1   **Revision 3**

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3   **IRON OXIDATION STATE IN PHYLLOSILICATE SINGLE CRYSTALS USING**

4   **FE-*K* PRE-EDGE AND XANES SPECTROSCOPY:**

5   **EFFECTS OF THE LINEAR POLARIZATION OF THE SYNCHROTRON X-RAY BEAM**

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23   **Abstract**

24   We investigated the influence of linear polarization of the synchrotron X-ray beam on the

25   determination of iron oxidation state in phyllosilicates. Fe *K*-edge XANES spectra and pre-edge

26   peaks have been recorded for various orientations of single crystals of biotite (Bt), clinochlore

27   (chlorite group; Cli), talc (Tc) and antigorite (serpentine group; Ant). *Ab initio* XANES

28   calculations, performed for 6 orientations of the biotite structure, support the experimental results.

29   Depending on crystal orientation, the experimental results show, 1) important changes both for

30   XANES and pre-edge peaks, 2) characteristic changes of spectral signatures regardless of the

31   mineral species, 3) uncorrelated changes between XANES and pre-edge peaks, 4) important

32   changes of the energy position of pre-edge peaks, but with no significant change for their integrated

33   areas. Regarding the crystal orientation, the pre-edge peak centroid varies in energy by ~0.4 eV in

34   the case of Bt and Tc, and by ~0.2 eV for Cli and Ant. Such variations correspond to #Fe^{3+} (i.e.,

35   Fe^{3+}/Fe_{total}) of 0.22 and 0.15, respectively. Comparison with the analysis of powdered samples show

36   that Fe-redox can be generally framed as follows: $-(2/3)$#Fe^{3+}<#$Fe^{3+}_{(powder)}$ < $+(1/3)$#Fe^{3+}. In good

37   agreement with the so-called "magic angle" theorem for powdered samples, we propose an ideal

38   orientation of the single crystals that provide similar pre-edge peaks as for powdered samples. With

39   the wavevector (i.e., beam direction) perpendicular to (100) or (010), measurements should be done

40   with an angle of 35° between the electric-field vector and the [001] crystal direction. Moreover,

41   measurements performed with the wavevector perpendicular to (001) systematically result in an

42   overestimation of #Fe^{3+} up to 0.07. Finally, we show that the appropriate positioning of single

43   crystals reduces the #Fe^{3+} uncertainty to the intrinsic error of pre-peak measurements. This

44   approach opens possibilities for *in situ* analyses of Fe-bearing phyllosilicates in thin sections that

45   are potentially relevant for scientific fields such as hydrothermal/metallogenic, metamorphic,

46   meteoritic or environmental mineralogy.

47   **1. Introduction**

48   Iron is the most abundant transition metal on Earth, and presents various oxidation states

49   according to the redox conditions of geological settings: elemental, ferrous and ferric iron, even

50   Fe(IV) as in amethyst (Di Benedetto et al., 2010). The oxidation state of iron in minerals is a

51   valuable indicator for the understanding of numerous mineralogical and petrological processes, such

52   as: *i*) metamorphic conditions prevailing in the continental crust (e.g., Diener and Powell, 2010;

53   Dyar et al., 2002b; Schmid et al., 2003; Vidal et al., 2006; Vidal et al., 2005); *ii*) ultra-high P-T

54   conditions prevailing in the Earth's mantle or at the core-mantle boundary (e.g., Andrault et al.,

55   2010; Canil et al., 1994; Frost and Langenhorst, 2002; McCammon et al., 2004); *iii*) high

56   temperature conditions of magmatic processes (e.g., Berry et al., 2008; Kelley and Cottrell, 2009);

57   *iv*) medium temperature and low pressure conditions typical of mid-oceanic ridges (e.g., Andréani

58   et al., 2008; Marcaillou et al., 2011), or environmental and biomineralogical processes (e.g.,

59   Benzerara et al., 2005; Brown et al., 2008; Miot et al., 2009).

60   Among the several analytical techniques that can be used to determine the oxidation state of

61   iron in minerals, XANES spectroscopy presents a large flexibility with beam size (from millimetric

62   down to a dozen nanometers by STXM; Scanning Transmission X-ray Microscopy), or detection

63   limits (down to a few tens of ppm), depending on the beam line and/or synchrotron source used.

64   The pre-edge peaks of XANES have been shown to be extremely sensitive to the oxidation state of

65   iron (e.g., Bajt et al., 1994; Berry et al., 2003; Farges, 2001; Galoisy et al., 2001; Petit et al., 2001;

66   Shulman et al., 1976; Wilke et al., 2001; Wilke et al., 2005). XANES spectroscopy requires the use

67   of a monochromatic synchrotron X-ray beam, which is generated with a horizontal linear

68   polarization due to the synchrotron ring geometry. This property of the X-ray beam does not affect

69   the characterization of mono-, or poly-mineral powders that show randomness in the crystalline

70   orientation of grains. In contrast, the X-ray absorption spectrum of a single crystal depends on its

71   orientation relative to the polarized X-ray beam (e.g., Dyar et al., 2001; Dyar et al., 2002a;

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72   Henderson et al., 1995; Manceau et al., 1988; Marcelli et al., 2006; Mottana et al., 2002; Schofield

73   et al., 1998; Van Der Laan et al., 1996).

74   Polarization effects at the iron K-edge (pre-edge peak and XANES) for various selected

75   micas were reported by Dyar et al. (2001) and Mottana et al. (2002). These studies aimed at

76   reporting uncertainties on the determination of the Fe^{3+}/Fe_{total} ratio ($\#Fe^{3+}$) for phyllosilicate single

77   crystals. Both studies report $\pm 10\%$ of absolute uncertainty for $\#Fe^{3+}$ if the measurement is made for

78   a crystal with unknown orientation. This uncertainty is much higher than that achievable on

79   randomly-oriented powders (about $\pm 3\%$ for octahedral cation exchanges; Wilke et al., 2001). This

80   is due to the complex dependence of the pre-edge (PE) peak as a function of mineral and beam

81   polarization. Hence, no satisfactory methodology has been proposed to achieve reliable values for

82   variably oriented mineral grains in natural rocks.

83   The present study aims at characterizing and quantifying the effect of linear polarization of

84   the X-ray beam on XANES spectra and PE peaks recorded for phyllosilicate single crystals at the

85   Fe K-edge. Notably, we intend to 1) better explore the angular-dependency without changing the

86   geometry of detection to avoid possible self-absorption effects, 2) improve data quality with better

87   signal-to-noise ratio, 3) improve data analysis and $\#Fe^{3+}$ determination using calibration curves of

88   Wilke et al. (2001). The angular dependency is evaluated for six orientations of euhedral biotite

89   single-crystal, cross-checked with theoretical *ab initio* XANES calculations for a similar structure

90   (FEFF8.2 package). Then, four single-crystals of biotite, clinochlore, talc and antigorite are

91   characterized by XANES spectroscopy (Fe K-edge) for specific orientations. PE peaks are used to

92   estimate the variations of the observed $\#Fe^{3+}$ according to the crystal orientation. Finally, specific

93   orientations of single crystals are proposed to measure "powder-equivalent" $\#Fe^{3+}$, and compared to

94   the so-called "magic-angle" (Pettifer et al., 1990).

95   **2. Experimental methods**

96   **2.1. Sample descriptions**

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97   Four single crystals of biotite (Bt), clinochlore (chlorite group; Cli), talc (Tc) and antigorite

98 (serpentine group; Ant) were selected from the mineralogy museum of the Institut Dolomieu at the

99 Université Grenoble 1, France; http://collections.obs.ujf-grenoble.fr. They show millimetric to

100 centimetric euhedral faces, and they are at least 1 mm thick, which enables X-ray absorption

101 measurements with a probe-size of a few hundreds of micrometers. Each single crystal was cut

102 perpendicularly to the (001) plane with a micrometric diamond-saw, to permit X-ray measurements

103 through this oriented section. (001) cleavage is clearly identified for each crystal. The biotite crystal

104 is translucent to opaque, depending on the thickness of the layers, and shows a typical dark-brown

105 color. The crystal presents a platy texture with "flexible" plates; its geological origin is

106 undocumented. The single crystal of talc is translucent, with a pale green color. This crystal was

107 collected at the Trimouns mines (Luzenac, France). The clinochlore crystal has a dark-green color

108 with a vitreous luster, and shows relatively massive layers. This crystal was collected in the Zermatt

109 area in Switzerland. The antigorite is translucent, massive and has a typical green color with a

110 greasy luster. This crystal was collected in the Mont-Cenis massif in the French Alps.

111 **2.2. Chemical analyses**

112   The composition of the crystals has been measured by X-Ray Fluorescence (XRF) analysis

113 performed with an EDAX Eagle-III micro-XRF at the Institut des Sciences de la Terre (Grenoble,

114 France). The fluorescence spectra (Fig. 1) were measured for 300 s with a vacuum of 0.3 mbar

115 using a Rh anode, at 20 kV/400 μA. The quantification of the XRF spectra was achieved with the

116 Vision32 software assuming a calibration based on a set of 12 oxide-, and silicate-standards

117 certified by Astimex Scientific Limited (MINM25-53 Mineral Mount) to reach less than 3% of

118 relative uncertainty for the concentration calculations. Element concentrations were obtained after 6

119 or 7 iterations between the matrix adjustment (i.e., concentration of major elements) and the

120 theoretical calculation of the corresponding XRF spectrum. The iterative calculation was stopped

121 when the predicted and measured intensities of the fluorescence lines differed by less than 0.1%.

122   The chemical analyses of the four starting crystals, expressed in weight percent (wt.%) and in atom

123   per formula unit (a.p.f.u.), are listed in Table 1. Following the XANES and PE peak data reduction

124   detailed later in this article, the iron contents were calculated assuming that iron in Bt, Cli and Tc is

125   in the ferrous state (FeO basis), and iron in Ant is in the ferric state (Fe_2O_3 basis). Iron oxide

126   contents of Bt, Cli, Tc and Ant are 3.88, 2.86, 1.28 and 1.16 wt.%, respectively.

127   **2.3. X-ray absorption spectroscopy**

128   Iron speciation (*K*-edge) was measured by X-ray absorption spectroscopy at the BM29

129   beamline – now moved on BM23 – of the ESRF (European Synchrotron Radiation Facility;

130   Grenoble, France). The storage ring was operating in the 16-bunch mode with an average current of

131   75 mA. X-rays were generated using a bending magnet, and monochromatized with a double-

132   crystal, fixed exit Si(111) monochromator. The low vertical divergence of the X-rays leads to a

133    $\Delta E/E$ of 2.8×10^{-4}, providing an energy resolution of ~1.99 eV at 7112 eV. XANES spectra were

134   collected at the iron *K*-edge in the fluorescence mode with a 13-element Ge-detector located on the

135   horizontal plane at 90 degrees from the incident X-ray beam direction. The sample surfaces were

136   positioned perpendicular to the X-ray beam to minimize self-absorption (Pfalzer et al., 1999).

137   Crystals were rotated around the propagation axis of the X-ray beam so that the geometry of

138   detection remains identical for all measurements (i.e., whatever the angle of rotation, the angle

139   between the sample surface and the incident beam is 90°). The energy sampling step for the

140   acquisition of the XANES spectra was optimized to properly resolve the different features. A first

141   linear region with a 5 eV step was used from 7070 eV to 7100 eV to collect a large pre-edge region

142   required for robust data normalization. Then we defined a second region that evolves polynomially

143   from 0.5 to 1 eV, respectively from 7100 to 7250 eV, to properly sample the PE peak and "white-

144   line" regions. XANES normalization and fits of PE features were performed in batch processing

145   mode thanks to the XasMap package, originally dedicated to dispersive micro-XANES mapping

146   applications (Muñoz et al., 2006; Muñoz et al., 2008; Pascarelli et al., 2006). According to the work

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147 of Wilke et al. (2001), the Fe-*K* PE peaks were fitted between 7108 and 7118 eV using Gaussian-

148 Lorentzian (GL) amplitude sum functions (i.e., pseudo-Voigt functions), which consider both the

149 Lorentzian broadening imposed by the core-hole lifetime and the Gaussian experimental resolution.

150 Considering the energy resolution of our experimental data, two peaks were sufficient to properly

151 fit the electronic transitions in the pre-edge features, i.e., local electric quadrupole transitions $1s \rightarrow$

152 $3d$, and/or local and non-local electric dipole transition $1s \rightarrow p$–d hybridized orbitals (see Cabaret et

153 al., 2010 and references therein). For each individual GL peak, we fixed the G/L ratio and the full-

154 width half-maximum (FWHM) to their best mean values obtained for the whole data set: 50% and 2

155 eV, respectively. It should be noted that energy positions and intensities modeled from PE features

156 have little physical significance since they result from the convolution of two distinct functions

157 (Gaussian and Lorentzian) that refer to different physical properties. Farges et al. (2004) showed

158 that the type of baseline used for the analysis of a pre-edge peak mainly affects its intensity but not

159 significantly the energy position of its centroid. Here, the baseline was empirically adjusted by the

160 tail of a Gaussian function since, for the energy range used for pre-edge fitting, the Lorentzian

161 percentage of the pseudo-Voigt naturally tends to 0 when the G/L ratio is not fixed. This method

162 provides best results in the peak-fitting procedure and is the least sensitive to the intrinsic noise of

163 the data. Finally, according to Wilke et al. (2001), the pre-edge variogram and calibration was based

164 on four powdered model compounds presenting different types of iron speciation, namely staurolite

165 ($^{[4]}Fe^{2+}$), unoxidized olivine ($^{[6]}Fe^{2+}$), andradite ($^{[6]}Fe^{3+}$) and sanidine ($^{[4]}Fe^{3+}$). This approach can be

166 used because no other local geometry (like square planar, cubic or antiprism geometry, etc.) is

167 expected around Fe in our phyllosilicates.

168 **3. Results**

169 **3.1. Detailed polarization dependence for biotite**

170 **3.1.1. *Ab initio* XANES calculations**

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171   A*b initio* XANES calculations were performed to evaluate the variations of XANES spectral

172   features as a function of the orientation of a single crystal relative to the horizontally polarized X-

173   ray beam. Calculations were achieved with the FEFF8.2 software (Ankudinov et al., 1998; Rehr et

174   al., 1992) at the Fe *K*-edge for biotite, based on the structure refinement of Sassi et al. (2008). A

175   self-consistent field (SCF card) multiple-scattering procedure was used to model charge transfer

176   between atoms during the photo-electric process up to 3.3 Å. Full multiple scattering (FMS card)

177   calculations were performed for the first eight shells of atoms (up to 4.6 Å) to achieve a close match

178   between the calculated and experimental spectrum of the powdered biotite. POLARIZATION and

179   ELLIPTICITY cards were used to simulate different orientations of the crystal exposed to a

180   horizontally-polarized X-ray beam.

181   Crystal positioning can be described by two vectors that characterize the polarized X-ray

182   beam: the wavevector **{{Rachet et al.: This vector symbol should be bold and on the same level**

183   **as the text, as all other symbols with vector symbol. MK}}** that indicates the direction of the

184   horizontal beam, and the electric-field vector that is also horizontal, but perpendicular to the

185   wavevector (see Figure 2). With parallel to the **a**-axis of the structure, can be either parallel to the

186   **c**-*,* or **b**-axis (see Figure 2a and 2b, respectively). The same reasoning can be conducted if is

187   parallel to the **b**-axis (i.e., parallel to **a**-, or **c**-axis), and to the **c**-axis (i.e., parallel to **a**-, or **b**-axis).

188   Then, six XANES spectra were computed for the six orientations (Fig. 3a). To distinguish between

189   them, each spectrum is labeled with two letters. The first letter indicates the crystallographic axis

190   that is parallel to the wavevector, and the second refers to the crystallographic axis parallel to the

191   electric-field vector.

192   The FEFF8.2 simulations mainly show two different shapes of XANES spectra among the

193   six orientations (Fig. 3a). These results show that XANES anisotropy is only a function of the

194   orientation of relative to the structure, regardless of the direction of the X-ray beam. This

195   observation is consistent with the *K*-edge probed here, i.e., the excitation of 1*s* electrons (spherical

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196   orbital) that leads to a dependence only as a function of   and the crystal structure in its

197   corresponding direction. Thus, we observe a perfect equivalence for the spectra *ac* and *bc*, *ab* and

198   *cb*, and *ca* and *ba*, respectively. Moreover, the pairs of spectra *ab-cb* and *ca-ba* are also very similar

199   to each other. In comparison, the pair *ac-bc* shows major differences, with a strong decrease and

200   widening of the D feature, a slight widening of E, and a significant shift towards lower energies for

201   the F feature. Note that, although the nature of electronic transitions is different, these observations

202   could be compared to polarized optical microscopy observations, for example for the pleochroic

203   properties of biotite. Indeed, light absorption is strong when the wavevector is perpendicular to

204   (001), *ca* or *cb* orientations, as well as for *ab* or *ba* orientations (dark brown color). In contrast, light

205   is less absorbed for *ac* or *bc* orientations (clear brown color). Such similarities most likely refer to

206   the atomic density that is observed from a 6-fold coordinated iron in the biotite structure: atomic

207   density in the direction [001] is much lower compared to [100] or [010]. Another comparison can

208   be made with isotropic minerals (cubic lattice): optical pleochroism is not observed, while polarized

209   XANES spectroscopy shows similar spectral signatures regardless of crystal orientation (e.g.,

210   Bordage et al., 2010).

211   **3.1.2. Experimental measurements (XANES and pre-edge peaks)**

212   Observations made for the calculated XANES spectra were crosschecked with experimental

213   measurements. For the six orientations defined above, experimental XANES spectra for biotite were

214   collected at the Fe-*K* edge. The euhedral faces of the single crystal were used as benchmarks for its

215   exposure to the X-ray beam. As predicted by theory, Figure 3b shows two well-contrasted XANES

216   shapes over the six orientations. For each group, the XANES overlap each other nearly perfectly: on

217   one hand, the spectra labeled *ac* and *bc* (in grey), on the other hand the spectra labeled *ab*, *cb*, *ca*

218   and *ba* (in black). Between these two contrasted shapes, changes observed for the features B, C, D,

219   E and F are very close to those obtained from *ab initio* calculations.

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220   Pre-edge features are displayed in the zoom inserted in Figure 3b. This figure shows that PE

221   peaks obtained for the orientations *ab* and *ba* (i.e., horizontal silicate sheets; see the lines with black

222   and white squares) have their centroid located at lower energies compared to the others. The

223   difference observed between *ca-cb* and *ac-bc* is simply due to their different baselines because of

224   the different spectral signatures in the white-line regions. However, similar values are observed for

225   their PE peak centroids (see Table 2).

226   As a consequence, while XANES spectra show different spectral signatures for the *ac-bc*

227   pair, the PE peaks show distinct shapes for the *ab-ba* pair. These contrasted observations between

228   the XANES and PE peaks are most likely due to their different photoelectron probing mechanism:

229   1) medium range order (i.e., ~ 3-10 Å) around the photo-absorber for the XANES; 2) the local

230   geometry of the 3d molecular orbitals (i.e., < 3 Å) for the PE peaks (considering only the crystal

231   field split transitions). The behavior of PE peaks can no longer be compared to optical microscopy

232   as for the XANES part of the spectrum (above the absorption edge). In the case of a given cubic

233   iron-bearing structure (such as garnet or wustite, etc.), the pre-edge varies while the XANES region

234   remains unchanged (Bolfan-Casanova et al., 2012; Bordage et al., 2010; Heumann et al., 1997).

235   **3.2. Comparative analysis for biotite, clinochlore, talc and antigorite**

236   **3.2.1. XANES polarization dependence**

237   According to the detailed study of polarization dependence for biotite (*ab initio* calculations

238   and experimental measurements), four series of spectra have been collected, with variable

239   orientations, for the biotite, clinochlore, talc and antigorite single crystals (Figure 4a, 4b, 4c and 4d,

240   respectively). Each crystal was first oriented with a vertical slice perpendicular to the beam (see

241   Figure 2a); this orientation is labelled *ac-bc* because of the spectral equivalence observed (Fig 3b).

242   Such orientation is noted as 0° in Figure 4. Then, the crystals were progressively rotated in steps of

243   15° to reach a 90° position where the horizontal slice is perpendicular to the beam (i.e., *ab-ba*).

244   Another spectrum was collected with (001) perpendicular to the beam (i.e., *ca-cb*). Finally, two

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245   more spectra are shown, which correspond to, 1) the powdered mineral, and 2) the average of the

246   three "end-member" spectra. These two spectra are systematically identical for each mineral, which

247   means that the spectrum of a randomly oriented powder is equivalent to the average of the three

248   end-members.

249   Figures 4a, 4b and 4c show that the XANES spectra for Bt, Cli and Tc are quite similar for a

250   given orientation. For these three minerals, the angular dependence of the different features is

251   similar to the description predicted by FEFF (Figure 3a). The feature A indicates the location of PE

252   peaks (detailed in Figure 5). Features B, C and D have relatively similar intensities at 0°, while D

253   becomes significantly higher for *ab-ba* (90°) and *ca-cb*. Moreover, from the 0 to 90°, feature E

254   slightly shifts towards lower energies and becomes narrower, while feature F shifts towards higher

255   energies. The strong similarities between the XANES spectral signatures of Bt, Cli and Tc are

256   consistent with the similar atomic local structure around Fe in these minerals, where iron is mainly

257   located in the octahedral sites, in the tri-octahedral layer of T-O-T sheets. On the other hand,

258   XANES spectra of the antigorite only show small variations depending on the crystal orientation

259   (see Fig. 4d). Compared to Bt, Cli and Tc, the XANES spectra of antigorite are clearly different,

260   most likely because of a well contrasted local structure of iron in this mineral – particularly in the

261   direction parallel to **c** – in which it is located in octahedral sites, in the tri-octahedral layer of T-O

262   sheets. Even so, such comparison of tri-octahedral T-O *vs.* T-O-T structures should highlight some

263   structural, and spectral, similarities in directions parallel to (001) for which the atomic landscape of

264   iron are similar. Therefore, another explanation could be the presence, in weak proportion, of 4-fold

265   coordinated iron in this mineral. This hypothesis is reinforced by the occurrence of high amounts of

266   Fe^{3+} relative to the Fe_{total} (see further in Figure 6), and agrees with the evidence of weak proportions

267   of tetrahedral iron proposed by Marcaillou et al. (2011) in experimental serpentines.

268   **3.2.2. Pre-edge polarization dependence**

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269   Figures 5a, 5b, 5c and 5d show the baseline-subtracted PE peaks that correspond to the

270   XANES spectra in Figure 4: Bt, Cli, Tc and Ant, respectively. Open circles indicate the series from

271   0 to 90° as well as the *ca-cb* orientation, black diamonds and black circles indicate the average and

272   powder spectra, respectively. Each PE peak is fitted using two pseudo-Voigt functions (dotted

273   lines), labeled A' and A" for the low and high-energy peak, respectively, and the fit results are

274   represented by solid lines. For each PE peak, the centroid energy position, integrated area and

275   corresponding #Fe^{3+} are listed in Table 3.

276   As observed for the XANES spectra, the evolutions of the PE peak features as a function of

277   crystallographic orientation are quite similar for the Bt, Cli and Tc. Rotating the samples from 0 to

278   90° by steps of 15° leads to a progressive decrease in intensity of the peak A" relative to A'.

279   However, in contrast to the XANES, similarities are observed between *ac-bc* and *ca-cb*, while *ab-*

280   *ba* is clearly different. For *ac-bc* and *ca-cb*, feature A' is slightly higher than A". For *ab-ba,* feature

281   A' is much more intense than the feature A", so the centroid energy is significantly shifted towards

282   lower energies. In the case of antigorite, the intensity of the peak A' is negligible while the intensity

283   of the peak A" is much higher, corresponding to a higher energy position of the PE peak centroid;

284   as for the XANES, only slight variations are observed with the crystal orientation.

285   In Figure 6, integrated area *versus* centroid energy are displayed in a variogram similar to

286   the one presented by Wilke et al. (2001). This variogram shows the end-member positions that

287   correspond to the four model compounds used in this study, and thus to the different Fe-speciation

288   end-members: $^{[4]}Fe^{2+}$, $^{[6]}Fe^{2+}$, $^{[6]}Fe^{3+}$, $^{[4]}Fe^{3+}$. Each model compound is located in a grey circular

289   region that is larger than the precision of the method (i.e., ± 0.05 eV in energy). This variogram also

290   shows the values obtained for the different orientations of the Bt, Cli, Tc and Ant crystals, from 0 to

291   90°. The values obtained are located near the line labeled [VI], which corresponds to mixtures

292   between $^{[6]}Fe^{2+}$ and $^{[6]}Fe^{3+}$. This observation confirms that iron is exclusively six-fold coordinated

293   in these minerals. Depending on their orientation, Bt, Cli and Tc show centroid positions varying

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294   from the $^{[6]}Fe^{2+}$ end-member to around 0.4 to 0.6 eV towards higher energies. The differences in

295   energy-range observed for these minerals are likely due to slight variations of either, i) the local

296   structure around Fe^{2+} in octahedral sites, e.g., site distortions, or ii) the averaged oxidation state of

297   iron. In contrast, centroid values obtained for antigorite are located around 7114.4 eV, close to the

298    $^{[6]}Fe^{3+}$ end-member and slightly above the [VI]-axis, which suggests that iron is mostly ferric and

299   octahedrally coordinated in this crystal. The relatively high integrated area values observed for

300   antigorite might be due to a weak proportion of tetrahedral iron, or possibly distortions of the

301   octahedral sites due to the large amount of ferric iron in the structure, which may lead to less

302   centrosymmetric site geometry.

303   The conversion from the centroid energy and integrated area, respectively to iron oxidation

304   state and coordination number is not straightforward. In particular, centrosymmetry is not a direct

305   function of the coordination. However, the phyllosilicates studied only present tetrahedral or

306   octahedral coordination geometries. This allows us to interpret the centrosymmetry information in

307   terms of averaged coordination numbers. Wilke et al. (2001) show that the relation between PE

308   peak intensity and averaged coordination number is quasi-linear, whereas the calibration curve for

309   the oxidation state quantification is not (see their figures 6 and 7). In the present study, we use their

310    $^{[6]}Fe^{2+}$–$^{[6]}Fe^{3+}$ calibration curve to derive #Fe^{3+} values. Our results reveal that crystal orientation

311   does not strongly affect the PE peak intensities, so that we mainly focus on the iron oxidation state

312   determination based on PE peak energies.

313   **3.2.3. #Fe^{3+} polarization dependence**

314   Figure 7a shows the dependence of the centroid energy according to the rotation angle

315   around the X-ray propagation direction. For each sample, including antigorite, the centroid position

316   decreases in energy from 0° to 90°, in perfect agreement with the qualitative observations made on

317   the PE peak shapes in Figure 5. Benchmarks for the $^{[6]}Fe^{2+}$, and $^{[6]}Fe^{3+}$ end-members are represented

318   as grey strips, with a width equivalent to the diameter of the grey circles in Figure 6. Since the

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319   intensity of the electric-field vector oscillates in a plane defined by itself and the wavevector (see

320   Figure 2), the periodicity for the crystal rotation relative to the X-ray beam is 180° (i.e., the

321   maximum contrast between 0 and 180° is observed at 90°). Therefore, each spectral signature

322   (XANES and/or PE peak) shows an angular dependence with a periodicity of 180°, and each series

323   of centroid energies (y) as a function of the angle (x) was fitted with a sine function defined as

324   follow:

325   Eq. 1

326   where α is the median value of the centroid energy range, and β is the amplitude of the variations.

327   The angular frequency (ω) and the phase-shift (φ) are, respectively, equal to $2\pi/180$ and $\pi/2$. The

328   parameters α and β for the data series of Bt, Cli, Tc and Ant are both listed in Table 4. For each

329   crystal, the range of values obtained for the centroid energies is defined by $\alpha \pm \beta$, and the energy

330   range is equal to 2β (see Table 4). Consequently, the maximum variation of the centroid energies is

331   observed for talc (0.40 eV) and biotite (0.39 eV). The lowest variation is observed for antigorite

332   (0.16 eV), and an intermediate value is observed for clinochlore (0.25 eV). For comparison, the

333   values of the centroid energy obtained for the powdered minerals are reported as horizontal grey

334   strips labelled "powder" in Figure 7a. In the 0-90° range, the strips intersect the sine models (Eq. 1)

335   at around $35 \pm 5°$ (considering about 0.05 eV of uncertainty). Based on that result, and on

336   similarities observed between PE peaks *ac-bc* and *ca-cb* (Figure 5), the centroid energy equivalent

337   to that of a powdered sample can be empirically approximated as:

338   Eq. 2

339   where ($\alpha + \beta$) is the centroid energy for the orientations *ac-bc* and *ca-cb*, and ($\alpha - \beta$) is the centroid

340   energy for the orientation *ab-ba*. Values obtained for the "powder-equivalent" centroid energies are

341   listed in Table 4.

342   Centroid energy values obtained for the oriented crystals were converted into $\#Fe^{3+}$ based on

343   the $^{[6]}Fe^{2+}$ – $^{[6]}Fe^{3+}$ calibration curve of Wilke et al. (2001). Note that these $\#Fe^{3+}$ values are not

14

344   "real" but "apparent" values, since all the Fe cations are simultaneously probed during

345   measurements, whatever the crystal orientation. Therefore, these apparent values do not correspond

346   to a sort of selective view of the different cations in the structure (sensitive to site-ordering for

347   example), but they are related to the crystal-field in the O_h geometry relative to the electric-field of

348   the X-ray beam. For each orientation of the crystals, the apparent $\#Fe^{3+}$ has been reported in Table 3

349   as well as in Figure 7b. As for the centroid energies, the apparent $\#Fe^{3+}$ values (*y*) were fitted as a

350   function of the angle (*x*) using the same type of equation:

351   Eq. 3

352   in which γ is the medium value of the $\#Fe^{3+}$ variability, δ is the amplitude of the variations. The

353   angular frequency ω and the phase-shift φ are equivalent to the ones used in Eq. 1. The parameters γ

354   and δ for the data series of Bt, Cli, Tc and Ant are both listed in Table 4, as well as 2δ that

355   represents the variability range for $\#Fe^{3+}$ (i.e., $\Delta\#Fe^{3+}$). This variability range is 0.22 for Bt and Tc

356   and 0.14 and 0.15 for Cli and Ant, respectively. At 35°, the $\#Fe^{3+}_{eq}$ values are 0.15, 0.17 and 0.18

357   for Bt, Cli and Tc, respectively. These results indicate that iron is mainly in the ferrous state in these

358   minerals. In contrast, iron in the antigorite characterized in this study is much more oxidized, with a

359    $\#Fe^{3+}_{eq}$ of 0.81. The values of $\#Fe^{3+}_{eq}$ obtained at 35° (Table 4) are in excellent agreement with

360   those obtained for the powdered minerals (Table 3).

361

362   **4. Discussion**

363   In agreement with the results of Dyar et al. (2001), the experimental and theoretical data

364   obtained for the phyllosilicates investigated here highlight important changes in the spectral

365   signatures with the orientation of the single crystals. Furthermore, we show additional information

366   such as the independent behavior between the XANES and PE peak shapes. For each crystal

367   investigated, the orientation *ac-bc* (i.e., electric-field vector parallel to the **c**-axis) shows contrasted

368   XANES compared to the other crystallographic orientations, while the orientations *ab-ba* and *ca-cb*

369   are quite equivalent to each other. Concerning the PE peaks, we show that the positioning *ab-ba* is

370   different from the others, whereas *ca-cb* and *ac-bc* are equivalent to each other. These uncorrelated

371   variations between the XANES (features above the edge) and the PE peak regions are due to

372   different types of interactions between the excited electron and the electronic/atomic structure

373   around the photoabsorber. On one hand, the XANES region reflects photoelectric multiple-

374   scattering effects at medium-range distance around the photoabsorber (Ankudinov et al., 1998; Rehr

375   et al., 1992; Rehr et al., 1995). So, the differences or similarities observed in the XANES shapes are

376   most likely due to the atomic "landscape" in the direction of . For *ab-ba* and *ca-cb*, is either

377   parallel to **a** or **b**. The photoelectric wave associated to the excited photon mostly interacts with

378   atoms in the octahedral plane of the TOT layer, i.e., within the (001) plane, and therefore "sees"

379   relatively similar atomic landscape. In contrast, for *ac-bc*, the photoelectric wave most likely

380   propagates perpendicularly to the TOT layers, i.e., in the [001] direction, and therefore sees well

381   contrasted atomic density/landscape when compared to the other orientations. On the other hand,

382   the PE peaks are related to 1s-3d (quadrupolar) and/or 1s-4p (dipolar) electronic transition (Dräger

383   et al., 1988; Heumann et al., 1997; Shulman et al., 1976; Westre et al., 1997), and thus can be

384   considered as a short-range structural probe around the photoabsorber (electronic cloud; below 3

385   Å). Differences observed between the pre-edge peaks likely result from the geometry of the

386   hybridized orbitals in crystal-field splitting of the octahedral sites (e.g., Cabaret et al., 2010; Galoisy

387   et al., 2001). A decrease of the average symmetry degree of iron sites, such as distortions or the

388   occurrence of tetrahedral iron, may cause strong changes in the pre-edge shapes depending on the

389   crystal orientation.

390   The XANES spectrum of biotite powder can be reproduced from the average of three

391   spectra measured on single-crystals with appropriate orientations (see Figure 4a). However, based

392   on our angle-dependency results, we show other ways to measure "powder-equivalent" spectra.

393   Figure 8 summarizes the crystal positioning that is required for measuring equivalent XANES or PE

16

394   peaks. For example the recording of a "powder-equivalent" XANES spectrum consists of rotating

395   the sample by 35° from *ab-ba* to *ac-bc*. Since *ab-ba* is equivalent to *ca-cb*, a rotation of 35° from

396   *ca-cb* to *ac-bc* also leads to the same result. On the other hand, we show that a "powder-equivalent"

397   PE edge peak is obtained when the sample is rotated by 35° from the *ac-bc* position to the *ab-ba*

398   position. The 35° angle obtained in this study is in excellent agreement with the "magic-angle"

399   theorem applied to X-ray absorption spectroscopy (Pettifer et al., 1990), which is defined as $sin^2(\theta_m)$

400   = 1/3 (i.e., θ_m = 35.26°). However, the approach of the latter authors was focused on the symmetry

401   properties of particle distributions in powdered samples, and did not consider symmetry properties

402   related to individual crystallites. Our results show that this angle should be used only between

403   specific crystal orientations. For example in the case of biotite and talc, a rotation of 35° from *ca-cb*

404   to *ac-bc* results in an overestimation of the centroid energy position, and leads to a 7%

405   overestimation of #Fe^{3+} (based on the sine model described in Figure 7b). Similarly, a rotation of

406   35° from *ab-ba* to *ca-cb* or *ac-bc* results in a 7% underestimate of #Fe^{3+}. The discrepancies can be

407   even larger if the crystals follow the *ab-ba* orientation (both electric-field vector and wavevector

408   parallel to the (001) plane): the underestimate of #Fe^{3+} reaches 15%. Therefore, the apparent

409   evolution of #Fe^{3+} with crystal orientation (for biotite or talc) is asymmetric: – 15% < #Fe^{3+} < + 7%.

410   It follows that the "real" #Fe^{3+} value (equivalent powder) of phyllosilicate single-crystal of

411   unknown orientation can be underestimated by 15%, or overestimated by 7%. For clinochlore or

412   antigorite, the #Fe^{3+} variability deduced from the sine model (Figure 7b) is smaller: – 10% < #Fe^{3+}

413   < + 5%. These are maximum values, and our results show that a proper orientation of the single

414   crystals, relative to the polarized X-ray beam, leads to the reduction of the uncertainty in the

415   determination of #Fe^{3+} down to the intrinsic error of the method. This latter is mainly due to the

416   error made on the determination of the centroid-energy of the pre-edge features, which is usually

417   considered to be about 0.05 eV according to the type of baseline used (e.g., Farges, 2001; Farges et

418   al., 2004; Wilke et al., 2001). Then, the errors propagated to the #Fe^{3+} depend on the type of

17

419   coordination for the ferrous and ferric cations, as well as their respective proportions. Typically,

420   based on the work of Wilke et al. (2001), a mixture composed of $^{[VI]}Fe^{2+}$ and $^{[VI]}Fe^{3+}$ will lead to

421   #Fe^{3+} uncertainties between 0.03 (near the ferrous pole) and 0.05 (near the ferric pole).

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26

586   **Figure captions**

587

588   **Figure 1.** μ-XRF spectra for biotite, clinochlore, talc and antigorite showing relative abundances of

589   the major and minor elements.

590

591   **Figure 2.** Schematic representation of the incident polarized X-ray beam relative to the orientation

592   of the macroscopic phyllosilicate single crystal: a) *ac*-positioning, also noted 0° in the text; b) *ab*-

593   positioning, also noted 90° in the text; c) *ca*-positioning.

594

595   **Figure 3.** Spectral signatures, at the Fe *K*-edge, for 6 different orientations of biotite single crystal

596   relative to the linearly polarized X-ray beam. a) Theoretical (FEFF) *ab initio* calculations of the

597   XANES spectra. b) Experimental XANES spectra and pre-edge peaks.

598

599   **Figure 4.** Experimental Fe *K*-edge XANES spectra measured for the crystals of biotite (a),

600   clinochlore (b), talc (c) and antigorite (d), as a function of their orientation relative to the polarized

601   incident X-ray beam. Spectra are collected from the orientation *ac-bc* to *ab-ba* by steps of 15°, and

602   for the orientation *ca-cb*. For each series, the spectrum resulting from the average of *ac-bc*, *ab-ba*

603   and *ca-cb* is shown, and compared to the spectrum obtained for the powder.

604

605   **Figure 5.** Fe *K*-edge pre-edge peaks obtained for the crystals of biotite (a), clinochlore (b), talc (c)

606   and antigorite (d), as a function of their orientation relative to the polarized X-ray beam: from 0°

607   (*ac-bc*) to 90° (*ab-ba*) by steps of 15°, and for the orientation *ca-cb*. Empty circles represent the

608   experimental data, dashed lines represent the pseudo-Voigt functions used for the fitting process,

609   and solid lines represent the fitting results.

610

27

611 **Figure 6.** Integrated area *vs.* centroid energy variogram reporting pre-edge peak data that

612 correspond to biotite, clinochlore, talc and antigorite measured between 0° and 90°. The diameter of

613 the circular regions (iron-speciation end-members) is similar to that of the variogram of Wilke et al.

614 (2001) and reflects the uncertainty of measurement.

615

616 **Figure 7.** Evolution of the pre-edge peak centroid energies (a) and the "apparent" Fe^{3+}/Fe_{total} ratios

617 (b) as a function of the positioning angle of the samples (dots). Sine fitting functions described by

618 Eq. 1 and 3 are represented with lines. Values obtained for powdered samples intersect the sine

619 functions at a "powder-equivalent" angle of 35°.

620

621 **Figure 8.** Sketch showing appropriate positioning of phyllosilicate single crystals that allow

622 measuring "equivalent-powder" XANES spectra (upper part) and pre-edge peaks (lower part). The

623 sketch view is from the incident X-ray beam. The arrows indicate rotations to apply in order to

624 obtain powder-like spectra.

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627

628 **Table 1.** μ-XRF chemical analyses (wt.% and a.f.p.u.) for the biotite, clinochlore, talc and

629 antigorite single crystals.

630

(wt.%)	biotite	clinochlore	talc	antigorite
SiO_2	39.57 ± 0.66	33.92 ± 1.02	62.15 ± 1.86	41.53 ± 1.25
TiO_2	1.59 ± 0.02	0.03 ± 0.00	0.00 ± 0.00	0.05 ± 0.00
Al_2O_3	14.51 ± 0.14	8.18 ± 0.24	0.63 ± 0.02	1.12 ± 0.03
Cr_2O_3	0.00 ± 0.00	0.66 ± 0.02	0.00 ± 0.00	0.13 ± 0.00
Fe_2O_3	-	-	-	1.16 ± 0.03
FeO	3.88 ± 0.12	2.86 ± 0.09	1.28 ± 0.04	-
MnO	0.03 ± 0.00	0.02 ± 0.00	0.00 ± 0.00	0.07 ± 0.00
NiO	0.00 ± 0.00	0.13 ± 0.00	0.05 ± 0.00	0.05 ± 0.00
MgO	25.63 ± 0.77	40.86 ± 1.23	30.73 ± 0.92	42.91 ± 1.29
CaO	0.05 ± 0.00	0.01 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
K_2O	10.62 ± 0.32	0.02 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
H_2O	4.20 ± 0.13	12.55 ± 0.38	4.70 ± 0.14	12.81 ± 0.38
Total	100.08	99.24	99.54	99.83
(a.p.f.u.)	biotite	clinochlore	talc	antigorite
Si	2.80 ± 0.08	3.24 ± 0.10	3.97 ± 0.12	1.92 ± 0.06
Ti	0.08 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Al	1.21 ± 0.04	0.92 ± 0.03	0.05 ± 0.00	0.06 ± 0.00
Cr	0.00 ± 0.00	0.05 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Fe(III)	-	-	-	0.04 ± 0.00
Fe(II)	0.23 ± 0.01	0.23 ± 0.01	0.07 ± 0.00	-
Mn	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Ni	0.00 ± 0.00	0.01 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Mg	2.70 ± 0.08	5.82 ± 0.17	2.92 ± 0.09	2.96 ± 0.09
Ca	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
K	0.96 ± 0.03	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
H_2O	0.98 ± 0.06	3.99 ± 0.24	1.00 ± 0.06	1.96 ± 0.12
O	11	14	11	7

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634 **Table 2.** Centroid energy (± 0.05 eV) and integrated area (± 0.025) of the pre-edge peaks, as well as

635 the apparent #Fe^{3+} (± 0.03) obtained for six orientations of the biotite crystal.

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biotite crystal orientation	centroid position (eV)	integrated area	#Fe^{3+}
ca	7113.68	0.083	0.242
cb	7113.68	0.085	0.242
ab	7113.23	0.079	0.000
ba	7113.26	0.086	0.010
ac	7113.67	0.096	0.235
bc	7113.69	0.106	0.245

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641 **Table 3.** Centroid energy ($\pm$ 0.05 eV), integrated area ($\pm$ 0.025) and corresponding #Fe^{3+} values

642 (from $\pm$ 0.03 to $\pm$ 0.05 for ferrous and ferric iron, respectively), obtained from pre-edge peaks of

643 biotite, clinochlore, talc and antigorite depending on the type of measurement (see explanations in

644 text).

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	centroid energy (eV)				integrated area							#Fe^{3+}
	Bt	Cli	Tc	Ant	Bt	Cli	Tc	Ant	Bt	Cli	Tc	Ant
0°	7113.68	7113.66	7113.62	7114.52	0.096	0.093	0.080	0.113	0.242	0.231	0.207	0.872
15°	7113.63	7113.64	7113.74	7114.50	0.096	0.091	0.105	0.128	0.209	0.215	0.278	0.858
30°	7113.51	7113.57	7113.66	7114.45	0.082	0.086	0.083	0.119	0.140	0.178	0.229	0.808
45°	7113.46	7113.48	7113.53	7114.41	0.087	0.083	0.077	0.128	0.111	0.121	0.150	0.775
60°	7113.35	7113.45	7113.39	7114.38	0.081	0.087	0.080	0.110	0.053	0.111	0.074	0.750
75°	7113.28	7113.42	7113.36	7114.36	0.077	0.089	0.090	0.136	0.020	0.091	0.057	0.735
90°	7113.27	7113.42	7113.30	7114.34	0.084	0.093	0.075	0.117	0.014	0.091	0.027	0.713
ca-cb	7113.67	7113.70	7113.63	7114.49	0.094	0.094	0.089	0.123	0.243	0.262	0.221	0.861
average	7113.54	7113.59	7113.51	7114.45	0.091	0.093	0.081	0.118	0.165	0.195	0.152	0.821
powder	7113.52	7113.56	7113.48	7114.43	0.089	0.094	0.096	0.128	0.155	0.173	0.139	0.808

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652 **Table 4.** Parameters α, β, γ and δ, fitted from Equations 1 and 3 for biotite, clinochlore, talc and

653 antigorite. $E_{eq.}$ and #Fe^{3+}_{eq} are "powder-equivalent" values (i.e., at the 35° angle) for the centroid

654 energy and the Fe^{3+}/Fe_{total} ratio, respectively.

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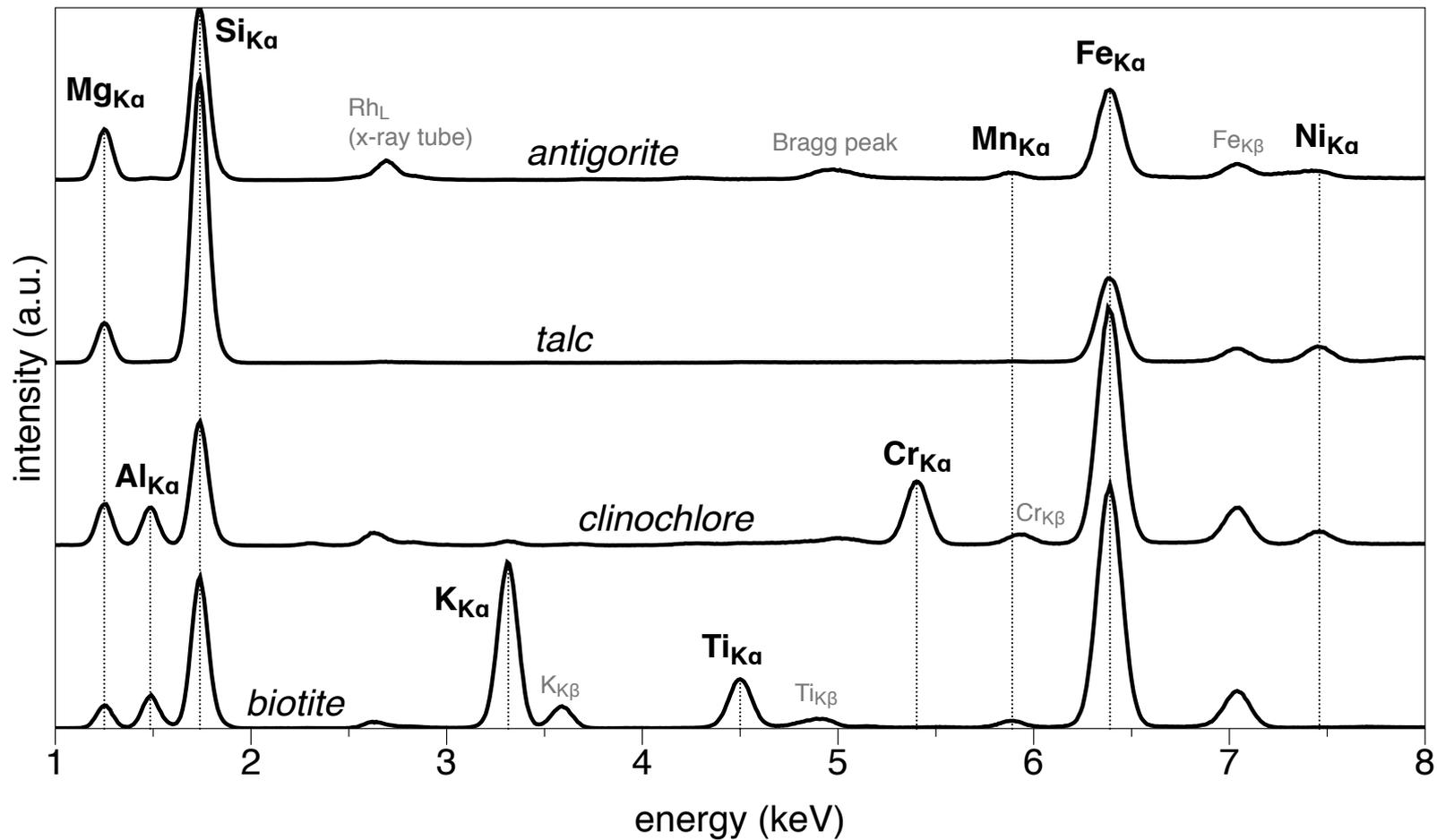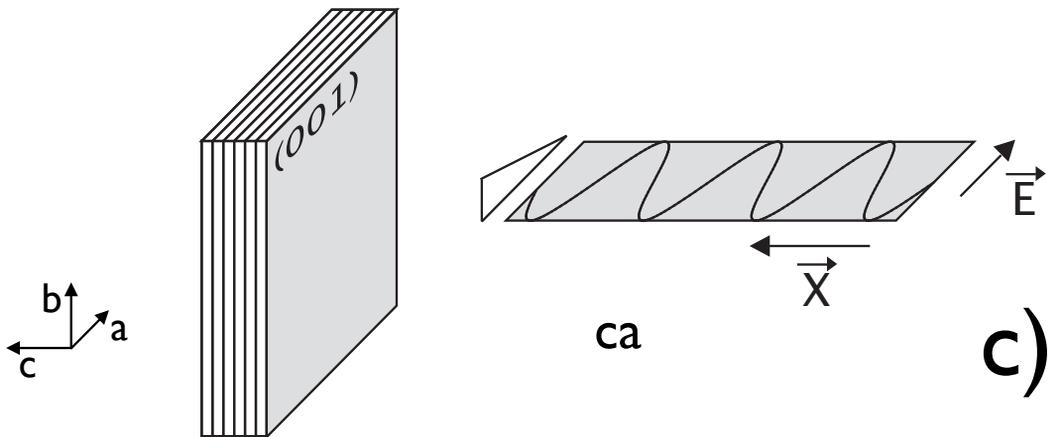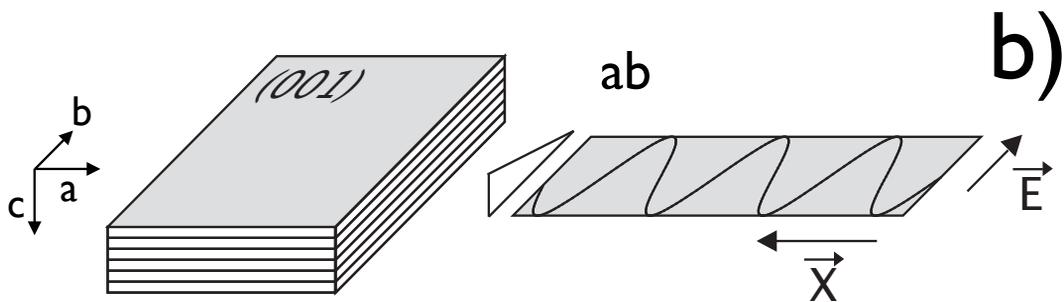|	biotite	clinochlore	talc	antigorite
$α$ (eV)	7113.45 ± 0.05	7113.52 ± 0.05	7113.51 ± 0.05	7114.42 ± 0.05
$β$ (eV)	0.197 ± 0.01	0.122 ± 0.01	0.198 ± 0.01	0.082 ± 0.01
$2β$ (eV)	0.39 ± 0.02	0.25 ± 0.02	0.40 ± 0. 02	0.16 ± 0. 02
$E_{eq.}$ (eV)	7113.52 ± 0.05	7113.56 ± 0.05	7113.58 ± 0.05	7114.45 ± 0.05
$γ$	0.113 ± 0.03	0.147 ± 0.03	0.146 ± 0.03	0.787 ± 0.05
$δ$	0.108 ± 0.01	0.070 ± 0.01	0.111 ± 0.01	0.073 ± 0.01
$2δ$	0.22 ± 0.02	0.14 ± 0.02	0.22 ± 0.02	0.15 ± 0.02
#$Fe^{3+}_{eq.}$	0.15 ± 0.03	0.17 ± 0.03	0.18 ± 0.03	0.81 ± 0.05

656

657

658

a)

normalized absorbance

D
C
B
E
F
A

b)

normalized absorbance

D
C
B
E
F
A

Legend:
- ·········· 0° (ac-bc)
- ——— 15°, 30°, 45°, 60°, 75°
- —•—•— 90° (ab-ba)
- ━━━ (001) (ca-cb)
- - - - - average
- ━━━ powder

c)

normalized absorbance

D
C
B
E
F
A

d)

D' D''
C
B
E' E''
F
A

energy (eV)

7100   7120   7140   7160   7180   7200

energy (eV)

7100   7120   7140   7160   7180   7200

a)

ca-cb (001)

A'

A"

ab-ba 90°

75°

60°

45°

30°

15°

ac-bc 0°

b)

ca-cb (001)

A'

A"

ab-ba 90°

75°

60°

45°

30°

15°

ac-bc 0°

average ◆   powder ●

c)

ca-cb (001)

A'

A"

ab-ba 90°

75°

60°

45°

30°

15°

ac-bc 0°

d)

ca-cb (001)

A'

A"

ab-ba 90°

75°

60°

45°

30°

15°

ac-bc 0°

intensity

intensity

energy (eV)

energy (eV)

7110   7112   7114   7116

7110   7112   7114   7116

Legend:
- ◆ standards
- ■ biotite
- □ clinochlore
- △ talc
- ○ antigorite

Axis labels: integrated area (y-axis); centroid position (eV) (x-axis)

Quadrant labels: $^{[4]}Fe^{2+}$, $^{[4]}Fe^{3+}$, $^{[6]}Fe^{2+}$, $^{[6]}Fe^{3+}$, [VI]