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 x 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-foitee and “NH4-dravite” join with the average structural formula 3[(NH4)0.08][Al1.72(Al,4Si1.72)2][Al1.80(Al,4Si1.80)2][Si6.06(Al,4Si4.06)2][BO4]2(OH)2.

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-foitee.

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 an important carrier of nitrogen between the crust and the deep Earth, which is important implications for a better understanding of the large-scale light element cycle.

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

INTRODUCTION

The transfer of nitrogen from the Earth’s surface to its interior occurs by subduction of ammonium-bearing sediments and altered oceanic crust (e.g., Boyd 2001; Hastings et al. 2013; Bebout et al. 2013a; Busigny and Bebout 2013, and references therein). Nitrogen released from organic matter is predominantly incorporated as NH4+ into clay minerals during diagenesis and may subsequently substitute for K+ in K-feldspar, muscovite, biotite, and other K-bearing silicates with increasing metamorphic grade (e.g., Williams et al. 1992). There is general agreement that during Barrovian-type metamorphism and during subduction a large proportion of the ammonium is continuously discharged by chemical dehydrogenation reactions (Bebout and Fogel 1992; Bebout et al. 1999; Sadofsky and Bebout 2000; Mingram and Bräuer 2001; Pöter et al. 2004; Pitcairn et al. 2005) and recycled to the surface, for example via arc volcanism. By contrast, high- and ultrahigh-pressure, low-temperature metasediments sometimes retain major amounts of NH4+ mainly in micas to at least 3.0 GPa and probably beyond (Busigny et al. 2003a; Bebout et al. 2013b). In addition, experiments by Watenphul et al. (2009) have shown that the NH4+ analogs of the high-pressure potassium-bearing silicates phengite, K-cymrite, K-hollandite, and K-Si-wadeite are stable to even much higher pressures at relevant temperatures. This indicates that significant amounts of nitrogen can indeed be transported into the deeper mantle. These results are in line with arguments presented by Cartigny and Marty (2013), suggesting that recycling of nitrogen into the mantle presently exceeds outgassing. There is, however, insufficient information about other NH4+-bearing minerals that may contribute to the deep nitrogen cycle, as all K-bearing silicates are potential carriers of nitrogen to depth.

Tourmaline has been long known as carrier of light elements such as boron and lithium in the Earth’s crust (e.g., Henry and Dutrow 1996; Busigny and Bebout 2013). It forms in various geochemical environments that have undergone diagenetic, metamorphic, metasomatic, or magmatic processes over a wide range of bulk compositions (Van Hinsberg et al. 2011), and has a large pressure and temperature stability field ranging from near-surface (Henry et al. 1999) to mantle conditions (Krosse 1995; Marschall et al. 2009). Tourmaline has a very flexible structure, which is able to adjust its composition in response to a wide range of chemical, pressure, and temperature variations (Dutrow and Henry 2011) as reflected by its complex general chemical formula, XY2Z1[TiO11](BO3)2V,W (Hawthorne and Henry 1999). The large X site is ninefold coordinated and typically contains...