

Nitrogen impacts on structural stabilities of silicates

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The nitrogen cycling between the surficial and deep Earth is vital for the evolution of the atmosphere and life. Silicate minerals are the main nitrogen carriers and their stabilities dictate the recycling efficiency of nitrogen to the deep Earth. However, the impacts of nitrogen on the stabilities of silicate minerals are poorly known. Phengite and feldspar are important nitrogen carriers. Nitrogen is mainly incorporated as ammonium in the interlayer sites in phengite and in the cavities in the feldspar framework structure. To investigate the impacts of nitrogen in different structural locations, the stabilities of a phengite with 0.2 wt.% ammonium and a feldspar with 0.12 wt.% ammonium are investigated using high temperature and high pressure spectroscopy and machine learning approach[1,2].

The results show that (1) No phase transition occurs in the nitrogen-bearing phengite up to ~ 20 GPa, and nitrogen has no impact on the lattice at high pressures. In contrast, the nitrogen-bearing feldspar experiences a structural transition near 15.3 GPa, with the transition pressure higher than that of the nitrogen-free feldspars; (2) Compared with their nitrogen-free counterparts, ammonium delays the softening of phengite lattice at high temperature and declines the thermal expansion coefficient of feldspar from $18.3 \pm 1.83 \text{ K}^{-1}$ to $14.9 \pm 0.5 \text{ K}^{-1}$; (3) By combining with previous studies, we reveal that ammonium enhances the thermal stability of phyllosilicates regardless of content while it reduces the thermal stability of tectosilicates when ammonium content is high enough. For phyllosilicates, the interactions of ammonium in the interlayer sites with the lattice at high temperature may enhance the thermal stability. For tectosilicates, hydrogen proton is left in the cavities after the decomposition of ammonium and its size is too small to hold the structure, which may cause structural instability.

These findings provide crucial constraints on the phase stabilities of nitrogen-bearing silicates and highlight the role of phyllosilicate, such as mica, for transporting nitrogen to the deep Earth.

[1] Huang, W. H. et al. (2021) *J. Earth Sci.* **32**, 1278–1286.

[2] Huang, W. H. et al. (2023) *Phys. Earth Planet. Inter.* **336**, 106997