Kinetics of dehydrogenation of riebeckite Na$_2$Fe$_{2+}^+$Fe$_{3+}^+$Si$_8$O$_{22}$(OH)$_2$: An HT-FTIR study

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ABSTRACT

In this work, we address the kinetics of dehydrogenation occurring at high temperatures (HT) in riebeckite, a sodic amphibole with the ideal composition Na$_2$Fe$_{2+}^+$Fe$_{3+}^+$Si$_8$O$_{22}$(OH)$_2$. We performed isothermal experiments on both powders and single-crystals up to 560 °C and monitored the O-H stretching signal by Fourier transform infrared (FTIR) spectroscopy. Single-crystals show an initial increase in IR absorption intensity due to increasing vibrational amplitudes of the O-H bond stretching, not observed for powders. The OH-intensities vs. time were fitted using the formalism for first-order reactions. The calculated activation energies for H$^+$ diffusion in riebeckite are 159 ± 15 kJ/mol for powders and 216 ± 20 kJ/mol for single crystals, respectively. The exponential factor in the Arrhenius-Erofeev equation obtained for crystals ranges between 1.02 and 1.31, suggesting that, unlike powders, the dehydration process in crystals is not a purely first-order reaction. This implies that a second energy barrier must be considered, i.e., diffusion of H$^+$ through the crystal. FTIR imaging showed that H$^+$ diffusion occurs mainly perpendicular to the silicate double-chain. Our results confirm that the release of H$^+$ from riebeckite occurs after the irreversible Fe$^{2+}$-to-Fe$^{3+}$ exchange, thus at temperatures >550 °C. To be effective, the process needs the presence of external oxygen that, by interacting with H$^+$ at the crystal surface, triggers the release of H$_2$O molecules. This implies that oxidizing conditions are required for the amphibole to be an efficient water source at depth.

Keywords: Riebeckite, HT-FTIR spectroscopy, FTIR imaging, Fe-oxidation, dehydration kinetics, activation energy

INTRODUCTION

Dehydration of H$_2$O/OH-bearing minerals as a function of increasing high-temperature/pressure (HT/HP) conditions is one of the most important processes in geology, being responsible for a wide spectrum of large-scale phenomena such as arc volcanism (e.g., Schmidt and Poli 1998), ore-forming processes (Robb 2005), mantle dynamics and properties (McCammon et al. 2004; Hu et al. 2018), and mantle partial melting (King et al. 2000). Amphiboles, together with layer silicates (Manthilake et al. 2016), play a significant role in this context; they are among the most important hydrous constituents of metamorphic rocks up to HP conditions and are believed to be among the main carriers of water into the mantle during geodynamic processes, considering that they constitute up to 50% by volume of the subduction plate (Christensen and Mooney 1995). Amphiboles have intriguing magnetic (Moukarika et al. 1983; Biedermann et al. 2015) and electrical (Schmidbauer et al. 2000) properties; the latter are enhanced at HT, and for this reason amphiboles are believed to play a major role in the conductive anomalies observed in subducted rocks at convergent plate margins (Wang et al. 2012; Hu et al. 2018). Therefore, the detailed knowledge of their stability and transformation processes at high P-T is mandatory in geological/geophysical research. For Fe-dominant compositions, this task is complicated by the connection between redox phenomena and dehydration/diffusion; the same also occurs at mantle conditions for a variety of Fe-bearing minerals (McCammon et al. 2004). Significant effort was made to define the HT stability of sodic Fe-amphiboles of commercial interest (“crocidolite”) during the 1960–1970s (Barnes 1930; Addison et al. 1962a, 1962b; Addison and Sharp 1962a, 1962b; Clark and Freeman 1967; Patterson 1965; Hodgson et al. 1965; Addison and White 1968; Ernst and Wai 1970; Rouxhet et al. 1972), with experiments aimed essentially at defining the Fe oxidation mechanism and the consequent dehydrogenation. Structural adjustments following iron oxidation were later addressed by Ungaretti (1980), Phillips et al. (1988, 1989, 1991), and Popp et al. (1995). Many studies have also focused on the stability of Fe-Ti amphiboles at mantle conditions and the oxo-substitution mechanisms for petrological purposes (King et al. 1999, 2000).

This topic has received renewed interest in recent years thanks to multidisciplinary work on the stability of Fe-rich amphiboles at non-ambient conditions (Welch et al. 2007; Oberti et al. 2016,