

Synthetic and natural ammonium-bearing tourmaline

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ABSTRACT

Due to the similar ionic radius of K⁺ and NH₄⁺, K-silicates can incorporate a significant amount of NH₄. As tourmaline is able to accommodate K in its crystal structure at high and ultrahigh pressure, we test if this also holds true for NH₄.

Piston-cylinder experiments in the system (NH₄)₂O-MgO-SiO₂-Al₂O₃-B₂O₃-H₂O at 4.0 GPa, 700 °C, with B₂O₃ and NH₄OH 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% (NH₄)₂O and are solid solutions mainly along the magnesio-foitite and “NH₄-dravite” join with the average structural formula $^{x}[(\text{NH}_4)_{0.08(1)}\square_{0.92(1)}]^{y}[\text{Mg}_{2.28(8)}\text{Al}_{0.72(8)}]^{z}[\text{Al}_{5.93(6)}\text{Si}_{0.07(6)}]^{t}[\text{Si}_{6.00(5)}\text{O}_{18}](\text{BO}_3)_3(\text{OH})_4$.

NH₄ 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, $V = 1567.9(2)$ Å³] relative to pure magnesio-foitite.

Incorporation of NH₄ 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 NH₄. The NH₄-concentrations in the three main NH₄-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