

Deprotonation of Fe-dominant amphiboles: Single-crystal HT-FTIR spectroscopic studies of synthetic potassic-ferro-richterite

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ABSTRACT

High-temperature Fourier transform infrared (HT-FTIR) spectroscopy was used to characterize the deprotonation process of synthetic potassic-ferro-richterite of composition $^A(K_{0.90}Na_{0.07})^B(Ca_{0.54}Na_{1.46})^C(Fe_{4.22}Fe_{0.78}^{3+})^T Si_8 O_{22}^W (OH_{1.70}O_{0.30}^2)$. Unpolarized single-crystal spectra were collected both in situ and on quenched samples, and heating experiments were conducted in air, at a rate of 10 °C/min. The room-*T* spectrum measured before annealing shows a main band at 3678 cm⁻¹ and a minor band at 3622 cm⁻¹; these are assigned to local configurations involving Fe²⁺ at *M*(1)*M*(1)*M*(3) and facing a filled and an empty alkali-site, respectively. At 400 °C, a new band grows at 3656 cm⁻¹; this is the most intense feature in the pattern at 450 °C. At $T \geq 500$ °C, all peaks decrease drastically in intensity, and finally disappear at $T > 600$ °C. The total absorbance measured in situ increases significantly in the 25 < *T* < 450 °C range, although the spectra collected on quenched samples show no OH loss in the same *T* range. This feature is consistent with an increase of the absorption coefficient (ϵ) with *T*, the reason for which is still unclear. However, this feature has significant implications for the quantitative use of FTIR data in HT experiments. Examination of the relevant OH-stretching bands shows that iron oxidation occurs preferentially at the *M*(1,3) sites associated with occupied *A* sites. The deprotonation temperature indicated by FTIR for single-crystals is around 100 °C higher than that obtained by HT-X-ray diffraction (XRD) on single crystal by Oberti et al. (2016), whereas that obtained by HT-XRD on powders is intermediate. This unexpected observation can be explained by considering that: (1) the iron oxidation process, which is coupled to deprotonation and is probed by XRD, occurs preferentially at the crystal surface where it is triggered by the availability of atmospheric oxygen; (2) the proton diffusion, probed by FTIR, is slower than the electron diffusion probed by XRD; thus, the temperature shift may be explained by a much longer escape path for H in single-crystals than in powders. These results suggest that possible effects due to crystals size should be carefully considered in HT experiments done on Fe-rich silicates.

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