

## Nomenclature of the Tourmaline-Group Minerals

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### 1. INTRODUCTION

The Subcommittee on Tourmaline Nomenclature (STN) of the International Mineralogical Association's Commission on New Minerals, Nomenclature and Classification (CNMNC) has made the following recommendations for a nomenclature of the tourmaline-group minerals. This was prompted by the general ambiguity in the assignment of names to specific tourmaline compositions. There are several reasons for this uncertainty (Hawthorne and Henry, 1999): (1) Some of the formal descriptions of tourmaline minerals specify the ideal end-member compositions but do not specify the limits of the use of the name. (2) Some of the formal descriptions of tourmaline minerals specify the general composition, but do not specify the end-member composition. (3) Tourmaline is commonly incompletely chemically characterized, with critical light elements (H, Li, and B) and the oxidation states of transition elements (Fe, Mn) generally being undetermined. (4) Site assignments can be equivocal in the absence of crystal-structure refinements. (5) Current graphical representations of tourmaline compositional variations are inadequate to express the actual substitutional nature of tourmaline. These considerations motivated Hawthorne and Henry (1999) and the STN to re-examine and, where necessary, redefine end members and potential new end members and species, and led to the development of several compositional diagrams that will aid in classification of the tourmaline-group minerals.

### 2. CRYSTAL-CHEMICAL ASPECTS OF TOURMALINE-GROUP MINERALS

Tourmaline is an acentric rhombohedral (R3m space group) borosilicate with the general chemical formula  $\text{XY}_3\text{Z}_6(\text{T}_6\text{O}_{18})(\text{BO}_3)_3\text{V}_3\text{W}$  (Hawthorne and Henry 1999). This general formula makes no assumptions about site occupancy, besides those sites known to be occupied exclusively by  $\text{O}^{2-}$ . Consequently, as knowledge of site occupancy in tourmaline progresses, it will be unnecessary to change the general formula, only the assignment of the chemical species to the letters of the general formula.

Table 1 gives the relative abundance of the generalized cations ( $R^{1+}$ ,  $R^{2+}$ ,  $R^{3+}$ ,  $R^{4+}$ ) and anions ( $S^{1-}$ ,  $S^{2-}$ ) at each of these sites, and presents the most common cation and anion substituents. Although tourmaline can accommodate a great variety of other cations in minor or trace amounts (Henry and Dutrow 1996), all current tourmaline species and most potential species will likely be represented by combinations of the cations, anions or vacancies described in Table 1.

**Table 1.** Relative site abundances of cations and anions in tourmaline-group minerals

Site	Relative abundance of ions with different valence states	Common cations and anions at each site in order of relative abundance
X	$R^+ > R^{2+} > \square$ (vacancy)	$\underline{R^+}$ : *Na <sup>1+</sup> >>K <sup>1+</sup> $\underline{R^{2+}}$ : Ca <sup>2+</sup>
Y	$R^{2+} > R^{3+} > R^+ > R^{4+}$	$\underline{R^{2+}}$ : Fe <sup>2+</sup> ~ Mg <sup>2+</sup> > Mn <sup>2+</sup> >>> Zn <sup>2+</sup> , Ni <sup>2+</sup> , Co <sup>2+</sup> , Cu <sup>2+</sup> $\underline{R^{3+}}$ : Al <sup>3+</sup> >> Fe <sup>3+</sup> > Cr <sup>3+</sup> >> V <sup>3+</sup> $\underline{R^+}$ : Li <sup>1+</sup> $\underline{R^{4+}}$ : Ti <sup>4+</sup>
Z	$R^{3+} >> R^{2+}$	$\underline{R^{3+}}$ : Al <sup>3+</sup> >> Fe <sup>3+</sup> > Cr <sup>3+</sup> > V <sup>3+</sup> $\underline{R^{2+}}$ : Mg <sup>2+</sup>
T	$R^{4+} >> R^{3+}$	$\underline{R^{4+}}$ : Si <sup>4+</sup> $\underline{R^{3+}}$ : Al <sup>3+</sup> > B <sup>3+</sup>
B	$R^{3+}$	$\underline{R^{3+}}$ : B <sup>3+</sup>
V	$S^- >> S^{2-}$	$\underline{S^-}$ : OH <sup>1-</sup> $\underline{S^{2-}}$ : O <sup>2-</sup>
W	$S^- \sim S^{2-}$	$\underline{S^-}$ : OH <sup>1-} \sim F<sup>1-</sup> <math>\underline{S^{2-}}</math>: O<sup>2-</sup></sup>

\* The bolded cations and anions represent the most common ions at these sites.

In addition to the ionic size and charge of the cations and anions, two other factors influence the actual content and location of the cations and anions in the tourmaline structure: short-range bond-valence requirements and order-disorder reactions. (1) In the Y site the incident bond-valence requirements mandate that only certain short-range configurations are stable (Hawthorne 1996). Table 2 gives the possible stable cation configurations at the Y site for generalized Li-free and Li-bearing tourmalines. For a given Y-site bulk composition, the tourmaline can have a single Y-site cation configuration or mixture of possible cation configurations. For example, the chemical composition of end-member liddicoatite has the stable Y-site configuration of Li<sub>2</sub>Al, whereas end-member elbaite, with a bulk Y site composition of Al<sub>1.5</sub>Li<sub>1.5</sub>, will have equal amounts of Al<sub>2</sub>Li and AlLi<sub>2</sub> clusters at the Y site (Hawthorne 1996). These relatively few cation configurations will constrain the number and type of potential stable end members possible in tourmaline. (2) Order-disorder in tourmaline affects the actual location of cations and anions in the tourmaline structure. Where O<sup>2-</sup> is located at the W site, short-range disordering develops at

the Y and Z sites (Hawthorne and Henry 1999). For example, Hawthorne (1996, 2002) showed that the occurrence of Mg at the Z site and Al at the Y site is due to disorder associated with the occurrence of  $O^{2-}$  at the W site and could be expressed as  $2^Y Mg^{2+} + ^Z Al^{3+} + ^W (OH)^{1-} = 2^Y Al^{3+} + ^Z Mg^{2+} + ^W O^{2-}$ . Effectively, the disordering enhances the amount of Mg that is located at the Z site.

**Table 2.** Stable short-range Y-site cation configurations for anions of different charge at the W site.

General chemical type of tourmaline	W-site anion	Stable short-range configurations
Li-free tourmaline	$(OH)^{1-}$ or $F^{1-}$	$*3R^{2+}$ or $R^{3+} + 2R^{2+}$
Li-free tourmaline	$O^{2-}$	$3R^{3+}$ or $2R^{3+} + R^{2+}$
Li-bearing tourmaline	$(OH)^{1-}$ or $F^{1-}$	$2Al^{3+} + Li^{1+}$ or $Al^{3+} + 2Li^{1+}$
Li-bearing tourmaline	$O^{2-}$	$3Al^{3+}$

\*R is a generalized divalent cation ( $R^{2+}$ ) or trivalent cation ( $R^{3+}$ ).

In terms of a classification scheme, most of the compositional variability occurs at the X, Y, Z, W and, to a lesser extent, V sites. Si and B typically dominate the T and B sites, respectively, and do not serve as primary parameters for classification. The complicating factor of disordering in the structure will be established only with certainty with crystal-structure refinement data. Consequently, in the absence of these structural data or methods to estimate the amount of disorder, classifications of mineral species are considered in terms of their ordered formulae.

### 3. TOURMALINE SUBGROUPS, END MEMBERS, ROOT NAMES AND SPECIES

There are several terms associated with mineral classification schemes that should be elucidated. **Mineral species** are defined on the basis of their unique chemical and crystallographic properties (Nickel and Grice 1998). Because tourmaline-group minerals are isostructural, tourmaline species are defined strictly in terms of chemical composition with the dominance of a chemical constituent of the dominant valency state at a given crystallographic site being the primary criterion. A “chemical constituent” designates a specific cation or anion, group of atoms with the same valency state, molecular group or vacancies. This dominance criterion is a statement of the **dominant-constituent rule** (Hatert and Burke, in press). Tourmaline solid solutions involve both homovalent substitutions at a given site and heterovalent coupled substitutions over single or multiple sites. An extension of the dominant-constituent rule is the **dominant-valency rule** (Hatert and Burke, in press). In accordance with recommendations of Nickel (1992) and Chopin (2006) the dominant-valency rule is expressed as: “In a relevant site, the dominant ion of the dominant valence state is considered for nomenclature”. However, there are exceptions to these criteria in some tourmaline species, e.g. the equal amounts of Al and Li at the Y site in elbaite.

An **end member** is an algebraic/chemical construct<sup>1</sup> that is chemically irreducible and is conformable with the crystal structure under consideration (Hawthorne 2002; see also Appendix A1.1 for more details). For example, the dravite end member  $[\text{NaMg}_3\text{Al}_6(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3\text{OH}]$  is irreducible in that it cannot be expressed as a combination of other tourmaline end members. In the case in which a tourmaline is determined to have *dominant* cation and anion occupancies of the crystallographic sites in accordance with this end member, it is given the **root name** dravite and is, by implication, considered to be the dravite **mineral species**.

In determining the systematics of mineral species, the STN recommends the following procedure be used:

- (1) In tourmaline-group minerals that are dominated by either  $\text{OH}^{1-}$  or  $\text{F}^{1-}$  in the W site, it is recommended that the  $\text{OH}^{1-}$ -dominant species be considered the reference **root composition** for that root name e.g. dravite.
- (2) For a tourmaline composition that has most of the chemical characteristics of a root composition, but is dominated by other cations or anions at one or more sites, mineral species is designated by the root name plus the appropriate prefix modifiers. For example, a tourmaline with a composition that is generally consistent with dravite, but containing dominant  $\text{F}^{1-}$  on the W site, the mineral species is termed a “fluor-dravite”. To take advantage of search capabilities, it is recommended that any modifiers to tourmaline root names be separated by hyphens. Hyphens are considered important to clarify the components of the species name.
- (3) If there are multiple prefix modifiers, the modifiers should be arranged in the order occurring in the structural formula i.e. X-site modifier, Y-site modifier, Z-site modifier, T-site modifier and then W-site modifier. This has the advantage of ordering the modifiers in a consistent and intuitive manner. For example, a composition that is generally consistent with dravite, but with dominant  $\text{K}^{1+}$  on the X site and  $\text{F}^{1-}$  on the W site, the hypothetical mineral species should be termed a “potassium-fluor-dravite”.

The cationic and anionic occupancy of the X and W sites serve as particularly convenient and petrologically meaningful ways to define generalized primary and secondary subgroupings of tourmaline species.

### 3.1 Principal Tourmaline Subgroups based on X-site Occupancy

Tourmaline can be classified into **principal subgroups** based on the dominant occupancy of the X site. Tourmalines have been described that contain dominant  $\text{Na}^{1+}$ ,  $\text{Ca}^{2+}$ ,  $\text{X}^{\square}$  and, rarely,  $\text{K}^{1+}$ . However, because of the rare occurrence of K-rich tourmalines, it is practical to combine the cations with like charges,  $\text{Na}^{1+}$  and  $\text{K}^{1+}$ , as an alkali subgroup. This results in principal

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<sup>1</sup> End members are important in a thermodynamic sense because the thermodynamic properties of end members can be defined, regardless of whether they exist as stable minerals or they are unstable as minerals, and are essential for modeling the behavior of solid solutions in petrological and geochemical processes.

subgroups that are termed the **alkali-, calcic- and X-vacant - tourmaline subgroups**. This general grouping makes petrologic sense because X-site occupancy generally reflects the paragenesis of the rock in which these tourmalines crystallize, analogous to similar general groupings in the amphibole- and pyroxene-group minerals. The alkali-, calcic-, X-vacant-ternary system for X-site occupancy can be plotted on the simple ternary diagram illustrated in Figure 1 (e.g. Nickel, 1992). Numerically, the primary X-site subgroups are defined as follows: *alkali* if  $(\text{Na}^{1+} + \text{K}^{1+}) \geq \text{Ca}^{2+}$  and  $(\text{Na}^{1+} + \text{K}^{1+}) \geq \text{X}\square$ ; *calcic* if  $\text{Ca}^{2+} > (\text{Na}^{1+} + \text{K}^{1+})$  and  $\text{Ca}^{2+} > \text{X}\square$ ; and *X-vacant* if  $\text{X}\square > (\text{Na}^{1+} + \text{K}^{1+})$  and  $\text{X}\square > \text{Ca}^{2+}$ . The dominance of  $\text{Na}^{1+}$  or  $\text{K}^{1+}$  in alkali-subgroup tourmaline is an example of the dominant-valency rule. In the uncommon case in which tourmaline is classified as an alkali-subgroup tourmaline and  $\text{K}^{1+}$  dominates over  $\text{Na}^{1+}$ , it is considered a “potassium-“ tourmaline. In this case, the root name should be prefixed by “potassium-“ e.g. “potassium-povondraite”. Numerically, to be considered a “potassium-“ tourmaline the following conditions must be satisfied:  $(\text{Na}^{1+} + \text{K}^{1+}) \geq \text{Ca}^{2+}$ ,  $(\text{Na}^{1+} + \text{K}^{1+}) \geq \text{X}\square$  and  $\text{K}^{1+} > \text{Na}^{1+}$ .

**Principal Tourmaline Subgroups - X site**

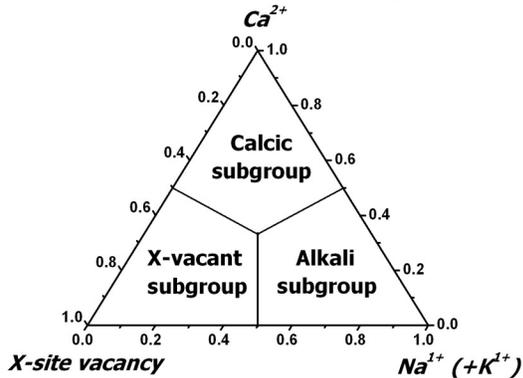


Figure 1. Ternary system for the principal tourmaline subgroups based on the dominant occupancy of the X site.

**Secondary Tourmaline Subgroups - W site**

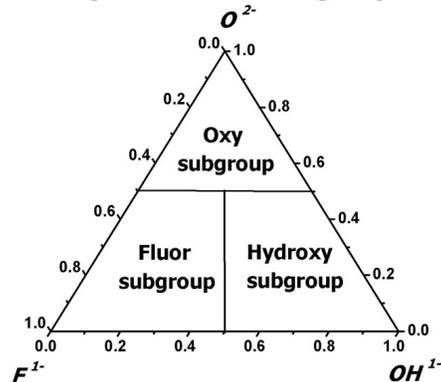


Figure 2. Ternary system for the secondary tourmaline subgroups based on the anion occupancy of the W site.

### 3.2 Secondary Tourmaline Subgroups based on the W-site Occupancy

Three distinct anions ( $\text{OH}^{1-}$ ,  $\text{F}^{1-}$  and  $\text{O}^{2-}$ ) can occur at the W site, and the occupancy of the W site forms the basis for secondary tourmaline subgroups: **hydroxy-, fluor- and oxy-subgroups** (Fig. 2). These are defined as follows: *hydroxy* if  $\text{OH}^{1-} + \text{F}^{1-} \geq \text{O}^{2-}$  and  $\text{OH}^{1-} \geq \text{F}^{1-}$ ; *fluor* if  $\text{OH}^{1-} + \text{F}^{1-} \geq \text{O}^{2-}$  and  $\text{F}^{1-} \geq \text{OH}^{1-}$ ; and *oxy* if  $\text{O}^{2-} > \text{OH}^{1-} + \text{F}^{1-}$ . The appearance of the secondary subgroup differs from Figure 1 because it involves two anions with a common 1- charge ( $\text{OH}^{1-}$  and  $\text{F}^{1-}$ ) and a single anion with a 2- charge ( $\text{O}^{2-}$ ). Consequently, for  $\text{O}^{2-}$  to be the dominant anion of the W site there must be  $> 50\%$   $\text{O}^{2-}$  (e.g. Nickel 1992, Chopin 2006). Despite the difficulty of measuring H contents in tourmaline, oxy-subgroup tourmalines do exist and must be considered in the tourmaline nomenclature. In the case of an oxy-subgroup, a coupled substitution involving another site is required, and a new root name is typically warranted rather than placing a modifying prefix on the root name.

### 3.3 Tourmaline Species

The number of currently recognized and plausible tourmaline species is potentially large. Prior to the publication of this nomenclature, the International Mineralogical Association (IMA) recognized 14 tourmaline species. Hawthorne and Henry (1999) and the STN re-examined the compositions of the holotype material of these species and, in some cases, redefined the end-member formulae and mineral species in accordance with guidelines suggested by Hawthorne and Henry (1999), Hawthorne (2002) and this proposal (Appendix A1.2).

Tourmaline can be broken into several general subgroupings and subtypes that are useful for classification purposes. The principal tourmaline subgroupings are based on occupancy of the X-site which serves as a convenient division into the alkali tourmaline subgroup, calcic tourmaline subgroup or the X-vacant tourmaline subgroup (Fig. 1). Because each of these subgroups involves a cation or vacancy with a different charge, coupled substitutions are required to compositionally shift among the subgroups (Tables 3, 4). Within a given subgroup there is a fundamental subtype, subtype 1, from which additional subtypes can be generated. Incorporation of  $\text{Li}^{1+}$  via coupled substitution (3) of Table 3 can result in additional Li-bearing subtypes which will warrant new root names (e.g. elbaite in Alkali-subtype 2 of Table 4). Likewise, the coupled substitution (4) of Table 3 can result in deprotonated tourmaline species (e.g. Alkali-subtypes 3 and 4 of Table 4), and these species should, by analogy, have distinct root names. Coupled substitutions (5) and (6) of Table 3 might yield tetrahedral-site dominant species and Ti species, but the existence of these species is currently unproven. Within a given tourmaline subtype there can be a number of homovalent substitutions that result in extensive or complete solid solution, but it does not change the fundamental character of a tourmaline subtype (e.g.  $\text{Fe}^{2+}$  for  $\text{Mg}^{2+}$  substitution that relates schorl and dravite in Alkali-subtype 1 tourmaline). Within each subgrouping, subtype 1 is generally the most common and has the most species. For instance, Alkali-subtype 1 contains 9 possible species, all variants with dravite or schorl root names. Table 5 presents several additional considerations associated with various substitutions in the tourmaline group minerals. This approach of identifying subgroups based on operation of general heterovalent coupled substitutions is similar to that used for the epidote-group nomenclature (Armbruster et al. 2006).

**Table 3. Significant tourmaline heterovalent coupled substitutions and associated exchange vectors**

	Generalized coupled substitutions*	Corresponding exchange vector	Resulting actions
(1)	${}^X\text{R}^{1+} + \text{R}^{2+} = {}^X\Box + \text{R}^{3+}$	$({}^X\Box\text{R}^{3+})(\text{R}^{1+}\text{R}^{2+})_{-1}$	relates alkali-calcic-X-vacant subgroups
(2)	${}^X\text{R}^{1+} + \text{R}^{3+} = {}^X\text{Ca} + \text{R}^{2+}$	$(\text{CaR}^{2+})(\text{R}^{1+}\text{R}^{3+})_{-1}$	relates alkali-calcic-X-vacant subgroups
(3)	${}^Y2\text{R}^{2+} = {}^Y\text{Li}^{1+} + {}^Y\text{Al}^{3+}$	$(\text{Li Al})(2\text{R}^{2+})_{-1}$	relates incorporation of Li in all subgroups
(4)	$\text{R}^{2+} + \text{OH}^{1-} = \text{R}^{3+} + \text{O}^{2-}$	$(\text{R}^{3+}\text{O}^{2-})(\text{R}^{2+}(\text{OH}^{1-}))_{-1}$	relates deprotonation in all

			types
(5)	$R^{2+} + {}^I\text{Si}^{4+} = R^{3+} + {}^I\text{R}^{3+}$	$(R^{3+} R^{3+})(R^{2+} \text{Si}^{4+})_{-1}$	relates tschermaks-like tetrahedral-octahedral substitution in all types
(6)	$0.5R^{2+} + \text{OH}^{1-} = 0.5\text{Ti}^{4+} + \text{O}^{2-}$	$(\text{Ti}_{0.5} \text{O}^{2-})(R^{2+}_{0.5}(\text{OH}^{1-}))_{-1}$	relates Ti-deprotonation in all types

\*R represents generalized cations such that  ${}^x\text{R}^{1+} = \text{Na}^{1+}, \text{K}^{1+}$ ;  $\text{R}^{2+} = \text{Mg}^{2+}, \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}$ ;  $\text{R}^{3+} = \text{Al}^{3+}, \text{Fe}^{3+}, \text{Cr}^{3+}, \text{V}^{3+}$ ; and no site designation reflects multiple site possibilities.

**Table 4. Generalized structural formula types for accepted or hypothetical tourmaline species (quotation marks) grouped by subtypes**

### Alkali tourmaline subgroup

Species	(X)	(Y <sub>3</sub> )	(Z <sub>6</sub> )	T <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	V <sub>3</sub>	W
<i>Alkali-subtype 1</i>	${}^x\text{R}^{1+}$	$\text{R}^{2+}_3$	$\text{R}^{3+}_6$	$\text{Si}^{4+}_6\text{O}_{18}$	$(\text{BO}_3)_3$	$(\text{OH}^{1-})_3$	$(\text{OH}^{1-}, \text{F}^{1-})$
Dravite	Na	Mg <sub>3</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)
Schorl	Na	Fe <sup>2+</sup> <sub>3</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)
Chromium-dravite	Na	Mg <sub>3</sub>	Cr <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)
Vanadium-dravite	Na	Mg <sub>3</sub>	V <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)
“Fluor-dravite”	Na	Mg <sub>3</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	F
“Fluor-schorl”	Na	Fe <sup>2+</sup> <sub>3</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	F
“Potassium-dravite”	K	Mg <sub>3</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)
<i>Alkali-subtype 2</i>	${}^x\text{R}^{1+}$	$\text{Li}^{1+}_{1.5} \text{Al}^{3+}_{1.5}$	$\text{Al}^{3+}_6$	$\text{Si}^{4+}_6\text{O}_{18}$	$(\text{BO}_3)_3$	$(\text{OH}^{1-})_3$	$(\text{OH}^{1-}, \text{F}^{1-})$
Elbaite	Na	Li <sup>1+</sup> <sub>1.5</sub> Al <sup>3+</sup> <sub>1.5</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)
“Fluor-elbaite”	Na	Li <sup>1+</sup> <sub>1.5</sub> Al <sup>3+</sup> <sub>1.5</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	F
<i>Alkali-subtype 3</i>	${}^x\text{R}^{1+}$	$\text{R}^{2+}_2 \text{R}^{3+}$	$\text{R}^{3+}_6$	$\text{Si}^{4+}_6\text{O}_{18}$	$(\text{BO}_3)_3$	$(\text{OH}^{1-})_3$	$\text{O}^{2-}$
Povondraite*	Na	Mg <sub>2</sub> Fe <sup>3+</sup>	Fe <sup>3+</sup> <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	O
“Oxy-dravite”**	Na	Mg <sub>2</sub> Al	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	O

“Oxy-schorl”**	Na	$\text{Fe}^{2+}_2\text{Al}$	$\text{Al}_6$	$\text{Si}_6\text{O}_{18}$	$(\text{BO}_3)_3$	$(\text{OH})_3$	O
“Na-Cr-O root name”	Na	$\text{Mg}_2\text{Cr}$	$\text{Cr}_6$	$\text{Si}_6\text{O}_{18}$	$(\text{BO}_3)_3$	$(\text{OH})_3$	O
“Potassium-povondraite”	K	$\text{Mg}_2\text{Fe}^{3+}$	$\text{Fe}^{3+}_6$	$\text{Si}_6\text{O}_{18}$	$(\text{BO}_3)_3$	$(\text{OH})_3$	O
<b><i>Alkali-subtype 4</i></b>	$^x\text{R}^{l+}$	$\text{Li}^{l+}_1\text{Al}^{3+}_2$	$\text{R}^{3+}_6$	$\text{Si}^{4+}_6\text{O}_{18}$	$(\text{BO}_3)_3$	$(\text{OH}^{l-})_3$	$\text{O}^{2-}$
“Na-Li-O root name ”	Na	$\text{Li}_1\text{Al}_2$	$\text{Al}_6$	$\text{Si}_6\text{O}_{18}$	$(\text{BO}_3)_3$	$(\text{OH})_3$	O
<b><i>Alkali-subtype 5</i></b>	$^x\text{R}^{l+}$	$\text{R}^{3+}_3$	$\text{R}^{3+}_6$	$\text{Si}^{4+}_6\text{O}_{18}$	$(\text{BO}_3)_3$	$(\text{O}^{2-})_3$	$(\text{OH}^{l-}, \text{F}^{l-})$
<b>Fluor-buergerite</b>	Na	$\text{Fe}^{3+}_3$	$\text{Al}_6$	$\text{Si}_6\text{O}_{18}$	$(\text{BO}_3)_3$	$(\text{O})_3$	<b>F</b>
<b>Olenite</b>	Na	$\text{Al}_3$	$\text{Al}_6$	$\text{Si}_6\text{O}_{18}$	$(\text{BO}_3)_3$	$(\text{O})_3$	<b>(OH)</b>
“Buergerite”	Na	$\text{Fe}^{3+}_3$	$\text{Al}_6$	$\text{Si}_6\text{O}_{18}$	$(\text{BO}_3)_3$	$(\text{O})_3$	(OH)
“Fluor-olenite”	Na	$\text{Al}_3$	$\text{Al}_6$	$\text{Si}_6\text{O}_{18}$	$(\text{BO}_3)_3$	$(\text{O})_3$	F
<b><i>Alkali-subtype 6</i></b>	$^x\text{R}^{l+}$	$\text{R}^{3+}_3$	$\text{R}^{3+}_6$	$\text{R}^{3+}_3\text{Si}^{4+}_3\text{O}_{18}$	$(\text{BO}_3)_3$	$(\text{O}^{2-})_3$	$(\text{OH}^{l-}, \text{F}^{l-})$
“Na-Al-Al- <sup>T</sup> Al root name”	Na	$\text{Al}_3$	$\text{Al}_6$	$\text{Al}_3\text{Si}_3\text{O}_{18}$	$(\text{BO}_3)_3$	$(\text{OH})_3$	(OH)
“Na-Al-Al- <sup>T</sup> B root name”	Na	$\text{Al}_3$	$\text{Al}_6$	$\text{B}_3\text{Si}_3\text{O}_{18}$	$(\text{BO}_3)_3$	$(\text{OH})_3$	(OH)
“Fluor- Na-Al-Al- <sup>T</sup> Al root name”	Na	$\text{Al}_3$	$\text{Al}_6$	$\text{Al}_3\text{Si}_3\text{O}_{18}$	$(\text{BO}_3)_3$	$(\text{OH})_3$	F
“Fluor-Na-Al-Al- <sup>T</sup> B root name”	Na	$\text{Al}_3$	$\text{Al}_6$	$\text{B}_3\text{Si}_3\text{O}_{18}$	$(\text{BO}_3)_3$	$(\text{OH})_3$	F
<b><i>Alkali-subtype 7</i></b>	$^x\text{R}^{l+}$	$\text{Ti}^{4+}_{1.5}\text{R}^{2+}_{1.5}$	$\text{R}^{3+}_6$	$\text{Si}^{4+}_6\text{O}_{18}$	$(\text{BO}_3)_3$	$(\text{O}^{2-})_3$	$(\text{OH}^{l-}, \text{F}^{l-})$
“Na-Ti-Mg-O root name”	Na	$\text{Ti}_{1.5}\text{Mg}_{1.5}$	$\text{Al}_6$	$\text{Si}_6\text{O}_{18}$	$(\text{BO}_3)_3$	$(\text{O})_3$	(OH)

\*The formula given in the table is the ordered form of povondraite, and by analogy “potassium-povondraite”. The IMA-accepted formula of the povondraite species is the disordered form  $\text{Na Fe}^{3+}_3(\text{Fe}^{3+}_4\text{Mg}_2)(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3\text{O}$  (Appendix A1.2).

\*\*Although a new root name is suggested under Section 3.3, because “oxy-dravite” and “oxy-schorl” have been used relatively commonly in the literature (e.g. Žáček et al. 2000; Novák et al. 2004; Henry et al. in press), it is recommended that these names be formally accepted as the species names for these end members.

### Calcic tourmaline subgroup

Species types	(X)	(Y <sub>3</sub> )	(Z <sub>6</sub> )	T <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	V <sub>3</sub>	W
<i>Calcic-subtype 1</i>	Ca <sup>2+</sup>	R <sup>2+</sup> <sub>3</sub>	R <sup>2+</sup> R <sup>3+</sup> <sub>5</sub>	Si <sup>4+</sup> <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH <sup>1-</sup> ) <sub>3</sub>	(OH <sup>1-</sup> , F <sup>1-</sup> )
Fluor-uvite	Ca	Mg <sub>3</sub>	MgAl <sub>5</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	F
Feruvite	Ca	Fe <sup>2+</sup> <sub>3</sub>	MgAl <sub>5</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)
“Uvite”	Ca	Mg <sub>3</sub>	MgAl <sub>5</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)
“Fluor-feruvite”	Ca	Fe <sup>2+</sup> <sub>3</sub>	MgAl <sub>5</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	F
<i>Calcic-subtype 2</i>	Ca <sup>2+</sup>	Li <sup>1+</sup> <sub>2</sub> Al <sup>3+</sup> <sub>1</sub>	Al <sup>3+</sup> <sub>6</sub>	Si <sup>4+</sup> <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH <sup>1-</sup> ) <sub>3</sub>	(OH <sup>1-</sup> , F <sup>1-</sup> )
Fluor-liddicoatite	Ca	Li <sup>1+</sup> <sub>2</sub> Al <sup>3+</sup>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	F
“Liddicoatite”	Ca	Li <sup>1+</sup> <sub>2</sub> Al <sup>3+</sup>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)
<i>Calcic-subtype 3</i>	Ca <sup>2+</sup>	R <sup>2+</sup> <sub>3</sub>	R <sup>3+</sup> <sub>6</sub>	Si <sup>4+</sup> <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH <sup>1-</sup> ) <sub>3</sub>	O <sup>2-</sup>
“Ca-Mg-O root name”	Ca	Mg <sub>3</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	O
“Ca-Fe-O root name”	Ca	Fe <sup>2+</sup> <sub>3</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	O
<i>Calcic-subtype 4</i>	Ca <sup>2+</sup>	Li <sup>1+</sup> <sub>1.5</sub> Al <sup>3+</sup> <sub>1.5</sub>	R <sup>3+</sup> <sub>6</sub>	Si <sup>4+</sup> <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH <sup>1-</sup> ) <sub>3</sub>	O <sup>2-</sup>
“Ca-Li-O root name ”	Ca	Li <sub>1.5</sub> Al <sub>1.5</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	O

### X-site vacant tourmaline subgroup

Species types	(X)	(Y <sub>3</sub> )	(Z <sub>6</sub> )	T <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	V <sub>3</sub>	W
<i>Vacancy-subtype 1</i>	□	R <sup>2+</sup> <sub>2</sub> R <sup>3+</sup>	R <sup>3+</sup> <sub>6</sub>	Si <sup>4+</sup> <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH <sup>1-</sup> ) <sub>3</sub>	(OH <sup>1-</sup> , F <sup>1-</sup> )
Foitite	□	Fe <sup>2+</sup> <sub>2</sub> Al	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)
Magnesio-foitite	□	Mg <sub>2</sub> Al	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)
“Fluor-foitite”	□	Fe <sup>2+</sup> <sub>2</sub> Al	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	F

“Fluor-magnesio-foitite”	□	Mg <sub>2</sub> Al	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	F
<b>Vacancy-subtype 2</b>	□	Li <sup>1+</sup> <sub>1</sub> Al <sup>3+</sup> <sub>2</sub>	Al <sup>3+</sup> <sub>6</sub>	Si <sup>4+</sup> <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH <sup>1-</sup> ) <sub>3</sub>	(OH <sup>1-</sup> , F <sup>1-</sup> )
Rossmannite	□	Li <sup>1+</sup> Al <sup>3+</sup> <sub>2</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)
“Fluor-rossmanite”	□	Li <sup>1+</sup> Al <sup>3+</sup> <sub>2</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	F
<b>Vacancy-subtype 3</b>	□	R <sup>2+</sup> <sub>1</sub> R <sup>3+</sup> <sub>2</sub>	R <sup>3+</sup> <sub>6</sub>	Si <sup>4+</sup> <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH <sup>1-</sup> ) <sub>3</sub>	O <sup>2-</sup>
“□-Mg-O root name”	□	MgAl <sub>2</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	O
“□-Fe-O root name”	□	Fe <sup>2+</sup> Al <sub>2</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	O
“□-Al-O root name”	□	Al <sub>3</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>2</sub> O	O
<b>Vacancy-subtype 4</b>	□	Li <sup>1+</sup> <sub>0.5</sub> Al <sup>3+</sup> <sub>2.5</sub>	R <sup>3+</sup> <sub>6</sub>	Si <sup>4+</sup> <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH <sup>1-</sup> ) <sub>3</sub>	O <sup>2-</sup>
“□-Li-O root name”	□	Li <sub>0.5</sub> Al <sub>2.5</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	O

Note: In natural tourmaline it is likely to be the case that a particular cation or anion may occupy more than one site. For example, in a tourmaline with [O<sub>3</sub>(OH)] at the V and W site, the OH can be distributed over both sites.

**Table 5. Additional considerations associated with homovalent and heterovalent substitutions in tourmaline group minerals:**

<p>(1) The most common <math>R^{1+}</math> homovalent substitution in the <b>X-site</b> is <math>Na^{1+} = K^{1+}</math> (KNa<sub>1</sub> exchange vector). The tourmaline is considered to be a member of the <i>alkali</i> subgroup (Alkali-subtype x) if <math>(Na^{1+}+K^{1+}) \geq Ca^{2+}</math> and <math>(Na^{1+}+K^{1+}) \geq X\Box</math>. In the uncommon case in which tourmaline is classified as an alkali subgroup tourmaline and <math>K^{1+} &gt; Na^{1+}</math>, it is considered a “potassium-tourmaline”. The tourmaline is considered part of the calcic subgroup (calcic subtype x) if <math>Ca^{2+} &gt; (Na^{1+}+K^{1+})</math> and <math>Ca^{2+} &gt; X\Box</math>. The tourmaline is considered part of the X-site vacancy subgroup (Vacancy-subtype x) if <math>X\Box &gt; (Na^{1+}+K^{1+})</math> and <math>X\Box &gt; Ca^{2+}</math>.</p>
<p>(2) <math>R^{2+}</math> homovalent substitutions involve a number of divalent cations such as Mg<sup>2+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>. For example, the most common substitution is probably Mg<sup>2+</sup> = Fe<sup>2+</sup> (FeMg<sub>1</sub> exchange vector). In this case the complicating factor is that Mg<sup>2+</sup> is the only <math>R^{2+}</math> cation that can be significantly accommodated on the <b>Z site</b> at concentrations up to 2 apfu, and this is most commonly with disordering associated with incorporation of O<sup>2-</sup> on the W site. Within a divalent group of elements on a given site, the dominant <math>R^{2+}</math> cations lead to a different modifier/root names. Except for Mg<sup>2+</sup>, the rest of the divalent cations are assumed to be on the <b>Y site</b>.</p>

- (3)  $R^{3+}$  homovalent substitutions occur on both the Y and Z sites and include trivalent cations such as  $Al^{3+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$  and  $V^{3+}$ . For example, a common substitution is  $Fe^{3+} = Al^{3+}$  ( $AlFe_{-1}$  exchange vector). The  $R^{3+}$  cations are most commonly found on the Z site, but the Y site and T site can contain up to 3 apfu  $R^{3+}$  cations. If there is  $O^{2-}$  on the W site, there is likely to be a disordering resulting in the displacement of the  $R^{3+}$  to the Y site with a concomitant substitution of  $Mg^{2+}$  on the Z site.
- (4) If there is **Li** in the tourmaline it is typically introduced via *heterovalent substitution (3)* ( $Li Al$ ) ( $2R^{2+}$ ) $_{-1}$ . Note that for each **Li** that is introduced there is 2  $R^{2+}$  displaced. That means that plotting parameters in the ternary elbaite-schorl-dravite system are  $2Li-Fe^{2+}-Mg$ .
- (5) The introduction of  $O^{2-}$  in the W or V site can take place via the *heterovalent deprotonation substitution (4)* ( $R^{3+} O^{2-}$ )( $R^{2+} (OH^{1-})$ ) $_{-1}$ . Note that for each  $O^{2-}$  there must be the introduction of an  $R^{3+}$  at the expense of an  $R^{2+}$ .
- (6) The introduction of  $R^{3+}$  (typically Al or B) into the tetrahedral site can take place via a tschermaks type of *heterovalent substitution (5)* ( $R^{3+} R^{3+}$ )( $R^{2+} Si^{4+}$ ) $_{-1}$ .
- (7) The introduction of the tetravalent **Ti** is probably introduced via the *heterovalent deprotonation substitution (6)* ( $Ti_{0.5} O^{2-}$ )( $R^{2+}_{0.5} (OH^{1-})$ ) $_{-1}$ .

For classification, it is recommended that the species is established as the dominant species of the dominant subtype of tourmaline, i.e. in accordance with the dominant-valency rule. For example, if there is a mixture of 40% elbaite, 35% schorl and 25% dravite the resulting subtypes would be 60% Alkali-subtype 1 and 40% Alkali-subtype 2. Alkali-subtype 1 is the dominant formula subtype and schorl is the dominant species within this dominant subtype such that the tourmaline should be considered a schorl. In this case, these relations can be illustrated graphically (Figs. 3, 4).

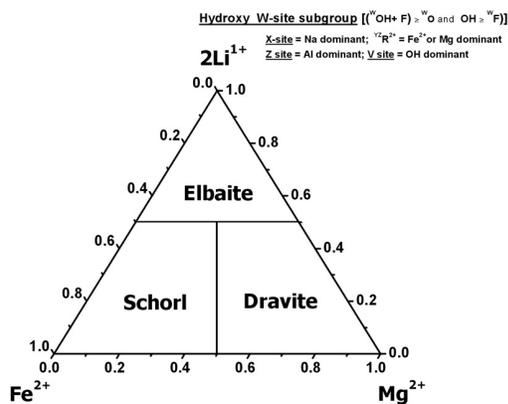


Figure 3. Ternary dravite-schorl-elbaite subsystem. Note that dravite and schorl are members of alkali-subtype 1 and elbaite is a member of alkali-subtype 2.

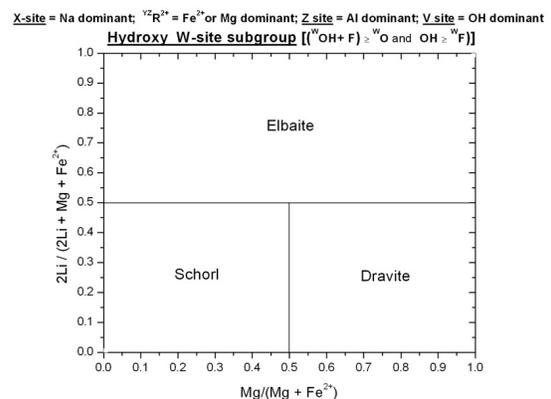


Figure 4. Binary diagram expressing an alternative plot of the ternary dravite-schorl-elbaite subsystem.

Identification of subtypes 1-4 for each of the X-site subgroup tourmalines can be established with a series of binary diagrams that use the X-site occupancy and  $(R^{2+}/(R^{2+} + 2Li))$  ratio as the primary discriminating factor, with the W-site occupancy as a further discriminator which will strictly define the subtype (Figs. 5-7). An alternative binary of  $(R^{2+}/(R^{2+} + 2Li))$  vs. W-site occupancy of  $O^{2-}$  results in a comparable discriminating diagram (Fig. 8). For the unusual,  $Y$ Ti-dominant and  $T$ Al-dominant subtypes (alkali-subtypes 5 and 6), other diagrams could be employed. Once the subtype is determined, the appropriate species name is given as the dominant species within that subtype (Table 4). Uncertainties arise when the tourmalines are incompletely analyzed (see section 5 for further discussion).

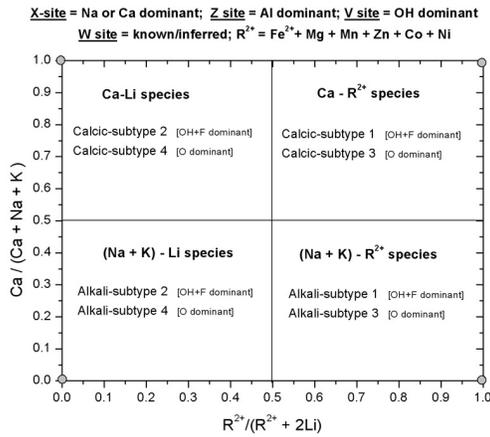


Figure 5. Binary system for determining alkali and calcic subtypes. Determination of the specific subtype requires information/inference of the W-site anion occupancy in accordance with the criteria given in section 3.2.

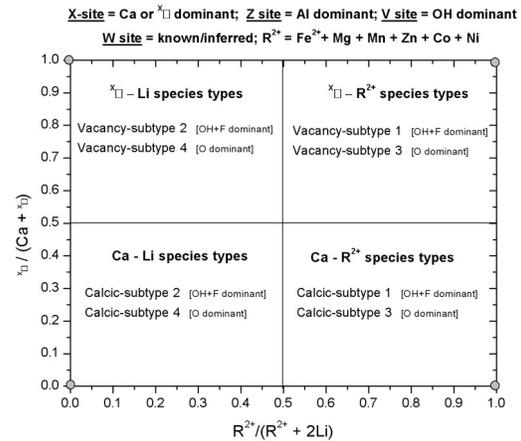


Figure 6. Binary system for determining vacancy and calcic subtypes. Determination of the specific subtype requires information/inference of the W-site anion occupancy in accordance with the criteria given in section 3.2.

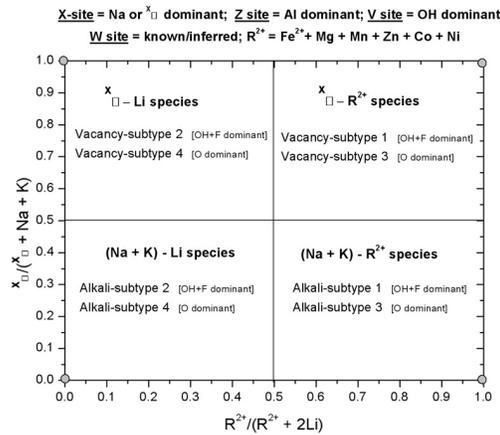


Figure 7. Binary diagram for determining alkali and vacancy subtypes. Determination of the specific subtype requires information/inference of the W-site anion occupancy in accordance with the criteria given in section 3.2.

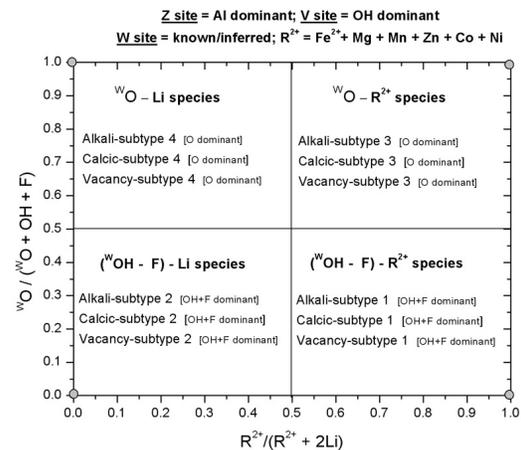


Figure 8. Binary diagram for determining the most general subtypes. Information/inference on the W-site anion occupancy is in accordance with the criteria given in section 3.2.

The hypothetical tourmaline species in Table 4 (in quotation marks) are considered to be species likely to be found naturally. These species are written in the ordered form at the Y and Z sites, with the understanding that some degree of disorder is likely, particularly in those end members with  $O^{2-}$  at the W site (e.g. Hawthorne 1996, 2002). Additional end members that have other cations dominant at one or more sites are likely, and these can be added as new tourmaline species when/if they are discovered and characterized. This proposed scheme is, therefore, easily expandable. Whenever possible or reasonable, new tourmaline species should be named using currently recognized root names with an appropriate prefix modifiers concatenated to the existing root name. For example, the IMA-accepted Mg-equivalent of foitite is magnesio-foitite (Table 4). Tourmaline compositions generated through heterovalent coupled substitutions of existing root compositions will generally mandate the introduction of new root names. **All proposed mineral species must be submitted to the IMA CNMNC and fulfill the requirements for new mineral species prior to IMA approval as a new mineral species.**

### 3.4.1. Additional adjectival modifiers

Tourmaline species can be further modified with a variety of adjectives that precede the species name (Table 4). In the past, the CNMNC recommended use of the “Schaller modifiers” in which the valency of the substituent ion is indicated by the suffix “-oan” (for the lower valency cation) and “-ian” (for the higher valency cation). However, this scheme has several shortcomings that have prompted the recent approval of alternative chemical-element adjectival modifiers in place of the Schaller-type modifiers (Bayliss et al. 2005). In the most general case, it is recommended that adjectival modifier such as “-rich” or “-bearing” be used together with the specific element(s) and, where equivocal, an indication of the oxidation state of the cation and/or the site it occupies, e.g., “Fe<sup>2+</sup>-rich”, “K-bearing” or “<sup>T</sup>Al-rich”. The chemical-element adjectival modifiers are not part of the name of the tourmaline species, and, consequently, authors are free to use chemical-element modifiers that are chemically correct and meet the needs of the author in expressing significant chemical information about the mineral species (Bayliss et al. 2005). However, it is recommended that the authors define what concentration levels are implied by these adjectival modifier terms. Multiple modifiers are possible, and the order of the modifiers should be such that the modifier with the greatest percentage of site occupancy is next to the mineral-species name, the modifier with the second most percentage preceding that one, etc. For example, a hypothetical tourmaline solid solution with 60% dravite-schorl, 40% uvite-feruvite and 2/1 ratio of Mg-Fe<sup>2+</sup> at the Y site, has a structural formula of (Na<sub>0.6</sub> Ca<sub>0.4</sub>) (Mg<sub>2</sub> Fe<sup>2+</sup>) (Mg<sub>0.4</sub> Al<sub>5.6</sub>) (Si<sub>6</sub>O<sub>18</sub>) (BO<sub>3</sub>)<sub>3</sub> (OH)<sub>3</sub> (OH) and the appropriate name would be expressed as Fe<sup>2+</sup>-, Ca-rich dravite i.e. reflecting 33% Fe<sup>2+</sup> at the Y site and 40% Ca at the X site.

## 4. SITE ALLOCATION OF CATIONS AND ANIONS

Hawthorne (1996) notes that chemical analyses of tourmaline merely establish which elements are present, but do not determine where they are located in the structure. Structural refinement and site assignment based on crystallographic evidence is required for accurate site allocation. Further, tourmaline site occupancies can be accurately modeled with appropriate optimization procedures (e.g. Wright et al. 2000). In the absence of site assignments directly established by crystal structure refinements, it is possible to make some "reasonable"

assumptions concerning site assignments of specific cations and anions (Table 1). With this basic information, it is recommended that cations and anions be allocated with the following procedure:

- (1) Based on the type of analytical data the most appropriate normalization scheme is used and any significant unanalyzed cations or anions are calculated (see procedures in Appendix A4).
- (2) Only  $B^{3+}$  is allocated to the B site. With compelling chemical, crystallographic or spectroscopic evidence, excess  $B^{3+}$  ( $B^{3+} > 3.0$  apfu) may be assumed to be in the T site. Compelling evidence includes NMR spectra indicating tetrahedral B, structural refinements with tetrahedral bond length determinations and well-constrained analytical evidence that demonstrate  $B > 3$  (e.g. Tagg et al. 1999; Hughes et al. 2000; Schreyer et al. 2002).
- (3)  $Na^{1+}$ ,  $Ca^{2+}$  and  $K^{1+}$  are assigned to the X site with any site deficiency assumed to represent an X-site vacancy ( $X\Box$ ).
- (4)  $Si^{4+}$  is assumed to be exclusively located in the T site with any deficiency made up by  $Al^{3+}$  (MacDonald and Hawthorne 1995). If there is compelling chemical, crystallographic or spectroscopic evidence for tetrahedral  $B^{3+}$ , this tetrahedral  $B^{3+}$  should be assigned to the T site prior to the assignment of the tetrahedral  $Al^{3+}$ .
- (5) The relative distribution of anions in the V and W sites are reasonably well known.  $F^{1-}$  is exclusively contained in the W site and  $O^{2-}$  tends to be preferentially contained in this site (Grice and Ercit 1993). Consequently, it can be assumed that all  $F^{1-}$  be assigned to the W site, and most of the  $O^{2-}$  contents that are determined for these sites. To date evidence from bond angle distortion of the  $ZO_6$  octahedron and Y-O distances indicates that most of the tourmaline species (except buergerite and some unusual Al-rich tourmalines) appear to have  $\sim 3(OH^{1-})$  on the V site (Ertl et al. 2002, 2006a; Cempírek et al. 2006).
- (6) The Y and Z site assignments can be more ambiguous. The least problematic assignment is the exclusive allocation of  $Li^{1+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Cu^{2+}$  and  $Ti^{4+}$  to the Y site. However, the small cation allocation between the Y and Z sites can be more uncertain.

*For the purposes of classification of tourmaline species*, the ordered form of the tourmaline is assumed in Table 4. Consequently, the procedure that is recommended for classification involves allocation of the small cations in the Z and Y sites as follows: Initially assign all  $Al^{3+}$  (in excess of that assigned to the T site) to the Z site. Next, successively assign  $V^{3+}$ ,  $Cr^{3+}$  and  $Fe^{3+}$ . If there is an excess of trivalent cations on the Z site, the excess trivalent cations go into the Y site. If there is a deficiency in the Z site (i.e.  $< 6.0$  cations), assign Mg to the Z-site (up to 2 apfu). Based on crystallographic and mineral chemical information, it is known that, with the presence of  $O^{2-}$  on the W site,  $Mg^{2+}$  is typically disordered into the Z site and trivalent cations (especially  $Al^{3+}$  and  $Fe^{3+}$ ) into the Y site (Tippe and Hamilton 1971; Tsang et al. 1971; Burns 1972; Hermon et al. 1973; Fortier and Donnay 1975; Henry and Dutrow 1990, 2001; Hawthorne et al. 1993; Taylor et al. 1995). Consequently, actual tourmaline structures can exhibit a significant amount of disordering and measurement or estimation of this feature is desirable. *In the absence of specific structural information for Y and Z site occupancies*, a procedure is recommended for allocating cations to the Z and Y

sites that accommodate the disordering that is common in tourmaline. Initially assign all Al<sup>3+</sup> (in excess of that assigned to the T site) to the Z site. Next, successively assign Mg<sup>2+</sup> (up to 2 apfu), V<sup>3+</sup>, Cr<sup>3+</sup> and Fe<sup>3+</sup>. If there is an excess of trivalent cations on the Z site, the excess trivalent cations go into the Y site.

There are other estimation procedures for assigning the Mg<sup>2+</sup> content on the Z site without requiring complete crystal-structure refinements.

**Method 1** – Relationship between unit cell parameters and Mg in the Z site. Grice and Ercit (1993) found an exponential relationship between the unit cell volume and Mg content on the Y site:  ${}^Z[\text{Mg}/(\text{Mg}+\text{Al})] = 0.209 \{ \exp[(V-1540)/40]-1 \}$ , where V is the unit cell dimension in Å<sup>3</sup>. This approach is subject to considerable uncertainty, especially in Al-rich tourmalines, and awaits future refinements.

**Method 2** – Relationship between Fe/(Fe+Mg) ratio and Mg<sup>2+</sup> in the Z site. Grice and Ercit (1993) found a good correlation between the partitioning of Mg and the total Fe/(Fe+Mg) ratio such that  ${}^Y\text{Mg}^{2+} \approx 3[1 - \text{Fe}/(\text{Fe}+\text{Mg})]$  and  ${}^Z\text{Mg}^{2+} \approx \text{Mg}_{\text{total}} - {}^Y\text{Mg}^{2+}$  for those tourmalines with FeO(total) > 7 wt%. Bloodaxe et al. (1999) noted that for the schorl-dravite series tourmalines, the amount of  ${}^Z\text{Mg}^{2+}$  increases as  ${}^Y\text{Fe}^{2+}$  decreases. When their structural refinement data and that of Ertl and Hughes (2002) and Ertl et al. (2003a) are fit with a linear-least squares curve, there is a clear inverse relation between  ${}^Y\text{Fe}^{2+}$  and  ${}^Z\text{Mg}^{2+}$  such that  ${}^Y\text{Fe}^{2+} = -1.65({}^Z\text{Mg}^{2+}) + 1.98$  [r = -0.87]. This latter expression provides an additional method for estimating  ${}^Z\text{Mg}$  for schorl-dravite tourmalines.

## 5. TOURMALINE CLASSIFICATION PROCEDURE - A HIERARCHICAL APPROACH

Tourmaline investigations generally have varying levels of information available. The tourmaline information may range from complete analytical and crystal structural data to incomplete chemical data or even basic color information. However, it is important that a hierarchical classification procedure be used to accommodate the level of information that is accessible.

### 5.1. Level 1 – complete analytical and structural data.

This level considers those tourmalines in which all elements are measured, including the oxidation states of transition elements, and the specific cation and anion site-occupancies are established by crystal-structure refinement. Note that an ordered structural formula is assumed for classification purposes only, and proper site occupancies should be included in the ultimate tourmaline structural formula. *This level of complete characterization of tourmaline is the optimum situation, but one which is currently relatively uncommon.*

### 5.2. Level 2 – complete analytical data.

This level implies direct knowledge of all elements (light elements and oxidation states of transition elements), but generally with assumed site assignments. Because an ordered structural formula is assumed, the site allocation procedure of section 4 can be used and is appropriate for classification purposes.

### 5.2.1. Recommended classification procedure for tourmaline with Level 1 and Level 2 data

With the complete analytical data and knowledge of site occupancies, the following procedure for systematically naming tourmaline is suggested:

- (1) Determine the dominant X-site cation or vacancy to establish the principal tourmaline subgroup (Fig. 1).
- (2) Establish the dominant anion ( $\text{OH}^{1-}$ ,  $\text{F}^{1-}$  or  $\text{O}^{2-}$ ) at the W site (Fig. 2).
- (3) Ascertain the dominant anion ( $\text{OH}^{1-}$  or  $\text{O}^{2-}$ ) at the V site. The current state of knowledge is that most tourmalines are dominated by  $\text{OH}^{1-}$  at the V site. The exceptions are buergerite and some Al-rich tourmalines (Ertl et al. 2005; Cempírek et al. 2006).
- (4) Establish the dominant Z-site cation ( $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$  or  $\text{V}^{3+}$ ). For tourmaline with low amounts of  $\text{Fe}^{3+}$ , the Al-V-Cr ternary can be used to graphically display Z-site dominant cation (Fig. 9). The most common Z-site dominant cation is  $\text{Al}^{3+}$ , and a procedure for graphically classifying 27 possible  $^{\text{Z}}\text{Al}$ -dominant tourmaline species is given in step 5. There are only a few  $\text{Cr}^{3+}$ -,  $\text{Fe}^{3+}$ -,  $\text{V}^{3+}$ -end-members have been described at this time (e.g., chromium-dravite, povondraite and vanadium-dravite) so comparable diagrams were not generated for these chemical systems. The  $\text{Fe}^{3+}$ -dominant end-member povondraite is commonly in solid solution with the “oxy-dravite” and dravite (Henry et al. 1999; Žáček et al. 2000). A convenient binary diagram that can be used to classify dravitic and povondraitic tourmalines is given in Fig. 10.

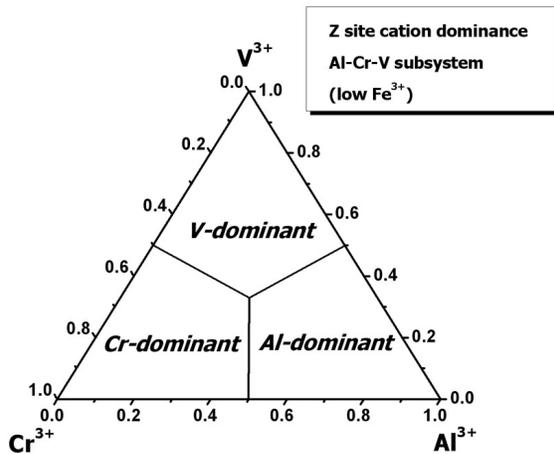


Figure 9. Al-V-Cr ternary system for the Z site subgroup tourmaline based on the dominant occupancy of the Z site for tourmaline with minor  $\text{Fe}^{3+}$  on the Z site.

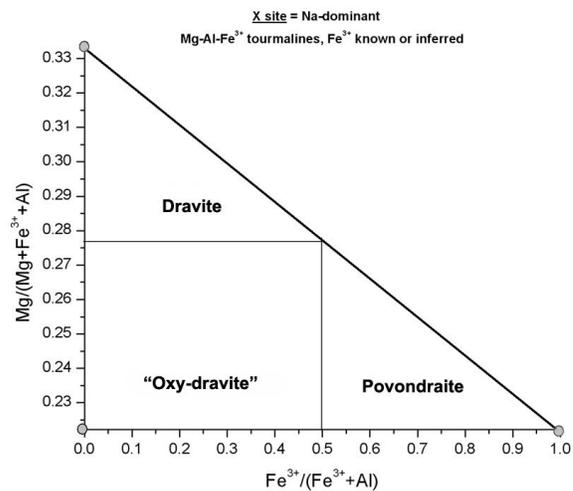


Figure 10. Binary diagram for Na-dominant tourmaline with Mg as the dominant divalent cation and  $\text{Fe}^{3+}$  measured, calculated or assumed. The values for the Mg,  $\text{Fe}^{3+}$  and Al include the Y and Z sites. For plotting purposes, any  $\text{Fe}^{2+}$  present should be added to Mg.

- (5) Determine the Y-site cation occupancy, recalling that an ordered form of the structural formula is used for classification purposes only (see section 4). The dominant subtype (subtype 1-4 of each of the three subgroups) can be established graphically from Figures 5-8. Once the dominant subtype is determined, the dominant species in that subtype defines the species name. This can be done by inspection or through the use of compositional diagrams such as Figures 11-15.

### Alkali subgroup

Z site = Al dominant

V site = OH dominant

$Y R^{2+} = Fe^{2+}$  or Mg dominant

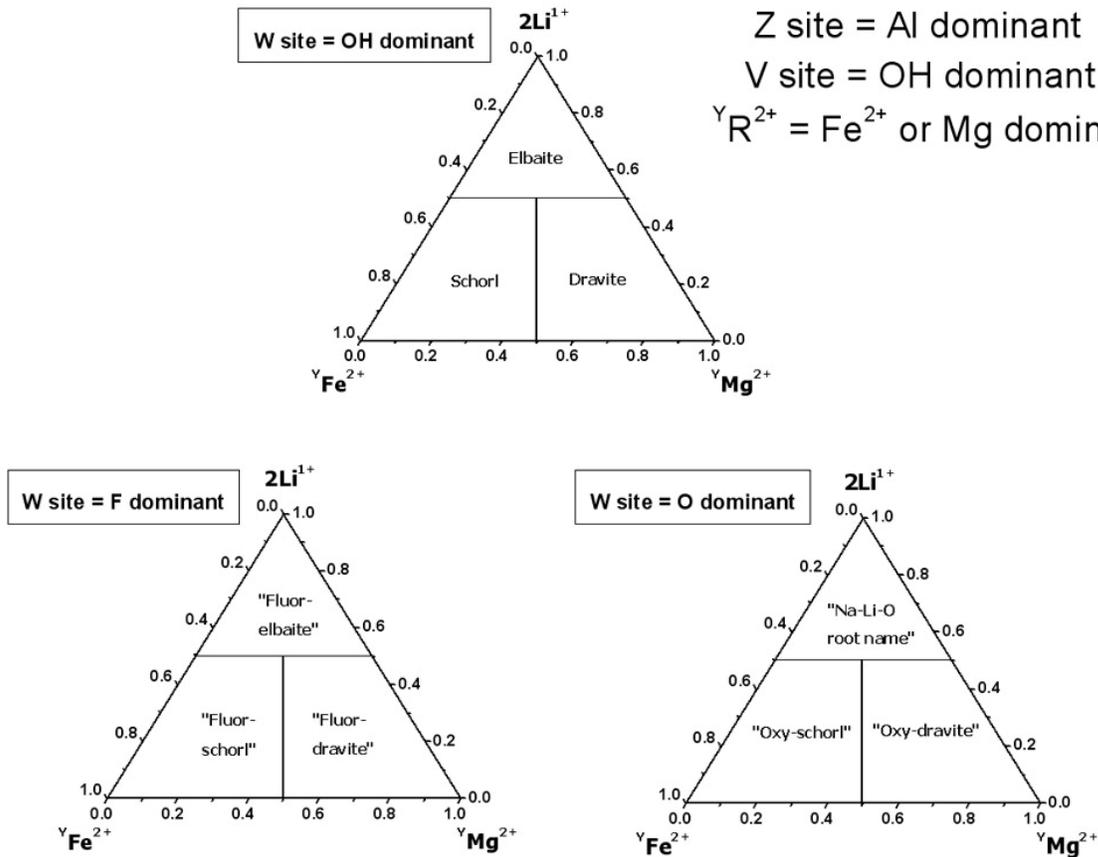


Figure 11. Alkali subgroup tourmaline species with  $Al^{3+}$  dominance at the Z site and  $OH^{1-}$  dominance at the V site. The three ternary subsystems represent dominance of  $OH^{1-}$ ,  $F^{1-}$ , or  $O^{2-}$  at the W site, respectively. Determination of the species is made by plotting Y-site cations on the appropriate ternary. The Y site occupancy is determined by an ordered structural formula (see section 4).

## Calcic subgroup

Z site = Al dominant

V site = OH dominant

$Y R^{2+} = Fe^{2+}$  or Mg dominant

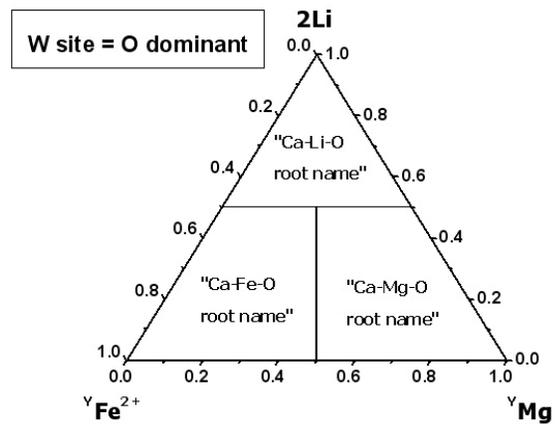
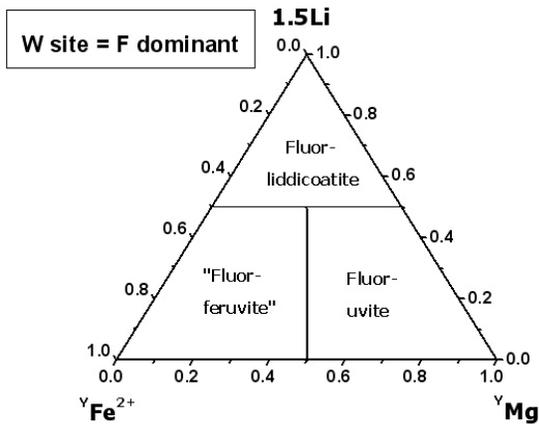
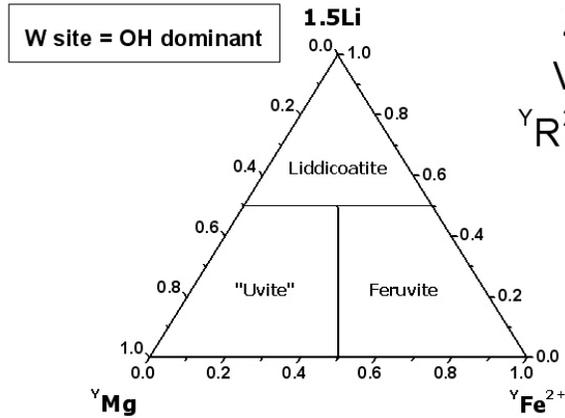


Figure 12. Calcic subgroup tourmaline species with  $Al^{3+}$  dominance at the Z site and  $OH^{1-}$  dominance at the V site. The three ternary subsystems represent dominance of  $OH^{1-}$ ,  $F^{1-}$ , or  $O^{2-}$  at the W site. Determination of the species is made by plotting Y-site cations on the appropriate ternary. The Y site occupancy is determined by an ordered structural formula (see section 4).

## Vacancy subgroup

Z site = Al dominant

V site = OH dominant

$Y_{R^{2+}} = Fe^{2+}$  or Mg dominant

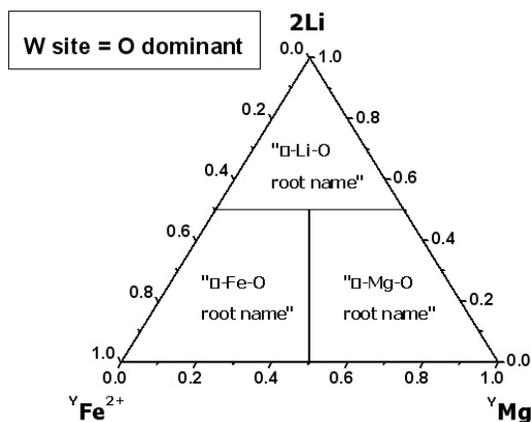
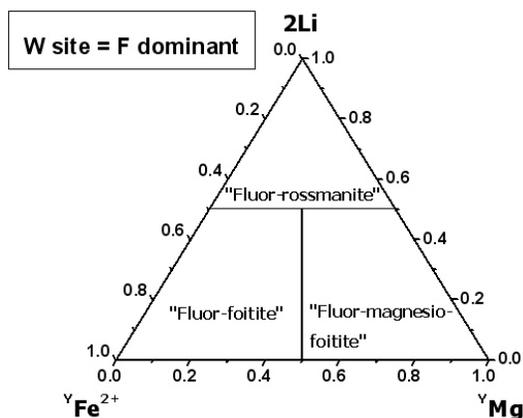
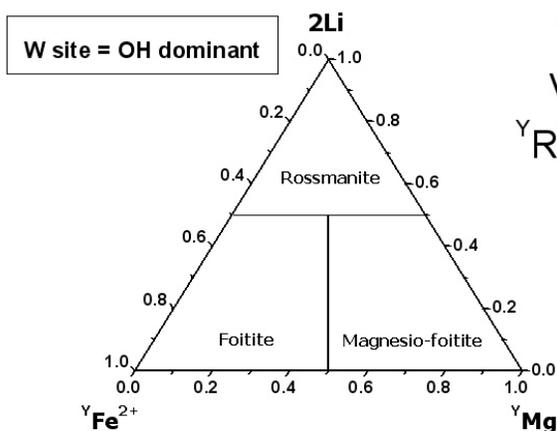


Figure. 13. X-site vacant subgroup tourmaline species with  $Al^{3+}$  dominance at the Z site and  $OH^{1-}$  dominance at the V site. The three ternary subsystems represent dominance of  $OH^{1-}$ ,  $F^{1-}$ , or  $O^{2-}$  at the W site. Determination of the species is made by plotting Y-site cations on the appropriate ternary. The Y site occupancy is determined by an ordered structural formula (see section 4).

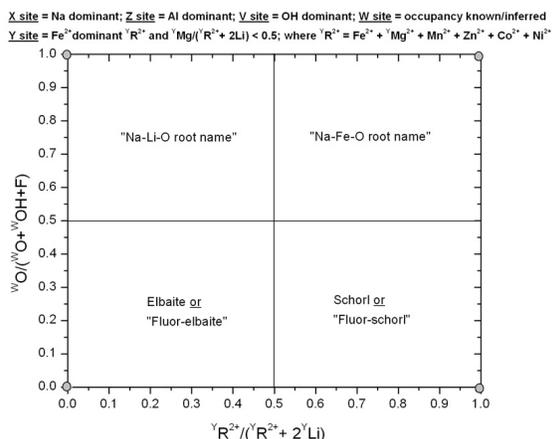


Figure 14. Na-subgroup tourmaline for Fe-rich and Li tourmaline species with level 1 characterization. Where there are multiple possible species in a field the species name will be a function of the dominant W-site anion. Site occupancies are known.

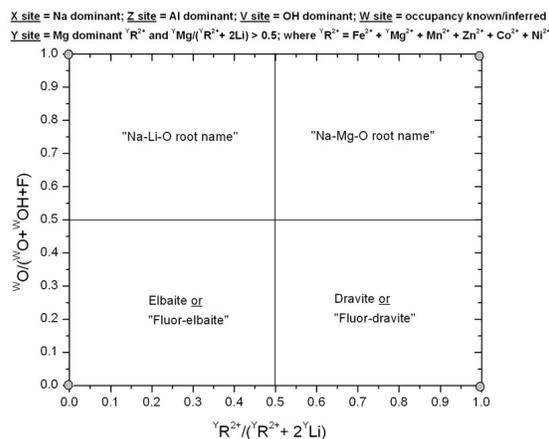


Figure 15. Na-subgroup tourmaline for Mg-rich and Li tourmaline species with level 1 characterization. Where there are multiple possible species in a field the species name will be a function of the dominant W-site anion. Site occupancies are known.

### 5.3. Level 3 - Partial tourmaline compositional data without direct measurement of B, H, Li and the oxidation states of transition elements.

This is the most common situation, typical of tourmalines analyzed only by the electron microprobe. The procedures outlined in Appendices A2 and A3 allow estimation of some of the undetermined cations and anions found in tourmaline. However, there can be considerable uncertainty associated with these procedures. As noted earlier, an ordered structural formula is assumed and the cations allocated accordingly (see section 4).

#### 5.3.1. Recommended classification procedure for tourmaline with Level 3 data

With the appropriate analytical data, estimation of unanalyzed elements and assumed site occupancies, the following procedure for systematically naming tourmaline is suggested:

- (1) Determine the dominant X-site cation or vacancy to establish the principal tourmaline subgroup (Fig. 1). This data is readily accessible from electron microprobe analysis.
- (2) Establish the dominant anion (OH<sup>1-</sup>, F<sup>1-</sup> or O<sup>2-</sup>) at the W site (Fig. 2). In the absence of direct measurement of H, the uncertainty associated with estimating H can be significant, and the resultant <sup>W</sup>O<sup>2-</sup> estimate inaccurate. In contrast, F<sup>1-</sup> can be accurately measured with the electron microprobe. If H is left undetermined, it is recommended that the criterion F > 0.5 apfu, be met for the tourmaline to be considered a fluor-species. The presence of a significant amount of an “oxy-component” can also be estimated or inferred from binary plots such as Figure 10.
- (3) Estimate the dominant anion (OH<sup>1-</sup> or O<sup>2-</sup>) at the V site. The current state of knowledge is that most tourmalines are dominated by OH<sup>1-</sup> at the V site. The exceptions are buergerite and some Al-rich tourmalines (Ertl et al. 2005; Cempírek et al. 2006).

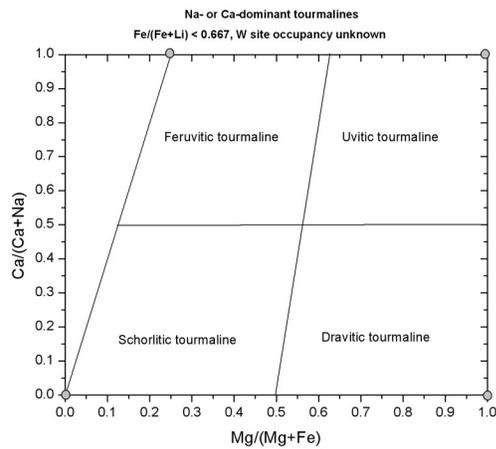
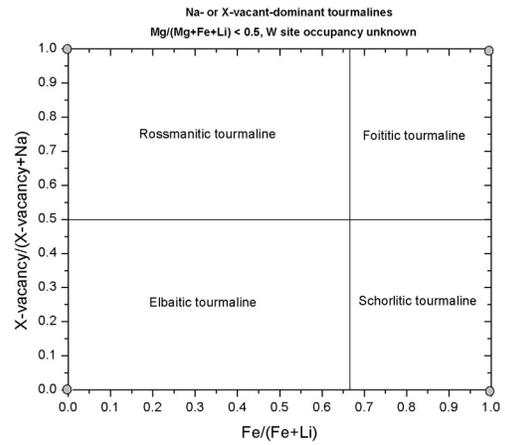
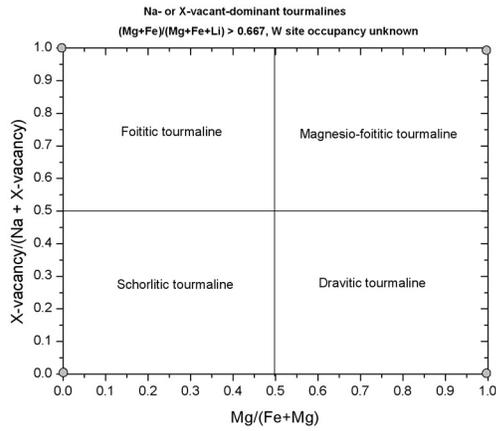
- (4) Establish the dominant Z-site cation ( $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$  or  $\text{V}^{3+}$ ). For tourmaline with low amounts of  $\text{Fe}^{3+}$ , the Al-V-Cr ternary can be used to graphically establish this Z-site subgroup (Fig. 9). The most common Z-site dominant cation is  $\text{Al}^{3+}$ , and a procedure for classifying 27 possible  $^{\text{Z}}\text{Al}$ -dominant tourmaline species is given in Figures 11-13. There are only a few  $\text{Cr}^{3+}$ -,  $\text{Fe}^{3+}$ -,  $\text{V}^{3+}$ -end-members have been described at this point (e.g., chromium-dravite, povondraite and vanadium-dravite) so comparable diagrams were not generated for these chemical systems. The  $\text{Fe}^{3+}$ -dominant end-member povondraite is commonly in solid solution with the “oxy-dravite” and dravite (Henry et al. 1999; Žáček et al. 2000). A convenient binary diagram that can be used to classify dravitic and povondraitic tourmalines is given in Fig. 10.
- (5) Determine the Y-site cation occupancy, recalling that an ordered form of the structural formula is used for classification purposes only (see section 4). The dominant subtype (subtype1-4 of each of the three subgroups) can be roughly established graphically from Figures 5-8. However, with the uncertainty of the W-site occupancy that assignment of a subtype can be equivocal, with the exception of the F-dominant tourmalines. If a dominant subtype is determined, the dominant species in that subtype defines the species name. This can be done by inspection or through the use of compositional diagrams such as Figures 11-15. In many instance that W site occupancy will remain undetermined. In this case it is recommended that a generalized name be used (Table 6, Figs. 16-18).

**Table 6. Recommended names for inadequately determined tourmalines**

dominant cations and anions in these sites	(X)	(Y <sub>3</sub> )	(Z <sub>6</sub> )	V <sub>3</sub> likely	W unknown
<b>Alkali tourmaline subgroup</b>					
<b>Elbaitic tourmaline</b>	Na	Li and Al	Al	(OH)	unknown
<b>Schorlitic tourmaline</b>	Na	$\text{Fe}^{2+}$	Al	(OH)	unknown
<b>Dravitic tourmaline</b>	Na	Mg	Al	(OH)	unknown
<b>Buergeritic tourmaline</b>	Na	$\text{Fe}^{3+}$	Al	(O)	unknown
<b>Olenitic tourmaline</b>	Na	Al	Al	(OH)	unknown
<b>Povondraitic tourmaline</b>	Na	$\text{Fe}^{3+}$	$\text{Fe}^{3+}$	(OH)	unknown
<b>Chromium-dravitic tourmaline</b>	Na	Mg	Cr	(OH)	unknown
<b>Vanadium-dravitic tourmaline</b>	Na	Mg	V	(OH)	unknown
<b>Calcic tourmaline subgroup</b>					
<b>Liddicoatitic tourmaline</b>	Ca	Li and Al	Al	(OH)	unknown
<b>Uvitic tourmaline</b>	Ca	Mg	Al	(OH)	unknown
<b>Feruvitic tourmaline</b>	Ca	$\text{Fe}^{2+}$	Al	(OH)	unknown

## X-site vacant tourmaline subgroup

<b>Rossmannitic tourmaline</b>	□	Li and Al	Al	(OH)	unknown
<b>Foitic tourmaline</b>	□	$\text{Fe}^{2+}$	Al	(OH)	unknown
<b>Magnesian-foititic tourmaline</b>	□	Mg	Al	(OH)	unknown



Figures 16, 17, 18. Binary diagrams that allow determination of the generalized name of a tourmaline.

## APPENDIX A1. TOURMALINE END-MEMBERS: MODIFICATIONS, ETYMOLOGY, TYPE LOCALITY AND REPRESENTATIVE CELL-DIMENSIONS

### A1.1. Tourmaline end members – general characteristics

There are inconsistencies in the earlier definitions of several of the tourmaline end-member formulae that prompt redefining some of these end members (Hawthorne and Henry 1999). In defining end-member compositions there are several characteristics that should be considered (Hawthorne 2002).

(1) An end-member composition must be fixed. Consequently, formulae expressed with variable cations or anions on a given site, such as  $(Al^{3+}, Fe^{3+})$  on the Y site or  $(F^-, OH^-)$  on the W site, can be factored into two or more end-member components of fixed composition. For example, in the case of the original end-member definition of foitite the composition was expressed as  $\square [Fe^{2+}_2 (Al, Fe^{3+})] Al_6 (Si_6O_{18}) (BO_3)_3 (OH)_4$  (MacDonald et al. 1993). However, this definition is incorrect because the composition is variable and can be factored into the two fixed compositions:  $\square [Fe^{2+}_2 Al] Al_6 (Si_6O_{18}) (BO_3)_3 (OH)_4$  and  $\square [Fe^{2+}_2 Fe^{3+}] Al_6 (Si_6O_{18}) (BO_3)_3 (OH)_4$ .

(2) An end-member may have more than a single cation or anion at a single given site if it is necessary to attain electroneutrality in the crystal structure. Electroneutrality in crystal structures mandate that in some instances two cations or anions may be required for charge balance on a single site. One of the best examples is the tourmaline end-member elbaite:  $Na [Li_{1.5} Al_{1.5}] Al_6 (Si_6O_{18}) (BO_3)_3 (OH)_3 (OH)$ . The X, Z, T, B, V and W sites are completely ordered (occupied by only one type of cation or anion) such that the aggregate charge is  $6^-$ . This requires that cations on the Y site have a total charge of  $6^+$ . In the case of elbaite, with a mix of  $Li^+$  and  $Al^{3+}$ , the aggregate charge is only met with the Y-site composition of  $[Li_{1.5} Al_{1.5}]$ .

(3) Anions are critical in defining end-members, and similar anions can occupy more than one crystallographically distinct site in a crystal structure. Anions such as  $OH^-$ ,  $F^-$  and  $O^{2-}$ , can define distinct end-members. Anions sites can have crystallographic distinctions that mandate preferences of certain anions for specific anion sites. For example, in the tourmaline structure the V site can be occupied by  $O^{2-}$  and  $OH^-$ , but the W site can be occupied by  $F^-$ ,  $O^{2-}$  and/or  $OH^-$ . In the case of homovalent anion substitution of  $F^-$  for  $OH^-$ , tourmaline will range from  $(OH)_3(OH)$  to  $(OH)_3(F)$ , thus defining the OH (hydroxy) and F (fluor) end-members. In the case of heterovalent anion substitution of  $O^{2-}$  for  $OH^-$  or  $F^-$ , coupled substitutions must involve other cations in the crystal structure to define an “oxy” end-member.

## A1.2. Tourmaline Species, End-member Formulae, Etymology, Type Localities and Representative Cell Dimensions

### Fluor-buergerite



*IMA number:* IMA 65-005. Original name: buergerite.

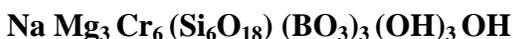
*Etymology:* Named for Martin Julian Buerger (1903-1986), a professor of mineralogy at M.I.T. and a pioneer of crystal structure analysis.

*Type locality:* Mexquitic, San Luis Potosí, Mexico

*Representative cell dimensions (type material):*  $a = 15.87 \text{ \AA}$ ,  $c = 7.19 \text{ \AA}$ ,  $V = 1568 \text{ \AA}^3$ .

*Selected References:* Donnay et al. (1966), Barton (1969) and Tippe and Hamilton (1971)

### Chromium-dravite



*IMA number:* IMA 82-055. Original name: chromdravite.

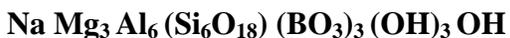
*Etymology:* Named for its relationship to dravite and chemical composition.

*Type locality:* Velikaya Guba uranium occurrence, Zaonezhskiy Peninsula, Karelia, Russia.

*Representative cell dimensions (type material):*  $a = 16.11 \text{ \AA}$ ,  $c = 7.27 \text{ \AA}$ ,  $V = 1634 \text{ \AA}^3$ .

*Selected References:* Nuber and Schmetzer (1979) and Rumyantseva (1983)

### Dravite



*IMA number:* Grandfathered status.

*Etymology:* Named in 1884 by Tschermak for the area of the locality from a Mg- and Na-rich tourmaline, the Drava river area, which is the district along the Drava river (in German: Drau; in Latin: Drave) in Austria and Slovenia (Ertl 2007).

*Type locality:* Unterdrauburg, Carinthia, Austria (today Dobrava pri Dravogradu, Slovenia); Ertl (2007).

*Representative cell dimensions (type material):*  $a = 15.96 \text{ \AA}$ ,  $c = 7.21 \text{ \AA}$ ,  $V = 1590 \text{ \AA}^3$ .

*Selected References:* Tschermak (1884), Kunitz (1929), Buerger et al. (1962) and Dunn (1977)

**Elbaite**

*IMA number:* Grandfathered status.

*Etymology:* Named after the type locality, on the island of Elba, Tuscany, Italy.

*Type locality:* San Piero in Campo, Campo nell'Elba, Elba Island, Livorno Province, Tuscany, Italy

*Representative cell dimensions (type material):*  $a = 15.85 \text{ \AA}$ ,  $c = 7.11 \text{ \AA}$ ,  $V = 1544.71 \text{ \AA}^3$ .

*Selected References:* Vernadsky (1913), Donnay and Barton (1972), Novák et al. (1999) and Ertl (2008).

**Foitite**

*IMA number:* IMA 92-034.

*Etymology:* Named for Franklin F. Foit, Jr., (1942- ), mineralogist at Washington State University, Pullman, in recognition of his work on tourmaline-group minerals

*Type locality:* Found as museum specimens designated only as from “southern California”, USA, probably from White Queen mine, Pala district, San Diego County, California, USA (Anthony et al. 1995).

*Representative cell dimensions (type material):*  $a = 15.97 \text{ \AA}$ ,  $c = 7.13 \text{ \AA}$ ,  $V = 1575 \text{ \AA}^3$ .

*References:* MacDonald et al. (1993) and Pezzotta et al. (1996)

*Modifications of the end-member definition:* The original end-member composition of foitite was given with a variable cation occupancy at the Y site i.e.  $Y_3 = [\text{Fe}^{2+}_2(\text{Al}, \text{Fe}^{3+})]$  (MacDonald et al. 1993). Because Al is dominant relative to  $\text{Fe}^{3+}$  in the holotype material, the Y-site composition of the end-member is considered  $\text{Fe}^{2+}_2\text{Al}$ .

**Feruvite**

*IMA number:* IMA 87-057.

*Etymology:* Named for its relationship to uvite and chemical composition.

*Type locality:* Repanga Island (Cuvier Island), Waikato, North Island, New Zealand

*Representative cell dimensions (type material):*  $a = 16.01 \text{ \AA}$ ,  $c = 7.25 \text{ \AA}$ ,  $V = 1609 \text{ \AA}^3$ .

*Selected References:* Grice and Robinson (1989) and Selway et al. (1998a)

*Modifications of the end-member definition:* The original formula for feruvite is  $\text{Ca Fe}_3 (\text{Al,Mg})_6 (\text{Si}_6\text{O}_{18}) (\text{BO}_3)_3 (\text{OH})_4$  (Grice and Robinson 1989). This is not considered to be a true end-member and does not specify the valence state of Fe. Crystal structure refinement demonstrates that all Fe is divalent, and that the Z site is  $(\text{Al}_{4.72}\text{Fe}^{3+}_{0.34}\text{Mg}_{0.82}\text{Fe}^{2+}_{0.12})$  which is to an  $(\text{Al}_5\text{Mg})$  end member.

### **Fluor-liddicoatite**

**Ca (Li<sub>2</sub>Al) Al<sub>6</sub> (Si<sub>6</sub>O<sub>18</sub>) (BO<sub>3</sub>)<sub>3</sub> (OH)<sub>3</sub> F**

*IMA number:* IMA 76-041. *Original name:* liddicoatite.

*Etymology:* Named for Richard T. Liddicoat (1918-2002), gemologist and president of the Gemological Institute of America.

*Type locality:* Pegmatitic area southwest of the towns of Antsirabé and Betafo, Vakinankaratra region, Antananarivo Province, Madagascar

*Representative cell dimensions (type material):*  $a = 15.87 \text{ \AA}$ ,  $c = 7.14 \text{ \AA}$ ,  $V = 1557 \text{ \AA}^3$ .

*Selected References:* Dunn et al. (1977b), Nuber and Schmetzer (1981) and Aurisicchio et al. (1999)

*Modifications of the end-member definition:* Dunn et al. (1977b) gave the structural formula for the holotype liddicoatite material as  $(\text{Ca}_{0.72}\text{Na}_{0.27}) (\text{Li}_{1.59}\text{Al}_{1.13}\text{Fe}_{0.11}\text{Ti}_{0.05}\text{Mn}_{0.04}\text{Mg}_{0.04}) \text{Al}_{6.00} \text{Si}_6\text{O}_{18} (\text{BO}_3)_3 [(\text{OH})_{2.73}\text{O}_{0.27}] [\text{F}_{0.87}(\text{OH})_{0.13}]$ . Based on this composition and the structural analogy with elbaite, they extrapolated the end-member composition of liddicoatite as  $\text{Ca} (\text{Li}_{1.74}\text{Al}_{1.26}) \text{Al}_6 (\text{Si}_6\text{O}_{18}) (\text{BO}_3)_3 [(\text{OH})_{2.48}\text{O}_{0.52}] (\text{F},\text{OH})$ , but stipulated that this is not a “pure end-member”. Further, they gave the “ideal” composition of liddicoatite as  $\text{Ca} (\text{Li},\text{Al})_3 \text{Al}_6 (\text{Si}_6\text{O}_{18}) (\text{BO}_3)_3 (\text{O},\text{OH})_3 (\text{OH},\text{F})$ . Several aspects of this formula warrant modification of the end-member structural formula to the one given here. (1) Because F partitions exclusively in the W site, the holotype material is an F-dominant species. (2) Any O at the W and V sites should be assigned to the W site in the holotype material structural formula (Hawthorne 1996). (3) The divalent charge of Ca requires an adjustment of the Li:Al ratio so the Y-site is  $(\text{Li}_2\text{Al})$ .

### **Magnesio-foitite**

**□ (Mg<sub>2</sub>Al) Al<sub>6</sub> (Si<sub>6</sub>O<sub>18</sub>) (BO<sub>3</sub>)<sub>3</sub> (OH)<sub>3</sub> OH**

*IMA number:* IMA 98-037.

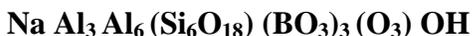
*Etymology:* Named for its relationship to foitite and chemical composition.

*Type locality:* Kyonosawa, Mitomi-mura, Yamanashi prefecture, Chubu region, Honshu Island, Japan

*Representative cell dimensions (type material):*  $a = 15.88 \text{ \AA}$ ,  $c = 7.18 \text{ \AA}$ ,  $V = 1568 \text{ \AA}^3$ .

*Selected References:* Hawthorne et al. (1999)

### **Olenite**



*IMA number:* IMA 85-006.

*Etymology:* Named for the type locality area, Olenek River basin, Russia.

*Type locality:* Olenek River basin, Olenii (Oleny) Range, Voron'i Tundry, Kola Peninsula, Murmansk region, Russia

*Representative cell dimensions (type material):*  $a = 15.80 \text{ \AA}$ ,  $c = 7.09 \text{ \AA}$ ,  $V = 1533 \text{ \AA}^3$ .

*Selected References:* Sokolov et al. (1986), Ertl et al. (1997), Hughes et al. (2000), Schreyer et al. (2002), Hughes et al. (2004) and Cempírek et al. (2006)

*Modifications of the end-member definition:* Sokolov et al. (1986) gave the formula for the type olenite as  $\text{Na}_{1-x} \text{Al}_3 \text{Al}_6 \text{B}_3 \text{Si}_6 \text{O}_{27} (\text{O},\text{OH})_4$ . To create an end-member formula with the ideal occupancy of one Na at the X site, three Al at the Y site, and where the T site is completely occupied by Si, the V and W site can only be occupied by  $[\text{O}_3(\text{OH})]$ . To create an ordered formula, the (OH) is eventually assigned to the W site, while  $\text{O}_3$  is assigned to the V site.

### **Povondraite**



*Renamed/redefined by IMA 90-E*

*Etymology:* Named for Pavel Povondra (1924- ), mineralogist and chemist at the Charles University, Prague, Czech Republic, for his extensive work on the tourmaline group.

*Type locality:* Alto Chapare district, Chapare Province, Cochabamba Department, Bolivia

*Representative cell dimensions (type material):*  $a = 16.19 \text{ \AA}$ ,  $c = 7.44 \text{ \AA}$ ,  $V = 1689 \text{ \AA}^3$ .

*Selected References:* Walenta and Dunn (1979), Grice et al. (1993) and Žáček et al. (2000)

*Modifications of the end-member definition:* Povondraite was redefined from the original “ferridravite” (Walenta and Dunn 1979) because the initially assumed site assignments were incorrect and did not correspond to the  $\text{Fe}^{3+}$ -equivalent of dravite (Grice et al. 1993). Hawthorne and Henry (1999) suggested that Mg is ordered at the Z site and should be part of the end-member formula.

### **Rossmanite**



*IMA number:* IMA 96-018.

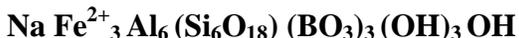
*Etymology:* Named after George R. Rossman (1945- ), California Institute of Technology, Pasadena, California, USA, in recognition for his work on the spectroscopy of the tourmaline minerals.

*Type locality:* Hradisko quarry, Rožná, Morava (Moravia), Czech Republic

*Representative cell dimensions (type material):*  $a = 15.77 \text{ \AA}$ ,  $c = 7.09 \text{ \AA}$ ,  $V = 1527 \text{ \AA}^3$ .

*References:* Selway et al. (1998b)

### **Schorl**



*Etymology:* Name probably derived from the early German mining term "Schor" (mud) or after the name of the former village "Schorl" (today: Zschorlau) in Saxony, Germany. The first relatively detailed description of schorl with the name "schürl" and its occurrence (various tin mines in the Saxony Ore Mountains) was written by Johannes Mathesius (1504-1565) in 1562 under the title "Sarepta oder Bergpostill" (Ertl 2006).

*Type locality:* Saxony Ore Mountains, Germany.

*Representative cell dimensions:*  $15.98 \text{ \AA}$ ,  $c = 7.16 \text{ \AA}$ ,  $V = 1583 \text{ \AA}^3$ .

*Selected References:* first described in 1562 by Mathesius (Mathesij 1562) as reported in Ertl (2006), Wallerius (1747), Romé de l'Isle (1772), Werner (1780), Fortier and Donnay (1975) and Foit (1989).

### **Fluor-uvite**



*Etymology:* Named for the type locality area, Uva Province, Sri Lanka.

*Type locality:* Uva Province, Sri Lanka.

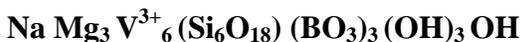
*Representative cell dimensions (type material):*  $a = 15.97 \text{ \AA}$ ,  $c = 7.21 \text{ \AA}$ ,  $V = 1592 \text{ \AA}^3$ .

*Selected References:* Kunitz (1929), Schmetzer et al. (1979) and Dunn et al. (1977a).

*Modifications of the end-member definition:* Uvite, originally defined by Kunitz (1929), was considered to have an ideal formula of  $\text{Ca Mg}_3 (\text{Al}_5\text{Mg}) (\text{Si}_6\text{O}_{18}) (\text{BO}_3)_3 (\text{OH})_4$ . This formula was based on the examination of tourmalines from Uva (Sri Lanka), De Kalb

(New York) and Gouverneur (New York) with OH contents of approximately 4 apfu. However, all other analyses from these localities contain F in the 0.5-1.0 apfu range. Dunn et al. (1977a) designated a sample of uvite from Uva, Sri Lanka as a neotype, and this sample has an anion content of  $(\text{OH}_{2.90}\text{F}_{0.76}\text{O}_{0.34})$ . This anion content would mandate that the W site would be dominated by F and that uvite should be an F-end-member.

#### **Vanadium-dravite**



*Etymology:* Named for its relationship to dravite and chemical composition.

*Type locality:* Slyudyanka complex, Lake Baikal region, Zabaikalye (Transbaikal), Siberia, Russia.

*Representative cell dimensions (type material):*  $a = 16.12 \text{ \AA}$ ,  $c = 7.39 \text{ \AA}$ ,  $V = 1663 \text{ \AA}^3$ .

*Selected References:* Reznitsky et al. (2001).

### **A1.3. Additional Potential Tourmaline Species Described in the IMA database**

#### **Unnamed 2575**



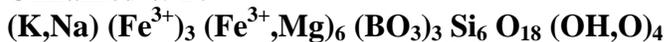
This is an F-dominant analogue of schorl (Ertl et al. 2006b).

#### **Unnamed 0918**



This is the fluorine-dominant analogue of elbaite. The suggested name fluor-elbaite was not approved by IMA.

#### **Unnamed 0920**



This is a K-dominant tourmaline (Žáček et al. 2000).

## **APPENDIX A2. ANALYTICAL CONSIDERATIONS AND NORMALIZATION PROCEDURES**

The crystal chemistry of tourmaline can be evaluated utilizing a variety of analytical procedures, each with strengths and weaknesses that should be carefully considered when assessing the results and classifying a given tourmaline. Several of the techniques used specifically for tourmaline analysis are briefly mentioned below. Special attention is given to normalization procedures used for the electron microprobe data of tourmaline.

### **A2.1. Bulk Tourmaline Analysis Techniques**

Several "bulk" sample techniques have been used to analyze tourmaline. The general disadvantage of these techniques is the averaging effect of "bulk" samples in which chemical zonation may be masked, and mineral and fluid inclusions may introduce contamination. (1) Wet chemical analysis was the standard procedure for analysis of materials prior to the widespread use of the electron microprobe (e.g., Peck 1964; Jarosowich 1966; Povondra and Čech 1976). The chief advantages were that light elements could be analyzed and oxidation states of transition elements were determined. (2) Inductively coupled plasma - atomic emission spectroscopy (ICP-AES) has commonly been used to supplement electron microprobe analysis by determining light element concentrations as well as trace element levels in tourmaline (e.g., Shearer and Papike 1986; Kantipuly et al. 1988). Sample amounts as small as 200-300 mg have been analyzed. (3) Induced neutron activation analysis (INAA) has been successfully used to determine REE in tourmaline (e.g., King et al. 1988; Roda et al. 1995).

### **A2.2. Tourmaline Structural Refinement and Spectroscopic Analysis Techniques**

Single crystal refinement and spectroscopic techniques provide valuable information about the local environments of specific cations, trace elements and oxidation states of transition elements. (1) Crystal structure refinement (SREF) is an electron-counting technique that, in combination with chemical analysis, helps determine the correct site assignments through definition of stereochemical relationships and refined site-scattering values (e.g., Hawthorne and Grice 1990; Hawthorne et al. 1995, Camára et al. 2002). This technique exhibits spatial resolution that will work on well-constrained analytical problems such as those encountered in elbaïtes (Burns et al. 1994). (2) Secondary ion microprobe spectroscopy (SIMS) has provided information on spatial distribution of light elements as well as trace and minor elements in tourmaline (e.g., Wilson and Long 1983; Grew et al. 1990; Harris et al. 1992; Hawthorne et al. 1995), (3) Mossbauer spectroscopy has been used to evaluate  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratios as well as the locations of the locations of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in the tourmaline structure (e.g., Hermon et al. 1973; Gorelikova et al. 1978; Saegusa 1979; Farrow et al. 1988; Farrow 1994; Dyar et al., 1998), but this approach also suffers from an averaging phenomenon. (4) Proton-induced gamma-ray emission (PIGE) has been used for light element analysis in tourmaline (e.g., Dyar et al. 1998).

### **A2.3. Tourmaline Electron Microprobe Analytical Techniques**

The electron microprobe is currently the most commonly used analytical tool for tourmaline analysis. However, there are several analytical limitations that must be considered when calculating a structural formula from electron microprobe data. Although it is possible to analyze most of the major elements in tourmaline, Li and H as well as the valence states of transition elements, cannot be directly measured. In addition, a critical constituent of tourmaline is the light element B. B has been analyzed with the electron microprobe (e.g., Bastin and Heijligers 2000; McGee and Anovitz 1991; Hawthorne et al. 1995), but the analytical accuracy and precision remain unsatisfactory for confident structural formula calculations. These shortcomings require that the normalization procedure for tourmaline be carefully considered to minimize the limitations of electron microprobe analysis. Because of a greatly improved understanding of tourmaline's crystal structure and chemistry as well as the constraints imposed by geochemical settings of tourmaline, estimation techniques for unanalyzed light elements and oxidation states are possible.

## APPENDIX A3. TOURMALINE NORMALIZATION PROCEDURES

### A3.1. Normalization of tourmaline with complete chemical characterization

Ultimately, the best approach for determination of the structural formula of tourmaline is to analyze tourmaline as completely as possible and by as many techniques as possible. With a complete analysis, normalization can be properly done on a 31 anion basis (Henry and Dutrow 1996; Clark 2007). The most accurate site assignments are made by means of crystal structure refinements with a combination of site-scattering and mean bond-length information (e.g., Hawthorne and Grice 1990; Hawthorne et al. 1993; Taylor et al. 1995; Hawthorne 1996; Ertl et al. 2003a,b).

### A3.2. Normalization of electron microprobe data and estimation of light elements and oxidation states of elements

Most widespread tourmaline normalization procedures make assumptions concerning the anionic and cationic assignments. In the absence of accurate analyses of B, O, H, Li and the oxidation states of transition elements, several procedures can be used to calculate a structural formula. Each of these procedures, in turn, can provide the basis for estimation of light elements and oxidation states of transition elements.

#### A3.2.1. Normalization procedure 1 – fixed number of oxygens.

Assume OH fills the four V+W sites after accounting for F and Cl. In essence, this implies normalization of the cations on the basis of 31 anions (O + F + OH), 29 oxygens (both normalization assuming B is calculated by stoichiometry,  $B = 3 \text{ apfu}$ ) or 24.5 oxygens (without B calculation). Generally, this approach provides a good first approximation (Clark 2007). However, if there is significant  $O^{2-}$  substitution for  $OH^{1-}$ , the oxygen normalization factor will be underestimated as will be the number of cations. In fact, significant amounts  $O^{2-}$  substitution for  $OH^{1-}$  have been demonstrated in uvite (Taylor et al. 1995) and in a number of other tourmaline compositions (e.g., Povondra 1981; Povondra and Novák 1986; Dyar et al. 1998). Consequently, this approach should be used with those tourmalines in which it is reasonably assured that  $OH+F+Cl \sim 4$  (e.g., Burns et al. 1994).

#### A3.2.2. Normalization procedure 2 – fixed Y+Z+T cations.

Normalize the sum of the T+Z+Y cations to 15. *This is the recommended normalization approach for tourmaline with low Li contents and minor B in the tetrahedral site.* It assumes that there are no vacancies in the Y, Z and T sites, a valid assumption based on a majority of crystal structure refinement data. It also assumes that the amount of tetrahedral B is not significant. However, some recent refinement results indicate small vacancies in Y and Z sites (<0.22 apfu; Ertl et al. 1997, Hughes et al. 2000, Ertl et al. 2003b, Prowatke et al. 2003). To the extent that all of the significant cations on these sites are accurately analyzed, the structural formula can be calculated without having to rely on estimates of the OH content or valence states of transition elements. Fortunately, those tourmaline containing even a moderate amount of Mg (>0.02 apfu)

and that coexist with minerals such as biotite, muscovite and staurolite typically have minor-to-insignificant amounts of Li due to the preferential partitioning of Li into these coexisting minerals (Henry and Dutrow 1996). This normalization procedure will be appropriate for virtually all metamorphic and most igneous tourmalines.

### **A3.2.3. Normalization procedure 3 – fixed Si.**

Normalize on the basis of Si = 6. This procedure is useful for normalization of tourmalines with significant amounts of unanalyzed elements, particularly Li. It assumes that there is no significant tetrahedral Al or B. For many, Li-rich tourmalines this general assumption is probably reasonable (e.g. Dutrow and Henry 2000). However, many low Li tourmalines are known to contain significant amounts of tetrahedral Al so that this procedure should be used with care in these instances (e.g. Hawthorne et al. 1993).

### **A3.2.4. Estimation of B.**

Based on the total B found in a series of high quality wet chemical analyses of tourmaline from a variety of lithologies, Henry et al. (2002) indicate that the assumption that B fully occupies the triangular B site and can be calculated using stoichiometric constraints (i.e. B = 3) is likely to be valid for most petrologic occurrences of tourmaline (see also Clark 2007). Further, crystal structure refinements and bond valence calculations indicate that there are essentially 3 B apfu in those tourmalines that have been determined to date (Hawthorne 1996). However, there are a few uncommon instances involving Al-rich tourmaline (e.g., olenite) in which some B may also be tetrahedral (Ertl et al. 1997; Tagg et al. 1999; Hughes et al. 2000; Ertl et al. 2006a). This feature indicates that the assumption of 3 B may not be valid in all cases, but is likely to be reasonable for most tourmalines

### **A3.2.5. Estimation of Li.**

Li can be approximated by assuming that Li fills any cation deficiency in the Y site. However, this requires that the formula be calculated either on a fixed cation basis (e.g. Si = 6, see Dutrow and Henry 2000) or that Li be iteratively calculated using a fixed number of oxygens and assuming OH+F=4 (e.g. Burns et al. 1994; Clark 2007). (1) The Si = 6 approach appears to work well for some Li-rich tourmaline (Li>0.7 apfu), but tends to underestimate the Li contents (Henry et al. 2002). The underestimate of Li is likely due to the existence of tetrahedral Al substituting for Si will result in calculated Li being too low. Henry and Dutrow (2002) indicate that this procedure should be within 0.1-0.3 apfu of the correct Li values. (2) The Li by iteration and OH+F=4.0 approach tends to result in high estimates of Li (Henry et al. 2002). For tourmalines with high values of Li (>0.7 apfu) this generally results in an overestimate of 0.1-0.3 Li apfu. This is a more significant problem in low-Li tourmalines, and generally appears to indicate that these tourmalines contain significant amounts of Li. The Li overestimates are a consequence of substantial amounts of substitution of O for OH+F in the W and V sites in many tourmalines or can result because of the occurrence of significant vacancies at the Y site in Al-rich tourmalines.

### **A3.2.5. Estimation of H.**

H contents can be determined by charge balance if oxidation states can be measured or inferred, and Li contents can be estimated. Putative oxidation state evidence can be derived from tourmaline optical properties or by mineral assemblages, particularly graphite-bearing assemblages. Minimal Li contents can be generally inferred by presence of significant Mg in tourmaline which is a function of coexisting mineral assemblages that tend to efficiently partition Li (Henry and Dutrow 1996). Charge balance estimates of H are subject to significant amounts of uncertainty, and likely result in minimum values of H. Despite the larger amounts of uncertainty, useful information on H contents can be derived using electron microprobe data (e.g. Henry et al. 2002).

### **A3.2.5. Estimation of Fe oxidation states.**

Fe<sup>3+</sup> contents can be determined by charge balance if H contents can be measured or inferred, and Li contents can be estimated. Despite the larger amounts of uncertainty, useful information on Fe<sup>3+</sup> contents can be derived using electron microprobe data (e.g. Henry et al. 1999). However, all these procedures can have relative large errors. The best way would be to employ techniques such as Mössbauer spectroscopy to determine the Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio (e.g. Dyar et al. 1998). In some instances, the Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio can be inferred for tourmalines found in certain mineral assemblages. For example, Dyar et al. (2002) found that tourmaline from graphite-bearing metapelites contained 20-34% of the total Fe as Fe<sup>3+</sup>.

## APPENDIX A4. COLOR-BASED TOURMALINE VARIETAL NAMES

Although mineral varietal names are not under the jurisdiction of the CNMNC, the STN notes the use of the color-based tourmaline varietal names. The following is a listing of some of the varietal names that have been used with possible general or tourmaline species associations.

### COLOR-BASED TOURMALINE VARIETAL NAMES

Achroite	colorless tourmaline, probably elbaite or rossmanite
Aphrizite	dark grey schorl
Brazilian chrysolite	yellow-green tourmaline resembling chrysolite
Brazilian emerald	green and transparent tourmaline resembling emerald
Brazilian peridot	honey yellow to green tourmaline resembling peridot
Brazilian ruby	transparent red tourmaline resembling ruby
Brazilian sapphire	transparent blue tourmaline resembling sapphire
Canary tourmaline	bright yellow tourmaline
Cat's eye tourmaline	chatoyant tourmaline in a variety of colors
Ceylon chrysolite	yellow-green tourmaline resembling chrysolite
Ceylon peridot	honey yellow tourmaline resembling peridot
Chameleonite	alexandrite-like tourmaline; color changes under different lighting conditions
Cromolite	green tourmaline, originally considered Cr-bearing tourmaline
Deuterolite	alexandrite-like tourmaline, probably a Cr-bearing dravite; color changes under different lighting conditions
Emeralite	emerald-green tourmaline
Indicolite	blue tourmaline, probably elbaite-schorl series
Iochroite	violet tourmaline
Moor's Head tourmaline	light-colored tourmaline with black top
Paraibaite	blue-green (neon blue) Cu-bearing elbaite, originally described from the Paraiba state of Brazil
Rubellite	pink or red tourmaline, probably elbaite
Siberian ruby	red tourmaline resembling ruby
Siberite	purple rubellite, probably elbaite
Verdelite	green tourmaline, probably elbaite-schorl series
Watermelon tourmaline	color-zoned tourmaline with pink interiors and green rims, generally elbaite

Sources of terms: Dietrich (1985)

## APPENDIX A5. OBSOLETE OR DISCREDITED TOURMALINE NAMES

Name	Additional information
Aluminobuergerite	Term for suggested end-member $\text{Na}_{1-x}\text{Al}_3\text{Al}_6(\text{BO}_3)_3\text{O}_{3-x}(\text{OH})_{1-x}$ or synthetic $\text{Na}_x\text{Al}_3\text{Al}_6(\text{BO}_3)_3\text{O}_3(\text{OH})$
Alumoelbaite	Elbaite
Chrome tourmaline	Green Cr-bearing tourmaline or chromdravite
Coronite	Dravite
Eicotourmaline	Tourmaline-like mineral without boron
Ferridravite	Povondraite
Ferroelbaite	Schorl
Ferroschorlite	Schorl
Gouverneurite	Dravite
Iochroite	Tourmaline
Jochroit	Tourmaline
Magnesioschorlite	Dravite
Magnodravite	Extremely Mg-rich uvite-like tourmaline
Mineral H	Ti-rich tourmaline from pegmatites
Oxytourmaline	Tourmaline with noteworthy replacement of O for (OH,F)
Pierrepontite	Schorl
Schorlite	Schorl
Schorlomite	Name mistakenly used for schorl; schorlomite is an accepted garnet group mineral
Taltalite	Mixture of tourmaline with Cu-ore or green tourmaline
Titanschorl (schörl)	Rutile
Titantourmaline	Ti-rich tourmaline
Titanturmaline	Ti-rich tourmaline
Tsilaisite	Mn-rich tourmaline, probably elbaite-schorl series
Zeuxite	Acicular tourmaline, $\text{Fe}^{3+}$ -rich tourmaline, green tourmaline

Sources of terms: Wang and Hsu (1966); Fleischer (1969); Chuchrov (1981); Dietrich (1985); Bayliss (2000)

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