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High-pressure ammonium-bearing silicates: Implications for nitrogen and hydrogen storage in the Earth's mantle

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Abstract

The ammonium analogues of the high-pressure potassium-bearing silicate phases K-hollandite, K-Si-wadeite, K-cymrite, and phengite were synthesized in the system $(NH_4)_2O$(-MgO)-Al_2O_3-SiO_2-H_2O [N(M)ASH] using multi-anvil and piston-cylinder equipment. Syntheses included NH_4-hollandite ($NH_4AlSi_3O_8$) at 12.3 GPa, 700 °C; NH_4-Si-wadeite [$(NH_4)_2Si_4O_9$] at 10 GPa, 700 °C; NH_4-cymrite ($NH_4AlSi_3O_8 \cdot H_2O$) at 7.8 GPa, 800 °C; and NH_4-phengite [$NH_4(Mg_{0.5}Al_{1.5})(Al_{0.5}Si_{3.5})O_{10}(OH)_2$] at 4 GPa, 700 °C. Run products were characterized by SEM, FTIR, and powder XRD with Rietveld refinements. Cell parameters of the new NH_4 end-members are: a = 9.4234(9) Å, c = 2.7244(3) Å, V = 241.93(5) Å^3 (NH_4-hollandite); a = 6.726(1) Å, c = 9.502(3) Å, V = 372.3(1) Å^3 (NH_4-Si-wadeite); a = 5.3595(3) Å, c = 7.835(1) Å, V = 194.93(5) Å^3 (NH_4-cymrite). NH_4-phengite consisted of a mixture of 1M, 2M_1, 2M_2, 3T, and 2Or polytypes. The most abundant polytype, 2M_1, has cell dimensions a = 5.2195(9) Å, b = 9.049(3) Å, c = 20.414(8) Å, β = 95.65(3)°, V = 959.5(5) Å^3. All unit-cell volumes are enlarged in comparison to the potassium analogues. Substitution of NH_4 for K does not cause changes in space group. NH_4 incorporation was confirmed by the appearance of NH_4-vibration modes ν_4 and ν_3 occurring in the ranges of 1397–1459 and 3223–3333 cm^{-1}, respectively.

Ammonium in eclogite facies metasediments is mainly bound in micas and concentrations may reach up to a few thousand parts per million. It can be stored to greater depths in high-pressure potassium silicates during ongoing subduction. This possibly provides an important mechanism for nitrogen and hydrogen transport into the deeper mantle.

Keywords: Hollandite, wadeite, cymrite, phengite, ammonium, high-pressure synthesis, nitrogen cycle