting the presence of Ti^0 or Ti^{2+} in these samples. Due to the small size and the scarcity of the “specks” in the equivalent XANES and XPEEM samples, however, they were unlikely to affect the Ti spectroscopic studies.

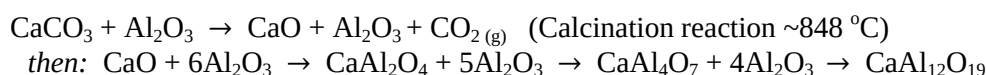
3.4.2 Ti-bearing synthetic hibonite

3.4.2.1 Saturation series

3.4.2.1.1 0Ti hibonite

Impurities were found in all 10 of the Ti-free sinter products, irrespective of fO_2 ($\Delta IW+6.5$, $\Delta IW-2.5$, $\Delta IW-6.5$), temperature (1300 °C and 1404 °C), and sample preparation method employed (single or multiple sinter(s); slow-cool or water quench). Al_2O_3 was observed in all the sinter products, some samples contained $CaAl_4O_7$, and a minor amount of $Ca_3Al_{10}O_{18}$ was found in some of the experimental products. The largest hibonite yield was produced under intermediate fO_2 conditions ($\Delta IW-2.5$), whereas the sample with the strongest Al_2O_3 signature in the powder XRD pattern was produced under oxidising conditions ($\Delta IW+6.6$).

The presence of Al_2O_3 and $CaAl_4O_7$, which is more abundant than $Ca_3Al_{10}O_{18}$, is in agreement with the reaction process detailed in Domínguez *et al.* (2001) and summarised below:



Pure hibonite is notoriously difficult to synthesise (Hofmeister *et al.*, 2004; Callender and Barron, 2000). Al_2O_3 is a common impurity in syntheses, regardless of the method employed (Holtstam, 1996; Callender and Barron, 2000; Vázquez *et al.*, 2003). Despite nine sinters at 1500-1625 °C and a product that appeared to be pure by XRD analysis, Geiger *et al.* (1988) found that SEM analysis revealed traces of Al_2O_3 in their samples. The stability of the simple oxide phases from the starting compositions is believed to attribute to the abundance of impurity phases (Hofmeister *et al.*, 2004). Indeed, their study found that their $CaO + Al_2O_3$ syntheses contained more impurities than the $CaO + CaAl_4O_7$ syntheses.

3.4.2.1.2 Ti^{3+} Saturation series

The Ti^{3+} saturation series samples from experiment IC31/8/09 were two or three toned: the area directly exposed to the gas was sky blue (2-3 mm) and the base of the sample was grey (2-6 mm). These two extremes graded into midnight blue (4-5 mm) in the central region of the Ti-rich samples HibG(75,0) and HibH(125,0). The blue and grey portions of HibF(20,0) were indistinguishable by XRD analysis, and the powders were therefore combined. SEM analysis later showed that hibonite grains in the grey portion of the sample were marginally Ti-poor ($Ca_{1.05}Al_{11.69}Ti_{0.21}O_{19}$) with respect to those in the blue region ($Ca_{1.06}Al_{11.63}Ti_{0.25}O_{19}$). The hibonite in the grey portion was interspersed with fine-grained Ti-oxide, whereas Al_2O_3 (corundum) was the only impurity observed in the blue region. Ti-oxide $\pm Al_2O_3$ were noted in samples with less than $\leq 0.75 Ti^{3+}$ pfu during EDS SEM analysis, and $CaTiO_3$ (perovskite) was found in the Ti-rich sample Hib7(100,0) by XRD and EDS SEM. A minor

Ca-bearing phase may be present in the Ti^{3+} hibonites with $\leq 0.75 \text{ Ti}^{3+}$ pfu, but it was not identified by XRD or EDS SEM.

3.4.2.1.3 Ti^{4+} Saturation series

The Ti^{4+} hibonite saturation series samples were white in colour. The unit cell increased in size with more Ti pfu, as shown by a shift in the XRD reflections to lower 2θ . The rate of increase slowed with more than 1Ti pfu and impurities such as $\text{CaTiO}_3 \pm \text{MgAl}_2\text{O}_4$ (spinel) $\pm \text{Al}_2\text{O}_3 \pm \text{Mg-Al-Ti-oxide}$ were noted in samples with $>1\text{Ti}$ pfu. Whereas multiple sinters usually reduce the number of impurities, the converse was true: no Al_2O_3 was detected by XRD after the second sinter of Hib9(44,43) and Hib10(150x2), but was present after the third sinter. The proportion of impurities after the fourth sinter (CO_2 , water quench) was greater for all the samples than the prior sinters (air, 600°C extraction). This may be due to the stability of Al_2O_3 (e.g. Hofmeister *et al.*, 2004), causing the exsolution of Al_2O_3 from the hibonite structure with more sinters. Alternatively, as Al_2O_3 is stable at higher temperature than hibonite, the water quench may have preserved a greater proportion of Al_2O_3 in the fourth sinter than the slow-cooled sinters in which Al_2O_3 may be resorbed into the hibonite structure as the temperature cools, analogous to hibonite formation in a gas of solar composition (Yoneda and Grossman, 1995).

The Ti^{4+} hibonite yield was maximised after two sinters, whereas the hibonite sintered under reducing conditions nucleated well during one sinter. This suggests that hibonite is more stable under reducing conditions, as observed by Domínguez *et al.* (2001) in the ceramic study of pure hibonite.

3.4.2.2 Large-volume samples

For the purposes of this study, “ Ti^{3+} hibonite(s)” refers to hibonite samples in which all the Ti is Ti^{3+} (HibF(20,0) and/or Hib5D(33,0)), and “ Ti^{4+} hibonite(s)” refers to hibonite samples in which all the Ti is Ti^{4+} (Hib9(44,43) and/or HibE(98,91)). The remaining samples are referred to as “mixed-valent” hibonites, with the qualification “ Ti^{4+} -bearing” referring to any hibonite containing Ti^{4+} and Mg^{2+} , and “ Ti^{3+} -rich” referring to hibonite with $>50\%$ of Ti as Ti^{3+} (HibF(20,0), Hib5D(33,0) and/or HibK(62,24)).

3.4.2.2.1 Material properties

As for the Ti^{3+} saturation series hibonites (IC31/8/09), the hibonites produced under reducing conditions were two (or three) toned. The Ti^{3+} hibonites HibF(20,0) and Hib5D(33,0) were blue where the sinter product was exposed to the gas, and grey where the sample was enclosed by the graphite mount. The mixed-valent hibonites with <1 Ti pfu were largely blue in colour, with minor grey in the shielded areas, and the hibonite with >1 Ti pfu (HibT(137,83)) was midnight blue in colour where enclosed in graphite. The Ti^{4+} hibonite sinter products were white in colour.

The sintered products were highly porous, the Ti^{3+} -bearing hibonites more so than the twice-sintered Ti^{4+} hibonites (Figure 3-5). The Ti^{3+} -bearing samples were platy with a hexagonal form, although the Ti^{3+} hibonite grains had a lower aspect ratio than the mixed-valent hibonite grains (4 ± 1 and 9 ± 3 respectively). In contrast, the Ti^{4+} hibonite grains were predominantly tabular in form.

The Fe-bearing hibonite crystals of Holtstam (1996) were tabular in form (15 μm max dimension), similar to the Ti^{4+} hibonite samples. Differences in crystal form can occur due to differences in element dispersion (Domínguez *et al.*, 2001). Indeed, the study by Domínguez *et al.* (2001) showed that mechanically stirred samples were more porous and platy than those prepared

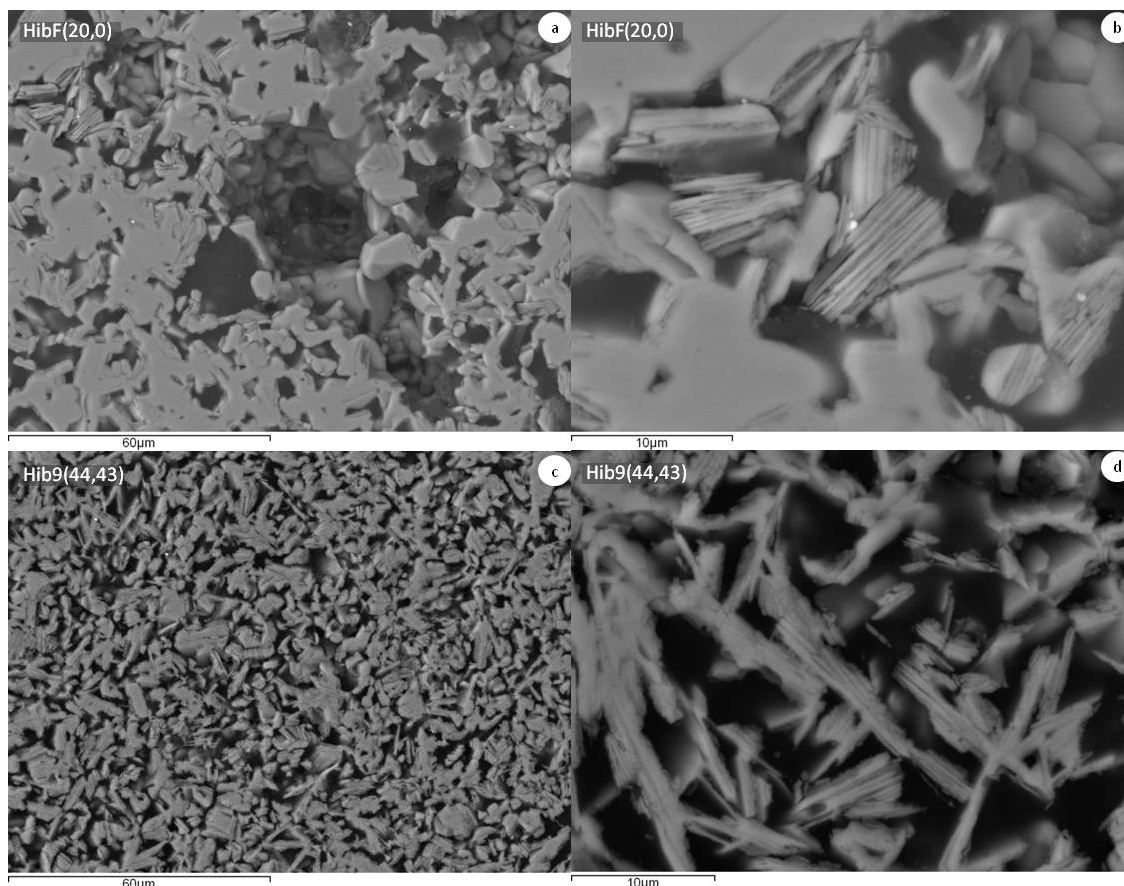


Figure 3-5 BEI of synthetic hibonites of (a,b) the Ti^{3+} hibonite HibF(20,0) and (c,d) the Ti^{4+} hibonite Hib9(44,43) showing the Ti^{3+} hibonite grains are platy and hexagonal, whereas those of the Ti^{4+} hibonite are predominantly tabular in form.

using attrition milling as the elements were more evenly dispersed in the latter method. Likewise, components of the Ti^{4+} hibonites would have been well dispersed after the powdering of the first sinter product.

3.4.2.2.2 Composition and calculated % Ti^{3+}

The average compositions of the synthetic hibonite samples (Table 3-9) were distinct from one another and close to the stoichiometry of the starting material. The average Ti content in the series ranged from 2.4 to 15.9 wt% TiO_2 , translating into 0.2 to 1.37 Ti pfu. The Ti^{3+} hibonites (HibF(20,0), Hib5D(33,0)), were compositionally distinct and well defined (Figure 3-6), as were the mixed-valent hibonite samples (HibK(62,24), Hib8C(73,49), HibT(137,83)) and the Ti^{4+} hibonite HibE(98,91). The

Table 3-9 The synthetic hibonite compositions: oxide weight%, cation proportions and %Ti³⁺/ΣTi vs. ideal %Ti³⁺/ΣTi

Sample	wt% oxide					Number of cations, calculated on 19 O					Number of cations		%Ti ³⁺ /ΣTi [§]		No. analyses
	CaO	Al ₂ O ₃	TiO ₂ ^{tot}	MgO	Total	Ca	Al	Ti	Mg	Total Cations	Ti ³⁺	Ti ⁴⁺	Calculated	Ideal	
HibF(20,0)	8.8 (0.4)	88.2 (0.6)	2.4 (0.5)	<Ild	99.4 (0.7)	1.07 (0.04)	11.69 (0.07)	0.20 (0.04)	<Ild	12.95 (0.02)	0.20	n.d.	100	100	37
Hib5D(33,0)	8.8 (0.3)	86.7 (0.6)	4.0 (0.4)	<Ild	99.5 (0.8)	1.07 (0.04)	11.51 (0.05)	0.33 (0.04)	<Ild	12.91 (0.02)	0.33	n.d.	100	100	30
HibK(62,24)	8.7 (0.3)	82.8 (0.5)	7.3 (0.5)	1.5 (0.1)	100.2 (0.7)	1.05 (0.04)	10.99 (0.06)	0.62 (0.04)	0.24 (0.02)	12.89 (0.02)	0.37	0.25	60 (4)	60	27
Hib8C(73,49)	8.8 (0.3)	79.9 (1.0)	8.6 (0.7)	2.9 (0.2)	100.2 (0.9)	1.07 (0.03)	10.66 (0.09)	0.73 (0.06)	0.49 (0.03)	12.94 (0.02)	0.24	0.49	33 (5)	33	42
HibJ(82,60) †	8.6 (0.3)	78.6 (2.5)	9.6 (2.2)	3.5 (0.6)	100.3 (0.9)	1.05 (0.04)	10.48 (0.32)	0.82 (0.19)	0.60 (0.10)	12.94 (0.04)	0.20	0.62	25 (12)	14	41
Hib9(44,43)	8.5 (0.3)	83.0 (1.9)	5.2 (1.4)	2.5 (0.6)	99.2 (0.6)	1.04 (0.03)	11.10 (0.22)	0.44 (0.12)	0.43 (0.11)	13.01 (0.02)	n.d.	0.44	0	0	26
HibE(98,91) ‡	8.3 (0.4)	74.8 (0.7)	11.4 (0.7)	5.4 (0.2)	100.0 (0.9)	1.01 (0.04)	10.07 (0.09)	0.98 (0.06)	0.91 (0.04)	12.98 (0.03)	n.d.	0.98	0	0	28
HibT(137,83)	8.6 (0.3)	71.0 (1.1)	15.9 (0.9)	4.9 (0.2)	100.4 (0.8)	1.05 (0.04)	9.59 (0.12)	1.37 (0.08)	0.83 (0.04)	12.84 (0.03)	0.54	0.83	39 (4)	40	18
HibN(46,40) ‡	8.6 (0.3)	82.8 (1.9)	5.4 (0.6)	2.4 (0.5)	99.2 (0.7)	1.05 (0.03)	11.08 (0.23)	0.46 (0.13)	0.40 (0.09)	13.00 (0.02)	0.05	0.41	10 (12)	12	31

Notes: EDS SEM analyses, calculated cations and %Ti³⁺/ΣTi (standard deviation in parentheses). Individual analyses in Appendix B.2.1.3.

Traces of sulphur were found in the hibonite samples produced under reducing conditions. From WDS EMP: The SiO₂ content of the hibonite was above detection limit, ranging between 0.23-0.68 wt% SiO₂. Na was detected in the Ti⁴⁺ hibonite samples: 0.27±0.06 wt% Na₂O in HibE(98,91) and 0.28 ±0.33 wt% in Na₂O Hib9(44,43). Analyses containing S, SiO₂ or Na₂O were not included in the average sample composition.

[§] Ideal %Ti³⁺/ΣTi = that determined by the stoichiometric mixture of Table 3-2.

† Average of the two different HibJ(82,60) portions:

HibJ(30_{body}) 30(4)% Ti³⁺/ΣTi 8.5(0.3) wt% CaO, 77.2(1.0) wt% Al₂O₃, 10.9(0.9) wt%TiO₂^{tot}, 3.8(0.2) wt% MgO, 100.5(0.9) wt% total (average of 27 analyses) Ca_{1.04}Al_{10.31}Ti_{0.93}Mg_{0.65}O₁₉
HibJ(14_{tail}) 14(15)% Ti³⁺/ΣTi 8.7(0.3) wt% CaO, 81.1(2.5) wt% Al₂O₃, 7.1(2.0) wt%TiO₂^{tot}, 3.0(0.7) wt% MgO, 99.9(1.0) wt% total (average of 14 analyses) Ca_{1.05}Al_{10.82}Ti_{0.61}Mg_{0.50}O₁₉

‡ Outliers not included in the average analyses above:

HibN(46,40) outlier 8.7 wt% CaO, 85.8 wt% Al₂O₃, 2.3 wt%TiO₂^{tot}, 2.6 wt% MgO, 99.4 wt% total (single analysis)
HibE(98,91) outlier(1) 8.8 wt% CaO, 79.7 wt% Al₂O₃, 8.3 wt%TiO₂^{tot}, 4.2 wt% MgO, 101.0 wt% total (single analysis)
HibE(98,91) outlier(2) 9.1 wt% CaO, 77.3 wt% Al₂O₃, 8.6 wt%TiO₂^{tot}, 4.8 wt% MgO, 99.9 wt% total (single analysis)

range in TiO_2 content of these samples was <3 wt% TiO_2 per sample. Approximately two-thirds of the HibJ(82,60) point analyses were well defined, but the composition of the remaining analyses showed a compositional range from 2.5 to 9.7 wt% TiO_2 . The samples Hib9(44,43) and HibN(46,40) also showed a compositional range with TiO_2 varying by 2.7-7.2 wt% TiO_2 for Hib9(44,43) and 2.3-7.6 wt% TiO_2 for HibN(46,40).

For the pure Ti^{4+} hibonite Hib9(44,43) the variation in Ti content clearly falls along the 1Ti:1Mg line. The compositional ranges of HibN(46,40) and HibJ(82,60) appear to trend toward the 1Ti:1Mg line from their ideal chemistries.

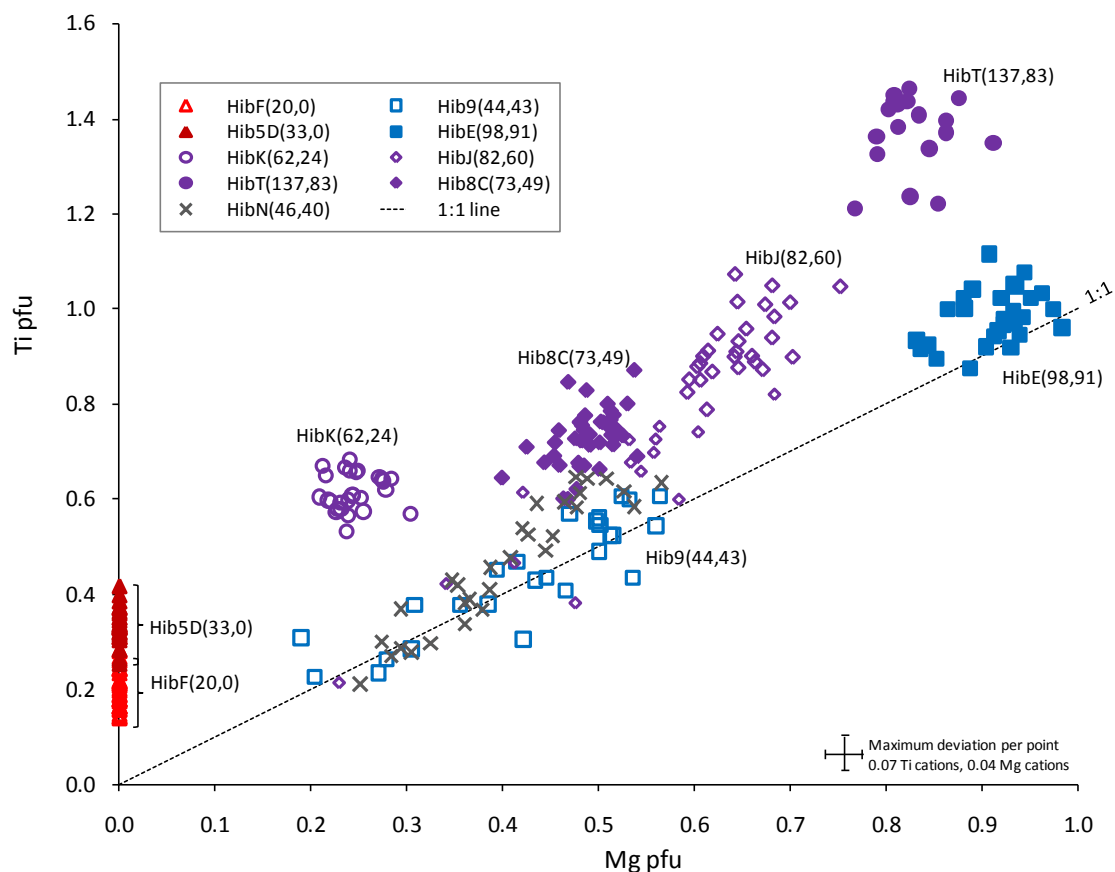


Figure 3-6 Ti vs. Mg cations pfu for the synthetic hibonites showing point analyses used to calculate the average compositions. The composition of six samples were distinct from one another, whereas Hib9(44,43), HibN(46,40) and a portion of HibJ(82,60) overlap compositionally along a 1:1 line (plotted as a guide to the eye).

Due to the simple stoichiometry of the samples prepared under known conditions, the $\text{Ti}^{3+}/\Sigma\text{Ti}$ may be calculated based on the assumption that $1\text{Ti}^{4+}:1\text{Mg}^{2+}$, with the remaining Ti being Ti^{3+} . Containing no Mg^{2+} , the Ti^{3+} hibonite compositions would be consistent with having 100% $\text{Ti}^{3+}/\Sigma\text{Ti}$. Furthermore, the blue colour of these samples is indicative of the presence of Ti^{3+} (Ihinger and Stolper, 1986). The white colour of the Ti^{4+} hibonite samples would be consistent with the samples being Ti^{3+} -free. The average $\text{Ti}^{3+}/\Sigma\text{Ti}$ for these samples was 0% $\text{Ti}^{3+}/\Sigma\text{Ti}$, although the variability in $\text{Ti}^{3+}/\Sigma\text{Ti}$ of Hib9(44,43) and HibE(98,91) was $\pm 14\%$ and $\pm 5\%$ $\text{Ti}^{3+}/\Sigma\text{Ti}$ respectively due to scatter along the 1Ti:1Mg composition line. This uncertainty reflects the compositional spread in Hib9(44,43) and the experimental error associated with EDS SEM for both samples (Figure 3-6). The

calculated $\text{Ti}^{3+}/\Sigma\text{Ti}$ in the mixed-valent samples HibK(62,24), Hib8C(73,49) and HibT(137,83) was similar to that expected from the ideal stoichiometry (Table 3-9). The HibJ(82,60) hibonite sample was compositionally complex, with approximately two thirds of the point analyses calculated to be Ti^{3+} -rich ($30 \pm 4\% \text{Ti}^{3+}/\Sigma\text{Ti}$), whereas the remaining analyses trended toward a 1Ti:1Mg line and were calculated to be within error of 0% $\text{Ti}^{3+}/\Sigma\text{Ti}$ ($14 \pm 15\% \text{Ti}^{3+}/\Sigma\text{Ti}$, see note in Table 3-9).

3.4.2.2.3 Impurities

Al_2O_3 and a Ti-oxide were found in the Ti^{3+} -bearing samples, whereas the Ti^{4+} -bearing samples contained MgAl_2O_4 and CaTiO_3 (Table 3-10). Microprobe analyses of the fine-grained impurities were compromised by Al contamination from the surrounding hibonite. Despite difficulties calculating accurate stoichiometries, the identity of the phases were confirmed by XRD. A minor Ca-bearing phase may be present in the Ti^{3+} -bearing hibonites, but no convincing identification could be made despite characterisation using XRD, EDS SEM and NPD.

Table 3-10 Impurity phases in the synthetic hibonite samples

Sample	Approximate % Ti in hibonite [†]	Impurity phases (mode of detection)
HibF(20,0)	85%	Al_2O_3 (SEM, HRPD), Ti-Oxide (SEM), possibly TiO
Hib5D(33,0)	73%	Al_2O_3 (NPD), Ti-Oxide (SEM), possibly TiO
HibK(62,24)	99%	Ti-Oxide (SEM), possibly TiO and/or Ti_2O_3
Hib8C(73,49)	98%	Al_2O_3 (NPD), Ti-Oxide (SEM), possibly TiO and Ti_2O_3
HibN(46,40)	99%	CaTiO_3 (SEM) CaAl_4O_7 (SEM), Ti-Oxide (SEM), possibly TiO and/or Ti_2O_3
HibJ(82,60)	96%	CaTiO_3 (SEM), MgAl_2O_4 (SEM, NPD), Ti-Oxide (SEM), possibly TiO and/or Ti_2O_3
HibT(137,83)	88%	CaTiO_3 (SEM), MgAl_2O_4 (SEM, NPD), Ti-Oxide (SEM), possibly Ti_2O_3
Hib9(44,43)	70%	CaTiO_3 (SEM), MgAl_2O_4 (NPD)
HibE(98,91)	86%	CaTiO_3 (SEM), MgAl_2O_4 (NPD)

Note: [†]The %Ti in hibonite was based on the proportion of Ti in the ideal hibonite stoichiometry vs. that in the hibonite produced.

Due to the stability of Al_2O_3 (e.g. Hofmeister *et al.*, 2004) and MgAl_2O_4 (e.g. Vázquez *et al.*, 2003) Ti-bearing impurities are inevitable, even at low Ti-concentrations, and thus also a Ca-bearing phase. The Ti-oxide impurities in the Ti^{3+} -bearing samples were difficult to verify by electron microprobe as the Ti-oxide stoichiometry was controlled by the stipulated valence state of Ti, and other cations were not present in order to better constrain the stoichiometry. Peaks just above the background in the XRD data of Hib5D(33,0) suggested the presence of TiO. The gradation in colour would be consistent with the presence of TiO, possibly due to more reducing conditions caused by the shielding of the powder pellet by the graphite holders. This would account for the blue-coloured hibonite in the areas exposed to the gas and the grey, Ti-O-bearing areas adjacent the graphite mount. The formation of Ti_2O_3 , violet in colour, would be consistent with the colour gradation between grey (shielded areas) and light blue (surface) in the Ti-rich hibonite samples, particularly HibT(137,83).

3.5 Chapter summary

Five Ti-bearing Ti-CMAS glass compositions were prepared over 17 log units in fO_2 in a vertical gas-mixing furnace with the fO_2 controlled by mixtures of CO_2 , CO and Ar in preparation for Ti K-edge XANES spectroscopy. An AD composition series was similarly prepared for EPR spectroscopy and an AD+Fo composition was prepared under five fO_2 conditions with a range of 13 log units in fO_2 for XPEEM studies. The glasses were colourless when equilibrated under oxidising conditions, with the colour deepening to pinky-purple as the conditions became more reducing, indicating an increase in the Ti^{3+} content. The bulk composition was as expected from the ideal stoichiometry, with 1 wt% TiO_2 . The EPR signal intensities of the graphite-mounted EPR series samples were less than that expected, suggesting the presence of Ti in a non-paramagnetic, reduced form (Ti^0 , Ti^{2+}). The EPR samples were optically different to the XANES sample series, containing numerous high backscatter co-efficient “specks”, which were scarce in the XANES samples prepared under equivalent conditions.

Nine synthetic hibonite compositions were prepared, with a range from 0-100% $Ti^{3+}/\Sigma Ti$. The Ti^{4+} hibonites were white in colour, whereas the Ti^{3+} -bearing hibonite samples were blue $\pm$ grey in colour. Six of the hibonite samples were compositionally well defined and distinct from one another, having TiO_2 ranges of 2-3 wt% TiO_2 per sample. The three remaining samples (or a portion thereof) had a wider range in TiO_2 content (~ 5 wt% TiO_2). Trace amounts of impurities such as Al_2O_3 , $MgAl_2O_4$, $CaTiO_3$ and Ti-oxide (possibly TiO and/or Ti_2O_3) were noted in the hibonite samples, however, mass-balance calculations show the majority of the initial Ti content entered the hibonite phase, particularly for the <1 Ti pfu mixed-valent hibonites ($>96\%$ initial Ti in hibonite).

4 Characterisation of meteoritic hibonites

4.1 Synopsis

Hibonite is found within calcium aluminium inclusions (CAIs) within undifferentiated meteorites. CAIs are dated to be the oldest material in the Solar System. Many CAIs have undergone reprocessing subsequent to their formation, and different classification schemes have been suggested to describe CAIs and hibonite based on petrography and/or mineral chemistry. Fifteen hibonite-bearing CAIs which represent four meteorite groups have been characterised as preparation for an X-ray absorption spectromicroscopy study of the $\text{Ti}^{3+}/\Sigma\text{Ti}$ ratios within these CAIs.

Blue hibonites with 6-8 wt% TiO_2 are found within two Type A CAIs from the unique Acfer094 carbonaceous chondrite that formed by direct condensation from the nebula gas. Greenish-blue hibonites within once molten CAI are found in a Type A CAI from the CR2 El Djouf001 carbonaceous chondrite and contain 6 wt% TiO_2 . Seven CAIs from the CM2 Murchison carbonaceous chondrite contain hibonite with 0 – 8 wt% TiO_2 and some also contain phyllosilicates, signifying that they have experienced low temperature alteration processes. Finally, six CAIs from R-type chondrites have hibonites containing 0 – 5 wt% TiO_2 , and may contain ilmenite and Fe,Zn-spinels, which are indicative of a period of extensive alteration.

4.2 Introduction

4.2.1 Background to calcium aluminium inclusions

Calcium aluminium inclusions (CAIs) are one of the five main components within chondritic meteorites (Figure 4-1). They may be 10 μm – 2 cm in size, and dated at 4.6 Ga are the oldest material in the Solar System (Amelin, 2002). The CAI mineral assemblages, rich in the refractory elements Ca, Al and Ti, are modelled to be the first minerals to condense from a gas having a solar composition (Lodders, 2003). Mineralogy, petrography, composition and isotopic systematics reveal a complex CAI formation history, involving processes such as condensation (Grossman, 1972; Simon *et al.*, 2002), evaporation (Ireland *et al.*, 1992) and melting (Beckett and Stolper, 1994; Ireland *et al.*, 1988). Many CAIs show evidence for reprocessing, although they are still thought to preserve pre-solar

signatures (e.g. Ireland *et al.*, 1991). Most CAIs are ^{16}O -rich and some from the CV3 chondrites contain evidence of the short-lived radionuclide ^{10}Be , suggesting that CAIs formed in a restricted area close to the proto-Sun (MacPherson, 2003). The period of CAI formation was believed to be short, on the order of 0.5 Ma (Makide *et al.*, 2009), and 2.5 Ma before chondrules began to form (Amelin, 2002, 2004; Krot *et al.*, 2006; Makide *et al.*, 2009). CAIs were then isolated from the place of formation, possibly relocated to the chondrule forming region (1-4 AU, Russell *et al.*, 2005; Scott and Krot, 2003) where some underwent a degree of reprocessing (e.g. Krot *et al.*, 2006) before incorporation into parent bodies.

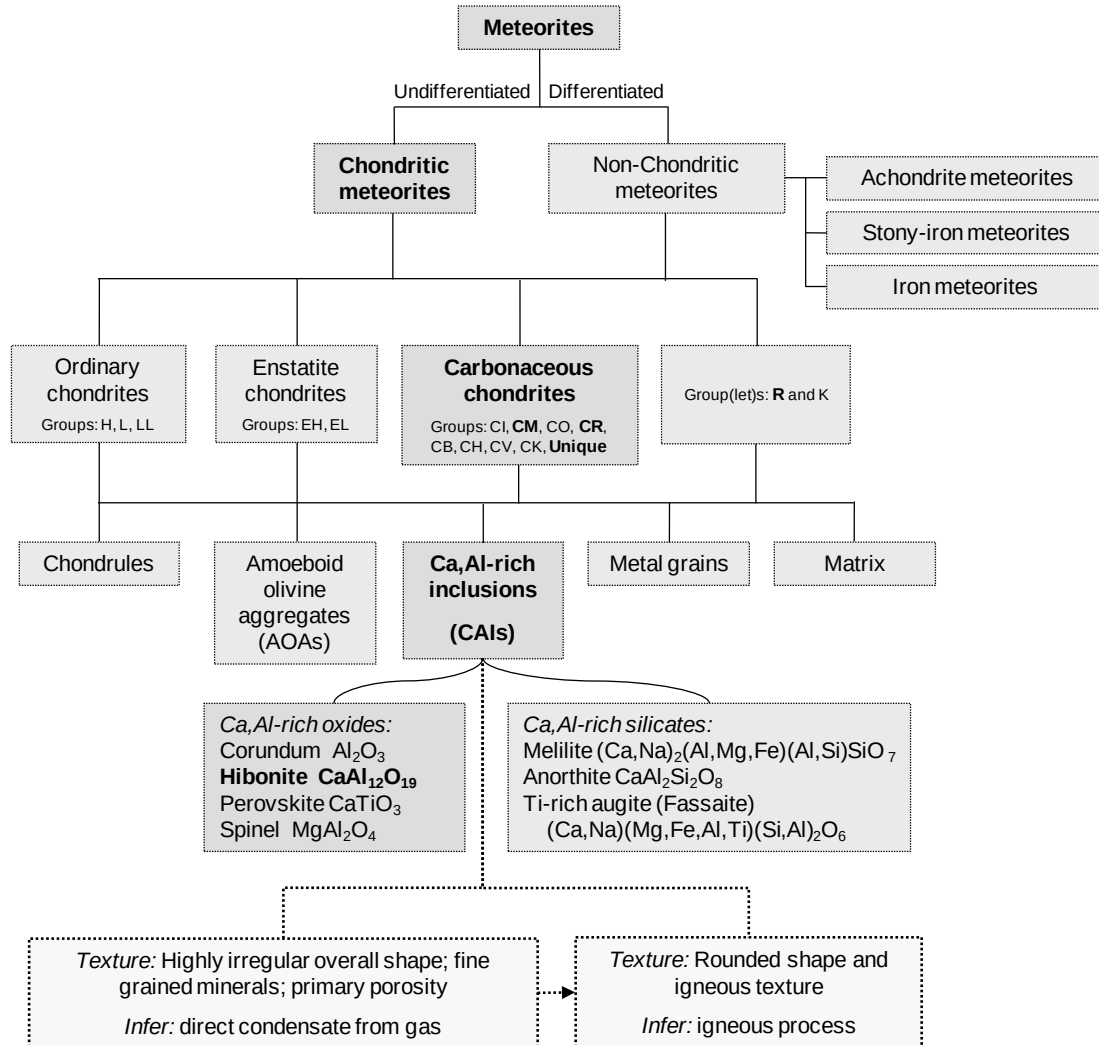


Figure 4-1 Schematic of meteorite nomenclature, with an emphasis on the chondritic meteorites and their components. The meteorite groups and meteoritic components represented in this study are highlighted in bold. This schematic is based on reviews by Krot *et al.* (2003), Scott and Krot (2003), MacPherson (2003) and Russell (2007).

4.2.2 CAI and hibonite classification schemes

The CV3 Allende meteorite fall in 1969 provided a large volume of material for analysis just as the planetary science community was preparing for the return of extraterrestrial samples from the NASA space missions (Davis, 2003). The CAI classification schemes subsequently developed during these investigations are still extensively used within the literature.

Three CAI groups were defined based on petrography, with Type A being pyroxene-poor and melilite-rich; Type B, pyroxene-rich; and Type C, anorthite-bearing (Grossman, 1975). Further studies split the Type A CAIs into two groups, such that CAIs with irregular perimeters and mineral aggregates were referred to as “fluffy” Type A, and those with igneous textures are referred to as “compact” Type A (Grossman, 1981).

An alternative classification scheme was developed using the REE patterns measured within CAIs, for which six distinctive signatures were identified (see summary by Ireland *et al.*, 1988). Hibonites characteristically have Group II or Group III REE signatures, with Group II REE patterns depleted in Eu and Yb (volatile REEs) and Er and Lu (refractory REEs), whereas Group III REE patterns are smooth and convex with heavy REE depletion.

Most studies refer to the Allende petrographic groupings, although meteorite-specific petrographic groups have also been developed (e.g. Rout and Bischoff, 2008) in order to account for variations in size, abundance and mineralogy of CAIs within different meteorite groups. For example, some CAIs in Acfer094 contain melilite (Krot *et al.*, 2004), and those in El Djouf001 contain grossite (Weber and Bischoff, 1994), whereas those in the Murchison meteorite contain very little melilite and grossite (MacPherson, 2003).

Extensive studies have been performed on hibonite-bearing CAIs from the CM2 Murchison meteorite (MacPherson, 2003) during which the CAIs were divided into five groups based on hibonite morphology and mineral associations (Ireland, 1988, 1990; Ireland *et al.* 1988, 1991). PLACs are PLATy Crystal fragments of hibonite; SHIBs are Spinel-HIBonite-perovskite CAIs; BAGs are rare, spinel-free Blue pleochroic AGgregates of hibonite grains; and Glass Spherules are hibonites with glassy fragments. The isotopic signatures and REE patterns of the hibonites within these groups are characteristic and have been used to interpret their genesis (Table 4-1).

Table 4-1: Summary of the chemical and petrographic characteristics of the hibonite-bearing CAI groups

Type	Mineralogy /morphology	wt% TiO ₂ content	Ti and Ca isotopic compositions	Mg isotope / (²⁶ Al/ ²⁷ Al) ₀ ratio	REE patterns	Process of formation
BAGs	Pleochroic blue hibonite plates	5.1-6.5	Large anomalies	Mass fractionated ²⁶ Mg	Group II (low abundance)	Condensate, then distillation
Glass spherule	Hibonite with glass	1.5-2.3	Large anomalies	Low	Variable	Melting ±distillation
PLAC	Platy hibonite crystals	0.5 - 2.0	Large anomalies	Low	Group III	First to form: condensate / distillation
HAL-type (FUN)	Hibonite crystals	<0.2	Mass fractionated	Low	Depleted Ce, Eu, Yb	Distillation
SHIB	Bladed hibonite crystals in spinel with perovskite	0.5 – 9.0 (variable within grains: 0.5-5.0)	Small anomalies	5 x 10 ⁻⁵ (“canonical”)	Variable usually Group II	Formed at a later stage: condensation processes, followed by melting

Note: Data compiled from Ireland (1988, 1990), Ireland *et al.* (1988) and Ireland *et al.* (1991.)

In addition, investigations of isotopes reveal that some CAI minerals show evidence for mass-dependant Fractionation and have isotopic anomalies in distinct nuclides. These are generally referred to as FUN CAIs, or more specifically, HAL-type CAIs (e.g. Ireland *et al.*, 1991) after the well characterised FUN-type HAL CAI from the Allende meteorite, as described by Allen *et al.* (1980).

4.3 Methodology and experimental techniques

4.3.1 Background to meteoritic samples

The hibonite-bearing CAIs in this study detailed in Table 4-2. The samples provided for this study were mounted in two ways: as probe sections on glass mounts, or as grain fragments pushed into gold foils on scanning electron microprobe (SEM) stubs.

The CAIs from the R-type meteorites in this study were described by Bischoff and Srinivasan (2003), Rout and Bischoff, (2008) and Rout *et al.* (2009). The O and Mg isotopes of the Hughes030/L hibonite were reported by Bischoff and Srinivasan (2003) and Rout *et al.* (2009). The O and Mg isotope signature of CAI minerals in Hughes030/L, NWA1476/124 and NWA2446/2L were obtained by Rout *et al.* (2009).

Hibonite-bearing CAIs from the Murchison meteorite have been described by Ireland (1988, 1990) and Ireland *et al.* (1991, 1992). Blue inclusions from a crushed Murchison meteorite sample were hand-picked by Ireland (1988) and subsequently analysed for trace elements (Ireland *et al.*, 1988) and Ti, Mg and Ca isotopes (Ireland *et al.*, 1986; Ireland and Compston, 1987; Ireland, 1988, 1990). Thereafter the CAIs were extracted from epoxy resin mounts, individually crushed, and the fragments pressed into gold foil for O isotope analysis (Ireland *et al.*, 1992). The CAIs from the Murchison meteorite in this study represent each of the groups defined by Ireland (1988, 1990), namely: PLAC, SHIB, BAG, GS, HAL-type hibonites.

Table 4-2 Hibonite-bearing CAIs in this study, their host meteorite and the sample source

Meteorite	Group	CAI name (Specimen number)	Sample source
Acfer094	Unique	Acfer094/22CAI (PL93022) Acfer094/40CAI (PL93040)	A Bischoff †
El Djouf001	CR2	El Djouf001/1CAI (PL91167)	A Bischoff †
Hughes030	R3-6	Hughes030/L (PL98015)	A Bischoff and S Rout †
Murchison	CM2	7-76; 7-505; 7-753; 7-971; 7-981; 10-43 (TRI1); 7-953 (TRI2)	T Ireland ‡
NWA1476	R3	NWA1476/124 (PL02154B)	A Bischoff and S Rout †
NWA2446	R3	NWA2446/2L (PL072096) NWA2446/5L (PL07041) NWA2446/8L (PL07041) NWA2446/12 (PL04157B)	A Bischoff and S Rout †

Note: † University of Münster, Germany, Probe sections; ‡ Australian Nation University, Australia, Grain mounts.

CAIs from six meteorites are characterised in this study. The meteorites represent four meteoritic groups which are thought to have experienced different evolutionary paths.

Acfer094 has been classified as a uniquely primitive carbonaceous chondrite breccia, with a fine-grained groundmass containing abundant chondrules (1200 μm in diameter), amoeboid olivine aggregates (1900 μm in diameter) and CAIs (1200 μm in diameter) (Newton *et al.*, 1995). Acfer094 is believed to be unaltered by hydrothermal, aqueous or metamorphic processing in the parent body (Newton *et al.*, 1995).

El Djouf001, also reported as Acfer059, is a primitive, unequilibrated CR2 carbonaceous chondrite (Bischoff *et al.*, 1993). The meteorite is described as a regolith breccia and consists of chondrules (average diameters of ~ 1000 μm), dark clasts, Fe-Ni-metal and CAIs (< 300 μm in diameter) in a very fine-grained groundmass (Bischoff *et al.*, 1993; Weber and Bischoff, 1992). The abundance of CAIs is low (< 1 vol%) and they are dominantly melilite rich compact Type A (MacPherson, 2003). Most CAIs from CR2 meteorites are mineralogically pristine (Makide *et al.*, 2009), and based on the low fayalite-content of the olivine (< 3 mol%) and the presence of Fe-Ni-metal (8-10 vol%), the conditions of formation for the majority of the high-temperature components of the El Djouf001 meteorite are reported to be reducing. Phyllosilicates have, however, been reported from the matrix, which indicates that some form of low-temperature alteration has occurred, potentially in an oxidising environment (Bischoff *et al.*, 1993).

The Murchison meteorite has been classified as a CM2 carbonaceous chondrite, containing chondrules, CAIs, xenolithic fragments of two other meteorite types, and abundant mineral and chondrule fragments, all within a fine-grained groundmass (Fuchs *et al.*, 1973; MacPherson *et al.*, 1983). Phyllosilicates are reported within CAIs, chondrules and the matrix (MacPherson *et al.*, 1983; MacPherson, 2003), indicating some degree of low temperature secondary alteration (Bischoff *et al.*, 1993).

There are three different R chondrites, and within these Hughes030 is a R3-6 chondrite, whereas NWA1476 and NWA2446 are R3 chondrites (Rout *et al.*, 2009). R chondrites are considered to be gas-rich regolith breccias that contain chondrules, sulphides, CAIs and mineral and chondrule fragments, all within an olivine-rich groundmass (Bischoff and Srinivasan, 2003). Many CAIs within these three meteorites contain altered regions and/or secondary minerals. In addition, the lack of Fe metal in the matrix indicates the R type meteorites experienced oxidising conditions (Rout *et al.*, 2009).

4.3.2 Sample characterisation and instrumental parameters

The probe sections were analysed optically using a Leitz DMRX microscope. Mineral chemistry and elemental maps were obtained using a JEOL 5900LV SEM with an energy dispersive spectrometer (EDS) and a SX100 Cameca electron microprobe (EMP) fitted with a wavelength dispersive spectrometer (WDS) at the Natural History Museum (NHM). The standards, peak counting times and operating conditions are detailed in Table 4-3.

Table 4-3 EDS SEM and WDS EMP calibration standards, with WDS analysing crystal (spectrometer) and peak counting times

Element	EDS SEM calibrations †		WDS EMP of Acfer094/22CAI			WDS EMP of Meteoritic samples ‡		
	TRI fragments	Thin sections	Standard	Crystal	Time (s)	Standard	Crystal	Time (s)
Ca	CaSiO ₃ (WOL)	CaSiO ₃ (WOL)	CaSiO ₃ (WOL4)	PET (Sp1)	20	CaSiO ₃ (WOL4)	PET (Sp1)	20
Al	Al ₂ O ₃ (COR)	Al ₂ O ₃ (COR)	Al ₂ O ₃ (COR)	TAP (Sp4)	20	Al ₂ O ₃ (COR4)	LTAP (Sp2)	15
Ti	TiO ₂ (RUT)	TiO ₂ (RUT)	TiO ₂ (RUT)	LPET (Sp3)	20	TiO ₂ (RUT)	LPET (Sp3)	15
Mg	Mg _{1.6} Fe _{0.4} SiO ₄ (EAG)	Mg ₂ SiO ₄ (FOR)	Mg ₂ SiO ₄ (FOR)	LTAP (Sp2)	20	Mg ₂ SiO ₄ (FOR)	LTAP (Sp2)	15
Na	-	NaAlSi ₂ O ₆ (JAD)	NaAlSi ₂ O ₆ (JAD)	LTAP (Sp2)	10	-	-	-
Si	-	Mg _{1.6} Fe _{0.4} SiO ₄ (EAG)	Mg ₂ SiO ₄ (FOR)	TAP (Sp4)	20	CaSiO ₃ (WOL4)	LTAP (Sp2)	15
S	-	ZnS (ZNS)	-	-	-	BaSO ₄ (BAR2)	LPET (Sp3)	15
Cr	-	-	-	-	-	FeCr ₂ O ₄ (CRO2)	LPET (Sp3)	15
Fe	-	Fe ₂ SiO ₄ (FAY)	-	-	-	Fe ₂ SiO ₄ (FAY)	LLIF (Sp5)	60
V	V (VV2)	V (PVV)	-	-	-	-	-	-

Notes: Operating conditions: EDS SEM (HV, 20 kV, 2 nA); WDS EMP (10 kV, 20 nA). Limits of detection detailed in Appendix B.2.1. † Murchison CAIs ‡ Acfer094/40CAI, El Djouf001/1CAI, Hughes030/L, NWA1476/124 and NWA2446/5L

Microprobe analyses of the CAI minerals often returned poor totals or contaminated analyses due to the small grain size of many CAI minerals (e.g. <3 x 15 µm) with respect to the excitation volume of the electron beam, as was also reported by Weber and Bischoff (1994) and Bischoff and Srinivasan (2003). In this case, average mineral chemistries with totals of 98 – 102% are included in Section 4.4.1 (hibonites) and Appendix C.2.1 (non-hibonite phases). Individual analyses are detailed in Appendix C.2.2. For phases with totals of 98 – 103% the stoichiometry of the phases were calculated and included in the text where relevant.

The Murchison CAI fragments were all <40 µm in longest dimension. Multiple fragments of the same CAI were mounted on a single gold foil, as indicated by circles in Figure 4-2. As data for only one hibonite-containing fragment from each CAI is presented in this thesis, the nomenclature in this text uses the name of the CAI as described by Ireland (1988) and Ireland *et al.* (1992). TRI1 contained 65 grain fragments from 18 different CAIs, of which 23 fragments were found to be hibonite-bearing. TRI2 contained 103 grains from 13 different CAIs, and 19 fragments were found to be hibonite-bearing.

The compositions of the Murchison CAI grain-fragments were determined using the JEOL 5900LV EDS SEM at the NHM, with the operating conditions detailed in Table 4-3. Due to the fragility of the mounts and the need to study them with other techniques, they were not carbon coated. The irregular, non-conductive surface resulted in low analytical totals which were normalised to 100%. Nevertheless, they were similar to those reported in literature, as summarised in Table 4-4.

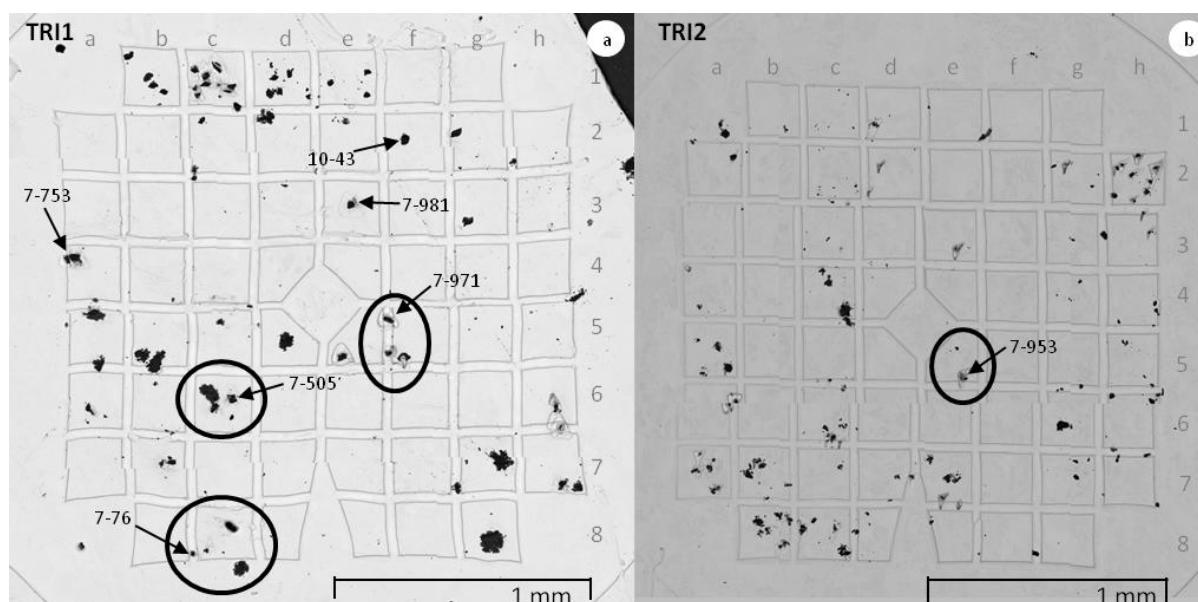


Figure 4-2 Backscatter electron image (BEI) of (a) the TRI1 mount and (b) the TRI2 mount. Clusters of grain-fragments (black) were located using the imprinted grid on the gold foil. Grain-fragments from a single CAI are circled, with the grains analysed by XANES spectroscopy are indicated by an arrow.

Table 4-4 Major element compositions of hibonite from grain-mounted Murchison CAIs (published and EDS SEM data)

Sample	Oxide wt% (standard deviation)						Ref. †	Stoichiometry
	CaO	Al ₂ O ₃	TiO ₂	MgO	FeO	Total		
7-76	8.5	88.8	1.8	0.9	<lld	100.0	1	Ca _{1.02} Al _{11.69} Ti _{0.15} Mg _{0.15} O ₁₉
7-505	8.5	83.3	5.5	2.8	<lld	100.0	2	Ca _{1.01} Al _{10.95} Ti _{0.46} Mg _{0.46} O ₁₉
7-753	8.6	88.5	1.9	0.9	nd	99.8	3	Ca _{1.03} Al _{11.68} Ti _{0.16} Mg _{0.14} O ₁₉
7-953	8.2	81.6	6.5	3.3	0.2	99.9	3	Ca _{0.99} Al _{10.88} Ti _{0.56} Mg _{0.56} O ₁₉
7-971	8.4	91.5	0.2	0.1	nd	100.0	3	Ca _{1.00} Al _{12.02} Ti _{0.02} Mg _{0.02} O ₁₉
7-981	8.5	89.7	1.2	0.7	nd	100.0	3	Ca _{1.01} Al _{11.78} Ti _{0.10} Mg _{0.12} O ₁₉
10-43	8.5	82.1	6.4	2.9	0.1	99.9	3	Ca _{1.03} Al _{10.93} Ti _{0.55} Mg _{0.48} O ₁₉

Note: † References: 1: This study, 1 EDS SEM analysis; 2: This study 2 EDS SEM analyses; 3: Ireland (1988). See Appendix C.2.2 for individual analyses and more detail.

4.4 Results

4.4.1 Description of hibonite-bearing CAIs

4.4.1.1 Unique Acfer094 meteorite

Two CAIs (Acfer094/22CAI and Acfer094/40CAI) from the unique Acfer094 carbonaceous chondrite are shown in Figure 4-3. Both CAIs have irregular perimeters and similar mineral assemblages, having a hibonite-rich core intergrown with melilite (Ca_{1.9}Al_{2.0}Si_{1.0}O₇), spinel (MgAl₂O₄) ±perovskite (CaTiO₃). The hibonite grains in both CAIs are blue in plane polarised light (ppl) and strongly pleochroic, and the pores between the hibonite grains appear to be primary, particularly for Acfer094/22CAI. The CAI cores are surrounded by a 14–45 µm wide melilite mantle (Ca_{2.0}Al_{1.9}Mg_{0.1}Si_{1.0}O₇) and a thinner Mg-rich silicate outer rim, the chemistry of which is diopside.

Acfer094/22CAI is 423 µm in the longest dimension and appears to be an irregularly shaped

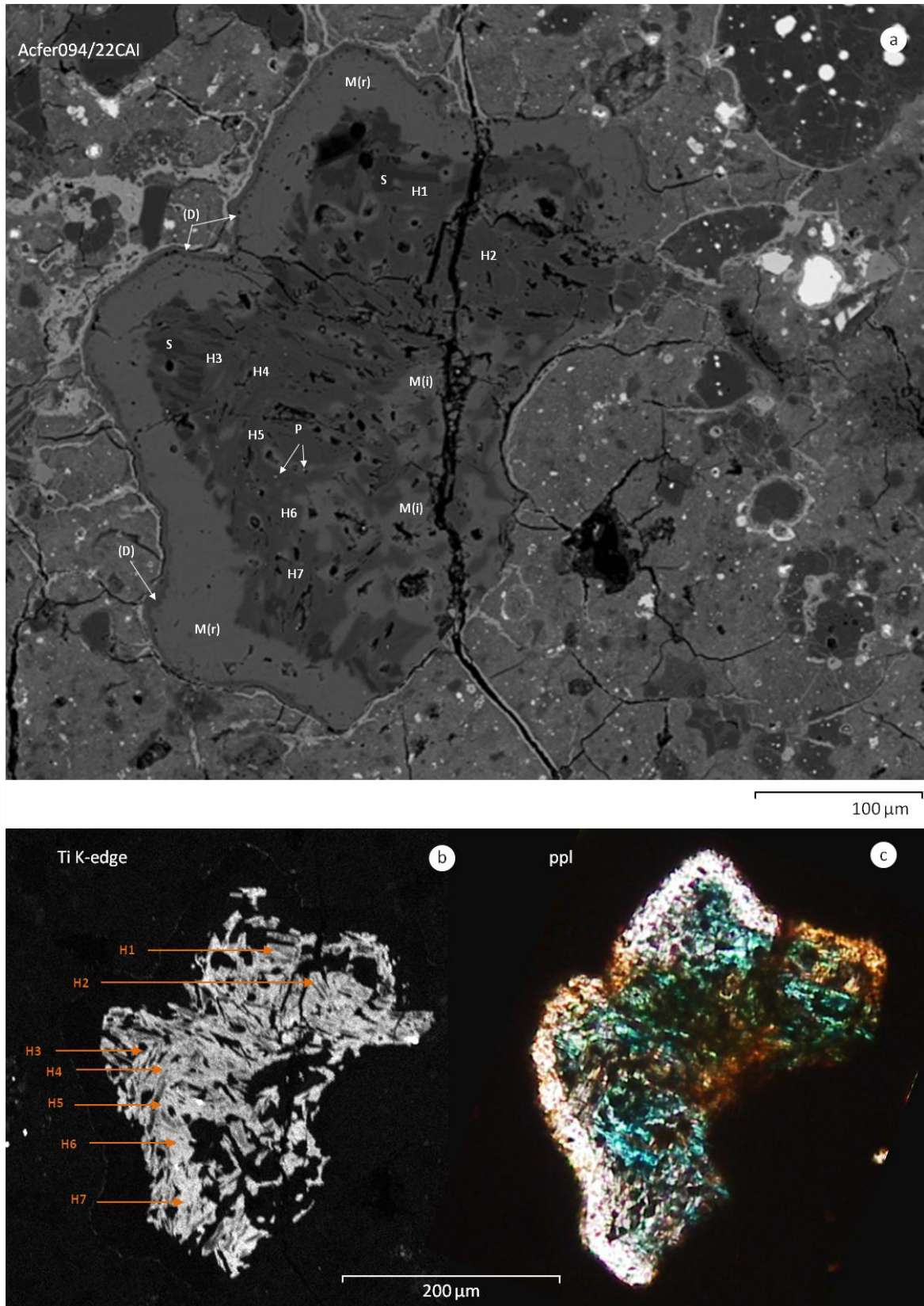


Figure 4-3 (a) BEI of Acfer094/22CAI showing an irregularly shaped perimeter, hibonite-rich core $\pm$ melilite (M(i)) and a wide melilite mantle (M(r)) and Mg-silicate rim (D); (b) Ti element map showing variable Ti content with the H-regions correspond to those marked in “(a)”; (c) The hibonite grains are blue under ppl.

fragment from a larger object. The hibonite grains are bladed, with the largest having dimensions on the order of $6 \times 28 \mu\text{m}$. Melilite and minor spinel are unevenly distributed throughout the CAI, and perovskite is rarely observed. Melilite appears to be infilling spaces between the hibonite blades in some regions within the CAI, and isolated spinel grains are intergrown with hibonite close to the melilite mantle. The MgO content of the hibonites vary across the CAI, ranging from 2.0 to 3.6 wt% MgO, and the average TiO_2 content of hibonites are $6.2 \pm 0.3 \text{ wt}\%$ TiO_2 (Table 4-5) with upper and lower limits of 3.5 and 7.2 wt% TiO_2 (Appendix C.2.2). The Ti elemental map of Acfer094/22CAI (Figure 4-3b,c) shows where hibonite is located within the CAI as hibonite is the main Ti-bearing phase. The Ti intensity is variable, and it appears that the hibonite grains in the melilite-rich region (H4, H6 and H7) are more Ti-rich than the hibonite in the melilite-poor regions (H1 and H2). This is in agreement with the calculated stoichiometry for the grains in these regions (Table 4-6).

Acfer094/40CAI is sub-rounded in shape and $170 \mu\text{m}$ in diameter, with anhedral $10 \times 13 \mu\text{m}$ hibonite grains in the core (Figure 4-4). The CAI core is also melilite-rich and contains coarse grained perovskite grains ($<5 \mu\text{m}$). These perovskite grains are often located on the boundary between hibonite and melilite. A near-continuous $30 \mu\text{m}$ wide spinel-rich region with fine-grained perovskite is located just within the melilite mantle. The Ti contents of the hibonite grains in Acfer094/40CAI were relatively constant ($7.6 \pm 0.4 \text{ wt}\%$ TiO_2), however, the MgO content of these hibonites varied between Mg-poor grains (3.0 wt% Mg) close to the spinel rim (H3, H4) compared to relatively Mg-rich hibonite (3.9 wt% Mg) on the rim (H2) and one in the central region (H1).

Both Acfer094/22CAI and Acfer094/40CAI are considered to be fluffy Type A CAIs using the Grossman (1975) nomenclature, with a mineral assemblage consistent with the SHIB CAIs using the classification scheme derived by Ireland (1988). The SHIB classification is also supported by the variable TiO_2 contents in hibonite from Acfer094/22CAI.

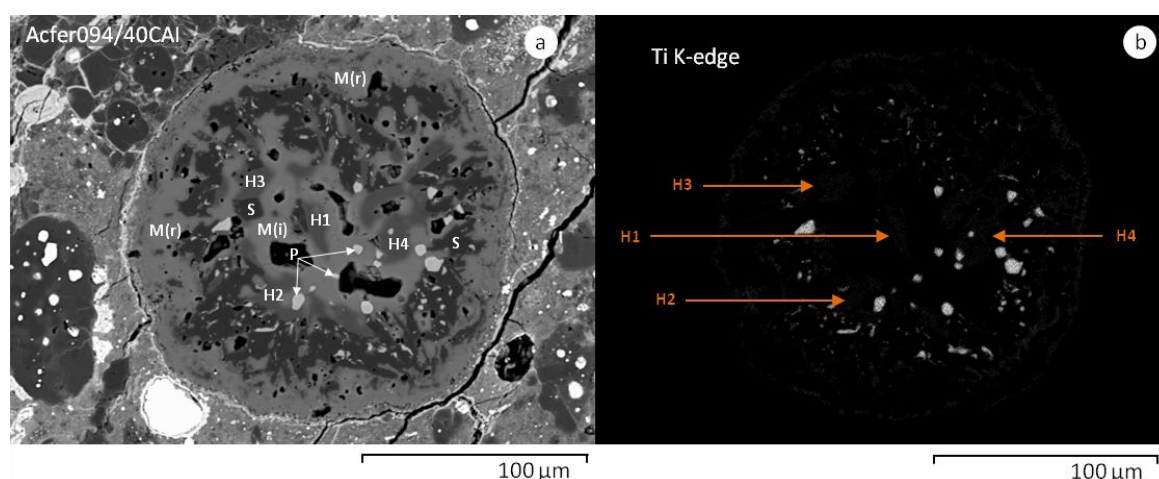


Figure 4-4 (a) BEI of Acfer094/40CAI showing anhedral hibonite (H) with melilite (Mi) infilling the pores. The core is surrounded by a spinel-rich zone (S) and melilite mantle (M(r)); (b) Ti element map showing Ti-bearing hibonite and coarse-grained perovskite in the core, with fine-grained perovskite in the spinel-rich region. The H-regions correspond to those marked in “(a)”.

Table 4-5 Average compositions of hibonites mounted in probe sections

Sample	Oxide wt% (standard deviation)							#	Stoichiometry
	CaO	Al ₂ O ₃	TiO ₂	MgO	FeO	SiO ₂	Total		
Acfer 094/22CAI	8.6 (<0.1)	83.5 (0.4)	6.2 (0.3)	3.1 (0.1)	nd	0.4 (0.1)	101.8 (0.2)	3	Ca _{1.02} Al _{10.90} Ti _{0.51} Mg _{0.51} Si _{0.04} O ₁₉
Acfer 094/40CAI	8.7 (0.1)	79.8 (0.7)	7.5 (0.4)	3.4 (0.4)	<lld	<lld	99.7 (0.8)	5	Ca _{1.06} Al _{10.69} Ti _{0.64} Mg _{0.58} O ₁₉
El Djouf 001/1CAI †	8.8 (0.2)	81.7 (0.8)	5.8 (0.7)	3.1 (0.3)	0.1 (0.1)	0.6 (0.2)	100.1 (0.6)	4	Ca _{1.06} Al _{10.86} Ti _{0.49} Mg _{0.51} Si _{0.06} Fe _{0.01} Cr _{0.01} O ₁₉
Hughes 030/L ‡	8.7 (0.1)	91.8 (0.3)	0.2 (0.1)	<lld	0.4 (0.1)	<lld	101.2 (0.4)	8	Ca _{1.03} Al _{11.93} Ti _{0.01} Fe _{0.04} O ₁₉
NWA1476/124 ‡	8.7 (0.1)	87.5 (0.2)	2.2 (0.2)	1.0 (0.1)	0.3 (0.1)	0.1 (0.1)	99.9 (0.3)	5	Ca _{1.04} Al _{11.57} Ti _{0.19} Mg _{0.17} Fe _{0.03} Si _{0.01} O ₁₉
NWA2446/2L ‡	8.6 (0.1)	88.6 (0.5)	1.4 (0.1)	0.6 (0.1)	0.5 (0.1)	<lld	99.6 (0.6)	5	Ca _{1.03} Al _{11.73} Ti _{0.12} Mg _{0.10} Fe _{0.05} O ₁₉
NWA2446/5L	8.5 (0.1)	88.3 (0.2)	2.6 (0.1)	1.3 (0.0)	0.6 (0.1)	0.1 (0.1)	101.5 (0.2)	4	Ca _{1.00} Al _{11.50} Ti _{0.22} Mg _{0.22} Fe _{0.06} Si _{0.01} O ₁₉
NWA2446/8L	8.2 (0.3)	81.0 (1.6)	5.0 (0.9)	2.8 (0.5)	1.3 (0.4)	<lld	98.4 (0.3)	3	Ca _{1.01} Al _{11.01} Ti _{0.43} Mg _{0.48} Fe _{0.13} O ₁₉
NWA2446/12 †	8.3 (0.1)	82.9 (2.7)	4.7 (1.5)	2.5 (0.9)	0.8 (0.2)	<lld	99.8 (1.4)	5	Ca _{1.01} Al _{11.04} Ti _{0.40} Mg _{0.42} Fe _{0.08} O ₁₉

Note: WDS EMP and EDS SEM analyses (standard deviation in parentheses). # = number of analyses. nd = not determined; lld = lower limit of detection. See Appendix C.2.2 for individual analyses. † SiO₂ and Cr₂O₃ were only detected in El Djouf001/1CAI (0.1 wt% Cr₂O₃); NWA2446/12 (0.4 wt% V₂O₅). ‡ The mineral compositions of hibonite-bearing CAIs from Hughes030/L and NWA1476 and NWA2446 are comparable to those in literature, however, trace Cr₂O₃ was noted by Rout and Bischoff (2008) in Hughes030/L hibonite (0.3 wt%) and NWA1476/124 hibonite (0.2 wt%); and Rout *et al.* (2009) reported trace NiO in NWA2446/2L hibonite (0.2 wt%).

Table 4-6 Variation in hibonite stoichiometry within Acfer094/22CAI and Acfer094/40CAI

Acfer094/22CAI		Acfer094/40CAI	
Region	Stoichiometry	Region	Stoichiometry
H1*	Ca _{1.1} Al _{11.2} Ti _{0.4} Mg _{0.4} O ₁₉	H1	Ca _{1.1} Al _{10.5} Ti _{0.7} Mg _{0.7} O ₁₉
H2*	Ca _{1.1} Al _{11.2} Ti _{0.3} Mg _{0.3} O ₁₉	H2	Ca _{1.1} Al _{10.7} Ti _{0.6} Mg _{0.7} O ₁₉
H3	Ca _{1.0} Al _{11.1} Ti _{0.4} Mg _{0.4} O ₁₉	H3	Ca _{1.1} Al _{10.7} Ti _{0.7} Mg _{0.6} O ₁₉
H4	Ca _{1.0} Al _{10.9} Ti _{0.5} Mg _{0.5} O ₁₉	H4	Ca _{1.1} Al _{10.8} Ti _{0.6} Mg _{0.5} O ₁₉
H5*	Ca _{1.0} Al _{11.0} Ti _{0.5} Mg _{0.5} O ₁₉	Average	Ca _{1.1} Al _{10.7} Ti _{0.6} Mg _{0.6} O ₁₉
H6	Ca _{1.0} Al _{10.9} Ti _{0.5} Mg _{0.5} O ₁₉		
H7*	Ca _{1.0} Al _{10.7} Ti _{0.6} Mg _{0.6} O ₁₉		
Average	Ca _{1.0} Al _{10.9} Ti _{0.5} Mg _{0.5} O ₁₉		

Note: * Stoichiometry of the hibonite blades were calculated from analyses with 98-103 wt% totals (analyses >102 wt% are excluded from the average detailed in Table 4-5).

4.4.1.2 CR2 El Djouf001 meteorite

One melilite-rich compact CAI from El Djouf001, about $84 \times 476 \mu\text{m}$ in size was included in the study. A melilite groundmass encloses perovskite, anhedral spinel ($<5 \mu\text{m}$) and sub- to euhedral hibonite grains ($<3 \times 15 \mu\text{m}$). The hibonite grains ($\text{Ca}_{1.1}\text{Al}_{10.9}\text{Ti}_{0.5}\text{Mg}_{0.5}\text{Si}_{0.1}\text{O}_{19}$; 5.8 wt% TiO_2 ; Table 4-5) are greenish-blue in plane polarised light and clustered in a region of $<80 \mu\text{m}^2$ (Figure 4-5). Hibonite grain H2 had variable TiO_2 contents ranging from 5.1 to 6.1 wt% TiO_2 . El Djouf001/1CAI is a compact Type A CAI, similar in form to the blocky melilite-rich Type A CAIs from the Allende meteorite (Grossman, 1975). The CAI may be classified as a SHIB as it has spinel, perovskite, an igneous texture and hibonite with variable TiO_2 contents.

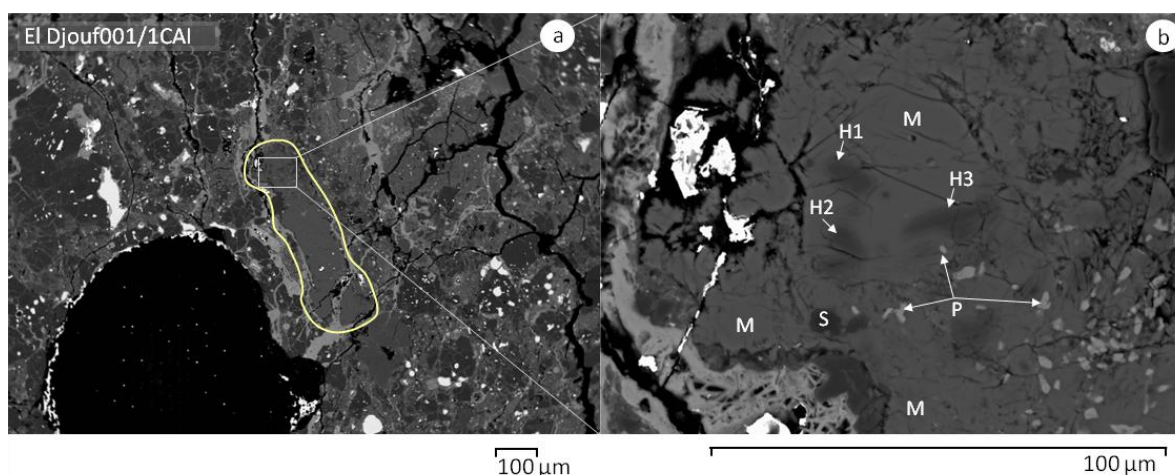


Figure 4-5 (a) BEI of the El Djouf001/1CAI with the blocky CAI circled so the sharp contacts between the CAI and meteorite matrix is still visible; (b) BEI of the hibonite-rich region of the El Djouf001/1CAI CAI showing sub- to euhedral hibonite grains (H) in a melilite groundmass (M) that also encloses spinel (S) and perovskite (P).

4.4.1.3 R-type meteorites: (1) Hughes030; (2) NWA1476; (3) NWA2446

Hibonite-bearing CAIs from three R-type meteorites are included in the study, one from Hughes030, one from NWA1476 and four from NWA2446. The petrographic descriptions from this study are augmented by the original descriptions by Rout and Bischoff (2008).

The Hughes030/L CAI was described by Rout and Bischoff (2008) as a simple concentric spinel-rich CAI. Figure 4-6 shows that the irregularly shaped CAI has large, well-cleaved, platy hibonite grains located mainly on the CAI perimeter. These hibonites are very Ti-poor, with less than 0.2 wt% TiO_2 detected. Indeed, the average mineral chemistry (Table 4-5) shows them to be close to ideal ($\text{Ca}_{1.0}\text{Al}_{11.9}\text{O}_{19}$). The CAI also contains Fe,Zn-spinel and secondary alteration minerals. Colour variation in some of the Hughes030/L hibonite grains has been reported by Rout and Bischoff (2008), with some grains orange in colour and others having a blue core and thick, colourless rim, although the colour variation was not observed in this study.

Hughes030/L is difficult to assign to the classical CAI groups of Grossman (1975) using the

mineral assemblages described. The primary mineral assemblage was probably a Type A CAI as the porosity in Hughes030 is thought to be due to the leaching out of melilite (Bischoff and Srinivasan, 2003). The irregular perimeter would be consistent with this classification. Using the Ireland (1988) nomenclature simple concentric spinel-rich CAIs, such as Hughes030/L, have features consistent with SHIB CAIs (Rout and Bischoff, 2008), although the large platy grains are also similar to PLAC CAIs. Irrespective of its mineralogy and grain morphology, Hughes030/L is classified as a HAL-type CAI based on Mg and O isotope data (Rout *et al.*, 2009).

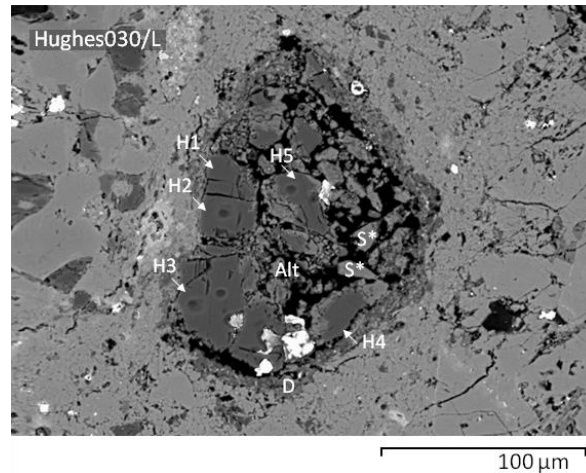


Figure 4-6 BEI of Hughes030/L, an irregularly shaped CAI with five main hibonite grains (H) predominantly on the perimeter, intergrown with Fe-Zn-spinel (S*). The CAI has large altered zones (Alt) and is surrounded by a diopside rim (D).

The NWA1476/124 CAI has been described as a fassaite-rich spherule (Rout and Bischoff, 2008) and is distinct from others within this study as it has a smooth, sub-circular perimeter and no rim sequence (Figure 4-7). The pyroxene groundmass of the CAI is zoned with respect to Ti, ranging from fassaite (4.4 wt % TiO₂) to Ti-poor augite (0.1 wt% TiO₂), as detailed in Appendix C.2.1. Three greenish-blue sub- to euhedral hibonite grains (Ca_{1.0}Al_{11.6}Ti_{0.2}Mg_{0.2}O₁₉; 2.2 wt% TiO₂, Table 4-5) were clustered together on one side of the CAI in association with perovskite. Petrographically the NWA1476/124 CAI is a Type B CAI, similar to those from the CV meteorites, but may also be classified as a glass spherule (Rout and Bischoff (2008).

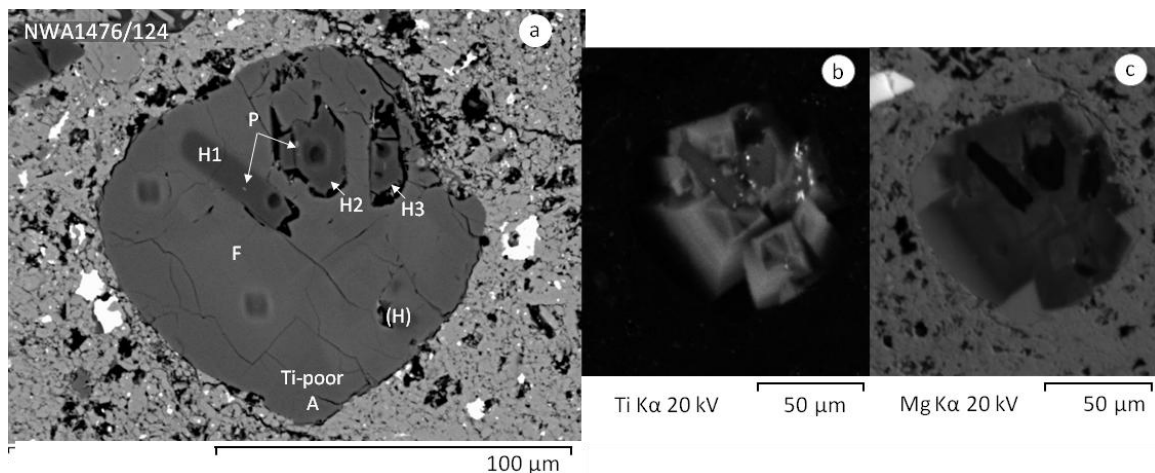


Figure 4-7 (a) BEI of the sub-circular NWA1476/124 CAI with three sub- to euhedral hibonite grains (H) in association with perovskite (P) within a fassaite (F) and Ti-poor augite matrix (A). (b,c) Ti and Mg K-edge elemental maps with zoning evident in the pyroxenitic groundmass of the CAI.

NWA2446/2L and NWA2446/8L are simple concentric spinel-rich CAIs (Rout and Bischoff, 2008), with a sub-circular shape and irregular perimeters. The hibonite in the core of NWA2446/2L is bladed ($\text{Ca}_{1.0}\text{Al}_{11.7}\text{Ti}_{0.1}\text{Mg}_{0.1}\text{O}_{19}$; 1.4 wt% TiO_2), whereas that in the core of NWA2446/8L is anhedral ($\text{Ca}_{1.0}\text{Al}_{11.0}\text{Ti}_{0.4}\text{Mg}_{0.5}\text{Fe}_{0.1}\text{O}_{19}$; 5.0 wt% TiO_2) and associated with a Fe,Zn-spinel perimeter, as shown in Figure 4-8. The hibonite grains in NWA2446/2L have a slight green hue in plane polarised light. In both CAIs, the hibonite grains were interspersed with ilmenite, and the central region was surrounded by secondary minerals in a large alteration zone which, in turn, was rimmed by diopside.

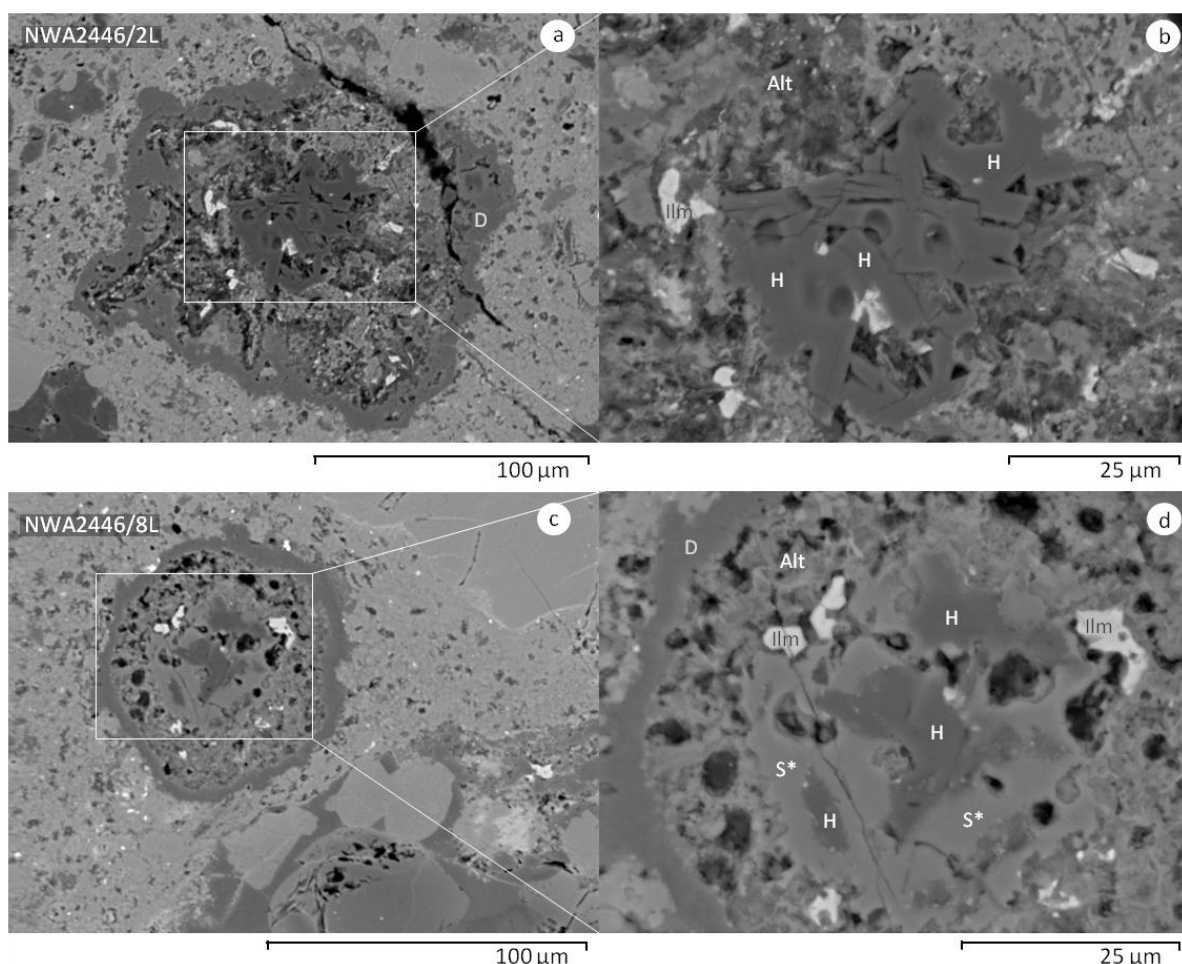


Figure 4-8 (a, b) BEI of the sub-circular NWA2446/2L with a porous, bladed hibonite core intergrown with ilmenite. The core is surrounded by a large altered zone and diopside rim forming an irregular perimeter. (c,d) BEI of the sub-circular NWA2446/8L CAI with an irregular perimeter and hibonite-rich core that is bound by Fe,Zn-spinel and ilmenite. An altered zone is rimmed by diopside. H = hibonite, D = diopside; S* = Fe-Zn spinel, Ilm = ilmenite; Alt = secondary alteration.

NWA2446/5L is classified as an Al-rich fragment and has colourless to slightly orange coloured hibonite (Rout and Bischoff, 2008). The hibonite grain ($\text{Ca}_{1.0}\text{Al}_{11.5}\text{Ti}_{0.2}\text{Mg}_{0.2}\text{Fe}_{0.1}\text{O}_{19}$; 2.6 wt% TiO_2 ; Table 4-5) has a well developed cleavage and is associated with minor Ti-poor augite (Figure 4-9).

NWA2446/12 is a complex spinel-rich CAI (Rout and Bischoff, 2008) in which the hibonite laths ($\text{Ca}_{1.0}\text{Al}_{11.0}\text{Ti}_{0.4}\text{Mg}_{0.4}\text{Fe}_{0.1}\text{O}_{19}$; 4.7 wt% TiO_2) are located in three regions on the CAI perimeter (Figure 4-9), in close association with ilmenite and Fe,Zn spinel. Al,Si-rich alteration minerals are interspersed throughout the CAI and the CAI is rimmed by diopside (Rout and Bischoff, 2008).

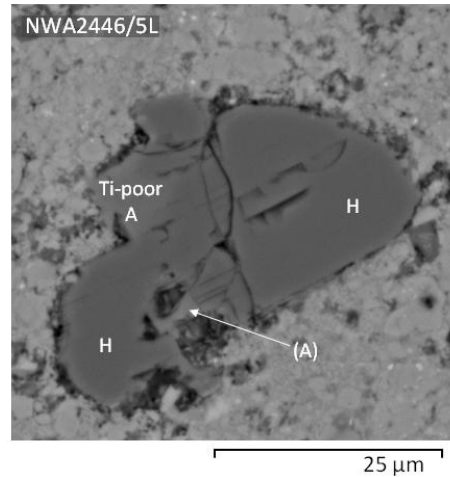


Figure 4-9 (a) BEI of NWA2446/5L, a biminerallitic CAI fragment consisting of hibonite (H) and Ti-poor augite (A).

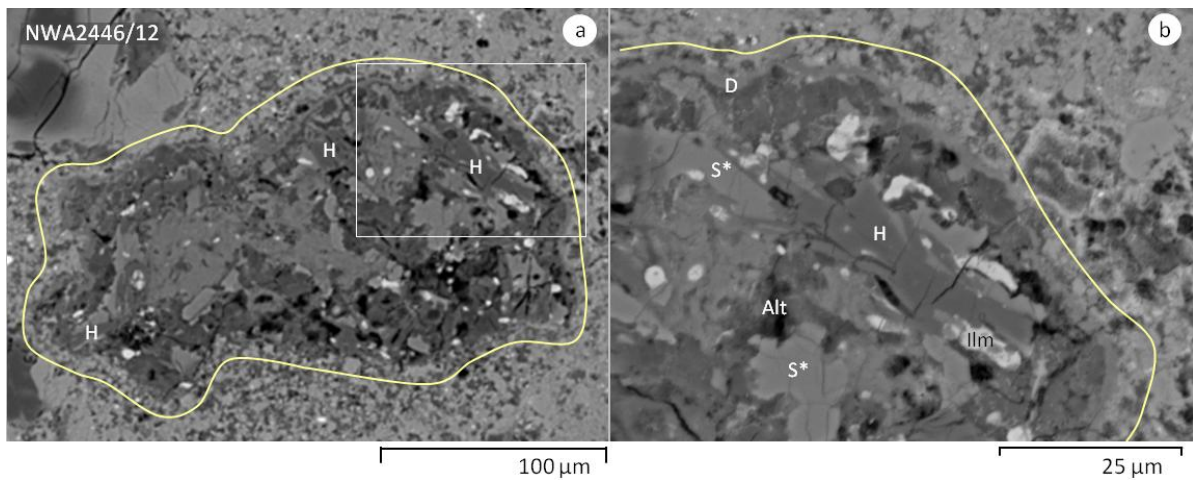


Figure 4-10 (a) BEI of the irregularly shaped, complex spinel-rich CAI NWA2446/12 CAI with the CAI outlined so as not to obscure the CAI-matrix boundary. The three distinct hibonite-rich regions are marked. (b) BEI of the region outlined “(a)” showing one group of hibonite laths intergrown with spinel (S) and ilmenite (Ilm), which are themselves interspersed with secondary alteration products. Also shown is the diopside rim (D).

As for Hughes030/L, the replacement of the primary mineral assemblages makes it difficult to classify the CAIs within NWA2446 in the manner of Grossman (1975). Rout and Bischoff (2008) suggest that the primary mineral assemblage contained melilite or anorthite, therefore the CAIs were likely to be Type A. NWA2446/2L, /8L and /12 can be classified as SHIBs (Rout and Bischoff, 2008). Indeed, hibonite cores intergrown with spinel, followed by concentric zones of spinel, Fe-silicate and finally clinopyroxene are characteristic of some SHIB-type CAIs from the Murchison meteorite. The biminerallitic CAI 2446/5L may be classified as a PLAC.

4.4.1.4 CM2 Murchison meteorite

Ireland (1988, 1990) described 37 hibonite-bearing CAIs from the Murchison meteorite and subdivided them into five groups depending on hibonite morphology, CAI mineralogy and isotopic signatures. A total of seven hibonites from the studies of Ireland (1988, 1990) were used in this investigation, including 1 PLAC, 3 SHIBs, 1 BAG, 1 glass spherule and 1 HAL-type CAI, and

backscatter electron images of the grains are presented in Figure 4-11. The mineralogy and mineral chemistry of the grain fragments were established using EDS SEM, whereas the petrography of the original CAI is summarised from Ireland (1988, 1990) and Ireland *et al.* (1988).

7-971 and 7-981 have hibonite morphologies typical of the PLAC group, namely large, platy grains 70 – 150 μm in the longest dimension. They were colourless to light-blue in colour and optically uniform, although SEM analysis by Ireland (1988) revealed the presence of perovskite films. 7-971 had mass fractionated Mg isotopes and was therefore re-classified as a HAL-type CAI (Ireland *et al.*, 1992), although both CAIs are classified as Type A using the nomenclature of Grossman (1975).

The three CAIs 7-76, 7-953, 7-505 possess mineral assemblages and hibonite morphology characteristic of the SHIB group. 7-76 is a compact aggregate comprising hibonite blades (<10 x 30 μm), anhedral perovskite inclusions (<10 μm) and spinel, rimmed by a Fe-silicate, clinopyroxene and spinel assemblage. 7-953 is an aggregate of hibonite blades (3 x 15 μm) and perovskite grains (1-2 μm) with minor spinel, surrounded by a rim of Fe-silicate. 7-505 is a broken fragment with six blades of hibonite (10 x 30 μm) interspersed with spinel (Ireland, 1990). These three CAIs are classified as Type A.

CAI 10-43 contained BAG-type hibonite grains with small euhedral perovskite grains (<2 μm) between the hibonite blades (Ireland *et al.*, 1988). SEM analysis of the 10-43 grain-fragment revealed a Mg-rich grain with a stoichiometry of MgAl_2O_4 , although BAGs are meant to be spinel-free (Ireland, 1988). This CAI is classified as Type A.

CAI 7-753 differs from the other Murchison CAI samples as it included a small pyroxenitic glass fragment and has therefore been classified as a glass spherule (Ireland, 1990). The CAI has a rounded hibonite core with a few perovskite inclusions, and is surrounded by a Fe-silicate rim, thought to be an alteration product. The glass spherule CAI (7-753) is a Type B CAI.

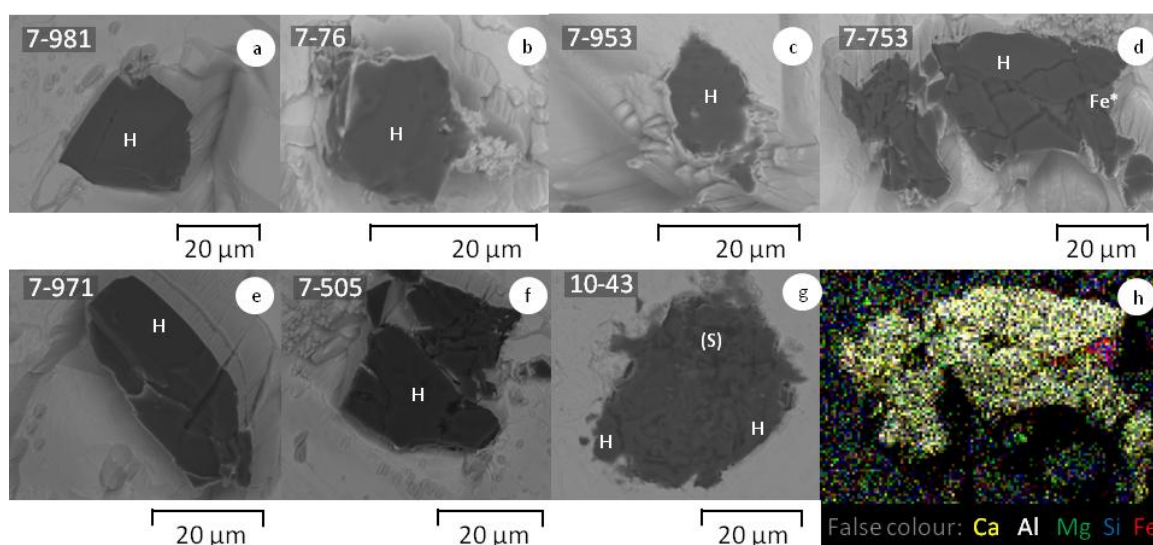


Figure 4-11 (a-g) BEI of hibonite-bearing CAI fragments mounted in gold foil showing the grain morphology and mineralogy as determined from literature descriptions, normalised EDS SEM analyses and element maps such as that shown in (g). (a,e) PLACs, (b,c,f) SHIBS, (g) BAG, (d,h) glassy spherule(GS). H = hibonite, Fe* = Fe-silicate, (S) = spinel?

4.4.2 CAI formation and subsequent reprocessing

Acfer094/22CAI has primary porosity and bladed hibonite grains, characteristics which have been used to support a condensation formation for CAIs in the Murchison and Acfer094 meteorites (Simon *et al.*, 2002; Krot *et al.*, 2004). Acfer094/40CAI also has primary porosity, and the mineral assemblages of both CAIs are as expected for a CAI that has condensed from a cooling gas of solar composition (Yoneda and Grossman, 1995). These CAIs are therefore considered to be direct condensates from the nebula gas.

Five of the compact Type A CAIs and the two Type B CAIs in this study have experienced either complete or partial melting. This is evident in the compact, blocky nature of El Djouf001/1CAI and the smooth, spherical outline of NWA1476/124 with Ti-zoning in the pyroxenitic groundmass (Rout *et al.*, 2009). The hibonite-bearing CAIs from Murchison with PLAC morphology (9-981) have REE patterns which suggest formation by a melt, and the SHIBs (7-76, 7-505, 7-953) have igneous textures (Ireland *et al.*, 1988; Ireland, 1990). The presence of pyroxenitic glass in the glass spherule 7-753 is indicative of melting (Ireland *et al.*, 1991).

The BAG and HAL-type CAIs have both experienced multiple reprocessing events. The BAG-type CAI 10-43 has REE patterns consistent with a condensation formation, but the mass-fractionated Mg isotopes suggest the CAI subsequently experienced a distillation event (Ireland, 1990), a process that is also described in terms of evaporation (Floss *et al.*, 1996). The HAL-type CAIs 7-971 and Hughes030/L contain either mass-fractionated or anomalous Mg or O isotopes, indicating reprocessing through distillation (Ireland *et al.*, 1992; Rout *et al.*, 2009). The Hughes030/L CAI has undergone extensive alteration since its formation (Rout *et al.*, 2009),

Alteration minerals, Fe,Zn-bearing spinels and ilmenite are characteristic of the CAIs from the R3 NWA2446 meteorite in this study. The irregular perimeters of NWA2446/2L and NWA2446/8L suggest these CAIs were direct condensates. Furthermore, NWA2446/2L has angular pore spaces between the hibonite blades, indicative of formation by condensation (e.g. Simon *et al.*, 2002). The pores in the core of the NWA2446/8L CAI may also be primary, although this is difficult to confirm as the resorption process in this CAI is advanced as indicated by the large spinel zone surrounding anhedral hibonite grains. The complex mineral assemblages in NWA2446/12 suggest that it may be a complex aggregate or have condensed from the nebula gas, and the biminerallitic fragment NWA2446/5L possibly formed through molten processes, as suggested for the PLACs (Ireland *et al.*, 1988). Chemical signatures of the formation process in all these CAIs have, however, been overprinted by the extensive secondary alteration processes. For example, the presence of Fe within the hibonites suggests they have re-equilibrated under oxidising conditions after CAI formation. It has been suggested that the alteration started in the nebula or planetesimals, before incorporation in the parent body (Bischoff and Srinivasan, 2003). Furthermore, this alteration may have occurred close to the water-ice thermal boundary zone (Rout *et al.*, 2009).

4.4.3 Mineral chemistry of hibonite

As Ti^{4+} and Mg^{2+} are considered to substitute for Al in the hibonite structure according to the coupled substitution Ti^{4+} and $\text{Mg} \leftrightarrow 2\text{Al}^{3+}$, stoichiometry may be used to estimate the $\text{Ti}^{3+}/\Sigma\text{Ti}$. In this case, any excess Ti after taking the coupled substitution into account would be present as Ti^{3+} . Figures 4-12 and 4-13, however, suggest that utilising this method will assign all the Ti to Mg, and thus no Ti^{3+} . For example, calculations of $\text{Ti}^{3+}/\Sigma\text{Ti}$ performed in this manner (Table 4-7) for the Acfer094 and El Djouf001 hibonites implies that there is no Ti^{3+} in these grains (Table 4-7). This is in apparent contradiction with the blue colour of the hibonite grains, which suggests the presence of Ti^{3+} (Ihinger and Stolper, 1986).

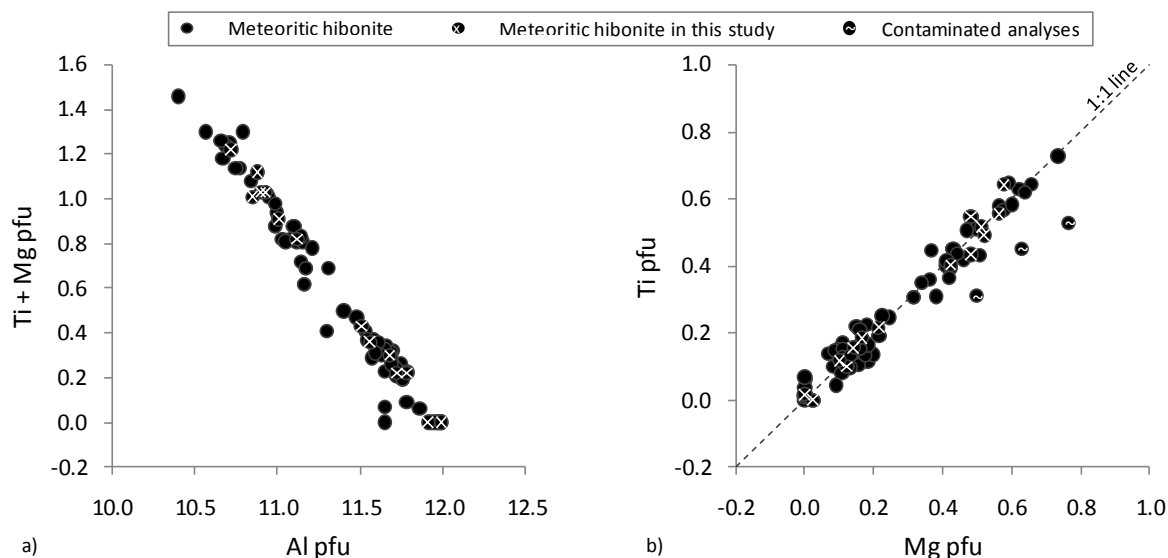


Figure 4-12 Cation comparisons for meteoritic hibonite from this study and literature, with (a) Ti + Mg pfu as a function of Al pfu showing a negative linear correlation; (b) Ti pfu as a function of Mg pfu showing a positive correlation along a 1:1 line. References detailed in Figure 4-14.

Table 4-7 Summary of TiO_2 contents, the colour of the meteoritic hibonite and the calculated $\text{Ti}^{3+}/\Sigma\text{Ti}$

Sample	Ti content †	Primary hibonite colour (ppl) ‡	%Ti ³⁺ /ΣTi		%Ti ³⁺ /ΣTi variability with 1[Ti+Si] 1[Mg+Fe]
			with Ti ⁴⁺ 1Ti ⁴⁺ :1Mg ²⁺	calculated assuming that: 1[Ti ⁴⁺ +Si ⁴⁺]:1[Mg ²⁺ +Fe ²⁺]	
Acfer094/22CAI	6.2 (0.3)	Blue	0	8 (2)	6-9
Acfer094/40CAI	7.5 (0.4)	Blue	9 (8)	9 (8)	0-16
El Djouf001/CAI	5.8 (0.7)	Greenish-blue	0	6 (6)	0-14
Hughes030/L	0.2 (<0.1)	Colourless	93 (19)	0	-
NWA1476/124	2.2 (0.2)	Greenish-blue	6 (6)	0	-
NWA2446/2L	1.4 (0.1)	Colourless	16 (14)	0	-
NWA2446/5L	2.6 (0.1)	Colourless	0 (2)	0	-
NWA2446/8L	5.0 (0.9)	Colourless	0	0	-
NWA2446/12	4.7 (1.5)	Colourless	0	0	-
7-76	1.8	Greenish-blue	0	0	-
7-505	5.5	Greenish-blue	0	0	-
7-753	1.9	Greenish-blue	9	9	-
7-953	6.5	Greenish-blue	0	0	-
7-971	0.2	Colourless	0	0	-
7-981	1.2	Colourless	0	0	-
10-43	6.4	Blue	12	11	-

Note: Fe was considered to be FeO. † See Table 4-4 (single analysis from the Murchison CAIs) and Table 4-5 (Compositional data gathered in this study for the probe-section mounted samples). ‡ The hibonite colour for CAIs Acfer094, El Djouf001, Hughes030, NWA1476 and NWA2446 are as seen under ppl. Subtle variations in colour are reported for the Hughes030,

NWA1476 and NWA2446 hibonite (Rout and Bischoff, 2008). Blue or greenish-blue CAIs were preferentially picked from a dense, non-magnetic fraction in the study by Ireland (1988), although under ppl the PLACs were reported to be colourless or near-colourless.

In meteoritic hibonite multiple element substitutions occur, including Si, Cr and Fe (e.g. Burns and Burns, 1984). Figure 4-13a shows a well constrained linear correlation, supporting a multi-element substitution mechanism, which makes stoichiometric calculations of $\%Ti^{3+}/\Sigma Ti$ complex. Indeed, the $\%Ti^{3+}/\Sigma Ti$ in hibonite may vary between 0 and 93% $Ti^{3+}/\Sigma Ti$ depending on the cation combinations used (e.g. Hughes030/L; Table 4-7). Additionally, due to the size of the grains, elemental analyses of hibonite may be contaminated by other phases (e.g. Weber and Bischoff, 1994), and the scatter in data shown in Figure 4-13b suggests many hibonite analyses are contaminated by neighbouring Si- or Fe-bearing phases. Due to the unreliable nature of quantifying $Ti^{3+}/\Sigma Ti$ by stoichiometry, direct determination of the Ti oxidation state in hibonite is necessary, and X-ray absorption spectroscopy was used for this purpose in this study.

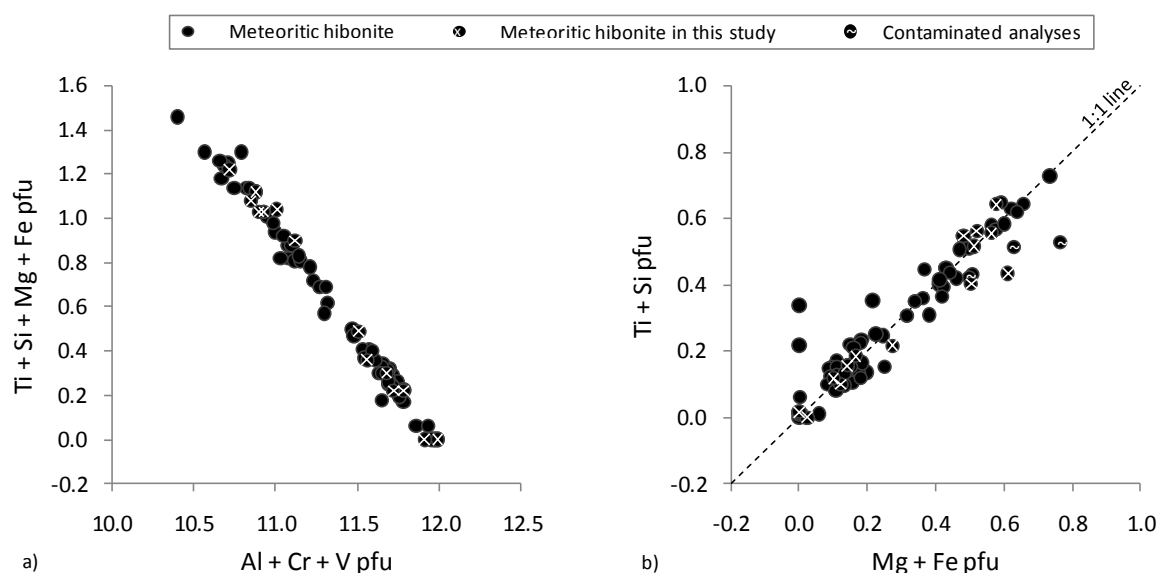


Figure 4-13 Plots of cations from meteoritic hibonite in this study and literature, with (a) Ti + Si + Mg + Fe pfu as a function of Al + Cr + V pfu showing a better constrained linear correlation than that in (Figure 4-12a); (b) Ti + Si pfu as a function of Mg + Fe pfu showing a correlation along a 1:1 line, but with more scatter. *Meteoritic hibonite data from:* Allen *et al.* (1978); Armstrong *et al.* (1982); Davis *et al.* (1982); Burns and Burns (1984); Ireland (1988); Weber and Bischoff (1994); Bischoff and Srinivasan (2003); Krot *et al.* (2004); Krot *et al.* (2006) Ushikubo *et al.* (2007); Rout *et al.* (2009); and average meteoritic hibonite data from this study. The meteoritic samples marked with ~ are likely contaminated by surrounding Mg-rich material (Weber and Bischoff, 1994).

The meteoritic hibonites in this study represent a range of CAI types from different meteorite groups and they have a wide range in Ti contents. Figure 4-14 shows meteoritic hibonite data plotted with the synthetic Ti-bearing hibonite data previously presented in Section 3.4.4. These synthetic hibonites have a wide range of Ti and Mg chemistries and represent the range of Ti-Mg variability displayed by natural meteoritic hibonite. Additionally, it is interesting to note that although Hib9(44,43) has a broad range in compositions, the Ti:Mg ratios plot along a 1:1 line suggesting that in oxidising conditions the ratios of Ti to Mg accurately measures the oxidation state.

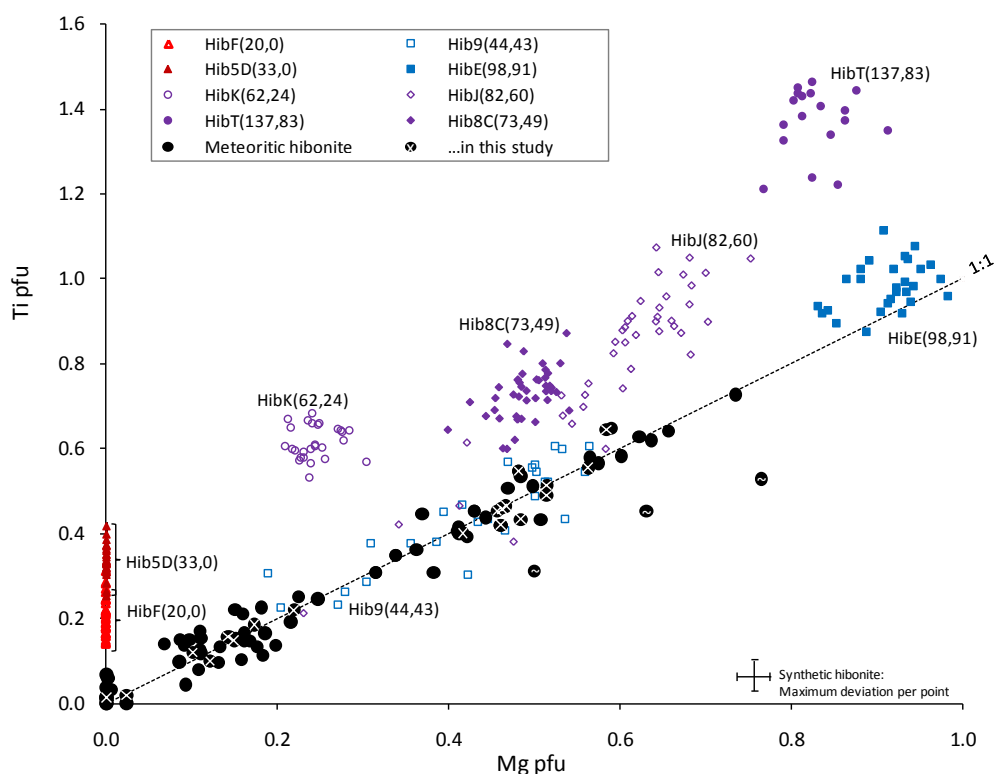


Figure 4-14 Ti pfu as a function of Mg pfu for both meteoritic hibonite (averages) and synthetic Ti-bearing hibonite (individual analyses).

4.5 Chapter summary

Fifteen hibonite-bearing CAIs from meteorites representing four different meteorite groups have been characterised. The two CAIs from the unique Acfer094 carbonaceous chondrite, considered to have formed from direct condensation, have hibonites that are blue in colour and are Ti-rich (6–8 wt% TiO_2). These CAIs show no evidence for any secondary extraterrestrial alteration. The CAI from the CR2 El Djouf001 carbonaceous chondrite, formed by complete or partial melting, contained hibonite that is greenish-blue in colour and contains 6 wt% TiO_2 . Seven hibonite-bearing CAIs from the CM2 Murchison carbonaceous chondrite were selected to represent each of the main hibonite groups defined by Ireland (1988) and Ireland *et al.* (1991), namely PLAC, SHIB, BAG, glass spherule and HAL-type. These hibonites range in colour from near-colourless to blue under plane polarised light, and vary in TiO_2 content from 0.2 to 6.5 wt% TiO_2 . The PLAC, SHIBs and glass spherule experienced melting, and the BAG and HAL-type CAI underwent distillation processes. Six CAIs from R chondrites that contain colourless, near-colourless or greenish-blue hibonites have been characterised. The hibonite in Hughes030/L contains 0.2 wt% TiO_2 , and has experienced distillation. The hibonite in NWA1476/124 was greenish-blue in colour and contained 2.2 wt% TiO_2 , whereas the colourless or near-colourless hibonites in NWA2446/2L, -5L, -8L and -/12 contain 1.4, 5.0, 2.6 and 4.7 wt% TiO_2 respectively. The NWA1476 and NWA2446 CAIs formed through condensation,

aggregation or melting processes, and have chemical signatures that appear to have been overprinted by alteration.

The CAIs from Acfer094, El Djouf001 and NWA1476 are unaltered, whereas some CAIs from Murchison contain phyllosilicates, indicating hydrothermal alteration, and CAIs from the Hughes030 and NWA2446 meteorites have undergone extensive alteration.

5 Neutron powder diffraction study of synthetic Ti-bearing hibonite

5.1 Synopsis

Hibonite ($\text{CaAl}_{12}\text{O}_{19}$) is crystal chemically complex, having five distinct Al sites onto which Ti may substitute. The preferred site occupancy of Ti is likely to be influenced by the oxidation state of Ti, therefore this study sought to investigate the substitution mechanisms of Ti^{3+} and Ti^{4+} in hibonite. Additionally, as changes to the Ti site geometry would modify the structure of Ti X-ray absorption spectra, a greater understanding of Ti site occupancy in hibonite would enable a better interpretation of such spectroscopic data.

X-ray diffraction data of powdered synthetic Ti-bearing hibonite was refined using the Rietveld refinement method and the results implied that Ti^{3+} and Ti^{4+} may occupy Al sites contradictory to those proposed in published literature. In order to clarify this Rietveld refinement of high resolution time-of-flight neutron powder diffraction data was used to determine Ti occupancy in a series of Ti^{3+} , Ti^{4+} and mixed-valent synthetic Ti-bearing hibonite samples. Ti in Ti^{3+} hibonite occupies the M4 octahedral site. Ti^{4+} undergoes a coupled substitution with Mg^{2+} for two Al^{3+} cations, with Mg occupying the tetrahedral M3 site. In Ti^{4+} hibonite Ti partitions between the M2 trigonal bipyramidal site and the M4 octahedral site. Similarly, Ti partitions between M2 and M4 in the mixed-valent hibonite samples. The results suggest that, for the Ti concentrations studied, Ti^{3+} occupies the octahedral M4 site and that Ti^{4+} occupies the M2 and M4 sites in a ratio close to 1:4, irrespective of Ti content and the proportion of Ti^{3+} in hibonite.

5.2 Introduction

5.2.1 The structure of hibonite

The structure of hibonite ($\text{CaAl}_{12}\text{O}_{19}$) was first characterised by Curien *et al.* (1956) using X-ray diffraction (XRD) data collected from terrestrial hibonite. It was subsequently refined by Kato and Saalfeld (1968), Bermanec *et al.* (1996), Hofmeister *et al.* (2004) and Nagashima *et al.* (2010).

Hibonite is hexagonal (space group $P6_3/mmc$, $Z=2$), with lattice parameters on the order of 5.6 Å and 22.0 Å (Hofmeister *et al.*, 2004).

The hibonite structure is dominated by O layers perpendicular to the c-axis (Figure 5-1a), with one 12-fold coordinated Ca-bearing site and five Al-bearing sites. The Ca site and a five-fold coordinated trigonal bipyramidal site (M2) lie within the O3 oxygen layer (Figure 5-1b). The M2 site is bound by three O atoms in the equatorial plane ($3 \times O3$), and an O (O1) atom above and below. The M2 atom is axially displaced from the equatorial plane (Utsunomiya *et al.*, 1988) in a static arrangement (Du and Stebbins, 2004) by 0.17-0.27 Å (Bermanec *et al.*, 1996; Hofmeister *et al.*, 2004).

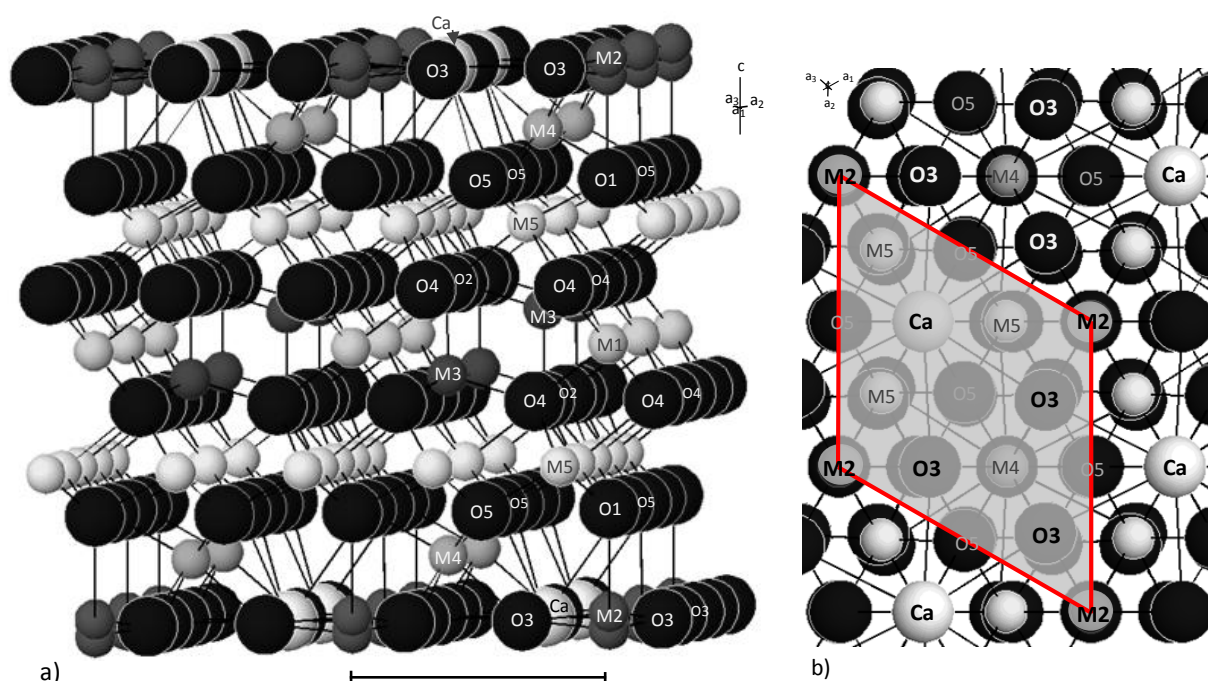


Figure 5-1 (a) The structure of hibonite showing O-layers perpendicular to the c-axis, interspersed by layers of Al on the M1, M3, M4 and M5 sites. The displacement of the M2 cation from the equatorial plane is indicated by the two equivalent M2 positions. Half a unit-cell is shown in the c-axis direction, and the scale bar indicates a unit-cell in the a-axis direction. (b) Cross-section within the O3 layer showing a unit-cell and the O3 layer atoms in bold.

The other four Al-sites form distinct layers between the O layers. A trigonally distorted tetrahedral (M3) site lies between the O2 and O4 oxygen layers (Burns and Burns, 1984). The three remaining cation sites are octahedral and distorted to varying degrees (Burns and Burns, 1984). M1 is undistorted (bonded by $6 \times O4$), whereas M4 is symmetrically distorted, having three long and three short M-O bonds (Bermanec *et al.*, 1996). The M5 site is the most abundant cation site and is asymmetrically distorted, being bound by four distinct O atoms ($1 \times O1$, $1 \times O2$, $2 \times O4$ and $2 \times O5$). The M1 and M5 sites form infinite chains of edge-sharing octahedra perpendicular to the c-axis, and the M4 site forms face-sharing pairs sub-parallel to the c-axis, sharing a face in the plane of the O3 layer (Burns and Burns, 1984). The multiplicity of the cation sites and their coordination geometries may be summarised as follows: $^{[12]}Ca^{[6]}M1^{[5]}M2^{[4]}M3_2^{[6]}M4_2^{[6]}M5_6O_{19}$ (where coordination numbers are in brackets and multiplicity is subscript, after Bermanec *et al.*, 1996).

5.2.2 Site occupancy in hibonite

A range of elements substitute into the hibonite structure, including: Mg^{2+} , Zn^{2+} , Fe^{2+} , Fe^{3+} , Cr^{3+} , V^{3+} , Ti^{3+} , Ti^{4+} , Si^{4+} , Th^{4+} and the rare earth elements (REEs) (e.g. Burns and Burns, 1984; Beckett *et al.*, 1988; Rakotondrazafy *et al.*, 1996). Previous studies have investigated the site occupancy of these elements in both terrestrial and synthetic hibonite, the findings of which are summarised in Table 5-1. An understanding of their substitution mechanisms, however, is not complete, as shown by differences in Ti^{4+} site occupancy determined by Bermanec *et al.* (1996) and Nagashima *et al.* (2010).

Of particular interest to this study is the site occupancy of Ti. Ti and Mg^{2+} substitute into meteoritic hibonite structure in significant quantities (up to 8.3 wt% TiO_2 , Allen *et al.*, 1978). Ti^{3+} may substitute directly for Al^{3+} , whereas Ti^{4+} undergoes a coupled substitution with Mg^{2+} for two Al^{3+} in order to maintain charge balance ($\text{Mg}^{2+} + \text{Ti}^{4+} \leftrightarrow 2\text{Al}^{3+}$).

Table 5-1 Hibonite M-site geometry and multiplicity, with the proposed site occupancy of substituting cations

Site †	Multi- plicity	M-Site characteristics		Proposed cation site occupancy ‡ in hibonite ($\text{CaAl}_{12}\text{O}_{19}$)	
		Geometry	Distortion		Reference
M1	1	Octahedral	Undistorted	Cr^{3+}	1
M2	1	Trigonal bipyramidal	Atom displaced from centre	Fe^{2+} ; Fe^{3+} ; V^{3+} ; Ti^{3+} ; Ti^{4+}	1, 2, 3, 4, 5
M3	2	Tetrahedral	Trigonally distorted	Mg^{2+} ; Fe^{2+} ; Fe^{3+} ; Zn^{2+} ; Si^{4+}	1, 3, 4, 5
M4	4	Octahedral	Symmetrically distorted	Fe^{2+} ; Cr^{3+} ; Ti^{4+} ; Si^{4+}	1, 3, 5
M5	6	Octahedral	Asymmetrically distorted	Cr^{3+}	1

Notes: †Using the nomenclature of Bermanec *et al.* (1996). **References:** (1) Burns and Burns (1984); (2) Beckett *et al.* (1988); (3) Bermanec *et al.* (1996); (4) Holtstam (1996); (5) Nagashima *et al.* (2010) ‡ An enhanced version of this table is included in Appendix D.1.

REEs occupy the 12-fold coordinated site in terrestrial hibonite (Bermanec *et al.*, 1996). Charge balance is maintained by the coupled substitution:



Numerous substitutions have been reported to occur on the trigonal bipyramidal M2 site (Table 5-1). Mössbauer spectra collected from terrestrial and Fe-doped hibonite by Burns and Burns (1984) and Holtstam (1996) were used to show Fe^{3+} occupies the M2 site. In addition, Burns and Burns (1984) reported Fe^{2+} on the M2 site. Using crystal field stabilisation theory, Burns and Burns (1984) suggested V^{3+} and Ti^{3+} should occupy the M2 site, and features in electron spin resonance spectra (Beckett *et al.*, 1988) and optical absorption spectra (Burns and Burns, 1984) were used to infer that Ti^{3+} occupies the M2 site. A single crystal XRD study of terrestrial gem quality Ti^{4+} -bearing hibonite identified 17% Ti^{4+} on the M2 site (Nagashima *et al.*, 2010).

In the single crystal XRD studies of terrestrial hibonite by Bermanec *et al.* (1996) and Nagashima *et al.* (2010) trace amounts of Zn^{2+} were refined onto the tetrahedral M3 site, whereas Mg^{2+} and Si^{4+} were placed on the tetrahedral M3 site. Optical absorption spectroscopy, Mössbauer spectroscopy and XRD were used to determine the presence of Fe^{2+} on this site (Burns and Burns, 1984; Holtstam, 1996; Bermanec *et al.*, 1996). Although most Fe^{3+} substituted onto M2 site in terrestrial hibonite, the

Mössbauer study of Burns and Burns (1984) suggested that some Fe^{3+} can simultaneously occupy the tetrahedral M3 site.

Fe^{2+} and Ti^{4+} have been reported on the M4 octahedral site (Burns and Burns, 1984; Bermanec *et al.*, 1996; Nagashima *et al.*, 2010). Despite the fact that octahedral Si^{4+} is very rare in minerals, Bermanec *et al.* (1996) suggested Si^{4+} may occupy the M4 site. No evidence has been reported for chemical substitution on the octahedral M1 and M5 sites in hibonite. However, Burns and Burns (1984) predicted that Cr^{3+} is likely to enter one of the octahedral sites in hibonite.

5.2.3 Site occupancy in structural analogues

The crystal chemical study of hibonite by Burns and Burns (1984) used hexagonal β -alumina ($\text{NaAl}_{11}\text{O}_{17}$) as a structural analogue for hibonite. Likewise, the magnetoplumbite group minerals ($\text{AB}_{12}\text{O}_{19}$), which are isostructural with hibonite (Wittmann *et al.*, 1956; Burns and Burns, 1984), may be used to elucidate cation substitution mechanisms within hibonite. The site occupancies within Ti- and Mg-bearing phases isostructural with hibonite are summarised in Table 5-2 and detailed in Appendix D.1.

In Ti^{4+} -rich phases isostructural with hibonite Ti^{4+} occupies four of the five M-sites. In $\text{SrTi}_6\text{Co}_6\text{O}_{19}$ Graetsch and Gebert (1995) found that Ti^{4+} fully occupies the M1 and M4 sites and partially occupies the M2 and M5 sites, with Co^{2+} occupying the M3 tetrahedral site. Similarly, using Mössbauer spectroscopy to study $\text{Ba}(\text{Fe},\text{Co},\text{Ti})_{12}\text{O}_{19}$, Kreber and Gonser (1976) found that Fe^{3+} preferentially occupies the M2 site, with Ti^{4+} and Co^{2+} potentially occupying any of the five M-sites at relatively low concentrations of Fe^{3+} (<4 Fe^{3+} per formula unit, pfu). Low concentrations of Ti^{3+} (<0.1 wt% Ti_2O_3) in β - and β'' -alumina (with formulae calculated to be $\text{Na}_{1.6}\text{Al}_{10.8}\text{O}_{17}$ and $\text{Na}_{1.7}\text{Al}_{10.6}\text{Mg}_{0.3}\text{O}_{17}$ respectively) were inferred to occupy the M1 and M5 octahedral sites from electron spin resonance (ESR) spectra (Barret *et al.*, 1984).

Table 5-2 Site occupancy in phases with magnetoplumbite or β -alumina structures

Site	Major component	Minor component (≤ 1 pfu)
M1	Co^{2+} ; Al^{3+} ; Cr^{3+} ; Fe^{3+} ; Ti^{4+}	Al^{3+} ; Ti^{3+}
M2	Co^{2+} ; Al^{3+} ; Fe^{3+} ; Ga^{3+} ; Mn^{4+} ; Ti^{4+}	-
M3	Co^{2+} ; Mn^{2+} ; Zn^{2+} ; Al^{3+} ; Fe^{3+} ; Ga^{3+}	Mg^{2+}
M4	Cr^{3+} ; Al^{3+} ; Fe^{3+} ; Mn^{4+} ; Ti^{4+}	Sb^{5+}
M5	Co^{2+} ; Al^{3+} ; Cr^{3+} ; Mn^{3+} ; Fe^{3+} ; Ti^{4+}	Al^{3+} ; Ti^{3+}

Note: Reference, and phase: Barret *et al.*, (1985), $\text{Na}_{1.6}\text{Al}_{10.8}\text{O}_{17}$ and $\text{Na}_{1.7}\text{Al}_{10.6}\text{Mg}_{0.3}\text{O}_{17}$; Bermanec *et al.* (1996), $\text{PbFe}_{9.3}(\text{Mn}^{2+}, \text{Mn}^{3+})_{1.8}\text{Sb}_{0.6}\text{Mg}_{0.3}\text{O}_{19}$ and $\text{PbFe}_{8.0}\text{Zn}_{1.9}(\text{Mn}^{3+}, \text{Mn}^{4+})_{2.5}\text{Ti}^{4+}_{0.4}\text{Al}_{1.0}\text{O}_{19}$; Bettman and Peters (1969), $\text{Na}_2\text{MgAl}_{10}\text{O}_{17}$; Graetsch and Gebert (1995), $\text{SrTi}_6\text{Co}_6\text{O}_{19}$; Graetsch and Gebert (1996), $\text{SrCr}_9\text{Ga}_3\text{O}_{19}$; Kreber and Gonser (1976), $\text{Ba}(\text{Fe},\text{Co},\text{Ti})_{12}\text{O}_{19}$. An enhanced version of this table is included in Appendix D.1.

The site occupancies of Mg^{2+} and Al^{3+} as minor components in phases isostructural with hibonite are also instructive for a study of Ti site occupancy. As reported for hibonite, Mg^{2+} occupies the tetrahedral M3 site in the β -alumina phase $\text{Na}_2\text{MgAl}_{10}\text{O}_{17}$ (Bettman and Peters, 1969). In nežilovite

($\text{PbFe}_{8.0}\text{Zn}_{1.9}(\text{Mn}^{3+}, \text{Mn}^{4+})_{2.5}\text{Ti}^{4+}_{0.4}\text{Al}_{1.0}\text{O}_{19}$) the Al^{3+} was reported to occupy the M1 and M5 octahedral sites (Bermanec *et al.*, 1996).

5.2.4 Rationale for a neutron diffraction study

According to the literature Ti^{3+} is thought to occupy the M2 trigonal bipyramidal site in hibonite (Beckett *et al.*, 1988; Burns and Burns, 1984) and Ti^{4+} is expected to occupy either the M4 octahedral site (Bermanec *et al.*, 1996), or both the M2 and M4 sites (Nagashima *et al.*, 2010). As part of this study, density functional theory (DFT) calculations performed by Dr Andrew Walker (University of Bristol) suggested that Ti^{3+} could substitute as a point-defect on the M2 site, but would occupy M4 in hibonite with 2 Ti^{3+} pfu. The DFT calculations also predicted that Ti^{4+} would substitute into either the M4 site (in a charged cell) or the M5 site (if co-substituted with Mg^{2+}). Rietveld refinement of in-house X-ray powder diffraction data from both Ti^{3+} and Ti^{4+} synthetic hibonites suggested that Ti^{3+} occupies either the M2 or M4 sites and that Ti^{4+} preferentially occupies the M4 site, but may also occupy the M5 site. As these findings were contrary to that expected from the literature, a more rigorous approach was sought in order to determine the mechanism of Ti substitution in hibonite.

Due to the different properties of X-rays (scattered by electrons) and neutrons (scattered by nuclei), the specific nature of the required study should determine which of these radiations are most suitable for a scattering experiment. Whereas refinement of X-ray and neutron data should accurately determine the structural positions of Al and Ti, the atomic coordinates of O are more precisely determined using neutron diffraction, especially when the concentration of heavy elements increases. Uncertainties in the site occupancy of Ti in hibonite extracted from in-house XRD data were exacerbated by difficulties in refining the O positions and the need to constrain the atomic displacement parameters (ADPs). With this in mind, neutron diffraction seemed the most appropriate method to use in order to refine the Ti-site occupancy in hibonite.

Determining Ti occupancy in an Al-dominated mineral using neutron diffraction has additional benefits. Ti has a negative scattering length (-3.44 fm; Sears, 1992), whereas the scattering length of Al (for which Ti substitutes) is positive (+3.45 fm; Sears, 1992). Substitution of Ti for Al would therefore vary the site scattering in a quantifiable way. For example, Kitamura *et al.* (1975) successfully used neutron diffraction data to show which of the three possible sites Ti occupied in oxykaersutite ($(\text{Na}_{0.73}\text{K}_{0.25}\text{Ca}_{1.72})(\text{Mg}_{2.42}\text{Fe}^{2+}_{0.61}\text{Fe}^{3+}_{1.04}\text{Al}_{0.48}\text{Mn}_{0.02}\text{Ti}_{0.67})(\text{Si}_{5.75}\text{Al}_{2.25})(\text{O},\text{OH})_{24}$). As in this study, the XRD refinements of Kitamura *et al.* (1975) were not definitive due to similarities of the atomic scattering factors of elemental pairs such as Mg and Al, and Ti and Fe. The neutron scattering lengths of these elements, however, differed sufficiently for Kitamura *et al.* (1975) to constrain the Ti site occupancy in the multi-element system.

5.3 Methodology and experimental techniques

5.3.1 Summary of sample characterisation

Eight synthetic Ti-bearing hibonite samples were prepared by sintering stoichiometric mixtures of elemental oxides in a CO-CO₂ vertical gas mixing furnace. The Ti content in the sample suite is 2.4 - 15.9 wt% TiO₂, ranging from 0 - 100% Ti³⁺/ΣTi (where ΣTi = Ti³⁺ + Ti⁴⁺), as shown in Table 5-3. Phase identification was made using powder XRD and the hibonite compositions were determined by energy dispersive spectroscopy (EDS) using a 5900 Jeol scanning electron microprobe (SEM; operating conditions: 10 kV, 2 nA). Full details of the sample synthesis and characterisation are provided in Chapter 3.

Table 5-3 Summary of the stoichiometry and Ti content in the synthetic Ti-bearing hibonite sample series

Sample [†]	Stoichiometry	Average wt% TiO ₂	%Ti ³⁺ ‡
HibF(20,0)	Ca _{1.07} Al _{11.69} Ti _{0.20} O ₁₉	2.4±0.5	100±0
Hib5D(33,0)	Ca _{1.07} Al _{11.51} Ti _{0.33} O ₁₉	4.0±0.4	100±0
HibK(62,24)	Ca _{1.05} Al _{10.99} Ti _{0.62} Mg _{0.24} O ₁₉	7.3±0.5	60±4
Hib8C(73,49)	Ca _{1.07} Al _{10.66} Ti _{0.73} Mg _{0.49} O ₁₉	8.6±0.6	33±5
HibJ(82,60)	Ca _{1.05} Al _{10.48} Ti _{0.82} Mg _{0.60} O ₁₉	9.6±2.2	25±12
Hib9(44,43)	Ca _{1.04} Al _{11.10} Ti _{0.44} Mg _{0.43} O ₁₉	5.2±1.4	0±0
HibE(98,91)	Ca _{1.01} Al _{10.07} Ti _{0.98} Mg _{0.91} O ₁₉	11.4±0.7	0±0
HibT(137,83)	Ca _{1.05} Al _{9.59} Ti _{1.37} Mg _{0.83} O ₁₉	15.9±0.9	39±4

Notes: Further compositional data are detailed in Table 3.7. [†] For ease of reference, the ratio of Ti:Mg cation ratio (x 100) is included within the sample name. [‡] %Ti³⁺ is based on stoichiometry (1Ti⁴⁺:1Mg²⁺).

For the purposes of this study, “Ti³⁺ hibonite(s)” refers to hibonite samples in which all the Ti is Ti³⁺ (HibF(20,0) and/or Hib5D(33,0)), and “Ti⁴⁺ hibonite(s)” refers to hibonite samples in which all the Ti is Ti⁴⁺ (Hib9(44,43) and/or HibE(98,91)). The remaining samples are referred to as “mixed-valent” hibonites, with the qualification “Ti⁴⁺-bearing” referring to any hibonite containing Ti⁴⁺ and Mg²⁺, and “Ti³⁺-rich” referring to hibonite with >50% of Ti as Ti³⁺ (HibF(20,0), Hib5D(33,0) and/or HibK(62,24)).

As described in Section 3.4.2.2, the Ti³⁺-rich samples (HibF(20,0), Hib5D(33,0) and HibK(62,24)) are compositionally well defined, as reflected in their narrow TiO₂ range (± 0.5 wt% TiO₂ per sample). Likewise, the Ti⁴⁺-rich hibonite samples HibT(137,83), Hib8C(73,49) and HibE(98,91) are compositionally well defined (± 0.9 wt% TiO₂ per sample). The Ti⁴⁺-rich hibonites Hib9(44,43) and HibJ(82,60) have wider compositional ranges (Figure 3.4), as reflected in the variation in TiO₂ contents: 5.2 ± 1.4 and 9.6 ± 2.2 wt% TiO₂ respectively.

5.3.2 Acquisition of neutron powder diffraction data

Time-of-flight (TOF) neutron powder diffraction (NPD) data were collected for a series of eight synthetic hibonite samples (Table 5-3) using the high-resolution powder diffractometer HRPD

(Ibberson *et al.*, 1992; Ibberson, 2009) at the ISIS neutron spallation source, Rutherford Appleton Laboratory, UK. A weighed sample was packed into an 8 mm diameter cylindrical vanadium can (Table 5-4) and positioned in line with the beam. Data were collected on three detector banks set at mean scattering angles of 168° , 90° and 30° over the TOF ranges: 32-126 ms, 32-130 ms and 32-132 ms respectively (corresponding to d-spacings of: 0.663-2.610 Å, 0.922-3.741 Å and 2.273-10.275 Å respectively). Ambient temperature data were collected from each sample with a total beam exposure of 100-152 μA (Table 5-4) and subsequently binned at $\Delta t/t$ 0.0003 ms (168° detector) and 0.0007 ms (90° detector). The data were focused, background subtracted, normalised and corrected for absorption before being formatted for refinement by the General Structure Analysis System (GSAS) of Larson and Von Dreele (2004).

Table 5-4 Sample weights and beam exposure

Sample	Sample holder	Weight (g)	Beam exposure (μA)
HibF(20,0)	vanadium can	2.82	145.5
Hib5D(33,0)	vanadium can	3.74	101.5
HibK(62,24)	vanadium can	4.38	152.0
Hib8C(73,49)	vanadium can	3.27	125.3
HibJ(82,60)	vanadium can	3.65	100.3
Hib9(44,43)	vanadium can	3.62	146.2
HibE(98,91)	vanadium can	3.63	113.2
HibT(137,83)	vanadium can	-	100.0
HibF(20,0)	Al-block (vanadium windows)	5.35	9 per temperature
HibT(137,83)	Al-block (vanadium windows)	5.39	9 per temperature

In order to investigate the effect of different Ti species on the thermal expansion of hibonite, NPD data were collected over a range of temperatures ($7 \leq T \leq 275$ K) for a Ti^{3+} hibonite (HibF(20,0)) and a mixed-valent hibonite (HibT(137,83)). Accurate modelling of thermal expansion data is best achieved through modelling the temperature dependence of the unit-cell parameters, thus the data collection times could be reduced from those of the ambient temperature structural study. A powdered sample was packed into an Al-sample block, loaded onto the end of a continuous cycle refrigerator (CCR) and positioned in line with the beam. HibF(20,0) was cooled to 8 K and then heated to 275 K in 5 K steps starting from 10 K, whereas HibT(137,83) was cooled to 7 K from 275 K in 5 K steps. In both experiments the equilibration times at each temperature step were 300 s. Data were collected for a total beam exposure of 9 μA in the TOF range 32-126 ms using the 168° backscatter detector bank and subsequently binned at $\Delta t/t$ 0.0003 ms. The data were focused, background subtracted, normalised and corrected for absorption before being formatted for refinement by GSAS.

5.3.3 Refinement of the hibonite structure

5.3.3.1 Preparation of a seed file

In order to prepare a seed file for use by subsequent refinements, the data from the 168° and 90° detector banks were refined simultaneously using GSAS interfaced with EXPGUI v1.82 (Toby, 2001).

Initial structural parameters were taken from Hofmeister *et al.* (2004), and the occupancy of M2 was set to 0.5 to account for the off-centre location of the M2 cation (Utsunomiya *et al.*, 1988). The peak profiles were modelled using the model-dependent Le Bail method with only three sample-dependent variables. The background was modelled using a five-term shifted Chebyshev function.

Thereafter the structure was refined using the Rietveld refinement method. The profiles of the two data banks were scaled and the structural parameters of additional phases (if any) were added, and then scaled relative to hibonite. The unit-cell parameters for hibonite were refined, after which the atomic coordinates and atomic displacement parameters (ADP) were added to the refinements.

5.3.3.2 Determining Ti site occupancy

Two procedures were employed in order to determine Ti site occupancy in the hibonite sample suite, namely: structure factor calculations and Rietveld refinement of NPD data. The Rietveld refinements were made with the above-mentioned seed file using two strategies: a site-elimination method, and a sequential Ti-substitution method.

5.3.3.2.1 Structure factor calculations

The intensity of XRD and NPD diffraction peaks are proportional to the square of the structure factor (Equation 5-1), where the structure factor (F) is a measure of all the reflections from a crystallographic plane. As shown in Equation 5-2 (XRD) and Equation 5-3 (TOF NPD), the structure factor is dependent upon the atomic X-ray scattering factor or the scattering length (NPD) of atoms on a plane.

Intensity (Cullity, 1978)

$$I \propto |F_{hkl}|^2 \quad \text{Equation 5-1}$$

Where:

F_{hkl} = the structure factor for reflection hkl
 h, k, l = miller indices

X-Ray structure factor (Cullity, 1978)

$$F_{hkl} = \sum_{n=1}^{n=N} f_n e^{2\pi i(hu_n + kv_n + lw_n)} \quad \text{Equation 5-2a}$$

$$= \sum_{n=1}^{n=N} f_n [\cos 2\pi(hu_n + kv_n + lw_n) + i \sin 2\pi(hu_n + kv_n + lw_n)] \quad \text{Equation 5-2b}$$

Where:

f_n = atomic scattering factor of atom n
 u_n, v_n, w_n = fractional coordinates of atom n

Neutron structure factor (Parise, 2006)

$$F_{hkl} = \sum_{n=0}^{n=N} b_n e^{-iK_{hkl} \cdot r_n} \quad \text{Equation 5-3}$$

Where:

b_n = neutron scattering length of atom n
 r_n = position vector of atom n
 $K_{hkl} = ha^* + kb^* + lc^*$
 $a^* = 2\pi/a$ = reciprocal lattice vector

When considering the neutron scattering lengths, substitution of Ti (negative scattering length) for Al-site (positive scattering length) should decrease the intensity of reflections from that site in a quantifiable manner. Structure factors were calculated for reflections within the 95-126 ms TOF range as these hibonite peaks were well-resolved (Figures 5-2 to 5-4). The fractional coordinates of Hofmeister *et al.* (2004) were used for three end-members, namely: $\text{CaAl}_{12}\text{O}_{19}$, $\text{CaAl}_{11}\text{Ti}^{3+}\text{O}_{19}$ and $\text{CaAl}_{10}\text{Ti}^{4+}\text{MgO}_{19}$. In order to simulate the Ti^{3+} hibonites, 1 Ti pfu was added to each site sequentially, and to simulate the Ti^{4+} hibonites Mg was added to the M3 tetrahedral site, after which 1 Ti pfu was added to the other sites sequentially. The calculated structure factor for each $\text{CaAl}_{12}\text{O}_{19}$ reflection was compared to that calculated for the equivalent reflection in the Ti-bearing hibonites. Any variation in the structure factors should be related to Ti site occupancy.

Direct comparison of the observed peak intensities to the calculated structure factors was, however, hindered by the compositional and structural complexity of the samples. Although the hibonite samples were compositionally distinct from one another, compositional variability within each sample (as described in Chapter 3) affected the peak profiles, with the Ti^{3+} samples having narrow, intense peaks, whereas the diffraction peaks of the Ti^{4+} samples are strongly asymmetric, broad and less intense. The overall outcome of the structure factor calculations suggested that Ti substitution in hibonite may not be a single-site mechanism. The results suggested that both the M2 and M4 sites may be involved in the Ti substitution mechanism.

5.3.3.2.2 Rietveld refinements: elimination and sequential-substitution methods

Unlike the method described above which considers individual reflections, the Rietveld refinement method (Rietveld, 1969, 2000) models the entire diffraction dataset simultaneously. Using an initial structural model, a diffraction pattern is calculated and compared to the observed dataset. The structural model is modified in an attempt to minimise the difference between the observed and calculated diffraction data (Young, 2000). The structural model and calculated diffraction pattern are thus iteratively refined with respect to the observed data using the least squares method.

With this approach any inaccuracy of the structural model would become evident by an excessive increase or decrease in one or more structural parameters, resulting in the calculation of unreasonable or non-physical values. In this case the ADP and site occupancy parameters proved to be particularly sensitive. It is not generally possible for Rietveld refinement of powder diffraction data from a complex structure to distinguish fully between different elements on the same site, as was the case in this study. As a consequence, the atomic coordinates and ADPs for atoms on the same site were constrained to be identical. Within the refinements the proportion of Ti (or Mg) and Al on a site were constrained to sum to 1 (or 0.5 for the M2 site). Consensus within the literature (Table 5-1) suggested that Mg^{2+} should occupy the tetrahedral M3 site, and this was found to be the case in initial refinements of the Ti^{4+} hibonites. In refinements of other Mg-bearing hibonites Mg^{2+} was set to

occupy the M3 site. The initial Mg content was defined to be the same as the average Mg content determined by EDS SEM and it was only refined if the associated structural parameters varied substantially from their equivalents across the sample series.

When using the site-elimination method, Ti was simultaneously allowed to refine onto all the pure Al-sites (that is, excluding the M3 site in Ti^{4+} -bearing hibonites). The unit-cell, atomic coordinates, ADP and proportion of Ti were iteratively refined. After convergence of the refinement, the proportion of Ti on each site was assessed. If the proportion of Ti on a site was less than the propagated uncertainty of the Ti pfu calculated from EDS SEM analyses, then the Ti-occupancy of that site was permanently set to zero. The refinement was then started afresh, with Ti occupying the remaining sites. This process was repeated until the refinement converged with Ti occupying specific sites above the EDS SEM Ti pfu uncertainty guide.

When using the sequential Ti-substitution method, Ti was placed on each site in turn. Initially Ti was placed in the M1 site to a value equating to that of the SEM analysis. The unit-cell, atomic coordinates and ADP were refined and assessed, after which the Ti content was adjusted if necessary and the refinement repeated. For the Ti^{3+} hibonites, Ti refined onto a single site and the corresponding ADP values agreed with those of synthetic hibonite described by Hofmeister *et al.* (2004). Using the ADP parameters as the main guide, it became evident that Ti^{4+} occupied two sites in the Ti^{4+} -bearing hibonites. The structures of Ti^{4+} -bearing samples were therefore refined by simultaneously changing the proportion of Ti on two sites.

The results from the two approaches concurred with respect to Ti site occupancy. For more detailed structural refinements, the results from the sequential substitution method were used as a base for further refinement. The results of these refinements are discussed in Section 5.4.

5.3.4 Refinement of thermal expansion data

NPD data collected for HibF(20,0) and HibT(137,83) within the temperature range $7 < T < 275$ K were refined using the model dependent Le Bail method within GSAS (Larson and Von Dreele, 2004). The HibF(20,0), structural data from Rietveld refinements of the ambient temperature data were used as an initial seed file for the HibF(20,0) dataset. For the 8 K HibF(20,0) data, the background was modelled using a five term shifted Chebyshev function and was refined together with the unit-cell parameters. The converged parameters from this analysis were then used as the initial parameters for the refinements of the 10 K data. The output from this dataset was used for the starting parameters for the dataset collected at the next temperature, and so on through the series.

For HibT(137,83), the 275 K data were used to prepare a seed file using the structural parameters from the ambient temperature HibF(20,0) refinements. The 275 K HibT(137,83) background was modelled with a five term shifted Chebyshev function, after which the unit-cell was refined using the model dependent Le Bail method. Thereafter the peak-shape was refined along with the background

and unit-cell. This structural model was used as a base for the model dependant Le Bail refinement of the 270 K HibT(137,83) data, during which the background was modelled using a five term shifted Chebyshev function and then refined together with the unit-cell parameters. The converged parameters from this analysis were then used as the initial parameters for the refinements of the 265 K data, and so on through the series.

5.3.5 Criteria for model assessment

Combinations of three independent methods were used to assess the quality and accuracy of the structural model, namely: numerical fit-indices, visual fit assessments and crystal chemical considerations. As the refinement strategy was identical for each dataset in the series these criteria can also be used in a systematic way.

5.3.5.1 Numerical measures of fit quality

Rietveld refinement optimises the calculated fit to the observed data by minimising the residual (M, Equation 5-4) at each step using the least-squares method. Therefore, quantitative measures of fit may be derived, such as the parameters R_p , R_{wp} and χ^2 which are used in GSAS (Equations 5-5a-c; Young, 2000; Von Dreele, 2006).

$$M = \sum w(Y_o - Y_c)^2 \quad \text{Equation 5-4}$$

$$R_p = \frac{\sum |(Y_o - Y_c)|}{\sum Y_o} \quad \text{Equation 5-5a}$$

$$R_{wp} = \sqrt{\frac{M}{\sum w Y_o^2}} \quad \text{Equation 5-5b}$$

$$\chi^2 = \frac{M}{N_{obs} - N_{var}} \quad \text{Equation 5-5c}$$

Where:

- w = $1/Y_o$ at each step
- Y_o, Y_c = Intensity of the observed data, and the calculated intensity (respectively) at each step
- N_{obs}, N_{var} = Number of data-points observed, and number of variables refined (respectively)

Numerical measures of fit, although useful in monitoring the progress of each refinement, may be misleading when used in isolation to interpret the reliability of the model. Unique features of each dataset will impact upon the absolute values of the goodness-of-fit parameters. Large backgrounds, low peak intensity and the number of variables in each refinement all influence the numerical fit indices. For this reason, numerical measures of fit should be considered in conjunction with a careful assessment of the appearance of a fit and crystal chemistry of the refined model. The numerical fit indices generated by GSAS for the converged refinements are shown in Table 5-5.

5.3.5.2 Visual assessment

A visual assessment of the fit gives a rapid indication as to the progress of the refinement. The refinement proceeds by minimising the residual, therefore changes to the model may be accepted or rejected as the refinements progress. A visual assessment of the fit also allows for the identification and inclusion of impurity phases (if any). As for the numerical fit indices, a visual assessment of the fit needs to take into account crystal chemical considerations. For example, a minimal residual may be achieved in a refinement, but the structural parameters may be unacceptable, whereas an apparently large residual may be acceptable if it can be justified by the model or the sample characteristics. The structural models with the smallest and largest fit residuals after convergence are shown in Figure 5-2 and Figure 5-3 respectively, with those for the entire sample series included in Appendix D.2.

5.3.5.3 Crystal chemical considerations

A key advantage of considering a suite of similar samples is the opportunity to consider systematics within the refined models. Although numerical fit indices and visual fits provided useful measures of the fit quality, the refined model must be both crystal chemically correct and reflect the sample chemistry. While assessing the success of the refinements, structural parameters which varied systematically across the series were used as a guide. For example, structural parameters were expected to vary either in a consistent manner or be broadly similar across the sample series. Additionally, the refined Ti and Mg contents should be similar to those obtained by EDS SEM.

5.3.6 Refinement complexities

As shown in Figure 5-4, the diffraction peaks of the Ti^{3+} -rich samples are narrow, intense and symmetrical. In contrast, however, the peaks of the Ti^{4+} -rich samples are broader, less intense and asymmetrical. The Ti^{4+} -rich samples Hib9(44,43) and HibJ(82,60) have significant compositional variability (Figure 3.7) and it seems likely that the reason for the asymmetric peak broadening can be correlated with this compositional variation. This type of line shape is hard to model within GSAS. An increased residual, although undesirable, therefore became inevitable and was only accepted if the crystal chemistry of the model was plausible.

Due to the similar magnitude but opposing signs of the scattering lengths of Ti (-3.44 fm; Sears, 1992) and Al (+3.45 fm; Sears, 1992), it is possible to encounter a scenario whereby the proportion of Ti on a site approached that of Al, such that there is apparently null scattering from that site. This is referred to as contrast matching and was found to occur for HibT(137,83). In this case the refinement is more difficult to control, requiring a more cautious approach for convergence to be achieved with a reliable structural model. In this case, the atomic coordinates and ADPs for sets of atoms were refined sequentially. First the atomic coordinates of the O atoms were refined, then those of the Ca,

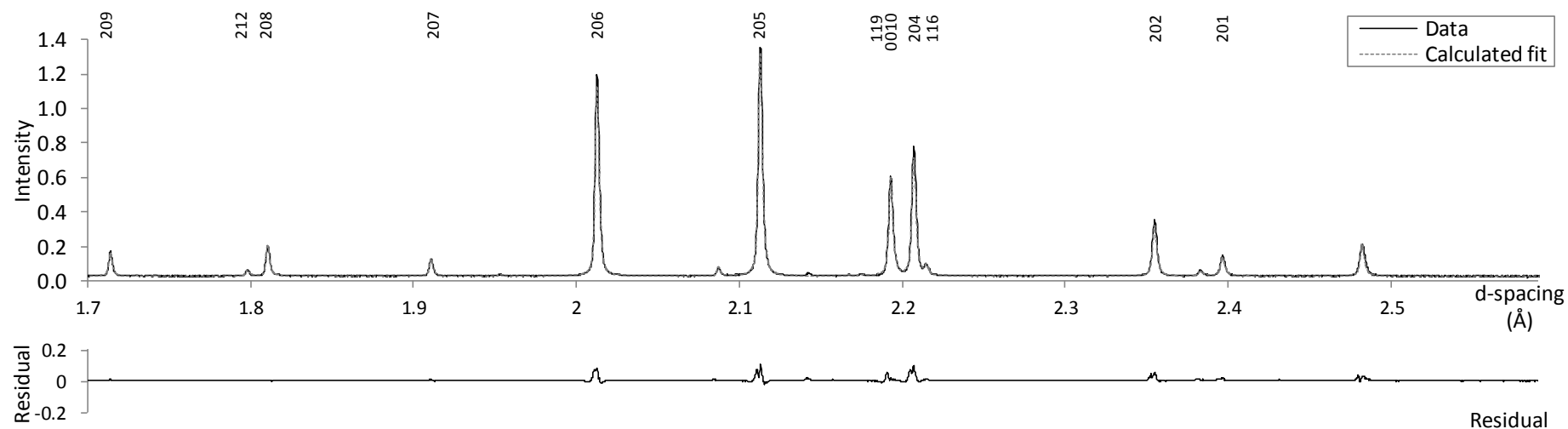


Figure 5-2 HibF(20,0) NPD data as a function of d-spacing with the calculated Rietveld refinement model and fit residual (below). The main hibernite reflections (hkl) are marked.

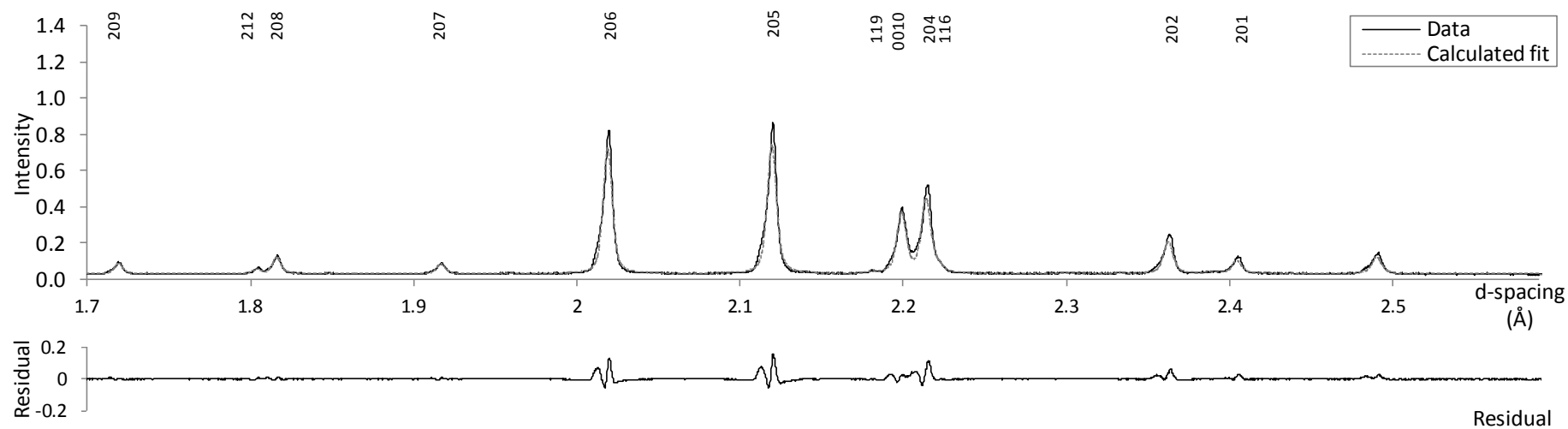


Figure 5-3 Hib9(44,43) NPD data as a function of d-spacing with the calculated Rietveld refinement model and fit residual (below). The main hibernite reflections (hkl) are marked.

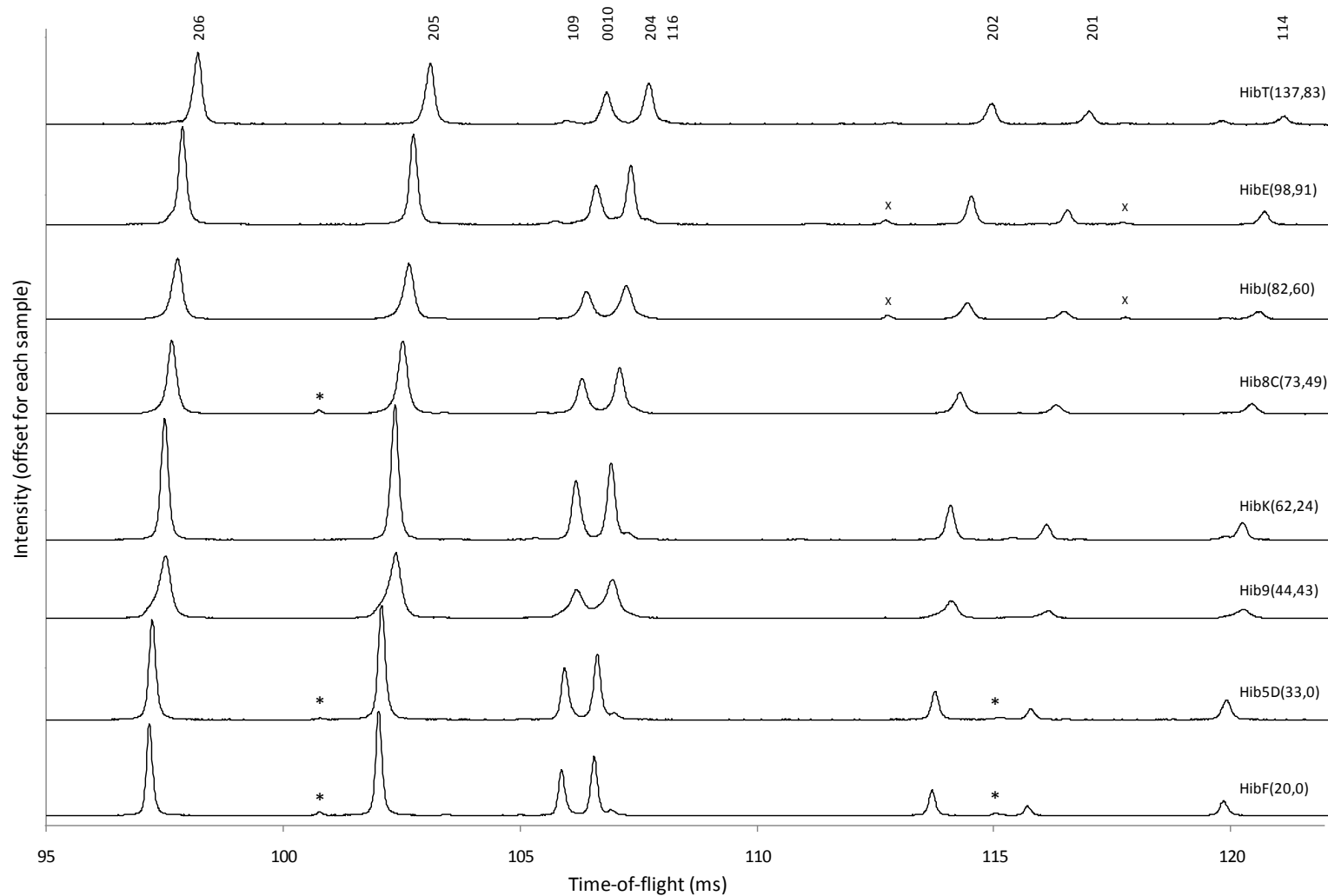


Figure 5-4 NPD data for the TOF range 95-126 ms collected on the backscatter detector (168°) at ambient temperature. The peaks of the Ti^{3+} -rich samples are narrow and intense, whereas the peaks of the Ti^{4+} -rich hibanite samples are broader and less intense. The peaks shift to higher TOF with increasing Ti pfu (samples increase in TiO_2 content away from the x-axis). Impurity peaks (* = Al_2O_3 , x = MgAl_2O_4) and hibanite reflections (hkl) are marked.

M1, M5 cations, followed by those of M3, then M2, and finally those of M4; after which the process was repeated until the model converged. At this point the ADPs were refined in an identical manner. Finally, with the same cautions approach, the atomic coordinates and ADPs of the atom-sets were refined together.

5.4 Results

The results of the Rietveld refinement of the NPD data are shown in Table 5-5, along with the refined structural parameters are the numerical fit indices. The results are shown in Figures 5-5 to 5-16. In particular, the lattice parameters are detailed in Table 5-6, and the site occupancies are presented in Table 5-7 and shown in Figure 5-7. Variation in axial lengths are discussed in Section 5.4.4 and shown in Figures 5-8 to 5-16.

Table 5-5 Site occupancy, fractional coordinates, ADP and fit statistics for synthetic hiconites (with uncertainties detailed for the last digit)

HibF(20,0)		Fit statistics:	N _{obs} 27711	χ^2 10.4	R _w 0.03	R _{wp} 0.02
Site	Occupancy	x	y	z	ADP	
Ca	1.000 (Ca)	0.66667	0.33333	0.25000	1.06 (3)	
M1	1.000 (Al)	0.00000	0.00000	0.00000	0.64 (2)	
M2	0.500 (Al)	0.00000	0.00000	0.26037 (7)	1.10 (3)	
M3	1.000 (Al)	0.33333	0.66667	0.02802 (4)	1.00 (2)	
M4	0.911 (1) (Al); 0.089 (1) (Ti)	0.33333	0.66667	0.19012 (4)	0.66 (2)	
M5	1.000 (Al)	0.1688 (6)	0.3375 (1)	-0.10889 (1)	0.82 (1)	
O1	1.000 (O)	0.00000	0.00000	-0.14952 (2)	0.80 (2)	
O2	1.000 (O)	0.66667	0.33333	0.05423 (3)	0.59 (1)	
O3	1.000 (O)	0.18094 (5)	0.3619 (1)	0.25000	1.13 (1)	
O4	1.000 (O)	0.15532 (3)	0.31075 (6)	0.05217 (1)	0.72 (1)	
O5	1.000 (O)	0.50336 (4)	1.00662 (9)	0.14897 (1)	0.75 (1)	
Hib5D(33,0)		Fit statistics:	N _{obs} 27703	χ^2 27.6	R _w 0.03	R _{wp} 0.03
Site	Occupancy	x	y	z	ADP	
Ca	1.000 (Ca)	0.66667	0.33333	0.25000	0.64 (4)	
M1	1.000 (Al)	0.00000	0.00000	0.00000	0.65 (4)	
M2	0.500 (Al)	0.00000	0.00000	0.2606 (1)	0.90 (5)	
M3	1.000 (Al)	0.33333	0.66667	0.02868 (6)	1.32 (3)	
M4	0.913 (1) (Al); 0.187 (1) (Ti)	0.33333	0.66667	0.18988 (8)	0.74 (4)	
M5	1.000 (Al)	0.1690 (1)	0.3379 (2)	-0.10881 (2)	1.06 (1)	
O1	1.000 (O)	0.00000	0.00000	-0.15008 (4)	1.16 (3)	
O2	1.000 (O)	0.66667	0.33333	0.05328 (5)	0.62 (2)	
O3	1.000 (O)	0.18156 (8)	0.3631 (2)	0.25000	1.50 (2)	
O4	1.000 (O)	0.15510 (5)	0.3102 (1)	0.05256 (2)	1.01 (1)	
O5	1.000 (O)	0.50323 (7)	1.0066 (2)	0.14882 (2)	0.99 (1)	

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Table 5-5 continued...

Hib K(62,24)		Fit statistics:	N _{obs} 27707	χ^2 26.6	R _w 0.04	R _{wp} 0.03
Site	Occupancy	x	y	z	ADP	
Ca	1.000 (Ca)	0.66667	0.33333	0.25000	1.78 (3)	
M1	1.000 (Al)	0.00000	0.00000	0.00000	0.46 (3)	
M2	0.474 (1) (Al); 0.026 (1) (Ti)	0.00000	0.00000	0.26284 (8)	1.05 (5)	
M3	0.890 (3) (Al); 0.110 (3) (Mg)	0.33333	0.66667	0.02843 (4)	0.99 (2)	
M4	0.748 (1) (Al); 0.252 (1) (Ti)	0.33333	0.66667	0.18861 (8)	0.93 (5)	
M5	1.000 (Al)	0.16931 (7)	0.3385 (1)	-0.10836 (2)	1.04 (1)	
O1	1.000 (O)	0.00000	0.00000	-0.14968 (3)	1.01 (2)	
O2	1.000 (O)	0.66667	0.33333	0.05505 (3)	0.74 (2)	
O3	1.000 (O)	0.18007 (6)	0.3602 (1)	0.25000	1.35 (1)	
O4	1.000 (O)	0.15429 (3)	0.30857 (7)	0.05237 (1)	1.01 (1)	
O5	1.000 (O)	0.50398 (4)	1.00805 (9)	0.14891 (1)	1.00 (1)	
HibT(137,83)		Fit statistics:	N _{obs} 27897	χ^2 27.4	R _w 0.03	R _{wp} 0.03
Site	Occupancy	x	y	z	ADP	
Ca	1.000 (Ca)	0.66667	0.33333	0.25000	2.52 (7)	
M1	1.000 (Al)	0.00000	0.00000	0.00000	0.49 (6)	
M2	0.468 (1) (Al); 0.032 (1) (Ti)	0.00000	0.00000	0.2676 (1)	1.0 (1)	
M3	0.500 (3) (Al); 0.500 (3) (Mg)	0.33333	0.66667	0.02904 (6)	0.71 (3)	
M4	0.385 (2) (Al); 0.615 (2) (Ti)	0.33333	0.66667	0.1891 (3)	1.0 (2)	
M5	1.000 (Al)	0.1676 (2)	0.3350 (3)	-0.10629 (3)	0.85 (2)	
O1	1.000 (O)	0.00000	0.00000	-0.14925 (6)	0.34 (4)	
O2	1.000 (O)	0.66667	0.33333	0.05705 (6)	0.93 (3)	
O3	1.000 (O)	0.1781 (1)	0.3563 (2)	0.25000	0.96 (2)	
O4	1.000 (O)	0.15307 (6)	0.3062 (1)	0.05319 (2)	0.65 (1)	
O5	1.000 (O)	0.50559 (7)	1.0113 (1)	0.14953 (3)	0.58 (2)	
Hib8C(73,49)		Fit statistics:	N _{obs} 27707	χ^2 22.7	R _w 0.05	R _{wp} 0.03
Site	Occupancy	x	y	z	ADP	
Ca	1.000 (Ca)	0.66667	0.33333	0.25000	1.63 (4)	
M1	1.000 (Al)	0.00000	0.00000	0.00000	0.46 (3)	
M2	0.455 (1) (Al); 0.045 (1) (Ti)	0.00000	0.00000	0.2633 (1)	1.08 (6)	
M3	0.750 (3) (Al); 0.250 (3) (Mg)	0.33333	0.66667	0.02826 (4)	0.99 (2)	
M4	0.694 (1) (Al); 0.306 (1) (Ti)	0.33333	0.66667	0.1876 (1)	0.99 (7)	
M5	1.000 (Al)	0.16883 (8)	0.3376 (2)	-0.10808 (2)	0.98 (1)	
O1	1.000 (O)	0.00000	0.00000	-0.15026 (3)	0.52 (2)	
O2	1.000 (O)	0.66667	0.33333	0.05601 (3)	0.74 (2)	
O3	1.000 (O)	0.18016 (6)	0.3604 (1)	0.25000	1.40 (1)	
O4	1.000 (O)	0.15351 (4)	0.30702 (8)	0.05276 (1)	0.99 (1)	
O5	1.000 (O)	0.50434 (5)	1.00875 (9)	0.14929 (1)	1.02 (1)	
HibJ(82,60)		Fit statistics:	N _{obs} 27707	χ^2 25.1	R _w 0.05	R _{wp} 0.04
Site	Occupancy	x	y	z	ADP	
Ca	1.000 (Ca)	0.66667	0.33333	0.25000	1.68 (4)	
M1	1.000 (Al)	0.00000	0.00000	0.00000	0.46 (4)	
M2	0.432 (1) (Al); 0.068 (1) (Ti)	0.00000	0.00000	0.2637 (1)	1.04 (8)	
M3	0.670 (3) (Al); 0.330 (3) (Mg)	0.33333	0.66667	0.02858 (4)	0.95 (2)	
M4	0.643 (1) (Al); 0.357 (1) (Ti)	0.33333	0.66667	0.1881 (2)	0.9 (1)	
M5	1.000 (Al)	0.1693 (1)	0.3385 (2)	-0.10789 (2)	1.02 (1)	
O1	1.000 (O)	0.00000	0.00000	-0.15076 (4)	0.51 (3)	
O2	1.000 (O)	0.66667	0.33333	0.05648 (4)	0.62 (2)	
O3	1.000 (O)	0.18056 (7)	0.3612 (2)	0.25000	1.41 (2)	
O4	1.000 (O)	0.15302 (4)	0.30605 (9)	0.05294 (2)	1.05 (1)	
O5	1.000 (O)	0.50456 (5)	1.0092 (1)	0.14925 (2)	0.97 (1)	

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Table 5-5 continued...

Hib9(44,43)		Fit statistics:	N _{obs} 27707	χ^2 26.5	R _w 0.05	R _{wp} 0.03
Site	Occupancy	x	y	z	ADP	
Ca	1.000 (Ca)	0.66667	0.33333	0.25000	1.48 (4)	
M1	1.000 (Al)	0.00000	0.00000	0.00000	0.57 (4)	
M2	0.452 (1) (Al); 0.048 (1) (Ti)	0.00000	0.00000	0.2627 (1)	1.17 (7)	
M3	0.790 (3) (Al); 0.210 (3) (Mg)	0.33333	0.66667	0.02778 (5)	0.91 (2)	
M4	0.802 (1) Al; 0.198 (1) (Ti)	0.33333	0.66667	0.18892 (8)	0.82 (5)	
M5	1.000 (Al)	0.16856 (9)	0.3370 (2)	-0.10832 (2)	0.96 (1)	
O1	1.000 (O)	0.00000	0.00000	-0.15037 (3)	0.38 (3)	
O2	1.000 (O)	0.66667	0.33333	0.05634 (4)	0.71 (2)	
O3	1.000 (O)	0.18109 (8)	0.3623 (2)	0.25000	1.26 (2)	
O4	1.000 (O)	0.15375 (4)	0.30750 (9)	0.05269 (2)	0.92 (1)	
O5	1.000 (O)	0.50347 (6)	1.0070 (1)	0.14937 (2)	0.96 (1)	
HibE(98,91)		Fit statistics:	N _{obs} 27707	χ^2 25.1	R _w 0.05	R _{wp} 0.03
Site	Occupancy	x	y	z	ADP	
Ca	1.000 (Ca)	0.66667	0.33333	0.25000	2.55 (4)	
M1	1.000 (Al)	0.00000	0.00000	0.00000	1.00 (3)	
M2	0.424 (1) (Al); 0.076 (1) (Ti)	0.00000	0.00000	0.26452 (1)	1.08 (7)	
M3	0.580 (3) (Al); 0.420 (3) (Mg)	0.33333	0.66667	0.02815 (4)	0.97 (2)	
M4	0.596 (1) (Al); 0.404 (1) (Ti)	0.33333	0.66667	0.1874 (2)	0.9 (1)	
M5	1.000 (Al)	0.16845 (8)	0.3368 (2)	-0.10732 (2)	1.24 (1)	
O1	1.000 (O)	0.00000	0.00000	-0.15061 (3)	0.98 (3)	
O2	1.000 (O)	0.66667	0.33333	0.05786 (3)	1.38 (2)	
O3	1.000 (O)	0.18067 (6)	0.3614 (1)	0.25000	1.29 (1)	
O4	1.000 (O)	0.15221 (4)	0.30442 (7)	0.05315 (1)	1.07 (1)	
O5	1.000 (O)	0.50403 (4)	1.00816 (8)	0.14961 (1)	1.08 (1)	

Table 5-6 Unit-cell of synthetic Ti-bearing hibonite

Sample	Unit-cell (Å) (uncertainty)		c/a		volume (Å ³)
	a	c			
HibF(20,0)	5.56686 (1)	21.92436 (4)	3.93837 (1)		588.408 (1)
Hib5D(33,0)	5.56960 (1)	21.93646 (6)	3.93861 (1)		589.310 (2)
HibK(62,24)	5.58523 (1)	21.98562 (5)	3.93639 (1)		593.952 (1)
Hib8C(73,49)	5.59471 (1)	22.00964 (6)	3.93401 (1)		596.622 (2)
HibJ(82,60)	5.60149 (1)	22.02502 (7)	3.93200 (1)		598.497 (7)
Hib9(44,43)	5.58464 (1)	21.98357 (7)	3.93644 (1)		593.771 (2)
HibE(98,91)	5.60643 (1)	22.07104 (6)	3.93674 (1)		600.794 (2)
HibT(137,83)	5.62790 (1)	22.11707 (9)	3.92990 (2)		606.669 (2)

Note: Uncertainty in last digit in brackets.

5.4.1 Ti content in hibonite

5.4.1.1 Ti saturation levels

As described in Section 3.3.1, the Ti saturation limits were explored by studying a series of either Ti³⁺ or Ti⁴⁺ hibonites with 0-1.25 Ti³⁺ pfu or 0-2.5 Ti⁴⁺ pfu respectively. Experimental products were examined using XRD to assess their purity. Under the experimental conditions used (1404 °C, $fO_2 = \Delta IW - 5.5$ (Ti³⁺) or $\Delta IW + 6.5$ (Ti⁴⁺), 1 atm) it was found that Ti³⁺ had saturated by 0.75 Ti³⁺ pfu and Ti⁴⁺ had saturated by 1 Ti⁴⁺ pfu. As Ti becomes incorporated in the hibonite structure the unit-cell expands, which became evident with shifts in the diffraction peaks to lower 2 Θ . Above 0.75 Ti³⁺ pfu

and 1 Ti^{4+} pfu no shifts in the diffraction peaks were observed. Furthermore, above these Ti contents, the proportions of impurities (Al_2O_3 , TiO_x , MgAl_2O_4 , CaTiO_3) increased dramatically. A range of mixed-valent Ti-bearing hibonites were produced within the Ti^{3+} and Ti^{4+} saturation limits defined above, and one sample was prepared with Ti^{3+} and Ti^{4+} just below their saturation limits, having 0.65 Ti^{3+} pfu and 0.8 Ti^{4+} pfu.

The maximum Ti pfu in natural hibonite was calculated to be 0.86 in terrestrial hibonite (Rakotondrazafy *et al.*, 1996) and 0.73 Ti pfu in meteoritic hibonite (Allen *et al.*, 1978) using composition data with Ti reported as TiO_2 . Up to 1.9 Ti^{3+} pfu was reported in synthetic $\text{Ca}(\text{Al,Ti})_{12}\text{O}_{19}$ single crystals grown as an impurity phase during an iron smelting process (Wittmann *et al.*, 1958). Ti^{4+} -rich phases isostructural with hibonite produced by sintering metal oxides in stoichiometric proportions have been reported with up to 6 Ti^{4+} pfu ($\text{SrTi}_6\text{Co}_6\text{O}_{19}$; Graetsch and Gebert, 1995). There has been no report of hibonite, natural or synthesised, with >1 Ti^{4+} pfu.

The synthesis conditions, the bulk composition and various active substitution mechanisms all have a direct bearing on the proportion of Ti that may be incorporated into the hibonite structure. At the structural level, Ti substitution may be controlled by site occupancy or by ordering characteristics on a single site or across several sites.

5.4.1.2 Refined composition versus EDS SEM composition

The initial Ti and Mg concentrations in the refinements were set to those determined by EDS SEM. During the refinement process, the Ti values were allowed to vary, as were the Mg contents (if necessary). It seems reasonable to expect a 1:1 correlation between the Rietveld refined and EDS determined Ti contents and likewise for the Mg content, and this is evident in Figure 5-5a. Therefore comparison of the refined structural parameters may be made using either the refined Ti pfu or Ti pfu determined by EDS. In this thesis the refined structural data has been plotted against Ti determined by EDS in order to maintain consistency with other chapters.

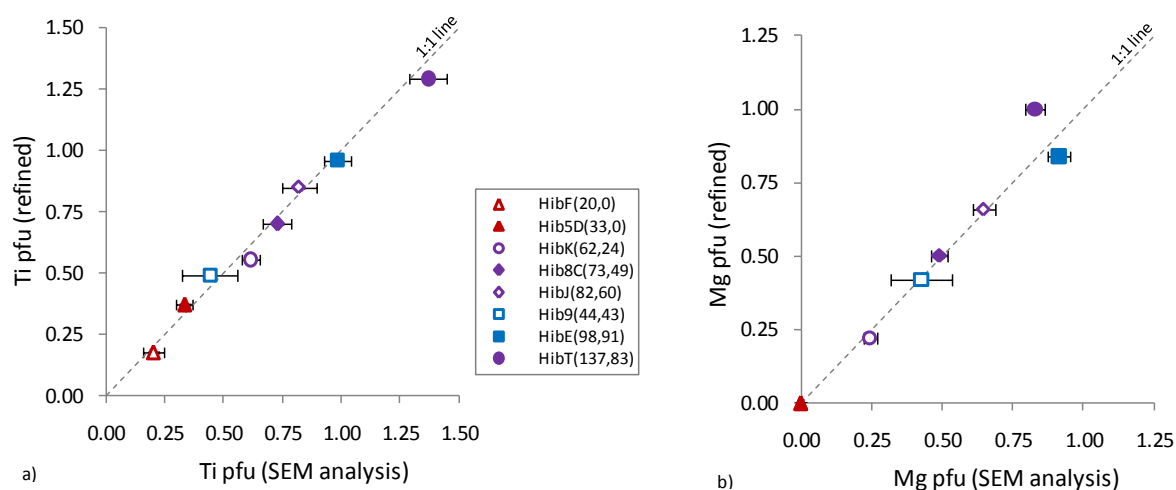


Figure 5-5 (a) Ti pfu as refined from NPD data versus that determined by EDS plotted along with a 1:1 reference line; and (b) Mg pfu as refined (if necessary) versus that determined by EDS. Uncertainties: SEM = 1σ standard deviation; refined data = $<$ data point size. Colour code: Ti^{3+} hibonite in red, Ti^{4+} hibonite in blue, mixed-valent hibonite in purple.

The Mg content of HibT(137,83) was refined to be slightly higher than that determined by EDS SEM (Figure 5-5b), although it should be noted that the refinements of the NPD data for this sample were prone to effects relating to contrast matching. It is important to be as precise as possible with the Mg content as this value will affect the calculated %Ti³⁺ in the mixed-valent hibonites. In order to maintain consistency across chapters therefore, the Mg pfu determined by EDS SEM will be used in further discussion and presentation of these data.

5.4.2 Cell parameters

The unit-cell parameters of the Ti-bearing hibonites of this study are shown in Figure 5-6 along with those of synthetic CaAl₁₂O₁₉ (Hofmeister *et al.*, 2004), synthetic CaAl_{10.1}Ti_{1.9}O₁₉ (Wittmann *et al.*, 1958) and terrestrial Ti⁴⁺ hibonite (Nagashima *et al.*, 2010).

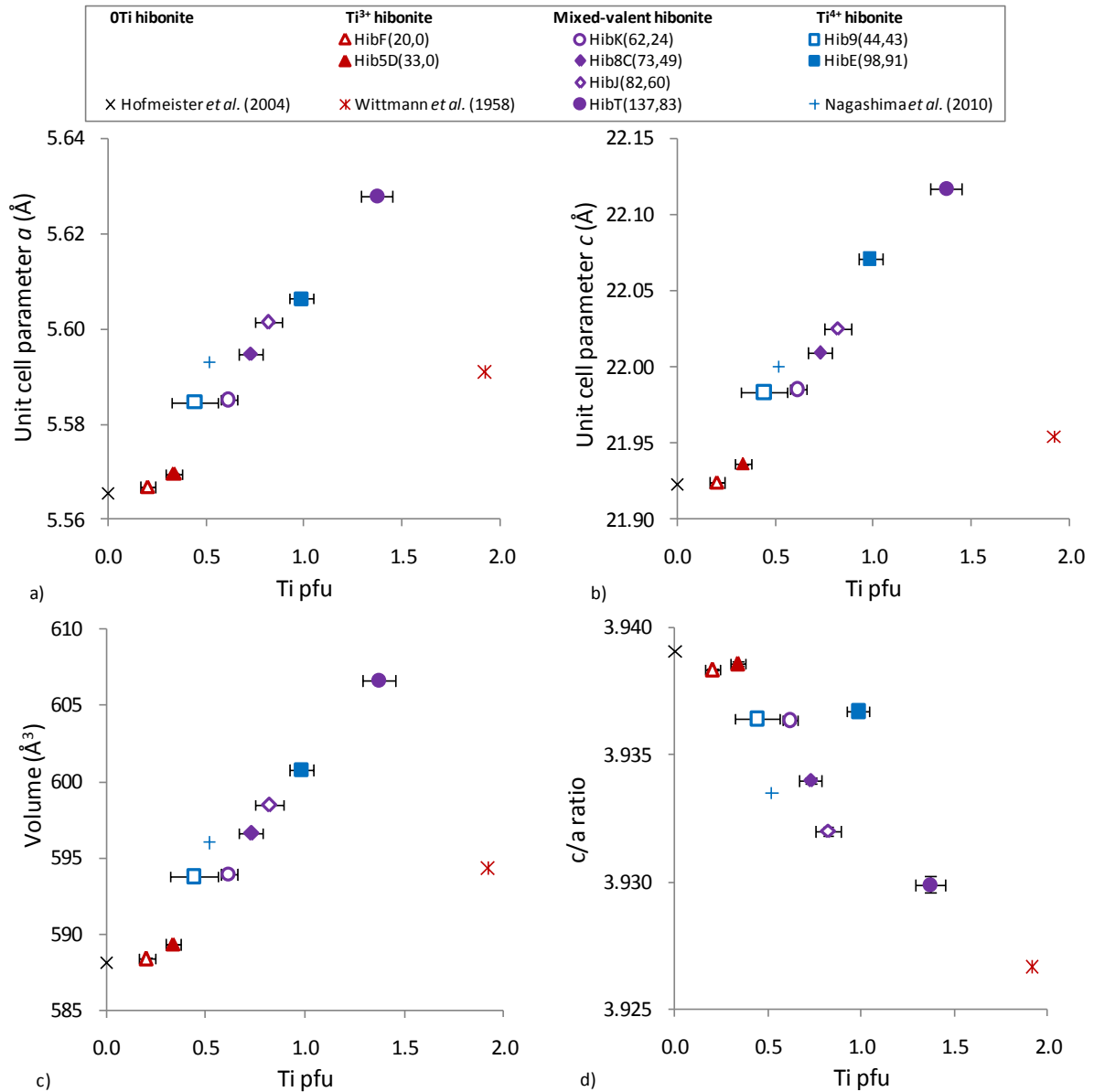


Figure 5-6 Hibonite unit-cell parameters (a) a and (b) c , (c) volume and (d) c/a ratio as a function of Ti-content as determined by EDS. Uncertainties in the refined parameters are smaller than the data points. Also shown are synthetic Ti³⁺

hibonite (Wittmann *et al.*, 1958); synthetic O-Ti hibonite (Hofmeister *et al.*, 2004); and terrestrial Ti^{4+} hibonite (Nagashima *et al.*, 2010). Data in Appendix D.3.2. Colour code: Ti^{3+} hibonite in red, Ti^{4+} hibonite in blue, mixed-valent hibonite in purple.

For the Ti^{3+} -bearing hibonites, substitution of Ti^{3+} appears to increase the unit-cell parameters linearly as a function of Ti pfu (Figure 5-6) from those of pure $\text{CaAl}_{12}\text{O}_{19}$. The unit-cell parameters of the pure Ti^{4+} -bearing hibonites also appear to increase linearly with Ti pfu from those of the synthetic hibonite of Hofmeister *et al.* (2004). The rate of increase of the unit-cell parameters as a function of Ti pfu is greater for the Ti^{4+} hibonites than for the Ti^{3+} hibonites. The unit-cell parameters of the mixed-valent hibonites increase as a function of Ti pfu between the trends defined by the Ti^{3+} and Ti^{4+} hibonites, with their proximity to these limits defined by their $\text{Ti}^{3+}/\text{Ti}^{4+}$ ratio. The c/a ratio of the sample series forms a linear trend with Ti pfu, showing that the rate of expansion of the unit-cell parameter *a* relative to the unit-cell parameter *c* remains constant, irrespective of the Ti oxidation state.

5.4.3 Ti substitution mechanism

The results of the NPD data refinements reveal the Ti site occupancy, and a summary of these data are presented in Table 5-7. Ti in the Ti^{3+} hibonites occupies the M4 octahedral site. In the Ti^{4+} hibonites, Mg^{2+} occupies the M3 tetrahedral site and Ti^{4+} partitions between the M2 trigonal bipyramidal site and the M4 octahedral site in a roughly constant ratio. Similarly, in the mixed-valent hibonites Mg^{2+} occupies M3 and Ti occupies both the M2 and M4 sites.

Table 5-7 Ti occupancy of the M2 and M4 sites

Sample	Ti occupancy		Ti occupancy M4 †		$\frac{\text{Ti}^{\text{Tot}}_{\text{M4}}}{\text{Ti}^{4+}_{\text{M2}}}$	$\frac{\text{Ti}^{4+}_{\text{M4}}}{\text{Ti}^{4+}_{\text{M2}}}$
	M2	M4	Ti^{3+}	Ti^{4+}		
HibF(20,0)	-	0.089 (1)	0.089 (1)	-	-	-
Hib5D(33,0)	-	0.187 (1)	0.187 (1)	-	-	-
HibT(137,83)	0.064 (2)	0.615 (2)	0.26 (3)	0.36 (3)	19.2 (6)	11.3 (9)
HibK(62,24)	0.052 (2)	0.252 (1)	0.16 (2)	0.09 (2)	9.7 (4)	3.3 (5)
Hib8C(73,49)	0.090 (2)	0.306 (1)	0.12 (2)	0.19 (2)	6.8 (2)	4.3 (4)
HibJ(82,60)	0.136 (2)	0.357 (1)	0.11 (2)	0.25 (2)	5.3 (1)	3.7 (3)
Hib9(44,43)	0.096 (2)	0.198 (1)	-	0.198 (1)	4.1 (1)	4.1 (1)
HibE(98,91)	0.152 (2)	0.404 (1)	-	0.404 (1)	5.3 (1)	5.3 (1)
Nagashima <i>et al.</i> (2010)	0.087 (4)	0.222 (5)	-	0.222 (5)	5.1 (3)	5.1 (3)

Notes: Uncertainty in last digit in brackets: from GSAS (Ti pfu) or the propagated uncertainty (Ti^{3+} or Ti^{4+} pfu).

† $\text{Ti}^{3+}_{\text{M4}} \text{ pfu} = \text{Ti}^{\text{Tot}}_{\text{M2,M4}} \text{ (as refined)} \times (\% \text{Ti}^{3+} / \Sigma \text{Ti})$ (by stoichiometry); $\text{Ti}^{4+}_{\text{M4}} \text{ pfu} = \text{Ti}^{\text{Tot}}_{\text{M4}} - \text{Ti}^{3+}_{\text{M4}}$

In previous studies (Section 5.2.2) Mg^{2+} was placed, rather than refined, on the M3 site in both terrestrial hibonite (<0.6 Mg pfu; Bermanec *et al.*, 1996), β -alumina ($\text{Na}_2\text{MgAl}_{10}\text{O}_{17}$; Bettman and Peters, 1969) and magnetoplumbite ($\text{PbFe}_{9.3}\text{Mn}_{1.8}\text{Sb}_{0.6}\text{Mg}_{0.3}\text{O}_{19}$; Bermanec *et al.*, 1996). One of the advantages of NPD is the ability to discriminate between Mg and Al (scattering lengths of +5.38 and

+3.45 fm respectively; Sears, 1992), whereas with XRD this is very difficult. Refinement of NPD data shows explicitly that Mg occupies the M3 tetrahedral site, whereas previous studies had to rely upon crystal chemical considerations to infer that Mg occupied the M3 site.

Refinement of the NPD data shows unambiguously that Ti^{3+} only occupies the M4 octahedral site and provides the first direct evidence for Ti^{3+} site occupancy. These results are, however, contrary to the findings of two previous studies that infer site occupancy from indirect spectroscopic data (Burns and Burns, 1984; Beckett *et al.*, 1988). Based on optical absorption spectra presented in an abstract by Stolper and Ihinger (1983), Burns and Burns (1984) reasoned that Ti^{3+} did not occupy an octahedral site as the Ti^{3+} absorption band in hibonite (~715 nm) was offset from that of Ti^{3+} in octahedral coordination in Al_2O_3 (~540 nm). Burns and Burns (1984) therefore suggested that Ti^{3+} occupies the M2 site, which they supported with crystal field theory reasoning. Similar spectroscopic data, however, for Ti^{3+} in a range of pyroxenes shows that the absorption band of Ti^{3+} in octahedral coordination shifts to much higher wavelengths (~640 nm), close to that measured for Ti^{3+} in hibonite (Burns and Huggins, 1973; Ihinger and Stolper, 1986), so it is possible that the absorption band could indeed relate to Ti^{3+} in an octahedral site in hibonite. ESR spectra collected in the study by Beckett *et al.* (1988) were interpreted to infer that Ti^{3+} occupied a strongly distorted site, which they identified as the M2 site, however ESR spectra of β -alumina, a phase with a similar structure to hibonite, were interpreted to arise from Ti^{3+} in octahedral coordination (Barret *et al.*, 1985). It is not unreasonable for Ti^{3+} to occupy octahedral sites in mineral structures, as reported for meteoritic pyroxene (Burns and Huggins, 1973), Ti-bearing pyrope (Rager *et al.*, 2003) and synthetic Ti-doped corundum (Vorobeveva *et al.*, 2009). Moreover, Beckett *et al.* (1988) stated that Ti^{3+} would favour the most distorted of the Al sites in hibonite, and this study will show that the M4 Ti^{3+} -bearing site is more distorted than they thought (Section 5.4.4.1).

This study found no evidence for Ti^{4+} occupying the M1 or M5 octahedral sites, despite the range of approaches to the structural refinements (Section 5.3.3). When Al^{3+} is a minor component in phases isostructural with hibonite, such as nežilovite ($\text{PbFe}_{8.0}\text{Zn}_{1.9}\text{Mn}_{2.5}\text{Ti}_{0.4}\text{Al}_{1.0}\text{O}_{19}$), it occupies the M1 and M5 sites (Bermanec *et al.*, 1996). This suggests that the affinity of Al^{3+} for the M1 and M5 sites precludes Ti substitution on these sites in an Al^{3+} -dominated phase such as hibonite, although in principle it is possible for Ti^{4+} to occupy the M1 and M5 (and M2, M4), as reported for Ti-rich magnetoplumbite phases such as $\text{SrTi}_6\text{Co}_6\text{O}_{19}$ (Graetsch and Gebert, 1995; Table 5-2).

Refinement of NPD data shows that Ti^{4+} in hibonites partitions between the M2 and M4 sites, in agreement with the single crystal XRD study of Nagashima *et al.* (2010). Previous single crystal XRD studies of terrestrial hibonite only reported Ti^{4+} on the M4 site (Bermanec *et al.*, 1996) and no Ti on the M2 site. The hibonite crystal of Bermanec *et al.* (1996), however, contained 0.3 Fe^{3+} pfu which was found to occupy the M2 site. It is possible that the presence of Fe^{3+} on the M2 site masks the presence of relatively small proportion of Ti^{4+} on M2, or even physically precludes Ti^{4+} from occupying this site. Such an argument is supported by the crystal chemistry of isostructural

Fe^{3+} bearing $\text{Ba}(\text{Fe,Ti,Co})_{12}\text{O}_{19}$ where Fe^{3+} was shown to occupy M2 preferentially with respect to Ti^{4+} . Indeed, Ti^{4+} only occupied the M2 site at $>4 \text{ Ti}^{4+}$ pfu.

In the mixed-valent samples, the Ti content on both M2 and M4 increased with increasing Ti pfu and there was no evidence for Ti occupying any other site, even up to 1.4 Ti pfu. Indeed, the Ti content on M2 is linearly correlated with Ti^{4+} (using Mg^{2+} as a proxy) in the hibonites with <1 Ti pfu, as shown in Figure 5-7a. Considering this, and the fact that refinements of the NPD data clearly show that in the Ti^{3+} hibonites, Ti^{3+} only occupies the M4 site, it seems reasonable to assume that in the mixed-valent samples the Ti on the M2 site is all Ti^{4+} . Furthermore, the ratio of Ti^{4+} on M4 to Ti^{4+} on M2 ($\text{Ti}^{4+}_{\text{M4}}/\text{Ti}^{4+}_{\text{M2}}$) remains constant at 4.3 for hibonite as a function of increasing Ti (up to 1 Ti pfu), as shown in Figure 5-7b. That is to say $19 \pm 3\%$ of the total Ti^{4+} in the Ti^{4+} -bearing hibonite samples, including the mixed-valent hibonites, occupies the M2 site. The partitioning of Ti^{4+} between M2 and M4 in the hibonite crystal analysed by Nagashima *et al.* (2010) agrees with this value.

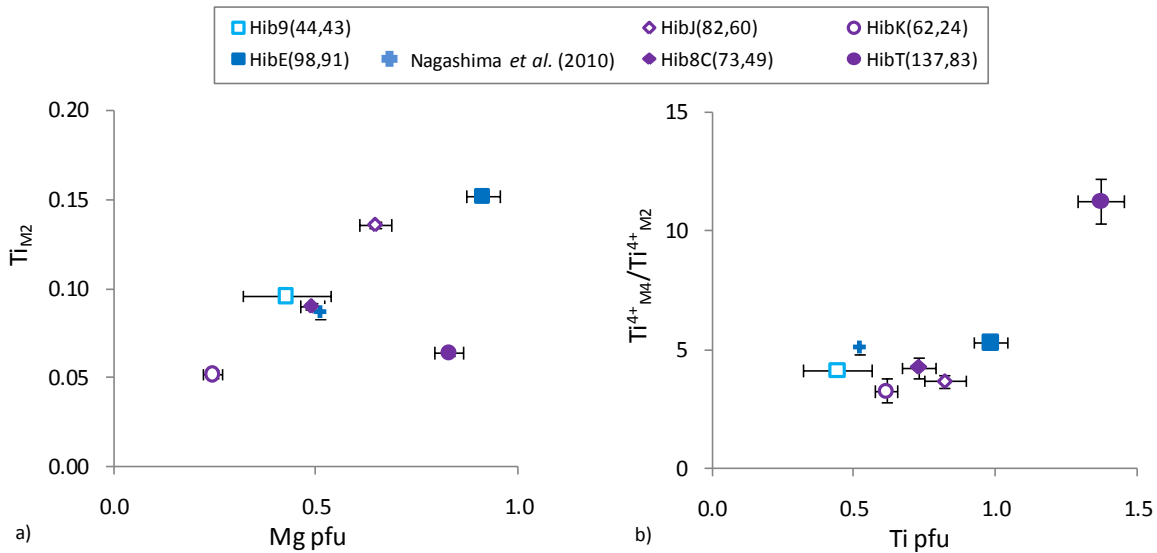


Figure 5-7 (a) Ti on M2 as a function of Mg pfu showing a near-linear correlation for hibonite with <1 Ti pfu; (b) $\text{Ti}^{4+}_{\text{M4}}/\text{Ti}^{4+}_{\text{M2}}$ as a function of Ti pfu showing that the $\text{Ti}^{4+}_{\text{M4}}/\text{Ti}^{4+}_{\text{M2}}$ ratio of hibonites with <1 Ti pfu is constant, whereas that of HibT(137,83) is higher. Included is the terrestrial Ti^{4+} hibonite of Nagashima *et al.* (2010). Colour code: Ti^{4+} hibonite in blue, mixed-valent hibonite in purple.

The $\text{Ti}^{4+}_{\text{M4}}/\text{Ti}^{4+}_{\text{M2}}$ ratio for HibT(137,83), which has >1 Ti pfu, appears, however, to deviate from this constant (Figure 5-7). This may be related to experimental uncertainty, especially as the refinement of the NPD data for this sample was complicated by apparent contrast matching effects. Alternatively, it may reflect some crystal chemical change associated with Ti >1 Ti pfu occurring within the hibonite structure. There are three potential explanations for this. Firstly, in order to avoid Ti-Ti interactions across the shared face of the M4 octahedra, the structure may impose a new substitution mechanism that does not involve M4 or M2. There is, however, no supporting evidence for Ti on any other site. Secondly, Ti-Ti interactions across the shared face of the M4 octahedra may be avoided by substituting more Ti on M2. This explanation however, contradicts what is observed in Figure 5-7 and the constant nature of the $\text{Ti}_{\text{M4}}/\text{Ti}_{\text{M2}}$ ratio of the other samples in the series. Figure 5-7

implies the Ti content on M4 has increased significantly with respect to that on M2. It is possible that Ti^{4+} on M2, displaced from the equatorial plane of the trigonal bipyramid, is ordered to be diagonally opposite the M4 octahedra that contains Ti. Above 1 Ti pfu this is no longer possible. Consequently, in order to minimise the effects of Ti-Ti interactions between M4 and M2, it is more sustainable to increase Ti on M4 and accommodate increased Ti-Ti interactions across the shared face of the M4 octahedral pair, correspondingly reducing the amount of Ti on M2. To be more conclusive in this matter, refinements of NPD data of more samples with >1 Ti pfu would be required.

5.4.4 Structural systematics

5.4.4.1 Systematic changes in bond-lengths

Interatomic distances calculated from the refinements are shown in Figures 5-8 to 5-16 and tabulated in Appendix D.3.3. The Ca, M1, M5 sites are not directly involved in the Ti substitution mechanism. Nevertheless, M-O distances of these sites vary systematically as a function of Ti pfu for hibonites with <1 Ti pfu (Figures 5-8 to 5-9). For sites involved with the Ti substitution mechanism, namely M3 (Mg), M2 and M4 (Ti), the M-O distances also vary systematically as a function of Ti pfu (Figures 5-10 to 5-12).

The 12-fold coordinated Ca atom is coordinated with O in two distinct geometries. The Ca-O3 distance (>2.78 Å) is longer than the Ca-O5 distance (2.72 Å). The Ca-O3 distance increases linearly as a function of Ti pfu with a total increase of 0.03 Å, whereas the Ca-O5 distance remains constant, regardless of the Ti content (Figure 5-8).

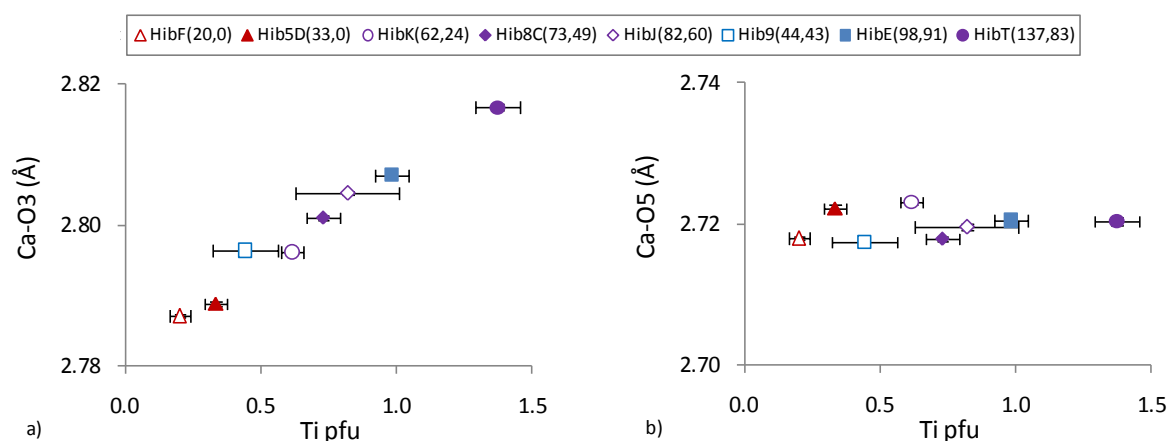


Figure 5-8 (a) Ca-O3 and (b) Ca-O5 distances as a function of Ti pfu showing a linear increase in the Ca-O3 distance (six bonds) with increasing Ti pfu, whereas the Ca-O5 distance (six bonds) remains constant. Colour code: Ti^{3+} hibonite in red, Ti^{4+} hibonite in blue, mixed-valent hibonite in purple.

The non-Ti-bearing M1 octahedral site has six M1-O4 bonds. The M1-O4 distance (~ 1.89 Å) remains unaffected by Ti content up to 1 Ti pfu, after which an increase of over 0.01 Å is observed (Figure 5-9a).

The M5 octahedral site is coordinated with four distinct O atoms and becomes progressively more distorted with greater Ti pfu (Figure 5-9b,c). Both the M5-O2 and M5-O4 bonds shorten with increasing Ti pfu (by 0.06 and 0.04 Å respectively), whereas the M5-O1 and M5-O5 bonds lengthen (by 0.04 and 0.05 Å respectively).

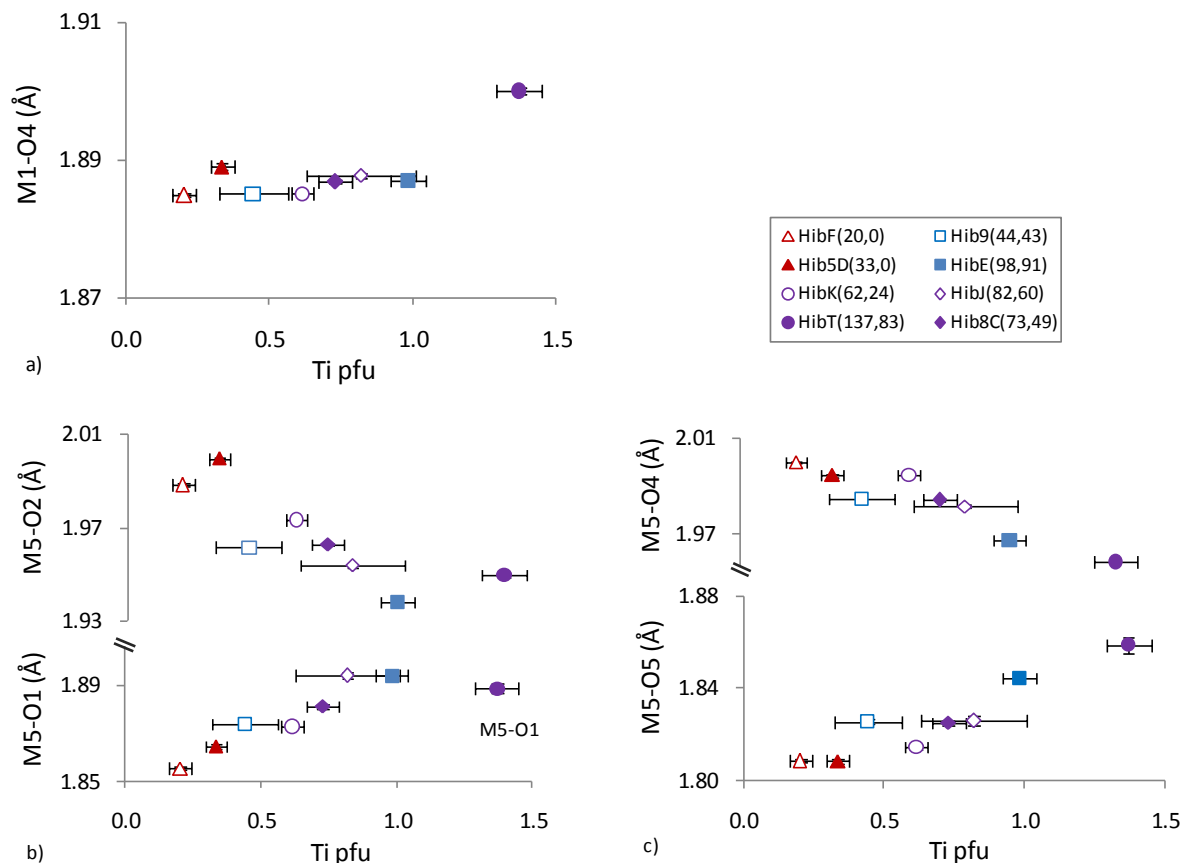


Figure 5-9 (a) M-O distances of the non-Ti-bearing octahedral M1 site as a function of Ti pfu, showing the M1-O4 distance (six bonds) remains unchanged for hibonite with <1 Ti pfu, whereas that of HibT(137,83) is larger. (b,c) M5-O2 and M5-O4 distances (one and two bonds respectively) generally decrease in length with increasing Ti pfu, whereas the M5-O1 and M5-O5 distances (one and two bonds respectively) increase with more Ti pfu. Colour code: Ti^{3+} hibonite in red, Ti^{4+} hibonite in blue, mixed-valent hibonite in purple.

Within the M3 tetrahedral site, the M3-O2 and M3-O4 distances of the Ti^{3+} hibonites are so similar that it appears that the Ti^{3+} (<0.33 Ti^{3+} pfu) content does not change the symmetrical nature of the tetrahedral site (Figure 5-10a,b). For the Ti^{4+} -bearing hibonites with <1 Ti pfu, the M3-O2 and M3-O4 distances increase linearly as a function of Ti pfu, with M3-O2 increasing by 0.11 Å and the M3-O4 distance lengthening by 0.05 Å, (Figure 5-10a,b). The lengthening of the M3-O2 distance parallel to the c-axis is approximately double the lengthening of the M3-O4 distance, which causes the M3 site to trigonally distort in the Ti^{4+} -bearing hibonites (Figure 5-10c). The lengthening of the M3-O distances is positively correlated with Mg content (e.g. Figure 5-10d) and it therefore appears that the Mg-content controls changes in the M3-O distance.

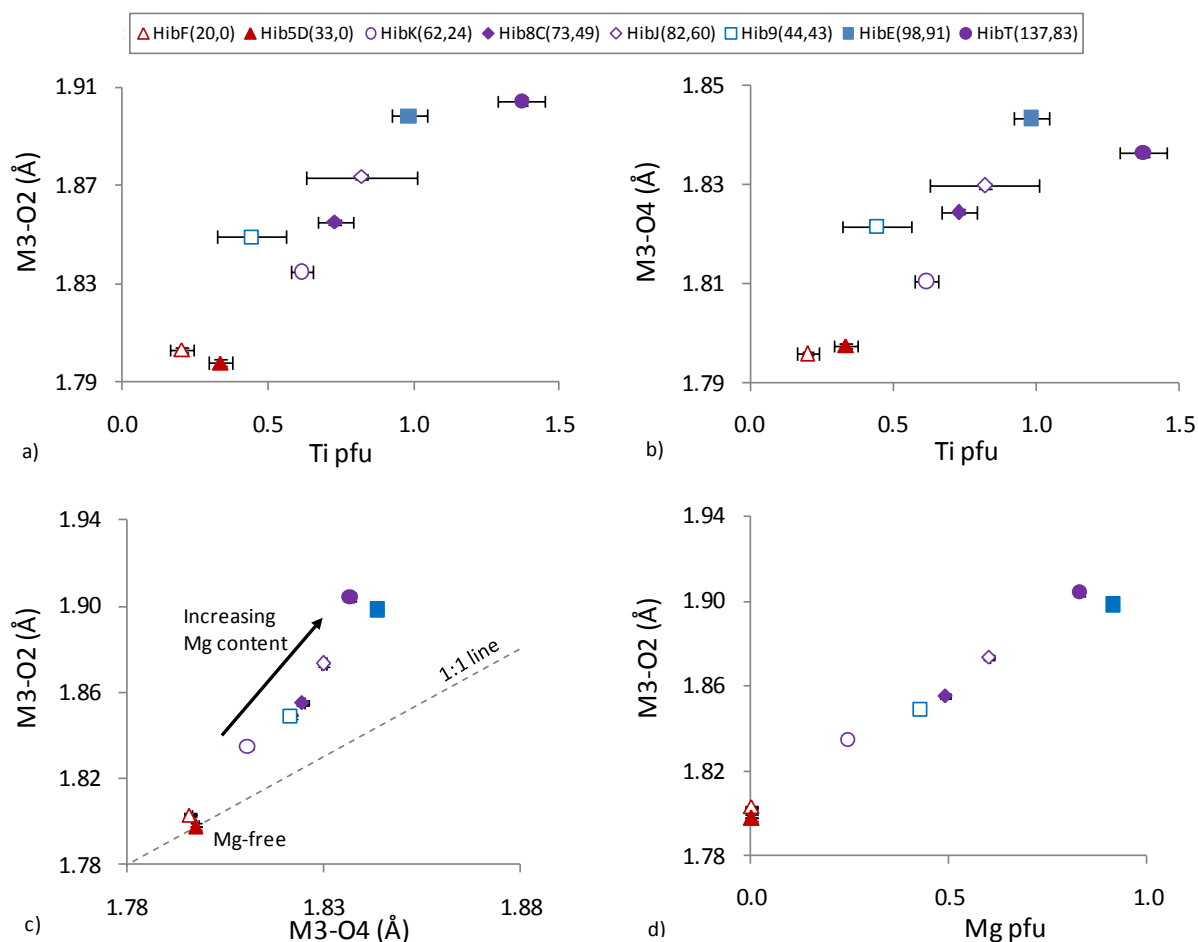


Figure 5-10 (a) M3-O2 and (b) M3-O4 distances as a function of Ti pfu showing an increasing in M-O bond lengths with increasing Ti pfu for the Ti^{4+} -bearing hibonites. (c) The axial M3-O2 distance (one bond) as a function of the M3-O4 distance (three bonds) showing the M3 site of the Ti^{3+} hibonites is undistorted, whereas the M3 site of the Ti^{4+} -bearing samples are trigonally distorted. (d) The M3-O2 distance as a function of Mg content showing a positive correlation. Colour code: Ti^{3+} hibonite in red, Ti^{4+} hibonite in blue, mixed-valent hibonite in purple.

The trigonal bipyramidal M2 site incorporates 19% of the total Ti^{4+} for Ti^{4+} -bearing hibonites with <1 Ti pfu. The M2-O3 distance for the three equatorial bonds does not vary greatly across the series, increasing by $0.02 \text{ \AA}$ as a function of increasing Ti. The M2-O1 bonds parallel to the c-axis, vary in an opposing manner: the longer of the two M2-O1 bonds lengthens by $0.19 \text{ \AA}$, whereas the shorter of the two M2-O1 bonds shortens by $0.14 \text{ \AA}$ (Figure 5-11a,b). The changes in the M2-O1 lengths reflect an axial displacement of the M2 cation further from the O3 equatorial plane with more Ti pfu, a correlation which is near-linear with an increase in displacement of $0.16 \text{ \AA}$ across the series and a total displacement of $0.39 \text{ \AA}$ (Figure 5-11c). The O1-O1 distance across the M2 site is fairly constant for the hibonites with <1 Ti pfu ($4.4 \text{ \AA}$), with HibT(137,83) showing about 6% increase in the O1-O1 distance (Figure 5-11d). This 6% increase is likely due to the substitution of >1 Ti pfu across both the M2 site and the adjacent M4 sites in HibT(137,83), which may distort this structure differently to the hibonite samples with <1 Ti pfu.

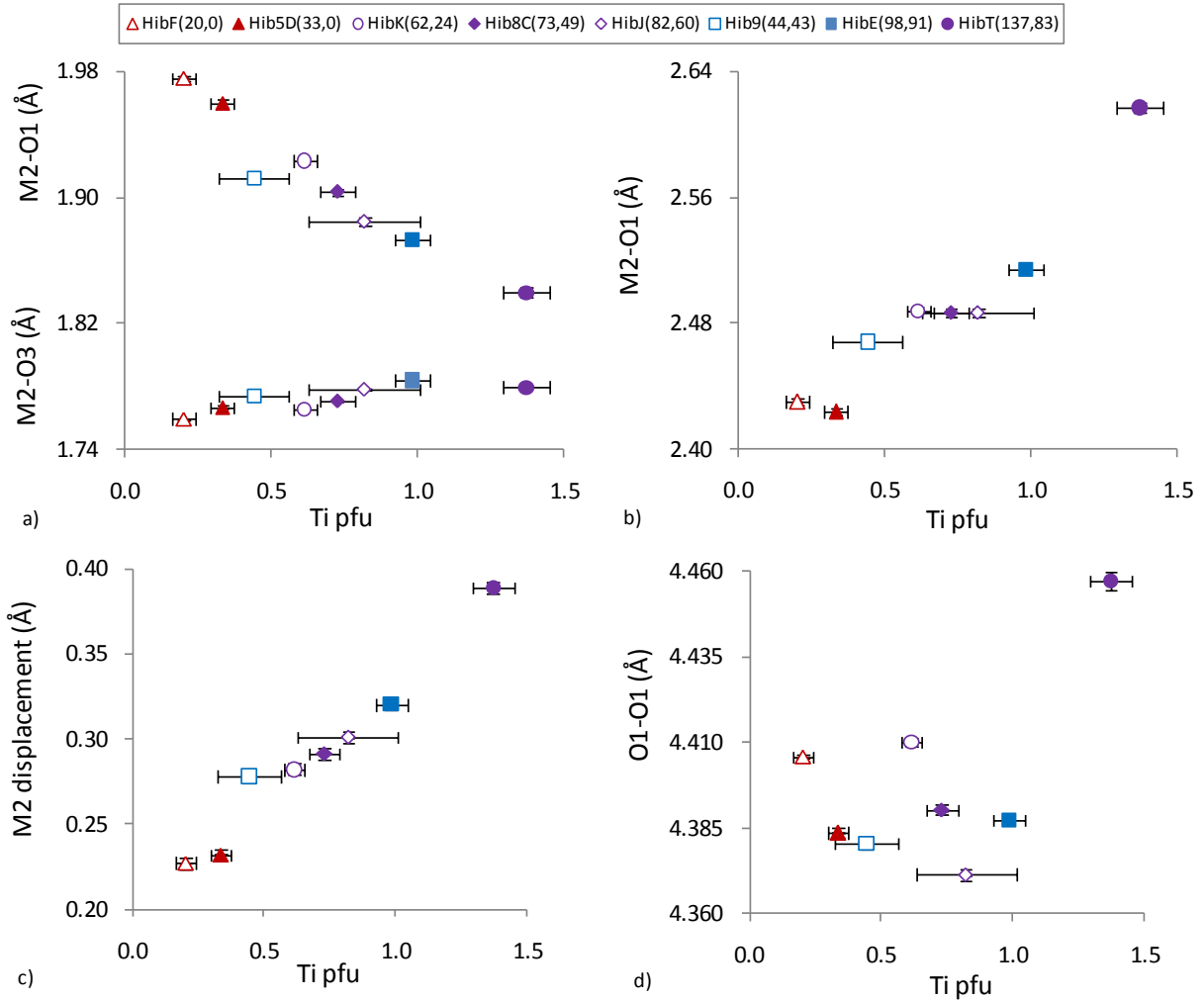


Figure 5-11 (a,b) M2-O distances as a function of Ti pfu, showing the shorter M2-O1 distance shortens, whereas the longer M2-O1 distance lengthens and the M2-O3 distances (three bonds) increases with more Ti pfu. (c) The M2 displacement from the O3 equatorial plane as a function of Ti pfu showing a positive correlation. (d) The O1-O1 distance across the M2 site as a function of Ti pfu showing the O1-O1 distance is fairly constant for <1 Ti pfu, with that of HibT(137,83) showing an increase of 6%. Colour code: Ti^{3+} hibonite in red, Ti^{4+} hibonite in blue, mixed-valent hibonite in purple.

All the Ti^{3+} cations and 81% of Ti^{4+} cations occupy the M4 site. There is no observable distortion to this octahedral site as Ti^{3+} increases up to 0.33 Ti pfu, whereas the M4-O3 distance of the Ti^{4+} -bearing hibonites lengthens linearly by 0.06 Å up to 1 Ti pfu, after which it appears to stabilize (Figure 5-12). The M4-O5 distance shortens slightly (by 0.01 Å) with increasing Ti pfu up to 1 Ti pfu, after which it increases. Increasing M4-O3 and decreasing M4-O5 distances in the Ti^{4+} -bearing hibonites with <1 Ti pfu indicate that the M4 site of these hibonites becomes more distorted with increasing Ti pfu.

An alternative approach to discussing the hibonite structure is to consider it in terms of a repetition of two distinct polyhedral layers perpendicular to the c-axis (e.g. Burns and Burns, 1984). In this case, the unit-cell is formed by stacking R- (Figure 5-13) and S-blocks (Figure 5-14) according to the sequence RSR'S', where R' and S' are rotated 180° relative to the other blocks (Bermanec *et al.*, 1996).

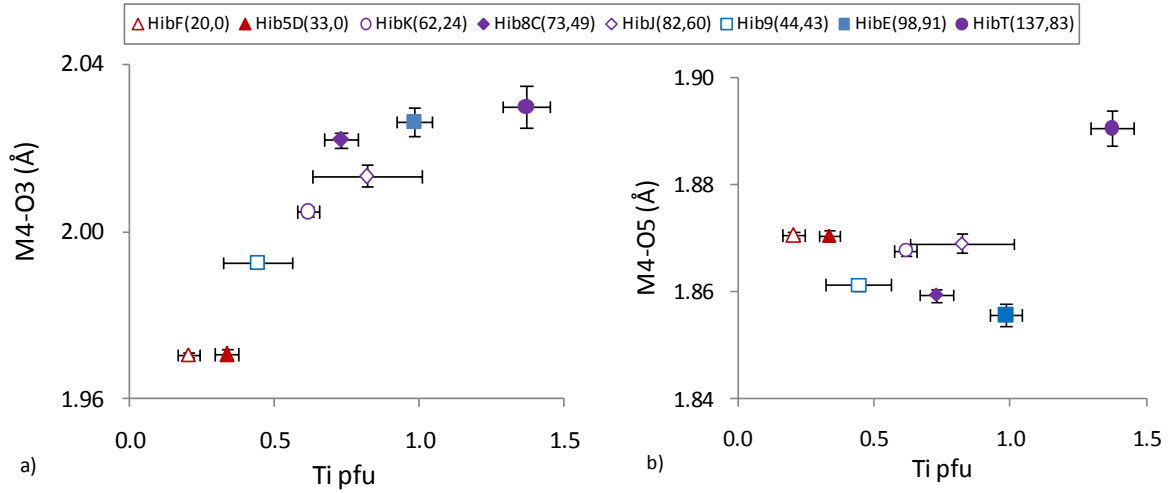


Figure 5-12 (a) M4-O3 and (b) M4-O5 distances (three bonds each) as a function of Ti pfu showing the M4-O3 distances increase as a function of Ti pfu, whereas the M4-O5 distances decrease slightly as a function of Ti for hibonites with <1 Ti pfu. The M4-O5 distance for HibT(137,83) is more than 0.02 Å larger than that of the hibonites with <1 Ti pfu. Colour code: Ti^{3+} hibonite in red, Ti^{4+} hibonite in blue, mixed-valent hibonite in purple.

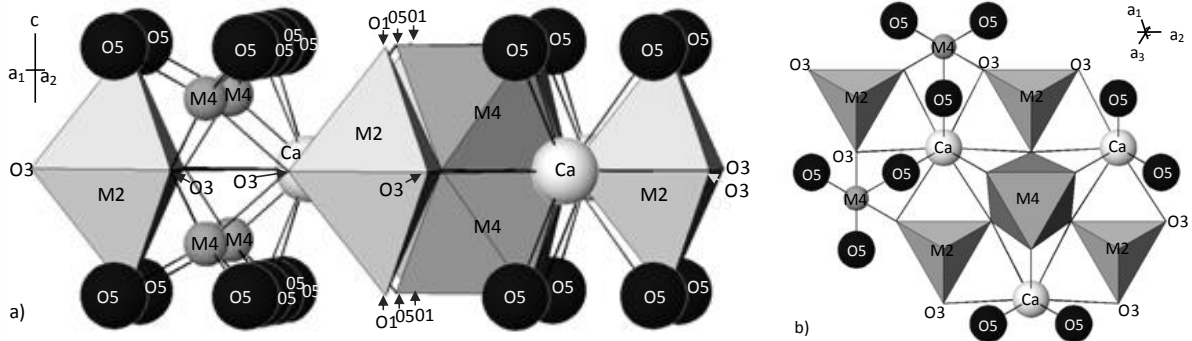


Figure 5-13 A section of the hibonite structure showing the face-sharing M4 octahedra in relation to the Ca and M2 atoms (a) with the c-axis in the plane of the page; and (b) with the c-axis normal to the page. The Ca, M2 and M4 sites are totally contained within the R-block of Bermanec *et al.* (1996).

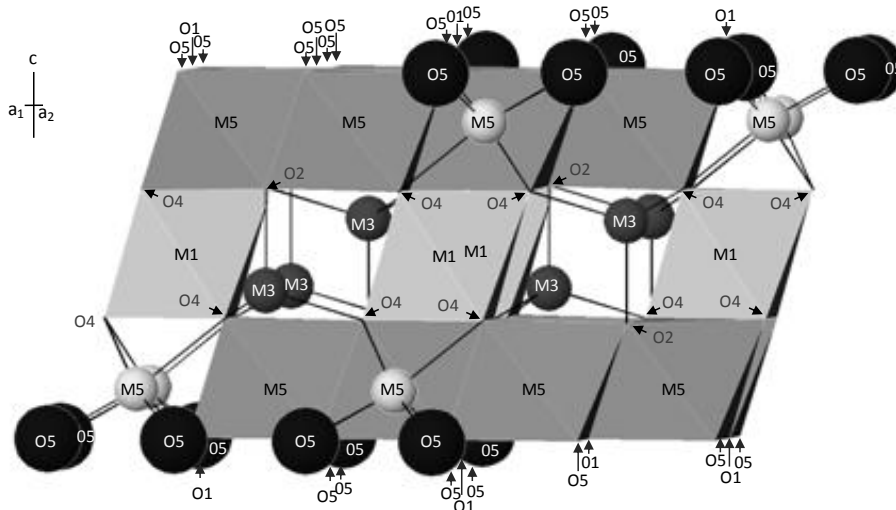


Figure 5-14 The S-block of the hibonite structure (as defined by Nagashima *et al.*, 2010) showing the M3-O2 distance parallel to the c-axis.

The M1 and M3 sites and half of the M5 sites are contained within the S block. The O1-O1 S-block distance, which spans the M1 and M3 sites, increases linearly as a function of both Ti pfu and the M3-O2 distance for hibonites with <1 Ti pfu (Figure 5-15). The M3-O2 bond is parallel to the c-

axis, and appears therefore to dominate the thickness of the S-block above contributions from the M1-O and M5-O distances.

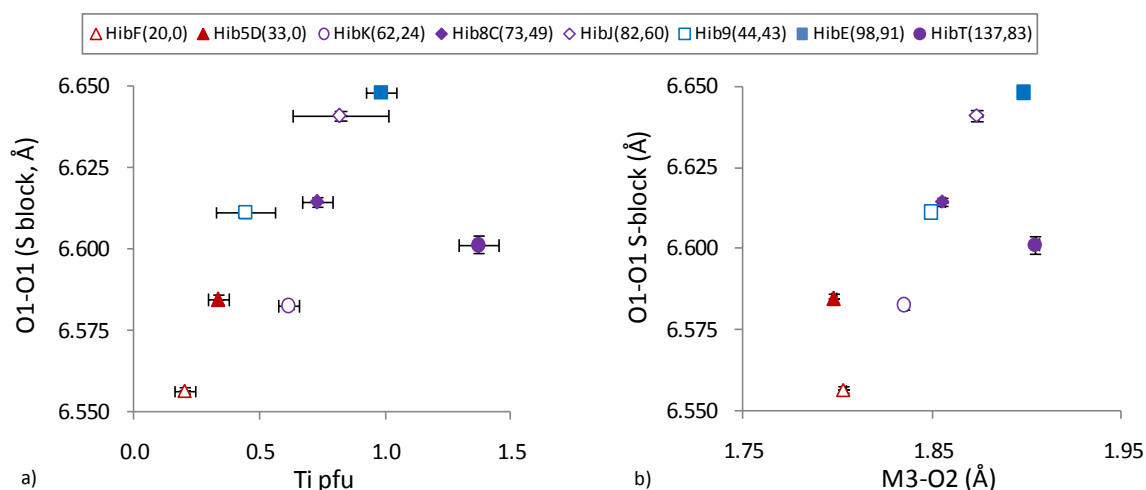


Figure 5-15 O1-O1 S-block distance as a function of (a) Ti pfu and (b) M3-O2 showing a positive correlation for both parameters for hibonites with <1 Ti pfu. Colours: Ti^{3+} hibonite in red, Ti^{4+} hibonite in blue, mixed-valent hibonite in purple.

The Ca, M2 and M4 sites are entirely contained within the R-block, and as Ti substitutes on M2 and M4 it is concentrated within the R-block. The M4 site within the R-block occurs in isolated face-sharing pairs sub-parallel to the c-axis, as shown in Figure 5-13. The M4-M4 distance across the shared face increases linearly as a function of Ti pfu for hibonites with <1 Ti pfu (Figure 5-16). In the hibonites with <1 Ti pfu the displacement of the M2 atom from the O3 layer is directly proportional to the distance M4 lies from the shared face of the M4 octahedra, with the shift of both atoms measured parallel to the c-axis (Figure 5-16). These shifts appear to be the result of Ti substitutions on one (or both) of the M-sites in the R-block, which may in part be due to the concentration of Ti^{4+} in the M2 and M4 sites, and the consequent repulsion between these atoms. This effect may also induce an ordering of Ti^{4+} between the M2 and M4 sites in which the Ti^{4+} on M2 is ordered diagonally opposite the Ti^{4+} on the M4 site, as shown in Figure 5-17.

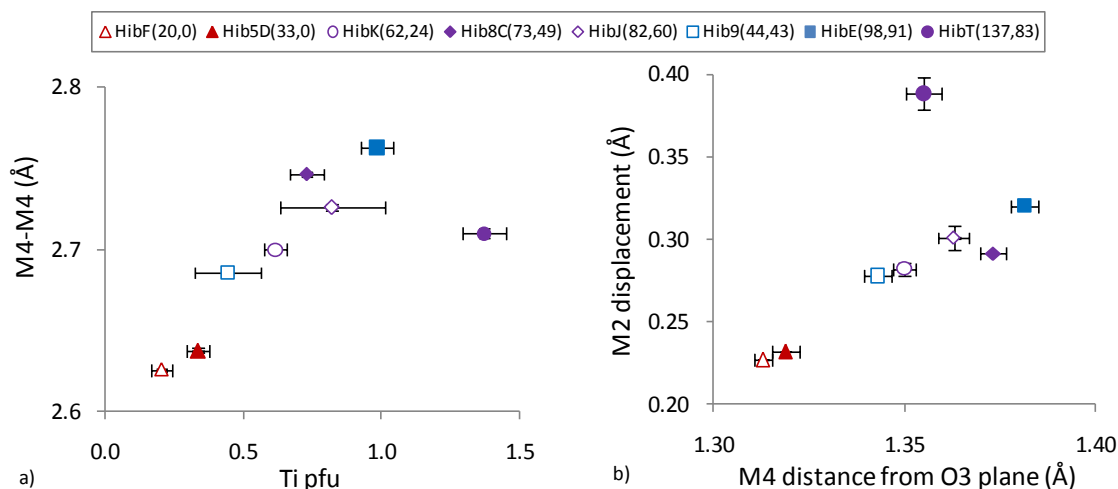


Figure 5-16 (a) The M4-M4 distance as a function of Ti pfu showing a linear increase in M4-M4 distance for hibonites with <1 Ti pfu. (b) The displacement of the M2 atom from the O3 equatorial plane as a function of the distance between M4 and the O3 plane of the shared face of the M4 octahedra showing a near-linear positive correlation for hibonites with <1 Ti pfu. Colour code: Ti^{3+} hibonite in red, Ti^{4+} hibonite in blue, mixed-valent hibonite in purple.

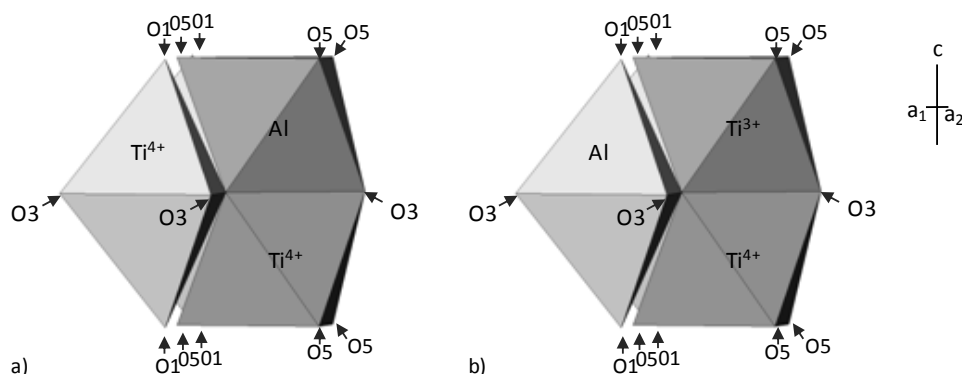


Figure 5-17 A section of the hibonite structure showing possible ordering of Al, Ti^{3+} and Ti^{4+} when occurring in adjacent M2 and M4 sites, with (a) <1 Ti pfu and (b) >1 Ti pfu. For simplicity the Al-Al- Ti^{4+} , Al-Al- Ti^{3+} and Al- Ti^{3+} - Ti^{4+} combinations are not shown, nor is the unlikely Ti^{3+} - Ti^{4+} - Ti^{4+} combination.

It would appear that Ti substitution on the M4 site causes the displacement of the M2 atom from the equatorial plane (Figure 5-11), regardless of the oxidation state of the substituting atom. This suggests the displacement is primarily related to the size of the substituting atom (0.67 Å for Ti^{3+} or 0.61 Å for Ti^{4+} vs. 0.54 Å for Al^{3+}); Shannon, 1976) on the adjacent M4 site. The structural modification caused by the increased displacement of M2 from the equatorial plane ripples through the structure, causing the M-O bonds associated with the M3, M4 and M5 sites to vary systematically as a function of Ti pfu (Figures 5-8 to 5-12). Structural changes within hibonite are enhanced by the coupled substitution of Ti^{4+} and Mg^{2+} as three sites are involved in this substitution mechanism. For example, the M3-O and M4-O distances only vary with more Ti^{4+} pfu (Figures 5-10 and 5-12). Furthermore, as the non-Ti-bearing M5 site is linked to the M3 site through O2 and O4, the M5-O2 and M5-O4 distances shorten as the M3-O distances increase with greater Mg pfu (Figure 5-10d). Similarly, the M5-O1 and M5-O5 bonds vary as a function of Ti pfu as the M5 site is linked to the M2 site through O1, and the M4 site through O5.

It is noticeable that the M-O distances change in a near-linear manner as a function of Ti below 1 Ti pfu, whereas the M-O distances of HibT(137,83) do not follow these trends. HibT(137,83) has >0.5 Ti occupancy on M4 and therefore Ti-Ti interactions across the M4 face-sharing octahedra within HibT(137,83) cannot be avoided. The Ti-Ti interactions and >1 Ti pfu, including 0.83 Ti^{4+} pfu, may cause the HibT(137,83) structure to distort differently to the hibonites with <0.5 Ti occupancy on M4. For example, the M2 O1-O1 and M4-O5 distances of HibT(137,83) are significantly greater than those for the hibonites with <1 Ti pfu (Figures 5-11d and 5-12b). This distortion may either be controlled by Ti-Ti interaction across the shared face of the M4 octahedra (Figure 5-17b) or by the large displacement of the M2 atom from the O3 equatorial plane. Figure 5-16 does not support a model in which the M4-M4 interactions result in the larger M-O distances in the R-block of HibT(137,83). Instead, the 0.39 Å displacement of M2 from the O3 equatorial plane in HibT(137,83) appears to be anomalously large compared to that for the other hibonites in the series (<0.32 Å) and 10 other phases with a magnetoplumbite structure, all of which have M2 atom displacements of <0.25 Å (Graetsch and

Gebert, 1995). The substitution of >1 Ti pfu in the R-block of HibT(137,83) appears to result in an increased displacement of the M2 atom from the equatorial plane, causing an increase in the O1-O1 distance across the M2 polyhedra which equates to the R-block thickness. As the O1 and O5 atoms form a layer either side of the R-block segment in Figure 5-13, the M4-O5 distance of HibT(137,83) is likely to be longer as a consequence of the increased O1-O1 distance of the R-block.

5.4.4.2 Thermal expansion of lattice parameters ($7 \leq T \leq 275$ K)

Lattice parameters for a Ti^{3+} hibonite (HibF(20,0)) and a mixed-valent hibonite (HibT(137,83)) were collected over the temperature range $7 \leq T \leq 275$ K. Thermal expansion of the unit-cell is evident from shifts in the diffraction peaks to higher TOF, as shown in Figure 5-18. The unit-cell parameters and volumes extracted from the Le Bail analysis of the NPD data and the goodness of fit parameters are tabulated in Tables 5-8 and 5-9, and are shown in Figure 5-19.

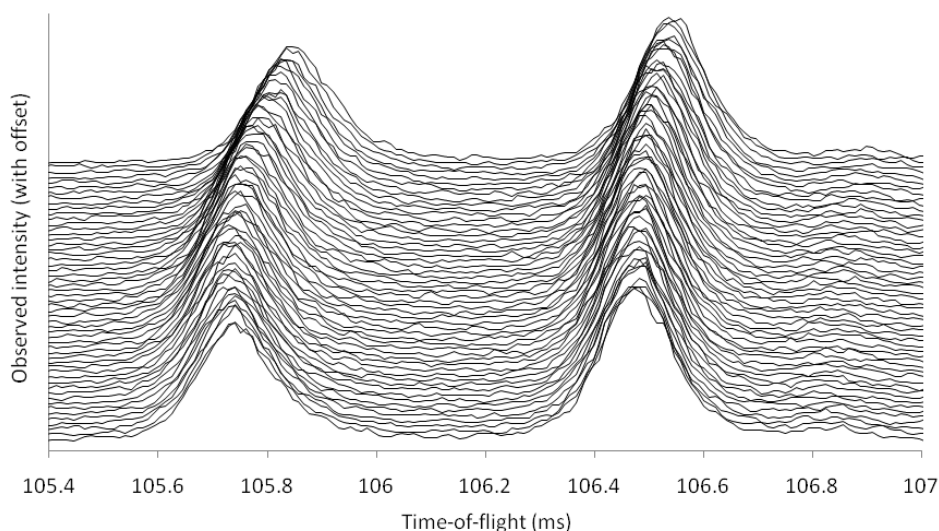


Figure 5-18 NPD data for HibF(20,0) collected over 268 K showing a larger peak shift to higher TOF for the 0010 reflection (~ 105.8 ms) compared to that of the 204 reflection ($\sim 106.5^\circ$ ms). A minor shift to lower TOF in the central region (60-85 K) of the 0010 reflection is just discernable. Sequence: 8 K data at the bottom, subsequent data offset.

Between 8 and 275 K the HibF(20,0) unit-cell parameters a and c increased as a function of temperature by $0.003 \text{ \AA}$ and $0.022 \text{ \AA}$ respectively (Figure 5-19a,b). The volume of HibF(20,0) at 10 K was $583.9 \text{ \AA}^3$, increasing by $1.24 \text{ \AA}^3$ at 275 K (Figure 5-19c). Over the temperature range 7 to 275 K, the HibT(137,83) unit-cell parameters a and c increased by $0.003 \text{ \AA}$ and $0.015 \text{ \AA}$ respectively, with the volume of HibT(137,83) increasing from $605.5 \text{ \AA}^3$ at 10 K by $1.16 \text{ \AA}^3$ at 275 K (Figure 5-19d).

The increase in the a parameter for both samples was the same, whereas the c parameter for HibF(20,0) increased by $0.008 \text{ \AA}$ more than that of HibT(137,83) and these differences are highlighted in Figure 5-19e. The c/a ratio of HibF(20,0) appears to decrease slightly up to 85 K, but above about 140 K it increases linearly. The c/a ratio of HibT(137,83) is near constant between 7 and 140 K, whereas above 140 K it increases slightly in a near-linear manner.

Table 5-8 HibF(20,0) lattice parameters collected between 8 K and 275 K

Temp (K)	Unit-cell parameter a (Å)	Unit-cell parameter c (Å)	Unit-cell Volume (Å ³)	R_w	R_{wp}
8	5.56305 (1)	21.89638 (8)	586.851 (2)	0.07	0.07
10	5.56303 (1)	21.89665 (8)	586.856 (2)	0.07	0.07
15	5.56304 (1)	21.89671 (8)	586.858 (2)	0.07	0.07
20	5.56306 (1)	21.89643 (8)	586.856 (2)	0.07	0.07
25	5.56307 (1)	21.89633 (8)	586.855 (2)	0.07	0.07
30	5.56308 (1)	21.89636 (8)	586.857 (2)	0.07	0.07
35	5.56307 (1)	21.89627 (7)	586.854 (2)	0.07	0.07
40	5.56309 (1)	21.89598 (8)	586.850 (2)	0.07	0.07
45	5.56311 (1)	21.89596 (8)	586.854 (2)	0.07	0.07
50	5.56314 (1)	21.89599 (8)	586.861 (2)	0.07	0.07
55	5.56312 (1)	21.89587 (8)	586.854 (2)	0.07	0.07
60	5.56319 (1)	21.89582 (8)	586.866 (2)	0.07	0.07
65	5.56318 (1)	21.89606 (8)	586.871 (2)	0.07	0.07
70	5.56318 (1)	21.89600 (8)	586.870 (2)	0.07	0.07
75	5.56322 (1)	21.89601 (7)	586.878 (2)	0.07	0.07
80	5.56328 (1)	21.89605 (8)	586.892 (2)	0.07	0.07
85	5.56330 (1)	21.89611 (8)	586.897 (2)	0.07	0.07
80	5.56328 (1)	21.89605 (8)	586.892 (2)	0.06	0.07
85	5.56330 (1)	21.89611 (8)	586.897 (2)	0.07	0.07
90	5.56329 (1)	21.89627 (7)	586.901 (2)	0.06	0.07
95	5.56338 (1)	21.89641 (7)	586.922 (2)	0.07	0.07
100	5.56338 (1)	21.89675 (7)	586.931 (2)	0.06	0.07
105	5.56343 (1)	21.89703 (8)	586.949 (2)	0.07	0.07
110	5.56347 (1)	21.89728 (8)	586.964 (2)	0.07	0.07
115	5.56350 (1)	21.89746 (8)	586.975 (2)	0.07	0.07
120	5.56354 (1)	21.89775 (8)	586.992 (2)	0.07	0.07
125	5.56359 (1)	21.89819 (8)	587.015 (2)	0.07	0.07
130	5.56364 (1)	21.89861 (8)	587.036 (2)	0.07	0.07
135	5.56368 (1)	21.89911 (7)	587.059 (2)	0.06	0.07
140	5.56373 (1)	21.89941 (7)	587.077 (2)	0.06	0.07
145	5.56377 (1)	21.89998 (8)	587.101 (2)	0.07	0.07
150	5.56383 (1)	21.90035 (8)	587.123 (2)	0.07	0.07
155	5.56387 (1)	21.90089 (8)	587.145 (2)	0.07	0.07
160	5.56398 (1)	21.90145 (8)	587.185 (2)	0.07	0.07
165	5.56402 (1)	21.90201 (7)	587.208 (2)	0.06	0.07
170	5.56410 (1)	21.90262 (8)	587.241 (2)	0.07	0.07
175	5.56418 (1)	21.90309 (8)	587.271 (2)	0.07	0.07
180	5.56422 (1)	21.90376 (8)	587.298 (2)	0.07	0.07
185	5.56433 (1)	21.90432 (8)	587.335 (2)	0.07	0.07
190	5.56438 (1)	21.90513 (8)	587.368 (2)	0.07	0.07
195	5.56446 (1)	21.90579 (8)	587.403 (2)	0.07	0.07
200	5.56458 (1)	21.90640 (8)	587.445 (2)	0.07	0.07
205	5.56464 (1)	21.90707 (8)	587.473 (2)	0.07	0.07
210	5.56473 (1)	21.90787 (8)	587.515 (2)	0.07	0.07
215	5.56484 (1)	21.90849 (8)	587.555 (2)	0.07	0.07
220	5.56494 (1)	21.90925 (8)	587.596 (2)	0.07	0.07
225	5.56501 (1)	21.91015 (8)	587.635 (2)	0.07	0.07
230	5.56509 (1)	21.91103 (8)	587.676 (2)	0.07	0.07
235	5.56520 (1)	21.91176 (8)	587.719 (2)	0.07	0.07
240	5.56530 (1)	21.91272 (8)	587.766 (2)	0.07	0.07
245	5.56540 (1)	21.91355 (8)	587.809 (2)	0.07	0.07
250	5.56551 (1)	21.91434 (8)	587.852 (2)	0.07	0.07
255	5.56565 (1)	21.91504 (8)	587.901 (2)	0.07	0.07
260	5.56575 (1)	21.91583 (8)	587.943 (2)	0.07	0.07
265	5.56585 (1)	21.91689 (8)	587.993 (2)	0.07	0.07
270	5.56597 (1)	21.91765 (8)	588.039 (2)	0.07	0.07
275	5.56611 (1)	21.91849 (8)	588.091 (2)	0.07	0.07

Table 5-9 HibT(137,83) lattice parameters collected between 7 K and 275 K

Temp (K)	Unit-cell parameter <i>a</i> (Å)	Unit-cell parameter <i>c</i> (Å)	Unit-cell Volume (Å ³)	R _w	R _{wp}
7	5.62441 (2)	22.1007 (1)	605.467 (3)	0.05	0.06
10	5.62447 (3)	22.1007 (2)	605.480 (5)	0.09	0.10
15	5.62440 (3)	22.1007 (2)	605.465 (5)	0.09	0.10
20	5.62447 (3)	22.1009 (2)	605.484 (5)	0.09	0.09
25	5.62443 (3)	22.1004 (2)	605.463 (5)	0.10	0.10
30	5.62444 (3)	22.1006 (2)	605.471 (5)	0.09	0.10
35	5.62441 (3)	22.1005 (2)	605.462 (5)	0.09	0.09
40	5.62443 (3)	22.1008 (2)	605.474 (5)	0.09	0.10
45	5.62441 (3)	22.1005 (2)	605.463 (5)	0.09	0.10
50	5.62443 (3)	22.1008 (2)	605.474 (5)	0.09	0.10
55	5.62446 (3)	22.1007 (2)	605.478 (5)	0.09	0.10
60	5.62449 (3)	22.1009 (2)	605.489 (5)	0.09	0.09
65	5.62450 (3)	22.1010 (2)	605.495 (5)	0.09	0.10
70	5.62448 (3)	22.1008 (2)	605.485 (5)	0.09	0.10
75	5.62447 (3)	22.1015 (2)	605.500 (5)	0.09	0.10
80	5.62453 (3)	22.1015 (2)	605.515 (5)	0.09	0.09
85	5.62460 (3)	22.1009 (2)	605.514 (5)	0.09	0.09
90	5.62453 (3)	22.1017 (2)	605.520 (5)	0.09	0.10
95	5.62464 (3)	22.1019 (2)	605.549 (5)	0.09	0.09
100	5.62462 (3)	22.1017 (2)	605.539 (5)	0.09	0.09
105	5.62475 (3)	22.1017 (2)	605.567 (5)	0.09	0.09
110	5.62473 (3)	22.1020 (2)	605.570 (5)	0.09	0.09
115	5.62478 (3)	22.1021 (2)	605.584 (5)	0.09	0.10
120	5.62484 (3)	22.1025 (2)	605.608 (5)	0.09	0.10
125	5.62487 (3)	22.1027 (2)	605.620 (5)	0.09	0.10
130	5.62493 (3)	22.1028 (2)	605.637 (5)	0.09	0.10
135	5.62498 (3)	22.1032 (2)	605.657 (5)	0.09	0.10
140	5.62507 (2)	22.1032 (2)	605.678 (5)	0.09	0.09
145	5.62508 (3)	22.1036 (2)	605.690 (5)	0.09	0.09
150	5.62518 (2)	22.1039 (2)	605.721 (5)	0.09	0.09
155	5.62526 (3)	22.1041 (2)	605.744 (5)	0.09	0.09
160	5.62528 (3)	22.1045 (2)	605.756 (5)	0.09	0.10
165	5.62539 (3)	22.1047 (2)	605.786 (5)	0.10	0.10
170	5.62543 (3)	22.1052 (2)	605.809 (5)	0.10	0.10
175	5.62559 (3)	22.1054 (2)	605.852 (5)	0.10	0.10
180	5.62564 (3)	22.1059 (2)	605.875 (5)	0.10	0.10
185	5.62572 (3)	22.1062 (2)	605.901 (5)	0.10	0.10
190	5.62582 (3)	22.1066 (2)	605.931 (5)	0.10	0.10
195	5.62588 (3)	22.1071 (2)	605.960 (5)	0.10	0.10
200	5.62602 (3)	22.1075 (2)	605.999 (5)	0.10	0.10
205	5.62613 (3)	22.1081 (2)	606.040 (5)	0.10	0.10
210	5.62621 (3)	22.1084 (2)	606.067 (5)	0.10	0.10
215	5.62632 (3)	22.1087 (2)	606.097 (5)	0.10	0.10
220	5.62644 (3)	22.1092 (2)	606.138 (5)	0.10	0.10
225	5.62660 (3)	22.1100 (2)	606.193 (5)	0.10	0.11
230	5.62668 (3)	22.1104 (2)	606.221 (5)	0.10	0.10
235	5.62678 (3)	22.1112 (2)	606.267 (5)	0.10	0.10
240	5.62689 (3)	22.1117 (2)	606.303 (5)	0.10	0.10
245	5.62707 (3)	22.1123 (2)	606.358 (5)	0.10	0.10
250	5.62720 (3)	22.1127 (2)	606.397 (5)	0.09	0.10
255	5.62734 (3)	22.1130 (2)	606.437 (5)	0.09	0.10
260	5.62747 (3)	22.1138 (2)	606.485 (5)	0.09	0.10
265	5.62758 (3)	22.1145 (2)	606.528 (5)	0.09	0.09
270	5.62770 (3)	22.1154 (2)	606.577 (5)	0.09	0.09
275	5.62784 (3)	22.1159 (2)	606.622 (5)	0.09	0.10

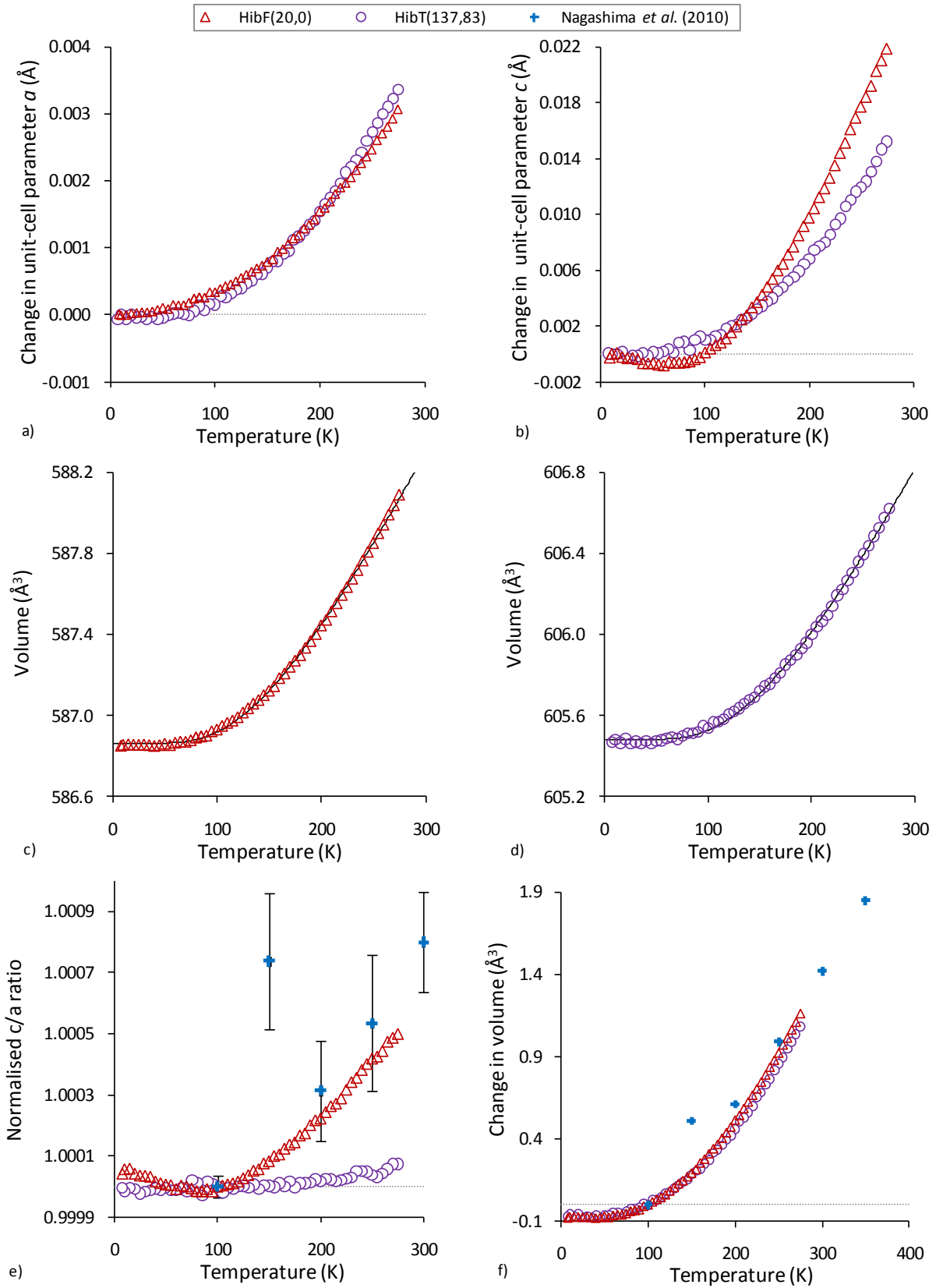


Figure 5-19 (a,b) Change in the unit-cell parameters a and c as a function of temperature (where $\Delta a_{xK} = a_{xK} - a_{10K}$, and $\Delta c_{xK} = c_{xK} - c_{10K}$). See text for detail. (c,d) Volume of HibF(20,0) and HibT(137,83) as a function of temperature, fitted with an Einstein function. (e) The c/a ratio of HibF(20,0), HibT(137,83) and Ti^{4+} hibonite from Nagashima *et al.* (2010) normalised to c/a_{100K} as a function of temperature showing the parabolic shape of the c/a ratio of HibF(20,0) and more constant ratio of HibT(137,83). (f) Change in unit-cell volume (where $\Delta V_{xK} = V_{xK} - V_{100K}$) for HibF(20,0), HibT(137,83) and Ti^{4+} hibonite of Nagashima *et al.* (201) as a function of temperature. Uncertainties < data points (unless shown). Ti^{3+} hibonite in red, Ti^{4+} hibonite in blue, mixed-valent hibonite in purple.

The thermal expansion of the HibF(20,0) unit-cell parameter c appears to be slightly negative below 60 K which is exaggerated by the c/a ratio (Figure 5-19e). Apparent negative thermal expansion at these temperatures has also been observed previously within other mineral systems (e.g. Schofield *et al.*, 1996, 2007). In the absence of supporting data within this study, however, the reason for the small change (~ 0.001 Å over 55 K) cannot be fully verified. Indeed, the apparent contraction along c below 60 K is not evident in the thermal expansion of the unit-cell volume of HibF(20,0), which has a similar temperature-dependant volume profile as HibT(137,83).

Recent studies on the thermal expansion of materials using unit-cell volumes calculated from temperature dependant diffraction data, have utilised a model with a rigorous physical basis rather than taking a purely empirical approach (e.g. Knight, 1996; Knight *et al.*, 1999; Knight and Price, 2008). This approach is based upon the assumption that the specific heat capacity can be described by an Einstein model such that the variation of the unit-cell volume as a function of temperature can be fitted with the Einstein expression described by Equation 5-6 (Knight, 1996; Schofield *et al.*, 1996).

$$V(T) = V_0 + \frac{K}{e^{v_E/T} - 1} \quad \text{Equation 5-6}$$

Where:

- V_0 = volume at 0 K
- K = Einstein constant
- v_E = effective Einstein temperature
- T = temperature

The temperature dependence of the unit-cell parameters for the Ti^{3+} hibonite HibF(20,0) and mixed-valent hibonite HibT(137,83) are well fitted by this model, and the results are presented in Figure 5-19 and Table 5-10.

Table 5-10 Fit parameters for temperature dependence of the unit-cell volume

Sample	V_0 (Å ³)	v_E (K)	K
HibF(20,0)	586.865 (2)	455 (5)	5.1 (1)
HibT(137,83)	605.483 (3)	475 (9)	5.2 (2)

The isobaric thermal expansion coefficient of the unit-cell volume ($\alpha(V)$) is defined by Equation 5-7.

$$\alpha(V) = \frac{1}{V_0} \cdot \frac{dV}{dT} = \frac{1}{V_0} \cdot \frac{K v_E}{T^2} \cdot \left(\frac{e^{v_E/T}}{(e^{v_E/T} - 1)^2} \right) \quad \text{Equation 5-7}$$

Where:

- V_0 = volume at 0 K
- dV = volume differential
- dT = temperature differential
- K = Einstein constant
- v_E = effective Einstein temperature
- T = temperature

At 275 K $\alpha(V)$ is calculated to be 1.53×10^{-5} for the Ti^{3+} hibonite HibF(20,0) and 1.41×10^{-5} for the mixed-valent hibonite HibT(137,83). Alternatively, assuming that $e^{v_E/T} \approx 1 + (v_E/T)$ at high temperatures (after Schofield *et al.*, 1996), Equation 5-7 can be simplified, resulting in Equation 5-8.

$$\alpha(V) = \frac{1}{V_0} \left(\frac{\Delta V}{\Delta T} \right) \approx \frac{K}{(V_0)(v_E)} \left[1 + \frac{v_E}{T} \right] \quad \text{Equation 5-8}$$

Where:

V_0 = volume at 0 K
 ΔV = change of volume
 ΔT = change of temperature
 K = Einstein constant
 v_E = effective Einstein temperature

$$\text{Thus for the Ti}^{3+} \text{ hibonite HibF(20,0) } \alpha(V) \approx 1.91439 \times 10^{-5} \left[1 + \frac{v_E}{T} \right]$$

$$\text{and for the mixed-valent hibonite HibF(20,0) } \alpha(V) \approx 1.79829 \times 10^{-5} \left[1 + \frac{v_E}{T} \right]$$

In order to further describe the differences between the thermal expansions of the Ti^{3+} and mixed-valent hibonites it is convenient to consider the hibonite structure in terms of the R- and S-blocks (Figures 5-13 and 5-14). As described in Section 5.4.4.1, the R-block encompasses the M2 and M4 sites into which Ti substitutes. The M2 site has M2-O1 bonds parallel to the c-axis and the M4-M4 distance is also parallel to c and perpendicular to the ab plane (Figure 5-13). Changes to Ti occupancy on the M2 and M4 sites appear to be the principle factor in differences to the thermal expansion between the samples, with M2-O1 and M4-M4 strongly influencing the variations of the c unit-cell parameter. Indeed, it has been shown that the mean expansion co-efficient for the M4 site of a Ti^{4+} -bearing terrestrial hibonite over the temperature range 100 - 923 K was larger than that predicted for an octahedrally coordinated Al-site (Nagashima *et al.*, 2010).

Within the S-block only the M3-O2 bond is parallel to the c-axis. Incorporation of Mg on this site causes the M3-O2 bond to lengthen, controlling increases in the S-block thickness as a function of increasing Mg and Ti pfu (*cf* Figure 5-10d and Figure 5-15b). It seems reasonable to assume that the presence of Mg on M3 will influence the thermal expansion of the S-block, and also be responsible for differences between the expansions of the S-block of the two samples. The study by Nagashima *et al.* (2010) found that the expansion co-efficient of the Mg-bearing M3 site was larger than expected, but smaller than that of the M4 site. Consequently, it seems reasonable that for the two samples studied here, the R-block will dominate the expansion of the c unit-cell parameter.

The thermal expansion of the a unit-cell parameter of the two samples is far smaller (~17%) than for the c unit-cell parameters, probably because the structure is more constrained within the layers parallel to the ab plane than across the layers parallel to c. Differences in the expansion of the a unit-cell parameter is still likely to be dominated by changes in the sites associated with the Ti onto the M2 and M4 sites and Mg onto the M3 site.

The thermal expansion of the lattice parameters of the Ti^{3+} hibonite HibF(20,0) are controlled by two mechanisms, namely that of the underlying Al hibonite structure, and secondly by the presence of Ti^{3+} on the M4 site. The mixed-valent hibonite HibT(137,83) has two additional mechanisms to

consider, with Ti^{4+} being present on the M2 and M4 sites, and Mg present on M3. Not only does HibT(137,83) expand less than HibF(20,0) across the temperature range showed, but it also expands at different rates along a and c with respect to HibF(20,0), as shown in Figure 5-19e. It appears that when all four mechanisms become active within a single phase their coupling acts to limit, rather than enhance, the thermal expansion. Furthermore, as evident in Figure 5-19, the thermal expansion becomes more isotropic in such a case.

Single crystal X-ray diffraction data over the temperature range 100 – 923 K were collected from a Ti^{4+} terrestrial hibonite by Nagashima *et al.* (2010). This allows for the comparison of the temperature dependant variation in unit-cell parameters of a Ti^{4+} hibonite with the Ti^{3+} and mixed-valent hibonites (Figure 5-19e,f). In general, aside from an apparent outlier at 150 K, the temperature-dependant unit-cell profile of the Ti^{4+} hibonites is similar to that of the Ti^{3+} and mixed-valent hibonites. The temperature dependence of the c/a ratio of the Ti^{4+} hibonite is very similar to that of the Ti^{3+} hibonite, although the uncertainty reported for the lattice parameters of the XRD data are larger than those in this study. The rate of increase in the c/a ratio of the Ti^{3+} and Ti^{4+} samples were similar above 150 K, whereas at 100 K the volume of the Ti^{4+} hibonite ($594.6 \text{ \AA}^3$) was intermediate between those of the Ti^{3+} hibonite HibF(20,0) and the mixed-valent hibonite Hib T(137,83), ($586.9 \text{ \AA}^3$ for HibF(20,0) and $605.5 \text{ \AA}^3$ for HibT(137,83) respectively).

5.5 Chapter Summary

Rietveld refinements of NPD data from eight Ti-bearing synthetic hibonite samples show unambiguously that Ti^{3+} in the Ti^{3+} hibonites occupies the M4 octahedral site, whereas Ti^{4+} in the Ti^{4+} hibonites partitions between the M2 trigonal bipyramidal site and the M4 octahedral site. Ti in the mixed-valent hibonites occupies the M2 and M4 sites. The results suggest that Ti^{4+} partitions between the M2 and M4 sites in a constant ratio of $\sim 1:4.3$, regardless of the presence of Ti^{3+} and total Ti content (for $<1 \text{ Ti pfu}$). In Ti^{4+} -bearing hibonite Mg^{2+} occupies the M3 tetrahedral site. A summary of the findings are included in Table 5-11.

Table 5-11 Summary of the stoichiometry and site occupancy of the synthetic hibonite sample series

Sample	% Ti^{3+} by stoichiometry	Stoichiometry (where $^{[12]}\text{Ca}^{[6]}(\text{Al})^{[5]}(\text{Al})^{[4]}(\text{Al})_2^{[6]}(\text{Al})_2^{[6]}(\text{Al})_{\text{O}1}$ = ideal hibonite)
HibF(20,0)	100±0	$^{[12]}\text{Ca}^{[6]}(\text{Al})^{[5]}(\text{Al}_{1.00})^{[4]}(\text{Al}_{2.00})^{[6]}(\text{Al}_{1.82}, \text{Ti}^{3+}_{0.18})^{[6]}(\text{Al})_6\text{O}_{19}$
Hib5D(33,0)	100±0	$^{[12]}\text{Ca}^{[6]}(\text{Al})^{[5]}(\text{Al}_{1.00})^{[4]}(\text{Al}_{2.00})^{[6]}(\text{Al}_{1.63}, \text{Ti}^{3+}_{0.37})^{[6]}(\text{Al})_6\text{O}_{19}$
HibK(62,24)	60±4	$^{[12]}\text{Ca}^{[6]}(\text{Al})^{[5]}(\text{Al}_{0.95}\text{Ti}^{4+}_{0.05})^{[4]}(\text{Al}_{1.78}, \text{Mg}_{1.22})^{[6]}(\text{Al}_{1.50}, \text{Ti}^{3+}_{0.33}, \text{Ti}^{4+}_{0.17})^{[6]}(\text{Al})_6\text{O}_{19}$
Hib8C(73,49)	33±5	$^{[12]}\text{Ca}^{[6]}(\text{Al})^{[5]}(\text{Al}_{0.91}\text{Ti}^{4+}_{0.09})^{[4]}(\text{Al}_{1.50}, \text{Mg}_{0.50})^{[6]}(\text{Al}_{1.39}, \text{Ti}^{3+}_{0.23}, \text{Ti}^{4+}_{0.38})^{[6]}(\text{Al})_6\text{O}_{19}$
HibJ(82,60)	25±12	$^{[12]}\text{Ca}^{[6]}(\text{Al})^{[5]}(\text{Al}_{0.86}\text{Ti}^{4+}_{0.14})^{[4]}(\text{Al}_{1.34}, \text{Mg}_{0.66})^{[6]}(\text{Al}_{1.29}, \text{Ti}^{3+}_{0.21}, \text{Ti}^{4+}_{0.50})^{[6]}(\text{Al})_6\text{O}_{19}$
Hib9(44,43)	0±0	$^{[12]}\text{Ca}^{[6]}(\text{Al})^{[5]}(\text{Al}_{0.90}\text{Ti}^{4+}_{0.10})^{[4]}(\text{Al}_{1.58}, \text{Mg}_{0.42})^{[6]}(\text{Al}_{1.60}, \text{Ti}^{4+}_{0.40})^{[6]}(\text{Al})_6\text{O}_{19}$
HibE(98,91)	0±0	$^{[12]}\text{Ca}^{[6]}(\text{Al})^{[5]}(\text{Al}_{0.85}\text{Ti}^{4+}_{0.15})^{[4]}(\text{Al}_{1.16}, \text{Mg}_{0.84})^{[6]}(\text{Al}_{1.19}, \text{Ti}^{4+}_{0.81})^{[6]}(\text{Al})_6\text{O}_{19}$
HibT(137,83)	39±4	$^{[12]}\text{Ca}^{[6]}(\text{Al})^{[5]}(\text{Al}_{0.94}\text{Ti}^{4+}_{0.06})^{[4]}(\text{Al}_{1.00}, \text{Mg}_{1.00})^{[6]}(\text{Al}_{0.77}, \text{Ti}^{3+}_{0.51}, \text{Ti}^{4+}_{0.72})^{[6]}(\text{Al})_6\text{O}_{19}$

The unit-cell increases with increasing Ti pfu, and systematic changes in bond lengths are observed in four of the M-sites (M2-M5), whereas the M1 octahedral site remains unchanged with increasing Ti pfu. The M2 cation on the trigonal bipyramidal site shifts progressively off the equatorial plane with increasing Ti pfu. The M3 tetrahedral site becomes trigonally distorted, and the distortion upon the M4 and M5 octahedral sites increases with more Ti^{4+} pfu.

The thermal expansion of unit-cell parameters from a Ti^{3+} hibonite are greater than those of a mixed-valent hibonite with >1 Ti pfu. Thermal expansion of the unit-cell parameters is accommodated in the R-block and is attributable to Ti content, particularly the Ti^{4+} content in hibonite.

6 Ti K-edge XANES study of Ti-bearing CMAS glasses, and synthetic and meteoritic hibonite

6.1 Synopsis

Ti K-edge X-ray absorption near edge structure (XANES) spectra were collected from a series of five Ti-bearing CaO-MgO-Al₂O₃-SiO₂ (Ti-CMAS) glass compositions, comprising 48 glass samples in total. Spectral features of each glass composition vary as a function of fO_2 , and this data were modelled with a theory-based fit, from which the $Ti^{3+}/\Sigma Ti$ for the glasses were calculated. The calculated $Ti^{3+}/\Sigma Ti$ are compared to the EPR data collected from a similar composition, and to $Ti^{3+}/\Sigma Ti$ in the literature. Additionally, compositional dependence of Ti^{4+} coordination and $Ti^{3+}/\Sigma Ti$ is discussed.

Ti K-edge XANES spectra were collected from six synthetic hibonite samples, the compositions of which spanned a 0-100% $Ti^{3+}/\Sigma Ti$ range (where $\Sigma Ti = Ti^{3+} + Ti^{4+}$). The energy of the minimum between the pre-edge feature and the edge was found to vary systematically as a function of $Ti^{3+}/\Sigma Ti$ as calculated by stoichiometry. This spectral parameter was fitted with an inverse quadratic. This Ti^{3+}/Ti^{4+} hibonite oxybarometer was applied to Ti K-edge XANES spectra that were collected from hibonite within 15 calcium aluminium inclusions (CAIs) in order to quantify the $Ti^{3+}/\Sigma Ti$ in these samples.

6.2 Introduction

The quantification of redox variable elements is crucial for the understanding of fO_2 -related processes (e.g. Berry *et al.*, 2008). Within the terrestrial system the oxidation state of Fe covers the redox conditions encountered in most geological systems (Frost, 1991), resulting in the extensive use of redox buffers such as the iron-wüstite (IW) and quartz-magnetite-fayalite (QFM) buffer curves (Myers and Eugster, 1983). In extra terrestrial environments much of the Fe is reduced to Fe-metal, with ordinary and carbonaceous chondrites reported to have equilibrated under conditions close to the IW buffer curve (Brett & Sato, 1984). Alternative oxybarometers have been suggested for extra terrestrial materials, including V^{2+} - V^{5+} in basaltic glasses using V K-edge XANES spectroscopy

(Sutton *et al.*, 2005) and $\text{Ti}^{3+}/\text{Ti}^{4+}$ in hibonite based on the proportion of Ti on different sites within hibonite (Beckett *et al.*, 1988).

The $\text{Ti}^{3+}/\text{Ti}^{4+}$ oxybarometer is particularly interesting as Ti is a refractory element (Lodders, 2003), which is found within minerals found in CAIs which are dated to be the oldest material in the Solar System (Amelin *et al.*, 2002). The $\text{Ti}^{3+}/\text{Ti}^{4+}$ in minerals such as hibonite and fassaite potentially records the $f\text{O}_2$ conditions during the earliest stages of the nebula formation (e.g. Beckett *et al.*, 1988; Simon *et al.*, 2005).

$\text{Ti}^{3+}/\Sigma\text{Ti}$ has commonly been determined using titration (e.g. Schreiber *et al.*, 1978; Tranell *et al.*, 2002). This technique is suitable for bulk analysis of Fe-free compositions, but produces anomalously high $\text{Ti}^{3+}/\Sigma\text{Ti}$ contents in Fe-bearing systems, as shown by Whipple (1979). Electron paramagnetic resonance (EPR) spectroscopy, also referred to as electron spin resonance (ESR) spectroscopy, may be used to measure the abundance of Ti^{3+} , from which $\text{Ti}^{3+}/\Sigma\text{Ti}$ may be determined (e.g. Beckett *et al.*, 1988). This technique is, however restricted to paramagnetic elements and the spectra may be complicated in multi-element systems (e.g. Schreiber *et al.*, 1978).

XANES spectroscopy is an element specific technique that measures the electronic structure of an atom. The technique is non-destructive and has micro-meter scale spatial resolution (Sutton *et al.*, 2005). These attributes are advantageous when analysing unique samples and samples on loan from museums and personal collections. Additionally, the spectra may be collected rapidly from geological samples prepared for electron microprobe analysis as the only sample preparation required is a polished sample surface. For these reasons XANES is ideal for the investigation of redox variable elements in geological systems.

XANES spectra may be divided into three main regions, namely the pre-edge region, edge and post-crest region. The pre-edge is caused by electronic transitions to empty or partially filled bound states. The interaction between Ti and the O first-neighbour atoms means the pre-edge is strongly influenced by the coordination state of the Ti atom (e.g. Farges *et al.*, 1996a). The edge feature corresponds to the energy at which an electron is excited beyond the bound state, and the structure within the post-crest region is a result of resonances caused by multi-scattering processes of non-bound electrons and is therefore influenced by the next-to-near neighbours of the target element (Brown *et al.*, 1988; Romano *et al.*, 2000).

In redox-variable elements, the core electrons are bound more tightly in higher oxidation states than lower oxidation states, therefore to a first order approximation the edge energy of an element will vary depending on its oxidation state (Brown *et al.*, 1988). Similarly, changes in oxidation state of the first row transition elements may be observed changes within the pre-edge region features as it is sensitive to the *d*-orbital configuration. A shift in energy to higher energy with higher oxidation state has been documented for either the pre-edge peak or edge features in many transition element systems, including: $\text{Ti}^{3+}/\text{Ti}^{4+}$ (Waychunas, 1987), $\text{V}^{2+}-\text{V}^{5+}$ (Sutton *et al.*, 2005); $\text{Cr}^{2+}/\text{Cr}^{3+}$ (Berry and O'Neill, 2004), and $\text{Fe}^{2+}/\text{Fe}^{3+}$ (Berry *et al.*, 2003).

Of particular interest to this study is the change in Ti K-edge XANES spectra with different oxidation states. Features in the pre-edge and the main edge energy collected from Ti_2O_3 and $\text{NaTi}^{3+}\text{Si}_2\text{O}_6$ were reported to be 2.0 eV lower than those collected from TiO_2 and Ti^{4+} -bearing acmitic pyroxene (Waychunas, 1987). The pre-edge feature was found to be more valence-sensitive than the edge, yet only semi-quantitative $\text{Ti}^{3+}/\Sigma\text{Ti}$ calculations were attempted by the study as shifts in the pre-edge feature due to chemical effects, such as coordination, could not adequately be separated from shifts in energy due to valence state (Waychunas, 1987).

There has been renewed interest in the quantification of $\text{Ti}^{3+}/\text{Ti}^{4+}$ using XANES spectroscopy, particularly with the increasing application of synchrotron-based techniques to geological investigations (Farges and Brown, 1997; Berry *et al.*, 2008). Ti K-edge XANES spectra have recently been collected from Ti^{3+} - and Ti^{4+} -bearing glasses (Yang *et al.*, 2008; Krawczynski *et al.*, 2009), synthetic garnet (Krawczynski *et al.*, 2009) and meteoritic pyroxene, spinel and hibonite (Simon *et al.*, 2007). $\text{Ti}^{3+}/\Sigma\text{Ti}$ has been quantified using two or three end-member calibrations (Simon *et al.*, 2007; Krawczynski *et al.*, 2009).

This study aims to investigate the systematics of $\text{Ti}^{3+}/\text{Ti}^{4+}$ in Ti K-edge XANES spectra collected from a suite of well characterised synthetic samples with 0 to 100% $\text{Ti}^{3+}/\Sigma\text{Ti}$ in order to develop robust Ti K-edge oxybarometers. The samples suite included both Ti-bearing $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ (Ti-CMAS) glasses and synthetic Ti-bearing hibonites. Additionally, Ti K-edge XANES spectra were collected from hibonites in 15 CAIs in order to use the spectral parameters to quantify the $\text{Ti}^{3+}/\Sigma\text{Ti}$ within these grains using the $\text{Ti}^{3+}/\text{Ti}^{4+}$ in hibonite oxybarometer.

6.3 Methodology and experimental techniques

6.3.1 Summary of sample characterisation and preparation

6.3.1.1 Ti-bearing standards

Well characterised Ti-bearing phases were used as standards, and included epoxy resin mounted minerals, powdered oxides and Ti foil. Table 6-1 details their stoichiometry and the Ti coordination state. TiO_2 and Ti_2O_3 powders were diluted with boron nitride (BN) powder (to 1 mol% Ti) and ground in an agate pestle and mortar before being pressed into 8 mm diameter pellets.

Table 6-1 Stoichiometry and Ti coordination within the Ti-bearing standards

Sample	Stoichiometry	Ti coordination	Source
Ti-Spinel (Ti-sp)	$\text{Ni}_{2.6}\text{Ti}_{0.7}\text{O}_4$	4	Berry <i>et al.</i> (2007)
Ti-Olivine (Ti-ol)	$\text{Mg}_{2.00}\text{Ti}_{0.01}\text{Si}_{0.99}\text{O}_4$	4	Berry <i>et al.</i> (2007)
Ti-Perovskite (Ti-pv)	BaTiO_3	6	Berry (pers. com)
Ti^{4+} -oxide (Ti(IV)-ox)	TiO_2	6	This study
Ti^{3+} -oxide (Ti(III)-ox)	Ti_2O_3	6	This study
Ti-foil (Ti-foil)	Ti	N/A	i18 standard

Notes: See Appendix B1.1 for details of the oxides used in this study.

6.3.1.2 Ti-bearing CMAS glasses

Five Ti-CMAS glass compositions were prepared in which Ti was the only redox variable element over the 17 log units in fO_2 investigated. As described in Section 3.3.1, 50 Ti-CMAS glasses were prepared between $\Delta IW+6.5$ and $\Delta IW-10.5$ in a vertical gas mixing furnace at 1404 ± 1 °C. The samples were quenched in water, and the $Ti^{3+}/\Sigma Ti$ ratios of the glasses are assumed to be equivalent to those in the melt. Sample preparation and characterisation are detailed in Section 3.3 and the average composition and calculated optical basicity (after Duffy, 1993) are summarised in Table 6-2. XANES spectra were collected from epoxy resin mounted glass fragments that had a polished surface suitable for analysis by electron microscopy.

Table 6-2 Average glass compositions (including 1 wt% TiO_2) and the calculated optical basicity

Sample	SiO_2	Al_2O_3	CaO	MgO	Total	O Basicity	#
AD	50.0 (0.5)	15.4 (0.2)	23.3 (0.3)	10.6 (0.1)	100.4 (0.7)	0.60 (0.01)	105
AD+En	54.1 (0.6)	9.5 (0.2)	14.3 (0.4)	21.7 (0.4)	100.8 (0.8)	0.58 (0.01)	134
AD+Fo	49.2 (0.6)	13.20 (0.1)	19.8 (0.3)	17.4 (0.2)	100.8 (0.8)	0.60 (0.01)	111
AD+Qtz	65.9 (0.4)	10.0 (0.3)	15.3 (0.3)	7.0 (0.1)	99.4 (0.4)	0.55 (0.02)	106
AD+Wo	51.5 (0.4)	6.3 (0.1)	37.4 (0.5)	4.3 (0.1)	100.6 (0.5)	0.62 (0.02)	117

Note: Analysis by WDS EMP (standard deviation in parentheses), with calculated optical basicity ("O Basicity") (standard deviation of the propagated error in parentheses). # = number of analyses. Further detail included in Tables 3-5 and 3-6.

6.3.1.3 Ti-bearing synthetic hibonite

Section 3.3 describes the synthesis and initial characterisation of a suite of nine Ti-bearing hibonite samples. Seven of these samples were selected for this study as they have a well constrained $Ti^{3+}/\Sigma Ti$, as determined by stoichiometry using $1Ti^{4+}:1Mg^{2+}$, with the remaining Ti as Ti^{3+} . The samples have a range in TiO_2 content from 2.4 to 15.9 wt%, which equates to 0.2 to 1.4 Ti per formula unit (pfu), as shown in Table 6-3.

Ti K-edge XANES spectra were collected from fragments mounted in epoxy resin which had a polished surface suitable for electron microscopy, and from powder pellets in which the powdered hibonite sample was either diluted in BN (1 mol% Ti) or undiluted.

Table 6-3 Summary of the stoichiometry and Ti content within the synthetic hibonite sample series

Sample†	Stoichiometry	Average wt% $TiO_2^{(tot)}$		% $Ti^{3+}/\Sigma Ti$		Analysed using‡
Hib5D(33,0)	$Ca_{1.07}Al_{11.51}Ti_{0.33}O_{19}$	4.0	(0.4)	100	(0)	Diffuse beam
HibF(20,0)	$Ca_{1.07}Al_{11.69}Ti_{0.20}O_{19}$	2.4	(0.5)	100	(0)	Micro-focus and diffuse beam
HibK(62,24)	$Ca_{1.05}Al_{10.99}Ti_{0.62}Mg_{0.24}O_{19}$	7.3	(0.5)	60	(4)	Micro-focus and diffuse beam
Hib8C(73,49)	$Ca_{1.07}Al_{10.66}Ti_{0.73}Mg_{0.49}O_{19}$	8.6	(0.7)	33	(5)	Micro-focus and diffuse beam
Hib9(44,43)	$Ca_{1.04}Al_{11.10}Ti_{0.44}Mg_{0.43}O_{19}$	5.2	(1.4)	0	(0)	Micro-focus and diffuse beam
HibE(98,91)	$Ca_{1.01}Al_{10.07}Ti_{0.98}Mg_{0.91}O_{19}$	11.4	(0.7)	0	(0)	Micro-focus and diffuse beam
HibT(137,83)	$Ca_{1.05}Al_{9.59}Ti_{1.37}Mg_{0.83}O_{19}$	15.9	(0.9)	39	(4)	Micro-focus and diffuse beam

Notes: Further compositional data and the uncertainties are detailed in Table 3.7

† For ease of reference, the ratio of Ti:Mg cations (x 100) are included within the sample name.

‡ Unless noted in the text, the data presented in this work was acquired using the microfocus beam.

6.3.1.4 Ti-bearing meteoritic hibonite

The hibonite-bearing CAIs used in this study are described and characterised in Section 4.4 and summarised in Table 6-4. The samples were either mounted as probe sections for optical and electron microscopy studies (e.g. Rout and Bischoff, 2008), or mounted as grain fragments pushed into gold foil for ion probe studies (e.g. Ireland *et al.*, 1992).

Prior to the beam time the CAI of interest was located using an optical microscope and circled using a Cu TEM disk (30 μm thickness) with an inner diameter of 1000 μm (Figure 6-1). The hibonite grains within the CAI were then centred within a 370 μm hole previously cut into Kapton tape (128 μm thickness) using a laser. At the beamline the CAI was located optically using the Kapton tape as a guide, after which XRF mapping was used with reference to both backscattered electron images (BEIs) and reflected light images to select points within the hibonite grains.

6.3.2 Experimental setup and data collection

Ti K-edge XANES spectra were recorded in fluorescence mode on beamline i18 (undulator source) at the Diamond Light Source (DLS) Oxfordshire (UK), which has a 3 GeV storage ring. The excitation energy was selected using a Si111 monochromator indirectly cooled by liquid nitrogen (Mosselmans *et al.*, 2009). The energy resolution of this experiment at the energy of the Ti K-edge (4966.4 eV; Bearden and Burr, 1967) is 0.70 eV, resulting in a spectral energy resolution of 1.2 eV when coupled with the Ti $K\alpha$ core-hole width of 0.94 eV (Krause and Oliver, 1979).

Spectra were collected from three occasions as follows: Ti-bearing standards in 2008, a suite of powdered synthetic hibonite samples and a meteoritic grain fragment (7-981) in 2009, and from a suite of Ti-CMAS glasses, and a suite of synthetic and meteoritic hibonites in 2010. The beam was collimated by the toroid (Figure 2-13) and defined by vertical and horizontal slits (Mosselmans *et al.*, 2009), after which it was focused onto the sample using KB mirrors, allowing either a 2 x 2 μm beam onto the hibonite samples, or a 3 x 3 μm beam onto the Ti-CMAS glasses. In 2009 a “diffuse beam” was achieved by moving the sample out of the focus plane of the beam.

In general the samples were mounted on Al plates attached to a kinematic stage that was orientated 45° to the incident beam and 45° to the fluorescence detector. The absorption length for the incident X-ray beam in hibonite is calculated to be 10-13 μm (after Henke *et al.*, 1993).

The step sizes used to collect data were as follows: 0.5 or 1.0 eV between 4950 and 4962 eV (before the pre-edge region); 0.1 eV between 4962 and 4975 eV (pre-edge region), 0.2 eV between 4975 and 5015 eV (post-crest region) and 2.5 or 5.0 eV up to 5200 eV (EXAFS region). Absorbance (iT) was measured by an ion chamber in line with the beam. Absorbance was only collected from a Ti foil that was used to perform an energy calibration. Fluorescence (iF) was measured using a nine-element monolithic germanium detector, which was orientated 90° to the incident beam. The total incoming count rate was roughly 130000 s^{-1} in order to remain within the linear response range of the

Table 6-4 Summary of CAI characteristics and hibonite stoichiometry

Sample	Stoichiometry	TiO ₂ wt%	Hibonite morphology	Mineral assemblage †	Classification ‡
Acfer094/CAI22	Ca _{1.02} Al _{10.90} Ti _{0.51} Mg _{0.51} Si _{0.04} O ₁₉	6.2±0.3	bladed (in CAI core)	Hibonite , melilite, spinel, minor-perovskite, (x)	Type A; SHIB
Acfer094/CAI40	Ca _{1.06} Al _{10.69} Ti _{0.64} Mg _{0.58} O ₁₉	7.5±0.4	amorphous (in CAI core)	Hibonite, melilite , spinel , perovskite, (x)	Type A; SHIB
El Djouf001/1CAI	Ca _{1.06} Al _{10.86} Ti _{0.49} Mg _{0.51} Si _{0.06} O ₁₉	5.8±0.7	sub-, euhedral (clustered)	Hibonite, melilite , spinel, perovskite	Type A; SHIB
Hughes030/L	Ca _{1.03} Al _{11.93} Ti _{0.01} O ₁₉	0.2±0.0	platy (on CAI perimeter)	Hibonite , spinel, alteration mineral , (x)	Type A; HAL-type (SHIB/PLAC)
NWA1476/124	CaAl _{11.57} Ti _{0.19} Mg _{0.17} O ₁₉	2.2± 0.2	sub-, euhedral (clustered)	Hibonite, Ti-rich augite , Ti-poor augite, perovskite	Type B; Glass spherule
NWA2446/2L	Ca _{1.03} Al _{11.73} Ti _{0.12} Mg _{0.10} O ₁₉	1.4± 0.1	bladed (core)	Hibonite , ilmenite, alteration , (x)	Type A; SHIB
NWA2446/5L	CaAl _{11.50} Ti _{0.22} Mg _{0.22} O ₁₉	2.6± 0.1	platy (fragment)	Hibonite , Ti-poor augite	Type A; PLAC
NWA2446/8L	Ca _{1.01} Al _{11.01} Ti _{0.43} Mg _{0.48} Fe _{0.13} O ₁₉	5.0±0.9	amorphous (in CAI core)	Hibonite , Zn-spinel, ilmenite, alteration , (x)	Type A; SHIB
7-76	Ca _{1.02} Al _{11.69} Ti _{0.15} Mg _{0.15} O ₁₉	1.8	bladed (possibly in CAI core)	Hibonite, perovskite, spinel (+, x)	Type A; SHIB
7-505	Ca _{1.01} Al _{10.95} Ti _{0.46} Mg _{0.46} O ₁₉	8.7/5.4	bladed (dispersed)	Hibonite , spinel, (+, x)	Type A; SHIB
7-753	Ca _{1.03} Al _{11.68} Ti _{0.16} Mg _{0.14} O ₁₉	1.9	rounded (in CAI core)	Hibonite , perovskite , (+)	Type B; Glass spherule
7-953	Ca _{0.99} Al _{10.88} Ti _{0.56} Mg _{0.56} O ₁₉	6.5	bladed (dispersed)	Hibonite , perovskite , spinel (+)	Type A; SHIB
7-971	Ca _{1.00} Al _{12.02} Ti _{0.02} Mg _{0.02} O ₁₉	0.2	platy (fragment)	Hibonite	HAL-type (PLAC morphology)
7-981	Ca _{1.01} Al _{11.78} Ti _{0.10} Mg _{0.12} O ₁₉	1.2	platy (fragment)	Hibonite	Type A; PLAC
10-43	Ca _{1.03} Al _{10.93} Ti _{0.55} Mg _{0.48} O ₁₉	6.4	platy	Hibonite , perovskite	Type A; BAG

Note: † (x) = diopside rim; (+) Fe-silicate rim. ‡ See Chapter 4 for explanation of hibonite grouping.

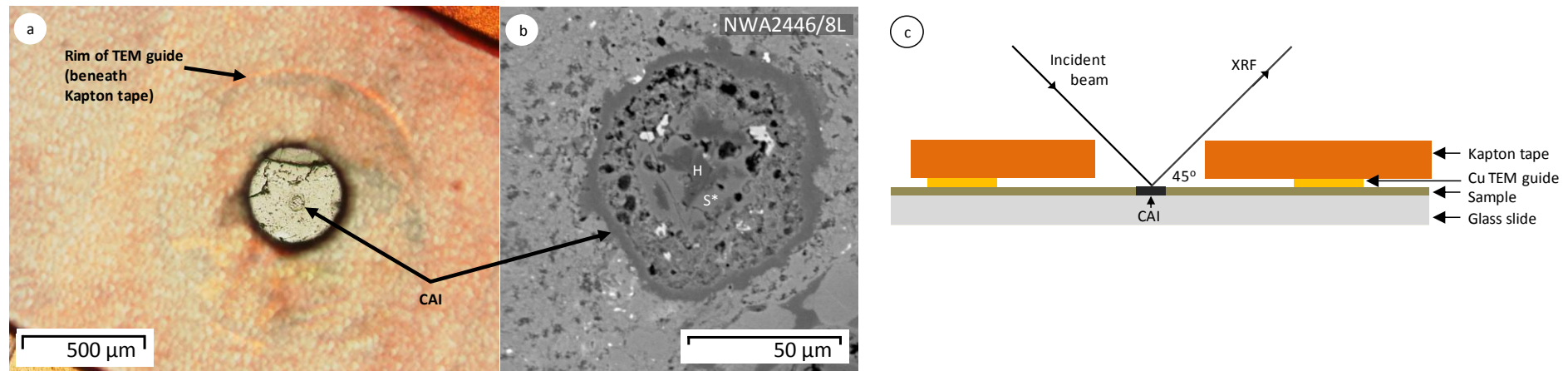


Figure 6-1 (a) Plan view of the Kapton tape highlighting the CAI position in reflected light; and (b) A magnified version of the hibonite-bearing CAI in a BEI with H= hibonite and S* = spinel; (c) Schematic cross section of the CAI mounting.

detector system, and the total scan time was 15-20 minutes. The data were collected and (for the 2010 dataset) deadtime corrected by the onsite-software.

The absorbance spectrum is defined by $\ln(I_0/I_T)$ where I_0 is the incident beam flux. The fluorescence data from nine detector channels were averaged and normalised to the incident beam flux (i.e. I_F/I_0). These spectra were brought to base by subtracting a horizontal background, and normalised to the average edge jump as defined by the intensity of the EXAFS region above 5145 eV.

The energy of the 2010 dataset was calibrated by defining the first derivative peak of Ti in Ti foil to be 4966.4 eV (Bearden and Burr, 1967). The datasets collected in 2008 and 2009 were calibrated by comparing spectra collected during these sessions and in 2010. Details of this calibration are tabulated in Appendix E.1.

The pre-edge was modelled empirically using a Gaussian-Lorentzian Cross Product (Amplitude) function in Peakfit v.4 (Equation 6-1) such that the peak widths were constant within a sample and across the sample series. The background from the continuum state was modelled by fitting a peak to the edge.

$$y = \frac{v_0}{1 + v_3 \left(\frac{(x-v_1)}{v_2} \right)^2} e^{\left[(1-v_3) \frac{1}{2} \left(\frac{(x-v_1)}{v_2} \right)^2 \right]} \quad \text{Equation 6-1}$$

Where:

v_0 = amplitude

v_1 = centre

v_2 = width

v_3 = shape

where: 0 = Gaussian (Amplitude); 1 = Lorentzian (Amplitude)

6.4 Results

6.4.1 Ti-bearing standards

Spectra were collected from Ti-bearing silicates and oxides in which Ti occupied different coordination states (Table 6-1). As can be seen in Figure 6-2, the intensity and energy of the crest (c) varies depending on the Ti oxidation state, coordination environment and bonding environment, and up to three main peaks were identified in each of the main regions within the XANES spectrum, namely the pre-edge (a_1 , a_2 , a_3), shoulder (b_1 , b_2 , b_3) and post-crest (d_1 , d_2 , d_3) regions. Similar features were reported for Ti K-edge XANES spectra collected from a range of Ti-bearing silicates and oxides (Waychunas, 1978; Berry *et al.*, 2007; Dhaussy *et al.*, 2007).

A single, intense pre-edge feature was observed in the spectra collected from ^{47}Ti -ol and ^{47}Ti -sp, whereas the pre-edge peak of ^{47}Ti -pv and ^{47}Ti (IV)-ox was less intense and split into three peaks. The pre-edge feature in spectra collected from ^{47}Ti (III)-ox was broad. The forms of the respective pre-edge features are as expected from Ti in the respective coordination states. The $1s \rightarrow 3d$ transition responsible for the pre-edge feature is Laporte forbidden, however, due to mixing of the Ti $3d$ and

O 2p orbitals, an electronic transition is allowed (Brown *et al.*, 1988; Farges, 1996). As the orbital mixing is greater on a non-centrosymmetric site, the pre-edge feature for Ti in tetrahedral coordination is greater than for Ti in octahedral coordination (Waychunas, 1987; Farges *et al.*, 1996a). Indeed, the pre-edge feature in spectra collected from Ti in a symmetrical octahedral site is reported to be almost nonexistent, whereas the pre-edge feature of Ti in a distorted octahedral site split into three peaks (Waychunas, 1987). In $^{61}\text{TiO}_2$ the a_2 and a_3 peaks (Figure 6-2b) are assigned to the t_{2g} and e_g crystal field states respectively, and the a_1 peak may be due to a multi-electron excitation process (Waychunas, 1987).

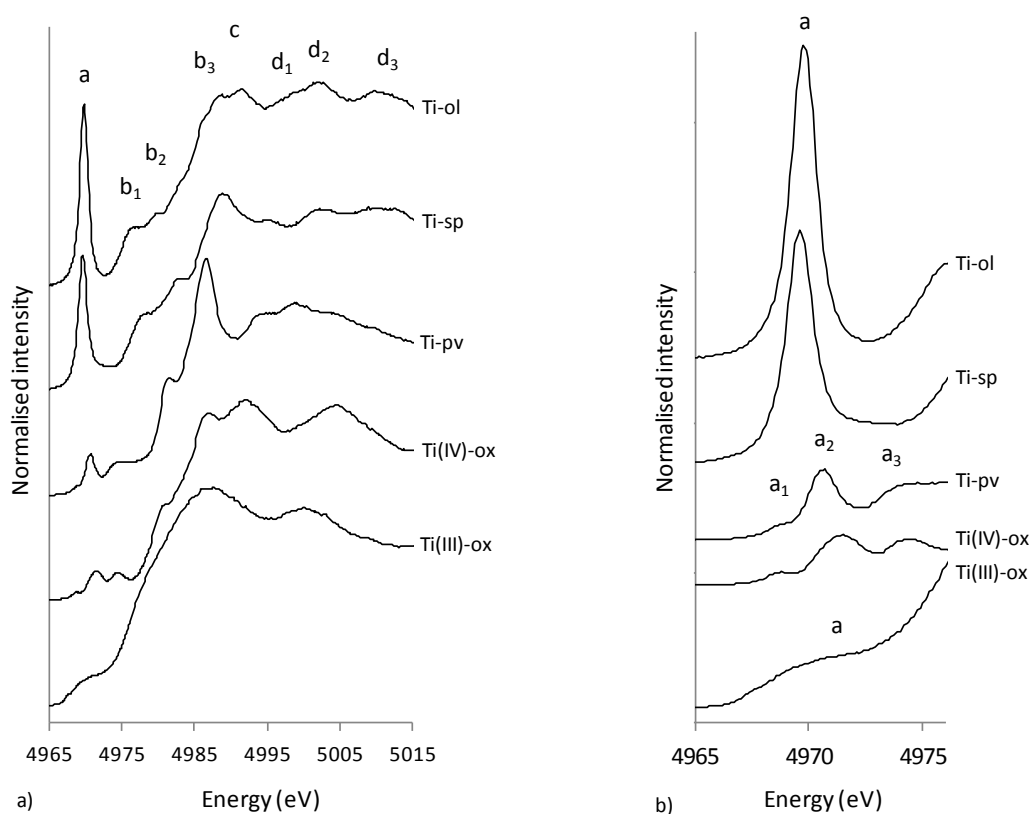


Figure 6-2 (a) Ti K-edge XANES spectra collected from a range of silicates and oxides with the pre-edge region (a, or a_1 , a_2 , a_3 as shown in figure 6-2b), and the main peaks marked for the shoulder (b_1 , b_2 , b_3), crest (c) and post-crest region (d_1 , d_2 , d_3); (b) The pre-edge region with the main peaks marked (a, or a_1 , a_2 , a_3).

The sensitivity of the pre-edge peak to coordination allows for energy and intensity fields to be defined for the respective coordination states (Farges *et al.*, 1996a). The pre-edge peak energy and intensity of $^{47}\text{Ti-sp}$ and $^{61}\text{Ti(IV)-ox}$ fit well within the 4- and 6-fold coordination fields (Figure 6-3). The $^{47}\text{Ti-ol}$ pre-edge peak intensity is higher than predicted by the Farges *et al.* (1996a) plot, although this sample plotted above this field in an independent study (Berry *et al.*, 2007). The $^{61}\text{Ti-Pv}$ pre-edge peak data plots outside the $^{61}\text{Ti}^{4+}$ field defined by Farges *et al.* (1996a), although the intensity of the $^{61}\text{Ti-pv}$ pre-edge feature is similar to that expected for Ti in octahedral coordination. The lineshape of the Ti K-edge spectrum collected from $^{61}\text{Ti-pv}$ (BaTiO_3), including the pre-edge feature, is similar to that collected from CaTiO_3 (Dhaussy *et al.*, 2007).

The pre-edge peak intensity of $^{61}\text{Ti(III)-ox}$ is similar to those collected from Ti^{4+} in octahedral coordination, and the energy of the pre-edge feature is shifted to lower energy (Figure 6-3).

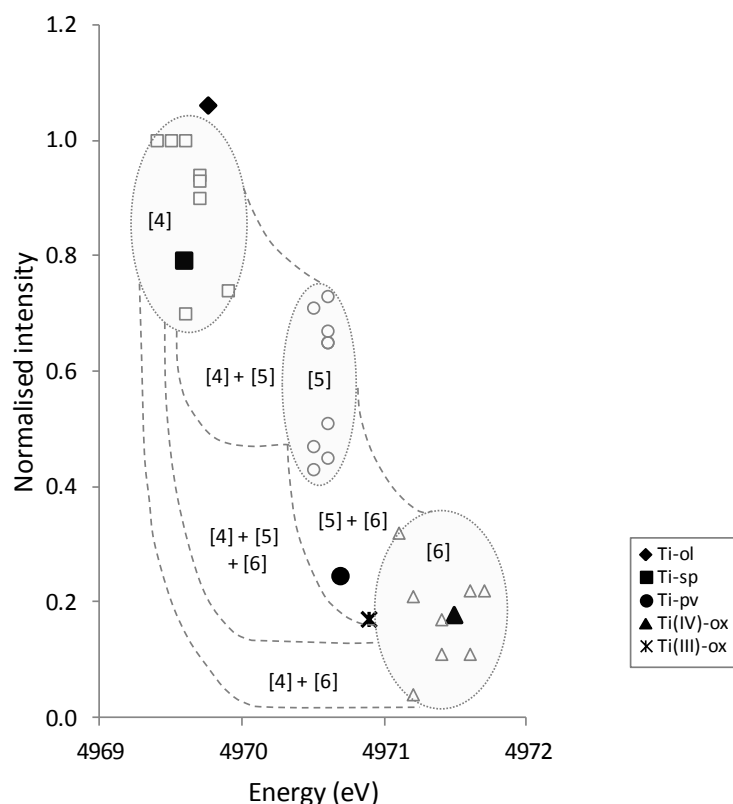


Figure 6-3 Ti K-edge XANES pre-edge peak intensity as a function of energy showing the Ti-bearing phases in this study (black points) with reference to the data of Farges *et al.* (1996a) (grey, unfilled points) and the fields defined by Farges *et al.* (1996a) for Ti in 4-, 5-, and 6-fold coordination (shaded areas) or Ti in two or more coordination states (regions enclosed by dashes).

6.4.2 Ti-CMAS glasses

6.4.2.1 Spectral characterisation

Ti K-edge XANES spectra for the five Ti-CMAS glasses are shown in Figure 6-4. The lineshape is similar across the compositions and is characterised by an asymmetric pre-edge (a), a shoulder on the edge (b), a single, broad crest (c) and a broad feature in the post-crest region at 5000 eV (d). The edge of the samples produced under reducing atmospheres ($\Delta\text{IW-10.5}$) were shifted 1.1-1.5 eV to lower energy than the samples produced under more oxidising conditions ($\Delta\text{IW+6.5}$).

There is an abrupt change in the spectral features of the samples prepared at $>\Delta\text{IW-6.5}$ and those prepared at $\leq\Delta\text{IW-6.5}$, particularly in the edge energy (Figure 6-4f) and the intensity of the pre-edge peak (Figure 6-5) between the samples produced at $\geq\Delta\text{IW-4.5}$. The synthesis conditions varied between these datasets as those prepared at $\geq\Delta\text{IW-4.5}$ using $\text{CO}_2 \pm \text{CO}$ were mounted on Pt or Re loops, whereas those prepared at $\leq\Delta\text{IW-6.5}$ using $\text{CO} \pm \text{Ar}$ were mounted in graphite. The graphite-mounted

glasses contain up to 0.5 wt% S and may have trace amounts of Ti-S, T-C, Ti^0 or dissolved Ti^{2+} present (Section 3.4.1).

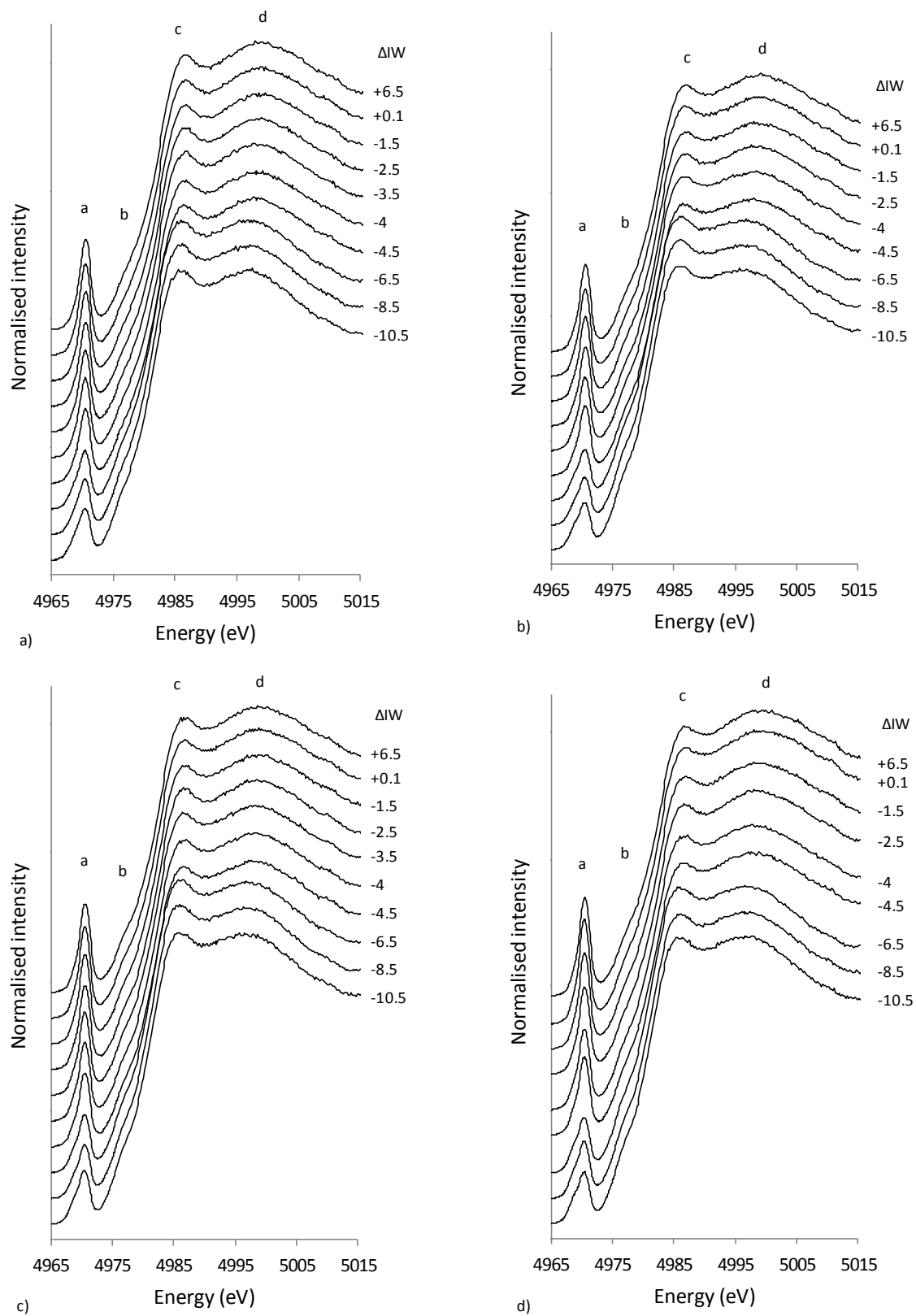


Figure 6-4 caption on following page.

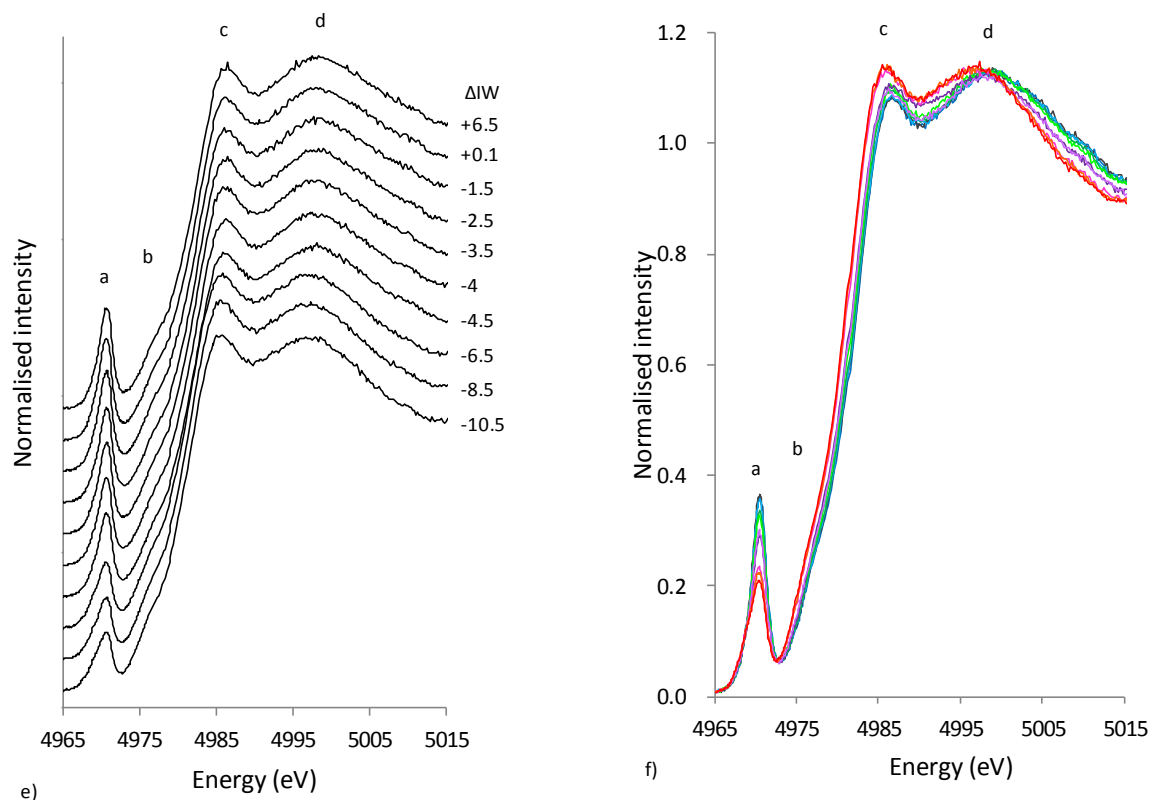


Figure 6-4 Ti K-edge XANES spectra collected from Ti-CMAS glasses prepared over 17 log units in fO_2 showing composition (a) AD; (b) AD+En; (c) AD+Fo; (d) AD+Qtz; and (e) AD+Wo (on following page), with the main features marked: asymmetric pre-edge feature (labelled a), shoulder (labelled b), crest (c) and broad feature in the post-crest region (d). Spectra offset for clarity. (f) The Ti K-edge XANES spectra collected from the AD glass composition prepared over 17 log units in fO_2 showing an offset in energy between the samples prepared at $<\Delta IW-6.5$ (in red, orange and pink) from those prepared at $>\Delta IW-4.5$.

The pre-edge was empirically modelled by three components (a_{fit1} , a_{fit2} , a_{fit3}) with a 99% Lorentzian lineshape, as shown for the AD glass composition (Figure 6-6). A Lorentzian lineshape is expected from an electronic transition, with the Gaussian component due to contributions from the experimental setup (Brown *et al.*, 1988). The full width half maximum for the five compositions was 1.64 eV, larger than the beamline resolution of 1.2 eV for the Ti K-edge (Section 6.3.2).

As shown in Figure 6-7, the pre-edge peak intensity and energy of the Ti^{4+} glass samples plot between the five- and six-fold coordination regions. Proportions of the two Ti coordination states present in the glasses were determined using the mixing line of Farges *et al.* (1996a) as this technique has successfully been used to quantify the proportion of Ti^{4+} in two coordination states in complex, multi-component glasses if present as $>10\%$ of total Ti (e.g. Farges and Brown, 1997; Romano *et al.*, 2000). Indeed, the technique is sufficiently sensitive to determine 5-fold co-orientated Ti ($^{[5]}Ti^{4+}$) from mixtures of Ti^{4+} in 4- and 6-fold coordination Ti ($^{[4]}Ti^{4+}$, $^{[6]}Ti^{4+}$).

The Ti coordination states in the CMAS glasses were dependant on composition, with the Ca-rich composition AD+Wo having equal proportions of Ti^{4+} in 5 and 6-fold coordination ($50^{[5]}Ti^{4+}:50^{[6]}Ti^{4+}$). In contrast, Ti in the SiO_2 -rich composition AD+Qtz was dominantly 5-fold coordinated ($70^{[5]}Ti^{4+}:30^{[6]}Ti^{4+}$), and the other compositions (AD, AD+En and AD+Fo) intermediate

($\sim 60^{[5]}\text{Ti}^{4+}:40^{[6]}\text{Ti}^{4+}$), as shown in Figure 6-8. The five-fold coordinated Ti^{4+} is probably square pyramidal, based on the findings of Ti coordination in $\text{TiO}_2\text{-SiO}_2\text{-(Al}_2\text{O}_3, \text{CaO, Na}_2\text{O, K}_2\text{O)}$ glasses (Farges *et al.*, 1996b).

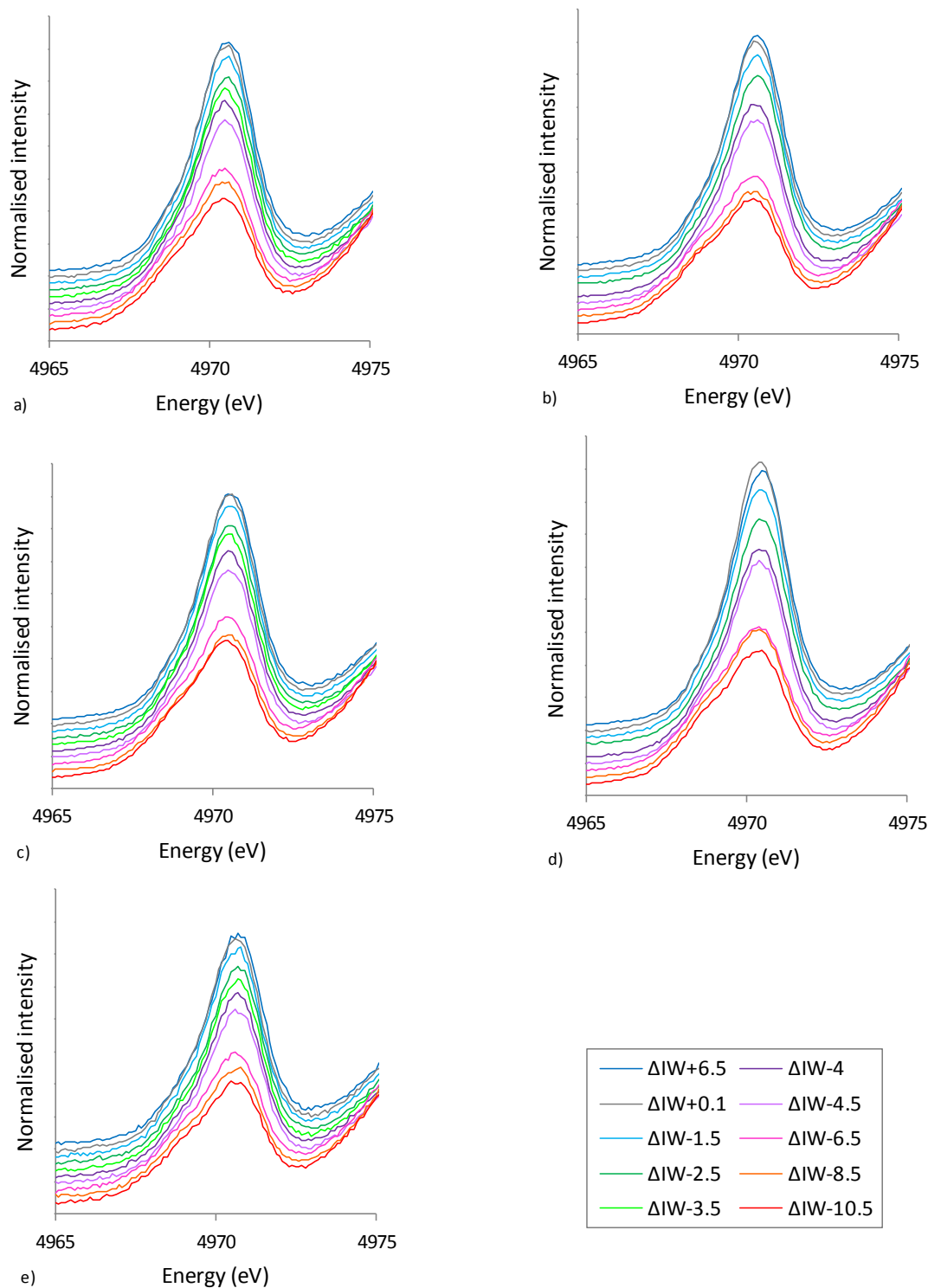


Figure 6-5 The Ti K-edge XANES pre-edge region for spectra collected from Ti-CMAS glasses prepared over 17 log units in $f\text{O}_2$ showing composition (a) AD; (b) AD+En; (c) AD+Fo; (d) AD+Qtz; and (e) AD+Wo. Spectra offset for clarity.

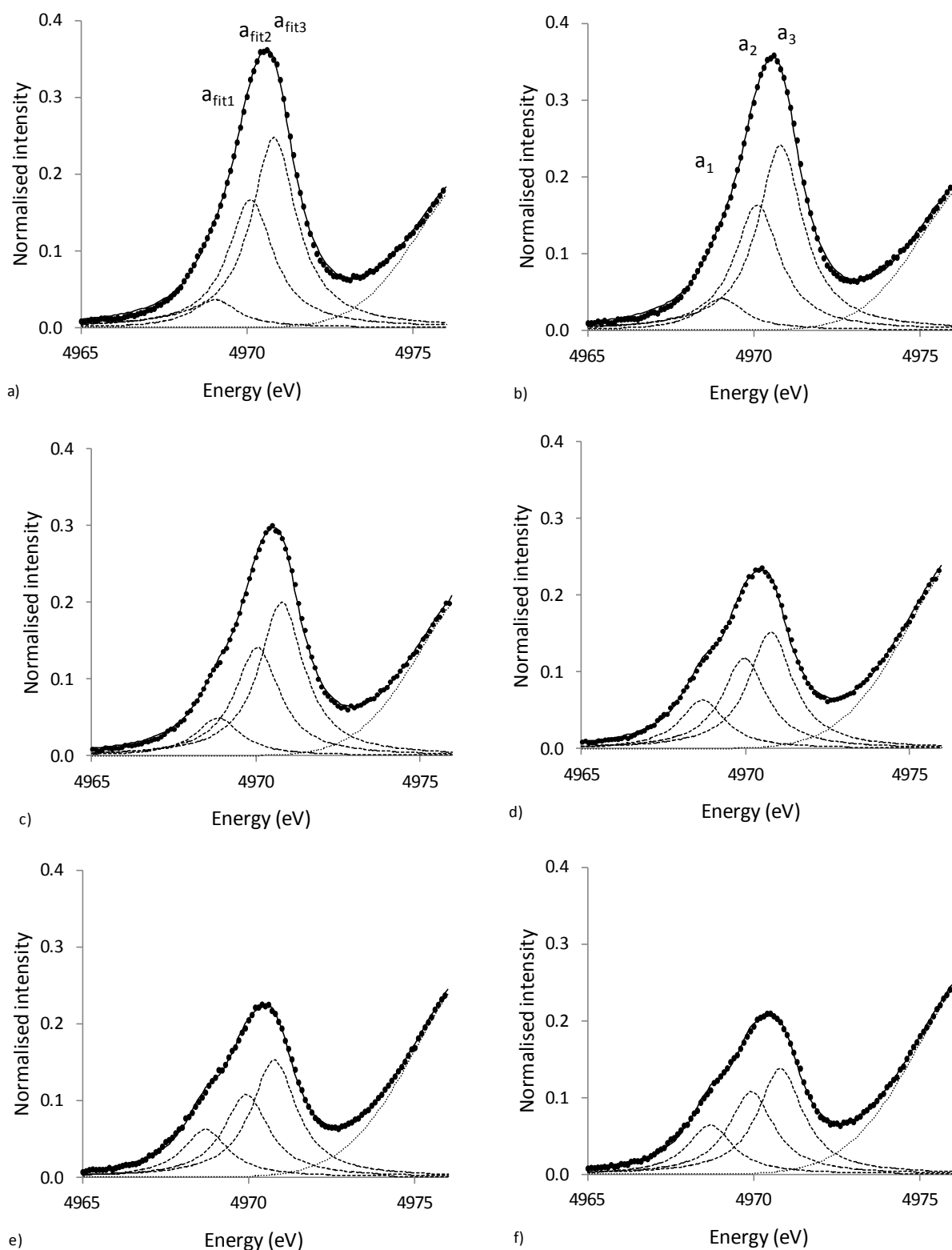


Figure 6-6 The pre-edge peak region of Ti K-edge XANES spectra collected from AD samples (dots) has been empirically modelled by three components (a_{fit1} , a_{fit2} and a_{fit3} ; dashed lines) and a background (small dotted/grey line). Samples representative of the series prepared over 17 log units in $f\text{O}_2$ are as follows: (a) $\Delta\text{IW}+6.5$; (b) $\Delta\text{IW}-1.5$; (c) $\Delta\text{IW}-4.5$; (d) $\Delta\text{IW}-6.5$; (e) $\Delta\text{IW}-8.5$; (f) $\Delta\text{IW}-6.5$.

These results agree with the findings of Farges and Brown (1997) and Romano *et al.* (2000), which showed that Ti^{4+} in rhyolitic compositions and $\text{SiO}_2\text{-TiO}_2$ mixtures are dominantly $^{[4]}\text{Ti}^{4+}$, whereas up to 50% of the Ti is $^{[5]}\text{Ti}^{4+}$ in basaltic, Ca-rich glasses with network modifying alkali and alkali earth elements (Farges *et al.*, 1996b). TiO_2 content also affects Ti^{4+} coordination, with $^{[4]}\text{Ti}^{4+}$ reported in $\text{TiO}_2\text{-SiO}_2$ and $\text{TiO}_2\text{-CaSiO}_3$ (Ti-S±C) glasses with >3.6 wt% TiO_2 , and $^{[5]}\text{Ti}^{4+}$ in the same glasses with <3.6 wt% TiO_2 (Henderson *et al.*, 2003). The dominance of $^{[5]}\text{Ti}^{4+}$ at low Ti contents in the Ti-S±C glasses is in agreement with the high proportion of $^{[5]}\text{Ti}^{4+}$ observed in the Ti-CMAS glasses in this study, with the presence of MgO and Al_2O_3 accounting for the presence of $^{[6]}\text{Ti}^{4+}$.

As melt structure is related to melt composition (e.g. Farges and Brown, 1997) and optical basicity is a function of melt composition, the structure of a melt may be expected to be related to optical basicity (Berry *et al.* 2006). As such, optical basicity is a useful measure by which to explain melt properties. The Ti^{4+} in octahedral coordination was directly correlated with calculated optical basicity (Figure 6-8). Empirically, the greater electron density round O in basic compositions appears to stabilise Ti in higher coordination than compositions with lower basicity.

In glasses Ti^{3+} is predicted to be in octahedral coordination (Tranell *et al.*, 2002), and Ti^{3+} occurs in octahedral coordination in many crystalline materials, such as meteoritic pyroxene (Burns and Huggins, 1973), Ti-bearing pyrope (Rager *et al.*, 2003) and synthetic Ti-doped corundum (Vorobeveva *et al.*, 2009). It is therefore not unreasonable to expect Ti^{3+} to be in octahedral coordination in the Ti-CMAS glasses. The decrease in the pre-edge peak intensity with more reducing conditions suggests a greater proportion of Ti^{3+} in octahedral coordination is present.

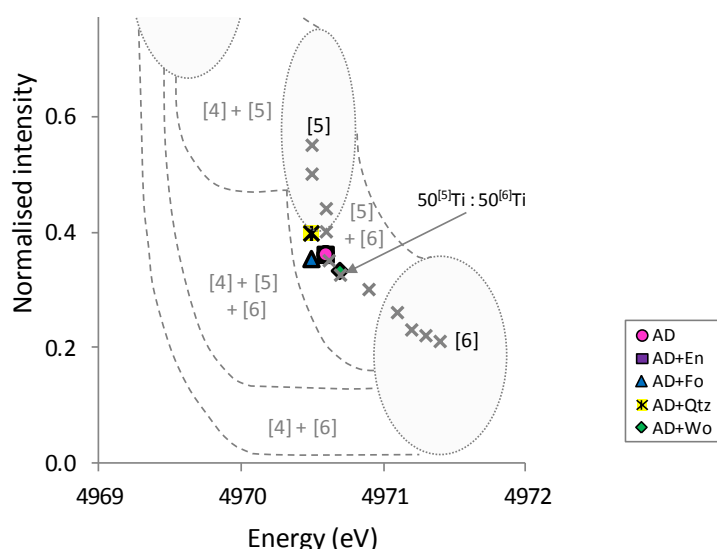


Figure 6-7 Ti K-edge pre-edge intensity and energy of the Ti^{4+} CMAS glasses prepared at $\Delta\text{IW}+6.5$. Included are the $^{[4]}\text{Ti}^{4+}$, $^{[5]}\text{Ti}^{4+}$, $^{[6]}\text{Ti}^{4+}$ fields (shaded areas, as per Figure 6-3) and the $^{[5]}\text{Ti}$ - $^{[6]}\text{Ti}$ mixing line (crosses) from Farges *et al.* (1996a) The error on the normalised intensity is smaller than the data point.

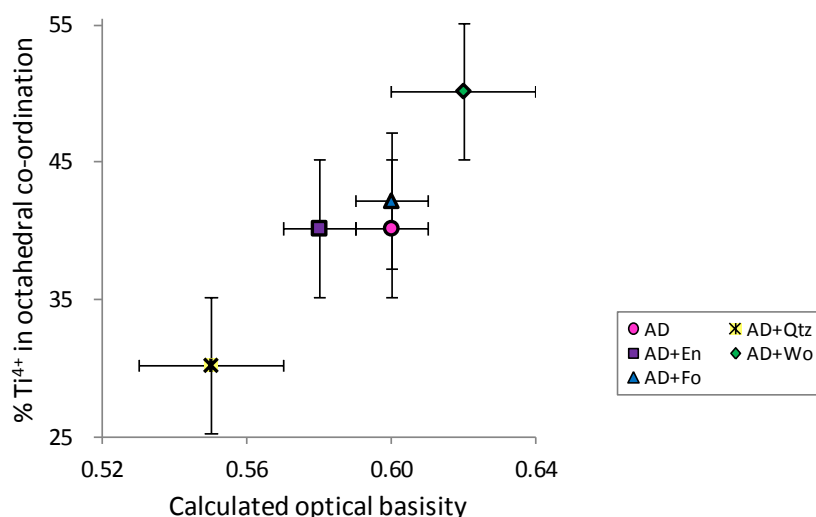


Figure 6-8 The proportion of Ti⁴⁺ in octahedral coordination as a function of calculated optical basicity.

6.4.2.2 Quantitative determination of Ti³⁺/ΣTi

Before the quantitative determination of Ti³⁺/ΣTi in the glasses, the stability of the Ti oxidation state in the CMAS glasses was investigated. For this purpose ten spectra were collected from a single point in each of three samples, with a scan in energy over the Ti K-edge XANES pre-edge region from 4962 eV to 4975 eV with 0.2 eV steps. Two samples (AD and AD+Fo) prepared at ΔIW-10.5 were potentially Ti³⁺-rich, whereas AD samples prepared at ΔIW-2.5 would have a greater proportion of Ti⁴⁺ present.

The pre-edge peak intensities of successive spectra are shown in Figure 6-9 and the data tabulated in Appendix E.3.2. The pre-edge peak intensity and energy varied randomly, and the standard deviations of these parameters were similar for all three samples. These results suggest that the Ti oxidation state is stable as a function of time.

Spectral features that varied over the 17 log units in *f*O₂ were investigated, including the energy and intensity of the pre-edge peak and crest (Table 6-5). Ratios of these spectral parameters, the energy and intensity of the pre-edge peak fit components were also plotted as a function of *f*O₂. The energy of the edge at normalised intensity 0.8 (*E*_{0.8}, Figure 6-10) varied most systematically over the *f*O₂ range investigated.

Spectral parameters that vary as a function of *f*O₂ may be fitted with a sigmoidal function (Equation 6-2), such that the variables in the fit relate to the number of electrons taking part in the reaction (*n*) and the composition (log*K'*), as shown by Berry and O'Neill (2004). This function assumes a linear relationship (Equation 6-3) between the valence-state dependant spectral parameter and the ratio of a redox variable element, as has been shown for Fe²⁺/(Fe²⁺+Fe³⁺) and Cr²⁺/(Cr²⁺+Cr³⁺) (Berry *et al.*, 2003; Berry and O'Neill, 2004). The parameters *a*₀ and *a*₁ in Equation 6-2 relate to this

linear relationship, as defined by Equation 6-3, and are determined by the fit to the spectral parameters plotted as a function of $f\text{O}_2$ (Equation 6-2).

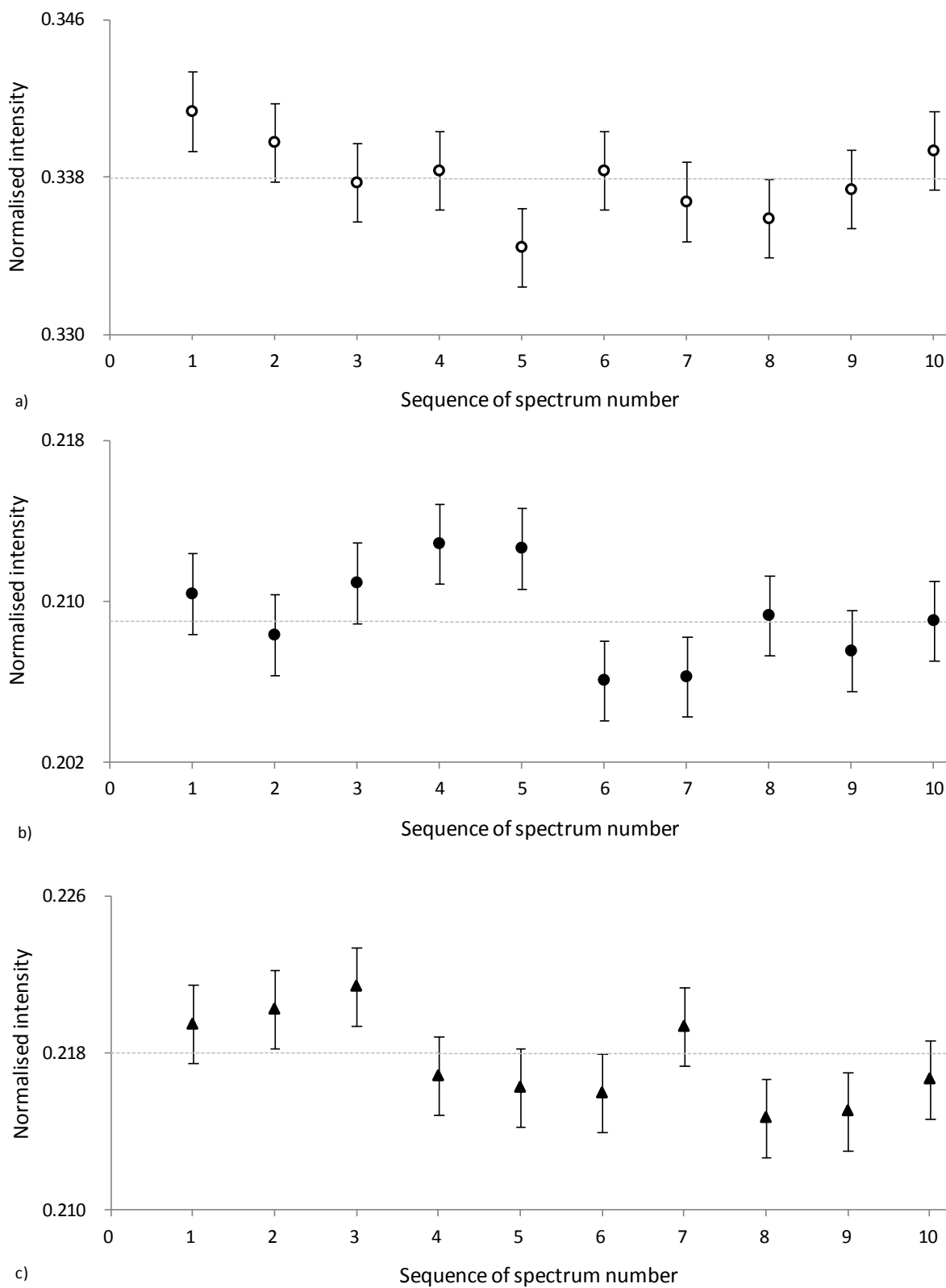


Figure 6-9 The pre-edge peak intensity (a) of 10 successive analyses for (a) AD prepared at $\Delta I\text{W}-2.5$; (b) AD prepared at $\Delta I\text{W}-10.5$; and (c) AD+Fo prepared at $\Delta I\text{W}-10.5$. The average pre-edge peak intensity is shown by the dashed line.

Table 6-5 Ti K-edge XANES spectral parameters from five Ti-CMAS glass compositions prepared over 17 log units in fO_2

Parameter	AD									
fO_2 (ΔIW)	+6.5	+0.1	-1.5	-2.5	-3.5	-4	-4.5	-6.5	-8.5	-10.5
Scan number	45977	46044	46026	46029	46051	45993	45969	46036	46038	45981
Pre-edge- a_2 (I)	0.361	0.362	0.358	0.338	0.329	0.320	0.301	0.236	0.225	0.209
Pre-edge- a_2 (E, eV)	4970.6	4970.6	4970.6	4970.6	4970.5	4970.5	4970.5	4970.5	4970.4	4970.5
Minimum- m_1 (I)	0.062	0.062	0.063	0.064	0.063	0.064	0.060	0.062	0.063	0.063
Minimum- m_1 (E, eV)	4973.1	4973.2	4973.1	4972.9	4972.8	4972.7	4972.8	4972.5	4972.7	4972.6
Energy when $I = 0.8$ ($E_{0.8}$, eV)	4983.1	4983.0	4983.0	4982.9	4982.7	4982.7	4982.6	4981.9	4981.8	4981.8
Crest-c (I)	1.082	1.086	1.089	1.098	1.107	1.094	1.099	1.134	1.144	1.143
Crest-c (E, eV)	4986.3	4986.7	4986.7	4986.5	4986.5	4986.7	4986.3	4985.9	4986.1	4985.5
Parameter	AD+En									
fO_2 (ΔIW)	+6.5	+0.1	-1.5	-2.5	-3.5	-4	-4.5	-6.5	-8.5	-10.5
Scan number	45972	46048	46024	46027	-	45998	45970	46033	46041	45996
Pre-edge- a_2 (I)	0.360	0.361	0.351	0.328	-	0.305	0.290	0.213	0.200	0.199
Pre-edge- a_2 (E, eV)	4970.6	4970.5	4970.6	4970.6	-	4970.5	4970.6	4970.5	4970.5	4970.5
Minimum- m_1 (I)	0.060	0.062	0.062	0.061	-	0.063	0.060	0.061	0.060	0.060
Minimum- m_1 (E, eV)	4973.0	4973.0	4973.1	4973.0	-	4972.8	4972.9	4972.5	4972.6	4972.4
Energy when $I = 0.8$ ($E_{0.8}$, eV)	4983.1	4982.9	4982.9	4982.8	-	4982.5	4982.5	4981.7	4981.6	4981.6
Crest-c (I)	1.084	1.101	1.096	1.109	-	1.114	1.108	1.155	1.162	1.153
Crest-c (E, eV)	4987.2	4986.5	4987.2	4987.0	-	4987.2	4986.3	4986.3	4986.1	4986.5
Parameter	AD+Fo									
fO_2 (ΔIW)	+6.5	+0.1	-1.5	-2.5	-3.5	-4	-4.5	-6.5	-8.5	-10.5
Scan number	45967	46045	46025	46028	46050	45994	45968	46035	46039	45997
Pre-edge- a_2 (I)	0.353	0.364	0.356	0.335	0.332	0.316	0.296	0.235	0.217	0.218
Pre-edge- a_2 (E, eV)	4970.5	4970.6	4970.6	4970.6	4970.6	4970.5	4970.5	4970.4	4970.5	4970.5
Minimum- m_1 (I)	0.059	0.062	0.063	0.062	0.062	0.062	0.061	0.062	0.060	0.063
Minimum- m_1 (E, eV)	4973.1	4972.8	4972.9	4973.2	4972.8	4972.9	4972.7	4972.5	4972.7	4972.4
Energy when $I = 0.8$ ($E_{0.8}$, eV)	4983.1	4983.0	4983.0	4982.8	4982.7	4982.6	4982.5	4981.9	4981.8	4981.7
Crest-c (I)	1.077	1.090	1.091	1.102	1.107	1.102	1.097	1.146	1.151	1.142
Crest-c (E, eV)	4986.5	4986.7	4987.0	4986.5	4986.3	4987.0	4986.7	4985.7	4985.9	4985.9
Parameter	AD+Qtz									
fO_2 (ΔIW)	+6.5	+0.1	-1.5	-2.5	-3.5	-4	-4.5	-6.5	-8.5	-10.5
Scan number	45976	46043	46023	46022	-	45999	45973	46034	46040	45982
Pre-edge- a_2 (I)	0.397	0.421	0.389	0.353	-	0.328	0.319	0.228	0.235	0.213
Pre-edge- a_2 (E, eV)	4970.5	4970.4	4970.4	4970.4	-	4970.4	4970.4	4970.4	4970.4	4970.5
Minimum- m_1 (I)	0.062	0.066	0.064	0.062	-	0.063	0.063	0.061	0.061	0.060
Minimum- m_1 (E, eV)	4973.0	4972.8	4973.0	4972.9	-	4972.8	4972.8	4972.6	4972.4	4972.4
Energy when $I = 0.8$ ($E_{0.8}$, eV)	4983.1	4982.9	4982.9	4982.9	-	4982.5	4982.5	4981.7	4981.7	4981.6
Crest-c (I)	1.075	1.100	1.089	1.077	-	1.094	1.083	1.141	1.133	1.140
Crest-c (E, eV)	4986.5	4987.1	4987.0	4986.5	-	4987.2	4986.7	4985.9	4985.9	4985.5
Parameter	AD+Wo									
fO_2 (ΔIW)	+6.5	+0.1	-1.5	-2.5	-3.5	-4	-4.5	-6.5	-8.5	-10.5
Scan number	45975	46047	46030	46031	46049	45995	45974	46032	46037	45978
Pre-edge- a_2 (I)	0.332	0.335	0.330	0.311	0.302	0.290	0.276	0.219	0.206	0.195
Pre-edge- a_2 (E, eV)	4970.7	4970.6	4970.8	4970.7	4970.7	4970.7	4970.6	4970.6	4970.8	4970.5
Minimum- m_1 (I)	0.059	0.060	0.064	0.061	0.060	0.063	0.061	0.062	0.061	0.062
Minimum- m_1 (E, eV)	4973.0	4973.0	4972.8	4973.0	4973.0	4972.7	4972.9	4972.8	4972.6	4972.8
Energy when $I = 0.8$ ($E_{0.8}$, eV)	4983.0	4982.9	4982.8	4982.8	4982.7	4982.6	4982.6	4982.0	4981.9	4981.8
Crest-c (I)	1.115	1.106	1.107	1.114	1.119	1.117	1.106	1.143	1.157	1.142
Crest-c (E, eV)	4986.5	4986.1	4986.1	4986.5	4985.9	4986.3	4985.9	4985.9	4985.7	4985.1

Note: I = intensity, E = energy. The uncertainties in these parameters are estimated to be: (I) 0.002 and (E) 0.05 eV.

During the curve fitting procedure a greater weighting was given to the Pt- and Re-mounted samples as the graphite-mounted samples were S-bearing and may contain a minor amount of Ti^0 or Ti^{2+} (Section 3.4.1). Without a constraint at low fO_2 , curve-fitting was difficult, and initial fits needed to be made using Excel. For this purpose Equation 6-2 was simplified to Equation 6-4 and then Equation 6-5, with A and B related to the valence-state dependant spectral parameters for the samples

prepared at $\Delta IW+6.5$ and $\Delta IW-10.5$ as shown. Equation 6-5 was used to obtain the initial fit-variables, after which a_0 , a_1 , n and $\log K'$ were refined using the curve fitting function within KaleidaGraph.

$$P = \frac{1}{a_1} \left(\frac{1}{1 + 10^{(n/4 \log fO_2 + \log K')}} - a_0 \right) \quad \text{Where:} \quad \text{Equation 6-2}$$

P = Valence-state dependant spectral parameter
 n = # of electrons involved in the oxidation reaction
 a_0 and a_1 = from Equation 6-3
 $\log K' = \log K - \log \frac{\gamma_{M^{(x+n)+} O_{(x+n)/2}}}{\gamma_{M^{x+} O_{x/2}}}$

Where the activity coefficient (γ) is assumed to be constant for low concentrations of element M.

$$\frac{M^{x+}}{(M^{x+} + M^{(x+n)+})} = a_0 + a_1 P \quad \text{Where:} \quad \text{Equation 6-3}$$

P = Valence-state dependant spectral parameter
 a_0 and a_1 = linear fit variables

$$P = \frac{1}{a_1} (C - a_0) \quad \text{Where:} \quad \text{Equation 6-4}$$

$$C = \frac{1}{1 + 10^{(n/4 \log fO_2 + \log K')}} \quad \text{with parameters as detailed in equations above}$$

$$P = BC + A \quad \text{Where:} \quad \text{Equation 6-5}$$

P = Valence-state dependant spectral parameter
 $A = -a_0/a_1$
 $= P_{\Delta IW+6.5} = P$ of the sample prepared at $\Delta IW+6.5$
 $B = 1/a_1$
 $= P_{\Delta IW-10.5} - P_{\Delta IW+6.5}$
 $C = \frac{1}{1 + 10^{(n/4 \log fO_2 + \log K')}} \quad \text{with parameters as detailed in equations above}$

The edge energy ($E_{0.8}$) parameter was fitted with a sigmoidal function after Berry and O'Neill (2004), as shown in Figure 6-10. The fit to the data resulted in an n parameter of approximately one, although that of AD and AD+Wo were a little higher and lower respectively (Table 6-6). These results would be consistent with a one electron reaction (e.g. Berry and O'Neil, 2004).

Table 6-6 Parameters obtained from fitting the data in Table 6-5 to Equation 6-2

Parameter	AD	AD+En	AD+Fo	AD+Qtz	AD+Wo
n	1.19	1.04	1.00	1.01	0.95
$\log K'$	4.34	3.72	3.60	3.68	3.58
a_0	3837.4	3323.7	3493.3	3344.8	4504.6
a_1	-0.7701	-0.6670	-0.7010	-0.6712	-0.9040
R^2	0.984	0.990	0.996	0.980	0.984

Note: The Pt- and Re-mounted samples were weighted with respect to the graphite-mounted samples. Based on the uncertainty of different weighting, the uncertainties are estimated to be as follows: 0.10 in n ; 0.35 in $\log K'$; 0.9 in a_0 ; and 0.0002 in a_1 .

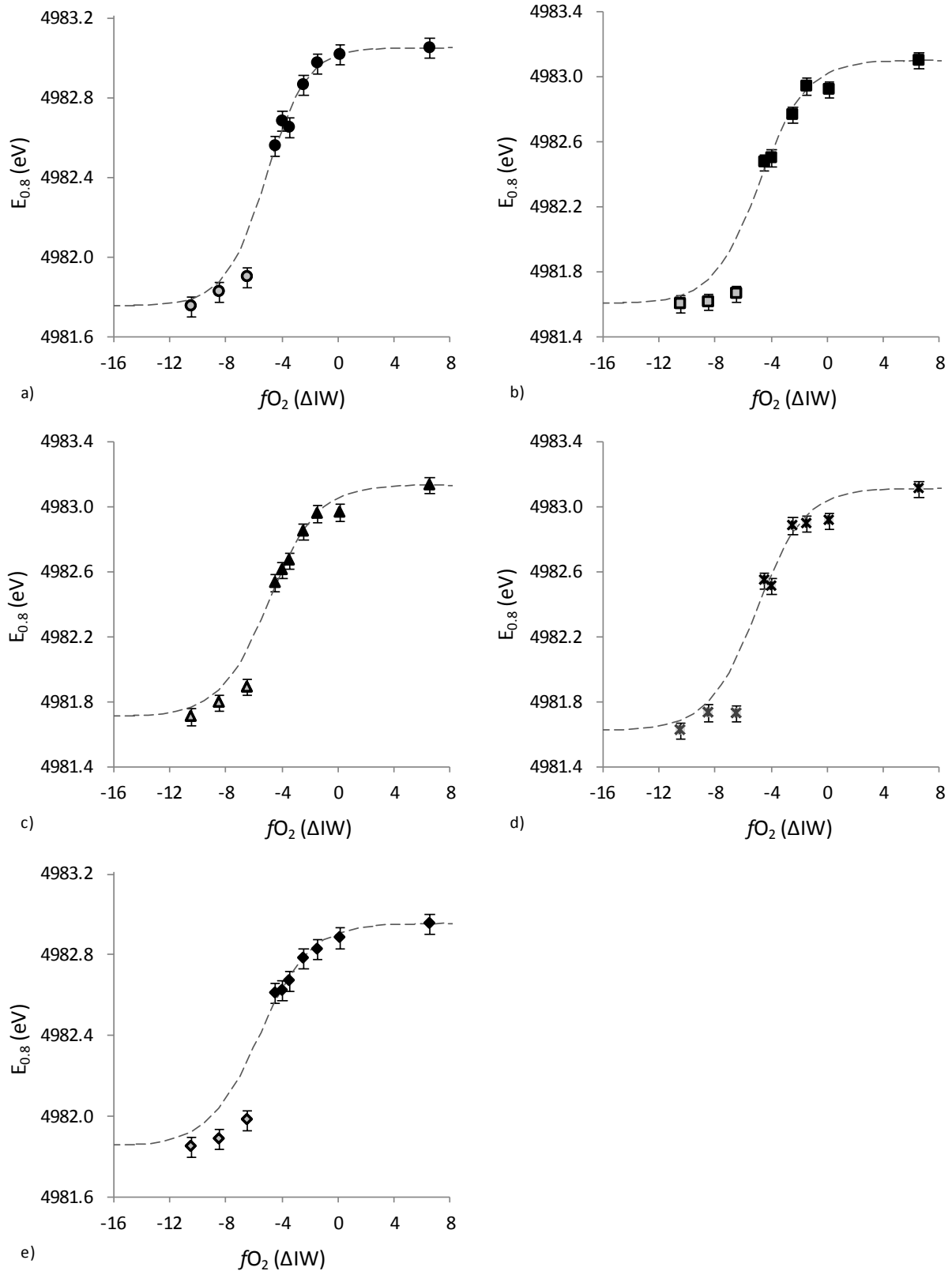


Figure 6-10 Spectral parameters $E_{0.8}$ of as a function of fO_2 for (a) AD, (b) AD+En, (c) AD+Fo, (d) AD+Qtz, (e) AD+Wo. A sigmoidal fit after Berry and O'Neill (2004) is shown.

The $Ti^{3+}/\Sigma Ti$ in the Ti-CMAS glasses may be calculated using Equation 6-3 and the fitted a_0 and a_1 parameters (Table 6-6) if a linear correlation is assumed between $Ti^{3+}/\Sigma Ti$ and $E_{0.8}$, which seems

reasonable based on the finding of Berry *et al.* (2003) and Berry and O'Neill (2004) for the $\text{Fe}^{2+}/\Sigma\text{Fe}$ and $\text{Cr}^{2+}/\Sigma\text{Cr}$ systems (respectively). The results are shown in Table 6-7, with non-physical $\text{Ti}^{3+}/\Sigma\text{Ti}$ calculated for AD at high $f\text{O}_2$, although this is only just outside the quoted uncertainty. This variability is possibly due to the uncertainty in the fit to the data and the deviation of the AD parameters from the ideal of one (Table 6-6). The calculated $\text{Ti}^{3+}/\Sigma\text{Ti}$ does, however, suggest that the samples prepared at $\Delta\text{IW}-10.5$ are close to a 100% $\text{Ti}^{3+}/\Sigma\text{Ti}$ end-member, despite the offset of the $E_{0.8}$ parameters from the sigmoidal fit to the data (Figure 6-10).

Figure 6-11 shows the results of mixing the Ti^{3+} and Ti^{4+} end-member spectra ($\Delta\text{IW}-10.5$ and $\Delta\text{IW}+6.5$ respectively) according to the calculated $\text{Ti}^{3+}/\Sigma\text{Ti}$ using Equation 6-3. The linear mixing of the two end-member spectra results in a spectrum with a similar lineshape to that collected from the sample with mixed-valent Ti. Moreover, the calculated $\text{Ti}^{3+}/\Sigma\text{Ti}$ from such a linear mixing model resulted in similar $\text{Ti}^{3+}/\Sigma\text{Ti}$ to that calculated by the sigmoidal fit after Berry and O'Neill (2004), as shown in Table 6-7.

Table 6-7 % $\text{Ti}^{3+}/\Sigma\text{Ti}$ calculated for the five Ti-CMAS glass compositions using either (S) Equation 6-3 and the parameters in Table 6-6 or (L) a linear mixing of the samples prepared at $\Delta\text{IW}+6.5$ (Ti^{4+} end-member) and $\Delta\text{IW}-10.7$ ($\sim\text{Ti}^{3+}$ end-member)

ΔIW	AD		AD+En		AD+Fo		AD+Qtz		AD+Wo	
	S	L	S	L	S	L	S	L	S	L
6.5	-5	1	-3	-1	-3	-2	-1	0	1	-1
0.1	-2	3	9	11	9	10	12	13	7	5
-1.5	1	7	8	10	10	10	13	15	12	11
-2.5	10	15	19	21	17	18	14	15	16	15
-3.5	26	31	nd	nd	30	31	nd	nd	27	25
-4	24	29	37	39	34	35	39	41	31	30
-4.5	33	39	39	40	40	41	36	38	32	31
-6.5	84	89	93	94	85	87	92	93	89	90
-8.5	90	95	96	98	91	94	91	93	97	99
-10.5	95	100	97	98	97	100	98	100	101	102

Notes: nd = no data. The propagated error is calculated to be 3% $\text{Ti}^{3+}/\Sigma\text{Ti}$ using an error of 0.05 eV in energy, which are based on the uncertainties associated with the Excel data-fit.

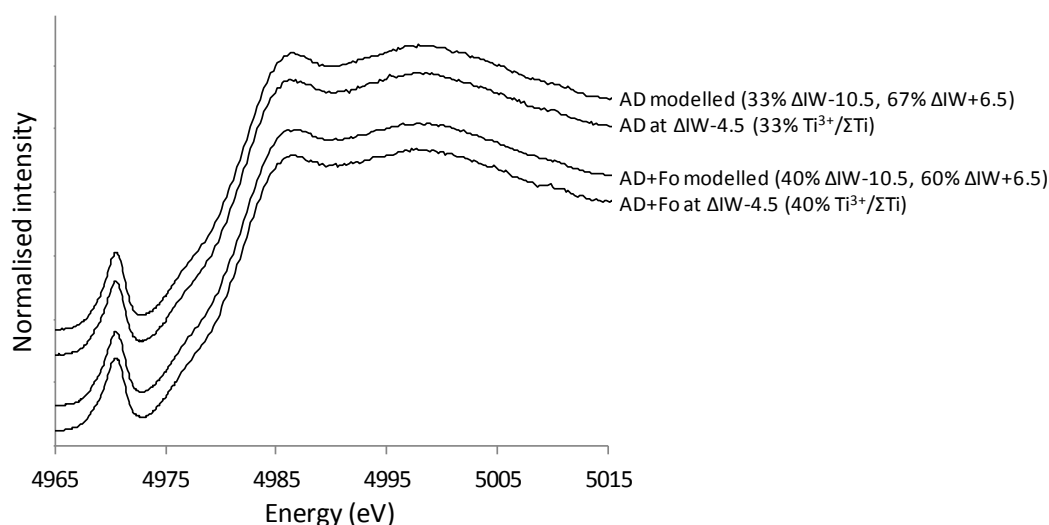


Figure 6-11 Ti K-edge XANES spectra collected from the AD and AD+Fo samples prepared at $\Delta\text{IW}-4.5$ and the modelled spectra from a linear mixing of the samples prepared at $\Delta\text{IW}+6.5$ and $\Delta\text{IW}-10.5$ for each composition.

The EPR signal intensity should be linearly correlated with the calculated $\text{Ti}^{3+}/\Sigma\text{Ti}$ as Ti^{3+} was the only paramagnetic element in the CMAS glasses over the $f\text{O}_2$ range investigated. It should, however, be noted that the samples from these two series were optically different, with the graphite-mounted samples from the EPR series containing numerous high backscatter coefficient “specks”, whereas those of the XANES sample series contained very few (Section 3.4.1). The EPR peak intensities for the Pt- and Re-mounted samples are linearly correlated with the calculated $\text{Ti}^{3+}/\Sigma\text{Ti}$ (Figure 6-12), whereas the graphite-mounted samples lie off this trend. The $\text{Ti}^{3+}/\Sigma\text{Ti}$ in the EPR sample prepared at $\Delta\text{IW}-10.5$ is approximately 48% less than expected, as based on the proportion of the measured EPR intensity and that expected from an extrapolation of the linear trend defined by the Pt- and Re-mounted samples. This finding supports the suggestion made in Section 3.4.1.4 that a non-paramagnetic Ti phase (Ti^0 , Ti^{2+} , Ti-C or Ti-S) is present in the graphite-mounted samples from the EPR sample series. If the graphite-mounted XANES samples contained even a small portion of such a phase, it may account for the offset in the spectral parameters from the fit to the $E_{0.8}$ data in Figure 6-10.

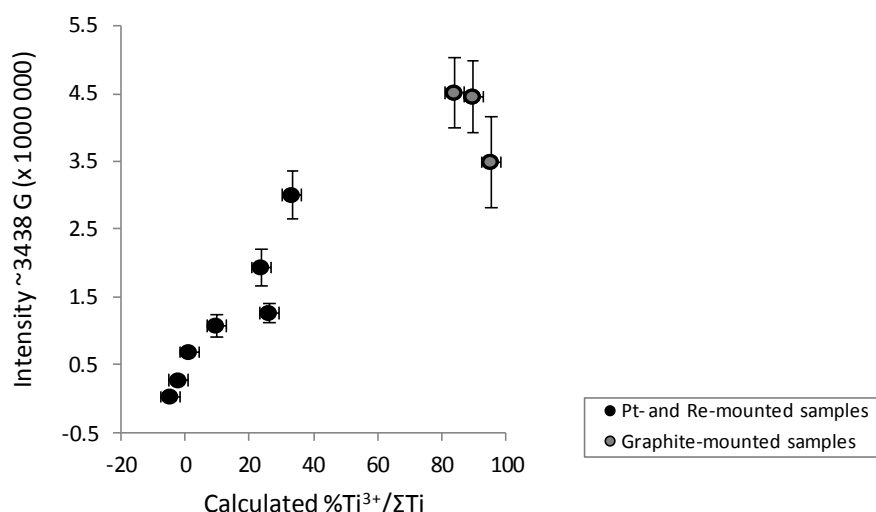


Figure 6-12 EPR peak intensity of the EPR sample series as a function of calculated $\text{Ti}^{3+}/\Sigma\text{Ti}$ for the XANES sample series for the same composition (AD).

The calculated $\text{Ti}^{3+}/\Sigma\text{Ti}$ may also be compared to values found in the literature for similar compositions. The Ti-bearing CMAS “FAD” composition of Schreiber *et al.* (1978) had a calculated optical basicity equal to that of the AD and AD+Fo compositions (0.60). Therefore, although the compositions differ, the $\text{Ti}^{3+}/\Sigma\text{Ti}$ characteristics of these samples should be similar. $\text{Ti}^{3+}/\Sigma\text{Ti}$ determined by titration (Schreiber *et al.*, 1978) is similar to that for the AD and AD+Fo series on a plot of $\text{Ti}^{3+}/\Sigma\text{Ti}$ versus $f\text{O}_2$ (Figure 6-13).

The $f\text{O}_2$ at which 50% $\text{Ti}^{3+}/\Sigma\text{Ti}$ is predicted to be present is $\Delta\text{IW}-5.1$, based on the partitioning of Ti between silicate melts (Fe-free and Fe-bearing) and minerals (olivine, orthopyroxene and clinopyroxene) as a function of $f\text{O}_2$ (Mallman and O’Neill, 2009). The composition of the glass used to define this $\text{Ti}^{3+}/\text{Ti}^{4+}$ - $f\text{O}_2$ relationship is not explicitly stated in their work, although the study used

CMAS glass compositions, including AD. It seems reasonable to expect that any modelling would be based on the simplest system, and therefore the AD composition. The predicted fO_2 at which 50% $Ti^{3+}/\Sigma Ti$ is predicted to be present (Mallmann and O'Neill, 2009) is shown on Figure 6-13, and it appears to continue the trend defined by the Pt- and Re-mounted glasses prepared at $\geq \Delta IW$ -4.5. This suggests that the calculated $Ti^{3+}/\Sigma Ti$ for these glasses is indeed accurate.

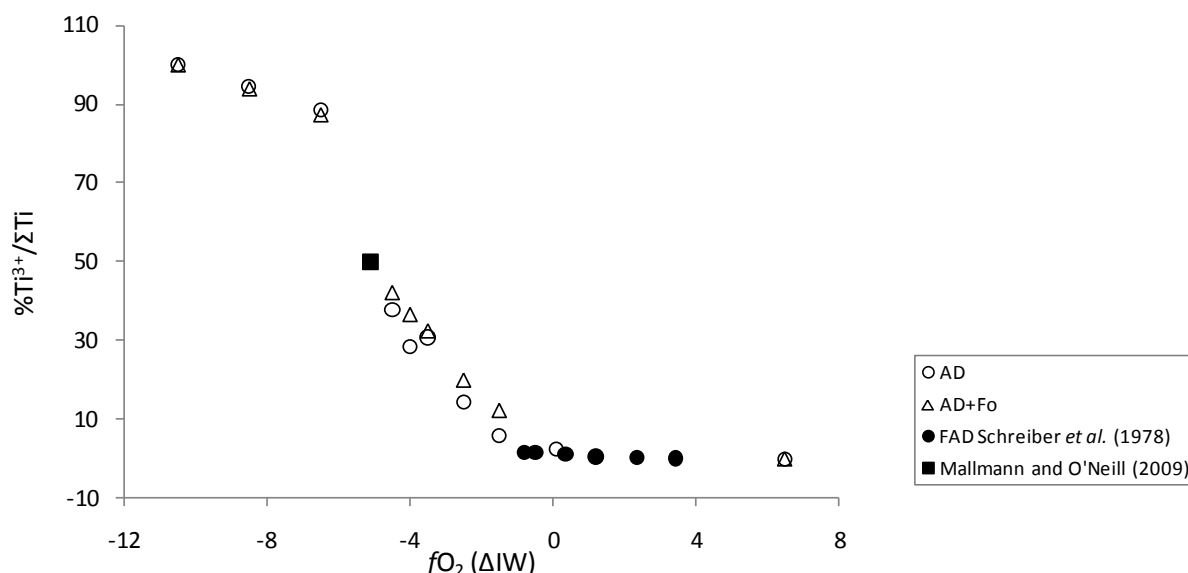


Figure 6-13 Calculated $\%Ti^{3+}/\Sigma Ti$ for the AD and AD+Fo compositions compared to literature values.

6.4.2.3 Compositional dependence of $Ti^{3+}/\Sigma Ti$

The ratio of redox variable elements at equivalent fO_2 s have been shown to be compositionally dependant, with $\log K'$ being a composition-dependant variable (Berry *et al.*, 2006). Within the glass compositions investigated, the $\log K'$ value of AD was higher than that of the other four glass compositions, which were near constant (Table 6-6). The fO_2 dependence of redox variable elements may be represented by a plot of $-\log fO_2$ vs. $\log(M^n/M^{n+1})$, with a slope of four expected for a one-electron reaction (Schreiber *et al.*, 1978). As shown in Figure 6-14 and detailed in Table 6-8, the samples prepared at $\geq IW$ -4.5 have a slope close to four. The graphite mounted samples are displaced from these trends, and for reasons already discussed will not be included in the discussion below.

In Figure 6-14 the data for the Ti-CAMS glasses are plotted along with the two Ti-CMAS compositions investigated by Schreiber (FAS and FAD). The calculated optical basicity of FAD is equivalent to that of AD and AD+Fo (0.60), and that of FAS (0.57) is close to that of AD+Qtz (0.55). The FAD and FAS data continue the trends defined by the AD, AD+Fo and AD+Qtz sample sets, with a similar amount of scatter in the data, and the E_M^* values of the two datasets were found to be similar. In particular, this composition-dependant variable was within error for the AD+Qtz and FAS compositions (Table 6-8). The E_M^* for the AD and AD+Fo compositions differed from that of FAD.

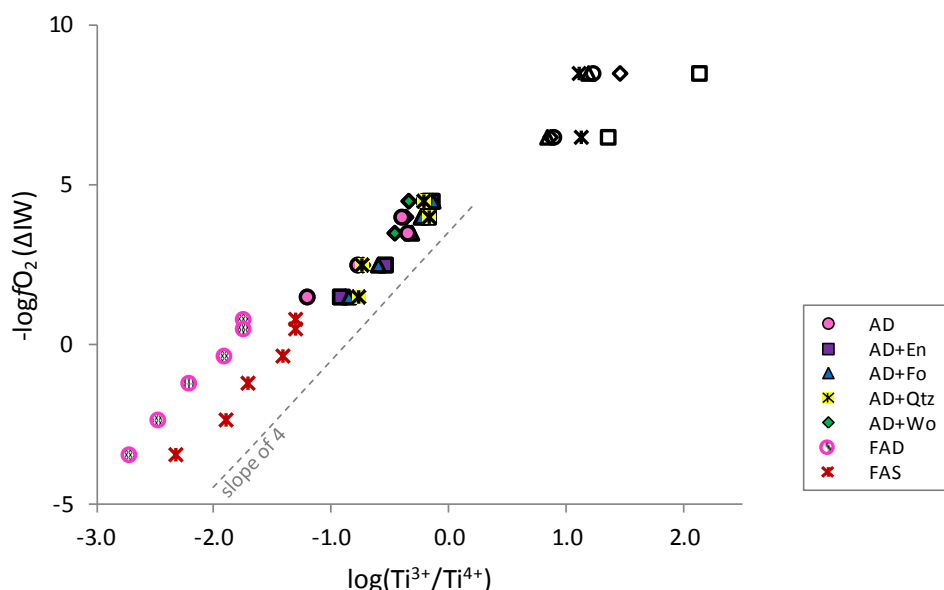


Figure 6-14 $-\log fO_2$ as a function of $\log(Ti^{3+}/Ti^{4+})$ showing the data from this study along with the FAS and FAD compositions of Schreiber *et al.* (1978). A line with a slope of 4 is shown (offset from the data for clarity). Glasses prepared in graphite shown in unfilled symbols (using the same symbol shape as the respective datasets).

Table 6-8 Fit parameters for $-\log fO_2 = m \times \log(Ti^{3+}/Ti^{4+}) - E^*_M$, fitting the data shown in Figure 6-14

Composition	Slope (m)	Linear fit	
		E^*_M	R^2
FAD (Schreiber <i>et al.</i> , 1978)	4	-16.7 (0.4)	-
FAS (Schreiber <i>et al.</i> , 1978)	4	-14.7 (0.5)	-
AD*	3.2 (0.3)	-14.5 (0.3)	0.98
AD+En	3.7 (1.0)	-14.3 (0.6)	0.97
AD+Fo	4.1 (0.3)	-14.5 (0.2)	0.99
AD+Qtz	4.0 (2.7)	-14.5 (1.2)	0.89
AD+Wo	5.0 (0.7)	-15.5 (0.4)	0.98

Note: Fit to data from ΔIW -1.5 to ΔIW -4.5 (1 σ error in parentheses).

A compositional difference was reported in FAS and FAD glass samples with 1.3 wt% TiO_2 (Schreiber *et al.*, 1978) and in $CaO-SiO_2-TiO_x$ glasses with 7.2 to 52.3 wt % TiO_2 (Tranell *et al.*, 2002). The clear compositional difference between the FAD and FAS compositions of Schreiber *et al.* (1978) is defined by glasses with $<5\% Ti^{3+}/\Sigma Ti$. Furthermore, the compositional difference reported by Tranell *et al.* (2002) was reported in Ti-rich glasses that contained up to 40% $Ti^{3+}/\Sigma Ti$. In the current study few glasses were prepared over this range as the goal was to produce a complete 0-100% $Ti^{3+}/\Sigma Ti$ Ti-CMAS glass series. The data in the $<50\% Ti^{3+}/\Sigma Ti$ region was therefore more sparse than the studies by Schreiber *et al.* (1978) and Tranell *et al.* (2002).

A CMAS glass series with 0-100% Cr^{2+} was investigated by Berry and O'Neill (2004) and Berry *et al.* (2006), and a strong composition-dependence of Cr^{2+}/Cr^{3+} as a function of fO_2 was reported. The data are presented in Figure 6-15 using the Schreiber *et al.* (1978) plot. Under more reducing conditions ($<\Delta IW$ +1.5) where the Cr^{2+} content increases above 50% the scatter in data becomes greater. The compositionally dependant trend-lines are therefore defined by the samples produced

under more oxidising conditions, as was suggested for the compositional dependence of $\text{Ti}^{3+}/\text{Ti}^{4+}$ as a function of $f\text{O}_2$ reported by Schreiber *et al.* (1978) and Tranell *et al.* (2002).

A compositional dependence of $\text{Ti}^{3+}/\text{Ti}^{4+}$ in the compositions in this study may therefore be proved if a greater number of samples with $<50\%$ $\text{Ti}^{3+}/\Sigma\text{Ti}$ were produced and analysed.

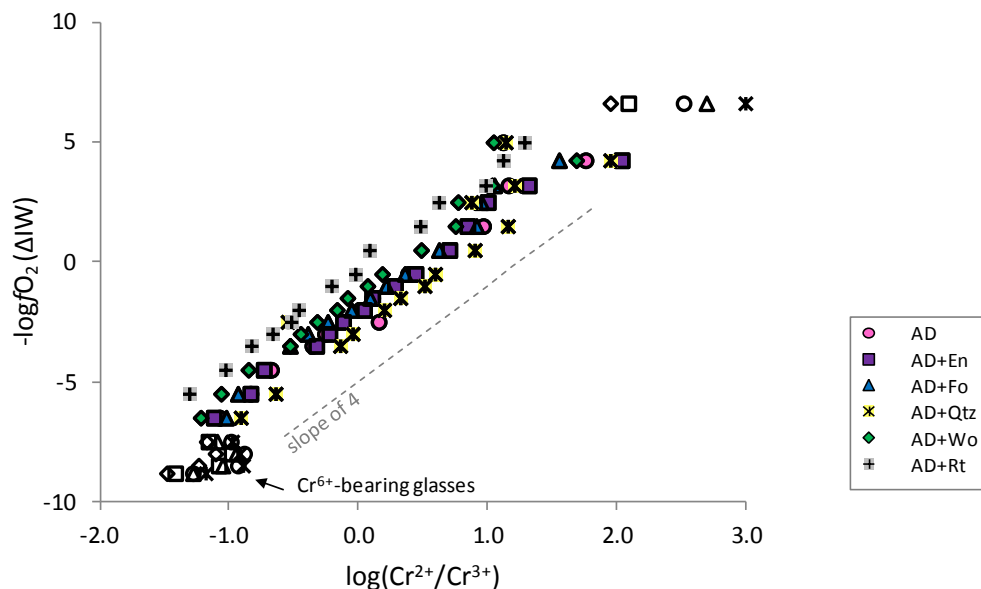


Figure 6-15 $-\log f\text{O}_2$ (in ΔIW) as a function of $\log(\text{Cr}^{2+}/\text{Cr}^{3+})$ for the Berry and O'Neill (2004) CMAS glass dataset. A line with a slope of 4 is shown (offset from the data for clarity). Cr^{6+} -bearing glasses and glasses prepared in graphite shown in unfilled symbols (using the same symbol shape as the respective datasets).

6.4.3 Ti-bearing synthetic hibonite

6.4.3.1 Spectral characterisation

The Ti K-edge XANES spectra collected from the synthetic hibonite series samples are shown in Figure 6-16. Three features are evident in the pre-edge peak (a_1 , a_2 , a_3), three on the shoulder (b_1 , b_2 , b_3) and four in the post-crest region (d_1 , d_2 , d_3 , d_4).

Up to 10 spectra were collected from random points on each sample such that the spectra are representative of hibonite crystals in different orientations. As shown in Figure 6-16, the four peaks in the post-crest region (d_1 - d_4) are particularly distinct in the Ti^{4+} -bearing hibonites (Hib9(44,43) and HibE(98,91)), and the ratio of the d_3 peak intensity and the intensity of the m_3 minimum varies (e.g. Figure 6-17), suggesting a spectral dependence on crystal orientation. The equivalent features in the post-crest region of the Ti^{3+} hibonite (HibF(20,0)) do not vary to the same degree. The Ti substitution mechanism differs between Ti^{3+} and Ti^{4+} , with Ti^{3+} occupying the M4 octahedral site which occurs in face-sharing pairs, whereas Ti^{4+} partitions between the M4 site and the trigonal bipyramidal M2 site, the three-fold axis of which is orientated parallel to the c-axis (Figure 6-18). In a trigonal bipyramidal site the z-axis of the d_{z^2} orbital is predicted to lie parallel to the crystallographic c-axis, and the d_{xz} and d_{yz} orbitals are preferentially stabilised relative to the d_{xy} and $d_{x^2-y^2}$ orbitals (Burns and Burns, 1984).

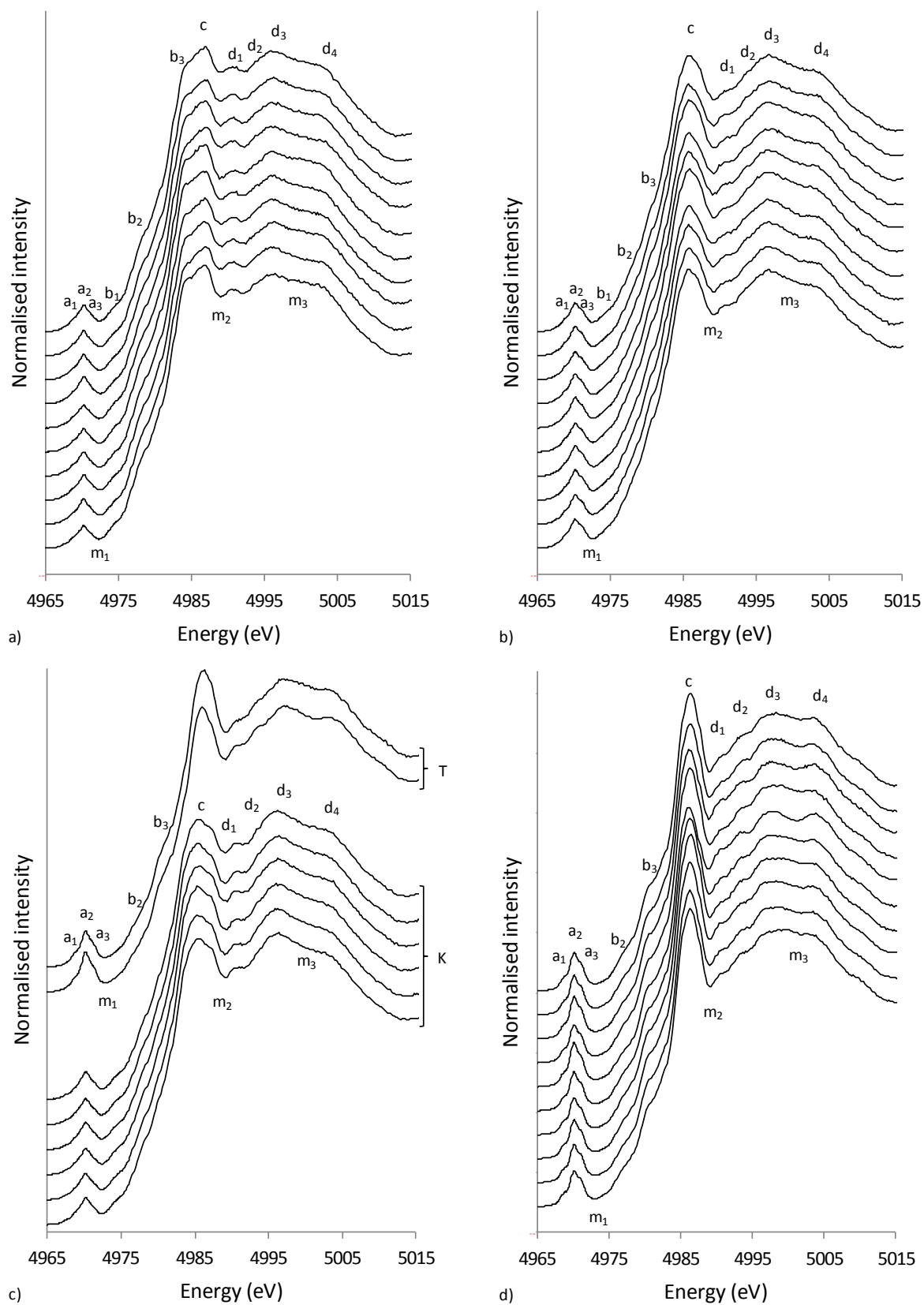
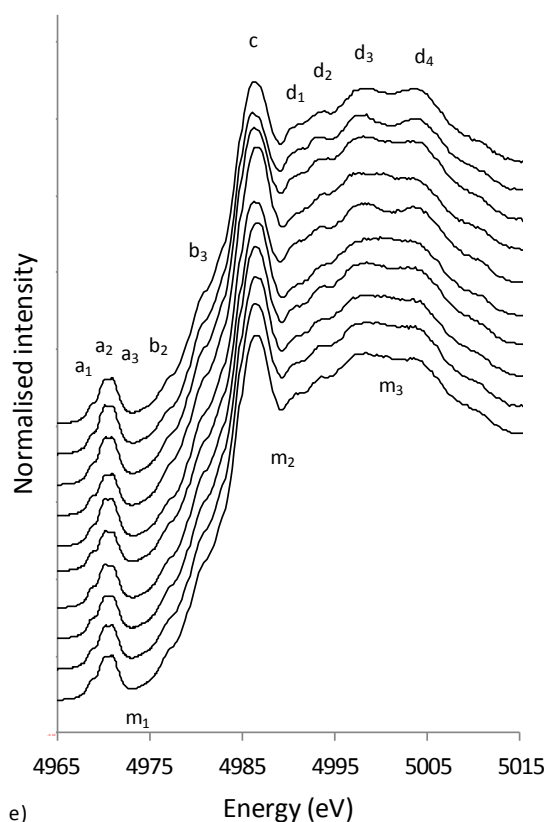


Figure 6-16 caption on following page.



e) Figure 6-16 Ti K-edge XANES spectra collected from different points within (a) the Ti^{3+} hibonite HibF(20,0), (b) the mixed-valent hibonite Hib8C(73,49), (c) the mixed-valent hibonites HibK(62,24) and HibT(137,83), (d) Ti^{4+} hibonite Hib9(44,43), (e) Ti^{4+} hibonite HibE(98,91). The main features are marked, including those in the pre-edge region (a_1 , a_2 , a_3), shoulder (b_1 , b_2 , b_3), crest (c) and post-crest region (d_1 , d_2 , d_3 , d_4).

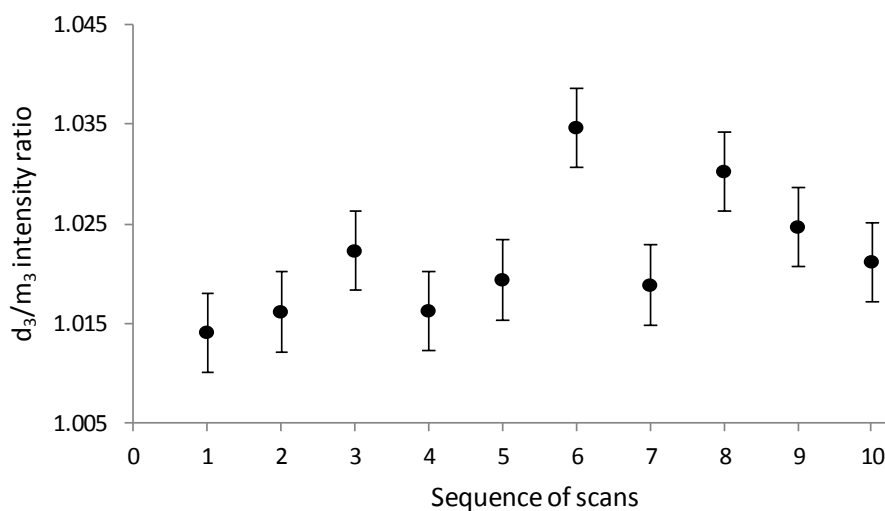


Figure 6-17 The d_3/m_3 intensity ratio as a function of the sequence of scans made for the Ti^{4+} hibonite Hib9(44,43). See Figure 6-16d, and Appendix E.4.2 for the tabulated data.

Electronic transitions involving the M2 site may therefore be expected to be made with d -orbitals orientated sub-parallel or parallel to the c -axis. Interaction of a polarised X-ray beam with Ti^{4+} on the M2 site would therefore account for the variation in the post-crest region of the Ti^{4+} -bearing hibonite spectra. The lack of obvious orientation effects in the Ti^{3+} hibonite may, in part, be due to the

dampening of any such signal by position of Ti in M4 sites which are a mirror image across the O3 layers.

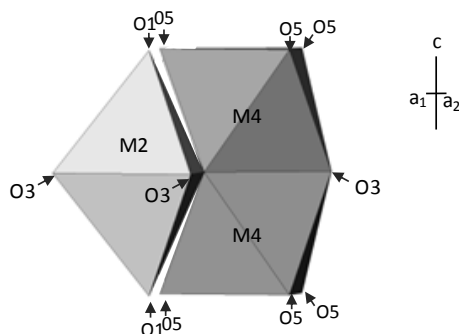


Figure 6-18 Section of the hibonite structure showing an M2 site and two M4 sites. The M2-O1 bonds are parallel to the c-axis and the M2 atom is displaced from the O3 equatorial plane, whereas the M4 octahedra share a face in the ab plane across the O3 oxygen layer.

Interestingly, little dependence on orientation is observed within the pre-edge feature of the Ti^{3+} and Ti^{4+} hibonites, as shown in Figure 6-19. The energy of the a_2 and m_1 spectral features vary by ≤ 0.1 eV for the 10 spectra collected from each sample, and the intensity of the a_2 feature varies by ± 0.01 , which is $\leq 6.4\%$ deviation on the average intensity. Despite hibonite being an anisotropic mineral, the deviation in pre-edge peak intensity is smaller than the 10% reported for the pre-edge peak intensity of V K-edge XANES spectra collected from the isotropic mineral spinel (Richter *et al.*, 2006). Variation in pre-edge peak intensities on this order therefore appears to be inherent with the measurement of XANES spectra under the experimental conditions used.

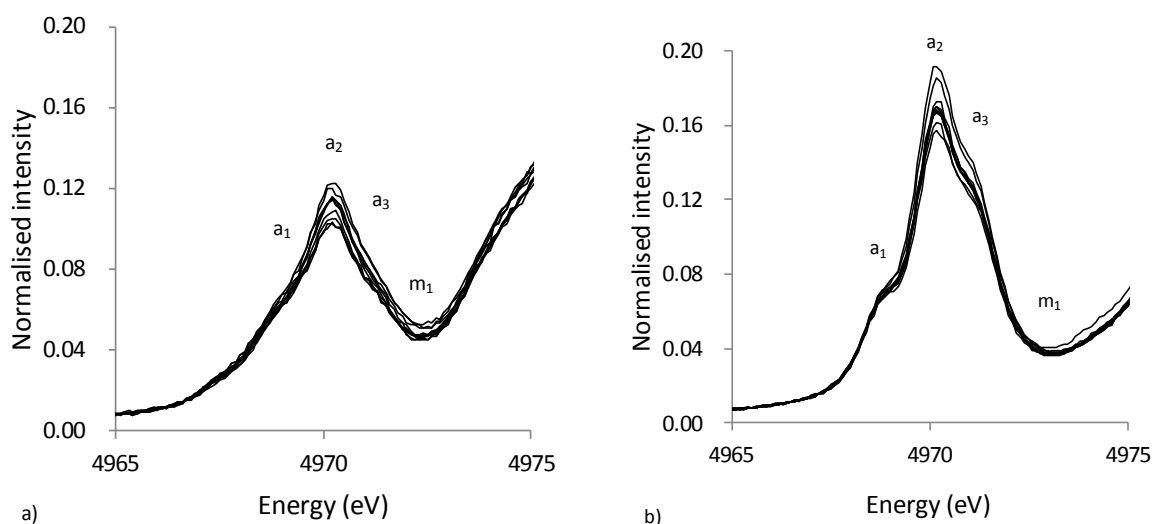


Figure 6-19 Ten Ti K-edge XANES spectra collected from (a) the Ti^{3+} hibonite HibF(20,0) and (b) the Ti^{4+} hibonite Hib9(44,43) are overlain, showing little variation in the pre-edge peak intensity with different orientation.

Ti K-edge XANES spectra collected from silicates and oxides have up to three features in the post-crest region (Waychunas, 1987). The additional, fourth peak in the post-crest region of the Ti K-

edge XANES spectra may be attributed to Ti occurring in two coordination states, particularly as the d_3 and m_3 features appear to be controlled by Ti on the M2 site.

Crystal chemical influences on the spectra are also observed in the post crest minimum (m_2). This feature varies as a function of Ti^{4+} refined onto the M2 site relative to the Ti pfu (Figure 6-20), which is a combination of Ti^{4+} on the M2 site and either Ti^{3+} or Ti^{4+} present on the connected M4 site. The post-crest region is a result of resonance between next-to-nearest neighbours (Farges *et al.*, 1996a), which would account for the variation observed when the proportion of Ti^{4+} increases on the M2 site relative to the abundance of Ti on the adjacent M4 site (Figure 6-15).

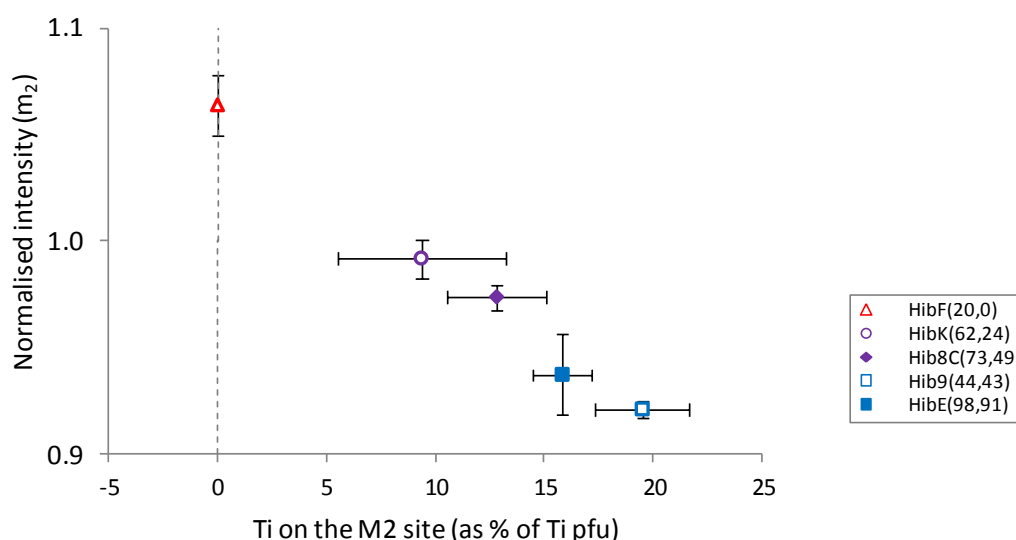


Figure 6-20 The normalised intensity of the m_2 feature in the post-crest region as a function of the refined Ti^{4+} on the M2 site as a function of Ti pfu.

Features in the pre-edge vary as a function of $Ti^{3+}/\Sigma Ti$, as defined using stoichiometry. In particular, the intensity of all three features in the pre-edge peak decrease with greater $Ti^{3+}/\Sigma Ti$, and the minimum between the pre-edge feature and the edge (m_1) shifts to lower energy. Interestingly, the pre-edge peak lineshape of the two Ti^{4+} hibonites (Hib9(44,43) and HibE(98,91)) differs, particularly that of the a_3 peak intensity. In contrast, the peak profile of the two Ti^{3+} hibonites (HibF(20,0) and Hib5D(33,0)) is similar (*cf* Figures 6-21 and 6-22).

These differences between the two Ti^{4+} hibonites are apparent in the fit components of the pre-edge feature (Figure 6-23). The fit was made such that peak widths were constant within a sample and across the sample series, resulting in an empirical fit of four peaks with a purely Lorentzian lineshape and a full width half maximum of 1.64 eV. Interestingly, this peak width is equivalent to that independently modelled for the Ti-CMAS glasses, but is larger than the energy resolution of the beamline (1.2 eV).

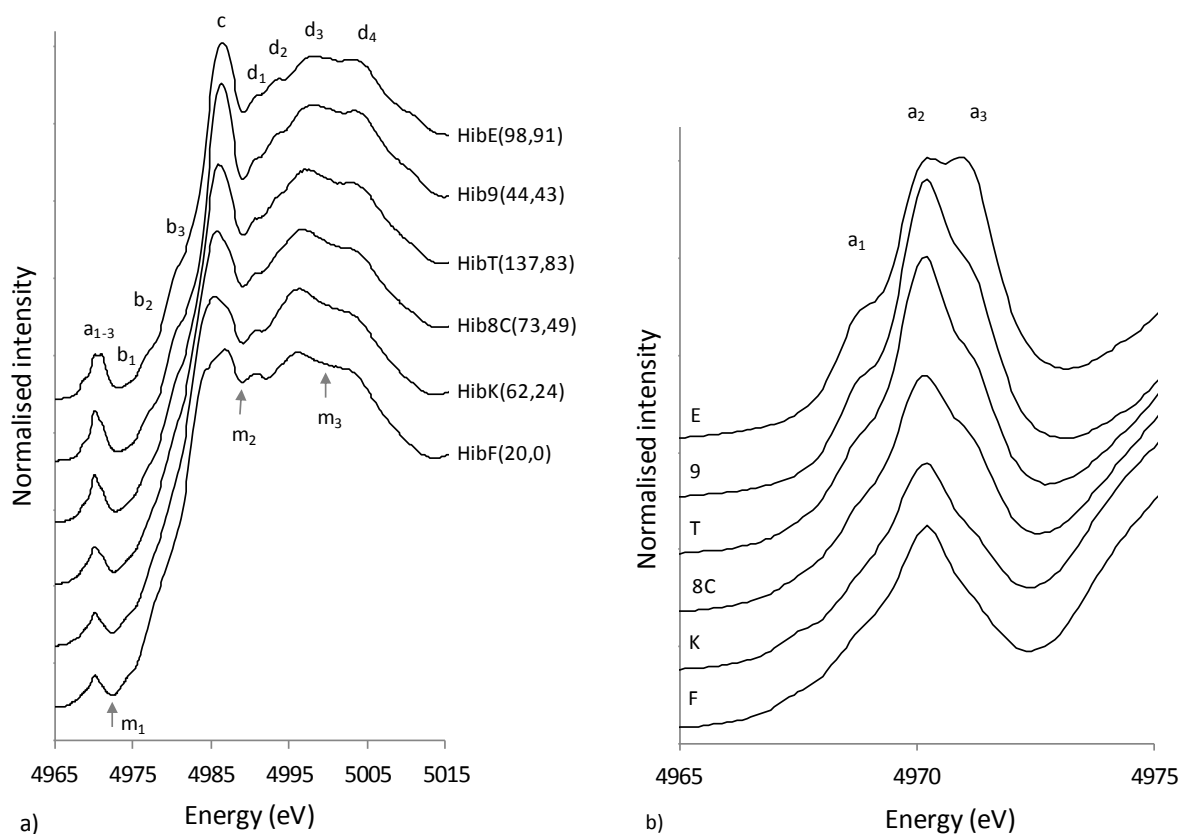


Figure 6-21 (a) Ti K-edge XANES spectra and (b) the pre-edge region collected from a synthetic hibonite series showing the main peaks in the pre-edge (a_1 , a_2 , a_3), on the shoulder (b_1 , b_2 , b_3), the crest (c) and the post-crest region (d_1 , d_2 , d_3 , d_4) and characteristic minima (m_1 , m_2 , m_3). HibF(20,0) is a Ti^{3+} hibonite, Hib9(44,43) and HibE(98,91) are Ti^{4+} hibonites and the remaining samples are mixed-valent hibonites.

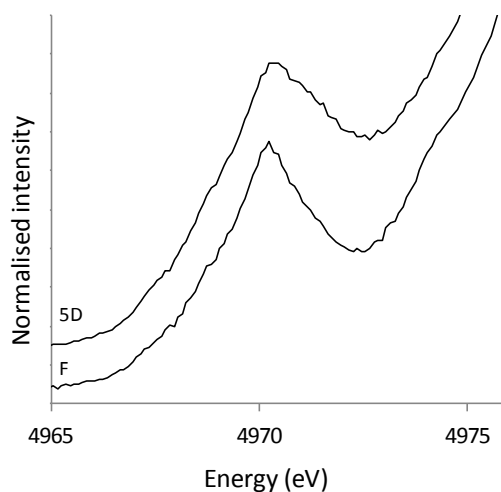


Figure 6-22 The Ti K-edge XANES pre-edge region for the two Ti^{3+} synthetic hibonite end-members (HibF(20,0) and Hib5D(33,0)). Offset for clarity (collected from powder pellets using a diffuse beam).

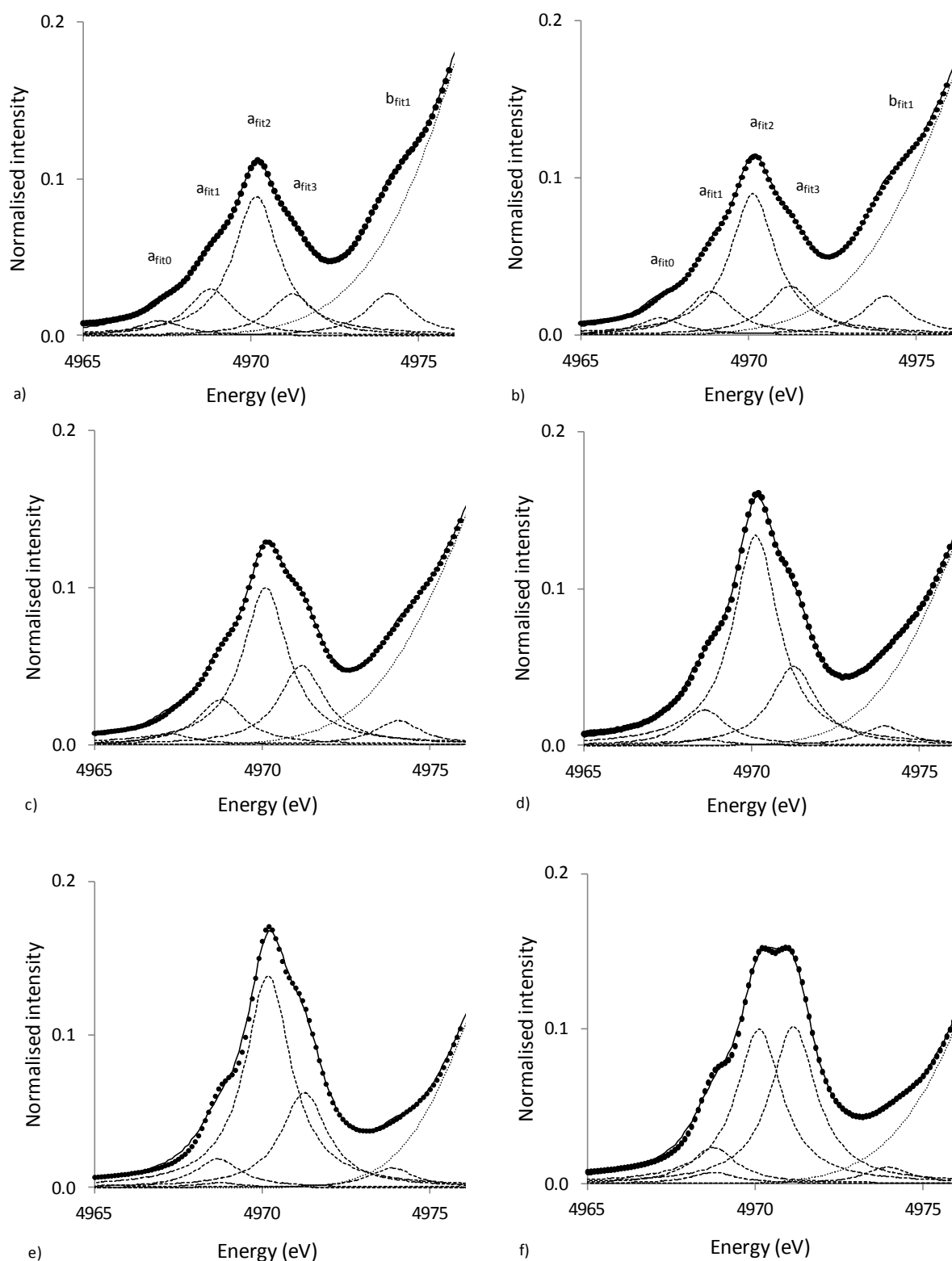


Figure 6-23 The Ti K-edge XANES pre-edge region collected from synthetic hibanite (dots) are modelled with components (dashed lines) for (a) the Ti^{3+} hibanite HibF(20,0); and the mixed-valent hibanites (b) HibK(62,24), (c) Hib8C(73,49) and (d) HibT(137,83); and the Ti^{4+} hibanites (e) Hib9(44,43) and HibE(98,91). The modelled background (thin dotted grey line) and the cumulative fit are shown (solid black line).

The neutron powder diffraction study showed that increasing Ti pfu caused the bond-lengths of the Ti-bearing sites to vary systematically. Differences between the pre-edge features of the Ti^{4+} hibonites Hib9(44,43) and HibE(98,91) may be explained by distortion of the Ti-bearing sites M2 and M4. The M2 atom is axially displaced further from the equatorial plane with increasing Ti pfu, and the displacement of the M2 atom is roughly correlated with the a_3 pre-edge peak intensity of the hibonites with <1 Ti pfu (Figure 6-24a). Similarly, the ratio of the a_2/a_3 peak intensities is negatively correlated with a ratio of the M4-O3/M4-O5 bond lengths, which is a measure of distortion of the M4 site (Figure 6-24b). Significantly, the distortion of the Ti-bearing sites (M2 and M4) differs for the two Ti^{4+} hibonites, whereas the bond-lengths of the M4 site of the Ti^{3+} hibonites HibF(20,0) and Hib5D(33,0) were equal (Section 5.4.4.1), thereby accounting for the similar pre-edge profiles of the Ti^{3+} hibonites (Figure 6-22).

A Ti K-edge XANES study of silicates reported a positive linear correlation between site distortion and the a_2 pre-edge peak intensity, but no such correlation for the oxide minerals in that study (Waychunas, 1987). This study shows that systematic distortion of the two Ti-bearing sites within a single-oxide series does result in systematic variation within the pre-edge parameters a_2 and a_3 .

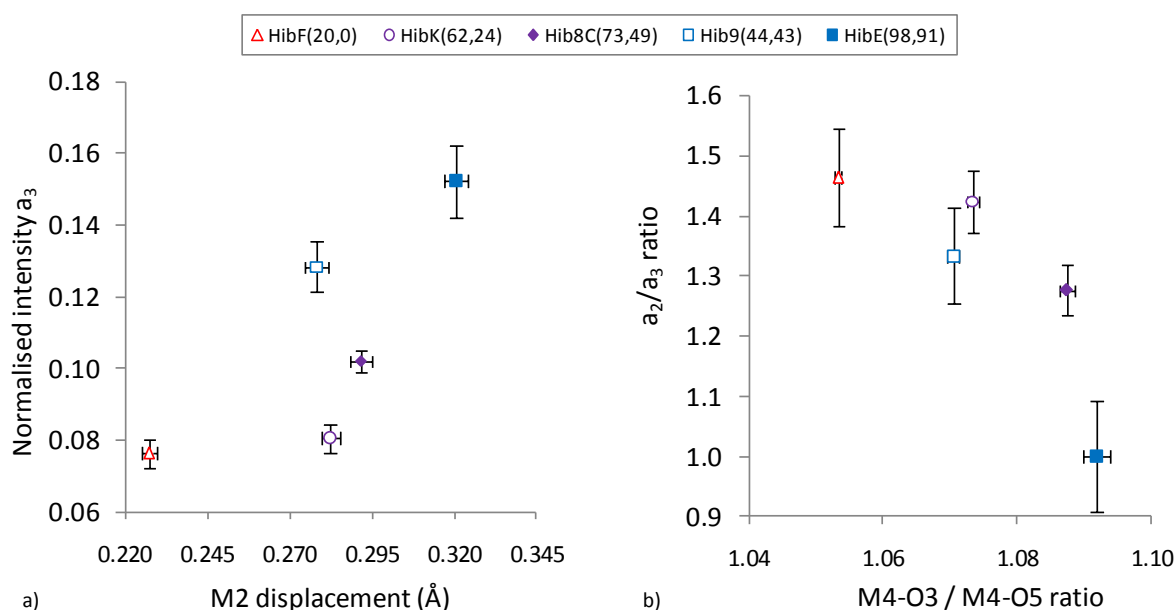


Figure 6-24 Pre-edge peak features as a function of structural parameters with (a) normalised intensity of the a_3 pre-edge peak as a function of the M2 atom displacement from the O3 equatorial plane, and (b) the ratio of the a_2/a_3 pre-edge peak intensities as a function of M4-O3/M4-O5, a measure of distortion of the M4 site.

The Ti-bearing M2 site is 5-fold coordinated, whereas the M4 site is 6-fold coordinated, as shown in the structural refinement of neutron powder diffraction data (Section 5.4.3). The Ti^{4+} hibonite pre-edge peak parameters, however, plot within the 4-, 5- and 6- fold coordination region defined by Farges *et al.* (1996a), as shown in Figure 6-25a. This plot is a classification tool sufficiently sensitive to determine Ti^{4+} in more than one coordination state in glasses (e.g. Farges and Brown, 1997), but has only been applied to Ti^{4+} in a single coordination states in crystals. The hibonite data from this study

suggests that the classification tool may not be suitable for crystalline material with Ti^{4+} in more than one coordination state.

Ti^{3+} in the Ti^{3+} hibonites occurs in the M4 octahedral site. The pre-edge peak parameters of the Ti^{3+} hibonite plot at lower energy and lower intensity than the Ti^{4+} hibonites (Figure 6-25b), which may be expected due to the change in oxidation state and no Ti in five-fold coordination.

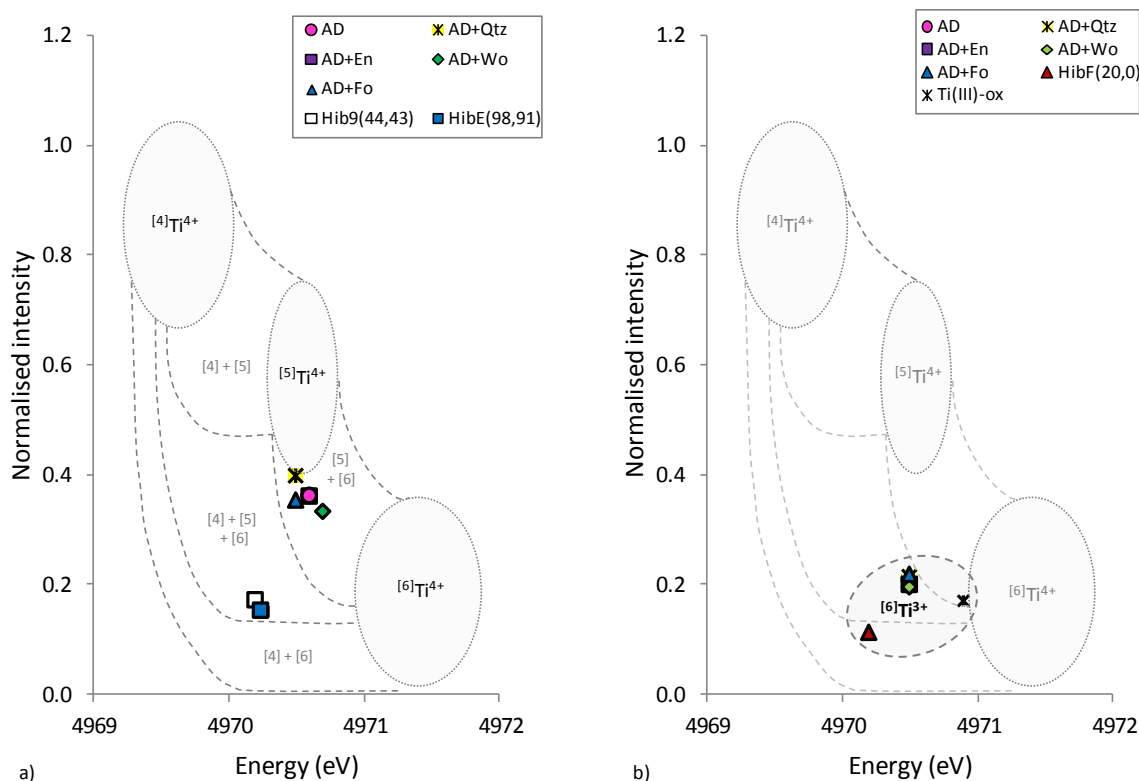


Figure 6-25 The pre-edge feature intensity and energy after Farges *et al.* (1996a) for (a) the Ti^{4+} glass end-members and the Ti^{4+} synthetic hibonite end-members; (b) the Ti^{3+} glass end-members and the Ti^{3+} synthetic hibonite end-members and Ti_2O_3 , which define a $[\text{Ti}^{3+}]$ region. Regions in grey are as described in Figure 6-3.

Fluorescence is normally collected from samples in which the target atom is dilute, having <2% element of interest, the matrix absorption is high or the sample is small (Brown *et al.*, 1988). In this study the sample mounting of the sintered pellets and the meteoritic grain mounts precluded recording absorption spectra. In samples with high abundance of the target atom, self absorption may modify spectral lineshapes, causing features to be dampened due to the reduction in fluorescence collected. This process, however, may be expected to affect the crest region more than the features in the pre-edge region.

There is no evidence for self absorption within the synthetic hibonite sample suite, despite the mixed-valent sample HibT(137,83) having up to 15.9 wt% TiO_2 . As shown in Figure 6-26, similar lineshapes were observed for spectra collected from hibonite samples mounted as sintered pellets and analysed by the microfocus beam (MF) and powder pellets analysed using a diffuse beam (DF) on both powder pellets, and BN diluted powders (+BN) such that the Ti content was 1 mol% Ti.

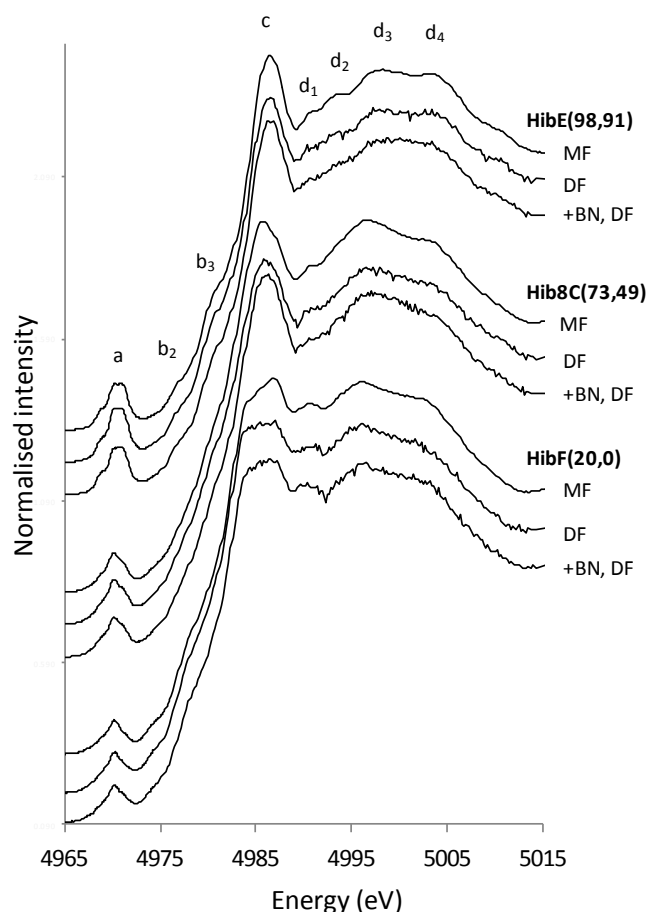


Figure 6-26 Ti K-edge XANES spectra collected from three hibonite samples which represent the TiO_2 range of the sample series with <1 Ti pfu: HibF(20,0) contains 2.4 wt% TiO_2 , Hib8C(73,49) contains 8.7 wt% TiO_2 , and HibE(98,91) contains 11.4 wt% TiO_2 . Only the main peaks are labelled. Samples mounted, and spectra collected as follows: MF = Sintered pellet, microfocus beam; DF = powder pellet, diffuse beam; +BN, DF = powder pellet diluted in BN, diffuse beam.

Furthermore, as shown in Figure 6-27, the crest height of the Ti^{3+} hibonite sample HibF(20,0) is within error of that of the Ti-rich Ti^{4+} hibonite HibE(98,91) and the mixed-valent samples Hib8C(73,49) and HibT(137,83), both of which are within error of the mixed-valent sample HibK(62,24). The crest height of the Ti-poor Ti^{4+} hibonite Hib9(44,43) is more intense than those of the other hibonites, but as crest height is related to order surrounding the target atom (Farges *et al.*, 1996a), it is possible that the intense crest of Hib9(44,43) reflects greater order within this sample as Ti^{4+} occupies two adjacent sites within the Ti^{4+} -bearing samples, and ordering may be induced such that the displacement of Ti^{4+} on the M2 site is diagonally opposite Ti^{4+} on the adjacent M4 site (Figure 6-18). A similar process would be occurring in the other Ti^{4+} -bearing hibonites, but as these hibonites have more Ti pfu than Hib9(44,43) the distortion of those Ti sites would be greater, decreasing the periodicity of the structure. Thus differences between the structures of the hibonites would account for the variation in crest height observed.

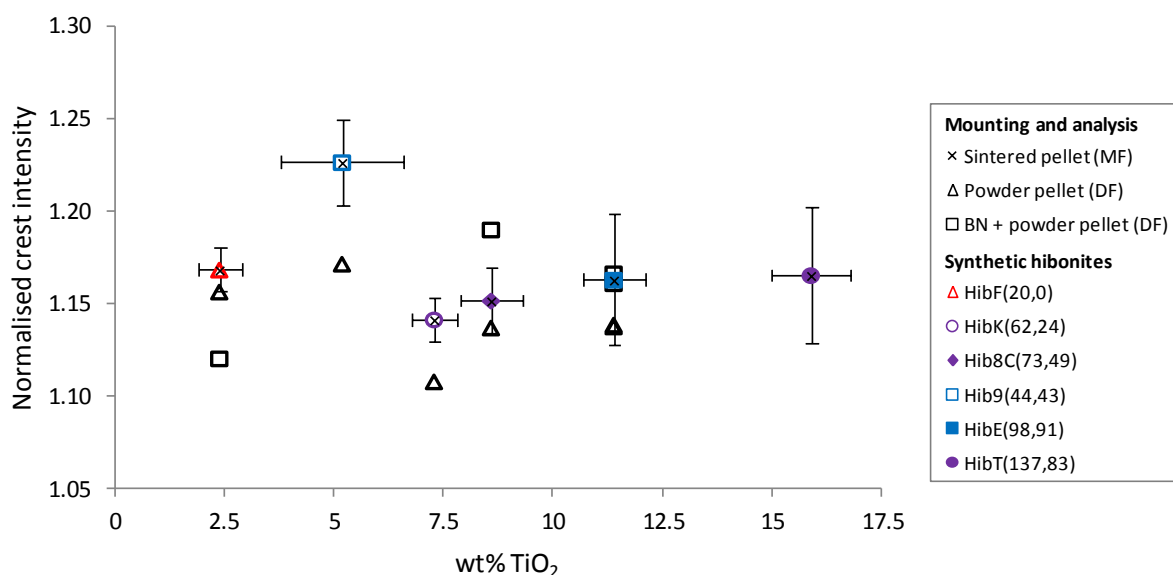


Figure 6-27 The normalised crest height for synthetic hibonite mounted as sintered pellets and analysed using the micro-focus beam (MF), compared with synthetic powder pellets analysed with a diffuse beam (DF) and synthetic hibonite in a BN powder pellet analysed with a diffuse beam (+BN, DF). The crest intensity error shown for the MF samples is the standard deviation of 10 analyses. Colour symbols shown for the MF samples. The spectral parameters are detailed in Appendix E.4.3.

6.4.3.2 Quantitative determination of $\text{Ti}^{3+}/\Sigma\text{Ti}$

Features that varied with $\text{Ti}^{3+}/\Sigma\text{Ti}$ as determined by stoichiometry were investigated, including the intensity and energy of the pre-edge peak (a_2), the minimum between the pre-edge features and the edge (m_1), the energy of the edge when the normalised intensity equalled 0.8 ($E_{0.8}$), the crest (c) and features in the post crest region. The positions of most features were determined using the first derivative of the Ti K-edge XANES spectrum (Figure 6-28), whereas a visual inspection of the spectrum was used to determine the parameters of the pre-edge features a_1 and a_3 , and features in the post-crest region (d_1 , d_2 , d_3 , d_4 , m_2 , m_3). The edge energy when the intensity was 0.8 ($E_{0.8}$) was calculated using a linear extrapolation between the recorded value on either side of 0.8 intensity. A summary of the spectral parameters are shown in Table 6-9, and Appendix E.4.3 details an extended list of spectral parameters for the individual spectra collected.

Table 6-9 Ti K-edge XANES spectral parameters for synthetic hibonite from the pre-edge feature (a_2), minima (m_1), the edge energy when normalised intensity = 0.8 ($E_{0.8}$) and crest (c) showing intensity (I) and energy (E , eV)

Parameter	a_2 (I)	a_2 (E , eV)	Em_1 (E , eV)	$E_{0.8}$ (E , eV)	c (I)	c (E , eV)
HibF(20,0)	0.112 (0.007)	4,970.20 (0.05)	4,972.30 (0.08)	4,982.22 (0.04)	1.2 (0.01)	4986.7 (0.1)
HibK(62,24)	0.115 (0.002)	4,970.21 (0.08)	4,972.40 (0.08)	4,982.36 (0.03)	1.1 (0.01)	4985.3 (0.1)
Hib8C(73,49)	0.130 (0.004)	4,970.16 (0.05)	4,972.60 (0.07)	4,982.90 (0.06)	1.2 (0.02)	4985.7 (0.1)
Hib9(44,43)	0.171 (0.010)	4,970.20 (0.00)	4,973.20 (0.12)	4,984.18 (0.03)	1.2 (0.02)	4986.3 (0.1)
HibE(98,91)	0.152 (0.010)	4,970.24 (0.05)	4,973.20 (0.04)	4,984.16 (0.07)	1.2 (0.04)	4986.5 (0.1)
HibT(137,83)	0.161 (0.011)	4,970.15 (0.07)	4,972.70 (0.14)	4,983.52 (0.07)	1.2 (0.04)	4985.9 (0.1)

Note: Standard deviation in parentheses. Number of analyses: 10 for the Ti^{3+} and Ti^{4+} hibonites and the mixed-valent hibonite Hib8C(73,49), 6 for the mixed-valent hibonite HibK(62,24) and 2 for the mixed-valent hibonite HibT(137,83)

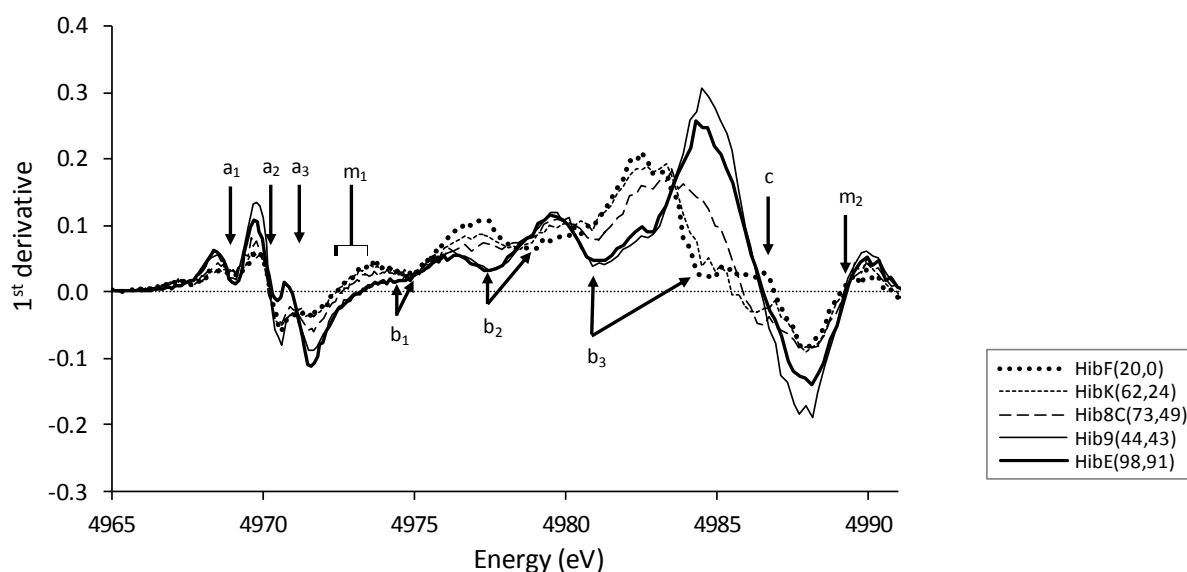


Figure 6-28 The first derivatives of the Ti K-edge XANES spectra collected from a suite of synthetic hibonites with <1 Ti pfu showing a Ti^{3+} hibonite (HibF(20,0)), two Ti^{4+} hibonites (Hib9(44,43) and HibE(98,91)) and mixed-valent hibonites (Hib8C(73,49) and HibK(62,24)). Shown are the pre-edge features (a_1 , a_2 , a_3), minima (m_1 , m_2) and crest (c).

Spectral parameters that varied as a function of $\text{Ti}^{3+}/\Sigma\text{Ti}$ but that also appeared to be strongly controlled by site distortion, such as peaks a_2 and a_3 , were excluded from further analysis. The energy of the minimum between the pre-edge feature and the edge (E_{m1}) and the edge energy ($E_{0.8}$) appeared to be promising oxybarometers (Figure 6-29). The three features on the edge add complexity to its interpretation, whereas the energy of the E_{m1} feature is primarily controlled by the intensity of the b_1 feature according to the empirical modelling of the pre-edge peak region (Figure 6-23), and to a lesser extent by contributions from the a_2 and a_3 peaks and the edge. Furthermore, the position of the E_{m1} feature may be accurately determined using the first derivative of a fluorescence spectrum (Figure 6-28), and a shift in the E_{m1} feature with $\text{Ti}^{3+}/\Sigma\text{Ti}$ can be modelled by the linear mixing of a Ti^{3+} and a Ti^{4+} hibonite spectrum (Figure 6-30).

The E_{m1} parameter as a function of $\text{Ti}^{3+}/\Sigma\text{Ti}$ was fitted with an inverse quadratic (Figure 6-29), resulting in Equation 6-6. The difference between the calculated $\text{Ti}^{3+}/\Sigma\text{Ti}$ and that determined by stoichiometry was less than 4%.

$$y = x / (a + bx + cx^2) + d$$

Equation 6-6

Where:

$$\begin{aligned} a &= -406390 \\ b &= 0.364 \\ c &= 0.0164 \\ d &= -26.1 \end{aligned}$$

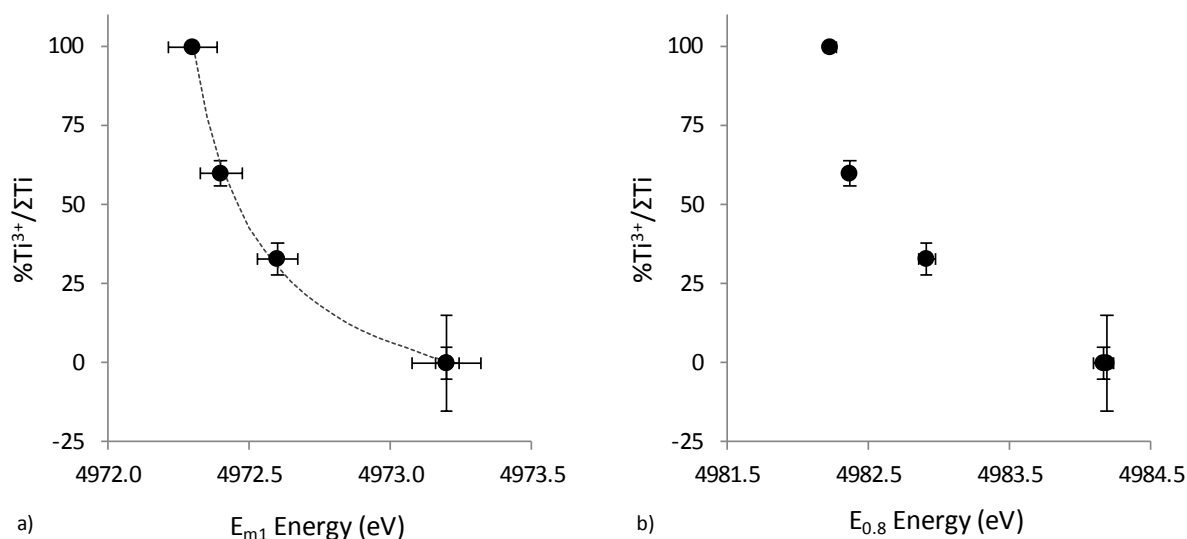


Figure 6-29 $\% \text{Ti}^{3+} / \Sigma \text{Ti}$ as determined by stoichiometry as a function of (a) $E_{0.8}$ and (b) E_{m1} , with E_{m1} fitted with an inverse quadratic.

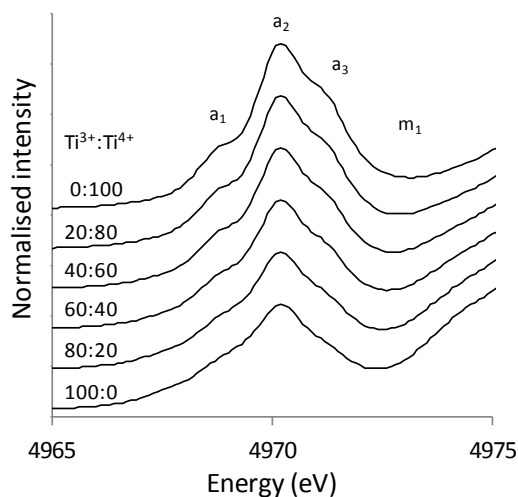


Figure 6-30 Modelled Ti K-edge XANES spectra based on the linear mixing of a Ti^{3+} hibonite (HibF(20,0)) and a Ti^{4+} hibonite (Hib9(44,43))

The curvature of the $\text{Ti}^{3+}/\text{Ti}^{4+}$ K-edge oxybarometer may be related to the unequal weighting of the spectral parameters of one end-member over another, crystal chemical controls or Ti content. For example, the $^{[5]}\text{Ti}^{4+}$ - $^{[6]}\text{Ti}^{4+}$ mixing line defined by Farges *et al.* (1996a) and shown in Figure 6-7 is curved, possibly due to the greater weighting of the intense pre-edge peak of $^{[5]}\text{Ti}^{4+}$ compared to that of $^{[6]}\text{Ti}^{4+}$. Alternatively, the structural influence of Ti^{4+} partitioning between two sites of different coordination ($^{[5]}\text{M2}$ and $^{[6]}\text{M4}$) relative to the total Ti in hibonite (Figure 6-20) may impose a strong influence on the spectral structure. Variation in Ti content between the two end-member spectra may also account for the curvature, particularly as the spectra collected from the mixed-valent hibonites with <1 Ti pfu could be modelled with a mixing of the Ti^{3+} and Ti^{4+} hibonite spectra in proportions defined by a mixing line of 0.2 Ti^{3+} pfu with 1 Ti^{4+} pfu, using 71% Ti^{3+} :29% Ti^{4+} for Hib8C(73,49) and 89% Ti^{3+} :11% Ti^{4+} for HibK(62,24). The results of the latter model are shown in Figure 6-31.

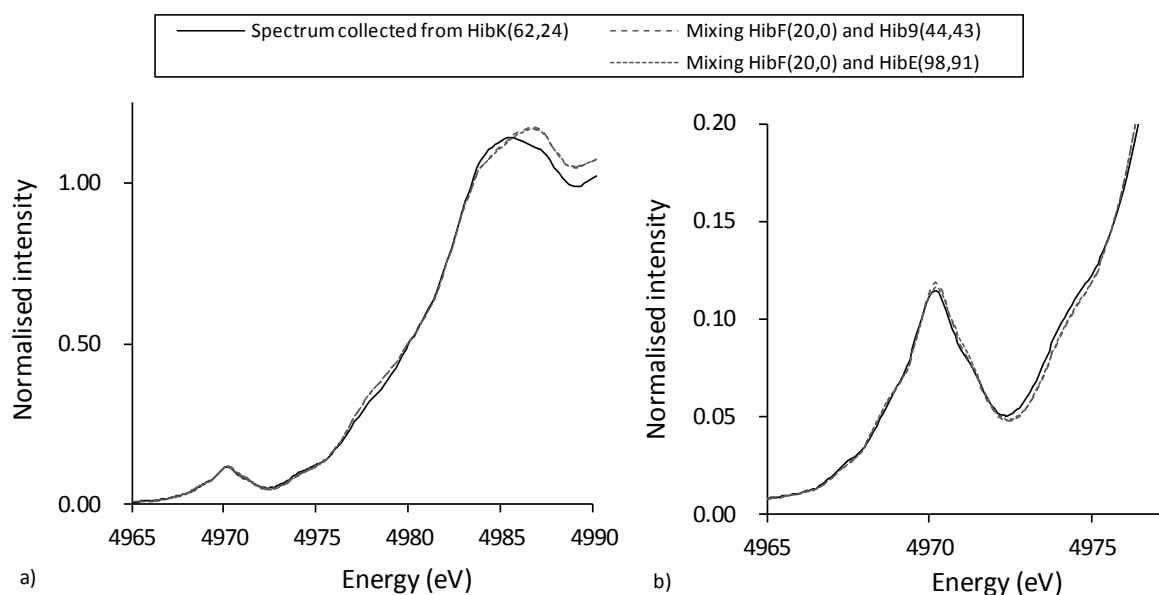


Figure 6-31 (a) Ti K-edge XANES region and (b) pre-edge region of the mixed-valent hibonite HibK(62,24) with modelled spectra using a linear mixing of the Ti^{3+} and Ti^{4+} synthetic hibonite spectra.

The results of this study show that, regardless of the mechanism, the spectral parameters of mixed-valent hibonites do not vary as a binary mixing of a Ti^{3+} hibonite spectrum with that of a Ti^{4+} hibonite spectrum, resulting in the $\text{Ti}^{3+}/\text{Ti}^{4+}$ K-edge oxybarometer shown in Figure 6-29. Similarly, curved oxybarometers have been developed for V^{2+} , V^{3+} , V^{4+} and V^{5+} using pre-edge parameters within V K-edge XANES spectra collected from basaltic glasses (Sutton *et al.*, 2005). Furthermore, features within L-edge EELS spectra collected from crystalline phases were used to develop $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Ti}^{3+}/\text{Ti}^{4+}$ oxybarometers (van Aken and Liebscher, 2002; Stoyanov *et al.*, 2007) which are also curved.

A recent Ti K-edge XANES study by Simon *et al.* (2007) has, however, quantified $\text{Ti}^{3+}/\Sigma\text{Ti}$ in fassaite using a binary mixing line of spectral parameters from a Ti^{3+} pyroxene and a Ti^{4+} pyroxene. The ratio of the pre-edge peaks used in their calibration (a_2/a_3) may, however, be susceptible to distortion of the Ti site in crystalline material, as shown for a range of silicate minerals (Waychunas, 1987) and in this study for the oxide hibonite (Figure 6-24). Furthermore, the Ti contents within the two standards used in the fassaite study (synthetic Ti^{3+} -bearing pyroxene and natural Ti^{4+} -bearing acmite) are likely to be different, with the Ti content in natural acmite (general formula: $\text{NaFe}^{3+}\text{Si}_2\text{O}_6$) likely to be less than that of $\text{NaTi}^{3+}\text{Si}_2\text{O}_6$. It is therefore possible that the spectral parameters of the mixed-valent fassaites do not lie on a binary mixing line defined by two end-members, as was the case for the mixed-valent hibonite in this study.

The results of the $\text{Ti}^{3+}/\Sigma\text{Ti}$ in fassaite study by Simon *et al.* (2007) show no difference in Ti^{3+} content between fassaite in the core CAI and fassaite in the CAI rim. This is in contradiction to the findings of electron microscopy studies by Haggerty (1978), Simon *et al.* (2005) and Dyl *et al.* (2011), in which the latter two investigations used the same samples analysed by Simon *et al.* (2007). The use

of a binary mixing line as a $\text{Ti}^{3+}/\text{Ti}^{4+}$ oxybarometer by Simon *et al.* (2007) may account for the discrepancy between the electron microscopy and XANES studies. If mixing of end-member spectra do not reproduce the experimentally measured spectra, as found by this study, then the preliminary $\text{Ti}^{3+}/\Sigma\text{Ti}$ quantification of garnet (Krawczynski, 2009) and hibonite, pyroxene and spinel (Simon *et al.*, 2009) reported in conference proceedings may need further investigation

As it appears that binary mixing models are unreliable oxybarometers, the ideal $\text{Ti}^{3+}/\text{Ti}^{4+}$ oxybarometer would be based on $\text{Ti}^{3+}/\Sigma\text{Ti}$ experimentally determined using Ti^{3+} , Ti^{4+} and mixed-valent samples, which would be enhanced if correlated with $f\text{O}_2$. This was the premise behind the studies by Beckett *et al.*, (1988), which showed the $f\text{O}_2$ at which hibonite formed could potentially be determined. The $\text{Ti}^{3+}/\text{Ti}^{4+}$ ESR oxybarometer was, however, based on the quantification of $\text{Ti}^{3+}/\text{Ti}^{4+}$ on the M2 site. As the Ti site occupancy determined in this NPD study shows unambiguously that Ti^{3+} occupies the M4 octahedral site (Section 5.4.3), the premise for the $\text{Ti}^{3+}/\text{Ti}^{4+}$ oxybarometer is unsupported. Attempts to amend the $f\text{O}_2$ to $\text{Ti}^{3+}/\text{Ti}^{4+}$ relationship defined by Beckett *et al.* (1988) with $\text{Ti}^{3+}/\text{Ti}^{4+}$ occupying the M4 site were unsuccessful. One reason for this may be that the fit to the experimental data shown in Figure 6 of Beckett *et al.* (1988) is plotted on a different axis to the experimental data shown. Another reason may be that the partitioning of Ti^{4+} across two sites complicates the mathematical relationship proposed by Beckett *et al.* (1988).

Furthermore, the mineral chemistry of hibonite influenced the $\text{Ti}^{3+}/\Sigma\text{Ti}$ ratio (Beckett *et al.*, 1988), and therefore a quantitative correlation between $f\text{O}_2$ and $\text{Ti}^{3+}/\Sigma\text{Ti}$ may not be possible. Nevertheless, the ESR study of Beckett *et al.* (1988) conclusively showed that Ti^{3+} was present in the blue-coloured hibonite grains, and not in the orange-coloured hibonite grains. As Ti^{3+} within the phase Ti_3O_5 is only stable below $\Delta\text{IW}-2.7$ (Ihinger and Stolper, 1986), the presence of Ti^{3+} in blue hibonite indicates they formed under reducing conditions, as proposed by the studies of Ihinger and Stolper (1986) and Beckett *et al.* (1988).

6.4.4 Ti-bearing meteoritic hibonite

6.4.4.1 Spectral characterisation

Ti K-edge XANES spectra were collected from 15 hibonite-bearing CAIs, which represent six meteorites from four meteorite groups. Ti-bearing phases such as perovskite, ilmenite and Ti-pyroxene occur in close proximity to hibonite within some CAIs, and hibonite spectra were occasionally contaminated by these phases, such as shown in Figure 6-32. Contamination was detected by characteristic features within the spectra such as a very intense crest and a peak in the XANES region at 5000 eV for perovskite (e.g. Dhaussy *et al.*, 2007). Contributions to the spectra from ilmenite were identified by a characteristically large shoulder before a symmetrical crest at 4990

eV, and spectra with a Ti-bearing pyroxene component were identified by a low-intensity pre-edge feature, sloping edge and intense crest (e.g. Waychunas, 1987).

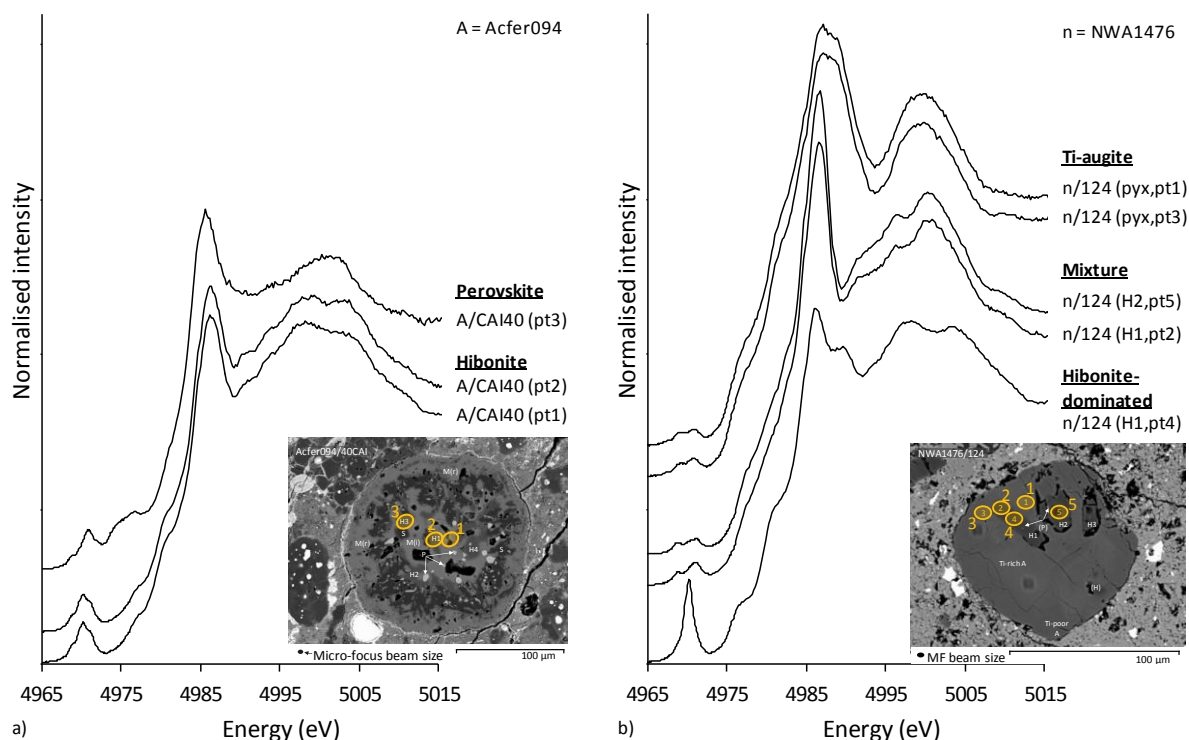


Figure 6-32 Ti K-edge XANES spectra collected from Ti-bearing phases within two CAIs shown as backscatter electron images (BEI) for (a) Acfer094/40CAI and (b) NWA1476/124. The point (pt) refers to the analysis point shown in the BEI. Appendix E.5.1 includes the hibonite spectra which appear to be contaminated by another phase, and the individual spectra collected from each CAI are shown in Appendix E.5.2, including BEI for the probe section mounted CAIs.

In total, hibonite spectra were collected from 12 CAIs, seven of which were prepared as polished probe mounts, and five of which were prepared as grain fragments mounted in gold foil. The hibonite spectra are shown in Figure 6-33, with the pre-edge region shown in Figure 6-34.

The lineshapes of the meteoritic hibonite spectra are similar to those of the synthetic hibonites. In particular, the four features in the post-crest region noted in the synthetic Ti^{4+} -bearing hibonites are clearly evident in the meteoritic hibonite spectra (Figure 6-33), which suggests that the meteoritic hibonites contain a significant proportion of Ti^{4+} . The features in the post-crest region and the three features on the edge are, however, better defined in the meteoritic hibonite than the synthetic hibonite spectra. The meteoritic hibonite grains were large, up to 40 μm in the grain mounts (e.g. 7-753), but typically 3 x 15 μm in the probe sections, both of which were larger than the synthetic hibonite gains ($\sim 3 \times 3 \mu\text{m}$). It is possible that features, particularly in the post-crest region, are accentuated in spectra collected from the larger meteoritic hibonite grains due to long range order, whereas the spectral features of the synthetic hibonites are dampened by the simultaneous analysis of more than one grain.

It is interesting to note that the main spectral features are clearly shown in spectra collected from hibonite with as little as 0.2 wt% TiO_2 (Hughes030/L and 7-971), although the signal-to-noise ratio is greater in spectra collected from hibonite with >1 wt% TiO_2 (e.g. 7-981), as shown in Figure 6-33.

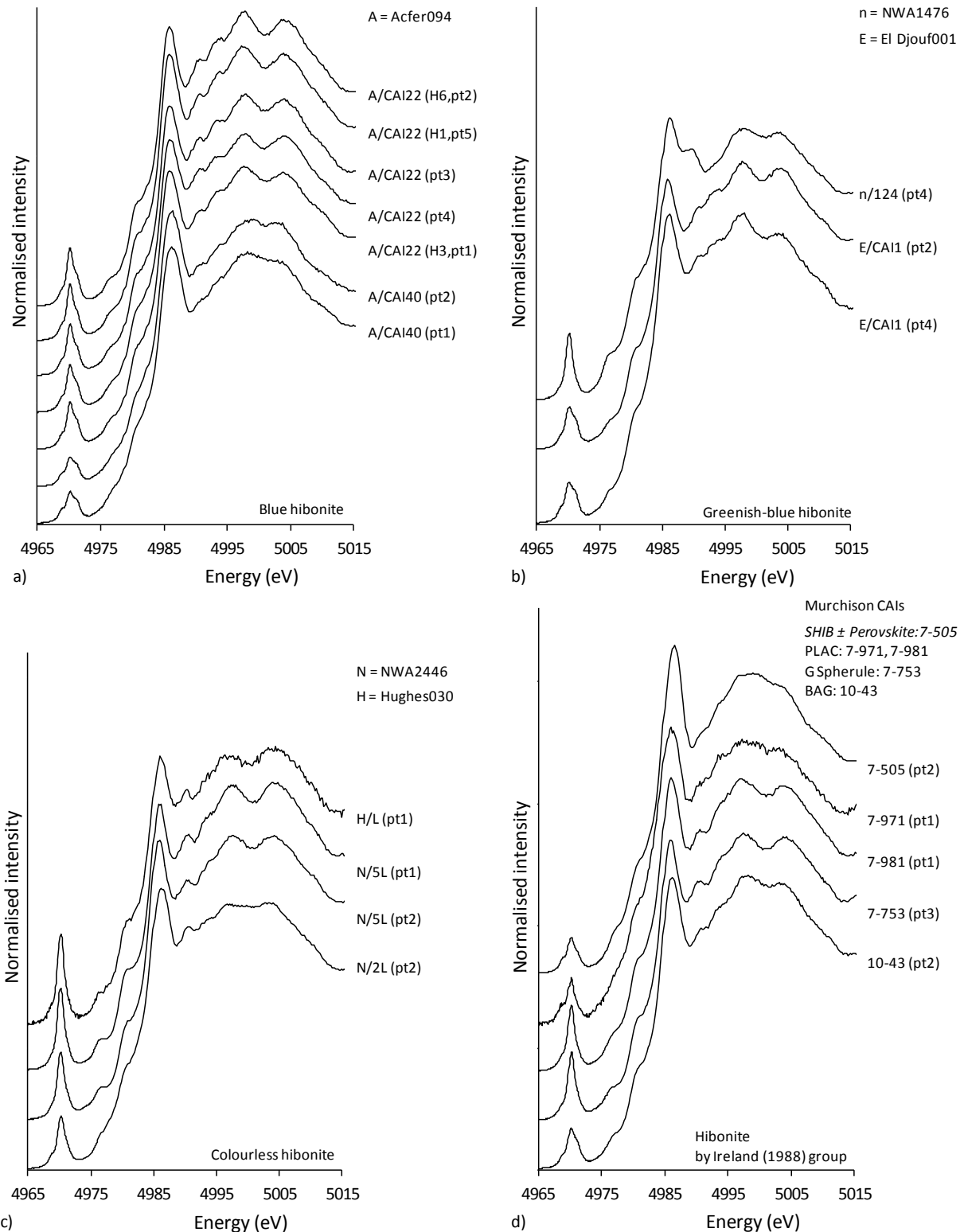


Figure 6-33 Ti K-edge XANES spectra from meteoritic hibonite: (a) blue-toned hibonite grains; (b) greenish-blue-toned hibonite grains; (c) colourless, platy hibonite grains; and (d) grain-mounted hibonite grains from a glass spherule CAI and hibonite grains from the three hibonite groups defined by Ireland (1988), namely: the SHIB, PLAC and BAG groups. All spectra plotted on the same vertical scale and offset for clarity. The NWA1476/124, NWA2446/2L and 7-505 CAI types are unique to this dataset and their spectra have been included for comparison, although the XANES regions of these samples suggest they may be contaminated by Ti-augite, ilmenite and perovskite (respectively). The point (pt) refers to the analysis point shown in Appendix E.4.2

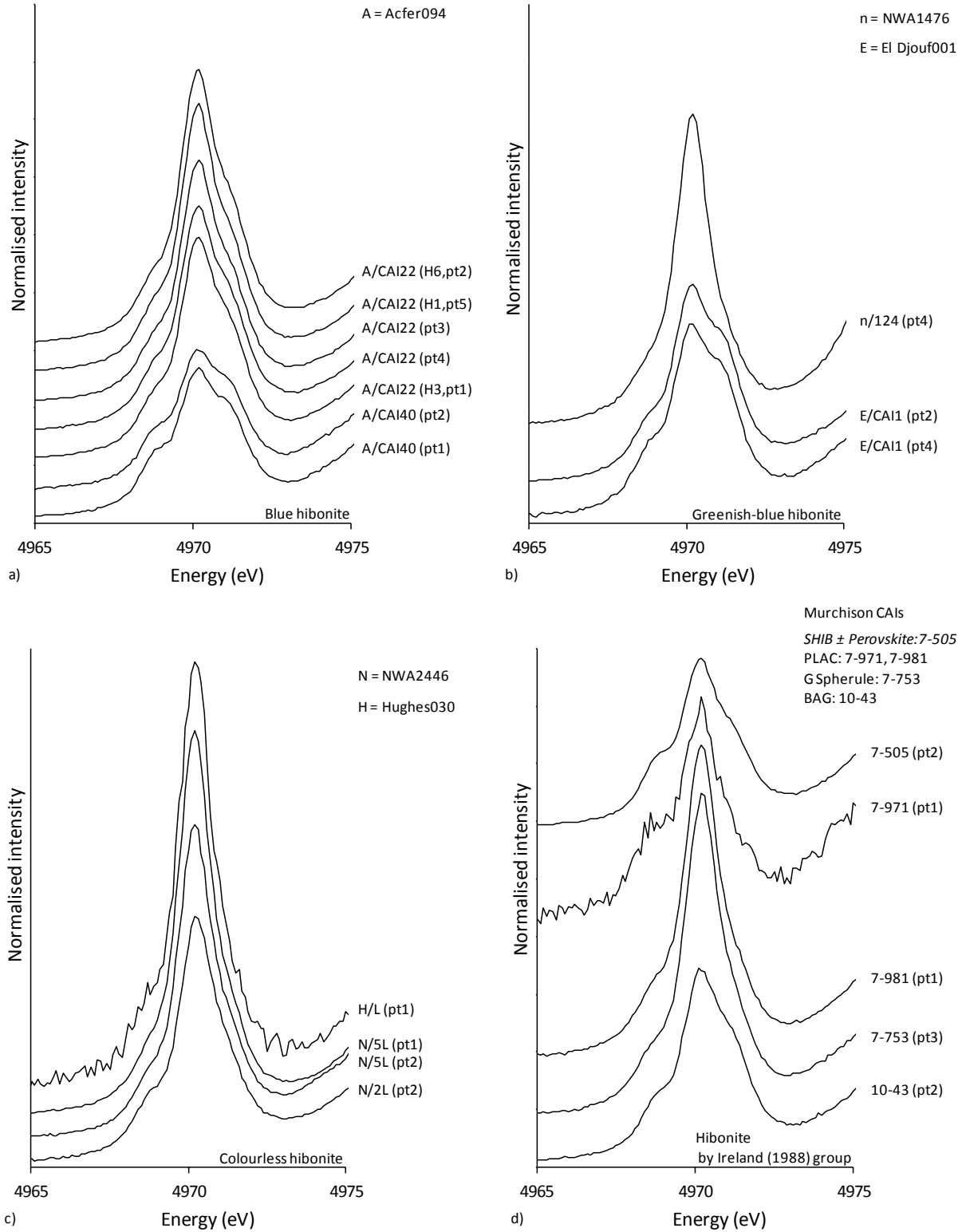


Figure 6-34 Ti K-edge XANES pre-edge regions for (a) blue-toned meteoritic hibonite grains; (b) greenish-blue toned meteoritic hibonite grains; (c) colourless, platy hibonite grains; and (d) meteoritic hibonite grains using the groupings defined by Ireland (1988).

The pre-edge lineshape is similar to that of the synthetic hibonites, having three features within the pre-edge region (Figure 6-34). The intensity of the a_2 peak of the platy hibonites is, however, greater than that of the synthetic hibonites (*cf* Figure 6-21). The reason for this is unclear, however, as the a_2 and a_3 peaks are influenced by distortion of the Ti-bearing site in the synthetic hibonite sample suite, this may account for the difference. Site distortion may be caused by the substitution of other elements into the hibonite structure, and trace amounts of Cr_2O_3 were reported in the hibonite in El Djouf001/1CAI, NWA1476/124 and Hughes030/L, and trace NiO in the hibonite from NWA2446/2L (Table 4-5). Such substitution does, however, not appear to be the cause of the a_2 peak intensity as the a_2 pre-edge peak of the hibonite within El Djouf001/1CAI and NWA2446/2L are less intense than those of the hibonite in NWA1476/124 and Hughes030/L and are more similar to that of the synthetic hibonites. It is interesting that many of the hibonites with the very intense a_2 peak either have PLAC-like morphologies (NWA2446/5L, Hughes030/L and 7-981) or are glass spherules (NWA1476/124 and 7-753). Both CAI types have experienced melting events (Ireland, 1988; Ireland *et al.*, 1991; Rout and Bischoff, 2008). It may be possible that the melting and subsequent quenching processes affected the structure of these hibonites and hence the Ti-bearing site, thereby accounting for the increased a_2 peak intensity observed.

The meteoritic hibonite crystals are larger than the synthetic hibonite crystals, with some grain fragments reaching up to $40\ \mu\text{m}$, in longest dimension. This makes an orientation study of a single grain potentially possible, therefore such a grain (7-981) was centred on a stage that rotated in a plane 45° to the incident beam. Fluorescence was collected from the grain orientated at discrete angles of 0° , 30° , 45° , 60° and 90° .

The four features in the post-crest region are clearly evident in the spectra collected at 30° and 60° , and to a lesser extent in those collected at 0° and 45° (Figure 6-35). The d_3/m_3 intensity ratio varies depending on orientation (Figure 6-36), but this is primarily due to a peak at 5000 eV in the spectra collected at 0° and 45° . This peak is characteristic of perovskite and suggests that at these orientations fluorescence is being collected from a contaminating perovskite phase, which is reported to occur in thin films within this sample (Ireland, 1988). The signal-to-noise ratio of the spectra collected at 30° and 60° was lower than for those collected at 0° and 45° . Together, these results suggest that topography of either the grain or the mount may be influencing the analysis, and that this effect is greater than any crystallographic orientation effects that may be observed within this sample.

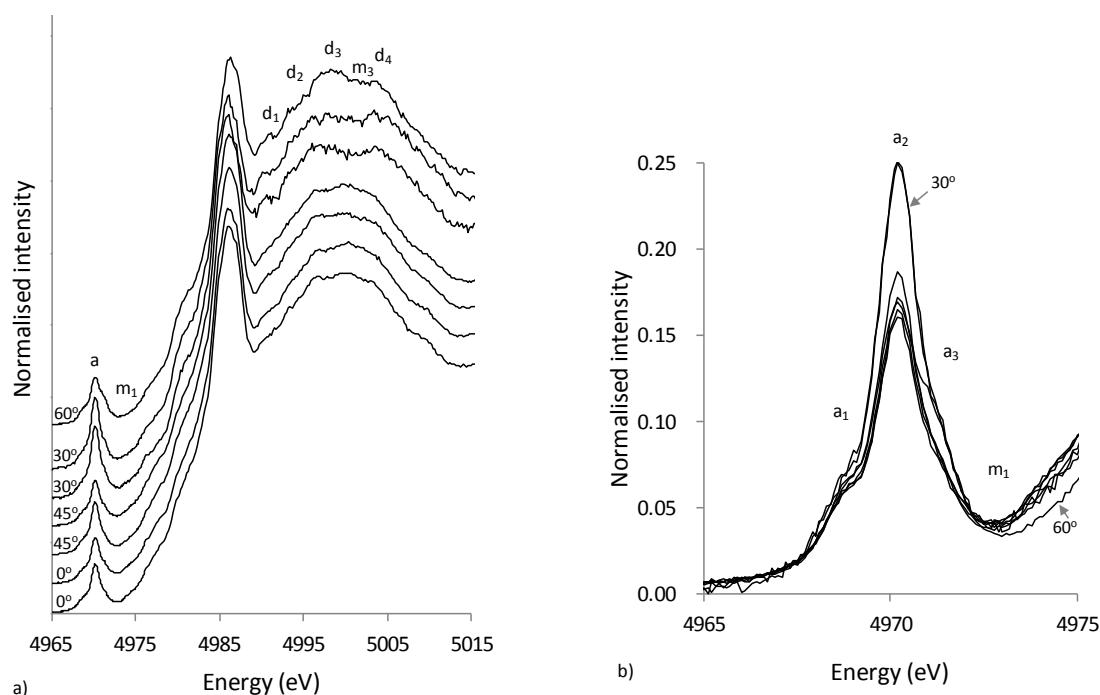


Figure 6-35 Ti K-edge (a) XANES spectra (offset) and (b) pre-edge feature (overlaid) for meteoritic hibonite 7-981 collected with the sample at different orientations.

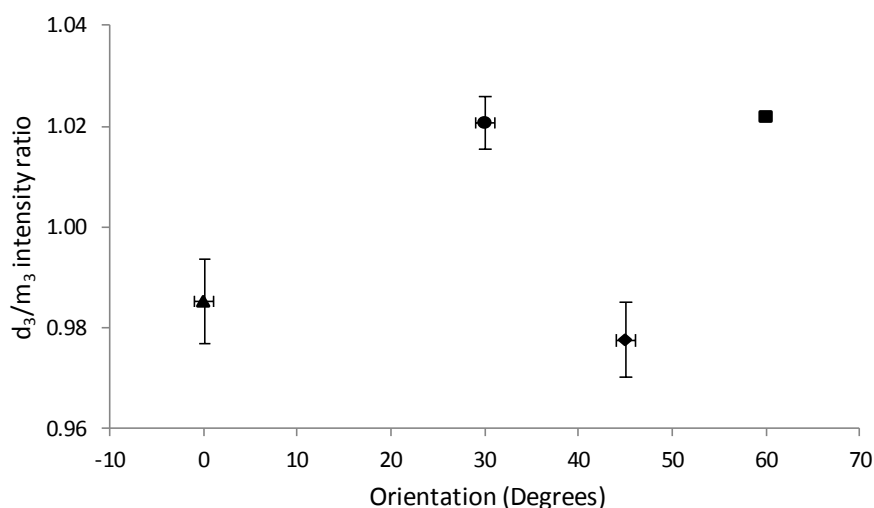


Figure 6-36 d_3/m_3 intensity ratio for the hibonite in 7-981, with repeat analyses shown for three orientations.

6.4.4.2 Quantitative determination of $Ti^{3+}/\Sigma Ti$

$Ti^{3+}/\Sigma Ti$ within the meteoritic hibonites was determined using the Ti^{3+}/Ti^{4+} K-edge oxybarometer defined by Equation 6-6, and the results are shown in Table 6-10 and Figure 6-37. The hibonite grains from Acfer094/40CAI and El Djouf001/1CAI contain variable amounts of $Ti^{3+}/\Sigma Ti$, having 0-6% and 0-10% $Ti^{3+}/\Sigma Ti$ respectively. The hibonites from Acfer094/40CAI all the Murchison CAIs contain 10% $Ti^{3+}/\Sigma Ti$. The hibonite within NWA1476/124 may contain up to 22% $Ti^{3+}/\Sigma Ti$, although this spectrum may be contaminated by Ti-bearing augite. The pyroxene surrounding the hibonite grains are estimated to contain 7% $Ti^{3+}/\Sigma Ti$, as calculated by stoichiometry, therefore it seems reasonable that

the hibonites in this CAI do contain Ti^{3+} , although the shift the spectral edge to lower energy is possibly causing an overestimate in $\text{Ti}^{3+}/\Sigma\text{Ti}$. The hibonite grains within Hughes030/L and NWA2446/5L contain less than 3% $\text{Ti}^{3+}/\Sigma\text{Ti}$.

Table 6-10 Calculated $\text{Ti}^{3+}/\Sigma\text{Ti}$ for meteoritic hibonite using Equation 6-6

Meteorite type	Sample	Colour of hibonite	Point	Grain	DLS scan#	E_{m1} (eV)	% $\text{Ti}^{3+}/\Sigma\text{Ti}$
Unique	Acfer094/CAI22	Blue	P1	H3	45744	4973.1	3
			P2	H6	45745	4973.1	3
			P3	H1	45746	4973.0	6
			P4	H1	45747	4973.3	-1
			P5	H1	45748	4973.1	3
	Acfer094/CAI40	Blue	P1	H1	45751	4972.9	10
			P2	H1	45752	4972.9	10
CM	10-43	BAG	P2	H	45829	4972.9	10
	7-753	GS	P3	H	45813	4972.9	10
	7-971	PLAC	P1	H	45819	4972.9	10
	7-981	PLAC	P1	H	45815	4972.9	10
CR	El Djouf001 /1CAI	Green	P2	H2	45804	4973.2	1
			P4	H2	45807	4972.9	10
R	NWA1476/124 †	Green	P4	H1	45771	4972.7	22
	Hughes030/L	Platy	P1	H3	45774	4973.2	1
	NWA2446/5L	Platy	P1	H	45733	4973.2	1
			P2	H	45735	4973.1	3

Note: The estimated uncertainty is 3% $\text{Ti}^{3+}/\Sigma\text{Ti}$. † The $\text{Ti}^{3+}/\Sigma\text{Ti}$ in this sample is probably overestimated. See text for detail.

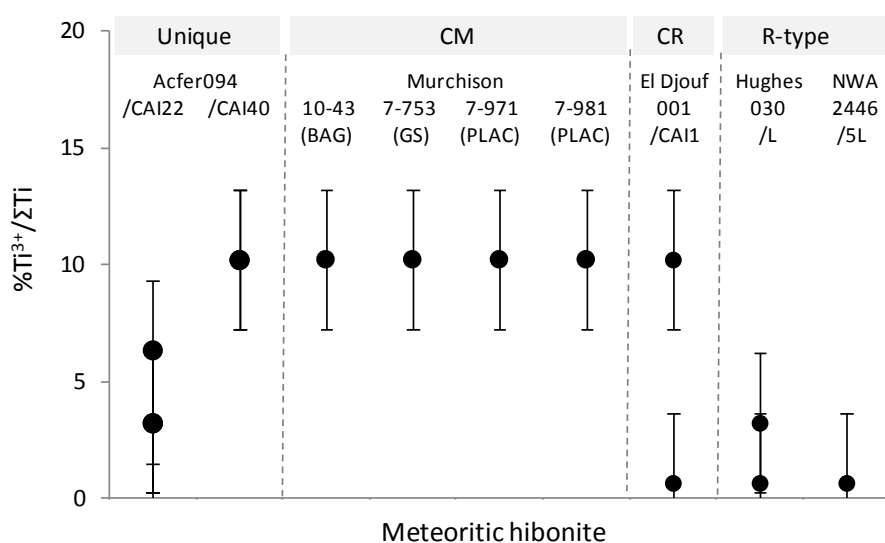


Figure 6-37 % $\text{Ti}^{3+}/\Sigma\text{Ti}$ for meteoritic hibonite calculated using E_{m1} , with the CAIs roughly ordered by the thermal stability field of the CAI minerals assemblage.

There is a correlation between the hibonite colour and alteration within the CAIs. The hibonite grains that were blue or greenish-blue in colour under plane polarised light were Ti^{3+} -bearing, namely: Acfer094/22CAI, Acfer094/40CAI and El Djouf001/1CAI, and the BAG sample 10-43 from the Murchison meteorite. In addition, the hibonite in the PLAC, SHIB and HAL-type samples from the Murchison meteorite were Ti^{3+} -bearing. Although these grains were colourless under plane polarised light (Ireland, 1988), blue-coloured inclusions were preferentially selected for inclusion in the study

by Ireland (1988), of which these grains were a part. When the TiO_2 content is low in hibonite, the grains may appear colourless under plane polarised light, whereas they are greenish-blue as a fragment (Simon *et al.*, 2002). In contrast, the colourless or slightly orange colour of the Hughes030/L and NWA2446/5L (Rout and Bischoff, 2008; Section 4.4.1.2) contained low Ti^{3+} contents ($<3\% \text{Ti}^{3+}/\Sigma\text{Ti}$). These findings are in agreement with the findings of Ihinger and Stolper (1986) that the colour in hibonite is correlated with the presence of Ti^{3+} .

Additionally, the CAIs that had no secondary alteration minerals had Ti^{3+} -bearing hibonite, namely Acfer094/22CAI, Acfer094/40CAI, El Djouf001/1CAI and NWA1476/124. Phyllosilicates are reported within CAIs and the matrix of the Murchison meteorite (MacPherson, 2003), yet the hibonite in the CAIs from the Murchison meteorite in this study were Ti^{3+} -bearing. In contrast, the CAIs that had undergone extensive alteration (e.g. Hughes030/L) or that has hibonite directly exposed to the meteorite matrix (NWA2446/5L) contained less $\text{Ti}^{3+}/\Sigma\text{Ti}$ than the hibonites from the unique Acfer094, CR2 El Djouf001, R3 NWA1476/124 and CM2 Murchison meteorites. The petrographic grade of the R3-6 Hughes030 and R3 NWA2446 meteorites indicates that they have undergone thermal metamorphism (Rout *et al.*, 2009). Hibonite is Ti^{3+} -bearing in CAIs that have undergone no alteration, low temperature alteration, or CAIs in which the hibonite grains were isolated from the meteorite matrix (e.g. NWA1476/124), whereas CAIs which have experienced extensive alteration contained less Ti^{3+} . The correlation between the presence of Ti^{3+} and alteration process is in agreement with the suggestion of Simon *et al.* (2001) that high temperature alteration processes ($>630^\circ\text{C}$) can result in re-equilibration of $\text{Ti}^{3+}/\Sigma\text{Ti}$ under oxidising conditions during an alteration event, whereas lower temperature alteration does not result in the re-equilibration of $\text{Ti}^{3+}/\Sigma\text{Ti}$.

6.5 Chapter summary

Within a series of Ti-CMAS glasses prepared over 17 log units in $f\text{O}_2$, the edge energy ($E_{0.8}$) varies as a function of $f\text{O}_2$ as expected for a one-electron redox reaction. Using this feature the $\text{Ti}^{3+}/\Sigma\text{Ti}$ content in the glasses were calculated using a theory-based fit to the data, and the findings were in agreement with published $\text{Ti}^{3+}/\Sigma\text{Ti}$ results. In addition, the study found that Ti^{4+} in the Ti-CMAS glasses occurred in five- and six-fold coordination, the proportion of which is compositionally dependent. The CaO-rich composition (AD+Wo) stabilised more Ti in octahedral coordination ($50\% [^6]\text{Ti}^{4+}$) and the SiO_2 -rich composition (AD+Qtz) the least ($30 [^6]\text{Ti}^{4+}$), with the other compositions intermediate ($\sim 40 [^6]\text{Ti}^{4+}$). These findings are in agreement with previous studies.

The synthetic hibonite spectra were modified by Ti oxidation state and crystal chemical controls, such as site occupancy and site symmetry. In a series of synthetic hibonite with 0-100% $\text{Ti}^{3+}/\Sigma\text{Ti}$, as determined by stoichiometry, the pre-edge-edge minimum energy (E_{m1}) and the edge energy ($E_{0.8}$) vary as a function of $\text{Ti}^{3+}/\Sigma\text{Ti}$. An inverse quadratic was fitted to the E_{m1} features as a function of $\text{Ti}^{3+}/\Sigma\text{Ti}$ in order to determine a $\text{Ti}^{3+}/\text{Ti}^{4+}$ K-edge oxybarometer. This oxybarometer was applied to the

spectral data collected from meteoritic hibonite grains. The results indicate that blue and greenish-blue hibonites are Ti^{3+} -bearing, and that $\text{Ti}^{3+}/\Sigma\text{Ti}$ varied between grains within two CAIs (Acfer094/22CAI and El Djouf001/1CAI). In contrast, colourless hibonites were Ti^{3+} -poor. In addition, hibonite within CAIs that were pristine or that had undergone low temperature alteration were Ti^{3+} -bearing, whereas hibonite in CAIs that had undergone extensive alteration were Ti^{3+} -poor.

7 Ti L-edge X-ray photo-emission electron microscopy study of Ti-bearing synthetic and meteoritic hibonite

7.1 Synopsis

Hibonite within five calcium aluminium inclusions (CAIs) that have different modes of formation and/or reprocessing have been studied on the sub-micron scale by X-ray photo-emission electron microscopy (XPEEM). Discrete mineral phases have been imaged at the 200 nm level, with detailed Ti L-edge X-ray absorption spectra extracted from regions as small as 32 x 32 nm.

XPEEM images were also collected from a series of synthetic hibonites with 0-100% $\text{Ti}^{3+}/\Sigma\text{Ti}$ from which X-ray absorption spectra were extracted. These Ti L-edge X-ray absorption spectra were modelled in an attempt to develop a $\text{Ti}^{3+}/\text{Ti}^{4+}$ L-edge oxybarometer.

Sub-micron scale zoning in Ti concentration was imaged within hibonite grains from Acfer094/22CAI and El Djouf001/1CAI, which has never previously been reported. The grain rims appear to be Ti-rich with respect to their cores, implying changing environmental conditions within the solar nebula during hibonite growth potentially consistent with the condensation model for the formation of many CAIs.

7.2 Introduction

XPEEM imaging is routinely used to study the components within functional materials and electronic devices at the nm scale (e.g. Humphrey *et al.*, 2009). The ability to extract spectroscopic data from XPEEM images means that oxidation state, chemical and chemical-speciation measurements and phase identifications are all possible with sub-micron spatial resolution (e.g. Tonner *et al.*, 1995; Smith *et al.*, 1998; Humphrey *et al.*, 2009). XPEEM is increasingly being applied to geological systems, including for example, nm scale element distribution in biominerals (Gilbert, 2005). Furthermore, X-ray absorption spectroscopy (XAS) can be coupled with the XPEEM images such that XAS spectra can be extracted from XPEEM images and used for the identification of minerals (Schofield *et al.*, 2002; Frazer *et al.*, 2004; Schofield *et al.*, 2008) in much the same way as shown for bulk powders (Cressey *et al.*, 1993; van der Laan *et al.*, 1992; Pattrick *et al.*, 1993; Schofield *et al.*, 1995). This has been demonstrated for oxide systems (Droubay *et al.*, 1997; Smith *et*

al., 1998), for a suite of silicates (Gilbert *et al.*, 2003), cosmic grains (Bernhard *et al.*, 2006) and trioctahedral clays (Vantalon *et al.*, 2009). Indeed, as XPEEM is a non-destructive technique it is ideal for characterising unique and rare specimens, leaving the sample available for future work (Smith *et al.*, 2003, 2004; Schofield *et al.*, 2010). In addition to the non-destructive nature of XPEEM, the spectral resolution equates to that of electron energy loss spectroscopy (EELS) within the transmission electron microscope (Smith *et al.*, 2004), and the spatial resolution can vary as required from 10's of microns down to ~30 nm (Feng and Scholl, 2007) and potentially down to 5 nm (MacDowell *et al.*, 2007).

In this study the aim was to image hibonite grains within calcium aluminium inclusions (CAIs) using XPEEM and to extract Ti L-edge XAS spectra, in order to compliment electron microscopy and X-ray absorption near edge structure (XANES) studies. Hibonite grains are rare within CAIs, but are of significant scientific interest as they are believed to be the second mineral to condense from a gas of solar composition (Yoneda and Grossman, 1995). As such, they potentially provide information about the earliest processes occurring within the solar nebula. An electron microscopy study of hibonite grains within two CAIs suggested that there is a variation in TiO₂ content (Section 4.4.1), and the quantitative assessment of Ti³⁺/ΣTi from Ti K-edge XANES spectra (Section 6.4.4) also suggests a degree of variation in the Ti oxidation states from the same samples. XPEEM has the potential to image any core-to-rim zoning for both the Ti content and Ti³⁺/ΣTi with spatial resolution not possible by electron microscopy or XANES microspectroscopy.

Valence state images and the corresponding L-edge XAS spectra of elements in different oxidation states have successfully been collected from a range of geological materials. These include a Martian meteorite (Cr²⁺/Cr³⁺), mantle minerals (Fe²⁺/Fe³⁺), Mn nodules (Mn²⁺/Mn⁴⁺, Fe²⁺/Fe³⁺), sulphide and oxide intergrowths (Mn²⁺, Mn³⁺, Mn⁴⁺; Fe²⁺ and Fe³⁺) and hydrothermal vent minerals (Fe²⁺/Fe³⁺, Cu²⁺/Cu⁺), as reported by Smith *et al.* (2003, 2004). Similarly, the speciation of Fe and Ni were determined using spectra extracted from an axinitic iron meteorite (Schofield *et al.*, 2010). So while XPEEM imaging of non-conducting, refractory phases is neither easy nor common, the potential scientific gain in imaging oxidation state variations in CAI minerals certainly makes the experiment worthwhile.

Investigations of the oxidation state of first row transition metals using the L-edge are advantageous for two main reasons (Cressey *et al.*, 1993). Firstly, the $2p_{3/2} \rightarrow 3d$ and $2p_{1/2} \rightarrow 3d$ electron transitions responsible for the L₃ and L₂ absorption edges respectively (van der Laan and Kirkman, 1992) are dipole allowed transitions, unlike the $1s \rightarrow 3d$ transitions of the pre-edge features of the K-edge XANES spectra. Secondly, the core hole lifetime of the transitions are 3 – 4 times smaller than those which give rise to the pre-edge feature in K-edge XANES spectra of the transition elements (Cressey *et al.*, 1993; de Groot *et al.* 1992). Consequently, the L-edge spectra are far more intense than the pre-edge features in K-edge XANES spectra and they also possess far more spectral structure allowing for detailed investigations of the electronic structure of the transition metals

(Cressey *et al.*, 1993; van der Laan and Kirkman, 1992). Spectral differences between Fe^{2+} and Fe^{3+} have been used to develop a $\text{Fe}^{2+}/\text{Fe}^{3+}$ calibration curve using a simple ratio of the L_3 and L_2 absorption peaks [$I(L_3)/I(L_2)$] from EELS spectra (van Aken and Liebscher, 2002). An EELS study by Otten and Buseck (1987) reported a 2 eV shift between the L-edges of Ti_2O_3 and TiO_2 , highlighting the potential for an equivalent $\text{Ti}^{3+}/\text{Ti}^{4+}$ L-edge calibration curve, and such a curve has recently been proposed by Stoyanov *et al.* (2007) based upon EELS spectra collected from a series of Ti-oxides.

Whereas the Fe calibration curve was applicable to many different minerals as Fe L-edge spectra are largely controlled by the oxidation state rather than coordination number (van Aken and Liebscher, 2002), the Ti L-edge XAS spectra are sensitive to oxidation state, coordination, site symmetry and bonding environment. As a consequence it is critical to use standards that are similar in composition and structure to the material being studied if any quantitative oxidation state ratios are to be determined. This issue is excellently demonstrated by the large differences in the Ti L-edge XAS spectra of the TiO_2 polymorphs (de Groot *et al.*, 1992). In addition to the sensitivity of L-edge XAS spectra to coordination environments, are challenges associated with the absolute concentration of Ti in the meteoritic hibonite, which ranges from 0.2 to 6.2 wt% TiO_2 and where no more than 23% of the Ti is expected to be present as Ti^{3+} (Beckett *et al.*, 1988). Nevertheless, in addition to imaging core-to-rim variations in the hibonite grains, this study attempted to quantitatively analyse Ti L-edge XAS spectra collected from a suite of well characterised synthetic hibonite samples with a range of Ti^{3+} from 0 to 100% $\text{Ti}^{3+}/\Sigma\text{Ti}$ in order to develop a $\text{Ti}^{3+}/\text{Ti}^{4+}$ oxybarometer that would complement the equivalent oxybarometer developed in Section 6.4.3 from the Ti K-edge XANES spectra.

7.3 Methodology and experimental techniques

7.3.1 Summary of samples

The samples analysed by XPEEM are detailed in Table 7-1, and include: Ti^{3+} , Ti^{4+} and mixed-valence synthetic hibonites, hibonite grains within CAIs from seven meteorites and a suite of Ti-bearing $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ (Ti-CMAS) glasses. The synthetic hibonite samples analysed by XPEEM are a subset from those characterised in Chapters 3 and 5 and were selected as the most suitable analogues of the meteoritic hibonites in this study. The meteoritic samples were standard probe sections and included hibonites within CAIs that had experienced different formation mechanisms, as described in Section 4.4.1. The AD+Fo glass sample series was specifically prepared for this experiment, as described in Section 3.3.1. The glasses were prepared at five $f\text{O}_2$ conditions spanning 12.7 log units of $f\text{O}_2$, and were quenched to the bottom of the furnace to produce unfractured samples with minimal surface topography.

Table 7-1 Summary of the stoichiometry, TiO₂ content and %Ti³⁺/ΣTi of the samples presented in this study

Sample†	Stoichiometry / composition	Average wt% TiO ₂	%Ti ³⁺ ‡	Analysed in
HibF(20,0)	Ca _{1.07} Al _{11.69} Ti _{0.20} O ₁₉	2.4 (0.5)	100 (0)	2010
HibK(62,24)	Ca _{1.05} Al _{10.99} Ti _{0.62} Mg _{0.24} O ₁₉	7.3 (0.5)	60 (4)	2009, 2010
Hib8C(73,49)	Ca _{1.07} Al _{10.66} Ti _{0.73} Mg _{0.49} O ₁₉	8.6 (0.7)	33 (5)	2009, 2010
HibJ(82,60)	Ca _{1.05} Al _{10.48} Ti _{0.82} Mg _{0.60} O ₁₉	9.6 (2.2)	25 (12)	2009, 2010
Hib9(44,43)	Ca _{1.04} Al _{11.10} Ti _{0.44} Mg _{0.43} O ₁₉	5.2 (1.4)	0 (0)	2010
Acfer094/22CAI	Ca _{1.02} Al _{10.90} Ti _{0.51} Mg _{0.51} Si _{0.04} O ₁₉	6.2 (0.3)	3-6 (4)	2010
El Djouf001/1CAI	Ca _{1.06} Al _{10.86} Ti _{0.49} Mg _{0.51} Si _{0.06} O ₁₉	5.8 (0.7)	0-10 (4)	2009
Hughes030/L	Ca _{1.03} Al _{11.93} Ti _{0.01} O ₁₉	0.2 (0.0)	0-1 (4)	2010
NWA1476/124	CaAl _{11.57} Ti _{0.19} Mg _{0.17} O ₁₉	2.2 (0.2)	≤22 (4)	2010
NWA2446/2L	Ca _{1.03} Al _{11.73} Ti _{0.12} Mg _{0.10} O ₁₉	1.4 (0.1)	unknown	2010
Acfer094/40CAI	Ca _{1.06} Al _{10.69} Ti _{0.64} Mg _{0.58} O ₁₉	7.5 (0.4)	10 (4)	2010
NWA2446/12	Ca _{1.01} Al _{11.04} Ti _{0.40} Mg _{0.42} Fe _{0.08} O ₁₉	4.7 (1.5)	unknown	2010
PSG	Ti-CMAS glasses prepared at IW+6.5, IW-3.5, IW-4.5, IW-6.5	1.0 (0.1)	0 - 85 (3)	2009, 2010

Notes: Further compositional data are detailed in Table 3.7 and Table 4-5.

† For ease of reference the Ti:Mg cation ratio (x 100) is included within the sample name for the synthetic hibonites.

‡ The synthetic hibonite %Ti³⁺/ΣTi is based on stoichiometry (1Ti⁴⁺:1Mg²⁺) as described in Section 3.4.2; %Ti³⁺/ΣTi in the meteoritic hibonites and the Ti-CMAS glasses was determined using the Ti³⁺/ΣTi K-edge XANES oxybarometers described in Section 6.4.3.

7.3.2 Sample preparation

XPEEM measurements were attempted during three beamtime allocations, one for beamline i06 (undulator source) of the Diamond Light Source (DLS) Oxfordshire (UK), and two for beamline 11.0.1 (undulator source) of the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory, Berkeley, California (USA).

The requirements for samples being loaded into the XPEEM on beamline i06 of the DLS were literal and unyielding. Samples embedded into the epoxy resin could not be ion etched, thus precluding their use, and there was apparently no way of accommodating probe sections in the XPEEM sample holders. To circumvent these constraints, fragments of synthetic hibonite were pressed into indium pellets, leaving inevitable topography at the sample/indium-substrate interface. The only meteoritic samples that could be loaded into the XPEEM microscope at i06 were those from the Murchison carbonaceous chondrite that had previously been embedded into gold foils (Ireland *et al.*, 1992), once these foils themselves had been removed from their Al SEM holder. Naturally these samples inherently possessed a great deal of topography. Attempts to use these samples were all unsuccessful, and even when a poor quality image of a hibonite grain could be stabilised, no Ti L-edge XAS spectra could be collected.

Despite the disappointment of the XPEEM experiments on beamline i06 at the DLS, beamtime was obtained on beamline 11.0.1 (PEEM3) at the ALS where geological materials have previously been imaged successfully (Schofield *et al.*, 2002; Smith *et al.*, 2003; Schofield *et al.*, 2008, 2010). The ALS beamline scientists designed and built two sample holders specifically to facilitate this experiment. The sample holders, shown in Figure 7-1, were suitable for most of the probe sections once the excess glass surrounding the meteorite sample had been removed. Even so, some meteorite sections could not be analysed as part of the meteorite would need to be destroyed for the CAI of

interest to fit within the 1 cm² field-of-view (FOV) of the XPEEM microscope. In addition to building sample holders dedicated to this experiment, etching and coating facilities were made available to permit the use of samples embedded in epoxy resin.

The preparation of the synthetic sample mounts for the two ALS beamtime allocations differed. For the November 2009 beamtime, three or four synthetic hibonite samples were mounted on carbon tape, fixed to an Al-disk and embedded in epoxy resin, whereas for the November 2010 beamtime synthetic hibonite grains from five samples were mounted in epoxy resin within an 8 x 8 mm square, along with a piece of Ti foil. In both cases the samples were thinned from both sides to a total thickness of approximately 1 mm, after which the sample face was polished. The samples were coated with approximately 15 nm of carbon directly after the mount preparation in an attempt to minimise degradation of the sample surface.



Figure 7-1 Schematic drawings of the XPEEM sample holders specially designed by the ALS 11.0.1 beamline scientists for probe sections of meteorite samples which were either (a) wide or (b) long and thin.

Once the samples were mounted within the ALS XPEEM sample holders, the x-y coordinates of the hibonite grains were recorded with respect to a fiducial mark using an offline optical microscope with a position calibrated stage. After being loaded into the XPEEM microscope, the CAI positions could be rapidly determined to within 50 – 100 μm of the grains of interest. Navigation was made within the maximum FOV of the XPEEM microscope, which was approximately 100 μm across, by tracking characteristic features observed in the live XPEEM images and related to the backscatter electron images (BEIs) and optical microscope images obtained prior to the experiment.

7.3.3 Surface preparation

For the 2009 experiment, the surface preparation was performed under UHV using the PEEM2 microscope on beamline 7.3.1.1 as the in-vacuum preparation chamber on the 11.0.1 PEEM3 beamline was still under development. As the sample transfer between PEEM2 and PEEM3 necessitated exposing the sample to air, a non-oxidising conductive coating was therefore selected from those available, which included Cu, Pd and Au. Pd was preferentially selected as evaporative application of Au can result in a heterogeneous coating (de Stasio *et al.*, 2003), and due to the high atomic number of Au, a gold surface coating is less likely to permit sufficient photo-electrons to leave the sample surface and enter the microscope, than for Pd. In this regard Cu would be more preferable than Pd, however, it is an important element in other studies of these meteorites, and any residual Cu remaining after the

experiment could interfere with such geochemical investigations planned for these samples. During the 2010 beamtime allocation the surface preparation was made using the in-vacuum preparation chamber attached to PEEM3.

During both the 2009 and 2010 experiments the mounted sample was inserted into a vented loading chamber, which was evacuated to a UHV of 10^{-8} torr in readiness for transfer to the surface preparation chamber. The sample surfaces were etched using Ar^+ ions in order to remove any surface degradation and oxidation, after which the clean sample surface was coated with a nm thick conductive Pd coat, as detailed in Table 7-2. The success of the surface etching process could only be assessed when the sample was in the XPEEM microscope. Therefore, an iterative trial-and-error approach was taken to ensure the surfaces were sufficiently clean. This method was successfully used by Smith *et al.* (2003, 2004) and Schofield *et al.* (2010). The Pd metal layer needed to be thick enough to prevent charge building up on the sample surface, yet sufficiently thin to allow the emission of photo-electrons from the top ~ 2.5 nm of the sample (e.g. Frazer *et al.*, 2003). Although methods have been developed to apply differential coating thicknesses to sample surfaces for XPEEM investigations (de Stasio *et al.*, 2003), it was still found that the ideal thickness could only be achieved through a trial-and-error process.

Table 7-2 Summary of surface preparation made under UHV

Sample	Analysed in	Mount type ‡	Etch time (minutes)	Pd Coating (nm)	Imaged	Spectra
PS3 (synthetic hibonite) †	2009	Normal	45	1.4	Yes	No
PS3 (synthetic hibonite) †	2009	Normal	80	0.3	No	No
PSY (synthetic hibonite) †	2009	Normal	60	0.6	Yes	Yes
El Djouf 89001/1CAI	2009	Large	180	0.8	Yes	Yes
PSG (synthetic Ti-glasses)	2009, 2010	Normal	40	0.6	Yes	No
PMD13 (synthetic hibonite)	2010	Normal	80	1.8	Yes	Yes
Acfer094/22CAI	2010	Large	75	1.2	Yes	Yes
Hughes030/L	2010	Large	40	0.6	Yes	Yes
NWA1476/124	2010	Normal	40	0.9	Yes	Yes
NWA2446/2L	2010	Large	90	0.8	Yes	Yes
Acfer094/40CAI	2010	Large	60	1.2	No	No
NWA2446/12	2010	Large	60	1.5	No	No

Note: † Example of the iterative surface preparation process. Only the final surface preparation protocol is shown for the other samples. ‡ Normal = Standard holder used on beamline; Large = specially designed sample holders.

7.3.4 XPEEM data collection and analysis

After etching and coating, the sample was transferred into the XPEEM chamber and placed under a UHV of 10^{-10} torr for analysis. During the 2009 beamtime, XPEEM images were collected at 1.0 eV increments before the Ti L_3 -edge (444.0 – 456.0 eV), 0.1 or 0.2 eV steps over the $L_{3,2}$ absorption edges (457.0 – 467.0 eV), and 0.3-0.5 eV after the L_2 edge (467.0 – 475.0 eV). In 2010, XPEEM images were collected at 0.2 – 1.0 eV increments before the Ti L_3 -edge (420.0 – 452.0 eV), 0.1 eV over the $L_{3,2}$ absorption edges (452.1 – 471.9 eV), and 0.2 – 0.5 eV after the L_2 edge (472.0 – 500.0 eV). Image exposure times ranged from 1 to 15 seconds, with most images captured at 2.5 seconds per

image resulting in a total acquisition time of approximately 35 minutes per energy scan. A minimum of three replicate scans were acquired from most samples.

The XPEEM images were subsequently analysed using the dedicated image analysis software PEEMVision (Scholl, 2010) which operates through the Research Systems IDL Virtual Machine 7.1. Images may be viewed individually or “stacked” as a function of the incident photon energy. Within PEEMVision individual images may be background subtracted, whereas a stack of images collected over an absorption edge may be integrated in order to image elemental distributions and relative proportions. Image stacks must be prepared such that individual images are sequentially aligned to account for any apparent shift in position during data collection. Additionally, to improve the resolution and signal-to-noise statistics on an image, a composite image may be compiled by aligning and combining equivalent images from replicate scans.

Using PEEMVision area-normalised spectra may be extracted from aligned image stacks by selecting different regions within the image. These extracted spectra need to be energy calibrated in order to account for the energy shift evident in the “vertical plane” of the images, which results from the energy differential associated with the oblique illumination of the sample. This differential was measured to be 1.4 eV over 30 μm for a 36 μm FOV (Figure 7-2).

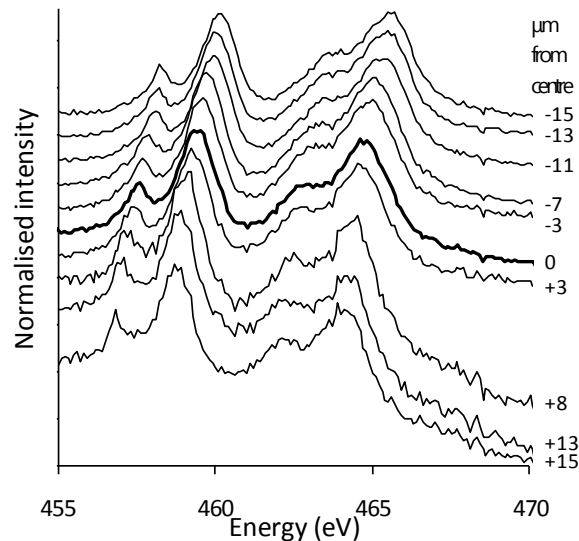


Figure 7-2 Ti L-edge XAS spectra extracted from 3 μm^2 areas of meteoritic hibonite within Acfer094/22CAI. The spectra were extracted along a vertical transect in a 36 μm field of view and shows a 1.4 eV shift over 30 μm .

The image stacks may be normalised to an image-specific I_0 , but in this study normalisation to I_0 was made offline in order to check for I_0 stability. Ti L-edge XAS spectra were extracted from those image stacks with the most stable I_0 over 450 – 475 eV, and normalised to I_0 . Large instabilities in I_0 can be catastrophic when attempting to systematically quantify subtle variations in L-edge XAS spectra. Unfortunately, in this study significant difficulties associated with I_0 stability were encountered. For example, Figure 7-3 shows three consecutive I_0 readings from data collected on the synthetic hibonite sample HibJ(82,60).

A background correction was made to the extracted spectra by fitting a straight line through the 448 – 451 eV region (2009 dataset) or the 451 – 456 eV region (2010 dataset). Unless otherwise noted, the spectra were normalised to the most intense L_3 peak (459.8 eV). The energy of the 2009 datasets were recalibrated to those of the 2010 datasets by comparing the energy of the main L_3 peak of Ti L-edge XAS spectra collected from a standard sample analysed during both beamtime allocations.

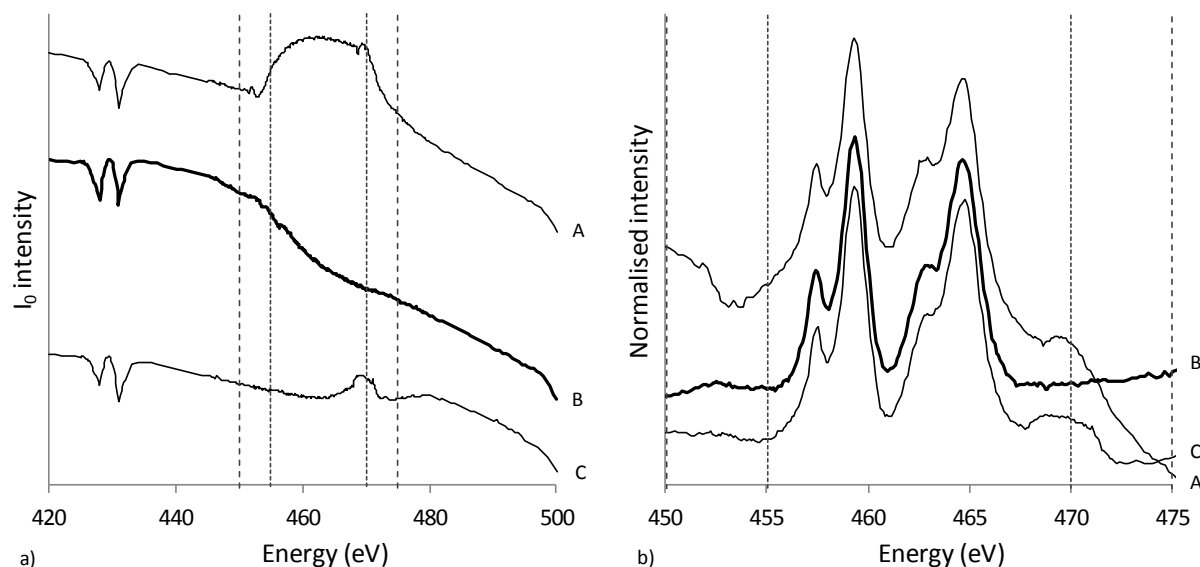


Figure 7-3 (a) I_0 intensity as a function of energy for three successive energy scans (A, B, C) over the Ti $L_{3,2}$ -edges collected from a mixed-valent synthetic hibonite (HibJ(82,60)). The spectra are offset for clarity. (b) Ti L-edge XAS spectra A, B and C extracted from the same region in HibJ(82,60), showing spectral variability. Spectrum B, normalised to the most stable I_0 , is in bold. The outer dashed lines demarcate the region over which the I_0 was required to be stable for the background subtraction, and the inner dashed lines show the region of interest plotted in most diagrams within this thesis.

7.4 Results

7.4.1 XPEEM Imaging

The quality of the XPEEM images is superior in terms of spatial resolution, contrast and clarity to those collected using electron microscopes, as shown in Figure 7-4. The edges of the 300 nm and 700 nm hibonite grains in secondary electron images (SEI) and backscatter electron images (BEI) captured at the same magnification as the XPEEM images are blurred by comparison to the XPEEM images (Figure 7-4). Moreover, spatially resolved composition data is captured within each XPEEM image, as shown by the zoning within the fassaite groundmass of NWA1476/124 (Figure 7-5).

XPEEM images were successfully captured from the Ti-bearing synthetic hibonite standards, as shown for a Ti^{3+} , Ti^{4+} and mixed-valent hibonite in Figure 7-6. Differences in grain morphology between these samples are apparent in the XPEEM images, in agreement with the findings of the electron microscopy study (Section 3.4.2.2). The Ti^{3+} hibonite grains are hexagonal and platy, whereas the Ti^{4+} hibonite grains are more tabular. The hibonite grains in four of the synthetic hibonites are homogeneous, but core-to-rim zoning is apparent within the mixed-valent hibonite

HibJ(82,60), as shown in Figures 7-6 and 7-7. This zoning is consistent with the variation of the chemical analyses from the electron probe. As described in Section 3.4.2.2, approximately two thirds of the sample was Ti^{3+} -rich ($10.9 \pm 0.9 \text{ wt\% TiO}_2$), whereas the remaining analyses tended toward a 1Ti:1Mg composition line, resulting in a wide range in composition ($7.1 \pm 2.0 \text{ wt\% TiO}_2$).

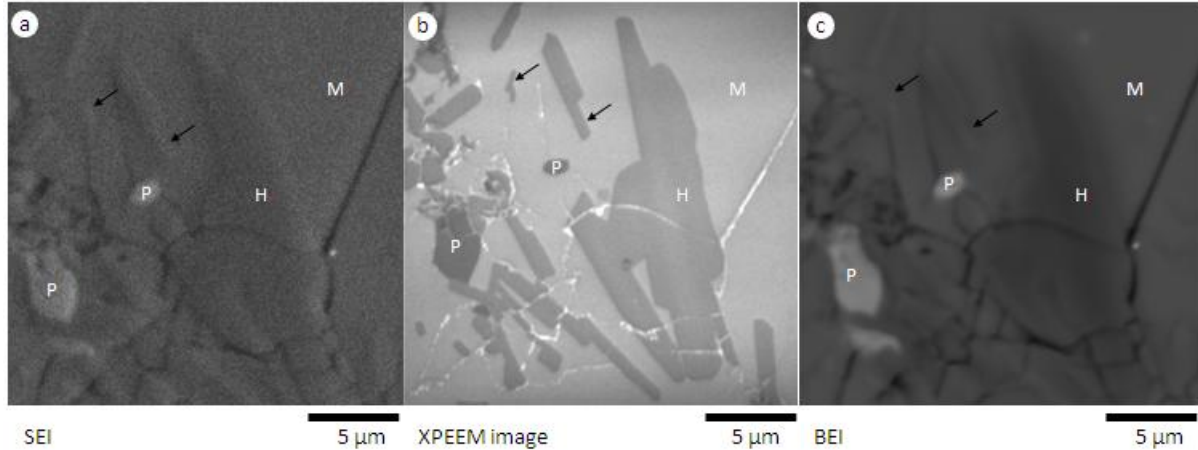


Figure 7-4 (a) SEI, (b) XPEEM image collected at 445.0 eV, and (c) BEI of hibonite (H), perovskite (P) and melilite (M) in El Djouf001/1CAI. The SEI and BEI were collected under normal analytical operating conditions (HV, 20 kV) with the same FOV as the XPEEM image. Hibonite grains with widths of 300 nm and 700 nm (respectively) are indicated by arrows to compare the spatial resolution of the XPEEM image to the BEI and SEI.

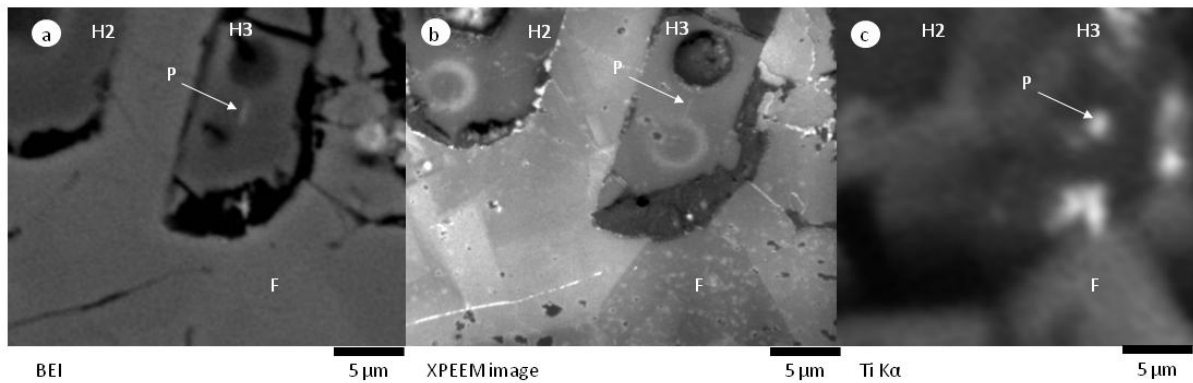


Figure 7-5 NWA1476/124 with two hibonite grains (H2, H3) in a fassaite groundmass (F) with perovskite (P) shown as (a) a BEI; (b) a XPEEM image at 460.0 eV with sharp grain boundaries and clear Ti zoning; and (c) a Ti element map from the electron microprobe with less detailed Ti zoning than is evident in the XPEEM image.

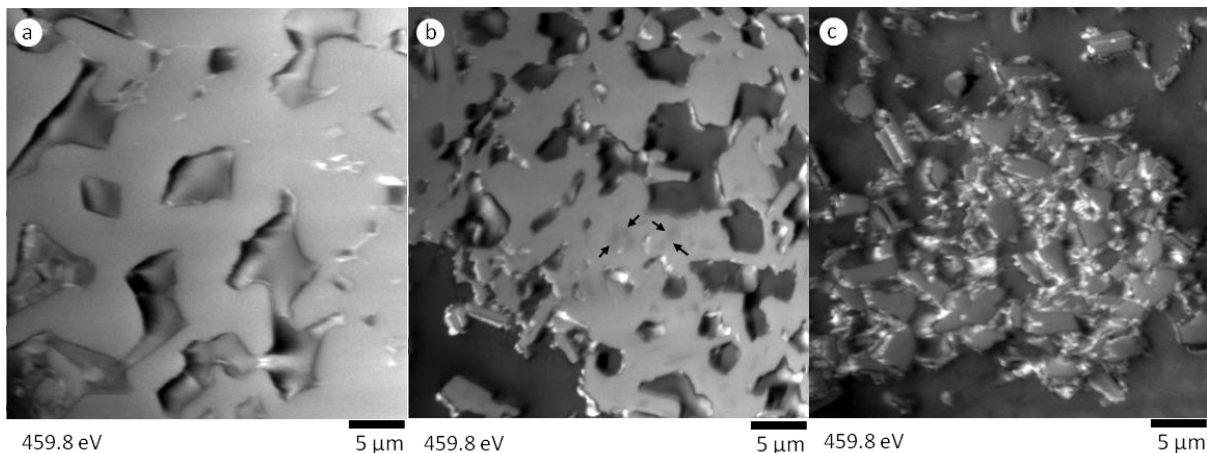


Figure 7-6 XPEEM images collected from Ti-bearing synthetic hibonites on the Ti L_3 edge showing (a) the Ti^{3+} hibonite HibF(20,0), (b) the mixed-valent hibonite HibJ(82,60), and (c) the Ti^{4+} hibonite Hib9(44,43) set in epoxy resin (darker grey). The platy, hexagonal Ti^{3+} hibonite grains are homogeneous, as are the more tabular Ti^{4+} hibonite grains crystals. Examples of the zoning within the mixed-valent hibonite HibJ(82,60) are indicated by arrows.

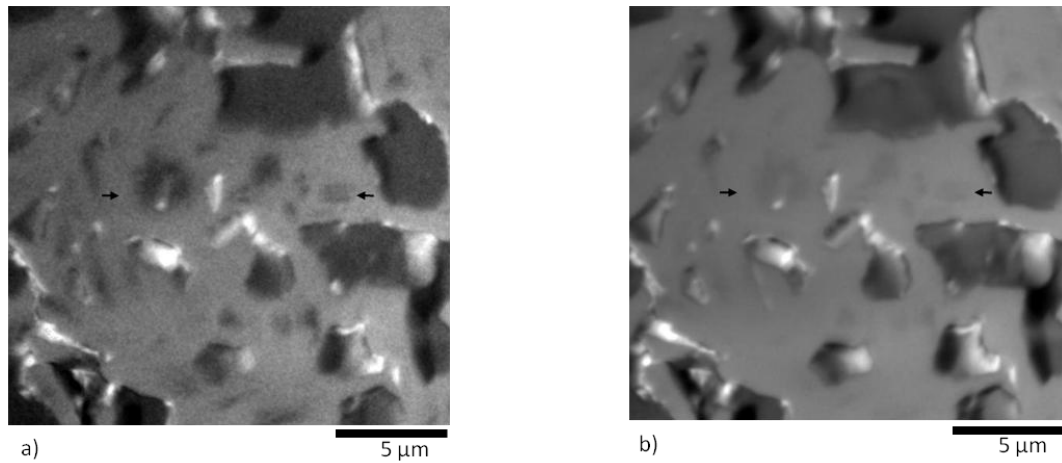


Figure 7-7 (a) XPEEM image of Ti on the L_3 edge (459.8 eV, with background subtracted) showing core-to-rim zoning in Hibl(82,60); and (b) an enhanced XPEEM image of the same region as “(a)”, with equivalent points indicated by arrows, showing differences in Ti content between core and rim regions (images integrated between 459.2 and 460.4 eV).

Similar quality images were collected from the Ti-CMAS glass (Figure 7-8a) and five CAIs (Figures 7-8 b-f). The hibonite grains from the Acfer094/22CAI are bladed, with angular interstitial pore spaces indicating these grains have not undergone resorption. The hibonite blades can be seen to range between 500 nm and 3 μm in width, whereas the pore spaces can be clearly observed down to 200 nm. Hibonite grains within El Djouf001/1CAI are far more clearly observed within the melilite groundmass than was the case in the scanning electron microprobe, and the XPEEM image quality for grains only 240 nm wide was as good as that for grains 5 μm across (Figure 7-8c). Figures 7-8 d-f all show ion probe holes about 2 μm in diameter from the destructive analysis of these samples during a previous investigation (Rout *et al.*, 2009). The image quality is such that even the initial spots (as opposed to ion probe pits) are evident within the hibonite grains. Indeed, compositional zoning may be observed within the fassaite of NWA1476/124 at the sub-micron level, and perovskite grains 200 nm in size are clearly evident (Figure 7-8d). Furthermore, the hibonite grains in NWA1476/124 and NWA2446/2L (Figures 7-8 d and f) occur in close association with perovskite and ilmenite such that electron microprobe analyses and XANES spectra may be contaminated. These perovskite and ilmenite grains are, however, sufficiently distinct within the XPEEM image that uncontaminated Ti L-edge XAS spectra may be extracted from the individual phases. Moreover, textural features and individual mineral grains on the 200 – 500 nm scale within the meteorite matrix and alteration regions are clearly distinguished (Figures 7-8 e and f).

Core-to-rim zoning can be observed in hibonite within two CAIs, namely Acfer094/22CAI and El Djouf001/1CAI. The zoning is evident within raw and background subtracted single images from the Ti L_3 edge and in an image integrated over the higher energy peak of the Ti L_3 edge (Figures 7-9 and 7-10). Interestingly, hibonite grains within these CAIs (Acfer094/22CAI and El Djouf001/1CAI) were found to have variable Ti contents (4 – 7 and 5 – 7 wt% TiO_2 respectively) and variable $\text{Ti}^{3+}/\Sigma\text{Ti}$ (0 – 6% and 0 – 10% $\text{Ti}^{3+}/\Sigma\text{Ti}$ respectively) from the meteorite characterisation study (Section 4.4.1) and XANES investigations (6.4.4).

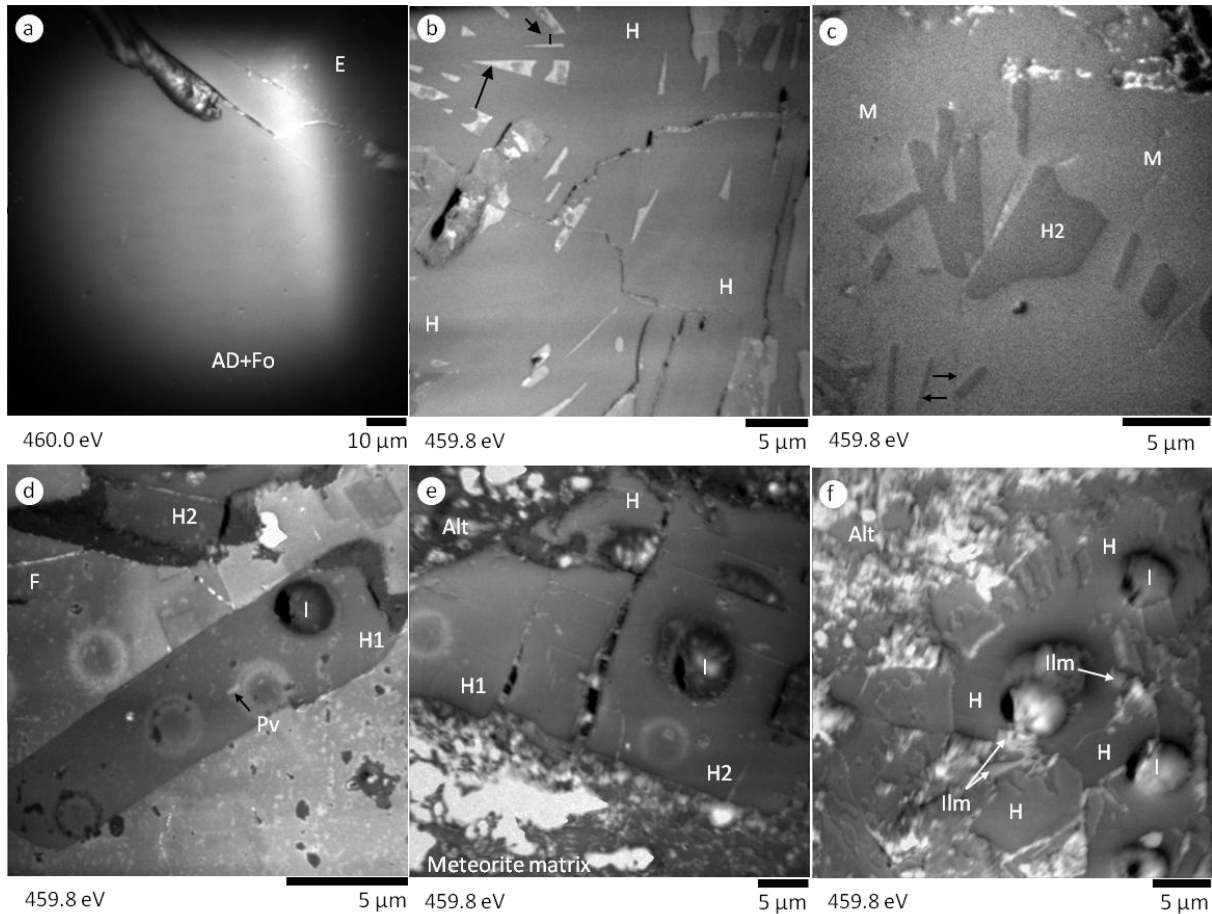


Figure 7-8 Raw, single energy XPEEM images captured from (a) a Ti-CMAS glass (AD+Fo) prepared at ΔT_W -4.5 showing a fracture on the grain boundary alongside epoxy resin (E); (b) hibonite grains (H) within Acfer094/22CAI with interstitial pore spaces. 500 nm and 3 μm wide grains are indicated by arrows. (c) Hibonite grain (H2) and smaller hibonite laths within a melilite (M) matrix within El Djouf001/1CAI. The hibonite grain indicated by an arrow is 240 nm wide, and smaller features are evident within the image, with a second arrow pointing to a fracture. (d) Two hibonite grains (H1, H2) within the fassaite (F) groundmass of NWA1476/124 in which composition is observed. (e) Hibonite grains (H1, H2, H) from the Hughes030/L CAI showing detail within the meteorite matrix alongside the CAI and alteration minerals (Alt) within the CAI. (f) Hibonite grains (H) within the core of NWA2446/2L, intergrown with ilmenite (Ilm) and surrounded by alteration minerals (Alt). The hibonite grains in the latter three images all show damage from an ion probe study (I).

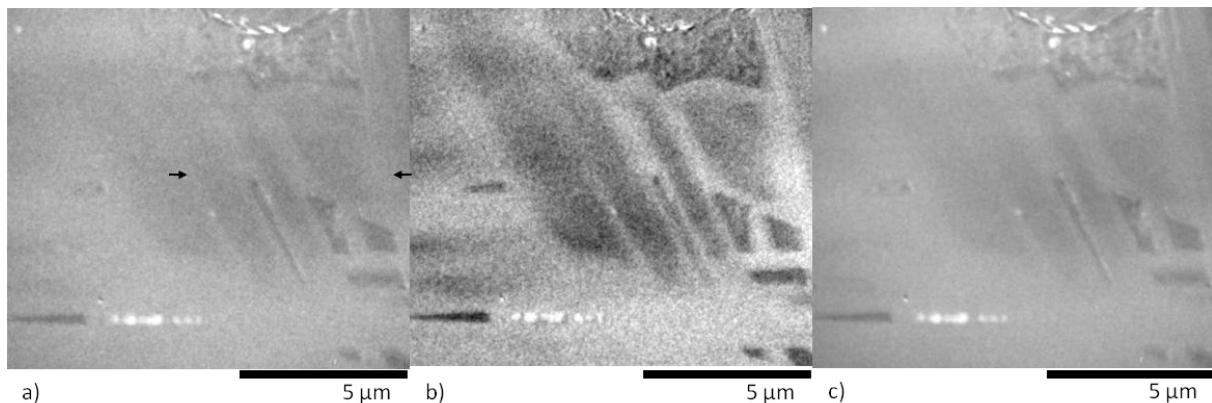


Figure 7-9 Core-to-rim zoning within bladed hibonite grains from Acfer094/22CAI with XPEEM images (a) captured at 459.8 eV (raw image), (b) a background subtracted image at 459.8 eV, and (c) an image integrated across the Ti L_3 edge. Spectra were extracted from 0.5 – 1 μm^2 areas in a line between the arrows (Figure 7-16).

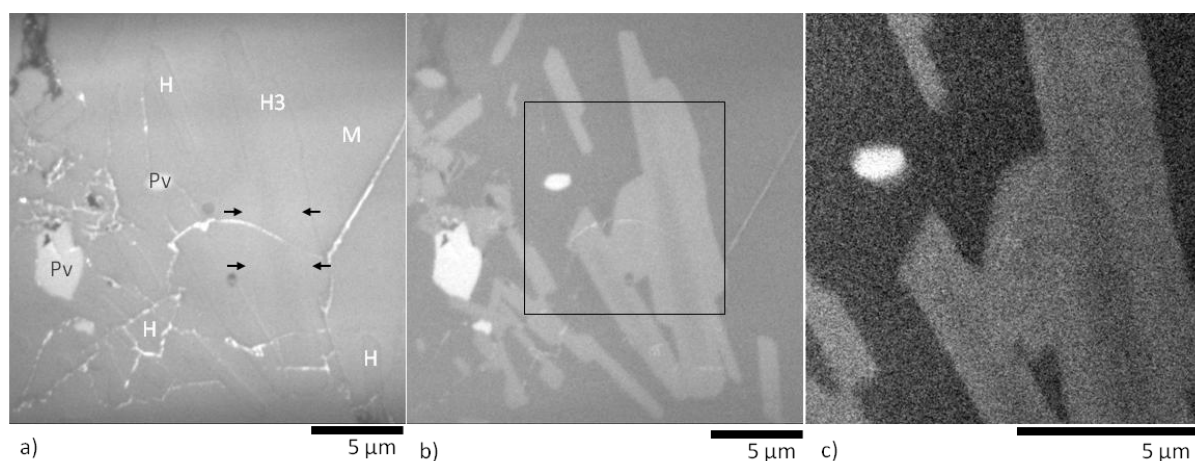


Figure 7-10 Core-to-rim zoning within bladed hibonite grains from El Djouf001/1CAI with XPEEM images (a) captured at 460.4 eV (raw image) showing different mineral phases, (b) a Ti L_3 image (background subtracted, 460.4 – 445.0 eV), and (c) a background subtracted Ti L_3 image captured at a smaller field of view, but less exposure time (460.4 eV). Spectra were extracted from $0.5 - 1 \mu\text{m}^2$ areas in a line between the arrows (Figure 7-17).

Surface preparation was undertaken on a further two meteoritic samples (Acfer094/40CAI and NWA2446/12), but stable images were not obtained from these CAIs. The surface preparation protocol was iterative and to a degree sample dependant, and perhaps the composition of these specific CAIs made them particularly difficult to image. In one case, stable images were collected from silicate minerals surrounding a CAI (El Djouf001/1CAI) when coated with 0.4 nm Pd, but the CAI itself could not be imaged until a total of 0.8 nm Pd was added. A thicker conductive coat potentially makes the images more stable, but spectroscopy becomes more difficult as the photo-electron emission from the sample surface is correspondingly reduced (e.g. Frazer *et al.*, 2003). Nevertheless, up to 1.5 nm Pd was applied to the two CAIs that could not be imaged (Table 7-2). Even though spectroscopy was not possible for these two samples, important information could potentially still have been obtained regarding compositional variations on the nm spatial scale, as shown by Schofield *et al.* (2010) for the Santa Catharina axinite. The hibonite grains in both these CAIs are in close association with either perovskite or ilmenite, which potentially contaminates Ti K-edge XANES spectra and compositional data collected using electron microscopy, so the inability to perform XPEEM experiments was particularly disappointing.

The spatial resolution for which useful Ti L-edge XAS spectra may be extracted from the XPEEM images will vary from sample to sample, and from one phase to another depending upon several factors, including Ti concentration. Figure 7-11 shows Ti L-edge XAS spectra extracted from different sized regions within perovskite, fassaite, and hibonite with different Ti contents. Although the signal-to-noise decreases as the area of extraction decreases, spectra with features suitable for phase identification could be extracted from regions as small as $32 \times 33 \text{ nm}$ within perovskite (Figure 7-11a). Detailed spectra with well resolved spectral features can be extracted from regions as small as $112 \times 112 \text{ nm}$ in fassaite with 2.6 wt% Ti, $98 \times 98 \text{ nm}$ within hibonite with 3.2 wt% Ti and $136 \times 136 \text{ nm}$ within hibonite with 1.3 wt% Ti. Despite the lower Ti content in the NWA1476/124 hibonite than in the Acfer094/22CAI hibonite, the signal-to-noise ratio of the spectra are better (Figure 7-11c,d).

This is likely to be related to the fact that for NWA1476/124 the FOV was almost 50% smaller and image exposure time was longer than those of Acfer094/22CAI.

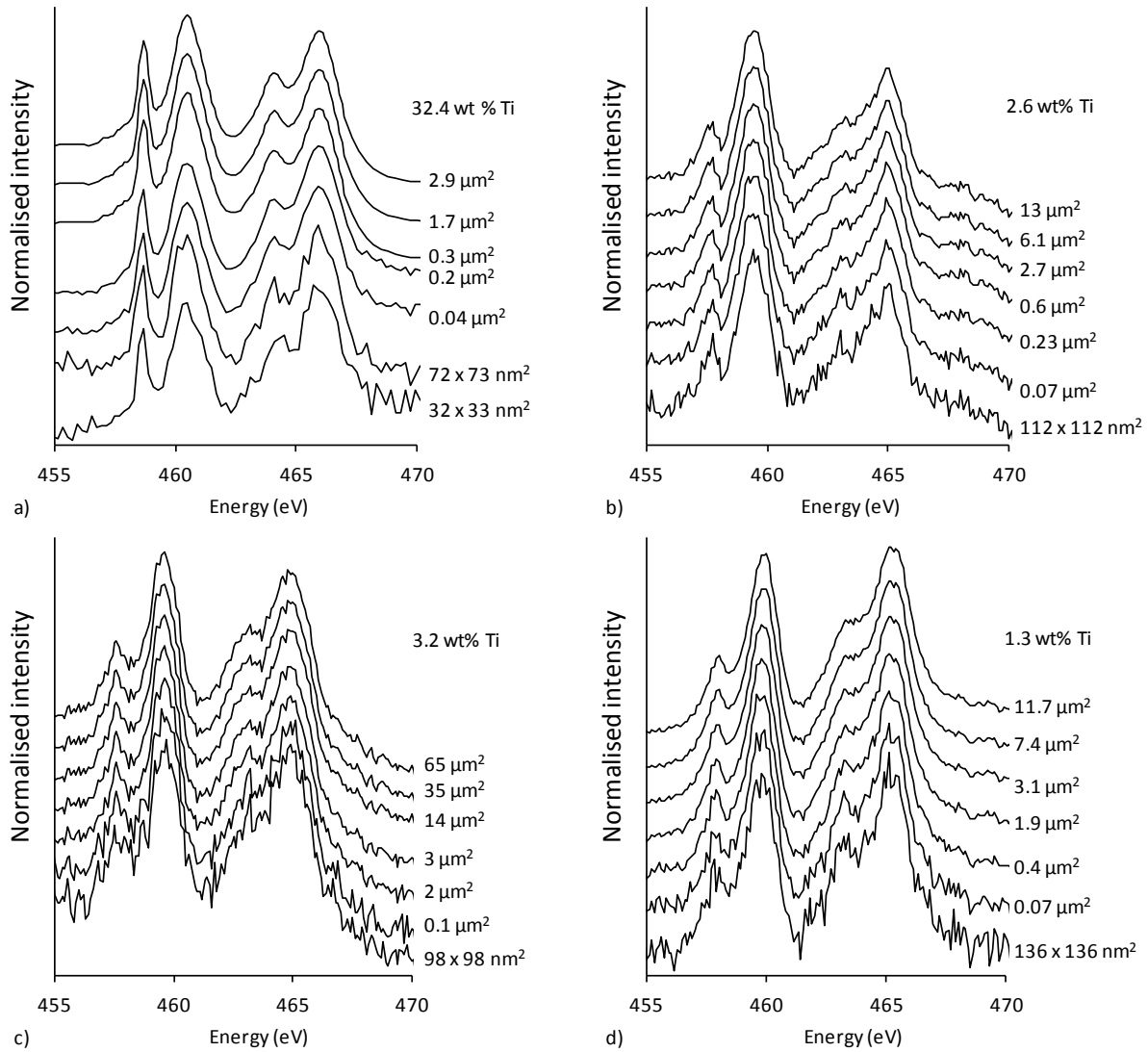


Figure 7-11 Ti L-edge XAS spectra extracted from different sized areas within (a) El Djouf001/1CAI from perovskite (CaTiO_3); (b) NWA1476/124 from fassaite ($\text{Ca}(\text{Mg}_{0.3}\text{Ti}_{0.1}\text{Al}_{0.5})(\text{Al}_{0.8}\text{Si}_{1.2})\text{O}_6$); (c) Acfer094/22CAI from hibonite ($\text{Ca}_{1.0}\text{Al}_{10}\text{Ti}_{0.5}\text{Mg}_{0.5}\text{O}_{19}$); and (d) NWA1476/124 hibonite ($\text{Ca}_{1.0}\text{Al}_{11.6}\text{Ti}_{0.2}\text{Mg}_{0.2}\text{O}_{19}$).

7.4.2 Spectroscopy

7.4.2.1 Ti L-edge XAS spectra

Ti L-edge XAS extracted from the synthetic hibonite series ranging from 0 – 100% Ti^{3+} are shown in Figure 7-12. Only spectra for which the I_0 was stable over the 450 – 475 eV range were included. Spectra were extracted from 2 – 5 μm^2 areas close to the centre of the XPEEM images with a 36 μm FOV. The edge energies and normalised peak intensities of spectra have been measured and are detailed in Table 7-3.

The hibonite Ti $L_{3,2}$ absorption edges are each split into two main peaks. This line-shape is characteristic of Ti^{4+} in octahedral coordination (e.g. de Groot *et al.*, 1992; Schofield *et al.*, 1995) and is in agreement with over 80% of the Ti in hibonite being octahedrally coordinated. Individual peaks within the Ti L-edge XAS spectra of Ti in octahedral coordination have been attributed based on crystal field theory, with the low energy peak in the L_3 and L_2 edges (peaks *a* and *c*) assigned to the t_{2g} level and the higher energy peak of the same edges (peaks *b* and *d*) assigned to the e_g orbital level (de Groot *et al.*, 1992). The broader nature of the L_2 peaks compared to the L_3 peaks is due to the increased core-hole width at the L_2 edge, with the Ti L_3 core-hole width calculated to be 0.22 eV and the Ti L_2 core-hole width calculated to be 0.24 eV (Krause and Oliver, 1979).

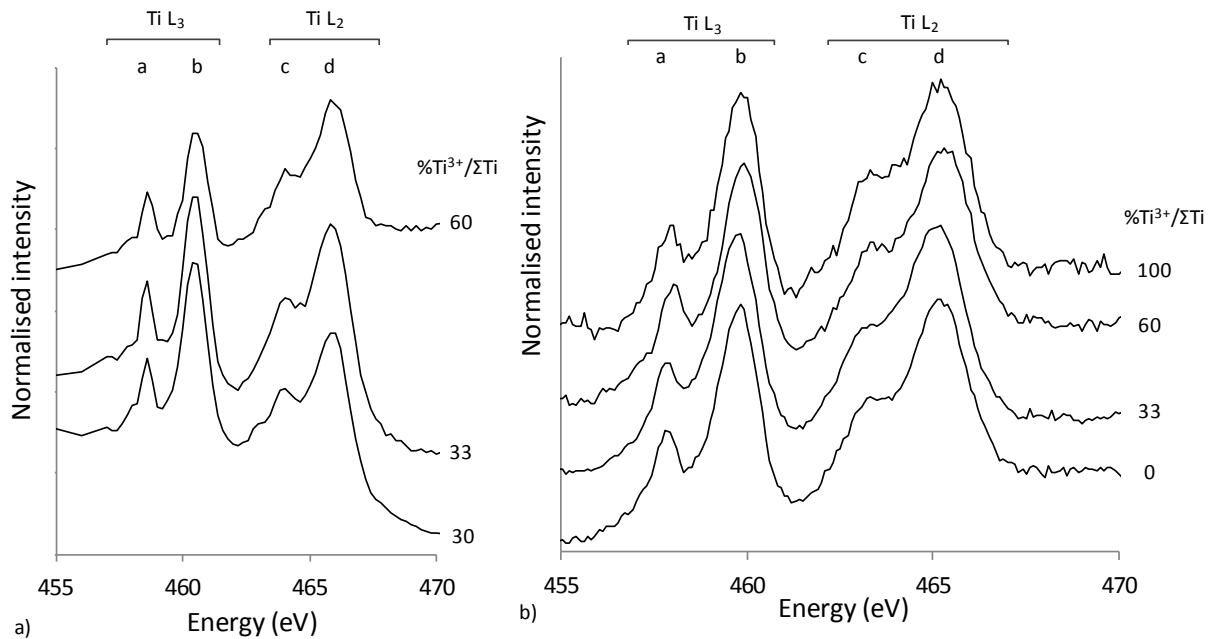


Figure 7-12 Synthetic hibonite Ti L-edge XAS spectra from (a) the 2009 dataset and (b) the 2010 dataset showing no variation in edge energy between the Ti^{3+} hibonite (HibF(20,0)) and the Ti^{4+} hibonite (Hib9(44,43)), nor for the mixed-valent hibonites HibK(60,24) with 60% $Ti^{3+}/\Sigma Ti$, Hib8C(73,49) with 33% $Ti^{3+}/\Sigma Ti$ and HibJ(82,60) with 30% $Ti^{3+}/\Sigma Ti$ in the Ti-rich regions.

Based upon calculated L-edge XAS spectra for Ti^{3+} and Ti^{4+} in octahedral coordination (van der Laan and Kirkman, 1992) observable shifts and differences in spectral structure would be expected for Ti^{3+} and Ti^{4+} in hibonite. Indeed, an EELS Ti L-edge study of TiO_2 , Ti_2O_3 , Ti_3O_5 , Ti_4O_7 and Ti_5O_9 (Stoyanov *et al.*, 2007) showed a systematic shift of the absorption peaks to lower energy as a function of Ti^{3+} content, with a change in the intensity of peaks *a* and *b*. Despite this, no systematic shift in energy was observed within the 0 – 100% Ti^{3+} synthetic hibonite sample series, and the variation in peak *a* intensity was less marked than observed by Stoyanov *et al.* (2007) for their Ti^{3+} -bearing sample series (Figure 7-12 and Table 7-3).

Table 7-3 Energy and intensity of the Ti $L_{3,2}$ -edges of XAS spectra from synthetic Ti-bearing hibonite

Data-set	Sample	Peak a		Peak b		Peak c		Peak d	
		E (eV)	Intensity	E (eV)	Intensity	E (eV)	Intensity	E (eV)	Intensity
2009	HibK(62,24)	458.61	0.63	460.41	1.00	464.00	0.78	465.80	1.20
	Hib8C(73,49)	458.61	0.49	460.41	1.00	464.00	0.38	465.80	0.84
	HibJ(82,60)	458.61	0.41	460.41	1.00	464.00	0.23	465.80	0.56
2010	HibF(20,0)	457.91	0.44	459.81	1.00	463.31	0.68	465.01	1.05
	HibK(62,24)	458.01	0.49	459.91	1.00	463.31	0.66	465.11	1.05
	Hib8C(73,49)	457.81	0.45	459.81	1.00	463.31	0.62	465.11	1.01
	HibJ(82,60) [†]	457.61	0.47	459.50	1.00	462.91	0.50	464.81	0.90
	Hib9(44,43)	457.81	0.47	459.81	1.00	463.21	0.61	465.11	1.02

Note: [†] The HibJ(82,60) I_0 was variable between 450 and 475 eV.

7.4.2.2 Quantitative $Ti^{3+}/\Sigma Ti$ determinations

Although the spectra for the synthetic hibonite series do not vary as much as had been expected, an attempt has been made to utilise the data presented in Table 7-3 and to produce a quantitative oxybarometer. Figure 7-13 shows the peak intensity ratios for the L_2 edge plotted as a function of $Ti^{3+}/\Sigma Ti$ showing a linear correlation between them. Unfortunately, the data from the two different beamtime allocations (2009 and 2010) are not constrained together and define different linear trends. This is possibly related to a combination of factors including spectra that show minimal changes with $Ti^{3+}/\Sigma Ti$ and an unreliable I_0 .

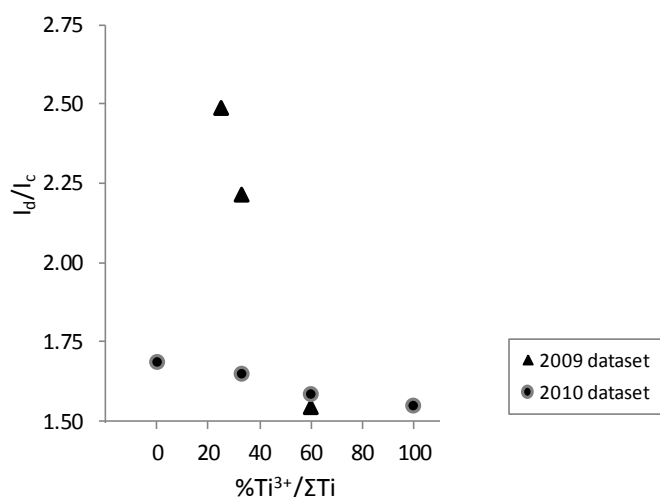


Figure 7-13 Ratios of the L_2 absorption edge peak intensities I_d/I_c of synthetic hibonite as a function of $\%Ti^{3+}$ showing near linear correlations for the 2009 and 2010 datasets.

It is not entirely clear why the Ti L-edge XAS spectra show such little variation as a function of $Ti^{3+}/\Sigma Ti$ for the synthetic hibonites. While it is possible that these spectra are naturally similar, it is also possible that some other factor is influencing the spectral structure. For example, potential intervalence charge transfer between Ti^{3+} and Ti^{4+} across the shared face of the M4 octahedra (Section 5.4.4.) could cause the Ti^{3+} and Ti^{4+} components of the spectra to merge, in a similar manner to that

observed for Fe^{2+} and Fe^{3+} in magnetite (Smith *et al.*, 1998). Inter-valence charge transfer, however, is only expected to occur in the mixed-valent hibonites, and not in the Ti^{3+} hibonites or the Ti^{4+} hibonites, therefore clear differences between their respective spectra should still be evident. It may also be possible that the samples were insufficiently etched, leaving a surface layer rich in Ti^{4+} , or even that the samples were etched for too long causing the Ti at the sample surface to become reduced. Whatever the reason for the similarity in the Ti L-edge XAS spectra of the standards, when coupled with instrumentation factors such as instabilities in I_0 , attempts at developing a $\text{Ti}^{3+}/\text{Ti}^{4+}$ oxybarometer were not successful.

Spectra from hibonite grains from five meteorites are shown in Figure 7-14. The L_3 line shapes (peaks *a* and *b*) of the meteoritic hibonites are consistent with those of the respective synthetic hibonite samples (Figure 7-12a,b). The L_2 line-shape of the meteoritic hibonites with greater than 1 wt% Ti is similar in form to that of the synthetic hibonite spectra, whereas the intensities of the L_2 absorption peaks and post-edge region decrease for hibonites with less than 1 wt% Ti. This is a function of the decreasing signal intensity as the concentration of Ti in the sample decreases coupled with the inherent structure of the I_0 spectrum and difficulties in the subsequent background subtraction. The hibonite in Acfer094/22CAI and El Djouf001/1CAI have similar TiO_2 contents (3.7 and 3.5 wt% Ti respectively). The signal-to-noise ratio of the El Djouf001/1CAI spectrum is better than that of the Acfer094/22CAI spectrum as the image exposure time was five times greater for the El Djouf001/1CAI image set than that of Acfer094/22CAI.

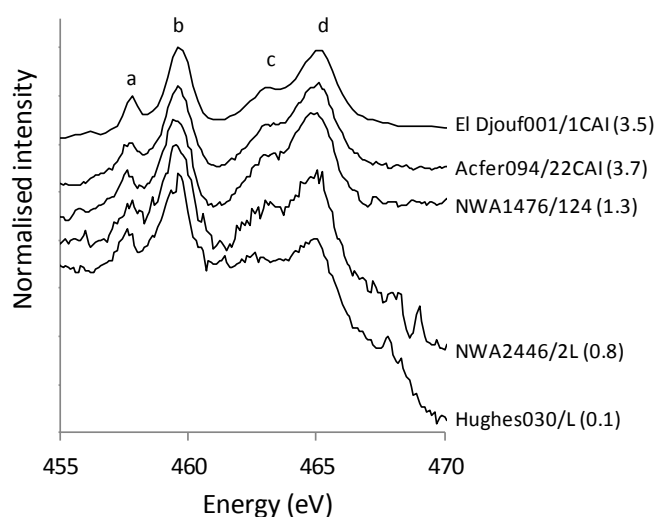


Figure 7-14 Ti L-edge XAS spectra from hibonite grains within five different meteorites showing L_3 peak shapes similar to the synthetic hibonite spectra. The signal-to-noise ratio decreases with TiO_2 contents below 1 wt% Ti (wt% Ti indicated in parentheses, see Table 7-1 for TiO_2 contents), as does the intensity of the L_2 peak.

7.4.2.3 Core-to-rim zoning

Core-to-rim zoning was observed within hibonite grains in a synthetic hibonite and hibonite grains within two CAIs, as shown in the XPEEM images in Figures 7-7 to 7-10. From the XPEEM images alone it has not been possible to ascertain whether this is related to Ti content or variation in $\text{Ti}^{3+}/\Sigma\text{Ti}$. In principle this can be resolved by extracting Ti L-edge XAS spectra from the relevant areas and these data are presented in Figures 7-15 to 7-17 for HibJ(82,60), Acfer094/22CAI and El Djouf001/1CAI respectively. Subtle variations in the spectral structure are indeed evident between the Ti L-edge XAS spectra from the core and from the rim, however, this is not definitive evidence for a change in the $\text{Ti}^{3+}/\Sigma\text{Ti}$. There are, however, unambiguous changes in spectral intensity between the core and the rim showing in both cases an increased intensity in the Ti L-edge XAS spectra from the rim by comparison to those from the core. The implication is that the concentration of Ti in the rims is higher than that of the core.

If the zoning observed for Ti within the hibonites of HibJ(82,60) correlates with the range in chemistries measured by the electron microprobe (Figure 3-6), then this zoning should also reflect corresponding changes in $\text{Ti}^{3+}/\Sigma\text{Ti}$. In this case, based on stoichiometry (note in Table 3-9), it is possible that the Ti-rich rims of the hibonite grains contain more Ti^{3+} than the cores which have lower Ti contents. This cannot be confirmed, however, by the Ti L-edge XAS spectra (Figure 7-15a), which show at best only subtle variations, perhaps for reasons described in the previous section.

As Acfer094/22CAI formed as a direct condensate, the hibonite may be recording changes in mineral formation sequences as the chemistry and temperature of the nebula gas passes through different mineral stability fields during a cooling event, as suggested by Krot *et al.* (2004) for a CAI with Ti-rich and Ti-poor hibonites. The Ti-rich rims and a Ti-poor core in the El Djouf001/1CAI would not be expected from grains undergoing evaporation as the rims would lose the volatile elements before the core. The core-to-rim variation is similar to that observed in the Acfer094/22CAI, and therefore probably reflects the initial formation environment, which was undergoing change.

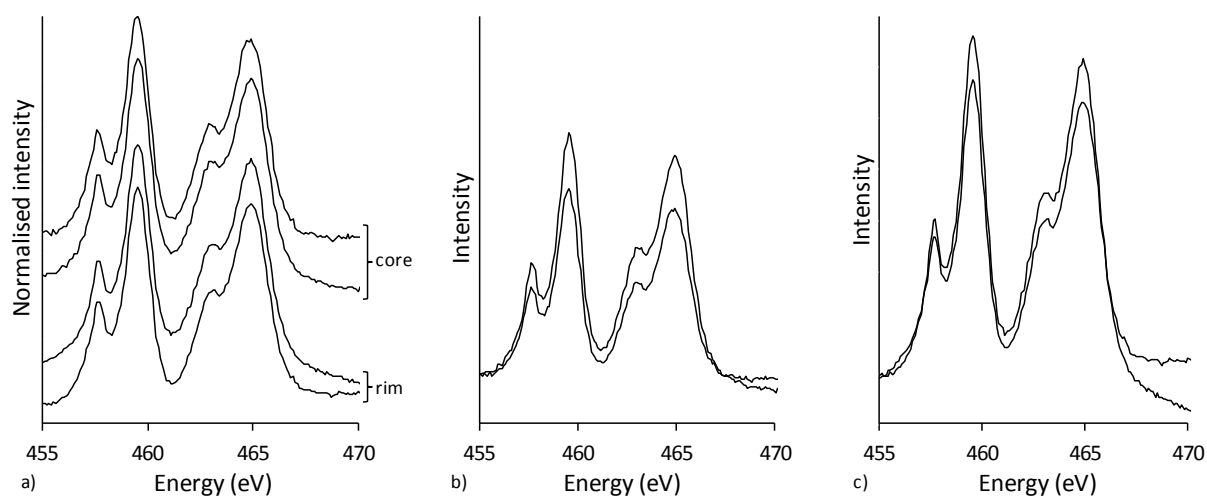


Figure 7-15 Ti L-edge XAS spectra collected from hibonite in the HibJ(82,60) (Figure 7-7) with (a) normalised spectra extracted from both the grain core and grain rims; (b) Intensity of spectra extracted from the core; and (c) the rim.

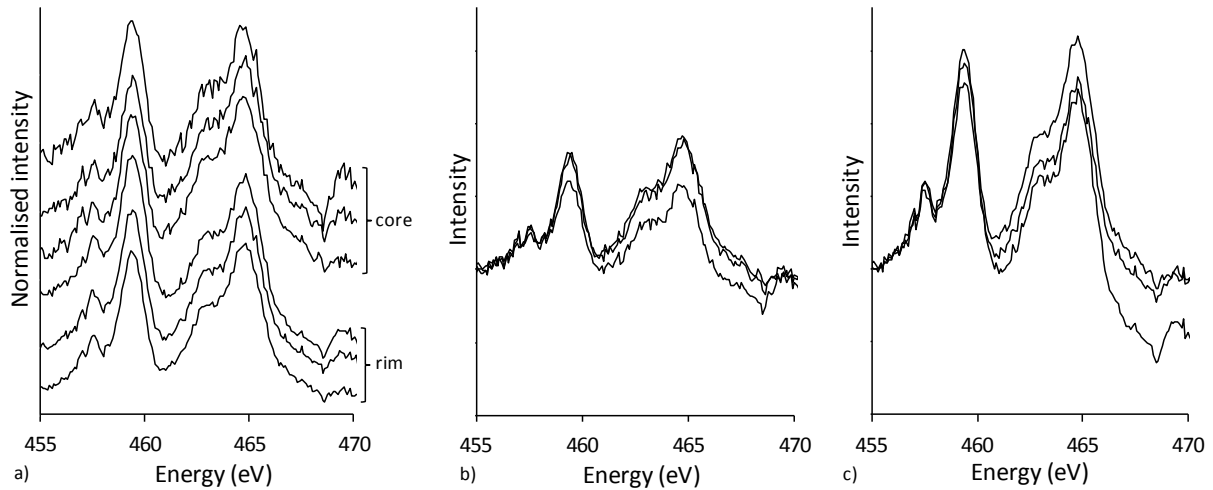


Figure 7-16 Ti L-edge XAS spectra collected from hibonite in the Acfer094/22CAI (Figure 7-9) with (a) normalised spectra extracted from both the grain core and grain rims; (b) absolute intensity of spectra extracted from the core and (c) the rim.

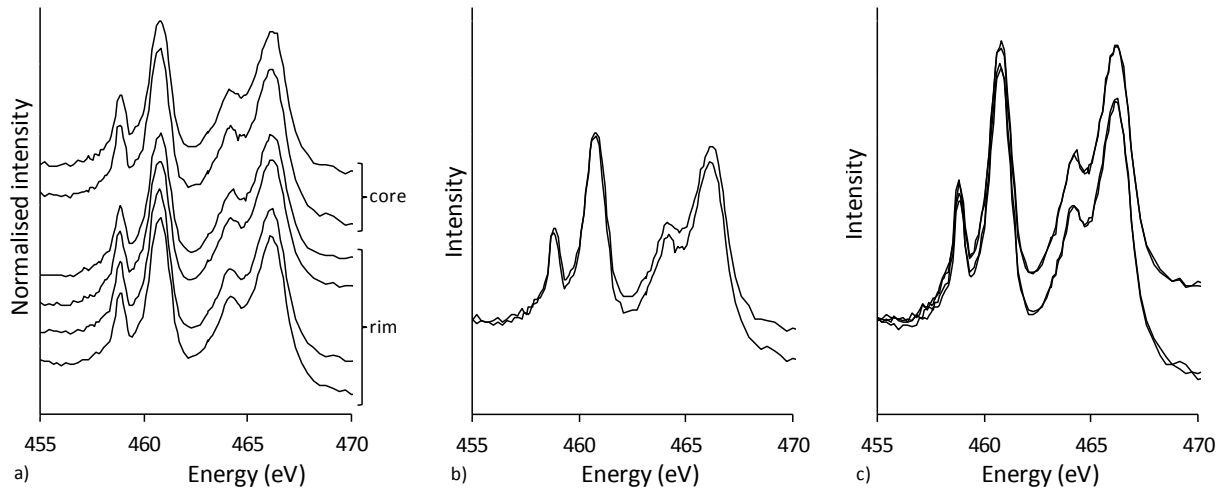


Figure 7-17 Ti L-edge XAS spectra collected from hibonite in the El Djouf001/1CAI (Figure 7-10) with (a) normalised spectra extracted from both the grain core and grain rims; (b) absolute intensity of spectra extracted from the core and (c) the rim.

7.4.2.4 Mineral identification

While the main focus of this study was to image the variation of the Ti and $\text{Ti}^{3+}/\Sigma\text{Ti}$ in hibonites from within CAIs, the simultaneous collection of data from the regions surrounding the hibonites also offers the ability to highlight another potential applications for XPEEM studies of meteorites. Being capable of extracting L-edge XAS spectra from areas down to $\sim 30 \times 30$ nm means that mineralogy at the sub-micron level, that cannot be accurately characterised by other techniques, can be studied both chemically and spectroscopically.

Many of the early studies in which L-edge XAS was applied to mineralogy highlighted the fact that in most cases the L-edge XAS spectra could be used as a fingerprint, such that unknown minerals could be identified (de Groot *et al.*, 1992; van der Laan *et al.*, 1992; Cressey *et al.*, 1993; Patrick *et al.*, 1993; Garvie and Craven, 1994; Schofield *et al.*, 1995). This has also been demonstrated by Droubay *et al.* (1997) and Smith *et al.* (1998, 2003) using XPEEM to study intergrowths of Fe-oxide

minerals and has been used in this fashion by Gilbert *et al.* (2003), Schofield *et al.* (2002, 2008, 2010) on other mineral systems. This study has demonstrated that very fine grained, very refractory and also mineral alteration products within meteoritic materials can all be imaged using XPEEM and that L-edge XAS spectra can be extracted from areas $\sim 30 \times 30$ nm. Figure 7-18 shows spectra from a range of Ti-bearing phases, all of which show spectral features sufficiently different so as to allow phase identification. For example, the spectra in Figure 7-18 for perovskite and ilmenite show differences in the L_3 edge peak widths and relative intensities, but an unambiguous phase identification based solely on these data would be challenging. If, however, XPEEM data at the Fe L-edge were collected for the same area as that for the Ti L-edge, then this identification could be confirmed. Similarly, elements such as O, Mg, Al and Si could also be studied along with the polyvalent first row transition metals providing that the absorption edges of the elements are accessible by the beamline (e.g. 150 – 2000 eV), increasing the accuracy and precision of the phase identification, in addition to enabling any chemical zoning and/or oxidation state zoning to be identified.

Even within this study many of the hibonites were too small to be chemically mapped by an electron microprobe, yet XPEEM was able to image core-to-rim zoning within such grains down to the ~ 100 nm level. Sub-micron mineralogy at the spatial resolutions offered by XPEEM are vital for many areas of cosmic mineralogy, from the study of CAIs as presented here, to the study of meteoritic matrix material (e.g. Bland *et al.*, 2007). If we are to begin to rationalise theories associated with the formation of the early solar nebula, then we must begin to study the minerals, their textures and their crystal chemistry at the sub-micron level.

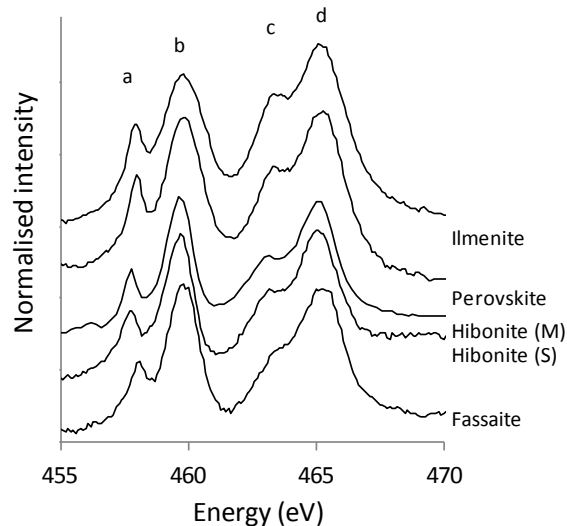


Figure 7-18 Ti L-edge X-ray absorption spectra extracted from the oxides ilmenite (FeTiO_3 , from NWA2446/2L) and perovskite (CaTiO_3 , from NWA1476/124) and hibonite ($\text{Ca}(\text{Al,Mg,Ti})_{12}\text{O}_{19}$; M = El Djouf001/1CAI and S = Hib9(44,43)) and the silicate fassaite ($\text{Ca}(\text{Mg}_{0.3}\text{Ti}_{0.1}\text{Al}_{0.5})(\text{Al}_{0.8}\text{Si}_{1.2})\text{O}_6$, from NWA1476/124). The energy of the spectra have been calibrated to the Ti L_3 peak of synthetic hibonite (459.8 eV, 2010 dataset) as the spectra were extracted from different regions within an XPEEM image stack.

7.5 Chapter summary

XPEEM images have been collected, non-destructively, from a suite of synthetic hibonites in which the $\text{Ti}^{3+}/\Sigma\text{Ti}$ varied from 0 – 100%, and from five CAIs with different formation and/or reprocessing mechanisms. Aspects of the mineralogy and mineral textures that are 200 nm in size were excellently resolved within the images, and features at the 100 nm scale were also evident. In addition, compositional zoning was clearly seen within fassaite of the pyroxenitic groundmass to a far higher spatial resolution than is possible with the electron microprobe.

Ti L-edge XAS spectra extracted from the synthetic hibonite series, showing subtle differences in their spectral structure as a function of $\text{Ti}^{3+}/\Sigma\text{Ti}$. Although these changes in spectral detail were not as large as expected, the potential for developing a $\text{Ti}^{3+}/\text{Ti}^{4+}$ L-edge XAS oxybarometer has been demonstrated. Furthermore, Ti L-edge XAS spectra showing the expected characteristic spectral features were obtained from hibonite with as little as 0.1 wt% Ti.

Furthermore, it has been demonstrated that Ti L-edge XAS spectra can be obtained from areas within the XPEEM images as small as 32 x 32 nm. These spectra were sufficient to distinguish between different minerals irrespective of their juxtaposition. That is to say that Ti L-edge XAS spectra could be extracted from hibonites (and other minerals) without any contamination from their neighbouring grains. This in turn shows that the XPEEM technique could facilitate non-destructive, mineralogical studies of rare and unique meteoritic material at the sub-micron level.

Core-to-rim zoning is observed in the XPEEM images of hibonite grains within the two CAIs Acfer094/22CAI and El Djouf001/1CAI and also from one synthetic hibonite sample (HibJ(82,60)). Spatially resolved Ti L-edge XAS spectra extracted from the different regions of these hibonite grains indicate that the rims are richer in Ti with respect to the cores. Additionally, subtle differences in the Ti L-edge XAS spectra extracted from the core and rim of these grains hint at possible differences in the $\text{Ti}^{3+}/\Sigma\text{Ti}$ between these areas. Although such a correlation cannot be confirmed for the meteoritic hibonites, zoning in Ti-content still supports the idea that the environmental conditions were changing rapidly during the short period of hibonite formation.

8 Synopsis and concluding remarks

8.1 The use of complementary analytical techniques

Two diffraction techniques and two X-ray absorption spectroscopy techniques have been used to characterise natural and synthetic Ti-bearing hibonites and synthetic glasses. X-ray powder diffraction (XRD) and neutron powder diffraction (NPD) were used to structurally characterise synthetic Ti-bearing hibonite standards. XRD allowed for the rapid determination of sample purity, requiring a relatively small sample for analysis compared to that needed for NPD. Due to differences between the XRD scattering factors and neutron scattering lengths, NPD can be used in a complementary manner with XRD. Indeed, in this study the particular advantages of NPD were utilised for the structural refinement of hibonite, as the positions of the oxygen atoms could be well constrained and the site occupancy of Mg could be directly observed. As a consequence, contradictory theories within the literature relating to the Ti substitution mechanism in hibonite have been corrected. Previous studies determined the site occupancy of Mg based on crystal chemical considerations, and that of Ti^{3+} was inferred through the interpretation of limited spectral information. In contrast, NPD directly measures scattering from Ti and Mg, therefore the results of this study reveal unambiguously the true site occupancy of Mg^{2+} , Ti^{3+} and Ti^{4+} in hibonite.

Knowledge of the Ti^{3+} and Ti^{4+} site occupancy subsequently aided interpretation of Ti X-ray absorption spectra collected from synthetic and meteoritic hibonite. The site occupancy of Ti^{4+} in the synthetic hibonites from this study differed to that determined for Fe^{3+} -bearing terrestrial hibonite (Bermanec *et al.*, 1996). Had this study relied upon previously published mechanisms for Ti substitution in hibonite, rather than standards structurally characterised using NPD, then the spectroscopic data may have been misinterpreted.

K- and L-edge studies using X-ray absorption near edge structure (XANES) spectroscopy and X-ray photo-emission electron microscopy (XPEEM), respectively, would ideally provide complimentary information. Spectra from both absorption edges are sensitive to oxidation state, coordination and site symmetry (Waychunas, 1987; de Groot *et al.*, 1992), and these characteristics were observed in the Ti X-ray absorption spectra collected from Ti-bearing materials in this study.

Ti K-edge XANES spectra are acquired in air and may be obtained rapidly from geological samples pre-mounted for electron microprobe analysis, as little additional sample preparation is required. Based on the results of the NPD study, features in the Ti K-edge XANES pre-edge region of the spectra from synthetic hibonite samples were correlated with structural distortions of the Ti-

bearing sites, and features in the post-crest region were shown to be sensitive to Ti site occupancy. Furthermore, the post pre-edge minimum (E_{m1}) and the edge feature ($E_{0.8}$) of the Ti K-edge XANES spectra of the hibonite and glasses, respectively, could be correlated with oxidation state. These features were used to develop Ti oxybarometers, allowing for the quantification of $Ti^{3+}/\Sigma Ti$ (where $\Sigma Ti = Ti^{3+} + Ti^{4+}$) in Ti-bearing CaO-MgO-Al₂O₃-SiO₂ (Ti-CMAS) glasses and meteoritic hibonite. Additionally, the Ti K-edge XANES pre-edge peaks of the Ti-CMAS glasses were used to determine the coordination state of Ti^{4+} in Ti-CMAS glasses, which proved to be composition-dependant.

In contrast to XANES spectroscopy, developing surface preparation protocols for XPEEM studies on insulating and refractory mineralogical material is neither straightforward nor predictable. Additionally, the sample size is restricted by the instrumentation, particularly the lack of space within the XPEEM chamber itself. The XPEEM technique, however, offers vastly increased spatial resolution and better spectral sensitivity relating to oxidation-states of polyvalent transition metals. In this study stable, high resolution XPEEM images were collected from non-conductive glasses, synthetic hibonites and meteoritic samples. The spatial resolution far exceeded that of secondary or backscatter electron images obtained by electron microscopy techniques used to obtain quantitative elemental analyses and microfocus XANES. Furthermore, the XPEEM images revealed sub-micron scale core-to-rim zoning in hibonite grains within two CAIs (Acfer094/22CAI and El Djouf001/1CAI) that could not be imaged or mapped by electron microscopy. The electron microscopy study and the XANES spectromicroscopy study both indicated that there may be compositional and speciation variability within these samples (respectively), but XPEEM proved to have the spatial resolution needed to resolve the source of the suggested variability in Ti content and $Ti^{3+}/\Sigma Ti$ in these samples.

8.2 Integrated analysis of $Ti^{3+}/\Sigma Ti$ in hibonite

8.2.1 Factors that may influence $Ti^{3+}/\Sigma Ti$ within hibonite

Apart from fO_2 , other factors may affect $Ti^{3+}/\Sigma Ti$ in meteoritic hibonite, including crystal chemistry, element availability, resorption and distillation processes, secondary alteration, and thermal metamorphism. All these need to be considered before the findings of this $Ti^{3+}/\Sigma Ti$ in hibonite study can be put into perspective with respect to early solar nebula processes.

Firstly, the role of Mg must be considered, with the possibility that due to the coupled substitution mechanism of Mg^{2+} and Ti^{4+} in hibonite, the $Ti^{3+}/\Sigma Ti$ may be overly influenced by Mg. That is to suggest that $Ti^{3+}/\Sigma Ti$ is purely crystal chemically controlled. While this was taken into account during the preparation of the synthetic hibonites, early solar nebula processes represent a far more complex and open system, in which other elements may also be incorporated into the hibonite structure.

It is therefore necessary to consider the thermodynamic stability of Ca, Al, Ti and Mg, as the volatility of these elements would affect their availability during hibonite forming processes in the early solar nebula. There is approximately 70 °C difference between the equilibrium condensation temperature of $\text{CaAl}_{12}\text{O}_{19}$ and Ti within CaTiO_3 (Lodders, 2003). Therefore in a cooling nebula model, early-formed hibonites would potentially be Ti-free, which seems plausible based on cooling rates of between 1 and 50 °C/hour (Davies and Richter, 2003; Russell, 2007). Even at these cooling rates hibonite grains could reach sizes large enough to accommodate chemical variations such as Ti compositional zoning. Indeed, the synthesis aspect of this study produced hibonite grains on the order of $3 \times 3 \mu\text{m}$ in just 36 hrs at 1404 °C and $\Delta\text{IW}-6.5$. Such a model would also be consistent with the idea that the formation of PLAC hibonites with 0.5 – 2.0 wt% TiO_2 occurred before the formation of the relatively Ti-rich SHIB hibonites with 0.5 – 9.0 wt% TiO_2 , as suggested by Ireland *et al.* (1991). Similarly, Ti^{3+} -bearing hibonite may be expected to form before mixed-valent hibonite during a 200 °C thermal range in which Ca, Al and Ti are stable, but not Mg (Lodders, 2003), but only if Mg^{2+} is necessary for the incorporation of Ti^{4+} within the hibonite structure.

Alternatively, if the $f\text{O}_2$ controls the $\text{Ti}^{3+}/\Sigma\text{Ti}$ in hibonite, irrespective of the availability of Mg, then the $\text{Ti}^{3+}/\Sigma\text{Ti}$ in hibonite would indeed record the $f\text{O}_2$ of the nebula gas during this thermal interval. If conditions were to change, as they would in an evolving nebula gas, then the $\text{Ti}^{3+}/\Sigma\text{Ti}$ in early-formed Ti^{3+} -rich hibonite may re-equilibrate rapidly with the $f\text{O}_2$ of the nebula itself after Mg becomes stable, providing Mg is able to enter and diffuse through hibonite structure. Such a re-equilibration process would be further enhanced by the small size of the hibonite grains, the high temperatures and the chemistry of the gas, increasing the likelihood that the reaction goes to completion.

Spatial distribution of the elements may also affect the mineral chemistry of hibonite. Whereas a homogeneous nebula is assumed based upon the isotopic studies of hibonite, it may not always have been homogeneous during the initial stages of CAI formation. Indeed, inhomogeneities are suggested by the anomalous isotopic ratios of the early-formed PLAC hibonites (Ireland, 1988).

Post hibonite formation processes could also influence the $\text{Ti}^{3+}/\Sigma\text{Ti}$ in hibonite. Hibonite has a finite thermal stability field, and in an equilibrium condensation sequence it reacts with the nebula gas to form melilite, and then spinel (Yoneda and Grossman, 1995). If Mg is leached out of the rims of the hibonite and utilised in the melilite forming reaction, Ti^{4+} may subsequently reduce to Ti^{3+} in order to maintain charge balance, and thus the hibonite rims may become enriched in Ti^{3+} . Alternatively, if the $f\text{O}_2$ of the nebula gas still imparts control over the $\text{Ti}^{3+}/\Sigma\text{Ti}$ in hibonite, as suggested by the experiments of Ihinger and Stolper (1986), then the removal of Mg may not necessarily alter the $\text{Ti}^{3+}/\Sigma\text{Ti}$. Charge balance must still be maintained however, and to account for this Beckett *et al.* (1988) invoked oxygen and/or cation vacancies, and even suggested that oxidation could induce exsolution of Ti into separate phases.

After the formation of the initial CAI, either through condensation and resorption processes, or from a melt, many CAIs are reprocessed by either partial or complete melting. Melting may be accompanied by distillation processes, during which the more volatile elements evaporate (Davis and Richter, 2003). Refractory minerals such as hibonite may not melt during such an event, although mass-fractionated Mg and Ti indicates that hibonite mineral chemistry may be partially influenced by distillation processes (e.g. Ireland *et al.*, 1992). Indeed, O is released by the evaporation of minerals, resulting in localised oxidising conditions in which Ce becomes volatile (Floss *et al.*, 1996), resulting in the Ce depletion reported in many PLACs (e.g. Ireland *et al.*, 1992). Geochemical signatures associated with the distillation processes may therefore be misleading when reconstructing fO_2 conditions during this process. Indeed, it may also influence the $Ti^{3+}/\Sigma Ti$ ratio in hibonite as the preferential loss of Mg may potentially cause an enrichment of $Ti^{3+}/\Sigma Ti$ in hibonite grain boundaries. Thus $Ti^{3+}/\Sigma Ti$ zoning would become apparent in hibonite grains within once molten or partially molten CAIs during distillation processes within the solar nebula. In order to preserve such a signature, cooling would have to be so rapid that the $Ti^{3+}/\Sigma Ti$ could not fully re-equilibrate with the melt.

Re-equilibration of $Ti^{3+}/\Sigma Ti$ in hibonite may also occur during alteration under oxidising conditions, as might be expected in a dust-rich environment within the solar nebula (Wood and Hashimoto, 1993). The temperature at which this alteration occurs appears to be crucial (Simon *et al.*, 2001). For example, orange, Ti^{3+} -poor hibonites exist within the Allende meteorite, reported to have experienced alteration at 630 °C (Simon *et al.*, 2001), whereas the Murchison meteorite which experienced alteration at 50 °C (Simon *et al.*, 2001) has blue, Ti^{3+} -bearing hibonite (this study; Beckett *et al.*, 1988).

8.2.2 CAI formation and associated $Ti^{3+}/\Sigma Ti$ ratios in hibonite

The CAIs in this study are representative of different formation and reprocessing mechanisms. Implications for the fO_2 of the early solar nebula with respect to CAI formation and/or reprocessing are discussed below in relation to the $Ti^{3+}/\Sigma Ti$ in hibonite determined using the Ti^{3+}/Ti^{4+} K-edge XANES oxybarometer.

Acfer094/22CAI and Acfer094/40CAI formed as direct condensates and are unaltered, potentially preserving chemical signatures relating to the initial conditions of CAI formation. The hibonite in both these CAIs are Ti^{3+} -bearing, with the hibonite in Acfer094/22CAI and Acfer094/40CAI measured in this study to contain up to 6% and 10% $Ti^{3+}/\Sigma Ti$ respectively. The nebula gas that these CAIs condensed from was therefore very reducing.

The compact Type A CAIs (El Djouf001/1CAI; and Murchison 7-76, 7-505, 7-953, 7-981) and Type B CAIs (NWA1476/124 and Murchison 7-753) have been either partially or fully melted, and

based on the ^{16}O -rich nature NWA1476/124 and Murchison CAIs (Ireland *et al.*, 1992; Rout *et al.*, 2009), this melting appears to have occurred in the nebula. If the $\text{Ti}^{3+}/\Sigma\text{Ti}$ in hibonite within these CAIs is in equilibrium with the melt, and this melt is in equilibrium with the nebula, then it should reflect the $f\text{O}_2$ of the nebula during the short melting episode experienced by these CAIs. The hibonites in the CAIs that experienced melting processes all possess Ti^{3+} . The hibonite in the El Djouf001/1CAI and the five Murchison CAIs contain up to 10% $\text{Ti}^{3+}/\Sigma\text{Ti}$. Furthermore, the $\text{Ti}^{3+}/\Sigma\text{Ti}$ of hibonites in El Djouf001 varied within hibonite grains from 0 to 10%. The hibonite within NWA1476/124 was measured to have up to 22% $\text{Ti}^{3+}/\Sigma\text{Ti}$, however there is the possibility that the XANES spectra for this sample were contaminated by the adjacent Ti^{3+} -rich fassaite. The $f\text{O}_2$ of the nebula during melting events experienced by these CAIs was therefore very reducing.

The BAG (Murchison 10-43) and HAL-type (Murchison 7-971 and Hughes030/L) CAIs experienced post formation distillation processes, which may increase the apparent $\text{Ti}^{3+}/\Sigma\text{Ti}$ in the rims of hibonite grains. The Murchison CAIs (10-43 and 7-791) were measured to have 10 % Ti^{3+} , whereas the hibonite in Hughes030/L is estimated to have <3% $\text{Ti}^{3+}/\Sigma\text{Ti}$. It is interesting to note that Hughes030/L has undergone extensive alteration, with the distinct possibility that the $\text{Ti}^{3+}/\Sigma\text{Ti}$ may have re-equilibrated.

The Type A CAIs NWA2446/2L, -5L, -8L and -12 have undergone extensive secondary alteration. Consequently, irrespective of how these CAIs may have formed, any chemical signatures reflecting their formation conditions has been subsequently overprinted by the alteration process. The $\text{Ti}^{3+}/\Sigma\text{Ti}$ of the hibonites in these CAIs is therefore likely to reflect the $f\text{O}_2$ conditions under which the alteration occurred. Ilmenite is seen to be in close proximity to hibonite in many of these CAIs, a common textural feature in altered CAIs. As a consequence, there is the distinct possibility that there is an ilmenite contribution to the Ti K-edge XANES spectra collected from some of these hibonites. Indeed, the intergrowth of ilmenite and hibonite in NWA2446/12 was at too fine a length scale for the XANES microbeam to resolve and therefore Ti K-edge XANES spectra were not even collected. Of all the NWA2446 CAIs, uncontaminated Ti K-edge XANES spectra of hibonites were most reliably collected from NWA2446/5L, and this contained <3% $\text{Ti}^{3+}/\Sigma\text{Ti}$.

As the hibonites within the R-type meteorites Hughes030 and NWA2446 contain less than 3% $\text{Ti}^{3+}/\Sigma\text{Ti}$, it is possible that during their formation the $f\text{O}_2$ of the nebula was oxidising. This, however, seems unlikely. Firstly, the observation that one grain in Hughes030/L had a blue core and colourless rim suggests the initial grain was Ti^{3+} -bearing, and partially re-equilibrated under oxidising conditions (Rout and Bischoff, 2008). Secondly, the hibonite in NWA2446/2L had a very light green hue, which also suggests the presence of Ti^{3+} (Ihinger and Stolper, 1986). Thirdly, meteorites are grouped based on their chemical signatures, therefore if CAIs in one R-type meteorite (e.g. NWA1476/124, this study) are Ti^{3+} -bearing, then it might be reasonable to suggest that all the CAI population sampled by the R-type meteorites formed under similarly reducing conditions. The extent of alteration experienced by the CAIs from NWA1476 and those from NWA2446 and Hughes030 differed.

NWA1476/124 contained no alteration minerals, whereas the CAIs NWA2446/2L, -/8L, -/12 and Hughes030/L were extensively altered. The CAIs from the NWA2446 and Hughes030 meteorites appear to have had primary porosity (Chapter 4), and thus the hibonites in these CAIs may have been more easily altered than the hibonite in NWA1476/124. It is therefore likely that the hibonite in the CAIs from NWA2446 and Hughes030 formed under reducing conditions, and the $\text{Ti}^{3+}/\Sigma\text{Ti}$ in hibonite subsequently re-equilibrated under oxidising conditions. These oxidising conditions could have existed during a high temperature alteration event such as thermal metamorphism, and any necessary crystal chemical charge balancing was facilitated by other elements such as Fe.

In conclusion, it therefore appears that $\text{Ti}^{3+}/\Sigma\text{Ti}$ in hibonite from CAIs which are unaltered or experienced low temperature alteration indicate reducing conditions in the early solar nebula, whereas the $\text{Ti}^{3+}/\Sigma\text{Ti}$ of hibonite in CAIs that have experienced high temperature alteration reflect the oxidising conditions under which that alteration occurred.

8.3 Implications for the understanding of solar nebula processes

If resorption and distillation processes are able to increase the Ti^{3+} content in hibonite, then determining a direct correlation between $f\text{O}_2$ and $\text{Ti}^{3+}/\Sigma\text{Ti}$ in hibonite may not be as straight forward as previously thought. Nevertheless, the presence of Ti^{3+} in CIAs implies that they formed or were reprocessed under very reducing conditions, at least $<\text{IW}-2.7$ based on the stability field of Ti_3O_5 (Ihinger and Stolper, 1986), and possibly as reducing as $\Delta\text{IW}-6.8$, the value of a gas of solar composition. This estimated $f\text{O}_2$ range may be represented in Figure 8-1a using the thermal stability field of hibonite at 10^{-3} atm (Yoneda and Grossman, 1995). These findings are in agreement with previous studies which report low $f\text{O}_2$ conditions of formation for fassaite in the CV3 Allende and Leoville meteorites (Haggerty, 1978; Simon *et al.*, 2005; Simon *et al.*, 2007; Dyl *et al.*, 2011) and hibonite from the CM2 Murchison meteorite (Ihinger and Stolper, 1986; Beckett *et al.*, 1988). As shown Figure 8-1b, the $f\text{O}_2$ of the early solar nebula appears to have become more oxidising over time as lower temperature mineral phases and many meteorites formed under conditions 3-7 log units in $f\text{O}_2$ more oxidising than hibonite and fassaite.

CAIs from different meteorite types have similar mineral chemistries, and are believed to have formed in a similar geochemical environment (Bischoff *et al.*, 1984; Guan *et al.*, 2000; MacPherson, 2003) during the short (~ 0.5 Ma) CAI formation period (Makide *et al.*, 2009). This model is supported by the findings of this study which shows that CAIs representative of four meteorite groups (unique, CR2, CM2, R) are Ti^{3+} bearing. This in turn indicates that the nebula in which these CAIs initially formed, or were reprocessed, was very reducing. CAIs from another meteorite type, namely the CV3 meteorites, are also reported to be Ti^{3+} -bearing (Haggerty, 1978; Simon *et al.*, 2005; Dyl *et al.*, 2011). There is increasing evidence that CAIs from most, if not all, chondritic meteorites formed under similarly reducing conditions in the early solar nebula.

There seems to be a consensus that all CAIs formed in a restricted region of the solar nebula, possibly in close proximity to the proto-sun (MacPherson *et al.*, 2005). If this is the case, then the fO_2 of that region was very reducing, and any Ti^{3+} -poor or oxidised signatures within alteration minerals in some CAIs may indicate either a change in the fO_2 of this region or simply reflects the fO_2 of a new region to which the CAIs had been extracted.

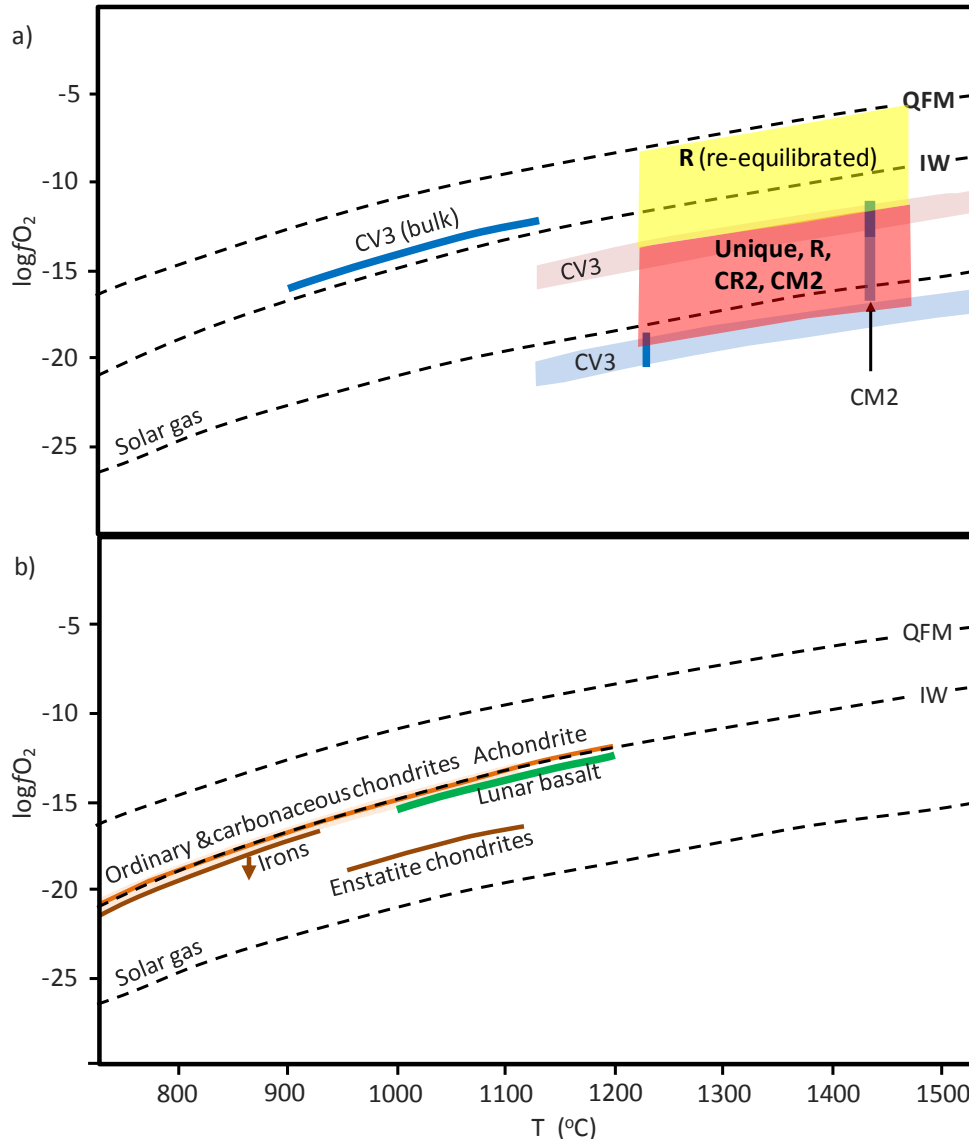


Figure 8-1 fO_2 as a function of temperature showing (a) the estimated fO_2 of formation of hibonite grains in this study, which represent four different meteorite groups are shown in the red (Ti^{3+} -bearing) and yellow fields (Ti^{3+} -poor); and (b) the fO_2 s under which the bulk of the extraterrestrial material formed, as described in Figure 1-1. The fO_2 of a solar composition gas and the iron-wüstite (IW) and quartz-fayalite-magnetite (QFM) buffer curves are shown.

Alternatively, it is also possible that CAIs formed in different parts of the solar nebula. The source of the ^{16}O -rich signature in CAIs remains a contentious issue, and isotopic systems thus far only show that CAIs from the CV3 and CM2 meteorites formed close to the proto-sun (Scott and Krot, 2001; MacPherson, 2003; Liu *et al.*, 2009). The CAI populations do differ between meteorite groups, therefore it is indeed possible that they may have formed elsewhere in the solar nebula. If this is the case and CAIs did form over a wide region, then reducing, ^{16}O -rich conditions were pervasive

throughout much of the early solar nebula. These reducing $f\text{O}_2$ conditions would be consistent with low dust contents over a wide region in the early solar nebula during CAI formation.

One final point for consideration relates to how the $f\text{O}_2$ dynamically changed over time within the solar nebula. PLACs are believed to have formed before SHIBs (Ireland, 1988), and the $\text{Ti}^{3+}/\Sigma\text{Ti}$ in hibonite for CAIs representative of these two groups are equal. It therefore appears that the $f\text{O}_2$ conditions were consistently reducing throughout these formation events. Furthermore, in the PLAC and SHIB CAIs formed in different locations within the solar nebula (Ireland, 1988) these results also imply that the $f\text{O}_2$ conditions were very similar over a wide area.

8.4 Conclusions

This study used a variety of analytical techniques in order to gain a better understanding of the Ti substitution mechanism in hibonite and the systematics of $\text{Ti}^{3+}/\text{Ti}^{4+}$ in Ti-CMAS glasses, synthetic hibonite and meteoritic hibonite. The techniques themselves provided different, but complementary information regarding Ti oxidation states and Ti distribution in hibonites. These results have been used to further constrain the geochemical conditions of the early solar nebula.

The main findings of this study are individually summarised below.

Ti^{3+} and Ti^{4+} saturation level in hibonite

Characterisation of the synthetic hibonite samples by X-ray diffraction showed that the hibonite structure may accommodate up to 0.75 Ti^{3+} or just over 1 Ti^{4+} per formula unit (pfu) under the synthesis conditions used (1404 °C, with pure CO or CO₂ respectively). A mixed-valent hibonite with more than 1 Ti pfu was prepared, but the Ti^{3+} and Ti^{4+} contents remained below their individual saturation limits. Additionally, results from the synthesis component of this study suggest that hibonite, including Ti-bearing hibonite, is more stable under reducing conditions than oxidising conditions.

Ti^{3+} , Ti^{4+} and Mg substitution mechanism

Rietveld refinement of neutron powder diffraction data from the synthetic Ti-bearing hibonites revealed that Mg^{2+} occupies the tetrahedral M3 site, Ti^{3+} only occupies the M4 octahedral site, and Ti^{4+} partitions between the M2 trigonal bipyramidal site and the M4 octahedral site. The results suggest that for <1 Ti pfu the partitioning of Ti^{4+} across these two sites is constant (1:4.3), irrespective of the amount of Ti^{3+} present.

Variations in M-O bond-lengths as a function of increasing Ti content are evident for those bonds involving M2, M3, M4 and M5. The M2 cation becomes increasingly displaced from the equatorial plane of the trigonal bipyramidal site with increasing Ti content such that hibonite with more than 1 Ti pfu (HibT(137,83)) has a larger displacement than is reported for the isostructural magnetoplumbites. Structural distortions for the hibonite with >1 Ti pfu do not conform to the systematics displayed by the hibonites with <1 Ti pfu, suggesting an additional influence from cation ordering.

In a thermal expansion study between 7 and 275 K, anisotropic thermal expansion was observed for a Ti^{3+} hibonite, whereas near-isotropic thermal expansion was observed for a Ti-rich mixed-valent hibonite sample. It is proposed that the differing thermal expansion of the two samples is related to different Ti substitution mechanisms within the structural unit referred to as the “R-block”.

Ti K-edge XANES oxybarometer for Ti-bearing CaO-MgO-Al₂O₃-SiO₂ (CMAS) glasses

Features in the Ti K-edge XANES spectra collected from a suite of Ti-CMAS glasses with 1 wt% TiO₂ were found to vary systematically as a function of fO_2 . The proportions of $Ti^{3+}/\Sigma Ti$ in the sample series was calculated using parameters derived from quantitative modelling of spectral features plotted as a function of fO_2 . The results are in good agreement with the $Ti^{3+}/\Sigma Ti$ content determined by Schreiber *et al.* (1978) for glasses of similar composition.

The Ti K-edge XANES pre-edge peak intensity and energy were used to determine Ti^{4+} coordination in the Ti-CMAS glasses, showing the Ti^{4+} occurred in five- and six-fold coordination. The proportion of Ti^{4+} in octahedral coordination was found to increase as the calculated optical basicity of the glass increased.

Ti K-edge XANES oxybarometer for Ti-bearing hibonite

Ti K-edge XANES spectra collected from a suite of synthetic hibonite samples with 0-100% $Ti^{3+}/\Sigma Ti$ varied systematically as a function of synthesis conditions. Spectral features that were correlated with the stoichiometrically determined $Ti^{3+}/\Sigma Ti$, were used to develop a Ti K-edge XANES oxybarometer.

This oxybarometer was applied to Ti K-edge XANES spectra collected from meteoritic hibonites from 15 CAIs. The results show that hibonite from the Acfer094 (unique), El Djouf001 (CR2), Murchison (CM2) and NWA1476 (R3) meteorites are Ti^{3+} -bearing. The blue hibonite from CAIs in the unique Acfer094 meteorite and greenish-blue hibonite from a CAI in the CR2 El Djouf001 meteorite have up to 10% $Ti^{3+}/\Sigma Ti$. Furthermore, the hibonites in the CAIs from these two meteorites (Acfer094 and El Djouf001) had variable $Ti^{3+}/\Sigma Ti$. Five CAIs with a range of morphologies from the CM2 Murchison meteorite contain 10% $Ti^{3+}/\Sigma Ti$. The highest $Ti^{3+}/\Sigma Ti$ was measured to be 22% and was from a greenish-blue hibonite in a CAI from the R3 NWA1476 meteorite. The $Ti^{3+}/\Sigma Ti$ measured from this sample however, may be an overestimate due to contamination from adjacent Ti^{3+} -bearing fassaite. Colourless hibonite grains from the R3-6 Hughes030 and R3 NWA2446 meteorites contain less than 3% $Ti^{3+}/\Sigma Ti$.

Implications for CAI formation

From Ti K-edge XANES spectra it appears that processes occurring in the early nebula during the formation and reprocessing of CAIs generally produce Ti^{3+} -bearing hibonite. High temperature alteration processes have caused the $Ti^{3+}/\Sigma Ti$ in hibonite to re-equilibrate thus reflecting the prevailing fO_2 conditions. Low temperature alteration does not appear to cause re-equilibration of the $Ti^{3+}/\Sigma Ti$ in hibonite and therefore such CAIs still maintain the $Ti^{3+}/\Sigma Ti$ that reflects the fO_2 of the early solar nebula.

Ti^{3+} was found in hibonite grains from four different meteorite types, namely a unique meteorite, CR2, CM2 and R-type meteorites. This suggests that CAIs from many, if not all, chondritic meteorite

groups initially formed under very reducing conditions. If CAIs formed in a restricted region, then the fO_2 of that region was very reducing. If CAI formation occurred over a wide region, then the reducing conditions were pervasive throughout the early solar nebula.

Nanometre scale zoning of Ti in CAI minerals

XPEEM images of non-conductive, synthetic and meteoritic hibonites were collected at the Ti L-edge. The spatial resolution was on the order of 200 nm, with features evident in the XPEEM images that could not be observed in the backscatter or secondary electron images. Ti L-edge X-ray absorption spectra were extracted from areas as small as 32 x 33 nm in the XPEEM image.

Sub-micron core-to-rim zoning was observed hibonite grains from CAIs in two meteorites (Acfer094 and El Djouf001) and in one synthetic hibonite sample. Neither the electron microprobe nor the analytical scanning electron microscope has sufficient resolution to observe this zoning. In the meteoritic hibonite, the Ti-zoning appears to be predominantly due to Ti-content, whereas the zoning in the synthetic hibonite may be related to $\%Ti^{3+}/\Sigma Ti$. Different hibonite grains within the meteorites were found to have different Ti contents and variable $Ti^{3+}/\Sigma Ti$. When coupled with the sub-micron variation in Ti within hibonite grains in the CAIs, these findings support a model of changing environmental conditions in the early stages of the solar nebula.

Data for the Acfer094/22CAI and the El Djouf001/1CAI collected using XANES, XPEEM and electron microscopy are all complementary and attest to changing environmental conditions during the formation of the early solar nebula. This is possibly due to changing mineral stability fields.

8.5 Ideas for future work

This thesis has described synthesis experiments, analyses including diffraction, microscopy and spectroscopy, the interpretation of the results of these analyses and the subsequent application of these interpretations to cosmic mineralogy. During this process many additional questions have arisen that could lead to further research in mineralogy and meteoritics that would complement and progress the work presented in this thesis. These ideas for follow-on research focus upon two main themes, (1) hibonite nucleation, crystal chemistry and physical properties, and (2) interpretation of the detailed mineralogy and crystal chemistry of CAIs.

Firstly, there are many interesting crystal chemical questions regarding hibonite that have arisen in light of the outcomes of this thesis. For example, “Does the Ti substitution mechanism change for hibonite when the concentration of Ti becomes greater than 1 Ti pfu?”. With this in mind, the work presented here may be complemented by performing additional crystal structure studies, using either neutron or synchrotron X-ray powder diffraction, on hibonites containing a range of Ti contents between 0.5 and 1.5 Ti pfu. Additionally, these studies could also monitor the effect, if any, of varying the $\text{Ti}^{3+}/\Sigma\text{Ti}$ ratios in such samples. The outcomes of these experiments could then be used to further inform computational studies, such as density functional theory (DFT) calculations, into the mechanisms of Ti incorporation into the hibonite structure.

Previous studies have attempted to explore the influence of $f\text{O}_2$ on the $\text{Ti}^{3+}/\Sigma\text{Ti}$ contents in hibonite using optical and electron spin resonance spectroscopies, however, as highlighted in this thesis the interpretation of such data can be quite complex and misleading. X-ray absorption near edge structure (XANES) spectroscopy and neutron powder diffraction (NPD) offer far more direct and accurate measures of Ti substitution and $\text{Ti}^{3+}/\Sigma\text{Ti}$ ratios in hibonites. An interesting set of experiments would thus be to apply XANES to the measurement of the $\text{Ti}^{3+}/\Sigma\text{Ti}$ in a suite of synthetic hibonites containing a range of Ti^{3+} and Ti^{4+} contents that have been re-equilibrated within melts under different $f\text{O}_2$ conditions and temperatures. Complementary XANES and XPEEM experiments could again be used, but this time to study the kinetics, mechanisms and progress of the re-equilibration process. In a similar manner, resorption processes could also be investigated by measuring the rate of diffusion of Mg and Ti through hibonite under different $f\text{O}_2$ conditions and temperatures.

Continuing to consider a hibonite-melt system, the work in Chapter 6 highlighted the fact that Ti^{4+} appears to occupy two distinct coordination sites within the CMAS glasses studied in this thesis. Considering the potential link between hibonites, CAIs and melts it may be useful to ascertain whether there is a preferred mechanism for the reduction of Ti^{4+} in glasses/melts considering Ti^{4+} occupies different coordination geometries. XANES as applied in this thesis, perhaps allied with extended X-ray absorption fine structure (EXAFS) spectra could be useful to try to quantify and model the mechanisms of reduction of Ti^{4+} in such glasses. Indeed, the reduction of Ti^{4+} to Ti^{3+} has

been reported previously to be accompanied by modifications in glass/melt structure (Tranell *et al.*, 2002) as has been schematically represented in Figure 8-2 calculated using data from the results of the Ti-CMAS glass study. Additionally, the effects of varying the concentration of Ti, incorporating Fe and other elements relevant to CAI chemistry could be similarly investigated under a range of environmental conditions relevant to the CAI formation process.

The thermal expansion of two different Ti-bearing hibonites was modelled as part of this thesis and it was shown that Ti^{3+} hibonites expand anisotropically as a function of temperature, whereas $\text{Ti}^{3+}/\text{Ti}^{4+}$ mixed-valent hibonite expands more isotropically. To understand and rationalise these differences it would be useful to study in an identical manner a pure $\text{CaAl}_{12}\text{O}_{19}$ hibonite and a Ti^{4+} bearing hibonite. The modelling of all these data could then be extended to calculate more fundamental properties (e.g. Grüneisen parameters, bulk moduli, internal energies) of hibonitic materials using the same approach as that developed by Knight and Price (2008).

Focussing more directly upon the mineralogy and mineral chemistry of CAIs, there is a great deal of scope for advancing our understanding of these inclusions, and other material formed in the early stages of the solar nebula, by using complementary XANES and XPEEM experiments. CAIs certainly indicate some process of changing $f\text{O}_2$ conditions or differing $f\text{O}_2$ conditions within the solar nebula. Imaging, measuring and quantifying these changes, however, at the micron and sub-micron level is very difficult and their interpretation can be quite contentious. The application of synchrotron based, non-destructive XANES and XPEEM spectromicroscopies to the study of mineralogical, chemical and oxidation state variations in CAIs, if performed systematically, could significantly enhance the understanding of, and potentially unify the interpretation of, these early solar materials.

Finally, while moving away from crystal chemical based studies, but still focussing upon CAIs, a systematic understanding of the ^{26}Al signatures within CAI minerals would offer an interesting approach to studying heterogeneity within the early solar nebula.

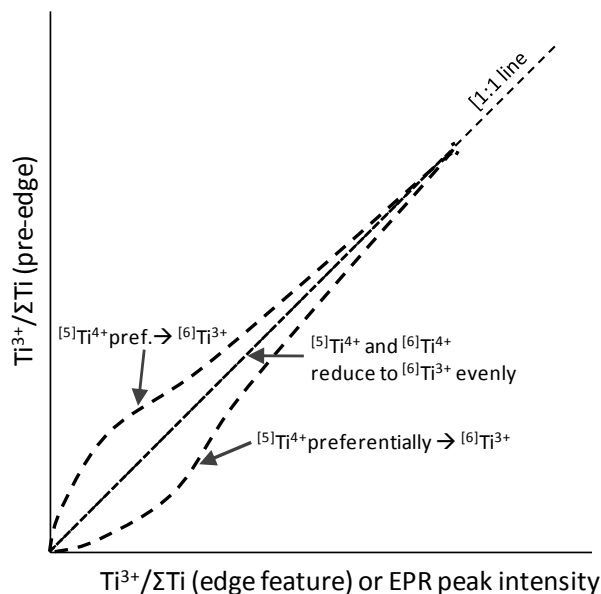


Figure 8-2 Schematic of the $\text{Ti}^{3+}/\Sigma\text{Ti}$ calculated using the pre-edge peak intensity (a) vs. that determined using the edge parameter ($E_{0.8}$) or the measured EPR peak intensity, as devised while analysing the spectral data collected from the Ti-CMAS glasses in this study.

9 References

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“How much better to get wisdom than gold; to choose understanding than silver!” Prov 16:16

A. Supplementary information for the calibration of the 1 atm gas-mixing furnace (Chapter 2)

A.1 Temperature calibration – the thermocouple experiment

Table A-1 Vertical thermal profile data for the IC furnace hotspot using three different conditions

T _p 1400 °C (no gas flowing)			T _p 1251 °C (100 sccm)			T _p 1417 °C (100 sccm)		
Distance (cm) †	Voltage (mV)	Temp (°C)	Distance (cm) †	Voltage (mV)	Temp (°C)	Distance (cm) †	Voltage (mV)	Temp (°C)
-	-	-	21.50	5.74	1096.0	22.00	-	-
-	-	-	22.90	6.15	1137.5	23.00	-	-
-	-	-	24.28	6.48	1170.2	23.85	8.14	1326.7
-	-	-	25.90	6.79	1200.4	26.00	8.52	1361.1
26.8	8.43	1352.8	27.00	6.93	1213.8	27.00	8.65	1372.7
27.9	8.54	1362.5	28.08	7.05	1225.3	28.00	8.75	1381.6
28.7	8.60	1368.1	29.29	7.15	1234.8	29.30	8.85	1390.5
29.8	8.66	1374.1	30.00	7.19	1238.6	30.05	8.89	1394.1
30.9	8.71	1378.6	30.95	7.24	1243.3	30.95	8.93	1397.7
31.9	8.75	1381.6	32.00	7.27	1246.1	32.28	8.97	1401.3
32.7	8.76	1383.4	33.05	7.30	1249.0	33.05	8.99	1403.0
33.7	8.78	1385.1	34.00	7.31	1249.9	34.15	9.00	1404.0
34.7	8.79	1386.1	35.00	7.32	1250.8	35.05	9.01	1404.8
35.7	8.80	1386.4	36.00	7.33	1251.8	36.00	9.01	1404.8
36.7	8.79	1386.1	37.00	7.32	1250.8	37.00	9.00	1404.0
37.7	8.78	1385.2	37.95	7.31	1249.9	38.00	8.99	1403.0
38.7	8.77	1383.8	39.00	7.29	1248.0	39.00	8.96	1400.4
39.7	8.74	1381.5	39.95	7.26	1245.2	40.00	8.93	1397.7
40.8	8.71	1378.2	40.95	7.23	1242.4	40.95	8.89	1394.1
41.8	8.67	1374.8	41.95	7.18	1237.6	42.00	8.84	1389.7
-	-	-	42.95	7.13	1232.9	43.20	8.76	1382.5
-	-	-	44.00	7.05	1225.3	44.00	8.69	1376.3
-	-	-	45.00	6.97	1217.6	45.00	-	-

Note: T_p = Programmed temperature. † Distance = Distance into furnace.

Table A-2 Temperature at the IC furnace hotspot with different gas flow

T _p (°C)	Distance into furnace (cm)	Voltage (mV)	Temperature (°C)	Gas flow (sccm)
1251	34.75	7.33	1251.8	200
1417	34.95	9.01	1404.8	80
	34.95	9.01	1404.8	100
	34.95	9.01	1404.8	200
	34.95	9.01	1404.8	200

Note: T_p = Programmed temperature.

Table A-3 Programmed temperature (T_p) and the hotspot temperature (T_H) 36 cm into the furnace with no gas flow

T _p (°C)	Voltage (mV)	T _H (°C)
1091	5.780	1100.0
1100	5.858	1108.0
1100	5.863	1108.5
1200	6.791	1200.4
1200	6.788	1200.1
1307	7.852	1300.4
1400	8.798	1385.9
1415	8.962	1400.5
1500	9.906	1483.3
1517	10.107	1500.6

A.2 Oxygen fugacity calibration

A.2.1 Gas mixtures

Table A-4 Gas mix ratios and fO_2 (1300 °C)

$\log fO_2$ at 1300°C	% gas flow	CO		% gas flow	CO ₂		Total sccm
		Channel (sccm)	sccm gas		Channel (sccm)	sccm gas	
-3	-	-	-	40.0	200	80.0	80.0
-11	42	200	84.0	9.5	200	19.0	103.0
-12	44	200	88.0	60.0	10	6.0	94.0
-13	44	200	88.0	20.0	10	2.0	90.0
-14	45	200	90.0	6.5	10	0.7	90.7
-16	40	200	80.0	-	-	-	80.0

Table A-5 - Gas mix ratios and fO_2 (1400 °C)

$\log fO_2$ at 1400°C	% gas flow	Ar [§]		% gas flow	CO		% gas flow	CO ₂		Total sccm
		Channel (sccm)	sccm gas		Channel (sccm)	sccm gas		Channel (sccm)	sccm gas	
-3	-	-	-	-	-	-	40	200	80	80.0
-9.4	-	-	-	50	200	100.0	20	200	40	140.0
-11	-	-	-	47	200	94.0	60	10	6	100.0
-12	-	-	-	50	200	100.0	20	10	2	102.0
-13	-	-	-	47	200	94.0	6	10	0.6	94.6
-13.5	-	-	-	70	200	140.0	5	10	0.5	140.5
-14	-	-	-	100	200	200.0	4	10	0.4	200.4
-16	-	-	-	40	200	80.0	-	-	-	80.0
-18	50	200	100	5.5	200	11.0	-	-	-	111.0
-20	50	200	100	10.1	10	1.0	-	-	-	101.0

Notes: [§] 100 sccm Ar flow regulated through the 200 sccm CO₂ mass flow controller set at 26%.

Additionally, the $\log fO_2$ of experiments prepared in air = -0.68 at 1400 °C (Berry and O'Neill, 2004).

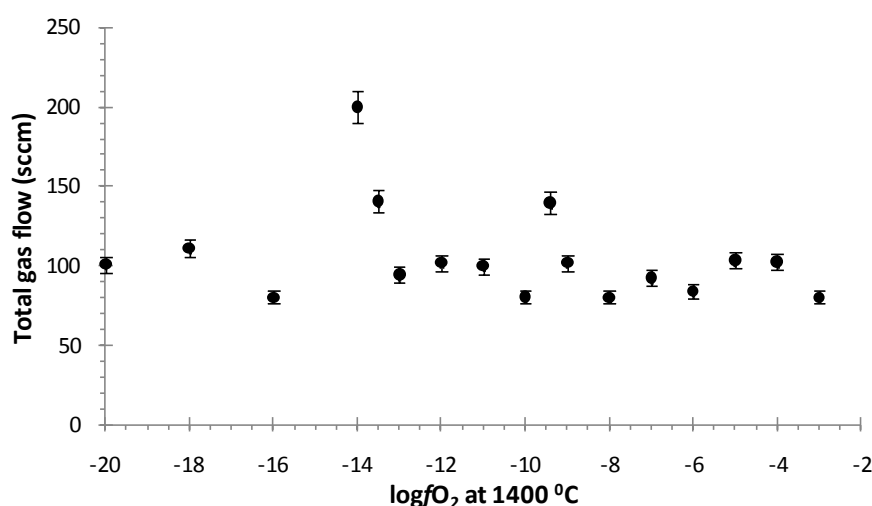


Figure A-1 Total gas flow (sccm) over the range of fO_2 studied, showing the averages flow is ~100 sccm. The error on the gas flow is shown as 5% (the tolerance level of the mass flow controller).

A.2.2 Fe-loop experiment

Table A-6 wt% Oxide elemental abundances of the Fe-loop glasses, and the calculated fO_2

Run number	Flow-controlled $\log fO_2$	Wt% oxide in glass †‡							Calculated number of moles							Calculated $\log X_{FeO}$	Calculated $\log fO_2$ §
		SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MgO	CaO	Total	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MgO	CaO	SUM		
IC25/08/09	-11	41.93	0.06	12.68	17.42	8.57	19.05	99.71	0.698	0.001	0.249	0.242	0.213	0.340	1.742	-0.86	-11.15
IC11/08/09	-12	47.81	0.06	14.42	5.72	9.88	21.97	99.86	0.796	0.001	0.283	0.080	0.245	0.392	1.796	-1.35	-12.14
IC15/08/09	-13	50.11	0.07	14.99	2.09	10.26	22.79	100.31	0.834	0.001	0.294	0.029	0.255	0.406	1.819	-1.80	-13.03
IC26/08/09	-13.5	49.57	0.06	14.72	1.22	9.98	22.56	98.11	0.825	0.001	0.289	0.017	0.248	0.402	1.781	-2.02	-13.48
IC06/08/09	-14	51.66	0.07	15.14	0.75	10.01	23.02	100.65	0.860	0.001	0.297	0.010	0.248	0.411	1.827	-2.24	-13.92

Note: †The initial oxide mixture was prepared by A Burnham. ‡ 10 analyses were made per sample using the WDS EMP by John Spratt (NHM). § The propagated error was calculated to be <0.1 $\log fO_2$ units by A Burnham who used the same dataset presented here.

Table A-7 Parameters for the step-wise solution of the fO_2 calibration

Parameter	Value	Data derived from:
Temperature in K	1677	Temp of experiment (1404 °C)
Y_{FeO}	1.367	O'Neill and Eggins (2002)
ΔG	-155838	Equation 9 of Holzheid <i>et al.</i> (1997), basis: $\Delta G = \Delta H - T\Delta S$
$\ln K$	11.177	$\Delta G = -RT \ln K$; where $R = 8.314472(15) \text{ JK}^{-1}\text{mol}^{-1}$
$\log K^{Fe-FeO(l)}$	4.854	From above; $K = (a_{FeO(l)}) / ((a_{Fe(s)})(a_{O_{2(g)}}^{0.5}))$; where a = activity of element or molecule

B. Supplementary information for the sample synthesis and characterisation (Chapter 3)

B.1 Sample synthesis

B.1.1 Starting material

Table B-1 Reagent information with oxide drying temperatures (where applicable)

Temp (°C)	Oxide	Ave % lost	Oxide from (Grade)	Product number	Batch / Lab number	Weight (g)
1000	Al ₂ O ₃	0%	BDH (AnalaR)	10008	91426300	1000
1000	MgO	24%	BDH (AnalaR)	10150	6651270	500
1000	SiO ₂	24%	BDH (Laboratory reagent)	15049	6693050	500
1000	TiO ₂ (1)	0%	Johnson Matthey Chemicals (SpecPure)	-	S.93895	10
1000	TiO ₂ (2)	1%	Johnson Matthey Chemicals (SpecPure)	Cat JMC435	S8074	5
1000	TiO ₂ (3)	0%	Koch-Light (laboratory reagent)	3N	29737	10
300	CaCO ₃	0%	BDH (AnalaR)	10068	6041830	500
300	Cr ₂ O ₃	0%	BDH (Laboratory reagent)	-	29721	500
300	Fe ₂ O ₃ (1)	1%	Johnson Matthey & Co. Ltd (SpecPure)	J.M. 850	S4559	50
300	Fe ₂ O ₃ (2)	0%	Johnson Matthey & Co. Ltd (SpecPure)	J.M.C. 850	581377	50
300	Fe ₂ O ₃ (3)		Sigma Aldrich Fe(III) oxide (99.98% pure)	203513	09405 MC	50
N/A	Ti ₂ O ₃	N/A	Sigma Aldrich Ti(III) oxide (99.9% pure)	481033	MKAA2345	10
N/A	Polyethylene Oxide	N/A	Alfa Aesar (Laboratory reagent)	K27N51	EG-500-038-2 25322-68-3	25

Notes: Oxide (#) = sequence of use. The table includes the product information for Polyethylene oxide (used as a binder) and Cr₂O₃ and Fe₂O₃ which were used for the synthesis of spinel in basaltic glass (Fe-isotope study).

B.1.2 Experimental details

Notes for Table B-2 and Table B-3:

Gas mixtures are detailed in Appendix A.2.1

Quench (Atm) = quenched to the furnace bottom;

Quench (Water) = quench into water beneath furnace (usually distilled water, 15 Ω MQ water).

“Glass series (x5)” = five samples, one of each composition (AD, AD+En, AD+Fo, AD+Qtz, AD+Wo).

Run number nomenclature: the date loaded, preceded by the furnace number:

B = produced at ANU (by ANU staff); IC = vertical CO-CO₂ gas-mixing furnace at Imperial College London.

Temperature of the hotspot was determined by the thermocouple experiment (error ~1 °C).

Table B-2 Details of synthesis experiments – Ti-bearing glasses

Run number	Sample	logfO ₂	°C	#Hrs	Mount	Extraction	Sample for
B17/4/08	AD (+1.5wt% TiO ₂)	-3	1404	1	Pt loop	Quench (Atm)	XPEEM
B18/4/08	AD (+1.5wt% TiO ₂)	-16	1404	12	Graphite	Quench (Atm)	XPEEM
IC3/8/09	Glass series (x5)	-16	1404	23	Small Graphite (6 pellet mount)	Quench (Water)	XANES
IC5/8/09	Glass series (x5)	-3	1404	22	Pt loop, Pt Chandelier	Quench (Water)	XANES
IC6/8/09	Glass series (x5)	-14	1404	20	Re Loop, Ceramic chandelier	Quench (Water)	XANES
IC11/8/09	Glass series (x5)	-12	1404	22	Pt loop, Pt Chandelier	Quench (Water)	XANES
IC15/8/09	Glass series (x5)	-13	1404	20	Re Loop, Ceramic chandelier	Quench (Water)	XANES
IC19/8/09	Glass series (x5)	-18	1404	20	Small Graphite (6 pellet mount)	Quench (Water)	XANES
IC20/8/09	Glass series (x5)	-20	1404	20	Small Graphite (6 pellet mount)	Quench (Water)	XANES
IC25/8/09	Glass series (x5)	-11	1404	19	Pt loop, Pt Chandelier	Quench (Water)	XANES
IC26/8/09	Glass series (x5)	-13.5	1404	19	Re Loop, Ceramic chandelier	Quench (Water)	XANES
IC20/10/09	AD+Fo (2 loops)	-3	1404	23	Pt loop, Pt Chandelier	Quench (Atm)	XPEEM
IC21/10/09	AD+Fo (2 loops)	-12	1404	41	Pt loop, Pt Chandelier	Quench (Atm)	XPEEM
IC23/10/09	AD+Fo (2 loops)	-13	1404	22	Re Loop, Ceramic chandelier	Quench (Atm)	XPEEM
IC24/10/09	AD+Fo (2 loops)	-14	1404	36	Re Loop, Ceramic chandelier	Quench (Atm)	XPEEM
IC26/10/09	AD+Fo (2 pellets)	-16	1404	24	Small Graphite (6 pellet mount)	Quench (Atm)	XPEEM
IC10/2/10	AD+Fo (x3); AD+En(x2)	-16	1404	40	Small Graphite (6 pellet mount)	Quench (Water)	XANES
IC12/2/10	Glass series (x5)	-9.4	1404	66	Re loops, Pt Chandelier	Quench (Water)	XANES
IC15/2/10	Glass series (x5)	-11	1404	41	Re loops, Pt Chandelier	Quench (Water)	XANES
IC17/2/10	Glass series (x5)	-12	1404	41	Re loops, Pt Chandelier	Quench (Water)	XANES
IC19/2/10	Glass series (x5)	-16	1404	44	Small Graphite (6 pellet mount)	Quench (Water)	XANES
IC10/1/11	AD (3 pellets)	-18	1404	20	Small Graphite (6 pellet mount)	Quench (Water)	EPR
IC11/1/11	AD (3 pellets)	-20	1404	20	Small Graphite (6 pellet mount)	Quench (Water)	EPR
IC12/1/11	AD (3 pellets)	-16	1404	20	Small Graphite (6 pellet mount)	Quench (Water)	EPR
IC13/1/11	AD (3 loops)	-3	1404	34	Pt loop, Pt Chandelier	Quench (Water)	EPR
IC15/1/11	AD (2 loops)	-13	1404	20	Re loop, Ceramic chandelier	Quench (Water)	EPR
IC16/1/11	AD (3 loops)	-12	1404	20	Re loop, Ceramic chandelier	Quench (Water)	EPR
IC17/1/11	AD (2 loops)	-11	1404	20	Re loop, Ceramic chandelier	Quench (Water)	EPR
IC18/1/11	AD (3 loops)	-13.5	1404	20	Re loop, Ceramic chandelier	Quench (Water)	EPR
IC20/1/11	AD (3 loops)	-14	1404	20	Re loop, Ceramic chandelier	Quench (Water)	EPR
IC21/1/11	AD (4 loops)	-9.4	1404	20	1 loop on Pt, 3 loops on Re; Pt Chandelier	Quench (Water)	EPR

Notes on page 217.

Table B-3 Details of synthesis experiments – Ti-bearing hibonite

Run number	Sample mixture	logfO ₂	°C	#Hrs	Mount	Extraction	Sinter
B15/04/08	Hib5, Hib7, Hib8	-16	1400	42	Graphite	Slow cool	Single sinter
B19/04/08	Hib1, Hib4, Hib3	-3	1400	14	Pt wire cage	Slow cool	Related to B14/4/08 (dropped off)
IC12/3/09	Hib11, Hib3, Hib10, Hib1, Hib9, Hib4	-0.68	1402	17	Pt chandelier	Slow cool	1 st sinter, IC23/3/09, IC27/3/09, 24/7/09 linked
IC23/3/09	Hib11, Hib3, Hib10, Hib1, Hib9, Hib4	-0.68	1402	36	Pt Baskets, Pt chandelier	Slow cool	2 nd sinter, IC12/3/09, IC27/3/09, 24/7/09 linked
IC27/3/09	Hib11, Hib3, Hib10, Hib1, Hib9, Hib4	-0.68	1402	71	Pt Baskets, Pt chandelier	Slow cool	3 rd sinter, IC12/3/09, IC23/3/09, 24/7/09 linked
IC24/7/09	Hib11, Hib3, Hib10, Hib1, Hib9, Hib4	-3	1402	63	Pt Baskets, Pt chandelier	Quench (Water)	4 th sinter, IC12/3/09, IC23/3/09, IC27/3/09 linked
IC31/7/09	Hib8	-16	1402	13	Small Graphite (6 pellets)	Slow cool	1 st sinter, IC1/8/09 linked
IC1/8/09	Hib8	-16	1402	36	Small Graphite (6 pellets)	Slow cool	2 nd sinter (combined with IC13/8/09 & IC18/8/09)
IC4/8/09	HibA	-3	1405	12	Pt Bucket	Slow cool	1 st sinter, IC7/8/09 linked
IC7/8/09	HibA	-3	1405	36	Pt Bucket	Slow cool	2 nd sinter, IC4/8/09 linked
IC9/8/09	Hib4,HibB	-3	1405	36	Pt Bucket	Slow cool	Single sinter (aborted due to loss of H ₂ O)
IC12/8/09	Hib9	-3	1405	12	Pt Bucket	Slow cool	1 st sinter, IC27/8/09 linked
IC13/8/09	HibC	-16	1402	22	Small Graphite (6 pellets)	Slow cool	Single sinter (combined with IC1/8/09 & IC18/8/09)
IC14/8/09	Hib7	-16	1402	12	Small Graphite (6 pellets)	Slow cool	Single sinter
IC16/8/09	Hib5	-16	1402	35	Small Graphite (6 pellets)	Slow cool	Single sinter (combined with IC21/8/09 & IC23/8/09)
IC18/8/09	HibC	-16	1402	20	Small Graphite (6 pellets)	Slow cool	Single sinter (combined with IC1/8/09 & IC13/8/09)
IC21/8/09	Hib5	-16	1402	31	Small Graphite (6 pellets)	Slow cool	Single sinter (combined with IC16/8/09 & IC23/8/09)
IC23/8/09	Hib5, HibD	-16	1402	24	Small Graphite (6 pellets)	Slow cool	Single sinter (combined with IC16/8/09 & IC21/8/09)
IC24/8/09	HibE	-3	1405	16	Pt Bucket	Slow cool	1 st sinter, IC1/9/09 linked
IC27/8/09	Hib9	-3	1405	32	Pt Bucket	Slow cool	2 nd sinter, IC12/8/09 linked
IC29/8/09	HibF	-16	1405	37	Large Graphite	Slow cool	Single sinter
IC31/8/09	Hib1, HibF, HibG, HibH, HibJ, HibK	-16	1402	24	Small Graphite (6 pellets)	Slow cool	Single sinter
IC1/9/09	HibE	-3	1405	33	Pt Bucket	Slow cool	2 nd sinter, IC24/9/09 linked
IC3/9/09	HibK	-16	1405	28	Large Graphite	Slow cool	Single sinter
IC6/9/09	HibT	-16	1405	22	Large Graphite	Slow cool	Single sinter
IC7/9/09	HibJ	-16	1405	33	Large Graphite	Slow cool	Single sinter
IC9/9/09	HibN	-16	1405	40	Large Graphite	Slow cool	Single sinter
IC12/9/09	Hib7, Hib1, HibG	-12	1402	40	Pt Baskets, Pt chandelier	Slow cool	Single sinter
IC14/9/09	Hib10, Hib1	-4	1300	43	Pt Bucket & Basket	Slow cool	Single sinter
IC16/9/09	HibG	-18	1300	46	Large Graphite	Slow cool	Single sinter
IC19/9/09	Hib7	-18	1300	42	Large Graphite	Slow cool	Single sinter

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B.2 Characterisation

B.2.1 Composition data

B.2.1.1 Microprobe Detection Limits

The lower limit of detection (lld) for the EDS SEM is calculated to be 3 x background (i.e. 3 x elemental wt% sigma). As such the lld of each analysis was individually determined.

Table B-4 Representative* lower limits of detection (lld) of the EDS SEM and WDS EMP for the major phases in this study.

Formula	Hibonite			Glass	
	SEM (10 kV)	SEM (20 kV)	EMP (20 kV)	SEM (20 kV)	EMP (20 kV)
SiO ₂	0.6	nd	0.06	1.5	0.04
Al ₂ O ₃	2.2	1.5	0.08	0.7	0.02
CaO	1.2	0.5	0.07	0.7	0.03
MgO	0.7	0.5	0.02	0.8	0.03
TiO ₂	2.3	0.7	0.08	0.4	0.03
FeO	nd	0.5	0.03	0.4	nd
Cr ₂ O ₃	nd	nd	0.03	nd	nd
V ₂ O ₅	nd	0.5	nd	nd	nd
Na ₂ O	0.5	nd	0.03	nd	nd
S	nd	nd	0.02	0.2	nd
Si	0.3	nd	0.03	0.7	0.02
Al	1.2	0.8	0.04	0.4	0.01
Ca	0.9	0.4	0.05	0.5	0.02
Mg	0.5	0.3	0.01	0.5	0.02
Ti	1.4	0.4	0.05	0.2	0.02
Fe	nd	0.4	0.02	0.3	nd
Cr	nd	nd	0.02	nd	nd
V	nd	0.3	nd	nd	nd
Na	0.4	nd	0.02	nd	nd
S	nd	nd	0.02	0.2	nd

Notes:

nd: The element was either not selected for EMP analysis (i.e. not determined), or below SEM lld (i.e. no detail).

* The hibonite lld (SEM, 10 kV) is the "upper" limit of 11 synthetic hibonite analyses (HibF, HibK, Hib8C, HibE, HibT). The hibonite lld (SEM, 20 kV) is based on 11 analyses from 3 CAIs (Acfer094/22CAI, NWA2446(PL04157B) and NWA2446(PL07041)); and the hibonite lld (EMP) based on 44 analyses in 2 CAIs (Acfer094/22CAI and El Djouf001/CAI). The lld for the SEM glass is an average of four AD+Qtz and AD+En glass analyses and one forsterite analysis.

In many cases the actual limit of detection is lower than that stated below, for example: the lld for HibF(20,0) was 1.3 wt% TiO₂, whereas that quoted in Table B-4 is for HibE(98,91) (2.3 wt% TiO₂).

B.2.1.2 XANES glasses: additional information

Table B-5 The AD glass composition in wt% oxide as an example of the effect of (a) different mount used and (b) different standard used when making analysis

<i>a or b</i>	<i>fO₂</i>	Run number	SiO ₂	Al ₂ O ₃	CaO	MgO	TiO ₂	S	FeO	Total	No. analyses
Pt	ΔIW-1.5	IC25/8/09	49.6 (0.6)	14.6 (0.1)	23.5 (0.3)	10.3 (0.1)	0.8 (0.1)	<lld	<lld	98.8 (0.5)	4
	ΔIW-2.5	IC11/8/09	51.2 (0.4)	14.9 (0.3)	23.6 (0.3)	10.6 (0.2)	0.6 (0.1)	<lld	<lld	100.8 (0.7)	3
Re	ΔIW-1.5	IC15/2/10	49.02 (0.22)	15.33 (0.05)	22.71 (0.14)	10.56 (0.04)	1.03 (0.02)	<lld	<lld	98.68 (0.33)	9
	ΔIW-2.5	IC17/2/10	50.51 (0.15)	15.27 (0.07)	23.27 (0.07)	10.53 (0.05)	1.02 (0.02)	<lld	0.05 (0.00)	100.64 (0.28)	12
ZnS	ΔIW-6.5	IC19/2/10	49.43 (0.47)	15.50 (0.16)	23.63 (0.06)	10.54 (0.05)	1.04 (0.01)	0.05 (0.01)	<lld	100.20 (0.68)	9
	ΔIW-8.5	IC19/8/09	50.16 (0.10)	15.67 (0.09)	23.57 (0.08)	10.70 (0.02)	1.05 (0.02)	0.11 (0.02)	<lld	101.28 (0.22)	9
	ΔIW-10.5	IC20/8/09	49.88 (0.26)	15.65 (0.12)	23.67 (0.05)	10.62 (0.07)	1.05 (0.01)	0.26 (0.01)	<lld	101.15 (0.45)	9
BaSO ₄	ΔIW-6.5	IC19/2/10	49.20 (0.62)	15.48 (0.27)	23.56 (0.10)	10.70 (0.11)	1.06 (0.02)	0.03 (0.01)	<lld	100.03 (0.91)	10
	ΔIW-8.5	IC19/8/09	49.77 (0.21)	15.56 (0.08)	23.47 (0.07)	10.76 (0.06)	1.05 (0.01)	0.08 (0.00)	<lld	100.70 (0.32)	12
	ΔIW-10.5	IC20/8/09	49.45 (0.26)	15.47 (0.10)	23.67 (0.07)	10.71 (0.05)	1.04 (0.01)	0.19 (0.01)	<lld	100.54 (0.41)	10

Notes: All analysed by WDS EMP apart from IC11/8/09 and IC25/8/09, which were analysed by EDS SEM (standard deviation in parentheses). The oxidation state of S is -2, but is reported as elemental wt%. A graphical representation of the S-content determined using the two standards is shown in Figure B-1.

Figure B-1 S-content determined using the ZnS standard ($S_{(ZnS)}$) compared to that determined from the BaSO₄ standard ($S_{(BaSO_4)}$) showing a positive linear correlation as detailed below

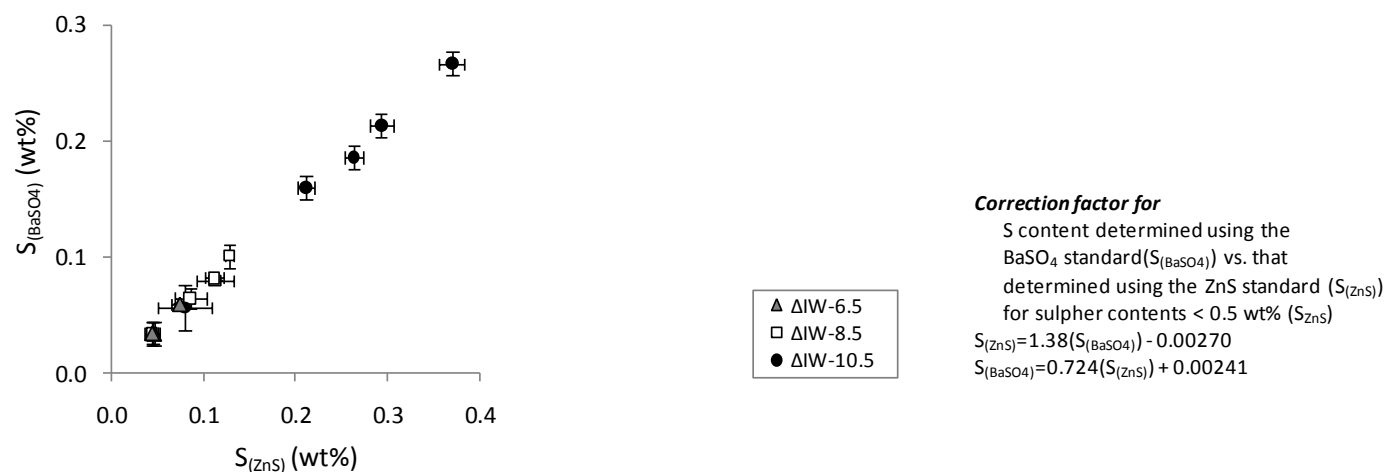


Table B-6 Mg₂SiO₄ crystals in AD+En

fO_2	$\log fO_2$ @ 1400 °C (run number)	SiO ₂	Al ₂ O ₃	CaO	MgO	TiO ₂	S	FeO	Total	No. analyses
$\Delta IW+6.5$	-3 (IC5/8/09)	42.73 nd	1.10 nd	1.36 nd	54.63 nd	0.12 nd	<lld	<lld nd	99.94 nd	1
$\Delta IW-2.5$	-12 (IC17/2/10)	41.97 (0.29)	<lld	0.36 (0.01)	57.75 (0.40)	<lld	<lld	0.04 (0.01)	100.17 (0.69)	4
$\Delta IW-4$	-13.5 (IC26/8/09)	42.84 (0.11)	<lld	0.39 (0.01)	57.90 (0.06)	0.04 (0.01)	<lld	0.27 (0.01)	101.46 (0.10)	4
$\Delta IW-4.5$	-14 (IC6/8/09)	42.78 (0.34)	0.03 (0.01)	0.40 (0.02)	58.00 (0.22)	0.04 (0.01)	<lld	0.21 (0.04)	101.46 (0.51)	9
$\Delta IW-6.5$	-16 (IC19/2/10)	41.62 (0.20)	0.04 (0.01)	0.38 (0.03)	56.98 (0.18)	0.06 (0.01)	<lld	<lld	99.09 (0.37)	4
$\Delta IW-8.5$	-18 (IC19/8/09)	42.53 (0.14)	0.03 (0.01)	0.40 (0.03)	57.71 (0.19)	0.07 (0.01)	<lld	<lld	100.74 (0.29)	6
$\Delta IW-10.5$	-20 (IC20/8/09)	42.99 (0.24)	0.04 (0.01)	0.40 (0.05)	57.82 (0.20)	0.07 (0.01)	<lld	<lld	101.31 (0.11)	2
Average		42.46 (0.54)	0.02 (0.02)	0.39 (0.02)	57.69 (0.36)	0.05 (0.03)	<lld	<lld	100.71 (0.94)	29

Notes: Analysis by WDS EMP (standard deviation in parentheses). Sample mounting material as follows: $\leq \Delta IW-6.5$ in Graphite, $\Delta IW-4.5$ to $\Delta IW+0.1$ on Re and $> \Delta IW+6.5$ on Pt.

The higher Al₂O₃ content in the crystals from IC5/8/09 show that the analysis is likely contaminated by the surrounding glass. It is retained in the table to show the crystals form in both reducing and oxidising conditions, and is not included in the average.

B.2.1.3 Hibonite compositions

Table B-7 Ideal composition of hibonite mixtures for the samples prepared for HRPD analysis.

Neutron Sample name	Idealised site Saturation	Ideal wt% oxide					%Ti ³⁺
		CaO	Al ₂ O ₃	TiO ₂	MgO	Total	
HibF(20,0)	25%satM2	8.3582	89.2620	2.9758	N/A	100.5961	100.0
Hib5D(33,0)	50%Sat M2	8.2692	86.4323	5.8883	N/A	100.5897	100.0
HibK(62,24)	75%SatM2;25%SatM4	8.2456	83.3748	7.3393	1.4811	100.4407	59.7
Hib8C(73,49)	50%SatM2;50%SatM4	8.2221	80.3352	8.7821	2.9537	100.2932	33.3
HibJ(80,62)	25%SatM2;75%SatM4	8.1988	77.3126	4.4180	10.2167	100.1461	14.7
Hib9(44,43)	25%SatM4	8.2856	82.8380	5.8999	2.9765	100.0000	0.0
HibE(98,91)	50%SatM4	8.1756	74.3073	11.6431	5.8740	100.0000	0.0
HibT(137,83)	65%SatM2;40%SatM4	8.0016	69.8169	17.0930	5.1741	100.0856	40.0
HibN(46,40)	7%SatTi ³⁺ 48%SatTi ⁴⁺	8.2723	82.4896	6.4453	2.8623	100.0695	12.7
Neutron Sample name	Ideal Stoichiometry (where Ca _{1.00} and O _{19.00})	Ideal wt% element					Total
		Ca	Al	Ti	Mg	O	
HibF(20,0)	CaAl _{11.75} Ti _{0.25} O ₁₉	5.9562	47.0995	1.7784	N/A	45.1658	100.0000
Hib5D(33,0)	CaAl _{11.50} Ti _{0.50} O ₁₉	5.9104	45.7423	3.5294	N/A	44.8179	100.0000
HibK(62,24)	CaAl _{11.13} Ti _{0.63} Mg _{0.25} O ₁₉	5.8935	44.1243	4.3992	0.8931	44.6899	100.0000
Hib8C(73,49)	CaAl _{10.75} Ti _{0.75} Mg _{0.50} O ₁₉	5.8767	42.5156	5.2640	1.7810	44.5627	100.0000
HibJ(80,62)	CaAl _{10.37} Ti _{0.88} Mg _{0.75} O ₁₉	5.8600	40.9160	2.6640	6.1239	44.4362	100.0000
Hib9(44,43)	CaAl _{11.00} Ti _{0.50} Mg _{0.50} O ₁₉	5.9221	43.8401	3.5364	1.7948	44.9066	100.0000
HibE(98,91)	CaAl _{10.00} Ti _{1.00} Mg _{1.00} O ₁₉	5.8434	39.3254	6.9789	3.5419	44.3103	100.0000
HibT(137,83)	CaAl _{9.60} Ti _{1.50} Mg _{0.90} O ₁₉	5.7535	37.1717	10.3073	3.1387	43.6288	100.0000
HibN(46,40)	CaAl _{10.97} Ti _{0.55} Mg _{0.48} O ₁₉	5.9130	43.6591	3.8636	1.7261	44.8382	100.0000

Note: Weighing error ~0.02 wt%, calculated as the difference between the target and actual TiO₂ weighed w.r.t. the target weight.

Table B-8 Individual hibonite analyses for the large-volume synthetic hibonite samples (EDS SEM analysis; composition/mixture name used)

Sample	wt% Oxide					wt% element						Number of cations based on 19 O						Analysis detail	
	CaO	Al ₂ O ₃	TiO ₂	MgO	Total	Ca	Al	Ti	Mg	O	Total	Ca	Al	Ti	Mg	O	%Ti ³⁺	SOI	Spectrum
Hib5	8.9	86.4	4.1	<lld	99.4	6.4	45.7	2.5	<lld	44.9	99.4	1.07	11.48	0.35	0.00	19	100	SOI1	Spectrum 1
Hib5	8.9	87.3	3.9	<lld	100.1	6.3	46.2	2.4	<lld	45.2	100.1	1.06	11.52	0.33	0.00	19	100	SOI1	Spectrum 2
Hib5	8.7	87.1	5.0	<lld	100.8	6.2	46.1	3.0	<lld	45.5	100.8	1.03	11.42	0.42	0.00	19	100	SOI1	Spectrum 3
Hib5	9.2	87.1	4.0	<lld	100.3	6.6	46.1	2.4	<lld	45.2	100.3	1.11	11.48	0.33	0.00	19	100	SOI1	Spectrum 4
Hib5	8.5	86.4	3.9	<lld	98.8	6.1	45.7	2.3	<lld	44.7	98.8	1.03	11.54	0.33	0.00	19	100	SOI3	Spectrum 1
Hib5	8.8	86.2	4.2	<lld	99.2	6.3	45.6	2.5	<lld	44.8	99.2	1.06	11.48	0.36	0.00	19	100	SOI3	Spectrum 2
Hib5	9.0	87.6	4.0	<lld	100.5	6.4	46.4	2.4	<lld	45.4	100.5	1.07	11.51	0.33	0.00	19	100	SOI3	Spectrum 3
Hib5	9.6	87.1	3.8	<lld	100.5	6.8	46.1	2.3	<lld	45.3	100.5	1.15	11.47	0.32	0.00	19	100	SOI3	Spectrum 4
Hib5	8.6	87.1	4.4	<lld	100.2	6.2	46.1	2.7	<lld	45.2	100.2	1.04	11.48	0.37	0.00	19	100	SOI3	Spectrum 5
Hib5	9.1	86.4	3.1	<lld	98.6	6.5	45.8	1.9	<lld	44.5	98.6	1.11	11.58	0.26	0.00	19	100	SOI4	Spectrum 1
Hib5	9.1	86.1	4.0	<lld	99.1	6.5	45.6	2.4	<lld	44.7	99.1	1.10	11.49	0.34	0.00	19	100	SOI4	Spectrum 2
Hib5	8.6	85.8	4.2	<lld	98.5	6.1	45.4	2.5	<lld	44.5	98.5	1.04	11.49	0.36	0.00	19	100	SOI4	Spectrum 3
Hib5	9.3	86.3	3.8	<lld	99.4	6.7	45.7	2.3	<lld	44.8	99.4	1.13	11.49	0.32	0.00	19	100	SOI4	Spectrum 4
Hib5	8.5	87.2	3.7	<lld	99.4	6.1	46.2	2.2	<lld	45.0	99.4	1.02	11.57	0.31	0.00	19	100	SOI4	Spectrum 5
Hib5	8.7	86.8	3.7	<lld	99.3	6.2	46.0	2.2	<lld	44.9	99.3	1.05	11.54	0.32	0.00	19	100	SOI6	Spectrum 2
Hib5	8.7	88.0	4.6	<lld	101.4	6.2	46.6	2.8	<lld	45.8	101.4	1.03	11.47	0.38	0.00	19	100	SOI6	Spectrum 3
Hib5	8.7	86.3	3.6	<lld	98.7	6.3	45.7	2.2	<lld	44.6	98.7	1.06	11.55	0.31	0.00	19	100	SOI6	Spectrum 4
Hib5	8.2	87.3	3.9	<lld	99.3	5.9	46.2	2.3	<lld	45.0	99.3	0.99	11.57	0.33	0.00	19	100	SOI6	Spectrum 5
Hib5	9.0	86.0	3.9	<lld	98.8	6.4	45.5	2.3	<lld	44.6	98.8	1.09	11.50	0.33	0.00	19	100	SOI6	Spectrum 6
Hib5	8.8	87.2	3.3	<lld	99.3	6.3	46.2	2.0	<lld	44.9	99.3	1.06	11.58	0.28	0.00	19	100	SOI7	Spectrum 1
Hib5	8.7	87.0	3.6	<lld	99.2	6.2	46.0	2.1	<lld	44.9	99.2	1.05	11.56	0.30	0.00	19	100	SOI7	Spectrum 2
Hib5	8.8	86.9	3.0	<lld	98.7	6.3	46.0	1.8	<lld	44.6	98.7	1.07	11.61	0.25	0.00	19	100	SOI7	Spectrum 3
Hib5	8.8	86.6	4.1	<lld	99.4	6.3	45.8	2.4	<lld	44.9	99.4	1.06	11.50	0.34	0.00	19	100	SOI7	Spectrum 4
Hib5	8.6	86.2	3.9	<lld	98.7	6.2	45.6	2.3	<lld	44.6	98.7	1.05	11.53	0.33	0.00	19	100	SOI7	Spectrum 5
Hib5	8.5	86.0	3.6	<lld	98.1	6.1	45.5	2.2	<lld	44.4	98.1	1.04	11.56	0.31	0.00	19	100	SOI7	Spectrum 6
Hib5	8.7	85.6	4.7	<lld	98.9	6.2	45.3	2.8	<lld	44.6	98.9	1.06	11.44	0.40	0.00	19	100	SOI8	Spectrum 1
Hib5	9.2	87.1	4.4	<lld	100.7	6.6	46.1	2.6	<lld	45.4	100.7	1.10	11.44	0.37	0.00	19	100	SOI8	Spectrum 2
Hib5	9.6	86.7	4.4	<lld	100.7	6.9	45.9	2.7	<lld	45.3	100.7	1.15	11.41	0.37	0.00	19	100	SOI8	Spectrum 3
Hib5	8.8	86.8	3.9	<lld	99.6	6.3	46.0	2.4	<lld	45.0	99.6	1.06	11.51	0.33	0.00	19	100	SOI8	Spectrum 4
Hib5	8.6	87.2	4.2	<lld	99.9	6.1	46.1	2.5	<lld	45.1	99.9	1.03	11.52	0.35	0.00	19	100	SOI8	Spectrum 5
Hib5	8.8	86.7	4.0	<lld	99.5	6.3	45.9	2.4	<lld	44.9	99.5	1.07	11.51	0.33	0.00	19	100	Average of 30	
	0.3	0.6	0.4		0.8	0.2	0.3	0.3		0.3	0.8	0.04	0.05	0.04	0.00			Standard deviation	

Continued...

Sample	CaO	Al ₂ O ₃	TiO ₂	MgO	Total	Ca	Al	Ti	Mg	O	Total	Ca	Al	Ti	Mg	O	%Ti ³⁺	SOI	Spectrum
HibF	9.2	87.2	2.5	<lld	98.9	6.6	46.1	1.5	<lld	44.7	98.9	1.12	11.63	0.22	0.00	19	100	SOI10	Spectrum 1
HibF	8.3	87.9	2.9	<lld	99.1	6.0	46.5	1.7	<lld	44.9	99.1	1.01	11.67	0.24	0.00	19	100	SOI10	Spectrum 2
HibF	9.0	87.4	1.9	<lld	98.3	6.4	46.3	1.1	<lld	44.5	98.3	1.10	11.72	0.16	0.00	19	100	SOI10	Spectrum 3
HibF	8.4	87.7	2.6	<lld	98.6	6.0	46.4	1.5	<lld	44.7	98.6	1.02	11.69	0.22	0.00	19	100	SOI10	Spectrum 4
HibF	8.5	88.5	2.2	<lld	99.2	6.1	46.8	1.3	<lld	45.0	99.2	1.03	11.73	0.19	0.00	19	100	SOI10	Spectrum 5
HibF	8.9	88.2	2.2	<lld	99.3	6.3	46.7	1.3	<lld	44.9	99.3	1.07	11.70	0.19	0.00	19	100	SOI11	Spectrum 1
HibF	9.0	88.7	1.9	<lld	99.7	6.4	47.0	1.2	<lld	45.1	99.7	1.08	11.73	0.16	0.00	19	100	SOI11	Spectrum 2
HibF	8.6	87.9	2.1	<lld	98.6	6.2	46.5	1.3	<lld	44.7	98.6	1.04	11.73	0.18	0.00	19	100	SOI11	Spectrum 3
HibF	8.6	88.8	2.1	<lld	99.5	6.2	47.0	1.3	<lld	45.1	99.5	1.04	11.74	0.18	0.00	19	100	SOI11	Spectrum 5
HibF	8.5	88.8	2.1	<lld	99.4	6.1	47.0	1.2	<lld	45.1	99.4	1.02	11.75	0.17	0.00	19	100	SOI11	Spectrum 6
HibF	8.7	88.3	1.7	<lld	98.7	6.2	46.7	1.0	<lld	44.7	98.7	1.05	11.77	0.14	0.00	19	100	SOI12	Spectrum 1
HibF	8.4	87.9	1.9	<lld	98.2	6.0	46.5	1.2	<lld	44.6	98.2	1.02	11.77	0.16	0.00	19	100	SOI12	Spectrum 2
HibF	8.5	87.6	2.4	<lld	98.5	6.1	46.3	1.5	<lld	44.6	98.5	1.04	11.70	0.21	0.00	19	100	SOI12	Spectrum 3
HibF	8.6	87.7	1.9	<lld	98.2	6.1	46.4	1.2	<lld	44.5	98.2	1.05	11.75	0.16	0.00	19	100	SOI12	Spectrum 5
HibF	8.9	89.4	1.6	<lld	99.9	6.3	47.3	1.0	<lld	45.3	99.9	1.06	11.77	0.14	0.00	19	100	SOI12	Spectrum 6
HibF	9.0	89.0	1.7	<lld	99.7	6.4	47.1	1.0	<lld	45.1	99.7	1.08	11.76	0.14	0.00	19	100	SOI13	Spectrum 1
HibF	8.9	87.8	2.1	<lld	98.8	6.4	46.5	1.3	<lld	44.7	98.8	1.08	11.71	0.18	0.00	19	100	SOI13	Spectrum 3
HibF	8.6	88.9	1.9	<lld	99.3	6.1	47.0	1.1	<lld	45.0	99.3	1.03	11.77	0.16	0.00	19	100	SOI13	Spectrum 4
HibF	9.0	89.1	1.9	<lld	100.1	6.5	47.2	1.2	<lld	45.3	100.1	1.08	11.73	0.16	0.00	19	100	SOI13	Spectrum 5
HibF	8.3	88.5	2.2	<lld	99.1	5.9	46.9	1.3	<lld	44.9	99.1	1.00	11.75	0.19	0.00	19	100	SOI14	Spectrum 1
HibF	9.2	87.4	2.5	<lld	99.1	6.6	46.2	1.5	<lld	44.7	99.1	1.12	11.64	0.21	0.00	19	100	SOI14	Spectrum 2
HibF	8.8	88.9	2.1	<lld	99.8	6.3	47.1	1.3	<lld	45.2	99.8	1.06	11.72	0.18	0.00	19	100	SOI14	Spectrum 3
HibF	8.7	88.7	1.7	<lld	99.1	6.2	47.0	1.0	<lld	44.9	99.1	1.05	11.78	0.15	0.00	19	100	SOI14	Spectrum 4
HibF	8.9	88.0	2.5	<lld	99.3	6.4	46.6	1.5	<lld	44.9	99.3	1.07	11.67	0.21	0.00	19	100	SOI15	Spectrum 1
HibF	8.5	89.3	2.4	<lld	100.2	6.1	47.3	1.4	<lld	45.4	100.2	1.01	11.73	0.20	0.00	19	100	SOI15	Spectrum 2
HibF	9.4	88.2	2.4	<lld	100.0	6.7	46.7	1.4	<lld	45.2	100.0	1.13	11.64	0.20	0.00	19	100	SOI15	Spectrum 4
HibF	9.3	88.2	2.6	<lld	100.1	6.6	46.7	1.5	<lld	45.2	100.1	1.11	11.64	0.21	0.00	19	100	SOI5	Spectrum 1
HibF	9.3	87.9	2.9	<lld	100.1	6.7	46.5	1.7	<lld	45.2	100.1	1.12	11.60	0.24	0.00	19	100	SOI5	Spectrum 2
HibF	9.1	88.8	2.8	<lld	100.6	6.5	47.0	1.7	<lld	45.5	100.6	1.08	11.64	0.23	0.00	19	100	SOI5	Spectrum 3
HibF	9.4	89.1	2.9	<lld	101.4	6.7	47.1	1.8	<lld	45.8	101.4	1.11	11.60	0.24	0.00	19	100	SOI5	Spectrum 4
HibF	9.0	88.3	3.7	<lld	100.4	6.5	46.4	2.2	<lld	45.3	100.4	1.08	11.53	0.31	0.00	19	100	SOI5	Spectrum 5
HibF	8.9	87.6	3.4	<lld	99.9	6.4	46.4	2.0	<lld	45.1	99.9	1.07	11.57	0.28	0.00	19	100	SOI7	Spectrum 2
HibF	9.1	87.2	3.2	<lld	99.4	6.5	46.1	1.9	<lld	44.9	99.4	1.10	11.58	0.27	0.00	19	100	SOI7	Spectrum 3
HibF	8.5	87.8	2.6	<lld	98.8	6.0	46.5	1.5	<lld	44.8	98.8	1.02	11.69	0.22	0.00	19	100	SOI8	Spectrum 1
HibF	8.7	87.8	3.3	<lld	99.8	6.2	46.5	2.0	<lld	45.1	99.8	1.04	11.60	0.28	0.00	19	100	SOI8	Spectrum 2
HibF	8.8	87.5	2.9	<lld	99.1	6.3	46.3	1.7	<lld	44.8	99.1	1.06	11.63	0.24	0.00	19	100	SOI8	Spectrum 3
HibF	9.9	87.5	3.1	<lld	100.5	7.1	46.3	1.9	<lld	45.3	100.5	1.18	11.53	0.26	0.00	19	100	SOI8	Spectrum 4
HibF	8.8	88.2	2.4	<lld	99.4	6.3	46.7	1.4	<lld	45.0	99.4	1.07	11.69	0.20	0.00	19	100	Average of 37	
	0.4	0.6	0.5		0.7	0.3	0.3	0.3		0.3	0.7	0.04	0.07	0.04	0.00			Standard deviation	

Sample	wt% Oxide					wt% element						Number of cations based on 19 O					%Ti ³⁺	Analysis detail	
	CaO	Al ₂ O ₃	TiO ₂	MgO	Total	Ca	Al	Ti	Mg	O	Total	Ca	Al	Ti	Mg	O		SOI	Spectrum
HibK	8.5	83.0	7.6	1.6	100.8	6.1	43.9	4.6	1.0	45.2	100.8	1.02	10.95	0.64	0.27	19	57	SOI1	Spectrum 1
HibK	8.6	83.2	7.1	1.4	100.3	6.1	44.0	4.2	0.9	45.0	100.3	1.03	11.02	0.60	0.24	19	60	SOI1	Spectrum 2
HibK	8.5	81.9	8.0	1.4	99.8	6.0	43.3	4.8	0.9	44.7	99.8	1.02	10.91	0.68	0.24	19	65	SOI1	Spectrum 3
HibK	8.3	82.5	6.8	1.3	98.9	5.9	43.7	4.1	0.8	44.5	98.9	1.01	11.07	0.58	0.23	19	61	SOI1	Spectrum 4
HibK	8.8	83.2	7.7	1.7	101.4	6.3	44.1	4.6	1.0	45.4	101.4	1.05	10.92	0.64	0.28	19	56	SOI1	Spectrum 5
HibK	8.7	83.4	6.3	1.4	99.8	6.2	44.2	3.8	0.9	44.8	99.8	1.05	11.10	0.53	0.24	19	55	SOI1	Spectrum 6
HibK	8.2	82.7	7.2	1.4	99.4	5.8	43.8	4.3	0.9	44.7	99.4	0.99	11.03	0.61	0.24	19	60	SOI2	Spectrum 1
HibK	9.2	82.3	7.9	1.4	100.8	6.6	43.6	4.7	0.9	45.1	100.8	1.11	10.88	0.67	0.24	19	65	SOI2	Spectrum 2
HibK	9.0	82.8	7.8	1.4	101.1	6.4	43.8	4.7	0.9	45.3	101.1	1.08	10.91	0.66	0.24	19	64	SOI2	Spectrum 3
HibK	8.6	82.6	7.8	1.5	100.4	6.1	43.7	4.7	0.9	45.0	100.4	1.03	10.94	0.66	0.25	19	62	SOI2	Spectrum 4
HibK	9.2	82.9	7.1	1.5	100.8	6.6	43.9	4.3	0.9	45.1	100.8	1.11	10.96	0.60	0.25	19	58	SOI3	Spectrum 1
HibK	9.2	82.2	7.6	1.7	100.5	6.6	43.5	4.5	1.0	45.0	100.5	1.10	10.90	0.64	0.28	19	57	SOI3	Spectrum 10
HibK	8.8	83.0	6.7	1.3	99.8	6.3	43.9	4.0	0.8	44.8	99.8	1.06	11.05	0.57	0.23	19	61	SOI3	Spectrum 3
HibK	8.5	83.7	6.7	1.4	100.4	6.1	44.3	4.0	0.9	45.1	100.4	1.02	11.07	0.57	0.24	19	58	SOI3	Spectrum 5
HibK	9.0	84.0	7.1	1.4	101.5	6.5	44.4	4.2	0.8	45.5	101.5	1.08	11.01	0.59	0.23	19	61	SOI3	Spectrum 8
HibK	9.1	82.6	6.7	1.8	100.3	6.5	43.7	4.0	1.1	44.9	100.3	1.10	10.98	0.57	0.30	19	47	SOI3	Spectrum 9
HibK	8.7	82.1	7.9	1.3	99.9	6.2	43.4	4.7	0.8	44.8	99.9	1.05	10.93	0.67	0.21	19	68	SOI4	Spectrum 2
HibK	8.7	82.7	7.8	1.5	100.8	6.2	43.8	4.7	0.9	45.2	100.8	1.05	10.92	0.66	0.25	19	62	SOI4	Spectrum 3
HibK	8.8	81.8	7.6	1.6	99.9	6.3	43.3	4.6	1.0	44.7	99.9	1.07	10.91	0.65	0.27	19	58	SOI4	Spectrum 4
HibK	8.1	82.4	7.6	1.3	99.3	5.8	43.6	4.6	0.8	44.6	99.3	0.98	11.01	0.65	0.22	19	67	SOI4	Spectrum 5
HibK	8.9	82.7	7.0	1.3	99.9	6.4	43.8	4.2	0.8	44.8	99.9	1.08	11.01	0.60	0.22	19	64	SOI4	Spectrum 6
HibK	9.0	82.7	7.1	1.2	100.0	6.4	43.8	4.3	0.8	44.8	100.0	1.09	11.00	0.60	0.21	19	65	SOI4	Spectrum 7
HibK	8.4	82.7	7.1	1.4	99.6	6.0	43.7	4.3	0.9	44.7	99.6	1.02	11.02	0.61	0.24	19	60	SOI5	Spectrum 2
HibK	8.3	83.3	6.8	1.4	99.9	6.0	44.1	4.1	0.8	44.9	99.9	1.01	11.07	0.58	0.23	19	60	SOI5	Spectrum 3
HibK	8.6	82.0	6.9	1.3	98.9	6.2	43.4	4.2	0.8	44.4	98.9	1.05	11.02	0.60	0.22	19	63	SOI5	Spectrum 4
HibK	8.2	82.9	6.7	1.5	99.4	5.9	43.9	4.0	0.9	44.7	99.4	1.00	11.07	0.57	0.25	19	56	SOI5	Spectrum 5
HibK	8.7	83.6	7.4	1.7	101.4	6.2	44.2	4.4	1.0	45.5	101.4	1.04	10.96	0.62	0.28	19	55	SOI5	Spectrum 6
HibK	8.7	82.8	7.3	1.5	100.2	6.2	43.8	4.4	0.9	44.9	100.2	1.05	10.99	0.62	0.24	19	60	Average of 27	
	0.3	0.5	0.5	0.1	0.7	0.2	0.3	0.3	0.1	0.3	0.7	0.04	0.06	0.04	0.02		4	Standard deviation	

Continued...

Sample	wt% Oxide					wt% element						Number of cations based on 19 O					%Ti ³⁺	Analysis detail	
	CaO	Al ₂ O ₃	TiO ₂	MgO	Total	Ca	Al	Ti	Mg	O	Total	Ca	Al	Ti	Mg	O		SOI	Spectrum
Hib8	8.5	80.1	8.9	2.9	100.3	6.1	42.4	5.3	1.7	44.8	100.3	1.03	10.65	0.76	0.48	19	36	(1a)SOI1-8	Spectrum 4
Hib8	8.7	79.7	8.6	2.9	99.9	6.2	42.2	5.2	1.8	44.6	99.9	1.06	10.65	0.74	0.49	19	33	(1a)SOI1-8	Spectrum 5
Hib8	9.1	78.7	8.4	2.8	99.0	6.5	41.7	5.0	1.7	44.1	99.0	1.11	10.64	0.72	0.48	19	33	(1a)SOI1-8	Spectrum 6
Hib8	8.5	81.7	8.9	2.8	101.8	6.0	43.2	5.3	1.7	45.5	101.8	1.01	10.70	0.74	0.46	19	38	(1a)SOI2-8	Spectrum 1
Hib8	9.3	81.1	8.0	2.9	101.2	6.6	42.9	4.8	1.7	45.2	101.2	1.12	10.70	0.68	0.48	19	29	(1a)SOI2-8	Spectrum 2
Hib8	8.7	80.4	7.9	2.9	99.8	6.2	42.5	4.7	1.7	44.6	99.8	1.06	10.74	0.67	0.48	19	28	(1a)SOI2-8	Spectrum 3

Sample	CaO	Al ₂ O ₃	TiO ₂	MgO	Total	Ca	Al	Ti	Mg	O	Total	Ca	Al	Ti	Mg	O	%Ti ³⁺	SOI	Spectrum
Hib8	8.8	80.4	7.0	2.7	99.0	6.3	42.6	4.2	1.6	44.3	99.0	1.08	10.84	0.60	0.46	19	23	(1a)SOI2-8	Spectrum 5
Hib8	8.7	79.9	8.4	2.9	99.9	6.2	42.3	5.0	1.8	44.6	99.9	1.06	10.68	0.71	0.49	19	31	(1a)SOI2-8	Spectrum 6
Hib8	8.8	79.7	9.0	2.9	100.3	6.3	42.2	5.4	1.7	44.7	100.3	1.06	10.62	0.76	0.48	19	37	(1a)SOI3-8	Spectrum 1
Hib8	8.6	79.8	9.0	3.0	100.4	6.2	42.2	5.4	1.8	44.8	100.4	1.04	10.62	0.76	0.50	19	34	(1a)SOI3-8	Spectrum 4
HibC	8.4	79.1	8.6	3.0	99.2	6.0	41.9	5.1	1.8	44.3	99.2	1.03	10.66	0.74	0.52	19	29	(1b)SOI1-C	Spectrum 1
HibC	8.4	79.2	9.4	3.0	100.1	6.0	41.9	5.6	1.8	44.7	100.1	1.02	10.58	0.80	0.51	19	36	(1b)SOI1-C	Spectrum 2
HibC	8.8	80.0	8.8	3.1	100.7	6.3	42.3	5.3	1.9	44.9	100.7	1.06	10.62	0.75	0.52	19	31	(1b)SOI1-C	Spectrum 4
HibC	8.8	81.4	8.2	2.7	101.2	6.3	43.1	4.9	1.6	45.2	101.2	1.06	10.74	0.69	0.45	19	34	(1b)SOI1-C	Spectrum 5
HibC	8.5	79.2	8.6	3.0	99.2	6.1	41.9	5.1	1.8	44.3	99.2	1.04	10.65	0.74	0.51	19	30	(1b)SOI1-C	Spectrum 6
HibC	8.6	80.6	7.9	2.7	99.9	6.2	42.7	4.7	1.6	44.7	99.9	1.05	10.77	0.67	0.46	19	32	(1b)SOI1-C	Spectrum 7
HibC	8.7	78.2	10.2	3.2	100.4	6.2	41.4	6.1	1.9	44.7	100.4	1.06	10.44	0.87	0.54	19	38	(1b)SOI2-C	Spectrum 2
HibC	8.5	79.3	8.0	3.2	98.9	6.1	41.9	4.8	1.9	44.2	98.9	1.04	10.69	0.69	0.54	19	22	(1b)SOI2-C	Spectrum 3
HibC	9.0	81.3	8.0	2.7	101.0	6.5	43.0	4.8	1.6	45.1	101.0	1.08	10.75	0.68	0.44	19	34	(1b)SOI2-C	Spectrum 4
HibC	8.9	78.4	8.3	2.9	98.5	6.4	41.5	5.0	1.8	43.9	98.5	1.10	10.64	0.72	0.50	19	30	(1b)SOI2-C	Spectrum 5
HibC	8.7	80.1	8.5	2.8	100.1	6.2	42.4	5.1	1.7	44.7	100.1	1.05	10.68	0.73	0.48	19	35	(1b)SOI3-C	Spectrum 1
HibC	9.3	78.8	9.1	2.9	100.0	6.7	41.7	5.4	1.7	44.5	100.0	1.14	10.55	0.78	0.49	19	37	(1b)SOI3-C	Spectrum 2
HibC	8.9	80.9	7.8	3.0	100.6	6.4	42.8	4.7	1.8	44.9	100.6	1.07	10.73	0.66	0.50	19	24	(1b)SOI3-C	Spectrum 3
HibC	8.8	79.6	9.5	3.2	101.1	6.3	42.2	5.7	1.9	45.0	101.1	1.06	10.54	0.80	0.53	19	34	(1b)SOI3-C	Spectrum 4
HibC	9.0	82.7	7.4	2.9	102.0	6.4	43.8	4.5	1.7	45.6	102.0	1.07	10.81	0.62	0.48	19	23	(1b)SOI3-C	Spectrum 5
HibC	9.3	78.9	8.9	2.8	100.0	6.6	41.8	5.3	1.7	44.5	100.0	1.13	10.58	0.76	0.48	19	37	(1b)SOI5-C	Spectrum 1
HibC	8.9	78.9	8.3	3.0	99.1	6.4	41.7	5.0	1.8	44.2	99.1	1.09	10.64	0.71	0.52	19	28	(1b)SOI5-C	Spectrum 2
HibC	8.5	80.8	7.0	2.8	99.0	6.1	42.8	4.2	1.7	44.4	99.0	1.04	10.86	0.60	0.47	19	22	(1b)SOI5-C	Spectrum 3
HibC	9.0	80.3	9.3	3.1	101.7	6.5	42.5	5.6	1.9	45.3	101.7	1.08	10.57	0.78	0.52	19	34	(1b)SOI5-C	Spectrum 5
HibC	9.0	78.7	8.5	3.1	99.3	6.4	41.7	5.1	1.9	44.3	99.3	1.10	10.60	0.73	0.53	19	28	(1c)SOI1-C	Spectrum 1
HibC	9.0	79.9	8.7	2.9	100.1	6.4	42.1	5.2	1.7	44.6	100.1	1.09	10.62	0.75	0.48	19	35	(1c)SOI1-C	Spectrum 2
HibC	8.5	79.9	9.0	3.0	100.3	6.1	42.3	5.4	1.8	44.8	100.3	1.03	10.63	0.76	0.51	19	34	(1c)SOI1-C	Spectrum 4
HibC	9.2	80.7	8.5	2.7	101.2	6.6	42.7	5.1	1.6	45.1	101.2	1.10	10.67	0.72	0.45	19	37	(1c)SOI2-C	Spectrum 1
HibC	8.8	79.4	8.8	3.0	99.9	6.3	42.0	5.3	1.8	44.6	99.9	1.07	10.62	0.75	0.51	19	31	(1c)SOI2-C	Spectrum 4
HibC	9.1	79.1	9.8	2.9	100.8	6.5	41.9	5.9	1.8	44.9	100.8	1.09	10.51	0.83	0.49	19	41	(1c)SOI2-C	Spectrum 5
HibC	8.8	80.5	8.3	2.5	100.1	6.3	42.6	5.0	1.5	44.7	100.1	1.06	10.73	0.71	0.42	19	40	(1c)SOI2-C	Spectrum 7
HibC	8.6	77.7	9.8	2.7	98.9	6.2	41.1	5.9	1.7	44.1	98.9	1.06	10.52	0.85	0.47	19	45	(1c)SOI2-C	Spectrum 8
HibC	8.7	80.7	9.1	3.1	101.7	6.2	42.7	5.5	1.9	45.4	101.7	1.04	10.61	0.77	0.51	19	33	(1c)SOI3-C	Spectrum 1
HibC	9.2	81.1	7.6	2.4	100.3	6.6	42.9	4.6	1.4	44.8	100.3	1.12	10.80	0.64	0.40	19	38	(1c)SOI3-C	Spectrum 2
HibC	8.5	80.2	9.3	3.1	101.0	6.0	42.4	5.6	1.9	45.1	101.0	1.02	10.60	0.79	0.51	19	35	(1c)SOI3-C	Spectrum 3
HibC	9.0	80.1	7.8	2.8	99.7	6.4	42.4	4.7	1.7	44.5	99.7	1.09	10.73	0.67	0.48	19	28	(1c)SOI3-C	Spectrum 4
HibC	8.7	79.2	8.7	3.1	99.7	6.2	41.9	5.2	1.9	44.5	99.7	1.06	10.62	0.74	0.52	19	30	(1c)SOI3-C	Spectrum 5
Hib8C	8.8	79.9	8.6	2.9	100.2	6.3	42.3	5.1	1.7	44.7	100.2	1.07	10.66	0.73	0.49	19	33	Average of 27	
	0.3	1.0	0.7	0.2	0.9	0.2	0.5	0.4	0.1	0.4	0.9	0.03	0.09	0.06	0.03		5	Standard deviation	

Continued...

Sample	wt% Oxide					wt% element						Number of cations based on 19 O					%Ti ³⁺	Analysis detail	
	CaO	Al ₂ O ₃	TiO ₂	MgO	Total	Ca	Al	Ti	Mg	O	Total	Ca	Al	Ti	Mg	O		SOI	Spectrum
HibJ _{tail}	7.9	82.6	7.2	3.5	101.2	5.7	43.7	4.3	2.1	45.4	101.2	0.94	10.85	0.60	0.58	19	3	SOI1	Spectrum 4
HibJ _{tail}	9.1	79.5	8.2	3.3	100.2	6.5	42.1	4.9	2.0	44.6	100.2	1.11	10.62	0.70	0.56	19	20	SOI2	Spectrum 10
HibJ _{tail}	8.8	77.7	8.6	3.5	98.5	6.3	41.1	5.1	2.1	43.9	98.5	1.08	10.55	0.74	0.60	19	19	SOI2	Spectrum 5
HibJ _{tail}	8.7	86.3	2.5	1.4	98.9	6.2	45.7	1.5	0.8	44.7	98.9	1.06	11.52	0.21	0.23	19	0	SOI3	Spectrum 1
HibJ _{tail}	8.5	81.8	7.2	2.5	100.1	6.1	43.3	4.3	1.5	44.8	100.1	1.03	10.88	0.61	0.42	19	31	SOI4	Spectrum 3
HibJ _{tail}	8.7	78.8	8.4	3.1	99.1	6.2	41.7	5.1	1.9	44.2	99.1	1.07	10.63	0.73	0.53	19	27	SOI5	Spectrum 8
HibJ _{tail}	9.1	79.3	8.9	3.4	100.6	6.5	42.0	5.3	2.0	44.8	100.6	1.10	10.55	0.75	0.56	19	25	SOI1	Spectrum 9
HibJ _{tail}	8.7	79.2	8.5	3.3	99.7	6.2	41.9	5.1	2.0	44.5	99.7	1.06	10.62	0.73	0.56	19	23	SOI5	Spectrum 3
HibJ _{tail}	8.5	82.3	5.4	2.4	98.6	6.1	43.6	3.3	1.5	44.3	98.6	1.04	11.08	0.47	0.41	19	11	SOI4	Spectrum 4
HibJ _{tail}	8.2	84.3	4.5	2.8	99.8	5.9	44.6	2.7	1.7	44.9	99.8	0.99	11.18	0.38	0.48	19	0	SOI5	Spectrum 4
HibJ _{tail}	8.5	80.5	8.0	3.2	100.1	6.0	42.6	4.8	1.9	44.8	100.1	1.02	10.73	0.68	0.53	19	21	SOI5	Spectrum 6
HibJ _{tail}	9.1	81.7	7.9	3.3	101.9	6.5	43.2	4.7	2.0	45.5	101.9	1.09	10.70	0.66	0.54	19	17	SOI5	Spectrum 7
HibJ _{tail}	8.9	83.7	5.0	2.0	99.5	6.3	44.3	3.0	1.2	44.7	99.5	1.08	11.16	0.42	0.34	19	19	SOI6	Spectrum 2
HibJ _{tail}	8.7	78.3	9.7	4.1	100.8	6.2	41.4	5.8	2.5	44.8	100.8	1.06	10.41	0.82	0.68	19	17	SOI6	Spectrum 6
HibJ(13)	8.7	81.4	7.1	3.0	99.9	6.2	42.9	4.3	1.8	44.7	99.9	1.05	10.82	0.61	0.50	19	17	Average of 13 (tail)	
	0.4	2.5	2.0	0.7	1.0	0.2	1.3	1.2	0.4	0.4	1.0	0.04	0.31	0.17	0.12		10	Standard deviation	
Sample	CaO	Al ₂ O ₃	TiO ₂	MgO	Total	Ca	Al	Ti	Mg	O	Total	Ca	Al	Ti	Mg	O	%Ti ³⁺	SOI	Spectrum
HibJ _{body}	8.8	78.0	10.5	4.0	101.3	6.3	41.3	6.3	2.4	45.0	101.3	1.06	10.33	0.89	0.66	19	25	SOI1	Spectrum 1
HibJ _{body}	8.5	76.1	10.0	3.6	98.1	6.1	40.3	6.0	2.2	43.6	98.1	1.06	10.39	0.87	0.62	19	29	SOI1	Spectrum 10
HibJ _{body}	8.7	76.2	12.7	3.8	101.4	6.2	40.3	7.6	2.3	44.9	101.4	1.04	10.11	1.07	0.64	19	40	SOI1	Spectrum 2
HibJ _{body}	8.8	77.5	10.6	3.8	100.8	6.3	41.0	6.4	2.3	44.8	100.8	1.07	10.33	0.90	0.64	19	29	SOI1	Spectrum 3
HibJ _{body}	8.7	75.9	11.5	4.0	100.1	6.2	40.2	6.9	2.4	44.4	100.1	1.06	10.19	0.98	0.68	19	31	SOI1	Spectrum 5
HibJ _{body}	9.2	77.5	10.0	3.6	100.3	6.6	41.0	6.0	2.2	44.5	100.3	1.12	10.38	0.85	0.61	19	29	SOI1	Spectrum 6
HibJ _{body}	8.9	78.2	10.5	3.6	101.2	6.3	41.4	6.3	2.2	45.0	101.2	1.07	10.37	0.89	0.61	19	32	SOI1	Spectrum 7
HibJ _{body}	8.9	77.2	10.3	3.8	100.2	6.4	40.9	6.2	2.3	44.5	100.2	1.08	10.34	0.88	0.65	19	26	SOI1	Spectrum 8
HibJ _{body}	8.4	76.7	10.6	3.6	99.3	6.0	40.6	6.4	2.2	44.2	99.3	1.03	10.36	0.91	0.61	19	33	SOI2	Spectrum 6
HibJ _{body}	8.5	77.6	10.6	4.2	100.8	6.0	41.1	6.4	2.5	44.8	100.8	1.02	10.32	0.90	0.70	19	22	SOI2	Spectrum 7
HibJ _{body}	8.4	77.9	9.6	3.5	99.4	6.0	41.3	5.8	2.1	44.3	99.4	1.02	10.49	0.83	0.59	19	28	SOI2	Spectrum 8
HibJ _{body}	8.7	78.8	10.1	3.5	101.0	6.2	41.7	6.0	2.1	45.0	101.0	1.04	10.44	0.85	0.59	19	30	SOI2	Spectrum 9
HibJ _{body}	8.7	78.7	9.3	3.6	100.3	6.2	41.6	5.6	2.2	44.7	100.3	1.05	10.50	0.79	0.61	19	22	SOI3	Spectrum 2
HibJ _{body}	8.9	78.7	10.5	3.6	101.6	6.3	41.7	6.3	2.2	45.2	101.6	1.06	10.39	0.88	0.60	19	31	SOI3	Spectrum 3
HibJ _{body}	9.1	77.8	10.7	3.6	101.2	6.5	41.2	6.4	2.2	44.9	101.2	1.10	10.33	0.90	0.61	19	32	SOI3	Spectrum 4
HibJ _{body}	8.2	76.9	11.9	4.0	101.0	5.9	40.7	7.1	2.4	44.9	101.0	0.99	10.21	1.01	0.67	19	33	SOI3	Spectrum 5
HibJ _{body}	8.4	75.4	12.2	4.0	100.1	6.0	39.9	7.3	2.4	44.4	100.1	1.02	10.13	1.05	0.68	19	35	SOI3	Spectrum 6
HibJ _{body}	8.9	77.1	10.2	4.0	100.2	6.4	40.8	6.1	2.4	44.5	100.2	1.09	10.33	0.87	0.67	19	23	SOI4	Spectrum 2
HibJ _{body}	8.4	77.7	11.4	3.9	101.4	6.0	41.1	6.8	2.4	45.1	101.4	1.01	10.28	0.96	0.65	19	32	SOI4	Spectrum 5
HibJ _{body}	8.6	75.8	12.4	4.5	101.2	6.2	40.1	7.4	2.7	44.8	101.2	1.04	10.08	1.05	0.75	19	28	SOI4	Spectrum 6
HibJ _{body}	8.4	77.2	10.5	3.9	100.0	6.0	40.9	6.3	2.4	44.5	100.0	1.02	10.34	0.90	0.66	19	27	SOI4	Spectrum 7

Sample	CaO	Al ₂ O ₃	TiO ₂	MgO	Total	Ca	Al	Ti	Mg	O	Total	Ca	Al	Ti	Mg	O	%Ti ³⁺	SOI	Spectrum
HibJ _{body}	7.8	77.6	11.1	4.1	100.5	5.6	41.1	6.6	2.4	44.8	100.5	0.94	10.33	0.94	0.68	19	27	SOI6	Spectrum 3
HibJ _{body}	8.4	76.1	11.9	4.1	100.6	6.0	40.3	7.1	2.5	44.6	100.6	1.02	10.17	1.01	0.70	19	31	SOI6	Spectrum 4
HibJ _{body}	8.3	76.0	11.9	3.8	99.9	5.9	40.2	7.1	2.3	44.4	99.9	1.01	10.21	1.02	0.65	19	36	SOI6	Spectrum 5
HibJ _{body}	8.9	78.2	10.8	3.9	101.8	6.4	41.4	6.5	2.3	45.2	101.8	1.07	10.31	0.91	0.64	19	29	SOI7	Spectrum 7
HibJ _{body}	8.1	76.4	10.8	3.8	99.1	5.8	40.4	6.5	2.3	44.1	99.1	1.00	10.33	0.93	0.65	19	31	SOI7	Spectrum 8
HibJ _{body}	8.5	77.2	11.1	3.7	100.5	6.1	40.8	6.7	2.2	44.7	100.5	1.03	10.30	0.95	0.62	19	34	SOI7	Spectrum 9
HibJ	8.6	77.2	10.9	3.8	100.5	6.1	40.9	6.5	2.3	44.7	100.5	1.04	10.31	0.93	0.65	19	30	Average of 28 (body)	
	0.3	1.0	0.9	0.2	0.9	0.2	0.5	0.5	0.1	0.4	0.9	0.04	0.11	0.07	0.04		4	Standard deviation	

Continued...

Sample	wt% Oxide					wt% element						Number of cations based on 19 O					%Ti ³⁺	Analysis detail	
	CaO	Al ₂ O ₃	TiO ₂	MgO	Total	Ca	Al	Ti	Mg	O	Total	Ca	Al	Ti	Mg	O		SOI	Spectrum
Hib9	8.8	86.6	2.7	1.2	99.2	6.3	45.8	1.6	0.7	44.8	99.2	1.07	11.52	0.23	0.20	19	10	SOI10	Spectrum 1
Hib9	8.2	83.3	5.1	2.6	99.3	5.9	44.1	3.1	1.6	44.7	99.3	1.00	11.12	0.44	0.45	19	0	SOI10	Spectrum 2
Hib9	9.0	86.6	3.1	1.7	100.4	6.4	45.8	1.9	1.0	45.3	100.4	1.08	11.41	0.26	0.28	19	0	SOI10	Spectrum 3
Hib9	8.5	81.7	6.6	3.0	99.7	6.1	43.2	4.0	1.8	44.7	99.7	1.03	10.90	0.56	0.50	19	11	SOI10	Spectrum 4
Hib9	8.6	81.4	5.7	2.9	98.7	6.1	43.1	3.4	1.8	44.2	98.7	1.05	10.98	0.49	0.50	19	0	SOI10	Spectrum 5
Hib9	8.7	82.4	5.1	3.2	99.3	6.2	43.6	3.0	1.9	44.5	99.3	1.05	11.03	0.43	0.54	19	0	SOI10	Spectrum 6
Hib9	8.7	84.3	4.4	1.8	99.2	6.2	44.6	2.7	1.1	44.6	99.2	1.05	11.26	0.38	0.31	19	18	SOI11	Spectrum 1
Hib9	8.9	86.1	2.8	1.6	99.3	6.3	45.6	1.7	1.0	44.8	99.3	1.07	11.46	0.23	0.27	19	0	SOI11	Spectrum 3
Hib9	9.0	82.6	6.6	3.0	101.2	6.4	43.7	4.0	1.8	45.3	101.2	1.08	10.88	0.55	0.50	19	10	SOI11	Spectrum 4
Hib9	8.4	81.5	6.1	3.0	99.0	6.0	43.1	3.7	1.8	44.4	99.0	1.03	10.94	0.52	0.52	19	2	SOI11	Spectrum 5
Hib9	8.7	81.4	7.2	3.1	100.4	6.2	43.1	4.3	1.9	44.9	100.4	1.05	10.81	0.61	0.52	19	14	SOI11	Spectrum 6
Hib9	8.5	82.3	5.4	2.4	98.6	6.1	43.5	3.3	1.5	44.3	98.6	1.04	11.08	0.47	0.41	19	11	SOI2	Spectrum 1
Hib9	8.2	83.8	4.4	2.3	98.8	5.9	44.4	2.7	1.4	44.5	98.8	1.00	11.24	0.38	0.38	19	0	SOI2	Spectrum 5
Hib9	8.5	81.3	6.7	2.8	99.2	6.0	43.0	4.0	1.7	44.5	99.2	1.03	10.91	0.57	0.47	19	18	SOI3	Spectrum 1
Hib9	8.3	80.8	6.3	2.9	98.4	5.9	42.8	3.8	1.8	44.1	98.4	1.02	10.92	0.55	0.50	19	8	SOI3	Spectrum 2
Hib9	8.6	81.4	6.1	3.0	99.1	6.1	43.1	3.7	1.8	44.4	99.1	1.05	10.93	0.52	0.51	19	2	SOI3	Spectrum 3
Hib9	8.3	81.2	7.0	3.1	99.7	5.9	43.0	4.2	1.9	44.7	99.7	1.01	10.84	0.60	0.53	19	11	SOI4	Spectrum 2
Hib9	8.5	82.9	5.3	2.3	99.0	6.1	43.9	3.2	1.4	44.5	99.0	1.04	11.11	0.45	0.39	19	13	SOI4	Spectrum 4
Hib9	8.7	84.6	3.3	1.8	98.4	6.2	44.8	2.0	1.1	44.3	98.4	1.06	11.37	0.29	0.30	19	0	SOI5	Spectrum 1
Hib9	8.0	81.0	6.3	3.3	98.5	5.7	42.8	3.8	2.0	44.2	98.5	0.98	10.92	0.54	0.56	19	0	SOI5	Spectrum 5
Hib9	7.9	86.5	3.6	1.1	99.2	5.7	45.8	2.2	0.7	44.9	99.2	0.95	11.49	0.31	0.19	19	39	SOI6	Spectrum 2
Hib9	8.6	84.2	4.4	2.1	99.3	6.2	44.5	2.7	1.3	44.7	99.3	1.05	11.23	0.38	0.36	19	6	SOI6	Spectrum 3
Hib9	8.0	85.1	3.6	2.5	99.2	5.7	45.1	2.2	1.5	44.8	99.2	0.96	11.34	0.30	0.42	19	0	SOI6	Spectrum 9
Hib9	8.5	80.2	7.1	3.3	99.1	6.1	42.5	4.2	2.0	44.3	99.1	1.04	10.79	0.61	0.56	19	7	SOI7	Spectrum 3
Hib9	8.5	82.6	4.8	2.7	98.7	6.1	43.7	2.9	1.7	44.3	98.7	1.04	11.11	0.41	0.47	19	0	SOI7	Spectrum 4
Hib9	8.9	83.0	5.0	2.6	99.0	6.4	43.6	3.0	1.5	44.4	99.0	1.09	11.08	0.43	0.43	19	0	SOI7	Spectrum 5
Hib9	8.5	83.0	5.2	2.5	99.2	6.1	43.9	3.1	1.5	44.6	99.2	1.04	11.10	0.44	0.43	19	7	Average of 26	
	0.3	1.9	1.4	0.6	0.6	0.2	1.0	0.8	0.4	0.3	0.6	0.03	0.22	0.12	0.11		9	Standard deviation	

Sample	wt% Oxide					wt% element						Number of cations based on 19 O					%Ti ³⁺	Analysis detail	
	CaO	Al ₂ O ₃	TiO ₂	MgO	Total	Ca	Al	Ti	Mg	O	Total	Ca	Al	Ti	Mg	O		SOI	Spectrum
HibE	9.1	75.1	11.4	5.5	101.1	6.5	39.8	6.8	3.3	44.7	101.1	1.10	10.02	0.97	0.93	19	4	SOI1	Spectrum 3
HibE	7.9	74.3	10.5	5.4	98.0	5.6	39.3	6.3	3.2	43.5	98.0	0.98	10.17	0.92	0.93	19	0	SOI1	Spectrum 4
HibE	8.4	74.4	11.4	5.5	99.7	6.0	39.4	6.8	3.3	44.2	99.7	1.03	10.04	0.98	0.94	19	4	SOI1	Spectrum 5
HibE	8.2	74.3	11.9	5.6	100.0	5.9	39.3	7.1	3.4	44.3	100.0	1.00	10.00	1.02	0.95	19	7	SOI1	Spectrum 7
HibE	8.8	74.9	11.8	5.8	101.2	6.3	39.6	7.1	3.5	44.8	101.2	1.06	9.97	1.00	0.97	19	3	SOI1	Spectrum 8
HibE	7.9	75.2	10.6	4.9	98.5	5.6	39.8	6.3	2.9	43.8	98.5	0.97	10.24	0.92	0.84	19	9	SOI10	Spectrum 1
HibE	8.0	74.6	11.2	5.4	99.2	5.7	39.5	6.7	3.3	44.0	99.2	0.99	10.10	0.97	0.92	19	5	SOI10	Spectrum 3
HibE	8.2	73.5	13.0	5.3	99.9	5.8	38.9	7.8	3.2	44.2	99.9	1.00	9.91	1.12	0.91	19	19	SOI2	Spectrum 3
HibE	8.3	74.5	12.3	5.5	100.7	6.0	39.4	7.4	3.3	44.6	100.7	1.01	9.97	1.05	0.93	19	11	SOI2	Spectrum 4
HibE	8.4	77.0	10.6	5.1	101.0	6.0	40.8	6.3	3.1	44.9	101.0	1.01	10.23	0.90	0.85	19	5	SOI2	Spectrum 5
HibE	8.5	75.1	11.7	5.2	100.5	6.1	39.7	7.0	3.1	44.5	100.5	1.03	10.06	1.00	0.88	19	12	SOI3	Spectrum 1
HibE	7.9	74.6	10.9	5.3	98.7	5.7	39.5	6.5	3.2	43.8	98.7	0.98	10.15	0.94	0.91	19	3	SOI3	Spectrum 2
HibE	8.7	74.8	12.0	5.5	101.0	6.2	39.6	7.2	3.3	44.7	101.0	1.06	9.98	1.02	0.92	19	10	SOI3	Spectrum 3
HibE	7.7	74.3	12.0	5.7	99.7	5.5	39.4	7.2	3.4	44.3	99.7	0.95	10.02	1.03	0.96	19	7	SOI3	Spectrum 4
HibE	8.1	74.5	12.2	5.5	100.4	5.8	39.4	7.3	3.3	44.5	100.4	0.99	9.99	1.05	0.94	19	11	SOI3	Spectrum 5
HibE	8.8	76.0	11.0	4.9	100.7	6.3	40.2	6.6	3.0	44.6	100.7	1.07	10.15	0.93	0.83	19	11	SOI4	Spectrum 1
HibE	7.8	75.5	12.3	5.3	100.9	5.6	40.0	7.4	3.2	44.8	100.9	0.95	10.05	1.04	0.89	19	15	SOI4	Spectrum 2
HibE	7.9	75.3	11.1	5.4	99.8	5.7	39.9	6.7	3.3	44.3	99.8	0.97	10.14	0.95	0.92	19	4	SOI4	Spectrum 4
HibE	8.9	74.9	11.7	5.1	100.6	6.3	39.7	7.0	3.1	44.5	100.6	1.08	10.04	1.00	0.87	19	13	SOI4	Spectrum 5
HibE	7.9	75.6	10.7	5.3	99.4	5.6	40.0	6.4	3.2	44.2	99.4	0.97	10.19	0.92	0.91	19	2	SOI4	Spectrum 6
HibE	8.7	74.5	11.4	5.4	100.1	6.2	39.5	6.8	3.3	44.3	100.1	1.06	10.03	0.98	0.92	19	6	SOI5	Spectrum 5
HibE	8.2	75.0	12.0	5.2	100.4	5.9	39.7	7.2	3.1	44.5	100.4	1.00	10.05	1.02	0.88	19	14	SOI5	Spectrum 6
HibE	8.9	74.4	11.2	5.8	100.3	6.4	39.4	6.7	3.5	44.4	100.3	1.09	10.00	0.96	0.98	19	0	SOI6	Spectrum 2
HibE	8.1	74.6	12.6	5.6	101.0	5.8	39.5	7.6	3.4	44.7	101.0	0.98	9.95	1.08	0.95	19	12	SOI6	Spectrum 3
HibE	8.0	74.9	11.6	5.5	100.3	5.7	39.8	7.0	3.3	44.5	100.3	0.98	10.07	0.99	0.93	19	6	SOI7	Spectrum 2
HibE	8.8	75.2	10.7	4.9	99.6	6.3	39.8	6.4	3.0	44.2	99.6	1.08	10.16	0.92	0.84	19	9	SOI7	Spectrum 3
HibE	8.4	73.6	10.8	5.4	98.2	6.0	38.9	6.5	3.3	43.5	98.2	1.04	10.08	0.95	0.94	19	1	SOI7	Spectrum 4
HibE	8.1	75.1	10.1	5.2	98.5	5.8	39.8	6.0	3.1	43.8	98.5	1.01	10.24	0.88	0.89	19	0	SOI7	Spectrum 5
HibE	8.3	74.8	11.4	5.4	100.0	5.9	39.6	6.9	3.2	44.3	100.0	1.01	10.07	0.98	0.91	19	7	Average of 28	
	0.4	0.7	0.7	0.2	0.9	0.3	0.4	0.4	0.1	0.4	0.9	0.04	0.09	0.06	0.04	0	5	Standard deviation	

Continued...

Sample	wt% Oxide					wt% element					Number of cations based on 19 O					%Ti ³⁺	Analysis detail	
	CaO	Al ₂ O ₃	TiO ₂	MgO	Total	Ca	Al	Ti	Mg	O	Total	Ca	Al	Ti	Mg	O	SOI	Spectrum
HibN	8.4	82.3	6.3	2.5	99.4	6.0	43.5	3.8	1.5	44.6	99.4	1.01	10.99	0.54	0.42	19	SOI1	Spectrum 1
HibN	8.6	84.3	4.6	2.2	99.6	6.1	44.6	2.8	1.3	44.8	99.6	1.03	11.21	0.39	0.37	19	SOI1	Spectrum 2
HibN	8.6	83.8	3.9	2.1	98.5	6.2	44.4	2.4	1.3	44.3	98.5	1.05	11.27	0.34	0.36	19	SOI1	Spectrum 3
HibN	9.0	83.3	4.8	2.3	99.4	6.5	44.1	2.9	1.4	44.6	99.4	1.10	11.13	0.41	0.39	19	SOI1	Spectrum 4
HibN	8.9	84.5	3.2	1.8	98.4	6.3	44.7	1.9	1.1	44.3	98.4	1.08	11.37	0.28	0.30	19	SOI1	Spectrum 5
HibN	8.5	80.2	7.5	2.9	99.0	6.1	42.4	4.5	1.7	44.3	99.0	1.04	10.79	0.64	0.49	19	SOI2	Spectrum 1
HibN	8.7	79.1	7.3	3.3	98.4	6.2	41.9	4.4	2.0	44.0	98.4	1.07	10.73	0.63	0.57	19	SOI2	Spectrum 2
HibN	8.7	83.6	5.9	2.7	100.8	6.2	44.3	3.5	1.6	45.2	100.8	1.04	11.02	0.49	0.45	19	SOI2	Spectrum 3
HibN	8.4	80.0	7.1	2.8	98.2	6.0	42.3	4.2	1.7	44.0	98.2	1.04	10.84	0.61	0.48	19	SOI2	Spectrum 4
HibN	8.3	83.8	5.0	2.1	99.2	5.9	44.4	3.0	1.2	44.6	99.2	1.01	11.19	0.43	0.35	19	SOI3	Spectrum 1
HibN	8.5	83.4	4.3	2.2	98.3	6.0	44.1	2.6	1.3	44.3	98.3	1.04	11.23	0.37	0.38	19	SOI3	Spectrum 2
HibN	8.7	85.3	3.2	1.7	98.9	6.2	45.2	1.9	1.0	44.6	98.9	1.06	11.42	0.27	0.28	19	SOI3	Spectrum 3
HibN	8.8	82.6	6.2	2.5	100.1	6.3	43.7	3.7	1.5	44.9	100.1	1.06	10.97	0.53	0.43	19	SOI3	Spectrum 4
HibN	9.1	85.3	2.5	1.5	98.3	6.5	45.2	1.5	0.9	44.3	98.3	1.11	11.48	0.21	0.25	19	SOI3	Spectrum 5
HibN	8.8	81.1	6.9	3.2	99.9	6.3	42.9	4.1	1.9	44.7	99.9	1.06	10.82	0.58	0.54	19	SOI3	Spectrum 7
HibN	8.7	84.5	4.3	1.8	99.3	6.2	44.7	2.6	1.1	44.7	99.3	1.06	11.27	0.37	0.29	19	SOI4	Spectrum 2
HibN	8.8	82.7	5.3	2.3	99.1	6.3	43.8	3.2	1.4	44.5	99.1	1.07	11.09	0.46	0.39	19	SOI4	Spectrum 3
HibN	8.7	84.6	3.5	1.6	98.4	6.2	44.8	2.1	1.0	44.3	98.4	1.07	11.37	0.30	0.27	19	SOI4	Spectrum 5
HibN	8.0	81.8	6.1	2.7	98.4	5.7	43.3	3.6	1.6	44.2	98.4	0.97	11.02	0.52	0.45	19	SOI5	Spectrum 2
HibN	8.7	81.9	7.0	2.6	100.1	6.2	43.3	4.2	1.6	44.8	100.1	1.05	10.89	0.59	0.44	19	SOI5	Spectrum 3
HibN	8.2	80.2	7.5	3.0	98.8	5.8	42.5	4.5	1.8	44.3	98.8	1.00	10.81	0.64	0.51	19	SOI5	Spectrum 5
HibN	8.4	80.2	6.7	2.8	98.1	6.0	42.5	4.0	1.7	44.0	98.1	1.04	10.88	0.58	0.48	19	SOI5	Spectrum 6
HibN	8.4	85.5	3.4	1.7	99.1	6.0	45.3	2.0	1.1	44.7	99.1	1.02	11.40	0.29	0.29	19	SOI6	Spectrum 1
HibN	8.8	84.1	4.5	2.2	99.5	6.3	44.5	2.7	1.3	44.7	99.5	1.06	11.21	0.38	0.36	19	SOI6	Spectrum 2
HibN	8.2	84.6	5.0	2.1	99.9	5.9	44.8	3.0	1.3	45.0	99.9	0.99	11.21	0.42	0.35	19	SOI6	Spectrum 3
HibN	8.9	82.8	5.6	2.4	99.7	6.3	43.8	3.4	1.5	44.7	99.7	1.07	11.04	0.48	0.41	19	SOI6	Spectrum 4
HibN	8.7	85.0	3.5	1.9	99.1	6.2	45.0	2.1	1.2	44.7	99.1	1.06	11.35	0.30	0.32	19	SOI6	Spectrum 5
HibN	9.0	80.5	7.6	2.8	99.9	6.4	42.6	4.5	1.7	44.6	99.9	1.09	10.76	0.65	0.48	19	SOI6	Spectrum 6
HibN	8.9	80.7	7.2	3.1	99.9	6.4	42.7	4.3	1.9	44.6	99.9	1.08	10.78	0.62	0.53	19	SOI6	Spectrum 7
HibN	8.7	82.8	6.9	2.7	99.1	6.2	42.7	4.2	1.7	44.4	99.1	1.07	10.86	0.59	0.47	19	SOI6	Spectrum 9
HibN	8.6	82.8	5.4	2.4	99.2	6.2	43.8	3.2	1.4	44.5	99.2	1.05	11.08	0.46	0.40	19	12	Average of 30
	0.3	1.9	1.6	0.5	0.7	0.2	1.0	0.9	0.3	0.3	0.7	0.03	0.23	0.13	0.09		9	Standard deviation

Continued...

Sample	wt% Oxide					wt% element						Number of cations based on 19 O					%Ti ³⁺	Analysis detail	
	CaO	Al ₂ O ₃	TiO ₂	MgO	Total	Ca	Al	Ti	Mg	O	Total	Ca	Al	Ti	Mg	O		SOI	Spectrum
HibT	8.2	73.3	14.1	4.5	100.1	5.8	38.8	8.5	2.7	44.3	100.1	1.00	9.87	1.21	0.77	19	37	SOI2	Spectrum 5
HibT	9.0	72.2	14.2	5.0	100.3	6.4	38.2	8.5	3.0	44.2	100.3	1.10	9.74	1.22	0.85	19	30	SOI1	Spectrum 4
HibT	8.6	72.2	14.3	4.8	99.9	6.2	38.2	8.6	2.9	44.1	99.9	1.06	9.76	1.24	0.83	19	33	SOI5	Spectrum 3
HibT	8.8	69.6	15.5	5.3	99.2	6.3	36.9	9.3	3.2	43.6	99.2	1.10	9.53	1.35	0.91	19	32	SOI2	Spectrum 6
HibT	8.3	72.5	15.5	4.7	101.0	5.9	38.4	9.3	2.8	44.6	101.0	1.00	9.71	1.33	0.79	19	40	SOI2	Spectrum 4
HibT	8.4	71.4	15.6	5.0	100.3	6.0	37.8	9.3	3.0	44.2	100.3	1.02	9.64	1.34	0.85	19	37	SOI2	Spectrum 2
HibT	8.0	71.0	15.7	4.6	99.3	5.7	37.6	9.4	2.8	43.8	99.3	0.99	9.66	1.36	0.79	19	42	SOI5	Spectrum 5
HibT	8.7	71.6	16.1	5.1	101.4	6.2	37.9	9.6	3.1	44.6	101.4	1.06	9.56	1.37	0.86	19	37	SOI5	Spectrum 6
HibT	8.8	71.3	16.2	4.8	101.1	6.3	37.7	9.7	2.9	44.4	101.1	1.08	9.56	1.38	0.81	19	41	SOI4	Spectrum 1
HibT	8.5	71.2	16.3	5.1	101.1	6.1	37.7	9.8	3.1	44.5	101.1	1.03	9.54	1.40	0.86	19	38	SOI2	Spectrum 3
HibT	8.5	70.7	16.4	4.9	100.4	6.1	37.4	9.8	3.0	44.2	100.4	1.05	9.53	1.41	0.83	19	41	SOI1	Spectrum 5
HibT	8.6	69.6	16.5	4.7	99.3	6.1	36.8	9.9	2.8	43.7	99.3	1.06	9.50	1.44	0.81	19	44	SOI1	Spectrum 2
HibT	9.2	70.7	16.6	4.7	101.1	6.6	37.4	9.9	2.9	44.4	101.1	1.12	9.49	1.42	0.80	19	44	SOI1	Spectrum 1
HibT	8.5	70.1	16.6	4.8	99.9	6.0	37.1	10.0	2.9	43.9	99.9	1.04	9.51	1.44	0.82	19	43	SOI4	Spectrum 2
HibT	8.9	70.6	16.7	4.8	100.9	6.3	37.4	10.0	2.9	44.3	100.9	1.08	9.50	1.43	0.81	19	43	SOI4	Spectrum 4
HibT	8.3	70.1	16.7	4.7	99.8	5.9	37.1	10.0	2.8	43.9	99.8	1.02	9.51	1.45	0.81	19	44	SOI5	Spectrum 2
HibT	8.4	69.6	16.9	4.8	99.7	6.0	36.9	10.1	2.9	43.8	99.7	1.04	9.47	1.46	0.82	19	44	SOI5	Spectrum 4
HibT	8.5	71.2	17.0	5.2	101.9	6.1	37.7	10.2	3.1	44.8	101.9	1.03	9.47	1.44	0.88	19	39	SOI4	Spectrum 3
HibT	8.6	71.0	15.9	4.9	100.4	6.1	37.6	9.5	2.9	44.2	100.4	1.05	9.59	1.37	0.83	19	39	Average of 18	
	0.3	1.1	0.9	0.2	0.8	0.2	0.6	0.6	0.1	0.3	0.8	0.04	0.12	0.08	0.04		4	Standard deviation	

B.2.2 EPR data

B.2.2.1 Notes regarding individual and repeat EPR analyses

Batch 1

Run #	logfO ₂ at 1404 °C
3751	-16(b)
3752	-20
3753	-9.4
3754	-3
3755	-18
3756	-11
3757	-16(a)
3758	-12
3759	-14
3760	-13.5
3761	-13

Notes:

Two spectra were recorded from each sample.
-16(a) and (b) refers to two different beads.

Batch 2

Run #	logfO ₂ at 1404 °C
3762	-16a
3763	-18
3764	-20
3765	-13.5
3766	-12
3767	-13

Notes:

-18 transferred to -9.4 sample tube;
-16(a) transferred to the -16(b) tube;
-13.5 transferred to the -3 tube;
3764 analyses 5 & 6 were made using a different portion of the -20 powder

B.2.2.2 Average data

Table B-9 Average EPR signal intensity ~3438 G

ΔIW	Intensity maximum
+6.5	43461 (2825)
+0.1	282045 (40694)
-1.5	699150 (29232)
-2.5	1089694 (159547)
-3.5	1275380 (130266)
-4.5	1948240 (265703)
-4.5	3013850 (354473)
-6.5	4523680 (528625)
-8.5	4465540 (527336)
-10.5	3503675 (670421)

Note: Standard deviation in parentheses.

B.2.2.3 Individual analyses

Table B-10 Individual EPR spectra of Ti-bearing glasses

$\Delta I W$	Run number	Time	Intensity	
			Max	Min
+6.5	3754X1	9:19	45458	-36394
+6.5	3754X2	9:20	41463	-37237
+0.1	3753X1	9:17	253270	-207370
+0.1	3753X2	9:16	310820	-250180
-1.5	3756X1	9:21	678480	-529760
-1.5	3756X2	9:21	719820	-562640
-2.5	3758X1	9:23	1198600	-923750
-2.5	3758X2	9:23	945980	-725320
-2.5	3766X1	15:18	1066900	-819170
-2.5	3766X2	15:18	1301700	-999290
-2.5	3766X3	15:19	935290	-720450
-3.5	3761X1	9:25	1498200	-1176800
-3.5	3761X2	9:25	1239400	-967590
-3.5	3767X1	15:17	1164900	-909820
-3.5	3767X2	15:17	1207100	-945540
-3.5	3767X3	15:17	1267300	-989720
-4	3760X1	9:24	2324100	-1748800
-4	3760X2	9:24	2130600	-1599100
-4	3765X1	14:36	1713200	-1280800
-4	3765X2	14:35	1772500	-1327500
-4	3765X3	14:35	1800800	-1344000
-4.5	3759X1	9:23	2763200	-2062300
-4.5	3759X2	9:23	3264500	-2451700
-6.5	3762X1	10:53	5476600	-4080600
-6.5	3762X2	10:52	4548100	-3380700
-6.5	3762X3	13:44	4277400	-3182100
-6.5	3762X4	13:40	3933400	-2920800
-6.5	3762X5	13:39	4768100	-3550400
-6.5	3762X6	13:39	4673500	-3485400
-6.5	3757X1	9:22	4911100	-3653400
-6.5	3757X2	9:22	4890100	-3646700
-6.5	3751X1	9:18	3887500	-2903600
-6.5	3751X2	9:19	3871000	-2887300
-8.5	3763X1	10:52	5110600	-3799800
-8.5	3763X2	10:51	4984400	-3708000
-8.5	3763X3	13:47	4277400	-3182100
-8.5	3763X4	13:47	4291100	-3182200
-8.5	3763X5	13:47	4338300	-3219800
-8.5	3763X6	13:47	4745900	-3519200
-8.5	3763X7	13:46	4341700	-3220500
-8.5	3763X8	13:46	5158300	-3829100
-8.5	3755X1	9:20	3679200	-2730300
-8.5	3755X2	9:20	3728500	-2776300
-10.5	3752X1	9:18	4159000	-3124200
-10.5	3752X2	9:17	4304700	-3216500
-10.5	3764X1	13:49	3446800	-2566400
-10.5	3764X2	13:49	4376800	-3269700
-10.5	3764X3	13:42	2928700	-2176700
-10.5	3764X4	13:42	2975700	-2200200
-10.5	3764X5	13:41	2828900	-2104400
-10.5	3764X6	13:40	3008800	-2236500

C. Supplementary information for the characterisation of meteoritic hibonite study (Chapter 4)

C.1 Thermal stability fields during equilibrium condensation

Table C-1 Condensation temperatures of Lodders (2003) and phase stability ranges of Yoneda and Grossman (1995)

Reference		Lodders (2003)	Yoneda and Grossman (1995)			
Pressure (atm)			10 ⁻⁴	10 ⁻⁴		10 ⁻³
Phase and End-member formula		Upper °C	Upper °C	Lower °C	Upper °C	Lower °C
Corundum	Al ₂ O ₃	1404	1426	1370	1497	1467
Hibonite	CaAl ₁₂ O ₁₉	1386	1374	1148	1470	1227
Perovskite	CaTiO ₃	1320	1336	1107	1415	1175
Ca titanite	Ca ₄ Ti ₃ O ₁₀	1305	-	-	-	-
Grossite	CaAl ₄ O ₇	1269	-	-	-	-
Ca titanite	Ca ₃ Ti ₂ O ₇	1266	-	-	-	-
Melilite ss	Ca ₂ (Mg,Al,Si)SiO ₇	1256	1273	1104	1355	1171
Ca titanite	Ca ₄ Ti ₃ O ₁₀	1239	-	-	-	-
Perovskite	CaTiO ₃	1168	-	-	-	-
Spinel	MgAl ₂ O ₄	1124	1148	1070	1228	1136
Anorthite	CaAl ₂ Si ₂ O ₈	1114	-	-	-	-
Rankinite	Ca ₃ Si ₂ O ₇	-	1104	1102	-	-
Fe alloy / Metal ss †	Fe _{ss}	1084	1097	-	1191	-
Fassaite ss	Ca(Mg,Al,Ti) (Ti,Si,Al) ₂ O ₆	-	1107	-	1176	-
Forsterite	Mg ₂ SiO ₄	1081	1098	-	1170	-
Plagioclase ss	(Na,Ca)(Si,Al) ₄ O ₈	-	1077	-	1143	-
Ti ₃ O ₅	Ti ₃ O ₅	-	-	-	1113	1088
Diopside	CaMgSi ₂ O ₆	1074	-	-	-	--
Enstatite	MgSiO ₃	1043	1030	-	1093	-
Ti ₄ O ₇	Ti ₄ O ₇	-	-	-	1088	944
Schreibersite	Fe ₃ P	975	-	-	-	-
Cr-spinel ss	(Mg,Fe)(Al,Cr) ₂ O ₄	-	-	-	948	-
Sphene	CaTiSiO ₅	-	-	-	944	-
Troilite	FeS	431	-	-	-	-
Magnetite	Fe ₃ O ₄	98	-	-	-	-
Water ice	H ₂ O	-91	-	-	-	-
Elemental abundances used		Lodders (2003)	Anders and Grevesse (1989)			

Note: †Fe alloy (Lodders, 2003); Metal ss (Yoneda and Grossman, 1995).

C.2 Major element concentrations within meteoritic hibonite and other CAI minerals

C.2.1 Compositional data – Perovskite, Ilmenite, Melilite, Spinel, Pyroxene

Table C-2a Major element composition of the accessory phases in the hibonite-bearing CAIs (portion b details the calculated stoichiometry)

Mineral	Sample	CaO ⁵	Al ₂ O ₃	TiO ₂	MgO	FeO	SiO ₂	Cr ₂ O ₃	ZnO	S	Total	#
Melilite (core)	Acfer094/22CAI	39.8 (0.4)	38.6 (1.5)	0.1 (0.1)	0.2 (0.1)	nd	21.4 (0.5)	nd	nd	nd	100.2 (0.7)	3
Melilite (rim)	Acfer094/22CAI	42.1 (0.1)	35.3 (1.3)	<lld	0.9 (0.6)	nd	23.0 (1.0)	nd	nd	nd	101.3 (0.4)	2
Melilite	Acfer094/40CAI	41.5 (0.5)	36.4 (0.1)	<lld	0.4 (0.1)	<lld	22.0 (0.6)	<lld	<lld	<lld	100.0 (0.7)	3
	El Djouf001/1CAI	41.0 (0.2)	34.7 (1.5)	0.1 (0.1)	1.0 (0.6)	0.1 (0.1)	23.2 (0.8)	<lld	nd	<lld	100.1 (0.3)	3
Perovskite*	Acfer094/40CAI	41.2	0.9	57.4	<lld	<lld	<lld	<lld	<lld	<lld	99.5	1
	El Djouf001/1CAI	40.1	9.6	44.2	0.2	0.1	5.2	<lld	nd	<lld	99.4	1
Spinel*	Acfer094/40CAI	0.3 (0.3)	69.4 (0.9)	<lld	28.4 (0.3)	0.4 (0.1)	<lld	<lld	<lld	<lld	98.8 (1.1)	4
	El Djouf001/1CAI	2.1	70.9	1.5	23.9	0.2	0.8	0.2	nd	<lld	99.6	1
Fe,Zn-spinel*	NWA2446/8L	<lld	59.7	<lld	10.4	23.0	0.7	<lld	3.6	1.3	98.8	1
Ti-poor augite	NWA2446/5L	25.6 (0.1)	36.6 (0.3)	0.7 (0.1)	4.5 (0.2)	0.9 (0.1)	33.6 (0.2)	<0.1 (0.1)	nd	<lld	101.8 (0.2)	2
	NWA1476/124	26.2 (0.1)	16.0 (3.7)	0.1 (0.1)	12.3 (1.9)	0.5 (0.1)	44.9 (2.6)	0.1 (0.1)	nd	<lld	100.0 (0.7)	2
Fassaite	NWA1476/124	25.5 (0.2)	29.8 (0.5)	4.4 (0.5)	5.6 (0.3)	0.4 (0.1)	33.6 (0.4)	0.1 (0.1)	nd	<lld	99.3 (0.3)	5
Ilmenite*	NWA2446/2L	1.7	18.7	40.5	1.3	35.5	1.7				99.5	1

Note: EDS SEM and WD EMP data (standard deviation in parentheses);* Contamination from adjacent phases; # = number of analyses. See Table C-3 for individual analyses.

Table C-2b Stoichiometry of the accessory phases

Mineral	Sample	Calculated Stoichiometry (based on number of O shown)
Melilite (core)	Acfer094/22CAI	Ca _{1.94} Al _{2.06} Mg _{0.02} Si _{0.97} O ₇
Melilite (rim)	Acfer094/22CAI	Ca _{2.04} Al _{1.88} Mg _{0.06} Si _{1.04} O ₇
Melilite	Acfer094/40CAI	Ca _{2.00} Al _{1.97} Mg _{0.05} Si _{1.00} O ₇
	El Djouf001/1CAI	Ca _{2.00} Al _{1.87} Mg _{0.07} Si _{1.06} O ₇
Perovskite*	Acfer094/40CAI	Ca _{1.00} Ti _{0.98} Al _{0.02} O ₃
	El Djouf001/1CAI	Ca _{0.94} Ti _{0.73} Al _{0.25} Si _{0.11} O ₃
Spinel*	Acfer094/40CAI	Mg _{1.02} Ca _{0.01} Al _{1.96} O ₄
	El Djouf001/1CAI	Mg _{0.85} (Ca,Ti,Si) _{0.10} Al _{2.00} O ₄
Fe,Zn-spinel*	NWA2446/8L	Mg _{0.42} Fe _{0.52} Zn _{0.07} Si _{0.02} Al _{1.91} O ₄
Ti-poor Augite	NWA2446/5L	Ca(Mg _{0.24} Ti _{0.02} Al _{0.74})(Al _{0.80} Si _{1.20})O ₆
	NWA1476	Ca(Mg _{0.67} Al _{0.32})(Al _{0.37} Si _{1.63})O ₆
Fassaite	NWA1476	Ca(Mg _{0.31} Ti _{0.12} Al _{0.54})(Al _{0.76} Si _{1.24})O ₆
Ilmenite*	NWA2446/2L	Fe _{0.68} Ti _{0.70} Al _{0.51} (Mg,Si,Ca) _{0.12} O ₃

C.2.2 Compositional data - Individual analyses

Table C-3 Major element abundance of meteoritic hibonite and accessory phases

Sample	Mineral	Point	CaO	Al ₂ O ₃	TiO ₂	MgO	FeO	SiO ₂	Cr ₂ O ₃	Na ₂ O	ZnO	MnO	V ₂ O ₅	S	Total	Calculated stoichiometry
Acfer094/CAI22	Mel rim	1 / 1 . (3)	41.97	36.18	<lld	0.47	nd	22.34	nd	0.04	nd	nd	nd	nd	101.06	
		2 / 1 . (3)	42.17	34.34	<lld	1.28	nd	23.68	nd	0.06	nd	nd	nd	nd	101.57	
	Mel rim(2)		42.07	35.26	<lld	0.88	nd	23.01	nd	0.05	nd	nd	nd	nd	101.32	Ca_{2.04}Al_{1.88}Mg_{0.06}Si_{1.04}O₇
	<i>Std Dev</i>		<i>0.14</i>	<i>1.30</i>		<i>0.57</i>		<i>0.95</i>		<i>0.01</i>					<i>0.36</i>	
	Mel (c)	6 / 1 . (3)	39.41	38.69	0.14	0.28	nd	21.51	nd	0.09	nd	nd	nd	nd	100.12	
		7 / 1 . (3)	39.71	39.99	<lld	0.18	nd	20.83	nd	0.11	nd	nd	nd	nd	100.91	
		11 / 1 . (3)	40.27	37.09	0.11	0.26	nd	21.77	nd	0.08	nd	nd	nd	nd	99.57	
	Mel (c) (3)		39.80	38.59	0.13	0.24	nd	21.37	nd	0.09	nd	nd	nd	nd	100.20	Ca_{1.94}Al_{2.06}Mg_{0.02}Si_{0.97}O₇
	<i>Std Dev</i>		<i>0.44</i>	<i>1.45</i>	<i>0.02</i>	<i>0.05</i>		<i>0.49</i>		<i>0.02</i>					<i>0.67</i>	
	Hib	1 / 8 . (2)	8.62	83.98	5.85	2.99	nd	0.47	nd	0.02	nd	nd	nd	nd	101.93	
		1 / 13 . (2)	8.60	83.18	6.50	3.27	nd	0.29	nd	0.04	nd	nd	nd	nd	101.87	
		1 / 19 . (2)	8.62	83.41	6.16	3.10	nd	0.31	nd	0.04	nd	nd	nd	nd	101.65	
	Hib(3)		8.61	83.52	6.17	3.12	nd	0.36	nd	0.03	nd	nd	nd	nd	101.82	Ca_{1.02}Al_{10.90}Ti_{0.51}Mg_{0.51}Si_{0.04}O₁₉
	<i>Std Dev</i>		<i>0.01</i>	<i>0.41</i>	<i>0.33</i>	<i>0.14</i>		<i>0.10</i>		<i>0.01</i>					<i>0.15</i>	
Acfer094/22CAI H1-H6 regions; * = totals 98-103 wt% † = totals 98-102 wt% and analysis used for average hibonite composition	Hib *	1 / 1 . (2)	8.96	86.34	4.77	2.52	nd	0.26	nd	<lld	nd	nd	nd	nd	102.86	
	Hib *	1 / 2 . (2)	9.04	86.34	4.28	2.41	nd	0.39	nd	<lld	nd	nd	nd	nd	102.48	
	Hib *	1 / 4 . (2)	9.01	87.22	3.79	2.13	nd	0.38	nd	<lld	nd	nd	nd	nd	102.55	
	Hib(3)H1		9.00	86.63	4.28	2.35	nd	0.34	nd	<lld	nd	nd	nd	nd	102.63	
	<i>Std Dev</i>		<i>0.04</i>	<i>0.51</i>	<i>0.49</i>	<i>0.20</i>		<i>0.07</i>							<i>0.20</i>	
	Hib *	1 / 5 . (2)	9.08	86.13	4.74	2.56	nd	0.36	nd	<lld	nd	nd	nd	nd	102.91	
	Hib *	1 / 7 . (2)	8.94	87.86	3.54	1.99	nd	0.46	nd	<lld	nd	nd	nd	nd	102.81	
	Hib †	1 / 8 . (2)	8.62	83.98	5.85	2.99	nd	0.47	nd	<lld	nd	nd	nd	nd	101.93	
	Hib(3)H3		8.88	85.99	4.71	2.51	nd	0.43	nd	<lld	nd	nd	nd	nd	102.55	
	<i>Std Dev</i>		<i>0.24</i>	<i>1.94</i>	<i>1.16</i>	<i>0.50</i>		<i>0.06</i>							<i>0.54</i>	
	Hib †	1 / 13 . (2)	8.60	83.18	6.50	3.27	nd	0.29	nd	0.04	nd	nd	nd	nd	101.87	
	Hib *	1 / 14 . (2)	8.84	85.93	4.97	2.51	nd	0.25	nd	<lld	nd	nd	nd	nd	102.52	
	Hib *	1 / 15 . (2)	9.56	83.53	5.68	2.99	nd	0.96	nd	0.04	nd	nd	nd	nd	102.75	
	Hib *	1 / 16 . (2)	8.93	85.10	5.42	2.88	nd	0.42	nd	<lld	nd	nd	nd	nd	102.78	
	Hib *	1 / 17 . (2)	8.78	83.62	6.65	3.30	nd	0.34	nd	0.04	nd	nd	nd	nd	102.73	
	Hib(5)H6		8.94	84.27	5.84	2.99	nd	0.45	nd	<lld	nd	nd	nd	nd	102.53	
	<i>Std Dev</i>		<i>0.37</i>	<i>1.18</i>	<i>0.72</i>	<i>0.32</i>		<i>0.29</i>							<i>0.38</i>	
	Hib (H2) *	1 / 18 . (2)	8.83	87.80	3.51	1.96	nd	0.44	nd	<lld	nd	nd	nd	nd	102.55	Ca_{1.06}Al_{11.18}Ti_{0.29}Mg_{0.32}Si_{0.05}O₁₉
	Hib (H4) †	1 / 19 . (2)	8.62	83.41	6.16	3.10	nd	0.31	nd	0.04	nd	nd	nd	nd	101.65	Ca_{1.02}Al_{10.91}Ti_{0.51}Mg_{0.51}Si_{0.04}O₁₉
	Hib (H7) *	1 / 20 . (2)	8.73	82.51	7.24	3.60	nd	0.29	nd	0.04	nd	nd	nd	nd	102.41	Ca_{1.03}Al_{10.74}Ti_{0.60}Mg_{0.59}Si_{0.03}O₁₉
	Hib (H5) *	1 / 21 . (2)	8.81	84.66	5.47	2.88	nd	0.44	nd	0.05	nd	nd	nd	nd	102.30	Ca_{1.04}Al_{10.99}Ti_{0.45}Mg_{0.47}Si_{0.05}O₁₉

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Continued...

Sample	Mineral	Point	CaO	Al ₂ O ₃	TiO ₂	MgO	FeO	SiO ₂	Cr ₂ O ₃	Na ₂ O	ZnO	MnO	V ₂ O ₅	S	Total	Calculated stoichiometry
Acfer094/CAI40	Hib(H1)	Spec 1	8.8	79.6	7.9	3.9	<lld	<lld	<lld	<lld	<lld	<lld	0.7	<lld	100.9	Ca _{1.06} Al _{10.54} Ti _{0.67} Mg _{0.65} O ₁₉
	Hib(H3)	Spec 2	8.8	79.7	8.0	3.4	<lld	<lld	<lld	<lld	<lld	<lld	<lld	<lld	99.8	Ca _{1.07} Al _{10.67} Ti _{0.68} Mg _{0.57} O ₁₉
	Hib(H4)	Spec 3	8.7	80.3	7.2	3.2	<lld	<lld	<lld	<lld	<lld	<lld	<lld	<lld	99.3	Ca _{1.06} Al _{10.78} Ti _{0.62} Mg _{0.54} O ₁₉
	Hib(H2)	Spec 4	8.6	79.0	7.5	3.8	<lld	<lld	<lld	<lld	<lld	<lld	<lld	<lld	98.8	Ca _{1.05} Al _{10.68} Ti _{0.64} Mg _{0.65} O ₁₉
	Hib(H4)	Spec 1 (SOI5)	8.8	80.7	7.1	3.0	<lld	<lld	<lld	<lld	<lld	<lld	<lld	<lld	99.7	Ca _{1.07} Al _{10.80} Ti _{0.61} Mg _{0.51} O ₁₉
	Hib(5)		8.7	79.8	7.5	3.4	<lld	<lld	<lld	<lld	<lld	<lld	<lld	<lld	99.7	Ca_{1.06}Al_{10.69}Ti_{0.64}Mg_{0.58}O₁₉
	Std Dev		0.1	0.7	0.4	0.4									0.8	
	Mel (c)	Spec 2 (SOI5)	42.0	36.3	<lld	<lld	<lld	21.9	<lld	<lld	<lld	<lld	<lld	<lld	100.1	
		Spec 5	41.4	36.4	<lld	<lld	<lld	21.5	<lld	<lld	<lld	<lld	<lld	<lld	99.2	
	Mel (r)	Spec 5 (SOI5)	41.1	36.5	<lld	0.4	<lld	22.6	<lld	<lld	<lld	<lld	<lld	<lld	100.5	
	Mel(3)		41.5	36.4	<lld	0.4	<lld	22.0	<lld	<lld	<lld	<lld	<lld	<lld	100.0	Ca_{2.00}Al_{1.97}Mg_{0.05}Si_{1.00}O₇
	Std Dev		0.5	0.1				0.6							0.7	
	Spinel	Spec 3 (SOI5)	0.0	69.0	<lld	28.6	<lld	<lld	<lld	<lld	<lld	<lld	0.6	<lld	98.2	
		Spec 4 (SOI5)	0.6	68.7	<lld	28.2	<lld	<lld	<lld	<lld	<lld	<lld	0.7	<lld	98.2	
		Spec 6	0.5	69.2	<lld	28.1	<lld	<lld	<lld	<lld	<lld	<lld	0.8	<lld	98.5	
		Spec 7	0.0	70.7	<lld	28.7	0.4	<lld	<lld	<lld	<lld	<lld	0.5	<lld	100.4	
	Spinel(4)		0.3	69.4	<lld	28.4	0.4	<lld	<lld	<lld	<lld	<lld	0.7	<lld	98.8	Mg_{1.02}Ca_{0.01}Al_{1.96}O₄
	Std Dev		0.3	0.9		0.3							0.1		1.1	
	Perov(1)	Spec 6 (SOI5)	41.2	0.9	57.4	<lld	<lld	<lld	<lld	<lld	<lld	<lld	<lld	<lld	99.5	Ca_{1.00}Ti_{0.98}Al_{0.02}O₃
El Djouf001/CAI	Hib(H2)	1 / 1 .	8.60	81.84	5.28	2.85	0.10	0.44	0.07	nd	nd	nd	nd	<lld	99.19	Ca _{1.05} Al _{10.96} Ti _{0.45} Mg _{0.48} Si _{0.05} Fe _{0.01} Cr _{0.01} O ₁₉
		1 / 2 .	8.89	82.58	5.09	2.79	0.10	0.80	0.06	nd	nd	nd	nd	<lld	100.29	Ca _{1.07} Al _{10.94} Ti _{0.43} Mg _{0.47} Si _{0.09} Fe _{0.01} Cr _{0.01} O ₁₉
		1 / 3 .	8.58	81.95	6.07	3.28	0.09	0.41	0.08	nd	nd	nd	nd	<lld	100.47	Ca _{1.03} Al _{10.85} Ti _{0.51} Mg _{0.55} Si _{0.05} Fe _{0.01} Cr _{0.01} O ₁₉
		1 / 4 .	9.01	80.58	6.68	3.32	0.06	0.63	0.08	nd	nd	nd	nd	<lld	100.37	Ca _{1.09} Al _{10.71} Ti _{0.57} Mg _{0.56} Si _{0.07} Fe _{0.01} Cr _{0.01} O ₁₉
	Hib(4)		8.77	81.74	5.78	3.06	0.09	0.57	0.07	nd	nd	nd	nd	<lld	100.08	Ca_{1.06}Al_{10.86}Ti_{0.49}Mg_{0.51}Si_{0.06}Fe_{0.01}Cr_{0.01}O₁₉
	Std Dev		0.21	0.84	0.73	0.28	0.02	0.18	0.01						0.60	
	Mel	1 / 5 .	41.02	36.30	0.09	0.43	0.14	22.26	<lld	nd	nd	nd	nd	<lld	100.24	
	Mel	1 / 6 .	40.75	33.36	0.05	1.51	0.18	23.88	<lld	nd	nd	nd	nd	<lld	99.76	
	Mel	1 / 9 .	41.20	34.51	0.04	1.10	0.10	23.42	<lld	nd	nd	nd	nd	<lld	100.39	
	Mel(3)		40.99	34.72	0.06	1.01	0.14	23.19	<lld	nd	nd	nd	nd	<lld	100.13	Ca_{2.00}Al_{1.87}Mg_{0.07}Si_{1.06}O₇
	Std Dev		0.23	1.48	0.03	0.55	0.04	0.83							0.33	
	Spinel(1)	1 / 8 .	2.14	70.94	1.50	23.91	0.15	0.77	0.20	nd	nd	nd	nd	<lld	99.60	Mg_{0.85}(Ca,Ti,Si)_{0.10}Al_{2.00}O₄
	Perov(1)	1 / 11 .	40.13	9.55	44.20	0.17	0.10	5.21	<lld	nd	nd	nd	nd	<lld	99.38	Ca_{0.94}Ti_{0.73}Al_{0.25}Si_{0.11}O₃

Continued...

Key for entire table:

Minerals: Hib = hibonite; Mel = melilite; Perov = perovskite; Ti-p Aug = Ti poor augite; Ti-r = Ti-rich augite.

Codes: (c) = core; (r) = rim; H# = hibonite grain number; Mineral(#) = number of analyses making up average.

Continued...

Sample	Mineral	Point	CaO	Al ₂ O ₃	TiO ₂	MgO	FeO	SiO ₂	Cr ₂ O ₃	Na ₂ O	ZnO	MnO	V ₂ O ₅	S	Total	Calculated stoichiometry
Hughes030/L	Hib (H2)	2 / 1 .	8.69	91.77	0.18	<lld	0.51	<lld	<lld	nd	nd	nd	nd	<lld	101.19	
		3 / 1 .	8.53	91.63	0.18	<lld	0.37	0.04	<lld	nd	nd	nd	nd	<lld	100.76	
	Hib (H3)	4 / 1 .	8.71	91.91	0.16	<lld	0.39	0.04	<lld	nd	nd	nd	nd	<lld	101.20	
		5 / 1 .	8.75	91.41	0.17	<lld	0.44	0.16	<lld	nd	nd	nd	nd	<lld	100.95	
		6 / 1 .	8.80	92.25	0.26	<lld	0.51	<lld	<lld	nd	nd	nd	nd	<lld	101.85	
	Hib (H4)	7 / 1 .	8.71	91.56	0.16	0.03	0.47	0.05	<lld	nd	nd	nd	nd	<lld	100.98	
		13 / 1 .	8.69	92.37	0.17	0.00	0.44	0.02	<lld	nd	nd	nd	nd	<lld	101.69	
	Hib (H5)	8 / 1 .	8.67	91.61	0.17	<lld	0.42	<lld	<lld	nd	nd	nd	nd	<lld	100.85	
	Hib(8)		8.69	91.81	0.18	<lld	0.44	<lld	<lld	nd	nd	nd	nd	<lld	101.18	Ca_{1.03}Al_{11.93}Ti_{0.01}Fe_{0.04}O₁₉
	<i>Std Dev</i>		<i>0.08</i>	<i>0.34</i>	<i>0.03</i>		<i>0.05</i>								<i>0.39</i>	
NWA1476/124	Hib	1 / 1 .	8.67	87.71	1.92	0.98	0.34	0.15	<lld	nd	nd	nd	nd	<lld	99.77	
		2 / 1 .	8.64	87.61	2.29	1.06	0.29	0.06	<lld	nd	nd	nd	nd	<lld	99.98	
		3 / 1 .	8.78	87.25	2.35	1.01	0.22	0.08	<lld	nd	nd	nd	nd	<lld	99.71	
		4 / 1 .	8.64	87.28	2.06	0.99	0.31	0.15	<lld	nd	nd	nd	nd	<lld	99.47	
		5 / 1 .	8.67	87.77	2.37	1.15	0.29	0.04	<lld	nd	nd	nd	nd	<lld	100.31	
	Hib(5)		8.68	87.52	2.20	1.04	0.29	0.10	<lld	nd	nd	nd	nd	<lld	99.85	Ca_{1.04}Al_{11.57}Ti_{0.19}Mg_{0.17}Fe_{0.03}Si_{0.01}O₁₉
	<i>Std Dev</i>		<i>0.06</i>	<i>0.24</i>	<i>0.20</i>	<i>0.07</i>	<i>0.04</i>	<i>0.05</i>							<i>0.32</i>	
	Ti-p Aug (r)	14 / 1 .	26.15	18.62	0.04	10.97	0.57	43.03	0.07	nd	nd	nd	nd	<lld	99.47	
	Ti-p Aug	10 / 1 .	26.17	13.39	0.07	13.69	0.43	46.71	0.05	nd	nd	nd	nd	<lld	100.49	
	Ti-p Aug (2)		26.16	16.01	0.06	12.33	0.50	44.87	0.06	nd	nd	nd	nd	<lld	99.98	Ca_{1.02}(Mg_{0.67}Al_{0.32})(Al_{0.37}Si_{1.63})O₆
	<i>Std Dev</i>		<i>0.01</i>	<i>3.70</i>	<i>0.02</i>	<i>1.92</i>	<i>0.10</i>	<i>2.60</i>	<i>0.01</i>						<i>0.72</i>	
	Ti-r Aug	9 / 1 .	25.70	30.47	3.84	5.33	0.31	33.59	0.06	nd	nd	nd	nd	<lld	99.32	
		8 / 1 .	25.44	29.42	4.11	6.04	0.34	34.14	0.07	nd	nd	nd	nd	<lld	99.57	
		13 / 1 .	25.68	29.68	4.24	5.56	0.38	33.78	0.08	nd	nd	nd	nd	<lld	99.39	
		7 / 1 .	25.46	30.06	4.81	5.48	0.46	33.17	0.10	nd	nd	nd	nd	<lld	99.54	
		11 / 1 .	25.26	29.40	4.92	5.50	0.41	33.30	0.08	nd	nd	nd	nd	<lld	98.86	
	Ti-r Aug (5)		25.51	29.81	4.38	5.58	0.38	33.60	0.08	nd	nd	nd	nd	<lld	99.34	Ca_{1.01}(Mg_{0.31}Ti_{0.12}Al_{0.50})(Al_{0.80}Si_{1.24})O₆
	<i>Std Dev</i>		<i>0.18</i>	<i>0.46</i>	<i>0.46</i>	<i>0.27</i>	<i>0.06</i>	<i>0.39</i>	<i>0.01</i>						<i>0.29</i>	
NWA2446/2L	Hib	Spec 1	8.6	89.1	1.5	0.8	0.5	<lld	<lld	<lld	<lld	<lld	<lld	<lld	100.5	
		Spec 2	8.7	88.5	1.4	0.6	0.5	<lld	<lld	<lld	<lld	<lld	<lld	<lld	99.6	
		Spec 3	8.6	88.0	1.5	0.5	0.5	<lld	<lld	<lld	<lld	<lld	<lld	<lld	99.1	
		Spec 4*	8.4	89.1	1.6	0.6	<lld	<lld	<lld	<lld	<lld	<lld	<lld	<lld	99.7	
		Spec 5	8.5	88.2	1.2	0.5	0.6	<lld	<lld	<lld	<lld	<lld	<lld	<lld	99.1	
	Hib(5)		8.6	88.6	1.4	0.6	0.5	<lld	<lld	<lld	<lld	<lld	<lld	<lld	99.6	Ca_{1.03}Al_{11.73}Ti_{0.12}Mg_{0.10}Fe_{0.05}O₁₉
	<i>Std Dev</i>		<i>0.1</i>	<i>0.5</i>	<i>0.1</i>	<i>0.1</i>	<i>0.0</i>								<i>0.6</i>	
	Ilm(1)	Spec 6	1.7	18.7	40.5	1.3	35.5	1.7	<lld	<lld	<lld	<lld	<lld	<lld	99.5	

Continued...

Continued...

Sample	Mineral	Point	CaO	Al ₂ O ₃	TiO ₂	MgO	FeO	SiO ₂	Cr ₂ O ₃	Na ₂ O	ZnO	MnO	V ₂ O ₅	S	Total	Calculated stoichiometry
NWA2446/5L	Hib	1 / 1 .	8.39	88.26	2.73	1.35	0.67	0.11	<lld	nd	nd	nd	nd	<lld	101.53	
		1 / 2 .	8.56	88.57	2.56	1.30	0.61	0.08	<lld	nd	nd	nd	nd	<lld	101.69	
		1 / 4 .	8.44	88.11	2.61	1.36	0.63	0.08	<lld	nd	nd	nd	nd	<lld	101.26	
		1 / 7 .	8.51	88.17	2.67	1.33	0.64	0.09	<lld	nd	nd	nd	nd	<lld	101.43	
	Hib(4)		8.48	88.28	2.64	1.34	0.64	0.09	<lld	nd	nd	nd	nd	<lld	101.48	Ca _{1.00} Al _{11.50} Ti _{0.22} Mg _{0.22} Fe _{0.06} Si _{0.01} O ₁₉
	Std Dev		0.08	0.20	0.07	0.03	0.025	0.01							0.18	
	Ti-p Aug	1 / 5 .	25.51	36.39	0.67	4.63	0.88	33.74	0.03	nd	nd	nd	nd	<lld	101.88	
		1 / 8 .	25.60	36.77	0.62	4.31	0.82	33.50	0.03	nd	nd	nd	nd	<lld	101.67	
NWA2446/8L	Ti-p Aug (2)		25.56	36.58	0.65	4.47	0.85	33.62	0.03	nd	nd	nd	nd	<lld	101.78	Ca _{0.98} (Mg _{0.24} Ti _{0.02} Al _{0.74})(Al _{0.80} Si _{1.20})O ₆
	Std Dev		0.06	0.27	0.04	0.23	0.042	0.17	0.00						0.15	
	Hib	Spec 1	8.3	82.3	4.3	2.6	1.3	<lld	<lld	<lld	<lld	<lld	<lld	<lld	98.7	
		Spec 2	7.9	79.3	6.0	3.4	1.7	<lld	<lld	<lld	<lld	<lld	<lld	<lld	98.2	
		Spec 3	8.5	81.6	4.8	2.5	0.9	<lld	<lld	<lld	<lld	<lld	<lld	<lld	98.3	
	Hib(3)		8.2	81.0	5.0	2.8	1.3	<lld	<lld	<lld	<lld	<lld	<lld	<lld	98.4	Ca _{1.01} Al _{11.01} Ti _{0.43} Mg _{0.48} Fe _{0.13} O ₁₉
	Std Dev		0.3	1.6	0.9	0.5	0.4								0.3	
NWA2446/12	Spinel(1)	Spec 5	<lld	59.7	<lld	10.4	23.0	0.7	<lld	<lld	3.6	<lld	<lld	1.3	98.8	Mg _{0.42} Fe _{0.52} Zn _{0.07} Si _{0.02} Al _{1.91} O ₄
	Hib	Spec 1	8.6	86.1	3.0	1.2	0.8	<lld	<lld	<lld	<lld	<lld	<lld	<lld	99.7	
		Spec 2	8.3	81.9	6.4	3.4	0.9	<lld	<lld	<lld	<lld	<lld	0.7	<lld	101.6	
		Spec 3	8.2	78.9	6.0	3.2	0.9	<lld	<lld	<lld	<lld	<lld	0.8	<lld	98.0	
		Spec 4	8.3	83.7	4.7	2.6	0.6	0.5	<lld	<lld	<lld	<lld	0.5	<lld	100.8	
		Spec 5	8.3	83.8	3.5	1.9	0.9	0.8	<lld	<lld	<lld	<lld	<lld	<lld	99.1	
	Hib(5)		8.3	82.9	4.7	2.5	0.8	<lld	<lld	<lld	<lld	<lld	0.4	<lld	99.8	Ca _{1.01} Al _{11.04} Ti _{0.40} Mg _{0.42} Fe _{0.08} O ₁₉
	Std Dev		0.1	2.7	1.5	0.9	0.2								1.4	
	Spinel (1) Ilm (1)	Spec 6 Spec 7	0.3 0.5	59.9 3.8	2.2 42.9	10.5 1.3	23.4 40.4	1.8 1.7	<lld <lld	<lld <lld	4.3 <lld	<lld <lld	<lld <lld	<lld <lld	102.2 90.5	
7-076	Hib	Spec 2	8.5	88.8	1.8	0.9	<lld	<lld	nd	<lld	nd	nd	<lld	<lld	100.0	Ca _{1.02} Al _{11.69} Ti _{0.15} Mg _{0.15} O ₁₉
7-505	Hib	Spec 1	8.3	82.8	5.5	2.8	<lld	<lld	nd	<lld	nd	nd	0.6	<lld	100.0	
		Spec 2	8.5	82.6	5.4	2.7	<lld	<lld	nd	<lld	nd	nd	0.8	<lld	100.0	
	Hib (2)		8.4	82.7	5.4	2.8	<lld	<lld	nd	<lld	nd	nd	0.7	<lld	100.0	Ca _{1.01} Al _{10.95} Ti _{0.46} Mg _{0.46} O ₁₉
	Std Dev		0.1	0.2	0.1	0.0							0.2			

Table C-4 Published major element abundance of meteoritic hibonite from the Murchison meteorite

Sample	Reference	CaO	Al ₂ O ₃	TiO ₂	MgO	FeO	SiO ₂	Total	Calculated stoichiometry
10-43	Ireland (1988)	8.51	82.09	6.44	2.86	0.04	nd	99.94	Ca _{1.03} Al _{10.93} Ti _{0.55} Mg _{0.48} O ₁₉
7-76†	Ireland <i>et al.</i> (1988)			1.83					
7-170	Ireland (1988)	8.61	84.12	4.99	2.76	0.21	nd	100.69	Ca _{1.03} Al _{11.10} Ti _{0.42} Mg _{0.46} O ₁₉
7-505†	Ireland <i>et al.</i> (1988)			8.70					
7-753	Ireland (1988)	8.60	88.49	1.86	0.85	nd	nd	99.8	Ca _{1.03} Al _{11.68} Ti _{0.16} Mg _{0.14} O ₁₉
7-953	Ireland (1988)	8.15	81.62	6.53	3.34	0.23	nd	99.87	Ca _{0.99} Al _{10.88} Ti _{0.56} Mg _{0.56} O ₁₉
7-971	Ireland (1988)	8.38	91.48	0.23	0.14	nd	nd	100.00	Ca _{1.00} Al _{12.02} Ti _{0.02} Mg _{0.02} O ₁₉
7-981	Ireland (1988)	8.46	89.66	1.19	0.73	nd	nd	100.04	Ca _{1.01} Al _{11.78} Ti _{0.10} Mg _{0.12} O ₁₉

† Only the TiO₂ content of 7-76 and 7-505 were published by Ireland *et al.* (1988). Published TiO₂ data from 7-76 (1.83 wt% TiO₂) is the same as the TiO₂ content determined by EDS SEM in this study, whereas the published TiO₂ content of 7-505 (8.70 wt% TiO₂) is higher than that determined in this study (5.5 wt% TiO₂). According to the EDS SEM analysis 7-505 contained 0.7 wt% V₂O₅ (0.2 wt% V). As the V energy peak overlaps that of Ti, it may account for the lower TiO₂ content determined by EDS SEM.

D. Supplementary information for the NPD study (Chapter 5)

D.1 Reported site occupancy

Table D-1 Reported site occupancy in hibonite

Site*	Experimentally determined occupancy	Cation	Predicted occupancy
A	XRD of terrestrial hibonite (Bermanec <i>et al.</i> , 1996)	Ca ²⁺ , REE	
M1		Cr ³⁺	Prediction as Cr ³⁺ has a strong preference for octahedral sites (Burns and Burns, 1984)
M2	Mössbauer spectroscopy of terrestrial hibonite (Burns and Burns, 1984)	Fe ²⁺	Prediction based on ionic radius and calculation of crystal field stabilisation energy (CFSE) (Burns and Burns, 1984)
	Mössbauer spectroscopy of terrestrial hibonite (Burns and Burns, 1984) and Fe-doped synthetic hibonite (Holtstam, 1996)	Fe ³⁺	Prediction based on ionic radius and calculation of CFSE (Burns and Burns, 1984)
	Optical spectroscopy (Burns and Burns, 1984)	V ³⁺	Prediction based on calculation of CFSE (Burns and Burns, 1984)
	Optical spectroscopy (Burns and Burns, 1984; Dyar <i>et al.</i> , 1986); Electron Paramagnetic Resonance (EPR) spectroscopy (Beckett <i>et al.</i> , 1988)	Ti ³⁺	Prediction based on CFSE (Burns and Burns, 1984); Prediction based on Density functional theory (DFT) (Walker, pers. comm. 2008)
	XRD of terrestrial hibonite (Nagashima <i>et al.</i> , 2010)	Ti ⁴⁺	Prediction based on ionic radius (Beckett <i>et al.</i> , 1988)
M3	XRD of terrestrial hibonite (Bermanec <i>et al.</i> , 1996; Nagashima <i>et al.</i> , 2010)	Mg ²⁺ ; Zn ²⁺ ; Si ⁴⁺	
	Mössbauer spectroscopy and optical absorption of synthetic Fe-doped hibonite (Holtstam, 1996); Mössbauer spectroscopy of terrestrial hibonite (Burns and Burns, 1984); XRD of terrestrial hibonite (Bermanec <i>et al.</i> , 1996)	Fe ²⁺	
	Mössbauer spectroscopy of terrestrial hibonite (Burns and Burns, 1984)	Fe ³⁺	
M4	Mössbauer spectroscopy of terrestrial hibonite (Burns and Burns, 1984)	Fe ²⁺	
	XRD of terrestrial hibonite (Bermanec <i>et al.</i> , 1996)	Si ⁴⁺	
	XRD of terrestrial hibonite (Bermanec <i>et al.</i> , 1996; Nagashima <i>et al.</i> , 2010); Optical spectroscopy (Burns and Burns, 1984)	Ti ⁴⁺	
		Cr ³⁺	Prediction as Cr ³⁺ has a strong preference for octahedral sites (Burns and Burns, 1984)
M5		Ti ⁴⁺	Predicted by DFT (in charge balanced with Mg ²⁺ on the M3 site) (Walker, pers. comm. 2008)
		Cr ³⁺	Prediction as Cr ³⁺ has a strong preference for octahedral sites (Burns and Burns, 1984)

* **Nomenclature:** M1 (Bermanec *et al.*, 1996, B) = Al1 (Hofmeister *et al.*, 2004, H) = Al4 (Kato and Saalfeld, 1968, K&S; Burns and Burns, 1984, B&B);

M2 (B) = Al2 (H) = Al5 (K&S, B&B); M3 (B) = Al3 (H) = Al2 (K&S, B&B); M4 (B) = Al4 (H) = Al3 (K&S; B&B); M5 (B) = Al5 (H) = Al1 (K&S; B&B)

Table D-2 Reported site occupancy in phases isostructural with hibonite

Site	Cation	Experimentally determined site occupancy
A	Pb, Ba, Ca	XRD of magnetoplumbite and nežilovite (Bermanec <i>et al.</i> , 1996)
M1	Al ³⁺ Cr ³⁺ Ti ³⁺ Fe ³⁺ Ti ⁴⁺	XRD of nežilovite PbFe _{8.0} Zn _{1.9} (Mn ³⁺ , Mn ⁴⁺) _{2.5} Ti ⁴⁺ _{0.4} Al _{1.0} O ₁₉ (Bermanec <i>et al.</i> , 1996); XRD of β-alumina (Na ₂ MgAl ₁₀ O ₁₇) (Bettman and Peters, 1969) XRD of SrCr ₉ Ga ₃ O ₁₉ (Graetsch and Gebert, 1996) ESR of Ti-bearing β- and β''-alumina (Na _{1.6} Al _{10.8} O ₁₇ and Na _{1.7} Al _{10.6} Mg _{0.3} O ₁₇) (Barret <i>et al.</i> , 1985) Mössbauer spectroscopy of Ba(Fe,Co,Ti) ₁₂ O ₁₉ (Kreber and Gonser, 1976); XRD of magnetoplumbite and nežilovite (Bermanec <i>et al.</i> , 1996) XRD of SrTi ₆ Co ₆ O ₁₉ (Graetsch and Gebert, 1995); Mössbauer spectroscopy of Ba(Fe,Co,Ti) ₁₂ O ₁₉ (Kreber and Gonser, 1976) Ti ⁴⁺ (and Co ²⁺ ?) only occupy this site when M3 and M4 contains no Fe.
M2	Co ²⁺ Al ³⁺ Fe ³⁺ Mn ⁴⁺ Ti ⁴⁺ Ga ³⁺	XRD of SrTi ₆ Co ₆ O ₁₉ (Graetsch and Gebert, 1995); Mössbauer spectroscopy of Ba(Fe,Co,Ti) ₁₂ O ₁₉ (Kreber and Gonser, 1976) Ti ⁴⁺ and Co ²⁺ only occupy this site <4 Fe pfu. XRD of β-alumina (Na ₂ MgAl ₁₀ O ₁₇) (Bettman and Peters, 1969) Mössbauer spectroscopy of Ba(Fe,Co,Ti) ₁₂ O ₁₉ (Kreber and Gonser, 1976); XRD of magnetoplumbite and nežilovite (Bermanec <i>et al.</i> , 1996) XRD of nežilovite PbFe _{8.0} Zn _{1.9} (Mn ³⁺ , Mn ⁴⁺) _{2.5} Ti ⁴⁺ _{0.4} Al _{1.0} O ₁₉ (Bermanec <i>et al.</i> , 1996) XRD of SrTi ₆ Co ₆ O ₁₉ (Graetsch and Gebert, 1995); Mössbauer spectroscopy of Ba(Fe,Co,Ti) ₁₂ O ₁₉ (Kreber and Gonser, 1976) Ti ⁴⁺ and Co ²⁺ only occupy this site <4 Fe pfu. XRD of SrCr ₉ Ga ₃ O ₁₉ (Graetsch and Gebert, 1996)
M3	Mg ²⁺ Mn ²⁺ Zn ²⁺ Co ²⁺ Al ³⁺ Fe ³⁺ Ga ³⁺	XRD of β-alumina (Na ₂ MgAl ₁₀ O ₁₇) (Bettman and Peters, 1969) XRD of magnetoplumbite PbFe _{9.3} (Mn ²⁺ , Mn ³⁺) _{1.8} Sb _{0.6} Mg _{0.3} O ₁₉ (Bermanec <i>et al.</i> , 1996) XRD of nežilovite PbFe _{8.0} Zn _{1.9} (Mn ³⁺ , Mn ⁴⁺) _{2.5} Ti ⁴⁺ _{0.4} Al _{1.0} O ₁₉ (Bermanec <i>et al.</i> , 1996) XRD of SrTi ₆ Co ₆ O ₁₉ (Graetsch and Gebert, 1995); Mössbauer spectroscopy of Ba(Fe,Co,Ti) ₁₂ O ₁₉ (Kreber and Gonser, 1976) XRD of β-alumina (Na ₂ MgAl ₁₀ O ₁₇) (Bettman and Peters, 1969) Mössbauer spectroscopy of Ba(Fe,Co,Ti) ₁₂ O ₁₉ (Kreber and Gonser, 1976); XRD of magnetoplumbite and nežilovite (Bermanec <i>et al.</i> , 1996) XRD of SrCr ₉ Ga ₃ O ₁₉ (Graetsch and Gebert, 1996)
M4	Al ³⁺ Cr ³⁺ Fe ³⁺ Mn ⁴⁺ Ti ⁴⁺ Sb ⁵⁺	XRD of β-alumina (Na ₂ MgAl ₁₀ O ₁₇) (Bettman and Peters, 1969) XRD of SrCr ₉ Ga ₃ O ₁₉ (Graetsch and Gebert, 1996) Mössbauer spectroscopy of Ba(Fe,Co,Ti) ₁₂ O ₁₉ (Kreber and Gonser, 1976); XRD of magnetoplumbite and nežilovite (Bermanec <i>et al.</i> , 1996) XRD of nežilovite PbFe _{8.0} Zn _{1.9} (Mn ³⁺ , Mn ⁴⁺) _{2.5} Ti ⁴⁺ _{0.4} Al _{1.0} O ₁₉ (Bermanec <i>et al.</i> , 1996) XRD of SrTi ₆ Co ₆ O ₁₉ (Graetsch and Gebert, 1995); Mössbauer spectroscopy of Ba(Fe,Co,Ti) ₁₂ O ₁₉ (Kreber and Gonser, 1976) XRD of magnetoplumbite PbFe _{9.3} (Mn ²⁺ , Mn ³⁺) _{1.8} Sb _{0.6} Mg _{0.3} O ₁₉ (Bermanec <i>et al.</i> , 1996)
M5	Cr ³⁺ Co ²⁺ Al ³⁺ Mn ³⁺ Fe ³⁺ Ti ³⁺ Ti ⁴⁺	XRD of SrCr ₉ Ga ₃ O ₁₉ (Graetsch and Gebert, 1996) XRD of SrTi ₆ Co ₆ O ₁₉ (Graetsch and Gebert, 1995); Mössbauer spectroscopy of Ba(Fe,Co,Ti) ₁₂ O ₁₉ (Kreber and Gonser, 1976) Ti ⁴⁺ and Co ²⁺ only occupy this site when M3 and M4 contain no Fe. XRD of nežilovite PbFe _{8.0} Zn _{1.9} (Mn ³⁺ , Mn ⁴⁺) _{2.5} Ti ⁴⁺ _{0.4} Al _{1.0} O ₁₉ (Bermanec <i>et al.</i> , 1996); XRD of β-alumina (Na ₂ MgAl ₁₀ O ₁₇) (Bettman and Peters, 1969) XRD of nežilovite PbFe _{8.0} Zn _{1.9} (Mn ³⁺ , Mn ⁴⁺) _{2.5} Ti ⁴⁺ _{0.4} Al _{1.0} O ₁₉ (Bermanec <i>et al.</i> , 1996) Mössbauer spectroscopy of Ba(Fe,Co,Ti) ₁₂ O ₁₉ (Kreber and Gonser, 1976); XRD of magnetoplumbite and nežilovite (Bermanec <i>et al.</i> , 1996) ESR of Ti-bearing β- and β''-alumina (Na _{1.6} Al _{10.8} O ₁₇ and Na _{1.7} Al _{10.6} Mg _{0.3} O ₁₇) (Barret <i>et al.</i> , 1985) XRD of SrTi ₆ Co ₆ O ₁₉ (Graetsch and Gebert, 1995); Mössbauer spectroscopy of Ba(Fe,Co,Ti) ₁₂ O ₁₉ (Kreber and Gonser, 1976) Ti ⁴⁺ and Co ²⁺ only occupy this site when M3 and M4 contain no Fe.

D.2 Measures of “good fit”

Table D-3 HibF(20,0) fractional coordinates, atomic displacement parameters and elemental occupancy.

HibF(20,0)	x	y	z	ADP	Occupancy (Element)
Ca	0.66670	0.33330	0.25000	1.059 (0.026)	1.000 (Ca)
M1	0.00000	0.00000	0.00000	0.639 (0.024)	1.000 (Al)
M2	0.00000	0.00000	0.26037 (0.00007)	1.101 (0.033)	0.500 (Al)
M3	0.33330	0.66670	0.02802 (0.00004)	1.000 (0.017)	1.000 (Al)
M4	0.33330	0.66670	0.19012 (0.00004)	0.655 (0.024)	0.911 (0.001) (Al); 0.089(0.001) (Ti)
M5	0.16882 (0.00006)	0.33754 (0.00012)	-0.10889 (0.00001)	0.823 (0.008)	1.000 (Al)
O1	0.00000	0.00000	-0.14952 (0.00002)	0.804 (0.018)	1.000 (O)
O2	0.66670	0.33330	0.05423 (0.00003)	0.585 (0.014)	1.000 (O)
O3	0.18094 (0.00005)	0.36189 (0.00010)	0.25000	1.130 (0.009)	1.000 (O)
O4	0.15532 (0.00003)	0.31075 (0.00006)	0.05217 (0.00001)	0.716 (0.006)	1.000 (O)
O5	0.50336 (0.00004)	1.00662 (0.00009)	0.14897 (0.00001)	0.751 (0.006)	1.000 (O)

Notes: Error as calculated by GSAS in brackets. Approximate error for Mg occupancy quoted.

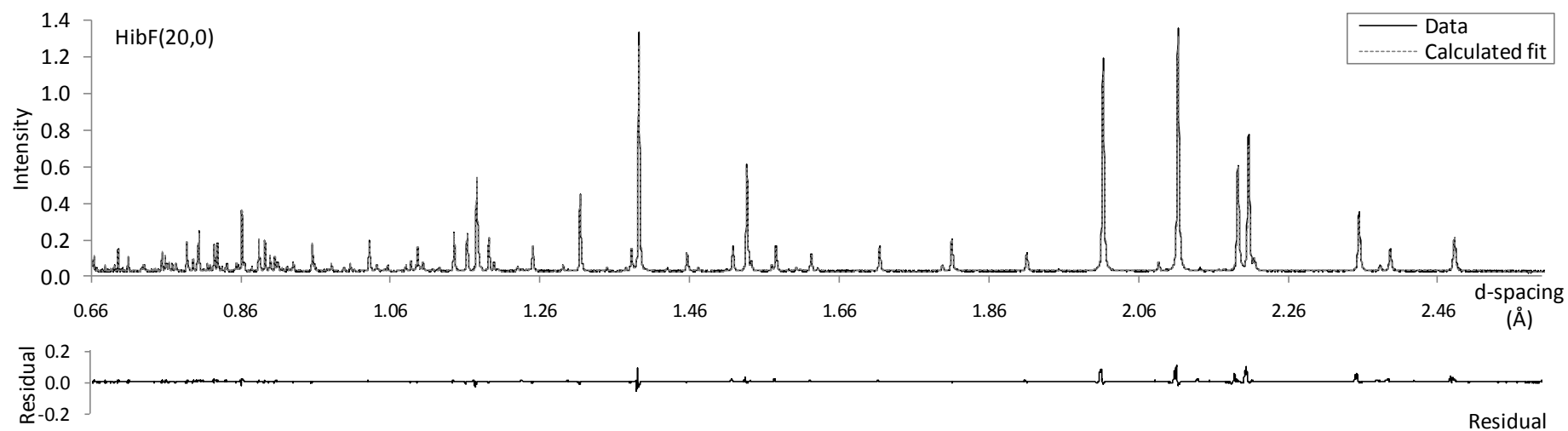


Figure D-1 HibF(20,0) neutron powder diffraction data and Rietveld refinement fit (above), and fit-residual (below).

Table D-4 Hib5D(33,0) fractional coordinates, atomic displacement parameters and elemental occupancy.

Hib5D(33,0)	x	y	z	ADP	Occupancy (Element)
Ca	0.66670	0.33330	0.25000	0.641 (0.040)	1.000 (Ca)
M1	0.00000	0.00000	0.00000	0.648 (0.037)	1.000 (Al)
M2	0.00000	0.00000	0.26058 (0.00011)	0.901 (0.050)	0.500 (Al)
M3	0.33330	0.66670	0.02868 (0.00006)	1.320 (0.029)	1.000 (Al)
M4	0.33330	0.66670	0.18988 (0.00008)	0.742 (0.044)	0.913 (0.001) (Al); 0.187 (0.001) (Ti)
M5	0.16901 (0.00010)	0.33793 (0.00020)	-0.10881 (0.00002)	1.060 (0.013)	1.000 (Al)
O1	0.00000	0.00000	-0.15008 (0.00004)	1.162 (0.030)	1.000 (O)
O2	0.66670	0.33330	0.05328 (0.00005)	0.621 (0.022)	1.000 (O)
O3	0.18156 (0.00008)	0.36311 (0.00017)	0.25000	1.500 (0.016)	1.000 (O)
O4	0.15510 (0.00005)	0.31022 (0.00010)	0.05256 (0.00002)	1.008 (0.010)	1.000 (O)
O5	0.50323 (0.00007)	1.00656 (0.00015)	0.14882 (0.00002)	0.994 (0.011)	1.000 (O)

Notes: Error as calculated by GSAS in brackets. Approximate error for Mg occupancy quoted.

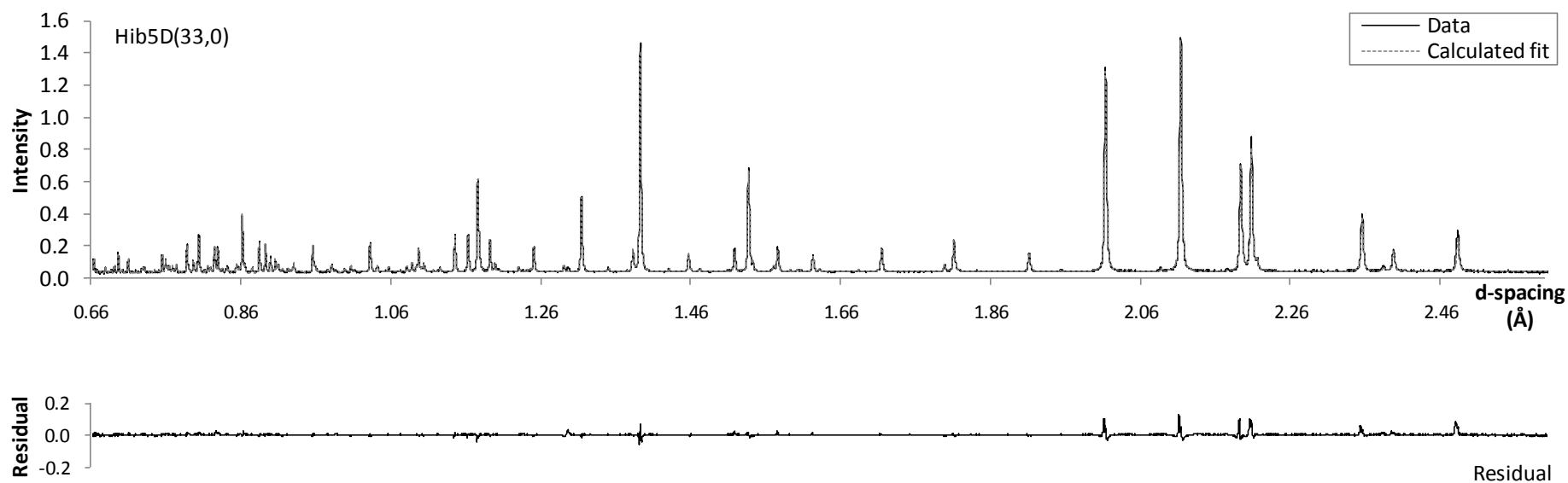


Figure D-2 Hib5D(33,0) neutron powder diffraction data and Rietveld refinement fit (above), and fit-residual (below).

Table D-5 HibK(62,24) fractional coordinates, atomic displacement parameters and elemental occupancy.

HibK(62,24)	x	y	z	ADP	Occupancy (Element)
Ca	0.66670	0.33330	0.25000	1.783 (0.033)	1.000 (Ca)
M1	0.00000	0.00000	0.00000	0.460 (0.028)	1.000 (Al)
M2	0.00000	0.00000	0.26284 (0.00008)	1.048 (0.046)	0.474 (0.001) (Al); 0.026 (0.001) (Ti)
M3	0.33330	0.66670	0.02843 (0.00004)	0.986 (0.019)	0.890 (0.003) (Al); 0.110 (0.003) (Mg)*
M4	0.33330	0.66670	0.18861 (0.00008)	0.932 (0.049)	0.748 (0.001) (Al); 0.252 (0.001) (Ti)
M5	0.16931 (0.00007)	0.33854 (0.00014)	-0.10836 (0.00002)	1.036 (0.010)	1.000 (Al)
O1	0.00000	0.00000	-0.14968 (0.00003)	1.013 (0.022)	1.000 (O)
O2	0.66670	0.33330	0.05505 (0.00003)	0.738 (0.016)	1.000 (O)
O3	0.18007 (0.00006)	0.36024 (0.00011)	0.25000	1.354 (0.011)	1.000 (O)
O4	0.15429 (0.00003)	0.30857 (0.00007)	0.05237 (0.00001)	1.011 (0.008)	1.000 (O)
O5	0.50398 (0.00004)	1.00805 (0.00009)	0.14891 (0.00001)	0.998 (0.008)	1.000 (O)

Notes: Error as calculated by GSAS in brackets. Approximate error for Mg occupancy quoted.

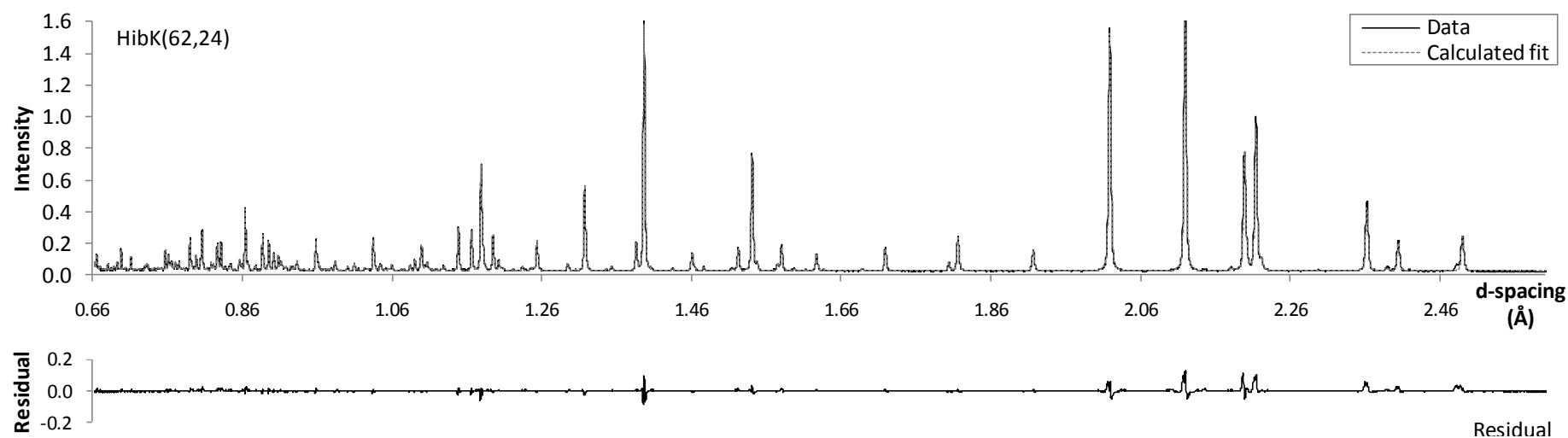


Figure D-3 HibK(62,24) neutron powder diffraction data and Rietveld refinement fit (above), and fit-residual (below).

Table D-6 Hib8C(73,49) fractional coordinates, atomic displacement parameters and elemental occupancy.

Hib8C(73,49)	x	y	z	ADP	Occupancy (Element)
Ca	0.66670	0.33330	0.25000	1.629 (0.037)	1.000 (Ca)
M1	0.00000	0.00000	0.00000	0.459 (0.032)	1.000 (Al)
M2	0.00000	0.00000	0.26325 (0.00010)	1.081 (0.057)	0.455 (0.001) (Al); 0.045 (0.001) (Ti)
M3	0.33330	0.66670	0.02826 (0.00004)	0.985 (0.019)	0.750 (0.003) (Al); 0.250 (0.003) (Mg)
M4	0.33330	0.66670	0.18761 (0.00012)	0.991 (0.069)	0.694 (0.001) (Al); 0.306 (0.001) (Ti)
M5	0.16883 (0.00008)	0.33758 (0.00017)	-0.10808 (0.00002)	0.983 (0.011)	1.000 (Al)
O1	0.00000	0.00000	-0.15026 (0.00003)	0.515 (0.023)	1.000 (O)
O2	0.66670	0.33330	0.05601 (0.00003)	0.743 (0.018)	1.000 (O)
O3	0.18016 (0.00006)	0.36044 (0.00013)	0.25000	1.398 (0.013)	1.000 (O)
O4	0.15351 (0.00004)	0.30702 (0.00008)	0.05276 (0.00001)	0.987 (0.008)	1.000 (O)
O5	0.50434 (0.00005)	1.00875 (0.00009)	0.14929 (0.00001)	1.018 (0.010)	1.000 (O)

Notes: Error as calculated by GSAS in brackets. Approximate error for Mg occupancy quoted.

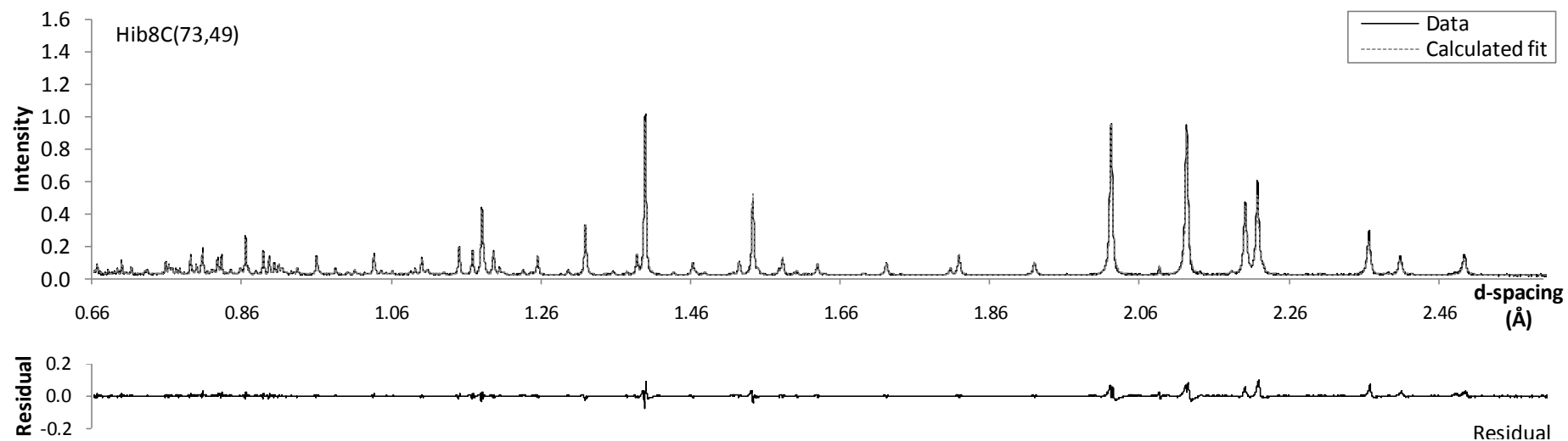


Figure D-4 Hib8C(73,49) neutron powder diffraction data and Rietveld refinement fit (above), and fit-residual (below).

Table D-7 HibJ(82,60) fractional coordinates, atomic displacement parameters and elemental occupancy.

HibJ(82,60)	x	y	z	ADP	Occupancy (Element)
Ca	0.66670	0.33330	0.25000	1.675 (0.042)	1.000 (Ca)
M1	0.00000	0.00000	0.00000	0.459 (0.037)	1.000 (Al)
M2	0.00000	0.00000	0.26367 (0.00012)	1.042 (0.075)	0.432 (0.001) (Al); 0.068 (0.001) (Ti)
M3	0.33330	0.66670	0.02858 (0.00004)	0.946 (0.021)	0.670 (0.013) (Al); 0.330 (0.013) (Mg)
M4	0.33330	0.66670	0.18811 (0.00017)	0.852 (0.105)	0.643 (0.001) (Al); 0.357 (0.001) (Ti)
M5	0.16927 (0.00010)	0.33845 (0.00020)	-0.10789 (0.00002)	1.022 (0.013)	1.000 (Al)
O1	0.00000	0.00000	-0.15076 (0.00004)	0.511 (0.027)	1.000 (O)
O2	0.66670	0.33330	0.05648 (0.00004)	0.621 (0.020)	1.000 (O)
O3	0.18056 (0.00007)	0.36123 (0.00015)	0.25000	1.405 (0.015)	1.000 (O)
O4	0.15302 (0.00004)	0.30605 (0.00009)	0.05294 (0.00002)	1.047 (0.010)	1.000 (O)
O5	0.50456 (0.00005)	1.00921 (0.00010)	0.14925 (0.00002)	0.971 (0.011)	1.000 (O)

Notes: Error as calculated by GSAS in brackets. Approximate error for Mg occupancy quoted.

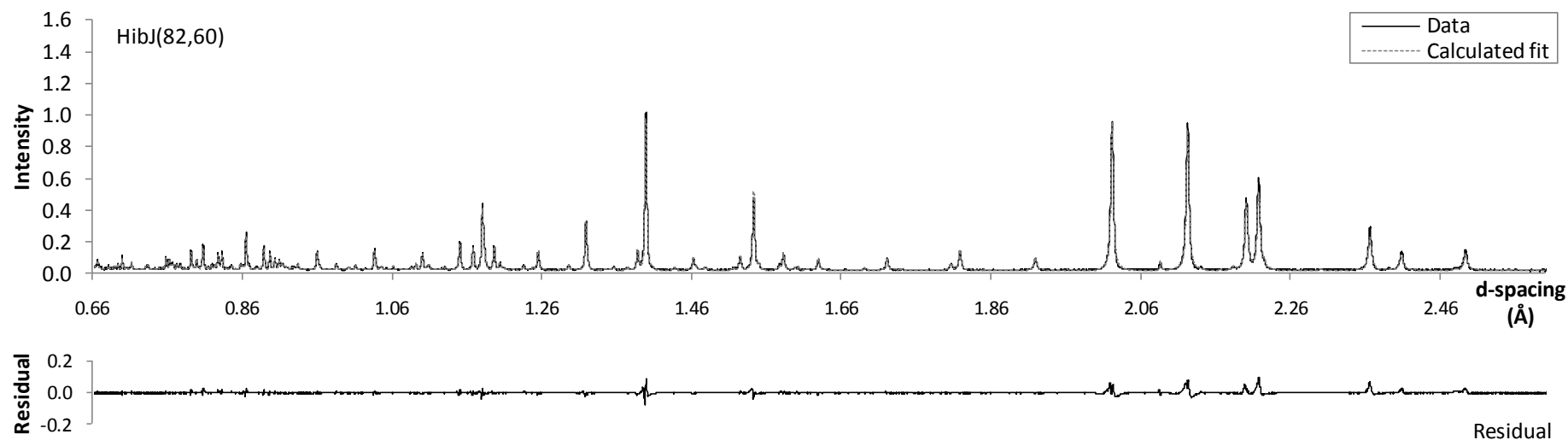


Figure D-5 HibJ(82,60) neutron powder diffraction data and Rietveld refinement fit (above), and fit-residual (below).

Table D-8 Hib9(44,43) fractional coordinates, atomic displacement parameters and elemental occupancy.

Hib9(44,43)	x	y	z	ADP	Occupancy (Element)
Ca	0.66670	0.33330	0.25000	1.484 (0.042)	1.000 (Ca)
M1	0.00000	0.00000	0.00000	0.570 (0.036)	1.000 (Al)
M2	0.00000	0.00000	0.26265 (0.00011)	1.169 (0.065)	0.452 (0.001) (Al); 0.048 (0.001) (Ti)
M3	0.33330	0.66670	0.02778 (0.00005)	0.908 (0.021)	0.790 (0.003) (Al); 0.210 (0.003) (Mg)
M4	0.33330	0.66670	0.18892 (0.00008)	0.816 (0.051)	0.802 (0.001) (Al); 0.198 (0.001) (Ti)
M5	0.16856 (0.00009)	0.33701 (0.00019)	-0.10832 (0.00002)	0.955 (0.013)	1.000 (Al)
O1	0.00000	0.00000	-0.15037 (0.00003)	0.379 (0.026)	1.000 (O)
O2	0.66670	0.33330	0.05634 (0.00004)	0.705 (0.020)	1.000 (O)
O3	0.18109 (0.00008)	0.36229 (0.00015)	0.25000	1.255 (0.015)	1.000 (O)
O4	0.15375 (0.00004)	0.30750 (0.00009)	0.05269 (0.00002)	0.924 (0.009)	1.000 (O)
O5	0.50347 (0.00006)	1.00701 (0.00011)	0.14937 (0.00002)	0.964 (0.011)	1.000 (O)

Notes: Error as calculated by GSAS in brackets. Approximate error for Mg occupancy quoted.

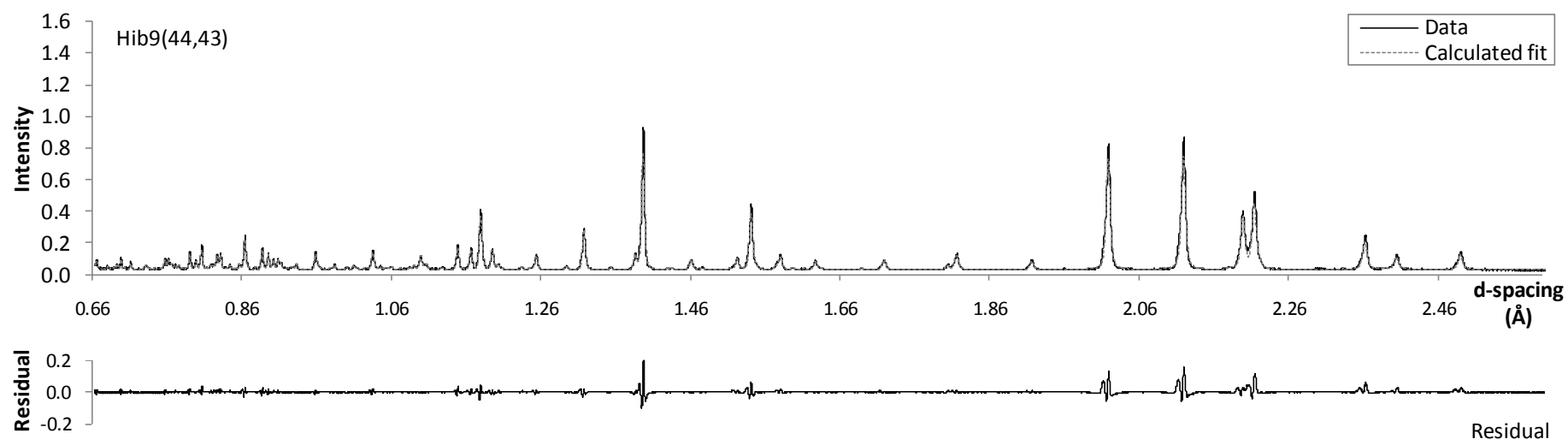


Figure D-6 Hib9(44,43) neutron powder diffraction data and Rietveld refinement fit (above), and fit-residual (below).

Table D-9 HibE(98,91) fractional coordinates, atomic displacement parameters and elemental occupancy.

HibE(98,91)	x	y	z	ADP	Occupancy (Element)
Ca	0.66670	0.33330	0.25000	2.546 (0.039)	1.000 (Ca)
M1	0.00000	0.00000	0.00000	0.999 (0.034)	1.000 (Al)
M2	0.00000	0.00000	0.26452 (0.00011)	1.083 (0.070)	0.424 (0.001) (Al); 0.076 (0.001) (Ti)
M3	0.33330	0.66670	0.02815 (0.00004)	0.968 (0.017)	0.580 (0.003) (Al); 0.420 (0.003) (Mg)
M4	0.33330	0.66670	0.18741 (0.00021)	0.855 (0.132)	0.596 (0.001) (Al); 0.404 (0.001) (Ti)
M5	0.16845 (0.00008)	0.33680 (0.00016)	-0.10732 (0.00002)	1.236 (0.012)	1.000 (Al)
O1	0.00000	0.00000	-0.15061 (0.00003)	0.977 (0.025)	1.000 (O)
O2	0.66670	0.33330	0.05786 (0.00003)	1.379 (0.018)	1.000 (O)
O3	0.18067 (0.00006)	0.36144 (0.00012)	0.25000	1.288 (0.013)	1.000 (O)
O4	0.15221 (0.00004)	0.30442 (0.00007)	0.05315 (0.00001)	1.073 (0.009)	1.000 (O)
O5	0.50403 (0.00004)	1.00816 (0.00008)	0.14961 (0.00001)	1.083 (0.009)	1.000 (O)

Notes: Error as calculated by GSAS in brackets. Approximate error for Mg occupancy quoted.

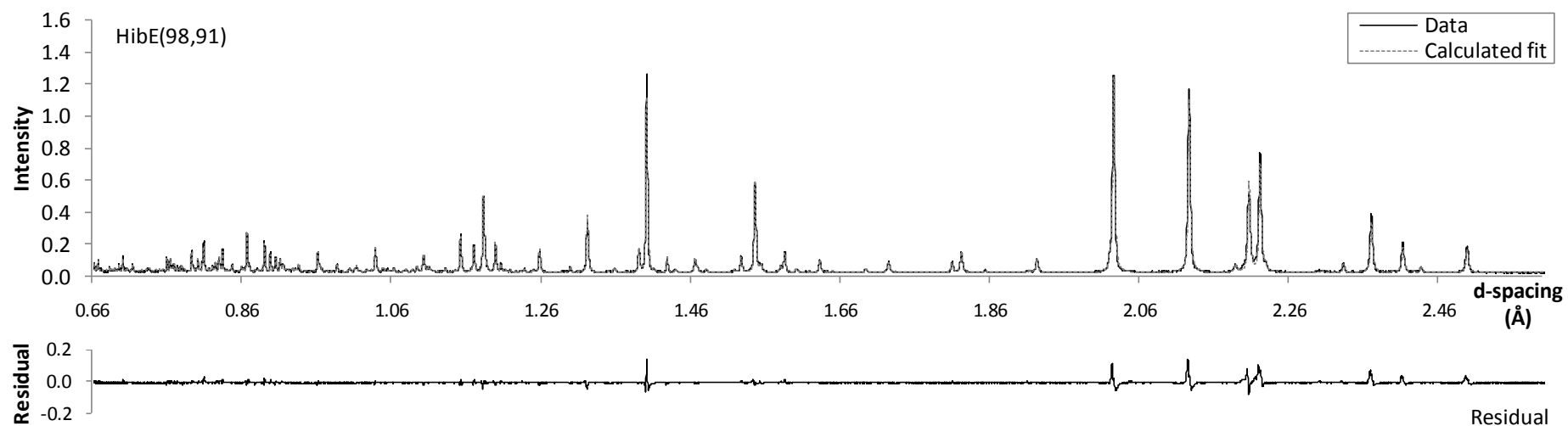


Figure D-7 HibE(98,91) neutron powder diffraction data and Rietveld refinement fit (above), and fit-residual (below).

Table D-10 HibT(137,83) fractional coordinates, atomic displacement parameters and elemental occupancy.

HibT(137,83)	x	y	z	ADP	Occupancy (Element)
Ca	0.66670	0.33330	0.25000	2.523 (0.070)	1.000 (Ca)
M1	0.00000	0.00000	0.00000	0.486 (0.055)	1.000 (Al)
M2	0.00000	0.00000	0.26758 (0.00014)	1.039 (0.099)	0.468 (0.001) (Al); 0.032 (0.001) (Ti)
M3	0.33330	0.66670	0.02904 (0.00006)	0.713 (0.028)	0.500 (0.005) (Al); 0.500 (0.005) (Mg)
M4	0.33330	0.66670	0.18908 (0.00032)	0.960 (0.211)	0.385 (0.002) (Al); 0.615 (0.002) (Ti)
M5	0.16757 (0.00016)	0.33504 (0.00033)	-0.10629 (0.00003)	0.846 (0.018)	1.000 (Al)
O1	0.00000	0.00000	-0.14925 (0.00006)	0.344 (0.040)	1.000 (O)
O2	0.66670	0.33330	0.05705 (0.00006)	0.931 (0.033)	1.000 (O)
O3	0.17809 (0.00011)	0.35628 (0.00021)	0.25000	0.957 (0.021)	1.000 (O)
O4	0.15307 (0.00006)	0.30615 (0.00012)	0.05319 (0.00002)	0.652 (0.014)	1.000 (O)
O5	0.50559 (0.00007)	1.01128 (0.00014)	0.14953 (0.00003)	0.576 (0.015)	1.000 (O)

Notes: Error as calculated by GSAS in brackets. Approximate error for Mg occupancy quoted.

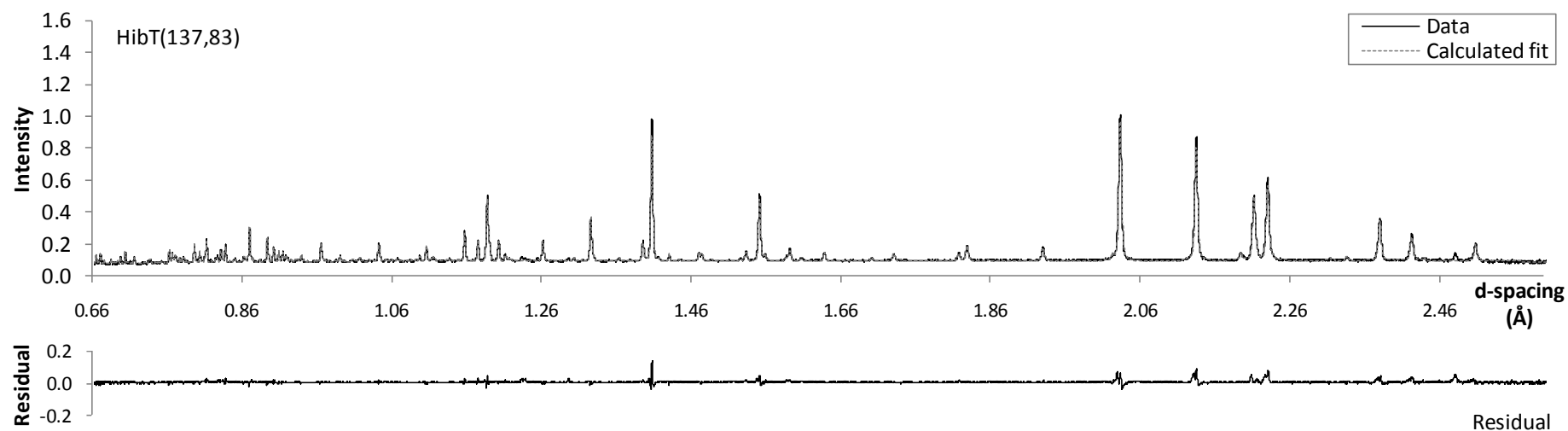


Figure D-8 HibT(137,83) neutron powder diffraction data and Rietveld refinement fit (above), and fit-residual (below).

Table D-11 Atomic displacement parameters for the synthetic Ti-bearing hibonite series ($100\text{\AA}^2$)

Site	CaAl ₁₂ O ₁₉ *	Terrestrial*	HibF(20,0)	Hib5D(33,0)**	HibK(60)	Hib8C(73,49)	HibJ(82,60)	Hib9(44)	HibE(98,91)	HibT(137,83)
Ca	1.6 (0.1)	2.0 (0.1)	1.06 (0.03)	0.64 (0.04)	1.78 (0.03)	1.63 (0.04)	1.68 (0.04)	1.48 (0.04)	2.55 (0.04)	2.52 (0.07)
M1	0.5 (0.1)	0.8 (0.1)	0.64 (0.02)	0.65 (0.04)	0.46 (0.03)	0.46 (0.03)	0.46 (0.04)	0.57 (0.04)	1.00 (0.03)	0.49 (0.06)
M2	0.9 (0.2)	2.0 (0.1)	1.10 (0.03)	0.90 (0.05)	1.05 (0.05)	1.08 (0.06)	1.04 (0.08)	1.17 (0.07)	1.08 (0.07)	1.0 (0.1)
M3	0.5 (0.1)	0.8 (0.1)	1.00 (0.02)	1.32 (0.03)	0.99 (0.02)	0.99 (0.02)	0.95 (0.02)	0.91 (0.02)	0.97 (0.02)	0.71 (0.03)
M4	0.6 (0.1)	0.9 (0.1)	0.66 (0.02)	0.74 (0.04)	0.93 (0.05)	0.99 (0.07)	0.85 (0.11)	0.82 (0.05)	0.9 (0.1)	1.0 (0.2)
M5	0.6 (0.1)	0.9 (0.1)	0.82 (0.01)	1.06 (0.01)	1.04 (0.01)	0.98 (0.01)	1.02 (0.01)	0.96 (0.01)	1.24 (0.01)	0.85 (0.02)
O1	0.6 (0.1)	1.1 (0.1)	0.80 (0.02)	1.16 (0.03)	1.01 (0.02)	0.52 (0.02)	0.51 (0.03)	0.38 (0.03)	0.98 (0.03)	0.34 (0.04)
O2	0.6 (0.1)	1.0 (0.1)	0.59 (0.01)	0.62 (0.02)	0.74 (0.02)	0.74 (0.02)	0.62 (0.02)	0.71 (0.02)	1.38 (0.02)	0.93 (0.03)
O3	0.8 (0.1)	1.8 (0.1)	1.13 (0.01)	1.50 (0.02)	1.35 (0.01)	1.40 (0.01)	1.41 (0.02)	1.26 (0.02)	1.29 (0.01)	0.96 (0.02)
O4	0.7 (0.1)	1.0 (0.1)	0.72 (0.01)	1.01 (0.01)	1.01 (0.01)	0.99 (0.01)	1.05 (0.01)	0.92 (0.01)	1.07 (0.01)	0.65 (0.01)
O5	0.6 (0.1)	1.0 (0.1)	0.75 (0.01)	0.99 (0.01)	1.00 (0.01)	1.02 (0.01)	0.97 (0.01)	0.96 (0.01)	1.08 (0.01)	0.58 (0.02)

Notes: * Synthetic hibonite (CaAl₁₂O₁₉) and terrestrial “brown” hibonite from Hofmeister *et al.* (2004).

D.3 Data tables for graphically presented data

D.3.1 Ti pfu refined vs. analysed by EDS SEM

Table D-12 Refined Ti pfu vs. Ti pfu obtained by EDS SEM

Sample	Number of Ti cations pfu		Number of Ti cations pfu	
	Refinement	EDS SEM	Refinement	EDS SEM
HibF(20,0)	0.177 (0.002)	0.20 (0.04)	-	<lld
Hib5D(33,0)	0.373 (0.002)	0.33 (0.04)	-	<lld
HibK(62,24)	0.556 (0.002)	0.62 (0.04)	0.22 (0.01)	0.24 (0.02)
Hib8C(73,49)	0.702 (0.002)	0.73 (0.06)	0.50 (0.01)	0.49 (0.03)
HibJ(82,60)	0.850 (0.002)	0.82 (0.19)	0.66 (0.01)	0.60 (0.10)
Hib9(44,43)	0.492 (0.002)	0.44 (0.12)	0.42 (0.01)	0.43 (0.11)
HibE(98,91)	0.960 (0.002)	0.98 (0.06)	0.84 (0.01)	0.91 (0.04)
HibT(137,83)	1.294 (0.004)	1.37 (0.08)	1.00 (0.01)	0.83 (0.04)

D.3.2 Unit cell parameters

Table D-13 Unit cell of synthetic Ti-bearing hibonite

Sample	Unit cell (Å) (error)		c/a	volume (Å ³)
	a	c		
HibF(20,0)	5.56686 (0.00001)	21.92436 (0.00004)	3.938	588.408 (0.001)
Hib5D(33,0)	5.56960 (0.00001)	21.93646 (0.00006)	3.939	589.310 (0.002)
HibK(62,24)	5.58523 (0.00001)	21.98562 (0.00005)	3.936	593.952 (0.001)
Hib8C(73,49)	5.59471 (0.00001)	22.00964 (0.00006)	3.934	596.622 (0.002)
HibJ(82,60)	5.60149 (0.00001)	22.02502 (0.00007)	3.932	598.497 (0.007)
Hib9(44,43)	5.58464 (0.00001)	21.98357 (0.00007)	3.936	593.771 (0.002)
HibE(98,91)	5.60643 (0.00001)	22.07104 (0.00006)	3.937	600.794 (0.002)
HibT(137,83)	5.62790 (0.00001)	22.11707 (0.00009)	3.930	606.669 (0.002)

Table D-14 Summary of published hibonite unit cell parameters

Reference	Unit cell (Å) (error)		c/a ratio	volume (Å ³)
	a	c		
Wittmann <i>et al.</i> (1958)	5.591 (0.003)	21.954 (0.005)	3.930	594.324 (0.001)
Kato and Saalfeld (1968)	5.564 (0.002)	21.892 (0.005)	3.930	586.935 (<0.000)
Utsunomiya <i>et al.</i> (1988)	5.5587 (0.0001)	21.8929 (0.0003)	3.940	585.841 (<0.000)
Bermanec <i>et al.</i> (1996)	5.613 (0.001)	22.285 (0.008)	3.970	608.042 (<0.000)
Hofmeister <i>et al.</i> (2004)	5.585 (0.000)	22.090 (0.001)	3.960	588.1 (0.1)
Hofmeister <i>et al.</i> (2004),	5.566 (0.001)	21.923 (0.004)	3.940	596.8 (0.1)
Nagashima <i>et al.</i> (2010),	5.5909 (0.0001)	21.9893 (0.0004)	3.933	595.26 (<0.000)

Notes: Cu K α λ = 1.5406 Å; Mo K α , λ =0.7093 Å (STOE win XPOW, v2.08).

For references 1-4 the volumes were not reported. They have therefore been calculated using $V = \sin 60^\circ \times a^2 \times c$.

Wittmann *et al.* (1958): determined by single crystal XRD on synthetic Ti-bearing hibonite crystals from FeTi-slag.

Kato and Saalfeld (1968): determined by XRD (Cu K α) on synthetic hibonite from the corrosion zone of a furnace.

Utsunomiya *et al.* (1988): determined by single crystal XRD (Mo K α) on a synthetic crystal.

Bermanec *et al.* (1996): determined by single crystal XRD (Mo K α) on natural hibonite from Madagascar.

Hofmeister *et al.* (2004): determined by single crystal XRD (Mo K α) on natural hibonite from Madagascar.

Hofmeister *et al.* (2004): determined by single crystal XRD (Mo K α) on synthetic hibonite.

Nagashima *et al.* (2010): determined by single crystal XRD (Mo K α) at 296 K on natural hibonite from Myanmar.

Stoichiometry recalculated based on 19 O: (Ca_{0.99}Na_{0.01})(Al_{10.76}Ti_{0.52}Mg_{0.51}Zn_{0.11}Si_{0.08}Fe²⁺_{0.04})O₁₉

D.3.3 Bond-lengths

Table D-15 Bond-lengths of the Ti-hibonite series

Sample	M2-O (Å)			M2-site O1-O1 (Å)	M2 displacement from centre (Å)	M4-O (Å)	
	M2-O1	M2-O1	M2-O3			M4-O3	M4-O5
HibF(20,0)	1.976 (2)	2.430 (2)	1.7594 (6)	4.406 (2)	0.227 (2)	1.9705 (7)	1.8707 (6)
Hib5D(33,0)	1.960 (2)	2.424 (3)	1.7667 (9)	4.384 (3)	0.232 (3)	1.971 (1)	1.871 (1)
HibK(62,24)	1.923 (2)	2.488 (2)	1.7652 (7)	4.411 (3)	0.282 (3)	2.005 (1)	1.8678 (9)
Hib8C(73,49)	1.903 (2)	2.487 (2)	1.7706 (8)	4.390 (3)	0.292 (3)	2.022 (2)	1.860 (1)
HibJ(82,60)	1.885 (3)	2.487 (3)	1.7780 (9)	4.371 (4)	0.301 (4)	2.013 (3)	1.869 (2)
Hib9(44,43)	1.912 (3)	2.468 (3)	1.7741 (9)	4.381 (4)	0.278 (4)	1.993 (1)	1.861 (1)
HibE(98,91)	1.873 (3)	2.514 (3)	1.7839 (8)	4.387 (4)	0.320 (4)	2.026 (3)	1.856 (2)
HibT(137,83)	1.840 (3)	2.617 (3)	1.780 (1)	4.457 (5)	0.389 (5)	2.030 (5)	1.891 (3)

Note: Refer to Figure D-9 for the number of bonds and to summary of the bond-length trends with increasing Ti pfu.

Table D-15 continued...

Sample	M1-O (Å)	M3-O (Å)		M5-O (Å)			
	M1-O4	M3-O2	M3-O4	M5-O1	M5-O2	M5-O4	M5-O5
HibF(20,0)	1.8849 (3)	1.8031 (8)	1.7959 (4)	1.8553 (6)	1.9886 (7)	2.0000 (4)	1.8087 (4)
Hib5D(33,0)	1.8890 (5)	1.798 (1)	1.7975 (6)	1.865 (1)	2.000 (1)	1.9946 (7)	1.8086 (7)
HibK(62,24)	1.8851 (3)	1.8350 (9)	1.8105 (4)	1.8727 (8)	1.9734 (8)	1.9948 (5)	1.8147 (5)
Hib8C(73,49)	1.8869 (3)	1.855 (1)	1.8245 (5)	1.8812 (9)	1.9629 (9)	1.9843 (5)	1.8250 (5)
HibJ(82,60)	1.8877 (4)	1.873 (1)	1.8299 (5)	1.894 (1)	1.954 (1)	1.9816 (6)	1.8261 (6)
Hib9(44,43)	1.8851 (4)	1.849 (1)	1.8215 (5)	1.874 (1)	1.962 (1)	1.9848 (6)	1.8255 (6)
HibE(98,91)	1.8870 (3)	1.8984 (9)	1.8435 (5)	1.8939 (9)	1.9384 (9)	1.9673 (5)	1.8445 (5)
HibT(137,83)	1.9000 (5)	1.904 (2)	1.8365 (7)	1.889 (2)	1.950 (2)	1.959 (1)	1.859 (1)

Note: Refer to Figure D-9 for the number of bonds and to summary of the bond-length trends with increasing Ti pfu.

Table D-15 continued...

Sample	Ca-O (Å)	
	Ca-O3	Ca-O5
HibF(20,0)	2.7871 (2)	2.7180 (3)
Hib5D(33,0)	2.7888 (4)	2.7222 (5)
HibK(62,24)	2.7962 (3)	2.7231 (3)
Hib8C73,49)	2.8011 (3)	2.7179 (4)
HibJ(82,60)	2.8046 (3)	2.7196 (4)
Hib9(44,43)	2.7964 (4)	2.7174 (4)
HibE(98,0)	2.8071 (3)	2.7205 (3)
HibT(137,83)	2.8168 (4)	2.7204 (6)

Note: Refer to Figure D-9 for the number of bonds and to summary of the bond-length trends with increasing Ti pfu.

Table D-16 O1-O1, M2-M4 and M4-M4 axial lengths

Sample	R-block O1-O1 (Å)	S-block O1-O1 (Å)	M2-M4 (Å)	M4-M4 (Å)
HibF(20,0)	4.406 (1)	6.556 (1)	3.564 (1)	2.626 (1)
Hib5D(33,0)	4.384 (2)	6.585 (2)	3.570 (1)	2.638 (1)
HibK(62,24)	4.410 (1)	6.583 (1)	3.615 (1)	2.700 (4)
Hib8C73,49)	4.390 (1)	6.615 (1)	3.634 (1)	2.747 (1)
HibJ(82,60)	4.371 (2)	6.641 (2)	3.637 (2)	2.726 (7)
Hib9(44,43)	4.380 (2)	6.611 (2)	3.609 (1)	2.686 (1)
HibE(98,0)	4.387 (1)	6.648 (1)	3.657 (2)	2.763 (1)
HibT(137,83)	4.457 (3)	6.601 (3)	3.687 (4)	2.71 (1)

Site	M1	M2	M3	M4	M5	A
O1		¹ ↑ ↓ ¹			¹ ↑ _(T)	
O2			¹ ↑ _(Ti⁴⁺)		¹ ↓	
O3		³ ↑		³ ↑ _(Ti³⁺)		⁶ ↑
O4	⁶ ~ _(T)		³ ↑		² ↓	
O5				³ ~ _(T)	² ↑	⁶ ~

Figure D-9 Summary of the effect increasing Ti pfu on bond-lengths (the number of bonds indicated by the numeral). Most bond-lengths increase with more Ti pfu (up arrow), with few remaining unchanged (~ symbol, a small increase or decrease indicated by the arrow). Notable differences to the general trend are indicated in brackets. (T=HibT(137,83))

E. Supplementary information for the Ti K-edge XANES spectromicroscopy study (Chapter 6)

E.1 Energy calibration

The energy calibration of the 2008 and 2009 datasets was based on the energy of the Ti K-edge XANES pre-edge peak of at least three samples for which equivalent spectra were collected in 2010. The energy corrections made were as follows: **Dec 08**: before scan 2738: +2.69; after scan 2738: +3.02 eV; **Sept 09**: -0.65 eV.

Table E-1 Energy calibration for 2008 and 2008, based on the first derivative peak of Ti-foil recorded in May 2010

Sample	DLS scan number		Date 2008- 2009	Pre-edge Peak Energy (eV)			Shift to correct 2008- 2009 data
	2010	2008- 2009		Uncorrected 2010	Corrected [†] 2010	Uncorrected 2008-2009	
Hib8C(73,49)PMD5 / Hib-8PMD powder	45796	27892	Dec-08	4969.1	4970.2	4967.5	2.72
HibE(98,91)PMD5 / Hib-4PMD powder	45780	27895	Dec-08	4969.1	4970.2	4967.6	2.62
7-753(SOI8,TRI1)	45811	27933	Dec-08	4969.1	4970.2	4967.5	2.72
7-753(SOI8,TRI1)	45811	27938	Dec-08	4969.1	4970.2	4966.7	3.52
Hib8C(73,49) / Hib-8PMD powder	45796	27940	Dec-08	4969.1	4970.2	4967.2	3.02
HibE(98,91) / Hib-4PMD powder	45780	27941	Dec-08	4969.1	4970.2	4967.2	3.02
HibF(20,0) / Hib-5PMD powder	45868	27946	Dec-08	4969.1	4970.2	4967.5	2.72
Hib8C(73,49)PMD5 / Hib8C powder	45796	37576	Sep-09	4969.1	4970.2	4970.8	-0.60
HibF(20,0)PMD4 / Hib-F powder	45868	37579	Sep-09	4969.1	4970.2	4970.9	-0.70
Hib9(44,43)PMD4 / Hib9 powder	45851	37586	Sep-09	4969.1	4970.2	4970.8	-0.60

Notes: 2010 spectra were deadtime corrected. Dec 2008 and Sept 2009 spectra were not deadtime corrected.

[†]1.10 eV was added to the energy of the May 2010 Ti-foil for the first derivative peak to be 4966.4 eV.

E.2 Ti-bearing standards

Table E-2 Pre-edge peak (a_2) parameters for the Ti-bearing standards

Sample	Pre-edge- a_2 (I)	Pre-edge- a_2 (E, eV)
Ti-OI (Ti-Olivine)	1.060	4969.8
Ti-pv (BaTiO ₃)	0.244	4970.7
Ti-Sp (Ti-Spinel)	0.791	4969.6
Ti(IV)-ox (TiO ₂)	0.177	4971.5
Ti(III)-ox (Ti ₂ O ₃)	0.169	4970.9

E.3 Ti-bearing CMAS glasses

E.3.1 Repeat scan Pre-edge normalisation

Table E-3 Pre-edge peak normalisation from the EXAFS region

Sequence	AD Δ IW-2.5				AD Δ IW-10.5				AD+Fo Δ IW-10.5			
	Scan number	Energy (eV)	Pre-edge		Scan number	Energy (eV)	Pre-edge		Scan number	Energy (eV)	Pre-edge	
			Norm1	Norm2			Norm1	Norm2			Norm1	Norm2
1	46010	4970.5	2.630	0.341	45983	4970.5	1.209	0.210	46000	4970.5	1.248	0.219
2	46011	4970.5	2.618	0.340	45984	4970.5	1.197	0.208	46001	4970.5	1.253	0.220
3	46012	4970.5	2.602	0.338	45985	4970.5	1.212	0.211	46002	4970.5	1.259	0.221
4	46013	4970.5	2.607	0.338	45986	4970.3	1.223	0.213	46003	4970.5	1.233	0.217
5	46014	4970.5	2.577	0.334	45987	4970.3	1.222	0.213	46004	4970.3	1.230	0.216
6	46015	4970.5	2.607	0.338	45988	4970.5	1.184	0.206	46005	4970.3	1.228	0.216
7	46016	4970.5	2.594	0.337	45989	4970.3	1.185	0.206	46006	4970.5	1.248	0.219
8	46017	4970.5	2.588	0.336	45990	4970.3	1.203	0.209	46007	4970.5	1.221	0.215
9	46018	4970.5	2.599	0.337	45991	4970.3	1.192	0.208	46008	4970.3	1.223	0.215
10	46019	4970.5	2.614	0.339	45992	4970.5	1.201	0.209	46009	4970.5	1.232	0.217
Average	-	4970.5	2.603	0.338	-	4970.4	1.203	0.209	-	4970.4	1.238	0.218
Std Dev	-	<0.1	0.015	0.002	-	0.1	0.014	0.002	-	0.1	0.013	0.002
%Std Dev on Average (%)	-	<0.1	0.588	0.588	-	<0.1	1.145	1.145	-	<0.1	1.069	1.069

Notes: Energy calibration applied

Norm1 = The observed pre-edge intensity was brought to base, and then normalised to the last 10 analyses (4973-4975 eV).

Norm2 = The observed pre-edge intensity was further normalised so that the average of the repeat-scans equalled the pre-edge peak intensity of the full spectra recorded (scan numbers 46029, 45981, and 45997).

E.3.2 Pre-edge peakfit data

Table E-4 Peakfit data for the pre-edge peak component- a_1 (centre, in eV)

logfO ₂	AD	AD+En	AD+Fo	AD+Qtz	AD+Wo
-3	4969.0	4969.1	4969.1	4969.0	4969.0
-9.4	4969.0	4969.1	4969.0	4969.0	4968.9
-11	4969.0	4969.0	4969.0	4969.0	4969.0
-12	4969.0	4969.0	4969.0	4968.9	4968.9
-13	4968.9	nd	4968.9	nd	4968.9
-13.5	4968.9	4968.8	4968.9	4968.8	4968.9
-14	4968.8	4968.8	4968.8	4968.8	4968.9
-16	4968.7	4968.6	4968.7	4968.6	4968.8
-18	4968.7	4968.6	4968.7	4968.6	4968.8
-20	4968.7	4968.6	4968.7	4968.6	4968.7

Table E-5 Peakfit data for the pre-edge peak components - a_1 , - a_2 , and - a_3 (Amplitude)

logfO ₂	AD			AD+En			AD+Fo			AD+Qtz			AD+Wo		
	a_1	a_2	a_3	a_1	a_2	a_3	a_1	a_2	a_3	a_1	a_2	a_3	a_1	a_2	a_3
-3	0.037	0.167	0.248	0.039	0.166	0.243	0.038	0.168	0.237	0.035	0.177	0.278	0.041	0.136	0.240
-9.4	0.040	0.167	0.248	0.044	0.161	0.247	0.041	0.168	0.246	0.041	0.212	0.262	0.033	0.133	0.246
-11	0.042	0.163	0.242	0.044	0.158	0.240	0.041	0.164	0.245	0.042	0.184	0.259	0.043	0.135	0.240
-12	0.045	0.160	0.223	0.045	0.144	0.230	0.043	0.159	0.224	0.043	0.176	0.227	0.042	0.127	0.226
-13	0.045	0.158	0.218	nd	nd	nd	0.048	0.164	0.211	nd	nd	nd	0.043	0.128	0.215
-13.5	0.050	0.154	0.207	0.049	0.140	0.211	0.051	0.154	0.202	0.052	0.155	0.219	0.043	0.114	0.216
-14	0.050	0.141	0.201	0.049	0.133	0.202	0.048	0.143	0.200	0.054	0.150	0.213	0.047	0.117	0.198
-16	0.064	0.118	0.153	0.063	0.098	0.152	0.062	0.116	0.152	0.069	0.114	0.151	0.056	0.095	0.156
-18	0.062	0.107	0.154	0.061	0.096	0.140	0.061	0.105	0.145	0.068	0.113	0.158	0.055	0.087	0.150
-20	0.064	0.107	0.139	0.066	0.096	0.137	0.063	0.108	0.144	0.069	0.107	0.140	0.053	0.086	0.143

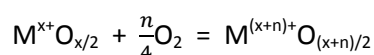
E.3.3 Parameterisation of the Ti-CMAS glass spectra

Table E-6 Pre-edge peak energy and intensity for the repeat scans

AD ($\Delta I W-2.5$)			AD ($\Delta I W-10.5$)			AD+Fo ($\Delta I W-10.5$)		
Scan number	Pre-edge intensity	Pre-edge energy (eV)	Scan number	Pre-edge intensity	Pre-edge energy (eV)	Scan number	Pre-edge intensity	Pre-edge energy (eV)
46010	2.63	4970.5	45990	1.203	4970.3	46000	1.248	4970.5
46011	2.618	4970.5	45991	1.192	4970.3	46001	1.253	4970.5
46012	2.602	4970.5	45992	1.201	4970.5	46002	1.259	4970.5
46013	2.607	4970.5	45983	1.209	4970.5	46003	1.233	4970.5
46014	2.577	4970.5	45984	1.197	4970.5	46004	1.23	4970.3
46015	2.607	4970.5	45985	1.212	4970.5	46005	1.228	4970.3
46016	2.594	4970.5	45986	1.223	4970.3	46006	1.248	4970.5
46017	2.588	4970.5	45987	1.222	4970.3	46007	1.221	4970.5
46018	2.599	4970.5	45988	1.184	4970.5	46008	1.223	4970.3
46019	2.614	4970.5	45989	1.185	4970.3	46009	1.232	4970.5

E.3.4 Derivation of the sigmoidal fit of Berry and O'Neill (2004)

Berry and O'Neill (2004) showed that for a one electron redox reaction (e.g. Equation E-1), the equilibrium constant (K, Equation E-2) may be arranged so that the $M^n/(M^n + M^{n+1})$ ratio was a sigmoidal function of $\log fO_2$ (Equation E-3). Valence-state dependent spectral parameters, such as the area beneath a feature in the edge in Cr K-edge XANES spectra, are linearly correlated with $M^n/(M^n + M^{n+1})$ according to Equation E-4 (Berry and O'Neill, 2004). By combining and rearranging Equations E-3 and E-4, a valence-state dependent spectra parameter (P) is defined as a sigmoidal function of $\log fO_2$ (Equation E-5).



Where:

n = number of electrons involved in the reaction

Equation E-1

$$K = \frac{X_{M^{(x+n)+}O_{(x+n)/2}} \gamma_{M^{(x+n)+}O_{(x+n)/2}}}{X_{M^{x+}O_{x/2}} \gamma_{M^{x+}O_{x/2}} (fO_2)^{n/4}}$$

Where:

X = the mole fraction

n = number of electrons involved in the reaction

γ = the activity coefficient

Equation E-2

$$\frac{M^{x+}}{(M^{x+} + M^{(x+n)+})} = \frac{1}{1 + 10^{(n/4 \log fO_2 + \log K')}}}$$

Where:

$$\log K' = \log K - \log \frac{\gamma_{M^{(x+n)+}O_{(x+n)/2}}}{\gamma_{M^{x+}O_{x/2}}}$$

Where γ_x is assumed to be constant for low Cr concentrations (~0.5 wt% Cr_2O_3).

$$\log \frac{X_{M^{n+}+}O_{(n+1)/2}}{X_{M^{n+}O_{n/2}}} = \log \frac{[M^{n+ + 1}]}{[M^{n+}]}$$

Equation E-3

$$\frac{M^{x+}}{(M^{x+} + M^{(x+n)+})} = a_0 + a_1 P$$

Where:

P = valence-state dependant spectral parameter

Equation E-4

$$P = \frac{1}{a_1} \left(\frac{1}{1 + 10^{(n/4 \log fO_2 + \log K')}} - a_0 \right)$$

Where:

parameters as defined above

Equation E-5

E.4 Ti-bearing synthetic hibonite

E.4.1 Self absorption check

Table E-7 Crest intensities of synthetic hibonite measured using the microfocus beam and diffuse beam

Analysis method	Sample	Wt%TiO ₂	Crest-c (I) †
Microfocus beam (average of up to 10 analyses)	HibF(20,0)	2.4 (0.5)	1.169 (0.12)
	HibK(62,24)	7.3 (0.5)	1.142 (0.12)
	Hib8C(73,49)	8.6 (0.7)	1.152 (0.18)
	Hib9(44,43)	5.2 (1.4)	1.227 (0.23)
	HibE(98,91)	11.4 (0.7)	1.163 (0.35)
	HibT(137,83)	15.9 (0.9)	1.166 (0.36)
Defocused beam on hibonite powder pellet	HibF(20,0)	2.4 (0.5)	1.157
	HibK(62,24)	7.3 (0.5)	1.108
	Hib8C(73,49)	8.6 (0.7)	1.137
	Hib9(44,43)	5.2 (1.4)	1.172
	HibE(98,91)	11.4 (0.7)	1.139
	HibE(98,91)	11.4 (0.7)	1.138
Defocused beam on BN + hibonite powder pellet	HibF(20,0)	2.4 (0.5)	1.121
	Hib8C(73,49)	8.6 (0.7)	1.190
	HibE(98,91)	11.4 (0.7)	1.167
	HibE(98,91)	11.4 (0.7)	1.161

† The uncertainty in the microfocus analysis is the standard deviation on repeat analysis. The estimated uncertainty for the pellet-mounted samples is 0.003 based on precision.

E.4.2 Orientation study data

Table E-8 Intensities of the Ti K-edge spectra for Hib9(44,43) and 7-981 showing variation in the d₃/m₃ intensity ratio

Sample	DLS scan	Measured angle	d ₃ intensity	m ₃ intensity	Ratio d ₃ /m ₃
Hib9(44,43) (PMD4)	45851	-	1.161	1.144	1.014
	45852	-	1.153	1.135	1.016
	45853	-	1.163	1.137	1.022
	45854	-	1.159	1.140	1.016
	45855	-	1.154	1.132	1.019
	45856	-	1.156	1.117	1.035
	45857	-	1.165	1.143	1.019
	45858	-	1.169	1.134	1.030
	45859	-	1.156	1.128	1.025
	45860	-	1.163	1.139	1.021
7-981 (TRI1)	45894	0°	1.160	1.177	0.985
	45920	0°	1.150	1.181	0.973
	45897	30°	1.220	1.191	1.025
	45907	30°	1.228	1.208	1.017
	45903	45°	1.168	1.188	0.983
	45904	45°	1.155	1.188	0.972
	45911	60°	1.226	1.200	1.022

Note: 7-981(TRI1): d₃ at 4996.7±0.7 eV; m₃ at 5000.6±0.6 eV; **Hib9(44,43):** d₃ at 4997.9±0.6 eV; m₃ at 5001.5±0.3 eV; propagated uncertainty on d₃/m₃ calculated to be 0.007.

E.4.3 Spectral parameters

Table E-9 Ti K-edge XANES spectral parameters for synthetic hibonite powder pellets analysed with a diffuse beam, with details for the pre-edge feature (a_2), the minima (m_1), the edge energy when normalised intensity = 0.8 ($E_{0.8}$) and crest (c), showing intensity (I) and energy (E, eV)

Parameter	Defocused beam synthetic hibonite powder pellet				Diffuse beam, synthetic hibonite powder in BN (~1mol% Ti)		
	Hib5D(33,0)	HibF(20,0)	Hib8C(73,48)	HibE(98,91)	HibF(20,0)	Hib8C(73,48)	HibE(98,91)
Sample	37577	37579	37576	37574	37580	37581	37573
Scan #	37577	37579	37576	37574	37580	37581	37573
a_2 (I)	0.155	0.135	0.146	0.176	0.113	0.130	0.157
a_2 (E, eV)	4971.1	4971.1	4971.0	4971.8	4971.1	4971.0	4971.7
E_{m1} (E, eV)	4973.5	4973.4	4973.7	4974.0	4973.3	4973.3	4974.1
$E_{0.8}$ (E, eV)	4982.8	4982.7	4983.9	4985.0	4983.1	4983.9	4984.9
c (I)	1.082	1.157	1.137	1.139	1.121	1.190	1.161
c (E, eV)	4987.5	4987.9	4986.7	4987.3	4987.3	4987.3	4987.1

Note:

Table E-10 Ti K-edge XANES spectral parameters for synthetic hibonite collected from the pre-edge features (a_2 , a_3), minima (m_1 , m_2 , m_3), the edge energy when normalised intensity = 0.8 ($E_{0.8}$), crest (c) and post-crest region (d_1 , d_2 , d_3 , d_4) showing intensity (I) and energy (E, eV)

Parameter	HibF(20,0)									
	45861	45862	45863	45864	45865	45866	45867	45868	45869	45874
Scan #	45861	45862	45863	45864	45865	45866	45867	45868	45869	45874
a_2 (I)	0.102	0.115	0.114	0.108	0.105	0.103	0.123	0.115	0.115	0.120
a_2 (E, eV)	4970.2	4970.2	4970.2	4970.2	4970.2	4970.2	4970.2	4970.2	4970.2	4970.2
a_3 (I)	0.070	0.078	0.077	0.074	0.074	0.075	0.083	0.076	0.076	0.081
a_3 (E, eV)	4971.2	4971.1	4971.2	4971.1	4971.1	4971.1	4971.2	4971.2	4971.1	4971.2
E_{m1} (E, eV)	4972.3	4972.3	4972.4	4972.3	4972.2	4972.3	4972.4	4972.3	4972.5	4972.4
$E_{0.8}$ (E, eV)	4982.2	4982.2	4982.2	4982.2	4982.2	4982.3	4982.3	4982.2	4982.3	4982.1
c (I)	1.182	1.159	1.163	1.161	1.174	1.179	1.157	1.163	1.157	1.191
c (E, eV)	4986.5	4986.7	4986.5	4986.7	4986.5	4986.5	4986.7	4986.5	4986.7	4986.7
m_2 (I)	1.049	1.069	1.064	1.052	1.060	1.044	1.078	1.067	1.066	1.090
m_2 (E, eV)	4989.0	4988.8	4988.8	4989.0	4989.0	4988.8	4988.8	4988.8	4988.8	4988.8
d_1 (I)	1.082	1.096	1.087	1.081	1.088	1.079	1.102	1.093	1.093	1.106
d_1 (E, eV)	4990.4	4990.4	4990.4	4990.4	4990.4	4991.0	4990.4	4990.4	4990.4	4990.4
d_2 (I)	1.100	1.107	1.118	1.104	1.116	1.097	1.120	1.119	1.103	1.133
d_2 (E, eV)	4993.4	4993.4	4993.8	4993.6	4993.8	4993.4	4993.8	4993.8	4993.4	4993.8

Parameters	HibK(62,24)						HibT(137,83)	
	45880	45881	45883	45884	45885	45886	45876	45877
Scan #	45880	45881	45883	45884	45885	45886	45876	45877
a_2 (I)	0.116	0.114	0.112	0.117	0.113	0.118	0.169	0.154
a_2 (E, eV)	4970.2	4970.2	4970.2	4970.2	4970.2	4970.3	4970.1	4970.2
a_3 (I)	0.086	0.078	0.078	0.084	0.076	0.082	0.116	0.112
a_3 (E, eV)	4971.0	4971.2	4971.2	4971.1	4971.2	4971.2	4971.1	4970.1
m_1 (I)	0.051	0.049	0.051	0.052	0.047	0.050	0.044	0.043
E_{m1} (E, eV)	4972.4	4972.4	4972.5	4972.3	4972.3	4972.4	4972.9	4972.7
$E_{0.8}$ (E, eV)	4982.3	4982.4	4982.3	4982.4	4982.4	4982.4	4983.7	4983.6
c (I)	1.147	1.147	1.159	1.140	1.131	1.126	1.140	1.191
c (E, eV)	4985.3	4985.3	4985.3	4985.5	4985.3	4985.3	4985.7	4985.9
m_2 (I)	1.001	0.987	0.989	1.002	0.978	0.996	0.939	0.944
m_2 (E, eV)	4988.8	4989.0	4988.9	4988.8	4988.8	4989.0	4989.0	4989.0
d_1 (I)	1.033	1.028	1.027	1.040	1.019	1.030	0.992	0.994
d_1 (E, eV)	4990.6	4990.4	4990.6	4990.6	4990.6	4990.4	4990.8	4990.6
d_2 (I)	1.113	1.108	1.099	1.093	1.087	1.087	1.071	1.074
d_2 (E, eV)	4993.8	4993.8	4993.6	4993.4	4993.6	4993.4	4993.8	4993.6

Table continued...

Table E-10 continued...

Parameter	Hib8C(73,49)									
Scan #	45790	45791	45792	45793	45794	45795	45796	45797	45798	45799
a ₂ (I)	0.129	0.131	0.133	0.132	0.127	0.135	0.134	0.124	0.131	0.126
a ₂ (E, eV)	4970.1	4970.2	4970.2	4970.2	4970.2	4970.2	4970.2	4970.1	4970.1	4970.1
a ₃ (I)	0.101	0.104	0.109	0.102	0.102	0.103	0.104	0.099	0.100	0.097
a ₃ (E, eV)	4971.1	4971.0	4970.9	4971.1	4971.0	4971.1	4991.0	4971.0	4971.1	4971.1
m ₁ (I)	0.048	0.049	0.049	0.047	0.048	0.047	0.047	0.048	0.048	0.047
E _{m1} (E, eV)	4972.5	4972.6	4972.5	4972.6	4972.6	4972.6	4972.5	4972.5	4972.4	4972.6
E _{0.8} (E, eV)	4982.9	4982.9	4982.9	4983.0	4982.8	4982.9	4983.0	4982.9	4983.0	4982.9
c (I)	1.167	1.149	1.153	1.127	1.182	1.151	1.130	1.169	1.137	1.153
c (E, eV)	4985.5	4985.5	4985.7	4985.5	4985.7	4985.5	4985.5	4985.7	4985.7	4985.7
m ₂ (I)	0.979	0.975	0.977	0.974	0.982	0.976	0.963	0.973	0.967	0.970
m ₂ (E, eV)	4989.0	4989.0	4989.0	4988.8	4989.0	4989.0	4989.2	4989.0	4989.0	4989.0
d ₁ (I)	1.017	1.016	1.025	1.017	1.020	1.025	1.011	1.017	1.011	1.012
d ₁ (E, eV)	4990.6	4990.8	4990.8	4990.8	4990.4	4991.2	4990.6	4990.9	4990.6	4991.0
d ₂ (I)	1.089	1.080	1.098	1.074	1.066	1.089	1.075	1.084	1.081	1.075
d ₂ (E, eV)	4993.6	4993.4	4993.8	4993.2	4992.8	4993.6	4993.4	4993.6	4993.6	4993.4
Energy Adj	Hib9(44,43)									
Scan #	45851	45852	45853	45854	45855	45856	45857	45858	45859	45860
a ₂ (I)	0.157	0.167	0.170	0.162	0.170	0.192	0.168	0.185	0.173	0.168
a ₂ (E, eV)	4970.2	4970.2	4970.2	4970.2	4970.2	4970.2	4970.2	4970.2	4970.2	4970.2
a ₃ (I)	0.121	0.125	0.127	0.120	0.129	0.140	0.129	0.140	0.132	0.121
a ₃ (E, eV)	4971.1	4971.1	4971.1	4971.1	4971.0	4971.1	4971.0	4971.0	4971.0	4972.0
m ₁ (I)	0.040	0.037	0.037	0.036	0.036	0.038	0.036	0.038	0.037	0.037
E _{m1} (E, eV)	4973.0	4973.0	4973.2	4972.9	4973.3	4973.1	4973.1	4973.0	4973.1	4973.2
E _{0.8} (E, eV)	4984.1	4984.2	4984.2	4984.2	4984.2	4984.2	4984.2	4984.2	4984.2	4984.2
c (I)	1.243	1.228	1.240	1.252	1.221	1.170	1.234	1.214	1.222	1.243
c (E, eV)	4986.1	4986.3	4986.1	4986.1	4986.1	4985.9	4986.1	4986.1	4986.3	4986.1
m ₂ (I)	0.925	0.918	0.927	0.920	0.914	0.919	0.921	0.925	0.919	0.923
m ₂ (E, eV)	4989.2	4989.0	4989.0	4989.0	4989.0	4988.8	4989.0	4989.0	4989.0	4989.0
d ₁ (I)	0.981	0.981	0.988	0.978	0.981	0.999	0.985	1.008	0.980	0.987
d ₁ (E, eV)	4990.6	4991.0	4990.4	4990.6	4990.8	4990.6	4990.8	4990.8	4990.6	4990.8
d ₂ (I)	1.064	1.062	1.072	1.074	1.066	1.070	1.068	1.081	1.071	1.079
d ₂ (E, eV)	4993.6	4993.6	4993.4	4993.8	4993.6	4993.4	4993.4	4993.8	4994.0	4993.8
d ₃ (I)	1.161	1.156	1.163	1.168	1.154	1.156	1.165	1.169	1.159	1.163
d ₃ (E, eV)	4999.3	4998.3	4998.1	4997.9	4997.4	4997.6	4997.9	4997.4	4997.6	4998.3
m ₃ (I)	1.144	1.135	1.138	1.140	1.133	1.123	1.143	1.134	1.128	1.139
m ₃ (E, eV)	5002.5	5001.7	5001.9	5001.7	5002.1	5000.9	5001.5	5000.9	5001.5	5001.7
d ₄ (I)	1.146	1.135	1.144	1.142	1.138	1.144	1.143	1.152	1.136	1.148
d ₄ (E, eV)	5002.9	5003.3	5003.3	5003.3	5003.5	5003.5	5003.5	5003.3	5003.3	5003.3
Parameter	HibE(98,91)									
Scan #	45780	45781	45782	45783	45784	45785	45786	45787	45788	45789
a ₂ (I)	0.151	0.150	0.146	0.150	0.138	0.165	0.141	0.163	0.167	0.153
a ₂ (E, eV)	4970.2	4970.3	4970.2	4970.2	4970.3	4970.2	4970.2	4970.3	4970.2	4970.3
a ₃ (I)	0.150	0.151	0.148	0.145	0.136	0.163	0.144	0.163	0.166	0.155
a ₃ (E, eV)	4970.9	4970.9	4970.9	4971.0	4970.9	4970.8	4971.0	4970.9	4970.9	4970.9
m ₁ (I)	0.043	0.045	0.043	0.041	0.040	0.042	0.042	0.046	0.044	0.043
E _{m1} (E, eV)	4973.2	4973.2	4973.2	4973.2	4973.2	4973.2	4973.1	4973.1	4973.2	4973.2
E _{0.8} (E, eV)	4984.1	4984.1	4984.1	4984.2	4984.3	4984.2	4984.1	4984.1	4984.2	4984.2
c (E, eV)	4986.3	4986.3	4986.3	4986.3	4986.3	4986.1	4986.3	4986.1	4985.9	4986.1
c (I)	1.195	1.200	1.183	1.181	1.135	1.128	1.207	1.167	1.116	1.119
m ₂ (E, eV)	4989.0	4989.2	4989.2	4989.2	4989.2	4989.0	4989.2	4989.0	4989.0	4988.9
m ₂ (I)	0.955	0.954	0.944	0.935	0.898	0.933	0.949	0.959	0.929	0.918
d ₁ (E, eV)	4990.8	4990.6	4990.6	4990.1	4990.8	4991.0	4990.6	4990.8	4990.8	4991.0
d ₁ (I)	1.005	1.001	0.989	0.988	0.938	0.999	0.987	1.014	0.997	0.985
d ₂ (E, eV)	4993.2	4993.4	4993.4	4993.4	4993.8	4993.4	4993.6	4993.8	4993.0	4993.4
d ₂ (I)	1.054	1.061	1.044	1.051	1.002	1.047	1.052	1.066	1.038	1.020

E.5 Ti-bearing meteoritic hibonite

E.5.1 Hibonite spectra collected, but contaminated by other Ti-bearing phases

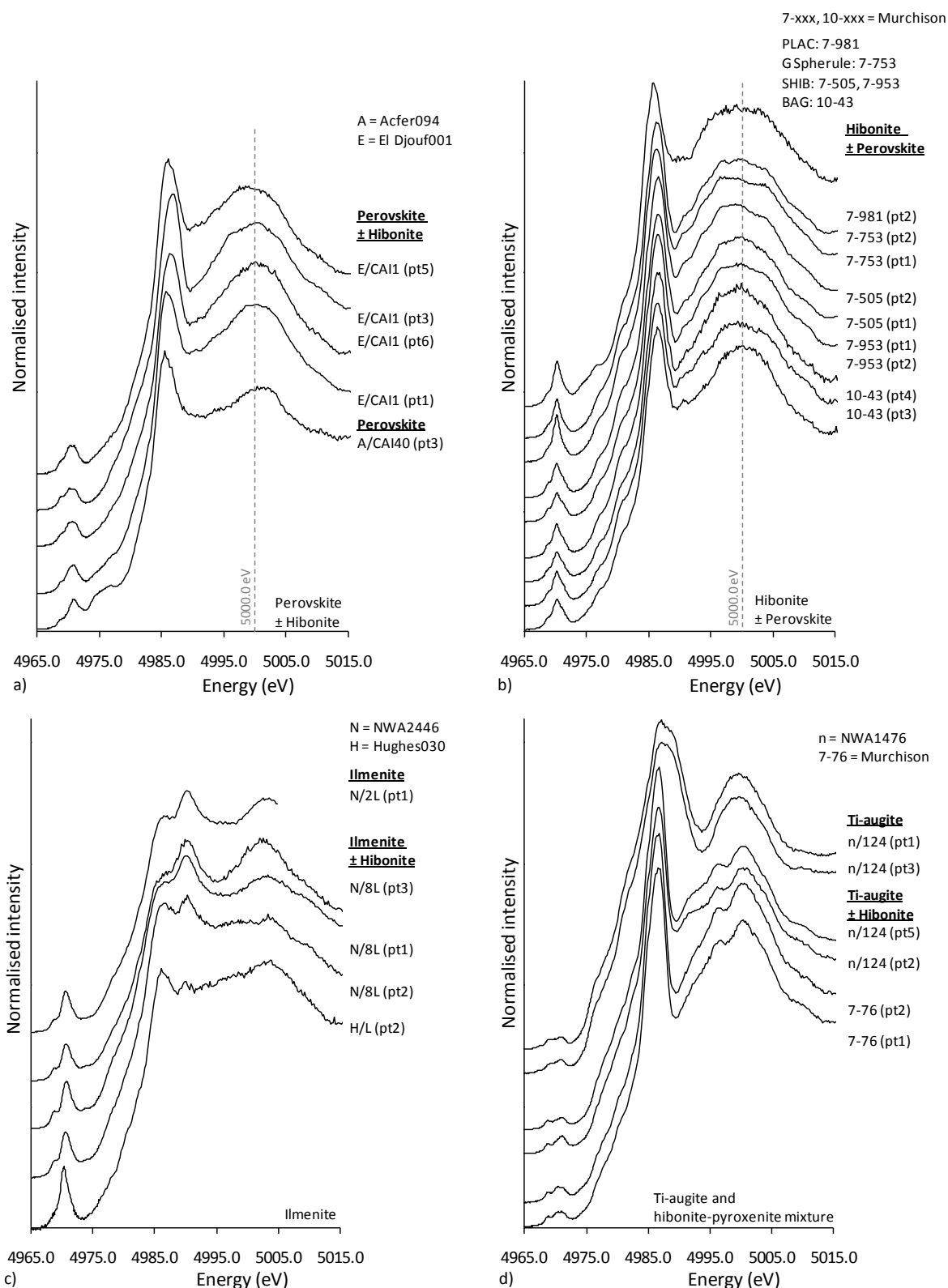


Figure E-1 Ti K-edge XANES spectra recorded from meteoritic minerals: (a) perovskite and perovskite-dominated spectra; (b) hibonite spectra with a minor perovskite component; (c) ilmenite spectra; and (d) Ti-bearing pyroxene spectra. The point (pt) refers to the analysis point shown in Appendix E.4.1. All spectra are plotted on the same vertical scale.

E.5.2 Spectra collected from each CAI (individually)

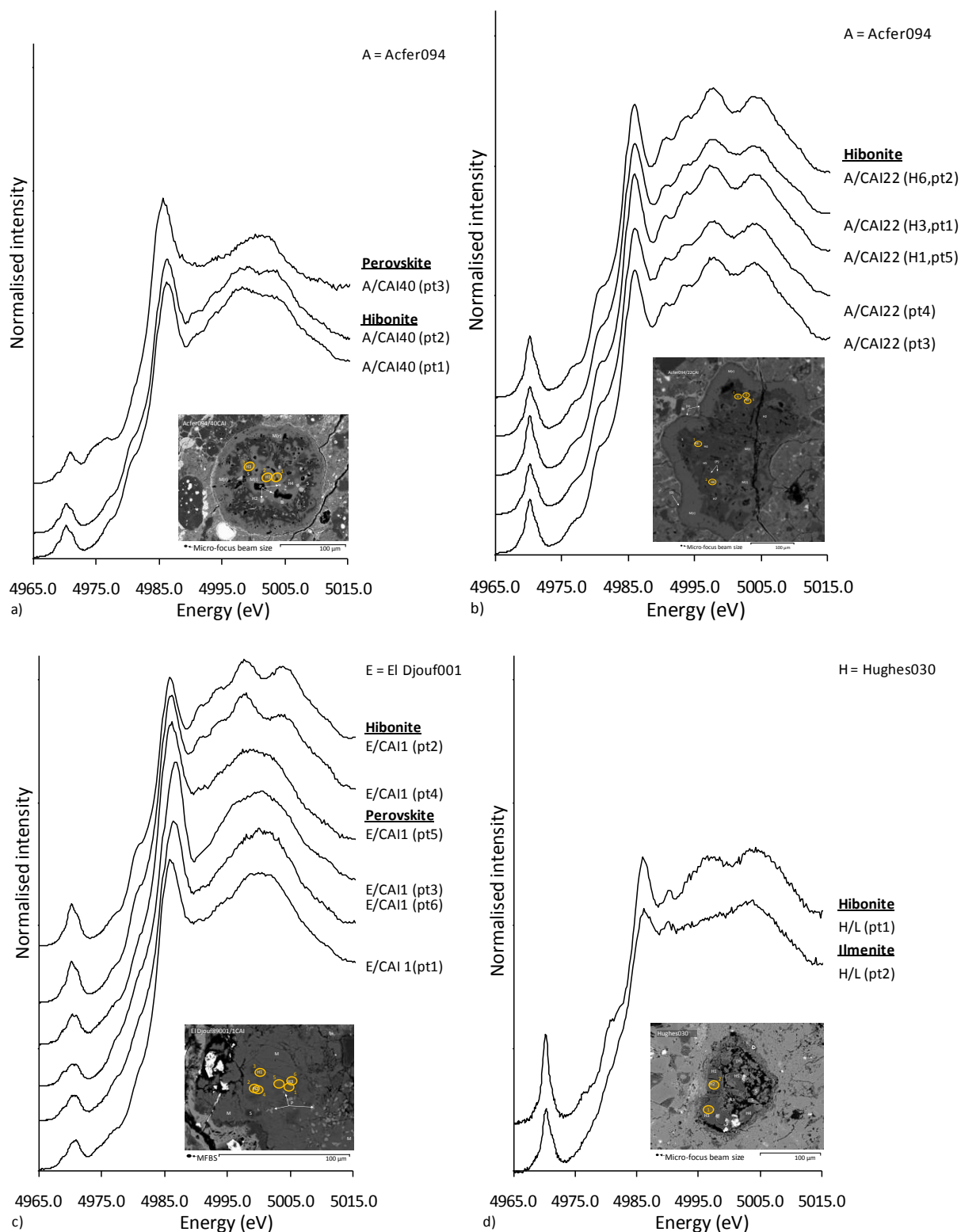


Figure E-2 (continued)

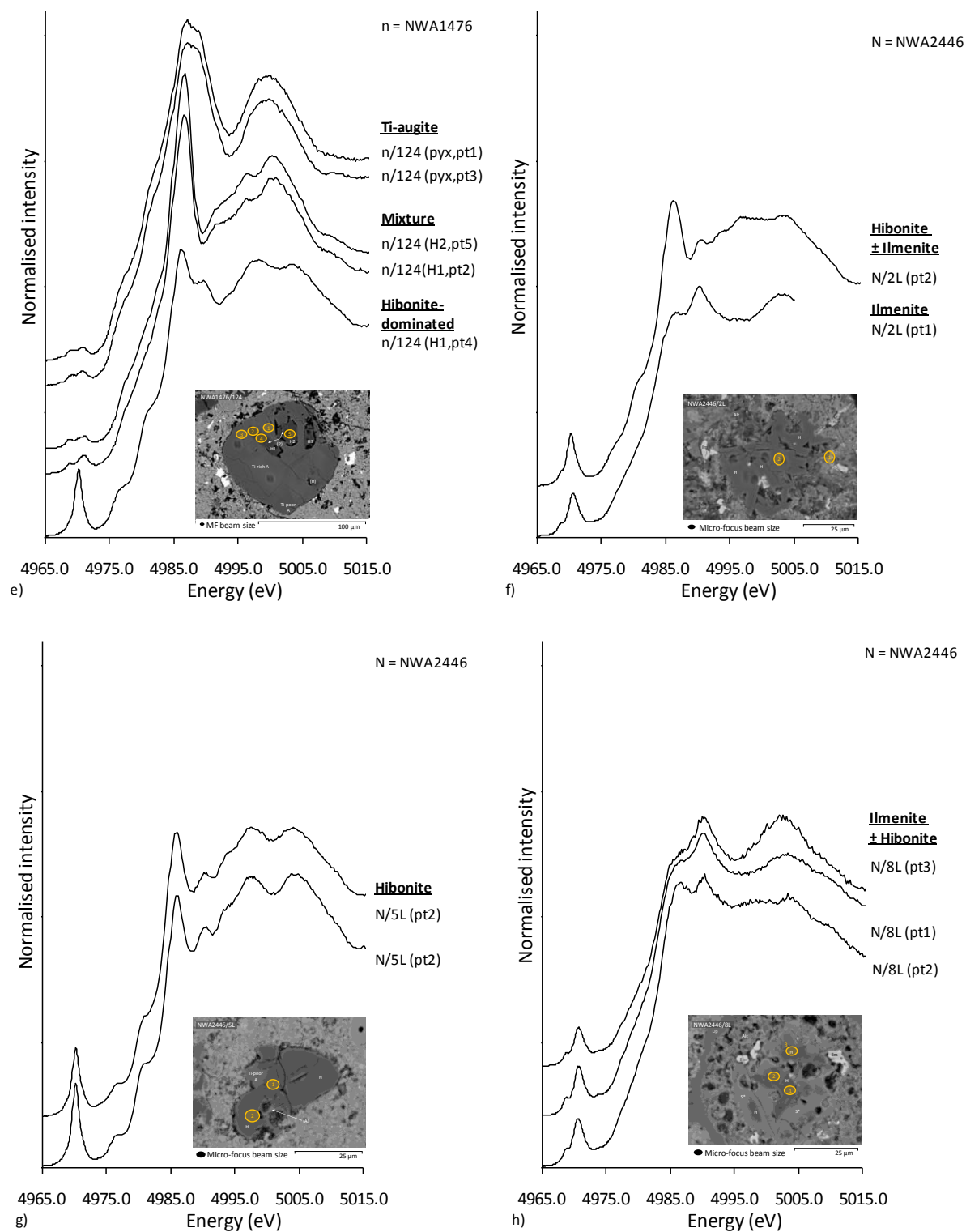


Figure E-2 (continued)

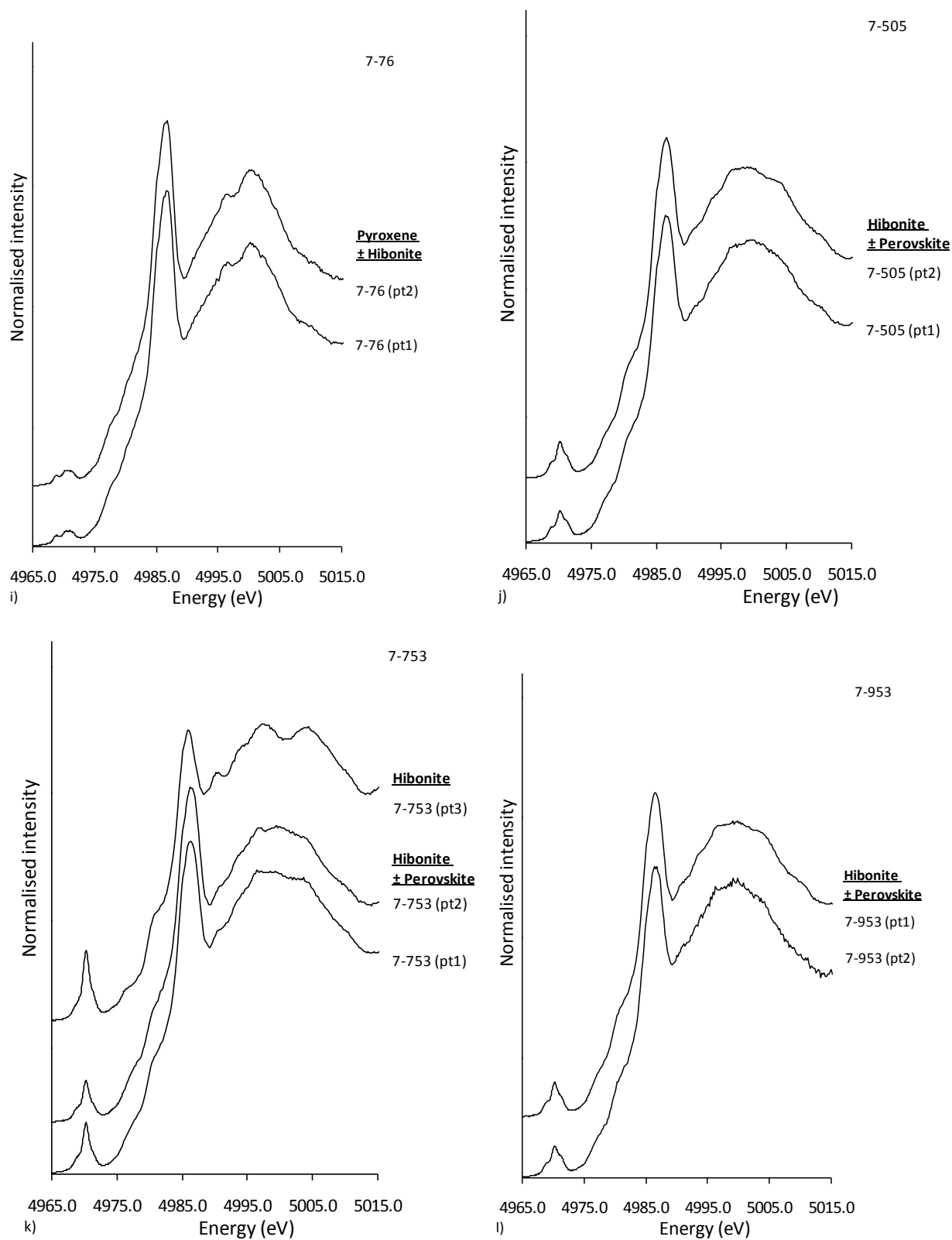


Figure E-2 (continued)

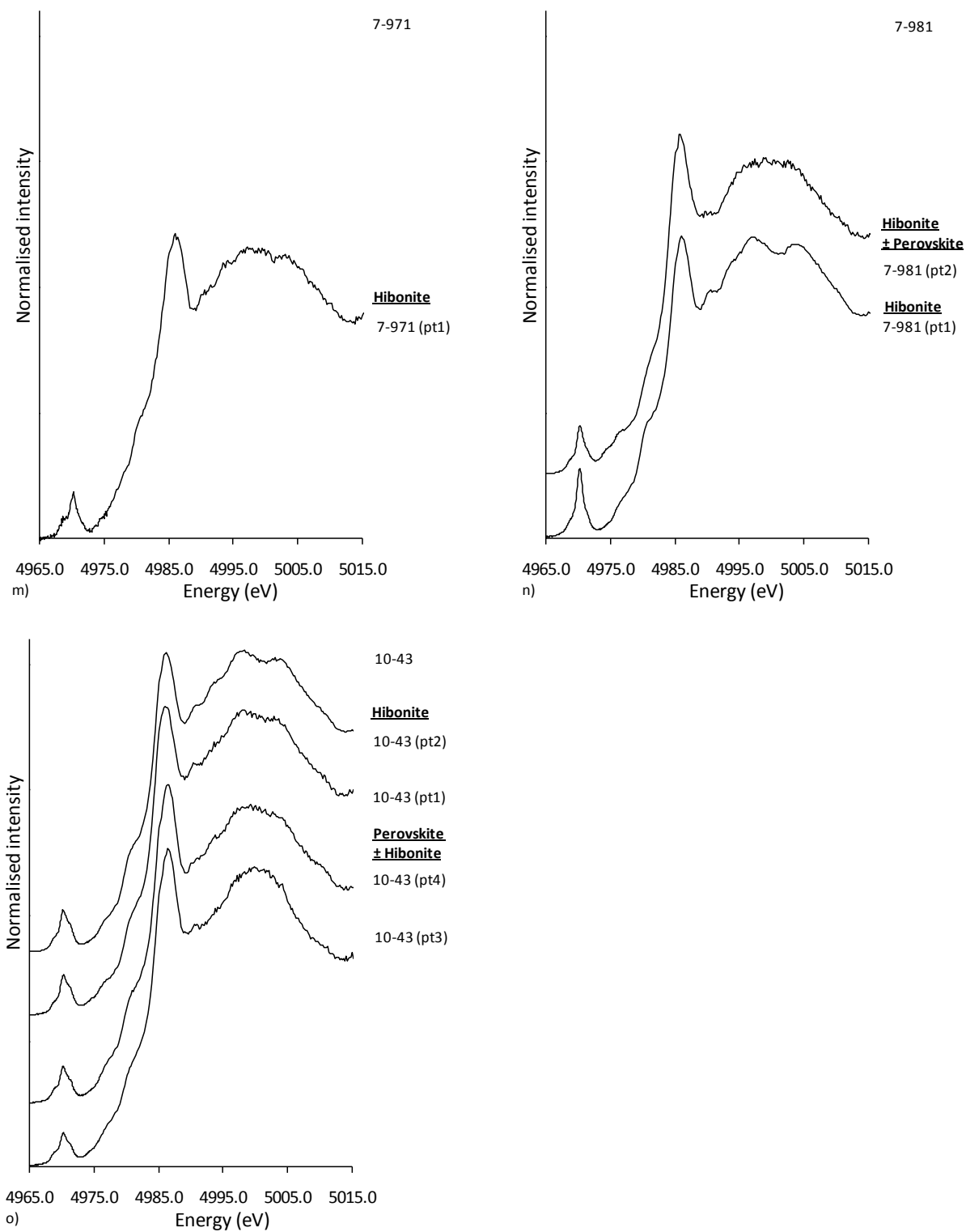


Figure E-2 Individual Ti K-edge XANES spectra recorded in each CAI.

E.5.3 Spectral parameters

Table E-11 Ti K-edge XANES spectra recorded on meteoritic hibonite (Blue toned)

Parameter	Acfer094/CAI22					Acfer094/CAI40			El Djouf001/CAI1
Scan number	45744	45745	45746	45747	45748	45751	45752	45753	45803
Type	Hib	Hib	Hib	Hib	Hib	Hib	Hib	Pv	Pv±Hib
Pre-edge-a ₂ (I)	0.198	0.243	0.215	0.200	0.239	0.135	0.125	0.133	0.125
Pre-edge-a ₂ (E, eV)	4970.2	4970.2	4970.2	4970.2	4970.2	4970.2	4970.1	4971.0	4970.9
Min - m ₁ (I)	0.039	0.037	0.036	0.039	0.036	0.037	0.035	0.087	0.058
E _{m1} (eV)	4973.1	4973.1	4973.0	4973.3	4973.1	4972.9	4972.9	4972.7	4972.8
E _{0.8} (eV)	4984.2	4984.3	4984.4	4984.3	4984.3	4984.3	4984.3	4983.7	4983.8
c-m ₁ (I)	0.301	0.300	0.289	0.321	0.307	0.299	0.292	0.223	0.266
c-m ₁ (E, eV)	4979.5	4979.5	4979.5	4979.6	4979.5	4979.5	4979.6	4979.1	4979.4
Crest-c (I)	1.136	1.140	1.100	1.111	1.168	1.126	1.122	1.171	1.266
Crest-c (E, eV)	4985.9	4985.9	4985.9	4985.9	4985.9	4986.1	4986.3	4985.5	4985.9

Table E-12 Ti K-edge XANES spectra recorded on meteoritic hibonite (Greenish-blue toned)

Parameter	El Djouf001/CAI1†					NWA1476/124				
Scan number	45804	45806	45807	45808	45809	45766	45767	45768	45771	45772
Type	Hib	Pv±Hib	Hib	Pv±Hib	Pv±Hib	Px	Hib+px	Px	Hib±px	Hib+px
Pre-edge-a ₂ (I)	0.177	0.096	0.173	0.128	0.106	0.058	0.079	0.065	0.274	0.055
Pre-edge-a ₂ (E, eV)	4970.2	4970.1	4970.1	4970.3	4970.3	4970.9	4971.1	4971.0	4970.2	4971.1
Min - m ₁ (I)	0.039	0.035	0.041	0.050	0.042	0.033	0.040	0.037	0.037	0.029
E _{m1} (eV)	4973.2	4972.8	4972.9	4972.9	4973.0	4972.2	4972.8	4972.4	4972.7	4972.7
E _{0.8} (eV)	4984.2	4983.9	4983.8	4983.7	4984.0	4982.4	4983.8	4982.5	4984.2	4983.8
c-m ₁ (I)	0.287	0.356	0.334	0.302	0.313	0.544	0.340	0.555	0.432	0.424
c-m ₁ (E, eV)	4979.5	4979.7	4979.5	4979.5	4979.7	4979.7	4979.7	4979.8	4979.4	4979.7
Crest-c (I)	1.100	1.324	1.259	1.321	1.226	1.365	1.433	1.373	1.149	1.498
Crest-c (E, eV)	4985.7	4986.5	4986.1	4986.1	4986.3	4987.2	4986.5	4987.2	4986.1	4986.7

Table E-13 Ti K-edge XANES spectra recorded on meteoritic hibonite (Colourless and platy)

Parameter	NWA2446/2L		NWA2446/5L			NWA2446/8L			Hughes030	
Scan number	45761	45762	45732	45733	45735	45739	45740	45741	45774	45775
Type	Im	Hib+Im	Hib	Hib	Hib	Im+Hib	Im+Hib	Im+Hib	Hib	Im
Pre-edge -a ₂ (I)	0.200	0.218	0.315	0.339	0.277	0.204	0.195	0.159	0.358	0.252
Pre-edge -a ₂ (E, eV)	4970.6	4970.2	4970.2	4970.2	4970.2	4970.8	4970.6	4970.7	4970.2	4970.3
Min - m ₁ (I)	0.100	0.042	0.031	0.035	0.043	0.085	0.072	0.060	0.029	0.033
E _{m1} (eV)	4973.1	4973.0	4973.4	4973.2	4973.1	4972.9	4972.9	4972.8	4973.2	4973.2
E _{0.8} (eV)	4984.8	4984.3	4984.7	4984.5	4984.2	4983.6	4983.5	4984.9	4984.5	4984.2
c-m ₁ (I)	0.400	0.326	0.280	0.276	0.268	0.512	0.521	0.399	0.285	0.324
c-m ₁ (E, eV)	4981.6	4979.6	4979.7	4979.5	4979.5	4981.4	4981.4	4981.4	4979.6	4979.7
Crest-c (I)	1.000	1.145	1.009	1.084	1.138	1.135	1.156	1.001	1.081	1.068
Crest-c (E, eV)	4990.2	4986.1	4985.9	4985.7	4985.9	4990.0	4990.0	4990.0	4985.9	4986.1