Cation partitioning among crystallographic sites based on bond-length constraints in tourmaline-supergroup minerals

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Abstract

Theoretical bond-length calculations from ideal bond valences for each ion and coordination allow for the prediction of ion site preference and partitioning in tourmaline structures at low-pressure conditions. A comparison of calculated data with published bond-length values enables the determination of the range of structurally stable bond lengths with a minimal induced distortion—the “Goldilocks zone.” The calculations following the data with published bond-length values enables the determination of the range of structurally stable bond lengths with a minimal induced distortion—the “Goldilocks zone.” The calculations following the data with published bond-length values enables the determination of the range of structurally stable bond lengths with a minimal induced distortion—the “Goldilocks zone.” The calculations following the data with published bond-length values enables the determination of the range of structurally stable bond lengths with a minimal induced distortion—the “Goldilocks zone.” The calculations following the data with published bond-length values enables the determination of the range of structurally stable bond lengths with a minimal induced distortion—the “Goldilocks 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Keywords: Tourmaline supergroup, crystal chemistry, bond length calculation, cation occupancy, trace elements; Lithium, Beryllium and Boron: Quintessentially Crystall

Introduction

Tourmaline supergroup minerals are cyclosilicates having the generalized structural formula $XY_2Z_2(T_1O_8)(BO_3)_2V_3W_3$, where the most common ions (or vacancy) at each site are the following: $X = \text{Na}^+$, $\text{K}^+$, $\text{Ca}^{2+}$, and vacancy; $Y = \text{Li}^+$, $\text{Fe}^{2+}$, $\text{Mn}^{2+}$, $\text{Mn}^{4+}$, $\text{Al}^{3+}$, $\text{Fe}^{3+}$, and $\text{Cr}^{3+}$; $Z = \text{Mg}^{2+}$, $\text{Al}^{3+}$, $\text{Fe}^{3+}$, and $\text{Cr}^{3+}$; $T = \text{Si}^{4+}$, $\text{Al}^{3+}$, and $\text{B}^{3+}$; $B = \text{B}^{3+}$; $V = (\text{OH})$ and $\text{O}^{2-}$; and $W = (\text{OH})$, $\text{F}^-$, and $\text{O}^{2-}$ (Henry et al. 2011). Their particular structure contains five different cationic crystallographic sites with various coordinations—one tetrahedral $T$ site, two octahedral $Z$ and $Y$ sites, a polyhedral ninefold-coordinated $X$ site, a triangular $B$ site, and eight different anionic sites, noted $O_1$–$O_8$ (Donnay and Bauer 1950). The structural complexity thus results in large variability of chemical elements, which can be incorporated in the tourmaline structure. The major elements include Si and B with small ionic radii, slightly larger Al, Mg, Fe, Li, Mn, Cr, V, and Ti, and also the largest Na, Ca, and K. Anionic sites comprise the dominant amount of O (as $\text{O}^{2-}$ and OH-) and usually a subordinate amount of F (Henry et al. 2011) or Cl (Bačík et al. 2015b).

Many other elements can occupy a tourmaline structure in minor to trace amounts. These include nearly the entire periodic table. Trace elements in tourmaline measured at the micrometer scale become important tracers of the rock evolution and fluids interacting with tourmaline. Tourmalines from various host environments can show a distinct chemical signature of their host, such as increased Li concentrations in evolved magmatic rocks (e.g., Keller et al. 1999; Selway et al. 1999, 2000), anomalous Sn concentrations in Sn deposits (Jiang et al. 1999; Williamson et al. 2000) and enrichment in Ni, V, and Cr in metabasic rocks and metabauxites (Henry and Dutrow 2001; Marschall et al. 2004). Subduction-zone fluids and their impact on arc-magmatism signatures were modeled based on ratios of Ba, Th, La, and Sm (Van Hinsberg et al. 2017). Trace amounts of Sr, Sc, V, Ni, Pb, Zr, Ta, Nb, Cr, Ga, and Sn and REE have been used as proxies for mineralizing fluids in ore deposits and in other rock environments (Duchoslav et al. 2017; Hazarika et al. 2017; Hong et al. 2017; Kalliomäki et al. 2017). Relatively high Cl contents in tourmaline are used to establish the unusual