1   **Revision 1**

2   **Cation partitioning among crystallographic sites based on bond-length constraints in**

3   **tourmaline-supergroup minerals**

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10   **Running title: Cation partitioning in tourmaline-supergroup minerals**

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12   ABSTRACT

13   Theoretical bond-length calculations from ideal bond valences for each ion and

14   coordination allows for the prediction of ion site preference and partitioning in tourmaline

15   structures at low-pressure conditions. A comparison of calculated data with published bond-

16   length values enables the determination of the range of structurally stable bond lengths with a

17   minimal induced distortion − the "Goldilocks zone". The calculations provided following

18   conclusions: the B-site occupancy is strictly limited to B^{3+}; the T site can freely accommodate

19   not only Si^{4+}, but also B^{3+} and Al^{3+}, although these substituents require shrinkage and

20   expansion of the TO_4 tetrahedron, respectively, and the Be^{2+} substitution results in a

21   significant difference in charge. Satisfactory bond lengths for octahedral sites were calculated

22   for Al^{3+} (Z-site preference), Ti^{4+}, Mn^{3+}, Ga^{3+}, V^{3+}, Fe^{3+} (mixed preference), Mg^{2+}, Fe^{2+}, Li^+,

23   Mn^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Sc^{3+} and Zr^{4+} (Y-site preference). Another group of cations, which

24   includes U^{4+}, Th^{4+}, Y^{3+} and lanthanoids from Tb to Lu and Ce^{4+}, have significantly longer

25   bonds than typical Y-O and very short bonds for the X site; therefore, it is likely they would

26   prefer an octahedron. The empirical bond length for the X site is met with Na^+, Ca^{2+}, Sr^{2+},

27   Pb^{2+} and lanthanoids from La to Gd, while K, Rb and Cs are too large in the low-pressure

28   conditions. However, the final tourmaline composition results from interaction of the structure

29   with the genetic environment in terms of P-T-X and geochemical conditions. This results in

30   structural and environmental constraints that limit the incorporation of elements into the

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31   structure. Consequently, major elements, such as Si, Al, B, Mg, Fe, Na and Ca usually occur

32   in abundance, whereas other elements (V, Cr, Mn, Ti, Pb) could form end-member

33   compositions, but rarely do because of their low abundance in the environment. The elements

34   with contents limited to trace amounts have either structural (Be, C, REE, Rb, Cs, U, Th) or

35   geochemical (Zr^{4+}, Sc^{3+} and Sr^{2+}) limits. However, environmental properties, such as high

36   pressure or specific local structural arrangements can overcome structural constraints and

37   enable the incorporation of elements (K).

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39   ***Key words***: tourmaline supergroup; crystal chemistry; bond length calculation; cation

40   occupancy; trace elements

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43   **Introduction**

44   Tourmaline supergroup minerals minerals are cyclosilicates having the generalized

45   structural formula $XY_3Z_6(T_6O_{18})(BO_3)_3V_3W$, where the most common ions (or vacancy) at

46   each site are the following: X = Na$^+$, K$^+$, Ca^{2+}, and vacancy; Y = Li$^+$, Fe^{2+}, Mg^{2+}, Mn^{2+}, Al^{3+},

47   Fe^{3+}, and Cr^{3+}; Z = Mg^{2+}, Al^{3+}, Fe^{3+}, and Cr^{3+}; T = Si^{4+}, Al^{3+}, and B^{3+}; B = B^{3+}; V = (OH)$^-$ and

48   O^{2-}; and W = (OH)$^-$, F$^-$, and O^{2-} (Henry et al. 2011). Their particular structure contains 5

49   different cationic crystallographic sites with various coordinations – one tetrahedral T site,

50   two octahedral Z and Y sites, a polyhedral 9-coordinated X site, a triangular B site, and 8

51   different anionic sites – O1-O8 (Donnay and Buerger 1950). The structural complexity thus

52   results in large variability of chemical elements, which can be incorporated in the tourmaline

53   structure. The major elements include Si and B with small ionic radii, slightly larger Al, Mg,

54   Fe, Li, Mn, Cr, V, and Ti, and also the largest Na, Ca and K. Anionic sites comprise dominant

55   amount of O (as O^{2-} and OH$^-$) and usually a subordinate amount of F (Henry et al. 2011) or

56   Cl (Bačík et al. 2015b).

57   Many other elements can occupy a tourmaline structure in minor to trace amounts. These

58   include nearly the entire periodic table. Trace elements in tourmaline measured at the

59   micrometer scale become important tracers of the rock evolution and fluids interacting with

60   tourmaline. Tourmalines from various host environments can show a distinct chemical

61   signature of their host, such as increased Li concentrations in evolved magmatic rocks (e.g.,

62   Keller et al. 1999; Selway et al. 1999, 2000), anomalous Sn concentrations in Sn deposits

63   (Jiang et al. 1999; Williamson et al. 2000) and enrichment in Ni, V and Cr in metabasic rocks

64   and metabauxites (Henry and Dutrow 2001; Marschall et al. 2004). Subduction-zone fluids

65   and their impact on arc-magmatism signatures were modelled based on ratios of Ba, Th, La

66   and Sm (Van Hinsberg et al. 2017). Trace amounts of Sr, Sc, V, Ni, Pb, Zr, Ta, Nb, Cr, Ga

67   and Sn and REE have been used as proxies for mineralizing fluids in ore deposits and in other

68   rock environments (Duchoslav et al. 2017; Hazarika et al. 2017; Hong et al. 2017; Kalliomäki

69   et al. 2017). Relatively high Cl contents in tourmaline are used to establish the unusual

70   hydrothermal setting for altered dioritic porphyries associated with a gold deposit (Bačík et al.

71   2015b).

72   However, due to their low content, it is usually not possible to determine the position of

73   these minor and trace elements exactly in the tourmaline structure based only on the chemical

74   and structural data. Although the site occupancy usually follows Goldschmidt rules, structural

75   and bond-valence requirements may result in disorder with various interchanging cations

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76   (Grice and Ercit 1993; Hawthorne et al. 1993). Moreover, the tourmaline structure can

77   accommodate ions which usually do not have an appropriate ionic radius for any structural

78   site in tourmaline (Bačík et al. 2015b). However, some assignements can be made based on

79   bond-length constraints for each ion at each site. Bond lengths can be derived from structural

80   data but can be applied only on ions which are abundant in the structure. However, theoretical

81   bond-length calculation from ideal bond valences for each ion and coordination can indicate

82   ion site preference in the structure. This could also help in the identification of internal

83   crystal-chemical and external genetic factors (including geochemical and P-T-X conditions)

84   that influence element partitioning, as well as the final tourmaline composition.

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Topology of tourmaline crystal structure

87   Tourmaline-group minerals have a relatively complex structure. The main structural

88   element is built from a 3D framework of edge-connected ZO_6 octahedra, interconnected by

89   periodically distributed structural "islands" (Fig. 1). These comprise six-member rings of TO_4

90   tetrahedra, triplets of YO_6 octahedra, 9-coordinated X sites, and BO_3 triangles (Bosi 2018).

91   Chains of ZO_6 octahedra are oriented in the c direction and provide support for the structure,

92   but also have sufficient flexibility for any local or long-distance structural distortion (Fig. 2).

93   Moreover, their orientation in the c direction manifests in the usual long-prismatic tourmaline

94   crystal habit (Bačík et al. 2015a).

TO_4 tetrahedron

96   The most apparent feature of the tourmaline structure is represented by a ring of six TO_4

97   tetrahedra, which are connected by the pairs of O^{2-} anions (Fig. 3). The apical atoms O (O6)

98   are directed towards the same ($-c$) pole of crystal, which is the basis for the crystallographic

99   asymmetry (Donnay and Buerger 1950; Barton Jr. 1969). Each TO_4 tetrahedron shares O

100   anions with the T (2×), Y, Z (3×) and X (2×) sites (Fig. 3). They have the lowest distortion in

101   bond lengths (Δ – the formulae for each site are in Ertl et al. 2002) from all cation sites, which

102   have Δ in the following general order: $T < Z < Y < X$ (Ertl et al. 2002). This is likely given by

103   their small size, high charge, and rigidity compared to other polyhedra (Ertl et al. 2002).

104   However, a correlation between the size of cations occupying the X site and the bond-angle

105   distortion of tetrahedra was found (Foit and Rosenberg 1979; Ertl et al. 2002). The T-site

106   bond-angle distortion increased from 4.73 to 16.07 in accordance with the X-site charge,

107   which results from sharing six of the nine ligands with XO_9 polyhedron (Ertl et al. 2002). The

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108   divalent X-site cations (Ca and other divalent cations) shift O4 and O5 bonds inwards to
109   accommodate at the X site with smaller ionic radii.

Triangular BO$_3$ groups

111   Triangular BO_3 groups lie parallel to the plane (0001) and connect to the vertices of ZO_6
112   and YO_6 octahedra (Fig. 4). The BO_3 group shares O with Z (4×), Y (2×), and X (3×) sites. The
113   presence of vacancies at B site was assumed to be possible, but with no spectroscopic or
114   structural evidence (Grice and Ercit 1993; Hawthorne 1996). A substitution mechanism that
115   requires vacancies at B would produce unacceptably short H-Y and H-Z bond lengths in all
116   cases except one, where H atoms at x = 0.94, y = 0.06, z = 0.72 can be bonded to O(2), only if
117   the X site is vacant (Hawthorne 1996). Therefore, the presence of B-site vacancies is highly
118   unlikely for these reasons.

ZO_6 and YO_6 octahedra

120   The rings of tetrahedra are connected to two types of octahedra – ZO_6 and YO_6. The ZO_6
121   octahedron (Fig. 5) is smaller than the YO_6 octahedron and is less distorted in terms of bond-
122   length distortion (Ertl et al. 2002), as well as in terms of angular distortion and quadratic
123   elongation (Bosi and Lucchesi 2007). It is connected to the T (2×), Z (3×), Y and B (2×) sites.

124   Foit and Rosenberg (1979) showed on a number of tourmaline samples that an angular
125   distortion of the ZO_6 octahedron negatively correlates to <Y-O> bond length. However, data
126   indicated a high negative correlation between the bond-angle distortion of the ZO_6 octahedron
127   and <Y-O> in all tourmalines, in which O3 (V) site is occupied by 3 (OH) pfu (Ertl et al.
128   2002). The only exception was in buergerite, in which O is dominant at the V site (OH = 0.29
129   apfu, Dyar et al. 1998). Since the V site represents a vertex of ZO_6 octahedron, it can be
130   presumed that the occupation of this site affects the degree of Δ in octahedron, which is
131   unconstrained (Ertl et al. 2002).

132   The YO_6 octahedron is more regular with a larger size than Z (Henry and Dutrow 1996).
133   The YO_6 octahedron is connected by O atoms with X (2×), T (2×), Z (2×), and B (2×) sites
134   (Fig. 6). Changes in bond and angular distortions of the YO_6 octahedron are larger than that of
135   the ZO_6 octahedron and are influenced by both the size of the central cation, as well as the
136   actions of neighbouring polyhedra. Quite commonly, it is difficult to separate the effects of
137   individual factors (Ertl et al. 2002). An influence of the central cation on the Δ of the
138   octahedron decreases from Li-Al tourmalines with the largest distortion to Mg tourmalines
139   (dravite, uvite) with the least distortion. Therefore, the smallest cations (Ti, Al) cause the

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140   greatest distortion (Ertl et al. 2002). Similarly, a significant difference in the size of the

141   cations in the X and Y sites induces local disorder and distortion in the YO_6 octahedron

142   (MacDonald and Hawthorne 1995).

143   ***XO_9 polyhedron***

144   The X site with the coordination number 9 is trigonal antiprism, which is located along a

145   threefold symmetry axis. The XO_9 polyhedron is connected through O atoms to T (6×), Y (3×),

146   and B (3×) sites (Fig. 7).

147   The reasons for distortion in bond lengths of XO_9 polyhedron are not certain, but it is

148   possible to infer the influence of the X, Y and W site occupancy. Tourmalines with high

149   contents of Li and Al (>1 Li apfu) and a relatively high content of F have higher Δ of XO_9

150   polyhedron – the highest Δ was found in fluor-liddicoatite (Ertl et al. 2002). The size of the

151   cation occupying the XO_9 polyhedron is positively correlated with the X-O2 distance (Ertl et

152   al. 2001), which may also affect the distortion in the XO_9 polyhedron (Ertl et al. 2002). Na-

153   bearing, Li-, and F-poor tourmalines generally have smaller Δ (olenite 1.04, schorl 1.33) than

154   Ca-dominant tourmalines (fluor-liddicoatite 4.47, uvite 3.06) (Ertl et al. 2002)

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156   **Methods**

157   Bond-length calculations are based on the following equation:

158   $$d_{ij} = R_0 - b \ln v_{ij}$$

159   where d_{ij} is the bond length (in Å) between the two given ions, the bond valence (v_{ij})

160   measures bond strength (in vu – valence units), R_0 is the length of a single bond (for which v_{ij}

161   = 1 vu), and b is the universal parameter for each bond (Brown 2006). The R_0 and b values for

162   each cation from the list of Gagné and Hawthorne (2015) were used, since this list provides

163   the most current and consistent data on the bonding parameters. For more details, see Bačík

164   and Fridrichová (2019). Bond lengths (Table 1) were calculated only for the most common

165   major, minor, and trace elements occurring in tourmaline, although a similar approach can be

166   used for any chemical element.

167   Empirical average bond lengths (Table 2) were calculated from structural-refinement data

168   of natural tourmaline samples collected in the American Mineralogist Crystal Structure

169   Database (Downs and Hall-Wallace 2003). Two methods were used for calculations with

170   regards to the available data: (1) calculation of average from samples with the composition

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171   closest to the end member, if the composition was less than 0.3 apfu deviated from the full

172   site occupancy (^{T}Si, ^{B}B, ^{Y}Mg, ^{Y}Fe); (2) calculation of bond length, assuming full site

173   occupancy from the trend line calculated as a linear equation from the samples, with the

174   composition deviating more than 0.3 apfu of selected element from the full site occupancy

175   (^{T}B, ^{Y}Mn, ^{Y}Li, ^{X}Na, ^{X}Ca, ^{X}□), (3) use of the published data (^{Z}Al – Bosi and Andreozzi 2013).

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177   **Results**

178   ***TO$_4$ tetrahedron***

179   The T site is dominantly occupied by Si^{4+}. The calculated Si^{4+}–O distance of 1.624 Å is

180   very similar to the empirical bond length of 1.621 Å (Table 1, Fig. 8). There are two typical

181   substituents for Si^{4+} – Al^{3+} and B^{3+}. Tetrahedral Al^{3+} have longer bonds (1.746 Å) and B^{3+}

182   shorter bonds (1.475 Å calculated, 1.482 Å empirical) than Si^{4+}. Consequently, B^{3+} shrinks

183   and Al^{3+} expands the tetrahedron. If any Be^{2+} was present in tourmaline structure, it would

184   prefer the T site with 1.635 Å calculated bond length. Other cations form very long bonds

185   (Ti^{4+} 1.819 Å, Fe^{3+} 1.870 Å); therefore, their presence at the T site is unlikely.

186   ***BO$_3$ site***

187   Boron is the only cation occupying the triangular B site. The calculated B^{3+}–O bond

188   length of 1.372 Å is similar to the empirical average bond length (Table 1). This indicates that

189   B-O bond in tourmaline is almost ideal, allowing only negligible variations. Other possible

190   cations have much larger calculated bond lengths (Si^{4+} 1.512 Å, Be^{2+} 1.594 Å) excluding their

191   possible substitution. In contrast, the bond length calculated for C^{4+}-O bond in triangular

192   coordination with 1.284 Å is significantly smaller than both the empirical data and calculated

193   B^{3+}–O bond length.

194   ***ZO$_6$ and YO$_6$ octahedron***

195   The octahedral Z site is usually dominated by Al^{3+} with the empirical distance of 1.906 Å

196   (Bosi and Andreozzi 2013) and calculated Al-O bond length of 1.904 Å (Fig. 9a). Shorter

197   empirical bond length results from angular and bond-length distortion of the ZO_6 octahedron.

198   Smaller bond lengths were calculated only for Si^{4+} (1.782 Å) and Be^{2+} (1.755 Å), which have

199   not yet been reported in octahedral coordination in tourmaline. All other cations have larger

200   octahedral bond lengths; Ti^{4+}, Mn^{3+}, Ga^{3+} and Cr^{3+} below 2.00 Å, V^{3+} and Fe^{3+} slightly larger

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201   than 2.00 Å, Mg^{2+}, Fe^{2+}, Li^+, Mn^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Sc^{3+}, Zr^{4+} and Bi^{5+} between 2.09 and

202   2.20 Å (Fig. 9).

203   The last group of cations which could occupy octahedral sites include cations with bond

204   lengths between 2.20 and 2.30 Å (Fig. 9b). These are usually only in trace amounts and

205   include U^{4+}, Th^{4+}, Y^{3+} and lanthanoids from Tb^{3+} to Lu^{3+} (HREE). Moreover, Ce^{4+} has a bond

206   length of 2.217 Å. These cations are not excluded, but their proportion is very limited and

207   would cause large distortion of the YO_6 octahedra, if present. Those with a bond length larger

208   than 2.30 Å (LREE from La^{3+} to Gd^{3+}, Bi^{3+}, Pb^{2+}) are highly unlikely to occupy octahedra in

209   tourmaline.

XO_9 polyhedron

211   Based on the empirical data, the bond lengths at the X site vary between 2.609 (Ca^{2+}) and

212   2.692 (Na^+) (Fig. 10). A perfect match with these bond lengths was calculated for Na^+ (2.618

213   Å), Sr^{2+} (2.678 Å) and Pb^{2+} (2.697 Å). The calculated Ca-O bond length of 2.522 Å is

214   significantly shorter than empirical data and similar to Na-O.

215   Other monovalent cations, including K^+, Rb^+ and Cs^+, have much larger bond lengths

216   (>2.90 Å) at low-P conditions, thus limiting their presence in the tourmaline structure almost

217   entirely. Barium also has a relatively large bond length (2.834 Å). In contrast, U^{4+}, Th^{4+}, Y^{3+},

218   lanthanoids from Tb^{3+} to Lu^{3+} (HREE) and Ce^{4+} have significantly smaller bond lengths

219   (<2.45 Å), which are probably too small for the X site. Only trivalent lanthanoids from La^{3+} to

220   Gd^{3+} with bond lengths similar to Ca^+ could likely occupy the X site.

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Discussion

The "Goldilocks zone" structural constraints

224   For the understanding of crystal-chemical properties and the prediction of the site

225   occupancy in any mineral, the Goldschmidt rules determining the possibility of substitutions

226   based on ionic radii are most often used. However, the bond-length calculation also provides

227   several advantages. For example, it can be used for various coordinations and cation charges

228   quite flexibly, only requiring a proper calculation of the bond valence. Moreover, it can be

229   easily compared to empirical analytical data from a structural refinement, as evidenced here.

230   For the evaluation of the allowed site occupancy, the "Goldilocks zone" for each site can

231   be defined. This term is derived from the "Goldilocks principle", indicating a narrow range of

232   proper conditions ("just the right amount") for certain phenomena and is used in a wide range

233   of disciplines, including biology and medicine (Martin 2011; Shander and Ferraris 2017),

234   astronomy (Levenson 2011), mathematics (Bharali and Zimmer 2017), and even geology

235   (Miller et al. 2002; Junod and Jacquet 2019). Used here, it defines the zone of structurally

236   stable bond lengths with a minimal induced distortion. It can be defined empirically by the

237   largest and shortest possible bond lengths in the extreme near-to-end-member compositions,

238   or theoretically, based on the selected deviation value – we used 10% deviation from the

239   empirical bond lengths for the most common occupants of selected sites.

240   The "Goldilocks zone" of bond lengths for each site is influenced by the short-range

241   effects in local structural arrangements around specific sites. According to the Bond Valence

242   Model, there is a tendency for the sum of the bond valences (BVS) around each atom to

243   approach its formal valence (FV); if a significant mismatch between BVS and FV occurs, it is

244   indicative of strained bonds that lead to an instability of the structure (Brown 2006; Bosi

245   2018). Based on the valence-sum rule, Hawthorne (1996, 2002) and Bosi (2010, 2011, 2013)

246   evaluated possible atomic arrangements around O1 and O3. The local arrangements

247   conforming the closest to the valence-sum rule are those that are most likely to occur in the

248   structure (Hawthorne 2016). In turn, the influence of O at the O1 site has a strong impact on

249   the disorder in the Y and Z sites (Hawthorne 1996, 2002).

250   The structural strain resulting from the bond-valence requirements of ions with variable

251   FV can be relaxed by the distortion of structural polyhedra. Variations in the tourmaline

252   octahedral occupancy influence the geometry of both Y and Z octahedra. The irregularity at

253   these sites is larger, when the difference of the occupying cations charge is larger. Elbaite,

254   which has the largest charge difference between Li and Al, displays the largest irregularity of

255   both octahedra. In contrast, fluor-buergerite with trivalent Fe and Al have only small

256   irregularity of octahedral sites that closely approach ideal octahedral metrics in both cases.

257   These variations mainly occur at the shared edge of the ZO_6 and YO_6 octahedra – not only at

258   the O3, but also at O6 site (Bačík 2018). Moreover, the Z- and Y-site occupancy influences the

259   distortion at the neighboring sites. Extremely large ZO_6 octahedra in povondraite, occupied

260   mostly by Fe^{3+} and Mg^{2+}, expands the structure and allows for presence of large K^+ at the X

261   site (Grice et al. 1993; Žáček et al. 2000).

262   The structural stability requirements, however, also involve long-range structural effects.

263   They are mainly determined by spatial/steric constraints (imposed by translational symmetry)

264   that restrict the number of ways in which ions can be bonded to each other in a three-

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265   dimensional space. In tourmaline, the three-dimensional framework of the ZO_6 polyhedra

266   must be able to accommodate the structural islands (Bosi 2018). On the basis of 127 structure

267   refinement (SREF) data, which were later extended to 322 datasets (Bosi 2018), a structural

268   stability field was determined for tourmaline as a function of $<Y\text{-}O>$ and $<Z\text{-}O>$, suggesting

269   that only limited variations between the $<Y\text{-}O>$ and $<Z\text{-}O>$ dimensions can be tolerated by the

270   structure (Bosi and Lucchesi 2007). Additionally, the influence of other structural motifs,

271   including tetrahedral rings and distribution of cations (Al^{3+} with the largest influence) among

272   structural sites (Bosi et al. 2010), also defines possible constraints for the determination of the

273   „Goldilocks zone".

274

Determination of the "Goldilocks zone" for crystallographic sites

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276   For the determination of the "Goldilocks zone", the relations between ideal and real

277   crystal structures must be considered. We can make some approximations using an

278   octahedron as an example of the coordination polyhedron.

279   As an initial approximation, we can consider an ideal octahedron (Fig. 11a). The largest

280   sphere, which is coordinated by six spheres, has the same radius as the largest circle

281   coordinated by 4-unit circles in the cross-section perpendicular to one of octahedron axis (Fig.

282   11b). The distance of circle centres corresponds to the bond length between the central cation

283   (R) and ligand (O) in octahedral coordination. It is equal to the square root of two squares of a

284   ligand ionic radius (Fig. 11b, outer circle). With regards to the O^{2-} ionic radius (1.36 Å in 3-

285   fold coordination, Shannon 1976), the R-O bond length is equal to 1.92 Å. By the subtraction

286   of O^{2-} ionic radius, we get the central-cation ionic radius of 0.56 Å (Fig. 11c). The ionic

287   radius of Al^{3+} in octahedral coordination is equal to 0.535 Å (Shannon 1976). It is very close

288   to the ideal value; consequently, isolated Al^{3+}-bearing octahedron should not be subjected to

289   any bond-length distortion in the rigid-sphere model. If any distortion occurs, it should be

290   attributed to the influence of surrounding polyhedra in a complex crystal structure.

291   As a second approximation, we need to involve the internal structure of the atomic shell

292   and electrostatic properties of bonds. The ideal Al-O bond length for octahedral coordination,

293   which is calculated using the bond-valence approach (Brown 2006), is slightly shorter – 1.904

294   Å. This indicates that an attractive electrostatic force of Al^{3+} results in significant shortening

295   of Al-O bonds compared to the ideal-octahedron model with bond-length determined by

296   cation+anion ionic radii. Individual Al-O bond lengths in the ZO_6 octahedron closely

297   approach 1.87 Å with an increasing Al content in tourmaline. For Al and other s and p
298   elements, including Li, B, Si, Mg, Na, and Ca as the most common in tourmaline, we can
299   assume homogeneous elongation or shortening of bonds in this approximation.

300   The situation gets more complicated for d elements, whose internal structure with unfilled
301   d orbitals allows for the reduction of symmetry due to Jahn-Teller distortion (Jahn et al.
302   1937). This was observed for Fe^{2+}, Mn^{3+}, and Cu^{2+} in similar silicates, such as epidote,
303   gadolinite-hingganite, chlorite and mica, as well as in tourmaline (Burns and Strens 1967;
304   Faye 1968; Ito and Hafner 1974; Burns and Hawthorne 1996; Bačík et al. 2014, 2017; Ertl et
305   al. 2015; Fridrichová et al. 2018). However, this distortion can be described in the second
306   approximation.

307   The third approximation involves the external short-range and long-range effects of
308   neighbouring atoms. Once again, Al at the tourmaline Z site can be used as an example. Both
309   the Z-O7 and Z-O8 bonds have a length close to 1.87 Å in the Al dominant compositions.
310   However, both the Z-O3 and Z-O7' bonds are longer. The Z-O3 bond length is expanded due
311   to OH group dominance at the O3 site, which also causes the elongation of the Z-O7' bond
312   (Bačík 2018). The O-H bond valence, which is slightly lower than 1 vu due to the hydrogen
313   bond, reduces in the Z-O3 bond valence to 0.36 vu (Bačík 2018). However, the Z-O6 bond
314   length in the most Al-rich tourmalines is distinctly lower, since it balances the bond valences
315   in a complex relationship between YO_6 and ZO_6 octahedra (Bačík 2018).

316   Consequently, the prediction of bond lengths in real structures, which is based on simple
317   idealistic bond-valence calculations, has its limits. However, it can be a good approximation
318   for the prediction of site occupancies.

319

320   ***Partitioning of cations***

321   The "Goldilocks zone" is quite narrow for small sites, such as B and T in tourmaline, but
322   larger in sites with a higher coordination number. It is well-documented on the tetrahedral T
323   site, which allows for only partly limited substitution of Al^{3+} and B^{3+}, as well as on the B-site
324   occupancy, which is strictly limited to B^{3+}. The substitution of B^{3+} for Si^{4+} at the T site is
325   more common in HP/UHP conditions, which compress the structure to enable this substitution
326   (Hughes et al. 2000; Ertl et al. 2006; Kutzschbach et al. 2016). Other structural short-range
327   effects can also allow for the substitution of B^{3+} for Si^{4+}; e.g. in tourmalines of fluor-

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328   liddicoatite-elbaite series – the excess of Al at the Y site in ^{Y}(Al$_2$Li) compositions results in

329   the presence of tetrahedral B (Ertl et al. 2006, 2018).

330   In contrast, extensive "tschermak-type" Al$_2$Si$_{-1}$Mg$_{-1}$ substitution indicates high-grade

331   metamorphism in the Al-rich and, to a lesser extent, silica-poor environment (Henry and

332   Dutrow 1996; Ertl et al. 2018). Higher ^{T}Al is quite often connected with oxy-tourmalines

333   (Cempírek et al. 2006; Bosi et al. 2010, 2017; Bačík et al. 2013, 2015b). In short, relatively

334   high amounts of ^{T}Al may be expected in Mg- and/or Fe^{2+}-rich tourmalines in aluminous bulk

335   compositions and high-temperature metamorphic conditions. Significant amounts of ^{T}Al are

336   also found in pegmatitic Al-rich and Li-bearing tourmaline species including Li-rich schorl,

337   elbaite, fluor-liddicoatite, olenite, "oxy-rossmanite" (Cámara et al. 2002; Bosi et al. 2005;

338   Lussier et al. 2008; Ertl et al. 2018). Moreover, adachiite, which was found in a hydrothermal

339   vein (with margarite and diaspore) crosscutting a lateritic metamorphic rock in Japan, is the

340   first end-member of the tourmaline supergroup formed via Tschermak–like substitution

341   (Nishio-Hamane et al. 2014).

342   Octahedral sites have the largest variety of possibilities of occupying cations. Bond-

343   length calculations can also help determine site preference for each cation. The Z site prefers

344   smaller cations that are more similar to Al^{3+} – Ti^{4+}, Mn^{3+}, Ga^{3+}, and Cr^{3+} with bond lengths

345   below 2.00 Å. Cations with bond lengths slightly larger than 2.00 Å – V^{3+} and Fe^{3+} may have

346   no significant site preference at low concentrations. Cations with bond lengths between 2.09

347   and 2.20 Å – Mg^{2+}, Fe^{2+}, Li$^+$, Mn^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Sc^{3+} and Zr^{4+} – prefer a larger YO$_6$

348   octahedron. If we consider that the average Z–O bond length in povondraite with 4.29 apfu

349   Fe^{3+}, 1.36 apfu Mg^{2+} and 0.32 apfu Al^{3+} was 2.007 Å (Grice et al. 1993), this value can be

350   used for discrimination of cation site-occupancy preference. Those forming bonds shorter

351   than 2.01 apfu tend to prefer the Z site, while larger cations usually occupy the Y site.

352   However, this cannot be considered a fixed rule when other structural features occur as

353   discussed later.

354   This is in accordance with the preference sequences of ^{Y}Fe^{3+} > ^{Y}V^{3+} > ^{Y}Cr^{3+} > ^{Y}Al^{3+} and

355   ^{Z}Al^{3+} > ^{Z}Cr^{3+} > ^{Z}V^{3+} > ^{Z}Fe^{3+} for trivalent and ^{Y}Mn^{2+} > ^{Y}Fe^{2+} > ^{Y}Co^{2+} > ^{Y}Mg^{2+} > ^{Y}Ni^{2+} and

356   ^{Z}Ni^{2+} > ^{Z}Mg^{2+} > ^{Z}Co^{2+} > ^{Z}Fe^{2+} > ^{Z}Mn^{2+} for divalent cations based on the ionic radii (Bosi

357   2018). Select relative element partitioning among tourmaline and other coexisting minerals in

358   (mostly) metapelitic rocks was determined as follows: B: tourmaline >> muscovite >

359   sillimanite > biotite, plagioclase > staurolite, garnet; Mg: tourmaline >> staurolite > gahnite;

360   Na: tourmaline > plagioclase; Ca: plagioclase > tourmaline; Li: staurolite > chlorite >

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361   cordierite > biotite > muscovite > tourmaline, garnet, chloritoid; F: tourmaline > biotite >

362   muscovite; Cr: chromite > tourmaline > margarite > muscovite > corundum; Ni: talc >

363   tourmaline > staurolite > muscovite > gahnite; Co: tourmaline > staurolite > muscovite >

364   gahnite; Zn: gahnite > staurolite > tourmaline > muscovite; LREE: average continental crust >

365   tourmaline (Henry and Dutrow 1996, 2001, 2018).

366   The excellent correlation between the $<X–O>$ distance and the average ionic radius of the

367   X-site occupants shows that the $<X–O>$ distance is essentially dependent on the X-site

368   occupants (Ertl and Tillmanns 2012). Consequently, calculated X–O bond lengths allow for

369   great prediction of the X-site occupants. Cations, which could occupy the X site, can be

370   divided into three groups. The first group comprises cations with calculated bond lengths

371   similar to the average empirical bond lengths – Na^+, Ca^{2+}, Sr^{2+} and Pb^{2+}. These cations,

372   including Bi^{3+} (Ertl and Bačík 2020), have no bond-length constraints in occupying the X site.

373   The second group involves cations with significantly larger bond lengths in the order of Ba^{2+}

374   $< K^+ < Rb^+ < Cs^+$. The substitution of these cations is usually limited (limitation increases

375   progressively in the specified order) and their incorporation into the tourmaline structure in

376   significant amounts requires specific structural adjustments (Grice and Ercit 1993; Žáček et

377   al. 2000; Henry and Dutrow 2012; Berryman et al. 2015; Lussier et al. 2016) usually at

378   specific PT-conditions (Berryman et al. 2015; Lussier et al. 2016).

379   The last group of potential X-site occupants contains cations with significantly smaller

380   bond lengths and a higher charge compared to the typical X-site occupants, but a larger bond

381   length than octahedral cations. This group includes U^{4+}, Th^{4+} and REE^{3+}. The difference in

382   charge and bond lengths could be the clear structural limit for their amount in tourmaline –

383   there is no structural site in the tourmaline structure that matches their requirements perfectly.

384   As a consequence, their content is limited to trace amounts, even in a REE-rich environment,

385   such as in REE-rich NYF pegmatites (Bačík et al. 2012). However, on the basis of affinity to

386   selected crystallographic sites, it could be assumed that larger cations, including $LREE^{3+}$ –

387   La^{3+} to Gd^{3+} (but there is no clear border line) prefer the X site, while smaller $HREE^{3+}$ and

388   Ce^{4+} have an affinity to the Y site. However, LREE fit better into the X-site "Goldilocks zone"

389   than HREE at the Y site. This corresponds to the LREE preference observed in REE-bearing

390   tourmalines (Bačík et al. 2012 and references therein). Actinoids have no clear preference, but

391   U^{4+} with a smaller bond length would have stronger affinity to octahedral sites than Th^{4+}.

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13

393   *Crystal chemistry vs. genetic environment*

394   The partitioning of cations in tourmaline structural sites results from both internal
395   structural and external environmental factors. It is not easy to distinguish the roles played by
396   these factors, since they always act simultaneously. Nevertheless, because it is necessary to
397   attempt sorting out the roles played by internal and external factors, we have identified a few
398   possible ways of achieving this objective.

399   The specific case partitioning of minor and trace elements between tourmaline and melt
400   can be determined from partition coefficients of two phases. Major elements directly
401   influence the thermodynamic stability of the mineral and are thus controlled by a different
402   process from the one operating for the trace elements (Van Hinsberg 2011). Partition-
403   coefficients calculated by Van Hinsberg (2011) are invariably close to unity, which shows
404   that tourmaline is unable to significantly fractionate trace elements. Partitioning is systematic
405   and corresponds to predictions based on the lattice-strain theory, which allows element
406   valence and element site-occupancy to be determined from partitioning data. Results indicate
407   occupancy of Na, K, Rb, Ag, Sr, Ba and Pb at the X site, Mn, Co, Ni, Cu, Zn, Sc, V, Ga, Sb,
408   REE, Ti, Hf and Zr at the Y and Z sites, and Be at the T site (Van Hinsberg 2011). This
409   distribution corresponds well to our calculations.

410   Cation partitioning based on the bond-length constraints shows similarities to partition
411   coefficients. The "Goldilocks zone" is quite narrow at small sites, such as B and T in
412   tourmaline, but larger in sites with a higher coordination number. This is one of the limits for
413   site occupancy. Cations with a larger deviation from the "Goldilocks zone" can still be
414   accommodated at the respective sites, but their substitution is limited. This is the case of Al
415   and B at the T site – they substitute for Si, but only in a limited proportion. Similarly, the
416   proportion of REE in tourmaline is limited, although it can be abundant in the environment.
417   This is a result of deviation from both the X- and Y-site "Goldilocks zones", as well as a
418   relatively high charge for the X site. However, on the basis of the data presented, if present,
419   REE likely divides between the Y (HREE) and X (LREE) site.

420   In contrast, some cations are perfectly placed in the "Goldilocks zone", yet are usually
421   only in trace amounts or even below the detection limits of frequently used analytical
422   methods. This can be explained by external geochemical properties of the genetic
423   environment. Such elements can be fractionated into different minerals with better structural
424   properties for their accommodation. This is the case of Be^{2+} at the T site, which, due to its
425   small charge, prefers other minerals, most commonly beryl, chrysoberyl, etc. An increased Be

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426   content was found in Al-rich tourmalines – 76 ppm Be in elbaite from the Himalaya Mine

427   pegmatite, California (Ertl et al. 2010c) and even 0.02 wt.% of BeO in olenite from Koralpe

428   metapegmatite, Austria (Kalt et al. 2001) with the formula refined to $^{T}[Si_{4.89}B_{0.83}Al_{0.27}Be_{0.01}]$

429   (Ertl et al. 2007). The highest Be content is in tourmaline enriched in tetrahedral B^{3+} and can

430   also be well correlated with Al at the Y site with $r^2 = 0.969$ (Ertl et al. 2010c). This link to Al-

431   rich tourmalines suggests that Be^{2+} with a smaller charge than Si^{4+}, similarly to B^{3+}, can

432   effectively substitute at the tetrahedral site only in tourmalines with excess in charge at both

433   octahedral sites dominated by Al^{3+}. The increased Be content in tourmaline can be also linked

434   to generally low bulk Be content in pegmatite insufficient to form Be minerals such as

435   Koralpe metapegmatite, in which no Be minerals phases have been found (A. Ertl, personal

436   communication, October 29, 2020).

437   In fact, there are no significant examples of direct Be^{2+} for Si^{4+} substitutions. In the

438   majority of Be minerals, such as beryl (Aurisicchio et al. 1988), gadolinite-supergroup

439   minerals (Bačík et al. 2017), and sapphirine-supergroup minerals (Grew et al. 2008), Be^{2+}

440   occupies an independent tetrahedron that prefers substitution for Al^{3+} or B^{3+} instead of Si^{4+}. In

441   the sapphirine supergroup mineral khmaralite, Be distribution and the strong preference for

442   Be/Al mixing over Be/Si mixing appear to satisfy the bonding requirements for the bridging

443   of O atoms by minimizing the number of Be-O-Be and Be-O-Al linkages (Barbier et al.

444   1999). In other Be-bearing minerals in the sapphirine supergroup, Be^{2+} cations are found to

445   occupy some of the most polymerized T sites that share corners with three other T sites (Grew

446   et al. 2007). Consequently, the substitution of Be^{2+} in tourmaline limited may result from a

447   relatively low degree of TO_4 polymerization; only two corners are shared with other T sites.

448   Likewise, Bi^{5+} can form bonds inside the boundaries of the "Goldilocks zone" for the

449   octahedral sites; however, its higher charge limits possible substitutions allowing for its

450   presence in the tourmaline structure (Ertl and Bačík 2020).

451   Some other elements are commonly found only in trace amounts in the tourmaline

452   environment or are already bound to other minerals – Zr^{4+}, Sn^{4+}, Bi^{3+}, Sc^{3+}, Sr^{2+}. These

453   elements, if enriched, are usually well below 1 wt. % – Sn^{4+} up to 0.42 wt % SnO_2 (Yu and

454   Jiang 2003), Bi^{3+} up to 0.49 wt % Bi_2O_3 (Johnson et al. 1997). Although some of these are

455   usually present only in trace amounts in tourmaline, several can accumulate in specific

456   conditions – Ti^{4+}, Cr^{3+}, V^{3+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+} and Pb^{2+}. There were tourmaline crystals

457   enriched in Ti^{4+} (up to 4.62 wt % TiO_2; Vezzoni et al. 2018), Cu^{2+} (up to 3.51 wt % CuO;

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458 Vereshchagin et al. 2013; Ertl et al. 2015), Ni^{2+} (up to 3.96 wt % NiO; Baksheev and

459 Kudryavtseva 2004), and Zn^{2+} (up to 7.37 wt % ZnO; Pieczka et al. 2018).

460 Some of these common trace elements can accumulate in specific conditions to form end-

461 member composition. Divalent manganese is dominant in the *Y*-site cation in tsilaisite (Bosi et

462 al. 2012b), fluor-tsilaisite (Bosi et al. 2015) and celleriite (Bosi et al. 2020). Chromium forms

463 several mineral species – chromium-dravite (Rumyantseva 1983), oxy-chromium-dravite

464 (Bosi et al. 2012a), chromo-alumino-povondraite (Reznitskii et al. 2014) and vanadio-oxy-

465 chromium-dravite together with vanadium (Bosi et al. 2014a). Vanadium is dominant in

466 vanadio-oxy-dravite (Bosi et al. 2014b) and oxy-vanadium-dravite (Bosi et al. 2013). Pb-rich

467 fluor-liddicoatite and Pb-dominant analogue of fluor-liddicoatite were described in the

468 elbaite-subtype granitic Minh Tien pegmatite in northern Vietnam (Kubernátová and

469 Cempírek 2019). Recently, the first Ti-rich tourmaline end-member was described as

470 dutrowite (Biagioni et al. 2019).

471 The flexibility of the tourmaline structure may allow for the incorporation of elements

472 from outside the "Goldilocks zone". The compression of the tourmaline structure under UHP

473 conditions allowed the incorporation of K into the structure of maruyamaite, which qualifies

474 for the end-member composition (Lussier et al. 2016). Recent experimental studies of K and

475 Na incorporation into dravitic tourmaline coexisting with a KCl-bearing fluid indicate that K

476 progressively increases at the *X*-site with an increase of pressure, temperature and KCl

477 concentration (Berryman et al. 2015). However, K can be introduced to the *X* site also in Fe^{3+}-

478 rich tourmalines with a properly expanded structure at lower pressures (Grice and Ercit 1993;

479 Žáček et al. 2000; Henry and Dutrow 2012). Povondraite, which allows for the incorporation

480 of K into the *X* site, has a significantly expanded ZO_6 octahedron (<Z–O> = 2.007 Å) and

481 consequently, *a* (16.186 Å), *c* (7.444 Å) and cell volume (1689 Å^3) compared to ^{Z}Al-

482 dominant tourmalines usually with *a* < 16 Å, *c* < 7.3 Å and *V* < 1610 Å^3 (Grice et al. 1993).

483 As a consequence, <*X*–O> increased to 2.738 Å in povondraite, while it is usually below 2.70

484 Å in ^{Z}Al-dominant tourmalines (Grice et al. 1993). It should also be mentioned that both

485 maruyamaite and povondraite are oxy-tourmalines. The distance between Na and H1 is 2.362

486 Å in oxy-dravite with occupancy of 0.245 H at the H1 site (Gatta et al. 2014). Interestingly

487 enough, the K content of 0.53 apfu is very similar to, yet slightly lower than the ^{W}O content of

488 0.60 apfu (Lussier et al. 2016). Therefore, the absence of H at the *W* site can minimize

489 electrostatic repulsion for a large cation at the *X* site, and it suggests that K prefers structural

490 arrangements of oxy-tourmalines.

491   Similar structural adjustment was observed in tourmaline crystallized in the Al-rich

492   environment in the Detva-Biely Vrch deposit, which resulted in the composition with a high

493   proportion of $^{V}O^{2-}$. This resulted in the shortening of Y-^{V}O bond and subsequent incorporation

494   of the disproportionally large Cl⁻ anion at the W site (Bačík et al. 2015b).

495   However, there is a limitation for simple bond-length prediction of the site preference

496   because the short- and long-range structural constraints influence the cationic distribution.

497   This is manifested in various cation disorder reactions at octahedral sites. Along with the Al-

498   Mg disorder (Grice and Ercit 1993; Hawthorne et al. 1993), the Cr-Al and V-Al disorder

499   between Y and Z sites was documented (Bosi and Lucchesi 2004; Cempírek et al. 2013; Bosi

500   et al. 2017), as well as disordering of Fe over Y and Z sites with temperature in treated

501   samples (Bosi et al. 2019). These were explained by several factors: the Fe/(Fe+Mg) ratio

502   (Grice and Ercit 1993), influence of the W-site (Hawthorne 1996, 2002) and X-site occupancy

503   (Ertl et al. 2010a), structural deformations (Foit 1989; Bosi and Lucchesi 2007), pressure (Ertl

504   et al. 2010b), and temperature (Bosi 2011).

505

506   **Implications**

507   Understanding the factors that influence the partitioning of chemical elements, including

508   trace elements among crystallographic sites in structurally complex minerals, such as

509   tourmaline-supergroup minerals, is necessary for the proper determination of mineral

510   composition and decoding of genetic properties and processes during the crystallization.

511   Predictions from bond-valence constraints, which are based on a theoretical bond-length

512   calculation from ideal bond valences for each ion and coordination, are a useful tool for the

513   identification of the internal crystal-chemical factors that determine cation distribution.

514   Moreover, it allows for the determination of geochemical factors that influence tourmaline

515   composition when there is no structural constraint. Therefore, the implications of this type of

516   theoretical study are not limited only to structural and crystal-chemical issues, but also extend

517   to mineralogic-genetic, geochemical, petrological, or ore-deposit research. They also create

518   the basis for further study of cation distribution in the tourmaline structure, as well as

519   understanding of all structural factors and constraints.

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816

817   **Table 1.** Calculated bond lengths (in Å) of chemical elements at selected structural sites

818   in tourmaline.

Bond	Bond length	Bond	Bond length	Bond	Bond length	Bond	Bond length
	T site		*Y* and *Z* site		*Y* and *Z* site		*X* site
Si^{4+}-O	1.6240	Al^{3+}-O	1.9043	Sn^{4+}-O	2.0929	Na^+-O	2.6178
B^{3+}-O	1.4747	Si^{4+}-O	1.7817	Ga^{3+}-O	1.9751	Ca^{2+}-O	2.5222
Be^{2+}-O	1.6349	Be^{2+}-O	1.7553	Sc^{3+}-O	2.0933	K^+-O	2.9215
Al^{3+}-O	1.7462	Mg^{2+}-O	2.0991	Cu^{2+}-O	2.0806	Rb^+-O	3.0433
Ti^{4+}-O	1.8190	Fe^{2+}-O	2.1536	Zn^{2+}-O	2.1086	Cs^+-O	3.1991
Fe^{3+}-O	1.8696	Fe^{3+}-O	2.0155	Ni^{2+}-O	2.0737	Sr^{2+}-O	2.6785
	B site	Mn^{2+}-O	2.2023	Zr^{4+}-O	2.0776	Ba^{2+}-O	2.8337
B^{3+}-O	1.3720	Mn^{3+}-O	1.9942	Pb^{4+}-O*	2.3664	Pb^{2+}-O*	2.6968
Be^{2+}-O	1.5494	Li^+-O	2.2110	U^{4+}-O	2.2512	U^{4+}-O	2.4025
C^{4+}-O	1.2842	Ti^{4+}-O	1.9577	Th^{4+}-O	2.2873	Th^{4+}-O	2.4576
Si^{4+}-O	1.5121	Cr^{3+}-O	1.9752	Ce^{3+}-O	2.3836	Ce^{3+}-O	2.5414
		V^{3+}-O	2.0036	Y^{3+}-O	2.2601	Y^{3+}-O	2.4251
				Yb^{3+}-O	2.2275	Yb^{3+}-O	2.3788
				Ce^{4+}-O	2.2147	Ce^{4+}-O	2.3833
				Bi^{5+}-O*	2.1389	Bi^{3+}-O*	2.4954
				Bi^{3+}-O*	2.3376		

819   * Data from (Ertl and Bačík 2020)

820

821   **Table 2.** Empirical bond lengths (in Å) of chemical elements at selected structural sites in

822   tourmaline with the +10% and –10% deviation for the most typical occupant of the selected

823   site determining the range of the "Goldilocks zone" for each site.

Bond	Bond length	+10%	–10%
$^T Si^{4+}$-O	1.6206	1.4586	1.7827
$^T B^{3+}$-O	1.4817		
$^B B^{3+}$-O	1.3722	1.2350	1.5094
$^Z Al^{3+}$-O	1.906*	1.7154	2.0966
$^Y Mg^{2+}$-O	2.0304	1.8274	2.2335
$^Y Fe^{2+}$-O	2.0421		
$^Y Mn^{2+}$-O	2.1579		
$^Y Li^+$-O	2.0902		
$^X Na$-O	2.6920	2.4228	2.9612
$^X \square$-O	2.7258		
$^X Ca^{2+}$-O	2.6091		
$^X K^+$-O	2.6866		

824   * Data from (Bosi and Andreozzi 2013)

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827 **Figure captions:**

828 **Figure 1.** One unit cell of the tourmaline crystal structure (Bačík et al. 2012) with
829 framework of ZO_6 octahedra enclosing structural islands with alternating T_6O_{18} tetrahedral
830 rings, triplets of YO_6 octahedra and BO_3 triangles.

831 **Figure 2.** Interconnected chains of ZO_6 octahedra oriented parallel to c forming 3D
832 framework.

833 **Figure 3.** Local environment of TO_4 tetrahedron in (**a**) polyhedral model and (**b**) as a
834 topological graph.

835 **Figure 4.** Local environment of BO_3 triangle in (**a**) polyhedral model and (**b**) as a
836 topological graph.

837 **Figure 5.** Local environment of ZO_6 octahedron in (**a**) polyhedral model and (**b**) as a
838 topological graph.

839 **Figure 6.** Local environment of YO_6 octahedron in (**a**) polyhedral model and (**b**) as a
840 topological graph.

841 **Figure 7.** Local environment of XO_4 trigonal antiprism in (**a**) polyhedral model, (**b**) as a
842 complete topological graph, topological graph of local environment in (**c**) $+c$ and (**d**) $-c$
843 direction.

844 **Figure 8.** Calculated bond lengths for each bond in the (**a**) tetrahedral T-site and (**b**)
845 triangular B-site coordination of cations. Horizontal dashed lines are for empirical bond
846 lengths at each site. The horizontal dotted line is the 10% deviation from the empirical bond
847 length. The "Goldilocks zone" is white. The substitution is significantly limited for cations in
848 the grey zone.

849 **Figure 9.** Calculated bond lengths for each bond in the octahedral Z- and Y-site
850 coordination of cations – (**a**) major and minor elements, (**b**) trace elements. Horizontal dashed
851 lines are for empirical bond lengths for each cation. The horizontal dotted line is the 10%
852 deviation from the empirical bond length. The "Goldilocks zone" is white. The substitution is
853 significantly limited for cations in the grey zone.

854 **Figure 10.** Calculated bond lengths for each bond in the 9-fold trigonal antiprismatic X-
855 site coordination of cations. Horizontal dashed lines are for empirical bond lengths for each
856 cation. The horizontal dotted line is the 10% deviation from the empirical bond length. The

30

857   "Goldilocks zone" is white. The substitution is significantly limited for cations in the grey

858   zone.

859   **Figure 11.** (**a**) Ideal octahedron with O anions; (**b**) the maximum size of cation in the

860   ideal octahedron is the square root of two squares of ligand ionic radius; (**c**) after the

861   subtraction of O^{2-} ionic radius the cation ionic radius is equal to 0.56 Å.

Fig 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

a

b

R-O = 1.92 Å
rO^{2-} = 1.36 Å
R
rO^{2-} = 1.36 Å
rO^{2-} = 1.36 Å

c

R-O = 1.92 Å
rO^{2-} = 1.36 Å
rR = 0.56 Å