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## Quantification of the ferric/ferrous iron ratio in silicates by scanning transmission X-ray microscopy at the Fe L<sub>2,3</sub> edges

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1 Quantification of the ferric/ferrous iron ratio in silicates by scanning transmission x-ray  
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35

36 **Abstract**

37

38 Estimation of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios in materials at the submicrometer scale has been a long-standing  
39 challenge in the Earth and environmental sciences because of the usefulness of this ratio in  
40 estimating redox conditions as well as for geothermometry. To date, few quantitative methods  
41 with submicrometric resolution have been developed for this purpose, and most of them have  
42 used electron energy-loss spectroscopy (EELS) carried out in the UHV environment of a  
43 transmission electron microscope (TEM). Scanning transmission x-ray microscopy (STXM)  
44 is a relatively new technique complementary to TEM and is increasingly being used in the  
45 Earth sciences. Here, we detail an analytical procedure to quantify the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio in  
46 silicates using Fe  $L_{2,3}$ -edge x-ray absorption near edge structure (XANES) spectra obtained by  
47 STXM, and we discuss its advantages and limitations. Two different methods for retrieving  
48  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios from XANES spectra are calibrated using reference samples with known  $\text{Fe}^{3+}$   
49 content by independent approaches. The first method uses the intensity ratio of the two major  
50 peaks at the  $L_3$ -edge. This method allows mapping of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios at a spatial scale better  
51 than 50 nm by the acquisition of 5 images only. The second method employs a 2-eV-wide  
52 integration window centred on the  $L_2$  maximum for  $\text{Fe}^{3+}$ , which is compared to the total  
53 integral intensity of the Fe  $L_2$ -edge. These two approaches are applied to metapelites from the  
54 Glarus massif (Switzerland), containing micrometer-sized chlorite and illite grains and  
55 prepared as ultrathin foils by Focused Ion Beam milling. Nanometer-scale mapping of iron  
56 redox in these samples is presented, and shows evidence of compositional zonation. The  
57 existence of such zonation has crucial implications for geothermometry and illustrates the  
58 importance of being able to measure  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios at the submicrometer scale in geological  
59 samples.

60

61 Keywords: ferric/ferrous iron, STXM, XANES spectroscopy,  $L_{2,3}$ -edge, redox mapping,  
62 silicate.

63

64 **Introduction**

65

66 Determination of the redox state of iron and its spatial variations in sediments and  
67 rocks is of critical importance in both geosciences and environmental sciences, because of the  
68 need to understand redox state during their deposition or formation as well as subsequent

69 changes in redox state due to weathering and other processes (e.g., de Andrade et al. 2006;  
70 Muñoz et al. 2006; Bernard et al. 2010; Benzerara et al. 2011; Bolfan-Casanova et al. 2012;  
71 Stagno et al. 2013). In addition, quantification of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios can yield a better insight into  
72 the chemistry of complex geological materials (e.g., Muñoz et al. 2006), or a better estimation  
73 of  $P$ - $T$  conditions by geothermobarometers, when variations of the  $\text{Fe}^{3+}$  content within the  
74 crystals are taken into account (e.g., Schmid et al. 2003; de Andrade et al. 2006; Bourdelle et  
75 al. 2013a). Therefore, assessment of the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio in minerals is an important and long-  
76 standing issue. Different techniques have been used extensively in the past for this purpose,  
77 including electron microprobe analysis (EMPA, e.g., Fialin et al. 2004), Mössbauer  
78 spectroscopy (e.g., Beaufort et al. 1992) x-ray photoelectron spectroscopy (XPS, e.g.,  
79 Raeburn et al. 1997a, b), or x-ray absorption near edge structure (XANES) spectroscopy at  
80 the K edge (e.g., Waychunas et al. 1983; Bajt et al. 1994; Wilke et al. 2001, 2009; Berry et al.  
81 2003, 2010). However, none of these methods provides spatial resolution at the few  
82 nanometers scale, which is particularly useful for studying chemical zonation patterns  
83 observed in low-temperature systems. Several studies (e.g., van Aken and Liebscher, 2002)  
84 have shown that electron energy-loss spectroscopy (EELS) carried out in a transmission  
85 electron microscope (TEM) is a powerful method for determining the redox state of iron at a  
86 submicrometer resolution. However it sometimes induces severe beam damage effects, such  
87 as electron beam-induced oxidation of iron (Lauterbach et al. 2000; Garvie et al. 2004), the  
88 effect of which can be corrected by measuring the signal as a function of time. Alternatively,  
89 XANES spectroscopy at the Fe  $L_{2,3}$  edges carried out with a scanning transmission x-ray  
90 microscope (STXM) has been increasingly used in the Earth and environmental sciences to  
91 infer qualitatively  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios in geological and environmental samples at a spatial  
92 resolution of  $\sim 50$ -nm (e.g., Wasinger et al. 2003; Carlut et al. 2010; Lam et al. 2010; de Groot  
93 et al. 2010; Miot et al. 2011; Boulard et al. 2012). This technique has several advantages such  
94 as offering a high energy resolution (better than 0.1 eV at existing synchrotron facilities) and  
95 the possibility of maintaining samples under anoxic conditions before and during the  
96 measurement (e.g., Miot et al. 2009). However, no calibration of the STXM-based Fe  $L_{2,3}$ -  
97 edge XANES approach has yet been carried out, whereas calibration of the EELS approach  
98 was quantified by van Aken and Liebscher (2002). Fe  $L_{2,3}$ -edges result from  $2p \rightarrow 3d$   
99 electronic transitions, as shown by Wasinger et al. (2003). These authors described in detail  
100 the physical basis of Fe L edges, and showed that information about iron valency can be  
101 retrieved from XANES spectra by a multiplet calculation approach (e.g., van der Laan and  
102 Kirkman, 1992; Cressey et al. 1993). This approach is difficult to apply when dealing with

103 mineral phases for which we do not know the structure. Alternatively, fitting of XANES  
104 spectra with a linear combination of normalized reference spectra has been performed by Miot  
105 et al. (2009), but requires appropriate  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  end-member reference compounds with  
106 Fe in the same local coordination environment as in the sample of interest. Van Aken and  
107 Liebscher (2002) have shown the possibility of a third approach that they calibrated for EELS  
108 and which uses an empirical correlation between  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios and a parameter (i.e.,  
109 modified integral white-line intensity ratio) which is directly retrieved from EELS spectra at  
110 the Fe  $L_{2,3}$  edges, and is independent of the coordination environment of Fe to a the first-order  
111 approximation.

112 Here we propose an empirical approach similar to that of van Aken and Liebscher  
113 (2002) to calibrate the correlation between  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio and some parameters extracted from  
114 the STXM-derived XANES Fe  $L_{2,3}$ -edge spectra of reference silicate glasses and  
115 phyllosilicates. Two empirical calibrations are proposed, both of which offer a compromise  
116 between speed and accuracy of the analytical measurement. An application of this approach to  
117 ultra-thin sections of natural chlorites and micas is presented to illustrate the methodology and  
118 to further assess the range of applicability of this calibration for STXM.

119

## 120 **Materials and Methods**

121

### 122 *Reference samples*

123

124 The samples used in this study were reference synthetic silicate glasses, natural  
125 phyllosilicates and fayalite, prepared as powders or ultra-thin sections cut by Focused Ion  
126 Beam (FIB) milling. The bulk chemical compositions of the five synthetic glasses were  
127 previously determined by Magnien et al. (2004). All samples are composed of similar  
128 proportions of Si, Mg, Ca, Na and Fe. The  $\text{SiO}_2$  and FeO contents are ~52 wt% and ~13 wt%,  
129 respectively. Bulk  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios were determined by wet chemistry, Mössbauer  
130 spectroscopy and EMPA and range from 0.09 to 0.94 (Table 1; Magnien et al. 2004). For  
131 STXM-XANES analyses, we ground these samples in deaerated and deionized water, inside  
132 an anoxic glovebox ( $p(\text{O}_2) < 50$  ppm) to avoid oxidation during sample preparation.

133 The phyllosilicate samples have 2:1 and 2:1:1 structures and their bulk compositions  
134 were investigated previously by Joswig et al. (1986), Keeling et al. (2000), Shingaro et al.  
135 (2005), Rigault et al. (2010), and in the present study by EMP analyses. Total Fe contents  
136 vary significantly between samples and bulk  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios ranging between 0.03 and 1.0

137 were measured by Mössbauer spectroscopy, EXAFS (extended x-ray absorption fine  
138 structure) and/or EELS (Table 1). In addition, a fayalite sample was used as a pure Fe<sup>2+</sup>  
139 reference. For STXM-XANES analyses, some samples (smectite Nau-2, chlorites GAB 42,  
140 VNI 92, VNI 114, fayalite) were prepared by grinding in deaerated and deionized water in an  
141 anoxic glovebox (p(O<sub>2</sub>) < 50 ppm). Other samples (clintonite, chlorite ‘prochlorite’, chlorite  
142 Ch1, Ti-mica) were prepared by FIB milling.

143 Samples transparent to soft x-rays are needed to measure XANES spectra in the  
144 transmission mode of STXM, therefore requiring the preparation of thin samples. FIB foils  
145 were cut with a FEI Model 200 TEM FIB system at University Aix-Marseille using the  
146 protocol detailed by Heaney et al. (2001). A 30 kV Ga<sup>+</sup> beam operating at ~20 nA excavated  
147 the sample to a depth of 5 µm. The sample foil was then further thinned to ~80-100 nm at  
148 lower beam voltage (5 kV) and current (~100 pA), in order to remove the layer damaged by  
149 high-energy ions (Bourdelle et al. 2012).

150

#### 151 *Glarus field samples*

152

153 The Glarus Alps (Switzerland) belongs to the Helvetic zone of the northern margin of  
154 the Central Alps, and was affected by low-grade metamorphism. Details about the location  
155 and composition of the samples analyzed by STXM in the present study are provided in  
156 Lahfid et al. (2010). The selected rock samples are metapelites, more or less clayey or sandy  
157 marls, with various proportions of quartz, calcite, and clay minerals. Three samples (noted  
158 Glarus GL07 13, 16, and 20, as in Lahfid et al. 2010), containing chlorites and K-deficient  
159 micas, were milled by FIB. The compositions of the chlorites and micas were obtained on the  
160 FIB foils by analytical electron microscopy analyses described elsewhere (Bourdelle et al.  
161 2012).

162

#### 163 *XANES spectroscopy*

164

165 Part of the STXM analyses were performed at the Advanced Light Source (ALS)  
166 (Lawrence Berkeley National Laboratory) on branch line 11.0.2.2 following the procedures  
167 described in Miot et al. (2009). The ALS storage ring was operated at 1.9 GeV and 500 mA  
168 current in a top-up mode. More details on the branch line 11.0.2.2 and beam characteristics  
169 are given by Bluhm et al. (2009). Stacks of images were obtained by scanning the sample in

170 the x–y directions of selected sample areas over the 690–730 eV energy range (Fe L<sub>2,3</sub>-edge)  
171 using an energy increment of 0.789 eV between 690 and 705 eV, 0.10 eV in the 705–713 eV  
172 energy range, 0.19 eV in the 713–719 eV energy range, 0.155 eV in the 719–726 eV energy  
173 range, and 0.475 eV in the 726–730 eV energy range. The dwell time per pixel and energy  
174 point was 1.3 ms.

175 Some data (chlorite Ch1, chlorite ‘prochlorite’ and Ti-mica) were acquired on the  
176 Pollux beamline at the Swiss Light Source (SLS, Villigen, Switzerland). The SLS synchrotron  
177 storage ring was operated at 2.4 GeV and 300 mA current in a top-up mode during data  
178 collection, and the characteristics of the beamline are detailed by Raabe et al. (2008). Stacks  
179 were obtained over the 690–730 eV energy range (Fe L<sub>2,3</sub>-edge) using an energy increment of  
180 0.667 eV between 690 and 700 eV, 0.15 eV in the 700–715 eV energy range, 0.40 eV in the  
181 715–727 eV energy ranges, and 0.89 eV in the 727–730 eV energy range. The dwell time per  
182 pixel and energy point was 3.5 ms.

183 At both the ALS and the SLS, focus was achieved systematically for each sample, and  
184 precision in the determination of the focus position was better than the focus depth. Image  
185 stacks were aligned and XANES spectra were derived from areas of interest using the  
186 aXis2000 software (Hitchcock, 2012). Potential beam damage caused by the incident photon  
187 beam was assessed by monitoring spectral changes at the Fe L<sub>2,3</sub>-edge with increasing dwell  
188 times up to a hundred milliseconds (10, 50, and 100 ms).

189

### 190 *Spectra processing*

191

192 Energy calibration was performed using the gaseous neon 1s → 3p electronic  
193 transition at 867.3 eV. As explained in Figure 1, the processing of spectra consisted of two  
194 steps. First, the contribution of lower energy absorption edges (i.e., background) was removed  
195 so that in the end, the pre-edge region is set to 0 optical density (noted OD) with a slope of  
196 zero. For that purpose, a “linear background” correction was applied to the spectrum. Second,  
197 the two edge steps resulting from transitions to unoccupied states in the continuum were  
198 subtracted using the following double arctan function (Chen et al. 1995; van Aken and  
199 Liebscher, 2002; Broton et al. 2007):

200

$$201 \quad f(\Delta E) = \frac{h_1}{\pi} \left( \arctan \left[ \frac{\pi}{w_1} (\Delta E - E_1) \right] + \frac{\pi}{2} \right) + \frac{h_2}{\pi} \left( \arctan \left[ \frac{\pi}{w_2} (\Delta E - E_2) \right] + \frac{\pi}{2} \right) \quad (1)$$

202

203 where  $h_1$  and  $h_2$  are the step heights of the two arctan functions,  $w_1$  and  $w_2$  are fixed peak  
204 widths, and  $E_1$  and  $E_2$  are the positions of the inflection points resulting in an energy near the  
205 edge onset. Here,  $w_1$  and  $w_2$  are fixed to 1 eV (Fig. 1). Broton et al. (2007) proposed setting  
206 the function slope  $w$  at 5 eV, to account for the slow onset of the continuum. They argued that  
207 a value smaller than 5 eV could induce spurious structures in the background-corrected  
208 spectrum. We observed that values of  $w = 1$  eV or  $w = 5$  eV provided similar results.

209

## 210 **Results and Discussion**

211

### 212 *Evolution of Fe L<sub>2,3</sub>-edge XANES spectra with changes in Fe<sup>3+</sup>/ΣFe*

213

214 XANES spectra at the Fe L<sub>2,3</sub>-edges of the reference phyllosilicates, fayalite and five  
215 Fe-bearing silicate glasses, corrected for continuum absorption, are shown in Figure 2, and the  
216 positions of major peaks are summarized in Table 1. These spectra are qualitatively similar to  
217 those described in several previous studies and were obtained using different analytical  
218 techniques (e.g., Crocombette et al. 1995; Heijboer et al. 2003; van Aken and Liebscher,  
219 2002). Four major Fe L<sub>2,3</sub>-edge XANES peaks are present in all samples. The two major  
220 peaks on the L<sub>3</sub> edge are noted as “L<sub>3</sub>-a” and “L<sub>3</sub>-b”, and similarly, the major peaks on the L<sub>2</sub>  
221 edge are noted as “L<sub>2</sub>-a” and “L<sub>2</sub>-b”. For all samples examined, the measured separations of  
222 the Fe L<sub>3</sub> and L<sub>2</sub> maxima, due to spin-orbit splitting (van Aken and Liebscher, 2002), are 12.9  
223 ± 0.4 eV and 14.2 ± 1.4 eV for peaks a and b, respectively in agreement with previous EELS  
224 and XANES studies (e.g., de Smit et al. 2008; de Groot et al. 2010). However, although most  
225 of the spectra show a single asymmetrical L<sub>3</sub>-a peak, some of them (i.e., VNI 92, VNI 114  
226 and GAB 42, fayalite) display an “L<sub>3</sub>-a” split into two peaks. In addition, these specific  
227 spectra show additional peaks on the L<sub>3</sub>-a side at ~706.3 and ~706.8 eV. According to  
228 Wasinger et al. (2003), the presence of these minor peaks may be due to a specific atomic  
229 environment and/or orbital co-valency of iron in these mineral phases. Similarly, several  
230 minor peaks can be observed at around 719.8 eV on the L<sub>2</sub>-edge for several samples (VNI 92,  
231 VNI 114, GAB 42, PyrNa 17R, fayalite).

232

233 The relative intensities of the different major peaks vary depending on the Fe<sup>3+</sup>/ΣFe  
234 ratio (Figure 2). With increasing Fe<sup>3+</sup>/ΣFe ratios, the relative intensity of the L<sub>3</sub>-a peak  
235 decreases compared to that of the L<sub>3</sub>-b peak; L<sub>3</sub>-a is more intense than L<sub>3</sub>-b in the XANES  
spectrum of the VNI 92 sample (Fe<sup>3+</sup>/ΣFe = 0.35), whereas the opposite is observed for PyrNa



236 5R ( $Fe^{3+}/\Sigma Fe = 0.61$ ). Likewise, the relative intensity of L<sub>2</sub>-a progressively decreases whereas  
237 that of L<sub>2</sub>-b increases as  $Fe^{3+}/\Sigma Fe$  increases. The energy position of L<sub>2</sub>-b changes very little  
238 between the samples, whereas peaks L<sub>3</sub>-a and L<sub>2</sub>-a shift slightly towards higher energies when  
239  $Fe^{3+}/\Sigma Fe$  increases.

240

241 *Quantification of  $Fe^{3+}/\Sigma Fe$  from XANES Fe L<sub>2,3</sub>-edge intensity ratios*

242

243 As documented in Figure 2, the main variations in the XANES spectra of reference  
244 samples with varying  $Fe^{3+}/\Sigma Fe$  ratios involve the L<sub>3</sub>-b/L<sub>3</sub>-a intensity ratio. More precisely, the  
245 L<sub>3</sub>-b/L<sub>3</sub>-a intensity ratio is linearly correlated with  $Fe^{3+}/\Sigma Fe$  ratio with only a little scatter ( $R^2$   
246 = 0.96) for both the phyllosilicates and silicate glasses (Figure 3). The correlation is described  
247 by equation (2):

248

$$249 \frac{Fe^{3+}}{\sum Fe} = \frac{R_{L_3} - 0.1867}{0.01991} \quad \text{with} \quad R_{L_3} = \frac{I(L_3 - b)}{I(L_3 - a)} \quad (2)$$

250

251 This approach requires only five XANES images to map  $Fe^{3+}/\Sigma Fe$  (see Figure 4 and below):  
252 two images in the pre-edge (needed to apply the “linear background correction” at each pixel  
253 of the image), one at 708.7 eV to quantify the L<sub>3</sub>-a peak, one at 710.25 eV to quantify the L<sub>3</sub>-  
254 b peak, and one at 718 eV, to remove the edge step of the arctan function. Finally, the ratio of  
255 the resulting 708.7 and 710.25 eV images can be used to determine the  $R_{L_3}$  parameter at each  
256 pixel of the image.

257

258 This calibration is useful but has some limitations. The L<sub>3</sub> peaks, which are much  
259 more intense than the L<sub>2</sub> peaks, are more susceptible to absorption saturation (see Hanhan et  
260 al. 2009, where saturation effects are described for Ca 2p edge spectra). This phenomenon  
261 occurs when the sample is too thick and/or highly concentrated in Fe implying that few  
262 photons are transmitted. This may trigger a non-linear response of the detection and an  
263 artifactual modification of the relative peak heights. The use of a spectral parameter correlated  
264 with  $Fe^{3+}/\Sigma Fe$  based on the less absorbing L<sub>2</sub>-edge may provide in this case an interesting way  
265 of circumventing absorption saturation issues encountered with the L<sub>3</sub>-edge.

266

267 Figure 2 shows that an increase of  $Fe^{3+}/\Sigma Fe$  is associated with a decrease of the  
268 intensity of L<sub>2</sub>-a. Figure 5 shows the correlation between  $Fe^{3+}/\Sigma Fe$  and  $R_{L_2}$ , a ratio that reflects  
269 the importance of L<sub>2</sub>-b relative to the total L<sub>2</sub>. Similar to the modified intensity defined by van  
270 Aken and Liebscher (2002), the L<sub>2</sub>-b contribution is computed as an integration window of 2

269 eV width centred around the maximum L<sub>2</sub>-b intensity; the ratio  $R_{L_2}$  is calculated from this  
 270 modified L<sub>2</sub>-b intensity and the total integral intensity of L<sub>2</sub>-edge. The correlation is high ( $R^2$   
 271 = 0.97), and is described by equation (3):

$$273 \quad \frac{Fe^{3+}}{\sum Fe} = \frac{R_{L_2} - 0.1476}{0.00297} \quad \text{with} \quad R_{L_2} = \frac{I(L_2 - b)_{\text{mod}}}{A(L_2)_{\text{total}}} \quad (3)$$

274  
 275 This approach requires the acquisition of a complete stack of images (i.e., as many images as  
 276 energy points are required to obtain a complete spectrum with a given spectral resolution)  
 277 between 715 and 730 eV, to cover the entire L<sub>2</sub>-edge, and to calculate the double arctan  
 278 function (equation (1)). As a consequence, the acquisition time required for this method is  
 279 longer than for the L<sub>3</sub>-b/L<sub>3</sub>-a intensity ratio method (e.g. 30-40 min *versus* 5-10 min for an  
 280 area of 150 by 150 pixels). However, this second method seems to be more accurate,  
 281 especially because (1) the calibration data are less scattered (Fig. 5 *versus* Fig. 3) and (2) the  
 282 intensity integration improves the signal-to-noise ratio. Several other methods of calibration  
 283 have been tested, sometimes giving equation with a high correlation (with a  $R^2$  up to 0.95),  
 284 but the two methods proposed here seem to be a good trade-off between  $Fe^{3+}/\sum Fe$  estimation  
 285 accuracy, acquisition time and ease of use.

### 287 *Assessment of saturation and beam damage effects*

289 When particles are sufficiently thin, the intensity of each spectral feature changes  
 290 linearly with thickness. However, Hanhan et al. (2009) showed that in the case of samples that  
 291 are too thick, one can observe distortions of the Ca 2p spectrum due to a saturation effects.  
 292 These observations led the authors of that study to set a maximum peak intensity, which  
 293 should not be exceeded to avoid saturation phenomena.

294 Similarly, we determined the maximum peak intensity below which the Fe L<sub>23</sub> spectra  
 295 are undistorted and vary linearly. For this purpose, a powder of the smectite Nau-2 sample  
 296 with grains of various sizes was analyzed by STXM. Figure 6 plots the difference between the  
 297 intensities at 710.35 (L<sub>3</sub>-b) and 723.54 eV (L<sub>2</sub>-b) (corrected from the pre-edge intensity) vs.  
 298 the intensity at 710.35 eV (L<sub>3</sub>-b, i.e., the peak of maximum intensity for Nau-2, hence the  
 299 most susceptible to saturation) for each pixel of the stack of images (i.e., a total of 6336  
 300 pixels). The difference between L<sub>3</sub>-b and L<sub>2</sub>-b intensities increases linearly when L<sub>3</sub>-b  
 301 intensity is lower than ~1.5 OD. Once the L<sub>3</sub>-b intensity exceeds 1.5 OD, the L<sub>3</sub>-b – L<sub>2</sub>-b

302 difference increases more slowly than L<sub>3</sub>-b, underlining (i) the distortion of the spectra for the  
303 considered pixels, and (ii) the faster increase of L<sub>2</sub>-b intensity compared to that of L<sub>3</sub>-b with  
304 increasing sample thickness. All the data presented in this study were therefore collected from  
305 areas presenting a L<sub>3</sub> peak intensity lower than 1.5 OD.

306 The spectrum may be also influenced by the crystal orientation relative to the direction  
307 of polarization of the x-ray beam, a process called linear dichroism. Therefore several  
308 XANES spectra were measured on the same part of a FIB foil after sequential rotation of the  
309 linear polarisation (see Benzerara et al., 2011 for details on the procedure). The variation of  
310 resulting Fe<sup>3+</sup>/ΣFe estimates is negligible, showing that sample orientation does not affect the  
311 Fe<sup>3+</sup> quantification.

312 Beam damage can also potentially alter assessment of the Fe<sup>3+</sup>/ΣFe ratio. Here, beam  
313 damage was evaluated by monitoring spectral changes at the Fe L<sub>2,3</sub>-edge with increasing  
314 dwell times from 10 up to 100 milliseconds. Figure 7 shows that Fe<sup>3+</sup>/ΣFe ratios derived from  
315 XANES spectra are only slightly affected by increasing dwell time. In particular, no  
316 significant change was observed for typical dwell times used during routine analyses of the  
317 samples (i.e., ~1.3 and 3.5 ms per energy- and image-point for ALS and SLS synchrotrons,  
318 respectively).

319

320 *Application to a geological case: chlorites and micas from Glarus (Central Alps, Switzerland)*

321

322 To go further, we have applied the methods proposed here on micrometer-sized  
323 chlorite and mica/illite-like grains sampled in the Glarus area of Switzerland and cut by FIB-  
324 milling. The temperatures of chlorite formation were calculated from analytical electron  
325 microscopy (AEM) chemical analyses, based on the thermometer by Bourdelle et al. (2013b),  
326 which does not require Fe<sup>3+</sup>/ΣFe input, and the thermometer by Inoue et al. (2009), which  
327 needs a previous estimation of Fe<sup>3+</sup> content. The Fe<sup>3+</sup>/ΣFe ratios were estimated for each FIB  
328 foil by XANES from equations (2) and (3). The results are given in Figure 8 and Table 2.

329 From images converted to optical density units taken at 708.7 eV, we can easily  
330 distinguish Fe-rich and Fe-poor minerals: chlorites appear as light grey and represent the Fe-  
331 rich phase, whereas micas are dark, i.e., Fe-poor. XANES spectra, acquired along the mica-  
332 chlorite contacts show that the Fe<sup>3+</sup>/ΣFe ratio is higher in illite than in chlorite: the Fe<sup>3+</sup>/ΣFe  
333 ratios estimated by equation (3) range from 22.3% to 27.9% in chlorite, whereas these ratios  
334 vary between 30 and 65.5% in illite-like phase. Equation (2) provides consistent estimations,  
335 suggesting that both calibrations are reliable. This analysis shows that K-deficient micas can

336 contain a high proportion of ferric iron (e.g. samples 13 and 20). Despite the relatively high  
337  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio in some illite-like crystals, the total  $\text{Fe}^{3+}$  content remains higher in chlorite.

338 Figure 8 also shows the variations of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios vs. the temperature of formation,  
339 which was estimated by chlorite thermometry (Table 2). In this respect,  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio  
340 increases slightly in chlorites with increasing temperature, whereas this ratio decreases in K-  
341 deficient micas. It should be noted that, contrarily to the Bourdelle et al. (2013b) model, some  
342 geothermometers based on thermodynamic models for chlorite (e.g., Inoue et al. 2009),  
343 require prior determination of the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio. When this value is not known, it is set to  
344 zero as the default in these types of models. Interestingly, the comparison of results provided  
345 by different thermometers in Table 2 shows that the Inoue and Bourdelle geothermometers  
346 yield very different temperature results (differences of up to  $76^\circ\text{C}$ ) when  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio is not  
347 known. In contrast, taking into account the  $\text{Fe}^{3+}/\Sigma\text{Fe}$ , the two thermometers provide more  
348 similar temperatures estimates (a maximum difference of less than  $28^\circ\text{C}$ , i.e., within the  
349 uncertainty of the thermometers), showing the cross-check validity of the  $\text{Fe}^{3+}/\Sigma\text{Fe}$   
350 estimation. A variation of the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio from 0 to  $\sim 23\%$  in chlorites implies a decrease in  
351 the temperatures calculated by the Inoue model of 20, 40, and  $46^\circ\text{C}$  depending on the sample.

352 Figure 9 displays an example of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  mapping at the nanometer-scale derived  
353 from images at 706, 708.7, 710.25, and 718 eV using Eq. (2) (see Figure 4). The analysis was  
354 carried out on the Glarus GL07 20 FIB foil. The scanned area measures  $3.3 \times 3.5$  micrometers  
355 with a pixel size of 88 nm x 88 nm. The analysis of the illite-chlorite contacts by AEM  
356 showed that they are approximately perpendicular to the FIB foil surface, i.e., there is only a  
357 little overlap between the two minerals at their contact. The spatial averaging effect of the x-  
358 ray beam over the pixel size (i.e., 88 nm) sets the limit of the minimum distance over which  
359 illite-chlorite contacts can be discriminated. Beyond this distance, the intracrystalline  
360 variation of the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio in the illite-like phase can be interpreted as an authentic  
361 zonation, from  $\sim 55\%$  in crystal rims (conforming to the spectra presented in Figure 8) to  
362  $\sim 85\%$  in several crystal core clusters. In the same way, the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio distribution draws a  
363 subtle zonation in the chlorite, with a  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio ranging from 18 to  $\sim 23\%$  on the crystal  
364 rim, in accordance with the spectra shown in Figure 8. Such variations of the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio  
365 within the crystals are equivalent to several degrees or tens of degrees in the temperature  
366 estimation, especially when this variation is associated with a variation in composition. One  
367 can expect that this zonation is a crucial issue in application of geothermometers (de Andrade  
368 et al. 2006; Bourdelle et al. 2013a), and the redox gap between illite and chlorite raises the  
369 issue of the crystallisation processes.

370 In summary, the STXM-based XANES study of FIB foils from the Glarus,  
371 Switzerland samples enables (i) estimation of the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio in each phase preserving the  
372 mineral texture, and (ii) establishment of iron redox mapping with high spatial resolution.

373

### 374 **Conclusion**

375

376 In this study, we have demonstrated the reliability of two methods that allow  
377 quantitative determination of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios in silicate phases using STXM coupled with  
378 XANES spectroscopy at the Fe  $L_{2,3}$ -edges. These approaches are similar to those proposed by  
379 van Aken and Liebscher (2002) for EELS measurements but are here calibrated for STXM.  
380 The two calibrations are based on reference samples with variable but known  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios,  
381 which were prepared as powders or as FIB foils. We tested these calibrations on three FIB  
382 foils extracted from field samples of phyllosilicates (Glarus, Switzerland chlorite and illite  
383 samples from metapelites), demonstrating the potential of these methods for quantifying  
384  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios at the submicrometer-scale. This approach will allow more quantitative  
385 mineralogical or geomicrobiological studies requiring estimation of the iron redox state at the  
386 nanoscale for terrestrial or extraterrestrial Fe-rich samples.

387

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398

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549

## 550 Tables

551

552 **Table 1** Reference samples used for XANES -  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio quantification

553

Type	Sample	Source	FeO %wt.*	$\text{Fe}^{3+}/\Sigma\text{Fe}$ Redox ratio	Position of maximum peak intensity (eV)			
					L <sub>3</sub> -a	L <sub>3</sub> -b	L <sub>2</sub> -a	L <sub>2</sub> -b
Silicate glass	PyrNa	Magnien et al. (2004)	12.83	0.73 ±0.03	708.57	710.04	721.68	723.54
Silicate glass	PyrNa17R	Magnien et al. (2004)	12.75	0.09 ±0.01	708.36	710.77	721.37	723.54
Silicate glass	PyrNa5R	Magnien et al. (2004)	12.92	0.61 ±0.01	708.57	710.04	721.68	723.54
Silicate glass	PyrNa750	Magnien et al. (2004)	12.68	0.94 ±0.03	708.67	710.25	721.68	723.54
Silicate glass	PyrNa1200	Magnien et al. (2004)	13.52	0.89 ±0.05	708.67	708.93	721.84	724.54
Nesosilicate	Fayalite	Neuville D.	70.50	0.00 ±0.00 <sup>‡</sup>	708.09	710.71	720.75	723.54
Phyllosilicate	Smectite Nau-2	Keeling et al. (2000)	34.10	1.00 ±0.00 <sup>‡</sup>	708.57	710.35	721.84	723.54
Phyllosilicate	Clintonite	Joswig et al. (1986)	3.01	0.69 ±0.03 <sup>‡</sup>	708.25	710.08	721.49	723.53
Phyllosilicate	Ti-mica	Shingaro et al. (2005)	19.38	0.03 ±0.03 <sup>‡</sup>	708.04	710.04	721.00	723.54
Phyllosilicate	Chlorite 'Prochlorite'	MNHN <sup>†</sup>	14.50	0.30 ±0.10 <sup>‡</sup>	708.26	710.21	721.51	723.51
Phyllosilicate	Chlorite Ch1	This study	40.10	0.17 ±0.05	708.04	710.19	721.00	723.54
Phyllosilicate	Chlorite GAB 42	Rigault (2010)	28.50	0.14 ±0.03	708.15	710.46	720.75	723.54
Phyllosilicate	Chlorite VNI 92	Rigault (2010)	20.73	0.35 ±0.03	708.15	710.25	720.75	723.54
Phyllosilicate	Chlorite VNI 114	Rigault (2010)	20.82	0.20 ±0.03	708.04	710.25	720.75	723.54

554 \*  $\Sigma\text{Oxides wt}\% = 100$  as basis and all iron reported as ferrous. <sup>†</sup> MNHN: Collection of Muséum National

555 d'Histoire Naturelle, France. <sup>‡</sup> assumed error deviation.

556

557 **Table 2** AEM chemical representative analyses of Glarus chlorites and comparison of  
 558 thermometers results taking into account  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios (Eq. (3)); regarding the scatter of  
 559 data on Figure 3, we infer a precision of  $\pm 5\%$  on the  $\text{Fe}^{3+}/\Sigma\text{Fe}$ . Analyses were carried out on  
 560 crystal rims, along the illite-chlorite contact, according to Bourdelle et al. (2013a).  
 561 Temperature estimations were performed with Bourdelle et al. (2013b) and Inoue et al. (2009)  
 562 thermometers, with and without consideration of  $\text{Fe}^{3+}$ , in accordance with the  
 563 recommendations made by each authors. Taking into account the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios in the Inoue  
 564 model allows to obtain similar results to those calculated with the Bourdelle model (which is  
 565 a pure  $\text{Fe}^{2+}$  model), i.e., with a difference less than  $30^\circ\text{C}$  (equivalent to the uncertainty of each  
 566 model)  
 567

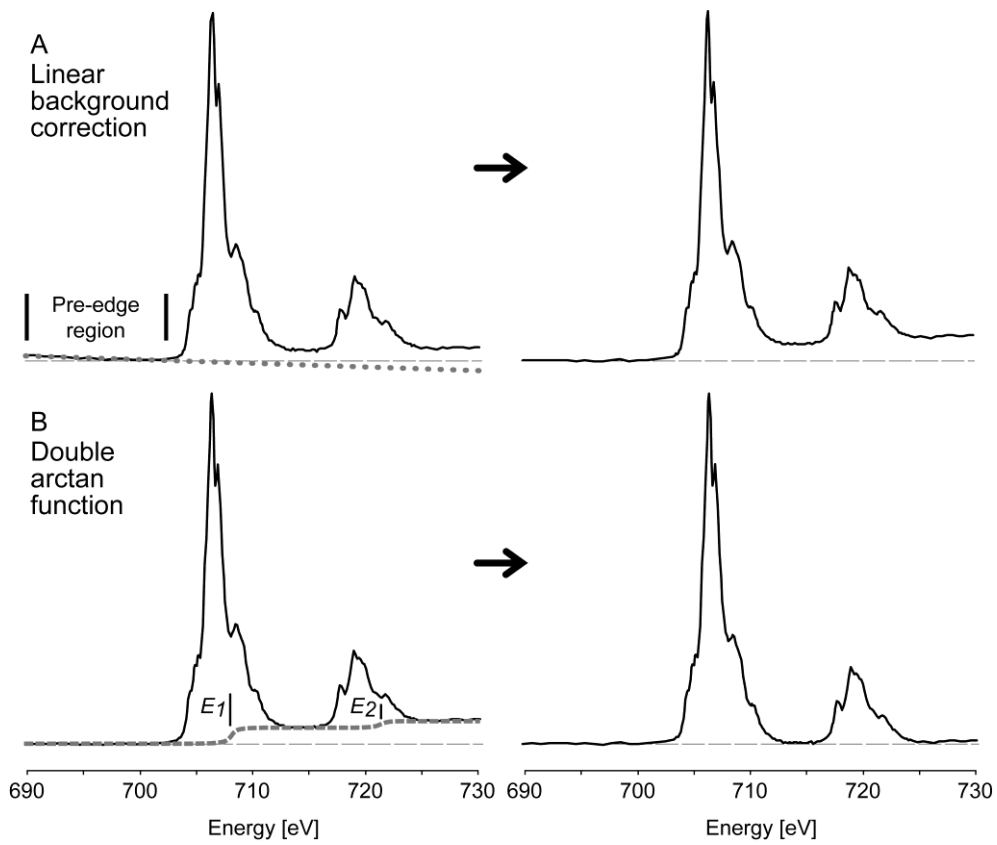
Chlorite [%wt]	GL07 13	GL07 20	GL07 16
$\text{SiO}_2$	32.70	31.40	31.57
$\text{TiO}_2$	0.07	0.06	0.04
$\text{Al}_2\text{O}_3$	26.41	25.56	26.02
$\text{FeO}$	26.63	28.53	25.13
$\text{MnO}$	0.00	0.00	0.00
$\text{MgO}$	13.75	13.97	16.70
$\text{CaO}$	0.06	0.10	0.29
$\text{Na}_2\text{O}$	0.00	0.04	0.00
$\text{K}_2\text{O}$	0.39	0.35	0.25
$\text{Fe}^{3+}/\Sigma\text{Fe}$ [%]	22.30	23.80	27.90
$T_{\text{BOU}} [^\circ\text{C}]$	135	170	182
$T_{\text{INO-Fe}^{2+}} [^\circ\text{C}]$	165 (+30)	236 (+66)	258 (+76)
$T_{\text{INO-Fe}^{3+}} [^\circ\text{C}]$	145 (+10)	196 (+26)	210 (+28)

568  $T_{\text{BOU}}$ : temperatures calculated with the  $\text{Fe}^{2+}$ -pure model of Bourdelle et al. (2013b), considering  $\text{Fe}_{\text{tot}} = \text{Fe}^{2+}$ .  
 569  $T_{\text{INO-Fe}^{2+}}$ : temperatures calculated with the Inoue et al. (2009) model, considering  $\text{Fe}_{\text{tot}} = \text{Fe}^{2+}$ .  $T_{\text{INO-Fe}^{3+}}$ :  
 570 temperatures calculated with the Inoue et al. (2009) model, using the estimated  $\text{Fe}^{3+}/\Sigma\text{Fe}$ .

571

## 572 **Figures**

573

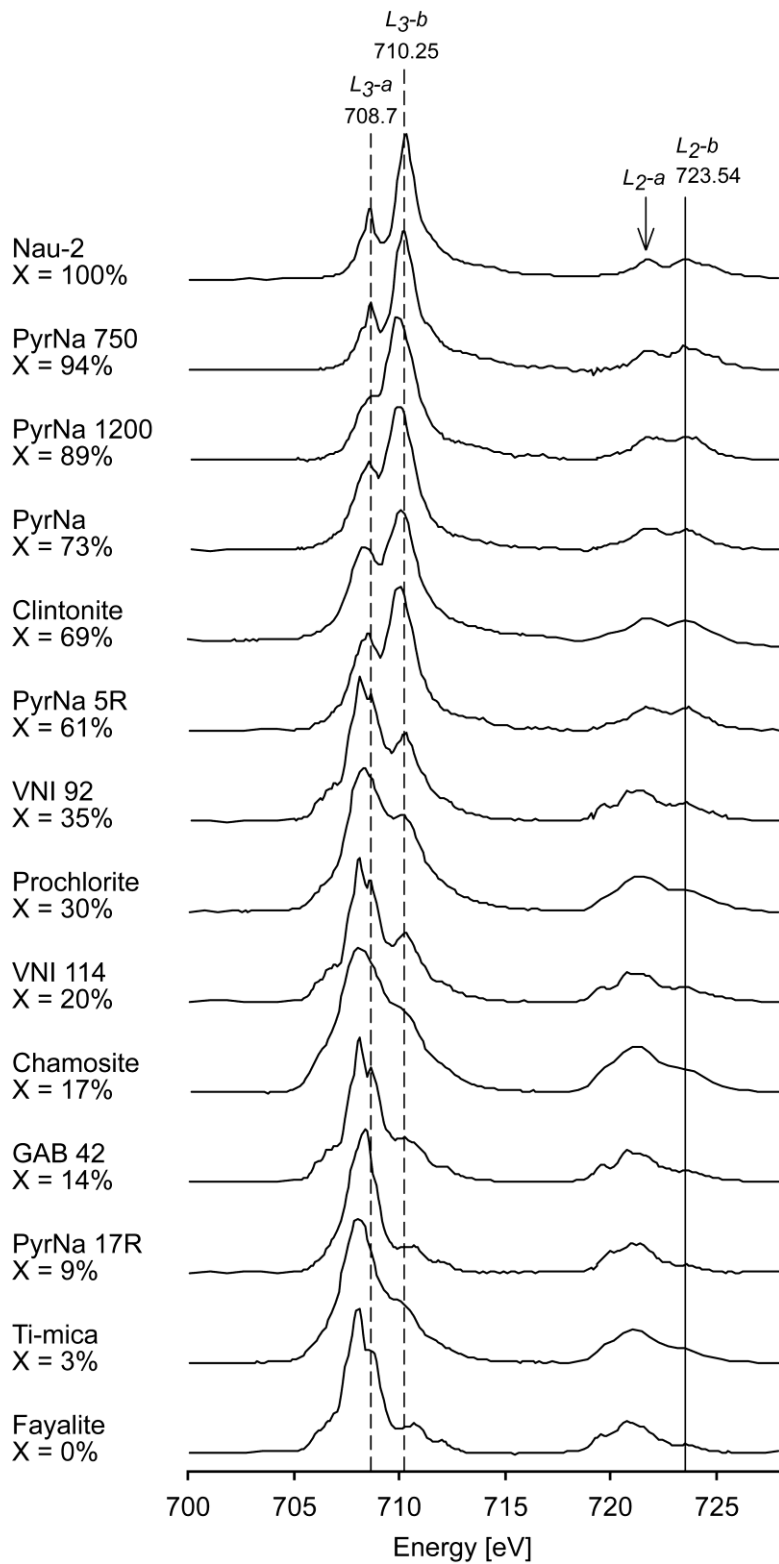


574

575 **Fig. 1** Subtraction of background from XANES spectra at Fe L-edge, using linear and double

576 arctan functions ( $w_1 = w_2 = 1$  eV), for chlorite GAB 42

577

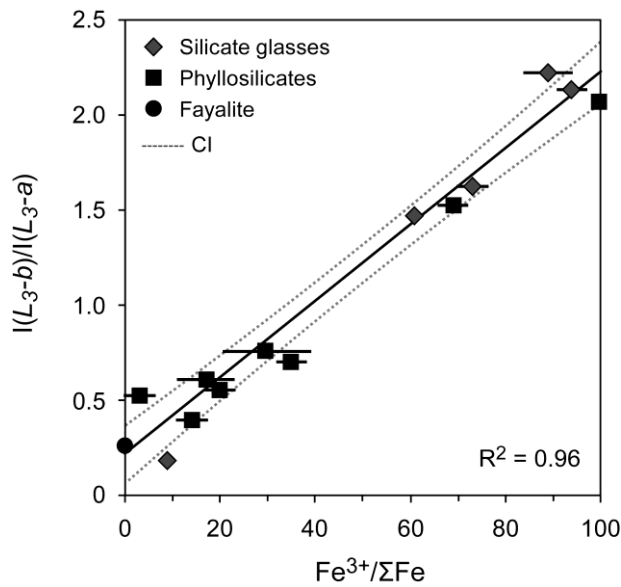


578

579 **Fig. 2** Representative XANES spectra at the Fe L<sub>2,3</sub>-edges for the reference silicates. The  
 580 spectra have been normalised to the integral Fe L<sub>3</sub>-edge intensity, and some of the spectra  
 581 have been shifted vertically for clarity (normalized intensity with arbitrary units). The dotted  
 582 lines represent the energies fixed to determine the Fe<sup>3+</sup> concentration from the Fe L<sub>3</sub>-peaks'

583 intensity ratio. The solid line underlines the position of  $L_{2-b}$  maximum intensity, which is  
584 identical for all spectra.  $X = Fe^{3+}/\Sigma Fe$  ratios of Table 1

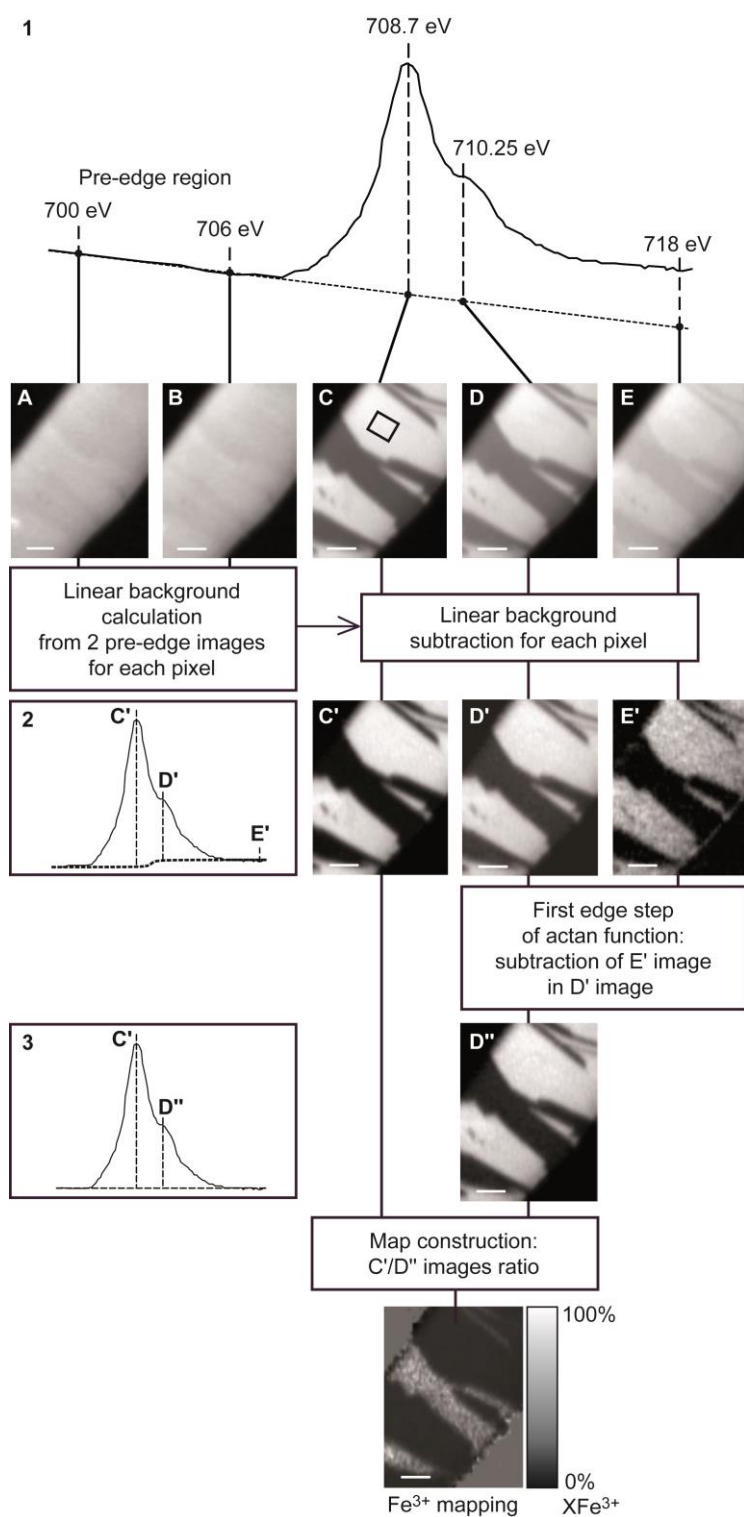
585



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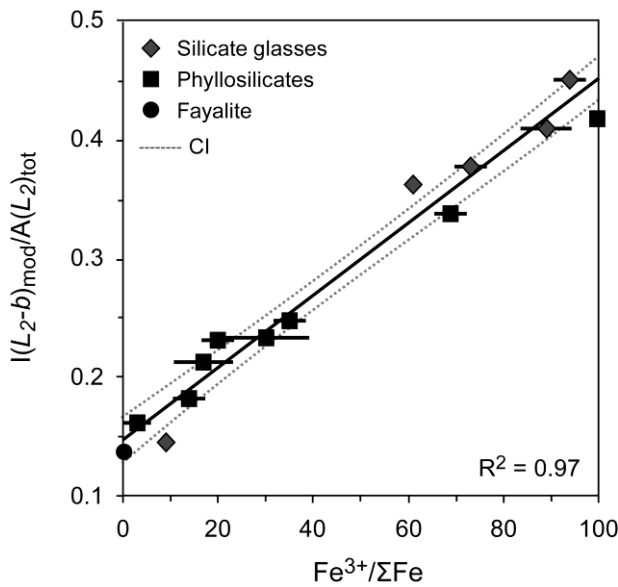
587 **Fig. 3**  $L_{3}$ -edge intensity ratio  $I(L_{3-b})/I(L_{3-a})$  from XANES spectra versus ferric iron  
588 concentration  $Fe^{3+}/\Sigma Fe$  quantified by independent methods for the selected silicates. CI:  
589 confidence interval (95%)

590



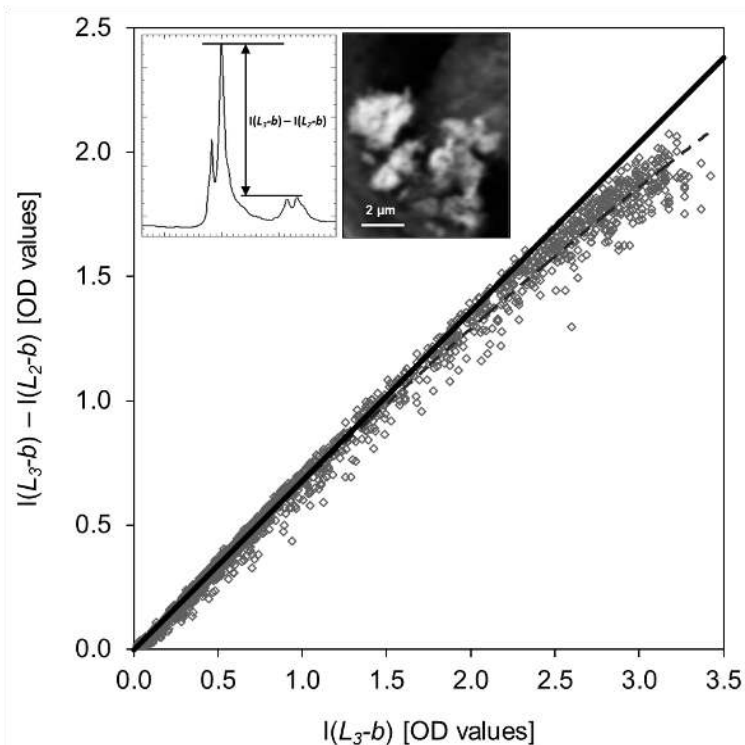
591  
 592 **Fig. 4** Determination of the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio from 5 selected energy images: two images in the  
 593 pre-edge (to apply the “linear background correction” at each pixel of the image), one at 708.7  
 594 eV to quantify the  $L_3$ -a peak, one at 710.25 eV to quantify the  $L_3$ -b peak, and one at 718 eV,  
 595 to remove the edge step of the arctan function. Finally, the ratio of the resulting 708.7 and  
 596 710.25 eV images can be used to determine the  $R_{L_3}$  parameter at each pixel of the image, and  
 597 obtain iron redox mapping. All images are OD images (70 x 90 pixels), where the illite and

598 chlorite are the dark- and light- grey phases, respectively. As an illustration, spectrum #1 was  
 599 retrieved from 110 images (i.e., 110 energy points) on a chlorite area (dark rectangle on image  
 600 C); spectrum #2 was obtained after the linear function subtraction from spectrum #1 and  
 601 spectrum #3 after the actan function subtraction from spectrum #2. Case of FIB foil of Glarus  
 602 GL07 20 sample.  
 603

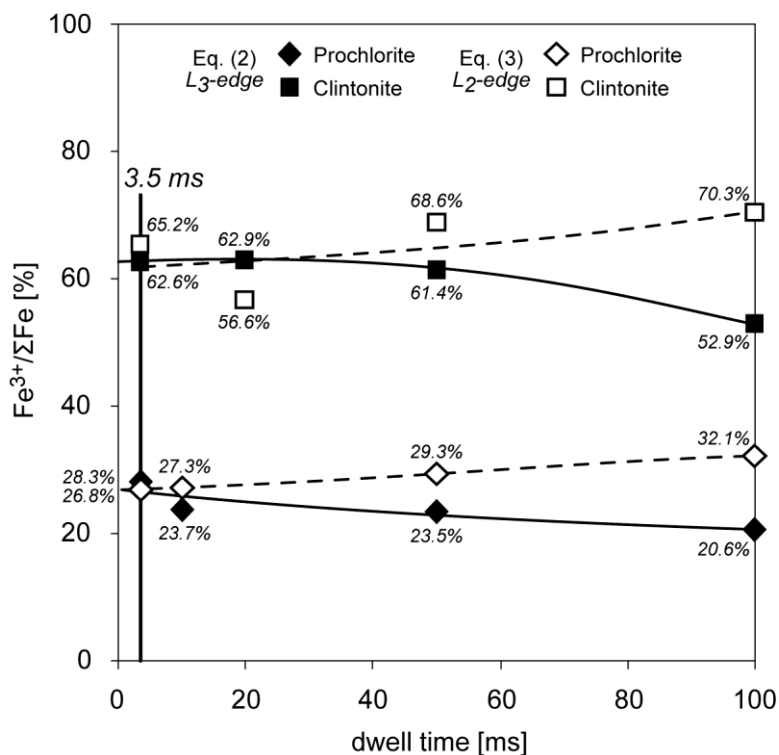


604  
 605 **Fig. 5**  $L_2$ -edge integral intensity ratio (i.e., integral intensity of maximum  $L_2$ -b  $\pm 0.1$  eV over  
 606 total integral intensity (area) of  $L_2$ -edge) from XANES spectra versus ferric iron  
 607 concentration  $Fe^{3+}/\Sigma Fe$  quantified by independent methods for the reference silicates. CI:  
 608 confidence interval (95%)  
 609

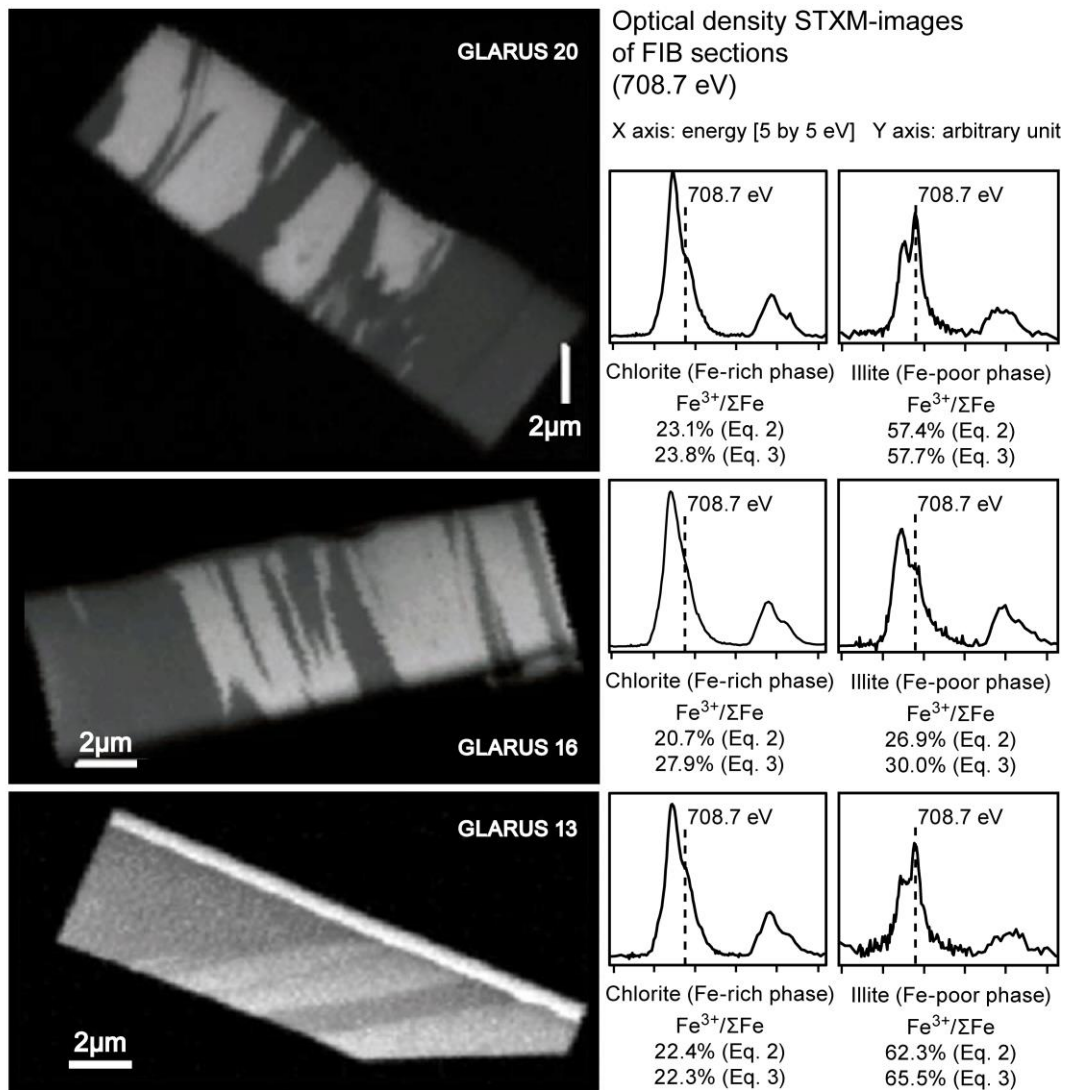




610  
 611 **Fig. 6** Difference, pixel by pixel, of intensity detected between the 710.25 and the 723.54 eV  
 612 images (in which a pre-edge image was not subtracted) versus the intensity of the 710.25 eV  
 613 image of a Smectite Nau-2 STXM-map (Nau-2, 72 x 88 pixels = 6336 points), i.e., the  $L_3$ -b –  
 614  $L_2$ -b intensity difference versus the  $L_3$ -b intensity for each pixel. The dashed line was  
 615 calculated from a quadratic equation. Inset: representative spectra and optical density image  
 616 (710.25 eV) for Nau-2 sample  
 617



618  
 619 **Fig. 7** Beam-induced radiation damage during STXM analyses of chlorite ‘prochlorite’  
 620 ( $X_{Fe^{3+}} = 30\%$ ) and clintonite ( $X_{Fe^{3+}} = 69\%$ ). Evolution of the  $Fe^{3+}/\Sigma Fe$  ratios as a function of  
 621 dwell time, estimated by Eq. (2) and (3) from XANES spectra. Data were fit by a quadratic  
 622 function. The beam radiations (increasing dwell) involve (1) a decrease of  $X_{Fe^{3+}}$  calculated  
 623 from L<sub>3</sub>-edge (Eq. 2) and (2) an increase of  $X_{Fe^{3+}}$  calculated from L<sub>2</sub>-edge (Eq. 3). Spectra of  
 624 reference samples and Glarus samples (see text) were recorded with a dwell time of 1.3-  
 625 3.5 ms per point and energy: the beam radiation damage is thus negligible with our analytical  
 626 conditions for data collection  
 627



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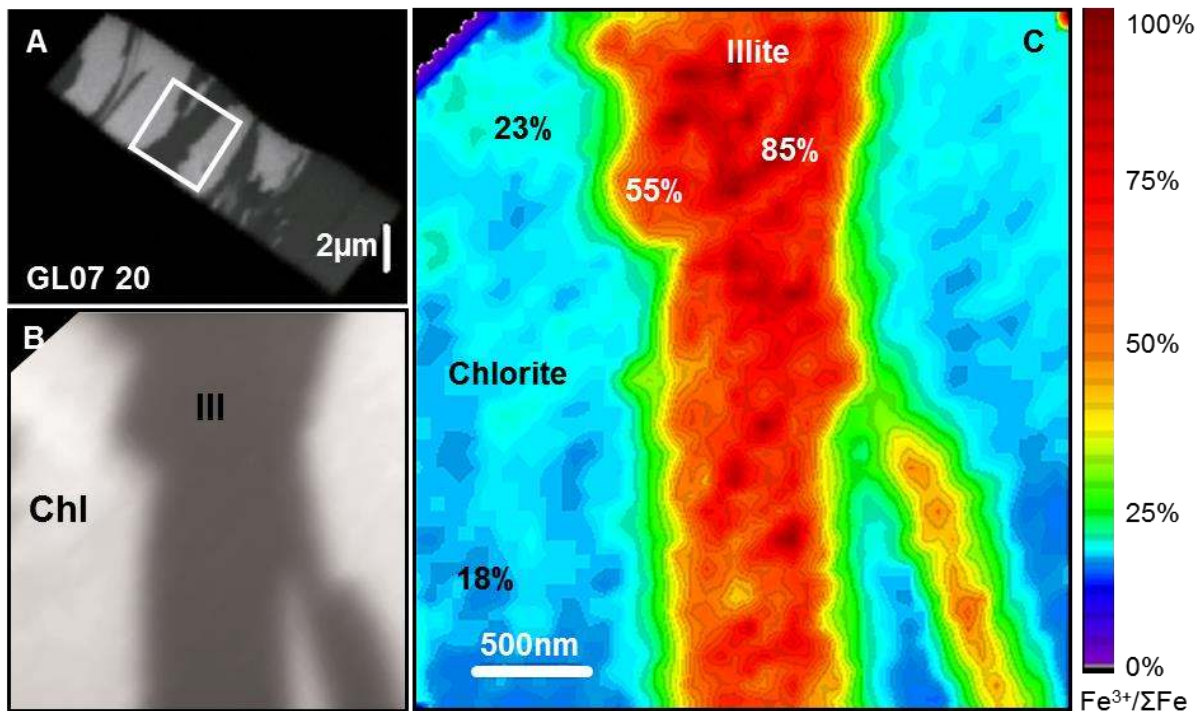
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**Fig. 8** Scanning transmission x-ray microscopy (STXM) and XANES analysis and Fe<sup>3+</sup>/ΣFe estimations for FIB foils of Glarus samples (chlorite and illite). [Left] Optical density images of FIB foils at 708.7 eV. The illite and chlorite are the dark- and light- grey phases, respectively. [Right] XANES spectra of areas of interest and calculated Fe<sup>3+</sup> concentrations associated (crystals rims)



635

636 **Fig. 9** Quantitative Fe redox nanomapping on FIB foil of Glarus GL07 20 sample. (a) Optical  
 637 density image at 708.7 eV of Glarus GL07 20 FIB section, where the illite and chlorite are the  
 638 dark- and light- grey phases, respectively. (b) Optical density image at 708.7 eV of the area of  
 639 interest. (c) iron redox mapping, calculated from the 708.7 to 710.25 eV images ratio coupled  
 640 with Eq. (2). The illite-chlorite contacts were analysed by AEM to check that they are  
 641 approximately perpendicular to the FIB foil surface, i.e., there is only a small overlap between  
 642 the two minerals at their contact. The spatial averaging effect of the x-ray beam over the pixel  
 643 size (i.e., 88 nm) sets the limit of the minimum distance over which illite-chlorite contacts can  
 644 be discriminated. Beyond this distance, the intracrystalline variation of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio in the  
 645 illite-like phase can be interpreted as an authentic zonation, from 55% to 85% in several  
 646 crystal core clusters

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