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 ± 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., \( \text{M}^{(1)}(\text{Fe}^{3+}\text{Fe}^{2+})\text{M}^{(2)}(\text{Fe}^{3+}\text{Fe}^{2+})\text{M}^{(3)}\text{Fe}^{2+} \); we call this phase “R” disordered riebeckite”. For T ≥ 800 °C, it decomposes to aegirine + fayalite + cristobalite + H₂O.

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 H₂O 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 Fe³⁺/Fe²⁺ composition up to higher temperatures.

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

Introduction

Riebeckite, ideally Na₂(Fe³⁺Fe²⁺)Si₆O₂₂(OH)₂, is a relatively common iron-rich member of the sodic amphibole subgroup; it is typically found in acid igneous rocks and as an important constituent of high-grade shists and meta-iron stones (Deer et al. 1997). The phase relations of riebeckite in the system Na₂O-FeO-SiO₂-H₂O under hydrothermal conditions have been experimentally determined by Ernst (1962, 1968) at varying oxygen fugacity, temperature, and pressure. According to these studies, end-member riebeckite is stable below ~500 °C, 1000 bars at an f₀₂ defined by the hematite-magnetite buffer; the effect of pressure was found to be rather limited with the stability increasing to ~600 °C at 2 kbar. The breakdown product included hematite + magnetite + quartz + acmite + fluid (Ernst 1962). Under more reducing conditions (magnetite-quartz-fayalite buffer), the stability of the amphibole increases to ~700 °C at 1 kbar. The fibrous form of riebeckite is the asbestos mineral known as “crocidolite.” Several studies on the thermal stability of crocidolite were done mostly in the 1960s and 1970s (see Della Ventura et al. 2018, 2021 for a complete list of references) mainly because crocidolite was used for efficient fire-resistant textiles. These studies were focused on the products of decomposition of crocidolite as a function of temperature, both in air and under an inert (Ar, N₂) atmosphere. In particular, Hodgson et al. (1965) and Whitfield and Freeman (1967) observed the appearance, at...