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## Revision 2

# Synthetic potassic-ferro-richterite: 2. Single-crystal HT-FTIR spectroscopy and hints on the deprotonation process of Fe-dominant amphiboles

GIANCARLO DELLA VENTURA<sup>1,2\*</sup>, UMBERTO SUSTA<sup>1</sup>, FABIO BELLATRECCIA<sup>1,2</sup>,  
AUGUSTO MARCELLI<sup>2</sup>, GÜNTHER J. REDHAMMER<sup>3</sup> AND ROBERTA OBERTI<sup>4</sup>

<sup>1</sup>*Dipartimento di Scienze, Università di Roma Tre, I-00146 Roma, Italy*

<sup>2</sup>*INFN-LNF, I-00044 Frascati, Italy*

<sup>3</sup>*Department of Materials Science & Physics, University of Salzburg,  
5020 Salzburg, Austria*

<sup>4</sup>*CNR-Istituto di Geoscienze e Georisorse, Sede secondaria di Pavia, I-27100 Pavia, Italy*

\* Corresponding author.

e-mail: [giancarlo.dellaventura@uniroma3.it](mailto:giancarlo.dellaventura@uniroma3.it)

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## ABSTRACT

20 High-Temperature Fourier Transform Infrared (HT-FTIR) spectroscopy was used to  
21 characterize the deprotonation process of synthetic potassic-ferro-richterite of composition  
22  $A(K_{0.90}Na_{0.07})^B(Ca_{0.54}Na_{1.46})^C(Fe^{2+}_{4.22}Fe^{3+}_{0.78})^T Si_8 O_{22}^W(OH_{1.70} O^{2-}_{0.30})$ . Unpolarized single-  
23 crystal spectra were collected both *in situ* and on quenched samples, and heating experiments  
24 were conducted in air, at a rate of 10°C/min. The room-*T* spectrum measured before  
25 annealing shows a main band at 3678 cm<sup>-1</sup> and a minor band at 3622 cm<sup>-1</sup>; these are assigned  
26 to local configurations involving Fe<sup>2+</sup> at *M*(1)*M*(1)*M*(3) and facing a filled and an empty  
27 alkali-site, respectively. At 400 °C, a new band grows at 3656 cm<sup>-1</sup>; this is the most intense  
28 feature in the pattern at 450 °C. At  $T \geq 500$  °C, all peaks decrease drastically in intensity, and  
29 finally disappear at  $T > 600$  °C. The total absorbance measured *in situ* increases significantly  
30 in the 25 °C <  $T$  < 450 °C range, although the spectra collected on quenched samples show no  
31 OH loss in the same  $T$  range. This feature is consistent with an increase of the absorption  
32 coefficient ( $\epsilon$ ) with  $T$ , the reason for which is still unclear. However, this feature has  
33 significant implications for the quantitative use of FTIR data in HT experiments. Examination  
34 of the relevant OH-stretching bands shows that iron oxidation occurs preferentially at the *M*  
35 sites associated with occupied *A* sites. The deprotonation temperature indicated by FTIR for  
36 single-crystals is around 100 °C higher than that obtained by HT-X-ray diffraction (XRD) on  
37 single-crystal by Oberti et al. (2016), whereas that obtained by HT- XRD on powders is  
38 intermediate. This unexpected observation can be explained by considering that: (1) the iron  
39 oxidation process, which is coupled to deprotonation and is probed by XRD, occurs  
40 preferentially at the crystal surface where it is triggered by the availability of atmospheric  
41 oxygen; (2) the proton diffusion, probed by FTIR, is slower than the electron diffusion probed  
42 by XRD; thus, the temperature shift may be explained by a much longer escape path for H in  
43 single-crystals than in powders. These results suggest that possible effects due to crystals size  
44 should be carefully considered in HT experiments done on Fe-rich silicates.

45

46 **Keywords:** HT-FTIR spectroscopy, amphiboles, potassic-ferro-richterite, deprotonation

47 process

48

## INTRODUCTION

49           The physical and crystal-chemical properties of solids strongly depend on temperature,  
50 and for this reason many disciplines, such as mineralogy, ceramic science, chemical, electrical  
51 and mechanical engineering, metallurgy and physics make use high-temperature (*HT*) studies.  
52 Most *HT* processes involve chemical transformations and phase transitions that need to be  
53 characterized by using combinations of *in situ* analytical techniques, such as *HT*-diffraction  
54 (either on single crystals or powders), thermal analysis (TG/DTA), and *HT* spectroscopies.  
55 Relevant to this point is the fact that many *HT* reactions in minerals involve the loss and  
56 subsequent migration of hydrogen or molecular species containing hydrogen. Also,  
57 deprotonation processes are associated with simultaneous oxidation of multivalent elements,  
58 such as Fe or Mn, with significant consequences for the physical properties of the mineral  
59 itself and of the rock where it occurs. For example, enhanced electrical conductivity in the  
60 Earth's crust and in the upper mantle has been related to similar processes occurring in  
61 subducted amphibolites (e.g., Schmidbauer et al. 2000; Wang et al. 2012). Hence, an accurate  
62 knowledge of the temperature effects on the physical properties of minerals is relevant to  
63 model geophysical phenomena. However, deprotonation reactions in Fe-rich or Fe-dominant  
64 hydrous minerals and their role on both electrical conductivity and magnetic properties are  
65 still poorly known.

66           Early *HT* studies on Fe-dominant amphiboles date back to the 1960-70s (Addison et  
67 al. 1962a, 1962b; Addison and Sharp, 1962, 1968; Addison and White, 1968; Ernst and Wai,  
68 1970), because of the emerging technological relevance of these materials for a variety of  
69 applications (e.g., fire-proof textiles, thermo-acoustic insulators, construction materials, water  
70 pipes, electrical components, etc.). Structural phenomena accompanying the oxidation of iron  
71 in amphiboles were later addressed by Ungaretti (1980), Clowe et al. (1988) and Phillips et al.  
72 (1988, 1989, 1991).

73 After the review provided by Welch et al. (2007), increasing efforts have been devoted  
74 to the study of different amphibole compositions at non-ambient conditions, and several  
75 features controlling the crystal-chemical and crystal-structural adjustments accompanying HT  
76 treatments have been discussed in detail (Welch et al. 2011; Zema et al. 2012; Oberti et al.  
77 2012, 2013, 2016). However, notable issues still need to be understood, including the  
78 mechanisms and kinetics of proton diffusion throughout the crystal structure, and the role of  
79 multiple-valence elements, notably Fe, in this process.

80 This study represents a further step of an ongoing project on the high-*T* study of Fe-  
81 rich amphiboles done by using a fully multidisciplinary approach, including microchemistry  
82 (EMP and SEM), X-ray diffraction, and spectroscopic methods (FTIR, Mössbauer). In this  
83 paper we describe, in particular, FTIR data obtained at HT on the same synthetic amphibole  
84 studied by HT single-crystal XRD (SC-XRD) by Oberti et al. (2016). This work is intended to  
85 (1) integrate the HT SC-XRD results for a better description of the deprotonation process, and  
86 (2) study the temperature dependence of the OH-stretching bands in a Fe-bearing amphibole  
87 with a simple and well-constrained composition, by combining measurements done *in situ*  
88 and on quenched materials. According to recent work (e.g., Zhang et al. 2007; Radica et al.  
89 2016a) the behavior of hydroxyl-related bands during HT-FTIR experiments still needs to be  
90 properly understood to allow using the spectroscopic data for quantitative studies.

91 To help following the discussion below, we schematically present in Figure 1 the  
92 relevant part of the *C2/m* amphibole structure sampled across the A site. The O-H group is  
93 directly bonded to a trimer of *M*(1)*M*(1)*M*(3) octahedra and is directed toward the alkali  
94 cation (in the present case K) which may occur at two different (split) positions centered at  
95 the A site (Fig. 1); for symmetry reasons, the same arrangement occurs on the opposite side of  
96 the alkali cation, which thus interacts with two OH groups bonded to two distinct strip of  
97 octahedra piling up along *a*\* (for more details, see Della Ventura et al. 2007). This local  
98 arrangement can be expressed via the *M*(1)*M*(1)*M*(3)-OH-A-OH-*M*(1)*M*(1)*M*(3) configuration

99 notation (Della Ventura et al. 1999). Robert et al. (1999) have shown that in amphiboles there  
100 is vibrational coupling between two O-H groups facing across the alkali site, while no  
101 coupling is observed across an unoccupied A site or along the O(3)-O(3) edge connecting two  
102 OH groups on both sides of the same strip of octahedra. When the A site is occupied, any  
103 perturbation of the anionic population at one of the two facing O(3) sites (e.g. substitution of  
104 OH<sup>-</sup> with F<sup>-</sup>, Cl<sup>-</sup> or O<sup>2-</sup>) involves a shift of the A cation (e.g. Hawthorne et al. 1996), and thus  
105 a change in the O-H...A repulsive interaction. In such a case, the O-H stretching frequency is  
106 also modified, whereas in A-site empty amphiboles it is not (Robert et al. 1999). In other  
107 words, the alkali cation acts as a bridge by vibrationally connecting two facing O(3) anions  
108 (Fig. 1), and this feature is extremely important for the interpretation of the IR spectra of  
109 amphiboles with complex compositions (Della Ventura et al. 2001, 2014). This effect has  
110 been verified in OH-F substituted richterites (e.g. Robert et al. 1989, 1999) and pargasite  
111 (Robert et al. 2000), while Della Ventura et al. (2007) have shown that the same is true for  
112 partially deprotonated amphiboles.

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114

## MATERIALS AND METHODS

115 The synthesis of the sample studied in this paper (labeled Ri1) has been described in  
116 detail by Redhammer and Roth (2002), and its structural characterization is reported in Oberti  
117 et al. (2016). These authors showed that the crystal-chemical formula of amphibole Ri1,  
118 obtained by combining EMP analysis, structure refinement of SC-XRD data and FTIR  
119 spectroscopy is:  $^A(K_{0.90}Na_{0.07})^B(Ca_{0.54}Na_{1.46})^C(Fe^{2+}_{4.22}Fe^{3+}_{0.78})^T Si_8 O_{22}^W (OH_{1.70} O^{2-}_{0.30})$ . The  
120  $Fe^{2+}/Fe^{3+}$  in particular was determined on the basis of refined bond-distances (Oberti et al.  
121 2016). Although still in the compositional field of richterite, this sample falls close to the  
122 richterite - arfvedsonite boundary (see Hawthorne and Oberti 2007 and Hawthorne et al.  
123 2012) for systematic issues on amphibole nomenclature).

124 Unpolarized single-crystal HT-FTIR spectra were collected both *in situ* and on  
125 quenched crystals at the Laboratori Nazionali di Frascati of the INFN (Frascati) using a  
126 Linkam 1400XY heating stage, fitted on a Bruker Hyperion 3000 FTIR microscope equipped  
127 with a 15X Schwarzschild objective and a MCT N<sub>2</sub>-cooled detector. The microscope was  
128 attached to a Vertex optical bench equipped with a KBr beamsplitter and a globar IR source;  
129 the beam was reduced to 50 μm, and 256 spectra were averaged for both mineral and  
130 background; the nominal resolution was 4 cm<sup>-1</sup>. The sample was prepared as a doubly  
131 polished 100 μm thick section, and cut into two fragments, for use in two different  
132 experiments. The orientation of the crystal slab was not determined, but considering that  
133 during polishing the sample tended to sit on the easy cleavage direction, it is believed to be  
134 approximately parallel to (110). In the first experiment, FTIR spectra were collected *in situ*  
135 every 25 °C for 25 < *T* < 500 °C and every 50 °C for 500 < *T* < 600 °C. The heating rate of 10  
136 °C/min was used, and the spectrum was collected immediately on reaching the set *T* in order  
137 to avoid the effects of the relatively fast kinetics of deprotonation at high temperature. The  
138 second experiment was carried out by using the same heating rate, but the FTIR spectra were  
139 collected every 50 °C on samples quenched to room-*T* after annealing the crystal at the  
140 desired temperature. After each room-*T* measurement, the sample was quickly (50 °C/min) re-  
141 heated to continue the ramp, and so on.

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## RESULTS

144 In this section, we compare the two sets of FTIR data. To the best of our knowledge,  
145 this comparison has never been done for amphiboles and is of general methodological interest  
146 to evaluate critically the results of FTIR analysis.

147 The spectrum collected on the crystal before annealing shows, in the principal OH-  
148 stretching region, a main band at 3678 cm<sup>-1</sup> and a minor band at 3622 cm<sup>-1</sup>; a shoulder at 3656  
149 cm<sup>-1</sup> is also evident on the lower frequency side of the main band (Fig. 2). Following the

150 systematic work on the FTIR spectroscopy of richterite specimens with different cation  
151 occupancies at the octahedral sites (e.g., Della Ventura 1992; Della Ventura et al. 1996, 1997,  
152 1998, 2005a, 2005b, 2016; Iezzi et al. 2004, 2005), and considering the well-defined  
153 composition of the sample under study, the main band at  $3678\text{ cm}^{-1}$  is assigned to the  
154  $M(1)Fe^{2+}M(1)Fe^{2+}M(3)Fe^{2+}$ -OH local environment, with the OH dipole pointing toward an  
155 occupied A site, while the lower-frequency band at  $3622\text{ cm}^{-1}$  can be assigned to the same  
156 local configuration but with the O-H group pointing toward an empty A site. According to the  
157 results of the structure refinement (Oberti et al. 2016), the shoulder at  $3656\text{ cm}^{-1}$  can be  
158 assigned to the presence of a minor, but nonetheless significant, oxo-component in the  
159 structure. This assignment is based on the work of Della Ventura et al. (2007) who showed  
160 that in A-site filled amphiboles, anytime  $Fe^{3+}$  occurs at the  $M(1)M(1)M(3)$  trimer of octahedra,  
161 at least one of the O(3) sites in the trimer is deprotonated to maintain electroneutrality; if no  
162  $Fe^{3+}$  occurs in the  $M(1)M(1)M(3)$  trimer facing on the other site of the A cavity (Fig. 1a), the  
163 local configuration is  $Fe^{2+}Fe^{2+}Fe^{2+}$ -OH-A-O<sup>2-</sup>- $Fe^{3+}Fe^{2+}Fe^{2+}$ . In such a case, the A cation  
164 moves away from the center of the A cavity in the direction of the deprotonated trimer, so that  
165 the  $H^+ \dots A^+$  interaction decreases and the O-H stretching band shifts by  $\sim 20\text{ cm}^{-1}$  towards  
166 lower wavenumbers because of the weakening of the O-H bond (Della Ventura et al. 2007);  
167 this is exactly what we observe in Figure 2.

168 In the NIR region, two relatively broad but well-defined peaks are observed at 4255  
169 and  $4155\text{ cm}^{-1}$ , respectively (Fig. 2). This region of the spectrum is poorly understood for  
170 amphiboles; according to literature data (e.g., Clark et al. 1990; Mustard 1992; Laukamp  
171 2012), these bands can be assigned to the combination of stretching and libration vibrations of  
172 the O-H dipole.

173 Finally, minor peaks are present at  $3730$  and  $3562\text{ cm}^{-1}$ , respectively. The frequency of  
174 the former would correspond to that of local arrangements containing only Mg (e.g., Robert et  
175 al. 1989, Della Ventura 1992, Gottschalk and Andrut 1998). However, as sample Ri1 does not

176 contain Mg, this band must be assigned to overtone/composition mode of framework  
177 vibrations; note that such absorptions are invisible in powder FTIR data, but may show up in  
178 single-crystal data. The minor peak at  $3562\text{ cm}^{-1}$  cannot be assigned to any of the cationic  
179 permutations compatible with the composition of the sample, and should be due to some  
180 mica-like local configurations (biopyribole defects) or again to overtone/composition modes  
181 of the silicate structure. In any case, because of their low intensity, these bands can be  
182 neglected in the following discussion.

183         Single-crystal HT-FTIR spectra were first collected *in situ* (Fig. 3a). Up to  $400\text{ }^{\circ}\text{C}$ , the  
184 main band at  $3678\text{ cm}^{-1}$  broadens, shifts to lower wavenumbers and increases in intensity. At  
185  $450\text{ }^{\circ}\text{C}$ , it is replaced by a broad and multicomponent band centered around  $3656\text{ cm}^{-1}$ . At  
186 higher temperatures, the bands disappear abruptly and the signal becomes extremely noisy. At  
187  $T \geq 550\text{ }^{\circ}\text{C}$  no peak can be resolved from the background. In the attempt to achieve a better  
188 resolution, FTIR spectra were collected at room- $T$  on quenched samples; they are plotted in  
189 Figure 3b using the same absorbance scale. Up to  $350\text{ }^{\circ}\text{C}$ , a very limited variation in band  
190 intensity and shape is observed. The band centered at  $3656\text{ cm}^{-1}$  becomes discrete at  $400\text{ }^{\circ}\text{C}$ ,  
191 but the  $3678\text{ cm}^{-1}$  band still is the major feature in the spectrum. The spectrum collected at  
192  $450\text{ }^{\circ}\text{C}$  is very different from the previous ones: the band at  $3656\text{ cm}^{-1}$  is now the most  
193 intense, and that at  $3678\text{ cm}^{-1}$  has lost most of its intensity. At  $T \geq 500\text{ }^{\circ}\text{C}$ , the absorbance  
194 decreases drastically, so that at  $600\text{ }^{\circ}\text{C}$  the sample retains a very minor amount of OH.

195         Figure 4 compares, as an example, the O-H stretching bands measured at  $400\text{ }^{\circ}\text{C}$  on  
196 the studied sample both *in situ* and after quenching. The resolution between the main bands at  
197  $3678$  and  $3656\text{ cm}^{-1}$  is lost in the spectrum collected *in situ*, due to the combined effects of a  
198 general broadening and of a different red shift of all the absorption components. Indeed, the  
199 downward shift of the  $3678\text{ cm}^{-1}$  component (assigned to the O-H dipole interacting with an  
200 alkali A cation), is twice that of the band at  $3622\text{ cm}^{-1}$ , (assigned to the O-H dipole pointing  
201 toward an empty A-site):  $\Delta\nu = 20\text{ cm}^{-1}$  vs.  $10\text{ cm}^{-1}$ . This feature is in agreement with the fact

202 that the increase in atom vibration at *HT* helps to reduce the repulsive coulombic interactions  
203 between the hydrogen of the O-H dipole and the A cation. Single-crystal XRD shows that the  
204 A cations at *HT* tend to order at the  $A(m)$  sub-site, which is displaced towards the side of the A  
205 cavity (Oberti et al. 2016). Moreover, the overall intensity (area) of the band varies  
206 significantly in the two experiments.

207 Figure 5 compares the evolution of the integrated intensity measured either *in situ* or  
208 after quenching at any temperature, scaled to the intensity at room- $T$  ( $T_I / RT_I \cdot 100$ ).  
209 Integration ranges were 3710-3600  $\text{cm}^{-1}$  for the OH-stretching region, and 4300-4100  $\text{cm}^{-1}$  for  
210 the combination region. In the OH-stretching region we observe a significant increase of the  
211 intensity collected *in situ*, which almost doubles in the 400-425 °C range, a result which is  
212 difficult to explain. In contrast, the intensity data collected after quenching indicate a constant  
213 OH content up to 400 °C, followed by an abrupt OH loss in the  $T$  range 400-500 °C. At 500  
214 °C, low amounts (~10%) of OH are still present in the amphibole, whereas almost no OH is  
215 present at  $T > 600$  °C. Focusing on the weak bands due to combination modes at 4255 and  
216 4155  $\text{cm}^{-1}$ , their total absorption measured *in situ* is constant up to 400 °C, and then decreases  
217 abruptly.

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219

## DISCUSSION

### 220 **Changes in the absorptivity of the OH-bond in potassic-ferro-richterite vs. $T$**

221 Previous *HT*-FTIR studies have clearly shown that absorption bands typically broaden  
222 and shift with increasing  $T$ . This feature has been observed in many different minerals (e.g.,  
223 Aines and Rossman 1985; Yamagishi et al. 1997; Tokiway and Nakashima 2010a,b; Zhang et  
224 al. 2005, 2006, 2007, 2010) and glasses (Keppler and Bagdassarov 1993). Zhang et al. (2007)  
225 discussed the occurrence of changes in the absorption coefficients with  $T$ , an issue that would  
226 have significant consequences for quantitative studies based on the Beer-Lambert  
227 relationship. Moreover, Zhang et al. (2007) and Radica et al. (2016a) noted that the

228 absorbance of the different vibrational modes (e.g., fundamental vs. multiphonon) measured  
229 on a single sample may vary as a function of  $T$  in different ways. In the Beer-Lambert  
230 relationship,  $\epsilon = A/d \cdot C$ ,  $\epsilon$  is the molar absorptivity,  $A$  the measured absorbance (either linear  
231 or integrated),  $d$  the sample thickness, and  $C$  the concentration of the molecule studied. Thus,  
232  $\epsilon$  is the coefficient relating the intensity measured experimentally to the amount of the  
233 molecule (or molecular group) absorbing the incoming radiation. In quantitative studies,  $\epsilon$   
234 must be either calibrated for any matrix or evaluated on the basis of empirical relationships  
235 (e.g., Paterson 1982; Libowitzky and Rossman 1997). In  $HT$  studies, it is generally assumed  
236 that  $\epsilon$  is constant over the temperature range examined, although there is increasing evidence  
237 (Yamagishi et al. 1997; Whitters et al. 1999; Okumura and Nakashima 2005; Zhang et al.  
238 2007, 2010; Tokiway and Nakashima 2010a; Radica et al. 2016b) that this is not the case.

239 For the amphibole studied in this work, two different trends are obtained for the  
240 intensity of the principal OH-band when collecting spectra *in situ* or after quenching (Fig. 5).  
241 Spectra collected on quenched samples show a constant OH concentration ( $C$ ) up to 400 °C.  
242 In the present case, the sample thickness can be considered constant because the expansion  
243 coefficients obtained by Oberti et al. (2016) are quite low. Therefore, in the Beer-Lambert  
244 relationship given above, the significant increase in absorption intensity observed during *in*  
245 *situ* measurements can be attributed solely to a  $T$ -induced increase in the integral molar  
246 absorptivity ( $\epsilon$ ).

247 The very intriguing point in Figure 5 is that the intensities measured *in situ* for the  
248 studied amphibole *increase* significantly in the  $T$  range considered, and even almost double  
249 close to the onset of deprotonation (around 400-425 °C). In contrast, all previous  $HT$ -FTIR  
250 studies so far published indicate, for the fundamental modes, a *decrease* in the  $H_2O/OH$   
251 intensity during heating (e.g., Zhang et al. 2007; Tokiway and Nakashima 2010a).  
252 Multiphonon (combination or overtone) bands have been shown to increase in intensity in  
253 some minerals, a notable case being provided by talc (Zhang et al. 2007); however, in

254 potassic-ferro-richterite the combination modes have a constant absorbance in the examined  
255 HT range (Fig. 5). It is also worth noting that a similar increase in the intensity of the  
256 fundamental stretching band as a function of  $T$  seems to be typical of  $\text{CO}_2$ ; this feature has  
257 been recently observed in cordierite (Radica et al. 2016a) and in different sodalite-group  
258 minerals (unpublished).

259         The first important consequence of this finding is that *in situ* FTIR data cannot be  
260 converted directly into quantitative information for the studied amphibole. The reason for the  
261 dependence of the molar absorptivity on temperature is still not clear (see also early literature,  
262 such as Hoover et al. 1969). In the case of muscovite, Tokiway and Nakashima (2010a)  
263 related the change in molar absorptivity to a tilting of the O-H vector with respect to the  $c^*$   
264 crystallographic direction for increasing  $T$ , namely from  $75^\circ$  at RT to  $43^\circ$  at  $650^\circ\text{C}$ . Indeed, a  
265 tilt of the O-H vector would change its projection on to the (001) plane (perpendicular to the  
266 IR beam), thus *reducing* the measured absorbance (see also Libowitzky and Rossman, 1996  
267 and Della Ventura et al. 2014 for a discussion of this issue). For potassic-ferro-richterite we  
268 have no evidence of a similar behavior because the position of the H atom in HT structure  
269 refinements done by Oberti et al. (2016) could not be determined.

270         The reason for the anomalous increase in the intensity reported in Figure 5 is therefore  
271 currently unknown. We can only note that it is being observed in other Fe-dominant  
272 amphiboles such as riebeckite (Susta 2016) and ferro-actinolite (unpublished), on both single-  
273 crystals and powders. Moreover, in all Fe-rich amphiboles we have examined so far the  
274 increase in absorption is not linear but is enhanced at higher  $T$ , similar to Figure 5, and such a  
275 behavior, although less pronounced, is observed also when using powders (Susta 2016).

276         An increase in intensity could in principle result from mode-mode coupling at HT of  
277 absorptions with close wavenumbers, and this could be the case for the  $3678$  and  $3656\text{ cm}^{-1}$   
278 bands. However at the present we have no elements to support this hypothesis. Additional  
279 work is needed on amphiboles with different compositions to understand whether this peculiar

280 absorption behavior is due to the chemistry, i.e. to the presence of Fe, and the phenomena  
281 accompanying its oxidation at *HT* conditions.

282

### 283 **The behavior of potassic-ferro-richterite during heating**

284 Figure 6 compares the evolution as a function of *T* of the unit-cell volume (data from  
285 Oberti et al. 2016) against the evolution of the OH-stretching absorbance (quenched data, see  
286 Figure 5) in sample Ri1. According to the work of Oberti et al. (2016), the unit-cell  
287 parameters expand linearly up to ~300 °C; in the *T* range 300-400 °C there is an abrupt  
288 contraction of all the edges, and then the expansion of the unit cell of the deprotonated phase  
289 continues steady until 800 °C (Fig. 6). Structure refinements at selected *T* revealed that in the  
290 300-400 °C *T* interval virtually all H is lost and electroneutrality at the anionic O(3) site is  
291 maintained by the oxidation of an equal amount of <sup>C</sup>Fe<sup>2+</sup> to <sup>C</sup>Fe<sup>3+</sup>. Careful inspection of the  
292 evolution of the refined site-scatterings and bond-lengths at the octahedral sites suggests that  
293 Fe oxidation occurs almost exclusively at the *M*(1) site, while the *M*(3) and *M*(2) sites are  
294 virtually unaffected. For 400 °C < *T* < 800 °C the related oxo-amphibole ("oxo-ferro-  
295 richterite") is stable, and its structure is perfectly retained upon reversal to room-*T*, with a  
296 linear decrease of all unit-cell parameters. Interestingly, an inverse trend as a function of *T* is  
297 observed for the β angle, which decreases with *T* in potassic-ferro-richterite but increases in  
298 its deprotonated counterpart (Oberti et al. 2016). It must be stressed, however, that the *T* range  
299 of stability reported for potassic-ferro-richterite is valid for 1 atmosphere in air, and that it is  
300 likely to change at different (water) pressures, typical of the deep crust, or under different  
301 oxidizing conditions.

302 The *HT*-FTIR data collected during the present work add further information to model  
303 the process described by *HT*-SC-XRD. The evolution of the overall intensity of the OH  
304 signal, measured on quenched samples for the 3710-3600 cm<sup>-1</sup> integration range (Fig. 6), is  
305 consistent with the behavior observed by X-ray diffraction: it does not indicate any significant

306 loss of hydrogen up to 400 °C, while deprotonation occurs in a relatively narrow  $T$  range (100  
307 °C). The intriguing point in Figure 6 is, however, that HT-SC-FTIR shows the onset of  
308 deprotonation at about 400 °C, which is about 100 °C higher than that reported by Oberti et  
309 al. (2016) for the same amphibole studied by HT-SC-XRD. This large  $T$  shift cannot be  
310 assigned to experimental artifacts. A malfunction or incorrect calibration of the thermocouple  
311 can be ruled out, because both heating systems (our HT stage and the microfurnace used by  
312 Oberti and co-workers) were calibrated against the melting point of a series of known  
313 substances. Although the duration of SC-FTIR (~ 2 hrs) and SC-XRD (~ 48 hrs) heating  
314 experiments is different, refinement of X-ray powder diffraction data collected *in situ* for the  
315 same sample (unpublished) using a heating regime very similar to that used for HT-SC-FTIR  
316 (~ 2 hrs) yielded a deprotonation onset of ~ 350 °C, hence intermediate between the values  
317 observed for single crystals. Useful information to solve this conundrum is provided by the  
318 results of Susta (2016) on riebeckite. Because a larger amount of sample was available, HT-  
319 FTIR data were collected *in situ* and under the same experimental conditions both on a single  
320 crystal and on powders. Again, the onset  $T$  of deprotonation is ~100 °C lower for powders  
321 than for single crystal. We can thus conclude that XRD techniques are not affected by crystal  
322 size, whereas FTIR spectroscopy yields a deprotonation  $T$  ~50/100 °C higher for single  
323 crystals than for powders. A possible explanation is that proton diffusion (probed by FTIR) is  
324 slower than electron diffusion. The way by which protons/hydrogen move across the  
325 amphibole crystal is not fully understood; a feasible model is by protons hopping between  
326 deprotonated O(3) sites along the strip of octahedra, hence along the  $c$  crystallographic  
327 direction (Susta 2016). The persistence of the O-H stretching absorption in the spectra at  $T$   
328 conditions where X-ray diffraction shows that the iron oxidation is proceeding (Fig. 6) is  
329 compatible with transient O-H bonds continuously created during the hopping of the proton  
330 towards the surface. The complete deprotonation is therefore observed at higher  $T$  on single-  
331 crystals where the diffusion path has to be order of magnitude longer than in powders.

332

333 **Local order in the deprotonation process of potassic-ferro-richterite**

334 Focusing on the crystal-chemical mechanisms involved in the deprotonation process,  
335 Figure 3b shows that for  $T < 350$  °C no significant change occurs in the OH-spectrum and  
336 hence in the local environment of the OH dipole (namely, the cation occurring at the adjacent  
337 sites). At 350 °C, a weak increase in the intensity of the  $3656\text{ cm}^{-1}$  component (the one  
338 assigned to the  $M^{(1)}\text{Fe}^{2+}M^{(1)}\text{Fe}^{3+}M^{(3)}\text{Fe}^{2+}\text{-OH-A-O}^{(3)}\text{O}^{2-}$  configurations) is observed, thus  
339 providing the first signal of Fe oxidation close to the O(3) site. This component becomes  
340 prominent at 400 °C, and is the main feature in the spectrum at  $T \geq 450$  °C. The spectra  
341 collected on quenched samples were decomposed using the Peakfit® program by Jandel  
342 Scientific; the background was treated as linear and all bands were modeled as symmetric  
343 Gaussian line-shapes (Della Ventura et al. 1996). The spectra were fitted to the smallest  
344 number of peaks needed for an accurate description of the spectral profile, based on the  
345 knowledge of the behavior of OH bands in this spectral region (see a review by Hawthorne  
346 and Della Ventura 2007). The spectral parameters (position and width) of some partially  
347 overlapping peaks (see for example the  $3656\text{ cm}^{-1}$  component) were refined where these  
348 peaks are most prominent, and then kept fixed during the refinement of the other samples. At  
349 convergence, the peak positions were released and the FWHM only were constrained to be  
350 roughly constant in all spectra. Figure 7 shows the results of the spectral decompositions.  
351 Residual intensity observed after fitting the  $3678$ ,  $3656$  and  $3622\text{ cm}^{-1}$  bands requires an  
352 additional peak around  $3641\text{ cm}^{-1}$  to be introduced in the model (Fig. 7). Given its frequency  
353 and the controlled chemistry of the system, this band must be related to some configuration  
354 involving  $\text{Fe}^{3+}$ ; however, because its intensity is very low we will neglect it in the following  
355 discussion.

356 Figure 8a shows the evolution with  $T$  of the relative integrated absorbance of the  $3678$   
357 and  $3656\text{ cm}^{-1}$  components obtained from Figure 7. Note that the spectra have been collected

358 systematically on the same point of a crystal chip with a constant thickness. The intensity of  
359 the higher-frequency band decreases only slightly between 300 and 400 °C, but disappears at  
360 500 °C. In contrast, the lower-frequency component at 3656 cm<sup>-1</sup> increases slightly between  
361 300 and 400 °C but increases significantly in the 400-500 °C range. Figure 8b shows the  
362 absolute intensities of these two bands plotted against *T*. The intensity of the 3678 cm<sup>-1</sup>  
363 component is almost constant up to 400 °C, then decreases drastically; that of the 3656 cm<sup>-1</sup>  
364 component increases slightly up to 400 °C and then starts dropping. At 500 °C, however, all  
365 the OH remaining in the amphibole is related to this band, i.e., to the <sup>*M*(1)</sup>Fe<sup>2+</sup><sup>*M*(1)</sup>Fe<sup>3+</sup><sup>*M*(3)</sup>Fe<sup>2+</sup>-  
366 configuration locally associated to a OH-A-<sup>O(3)</sup>O<sup>2-</sup> bridge.

367         The behavior of the OH-bands in Figure 8b confirms that the oxidation process occurs  
368 via the creation of a local <sup>O(3)</sup>O<sup>2-</sup>-A-<sup>O(3)</sup>O<sup>2-</sup> order (Della Ventura et al. 2007). As a matter of  
369 fact, if the oxidation of Fe at *M*(1) occurred randomly, we would have observed in Figure 8b a  
370 significant increase in the 3656 cm<sup>-1</sup> component at the expense of the 3678 cm<sup>-1</sup> component,  
371 but this is not the case because both bands decrease for *T* > 450 °C. Useful information is  
372 provided by the evolution with temperature of the 3622 cm<sup>-1</sup> band (assigned to the  
373 configurations including a vacant A-site), which is reported in Figure 9. The trends show that  
374 although this band disappears rapidly at *T* > 400 °C (Fig. 9b), its intensity actually *increases*  
375 relative to all other components (Fig. 9a). We can conclude that the local configurations  
376 associated with a vacant A-site are less affected by the deprotonation process than those  
377 associated with an occupied A site. As a matter of fact, the presence of the A cation helps in  
378 providing local electroneutrality to those anionic O(3) sites, which remain underbonded after  
379 H loss, a suggestion first made by Ungaretti (1980).

380         The evidence discussed above suggests a crucial role played by local configuration on  
381 the deprotonation process. This results is consistent with the relatively lower thermal stability  
382 observed in nature for A-filled Fe-dominant amphiboles. However, the great compositional  
383 variety of amphibole requires a more systematic approach to this issue. The higher stability of

384 A-vacant Fe-rich or Fe-dominant amphiboles is also in agreement with previous findings on  
385 layer silicates (Zhang et al. 2007), where the presence of K at the interlayer site decreases  
386 thermal stability, so that sericite (Zhang et al. 2005) has a lower deprotonation temperature  
387 than talc (Ward 1975) and phyllophylite (Wang et al. 2002).

388

389

### IMPLICATIONS

390 The stability of Fe-rich rock-forming minerals at non ambient conditions, particularly  
391 at high temperatures, is of great relevance in Earth and planetary sciences; evolving  $\text{Fe}^{3+}/\text{Fe}^{2+}$   
392 ration in response of varying boundary conditions may affect properties such as rock's  
393 magnetism and electrical conductivity, and may thus have significant consequences onto  
394 geophysics (e.g., Wang et al. 2012).

395 By integrating HT-SC-FTIR spectroscopy with previous HT-SC-XRD results on a  
396 synthetic potassic-ferro-richterite we significantly improved our knowledge of the  
397 deprotonation process in amphiboles, which may be extended to other hydrous minerals. The  
398 main implications of our work are:

399 (1) The deprotonation process of the studied amphibole proceeds via a simultaneous loss of  
400 proton and oxidation of ferrous iron in order to maintain electroneutrality. Fe oxidation occurs  
401 preferentially at the *M*(1) site coordinating an OH group interacting with an alkali A cation.

402 (2) The results of HT-FTIR analysis are strongly dependent on crystal size. This point is far  
403 less important with XRD because this technique provides data that are averaged over the  
404 crystal, while FTIR spectroscopy in the mid-IR range yields information at a molecular scale.  
405 Hence, deprotonation is detected by FTIR at lower *T* on powders than on single-crystals, also  
406 suggesting a surface-driven process ruled by the availability of atmospheric oxygen (Addison  
407 et al. 1962a, Hodgson et al. 1965, and Susta 2016).

408 (3) We provide the first evidence of a significant increase in the absorption coefficient with *T*,  
409 which should be related to a change in the electronic properties of the sample. Although this

410 feature still needs to be fully understood, this work implies that SC-FTIR spectroscopy in  
411 non-ambient  $T$  studies should be done on quenched materials, or at least comparing  
412 measurements done *in situ* with those done on quenched materials.

413

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417

418

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599

600

## FIGURE CAPTIONS

601 Figure 1. Schematic local structure of the amphiboles across the *A* site.

602

603 Figure 2. Room-*T* single-crystal unpolarized spectra, collected on a 100  $\mu\text{m}$  thick, section.

604

605 Figure 3. HT-FTIR spectra (temperature in  $^{\circ}\text{C}$ ) collected (a) *in situ* during the heating ramp,  
606 and (b) after quenching the sample annealed at the target *T*. Spectra plotted in each Figure  
607 with the same absorbance scale.

608

609 Figure 4. Comparison of the FTIR spectra collected *in situ* at 400  $^{\circ}\text{C}$  and after quenching the  
610 sample annealed at the same *T*. Spectra plotted with the same absorbance scale.

611

612 Figure 5. Comparison of the OH-stretching absorbance measured *in situ* (filled triangle) and  
613 quenched samples (empty triangle) and the combination modes absorbance *in situ* (filled  
614 diamond), as a function of increasing *T*. Integrated intensities obtained scaling the absorbance  
615 at any temperature ( $T$ ) to that at room-*T* ( $^{RT}T$ ). Integration ranges: 3710-3600  $\text{cm}^{-1}$  for the OH-  
616 stretching region and 4300-4100  $\text{cm}^{-1}$  for the combination region.

617

618 Figure 6 Evolution of the cell volume of potassic-ferro-richterite (from Oberti et al. 2016) vs.  
619 the OH-stretching absorbance (quenched data) obtained in this study.

620

621 Figure 7. Fitted OH-stretching spectra collected on quenched samples after annealing at the  
622 indicated *T*. All spectra plotted with the same absorbance scale.

623

624 Figure 8. Temperature dependence of the 3678 vs. 3660  $\text{cm}^{-1}$  components as a function of *T*.  
625 (a) relative intensity, (b) absolute intensity.

626

627 Figure 9. Temperature dependence of the 3622  $\text{cm}^{-1}$  band as a function of *T*. (a) relative  
628 intensity, (b) absolute intensity.





















