The influence of cationic partitioning among crystallographic sites based on bond-valence constraints and the genetic environment geochemistry on the composition of tourmaline-supergroup minerals

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Abstract: Theoretical bond-length calculation from ideal bond valences for each ion and coordination can predict ion site preference in the structure. It revealed that the B-site occupancy is strictly limited to B^{3+}, T site can freely accommodate Si^{4+} and Be^{2+}, B^{3+} and Al^{3+} substitution requires compression or expansion of TO_4 tetrahedron. Proper 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 including U^{4+}, Th^{4+}, Y^{3+}, lanthanoids from Tb^{3+} to Lu^{3+} and Ce^{4+} have significantly longer bonds than typical Y-O but form too short bonds for the X site. Therefore, they probably prefer octahedron. The usual empirical bond length for the X site is met with Na^+, Ca^{2+}, Sr^{2+}, Pb^{2+} and lanthanoids from La^{3+} to Gd^{3+}, while K^+, Rb^+ and Cs^+ are too big. However, the tourmaline composition results from interaction of structure with the genetic environment. The proportion of REE, U^{4+} and Th^{4+} in tourmaline is structurally limited, while e.g. Zr^{4+}, Sc^{3+}, Sr^{2+}, Pb^{2+} have only geochemical limits with no obvious structural constraints. Moreover, environmental properties such as pressure or specific local structural arrangements can overcome structural constraints.

Introduction

Tourmaline supergroup minerals belong to cyclosilicates with a relatively complex structure. It contains 5 different cationic crystallographic sites at different coordination – one tetrahedral T site, two octahedral Z and Y sites, polyhedral X site, triangular B site, and 8 different anionic sites — O1–O8 (Donnay & Buerger 1950). This structural complexity results in large variability of chemical elements which can be incorporated in the tourmaline structure. The major elements include small Si and B, slightly larger Al, Mg, Fe, Li, Mn, Cr, V, and Ti, and also the largest Na, Ca and K. Anionic sites comprise dominant O (as O^{2-} and OH^- anions) and minor F (Henry et al. 2011). However, many other elements can occupy tourmaline structure in minor to trace amounts.

Although the site occupancy usually follows Goldschmidt rules, local structural and bond-valence requirements may result in various disorder. Moreover, the tourmaline structure can accommodate cations which usually should be improper for specific structural site. Although it is usually not possible to analytically determine the position of each ion, mainly for trace elements, some predictions can be made based on bond-valence constraints for each ion at each site. Bond lengths can be derived from structural data, but it can be applied only on ions which are abundant in the structure. However, theoretical bond-length calculation from ideal bond valences for each ion with various coordination can predict the ion site preference in the structure. It could also help to identify internal crystal-chemical and external genetical and geochemical factors influencing tourmaline composition.

Topology of tourmaline crystal structure

Tourmaline group minerals has a relatively complex structure. The main structural element is built from the 3D framework of edge-connected ZO_6 octahedra, interconnected by regularly distributed structural "islands". These comprise six-member rings of TO_4 tetrahedra, triplets of YO_6 octahedra, large 9-coordinated X sites and BO_3 triangles (Bosi 2017). Chains of ZO_6 octahedra are oriented in the c direction and provide support for the structure but also sufficient flexibility for any local or long-distance structural distortion.

Moreover, their direction manifests in long-prismatic tourmaline crystal habitus (Bačík et al. 2015a).

Site occupancy based on bond-valence constraints

TO_4 tetrahedron

The most prominent feature of the tourmaline structure, which defines it as cyclosilicate, is represented by the ring of six TO_4 tetrahedra, which are connected by the pairs of O^{2-} anions. The apical atoms O (O6) are directed to the same (–c) pole of crystal (Donnay & Buerger 1950). Each TO_4 tetrahedron shares O anions with the X (2×), Y and Z (2×) sites.

The most abundant cation at the T site is Si^{4+}. The calculated Si–O distance of 1.624 Å is very similar to the empirical bond length of 1.621 Å. There are two typical substituents for Si^{4+} — Al^{3+} and B^{3+}. Tetrahedral Al have longer bonds (1.746 Å) and B shorter bonds (1.475 Å calculated, 1.482 Å empirical) than Si^{4+}. Consequently, B^{3+} causes compression and Al^{3+} expansion of tetrahedron. If any Be^{2+} is present in tourmaline structure, it likely prefers the T site with 1.635 Å calculated bond length. Other cations form very long bonds (Ti^{4+} 1.819 Å, Fe^{3+} 1.870 Å), therefore, their presence at the T site is unlikely.

BO_3 site

Triangular BO_3 groups lie parallel to the (0001) plane and connect to the vertices of ZO_6 and YO_6 octahedra. The BO_3 group shares O with Z (2×), Y (2×), and X (3×) sites.

Boron is the only cation occupying the B site. The calculated B–O bond length of 1.372 Å is similar to empirical average bond length. This indicates that B–O bond length in tourmaline is almost ideal allowing only minute variations. Other possible cations have much larger calculated bond lengths (Si^{4+} 1.512 Å, Be^{2+} 1.594 Å) excluding their possible substitution.

The presence of vacancies at B site was presumed but with no spectroscopic or structural evidence (Grice & Ercit 1993; Hawthorne 1996). Substitution mechanism that would result in vacancies at B produces unacceptably short H−Y and H−Z distances (Hawthorne 1996).

ZO_6 and YO_6 octahedron

The rings of tetrahedra are connected to two types of octahedra — ZO_6 and YO_6, which combined form brucite layer. The ZO_6 octahedron is smaller than YO_6 octahedron and is more distorted. It is connected to the T (3×), Y (2×), and B (2×) sites. The Y site is relatively regular octahedron with larger size than Z. The YO_6 octahedron is connected by O atoms with X (2×), T (2×), Z (3×), and B (2×) sites.

The Z site is usually dominated by Al^{3+} with calculated Al–O bond length of 1.904 Å and empirical distance of 1.868 Å. Smaller empirical bond length results from angular and bond-length distortion of the ZO_6 octahedron. Smaller bond lengths were calculated only for Si^{4+} (1.782 Å) and Be^{2+} (1.755 Å) which were never evidenced in octahedral coordination in tourmaline. All other cations have larger octahedral bond lengths; Ti^{4+}, Mn^{3+}, Ga^{3+} and Cr^{3+} below 2.00 Å, V^{3+} and Fe^{3+} slightly larger than 2.00 Å, Mg^{2+}, Fe^{2+}, Li^+, Mn^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Sc^{3+} and Zr^{4+} between 2.09 and 2.20 Å. These are proper values for the Y site in tourmaline evidenced in comparison to empirical data. Empirical bond lengths are always smaller due to octahedral distortions influencing bond valences in real structure.

The last group of cations which could occupy octahedral sites include cations with bond lengths between 2.20 and 2.30 Å. These are usually only in trace amounts and include U^{4+}, Th^{4+}, Y^{3+} and lanthanoids from Tb to Lu (HREE). Moreover, Ce^{4+} has bond length of 2.217 Å. These cations are not excluded but their proportion is very limited and would cause large distortion of the YO_6 octahedra, if present. Those with bond length larger than 2.30 Å (LREE from La^{3+} to Gd^{3+}, Pb^{4+}) are highly unlikely to occupy octahedra in tourmaline.

XO_9 polyhedron

The X site with coordination number of 9 is the trigonal antiprism located along threefold symmetry axis. The XO_9 polyhedron is connected through O atoms to T (6×), Y (3×), and B (3×) sites.

Based on the empirical data, the bond lengths at this site varies between 2.609 (Ca^{2+}) and 2.692 (Na^+). This can be considered the "Goldilocks zone" (similar to astronomical term, the zone of structurally stable bond lengths with minimal induced distortion) of the X site; cations with larger or smaller bond lengths have a limited occupancy. The perfect match with the "Goldilocks" bond lengths was calculated for Na^+ (2.618 Å), Sr^{2+} (2.678 Å) and Pb^{2+} (2.697 Å). The calculated Ca-O bond length of 2.522 Å is, similarly to Na-O, significantly shorter than empirical. This results from the contraction of neighbouring octahedral Y–O bonds leaving smaller bond valence for the X-site cations.

Other monovalent cations including K^+, Rb^+ and Cs^+ have much larger bond lengths (>2.90 Å) limiting their presence at tourmaline structure almost entirely. Barium has also relatively large bond length (2.834 Å). In contrast, U^{4+}, Th^{4+}, Y^{3+}, lanthanoids from Tb^{3+} to Lu^{3+} (HREE) and Ce^{4+} have significantly smaller bond lengths (<2.45 Å), probably too small for the X site. Only trivalent lanthanoids from La^{3+} to Gd^{3+} with bond lengths similar to Ca^+ are likely occupying the X site.

Crystal chemistry vs. genetic environment

For the understanding crystal-chemical properties and prediction of the site occupancy and substitutions in any mineral, Goldschmidt rules are usually used. However, the bond-length calculation provides a few advantages. It can be used for various coordination and cation charges very flexibly, only requiring a proper calculation of the bond valence. Moreover, it can be easily compared to empirical analytical data from structural refinement as evidenced here.

For every structural site, the "Goldilocks zone" of bond lengths can be assumed. This defines the range of bond length, which does not induce large structural tension and distortion. It is quite narrow in small sites such as B and T in tourmaline, but larger in sites with higher coordination number. This is one of limits for the site occupancy. Cations with larger deviation from the "Goldilocks zone" can still be accommodated at the respective site but their substitution is limited. This is the case of Al and B at T site — they substitute for Si but only in a limited proportion. Similarly, the proportion of REE in tourmaline is limited, although these can be abundant in the environment. It results from the deviation from the "Goldilocks zone" for both X and Y site and also relatively high charge for the X site. However, based on the present data, if present, REE likely divide between the Y (HREE) and X (LREE) site.

In contrast, some cations are straight in the "Goldilocks zone" but are usually absent or only in trace amounts. This can be only explained by external geochemical properties of the genetic environment. Such elements can be fractionated into different minerals with better structural properties for their accommodation. This is the case of Be^{2+} at T site, which, due to small charge, prefers other minerals such as beryl, chrysoberyl, etc. Some other elements are usually only in trace amounts in tourmaline environment or are already bound in other minerals — Zr^{4+}, Sn^{4+}, Sc^{3+}, Zn^{2+}, Ni^{2+}, Sr^{2+}. However, some of these can accumulate in tourmaline in specific conditions although usually also only in trace amounts — Cr^{3+}, V^{3+}, Cu^{2+}, and Pb^{2+}.

However, elasticity of the tourmaline structure can allow incorporation of elements from the outside of the "Goldilocks zone". The compression of the tourmaline structure at UHP conditions allowed the incorporation of K into the structure of maruyamaite (Hawthorne et al. 2016). However, K can be introduced at the X site also in Fe^{3+}-rich tourmalines with properly expanded structure (Žáček et al. 2000). In contrast, Al-rich environment in Detva-Biely vrch deposit resulted in composition with high proportion of $^VO^{2-}$. This resulted in the compression of Y–^VO bond and subsequent incorporation of the disproportionally large Cl^- anion at W site (Bačík et al. 2015b). And although never observed in natural samples or in experiments, octahedral Si at Z site could be present in tourmaline at UHP conditions (Broska et al. 2019).

However, there is a limit for a simple bond-length prediction of the site preference because the local and long-distance structural requirements also influence the cationic distribution. It is manifested in various cationic disorder reactions at octahedral sites. Along with the Al–Mg disorder (Hawthorne et al. 1993), the Cr and V disorder between Y and Z sites was documented (Bosi et al. 2004, 2017; Cempírek et al. 2013). These were explained by several external factors: the Fe/(Fe+Mg) ratio (Grice & Ercit 1993), influence of the X-site occupancy (Ertl et al. 2010a), structural deformations (Foit 1989; Bosi & Lucchesi 2007), pressure (Ertl et al. 2010b) and temperature (Bosi 2011). However, none of them was proved to be decisive. Nevertheless, more complex bond-valence calculations have shown possible mechanisms allowing disorder (Bačík 2015, 2018).

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