

1 Variation in XANES in biotite as a function of  
2 orientation, crystal composition and metamorphic  
3 history: Revision 2

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6 **Abstract**

7 Microscale analysis of ferrous:ferric iron ratios in silicate minerals has  
8 the potential to constrain geological processes but has proved challeng-  
9 ing because textural information and spatial resolution are limited with  
10 bulk techniques, and in-situ methods have limited spatial resolution. Syn-  
11 chrotron methods, such as XANES, have been hampered by the sensitivity  
12 of spectra to crystal orientation and matrix effects.

13 In an attempt to break this nexus, biotites from Tanzania were char-  
14 acterised with a combination of optical microscopy, electron microprobe,

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15 Mössbauer analysis, Electron Back Scatter Diffraction (EBSD) and X-ray  
16 Absorption Near Edge Structure (XANES) spectroscopy. Pre-edge and  
17 edge characteristics of the Fe  $K\alpha$  absorption feature were compared to  
18 orientation information derived by EBSD and ferric iron content derived  
19 from Mössbauer analysis.

20 Statistically significant correlations between measured spectral fea-  
21 tures and optic/crystallographic orientation were observed for individual  
22 samples. However, orientation corrections derived from these correlations  
23 did not reduce the uncertainty in  $Fe^{3+}/Fe_{tot}$ . The observations are consis-  
24 tent with matrix- and ordering-dependency of the XANES features, and  
25 further work is necessary if a general formulation for orientation correc-  
26 tions is to be devised. (185 words)

27 Keywords: Fe, oxidation, XANES, biotite, orientation

## 28 **Introduction**

29 The oxidation state of iron in minerals is a critical control on mineral properties  
30 and is a strong determinant of the oxidation state of the host rock, which in  
31 turn, affects parameters such as rheology (Mackwell et al., 1990; Keefner et al.,  
32 2011), melting characteristics (Wyllie, 1995; Foley, 2011), and the release of  
33 elements of environmental and economic interest (e.g. S, C, Cu, Au) by melting  
34 and devolatilisation (Mavrogenes and O'Neill, 1999; Jugo et al., 2005; Jugo,  
35 2009).

36  $Fe^{3+}/Fe_{tot}$  in minerals can vary on a micron scale (Schmid et al., 2003; De-

laney et al., 1998; Berry et al., 2010), and acquisition of this information could provide invaluable information on geological processes. However, measurement of  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  is challenging. Wet chemical and bulk Mössbauer methods (Meyrowitz, 1963; Li et al., 2005) require a bulk sample and so cannot resolve micron scale spatial variation of  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ . In-situ Mössbauer has the potential to reach 50 micron spatial resolution, but the measurements are time-consuming and impractical for detailed studies of within-grain  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  variation (McCammon et al. 2004, McCammon 2005). EELS (Electron Energy Loss Spectroscopy) also has potential (e.g. Garvie et al., 2004; Keast et al., 2001) but requires a TEM thickness sample, so textural information is often lost during sample preparation.

Synchrotron XANES-based methods provide a promising opportunity for in-situ  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  analysis on beamlines with micro-focus capability. Spatial resolution is typically less than 10 microns and potentially less than 1  $\mu\text{m}$  on the new high-resolution beamlines. Analysis can be achieved in minutes to tens of minutes, even at iron concentrations less than one weight percent. Early work provided calibrations based on the position of the centroid of the 1s to 3d Fe K pre-edge peak for iron in octahedral compounds (Bajt et al., 1994) and glasses (Berry et al., 2003, 2004). Further study revealed that the characteristics of the pre-edge peak are a complex function of site geometry, co-ordination, matrix composition, and mineral orientation. These functional relationships have been studied by a combination of experimental and theoretical methods (Randall et al., 1995; Arrio et al., 2000; Dyar et al., 2001, 2002a,b; Petit et al., 2001;

60 Wilke et al., 2004, 2005; Delaney et al., 2005; Wilke et al., 2007).

61 Results from these studies indicate that, for minerals with a high-spin elec-  
62 tron arrangement such as biotite, the pre-edge peak intensity is mostly a function  
63 of the extent of electric dipole coupling induced by hybridisation of the 3d-4p  
64 orbitals, because the 1s to 3d transition is forbidden unless hybridisation occurs.  
65 Such hybridisation is facilitated by non-centrosymmetric site geometries for iron  
66 and thus peak intensities are higher for tetrahedrally coordinated than for oc-  
67 tahedrally coordinated iron. The asymmetry of coordination polyhedra is also  
68 enhanced when bond lengths decrease. So, pre-edge peaks for  $\text{Fe}^{3+}$  are more  
69 intense than those for  $\text{Fe}^{2+}$  because the higher charge on  $\text{Fe}^{3+}$  results in shorter  
70 Fe-O distances. The more intense pre-edge peaks for  $\text{Fe}^{3+}$  are also caused by  
71 the greater probability of 1s to 3d transitions for  $\text{Fe}^{3+}$ , which occurs because  
72 there are more vacancies in the *d* levels for the higher valence oxidation state.

73 There is a broad correlation between pre-edge peak energy and oxidation  
74 state. Electrons are more tightly held in  $\text{Fe}^{3+}$  because of the greater charge,  
75 so transitions related to this oxidation state are at slightly higher energy (1-2  
76 eV) than for  $\text{Fe}^{2+}$ . The number of sub-peaks in the composite pre-edge can  
77 be predicted via molecular orbital (MO) calculations (Rehr et al., 2009; Westre  
78 et al., 1997b). Octahedral  $\text{Fe}^{2+}$  should have three peaks, while tetrahedral  $\text{Fe}^{2+}$   
79 has four. Octahedral  $\text{Fe}^{3+}$  and tetrahedral  $\text{Fe}^{3+}$  should both have two peaks,  
80 but only those for octahedral  $\text{Fe}^{3+}$  are expected to be resolvable. Tetrahedral  
81  $\text{Fe}^{3+}$  is expected to produce a single intense peak because the separation of  
82 the two sub-peaks is small ( $< 0.7$  eV). However, with typical configurations for

83 X-ray spectroscopy it is difficult to deconvolute XANES pre-edge peak informa-  
84 tion properly for minerals such as biotite with octahedral and tetrahedral ferric  
85 and ferrous iron, because spectrometer resolution, even with a high resolution  
86 monochromator, is insufficient.

87 The difficulty associated with resolution of individual peaks within the pre-  
88 edge peak for specific mineral phases means that existing calibrations (Wilke  
89 et al., 2001; Berry et al., 2003, 2004; Wilke et al., 2007, 2009), are largely em-  
90 pirical, although if the Fe co-ordination is known then plots of the type first  
91 reported by Wilke et al. (2001) can be used as a generalised calibration for the  
92 pre-edge peak. An empirical calibration for  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  in garnet (Berry et al.,  
93 2010) that uses main edge and post-main edge features has also been produced,  
94 and, at least for garnet, the main edge calibrations are more sensitive and pro-  
95 vide higher precision than those based on pre-edge features. However, features  
96 at and above the main edge are strongly related to structural environment and  
97 thus display greater matrix dependence than pre-edge features, which record  
98 local environment to a greater extent. Existing calibrations allow accurate and  
99 precise measurements of  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  in isotropic or powdered material, so long as  
100 excellent matrix-matched calibration standards are available. It is also possible  
101 to make measurements of relative  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  within single anisotropic grains  
102 (Schmid et al., 2003; Vidal et al., 2006; Munoz et al., 2006). However, measure-  
103 ment of absolute  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  in-situ for anisotropic grains is still hampered by  
104 uncertainties related to matrix composition and crystal orientation (Dyar et al.,  
105 2001, 2002a) which limit precision in  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  to 10 – 15% absolute. Brouder

106 (1990) derives and presents relationships between X-ray absorbance and crystal  
107 orientation for a wide range of crystal symmetries. It is therefore theoretically  
108 possible to account for orientation effects if crystal orientation is known.

109 Electron Back Scatter Diffraction (EBSD) provides a non-destructive way to  
110 precisely and accurately determine the orientation of crystals accurately with  
111 respect to a sample reference frame, and it is therefore possible that combination  
112 of this technique with XANES could eliminate, or substantially reduce, crystal  
113 orientation-related uncertainties in  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ . In this study, we examine the  
114 characteristics of XANES spectra as a function of EBSD-derived mineral orien-  
115 tation, and assess the potential utility of the combined technique. Biotite grains  
116 from three samples are characterised using microprobe, Mössbauer, XANES and  
117 EBSD. Pre-edge peak and main edge XANES features were examined, and rela-  
118 tionships between the areas of the component peaks and orientation parameters  
119 were investigated, and the potential for quantitative predictive calibrations as-  
120 sessed.

## 121 **Material and Methods**

122 The criteria for sample selection were that: the samples should contain sig-  
123 nificant modal proportions of biotite with homogeneous composition; the sam-  
124 ples should not contain excessive magnetite that could contaminate the picked  
125 minerals; and that samples should cover a range of ferromagnesian assem-  
126 blages, with the expectation that this would produce a range of ferric:ferrous

127 ratios in the biotites. Three samples were chosen from a suite of partially  
128 retrogressed eclogites and granulites from western Tanzania. Samples T01-  
129 23 (S07°08'7.2" E036°08'10.9") and T01-28A (S07°07'49.0" E036°07'22.4") are  
130 Palaeoproterozoic metamorphic rocks of the Isimani Unit of the Usagaran Oro-  
131 gen (Reddy et al., 2003; Collins et al., 2004). Both samples are high-grade  
132 quartzo-feldspathic gneiss that show minor signs of lower grade metamorphic  
133 overprints (e.g. trace epidote and actinolite).  $^{40}\text{Ar}/^{39}\text{Ar}$  data from micas in this  
134 region record an isotopic disturbance consistent with a weak Pan-African green-  
135 schist facies thermal overprint (Reddy et al., 2004). Sample T01-54 (S07°34'44.0"  
136 E036°45'45.0") is a strongly foliated banded gneiss comprising alternating lay-  
137 ers of amphibole-rich and amphibole-poor quartzo-feldspathic layers. The sam-  
138 ple analysed contains red-brown biotite, garnet and amphibole, plagioclase, K-  
139 feldspar and quartz. The sample was collected from the road section adjacent  
140 to the Great Ruaha River, close to the entrance of the Udzungwa Mountains  
141 National Park and is probably a Neoproterozoic protolith reworked at high-grade  
142 conditions during Neoproterozoic Pan-African orogeny (Vogt et al., 2006).

143 Each sample was crushed for about 5 seconds in a tungsten carbide TEMA  
144 mill to produce grains a few hundred microns in size. The crushed sample was  
145 then passed repeatedly through a Frantz magnetic separator to concentrate the  
146 ferromagnesian fraction. 30 micrograms of biotite was hand-picked from each  
147 sample for Mössbauer analysis. Microprobe analysis, EBSD and XANES analy-  
148 sis were performed on polished thin sections. Thin sections were prepared in the  
149 normal way, plus a final polish with 0.06  $\mu\text{m}$  colloidal silica NaOH suspension

150 (pH 9.8) for ca. 2 hours on a Buehler Vibromet II polisher. A thin ( $\sim 5$  nm)  
151 carbon coat was applied before EBSD analyses to reduce surface charging.

### 152 **Mineral composition analysis**

153 Mineral compositions were analysed using the JEOL JXA-8530F hyperprobe  
154 located at the CMCA (Centre for Microscopy, Characterisation and Analysis)  
155 at the University of Western Australia. Accelerating voltage was 15 KeV, and  
156 the beam current was 20nA. Cation occupancies were calculated using the Ax  
157 software (Holland, pers. comm.)

### 158 **Mössbauer**

159 Approximately 30 mg of the sample was crushed to a fine powder with sugar un-  
160 der acetone before mounting in a sample holder confined by sellotape. Mössbauer  
161 spectra were acquired at 295K using a source of 80 mCi  $^{57}\text{Co}$  in Rh on a WEB  
162 Research Co. model WT302 spectrometer (Mount Holyoke College). Run times  
163 were 6 – 24 hours, and results were calibrated against  $\alpha$ -Fe foil; baseline counts  
164 ranged from 2 – 8 million.

165 Mössbauer spectra were modeled using the Mex-Fieldd program, which was  
166 acquired from the University of Ghent courtesy of E. DeGrave. The program  
167 uses Lorentzian line shapes and solves full Hamiltonians for isomer shift and  
168 quadrupole splitting. Errors are 0.02 mm/s on isomer shift and as high as 0.05



169 mm/s for quadrupole splitting (Dyar et al., 2008). Errors on  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  are  
170 1-3% absolute based on repeated fits to the same spectra. Doublet areas are  
171 assumed to correspond directly to the abundances of the species present (but  
172 see Dyar et al. (2008)).

173 Two of the samples appeared to contain a small amount of impurity that  
174 is a magnetic phase; only the center two peaks of the sextet are visible at this  
175 velocity range. Their locations suggest that this phase is hematite, which is  
176 weakly magnetic. However, the emphasis of this work is to use Mössbauer  
177 spectroscopy to determine the ferric iron proportion in biotite so confirmation  
178 of this suggestion is not necessary.

## 179 **EBSD**

180 EBSD mapping was undertaken at the Microstructural Analysis Facility, Curtin  
181 University, Western Australia, using a W-source Philips XL30 SEM operating at  
182 20 kV and a 15 mm working distance. The SEM is fitted with a Nordlys I EBSD  
183 acquisition camera, two forescatter OCI detectors, and an Oxford Instruments  
184 (formerly HKL Technologies) EBSD system. All EBSD data were acquired and  
185 processed using Oxford Instruments Channel 5 (SP9) software.

186 Biotite has significant issues with multiple solutions because of the pseudo  
187 threefold axis around the pole to (001), i.e.  $\langle 103 \rangle$ . Such pseudosymmetry is-  
188 sues can create significant systematic misindexing of EBSD data. To reduce the  
189 effect of this misindexing problem the camera distance was selected to increase

190 the number of visible Kikuchi bands within each diffraction pattern. Prior to  
191 data collection individual diffraction patterns were collected and calibrated man-  
192 ually using >7 bands and solutions were checked against the empirically-derived  
193 electron backscatter pattern (EBSP). During this process it became clear that  
194 recognition of the correct solution is not possible by visually comparing so-  
195 lutions with the EBSP. To facilitate the correct identification of biotite lattice  
196 orientation multiple analyses of the biotite grains using automated mapping was  
197 employed. Following this mapping, data were noise reduced to remove isolated  
198 points with anomalous orientations from the data using the Tango wildspike cor-  
199 rection tool, and a 6 nearest-neighbour extrapolation to reduce the proportion  
200 of zero solutions.

## 201 **XANES**

202 XANES spectra were collected at beamline X26A at the National Synchrotron  
203 Light Source (NSLS), which is sited at the Brookhaven National Laboratory,  
204 Upton, New York, USA. Energy scans were made across the Fe K edge in four  
205 regions: (i) from 7020 to 7096eV in 10eV steps with a 1 second counting time;  
206 (ii) from 7096 to 7118 eV, which is the pre-edge peak region, with 0.1 eV steps  
207 and five second count time; (iii) from 7118.2 eV to 7140 eV in 0.4 eV steps and  
208 2 second count time; and finally (iv) from 7141 to 7220 eV in 3 eV steps with a  
209 2 second count time. Spectra collection for each sample required approximately  
210 30 minutes. The beam was located and beam size assessed by scans across the

211 edge of a razor blade. Beam size was measured to be  $7\ \mu\text{m} \times 11\ \mu\text{m}$ , with the  
212 larger dimension in the horizontal plane; the beam was also highly polarised to  
213 produce an electric vector lying in the horizontal plane. The extent of polarisa-  
214 tion was not measured but for an NSLS bending magnet source is assumed to  
215 be  $> 96\%$  (Janssens et al., 1993). Beam energy was tuned by a Si(311) lattice,  
216 channel-cut, monochromator, the crystals are cut to a 7 mm gap and cooled  
217 to  $11^\circ\text{C}$  using a Neslab chiller. The Si(311) with a 0.2 mm upstream aperture  
218 has an instrumental resolution of 0.36 eV at 6 keV. Adding this resolution in  
219 quadrature with the natural Fe K width for the 1s electron level of 1.08 eV  
220 (Krause and Oliver, 1979), and accounting for instrumental broadening of the  
221 overall resolution yields an overall resolution of 1.3 eV. Microfocus is achieved  
222 via a pair of 100 mm long rhodium-coated, grazing-incidence silicon mirrors in  
223 a Kirkpatrick-Baez (KB) geometry. Photon flux at 7 keV is roughly  $2.5 \times 10^8$   
224 photons  $\text{second}^{-1}$  with the Si(311) monochromator. A 5X Mitutoyo long work-  
225 ing distance objective with CCD digital image capture is mounted horizontally  
226 so that the sample surface can be viewed normally.

227 Energy calibration was performed against samples of NMNH (National Mu-  
228 seum of Natural History) magnetite and Balmat magnetite. Calibration was  
229 based on the assumption that the centroid of the magnetite pre-edge peak was  
230 at 7113.25 eV. Use of natural magnetites as reference standards requires caution  
231 because natural samples with appreciable Cr and Ti may not be fully ordered  
232 in the inverse spinel structure with all  $\text{Fe}^{2+}$  on the octahedral site (Wilke et al.,  
233 2001). If this is the case then the centroid position could vary from sample to

234 sample. However, in this case, the Balmat and NMNH magnetites were mea-  
235 sured sequentially and found to have identical Fe K pre-edge and main-edge  
236 absorption energies, within the resolution of the system. Magnetite standards  
237 were run after every beam fill, and every three to five samples to monitor for any  
238 energy drift. Energy corrections were performed assuming that any monochro-  
239 mator drift involved a linear relationship between time and drift between stan-  
240 dard measurements as photon flux decreased relative to decaying current in the  
241 NSLS X-ray storage ring. Total drift over the two day run was 0.25 eV. Spectra  
242 were collected in a fluorescence geometry, and the thin sections were mounted  
243 vertically at 45 degrees to the beam direction. After spectra from each grain  
244 of interest on the thin section had been collected, the sample was rotated by  
245 90° within the plane of the section and a second spectra was collected. Fluores-  
246 cent X-rays were detected using a 9-element Canberra high purity germanium  
247 (HPGe) detector. Count rates were normalised to the incident beam current  
248 and corrected for dead time.

## 249 **Data Processing**

250 Spectra were corrected for monochromator energy drift using the Balmat mag-  
251 netite analyses described above. The background was removed and the signal  
252 was normalised using the Athena software (Ravel and Newville, 2005). Nor-  
253 malisation involved division of the signal by an estimation of the signal at the  
254 edge energy, taken to be 7120 eV. The estimated signal is calculated from the

255 difference between pre-edge and post-edge lines extrapolated to 7120 eV. The  
256 pre-edge line was constructed by regression of the data between 7050 and 7090  
257 eV. The post-edge line is a quadratic polynomial regressed to the data between  
258 35 and 100 eV above the edge. These values were chosen to encompass a single  
259 oscillation in the post-edge spectra.

260 The biotite is Fe-rich (~20 wt%) so self absorption must be considered.  
261 Absorption lengths were calculated using the Hephaestus software (Ravel and  
262 Newville, 2005) and the microprobe-derived mineral formulae and were found  
263 to be 60 microns in the pre-edge region and around 30 microns in the post-edge  
264 region. The contribution of iron to the absorption is around 10% in the pre-edge  
265 region and over 60% in the post-edge region. The thin sections are 30 microns  
266 thick and the angle between the beam and the sample was 45 degrees, so the  
267 effective thickness of biotite grains was a maximum of 42 microns. Thus, in  
268 the pre-edge region  $\mu t$  is around 0.7, whereas it around 1.4 in the main edge  
269 and post-edge regions. If self absorption is to be ignored then the element  
270 of interest needs to be relatively dilute or  $\mu t$  needs to be significantly less, or  
271 significantly greater than 1 (Pfalzer et al., 1999). The biotite analysed fulfils this  
272 criteria in the pre-edge region, since Fe contributes only 10% of the absorption.  
273 This conclusion is consistent with those of Bajt et al. (1994) and Berry et al.  
274 (2010). However, self-absorption is likely to affect main edge characteristics -  
275 see discussion in Berry et al. (2010) and below. Self-absorption may also affect  
276 magnetite spectra, even in the pre-edge. However, magnetite was only used as  
277 a monitor for monochromator calibration and each measurement would have

278 suffered the same self absorption effects, so self absorption is not be a problem  
279 for this application.

280 Subsequent processing was performed using custom-built functions written  
281 in Mathematica<sup>TM</sup>. The pre-edge peak was extracted from the data by subtrac-  
282 tion of a baseline. The baseline was derived from an arctan function fit to the  
283 data between 7100 and 7119 eV, excluding the peak which was considered to lie  
284 between 7109 eV and 7116.5 eV. Variations on the fit windows described above  
285 were tried and the chosen values were found to produce reproducible results  
286 for all three samples with minimal artefacts. The pre-edge peak was then fit  
287 to a combination of three Lorentzians in two stages. Initially, peak positions  
288 and areas were fit. In all fits, peak widths were constrained to 1.3 eV, the the-  
289 oretical width derived from the monochromator resolution and values for core  
290 hole width at the Fe K edge. The most consistent fits were obtained with three  
291 component peaks; fits with two peaks could not reproduce the data, and fits to  
292 four peaks were non-unique and therefore underdetermined.

293 Fits that utilised pseudo-Voigt peaks were also attempted, where the pseudo-  
294 Voigt peak is constructed from the sum of a Gaussian and Lorentzian peak.  
295 Theoretically, Voigt or pseudo-Voigt peaks are better suited to XANES peak  
296 fitting than simple Lorentzians (Wilke et al., 2001). The Lorentzian contribution  
297 accounts for the true peak shape, while the Gaussian contribution is produced  
298 by peak broadening due to limitations in the experimental energy resolution. A  
299 number of strategies were tried that included Voigt peaks in the fit. First, the  
300 Mathematica routine was modified to fit to three Voigt peaks, with Gaussian

301 broadening of 1.3 eV and Lorentzian broadening of 1.08 eV. Fits utilising these  
302 parameters were worse than those with simple Lorentzians. Fit attempts were  
303 also made specifying the Lorentzian broadening parameters as fit parameters.  
304 No improvement in fit was noted and strict limits on the fit parameters were required  
305 as the system started to become underdetermined. If these limits were omitted  
306 then the fit parameters were often found to take physically unrealistic values.  
307 The inclusion of pseudo-Voigt peaks, where the peaks are constructed from a  
308 simple sum of Gaussian and Lorentzian terms was also considered. However,  
309 the number of fit parameters introduced by the need to specify Gaussian and  
310 Lorentzian proportions plus parameters to specify different peak widths for the  
311 two components meant that the data available was insufficient to uniquely de-  
312 termine the fit parameters. The failure of Voigt peaks to replicate the data any  
313 better than the simple sum of Lorentzians led to retention of the Lorentzians.

314 Peak positions from the preliminary fit for each sample were plotted on a  
315 histogram, and subsequent fitting exercises used the highest frequency peak en-  
316 ergies from this histogram. The final fit to the data utilised these peak positions,  
317 and peak areas were fit for set peak positions and widths. This two-step strategy  
318 allowed a good combination of flexibility and consistency. Uncertainties were  
319 derived from the residuals to the non-linear regression and propagated to give  
320 uncertainties on the centroid and on the calculated  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ . The position of  
321 the centroid was calculated from the peak areas and positions, and an estimate  
322 of the apparent proportion of ferric iron was made using the expression derived  
323 for micas by Dyar et al. (2001).

324 Additionally, the energy at a normalised peak intensity of 0.9 ( $I_N = 0.9$ ) was  
325 measured, after correction for any monochromator drift, and used as a potential  
326 calibration parameter. This was performed because Berry et al. (2010) found  
327 that  $I_N = 0.9$  in garnet correlated better with  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  than any of the pre-  
328 edge parameters. However, it should be noted that caution is necessary in the  
329 application of main edge features to calculate  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  because main edge  
330 features are much more sensitive to mineral characteristics on longer length  
331 scales than the individual atom, such as ordering and the identity of an atom's  
332 nearest neighbours. Main edge features are also more likely to suffer from issues  
333 related to self absorption.

334

### Theory

335 EBSD results provided measurements of the orientations of the crystallographic  
336 axes, and of the angle between the  $a$  and  $c$  axes. This allowed the orientations  
337 of the indicatrix axes,  $\alpha$ ,  $\beta$ , and  $\gamma$  to be calculated. The angles between the  
338 electric vector ( $E$ ) and the crystallographic and indicatrix axes, and  $[001]$ , and  
339 were calculated using stereonets and the program OSXStereonet (Allmendinger  
340 et al., 2012).

341 The absorbance cross section due to the dipole transition in biotite, which



342 belongs to the space group  $C2/m$  is

$$\sigma^D(\epsilon) = \sigma^D(0, 0) - \sqrt{3} \sin^2 \phi_Z [\cos 2\psi \sigma^{Dr}(2, 2) + \sin 2\psi \sigma^{Di}(2, 2)] - \left(\frac{1}{\sqrt{2}}\right) (3 \cos^2 \phi_Z - 1) \sigma^D(2, 0) \quad (1)$$

343 (Brouder, 1990).  $\sigma^D(\epsilon)$  is absorbance as a function of the polarisation vector  
344  $\epsilon$ ,  $\sigma^D(0, 0)$  is the isotropic absorption cross section, which is the same as that  
345 which would be measured on powders.  $\sigma^D(2, 0)$  is related to absorption of the  
346 most anisotropic section, and  $\sigma^{Dr}(2, 2)$  and  $\sigma^{Di}(2, 2)$  refer to real and imaginary  
347 parts of absorbance for (2,2) respectively.  $\phi_Z$  is the angle between the  $Z$  axis of  
348 the absorbance ellipsoid and the electric vector and  $\psi$  is the angle of the electric  
349 vector with respect to the  $X$  axis of the absorbance ellipsoid (Figure 1).

350 Interpretation of the spectra using Eqn 1 is problematic, partly because of  
351 the pseudosymmetry issues encountered during the EBSD analysis, and partly  
352 because the unknown orientation of the absorbance ellipsoid relative to the  
353 indicatrix provides a number of unknowns too large to be determined with the  
354 dataset acquired for this study. However, fortunately, the symmetry is close to  
355 trigonal;  $\alpha$  and  $\gamma$  diverge from the  $c$  and  $a$  axes respectively by less than 5 degrees  
356 for the samples studied here, and the  $\beta$  and  $\gamma$  refractive indices have very similar  
357 values, as indicated by the low birefringence of (001) sections. The absorbance  
358 cross-section due to electric dipole interactions for crystal symmetries with a  
359 rotation axis of order greater than two is

$$\sigma^D(\epsilon) = \sigma^D(0, 0) - \left(\frac{1}{\sqrt{2}}\right) (3 \cos^2 \phi_Z - 1) \sigma^D(2, 0) \quad (2)$$

360 Brouder (1990). Eqn 2 can be simplified to

$$\sigma^D(\epsilon) = A1 + A2 \cos^2 \phi_Z \quad (3)$$

361 where  $A1$  is  $\sigma^D(0, 0) - \frac{\sigma^D(2,0)}{\sqrt{2}}$  and  $A2$  is  $\frac{3\sigma^D(2,0)}{\sqrt{2}}$ .

362 For this reason, preliminary interpretations of the data are made assuming  
363 that biotite symmetry is pseudo-trigonal and that Eqn 3 can be used to describe  
364 the relationship between crystal and absorbance orientation. In this case the  $z$   
365 axis of biotite is assumed to be parallel to the  $Z$  axis of the absorbance ellipsoid  
366 and approximately parallel to the  $\alpha$  axis of the absorbance ellipsoid. The  $\beta$  axis  
367 of the indicatrix is parallel to the  $b$  crystallographic axis, and to the  $Y$  axis of  
368 the absorbance ellipsoid. The  $\gamma$  axis of the indicatrix is assumed parallel to the  
369  $a$  crystallographic axis, and to the  $X$  axis of the absorbance ellipsoid.

370 Additional absorbance may result from electric quadrupole interactions with  
371 the X-ray beam (Brouder, 1990). Theoretically, absorbance due to electric  
372 quadrupole interactions have been calculated to be around two orders of mag-  
373 nitude weaker than that for electric dipole interactions, and quadrupole ab-  
374 sorbance has been neglected in a number of studies of the angular dependence  
375 of XAFS (e.g. Heald and Stern, 1977; Manceau et al., 1990; Dyar et al., 2002a;  
376 Berry et al., 2010). However, the 1s to 3d transition, which is invoked as the  
377 main cause of the Fe pre-edge peak (Shulman et al., 1976), is forbidden for com-  
378 plexes in centrosymmetric environments (Westre et al., 1997a). In such cases,  
379 quadrupole interactions can form a significant part of a weak pre-edge feature,

380 as is observed for  $\text{Cr}^{3+}$  and  $\text{V}^{3+}$  in garnet (Cabaret et al., 2010). In non centro-  
381 symmetric environments, the mixing of 4p with 3d orbitals allows electric dipole  
382 1s to 4p transitions, and it is this transition that dominates the pre-edge peak  
383 (e.g. Westre et al., 1997a). Brouder (1990) provides an equation for electric  
384 quadrupole interactions as a function of  $\phi_Z$  and  $\psi$ . Ideally, it would be possible  
385 to assess the quadrupole interaction contribution to the pre-edge peak using this  
386 equation. However, the quadrupole equation contains four calibration parame-  
387 ters, and the signal is likely to be weak, due to the relatively asymmetric nature  
388 of the iron-bearing sites in biotite. Under these circumstances it was considered  
389 that the data set was insufficient to properly calibrate the electric quadrupole  
390 signal and this contribution to the pre-edge peak was not considered further.

391 To test the applicability of Eqn 3, the areas and proportions of the three  
392 Lorentzian peaks, the position of the centroid, and the energy of the normalised  
393 spectra at  $I_N=0.9$  were plotted against  $\cos^2 \phi_Z$ , and correlation coefficients were  
394 calculated for each of the datasets.

395 Other potential orientation – XANES relationships were also tested. These  
396 included testing for a link between absorbance and the angle between the {110}  
397 lattice vectors and the electric vector, which is equivalent to testing for a rela-  
398 tionship with  $\psi$ , as in Eqn 1. None of the more complex approaches produced  
399 results any better than those derived from the simple approach based on the  
400 assumption of pseudosymmetry, so only results based on Eqn 3 are presented  
401 here.

## Results

402

403 The biotites measured (Fig. 2) were compositionally homogeneous (Table 1)  
404 both within grains and between grains in a thin section.  $\text{Fe}/(\text{Fe}+\text{Mg})$  was  
405 between 0.46 – 0.56. Total Al varied between 1.3 and 1.5 cations per 11 oxygens,  
406 and calculated Ti was 0.15 to 0.22 cations per 11 oxygens. The highest Ti values  
407 occurred in the samples with red-brown biotite (T01-54). The site occupancy  
408 calculations did not indicate any ferric iron, or iron on the tetrahedral sites, but  
409 such calculations are not a reliable way to determine these parameters. The  
410 interlayer cation site was dominated by K with  $\text{K}/(\text{K}+\text{Na})$  values greater than  
411 0.99.

412 Results of the Mössbauer analysis (Table 1; Fig 3) indicate ferric iron pro-  
413 portions of 0.10, 0.23 and 0.21 for samples T01-23, T01-28, and T01-54 respec-  
414 tively. Fit diagnostics indicate an excellent fit of the model to the data (Table  
415 4). The ferric iron content does not correlate with the  $\text{Fe}/(\text{Fe}+\text{Mg})$  value, Al  
416 content or Ti content, or with the colour of the biotite. The two samples with  
417 the green-brown biotites (T01-23 and T01-28) had the lowest and highest ferric  
418 iron proportions respectively.

419 Despite the difficulty in polishing biotites for EBSD analysis, EBSPs for the  
420 biotites were of acceptable quality (e.g. Fig. 4a) and were routinely indexed  
421 by the Channel 5 software (Fig. 4b). For individual grains the proportion  
422 of points indexed successfully was generally greater than 50% (e.g. Fig. 4c).  
423 However, the indexed grains contain multiple solutions because of the pseudo-

424 hexagonal symmetry of biotite (Fig. 4c). The different solutions represent 60  
425 degree rotations around the pole to (001) and, as a result, poles to (001) record  
426 only a single solution (Fig. 4d).

427 In detail, the orientation of (001) poles is seen to vary systematically along  
428 small circles by up to 15 degrees (Fig. 4d). This is also reflected in the distribu-  
429 tion of most of the other poles, with the exception of one pole, around which the  
430 other poles appear to be dispersed (Fig. 4d). This pattern of dispersion is com-  
431 monly seen in minerals deforming by dislocation creep and can be interpreted in  
432 terms of the formation of tilt boundaries associated with the operation of par-  
433 ticular slip systems (Reddy et al., 2007) associated with bending of the mineral  
434 lattice. In the case of biotite, deformation commonly occurs by slip on the (001)  
435 basal plane with  $\langle 100 \rangle$  being a common Burgers vector. In this slip system  
436 scenario, the pole to (010) would be expected to be the axis about which all  
437 other poles are dispersed. In the example shown here, where the biotite grain is  
438 bent through about 15 degrees, only one of the (010) poles records no dispersion  
439 (Fig. 4d) so this must be the correctly indexed (010) pole. Consequently, the  
440 analysis of slightly bent grains provides an opportunity to overcome the inherent  
441 problem of systematic misindexing when trying to establish the orientation of  
442 biotite grains.

443 Even using the methodology outlined above, very few of the analysed biotites  
444 could be uniquely oriented because of the general absence of deformation within  
445 individual biotite grains. Hence, most of the orientation data have uniquely  
446 oriented poles to (001) but less well-constrained  $\{100\}$  and  $\{010\}$  orientations.

447 Fortunately,  $\phi_Z$  depends only on  $\{001\}$  so the potential misindexing does not  
448 affect results acquired from Eqn 3.

449 XANES spectra showed significant variation in the characteristics of the pre-  
450 edge peak, main edge, and post-edge features between samples, between grains  
451 in a single sample, and as a function of orientation of individual grains (Fig.  
452 5, Tables 5 – 7). A number of features showed consistent trends as a function  
453 of  $\phi_Z$  if spectra collected at the highest and lowest values of  $\phi_Z$  are compared.  
454 Spectra from samples oriented with a low  $\phi_Z$  showed a smaller pre-edge peak,  
455 with, potentially, a slight skew to lower energy values, compared to spectra  
456 collected from samples oriented with a high  $\phi_Z$ . The shape of the shoulder  
457 on the main edge also varied, and was found to occur at a higher normalised  
458 absorption for the spectra collected at low  $\phi_Z$ . This feature may contribute  
459 towards variation in the value of the energy at a normalised intensity of 0.9 ( $I_N$   
460 =0.9; Fig. 5a). With respect to edge and post-edge features, the total overall  
461 intensity of the second peak (MP2 on Fig. 5) is higher for the high  $\phi_Z$  spectra,  
462 and the ratio of the intensities of the first two peaks, MP1:MP2, is lower for the  
463 high  $\phi_Z$  spectra. Systematic differences continue at higher energies. The fall  
464 in energy after the third peak (MP3) occurs at higher energies for the spectra  
465 collected at low  $\phi_Z$ . However, these systematic differences may be small relative  
466 to the variation between grains and between samples, because the relationships  
467 described above are not statistically significant if the full dataset is considered.

468 The isolated pre-edge peak data fit well to the combination of three Lorentzians  
469 (Fig. 6). The relative proportions of the three peaks vary with the angle be-

470 tween the electric vector and [001], and it appears, qualitatively, as though the  
471 sample out of any pair of measurements with a greater value for  $\phi_Z$  also has  
472 a greater proportion of the pre-edge peak accommodated in the lowest energy  
473 peak, which is referred to as P1 (Figs 6a, c and e versus b, e and f). The  
474 middle and highest energy peaks are referred to as P2 and P3 respectively, but  
475 there is little sign of a systematic relationship between the proportions of these  
476 peaks and the grain orientation. Additionally, while the general trend of the  
477 differences in relative peak area between measurements on a single grain seems  
478 reasonably consistent, there appears to be significant variation between grains  
479 and between samples.

480 The preliminary peak fitting exercise revealed three relatively well separated  
481 groups of Lorentzian positions (Fig. 7). The P1 peak at 7111.4 eV was well  
482 defined and in the same position for all three samples. The P2 peak varied more  
483 and samples T01-23 and T01-28 was at slightly lower energies (7112.1 – 7112.9  
484 eV) than for T01-54 (7112.7 – 7113.1 eV). A similar trend was observed for the  
485 P3 peak, with the bulk of measurements for T01-23 and T01-28A at 7113.3 –  
486 7114.1 eV and T01-54 at 7114.1 – 7114.4 eV. The similarity of T01-23 and T01-  
487 28A, and the difference between these samples and T01-54 is not related to the  
488 Mössbauer-derived estimates of  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  (Table 4), which indicate that T01-  
489 28A and T01-54 have very similar ferric iron contents whereas that of T01-23  
490 is significantly less. However, T01-54 does differ in having significantly higher  
491 Ti content (Table 3).

492 Ferric iron contents calculated using the formula of Dyar et al. (2001) are

493 within error of the values measured by Mössbauer (compare Table 4 to Tables  
494 5 to 7). However, the uncertainties are relatively large, and there is no signifi-  
495 cant difference between T01-23, which has Mössbauer-derived  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  of 0.1,  
496 and the other two samples, which have Mössbauer-derived values of  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$   
497 of around 0.22. The standard deviation of the measurements of centroid and  
498  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  for grains within a sample is much larger than the propagated error  
499 on the individual measurements, which indicates that the observed variation as  
500 a function of crystal orientation is real and not simply derived from uncertainties  
501 associated with analysis and the fitting process.

502 Calculated correlation coefficients (Table 8) show that the measured param-  
503 eter that has the most convincing relationship with  $\cos^2\phi_Z$  is the energy at  
504  $I_N = 0.9$ , which correlates significantly with  $\cos^2\phi_Z$  for two of the three samples  
505 and with a  $p$  value of less than 0.06 for the third (T01-54). The slope of the  
506 data in  $\cos^2\phi_Z - I_N = 0.9$  space (Fig. 8a) was also similar for the three samples  
507 considered. T01-23 and T01-28A (low Ti samples), which have significantly dif-  
508 ferent  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ , plotted in approximately the same region, while the higher  
509 Ti sample (T01-54) plotted at lower  $I_N = 0.9$  values. There were no consistent  
510 significant, or nearly significant, correlations between  $\cos^2\phi_Z$  and the measured  
511 centroid characteristics (e.g. Table 8; Figs 8b, c, d), though a significant corre-  
512 lation was observed between the area of P1 and  $\cos^2\phi_Z$  for T01-28A ( $p = 0.01$ );  
513 a low  $p$ -value was calculated for the same pair of parameters for sample T01-54  
514 ( $p=0.02$ ). The other significant correlation was between the proportion of P3  
515 and  $\cos^2\phi_Z$  for T01-23 ( $p=0.009$ ).



516

## Discussion and Concluding Remarks

517  $I_N = 0.9$  is the spectral characteristic that appears most reliably sensitive to  
518 crystal orientation (Fig. 8a). However, there doesn't seem to be any consistent  
519 relationship between the energy at  $I_N = 0.9$  and ferric iron content (Fig. 8a),  
520 although Berry et al. (2010) record a positive correlation between  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$   
521 and the energy at  $I_N = 0.9$  in garnet. It may be that  $I_N = 0.9$  is insensitive to  
522 biotite composition at the limits of resolution imposed by the analysis, or that  
523 additional factors related to the sample matrix contribute to the edge position  
524 and characteristics and obscure trends that might otherwise be discernible. The  
525 size of the error bars suggests the former. However, it is also useful to consider  
526 the potential effects of sample matrix.

527 It has been proposed that the shoulder on the main edge in biotite is caused  
528 by interactions between photoelectrons ejected from Fe atoms and neighbouring  
529 or second nearest neighbour Fe atoms, and that the characteristics of the feature  
530 record Fe-ordering (Dyar et al., 2001). The position and size of this shoulder  
531 affects  $I_N = 0.9$ , so it is possible that the characteristics of the shoulder are  
532 sensitive to the composition of the matrix and depend on compositional param-  
533 eters such as  $\text{Fe}/(\text{Fe}+\text{Mg})$ , the Al content of the biotite, the Ti content, as well  
534 as other factors such as the temperature of equilibration, which would affect the  
535 extent of ordering.

536 The temperature of equilibration, which affects ordering, also affects  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$   
537 in biotite via the stability of other minerals in the assemblage, if bulk rock

538  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  is fixed or approximately fixed. This combination of causal links  
539 could produce a false correlation. For example, the presence of moderate quan-  
540 tities of epidote in the T01-23 sample could be interpreted to indicate that  
541 this sample equilibrated at a lower temperature than the other two, which are  
542 epidote-absent, and therefore have different ordering. Additionally, epidote,  
543 which contains ferric iron, may have sequestered ferric iron present in the rock  
544 so that the ferric iron in biotite is less than in the other two samples. Under  
545 these circumstances, temperature could have controlled both  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ , and  
546 the energy at  $I_N = 0.9$  via mineral stability and ordering, respectively. In this  
547 case the presence or absence of correlation between the energy at  $I_N = 0.9$  and  
548  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  should be treated cautiously.

549 Mineral assemblages do not provide evidence of a difference in temperature  
550 between the three samples examined. Sillimanite is present in T01-23 and T01-  
551 28A, while K-feldspar is present in T01-28A and T01-54. The presence of silli-  
552 manite indicates that the rocks equilibrated at temperatures in excess of 600°C  
553 for reasonable geothermal gradients, and the presence of K-feldspar indicates  
554 that temperatures were higher than the muscovite-out reaction which is consis-  
555 tent with temperatures higher than around 650°C, for these bulk compositions.  
556 Samples T01-23 and T01-28A were collected about 1500 m apart, and there is  
557 no evidence of a major structural discontinuity between them, while the T01-54  
558 sample site is separated from the other two by a significant shear zone. The  
559 mineral assemblages in the three sections are too different and/or high variance  
560 for reliable comparative thermobarometry and a full pseudosection approach

561 is beyond the scope of this paper. For this reason, the Ti-in-biotite geother-  
562 mometer of Henry et al. (2005) was applied to obtain a preliminary assessment  
563 of temperature differences between the three samples. This geothermometer is  
564 empirically calibrated for rutile-bearing assemblages in aluminous metapelites  
565 and may, therefore, be unreliable for more mafic rocks such as T01-28A. Tem-  
566 peratures calculated for the three samples are  $677 \pm 20$  °C for T01-23;  $682 \pm 20$   
567 °C for T01-28A, and  $713 \pm 20$  C for T01-54. These temperatures are within  
568 uncertainty of each other, so it is not possible to confirm any significant differ-  
569 ence in the temperature of equilibration between the three samples. However,  
570 differences in temperature may affect ordering, and hence XANES features, and  
571 this needs to be assessed in detail as part of any further development of the use  
572 of XANES to measure  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ .

573 Features of the pre-edge peak, on which most attention has been focussed  
574 in previous work on  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ , do not exhibit consistent relationships with  
575 crystal orientation (Table 8). The area of the P1 peak presents the best pos-  
576 sibility, because significant or nearly significant correlations were observed for  
577 two samples (T01-23 and T01-54) but further work on this parameter is not  
578 useful because after orientation corrections only two points would be obtained,  
579 which are insufficient for determination of trends.

580 **Orientation corrections**

581 The simplest possible orientation correction is to fit the parameter of interest as  
582 a linear function of  $\cos^2 \phi_Z$ , (Eqn 3), and to project the parameter of interest to  
583 a chosen value of  $\phi_Z$ . This correction was performed for the energy at  $I_N = 0.9$ .  
584 The data were fit to

$$E_{I_N=0.9} = m_1 \cos^2 \phi_Z + c_1 \quad (4)$$

585 where  $E_{I_N=0.9}$  is the energy at  $I_N = 0.9$ , and  $m_1$  and  $c_1$  are constants. Eqn  
586 4 has the same form as Eqn 3. The data from each sample were fit to Eqn  
587 4 to provide expressions that allow calculation of  $E_{I_N=0.9}$  as a function of  $\phi_Z$ .  
588 The value chosen was  $45^\circ$ , which is convenient because this value of  $\phi_Z$  can  
589 be obtained if the cleavage of biotite in any  $(hk0)$  section is aligned vertically  
590 during measurement. Values of the fit parameters, and their uncertainties are  
591 shown in Table 9.

592 Values of  $I_N = 0.9$  for  $\phi_Z = 45^\circ$  were plotted against Mössbauer-derived  
593  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  (Fig. 9). The results should be treated with caution since there are  
594 only three data points, and two of these have similar  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  values; however,  
595 it can be seen that  $I_N = 0.9$  is not a function of  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ .

596 Orientation correction parameters for each of the samples are different (Table  
597 9). This supports the possibility discussed above, i.e. that XANES characteris-  
598 tics depend on factors other than orientation, such as biotite composition and  
599 the extent of ordering. This proposal is supported by the work of Wong et al.  
600 (1984) on vanadium spectra. Wong et al. (1984) recorded pre-edge peaks for

601 octahedral trivalent V that were more intense when the V was held in roscoel-  
602 lite, a V-bearing mica, relative to those caused by V in  $V_2O_3$ . The difference  
603 was attributed to the fact that the Al neighbours of V in roscoelite are smaller  
604 and more highly charged than V neighbours. Bonds in roscoelite would there-  
605 fore take on a more ionic character, and the probability of transitions into the  
606  $3d$  orbitals would be enhanced as these bonding orbitals would be, on average,  
607 more empty.

608 Under these circumstances, any biotite calibration, including the orientation  
609 correction, would have to be very closely matrix-matched, although relative  
610 changes in  $Fe^{3+}/Fe_{tot}$  within grains or between grains with similar compositions  
611 could be considered robust. The need for matrix correction is further supported  
612 by the distinctly different positions of the preliminary fit P2 and P3 Lorentzians  
613 (Fig. 7) for the green-brown Ti-poor biotites, T01-23 and T01-28A, and the red-  
614 brown Ti-rich biotite, T01-54. Further work, both experimental and theoretical,  
615 is necessary to elucidate the nature of the matrix-dependency.

616 Alternatively, it may be that the simplifying assumptions made in the de-  
617 velopment of the orientation correction are not justified and an improved ori-  
618 entation correction might be devised if the obstacles that necessitated the as-  
619 sumptions were removed. For example, it was assumed that the monoclinic  
620 biotite symmetry could be approximated by trigonal symmetry because this as-  
621 sumption greatly simplified the relationship between measured absorbance and  
622 crystal orientation, since in trigonal systems the axes of the absorbance ellipsoid  
623 are aligned with both the indicatrix axes and the  $[001]$  crystal axis.

624 If electric quadrupole interactions contributed significantly to the pre-edge  
625 peak then the use of Eqn 2 is inappropriate and a good fit of the data to the  
626 model would not be expected. Previous workers (e.g. Heald and Stern, 1977;  
627 Manceau et al., 1990; Dyar et al., 2002a; Berry et al., 2010) have neglected  
628 quadrupole interactions for fits of iron pre-edge peaks, and the large number  
629 of calibration parameters necessary to fit an electric quadrupole contribution  
630 to the data made it impossible to fit the data to the more complex model.  
631 However, in future, it would be informative to use ab-initio calculations to  
632 constrain the contribution of the electric quadrupole contribution, and perform  
633 a proper assessment on the likely significance of this feature.

634 It is also possible that orientation of the absorbance ellipsoid varies with the  
635 energy of the X-ray beam, since the different bonds which absorb at energies  
636 determined by crystal field splitting and symmetry constraints are oriented dif-  
637 ferently within the crystal. The detailed data needed to resolve the potentially  
638 complex nature of this problem was beyond the scope of the measurements made  
639 for this study, and indeed, the good correlations between orientation and key  
640 parameters such as  $E_{I_N=0.9}$  indicate that these effects are likely to be second  
641 order. However, further work focussed on measurement of the orientation of  
642 the absorbance ellipsoid might prove useful and allow reduction in orientation-  
643 related uncertainties.

644 It was also assumed that the beam was fully polarised, whereas, in reality,  
645 the use of the Kirkpatrick-Baez mirrors for focussing introduces a small degree  
646 of elliptical polarisation. Under these circumstances the electric vector has

647 an additional orthogonal component. If the extent to which the synchrotron  
648 beam was elliptically polarised was known then it would be possible, though not  
649 trivial (compare Sambridge et al. (2008) to Libowitzky and Rossman (1996)),  
650 to develop equations for a two dimensional beam. If the extent of polarisation  
651 could be controlled then this feature could be used to constrain the orientation  
652 of the absorbance ellipsoid. However, the precise shape of the beam was not  
653 determined for this study.

654 It would also be possible to improve the resolution of the data if a standard  
655 were continuously monitored, such that the drift corrections did not involve  
656 interpolation in time. However, the drift corrections noted for this project were  
657 small relative to the variation in the energy at  $I_N = 0.9$  and the variation in  
658 centroid position so it is unlikely that the lack of an off-line standard had a  
659 serious impact on the quality of the results.

660 To summarise, pre-edge peak parameters do not correlate with biotite crystal  
661 orientation, but  $E_{I_N=0.9}$  is significantly correlated with  $\phi_Z$  in two of the three  
662 samples and relatively well correlated in the third. Once the measurements are  
663 corrected for orientation, there is no significant relationship between  $E_{I_N=0.9}$   
664 and  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ . The absence of a correlation is attributed to composition-  
665 or temperature-related differences in ordering and/or simplifying assumptions  
666 used in the development of the model. Further work should include careful  
667 calibrations on matrix-matched standards and ab-initio modelling to assess the  
668 relative contributions of electric dipole and quadrupole to the pre-edge peak. If  
669 this work were performed then it may be possible to improve the precision and

670 accuracy of synchrotron measurement of  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  in non-powdered samples.

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## References

- 684 Allmendinger, R., Cardozo, N., and Fisher, D. (2012) Structural Geology Algo-  
685 rithms: Vectors and Tensors. Cambridge University Press, Cambridge.
- 686 Arrio, M.A., Rossano, S., Brouder, C., Galois, L., and Calas, G. (2000) Calcu-  
687 lation of multipole transitions at the FeK pre-edge through p-d hybridization  
688 in the Ligand Field Multiplet model. *Europhysics Letters*, 51, 454–460.
- 689 Bajt, S., Sutton, S.R., and Delaney, J.S. (1994) X-Ray Microprobe Analysis of  
690 Iron Oxidation-States in Silicates and Oxides Using X-Ray-Absorption near-  
691 Edge Structure (Xanes). *Geochimica Et Cosmochimica Acta*, 58, 5209–5214.
- 692 Berry, A.J., O'Neill, H.S., and Foran, G.J. (2004) The in situ determination of  
693 redox states in silicate melts. *Lithos*, 73, S9–S9.
- 694 Berry, A.J., O'Neill, H.S., Jayasuriya, K.D., Campbell, S.J., and Foran, G.J.  
695 (2003) XANES calibrations for the oxidation state of iron in a silicate glass.  
696 *American Mineralogist*, 88, 967–977.
- 697 Berry, A.J., Yaxley, G.M., Woodland, A.B., and Foran, G.J. (2010) A XANES  
698 calibration for determining the oxidation state of iron in mantle garnet. *Chem-  
699 ical Geology*, 278, 31–37.
- 700 Brouder, C. (1990) Angular-Dependence of X-Ray Absorption-Spectra. *Journal  
701 of Physics-Condensed Matter*, 2, 701–738.
- 702 Cabaret, D., Bordage, A., Juhin, A., Arfaoui, M., and Gaudry, E. (2010) First-

- 703 principles calculations of X-ray absorption spectra at the K-edge of 3d transi-  
704 tion metals: an electronic structure analysis of the pre-edge. *Physical Chem-*  
705 *istry Chemical Physics*, 12, 5619–5633.
- 706 Collins, A.S., Reddy, S.M., Buchan, C., and Mruma, A. (2004) Temporal con-  
707 straints on Palaeoproterozoic eclogite formation and exhumation (Usagaran  
708 Orogen, Tanzania). *Earth and Planetary Science Letters*, 224, 175–192.
- 709 Delaney, J.S., Dyar, M.D., Gunter, M.E., Sutton, S.R., and Lanzarotti, A. (2005)  
710 Geometric constraints of in situ synchrotron micro-XANES determinations of  
711 oxidation state. *Geochimica Et Cosmochimica Acta*, 69, A793–A793.
- 712 Delaney, J.S., Dyar, M.D., Sutton, S.R., and Bajt, S. (1998) Redox ratios with  
713 relevant resolution: Solving an old problem by using the synchrotron microX-  
714 ANES probe. *Geology*, 26, 139–142.
- 715 Dyar, M.D., Delaney, J.S., and Sutton, S.R. (2001) Fe XANES spectra of iron-  
716 rich micas. *European Journal of Mineralogy*, 13, 1079–1098.
- 717 Dyar, M.D., Gunter, M.E., Delaney, J.S., Lanzarotti, A., and Sutton, S.R.  
718 (2002a) Systematics in the structure and XANES spectra of pyroxenes, am-  
719 phiboles, and micas as derived from oriented single crystals. *Canadian Min-*  
720 *eralogist*, 40, 1375–1393.
- 721 Dyar, M.D., Lowe, E.W., Guidotti, C.V., and Delaney, J.S. (2002b) Fe<sup>3+</sup> and  
722 Fe<sup>2+</sup> Partitioning Among Silicates in Metapelites: a Synchrotron Micro-  
723 Xanes Study. *American Mineralogist*, 87, 514–522.

- 724 Dyar, M.D., Schaefer, M.W., Sklute, E.C., and Bishop, J.L. (2008) Mossbauer  
725 spectroscopy of phyllosilicates: effects of fitting models on recoil-free fractions  
726 and redox ratios. *Clay Minerals*, 43, 3–33.
- 727 Foley, S.F. (2011) A Reappraisal of Redox Melting in the Earth's Mantle as a  
728 Function of Tectonic Setting and Time. *Journal of Petrology*, 52, 1363–1391.
- 729 Heald, S.M. and Stern, E.A. (1977) Anisotropic X-Ray Absorption in Layered  
730 Compounds. *Physical Review B*, 16, 5549–5559.
- 731 Henry, D.J., Guidotti, C.V., and Thomson, J.A. (2005) The Ti-saturation sur-  
732 face for low-to-medium pressure metapelitic biotites: Implications for geother-  
733 mometry and Ti-substitution mechanisms. *American Mineralogist*, 90, 316–  
734 328.
- 735 Janssens, K., Vincze, L., Vanespen, P., and Adams, F. (1993) Monte Carlo simu-  
736 lation of conventional and synchrotron energy-dispersive x-ray spectrometers.  
737 *X-Ray Spectrometry*, 22, 234–243.
- 738 Jugo, P.J. (2009) Sulfur content at sulfide saturation in oxidized magmas. *Ge-*  
739 *ology*, 37, 415–418.
- 740 Jugo, P.J., Luth, R.W., and Richards, J.P. (2005) An experimental study of the  
741 sulfur content in basaltic melts saturated with immiscible sulfide or sulfate  
742 liquids at 1300 degrees C and 1 center dot 0 GPa. *Journal of Petrology*, 46,  
743 783–798.
- 744 Keefner, J.W., Mackwell, S.J., Kohlstedt, D.L., and Heidelbach, F. (2011) De-

- 745 pence of dislocation creep of dunite on oxygen fugacity: Implications for  
746 viscosity variations in Earth's mantle. *Journal of Geophysical Research-Solid*  
747 *Earth*, 116.
- 748 Krause, M.O. and Oliver, J.H. (1979) Natural Widths of Atomic K-Levels and L-  
749 Levels, K-Alpha X-Ray-Lines and Several Kll Auger Lines. *Journal of Physical*  
750 *and Chemical Reference Data*, 8, 329–338.
- 751 Li, Y.L., Zheng, Y.F., and Fu, B. (2005) Mossbauer spectroscopy of omphacite  
752 and garnet pairs from eclogites: Application to geothermobarometry. *Ameri-*  
753 *can Mineralogist*, 90, 90–100.
- 754 Libowitzky, E. and Rossman, G.R. (1996) Principles of quantitative absorbance  
755 measurements in anisotropic crystals. *Physics and Chemistry of Minerals*, 23,  
756 319–327.
- 757 Mackwell, S.J., Bai, Q., and Kohlstedt, D.L. (1990) Rheology of Olivine and  
758 the Strength of the Lithosphere. *Geophysical Research Letters*, 17, 9–12.
- 759 Manceau, A., Bonnin, D., Stone, W.E.E., and Sanz, J. (1990) Distribution  
760 of Fe in the Octahedral Sheet of Trioctahedral Micas by Polarized Exafs -  
761 Comparison with Nmr Results. *Physics and Chemistry of Minerals*, 17, 363–  
762 370.
- 763 Mavrogenes, J.A. and O'Neill, H.S.C. (1999) The relative effects of pressure,  
764 temperature and oxygen fugacity on the solubility of sulfide in mafic magmas.  
765 *Geochimica Et Cosmochimica Acta*, 63, 1173–1180.

- 766 Meyrowitz, R. (1963) A semimicroprocedure for the determination of ferrous iron  
767 in nonrefractory silicate minerals. *American Mineralogist*, 48, 340–347.
- 768 Munoz, M., De Andrade, V., Vidal, O., Lewin, E., Pascarelli, S., and Susini, J.  
769 (2006) Redox and speciation micromapping using dispersive X-ray absorption  
770 spectroscopy: Application to iron chlorite mineral of a metamorphic rock thin  
771 section. *Geochemistry Geophysics Geosystems*, 7.
- 772 Petit, P.E., Farges, F., Wilke, M., and Sole, V.A. (2001) Determination of the  
773 iron oxidation state in Earth materials using XANES pre-edge information.  
774 *Journal of Synchrotron Radiation*, 8, 952–954.
- 775 Pfalzer, P., Urbach, J.P., Klemm, M., Horn, S., denBoer, M.L., Frenkel, A.I.,  
776 and Kirkland, J.P. (1999) Elimination of self-absorption in fluorescence hard-  
777 x-ray absorption spectra. *Physical Review B*, 60, 9335–9339.
- 778 Randall, C.R., Shu, L.J., Chiou, Y.M., Hagen, K.S., Ito, M., Kitajima, N.,  
779 Lachicotte, R.J., Zang, Y., and Que, L. (1995) X-Ray-Absorption Pre-Edge  
780 Studies of High-Spin Iron(II) Complexes. *Inorganic Chemistry*, 34, 1036–1039.
- 781 Ravel, B. and Newville, M. (2005) ATHENA, ARTEMIS, HEPHAESTUS: data  
782 analysis for X-ray absorption spectroscopy using IFEFFIT. *Journal of Syn-*  
783 *chrotron Radiation*, 12, 537–541.
- 784 Reddy, S.M., Collins, A.S., Buchan, C., and Mruma, A.H. (2004) Heterogeneous  
785 excess argon and Neoproterozoic heating in the Usagaran Orogen, Tanzania,  
786 revealed by single grain Ar-40/Ar-39 thermochronology. *Journal of African*  
787 *Earth Sciences*, 39, 165–176.

- 788 Reddy, S.M., Collins, A.S., and Mruma, A. (2003) Complex high-strain defor-  
789 mation in the Usagaran Orogen, Tanzania: structural setting of Palaeopro-  
790 terozoic eclogites. *Tectonophysics*, 375, 101–123.
- 791 Reddy, S.M., Timms, N.E., Pantleon, W., and Trimby, P. (2007) Quantitative  
792 characterization of plastic deformation of zircon and geological implications.  
793 *Contributions to Mineralogy and Petrology*, 153, 625–645.
- 794 Rehr, J.J., Kas, J.J., Prange, M.P., Sorini, A.P., Takimoto, Y., and Vila, F.  
795 (2009) Ab initio theory and calculations of X-ray spectra. *Comptes Rendus*  
796 *Physique*, 10, 548–559.
- 797 Sambridge, M., Gerald, J.F., Kovacs, I., O'Neill, H.S.C., and Hermann, J. (2008)  
798 Quantitative absorbance spectroscopy with unpolarized light: Part I. Physical  
799 and mathematical development. *American Mineralogist*, 93, 751–764.
- 800 Schmid, R., Wilke, M., Oberhansli, R., Janssens, K., Falkenberg, G., Franz,  
801 L., and Gaab, A. (2003) Micro-XANES determination of ferric iron and its  
802 application in thermobarometry. *Lithos*, 70, 381–392.
- 803 Shulman, G.R., Yafet, Y., Eisenberger, P., and Blumberg, W.E. (1976) Ob-  
804 servations and interpretation of x-ray absorption edges in iron compounds  
805 and proteins. *Proceedings of the National Academy of Sciences of the United*  
806 *States of America*, 73, 1384–8.
- 807 Vidal, O., De Andrade, V., Lewin, E., Munoz, M., Parra, T., and Pascarelli,  
808 S. (2006) P-T-deformation-Fe<sup>3+</sup>/Fe<sup>2+</sup> mapping at the thin section scale

- 809 and comparison with XANES mapping: application to a garnet-bearing  
810 metapelite from the Sambagawa metamorphic belt (Japan). *Journal of Meta-*  
811 *morphic Geology*, 24, 669–683.
- 812 Vogt, M., Kroener, A., Poller, U., Sommer, H., Muhongo, S., and Wingate,  
813 M.T.D. (2006) Archaean and Palaeoproterozoic gneisses reworked during a  
814 Neoproterozoic (Pan-African) high-grade event in the Mozambique belt of  
815 East Africa: Structural relationships and zircon ages from the Kidatu area,  
816 central Tanzania. *Journal of African Earth Sciences*, 45, 139–155.
- 817 Westre, T.E., Kennepohl, P., DeWitt, J.G., Hedman, B., Hodgson, K.O., and  
818 Solomon, E.I. (1997a) A multiplet analysis of Fe K-edge 1s- $\rightarrow$ 3d pre-edge fea-  
819 tures of iron complexes. *Journal of the American Chemical Society*, 119, 6297–  
820 6314.
- 821 — (1997b) A multiplet analysis of Fe K-edge 1s to 3d pre-edge features of  
822 iron complexes. *Journal of the American Chemical Society*, 119, 6297–6314.
- 823 Wilke, M., Farges, F., Petit, P.E., Brown, G.E., and Martin, F. (2001) Oxidation  
824 state and coordination of Fe in minerals: An FeK-XANES spectroscopic study.  
825 *American Mineralogist*, 86, 714–730.
- 826 Wilke, M., Partzsch, G.M., Bernhardt, R., and Lattard, D. (2004) Determina-  
827 tion of the iron oxidation state in basaltic glasses using XANES at the K-edge.  
828 *Chemical Geology*, 213, 71–87.
- 829 — (2005) Determination of the iron oxidation state in basaltic glasses using  
830 XANES at the K-edge (vol 213, 71, 2004). *Chemical Geology*, 220, 141–+.

- 831 Wilke, M., Farges, F., Partzsch, G.M., Schmidt, C., and Behrens, H. (2007)  
832 Speciation of Fe in silicate glasses and melts by in-situ XANES spectroscopy.  
833 American Mineralogist, 92, 44–56.
- 834 Wilke, M., Hahn, O., Woodland, A.B., and Rickers, K. (2009) The oxidation  
835 state of iron determined by Fe K-edge XANES-application to iron gall ink in  
836 historical manuscripts. Journal of Analytical Atomic Spectrometry, 24, 1364–  
837 1372.
- 838 Wong, J., Lytle, F.W., Messmer, R.P., and Maylotte, D.H. (1984) K-Edge  
839 Absorption-Spectra of Selected Vanadium Compounds. Physical Review B,  
840 30, 5596–5610.
- 841 Wyllie, P.J. (1995) Experimental Petrology of Upper-Mantle Materials, Process  
842 and Products. Journal of Geodynamics, 20, 429–468.



843

## Figure Captions

844 Figure 1: Schematic illustration of the absorption ellipsoid, showing the direc-  
845 tion of the beam, the electric vector and angles discussed in the text.

846 Figure 2: Plane polarised photomicrographs of (a) T01-23; (b) T01-28A; (c)  
847 T01-54. Labels indicate the biotite grains analysed.

848 Figure 3: Results of Mössbauer spectroscopy on (a) T01-23; (b) T01-28A; (c)  
849 T01-54.

850 Figure 4. Electron backscatter diffraction data from biotite grain EB5 (Sam-  
851 ple T01-23). a) Typical EBSP from the grain. Although the bands can  
852 be seen they are relatively faint due to the difficulty in polishing biotite.  
853 b) the indexed orientation derived from comparison of bands identified in  
854 (a) with a theoretical diffraction pattern for biotite. c) Orientation map  
855 created by applying red, green and blue colours to each of the 3 Euler ori-  
856 entations required to define the orientation of the lattice at each pixel. The  
857 variation in colour indicates an apparent change in orientation associated  
858 with a systematic misindexing due to the pseudo-hexagonal symmetry of  
859 biotite. d) pole figures for  $\{100\}$ ,  $\{010\}$  and  $\{001\}$  for the grain shown in  
860 (c). Colours represent the orientations shown in (c) The misindexing is  
861 shown by the presence of three clusters in the  $\{100\}$  and  $\{010\}$  data. Only  
862  $\{001\}$  shows a single orientation indicating that the misindexing represents  
863 an apparent 60 rotation around the  $\{001\}$  pole. The dispersion of data for

864 most of the poles by  $15^\circ$  around small circles are consistent with deforma-  
865 tion by dislocation creep. The absence of dispersion around the centrally  
866 located  $\{010\}$  pole, combined with the knowledge of biotite deformation  
867 mechanisms allows this pole to be identified as the real orientation of the  
868 grain despite the systematic misindexing problem (see text for details).

869 Figure 5. XANES. (a,b) absorption edge and pre-edge peak for T01-23; (c,d)  
870 absorption edge and pre-edge peak for T01-28A; (e, f) absorption edge  
871 and pre-edge peak for T01-54. Orientations chosen to show high and low  
872  $\phi_Z$  for a given grain.

873 Figure 6. Fit to pre-edge peak for spectra shown in Fig. 5 (a, b) T01-23; ((c,  
874 d) T01-28A; (e, f) T01-54. Dots indicate measured absorption values with  
875 background removed. Lines indicate the fit Lorentzian peaks.

876 Figure 7. Histogram illustrating the positions of Lorentzians obtained during  
877 preliminary pre-edge peak analysis.

878 Figure 8. Relationships between  $\cos^2\phi_Z$  and measured parameters for the three  
879 samples investigated. (a) Energy at  $I_N = 0.9$ ; (b) Centroid energy; (c)  
880 Proportion of pre-edge peak component at 7111.4 eV (P1); (d) Proportion  
881 of pre-edge peak component P3.

882 Figure 9. Orientation-corrected values of energy at  $I_N = 0.9$  plotted against  
883 Mössbauer-derived  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ . Energy at  $I_N = 0.9$  values are corrected  
884 to a value of  $\phi_Z$  using Eqn 4.

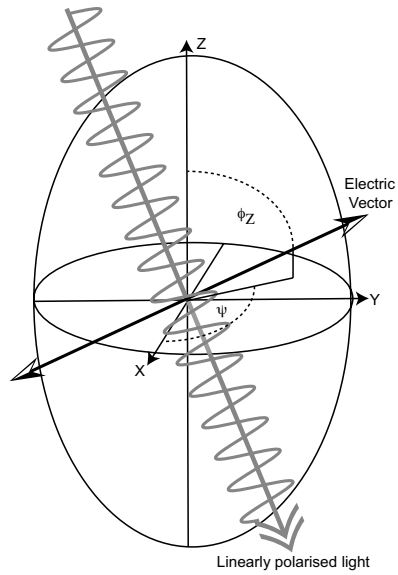


Figure 1:

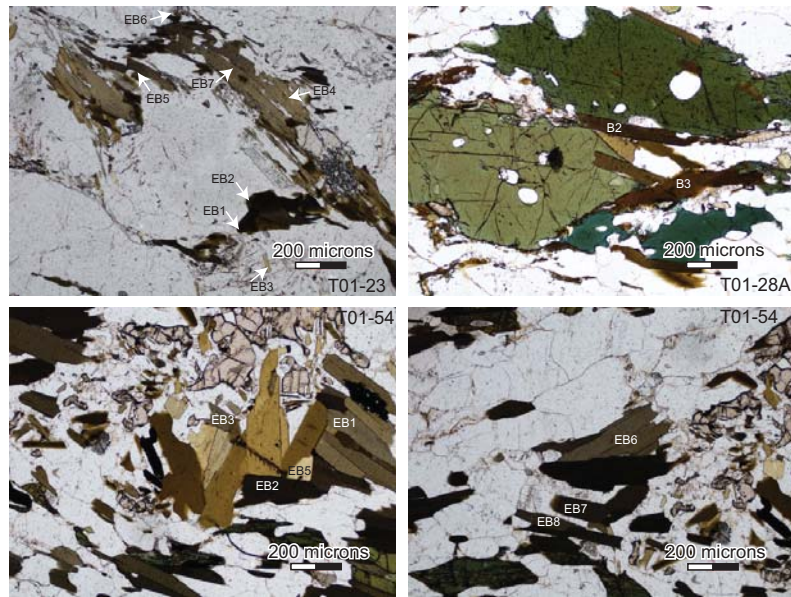


Figure 2:

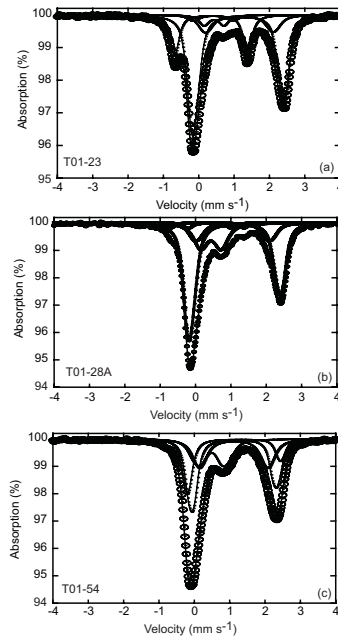


Figure 3:

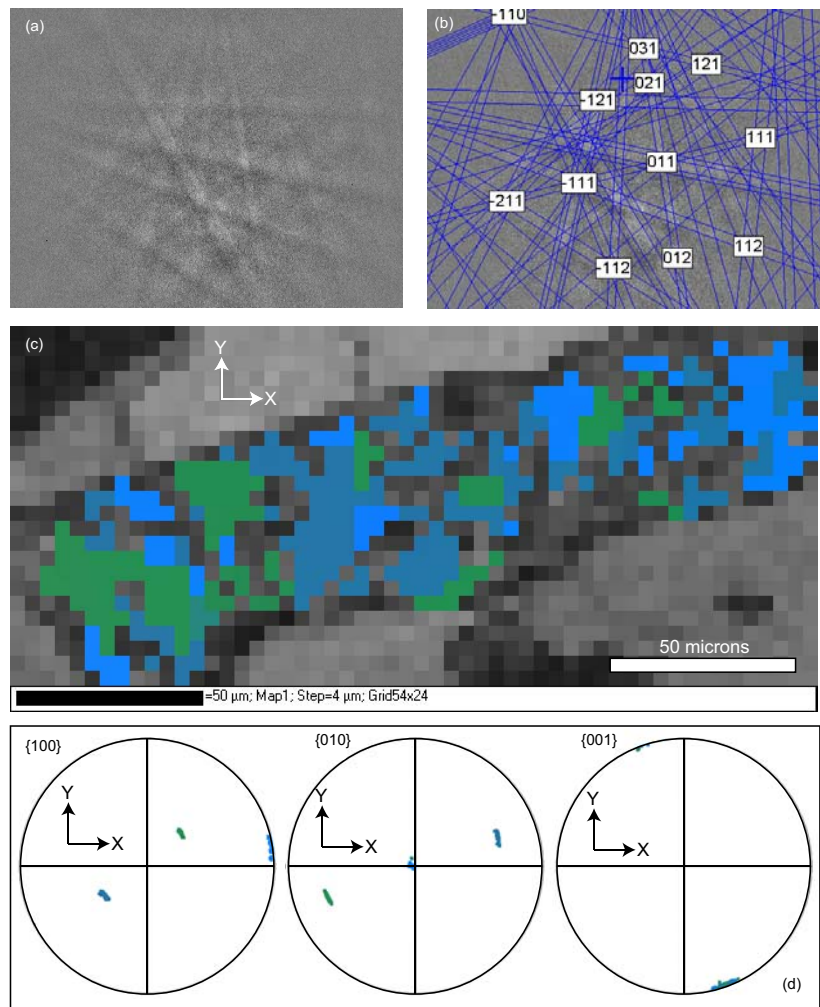


Figure 4:

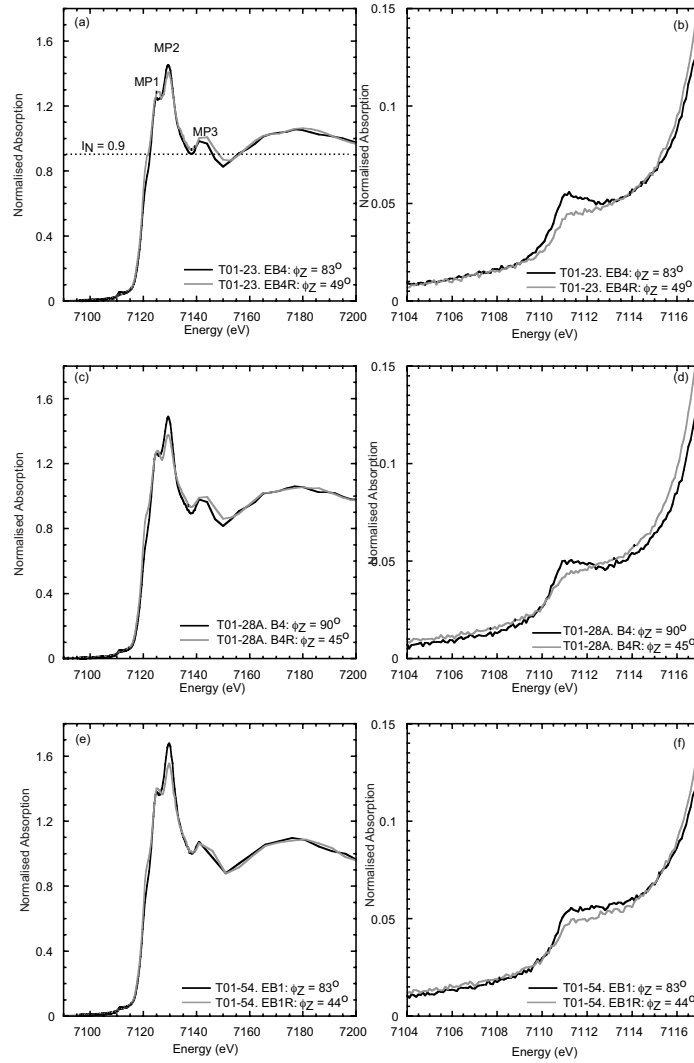


Figure 5:

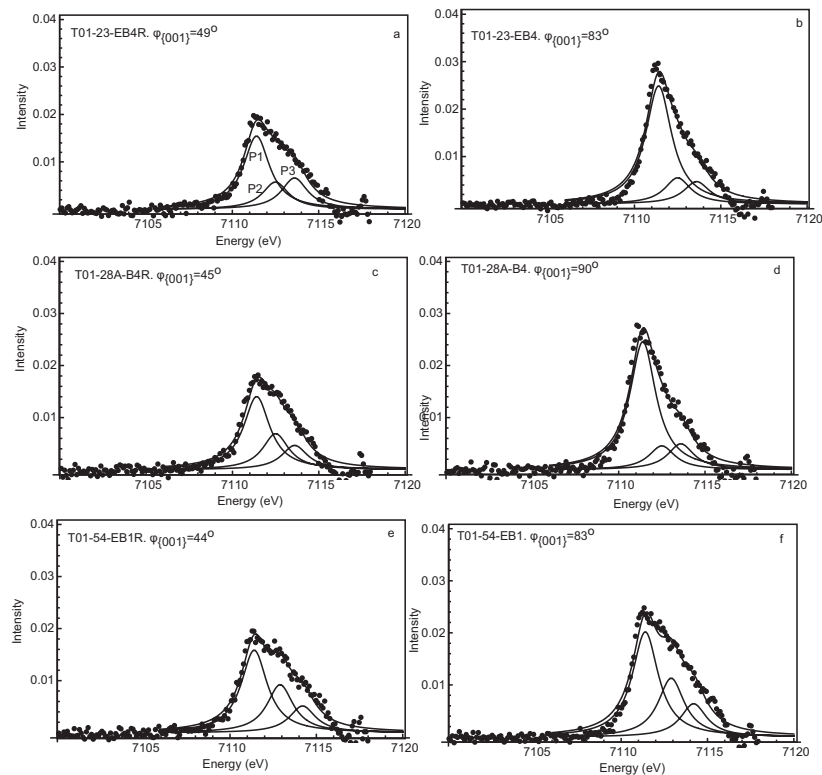


Figure 6:



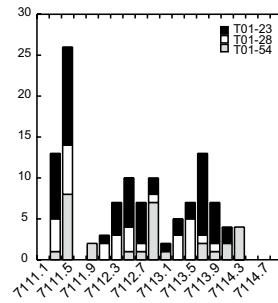


Figure 7:

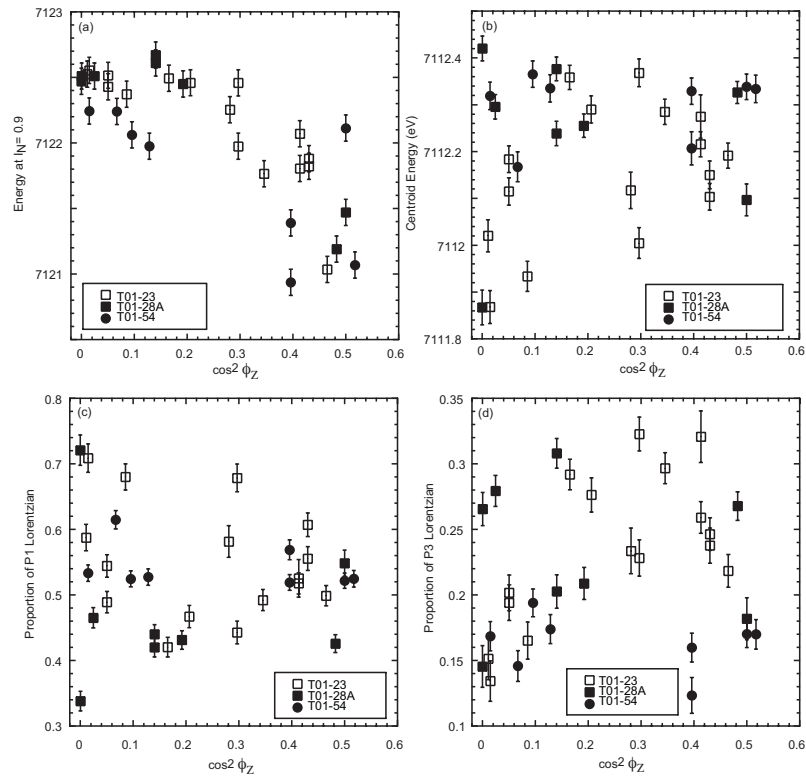


Figure 8:

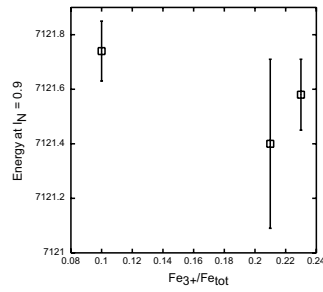


Figure 9:

## Tables

Table 1: T01-23 biotite composition data

wt% ox	EB1	$\sigma$	EB3	$\sigma$	EB4	$\sigma$	EB5	$\sigma$
SiO <sub>2</sub>	35.84	0.30	36.13	0.16	35.65	0.35	36.22	0.55
TiO <sub>2</sub>	2.61	0.03	2.54	0.01	2.66	0.03	2.81	0.02
Al <sub>2</sub> O <sub>3</sub>	16.40	0.19	15.70	0.03	15.83	0.09	15.95	0.02
Cr <sub>2</sub> O <sub>3</sub>	0.02	0.01	0.01	0.00	0.03	0.01	0.02	0.01
FeO	20.26	0.21	20.86	0.26	21.25	0.46	21.17	0.10
MnO	0.20	0.01	0.22	0.02	0.23	0.01	0.23	0.00
MgO	9.40	0.21	9.54	0.07	9.58	0.20	9.55	0.06
Na <sub>2</sub> O	0.02	0.02	0.02	0.01	0.03	0.02	0.06	0.03
K <sub>2</sub> O	6.87	0.87	9.16	0.10	9.14	0.11	9.04	0.15
Cl	0.51	0.02	0.49	0.01	0.51	0.01	0.49	0.01
F	0.14	0.12	0.13	0.20	0.14	0.07	0.12	0.06
H <sub>2</sub> O	7.55	0.05	3.74	0.01	3.73	0.01	3.74	0.01
Total	99.82		98.54		98.78		99.40	
X(Mg)	0.45		0.45		0.45		0.45	
Fe <sup>3+</sup> /Fe <sub>tot</sub>	0.07		0.00		0.00		0.00	
Si	2.802		2.807		2.772		2.789	
Ti	0.153		0.148		0.156		0.163	
Al	1.511		1.438		1.452		1.448	
Cr	0.001		0.001		0.002		0.001	
Fe(III)	0.09		0		0		0	
Fe(II)	1.235		1.356		1.382		1.363	
Mn	0.013		0.014		0.015		0.015	
Mg	1.095		1.105		1.11		1.096	
Na	0.003		0.003		0.005		0.009	
K	0.685		0.908		0.907		0.888	
totals	7.589		7.781		7.802		7.773	

$\sigma$  is the standard deviation on 3 – 5 measured points on each grain

Table 2: T01-28A biotite composition data

	B2	$\sigma$	B3	$\sigma$	B4	$\sigma$	B5	$\sigma$	B6	$\sigma$
SiO <sub>2</sub>	36.31	0.26	36.68	0.11	36.92	0.16	36.57	0.14	36.15	0.35
TiO <sub>2</sub>	2.81	0.08	2.86	0.03	2.76	0.03	2.89	0.04	2.39	0.05
Al <sub>2</sub> O <sub>3</sub>	15.51	0.14	15.48	0.07	15.57	0.20	15.29	0.03	15.37	0.15
Cr <sub>2</sub> O <sub>3</sub>	0.06	0.01	0.04	0.01	0.05	0.01	0.06	0.02	0.01	0.01
FeO	21.08	0.39	21.36	0.22	21.53	0.10	21.67	0.36	20.99	0.12
MnO	0.22	0.03	0.25	0.01	0.25	0.03	0.25	0.01	0.24	0.01
MgO	10.48	0.07	10.36	0.16	10.47	0.03	10.17	0.07	10.65	0.08
Na <sub>2</sub> O	0.03	0.01	0.05	0.02	0.03	0.00	0.03	0.02	0.04	0.01
K <sub>2</sub> O	8.78	0.22	7.64	0.10	8.95	0.28	9.12	0.37	8.48	0.16
Cl	0.25	0.02	0.24	0.00	0.25	0.01	0.24	0.01	0.25	0.02
F	0.10	0.08	0.18	0.04	0.17	0.08	0.09	0.11	0.26	0.12
H <sub>2</sub> O	3.76	0.01	3.78	0.01	3.75	0.01	3.74	0.02	3.75	0.01
Total	99.39		98.93		100.70		100.12		98.58	
X(Mg)	0.47		0.47		0.47		0.46		0.48	
Fe <sup>3+</sup> /Fe <sub>tot</sub>	0.04		0.11		0.03		0.00		0.10	
Si	2.778		2.793		2.793		2.794		2.781	
Ti	0.161		0.164		0.157		0.166		0.138	
Al	1.399		1.39		1.389		1.377		1.394	
Cr	0.004		0.003		0.003		0.004		0.001	
Fe(III)	0.057		0.145		0.04		0.006		0.129	
Fe(II)	1.291		1.215		1.322		1.378		1.221	
Mn	0.015		0.016		0.016		0.016		0.016	
Mg	1.195		1.175		1.181		1.158		1.22	
Na	0.004		0.007		0.005		0.004		0.006	
K	0.857		0.743		0.864		0.889		0.832	
totals	7.762		7.651		7.77		7.794		7.739	

$\sigma$  is the standard deviation on 3 – 5 measured points on each grain, except B6 which has only two good analyses

Table 3: T01-54 biotite composition data

	B1	$\sigma$	B2	$\sigma$	B4	$\sigma$	B5	$\sigma$	B6	$\sigma$	B7	$\sigma$	B8	$\sigma$
SiO <sub>2</sub>	36.29	0.08	36.29	0.29	37.24	0.29	37.16	0.30	36.74	0.16	37.05	0.21	36.75	0.28
TiO <sub>2</sub>	3.96	0.05	3.97	0.05	3.96	0.20	3.98	0.05	4.19	0.09	3.94	0.08	3.93	0.06
Al <sub>2</sub> O <sub>3</sub>	14.84	0.07	14.79	0.10	15.42	0.62	15.01	0.08	15.25	0.18	14.71	0.06	14.76	0.07
Cr <sub>2</sub> O <sub>3</sub>	0.06	0.02	0.07	0.01	0.07	0.01	0.08	0.01	0.07	0.02	0.06	0.03	0.06	0.02
FeO	17.87	0.15	18.25	0.55	18.12	0.47	17.76	0.16	17.76	0.29	18.48	0.45	18.39	0.66
MnO	0.05	0.01	0.03	0.01	0.01	0.01	0.03	0.01	0.02	0.01	0.05	0.02	0.04	0.02
MgO	12.71	0.07	12.78	0.08	11.90	0.92	12.57	0.05	12.39	0.19	12.58	0.04	12.60	0.04
Na <sub>2</sub> O	0.03	0.01	0.04	0.01	0.04	0.02	0.04	0.01	0.03	0.02	0.03	0.03	0.03	0.01
K <sub>2</sub> O	8.59	0.15	8.72	0.22	8.67	0.34	8.87	0.48	8.74	0.11	8.79	0.25	8.94	0.14
Cl	0.49	0.02	0.48	0.01	0.50	0.02	0.47	0.02	0.48	0.02	0.47	0.01	0.47	0.01
F	0.38	0.11	0.43	0.11	0.26	0.11	0.37	0.07	0.41	0.12	0.34	0.16	0.36	0.04
H <sub>2</sub> O	3.79	0.01	3.77	0.01	3.80	0.01	3.79	0.01	3.79	0.01	3.78	0.01	3.77	0.01
Total	99.05		99.63		100.00		100.13		99.88		100.27		100.10	
X(Mg)	0.56		0.56		0.54		0.56		0.56		0.55		0.55	
Fe <sup>3+</sup> /Fe <sub>tot</sub>	0.05		0.07		0.00		0.00		0.00		0.01		0.02	
Si	2.76		2.749		2.801		2.795		2.772		2.79		2.776	
Ti	0.227		0.226		0.224		0.225		0.238		0.223		0.223	
Al	1.33		1.32		1.367		1.331		1.357		1.306		1.315	
Cr	0.003		0.004		0.004		0.005		0.004		0.004		0.004	
Fe(III)	0.056		0.078		0		0		0		0.016		0.018	
Fe(II)	1.08		1.078		1.14		1.117		1.121		1.147		1.144	
Mn	0.003		0.002		0.001		0.002		0.001		0.003		0.003	
Mg	1.44		1.443		1.333		1.409		1.394		1.411		1.418	
Na	0.004		0.005		0.006		0.005		0.005		0.005		0.004	
K	0.833		0.843		0.832		0.851		0.841		0.844		0.861	
totals	7.738		7.749		7.708		7.741		7.733		7.75		7.766	

$\sigma$  is the standard deviation on 3 – 5 measured points on each grain

Table 4: Mössbauer data

		T01-23	T01-28A	T01-54
Fe <sup>2+</sup> in biotite	$\delta$			1.13
	$\Delta$			2.34
	$\Gamma$			0.24
	area			36
Fe <sup>2+</sup> in biotite	$\delta$	1.13	1.13	1.13
	$\Delta$	2.6	2.61	2.63
	$\Gamma$	0.24	0.24	0.24
	area	58	60	20
Fe <sup>2+</sup> in biotite	$\delta$	1.15	1.07	1.12
	$\Delta$	1.98	2.09	1.97
	$\Gamma$	0.38	0.35	0.4
	area	13	15	23
Fe <sup>3+</sup> in biotite	$\delta$	0.43	0.45	0.48
	$\Delta$	0.56	0.57	0.58
	$\Gamma$	0.3	0.41	0.34
	area	6	20	21
Fe <sup>2+</sup> in biotite	$\delta$	0.4	0.42	
	$\Delta$	1.14	1.22	
	$\Gamma$	0.37	0.3	
	area	4	3	
Center 2 peaks from Fe <sup>3+</sup> oxide	$\delta$	0.35	0.35	
	$\Delta$	2.04	2.08	
	$\Gamma$	0.24	0.24	
	area	19	3	
	$\chi^2$	0.99	0.85	1.15
%Fe <sup>3+</sup> in biotite		10	23	21
$\sigma$ %Fe <sup>3+</sup> in biotite		2	2	2



Table 5: Orientation and XANES parameters for T01-23

Grain	E (eV) @I <sub>N</sub> =0.9	φ <sub>z</sub>	Area			σ			centroid (eV)	σ centroid	Fe <sup>3+</sup> / Fe <sub>tot</sub> mol %	σ			Fe <sup>3+</sup> / Fe <sub>tot</sub>
			P1	P2	P3	P1	P2	P3				P1	P2	P3	
T01-23-EB9r	7121.04	47	0.061	0.034	0.027	0.002	0.002	0.002	7112.19	0.03	14.6	0.50	0.28	0.22	1.5
T01-23-EB4r	7121.82	49	0.063	0.023	0.027	0.002	0.003	0.002	7112.15	0.03	12.6	0.56	0.21	0.24	1.5
T01-23-EB5r	7121.88	49	0.073	0.018	0.030	0.002	0.003	0.002	7112.10	0.03	10.3	0.61	0.15	0.25	1.4
T01-23-EB10r	7121.80	50	0.068	0.029	0.034	0.002	0.003	0.002	7112.22	0.03	15.8	0.52	0.22	0.26	1.3
T01-23-EB8r	7122.07	50	0.057	0.017	0.035	0.003	0.004	0.003	7112.27	0.05	18.7	0.53	0.15	0.32	2.3
T01-23-EB1r	7121.76	54	0.063	0.027	0.038	0.002	0.003	0.002	7112.28	0.03	19.2	0.49	0.21	0.30	1.3
T01-23-EB1	7122.46	57	0.050	0.026	0.036	0.002	0.003	0.002	7112.37	0.03	23.3	0.44	0.23	0.32	1.5
T01-23-EB3r	7121.97	57	0.089	0.012	0.030	0.002	0.003	0.002	7112.00	0.03	5.4	0.68	0.09	0.23	1.6
T01-23-EB2r	7122.25	58	0.068	0.022	0.027	0.003	0.004	0.003	7112.12	0.04	11.0	0.58	0.18	0.23	1.9
T01-23-EB2	7122.46	63	0.058	0.032	0.034	0.002	0.003	0.002	7112.29	0.03	19.5	0.47	0.26	0.28	1.4
T01-23-EB3	7122.49	66	0.066	0.045	0.046	0.003	0.003	0.003	7112.36	0.03	22.9	0.42	0.29	0.29	1.3
T01-23-EB9	7122.37	73	0.102	0.023	0.025	0.003	0.003	0.003	7111.93	0.03	1.9	0.68	0.15	0.17	1.6
T01-23-EB10	7122.43	77	0.081	0.039	0.029	0.002	0.003	0.002	7112.11	0.03	10.8	0.54	0.26	0.19	1.4
T01-23-EB5	7122.52	77	0.074	0.047	0.030	0.003	0.003	0.003	7112.18	0.03	14.2	0.49	0.31	0.20	1.4
T01-23-EB4	7122.55	83	0.102	0.022	0.019	0.003	0.003	0.003	7111.87	0.04	-1.3	0.71	0.16	0.13	1.7
T01-23-EB8	7122.52	84	0.082	0.036	0.021	0.003	0.004	0.003	7112.02	0.03	6.2	0.59	0.26	0.15	1.7
Average			0.072	0.028	0.030				7112.15		12.8	0.55	0.21	0.24	
1σ			0.015	0.010	0.007			0.15			7.2	0.09	0.06	0.06	

Table 6: Orientation and XANES parameters for T01-28A

Grain	E (eV) @I <sub>N</sub> =0.9	φz	Area			σ			centroid (eV)	σ centroid	Fe <sup>3+</sup> / Fe <sub>tot</sub> mol %	Prop			σ Fe <sup>3+</sup> / Fe <sub>tot</sub>	
			P1	P2	P3	P1	P2	P3				P1	P2	P3		
T01-28A-B4r	7121.47	45	0.057	0.028	0.019	0.002	0.002	0.003	0.002	7112.10	0.03	9.9	0.55	0.27	0.18	1.7
T01-28A-B3	7121.19	46	0.064	0.046	0.041	0.002	0.002	0.003	0.002	7112.33	0.02	21.3	0.43	0.31	0.27	1.2
T01-28A-B5	7122.45	64	0.068	0.056	0.033	0.002	0.002	0.003	0.002	7112.26	0.03	17.8	0.43	0.36	0.21	1.2
T01-28A-B5r	7122.61	68	0.060	0.038	0.044	0.002	0.002	0.003	0.002	7112.38	0.03	23.8	0.42	0.27	0.31	1.3
T01-28A-B6	7122.67	68	0.065	0.053	0.030	0.002	0.002	0.003	0.002	7112.24	0.03	17.0	0.44	0.36	0.20	1.3
T01-28A-B6r	7122.51	81	0.057	0.031	0.034	0.002	0.002	0.003	0.002	7112.30	0.03	19.8	0.47	0.26	0.28	1.3
T01-28A-B3r	7122.51	89	0.047	0.055	0.037	0.002	0.002	0.003	0.002	7112.42	0.03	25.9	0.34	0.40	0.27	1.3
T01-28A-B4	7122.47	90	0.100	0.019	0.020	0.003	0.003	0.003	0.003	7111.87	0.04	-1.4	0.72	0.13	0.15	1.8
Average			0.065	0.041	0.032					7112.23		16.7	0.47	0.29	0.23	
1σ			0.016	0.014	0.009					0.18		8.8	0.12	0.08	0.06	

Table 7: Orientation and XANES parameters for T01-54

Grain	E (eV) @I <sub>N</sub> =0.9	φz	Area			σ			centroid (eV)	σ centroid	Fe <sup>3+</sup> / Fe <sub>tot</sub> mol %	Prop			σ Fe <sup>3+</sup> / Fe <sub>tot</sub>	Prop		
			P1	P2	P3	P1	P2	P3				P1	P2	P3		P1	P2	P3
T01-54-EB1r	7121.07	44	0.065	0.038	0.021	0.002	0.002	0.002	7112.33	0.03	21.6	1.5	0.52	0.31	0.17	0.52	0.31	0.17
T01-54-EB5	7122.11	45	0.079	0.047	0.026	0.002	0.002	0.002	7112.34	0.03	21.9	1.3	0.52	0.31	0.17	0.52	0.31	0.17
T01-54-EB2r	7120.94	51	0.069	0.037	0.015	0.002	0.002	0.002	7112.21	0.04	15.4	1.8	0.57	0.31	0.12	0.57	0.31	0.12
T01-54-EB6r	7121.39	51	0.070	0.043	0.022	0.002	0.002	0.002	7112.33	0.03	21.4	1.4	0.52	0.32	0.16	0.52	0.32	0.16
T01-54-EB6	7121.98	69	0.077	0.044	0.025	0.002	0.002	0.002	7112.34	0.03	21.7	1.4	0.53	0.30	0.17	0.53	0.30	0.17
T01-54-EB5r	7122.06	72	0.083	0.045	0.031	0.002	0.002	0.002	7112.37	0.03	23.2	1.4	0.52	0.28	0.19	0.52	0.28	0.19
T01-54-EB2	7122.24	75	0.087	0.034	0.021	0.002	0.002	0.002	7112.17	0.03	13.4	1.6	0.61	0.24	0.15	0.61	0.24	0.15
T01-54-EB1	7122.24	83	0.082	0.046	0.026	0.002	0.002	0.002	7112.32	0.03	20.9	1.4	0.53	0.30	0.17	0.53	0.30	0.17
Average			0.076	0.042	0.023				7112.30		20.0		0.54	0.29	0.16	0.54	0.29	0.16
1σ			0.008	0.005	0.005			0.07			3.5		0.03	0.03	0.03	0.03	0.03	0.02

Table 8: Correlation information.

	T01-23		T01-28A		T01-54	
	$I_N=0.9$	$\cos^2\phi_{\{Z\}}$	$I_N=0.9$	$\cos^2\phi_{\{Z\}}$	$I_N=0.9$	$\cos^2\phi_{\{Z\}}$
$\cos^2\phi_{\{Z\}}$	Pearson Correlation Coefficient	-0.844	n.a.	-0.918	n.a.	-0.681
	p-value	0.00004	n.a.	0.001	n.a.	0.063
Area (P1)	Pearson Correlation Coefficient	0.369	-0.624	0.085	-0.197	0.915
	p-value	0.160	0.010	0.841	0.640	0.001
Area (P2)	Pearson Correlation Coefficient	0.279	-0.467	0.094	0.013	0.482
	p-value	0.296	0.068	0.824	0.976	0.226
Area (P3)	Pearson Correlation Coefficient	-0.037	0.312	0.128	-0.091	0.761
	p-value	0.893	0.239	0.763	0.830	0.028
Centroid	Pearson Correlation Coefficient	-0.176	0.434	0.081	0.005	0.191
	p-value	0.515	0.093	0.849	0.990	0.650
Total Area	Pearson Correlation Coefficient	0.526	-0.781	0.225	-0.220	0.932
	p-value	0.036	0.0004	0.592	0.600	0.001
Proportion (P1)	Pearson Correlation Coefficient	0.100	-0.247	-0.065	-0.039	0.020
	p-value	0.713	0.357	0.879	0.926	0.962
Proportion (P2)	Pearson Correlation Coefficient	0.101	-0.247	0.022	0.100	-0.477
	p-value	0.711	0.356	0.958	0.814	0.232
Proportion (P3)	Pearson Correlation Coefficient	-0.257	0.632	0.100	-0.066	0.536
	p-value	0.337	0.009	0.813	0.877	0.171
						0.593

Table 9: Orientation correction function information

	T01-23	T01-28	T01-54
$m(I_N = 0.9)$	-2.25	-2.52	-1.91
$\sigma_{m(I_N=0.9)}$	0.38	0.45	0.84
$c(I_N = 0.9)$	7122.87	7122.85	7122.35
$\sigma_{c(I_N=0.9)}$	0.11	0.12	0.27
$I_N = 0.9 @ 45^\circ$	7121.74	7121.58	7121.40
$\sigma_{I_N=0.9 @ 45^\circ}$	0.11	0.13	0.31