

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

PETER BAČÍK<sup>1,\*</sup>,† AND JANA FRIDRICHOVÁ<sup>1</sup>

<sup>1</sup>Faculty of Natural Sciences, Department of Mineralogy and Petrology, Comenius University in Bratislava, Mlynská dolina, 842 15 Bratislava, Slovak Republic

### 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 provided the following conclusions: the *B*-site occupancy is strictly limited to  $B^{3+}$ ; the *T* site can freely accommodate not only  $Si^{4+}$  but also  $B^{3+}$  and  $Al^{3+}$ , although these substituents require shrinkage and expansion of the  $TO_4$  tetrahedron, respectively; and the  $Be^{2+}$  substitution results in a significant difference in charge. Satisfactory bond lengths for octahedral sites were calculated for  $Al^{3+}$  (*Z*-site preference),  $Ti^{4+}$ ,  $Mn^{3+}$ ,  $Ga^{3+}$ ,  $V^{3+}$ ,  $Fe^{3+}$  (mixed preference),  $Mg^{2+}$ ,  $Fe^{2+}$ ,  $Li^+$ ,  $Mn^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Sc^{3+}$ , and  $Zr^{4+}$  (*Y*-site preference). Another group of cations, which includes  $U^{4+}$ ,  $Th^{4+}$ ,  $Y^{3+}$ , and lanthanoids from Tb to Lu and  $Ce^{4+}$ , have significantly longer bonds than typical *Y*-O and very short bonds for the *X* site; therefore, it is likely they would prefer an octahedron. The empirical bond length for the *X* site is met with  $Na^+$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Pb^{2+}$ , and lanthanoids from La to Gd, while K, Rb, and Cs are too large in the low-pressure conditions. However, the final tourmaline composition results from the interaction of the structure with the genetic environment in terms of *P-T-X* and geochemical conditions. This results in structural and environmental constraints that limit the incorporation of elements into the structure. Consequently, major elements, such as Si, Al, B, Mg, Fe, Na, and Ca usually occur in abundance, whereas other elements (V, Cr, Mn, Ti, Pb) could form end-member compositions, but rarely do because of their low abundance in the environment. The elements with contents limited to trace amounts have either structural (Be, C, REE, Rb, Cs, U, Th) or geochemical ( $Zr^{4+}$ ,  $Sc^{3+}$ , and  $Sr^{2+}$ ) limits. However, environmental properties, such as high pressure or specific local structural arrangements, can overcome structural constraints and enable the incorporation of elements (K).

**Keywords:** Tourmaline supergroup, crystal chemistry, bond length calculation, cation occupancy, trace elements; Lithium, Beryllium and Boron: Quintessentially Crustal