1 # Use of Multivariate Analysis for Synchrotron Micro-XANES Analysis of Iron

2 # Valence State in Amphiboles

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## ABSTRACT

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27    Microanalysis of $Fe^{3+}/\Sigma Fe$ in geological samples using synchrotron-based X-ray

28    absorption spectroscopy has become routine since the introduction of standards and model

29    compounds. Existing calibrations commonly use least squares linear combinations of pre-edge

30    and edge data from standard reference spectra with known coordination number and valence

31    state acquired on powdered samples to avoid preferred orientation. However, application of these

32    methods to single mineral grains is appropriate only for isometric minerals and limits their

33    application to analysis of *in situ* grains in thin sections. In this work, a calibration suite

34    developed by acquiring X-ray absorption near-edge spectroscopy (XANES) data from amphibole

35    single crystals with the beam polarized along the major optical directions (X, Y, and Z) is

36    employed. Seven different methods for predicting %$Fe^{3+}$ were employed based on 1) area-

37    normalized pre-edge peak centroid, 2) the energy of the main absorption edge at the location

38    where the normalized edge intensity has the highest $R^2$ correlation with $Fe^{3+}/\Sigma Fe$, 3) the ratio of

39    spectral intensities at two energies determined by highest $R^2$ correlation with $Fe^{3+}/\Sigma Fe$, 4) use of

40    the slope (first derivative) at every channel to select the best predictor channel, 5,6) partial least-

41    squares models with variable and constant numbers of components, and 7) least absolute

42    shrinkage and selection operator models. The latter three sophisticated multivariate analysis

43    techniques for predicting $Fe^{3+}/\Sigma Fe$ show significant improvements in accuracy over the former

44    four types of univariate models. $Fe^{3+}/\Sigma Fe$ can be measured in randomly-oriented amphibole

45    single crystals with an accuracy of ±5.5-6.2% absolute. Multivariate approaches demonstrate that

46    for amphiboles main edge and EXAFS regions contain important features for predicting valence

47    state. This suggests that in this mineral group, local structural changes accommodating site

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48    occupancy by $Fe^{3+}$ vs. $Fe^{2+}$ have a pronounced (and diagnostic) effect on the XAS spectra that

49    can be reliably used to precisely constrain $Fe^{3+}/\Sigma Fe$.

## INTRODUCTION

A growing worldwide community of synchrotron users is pursuing studies of the redox state of iron at microscales within minerals and glasses using Fe K-edge X-ray absorption near-edge structure (XANES) spectroscopy. For these materials, there is a general consensus that calibrations based on the intensity and energy of the Fe K-edge pre-edge signal, which is composed of contributions from Fe cations in different valence states and coordination polyhedra, provides a fairly representative measure of Fe valence state. The area-weighted average peak centroid energy of the pre-edge multiplets has been shown to be representative of contributions from the composite transitions, as first pioneered by Bajt et al. (1994). Subsequently it was recognized that the intensity of the pre-edge signal is also a function of site distortion and coordination, so Galoisy et al. (2001) utilized pseudo-Voigt line shapes of minerals with known coordination geometries to deconvolute XANES pre-edge spectra into component peaks, e.g., andradite spectra are used for $^{[6]}Fe^{3+}$, augite glass for $^{[4,5]}Fe^{2+}$, berlinite for $^{[4]}Fe^{3+}$, staurolite for $^{[4]}Fe^{2+}$, and siderite for $^{[6]}Fe^{2+}$. This work was generalized by Wilke et al. (2001) and Petit et al. (2001), who characterized and fit 30 minerals and synthetic compounds to correlate energy and intensity of pre-edge features with oxidation state and local coordination environments. The Wilke et al. (2001) calibration has been used often to predict $Fe^{3+}$ and $Fe^{2+}$ contents in geological materials, but it is inherently limited by its requisite use on powders and the known differences in site geometry between their reference materials and the unknown minerals.

For petrologic applications, the true "Holy Grail" for microanalysis of $Fe^{3+}/\Sigma Fe$ is *in situ* microanalysis of individual minerals grains in thin sections which preserves the petrological relationship between mineral grains in the section, an endeavor complicated by anisotropy of

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73    most common rock-forming minerals. To test the effects of orientation, Dyar et al. (2002a,b)

74    aligned the vibration direction of the polarized synchrotron beam along the major optical

75    directions (X, Y, and Z) of single crystals of biopyriboles, olivine, scapolite, and feldspar. Their

76    results show significant variation over the entire XANES energy range (pre-edge and main-edge)

77    that propagates 10-20% absolute errors on measurements of %$Fe^{3+}$ using pre-edge-based

78    techniques for quantification. It is apparent from this work and that of others (Dräger et al. 1988,

79    Scordari et al. 2010, Mino et al. 2014, Evans et al. 2014) that useful predictions of $Fe^{3+}/\Sigma Fe$ in

80    single crystals must consider the full range of possible optical orientations in order to encompass

81    all possible electronic transitions in each mineral of interest. This process should be

82    fundamentally analogous to determinations of species abundances based on spectral features in

83    the visible and infrared wavelengths.

84          In this paper, we focus on the amphibole mineral group, which has a range of four

85    possible [6] or [6+2] coordinated polyhedra that can be occupied by $Fe^{3+}$ and $Fe^{2+}$. We use a

86    suite of samples characterized both chemically and by single-crystal X-ray diffraction to relate

87    peak energies and intensities directly to the geometry of the $M(1)$-$M(4)$ sites. We use spectra

88    acquired with the crystals oriented such that the polarization direction of the synchrotron beam is

89    parallel to their X, Y, and Z optical orientation directions, choosing samples that cover a range of

90    composition and extremes of $Fe^{3+}/\Sigma Fe$, enabled in part by thermal heating and resultant

91    oxidation of a subset of samples. We extract the pre-edge region of the XANES spectra to fit

92    component peaks representing contributions from both $Fe^{2+}$ and $Fe^{3+}$ in this region, and compare

93    those peaks to known $Fe^{3+}/\Sigma Fe$ from bulk methods. We also examine $R^2$ correlation of three

94    derived spectral features (normalized intensity in the main edge, intensity ratios, and slope) with

95    $Fe^{3+}/\Sigma Fe$ to select the channels best used for univariate prediction of $Fe^{3+}/\Sigma Fe$. Finally, we use

96 multivariate analysis techniques and the spectra from the entire XANES region to predict

97 $Fe^{3+}/\Sigma Fe$, providing a dramatic improvement over the accuracy of univariate methods. This work

98 establishes a protocol for XANES analysis of other anisotropic mineral groups, and lays the

99 groundwork for producing precise and accurate routine XANES analyses of $Fe^{3+}/\Sigma Fe$ in

100 randomly-oriented grains in thin sections using partial least squares (PLS) and least absolute

101 shrinkage and selection operator (lasso) regression.

<div align="center">

**BACKGROUND**

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103   Bajt et al. (1994) were the first to suggest that a calibration curve for quantitative

104 prediction of $Fe^{3+}/\Sigma Fe$ in minerals could be established using the area-weighted centroid energy

105 of the composite pre-edge in three standards: olivine (0% $Fe^{3+}$), magnetite (67% $Fe^{3+}$), and

106 hematite (100% $Fe^{3+}$). Delaney et al. (1998) soon thereafter pointed out that olivine, pyroxene,

107 amphibole, mica, and tourmaline groups each required independent calibration curves due to the

108 differences in coordination polyhedra among them. Galoisy et al. (2001), Wilke et al. (2001), and

109 Petit et al. (2001) chose a different, more generalized approach using representative minerals

110 from several different groups as model compounds for $Fe^{2+}$ and $Fe^{3+}$ in a variety of site

111 geometries and coordination polyhedra. Wilke et al. (2001) noted that the area-weighted

112 composite pre-edge position varies non-linearly with oxidation state. Their results show a

113 calibration curve similar to that of Bajt et al. (1994) though customized to distinguish between

114 $^{[4]}Fe^{2+}$, $^{[6]}Fe^{2+}$, $^{[4]}Fe^{3+}$, and $^{[6]}Fe^{3+}$. Many hundreds of workers (e.g., Giuli et al. 2003, 2005,

115 Schmid et al. 2003, Grossemy et al. 2007, Beck et al. 2012, Bonadiman et al. 2014, Debret et al.

116 2014) have subsequently used the generalized Figure 6 from the Wilke et al. (2001) paper to

117 determine redox ratios in a variety of silicate minerals and glasses.

118     However, there are issues with such a generalized technique, acknowledged by Wilke et

119     al. (2001) to have ±10% (absolute) errors on $Fe^{3+}/\Sigma Fe$. It applies only to finely ground powders

120     that are effectively isotropic with no preferred orientation. Deviations from their calibration are

121     attributed to the method for numerically extracting the pre-edge from the main edge, and to

122     differences in site geometry between their references and the unknown minerals. Because the $1s$

123     $\rightarrow 3d$ transition is also sensitive to $3d + 4p$ orbital mixing, the intensity of the pre-edge peaks

124     (and thus their calculated areas) is sensitive to site geometry. Pre-edge peak intensities will

125     increase progressively with site distortion from centrosymmetric. The calibration lines are not

126     necessarily linear (Delaney et al., 1996). Wilke et al. (2001) weight the calibration line toward

127     whichever Fe atom is in a more distorted site, and use exclusively the pre-edge region, ignoring

128     potentially significant features associated with the rising-edge and white line ($1s \rightarrow 4s$ and $1s \rightarrow$

129     $4p$ transitions) and Extended X-ray Absorption Fine Structure (EXAFS) regions ($1s$ to

130     continuum) of the spectra. Mixtures of Fe in different sites tend to average out in the Wilke

131     method (Forder et al. 2009) making some solutions non-unique.

132     The intervening decade since this work was done has seen the widespread introduction of

133     high-resolution monochromators that offer the capability to better resolve within the Fe K edge

134     spectra the individual features associated with each type of coordination polyhedron and valence

135     state. An area-weighted approach like that of Wilke et al. (2001) is sensitive to differences in

136     energy resolution of the beamlines used, the particular fitting model used to fit each multiplet

137     peak in the pre-edge and the choice of baseline fit beneath the peaks. All impact the relative area

138     of measured peaks and thus leads to small inconsistencies in calculated area-weighted centroids

139     between research groups and facilities, particularly for highly oxidized or reduced species where

140  the tail of the main edge absorption feature can be difficult to deconvolute accurately. There is a

141  need for alternative approaches.

142  Although the XANES technique works well for isotropic and powdered materials

143  generally irrespective of orientation during analysis, in anisotropic minerals the high degree of

144  linear polarization of the X-ray beam within the orbital plane of the synchrotron storage ring

145  results in variations in XANES spectral intensities as a consequence of X-ray pleochroism. One

146  of the original papers to address this was Dräger et al. (1988), who used thin plates cut from

147  oriented single crystals. They confirmed that isometric samples show identical spectra when the

148  polarization direction is either parallel or perpendicular to an oriented crystal. They observed a

149  conspicuous angular dependence of pre-edge absorption in the anisotropic (hexagonal) minerals

150  hematite and siderite. In hematite, for example, the intensity of a pre-edge peak at 7114 eV is

151  twice as intense with the beam polarization parallel to (001) than it is perpendicular to (001).

152  Delaney et al. (2001), Dyar et al. (2002a,b), Scordari et al. (2010) and Mino et al. (2014)

153  observed similar phenomenon in other oriented mineral samples.

154  Subsequent studies documented the differential interactions of the linearly polarized X-

155  ray beam with anisotropic crystals. Orientation effects were first recognized and extensively

156  characterized in sheet silicates (Manceau et al. 1998, Giuli et al. 2001, Dyar et al. 2001, Mino et

157  al. 2014, Evans et al. 2014). For example, Munoz et al. (2013) applied the magic angle geometry

158  for measurement of Fe-K XANES and pre-edges of phyllosilicates. The "magic tilt angle" for

159  incident X-rays is the angle at which orientation dependent terms vanish from resonant intensity

160  terms (Pettifer et al. 1990, Stöhr 1992). It theoretically reflects the relatively high rotational

161  symmetry of the mica lattice in the basal plane, and provides a fundamental starting point for the

162  determination of the magnitude of angle dependent intensity for oriented slices such as those in

163  thin section (Brouder 1990). However, no magic angle spectra acquired at a constant

164  crystallographic orientation can represent all potential electronic transitions at all

165  crystallographic orientations.

166       The only way to ensure that all possible transitions are represented in crystalline

167  standards is to acquire XANES spectra with the vibration direction of the synchrotron beam

168  parallel to the known optical orientations of each single crystal. We use optical (rather than

169  crystallographic) orientations for two reasons: 1) this is the historical convention for acquisition

170  of visible and infrared spectra, and 2) future users of our techniques could use observable optical

171  directions in a thin section to aid in data collection. We note, however, that in future studies we

172  plan to collect data along both the optical, as well as crystallographic directions when they differ,

173  as occurs for monoclinic amphiboles.

174       The measurements are extremely challenging because they require that crystals be

175  mounted on fibers in goniometer heads and be oriented either through X-ray diffraction or

176  spindle stage microscopy to determine the proper orientations of the crystals on the X-ray

177  absorption (XAS) beamlines. For this reason, there are only a handful of data where spectra were

178  truly acquired along the optical directions X, Y, and Z. Dyar et al. (2002a,b) studied oriented

179  crystals of orthopyroxene (opx), clinopyroxene (cpx), amphibole, biotite, and muscovite. Spectra

180  acquired along the length of the chains (*c* for px, *c* for amph, and *a* for sheet silicates) are similar,

181  with corresponding changes in the optical directions, such that $Y_{musc} \approx Z_{bt} \approx Z_{amph} \approx Z_{opx} \approx$

182  $X_{aegirine}$ (cpx is intermediate). Spectra taken along the *b* crystallographic axes (along the

183  octahedral layer, across the I-beam) are similar for all groups ($Z_{musc} \approx Y_{bt} \approx Y_{amph} \approx X_{opx} \approx Y_{cpx}$),

184  and more similar for the amphiboles and micas. Finally, spectra acquired along the stacking

185  direction, which is the *a* crystallographic direction for pyroxene and amphiboles and the *c*

186    crystallographic direction in sheet silicates, are analogous. From these relationships, and from

187    hints of fundamental peaks within the pre-edge envelopes, it became clear that higher resolution

188    data on pre-edge spectra of oriented samples could potentially elucidate transitions specific to

189    different optical orientations, with energies that can be related to their crystal structures.

190    Moreover, this work demonstrated quantitatively that the effect of orientation on calculated

191    $Fe^{3+}/\Sigma Fe$ generates $\pm$10-20% errors in randomly-oriented crystals using the position of the area-

192    weighted centroid of the pre-edge peaks.

193         The sensitivity of Fe K pre-edges region to valence state reflects the sensitivity of these

194    electronic transitions to valence states of the excited atom. However, other parts of the XANES

195    and EXAFS regions of the absorption spectra also reflect changes that arise from permutations to

196    the local structure around the Fe cations due to the difference in size and charge between $Fe^{2+}$

197    and $Fe^{3+}$ (Marcus et al. 2008), though the magnitude of such changes will be highly dependent

198    on the specific phase and structure. It stands to reason that an alternative and perhaps more

199    sensitive method for predicting valence state from XAS of any material would be one that

200    utilizes information not only in the pre-edge region, but also extending into the EXAFS energies.

201         For example, Berry et al. (2010) suggest several empirical alternative approaches to

202    calibration of garnet XANES spectra. They report that the average centroid energy of garnet pre-

203    edges is relatively insensitive to $Fe^{3+}/\Sigma Fe$, and propose two alternative methods of prediction.

204    The first is to use the absorption edge energy at an arbitrary normalized intensity value of 0.9,

205    though a small offset in the resultant calibration plot is caused by varying size and geometry of

206    the average coordination polyhedra (which are a function of composition) and may diminish its

207    effectiveness. As an alternative, Berry et al. (2010) used information in the main-edge XANES

208    and near-EXAFS regions of their spectra to demonstrate that the ratio of spectral intensities at

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209   7138.4 and 7161.7 eV was an accurate predictor of $Fe^{3+}/\Sigma Fe$ in mantle garnets. This technique

210   shows great promise, but its choice of which channels to use in predictions is somewhat *ad hoc*

211   and subjective. Moreover, it relies on prior knowledge based on wet chemical or Mossbauer

212   analysis on a painstakingly acquired or synthesized set of matrix-matched mineral standards.

213         Dyar et al. (2012) instead used a multivariate analysis method (partial least squares

214   regression, or PLS) to examine use of full XANES spectra in predicting $Fe^{3+}/\Sigma Fe$ in garnets.

215   Previously-proposed techniques for using simple linear regression methods to predict $Fe^{3+}/\Sigma Fe$

216   (including those of Berry et al. 2010) were evaluated, along with PLS. Results showed that PLS

217   analysis of the entire XANES spectral region yields significantly better predictions of $Fe^{3+}$ in

218   garnets, with both robustness and generalizability, than approaches based solely on pre-edges.

219   Moreover, their PLS coefficients and loadings clearly demonstrate that the vast majority of the

220   useful information in the XANES spectra for predicting $Fe^{3+}/\Sigma Fe$ in garnets is found in the main

221   edge and at higher energies. This result emphasizes that in garnet changes in local coordination

222   and nearest neighbors, which are manifest in the EXAFS region, in part reflect valence state

223   differences. Expanding such calibrations to a wider range of mineral structure types may

224   dramatically improve the accuracy of redox predictions in glasses and minerals. The current

225   paper and work on silicate glasses (Dyar et al., 2014 and submitted) demonstrate such a potential

226   approach where multivariate analysis of the entire XAS region provides $Fe^{3+}/\Sigma Fe$ values that are

227   more consistent with values measured using Mössbauer in non-isometric materials such as the

228   amphiboles described here.

### SAMPLES STUDIED

230         Provenance and references to localities from which amphiboles were obtained for this

231   study are listed in Table 1, and their compositions and crystal-chemical formulae in Table 2. All

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232   samples were analyzed not only for major elements by electron microprobe, but also for

233   $Fe^{3+}/\Sigma Fe$ by Mössbauer (see Dyar et al. 1993 and Oberti et al. 2012) and $H_2O$ by one of two

234   techniques. The bulk technique of uranium extraction was used for the majority of samples

235   studied; it determines $H_2O$ contents by means of a procedure for collecting and measuring all the

236   structural H using a volumetric measurement of water vapor extracted from silicates (see

237   Bigeleisen et al. 1952 and Holdaway et al. 1986 for details of the technique). Samples DL-5, Fr-

238   12, and Z2124 were analyzed for H by secondary ion mass spectrometry (SIMS), based on very

239   careful single-crystal structure refinement (SREF) calibrations that take into account the Fe/Mg

240   ratio (one of the main factors affecting ion yield in amphiboles). More details on the procedures

241   are reported in Ottolini et al. (1995), Ottolini and Oberti (2000) and Oberti et al. (2007).

242        Single crystal x-ray diffraction was used to characterize site occupancies and crystal

243   structures of seven of the samples studied here. Previous high temperature studies on amphibole

244   single crystals (Oberti et al. 2010, 2013) had shown that thermal annealing in un-buffered sealed

245   vials induces Fe oxidation and deprotonation, and that these processes can be monitored

246   accurately by single-crystal X-ray diffraction. In particular, the results of the structure

247   refinements done at different temperatures were interpreted in the light of the experience

248   developed at CNR-IGG Pavia, and allowed precise determination of the site populations and thus

249   of the crystal-chemical formulae. Full details of the structure refinements will be given in a series

250   of papers focussed on thermal expansion and deprotonation in monoclinic calcium and sodium-

251   calcium amphiboles (Oberti et al. 2016, in preparation).

252        For this work, two kaersutites, one potassic-magnesio-hastingsite, and one pargasite

253   samples were selected (Fr-12, DL-5, KAR, and Z2124) and studied both as crystallized in nature

254   and after being heat treated in air at 900°C for 20 hours. In this way, we could obtain samples

255  with the same overall composition but with different cation ordering and values of the $Fe^{3+}/Fe^{2+}$

256  ratios. The response of each sample to annealing depends on the amount of the $Fe^{2+}$ content. For

257  kaersutite Fr-12 (0.05 $Fe^{2+}$ *apfu*), only minimal oxidation change could be observed, and hence

258  this sample was examined here only as untreated. In kaersutite DL-5, the $Fe^{2+}$ content (1.14 *apfu*)

259  is high enough to allow complete dehydrogenation under the above conditions for thermal

260  annealing and to maintain a low but significant amount of $Fe^{2+}$ (0.16 *apfu*). In contrast, the

261  potassic-magnesio-hastingsite KAR did not have sufficient $Fe^{2+}$ to allow complete

262  dehydrogenation; thus all Fe was oxidized but residual H remained also after thermal annealing.

263  In pargasite Z2124, the low $Fe^{2+}$ content (0.29 *apfu*) allowed only the same amount of H loss. It

264  is also important to note that significant amounts of cation exchange were observed in samples

265  DL-5 and Z2124, where all $^{B}Fe^{2+}$ (at the *M*(4) site) exchanged with $^{C}Mg$ (occurring at the *M*(1)

266  and *M*(3) sites, which are both coordinated with the OH groups). All these processes were

267  assessed by structure refinement and crystal chemical analyses of the same crystals which were

268  later oriented and used for XANES analyses.

269                                          **METHODS**

270  **Experimental methods**

271      In preparation for each beam session, single crystals were oriented optically using a

272  polarizing light microscope with a spindle stage. Each crystal was mounted with the Z optical

273  orientation parallel to the rotation axis of a spindle stage, permitting acquisition of polarized

274  XANES spectra perpendicular to the double chains (the *a sin β* direction) or within them (either

275  the *b* or *c* crystallographic axes). Ten samples were analyzed in known orientations to the

276  incident beam and 14 samples were analyzed with unknown, random orientation to the incident

277  beam. XANES measurements used a special beam geometry described in Dyar et al. (2002b).

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278    Samples were analyzed over the course of three sessions at beamline X26A at the

279    National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory in Upton, NY.

280    Using mutually-orthogonal Kirkpatrick-Baez mirrors, the beam was focused to a ~7×9 μm area.

281    Incident beam energy was controlled by a water-cooled (9° C) Si(311) channel-cut

282    monochromator. The structure of the Fe K absorption edge was scanned in the near-edge region

283    from 7020-7220 eV. XANES spectra were collected in fluorescence mode using Si drift diode

284    detectors. Acquisition parameters varied between sessions, but all spectra were acquired at a

285    sampling resolution of at least 5.0 eV from 7020-7105 eV, 0.1 eV from 7105-7118 eV, 0.5 eV

286    from 7118-7140 eV, and 1.0 eV from 7140-7220 eV. Because prevailing theory at the time these

287    measurements were made suggested that Fe redox state is primarily evidenced in the pre-edge

288    region, these scans favored 7105-7140 eV in time and energy resolution. The scans were carried

289    out to a maximum energy of 7220 eV to include most significant post-edge oscillations in the

290    absorption spectra to achieve reasonable edge-step normalization.

291    Monochromator energy drift, primarily caused by changing thermal expansion of the

292    silicon monochromator correlated to decrease in storage ring current at the NSLS over time, was

293    monitored with a National Museum of Natural History (NMNH) magnetite standard, and was

294    always analyzed before and after every 2-3 samples from 1995-the present. An energy offset was

295    determined using repeated measurements of the observed pre-edge centroid of the NMNH

296    magnetite standard relative to a reference energy of 7113.25 eV (cf. Westre et al. 1997). Drift of

297    up to 0.6 eV over the NSLS injection cycle, measured by successive magnetite analyses, was

298    modeled linearly and used to correct sample spectra. The magnitude of the observed drift for the

299    X26A monochromator was of similar magnitude to that reported by Cottrell et al. (2009). Sample

300    spectra were not acquired in the first hour following electron injection of the storage ring, when

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301 monochromator thermal drift is most non-linear. Resultant XANES spectra covering the entire

302 energy range studied are shown in Figure 1.

303 **Datasets**

304        Two distinct processing treatments were performed to determine the sensitivity of the

305 predictions of $Fe^{3+}/\Sigma Fe$ to pre-processing routines, specifically edge-step normalization and

306 over-absorption correction. **Minimal Treatment** required the least user input and included

307 normalization to incident beam intensity, edge-step normalization to an average of the last five

308 data points in the spectrum, and no over-absorption correction. **Full Treatment** included

309 normalization to incident beam intensity, edge-step normalization with a polynomial fit to a user-

310 specified portion of the post-edge, and correction for over-absorption using the PAXAS software

311 described below.

312        Each treatment was performed eight ways, and its effect on the prediction of $\%Fe^{3+}$ was

313 evaluated:

314     1. Predict each X orientation spectrum from all other X orientation spectra.

315     2. Predict each Y orientation spectrum from all other Y orientation spectra.

316     3. Predict each Z orientation spectrum from all other Z orientation spectra.

317     4. Predict each X or Y oriented spectrum from all other X or Y oriented spectra.

318     5. Predict each X, Y, or Z-oriented spectrum from all other X, Y, and Z-oriented

319        spectra.

320     6. Predict each spectrum from crystals that were randomly-oriented using all other data

321        for which crystals were randomly-oriented.

322     7. Predict each spectrum of samples for which crystals were randomly-oriented from

323        spectra of all X, Y, and Z-oriented spectra.

324    8.  Predict each oriented or randomly-oriented crystal spectrum from all other spectra of

325        oriented and randomly-oriented samples.

326    Prediction of $Fe^{3+}/\Sigma Fe$ was undertaken for four univariate and three multivariate models

327    for each of the two pre-processing treatments and eight subsets of spectra, as described below.

**Data Pre-Processing**

329    The two different methods of edge-step normalization used in the Minimal Treatment

330    (average of the last five data points) and Full Treatment (the more widely used polynomial fit)

331    were compared in case significant oscillations continued beyond 7220 eV where the scans ended.

332    If significant oscillations remained past 7220 eV, error could result in polynomial modeling of

333    the post-edge due to uncertainty in the location of appropriate nodes required to constrain the

334    polynomial function. Normalizing to the last five data points as in the Minimal Treatment

335    eliminates the need for the user to specify node locations, though could result in poor modeling

336    of the background shape for spectra with slope in the post-edge.

337    Examination of the raw spectra (normalized to incident beam intensity only) shows that

338    these amphibole spectra are similar in the shape of the post-edge regardless of oxidation state

339    and have a relatively flat slope (Figure 1, top). This suggests that a simple scaling of intensity as

340    in the Minimal Treatment rather than a correction for shape will suffice to normalize spectra.

341    Indeed, simply normalizing these raw spectra to total spectral intensity (dividing each pixel by

342    the sum of all pixels in the spectrum), brings all spectra within 20% in magnitude at 7140 eV, the

343    region of greatest spread (Figure 1, bottom). This indicates that scaling for variations in signal

344    return due to beam-to-sample coupling and inter-session variability accounts for the majority of

345    signal variation. The Full Treatment spectra in Figure 2 do have intensity variation at 7220 eV,

346    suggesting that some oscillation continued beyond 7220 eV. Predictions of $Fe^{3+}/\Sigma Fe$ for Full

347     Treatment and Minimal Treatment models are comparable, however, suggesting that differences

348     in edge-step normalization methods have little impact for this data set.

349         Spectra used for prediction of $Fe^{3+}/\Sigma Fe$ by Full Treatment Models (see description above)

350     were processed using the PAXAS (Python Analysis for XAS) software package written for this

351     project by Mirna Lerotic. The program automates, as a batch process, $I_0$ and edge-step

352     normalization for XANES spectra, correction for over-absorption effects using the FLUO

353     algorithm (Haskel 1999), and spectral fitting including background removal and Gaussian fitting

354     of pre-edge centroids, fitting of the rising edge and the white line of the absorption spectra.

355     PAXAS works in batch processing mode taking as input an ascii list of files that points to the file

356     name of raw spectra data (multi-column data of energy bins, fluorescence intensities and incident

357     flux intensities), a listing of sample compositions for OA corrections and optional energy shifts

358     for each spectra. Input data files are in the form of $\chi\mu$ (*.xmu) format as output by the ATHENA

359     program as "project files." Output is as normalized $\mu(E)$ (Ravel and Newville 2005), though

360     PAXAS can also fit peaks to the pre-edge region. PAXAS assumes that input data has already

361     been corrected for detector dead-time effects. The software is currently being configured to

362     output predicted $\%Fe^{3+}$ using the optimal algorithm described in this paper for amphiboles.

363         Background removal and edge-step normalization in PAXAS were performed using a

364     linear fit to the pre-edge region (~7045-7095 eV) and a third-order polynomial fit to the post-

365     edge region (~7190-7210 eV) (using the algorithm of Ravel and Newville 2005). The edge-step

366     normalization constant, $\mu_0(E_0)$, represents the value of the background function evaluated at the

367     absorption edge energy $E_0$. It is determined by extrapolating the pre- and post-edge fits to $E_0$ and

368     subtracting the $E_0$-crossing of the pre-edge fit from the $E_0$-crossing of the post-edge fit. The pre-

369    edge fit is extrapolated to all energies and subtracted from $\mu(E)$. These pre-edge subtracted data

370    are divided by $\mu_0(E_0)$ to yield background removed, edge-step normalized spectra.

371          Spectra were corrected for over-absorption (OA) using an adaptation of the FLUO

372    algorithm (http://www.aps.anl.gov/~haskel/fluo.html) as implemented in PAXAS. Over-

373    absorption is the reason why transmission x-ray absorption analysis is typically the preferred

374    XAS technique at high absorber concentrations. Over-absorption is sometimes referred to as

375    "self-absorption" but that term is something of a misnomer because the observed attenuation has

376    nothing to do with re-absorption of the fluorescence radiation (Manceau et al. 2002). In fact, the

377    absorption of the fluorescence is independent of the incident energy, and hence does not

378    contribute to any non-linearity. What is important is that the penetration depth for the incident

379    radiation depends on the quantity to be measured, which changes over the energy range of the

380    absorption edge. The effect of over-absorption in high-Fe (i.e., most geologically-relevant)

381    samples is to reduce the ratio of feature height to background relative to that predicted from a

382    simple correlation between X-ray intensity and composition.  As part of this study, we seek to

383    test the importance of this correction on quantitative results for predicting $Fe^{3+}$ contents.

384    Accordingly, the major element compositions used in the correction are shown in Table 2.

385    Absorption cross-sections used to approximate the absorption coefficient for OA correction are

386    from McMaster et al. (1969). PAXAS assumes no OA correction is required when no

387    composition is supplied. Background removal, edge-step normalizations and OA corrections

388    were all conducted in a manner so as to provide comparable normalizations and corrections to

389    those used for data presented for garnets in Dyar et al. (2012).

390    **Univariate models (simple linear regression)**

391    Four simple linear regression models (SLR) were employed to predict $Fe^{3+}/\Sigma Fe$ from

392    minimally and fully pre-processed spectra using the eight data subsets described above: 1) area-

393    normalized pre-edge centroid method, 2) absorption edge energy method, 3) intensity ratio

394    method, and 4) slope method. For all SLR models, a calibration curve was generated between the

395    selected predictor variable and $Fe^{3+}/\Sigma Fe$. All spectra belonging to the sample being predicted

396    were left out of the calibration curve when predicting that sample.

397    For the area-normalized pre-edge centroid method, the pre-edge region defined in the

398    PAXAS configuration file is extracted. The background (the contribution of the main edge to the

399    pre-edge spectrum) is fitted with a linear offset and a portion of a Lorentzian line (Hecht 1987)

400    and subtracted, with no constraints on wavelength. Pre-edge peaks are fitted using a user-defined

401    number of Gaussian curves (2 or 3 in this study, depending on the spectrum). An area-

402    normalized centroid energy is calculated for each spectrum as the sum of the products of each

403    Gaussian relative area (expressed as a percentage) and its centroid energy, as done by Wilke et

404    al. (2001):

405    $\mathrm{Centroid_{area\text{-}normalized}} = \%\mathrm{Area_{peak1}} \times \mathrm{Centroid_{peak1}} + \%\mathrm{Area_{peak2}} \times \mathrm{Centroid_{peak2}} + \%\mathrm{Area_{peak3}} \times \mathrm{Centroid_{peak3}}.$

406    The area-normalized centroid energies were then used as input for simple regression expressions

407    to quantify $\%Fe^{3+}$.

**Multivariate models**

409    Two different multivariate techniques were used to process the XANES data. The first is

410    partial least squares (PLS), also known as projection to latent structures, which was developed

411    for use in situations where explanatory variables ($p$) significantly outnumber observations ($N$). It

412    has been used to analyze data from a variety of types of spectroscopy, including, but not limited

413    to, laser-induced breakdown spectroscopy (Clegg et al 2009, Dyar et al. 2012), near infrared

414    reflectance (NIR) spectroscopy (Kramchote et al. 2014, Zhang et al. 2015), Fourier transform

20

415    infrared (FTIR) spectroscopy (Hayes et al. 2014, Anjos et al. 2015), and Fourier transform-

416    Raman (FT-Raman) spectroscopy (Lopez-Reyes et al. 2014). PLS calculates components that

417    maximize the covariance between the feature and response matrices (Wegelin 2000). It is

418    especially well suited for problems with many highly correlated features and multiple responses

419    (Erdas et al. 2010, Kalivas 1999).

420         PLS sequentially chooses directions, or components, of maximal covariance from the

421    feature matrix, **X**, and the response matrix, **Y**, to determine the model coefficients using a two-

422    step process. The first step is the shrinkage step, in which the shrinkage penalty determines the

423    number of factors to be included in the regression. This shrinks the feature matrix by projecting

424    it from the original $p$-dimensional space into a smaller $q$-dimensional vector space. In the context

425    of this project, $p = 434$, the number of channels (wavelength values) at which the signal is

426    measured, and $q$, the number of components, is either allowed to vary from 1-10 or held constant

427    at some generalized value within that range. The choice of an appropriate number of components

428    does not relate directly to any of the variables (such as $\%Fe^{3+}$) but rather is analogous to the

429    order of a polynomial line used to fit a complex set of data. As in that example, higher numbers

430    of components train the model more closely to the specific training set, while use of fewer

431    components makes the model more generalizable. The components themselves are a set of linear

432    combinations of channel intensities that best explain the variation in the data set. They are

433    constructed by the algorithm, which solves for the best linear combination of channels. The

434    second step follows ordinary least squares by regressing the response on the components

435    generated in the first step to minimize the residual sum of squared error. For this project, a single

436    response model, PLS-1, was trained for prediction of our variable of interest, which is $Fe^{3+}/\Sigma Fe$.

437    **Lasso**. Least absolute shrinkage and selection operator (lasso) regression is an ordinary

438    least squares regression model with an $l_1$ penalty on the model coefficients to induce sparsity

439    (Hastie et al 2009). The lasso provides a sparse model by shrinking some coefficients and setting

440    most other coefficients to zero. In other words, the lasso removes channels (in our application,

441    energies) where the signal is not useful for predicting $\%Fe^{3+}$. It is assumed that a smaller (<434)

442    subset of the predictor variables is driving the prediction results. Thus, other coefficients can be

443    excluded from the model (i.e., set to zero) with no significant performance loss. This reduces a

444    sizable, largely uninterpretable model to a sparse, more interpretable model:

445        To calculate its model coefficients, the lasso fits a linear model

446    $$\hat{y} = b_0 + (b_1 \times x_1) + (b_3 \times x_3) + \cdots (b_p \times x_p) \tag{1}$$

447    with a goal of minimizing $\sum(y - \hat{y})^2$ and keeping the sum of the absolute values of the weights

448    at a minimum, such that $\sum|b_j| \leq s$. Adding that constraint on $s$ as a boundary condition to

449    ordinary least squares prevents the model from overfitting the training data.

450    Choice of a value for $s$ is difficult, so an alternate parametrization is helpful. The lasso penalty,

451    $L_q$, is used to select specific channels (wavelengths) for each element that explain the most

452    variance in its predicted concentration.  The lasso penalty, $L_q$, can be generalized as:

453    $$b^* = argmin_b \left\{ \sum_{i=1}^{n} \left( y_i - b_0 - \sum_{j=1}^{p} x_{ij}b_j \right)^2 + \lambda \sum_{j=1}^{p} |b_j|^q \right\} \; for \; q \geq 0. \tag{4}$$

454    Here b* is the value that minimizes the overall error in $y$ and the weights of the individual

455    channels, $x_{ij}$ is the ith example in the jth channel, l (sometimes called a) is a variable term that

456    restrict the sparsity of the result, and $q$ is set to one, which shrinks some coefficients and sets

457    other, less influential coefficients to zero. For problems with many features, the lasso can

458    eliminate noisy features that may otherwise hinder the model. These parsimonious models have

459    shown to be effective in many types of chemometric models (Andries 2013, Filmozer et al.

460    2012).

461        The open-source machine learning Python library Scikit-learn (Pedregosa et al. 2011)

462    was used to train and test all models.

463                                        **RESULTS**

464        Spectra from oriented and randomly-oriented amphiboles were acquired and processed

465    using the Full Treatment and Minimum Treatment methods described above (Tables 3, 4, and 5).

466    The only exception was that only Full Treatment pre-edge data were fit for determination of the

467    area-normalized pre-edge centroid for comparison with published calibrations processed in the

468    same manner. Several different strategies for predicting $Fe^{3+}/\Sigma Fe$ were undertaken.

**Area-Normalized Pre-edge Centroid Energy vs. $Fe^{3+}/\Sigma Fe$**

470        In this method, component peaks are fit to the pre-edge, and then an area-normalized

471    centroid energy is calculated for use in calibration. This energy is the point dividing the total

472    integrated intensity in half (Table 3). This is the method first used by Bajt et al. (1994) and

473    adapted and described in detail by many subsequent users including Wilke et al. (2001) and

474    Cottrell et al. (2009). The highest $R^2$ value for a fit of area-normalized pre-edge centroid fit to

475    predicted $\%Fe^{3+}$ vs. true $\%Fe^{3+}$ was 0.91 for predictions of $Fe^{3+}$ in Y-oriented crystals from other

476    Y-oriented crystals (Figure 3A, B). The root of the mean-squared errors (RMSE) of the eight

477    different sample combinations ranged from 9.7-18.1% (absolute, in units of $\%Fe^{3+}$). So even

478    when like orientations are used to predict the same optical orientations, use of a single peak

479    centroid based on its area-normalized energy does not produce very accurate results.

480        The reason for this high error is apparent in Figure 4, which shows the variations in pre-

481    edge intensity and position as a function of orientation for seven representative samples. The

482    three heat treated, ["HT"] samples are all nearly completely oxidized, yet their peak intensities

483    are only somewhat similar to one another. The shape of the pre-edge is dramatically different for

484    each sample at each orientation.

485    **Alternate Methods for Predicting $Fe^{3+}$ using Linear Correlations**

486    Berry et al. (2010) evaluated two other univariate methods for predicting $Fe^{3+}$ using XAS

487    spectra. Note that those studies used only garnets, which are isotropic. Results of similar

488    methods applied to our amphiboles are shown in Figure 5 and accuracies and $R^2$ values are given

489    in Table 4.

490    The absorption edge energy method is based on work done with garnet spectra by Berry

491    et al. (2010). They found high $R^2$ correlation between $Fe^{3+}/\Sigma Fe$ and the energy at which the

492    absorption edge reaches a normalized intensity of 0.9 for each spectrum, with samples with

493    greater $Fe^{3+}/\Sigma Fe$ reaching that intensity at higher energies. In this study, $R^2$ with $Fe^{3+}/\Sigma Fe$ was

494    calculated for all absorption edge energies at normalized intensities from $0.04 - 1.4$ at an interval

495    of 0.01. The absorption edge energy with the highest $R^2$ was used to predict $Fe^{3+}/\Sigma Fe$. The best-

496    performing absorption edge model is for full treatment pre-processing, predicting Z-oriented

497    spectra from Z-oriented spectra. RMSE for this model is 3.7% $Fe^{3+}$ and $R^2$ between true and

498    predicted $Fe^{3+}/\Sigma Fe$ is 0.99 (Table 4). Energy at a normalized intensity of 0.29, corresponding to a

499    range of $7119.2 - 7122.4$ eV for the Z-oriented spectra, was selected as the best predictor of

500    $Fe^{3+}/\Sigma Fe$.

501    For the intensity ratio method, normalized intensity at each channel was divided by

502    normalized intensity at every other channel. $R^2$ was calculated between those 41,209 ratios per

503    spectrum and $Fe^{3+}/\Sigma Fe$, and the ratio with the highest correlation was used to predict $Fe^{3+}/\Sigma Fe$.

504    This method was also inspired by Berry et al. (2010), who found high correlation between

505    normalized intensity ratio at two spectral features that occur at 7138.4 and 7161.7 eV in garnet

24

506  spectra. While acknowledging that this is a somewhat ad-hoc approach because the features lie in

507  the region caused by multiple scattering processes, Berry et al. (2010) plotted the ratio of

508  intensities at those two wavelengths vs. $Fe^{3+}$, which resulted in a useful prediction of $Fe^{3+}$. Our

509  method examines every possible intensity ratio for correlation with $Fe^{3+}/\Sigma Fe$ regardless of the

510  presence or absence of distinguishing spectral features. The best-performing intensity ratio

511  model is also for full treatment pre-processing, predicting Z-oriented spectra from Z-oriented

512  spectra. RMSE for this model is 1.7% $Fe^{3+}$ and $R^2$ between true and predicted $Fe^{3+}/\Sigma Fe$ is 1.00

513  (Table 4). The ratio of normalized intensity at 7119.5 eV (main edge) to that at 7149.0 eV (post-

514  edge) was selected as the best predictor of $Fe^{3+}/\Sigma Fe$ for the Z-oriented spectra.

515        For the slope method, the first derivative of the spectrum was computed for every

516  channel. The slope at the channel with the highest $R^2$ was used to predict $Fe^{3+}/\Sigma Fe$. This method

517  was undertaken because samples with greater $Fe^{3+}/\Sigma Fe$ appear to have sharper features in both

518  the pre-edge and the main edge. The best-performing slope model is also for full treatment pre-

519  processing, predicting Z-oriented spectra from Z-oriented spectra. RMSE for this model is 6.0%

520  $Fe^{3+}$ and $R^2$ between true and predicted $Fe^{3+}/\Sigma Fe$ is 0.97 (Table 4). The slope at 7117.2 eV

521  (between pre-edge and main edge) was selected as the best predictor of $Fe^{3+}/\Sigma Fe$ for the Z-

522  oriented spectra.

523  **Partial Least Squares**

524        While working with the existing methods for $Fe^{3+}$ predictions discussed above, it became

525  apparent that more sophisticated statistical analysis of these data might improve our results, as

526  was the case for garnet spectra detailed in Dyar et al. (2012). PLS models were built for each

527  data set (Table 5) in two different ways. The first (labelled "PLS" in Table 5) tuned the

528  hyperparameter, $q$, differently for each model using the number of components among the first

25

529   ten that provides the global minimum RMSE. The second set of models ("PLS*" in Table 5)

530   used a constant number of components (6, chosen from the most common value of the global

531   minimum) in all models. PLS coefficients for each channel are superimposed on plots of all

532   spectra in each model in Figure 6. The largest positive and negative coefficients in each PLS

533   model lie at predictor channels in the main edge and EXAFS region rather than in the pre-edge.

534   **Lasso**

535   Lasso models were also built for both minimal and full treatments of all data, in eight

536   combinations as listed in Table 5 and shown in Figure 7. Relative performance of the lasso

537   models is in many cases inferior to that of the PLS models. However, the lasso models are

538   extremely sparse and thus likely to be more generalizable. For example, the model of spectra

539   with the beam polarization along the Y optical orientation uses only five channels, suggesting

540   that all the information needed to predict $Fe^{3+}$ with Y-oriented samples is contained in only five

541   channels – likely representing important transitions in that orientation. Moreover, Figure 8 shows

542   that the eight different models are all picking nearly the same channels, with only small offsets

543   between the full and minimal treatment models that result from the over-absorption correction.

544   Theory has not yet advanced to the point of understanding the transitions to which these energies

545   correspond in such a complex mineral structure with four different sites for Fe. However, it is

546   clear that the XAS energies at channels corresponding to 7120, 7153, and 7217 eV for the

547   minimal models and 7129, 7154, 7162, and 7194 eV for the full treatment models  must be

548   associated with the phenomena (key transitions) that differentiate between $Fe^{2+}$ and $Fe^{3+}$ in

549   amphiboles.. Reducing the number of channels needed for $Fe^{3+}$ prediction to such a small

550   number is critically important because it enables rapid analyses and facilitates development of

551   methodology for acquisition of high-resolution redox maps with 1-μm pixel sizes.

552 **First Derivative Models for PLS and Lasso**

553     The multivariate models clearly depend upon data channels in the main edge and EXAFS

554 regions to predict $Fe^{3+}$ contents. To test whether this occurs because of the absolute magnitude of

555 the peaks, we ran the full set of PLS and Lasso models on first derivatives of the spectra rather

556 than raw spectral intensity to see if the channels that are picked are the same. Results are shown

557 in Figure 9 and Table 5. They demonstrate that multivariate models based on first derivative

558 spectra do not choose channels in the pre-edge region either, and moreover, they produce results

559 that are comparable to but slightly less accurate as measured by RMSE.

560                                                      DISCUSSION

561     Amphiboles are either monoclinic (like those studied here) or orthorhombic minerals,

562 with varying atom densities at different orientations that gives rise to the familiar pleochroism

563 observed in amphiboles in thin section. These variations are manifested in optical spectra of

564 amphiboles, which exhibit strong variations as a function of orientation because specific

565 electronic interactions are most favored along specific directions in the crystal structure. A strong

566 absorption band at ~1,000 nm corresponds to $Fe^{2+}$ in the $M(4)$ site and is most active in the β

567 (=Y) optical orientation across the I-beams in the amphibole structure. Optical wavelength

568 interactions from the $Fe^{2+}$ $M(1)$-$M(3)$ site band are strongest in the sharp peak at 1,400 nm,

569 which arises from Fe interactions along the α sin β (closest to X) orientation perpendicular to the

570 plane of the I-beams (Figure 10). XANES spectra should also reveal atomic interactions with

571 electromagnetic radiation of much higher energy. This is suggested in our spectra, in which the

572 highest energy pre-edge peak (ca. 7114.1 eV) is consistently the most intense in the X

573 orientation, consistent with it being caused by $Fe^{2+}$ hosted at the $M(1)$-$M(3)$ sites. However,

574   sample Z2124 HT, which contains 100% $Fe^{3+}$, also has a feature at this energy, so there must

575   also be some contribution there from $Fe^{3+}$.

576          Within the chemistry literature, Fe XANES pre-edge spectra have been modeled based on

577   molecular orbital calculations; for simple compounds, normalized pre-edge positions and

578   intensities can successfully be predicted. For example, Randall et al. (1995) quantified the

579   coordination number and symmetry of $Fe^{2+}$ atoms in synthetic high-spin $Fe^{2+}$ complexes, and

580   Westre et al. (1997) used ligand field theory to describe systematic relationships between spin

581   state, oxidation state, and site geometry and the energy (i.e., position), splitting, and intensity

582   distribution in a large variety of ferrous and ferric model compounds. These workers and many

583   others subsequently have shown that the Fe K edge is extremely sensitive to the electronic

584   structure of the Fe cation. In general, pre-edge intensities are greater in $Fe^{3+}$-bearing minerals

585   because of the additional hole that is present in their ground state. This is also consistent with the

586   observation that the highest energy peak in our pre-edge fits should be assigned to $Fe^{3+}$ as noted

587   in the previous paragraph.

588          Moreover, Westre et al. (1997) show that distortions from ideal octahedral symmetries to

589   tetrahedral and square pyramidal geometries (as are found in most mineral spectra) allow for $3d$

590   $\rightarrow 4p$ mixing, and affect both the intensity and energy distribution in the pre-edge region. The

591   effect of symmetry on pre-edge intensity is commonly observed in minerals. For example, $Fe^{2+}$

592   with a perfect octahedral coordination would have no pre-edge; we have observed this scenario

593   in wüstite XAS data (unpublished data). If site geometry is the dominant effect on pre-edge

594   intensity and specific pre-edge features result from the distinct $M$ sites in amphiboles, then the

595   distortion in cation polyhedra ought to correlate with the intensity of peaks in the pre-edge.

596    Because we have done SREF of seven of the samples used in this study, we are able to address

597    this issue, albeit inconclusively.

598        The geometry of coordination polyhedra can be described using two parameters devised

599    by Robinson et al. (1971), who quantified polyhedral distortion using data derived from single

600    crystal structure refinement. The first parameters is angular variance, $\sigma$, calculated using the

601    expression, where

602
$$\sigma = \frac{\sum_{i=1}^{n}(\theta_i - \theta_{avg.})^2}{n-1}. \tag{2}$$

603    Here $\theta_i$ is the measured O-cation-O angle in the crystal structure (there are $n = 12$ angles in a 6-

604    coordinated site), and $\theta_{avg}$ is theoretical value for a perfect octahedron (all angles are 90º).  Units

605    are in degrees squared. Values of $\sigma$ directly reflect how distorted the polyhedra are. The second

606    parameter is the quadratic elongation ($\lambda$), where

607
$$\lambda = \sum_{i=1}^{n}\left(\frac{l_i}{l_0}\right)^2 / n. \tag{3}$$

608    In this expression, $l_i$ is the measured cation- oxygen bond distance (where $n = 6$ for 6-

609    coordination) and $l_0$ is the bond distance in a perfect (undistorted, equal volume) octahedron.

610    Values for octahedral $\lambda$ range from ~1.00 for wustite and garnets, up to 1.06 for some olivines

611    and pyroxenes, and can be as high as 1.15 in staurolite, which indeed has a very intense pre-edge

612    (Wilke et al. 2001). This parameter is unitless. Of the two parameters, quadratic elongation is

613    generally considered to provide the best measure of polyhedral distortion (Robinson et al. 1971).

614    Note also that octahedra containing smaller trivalent and divalent cations (e.g., $Al^{3+}$, $Fe^{3+}$, and

615    $Mg^{2+}$) are generally less distorted that those containing larger divalent cations (Robinson et al.

616    1971; Brown 1970). If polyhedral distortion is the dominant factor controlling peak intensity,

617    then large values of $\lambda$ and $\sigma$ ought to relate to intense peaks.

618    Table 6 shows occupancies of Fe cations in the $M(1)$-$M(4)$ sites of seven of the samples

619    studied here, and Figure 11 plots summed pre-edge areas against $\lambda$ and $\sigma$ for the [6-coordinated]

620    $M(1)$, $M(2)$, and $M(3)$ polyhedra. Overall, there is little correlation between $\lambda$ and the pre-edge

621    area. For the $M(3)$ octahedron, there is a clear inverse correlation between $\lambda$ ($R^2 = 0.90$) and

622    $\sigma$ ($R^2 = 0.91$) versus peak area. Perhaps this relationship occurs because the $M(3)$ polyhedron - in

623    the center of the strip (Figure 12) – when occupied by $Fe^{3+}$, is strongly affected by the

624    dimension/conformation of the other octahedra, in particular of $M(1)$, where most of the

625    oxidation related to deprotonation occurs. Overall, these data suggest that the dominant control

626    on peak area is not site distortion. However, note that in every pair of natural vs. heat-treated

627    spectra, at every orientation, the maximum peak intensity does correlates with the amount of $Fe^{3+}$

628    present (Figure 4). Thus, valence state is a far more important factor in pre-edge intensity than

629    symmetry, at least for the amphibole group studied here.

630                                        **IMPLICATIONS**

631    **Recommendations for Measuring $Fe^{3+}$ in Amphiboles using XAS**

632        Figure 13 shows a comparison of the accuracy of all models used in this study for

633    predicting $Fe^{3+}$ contents in amphiboles. The most important conclusion of this research is that it

634    provides clear evidence for the utility of the entire XANES region in predicting Fe valence

635    states. Our PLS and lasso loading and coefficients show that there is key diagnostic information

636    in other regions of their spectra arising from changes to the local structural environment resulting

637    from the difference in size and charge between $Fe^{2+}$ and $Fe^{3+}$. The community would benefit

638    greatly from a new study of powdered mineral spectra of reference materials using multivariate

639    analyses to predict valence state and, potentially, coordination number. These authors will

640    support that effort in any way possible.

641    In the meantime, the model from this study will be made broadly available for studies

642    associated with interpreting conditions of geological formations of amphiboles; the PAXAS code

643    and associated multivariate models are available upon request from the senior author. Another

644    important use of this technique will be to health-related fields for the study of asbestiform

645    minerals, many of which are amphibole species (Gunter et al. 2007). Gunter et al. (2011) used

646    synchrotron methods to document differences in the oxidation state of Fe between asbestiform

647    and non-asbestiform samples, and suggested that iron oxidation, mineral morphology, and

648    potential health effects may all be interrelated. Implementation of our method for measuring

649    redox states in amphibole particles will enable further research to understand the role of

650    oxidation state in the causation of disease between these differing morphologies.

651    Results of this study also have broad implications for many types of synchrotron

652    applications in which single phases are studied without careful attention to orientation effects. As

653    with optical spectra of the visible region and infrared spectra, pleochroism effects as evidenced

654    in XAS transitions are significant and ubiquitous in anisotropic materials. Many workers have

655    attempted to document orientation effects by rotating their samples on the stage, but this practice

656    can be misleading. At best, when the stage is oriented at a 90° angle to the beam, rotation

657    samples two of the three optical orientations of a crystal, but only if it is orthorhombic. Most

658    microprobe beamlines are configured with the beam impinging on the sample at a 45° angle with

659    fluorescence detectors placed at 90° to the incident beam and in the plane of the storage ring to

660    reduce measured X-ray scatter and significantly improving measured peak to background for a

661    given emission line. In this geometry, rotation within the sample plane simply samples assorted

662    angles within the crystal. To acquire spectra from at least two optical orientations, a back-

663    fluorescence configuration in which the beam impinges on the thin section's surface at a 90°

664 angle with the beam co-located with the stage's rotation axis is optimal. This geometry is

665 analogous to that used in the current study as depicted in Figure 1 of Dyar et al. (2002b) and used

666 in several experimental papers by Cibin et al. (2006, 2010).

667        Many of the previous calibrations for predicting $Fe^{3+}$ on the basis of pre-edge

668 spectroscopy are limited to analyses of powders (e.g., Galoisy et al. 2001, Wilke et al. 2001), but

669 this limits their usefulness in petrologic contexts where it is desirable to analyze minerals in situ

670 in thin sections. Dyar et al. (2002a) determined that the effect of orientation on calculated

671 $Fe^{3+}/\Sigma Fe$ would be ±10-20% errors in randomly-oriented crystals using the position of the peak

672 area-normalized pre-edge. In this study, Table 4 quantifies this effect for seven different

673 prediction methods. Results show that the worst errors (±33% and ±11% $Fe^{3+}$ relative to total Fe)

674 arise from predicting $Fe^{3+}$ in randomly-oriented crystals using a calibration based only on spectra

675 acquired with the beam polarized along X, Y, and Z using the minimal and full treatment

676 models, respectively. The situation improves when the entire data set (spectra of oriented and

677 randomly-oriented crystals) is used for training, with RMSEP errors of ±14% and ±7% $Fe^{3+}$,

678 again respectively. These error bars do not come close to the ±1-3% absolute errors associated

679 with %$Fe^{3+}$ measurements from Mössbauer spectroscopy and wet chemistry. Although the ±7%

680 error using the full treatment model is probably the best that can be achieved for random grains

681 in a thin section using currently-available data and technology, it will still be useful for many

682 applications, and is markedly better than picking out grains and powdering them for analysis by

683 other methods! Combination of XANES results with in-situ EBSD measurements or single-

684 crystal X-ray diffraction would have the potential to provide precise orientation data for all spots

685 measured in thin section.

686 **Comparison with Garnet Results**

687      Given the success of the lasso predictions for the amphiboles when orientation was held

688      constant, we undertook lasso predictions of the garnet data set from Dyar et al. (2012) for

689      comparison. The 19 samples studied cover a range from almandine, andradite, grossular, and

690      melanite. Results are shown in Figures 14 and 15. Two themes are again apparent. Prediction of

691      $Fe^{3+}$ utilizes primarily the main edge regions of the spectra rather than the pre-edge, as indicated

692      by the positions of the vertical red lines in Figure 15. Note that the number of channels needed to

693      accurately predict $Fe^{3+}$ is larger for garnet than for amphiboles. This difference may be explained

694      by the wide range of garnet compositions represented in the study, or by a large number of

695      possible transition for garnet relative to amphibole – theory is insufficient to explain. Second, for

696      garnets the lasso provides significantly more accurate measurement of $Fe^{3+}/\Sigma Fe$ than PLS, with

697      an error of $\pm 0.01\%$ $Fe^{3+}$. This success of this model can be attributed to both the isometric nature

698      of the garnet structure and the fact that only two sites are present. However, Dyar et al. (2016)

699      showed that $Fe^{3+}$ contents in silicate glasses with widely-ranging compositions and $Fe^{3+}$ from 0-

700      100% could be predicted with an accuracy of $\pm 3.6\%$ $Fe^{3+}$ (absolute) even though glass by

701      definition has a wide variety of sites for $Fe^{2+}$ and $Fe^{3+}$. These results reinforce the conclusions of

702      the amphibole work, which also show that when orientation effects are mitigated (i.e., for

703      predicting Y from Y), extremely accurate results can be obtained.

704      The success of this paper and the previous work on garnet suggests that multivariate

705      analysis may be the key to quantifying Fe redox states across a wide variety of geological (and

706      other) materials. The contrast between the garnet, putative glass, and amphibole results

707      highlights the fact that anisotropy is the primary source of error is predicting $Fe^{3+}$ in amphiboles.

708      Optimal accuracy in thin section analyses can be obtained by carefully orienting crystals of

709      unknowns with respect to their optical orientations and then interpreting those results using a

710    model built on standards also acquired at the same orientation. If random orientations are probed

711    without knowledge of their orientations, then reduced accuracy must be accepted.

712        This study also highlights the need for further analogous studies of other mineral groups

713    commonly studied at microscales. The magnitude of error introduced by failure to correct for

714    crystal orientation will likely scale with the magnitude of optical birefringence (the difference in

715    refractive index between two directions of a crystal), which is a convenient measure of

716    dissimilarity between two orientations. For example, minerals in the feldspar group are

717    framework silicates in which all the corners of every Si and Al tetrahedron are shared. This

718    creates a 3-D tetrahedral network, with similar electron densities and charges in all directions. As

719    a result, feldspars have very low birefringence. So in feldspars, there should not be such dramatic

720    differences in XAS spectra acquired along X, Y, and Z orientations. At the other extreme (e.g.,

721    Dyar et al. 2002), layer silicates have only three of the four corners of the tetrahedra shared. In

722    minerals like biotite and muscovite, there are roughly similar atomic and electronic densities

723    within the sheets (i.e., the *a-b* plane), so a mica section where the light vibrates only in the sheet

724    will have low birefringence and a small difference between the two crystal orientations.

725    However, a grain oriented where one of the orientations represents light vibrating perpendicular

726    to the sheets in the *a-b* plane (i.e., along *c*), shows marked birefringence. This would be

727    manifested in XAS by similar spectra in the X and Y directions that would be quite different

728    from those acquired with the vibration direction along Z. Finally, chain silicates like pyroxene,

729    which share only two of four corners of their tetrahedral, usually have the largest refractive index

730    and highest retardation along the chains. So maximum retardation will occur when looking at

731    any slice that includes the direction along which the chains lie, but X, Y, and Z would all be

732    expected to be different. So for biopyribole groups like layer silicates and pyroxenes, it is

733 imperative that XAS data from end-member optical orientations be acquired to ensure optimal

734 accuracy in predicting $Fe^{3+}$.

735      Although detailed studies like this current paper are time-consuming and difficult, they

736 are necessary to obtain accurate and truly quantitative analyses of $Fe^{3+}/Fe^{2+}$ at microscales. The

737 potential pay-off for these detailed studies will be the unveiling of a new capability for

738 understanding variations of Fe redox state and oxygen fugacity at micron and sub-micron scales.

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964

# FIGURE CAPTIONS

965

966    Figure 1. Raw XANES spectra of oriented crystals normalized to incident beam intensity (top).

967    The shape of the post-edge is similar regardless of oxidation state and all spectra have a

968    relatively flat slope. Normalizing these raw spectra to total spectral intensity (dividing each pixel

969    by the sum of all pixels in the spectrum), brings all spectra within 20% in magnitude at 7140 eV,

970    the region of greatest spread (bottom).

971    Figure 2.  Pre-processed XANES spectra of oriented crystals covering the entire energy range

972    studied (top) and the pre-edge region (bottom). Intensity variations at 7220 eV in the Full

973    Treatment spectra, for which the post-edge background was modeled with a user-defined

974    polynomial, suggest oscillations continuing beyond 7220 eV. To remediate this, spectra were

975    also edge-step normalized to the average of the last five points in the spectrum in the Minimal

976    Treatment method.

977    Figure 3A. Results of $Fe^{3+}$ predictions based on fits of the energy of the area-normalized pre-

978    edge centroid vs. $Fe^{3+}$ measured by Mössbauer. Best-fit lines are shown with long dashes in red;

979    1:1 lines are shown as green dotted lines. Error bars are ±3% on the *x* axis (the maximum error

980    associated with Mössbauer %$Fe^{3+}$ measurements) and ±RMSEP from Table 4 for the *y* axis.

981    Figure 3B. Results of $Fe^{3+}$ predictions based on fits of the energy of the area-normalized pre-

982    edge centroid vs. $Fe^{3+}$ measured by Mössbauer. Best-fit lines are shown with long dashes in red;

983    1:1 lines are shown as green dotted lines. Error bars are ±3% on the *x* axis (the maximum error

984    associated with Mössbauer %$Fe^{3+}$ measurements) and ±RMSEP from Table 4 for the *y* axis.

985    Figure 4. Extracted pre-edges from oriented crystals along with crystal structure diagrams of the

986    M[1]-M[3] sites in each crystal (M[1] at left, M[2] in center column, M[3] at right), viewed

46

987    down the corresponding axis. The range of the y axis scale is the same for all three orientations

988    of each individual crystal, but note that the y axis maximum is different for each sample based on

989    characteristics of that particular composition. Fitted peaks are color-coded with red as lowest

990    energy, green as middle, and blue as highest energy peak.

991    Figure 5. Predicted vs. "true" Mössbauer $\%Fe^{3+}$ values for randomly-oriented crystals of

992    amphibole from this study using models analogous to those described by Berry et al. (2010).

993    (left) Predictor was pre-edge energy at edge intensity of 0.38 for minimal treatment, edge

994    intensity of 0.31 for full treatment. (center) Predictor was intensity at 7111.70/7112.80 eV for

995    minimal treatment and 7111.70/7112.70 eV for full treatment (right) Predictor was first

996    derivative at 7119.00 eV for minimal treatment and 7112.4 eV for full treatment. For each of

997    these models, we regressed against every possible predictor and chose the predictor with highest

998    $R^2$ with $\%Fe^{3+}$.

999    Figure 6. PLS coefficients and loadings for full treatment spectra. Models used here tuned the

1000    hyperparameter, $q$, differently for each model using the global minimum number of components

1001    among the first ten. On each pair of plots, intensity is plotted in blue relative to the left axis and

1002    the PLS loadings (top of each pair) and coefficients (bottom of each pair) are plotted in red

1003    dashed lines relative to the right vertical axes.

1004    Figure 7. Locations and magnitudes of lasso coefficients in the full treatment models. On each

1005    plot, the left axis in blue is intensity, and the right axis shows the magnitude of the lasso

1006    coefficients, which are indicated as red lines ending in circles. When compared to Figure 5, it is

1007    apparent that the lasso models use many fewer channels (as few as five); moreover, such sparser

1008    models are also considered to be more generalizable.

1009   Figure 8. Comparison of lasso coefficients for the full-treatment and minimal-treatment models.

1010   Only one coefficient does not fall in these energy ranges: in the X from X model (only), channel

1011   7137 eV has a coefficient of 117. An average XANES spectrum of the amphiboles is shown as

1012   dashed magenta lines for reference. The chosen channels are very similar but not identical due to

1013   a slight offset introduced by the over-absorption correction.

1014   Figure 9. Full treatment PLS and lasso models run using all data to predict all data, with input as

1015   first derivatives of the spectra rather than raw spectral intensity.

1016   Figure 10. Visible Spectra of two amphiboles from the Mineral Spectroscopy Server at Caltech

1017   (http://minerals.gps.caltech.edu/). Pargasite is from Oxbrow, NJ, plotted as 1.00 mm thick, while

1018   kaersutite is GRR #1029, plotted for 0.05 mm. The kaersutite spectrum is dominated by

1019   intervalence charge transfer bands, but the pargasite shows characteristic features arising from

1020   Fe2+ in M[4] (~1,000 nm, or 10,000 cm-1) and M[1] and M[3] (1400 nm, or 7,100 cm-1). The

1021   M[1]- M[3] site band is strongest in the alpha orientation perpendicular to the plane of the I-

1022   beams. The asymmetric M[4] site band is most intense in the beta direction across the I-beams.

1023   Figure 11. Normalized total pre-edge area plotted against the site distortion parameters angular

1024   variance, σ (left *y* axis) and quadratic elongation λ (right *y* axis, solid symbols). Error bars on

1025   these parameters are estimated to be ±0.001 for total pre-edge area, ±1° for σ, and ±0.001 for λ.

1026   These data indicate that overall pre-edge intensity is poorly correlated with site distortion as

1027   measured by these parameters.

1028   Figure 12. View down the x axis of the amphibole structure, with tetrahedral chains removed

1029   (top) and superimposed (bottom), showing how the M[3] site is surrounded by M[1] and M[2].

1030   The geometry of the M[3] site is strongly affected by the dimension/conformation of the other

1031    octahedra, in particular of M[1], where most of the oxidation related to deprotonation occurs.

1032    This arrangement may explain the trend in Figure 10 showing that the relationship between pre-

1033    edge area and site geometry is most apparent for the M[3] site.

1034    Figure 13. Summary diagram comparing root mean squared prediction errors associated with

1035    minimal (top) and full treatment (bottom) models. Shown are prediction errors for methods listed

1036    as Linear Edge, which uses the energy of the main absorption edge at the location where the

1037    normalized edge intensity has the highest $R^2$ correlation with $Fe^{3+}/\Sigma Fe$; Linear Ratio, which uses

1038    pre-edge energy at edge intensity of 0.38 for minimal treatment, edge intensity of 0.31 for full

1039    treatment; Linear Slope, which uses of the first derivative at every channel to select the best

1040    predictor channel; partial least-squares models on data and their first derivatives; and least

1041    absolute shrinkage and selection operator models (Lasso) results from data and their first

1042    derivatives.

1043    Figure 14. Comparison of PLS and lasso models for garnet data (left) from Dyar et al. (2012)

1044    against PLS and lasso results from this study for amphibole (right). Error bars in the direction of

1045    the x axis on all plots are ±1-3% absolute for Mossbauer data corrected for recoil-free fraction.

1046    The amphibole predictions are slightly less accurate than those for garnet because amphiboles

1047    are not isometric and thus display different spectra along the X, Y, and Z optical orientation

1048    directions.

1049    Figure 15.  PLS loadings and coefficients and lasso coefficients for garnet models from Figure

1050    12. As for amphibole, the predominance of information about Fe valence state is in the main-

1051    edge and EXAFS region indicated by the dashed lines for PLS and the vertical lines for the lasso.

49

**Table 1. Selected previous mineral and glass studies quantifying $Fe^{3+}/\Sigma Fe$ using XANES**

| Material | Method and part of spectrum used for quantification, notes | Citation |
|---|---|---|
| silicate glasses, minerals | Changes in amplitude of $Fe^{2+}$ and $Fe^{3+}$ Lorentzian peaks fit to pre-edge | Calas and Petiau (1983a) |
| pyrite, hematite, siderite, Fe metal | Observed orientation dependence for non-cubic minerals and varying magnitudes of **pre-edge** features | Dräger et al. (1988) |
| hematite, magnetite, and olivine | Universal calibration line based on **pre-edge** centroid area and hematite, magnetite, and olivine standards to predict $Fe^{2+}$ and $Fe^{3+}$ | Bajt et al. (1994) |
| almandine, fayalite, staurolite, aegirine, leucite, orthoclase | **Pre-edge** peak heights of model compounds | Henderson at al. (1995) |
| model compounds | **Pre-edge** intensities of 50 Fe complexes to assess pre-edge features as a function of symmetry and coordination | Westre et al. (1997) |
| olivine, pyroxene, amphibole, mica, tourmaline | Centroids of area-normalized **pre-edge** peaks for mineral groups shown to be distinct, requiring difference calibrations for each group | Delaney et al. (1998) |
| biotite, nontronite | **Pre-edge** peak position of oxidized vs. reduced samples | Manceau et al. (2000) |
| silicate glasses | Components fit to **pre-edge** used to create calibration curve | Bonnin-Masbah et al. (2001) |
| biotite | Created calibration for mica $Fe^{3+}/\Sigma Fe$ using pre-edge features | Dyar et al. (2001) |
| 8 grandidierites and some model compounds | Peak-area normalized **pre-edge** centroids of $^{[5]}Fe^{2+}$ are affected by substitution of $^{[6]}Fe^{3+}$ so Wilke et al. (2001) calibration standards must be carefully selected | Farges (2001) |
| mineral standards | Linear combination of fits to $Fe^{3+}$ and $Fe^{2+}$ peaks in **pre-edge** of standards used to identify valence state and coordination number in glasses | Galoisy et al. (2001) |
| 35 minerals and synthetic compounds | Position of peak-area normalized **pre-edge** centroid varies by 1.4±0.1 eV for $Fe^{2+}$ and $Fe^{3+}$ | Petit et al. (2001) |
| 30 minerals and synthetic compounds | Position of peak-area normalized **pre-edge** modeled with ≤3 pseudo-Voigt lineshapes to predict $Fe^{2+}$ and $Fe^{3+}$ with ±10mol% accuracy | Wilke et al. (2001) |
| enstatite, augite, aegirine, kaersutite, annite, phlogopite | Centroids of **pre-edge** spectra acquired along X, Y, Z optical orientations vary greatly, resulting in ±20% in $Fe^{3+}/\Sigma Fe$ for pyroxenes and amphiboles and ±10-15% for micas | Dyar et al. (2002a) |
| almandine, buergerite, scapolite, fayalite | Centroids of **pre-edge** spectra acquired along X, Y, Z optical orientation show no variation for isotropic garnet but considerable shift for uniaxial minerals | Dyar et al. (2002b) |
| orthopyroxenes | Non-linear changes in **main Fe K-edge** with composition, no change in $Fe^{3+}/\Sigma Fe$ | Giuli et al. (2002) |
| obsidian, magnetite, FeO | Used **main edge** position to infer $Fe^{3+}$ contents | Lytle and Pingitore (2002) |
| silicate glasses | Position of peak-area normalized **pre-edge** used | Wilke et al. (2002) |
| silicate glasses, fayalite, hematite, magnetite | Determined using linear combinations of end-member **pre-edge** spectra with 0% and 100% $Fe^{3+}$. Found that mineral standards were poor predictors of $Fe^{3+}/\Sigma Fe$ but glass standards worked well. | Berry et al. (2003) |
| Libyan desert glass | Used **pre-edge** spectra of mineral standards to predict $Fe^{3+}/\Sigma Fe$ in silicate glasses along with fits to pseudo-Voigt functions following Wilke et al. (2001) | <span style="color:red">Giuli et al. (2003)</span> |
| eclogite minerals | Applied Wilke et al. (2001) **pre-edge** calibration to predict $Fe^{3+}/\Sigma Fe$ in thin sections; used rotation test. | <span style="color:red">Schmid et al. (2003)</span> |
| silicate glass | Used **pre-edges** of 27 silicate glasses; showed no change in CN with oxidation for constant composition | Farges et al. (2004) |
| silicate glass | Compared wet chemical, Mössbauer, and XANES **pre-edge** results | Magnien et al. (2004) |
| basaltic glass | Compared wet chemical, Mössbauer, and XANES **pre-edge** results | Wilke et al. (2004, 2005) |
| impact glass | Applied Giuli et al. (2002) and Wilke et al. (2001) **pre-edge** calibrations to predict $Fe^{3+}/\Sigma Fe$ in impact glasses | <span style="color:red">Giuli et al. (2005)</span> |
| peralkaline glass | Applied **pre-edge** data from their own reference glasses and Wilke et al. (2001) calibration | Métrich et al. (2006) |
| silicate glass | Applied Berry et al. (2003 calibration and intensity-weighted **pre-edge** energy | O'Neill et al. (2006) |
| silicate glass | Applied Wilke et al. (2001) **pre-edge** calibration to predict $Fe^{3+}/\Sigma Fe$ in thin sections | Wilke et al. (2006) |
| Stardust extraterrestrial grains | Used intensity-weighted average of **pre-edge** components and Wilke et al. (2001) methods | <span style="color:red">Grossemy et al. (2007)</span> |

| silicate glass | Studied **pre-edges** and EXAFS of glasses to understand Fe coordination | Wilke et al. (2007) |
|---|---|---|
| komatiites | Compared **pre-edge** data of unknowns to their own MORB reference glasses | Berry et al. (2008) |
| impact glass | Applied Wilke et al. (2001) **pre-edge** calibrations to predict $Fe^{3+}/\Sigma Fe$ and Fe coordination in impact glasses | Giuli et al. (2008) |
| oxide and silicate glasses | Matched glass XAS spectra against powdered oxide standards to identify oxides and Wilke methods | Hurai et al. (2008) |
| iron-phosphate glasses | Assessed $Fe^{3+}$ contents in powdered samples using FeO, $Fe_2O_3$, $Fe_3O_4$, and $Fe_2(SO)_4$ standards | Qiu et al. (2008) |
| nuclear waste glass | Used Magnien et al. (2004) glass calibration based on **pre-edge** | Cochain et al. (2009) |
| silicate glasses | Compared **pre-edge** data of unknowns to their own reference glasses to create reference glasses | Cottrell et al. (2009) |
| minerals and glasses | Compared **pre-edge** data on mixed-valence reference glass standards | Forder et al. (2009) |
| silicate glasses | Compared **pre-edge** data of unknowns to their own reference glasses to create reference glasses | Kelley and Cottrell (2009) |
| LAP04840 chondrite | Compared **pre-edge** spectra from single crystal amphiboles to spectra from their own amphibole standards | Ota et al. (2009) |
| garnet | Compared **pre-edge** and **main-edge** data on garnet standards to develop calibration | Berry et al. (2010) |
| vivianite | Used Fityk program to fit **pre-edge** and derive valence information | Figueiredo et a. (2010) |
| phlogopite | Used Bajt et al. (1994) **pre-edge** calibration, different orientations of crystals, compared against Mössbauer | Scordari et al. (2010) |
| phonolite glass | Used **pre-edge** spectra of mineral standards to predict $Fe^{3+}/\Sigma Fe$ in silicate glasses along with fits to pseudo-Voigt functions following Wilke et al. (2001) | Giuli et al. (2011) |
| CI, CM chondrites | <span style="color:red">Applied Wilke et al. (2001) **pre-edge** calibrations and in-house powdered mineral standards</span> | <span style="color:red">Beck et al. (2012)</span> |
| garnet | Used Berry et al. (2010) **pre-edge** and **main-edge** data from garnet standards for calibration | Borfecchia et al. (2012) |
| garnet | Used multivariate analysis of **pre-edge** and **main-edge** data from in-house garnet standards for calibration | Dyar et al. (2012) |
| rhyolitic glass | Used **pre-edge** spectra of powdered mineral standards to predict $Fe^{3+}/\Sigma Fe$ in silicate glasses along with fits to pseudo-Voigt functions following Wilke et al. (2001) | Giuli et al. (2012) |
| basaltic glass | Used Cottrell et al. (2009) **pre-edge** glass calibration | Kelley and Cottrell (2012) |
| serpentine | Applied Wilke et al. (2001) **pre-edge** calibrations | Andreani et al. (2013) |
| garnet | Used Berry et al. (2010) **pre-edge** and **main-edge** data from garnet standards for calibration | Berry et al. (2013) |
| soda-lime silicate glass | Applied Wilke et al. (2001) **pre-edge** calibrations, showed that low-iron glasses can be photoreduced | Gonçalves Ferreira et al. (2013) |
| silicate glass | Used **pre-edge** peak position to confirm lack of $Fe^{2+}$ | Bingham et al. (2014) |
| amphibole | Applied Wilke et al. (2001) **pre-edge** calibrations to study of amphibole powders | <span style="color:red">Bonadiman et al. (2014)</span> |
| serpentine | Applied Wilke et al. (2001) **pre-edge** calibrations | <span style="color:red">Debret et al. (2014)</span> |
| biotite | Used Dyar et al. (2001) pre-edge calibration based on micas | Evans et al. (2014) |
| nakhlites | Fitted components to **pre-edge** and used method similar to Wilke et al. (2001) and Berry et al. (2003) | Hicks et al. (2014) |
| garnet, omphacite | Used **pre-edge** positions in almandine, augite, aegirine standards as references, noted orientation effects | Mino et al. (2014) |
| shergottites | Ratioed $Fe^{3+}$ to $Fe^{2+}$ components in **pre-edge** | Satake et al. (2014) |

## Table 2. Samples studied

| Sample code | Species* | Locality | Reference |
|---|---|---|---|
| 84-BM | magnesio-hastingsite | Dreiser Weiher, Germany, Brück-Raders cone, cognate | Dyar et al. (1993) |
| 86-BM | pargasite | Bullenmerri maar, Victoria, Australia | Dyar et al. (1993) |
| AK-M2 | pargasite | Harrat al Kishb, Saudi Arabia, Coleman locality H271 | Dyar et al. (1993) |
| DL-5 | kaersutite | Deadman Lake, California, Hill 2237 | Dyar et al. (1993); Oberti et al. (2012) |
| DL-5 HT | kaersutite | Deadman Lake, California, Hill 2237 | Oberti et al. (2012) |
| DL-7 | ferri-kaersutite | Deadman Lake, California, Hill 2237 | Dyar et al. (1993) |
| FA-861 | pargasite | Grenville Orogen, Ontario | Cosca et al. (1991) |
| Fr-11 | ferri-kaersutite | Massif Central, France, just east of Alleyras basalt flow | Dyar et al. (1993) |
| Fr-12 | ferri-kaersutite | Massif Central, France, Montgros, from oxidized vent agglomerate | Dyar et al. (1993); Oberti et al. (2012) |
| Fr-12 HT | ferri-kaersutite | As above, except heat-treated | Oberti et al. (2012) |
| Kakanui | Ti-rich pargasite | Kakanui, New Zealand, USNM 109647/50 | Dyar et al. (1993) |
| KAR | potassic-pargasite | Old Orefield, Pitkaranta, Karelia, Russia | Oberti et al. (2012) |
| KAR HT | "oxo-potassic-pargasite" | As above, except heat-treated | Oberti et al. (2012) |
| MIN-864 | magnesio-hornblende | Grenville Orogen, Ontario | Cosca et al. (1991) |
| PBM1B | tremolite | O'Neill Iron Mine, Sterling New Jersey | This study |
| PBM2 | pargasite | Location 2 Edenville (Warwick Town) NY | This study |
| PBM5 | pargasite | Warwick Location 5 Adams Property, Mountainside x Big Island Rds, Edenville, NY | This study |
| PBM6 | ferri-edenite | Warwick Location 6 PMB 15A pty, Swale with scapolite rock, pegmatite (ridge), FM (lower part) | This study |
| Tm | kaersutite | Easy Chair Crater, Lunar Crater, Nevada | Dyar et al. (1993) |
| Z2124 | pargasite | Zabargad island, Red Sea | Piccardo et al. (1993), Oberti et al. (2012) |
| Z2124-HT | "oxo-pargasite" | As above, except heat-treated | Oberti et al. (2012) |

 * Amphibole names are given according to Hawthorne et al. (2012). Names between "" refer to heat-treated samples.

**Table 3. Sample compositions and crystal-chemical formulas***

| | 84-BR | 86-BM | AK-M2 | DL-5 SREF | DL-5-HT SREF | DL-7 | FA861 | Fr-11 | Fr-12 SREF | Fr-12-HT SREF | Kakanui |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Oriented? | random | random | both | oriented | oriented | random | random | random | oriented | oriented | random |
| SiO$_2$ | 39.29 | 41.91 | 39.93 | 39.62 | 39.62 | 39.85 | 40.94 | 40.05 | 39.56 | 39.56 | 39.32 |
| Al$_2$O$_3$ | 13.85 | 14.46 | 14.83 | 13.54 | 13.54 | 14.39 | 13.28 | 14.48 | 13.8 | 13.8 | 13.54 |
| TiO$_2$ | 3.27 | 3.23 | 5.31 | 4.64 | 4.64 | 4.51 | 2.69 | 4.49 | 5.15 | 5.15 | 4.89 |
| FeO$_T$ | 10.51 | 7.97 | 11.04 | 11.80 | 11.80 | 13.90 | 15.97 | 12.88 | 10.46 | 10.46 | 11.02 |
| Cr$_2$O$_3$ | 0.02 | 0.77 | 0.02 | 0.01 | 0.01 | 0.00 | 0.00 | 0.02 | 0.03 | 0.03 | 0.00 |
| MgO | 13.77 | 15.16 | 12.84 | 11.61 | 11.61 | 11.26 | 10.01 | 11.92 | 12.71 | 12.71 | 12.31 |
| MnO | 0.10 | 0.11 | 0.09 | 0.13 | 0.13 | 0.20 | 0.27 | 0.09 | 0.10 | 0.10 | 0.14 |
| ZnO | n.a. | n.a. | n.a. | 0.10 | 0.10 | n.a. | n.a. | n.a. | 0.03 | 0.03 | n.a. |
| NiO | n.a. | n.a. | n.a. | 0.01 | 0.01 | n.a. | n.a. | n.a. | 0.03 | 0.03 | n.a. |
| CaO | 12.10 | 10.74 | 9.87 | 10.87 | 10.87 | 10.82 | 10.57 | 10.73 | 11.27 | 11.27 | 9.96 |
| Na$_2$O | 1.96 | 3.18 | 2.91 | 2.35 | 2.35 | 2.74 | 3.12 | 2.73 | 2.33 | 2.33 | 2.56 |
| K$_2$O | 2.18 | 1.21 | 1.10 | 1.64 | 1.64 | 1.50 | 1.04 | 1.35 | 1.48 | 1.48 | 2.06 |
| F | 0.00 | 0.00 | 0.00 | 0.14 | 0.14 | 0.20 | 0.05 | 0.00 | 0.09 | 0.09 | 0.18 |
| Cl | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 | 0.02 | 0.46 | 0.00 | 0.03 | 0.03 | 0.02 |
| H$_2$O | 1.41 | 1.13 | 1.03 | 0.86 | 0.00 | 0.90 | 1.43 | 0.48 | 0.07 | 0.02 | 1.14 |
| - O=F | - | - | - | 0.06 | 0.06 | 0.08 | 0.02 | - | 0.04 | 0.04 | 0.08 |
| - O=Cl | - | - | - | 0.00 | 0.00 | 0.00 | 0.10 | - | 0.01 | 0.01 | 0.00 |
| Sum | 98.37 | 99.87 | 98.97 | 97.07 | 96.40 | 100.29 | 102.71 | 99.22 | 97.07 | 97.02 | 97.06 |
| Mössbauer %Fe$^{3+}$† | 44 | 23 | 25 | 34 | 89 | 41 | 18 | 72 | 72 | 100 | 28 |
| Si | 5.874 | 6.066 | 5.944 | 6.051 | 6.051 | 5.922 | 5.985 | 5.945 | 5.972 | 5.972 | 5.990 |
| Al | 2.126 | 1.934 | 2.056 | 1.949 | 1.949 | 2.078 | 2.015 | 2.055 | 2.028 | 2.028 | 2.010 |
| Σ T cations | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 |
| Al | 0.315 | 0.533 | 0.547 | 0.489 | 0.489 | 0.443 | 0.481 | 0.479 | 0.428 | 0.428 | 0.422 |
| Fe$^{3+}$ | 0.582 | 0.230 | 0.344 | 0.666 | 1.348 | 0.699 | 0.346 | 1.158 | 1.274 | 1.321 | 0.414 |
| Ti | 0.368 | 0.352 | 0.594 | 0.533 | 0.533 | 0.504 | 0.494 | 0.501 | 0.585 | 0.585 | 0.560 |
| Cr | 0.002 | 0.088 | 0.002 | 0.001 | 0.001 | 0.011 | 0.000 | 0.002 | 0.004 | 0.004 | 0.000 |
| Zn | - | - | - | 0.011 | 0.011 | - | - | - | 0.003 | 0.003 | - |
| Ni | - | - | - | 0.000 | 0.000 | - | - | - | 0.000 | 0.000 | - |
| Mg | 3.066 | 3.268 | 2.847 | 2.641 | 2.618 | 2.492 | 2.180 | 2.635 | 2.706 | 2.659 | 2.793 |
| Fe$^{2+}$ | 0.667 | 0.529 | 0.666 | 0.659 | 0.000 | 0.851 | 1.499 | 0.211 | 0.000 | 0.000 | 0.811 |
| Mn$^{2+}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Σ C cations | 5.000 | 5.000 | 5.000 | 5.000 | 5.000 | 5.000 | 5.000 | 5.000 | 5.000 | 5.000 | 5.000 |
| Mg | 0.000 | 0.000 | 0.000 | 0.000 | 0.023 | 0.000 | 0.000 | 0.000 | 0.152 | 0.199 | 0.000 |
| Fe$^{2+}$ | 0.065 | 0.206 | 0.365 | 0.182 | 0.159 | 0.178 | 0.108 | 0.230 | 0.047 | 0.000 | 0.179 |
| Mn | 0.013 | 0.013 | 0.011 | 0.017 | 0.017 | 0.025 | 0.033 | 0.011 | 0.013 | 0.013 | 0.018 |
| Ca | 1.922 | 1.666 | 1.574 | 1.779 | 1.779 | 1.723 | 1.656 | 1.707 | 1.788 | 1.788 | 1.626 |
| Na | 0.000 | 0.115 | 0.050 | 0.022 | 0.022 | 0.074 | 0.203 | 0.052 | 0.000 | 0.000 | 0.177 |
| Σ B cations | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 |
| Ca | 0.016 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.035 | 0.035 | 0.000 |
| Na | 0.568 | 0.777 | 0.790 | 0.674 | 0.674 | 0.715 | 0.681 | 0.734 | 0.682 | 0.682 | 0.579 |
| K | 0.416 | 0.223 | 0.209 | 0.320 | 0.320 | 0.284 | 0.194 | 0.256 | 0.285 | 0.285 | 0.400 |
| Σ A cations | 1.000 | 1.000 | 0.999 | 0.994 | 0.994 | 0.999 | 0.875 | 0.990 | 1.002 | 1.002 | 0.979 |
| OH | 1.476 | 1.496 | 1.023 | 0.682 | 0.000 | 0.892 | 1.394 | 0.475 | 0.070 | 0.020 | 1.158 |
| F | 0.000 | 0.000 | 0.000 | 0.068 | 0.068 | 0.094 | 0.023 | 0.000 | 0.043 | 0.043 | 0.087 |
| Cl | 0.000 | 0.000 | 0.000 | 0.003 | 0.003 | 0.005 | 0.114 | 0.000 | 0.008 | 0.008 | 0.005 |
| O | 0.524 | 0.504 | 0.977 | 1.247 | 1.929 | 1.009 | 0.469 | 1.525 | 1.879 | 1.929 | 0.750 |
| Σ W anions | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 |
| Calc. %Fe$^{3+}$ | 44 | 24 | 25 | 44 | 89 | 41 | 18 | 72 | 96 | 100 | 29 |

*Formulas calculated based on 24 (O,Cl,F) apfu and 2 (O,OH,Cl,F) apfu and taking into account the Fe$^{3+}$/Fe$^{2+}$ ratio obtained from Mössbauer or SREF analysis; n.a. = not analyzed.
†%Fe$^{3+}$ calculated from Mössbauer peak areas and then corrected for differential recoil-free fraction as described in Dyar et al. (1993).

# Table 3, continued. Sample Compositions and crystal-chemical formulas *

| | KAR SREF | KAR-HT SREF | MIN864 | PBM1B | PBM2 | PBM5 | PBM6 | Tm | Z2124 SREF | Z2124-HT SREF |
|---|---|---|---|---|---|---|---|---|---|---|
| Oriented? | oriented | oriented | random | random | random | random | random | both | oriented | oriented |
| $SiO_2$ | 39.54 | 39.54 | 44.53 | 57.53 | 43.42 | 40.48 | 47.95 | 39.52 | 47.48 | 47.48 |
| $Al_2O_3$ | 0.79 | 15.47 | 10.15 | 0.67 | 10.40 | 14.68 | 8.19 | 14.03 | 9.56 | 9.56 |
| $TiO_2$ | 15.47 | 0.79 | 0.91 | 0.00 | 1.13 | 0.32 | 0.32 | 5.87 | 0.34 | 0.34 |
| $FeO_T$ | 0.01 | 14.78 | 16.81 | 4.38 | 13.50 | 10.32 | 2.38 | 12.22 | 4.65 | 4.65 |
| $Cr_2O_3$ | 14.78 | 0.01 | 0.00 | 0.00 | 0.00 | 0.01 | 0.03 | 0.00 | 1.38 | 1.38 |
| MgO | 0.59 | 10.31 | 10.40 | 21.75 | 12.70 | 12.93 | 21.81 | 11.71 | 19.48 | 19.48 |
| MnO | 0.00 | 0.59 | 0.33 | 0.06 | 0.24 | 0.38 | 0.05 | 0.17 | 0.02 | 0.02 |
| ZnO | 0.00 | 0.00 | n.a | n.a | n.a | n.a | n.a | n.a | 0.00 | 0.00 |
| NiO | 0.00 | 0.00 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | 0.00 | 0.00 |
| CaO | 10.31 | 12.03 | 11.59 | 13.26 | 11.63 | 11.96 | 12.39 | 11.10 | 10.49 | 10.49 |
| $Na_2O$ | 12.03 | 1.30 | 1.48 | 0.24 | 2.82 | 2.31 | 2.72 | 2.81 | 3.77 | 3.77 |
| $K_2O$ | 1.30 | 2.64 | 1.21 | 0.15 | 1.05 | 1.79 | 0.65 | 1.29 | 0.56 | 0.56 |
| F | 2.64 | 1.30 | 0.15 | 1.29 | 2.30 | 2.01 | 2.39 | 0.00 | 0.10 | 0.10 |
| Cl | 1.20 | 0.00 | 0.08 | 0.03 | 0.16 | 0.33 | 0.09 | 0.00 | 0.00 | 0.00 |
| $H_2O$ | 1.30 | 0.00 | 1.55 | 1.35 | 0.70 | 1.04 | 0.95 | 0.27 | 2.00 | 1.52 |
| - O=F | 0.55 | 0.55 | 0.08 | 0.54 | 0.97 | 0.85 | 1.01 | - | 0.10 | 0.10 |
| - O=Cl | 0.00 | 0.00 | 0.06 | 0.01 | 0.04 | 0.07 | 0.02 | - | 0.00 | 0.00 |
| Sum | 99.41 | 99.51 | 99.10 | 99.93 | 99.05 | 97.64 | 98.89 | 98.99 | 99.79 | 99.31 |
| Mössbauer $\%Fe^{3+}$† | 28 | 100 | 33 | 26 | 18 | 15 | 4 | 77 | 36 | 100 |
| Si | 5.934 | 5.934 | 6.655 | 7.934 | 6.501 | 6.095 | 6.817 | 5.895 | 6.729 | 6.729 |
| Al | 2.066 | 2.066 | 1.345 | 0.066 | 1.499 | 1.905 | 1.183 | 2.105 | 1.271 | 1.271 |
| Σ T cations | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 |
| Al | 0.671 | 0.671 | 0.443 | 0.043 | 0.337 | 0.701 | 0.190 | 0.362 | 0.326 | 0.326 |
| $Fe^{3+}$ | 0.651 | 1.852 | 0.685 | 0.130 | 0.297 | 0.195 | 0.012 | 1.166 | 0.090 | 0.551 |
| Ti | 0.089 | 0.089 | 0.102 | 0.000 | 0.127 | 0.036 | 0.034 | 0.658 | 0.036 | 0.036 |
| Cr | 0.001 | 0.001 | 0.000 | 0.000 | 0.000 | 0.001 | 0.003 | 0.000 | 0.155 | 0.155 |
| Zn | 0.000 | 0.000 | - | - | - | - | - | - | 0.000 | 0.000 |
| Ni | 0.000 | 0.000 | - | - | - | - | - | - | 0.000 | 0.000 |
| Mg | 2.305 | 2.305 | 2.315 | 4.468 | 2.832 | 2.900 | 4.618 | 2.602 | 4.112 | 4.112 |
| $Fe^{2+}$ | 1.205 | 0.004 | 1.417 | 0.359 | 1.393 | 1.105 | 0.143 | 0.212 | 0.281 | 0.000 |
| $Mn^{2+}$ | 0.075 | 0.075 | 0.038 | 0.000 | 0.014 | 0.048 | 0.000 | 0.000 | 0.000 | 0.000 |
| Σ C cations | 4.997 | 4.997 | 5.000 | 5.000 | 5.000 | 4.986 | 5.000 | 5.000 | 5.000 | 5.000 |
| Mg | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.180 |
| $Fe^{2+}$ | 0.000 | 0.000 | 0.000 | 0.016 | 0.000 | 0.000 | 0.128 | 0.146 | 0.180 | 0.000 |
| Mn | 0.000 | 0.000 | 0.004 | 0.007 | 0.016 | 0.000 | 0.006 | 0.021 | 0.002 | 0.002 |
| Ca | 1.935 | 1.935 | 1.856 | 1.960 | 1.866 | 1.930 | 1.866 | 1.774 | 1.593 | 1.593 |
| Na | 0.065 | 0.065 | 0.140 | 0.017 | 0.118 | 0.070 | 0.000 | 0.059 | 0.255 | 0.255 |
| Σ B cations | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 |
| Ca | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.022 | 0.000 | 0.000 | 0.000 |
| Na | 0.313 | 0.313 | 0.289 | 0.047 | 0.701 | 0.604 | 0.750 | 0.754 | 0.811 | 0.811 |
| K | 0.505 | 0.505 | 0.231 | 0.026 | 0.201 | 0.344 | 0.118 | 0.245 | 0.101 | 0.101 |
| Σ A cations | 0.818 | 0.818 | 0.520 | 0.073 | 0.902 | 0.948 | 0.890 | 0.999 | 0.912 | 0.912 |
| OH | 1.201 | 0.000 | 1.540 | 1.269 | 0.699 | 1.044 | 0.901 | 0.318 | 1.890 | 1.437 |
| F | 0.617 | 0.617 | 0.071 | 0.563 | 1.089 | 0.957 | 1.075 | 0.000 | 0.045 | 0.045 |
| Cl | 0.000 | 0.000 | 0.020 | 0.007 | 0.041 | 0.084 | 0.022 | 0.000 | 0.000 | 0.000 |
| O | 0.182 | 1.383 | 0.369 | 0.161 | 0.171 | 0.000 | 0.002 | 1.682 | 0.065 | 0.518 |
| Σ W anions | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.085 | 2.000 | 2.000 | 2.000 | 2.000 |
| Calc. $\%Fe^{3+}$ | 35 | 100 | 33 | 26 | 18 | 15 | 4 | 77 | 36 | 100 |

*Formulas calculated based on 24 (O,Cl,F) apfu and 2 (O,OH,Cl,F) apfu and taking into account the $Fe^{3+}/Fe^{2+}$ ratio obtained from Mössbauer or SREF analysis; n.a.= not analyzed. †$\%Fe^{3+}$ calculated from Mössbauer peak areas and then corrected for differential recoil-free fraction as described in Dyar et al. (1993).

**Table 4. Parameters of pre-edge fits using full treatment models**

| | MS %$Fe^{3+}$ | Area | Centroid | FWHM | %Area | Area | Centroid | FWHM | %Area | Area | Centroid | FWHM | %Area | Area | Centroid | FWHM | %Area | $\chi2$ | ANPC |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Oriented Crystals** | | | | | | | | | | | | | | | | | | | |
| DL-5-HT X | 89 | | | | | 0.01 | 7112.57 | 1.34 | 13 | 0.08 | 7114.16 | 1.68 | 87 | | | | | 0.86 | 7113.95 |
| DL-5-HT Y | 89 | | | | | 0.01 | 7112.47 | 1.30 | 15 | 0.05 | 7113.99 | 1.72 | 85 | | | | | 0.18 | 7113.76 |
| DL-5-HT Z | 89 | | | | | 0.03 | 7112.65 | 1.45 | 48 | 0.03 | 7114.08 | 1.57 | 52 | | | | | 0.27 | 7113.39 |
| DL-5 X | 32 | 0.04 | 7111.63 | 2.37 | 49 | 0.01 | 7112.94 | 1.06 | 8 | 0.04 | 7113.94 | 2.26 | 43 | | | | | 0.21 | 7112.74 |
| DL-5 Y | 32 | 0.04 | 7111.64 | 2.43 | 50 | 0.01 | 7112.91 | 1.00 | 8 | 0.03 | 7113.97 | 2.24 | 42 | | | | | 0.15 | 7112.71 |
| DL-5 Z | 32 | 0.03 | 7111.76 | 2.39 | 48 | 0.00 | 7113.04 | 0.88 | 3 | 0.03 | 7114.01 | 2.51 | 49 | | | | | 0.08 | 7112.90 |
| Fr-12-B X | 95 | | | | | 0.03 | 7112.68 | 1.37 | 38 | 0.04 | 7114.11 | 1.68 | 62 | | | | | 0.18 | 7113.56 |
| Fr-12-B Y | 95 | | | | | 0.03 | 7112.66 | 1.40 | 38 | 0.05 | 7114.15 | 1.61 | 62 | | | | | 0.24 | 7113.59 |
| Fr-12-B Z | 95 | | | | | 0.02 | 7112.71 | 1.26 | 29 | 0.04 | 7114.16 | 1.60 | 71 | | | | | 0.24 | 7113.74 |
| PAR-HT X | 100 | | | | | 0.04 | 7112.68 | 1.38 | 40 | 0.05 | 7114.12 | 1.71 | 60 | | | | | 0.57 | 7113.54 |
| PAR-HT Y | 100 | | | | | 0.03 | 7112.68 | 1.43 | 41 | 0.05 | 7114.16 | 1.67 | 59 | | | | | 0.53 | 7113.56 |
| PAR-HT Z | 100 | | | | | 0.03 | 7112.74 | 1.29 | 44 | 0.03 | 7114.17 | 1.60 | 56 | | | | | 0.38 | 7113.54 |
| PAR X | 28 | 0.05 | 7112.05 | 2.85 | 65 | 0.00 | 7113.20 | 0.90 | 5 | 0.02 | 7114.27 | 1.82 | 29 | | | | | 0.13 | 7112.77 |
| PAR Y | 28 | 0.05 | 7112.08 | 2.78 | 62 | 0.01 | 7113.16 | 1.00 | 7 | 0.02 | 7114.30 | 1.76 | 31 | | | | | 0.09 | 7112.85 |
| PAR Z | 28 | 0.02 | 7111.89 | 2.21 | 40 | 0.00 | 7112.17 | 0.50 | 1 | 0.03 | 7113.83 | 2.25 | 59 | | | | | 0.12 | 7113.04 |
| Z2124-HT X | 100 | | | | | 0.01 | 7112.68 | 1.38 | 16 | 0.08 | 7114.19 | 1.66 | 84 | | | | | 0.78 | 7113.95 |
| Z2124-HT Y | 100 | | | | | 0.01 | 7112.44 | 1.20 | 10 | 0.08 | 7114.04 | 1.86 | 90 | | | | | 0.76 | 7113.88 |
| Z2124-HT Z | 100 | | | | | 0.03 | 7112.64 | 1.37 | 35 | 0.05 | 7114.14 | 1.90 | 65 | | | | | 0.53 | 7113.62 |
| Z2124 X | 36 | 0.03 | 7112.00 | 2.23 | 44 | 0.01 | 7113.06 | 1.03 | 20 | 0.02 | 7114.30 | 1.45 | 37 | | | | | 0.29 | 7113.06 |
| Z2124 Y | 36 | 0.05 | 7112.12 | 2.35 | 59 | 0.01 | 7112.97 | * | 10 | 0.02 | 7114.30 | 1.54 | 30 | | | | | 0.35 | 7112.87 |
| Z2124 Z | 36 | 0.01 | 7111.20 | 1.54 | 16 | 0.03 | 7112.64 | 1.80 | 49 | 0.02 | 7114.25 | 1.57 | 35 | | | | | 0.30 | 7112.97 |
| AK-M2 X | 25 | 0.07 | 7112.58 | 2.93 | 79 | 0.00 | 7113.36 | 0.66 | 1 | 0.02 | 7114.39 | 1.62 | 19 | | | | | 0.17 | 7112.94 |
| AK-M2 Y | 25 | 0.08 | 7111.90 | 2.51 | 66 | 0.01 | 7113.25 | 1.22 | 8 | 0.03 | 7114.48 | 1.93 | 26 | | | | | 0.44 | 7112.68 |
| AK-M2 Z | 25 | 0.03 | 7111.64 | 1.82 | 48 | 0.02 | 7113.06 | 1.46 | 29 | 0.02 | 7114.38 | 1.67 | 23 | | | | | 0.19 | 7112.68 |
| Fr-12 X | 95 | | | | | 0.03 | 7112.83 | 1.43 | 28 | 0.07 | 7114.28 | 1.55 | 72 | | | | | 0.09 | 7113.87 |
| Fr-12 Y | 95 | | | | | 0.02 | 7112.86 | 1.31 | 32 | 0.05 | 7114.27 | 1.57 | 68 | | | | | 0.07 | 7113.82 |
| Fr-12 Z | 95 | | | | | 0.02 | 7112.87 | 1.30 | 31 | 0.05 | 7114.30 | 1.51 | 69 | | | | | 0.08 | 7113.85 |
| Tm X | 77 | 0.01 | 7111.50 | 1.50 | 13 | 0.03 | 7112.84 | 1.42 | 40 | 0.04 | 7114.29 | 1.61 | 47 | | | | | 0.08 | 7113.36 |
| Tm Y | 77 | 0.01 | 7111.64 | 1.50 | 12 | 0.02 | 7112.89 | 1.35 | 29 | 0.04 | 7114.08 | 2.07 | 59 | | | | | 0.08 | 7113.43 |
| Tm Z | 77 | 0.01 | 7111.15 | 1.50 | 11 | 0.03 | 7112.99 | 1.92 | 50 | 0.02 | 7114.45 | 1.42 | 39 | | | | | 0.27 | 7113.37 |
| **Randomly-Oriented** | | | | | | | | | | | | | | | | | | | |
| Tm | 77 | | | | | 0.03 | 7112.31 | 2.50 | 40 | 0.01 | 7112.82 | 1.01 | 14 | 0.03 | 7114.23 | 1.88 | 47 | 0.06 | 7113.28 |
| PBM-6 | 4 | 0.02 | 7111.26 | 1.47 | 31 | 0.02 | 7112.56 | 1.83 | 23 | 0.04 | 7113.97 | 2.90 | 46 | | | | | 0.18 | 7112.81 |
| PBM-5 | 15 | 0.03 | 7111.42 | 1.70 | 47 | 0.00 | 7112.34 | 0.63 | 2 | 0.01 | 7113.05 | 1.35 | 16 | 0.03 | 7113.96 | 2.63 | 35 | 0.18 | 7112.59 |
| PBM-2 | 18 | 0.00 | 7109.72 | 1.27 | 3 | 0.03 | 7111.38 | 1.69 | 35 | 0.02 | 7112.82 | 1.85 | 24 | 0.03 | 7114.16 | 3.18 | 38 | 0.06 | 7112.74 |
| PBM-1B | 26 | 0.03 | 7111.50 | 1.89 | 42 | 0.00 | 7112.39 | 0.44 | 2 | 0.03 | 7114.12 | 2.11 | 40 | 0.01 | 7113.00 | 1.09 | 17 | 0.27 | 7112.81 |
| MIN-864 | 38 | 0.03 | 7112.00 | 2.39 | 51 | 0.03 | 7114.36 | 1.89 | 41 | 0.00 | 7112.37 | 0.72 | 2 | 0.00 | 7113.20 | 0.92 | 6 | 0.05 | 7113.04 |
| Kakanui | 29 | 0.02 | 7111.55 | 1.82 | 42 | 0.02 | 7113.18 | 1.71 | 42 | 0.00 | 7114.29 | 0.96 | 8 | 0.00 | 7115.03 | 1.15 | 8 | 0.08 | 7112.73 |
| Fr-12 | 95 | | | | | | | | | 0.02 | 7112.82 | 1.36 | 31 | 0.05 | 7114.31 | 1.42 | 69 | 0.09 | 7113.85 |
| Fr-11 | 66 | 0.04 | 7111.83 | 2.25 | 44 | 0.01 | 7113.06 | 1.34 | 17 | 0.03 | 7114.33 | 1.74 | 35 | 0.00 | 7115.79 | 1.15 | 4 | 0.08 | 7113.05 |
| FA-861 | 21 | 0.03 | 7111.53 | 1.92 | 45 | 0.02 | 7113.10 | 1.64 | 32 | 0.01 | 7114.54 | 1.72 | 21 | 0.00 | 7115.62 | 0.74 | 2 | 0.08 | 7112.74 |
| DL-7 | 40 | 0.03 | 7112.13 | 2.42 | 51 | 0.01 | 7114.94 | 1.30 | 13 | 0.01 | 7113.03 | 1.10 | 9 | 0.02 | 7114.06 | 1.53 | 27 | 0.05 | 7113.10 |
| AK-M2 | 25 | 0.02 | 7111.50 | 1.80 | 44 | 0.01 | 7112.90 | 1.12 | 16 | 0.02 | 7114.02 | 1.92 | 35 | 0.00 | 7115.49 | 1.04 | 5 | 0.10 | 7112.80 |
| 86-BM | 24 | 0.06 | 7112.64 | 3.26 | 80 | 0.01 | 7114.54 | 1.36 | 13 | 0.00 | 7111.65 | 1.51 | 6 | 0.00 | 7113.38 | 0.64 | 1 | 0.11 | 7112.84 |
| 84-BR | 43 | 0.03 | 7111.81 | 2.27 | 36 | 0.00 | 7113.08 | 1.12 | 6 | 0.05 | 7114.00 | 2.31 | 58 | | | | | 0.09 | 7113.16 |

MS %$Fe^{3+}$ = Percentage of $Fe^{3+}$ as measured by Mössbauer spectroscopy and corrected for recoil-free fraction. Area is in units of normalized intensity. Centroid and FWHM (full width at half peak maximum) are in units of eV, and % area is the relative % of the total pre-edge energy in that peak. $\chi^2$ is the fit of the summed peaks to the data, and ANPC is the area-normalized peak centroid that divides all the spectra area in half.

**Table 5. RMSE accuracies and $R^2$ values for linear prediction models tested**

| Treatment | Method | Linear Centroid RMSE | $R^2$ | Linear Edge RMSE | $R^2$ | Linear Ratio RMSE | $R^2$ | Linear Slope RMSE | $R^2$ |
|---|---|---|---|---|---|---|---|---|---|
| Minimal | X from X | n.a. | n.a. | 8.9 | 0.93 | 9.7 | 0.92 | 6.9 | 0.96 |
| Minimal | Y from Y | n.a. | n.a. | 10.3 | 0.91 | 14.7 | 0.81 | 15.2 | 0.81 |
| Minimal | Z from Z | n.a. | n.a. | 5.0 | 0.98 | 5.9 | 0.97 | 6.9 | 0.96 |
| Minimal | X or Y from X and Y | n.a. | n.a. | 9.7 | 0.91 | 15.2 | 0.78 | 20.0 | 0.68 |
| Minimal | X, Y, or Z from all X, Y, and Z | n.a. | n.a. | 10.9 | 0.89 | 15.0 | 0.79 | 11.9 | 0.87 |
| Minimal | random from random | n.a. | n.a. | 14.5 | 0.72 | 14.6 | 0.73 | 14.1 | 0.73 |
| Minimal | random from X, Y, and Z | n.a. | n.a. | 15.4 | 0.69 | 11.4 | 0.84 | 16.2 | 0.65 |
| Minimal | all from all | n.a. | n.a. | 13.8 | 0.84 | 11.9 | 0.88 | 23.4 | 0.58 |
| Full | X from X | 16.2 | 0.77 | 9.1 | 0.93 | 5.5 | 0.97 | 5.5 | 0.97 |
| Full | Y from Y | 10.4 | 0.91 | 12.7 | 0.87 | 9.2 | 0.93 | 15.0 | 0.83 |
| Full | Z from Z | 13.1 | 0.85 | 2.7 | 0.99 | 9.3 | 0.93 | 2.6 | 0.99 |
| Full | X or Y from X and Y | 13.2 | 0.84 | 10.6 | 0.90 | 8.2 | 0.94 | 19.3 | 0.70 |
| Full | X, Y, or Z from all X, Y, and Z | 12.5 | 0.85 | 10.7 | 0.89 | 8.6 | 0.93 | 17.3 | 0.72 |
| Full | random from random | 13.7 | 0.76 | 18.1 | 0.56 | 25.4 | 0.38 | 13.3 | 0.76 |
| Full | random from X, Y, and Z | 12.2 | 0.80 | 14.7 | 0.72 | 12.6 | 0.80 | 17.1 | 0.63 |
| Full | all from all | 12.5 | 0.87 | 12.3 | 0.87 | 10.7 | 0.90 | 23.9 | 0.54 |

n.a. = not analyzed

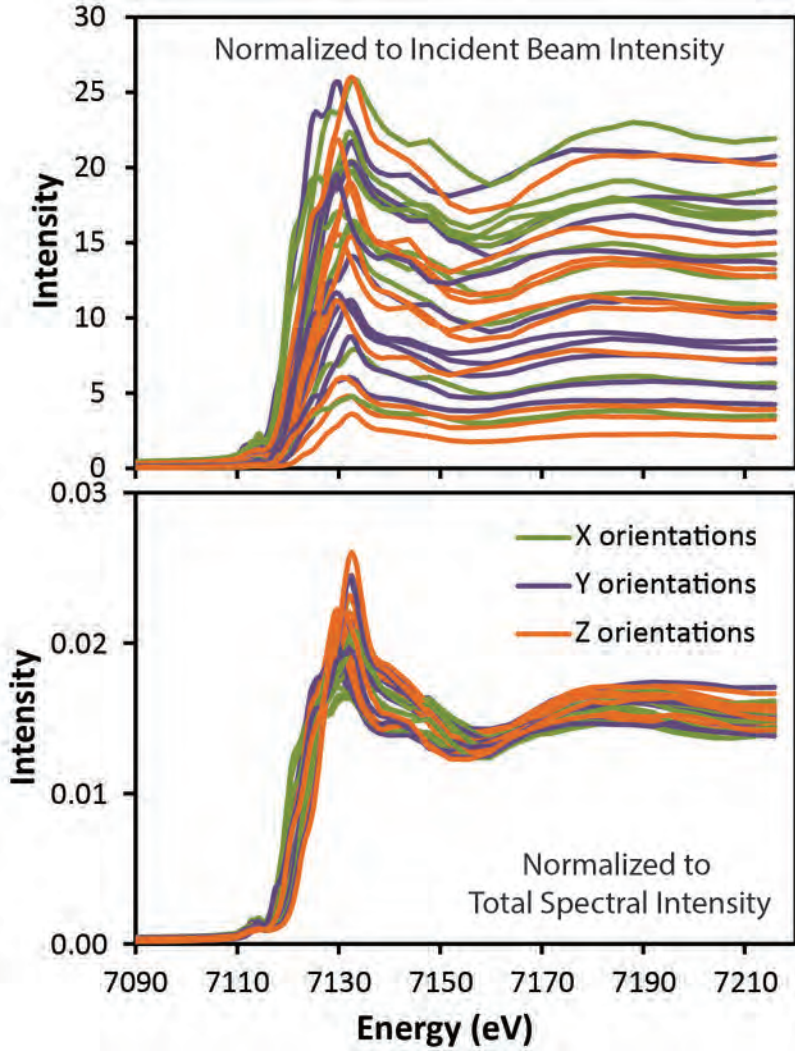**Table 6. RMSE accuracies and $R^2$ values for multivariate prediction models tested**

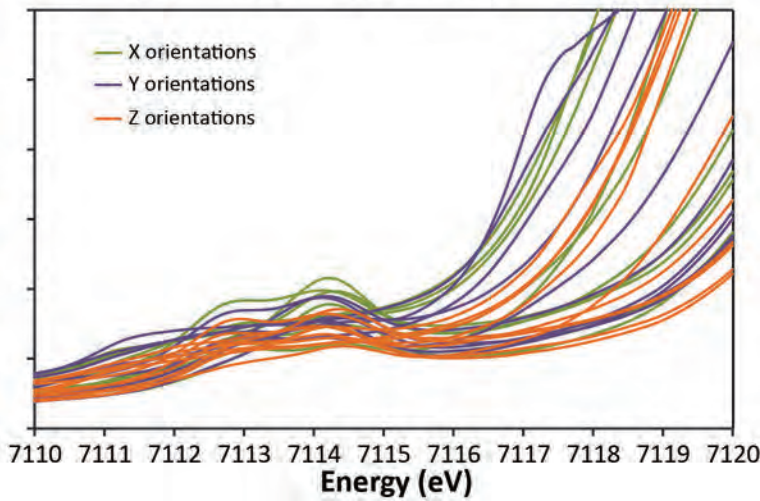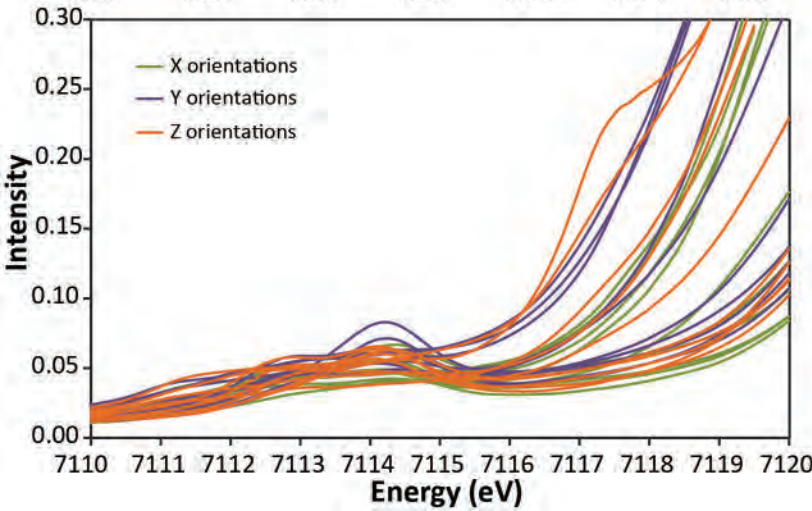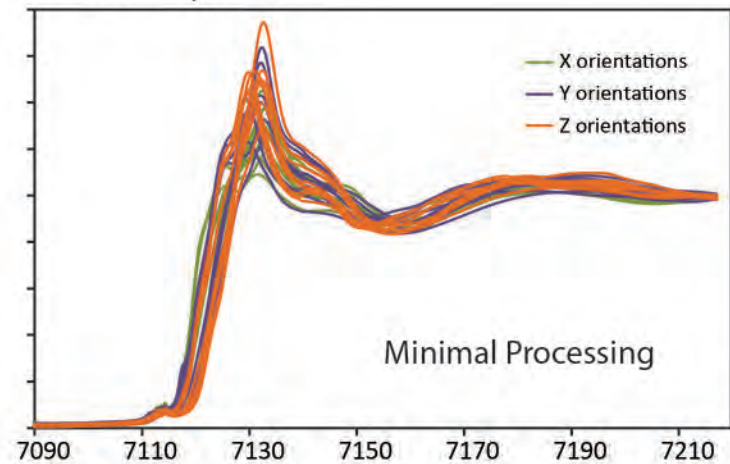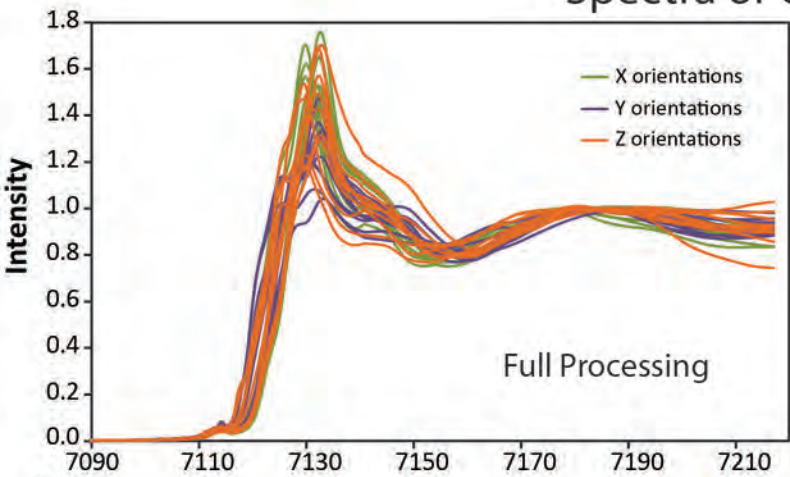| Treatment | Method | Raw Spectra PLS* RMSE | Raw Spectra PLS* $R^2$ | Raw Spectra Lasso RMSE | Raw Spectra Lasso $R^2$ | First Derivative Spectra PLS* RMSE | First Derivative Spectra PLS* $R^2$ | First Derivative Spectra Lasso RMSE | First Derivative Spectra Lasso $R^2$ |
|---|---|---|---|---|---|---|---|---|---|
| Minimal | X from X | 1.06 | 1.00 | 0.00 | 1.00 | 1.06 | 1.00 | 0.00 | 1.00 |
| Minimal | Y from Y | 0.24 | 1.00 | 7.22 | 0.95 | 0.24 | 1.00 | 7.22 | 0.95 |
| Minimal | Z from Z | 0.34 | 1.00 | 9.26 | 0.91 | 0.34 | 1.00 | 9.26 | 0.91 |
| Minimal | X or Y from X and Y | 2.67 | 0.99 | 6.23 | 0.96 | 2.67 | 0.99 | 6.24 | 0.96 |
| Minimal | X, Y, or Z from all X, Y, and Z | 3.35 | 0.99 | 7.87 | 0.94 | 3.36 | 0.99 | 7.87 | 0.94 |
| Minimal | random from random | 1.60 | 0.99 | 31.15 | 0.39 | 1.60 | 1.00 | 31.14 | 0.40 |
| Minimal | random from X, Y, and Z | 15.61 | 0.65 | 19.42 | 0.45 | 15.61 | 0.64 | 19.42 | 0.46 |
| Minimal | all from all | 5.48 | 0.97 | 9.73 | 0.92 | 5.48 | 0.97 | 9.74 | 0.92 |
| Full | X from X | 0.36 | 1.00 | 0.00 | 1.00 | 0.36 | 1.00 | 0.00 | 1.00 |
| Full | Y from Y | 0.31 | 1.00 | 11.84 | 0.86 | 0.31 | 1.00 | 11.84 | 0.86 |
| Full | Z from Z | 0.31 | 1.00 | 9.69 | 0.91 | 0.31 | 1.00 | 9.69 | 0.91 |
| Full | X or Y from X and Y | 3.75 | 0.98 | 9.32 | 0.92 | 3.75 | 0.99 | 9.33 | 0.92 |
| Full | X, Y, or Z from all X, Y, and Z | 3.50 | 0.99 | 9.89 | 0.91 | 3.50 | 0.99 | 9.89 | 0.90 |
| Full | random from random | 1.94 | 0.99 | 27.85 | 0.11 | 1.92 | 0.99 | 27.85 | 0.11 |
| Full | random from X, Y, and Z | 13.70 | 0.73 | 14.12 | 0.71 | 13.70 | 0.72 | 14.11 | 0.71 |
| Full | all from all | 6.18 | 0.97 | 10.56 | 0.91 | 6.17 | 0.97 | 10.56 | 0.90 |

*PLS models all using 6 components.

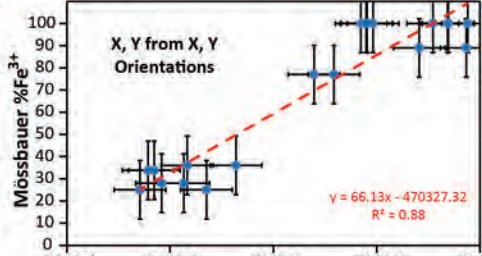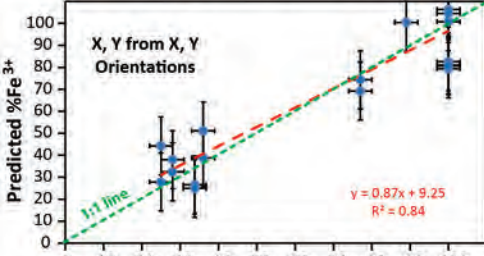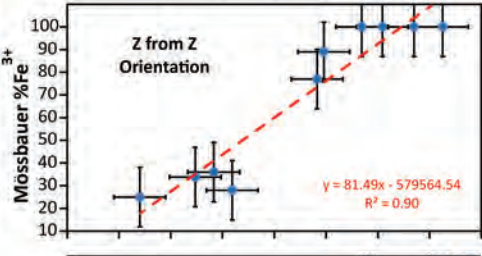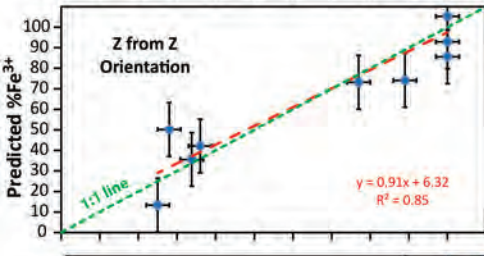Table 7. Relevant Structure REFinement (SREF) data for selected samples*

| | $M(1)$ $Fe^{2+}$ | $M(1)$ $Fe^{3+}$ | $M(2)$ $Fe^{2+}$ | $M(2)$ $Fe^{3+}$ | $M(3)$ $Fe^{2+}$ | $M(3)$ $Fe^{3+}$ | $M(4)$ $Fe^{2+}$ |
|---|---|---|---|---|---|---|---|
| | Site populations (atoms per formula unit) | | | | | | |
| DL-5 | 0.50 | 0.09 | 0.00 | 0.43 | 0.25 | 0.15 | 0.10 |
| DL-5-HT | 0.16 | 0.76 | 0.00 | 0.19 | 0.00 | 0.40 | 0.00 |
| Fr-12 | 0.04 | 0.74 | 0.00 | 0.25 | 0.01 | 0.28 | 0.00 |
| Fr-12-HT | 0.00 | 0.78 | 0.00 | 0.25 | 0.00 | 0.29 | 0.00 |
| KAR | 0.73 | 0.00 | 0.02 | 0.65 | 0.46 | 0.00 | 0.00 |
| KAR-HT | 0.00 | 1.11 | 0.00 | 0.46 | 0.00 | 0.28 | 0.00 |
| Z2124 | 0.11 | 0.00 | 0.09 | 0.09 | 0.08 | 0.00 | 0.18 |
| Z2124-HT | 0.00 | 0.38 | 0.00 | 0.08 | 0.00 | 0.09 | 0.00 |
| | % of total Fe in each valence state and site | | | | | | |
| DL-5 | 33 | 6 | 0 | 28 | 17 | 10 | 6 |
| DL-5-HT | 11 | 50 | 0 | 13 | 0 | 26 | 0 |
| Fr-12 | 3 | 56 | 0 | 19 | 1 | 21 | 0 |
| Fr-12-HT | 0 | 59 | 0 | 19 | 0 | 22 | 0 |
| KAR | 39 | 0 | 1 | 35 | 25 | 0 | 0 |
| KAR-HT | 0 | 60 | 0 | 25 | 0 | 15 | 0 |
| Z2124 | 30 | 0 | 24 | 24 | 22 | 0 | 0 |
| Z2124-HT | 0 | 68 | 0 | 16 | 0 | 16 | 0 |
| | Distortion parameters for the $M(1\text{-}3)$ sites | | | | | | |
| | $M(1)$ $\lambda^{\dagger}$ | $M(1)$ $\sigma^{\dagger}$ | $M(2)$ $\lambda$ | $M(2)$ $\sigma$ | $M(3)$ $\lambda$ | $M(3)$ $\sigma$ | |
| DL-5 | 1.0146 | 45.88 | 1.0091 | 27.98 | 1.0229 | 72.61 | |
| DL-5-HT | 1.0178 | 53.09 | 1.0111 | 34.06 | 1.0218 | 68.54 | |
| Fr-12 | 1.0179 | 52.82 | 1.0106 | 32.37 | 1.0217 | 68.33 | |
| Fr-12-HT | 1.0172 | 51.34 | 1.0108 | 33.04 | 1.0211 | 66.53 | |
| KAR | 1.0163 | 51.23 | 1.0073 | 22.71 | 1.0276 | 87.09 | |
| KAR-HT | 1.0188 | 58.07 | 1.0110 | 34.06 | 1.0228 | 70.85 | |
| Z2124 | 1.0129 | 41.79 | 1.0072 | 22.99 | 1.0181 | 58.19 | |
| Z2124-HT | 1.0120 | 38.47 | 1.0086 | 26.97 | 1.0158 | 51.06 | |

*Site populations from Oberti et al., in preparation. [†]Site distortion parameters as described in the text.

**Spectra of Oriented Crystals**

Full Processing

Minimal Processing

X orientations
Y orientations
Z orientations

Left column figures (Predicted %Fe³⁺ vs Mossbauer %Fe³⁺):

**X from X Orientation**
$y = 0.83x + 12.42$
$R^2 = 0.77$

**Y from Y Orientation**
$y = 0.93x + 5.10$
$R^2 = 0.91$

**Z from Z Orientation**
$y = 0.91x + 6.32$
$R^2 = 0.85$

**X, Y from X, Y Orientations**
$y = 0.87x + 9.25$
$R^2 = 0.84$

Right column figures (Mössbauer %Fe³⁺ vs Anorm Centroid (eV)):

**X from X Orientation**
$y = 65.07x - 462823.16$
$R^2 = 0.84$

**Y from Y Orientation**
$y = 67.68x - 481383.61$
$R^2 = 0.93$

**Z from Z Orientation**
$y = 81.49x - 579564.54$
$R^2 = 0.90$

**X, Y from X, Y Orientations**
$y = 66.13x - 470327.32$
$R^2 = 0.88$

Left column (top to bottom):
- X, Y, Z Orientations from X, Y, Z; y = 0.87x + 9.56, R² = 0.85; 1:1 line
- Random from Random Orientations; y = 0.84x + 6.32, R² = 0.76; 1:1 line
- Random from X, Y, Z Orientations; y = 0.74x + 15.61, R² = 0.80; 1:1 line
- All from All Orientations; y = 0.88x + 6.96, R² = 0.87; 1:1 line

Right column (top to bottom):
- X, Y, Z Orientations from X, Y, Z; y = 69.88x − 497037.53, R² = 0.88
- Random from Random Orientations; y = 76.59x − 544718.09, R² = 0.81
- Random from X, Y, Z Orientations; y = 69.88x − 497037.53, R² = 0.88
- All from All Orientations; y = 73.49x − 522663.49, R² = 0.88

Left x-axis: Mössbauer %Fe³⁺
Right x-axis: Anorm Centroid (eV)
Left y-axis: Predicted %Fe³⁺
Right y-axis: Mössbauer %Fe³⁺

Pre-Edge Energy at Intensity of 0.38 (Minimal), 0.31 (Full) eV

Ratio of Peak Intensities at 7111.7/7112.8 (Minimal) & 7111.7/7112.7 (Full) eV

Slope Method using First Derivative at 7119.0 (Minimal) & 7112.4 (Full) eV

Left panel:
$R^2 = 0.70$
$R^2 = 0.66$

Middle panel:
$R^2 = 0.79$
$R^2 = 0.75$

Right panel:
$R^2 = 0.63$
$R^2 = 0.61$

Y-axis (all panels): Predicted %$Fe^{3+}$

X-axis (all panels): Mössbauer %$Fe^{3+}$

Pargasite
UCLA MS2858

M4Fe$^{2+}$

M1, M3Fe$^{2+}$

Alpha
Beta
Gamma

Kaersutite
Luchkow

Fe$^{2+}$ - Ti$^{4+}$ IVCT

Alpha
Beta
Gamma

Wavelength (nm)