Ammonium promotes hydrogen bond symmetrization in phengite under high pressures

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Phengite is critical for carrying both hydrogen and nitrogen into the deep Earth through subduction. Our previous studies have investigated the mechanism and kinetics of ammonium release in phengite[1][2]. Ammonium loss is easier comparing with dehydation and ammonium itself can facilitate the dehydration in phengite.

The behavior of hydroxyl and lattice during subduction process, which relate to stability and physical properties of phengite, is an essential component of the deep Earth's water cycle. Here, we applied in situ high temperature and high pressure IR and Raman spectroscopy to characterize the behavior of hydroxyl and lattice in the ammonium-bearing and the ammonium-free phengite samples. No matter with increasing temperature or pressure, the OH band shifts to lower frequencies for both ammonium-bearing and ammonium-free phengites. The frequency shift of the OH band is larger for the ammonium-bearing phengite than the ammonium-free phengite upon compression. Ammonium can promote hydrogen bond symmetrization in phengite under high pressures. During either heating or compressing processes, the ammonium-bearing phengite dehydrates, while the ammonium-free phengite show negligible water loss. Ammonium have little impact on the lattice vibration of phengite as there is no phase transition and the frequency shift of the lattice mode in both the ammonium-bearing phengite and ammonium-free phengite are similar during compression. The study is for the first time to investigate the impact of ammonium on behavior of hydroxyl and lattice in phengite at high temperature and high pressure. The transportation of water in the ammonium-bearing phengite would be at shallow depth in the deep earth. These results may call our attention to the link between ammonium and the deep Earth's water cycle.

[1] Yang et al., 2017. *Am. Mineral.* 102, 2244-2253.
[2] Liu et al., 2019. *Earth Planet. Sci. Lett.* 513, 95-102.