

## **The dynamics of Fe oxidation in riebeckite: A model for amphiboles**

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### **ABSTRACT**

In this work, we investigate the oxidation behavior of a nearly end-member riebeckite, ideally  $\text{Na}_2(\text{Fe}_3^{2+}\text{Fe}_2^{3+})\text{Si}_8\text{O}_{22}(\text{OH})_2$ , by using vibrational FTIR and Raman spectroscopies. Combining these results with previous studies performed on the same sample by single-crystal structure refinement and Mössbauer spectroscopy, we conclude that iron oxidation in riebeckite is a multi-step process. (1) In the  $\sim 523 \text{ K} < T < 623 \text{ K}$  temperature range, the O-H bond lengthens and both the electrons and the hydrogen cations delocalize. Raman analysis shows that this step is reversible upon cooling to room temperature. (2) In the  $623 \text{ K} < T < 723 \text{ K}$  range, the kinetic energy increases so that the electrons can be ejected from the crystal; beyond 723 K an irreversible oxidation of Fe occurs that couples with irreversible changes in the  $\text{SiO}_4$  double-chains leading to a contraction of the unit-cell volume, i.e., to structural changes detectable at the long-range scale. (3) Beyond 823 K, the irreversible oxidation is completed and  $\text{H}^+$  ions are forced to leave the crystal bulk. Because of this multi-step process, the onset of the deprotonation process is detected at  $\sim 700 \text{ K}$  by single-crystal XRD analysis of the unit-cell parameters, but starts at 623 K as indicated by Mössbauer spectroscopy on powders (and by changes in the cation distribution observed by structure refinement). Also, Raman scattering shows that the release of  $\text{H}^+$  from the crystal surface starts  $\sim 100 \text{ K}$  before the complete deprotonation of the crystal bulk is witnessed by FTIR absorption. Hence, the oxidation of Fe starts at the crystal surface and induces electron and  $\text{H}^+$  migration from the crystal interior to the rim and thus subsequent oxidation through the crystal bulk. No deprotonation is observed by FTIR either in powders embedded in KBr or in crystals heated in  $\text{N}_2$  atmosphere, implying that the release of  $\text{H}^+$  needs surficial (atmospheric) oxygen to form  $\text{H}_2\text{O}$  molecules.  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  oxidation produces a flux of electrons throughout the crystal matrix, which generates electrical conductivity across the amphibole. An important implication of this work, which might have interesting applications in material science, is that iron oxidation in riebeckite (and possibly in other Fe-rich silicates) is reversible in a given range of temperature. Also, this work shows that complex processes cannot be fully understood or even monitored accurately without using a proper combination of independent techniques.

**Keywords:** Riebeckite, HT spectroscopy, FTIR, Raman, iron oxidation, deprotonation