Tourmaline crystal chemistry

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ABSTRACT

Tourmalines form the most important boron rock-forming minerals on Earth. They belong to the cyclosilicates with a structure that may be regarded as a three-dimensional framework of octahedra $\text{ZO}_6$ that encompass columns of structural “islands” made of $\text{XO}_9$, $\text{YO}_6$, $\text{BO}_3$ and $\text{TO}_4$ polyhedra. The overall structure of tourmaline is a result of short-range and long-range constraints depending respectively on the charge and size of ions. In this study, published data are reviewed and analyzed to achieve a synthesis of relevant experimental results and to construct a crystal-chemical model for describing tourmalines and their compositional miscibility over different length scales. Order-disorder substitution reactions involving cations and anions are controlled by short-range structural constraints, whereas order-disorder intracrystalline reaction involving only cations are controlled by long-range structural constraints. The chemical affinity of a certain cation to a specific structural site of the tourmaline structure has been established on the basis of structural data and crystal-chemical considerations. This has direct implications for the tourmaline nomenclature, as well as on petrogenetic and provenance information. Some assumptions behind the classification scheme of tourmaline have been reformulated, revealing major agreement and significant improvements compared to earlier proposed scheme.

Keywords: Tourmaline, order-disorder, crystal structure, nomenclature
INTRODUCTION

The tourmaline supergroup minerals are chemically complex cyclosilicates rich in boron. They are the most common and the earliest boron minerals formed on Earth (Grew et al. 2016). Tourmalines are widespread in Earth’s crust, typically occurring in granites and granitic pegmatites but also in sedimentary and metamorphic rocks (Dutrow and Henry 2011; van Hinsberg et al. 2011). In recent years it was demonstrated that tourmalines preserve important records of the geological conditions in which they form in the lithosphere, thus it is important that we can understand how to read those records (e.g., Dutrow and Henry 2011). The general formula may be written as: $XY_3Z_6T_6O_{18}(BO_3)_3V_3W$, with $X = Na^+, K^+, Ca^{2+}, □$ (= vacancy); $Y = Al^{3+}, Cr^{3+}, V^{3+}, Fe^{2+/3+}, Mg^{2+}, Mn^{2+}, Li^+$; $Z = Al^{3+}, Cr^{3+}, V^{3+}, Fe^{2+/3+}, Mg^{2+}$; $T = Si^{4+}, Al^{3+}, B^{3+}$; $B = B^{3+}, V = (OH)^-, O^{2-}$; $W = (OH)^-, F^-, O^{2-}$ being the most common constituents. The letters in the formula ($X, Y, Z, T$ and $B$, not italicized) represent groups of cations at the $[^9X], [^6Y], [^6Z], [^4T]$ and $[^3B]$ crystallographic sites (letters italicized). The letters $V$ and $W$ represent groups of anions at the $[^3O3]$ and $[^3O1]$ sites, respectively. The H atoms occupy the H3 and H1 sites which are related to O3 and O1, respectively.

Since the publication of the nomenclature of the tourmaline-supergroup minerals (Henry et al. 2011), several new members of tourmaline have been approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA). These include oxy-species characterized by high contents of $Al^{3+}, Cr^{3+}, V^{3+}$ and $Fe^{2+/3+}$, which have provided a better understanding of the tourmaline crystal chemistry. This paper will present a general picture of the tourmaline structure and crystal chemistry, showing major factors controlling stability and chemical constraints from a short- and long-range structural viewpoint. The critical recognition of the importance of charge and size of atoms in determining...
crystal-chemical properties and miscibility behavior will be emphasized as well as critical comments on the assumptions behind the classification scheme of tourmaline. The importance of the crystal-chemical control of the tourmaline composition has direct implications on nomenclature as well as on the petrogenetic and provenance information (e.g., Hawthorne and Henry 1999).

**Tourmaline Constituents and Species**

The compositional range of tourmaline is remarkable, including important constituents with more than one oxidation state (e.g., Fe$^{2+}$-Fe$^{3+}$ and Mn$^{2+}$-Mn$^{3+}$) and other characterizing synthetic tourmalines (e.g., Ag$^+$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$ and Ga$^{3+}$; London et al. 2006; Rozhdestvenskaya et al. 2012; Vereshchagin et al. 2013, 2015, 2016). A total of (at least) 26 relevant constituents, in terms of concentration or occurrence, have been unambiguity identified in tourmaline (Table 1). These constituents are very different in charge and size and accommodate into seven crystallographic sites (X, Y, Z, T, B, O1 and O3); the other sites (O2, O4, O5, O6, O7 and O8) are solely occupied by oxygen. Moreover, the number of constituent-coordination environments is relatively large, compared to most other minerals: [3], [4], [6] and [9] coordination. Thus, tourmaline violates the Pauling’s parsimony rule, which emphasizes that the number of topochemically different environments in a structure tends to be small (Hawthorne 2006). In theory, this relatively large number of substantially different sites would decrease the stability, but tourmaline exists over environments that extend from the surface of the crust to the upper mantle (e.g., Marschall et al. 2009; Lussier et al. 2016) in the presence of H$_2$O, B- and F-bearing fluids.

The dominance of tourmaline constituents at one or more sites of the structure gives rise to a range of mineral species. At present, the tourmaline supergroup consists of 33 mineral species approved by the IMA-CNMNC (Table 2).
The tourmaline structure is typically rhombohedral, space-group $R3m$ with $Z = 3$, although some studies report lower symmetry such as orthorhombic, monoclinic or triclinic (e.g., Akizuki et al. 2001; Shtukenberg et al. 2007; Hughes et al. 2011). Tourmaline has an intermediate structural complexity of about 200 bits per unit cell (Krivovichev 2013), which is larger than that of amphibole (about 150 bits per unit cell), but smaller than that of some other minerals such as analcime (usually much over 200 bits per unit cell).

The tourmaline structure may be regarded as one of the most elegant of all crystal structures. It belongs to the subclass of cyclosilicate as consists of rings of six $TO_4$ tetrahedra, lying in a plane parallel to (0001). Because all tetrahedra point in the same direction, tourmaline lacks center symmetry (polar character) and is both pyroelectric and piezoelectric (electrical properties). Each tetrahedron shares one edge with the trigonal antiprism $XO_9$, which is located along the 3-fold axis passing through the center of each six-membered ring [$T_6O_{18}$]. The $X$-site occupancy usually reflects the paragenesis of the rock in which tourmaline crystallizes (petrologic information), and tourmaline supergroup is classified into primary groups based on the dominant occupancy of the $X$ site: vacant, alkali and calcic groups (Henry et al. 2011). The antiprism $XO_9$ and the ring [$T_6O_{18}$] combine with two sets of three octahedra $YO_6$: an [$Y_3O_{15}$] triplet of octahedra caps the $XO_9$ polyhedron toward the $+c$ axis and the other [$Y_3O_{13}$] caps the [$T_6O_{18}$] ring of tetrahedra toward the $-c$ axis. The most extensive compositional variation occurs at the $Y$ site, which is able to incorporate constituents of different sizes and charges (including vacancies) that makes tourmaline famous for its extensive range of colors (all rainbow colors) even within individual crystals (oscillatory and sector zoning). The $BO_3$ groups oriented sub-parallel to (0001) lie between the tetrahedral rings and are fully occupied by B, which makes tourmaline one of the most important B-bearing minerals (reservoir of B) in the Earth. The structural arrangement of [$T_6O_{18}$], $XO_9$, [$Y_6O_{18}$] and $(BO_3)_3$ form “islands” that are stacked in columns along the $c$ axis. These islands are attached to one another.
along the a and b crystallographic axes by spiral chains of ZO₆ octahedra (Fig. 1), which also extend along to the c axis according to a 3₁ triad screw axis. The three-dimensional framework of the tourmaline structure is therefore given by the screw-like arrangement of ZO₆ (Fig. 2). This framework is characterized by similar strong Z-O bonds (~ 0.5 valence units) which would explain some physical properties: hardness (~ 7-7½ Mohs), lack of cleavage, resistance to weathering in clastic sediments (like rutile and zircon), and extensive pressure-temperature stability up to about 7 GPa and 950 °C. Finally, another important feature of the tourmaline structure is provided by the orientation of the hydrogen atoms, which are sub-parallel to the c axis: H₁-hydrogen point down –c towards the oxygen at O₁, and H₃-hydrogen points up +c towards the oxygen at O₃. Owing to this orientation of (OH) dipoles, the fundamental (OH)-stretching bands in infrared spectra of tourmalines will display a very strong pleochroism, with ε >> ω (e.g., Skogby et al. 2012). All polyhedra discussed above are distorted. With respect to the ideal volume, bond distance or bond angle, the distortion of polyhedra decrease with decreasing coordination number according to the sequence: XO₉ > YO₆ > ZO₆ > TO₄ > BO₃ (Ertl et al. 2002; Bosi and Lucchesi 2007).

In summary, the tourmaline structure may be considered as a three-dimensional framework of octahedra ZO₆ that must be able to accommodate the structural islands.

**STRUCTURAL CONSTRAINTS**

Henry and Dutrow (2011) showed that the accommodation of F at the O₁ site is influenced by the cation occupancy (total charge) of the X and the Y sites. They suggested that the manner in which chemical constituents are incorporated into the tourmaline structure depends on external influences (temperature, pressure, mineral local assemblages and fluid composition) and on internal influences (crystallographic constraints). Moreover, tourmaline may be extremely optically, chemically, and isotopically zoned due to the occurrence of extensive short-range order of atoms.
that may strongly decrease the diffusion rates of atoms in the structure (e.g., Hawthorne and Dirlam 2011).

In general, the tourmaline chemical composition and zoning is a result of external and internal constraints. The latter act from a scale of a few Å (short-range structure) to a scale that involve the complete crystal (long-range structure).

**Short-range structure**

Short-range structure involves a set of atoms (cluster) that do not obey to the translational symmetry. Each cluster is controlled by bond-valence requirements, i.e., the charge of ions needs to be neutralized locally by nearest neighbors. Of particular relevance for tourmaline are the local atomic arrangements around the O1 (bonded to $3\text{Y}$) and O3 (bonded to $\text{Y}^{+2}\text{Z}$) sites which show a greater chemical variability. Hawthorne (1996; 2002) and Bosi (2010; 2011; 2013) evaluated possible atomic arrangements around O1 and O3, constrained by the valence-sum rule. According to the Bond Valence Model (e.g., Brown 2016), there is a tendency for the sum of the bond valences (BVS) around each atom to approach its formal valence (FV); if a large mismatches between BVS and FV occur, it is indicative of strained bonds which lead to instability in the structure. As a result, those local arrangements that most closely conform to the valence-sum rule are the arrangements that are most likely to occur in the structure (Hawthorne et al. 2005; Hawthorne 2016). The allowed stable short-range arrangements expressed as charge arrangements around O1 and O3 of tourmaline are summarized in Table 3. These arrangements can be considered as short-range constraints and have significant effects on the chemistry of short-range structure. For example, in oxy-foitite, ideally $\square^Y(\text{Fe}^{2+}\text{Al})_2^Y(\text{Al}_6(\text{Si}_6\text{O}_{18})(\text{BO}_3))_{0^3}(\text{OH})_{0^1}(\text{O})$, the Y and O1 sites composition would require the short-range arrangement $^Y(\text{Fe}^{2+} + 2\text{Al}) -^0\text{I}(\text{O}^2^-)$ rather than the chemically equivalent proportion of 33% $^Y(3\text{Fe}^{2+}) -^0\text{I}(\text{O}^2^-)$ plus 67% $^Y(3\text{Al}) -^0\text{I}(\text{O}^2^-)$, because the arrangement $^Y(3\text{Fe}^{2+}) -^0\text{I}(\text{O}^2^-)$ is unstable from a bond valence perspective. Similarly, the Y, Z and O3 sites composition
requires specific proportions of short-range arrangements, 33% $[^7\text{Fe}^{2+} + Z\text{(2Al)}]^{-\text{O}_3}\text{(OH)}$ plus 67%

\[[^7\text{Al} + Z\text{(2Al)}]^{-\text{O}_3}\text{(OH)}.\]

Therefore, the short-range constraints will tend to favor specific cation arrangements around the anions at the O1 and O3 sites. We can also note that the local arrangements around O$^2-$ of Table 3 can be associated with occupants having a total charge higher than that of occupants around (OH,F). This is consistent with the study of Bosi (2013), who examined the bond valences of a large number of refined tourmaline structures and showed a well-developed linear correlation between BVS at the O1 site and MFV (mean formal valence = total charge divided by the site multiplicity) at the Y site: BVS(O1) = 0.99 · MFV(Y) – 1.20 (see also Fig. 1 of Bosi 2013). Such a correlation indicates that O$^1$O$^2-$ content increases with increasing of $^7\text{R}^{3+}$content as suggested by Table 3, and may hence be considered as the linking between what predicted by bond valence arguments in the short-range structure with what observed by the diffraction techniques in the long-range structure.

As the sum of all different stable short-range arrangements corresponds to occupancies of the sites averaged over the complete crystal, it is apparent that (i) the stable short-range structures affects the long-range structure, (ii) the short-range constraints may have significant effects on the variation in chemical composition of tourmalines such as atomic substitutions and order-disorder mechanisms. In this regard, consider that the relation between dravite and oxy-dravite can be formulated by the chemical substitution:

\[\text{Mg}^{2+} + (\text{OH})^- \leftrightarrow \text{Al}^{3+} + \text{O}^{2-}\]

corresponding to the order-disorder mechanism

\[[^7(3\text{Mg}^{2+}) + \text{O}^1(\text{OH})^-] + Z\text{Al}^{3+} \leftrightarrow [^7(2\text{Al}^{3+} + \text{Mg}^{2+}) + \text{O}^1(\text{O}^-)] + Z\text{Mg}^{2+}\]

This mechanism involves the stable short-range arrangements $[^7(3\text{R}^{2+})^1(\text{OH})]$ and $[^7(2\text{R}^{3+} + \text{R}^{2+})^1(\text{O})]$ compatible respectively with dravite and oxy-dravite (or maruyamaite), and it can be
simplified to $2^\gamma \text{Mg}^{2+} + \text{O}^1(\text{OH})^- + Z \text{Al}^{3+} \leftrightarrow 2^\gamma \text{Al}^{3+} + \text{O}^1(\text{O}^2^-) + Z \text{Mg}^{2+}$ (Hawthorne 1996). Similarly, dravite and povondraite are related by the chemical substitution:

$$\text{Mg}^{2+} + 6\text{Al} + (\text{OH})^- \leftrightarrow 7\text{Fe}^{3+} + \text{O}^2^-$$

corresponding to the order-disorder mechanism

$$[ ^\gamma (3\text{Mg}^{2+}) + \text{O}^1(\text{OH})^- ] + 6Z \text{Al}^{3+} \leftrightarrow [ ^\gamma (3\text{Fe}^{3+}) + \text{O}^1(\text{O}^2^-) ] + 2Z \text{Mg}^{2+} + 4Z \text{Fe}^{3+}$$

This mechanism involves the stable short-range arrangements $[^\gamma (3\text{R}^{2+})-\text{O}^1(\text{OH})]$ and $[^\gamma (3\text{R}^{3+})-\text{O}^1(\text{O})]$ compatible with dravite and povondraite, respectively.

The two mechanisms reported above can be generalized to:

$$2^\gamma \text{R}^{2+} + Z^\gamma \text{R}^{3+} + \text{O}^1(\text{OH},\text{F})^1^- \leftrightarrow 2^\gamma \text{R}^{3+} + Z^\gamma \text{R}^{2+} + \text{O}^1(\text{O}^2^-) \quad (1)$$

$$3^\gamma \text{R}^{2+} + 2Z^\gamma \text{R}^{3+} + \text{O}^1(\text{OH},\text{F})^1^- \leftrightarrow 3^\gamma \text{R}^{3+} + 2Z^\gamma \text{R}^{2+} + \text{O}^1(\text{O}^2^-) \quad (2)$$

which are actually order-disorder substitution reactions involving cations and anions and controlled by local bond-valence requirements at the O1 site, i.e., short-range constraints.

Besides order-disorder substitution reactions (1) and (2), there is another type of order-disorder reaction that involves only cations:

$$^\gamma Z^\gamma \text{R}^{3+} + Z^\gamma \text{R}^{2+} \leftrightarrow ^\gamma Z^\gamma \text{R}^{2+} + Z^\gamma \text{R}^{3+} \quad (3)$$

The latter is an intracrystalline reaction usually controlled by long-range constraints (see below).

**Long-range structure**

The short-range constraints control which atoms can be nearest neighbors and hence determine the short-range structure. The sum of all of the short-range arrangements leads to a long-range structure. The latter is determined mainly by spatial/steric constraints (imposed by translational symmetry) that restrict the number of ways in which ions can be bonded to each other in the three-dimensional space. For a long-range structure to be formed, both short-range and long-range constraints must be satisfied. Consequently, all involved short-range arrangements need to be consistent with geometrical requirements, that is, with specific long-range interatomic distances.
In tourmaline, the three-dimensional framework of the $\text{ZO}_6$ polyhedra must be able to accommodate the structural islands (Fig. 2). On the basis of 127 structure refinement (SREF) data, Bosi and Lucchesi (2007) presented a structural stability field for tourmaline as a function of $<Y\text{-O}>$ and $<Z\text{-O}>$, suggesting that only a limited mismatch in the dimensions between $<Y\text{-O}>$ and $<Z\text{-O}>$ can be tolerated by the structure. At present, additional SREF can be found in the literature (at least 195, for a total of 322 data sets), which confirm the occurrence of a dimensional difference $\Delta_{Y-Z} = <Y\text{-O}> - <Z\text{-O}>$ in the range between 0.00 Å and 0.15 Å (Fig. 3). All known tourmalines fall within the delineated field indicating the presence of a long-range structural constraint. As values outside the range 0.00-0.15 Å have never been correctly observed so far, possible anomalous data need to be carefully checked: for example, the mean bond distances of lucchesiite from Czech Republic (Bosi et al. 2017a), $<Y\text{-O}> = 2.095$ Å and $<Z\text{-O}> = 1.932$ Å, yielded $\Delta_{Y-Z} = 0.16$ Å ($> 0.15$ Å).

However, a careful check of the $Y$-$O$ distances showed a mistake in the calculation of $<Y\text{-O}>$. The correct value is actually 2.065 Å which is fully consistent with the empirical structural constraint mentioned above: $\Delta_{Y-Z} = 0.13$ Å ($< 0.15$ Å).

The stability field $<Z\text{-O}>$ versus $<Y\text{-O}>$ also describes and predicts the effects of the tourmaline structural stability on its chemical variability. For instance, Bosi and Lucchesi (2007) predicted that the end-member compositions of dravite, schorl and tsilaisite (i.e., species with the $Y$ site occupied by $R^{2+}$-cations and the $Z$ site occupied by Al) should never occur, neither as natural samples nor as synthetic samples, because their structures should be unstable: $<^Y\text{Mg}\text{-O}>$, $<^Y\text{Fe}^{2+}\text{-O}>$ and $<^Y\text{Mn}^{2+}\text{-O}>$ distances are too large with respect to $<^Z\text{Al}\text{-O}>$. In this regard, the case of fluor-dravite (an oxy-free species) nicely illustrates the effect of long-range constraint on tourmaline site populations. According to the chemical analysis (Clark et al. 2011), the structural formula of fluor-dravite is expected as follows: $\text{Na}^Y(\text{Mg}_2\text{Fe}^{2+})^Y(\text{Al}_6)(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3[\text{F}_{0.7}^{\text{OH}}_{0.3}]$, with expected $<Y\text{-O}>$ ~ 2.100 Å and $<Z\text{-O}>$ ~ 1.907 Å, derived from the ionic radii (see below). These expected distances yield $\Delta_{Y-Z} = 0.19$ Å $> 0.15$ Å, indicating that the fluor-dravite structure is...
unstable. However, SREF data clearly show that the observed $<Y-O> = 2.053 \, \text{Å}$ and $<Z-O> = 1.913 \, \text{Å}$ are consistent with the long-range constraint ($\Delta Y-Z = 0.14 \, \text{Å} < 0.15 \, \text{Å}$) because the $Y$ and $Z$ site population is actually disordered: $\ldots^Y(Mg_{1.4}Al_{0.6}Fe^{2+}_{1.0})_{\Sigma 3.0}^Z(Al_{5.4}Mg_{0.6})_{\Sigma 6.0} \ldots$ (Clark et al. 2011). In fact, the intracrystalline order-disorder reaction $^YAl^{3+} + ^ZMg^{2+} \leftrightarrow ^YMg^{2+} + ^ZAl^{3+}$, not involving anions, occurs to shorten $<Y-O>$ (by introducing $Al^{3+}$) and to enlarge $<Z-O>$ (by introducing $Mg^{2+}$), thus to accommodate the potential misfit between $^YMgO_6$ and $^ZAlO_6$.

In summary, the tourmaline structure is a result of short-range constraints depending on the charge of ions, and long-range constraints depending on the size of ions. Order-disorder substitution reactions such as (1) and (2) involve cations and anions and are controlled by the short-range constraints, whereas order-disorder (usually) intracrystalline reaction (3) involves only cations and are controlled by the long-range constraints.

THE IONIC RADIUS

Variations in mean bond distances are often encountered in mineral crystal structures. In accordance with the Bond Valence Model, these variations may be explained as function of the degree of strain occurring in coordination environments of cations (Bosi 2014). In line with the mineralogical convention, any variation in mean bond distance is expressed as a variation in the cation radius by keeping the anion radius fixed, although the oxide anion radius can show a wide range of values (e.g., Gibbs et al. 2014).

Bosi and Lucchesi (2007) refined empirical ionic radii for six-fold coordinated ions in tourmaline and showed that the $^{[6]}Al$ ionic radius varies in a range of values larger than the expected one: the observed variation of $<Z-Al-O>$, $1.900-1.912 \, \text{Å}$ with a grand mean value $1.906 \, \text{Å}$ (Fig. 3 of Bosi and Andreozzi 2013), is larger than $1.892 \, \text{Å}$ calculated from Shannon (1976). A significant size variation was also reported for the $^{[6]}Fe^{3+}$ ionic radius ($0.645-0.705 \, \text{Å}$) as well as for the other ions depending on the $Y$ or $Z$ site occupancy. The reasons of these variations may be ascribed to
experimental errors (e.g., Bosi and Andreozzi 2013), inductive effects from other parts of the
structure (e.g., Ertl et al. 2012a), different occupancies at the octahedrally coordinated sites (e.g.,
Bosi and Lucchesi 2007), or more generally to different degree of strain experienced by atoms in
the bonding environment (Bosi 2014).

Although the $Y$ and $Z$ ionic radii of Bosi and Lucchesi (2007) fitted with 93% of the $Y$ and $Z$
mean bond distances analyzed, their size variations are of little practical interest for crystal-
chemical considerations. It is convenient to report such ionic radii by a unique mean value with its
standard error ($\pm \sigma$). The latter can be estimated as the difference between the maximum and
minimum radius reported in Table 2 of Bosi and Lucchesi (2007) divided by 4 or from the above
mentioned distance variations for Al: $2\sigma_{Al} = \pm \frac{(1.912 - 1.900)}{2} = \pm 0.006 \text{ Å}$, then $\sigma_{Al} = \pm 0.003 \text{ Å}$.

Table 4 shows such mean ionic radii for [6]-coordinated ions in tourmaline.

**CATION SITE PREFERENCE FOR $Y$ AND $Z$**

Because $<Y$-O$>$ is always greater than $<Z$-O$>$ in tourmaline, the $Y$ site will tend to
incorporate relatively large cations, whereas the $Z$ site will tend to incorporate relatively small
cations. Moreover, the chemical affinity of a certain cation to a specific structural site of the
tourmaline structure can be established on the basis of structural data and crystal-chemical
considerations. Bosi et al. (2017b) proposed that the preference of $R^{3+}$-cations for the $Y$ and $Z$ sites
is mainly controlled by their ionic radius according to the sequence: $^{Y}V^{3+} > ^{Y}Cr > ^{Y}Al$ and $^{Z}Al > ^{Z}Cr$
$> ^{Z}V^{3+}$. This conclusion is consistent with the cation distributions over $Y$ and $Z$ observed for the
oxy-species such as vanadio-oxy-chromium-dravite, vanadio-oxy-dravite and chromo-alumino-
povondraite (Table 2) as well as with the fact that no tourmaline species with atomic arrangements
such as “$^{Y}(Al,Cr)_{3}Z(Mg_{2}V_{4})$...” have been documented so far. Ferric iron can also be included in
this sequence on the basis of the $Fe^{3+}$-Al crystal-chemical behavior in bosiite,
“…(Fe³⁺)₃(Mg₂Al₄)…” (Ertl et al. 2016), and the relatively large ionic radius of Fe³⁺. Therefore, the preference for the R³⁺-cations to occupy the Y and Z sites is of type:

\[ \text{YFe}^{3+} > \text{YV}^{3+} > \text{YCr}^{3+} > \text{YAl}^{3+} \]

\[ \text{ZAl}^{3+} > \text{ZCr}^{3+} > \text{ZV}^{3+} > \text{ZFe}^{3+} \]

Similar arguments apply to the R²⁺-cations (Bosi and Skogby 2013; Bosi et al. 2015a; Vereshchagin et al. 2015): the preference of R²⁺ for the Z site increases with decreasing ionic radius. An opposite preference is expected for the Y site. Therefore, the preference for the R²⁺-cations to occupy the Y and Z sites is of type:

\[ \text{YMn}^{2+} > \text{YFe}^{2+} > \text{YCo}^{2+} > \text{YMg}^{2+} > \text{YNi}^{2+} \]

\[ \text{ZNi}^{2+} > \text{ZMg}^{2+} > \text{ZCo}^{2+} > \text{ZFe}^{2+} > \text{ZMn}^{2+} \]

**On the degree of R²⁺-R³⁺ order-disorder over the Y and Z sites**

In minerals, cation substitutions in a structural site are usually controlled by ion sizes (Goldschmidt’s rules). In this regard, the cation-size mismatch is a useful parameter to predict the extension of chemical substitution series: size difference between ions less than ~15% indicates a wide substitution; by ~15 to ~30% indicates a partial substitution; more than ~30% indicates little substitution.

In tourmaline, the cation-size mismatch can explain the amount of R²⁺ replacing R³⁺ at the Z site, which occurs in the chemical reactions (1), (2) and (3). Using the ionic radii of Table 4, the difference in size between Al³⁺ and R²⁺-cations are: Al-Ni²⁺ ~ 21%, Al-Mg²⁺ ~ 24%, Al-Co²⁺ ~ 27%, Al-Fe²⁺ ~ 30% and Al-Mn²⁺ ~ 32%. These values suggest the occurrence of a partial and little substitution between ZAl and ZR²⁺-cations. The negative correlation between Al-R²⁺ cation-size mismatch and the maximum ZR²⁺-occupancy observed for tourmalines with Al > 5 apfu, strongly supports the dependence of ionic radius on substitution degree (Fig. 4). Similarly, the different crystal-chemical behavior of ZMg observed in Cr- and Al-oxy-tourmalines can be explained.
difference in size Cr$^{3+}$-Mg$^{2+}$ (~15%) is smaller than Al-Mg$^{2+}$ (~24%), the $Z$Mg content in Cr-oxy-tourmalines is expected to be larger than that in Al-oxy-tourmalines. This is confirmed by the site populations of oxy-chromium-dravite and oxy-dravite (or maruyamaite): “…$Y$(Cr)$_3$$Z$(Mg$_2$Cr$_4$)…” and “…$Y$(MgAl)$_3$$Z$(MgAl$_3$)…”, respectively (Bosi et al. 2012; Bosi and Skogby 2013; Lussier et al. 2016).

**NOMENCLATURE ISSUES**

Tourmaline site occupancies depend essentially on the charge and size of atoms forming specific arrangements that obey both the short-range and long-range structural constraints. This crystal-chemical control of tourmaline composition should be reflected in systematic procedure for classification.

The tourmaline nomenclature is based on the determination of the chemical content at each non-equivalent site of the crystal structure (Hawthorne and Henry 1999). Consequently, a structural formula $XY_3Z_6T_6O_{18}(BO_3)_3V_3W$ is required for classification purposes. In accordance with the IMA-CNMNC guidelines (e.g., Nickel and Grice 1998; Hatert and Burke 2008), this means that the chemical information of the $Y$ and $Z$ site should not be merged, because such sites have different crystal-chemical response to the atom accommodations. For identifying tourmaline species, Henry et al. (2011, 2013) pointed out the importance of the empirical structural formula stating that the “actual tourmaline structural information of the $Y$- and $Z$-site occupancy is an overriding consideration for the definition of a tourmaline species”.

Only in absence of specific structural information on $Y$ and $Z$ occupancy, Henry et al. (2013) recommended the following site allocation procedure for the $Z$ and $Y$ sites: “Initially assign all Al (in excess of that assigned to the $T$ site) to the $Z$ site. Next, successively assign Mg$^{2+}$ (up to 2 apfu), V$^{3+}$, Cr$^{3+}$, and Fe$^{3+}$. If there is an excess of trivalent cations on the $Z$ site, the excess trivalent cations go into the $Y$ site”. As a result, tourmaline species can also be classified by combining chemical
data with assumptions on the site allocation of atoms, which lead to a calculated structural formula. However, the application of such nomenclature rules results in ambiguity for identifying oxy-tourmalines.

Table 5 shows that the empirical and calculated structural formulae of selected oxy-tourmaline species do not converge to same mineral name. In detail, sample PR1973 and TM84a can be only identified by the empirical structural formula. Sample PR85m is identified as oxy-schorl by the empirical formula and as oxy-dravite by the calculated formula. Sample drv18 is quite anomalous as both its empirical and its calculated formula lead to two new end-member formulae:

\[
\text{Na(Mg}_{2}\text{Fe}_{3+})\text{Al}_{6}\text{Si}_{6}\text{O}_{18}(\text{BO}_{3})_{3}\text{(OH)}_{3}\text{O} \quad \text{and} \quad \text{Na(Fe}_{2+}\text{Fe}_{3+})\text{Al}_{6}\text{Si}_{6}\text{O}_{18}(\text{BO}_{3})_{3}\text{(OH)}_{3}\text{O},
\]

These formulae, however, appear to represent an unresolved issue in the classification scheme rather than the occurrence of new species.

The unsuccessful application of the procedure of Henry et al. (2013) for naming tourmaline species may be ascribed to inaccurately developed cation site distributions, concerning in particular (i) the incorrect site preference of V$^{3+}$ and Cr$^{3+}$ for the Z site, which should be reversed as first ZCr$^{3+}$ and then ZV$^{3+}$ (see above), and (ii) the assumed qualitative Al site distribution, which incorrectly increases the actual amount of Al at the Z site. In order to improve this procedure, the site partitioning of important cations such as Al should be correctly modelled. Of particular relevance in this regard is the plot of $Z\text{Al}$ versus $[6]\text{Al} (= \text{Al}_{\text{tot}} - T\text{Al})$, obtained using cation-distribution data of 83 oxy-tourmalines accompanied by SREF, showing a strong positive nonlinear relation (Fig. 5). In detail, the plot displays the occurrence of an almost linear trend with $Z\text{Al}/[6]\text{Al}$ ratio very close to 1 for $[6]\text{Al} < 4$ apfu, and a nonlinear trend for $[6]\text{Al} > 4$ apfu. In order to make prediction from experimental data, the following quadratic equation may be used:

\[
Z\text{Al} = -0.1155 + 1.1713 \cdot [6]\text{Al} - 0.0522 \cdot [6]\text{Al}^2 \tag{4}
\]

Equation (4) allows assigning amounts of Al at the Z site using only chemical data. Notice that this quadratic fitting does lead to non-physical values for extrapolated values of $[6]\text{Al}$ ranging from...
0.000 to 0.098 apfu (\(^{\text{Z}}\)Al assumes slightly negative values) and from 8.270 to 9.000 apfu (\(^{\text{Z}}\)Al assumes values slightly larger than 6.000 apfu). An empirical site assignment model could also be attained for Mg, but the correlation of \(^{\text{Z}}\)Mg versus \([^{6}\text{Al}]_{\text{tot}}\) (not shown) is not yet sufficiently accurate to make prediction. Similarly, it is not yet possible to define a reliable mathematical model for the \(Y\) and \(Z\) site assignments of other trivalent cations (Fe, V, Cr), although important indications on their crystal-chemical behavior have been mentioned above.

**Possible improvements of the nomenclature of oxy-tourmalines**

Based on the strong correlation between \(^{\text{Z}}\)Al and \([^{6}\text{Al}]_{\text{tot}}\), and on the preference of R\(^{2+}\) and R\(^{3+}\)-cations for the \(Y\) and \(Z\) sites, the recommended procedure of Henry et al. (2013) for allocating cations to \(Z\) and \(Y\) can be reformulated as follows.

(i) Initially assign Al\(^{3+}\) (in excess of that assigned to the \(T\) site) to the \(Z\) site according to equation (4), and then assign the remaining Al\(^{3+}\) to the \(Y\) site.

(ii) Next, successively assign Mg\(^{2+}\) to \(Z\) (up to 2 apfu), Cr\(^{3+}\), V\(^{3+}\) and Fe\(^{3+}\).

(iii) If there is an excess of trivalent cations at the \(Z\) site, the excess trivalent cations go into the \(Y\) site.

In this way, the resulting cation distributions should more closely conform to the actual \(Y\)- and \(Z\)-site occupancy with respect to the previous procedure. Therefore, for the given bulk composition, the combination of the new procedure for the \(Y\) and \(Z\) cation distributions with the recommendations of Henry et al. (2011) for the allocation of constituents over the \(X\), \(T\), \(B\), \(O1\) and \(O3\) sites would yield a calculated structural formula leading to an end-member formula of a recognized tourmaline species. With regard to samples of Table 5, they can be univocally identified by applying the present procedure. In particular, sample drv18 may be identified as bosiite, ruling out the occurrence of a new species.
The definition of the crystal-chemical behavior of important constituents of tourmaline has allowed developing of a better scheme for site assignment that reveal major agreement and significant improvements compared to the earlier proposed scheme. The development of an unambiguous classification scheme is not just a question about terminology, but is a necessary step to understand the processes that govern the mineral diversity and has direct implications on the petrogenetic and provenience information of minerals. For example, ambiguity in the naming of a tourmaline species will not assist direct comparisons of tourmalines originating from different deposits. Therefore, for classification purposes, it would be better to treat all tourmalines alike, that is, follow recommendations based on assumptions whether or not a set of structural and spectroscopic data are available to determine real site occupancies. In this way, the naming of a tourmaline composition would be comparable for fully characterized tourmalines and for tourmalines for which only a chemical analysis is available. It would be appropriate to use the empirical structural formula to define new species, and the calculated structural formula to classify known species.

Acknowledgements

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$\text{Fe}^{2+}$ disorder at the $Y$ and $Z$ sites of tourmaline: a combined EMP, SREF, MS, IR and OAS 

$\text{NaMn}_3\text{Al}_6(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3\text{F}$, a new tourmaline from San Piero in Campo (Elba, Italy) 
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Bosi, F., Skogby, H., and Hålenius, U. (2017d) Oxy-foitite, \( \square(\text{Fe}^{2+}\text{Al}_2)\text{Al}_6(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3\text{O} \), a new mineral species of the tourmaline supergroup. European Journal of Mineralogy, DOI 10.1127/ejm/2017/0029-2631.


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**Figure 4.** Plot of maximum occupancy of $Z^R_{2+}$ observed in tourmalines with Al > 5 apfu against $R_{2+}$-Al$_{3+}$ cation-size mismatch. Solid line is linear regression. Data from Rozhdestvenskaya et al. (2012), Filip et al. (2012), Bosi and Skogby (2013) and Bosi et al. (2015b).

Table 1. The 26 relevant constituents occurring in tourmaline

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<tr>
<th>Valence</th>
<th>zero</th>
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<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>[6]Cu²⁺</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes: Vacancy (=□) is considered as a constituent in accord with the IMA-CNMC rules. In brackets are indicated coordination numbers. In bold are indicated constituents characterizing the 33 species of the tourmaline-supergroup minerals.
Table 2. The 33 mineral species of tourmaline recognized by the IMA-CNMNC

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adachiite</td>
<td>CaFe$_{2+}$Na$_8$Si$<em>6$AlO$</em>{18}$BO$_3$OH</td>
</tr>
<tr>
<td>Bosiite</td>
<td>NaFe$_{2+}$Na$_8$Mg$_2$Si$<em>6$O$</em>{18}$BO$_3$OH</td>
</tr>
<tr>
<td>Chromium-dravite</td>
<td>NaMg$_2$Cr$_6$Si$<em>6$O$</em>{18}$BO$_3$OH</td>
</tr>
<tr>
<td>Chrome-alumo-povondraite</td>
<td>NaCr$_{3+}$Na$_8$Si$<em>6$O$</em>{18}$BO$_3$OH</td>
</tr>
<tr>
<td>Darrellhenryite</td>
<td>NaLi$_8$Al$_6$Si$<em>6$O$</em>{18}$BO$_3$OH</td>
</tr>
<tr>
<td>Dravite</td>
<td>NaMg$_2$Al$_6$Si$<em>6$O$</em>{18}$BO$_3$OH</td>
</tr>
<tr>
<td>Elbaite</td>
<td>Na(Li$<em>{1.5}$Al$</em>{1.5}$)Al$_6$Si$<em>6$O$</em>{18}$BO$_3$OH</td>
</tr>
<tr>
<td>Feruvice</td>
<td>CaFe$_{2+}$Mg$_6$Si$<em>6$O$</em>{18}$BO$_3$OH</td>
</tr>
<tr>
<td>Fluor-buergerite</td>
<td>NaFe$_{2+}$Na$_8$Si$<em>6$O$</em>{18}$BO$_3$OH F</td>
</tr>
<tr>
<td>Fluor-dravite</td>
<td>NaMg$_2$Al$_6$Si$<em>6$O$</em>{18}$BO$_3$OH</td>
</tr>
<tr>
<td>Fluor-elbaite</td>
<td>Na(Li$<em>{1.5}$Al$</em>{1.5}$)Al$_6$Si$<em>6$O$</em>{18}$BO$_3$OH</td>
</tr>
<tr>
<td>Fluor-liddicoatite</td>
<td>Ca(Li$_2$Al)Al$_6$Si$<em>6$O$</em>{18}$BO$_3$OH</td>
</tr>
<tr>
<td>Fluor-schorl</td>
<td>NaFe$_{2+}$Na$_8$Si$<em>6$O$</em>{18}$BO$_3$OH F</td>
</tr>
<tr>
<td>Fluor-tsilaisite</td>
<td>NaMn$_{2+}$Na$_8$Si$<em>6$O$</em>{18}$BO$_3$OH F</td>
</tr>
<tr>
<td>Fluor-uvite</td>
<td>CaMg$_3$(Al$_6$Mg)Si$<em>6$O$</em>{18}$BO$_3$OH F</td>
</tr>
<tr>
<td>Foitite</td>
<td>(Fe$_{2+}$Al)$_8$Al$_6$Si$<em>6$O$</em>{18}$BO$_3$OH F</td>
</tr>
<tr>
<td>Lucchesiite</td>
<td>CaFe$_{2+}$Na$_8$Si$<em>6$O$</em>{18}$BO$_3$OH</td>
</tr>
<tr>
<td>Luinaite-(OH) a</td>
<td>(Na$<em>{3+}$Fe$</em>{2+}$Mg)$_8$Al$_6$Si$<em>6$O$</em>{18}$BO$_3$OH</td>
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<tr>
<td>Magnesio-foitite</td>
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</tr>
<tr>
<td>Maruyamaite</td>
<td>K(Al$_2$Mg)(Al$_3$Mg)Si$<em>6$O$</em>{18}$BO$_3$OH</td>
</tr>
<tr>
<td>Olenite</td>
<td>NaAl$_8$Al$_6$Si$<em>6$O$</em>{18}$BO$_3$OH</td>
</tr>
<tr>
<td>Oxy-chromium-dravite</td>
<td>NaCr$<em>{3+}$Cr$</em>{3+}$Si$<em>6$O$</em>{18}$BO$_3$OH</td>
</tr>
<tr>
<td>Oxy-dravite</td>
<td>Na(Al$_2$Mg)(Al$_2$Mg)Si$<em>6$O$</em>{18}$BO$_3$OH</td>
</tr>
<tr>
<td>Oxy-foitite</td>
<td>(Al$<em>2$Fe$</em>{2+}$)$_8$Al$_6$Si$<em>6$O$</em>{18}$BO$_3$OH</td>
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<tr>
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</tr>
<tr>
<td>Oxy-vanadium-dravite</td>
<td>NaV$_3$(V$_4$Mg$_2$)Si$<em>6$O$</em>{18}$BO$_3$OH</td>
</tr>
<tr>
<td>Povondraite</td>
<td>NaFe$_{2+}$Na$_8$Si$<em>6$O$</em>{18}$BO$_3$OH F</td>
</tr>
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<td>Rossmanite</td>
<td>(Al$_2$Li)$_8$Al$_6$Si$<em>6$O$</em>{18}$BO$_3$OH</td>
</tr>
<tr>
<td>Schorl</td>
<td>NaFe$_{2+}$Na$_8$Si$<em>6$O$</em>{18}$BO$_3$OH F</td>
</tr>
<tr>
<td>Tsilaisite</td>
<td>NaMn$_{2+}$Na$_8$Si$<em>6$O$</em>{18}$BO$_3$OH F</td>
</tr>
<tr>
<td>Uvite</td>
<td>CaMg$_3$(Al$_6$Mg)Si$<em>6$O$</em>{18}$BO$_3$OH</td>
</tr>
<tr>
<td>Vanadio-oxy-chromium-dravite</td>
<td>NaV$_3$(Cr$_2$Mg$_2$)Si$<em>6$O$</em>{18}$BO$_3$OH</td>
</tr>
<tr>
<td>Vanadio-oxy-dravite</td>
<td>NaV$_3$(Al$_4$Mg$_2$)Si$<em>6$O$</em>{18}$BO$_3$OH</td>
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</table>

* Mineral (IMA 2009-046) description has not yet been published in the scientific literature.
<table>
<thead>
<tr>
<th>Composition</th>
<th>Formal valence</th>
<th>Charge arrangement</th>
<th>MFV $^a$</th>
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<td>O1</td>
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<td>YYY</td>
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<tr>
<td>(OH) or F</td>
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<td>$(R^{3+} + 2R^+)$</td>
<td>1.67</td>
</tr>
<tr>
<td>(OH) or F</td>
<td>–1</td>
<td>$(R^{3+} + R^{2+} + \square)$</td>
<td>1.67</td>
</tr>
<tr>
<td>(OH) or F</td>
<td>–1</td>
<td>$(R^{3+} + R^{2+} + R^{+})$</td>
<td>2.00</td>
</tr>
<tr>
<td>(OH) or F</td>
<td>–1</td>
<td>$(R^{3+} + R^{3+} + \square)$</td>
<td>2.00</td>
</tr>
<tr>
<td>(OH) or F</td>
<td>–1</td>
<td>$(3R^{2+})$</td>
<td>2.00</td>
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<tr>
<td>(OH) or F</td>
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<td>$(2R^{3+} + R^{+})$</td>
<td>2.33</td>
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<tr>
<td>(OH) or F</td>
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<td>$(2R^{2+} + R^{3+})$</td>
<td>2.33</td>
</tr>
<tr>
<td>O</td>
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<td>$(R^{2+} + 2R^{3+})$</td>
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<tr>
<td></td>
<td></td>
<td>$(3R^{3+})$</td>
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<table>
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<tr>
<th>O3</th>
<th>O3 $^b$</th>
<th>YZZ</th>
<th>$&lt;YZZ&gt;$</th>
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<td>(OH)</td>
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<td>$\gamma R^+ + \zeta (R^{2+} + R^{3+})$</td>
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</tr>
<tr>
<td>(OH)</td>
<td>–1</td>
<td>$\gamma \square + \zeta (2R^{3+})$</td>
<td>2.00</td>
</tr>
<tr>
<td>(OH)</td>
<td>–1</td>
<td>$\gamma R^{2+} + \zeta (2R^{3+})$</td>
<td>2.33</td>
</tr>
<tr>
<td>(OH)</td>
<td>–1</td>
<td>$\gamma R^{3+} + \zeta (2R^{2+})$</td>
<td>2.33</td>
</tr>
<tr>
<td>(OH)</td>
<td>–1</td>
<td>$\gamma R^{2+} + \zeta (2R^{3+})$</td>
<td>2.67</td>
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<td>(OH)</td>
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<td>$\gamma R^{3+} + \zeta (2R^{2+})$</td>
<td>2.67</td>
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<td>–1</td>
<td>$\gamma R^{3+} + \zeta (2R^{3+})$</td>
<td>3.00</td>
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<tr>
<td>O</td>
<td>–2</td>
<td>$\gamma R^{3+} + \zeta (2R^{3+})$</td>
<td>3.00</td>
</tr>
</tbody>
</table>

Abbreviation: $R^+$, $R^{2+}$ and $R^{3+}$ = generalized monovalent (+1), divalent (+2) and trivalent (+3) cation

$^a$ MFV = mean formal valence = total charge/3

$^b$ Because of the hydrogen bond, the bond-valence sum at the O1 and O3 sites occupied by (OH) are 1.05 vu and 1.15 vu, respectively (e.g., Hawthorne 2002; Gatta et al. 2014)
### TABLE 4. Empirical mean ionic radii (Å) for [6]-coordinated ions in tourmaline

<table>
<thead>
<tr>
<th>Ion</th>
<th>This work</th>
<th>Shannon (1976)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al³⁺</td>
<td>0.547(3)</td>
<td>0.535</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>0.615(1)</td>
<td>0.615</td>
</tr>
<tr>
<td>V³⁺</td>
<td>0.655(1)</td>
<td>0.64</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>0.675(15)</td>
<td>0.645</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>0.776(1)</td>
<td>0.78</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.722(1)</td>
<td>0.72</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>0.809(1)</td>
<td>0.83</td>
</tr>
<tr>
<td>Li⁺</td>
<td>0.751(9)</td>
<td>0.76</td>
</tr>
</tbody>
</table>

**Notes:** Empirical ionic radii from Shannon (1976) apply to the other ions such as Ti⁴⁺ = 0.605 Å, Ni²⁺ = 0.69 Å, Co²⁺ = 0.745 Å, etc.

The mean anionic radii \(<O>\) related to the \(Y\) and \(Z\) sites is a function of the constituent-anion radius of Shannon (1976). The \(<O>\) varies from 1.353 to 1.363 Å; \(<\bar{O}>\) varies from 1.357 Å for tourmalines with \(O_3 = (OH)\) to 1.360 Å for tourmalines with \(O_3 = O^2-\).

Estimated standard error (±σ) in brackets.
### Table 5. Examples of identification of selected oxy-tourmalines

<table>
<thead>
<tr>
<th>Sample</th>
<th>PR1973</th>
<th>TM84a</th>
<th>PR85m</th>
<th>drv18</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical site population</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>(V_{2.21}Cr_{0.54}Mg_{0.11}Fe^{3+}<em>{0.12}Ti</em>{0.01}Zn_{0.01})</td>
<td>(Al_{1.52}Fe^{3+}<em>{0.06}Fe^{2+}</em>{1.07}Mg_{0.26}Mn^{2+}<em>{0.05}Zn</em>{0.01}Ti^{4+}_{0.03})</td>
<td>(Al_{1.23}Fe^{2+}<em>{0.90}Mg</em>{0.63}Fe^{3+}<em>{0.15}Ti^{4+}</em>{0.09})</td>
<td>(Mg_{1.35}Fe^{2+}<em>{0.94}Fe^{3+}</em>{0.49}Ti^{4+}_{0.20})</td>
</tr>
<tr>
<td>Z</td>
<td>(Cr_{3.01}Al_{0.96}Mg_{2.03})</td>
<td>(Al_{5.48}Fe^{3+}<em>{0.08}Mg</em>{0.36}Fe^{2+}_{0.08})</td>
<td>(Al_{5.05}Mg_{0.89}Fe^{3+}_{0.06})</td>
<td>(Al_{4.58}Mg_{0.80}Fe^{3+}_{0.62})</td>
</tr>
<tr>
<td>Name</td>
<td>vanadio-oxy-chromium-dravite</td>
<td>oxy-folitite</td>
<td>oxy-schorl</td>
<td>oxy-?</td>
</tr>
<tr>
<td><strong>Calculated site population according to Henry et al. (2013)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>(Cr_{2.72}Mg_{0.14}Fe^{3+}<em>{0.12}Ti</em>{0.01}Zn_{0.01})</td>
<td>(Al_{1.00}Fe^{3+}<em>{0.14}Fe^{2+}</em>{1.15}Mg_{0.61}Mn^{2+}<em>{0.05}Zn</em>{0.01}Ti^{4+}_{0.03})</td>
<td>(Mg_{1.52}Fe^{2+}<em>{0.90}Al</em>{0.28}Fe^{3+}<em>{0.21}Ti^{4+}</em>{0.09})</td>
<td>(Mg_{0.73}Fe^{2+}<em>{0.94}Fe^{3+}</em>{1.11}Ti^{4+}_{0.20})</td>
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<tr>
<td>Z</td>
<td>(Al_{0.96}Mg_{2.00}V_{2.21}Cr_{0.83})</td>
<td>(Al_{6.00})</td>
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<tr>
<td>Name</td>
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<td>oxy-?</td>
</tr>
<tr>
<td><strong>Calculated site population according to this work</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>(V_{2.21}Cr_{0.51}Mg_{0.14}Fe^{3+}<em>{0.12}Ti</em>{0.01}Zn_{0.01})</td>
<td>(Al_{1.47}Fe^{3+}<em>{0.14}Fe^{2+}</em>{1.15}Mg_{0.14}Mn^{2+}<em>{0.05}Zn</em>{0.01}Ti^{4+}_{0.03})</td>
<td>(Al_{1.10}Fe^{2+}<em>{0.90}Mg</em>{0.70}Fe^{3+}<em>{0.21}Ti^{4+}</em>{0.09})</td>
<td>(Al_{0.43}Mg_{0.30}Fe^{2+}<em>{0.94}Fe^{3+}</em>{1.11}Ti^{4+}_{0.20})</td>
</tr>
<tr>
<td>Z</td>
<td>(Al_{0.96}Mg_{2.00}Cr_{0.04})</td>
<td>(Al_{5.53}Mg_{0.47})</td>
<td>(Al_{1.18}Mg_{0.82})</td>
<td>(Al_{1.15}Mg_{1.15})</td>
</tr>
<tr>
<td>Name</td>
<td>vanadio-oxy-chromium-dravite a</td>
<td>oxy-folitite b</td>
<td>oxy-schorl c</td>
<td>biosilite d</td>
</tr>
</tbody>
</table>

#### Empirical structural formula for:

- **sample PR1973 (Bosi et al. 2014),**
  \((Na_{0.97}K_{0.02}Ca_{0.02})^2(V_{2.21}Cr_{0.54}Fe^{3+}_{0.12}Mg_{0.11}Ti^{4+}_{0.01}Zn_{0.01})^2(Cr_{3.01}Al_{0.96}Mg_{2.03})^2[(Si_{6.99}Al_{0.03})O_{18}][BO_{3}]_3(OH_{2.87}O_{0.13})(O_{0.71}F_{0.29})^2;\)

- **sample TM84a (Bosi et al. 2017d),**
  \((-0.5)Na_{0.45}Ca_{0.00}K_{0.01})^2(AL_{1.52}Fe^{3+}_{0.06}Fe^{2+}_{1.07}Mg_{0.25}Mn^{2+}_{0.06}Zn_{0.01}Ti^{4+}_{0.03})^2(Al_{5.48}Fe^{3+}_{0.08}Mg_{0.36}Fe^{2+}_{0.08})^2[(Si_{5.69}Al_{0.11})O_{18}][BO_{3}]_3(OH_{3})_3[O_{0.57}F_{0.04}](OH_{0.39})^3;\)

- **sample PR85m (Bosi et al. 2017c),**
  \((Na_{0.69}K_{0.02}-0.16Ca_{0.11})^2[(Al_{1.22}Fe^{3+}_{0.90}Mg_{0.63}Fe^{3+}_{0.15}Ti^{4+}_{0.09})^2(Al_{5.05}Mg_{0.89}Fe^{3+}_{0.06})^2][Si_{5.95}Al_{0.01}]O_{18}][BO_{3}]_3(OH)_{3}[OH_{0.59}](OH_{0.35}F_{0.06});\)

- **sample drv18 (Câmara et al. 2002),**
  \((Na_{0.49}K_{0.01}Ca_{0.48})^2(Mg_{1.35}Fe^{3+}_{0.94}Fe^{3+}_{0.49}Ti_{0.20})(Al_{4.58}Fe^{3+}_{0.62}Mg_{0.80})^2[(Si_{5.95}Al_{0.01})O_{18}][BO_{3}]_3(OH)_{3}[OH]_{0.18}F_{0.19}O_{0.64}];\)

\[a\] Ideally Na\(V^{3+}_{0.3}(Mg_{2}Al_{2})(SiO_{18})(BO_{3})_3(OH)_3O\)

\[b\] Ideally \(((Fe^{2+}_{0.2}Al)_{2}Al_{6}(SiO_{18})(BO_{3})_3(OH)_3O\)

\[c\] Ideally Na\((Fe^{2+}_{0.2}Al)_{2}Al_{6}(SiO_{18})(BO_{3})_3(OH)_3O\)

\[d\] Ideally Na\(Fe^{3+}_{0.3}Al_{6}(SiO_{18})(BO_{3})_3(OH)_3O\)
Figure 4

Max. $R^2^+$ at Z (atoms/site %)

$R^2^+$-Al cation-size mismatch (%)

$r^2 = 0.98$

Ni$^{2+}$

Mg$^{2+}$

Co$^{2+}$

Fe$^{2+}$

Mn$^{2+}$

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Figure 5

\[ Z\text{Al} = -0.1155 + 1.1713 \times [6]\text{Al} - 0.0522 \times [6]\text{Al}^2 \]

\( r^2 = 0.99 \)