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Synthetic and natural ammonium-bearing tourmaline

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Abstract

Due to the similar ionic radius of K^+ and NH_4^+, K-silicates can incorporate a significant amount of NH_4. As tourmaline is able to accommodate K in its crystal structure at high and ultrahigh pressure, we test if this also holds true for NH_4.

Piston-cylinder experiments in the system $(NH_4)_2O$-MgO-SiO_2-Al_2O_3-B_2O_3-H_2O at 4.0 GPa, 700 °C, with B_2O_3 and NH_4OH in excess produce an assemblage of tourmaline, phengite, and coesite. The tourmaline crystals are up to 10 × 40 μm in size. EMP analyses indicate that the tourmalines contain 0.22 (±0.03) wt% $(NH_4)_2O$ and are solid solutions mainly along the magnesio-foitite and "NH_4-dravite" join with the average structural formula $^X[(NH_4)_{0.08(1)}\square_{0.92(1)}]^Y[Mg_{2.28(8)}Al_{0.72(8)}]^Z[Al_{5.93(6)}Si_{0.07(6)}]^T[Si_{6.00(5)}O_{18}](BO_3)_3(OH)_4$.

NH_4 incorporation is confirmed by characteristic <N-H> stretching and bending modes in the IR-spectra of single crystals on synthetic tourmaline. Further evidence is the increased unit-cell parameters of the tourmaline [a = 15.9214(9) Å, c = 7.1423(5) Å, V = 1567.9(2) Å^3] relative to pure magnesio-foitite.

Incorporation of NH_4 in natural tourmaline was tested in a tourmaline-bearing mica schists from a high-P/low-T (>1.2 GPa/550 °C) metasedimentary unit of the Erzgebirge, Germany, rich in NH_4. The NH_4-concentrations in the three main NH_4-bearing phases are: biotite (~1400 ppm) > phengite (~700 ppm) > tourmaline (~500 ppm). This indicates that tourmaline can act as important carrier of nitrogen between the crust and the deep Earth, which has important implications for a better understanding of the large-scale light element cycle.

Keywords: Tourmaline, high-pressure synthesis, ammonium, Erzgebirge mica-schists, nitrogen cycle