

## Oxidation or cation re-arrangement? Distinct behavior of riebeckite at high temperature

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### ABSTRACT

In this work we address the stability of riebeckite at high temperatures and compare the different behaviors observed under various oxidation conditions. For this purpose, we annealed powders of a sample from Mt. Malosa (Malawi), which is compositionally close to the end-member; the run products obtained after annealing in air vs. in vacuum were studied by Mössbauer spectroscopy and powder X-ray diffraction. The results show that riebeckite follows two distinct paths depending on the external environment. Under oxidizing conditions, it is stable in the hydrous form up to relatively low temperatures (400–450 °C), then it undergoes a rapid (within ~50 °C) dehydrogenation, forming oxo-riebeckite, which is stable up to ~900 °C. The final breakdown products of the oxo-amphibole include aegirine + cristobalite + hematite. Based on the relative intensity of the (310) Bragg reflection, the activation energy ( $E_a$ ) for the riebeckite to oxo-riebeckite transition is  $166 \pm 6$  kJ/mol.

Under vacuum conditions, no Fe oxidation is observed, and riebeckite is stable up to much higher temperatures (750–800 °C); however, in the  $550 < T < 700$  °C range, it undergoes a significant re-arrangement of the C cations (those hosted in the strip of octahedra). Indeed, the amphibole stable in the 700–800 °C range has the same chemical formula as riebeckite but has a disordered and non-standard cation distribution at the octahedra, i.e.,  $^{M(1)}(\text{Fe}^{3+}\text{Fe}^{2+})^{M(2)}(\text{Fe}^{3+}\text{Fe}^{2+})^{M(3)}\text{Fe}^{2+}$ ; we call this phase “ $\text{R}^{3+}$  disordered riebeckite”. For  $T \geq 800$  °C, it decomposes to aegirine + fayalite + cristobalite +  $\text{H}_2\text{O}$ .

External oxygen is required for the release of water into the surrounding system, being a prerequisite for the Fe-amphiboles to be a carrier of  $\text{H}_2\text{O}$  in the lower crust and upper mantle. One important implication of our results is that characterization of the overall oxidation state of iron does not necessarily provide the redox conditions of the environment of formation because a crystal-chemical re-arrangement under reducing conditions allows riebeckite to maintain its  $\text{Fe}^{3+}/\text{Fe}^{2+}$  composition up to higher temperatures.

**Keywords:** riebeckite, HT experiments, vacuum conditions, Mössbauer spectroscopy, X-ray powder diffraction