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The fate of ammonium in phengite at high temperature

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Abstract

Nitrogen (N) is the main component of the atmosphere and is largely considered as a volatile element. However, most researchers now agree that a significant amount of N, in the form of ammonium (NH_4^+) substituting for K^+ in some K-bearing minerals such as clays, micas, and feldspars, can be transferred to the deep Earth through subduction. The fate of ammonium in those minerals during subduction is still poorly known but is likely controlled by temperature and pressure pathways. In an attempt to contribute to understanding the fate of N during high-temperature processes, we carried out in situ high-temperature IR and Raman spectra measurements to investigate the rate and mechanism of NH_4^+ loss in phengite. We observed that a new OH band at 3425 cm^{-1} became prominent above 400 °C, and did not change with times during isothermal annealing at 500 and 700 °C. The N-H stretching band shifted to higher wavenumbers in the temperature interval from –150 to 20 °C, while linearly shifted to lower wavenumbers in the temperature interval from 20 to 500 °C and remained stable above 500 °C. The N-H bending band linearly shifted to lower wavenumbers in the temperature interval from –150 to 400 °C and remained stable. The K-O stretching frequency decreased with increasing temperature to 600 °C, and then remained stable. These processes were reversible until dehydration and ammonium loss from phengite starting at 800 °C. The results suggest that (1) at low temperatures, ammonium is ordered and hydrogen bonding between ammonium and the framework evolves during cooling; (2) at high temperatures, the N-H interatomic distance of NH_4^+ lengthens with increasing temperature until 500 °C. N-H bond subsequently no longer lengthens, accompanied by H transferring from N to neighboring O and forming a new OH band at 3425 cm^{-1}. At 800 °C, H^+ starts breaking from N and leaving others to form NH_3 and OH^-. This study has implications for evaluating the extent to which these minerals can preserve information regarding nitrogen behavior during high-temperature processes.

Keywords: Phengite, nitrogen, ammonium, high temperature, IR, Raman