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BOND-VALENCE CONSTRAINTS ON THE CHEMICAL COMPOSITION OF TOURMALINE

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Abstract

Bond-valence theory is used to examine the stability of possible end-member compositions for the tourmaline structure, with a focus on heterovalent-cation and -anion solid-solutions. Of particular importance in this regard are the O(1) and O(3) sites, the *V* and *W* anions in the general formula of tourmaline. The O(1) anion is coordinated by three *Y* cations, and hence the *local* occupancies of the *Y* and O(1) sites are constrained by the valence-sum rule. The O(3) anion is coordinated by one *Y* and two *Z* cations, and the *local* occupancy of the *Z* and O(3) sites is strongly constrained by the valence-sum rule. As the O(1) site can be occupied by O, OH and F, and the O(3) site can be occupied by O and OH, these constraints on local order dominate the behavior of heterovalent substitutions in the tourmaline structure. All possible local configurations around the O(1) and O(3) sites are examined for all possible heterovalent occupancies of these sites, and the *local* bond-valence arrangements (required by the valence-sum rule) are assessed. From these local bond-valence arrangements, the associated bond-lengths are calculated. Those bond lengths that are realistic for the cation–anion pairs involved in the bonds denote structures that are possibly stable; those bond lengths that are not realistic denote structures that cannot be stable. In this way, the stability (*i.e.*, existence) or non-stability of end-member tourmaline compositions is evaluated.

Keywords: tourmaline, bond-valence theory, stability, end member.

Sommaire

La théorie des valences de liaisons est utilisée pour un examen de la stabilité possible de pôles pour la structure de la tourmaline, avec une attention particulière sur les solutions solides impliquant des couples de cations et d'anions hétérovalents. D'importance primordiale à cet égard sont les sites O(1) et O(3), les anions appelés *V* et *W* dans la formule générale d'une tourmaline. L'anion O(1) est coordonné par trois cations *Y*, et donc les occupations *locales* des sites *Y* et O(1) sont limitées par la règle des sommes des valences. L'anion O(3) est coordonné par un cation *Y* et deux cations *Z*, et l'occupation *locale* des sites *Z* et O(3) est fortement régie par le même principe. Parce que le site O(1) peut contenir O, OH et F, et le site O(3) peut contenir O et OH, ces restrictions sur le degré d'ordre local exercent un contrôle prédominant sur les substitutions hétérovalentes dans la structure. Tous les agencements locaux possibles autour des sites O(1) et O(3) sont examinés pour tous les schémas possibles d'occupation hétérovalente de ces sites, et les arrangements *locaux* des valences de liaison (tels que requis selon la règle de la somme des valences) sont évalués. A partir de ces arrangements locaux, les longueurs de liaison associées sont calculées. Les longueurs qui sont réalistes pour les paires cation–anion impliquées dans ces liaisons indiquent les structures qui pourraient être stables; les longueurs considérées non réalistes sont celles appartenant aux structures qui ne peuvent pas être stables. De cette façon, la stabilité (c'est-à-dire, l'existence) ou l'instabilité de la composition de pôles de la famille de la tourmaline est évaluée.

(Traduit par la Rédaction)

Mots-clés: tourmaline, théorie des valences de liaison, stabilité, pôle.

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INTRODUCTION

The chemical formula of tourmaline may be written as

$$X\,Y_3\,Z_6\,[T_6O_{18}]\,[BO_3]_3\,V_3\,W$$

where X = Ca, Na, K, □ (vacancy)

Y = Li, Mg, Fe^{2+}, Mn^{2+}, Al, Cr^{3+}, V^{3+}, Fe^{3+}, (Ti^{4+})

Z = Mg, Al, Fe^{3+}, V^{3+}, Cr^{3+}

T = Si, Al, B

B = B, (□)

V = OH, O, (F)

W = OH, F, O

and where the species in parentheses are not yet proven to occur at these sites. If one permutes all possible site-occupancies, as indicated by the above formula, under the constraint of electroneutrality, one derives a large number of potential end-member compositions. However, only thirteen of these compositions are currently valid mineral species. This situation contrasts, for example, with the amphiboles, where a formula and structure of comparable complexity give rise to a far larger number of distinct minerals. Why is this so? This is a significant question as it challenges our knowledge of what factors affect the stability of a mineral.

CHEMICAL SUBSTITUTIONS IN THE TOURMALINE STRUCTURE

Chemical substitutions in mineral structures can be divided into two types: (1) homovalent, and (2) heterovalent. Homovalent substitutions are usually straightforward and commonly involve simple solid-solutions (*e.g.*, Mg $\rightleftharpoons$ Fe^{2+} in olivine) with rapid diffusion and exchange (*e.g.*, Mg–Fe^{2+} ordering in orthopyroxenes) and exsolution (*e.g.*, K $\rightleftharpoons$ Na in alkali feldspars). Heterovalent substitutions are more complicated. They occur in pairs (or more complex combinations) in order to maintain overall electroneutrality in the crystal, and the usually much greater range in the strength of chemical bonding of the active species constrains the response of a mineral to variations in temperature and pressure; they commonly involve complex solid-solutions with slow diffusion and exchange (*e.g.*, Mg $\rightleftharpoons$ Al and Si $\rightleftharpoons$ Al in amphiboles) and complex exsolution (*e.g.*, Ca $\rightleftharpoons$ Na and Al $\rightleftharpoons$ Si in plagioclase). Here, I will focus on heterovalent substitutions in tourmaline, as these are of primary importance in controlling the stability of the structure. In order to simplify the arguments, I will use the following site-constituents: X = □, Na, Ca; Y = Li, Mg, Al; Z = Mg, Al; T = Al, Si; V = OH, O; W = OH, O; Hawthorne (1996) has considered the factors affecting the (as yet) hypothetical □ $\rightleftharpoons$ B substitution in tourmaline.

END MEMBERS

Hawthorne & Henry (1999) have discussed the compositions of currently valid species of tourmaline (Table 1). Ignoring homovalent substitutions (see above), these end-members reduce to seven distinct arrangements of charges over the tourmaline structure: magnesiofoitite, rossmanite, dravite, olenite, elbaite, uvite and liddicoatite. There are two important characteristics of end-member compositions. First, they must have a fixed chemical composition. Second, they must show the maximum degree of order possible; only one site can contain more than one species. Thus elbaite is an end-member because the X, Z, T(1), T(2), O(1) and O(3) sites are completely ordered, and Y contains ($Li_{1.5}Al_{1.5}$) as required by the constraint of electroneutrality.

Potential end-member compositions with $T = Si_6$ are listed in Table 2. Only one composition has $V = (OH)_3$ and W = (OH); the other eleven compositions all have OH less than 4 *apfu* (atoms per formula unit). Potential end-members with $T = (Si,Al)_6$ are listed in Table 3; of the eight distinct compositions, four have less than 4 OH *pfu*. So in addition to the seven known heterovalent-distinct end-members of the tourmaline group, there are an additional twenty heterovalent-distinct potential end-members of the tourmaline group. How many of these compositions are crystal-chemically possible as tourmaline minerals?

TABLE 1. END-MEMBER COMPOSITIONS FOR CURRENTLY VALID TOURMALINE SPECIES

	X	*Y*	*Z*	*T*(1)	*T*(2)	O(3)	O(1)	[Ref.]
				***X*-site-vacant tourmalines**				
Magnesiofoitite	□	Mg_2Al	Al_6	(Si_6O_{18})	$(BO_3)_3$	$(OH)_3$	(OH)	[1]
Foitite	□	$Fe^{2+}{}_2Al$	Al_6	(Si_6O_{18})	$(BO_3)_3$	$(OH)_3$	(OH)	[2]
Rossmanite	□	$LiAl_2$	Al_6	(Si_6O_{18})	$(BO_3)_3$	$(OH)_3$	(OH)	[3]
				Alkali tourmalines				
Dravite	Na	Mg_3	Al_6	(Si_6O_{18})	$(BO_3)_3$	$(OH)_3$	(OH)	[4]
Schorl	Na	$Fe^{2+}{}_3$	Al_6	(Si_6O_{18})	$(BO_3)_3$	$(OH)_3$	(OH)	[4]
Chromdravite	Na	Mg_3	$Cr^{3+}{}_6$	(Si_6O_{18})	$(BO_3)_3$	$(OH)_3$	(OH)	[5]
Povondraite	Na	$Fe^{3+}{}_3$	$Fe^{3+}{}_4Mg_2$	(Si_6O_{18})	$(BO_3)_3$	$(OH)_3$	O	[6]
Buergerite	Na	$Fe^{3+}{}_3$	Al_6	(Si_6O_{18})	$(BO_3)_3$	O_3	F	[7]
Elbaite	Na	$Li_{1.5}Al_{1.5}$	Al_6	(Si_6O_{18})	$(BO_3)_3$	$(OH)_3$	(OH)	[4]
Olenite	Na	Al_3	Al_6	(Si_6O_{18})	$(BO_3)_3$	$O_2(OH)$	O	[8]
				Calcic tourmalines				
Uvite	Ca	Mg_3	Al_5Mg	(Si_6O_{18})	$(BO_3)_3$	$(OH)_3$	(OH)	[9]
Feruvite	Ca	$Fe^{2+}{}_3$	Al_5Mg	(Si_6O_{18})	$(BO_3)_3$	$(OH)_3$	(OH)	[10]
Liddicoatite	Ca	Li_2Al	Al_6	(Si_6O_{18})	$(BO_3)_3$	$(OH)_3$	F	[11]

References: [1] Hawthorne *et al.* (1999); [2] MacDonald *et al.* (1993); [3] Selway *et al.* (1998); [4] Dietrich (1985); [5] Rumyantseva *et al.* (1983); [6] Grice *et al.* (1993); [7] Donnay *et al.* (1966); [8] Sokolov *et al.* (1986); [9] Kunitz (1929); [10] Grice & Robinson (1989); [11] Dunn *et al.* (1977)

Bond-Valence Theory

Bond-valence theory was developed initially as an extension of Pauling's second rule, and the term *bond valence* has evolved as a measure of the strength of a chemical bond. On the basis of this approach, Brown (1981, 1992) and O'Keeffe (1989, 1990) have developed a simple yet coherent picture of chemical bonding in inorganic structures. A crystal is considered as an array of atoms connected by a network of chemical bonds. For oxysalt minerals, any path through this network consists of alternating cations and anions, and the total network is subject to the law of electroneutrality: the total valence of the cations is equal to the total valence of the anions. Bond valence, *s*, can be calculated from the curves of Brown & Shannon (1973) and Brown & Altermatt (1985) if the bond lengths are known, and can be estimated from Pauling's second rule if only the topology of the bond network is known. The valence-sum rule states that the sum of the bond valences incident at each atom is (approximately) equal to the magnitude of the formal valence of that atom: $\Sigma s(0) \approx |Z^o|$. Bond-valence considerations are usually applied to long-range aspects of structure. However, this is not an intrinsic restriction of this approach. Bond-valence arguments may be used to characterize short-range order (SRO) (Hawthorne 1997) in much the same way as it has been used to characterize long-range order (LRO), with the exception that the true interatomic distances are not known, and hence local bond-valences must be approximated where long-range disorder is present. This is done in the following way. The total bond-valence incident at an anion is known ideally (from the valence-matching principle). For a specific local arrangement of coordinating cations, bond valences are assigned such that the ratio of the individual values is the ratio of the formal charges of the cations, and the sum of the bond valences is equal to the ideal bond-valence incident at the anion. The corresponding bond-lengths can then be calculated from the curves of Brown (1981). Significant error could be introduced into this procedure if one or more of the anions in the tourmaline structure deviates significantly from the valence-sum rule. Such deviations are fairly common in rock-forming minerals; typical examples are the O(2) anion in monoclinic pyroxenes (*e.g.*, 1.79 valence units, *vu*, in diopside) and the O(4) anion in monoclinic amphiboles (*e.g.*, 1.84 *vu* in tremolite). However, tourmaline does not show such large deviations at the divalent anion sites. Hawthorne *et al.* (1993) and MacDonald & Hawthorne (1995) listed the following incident bond-valence sums at the divalent-anion sites: O(2) 2.01, 2.01; O(4) 2.05, 2.06; O(5) 1.97, 1.99; O(6) 1.98, 1.98; O(7) 1.99, 1.99; O(8) 1.99, 1.99 *vu*. Hence for the tourmaline structure, the valence-sum rule is obeyed very closely at the divalent-anion sites, and the accuracy of the arguments given here should not be affected significantly by deviations from the valence-sum rule.

TABLE 2. POTENTIAL END-MEMBER COMPOSITIONS OF TOURMALINE FOR $Y = (Li,Mg,Al)_3$ AND $T(1) = Si_6$

	X	*Y*	*Z*	*T*	*B*	O(3)	O(1)
				X-site vacant tourmalines			
[2.1]	□	$MgAl_2$	Al_6	(Si_6O_{18})	$(BO_3)_3$	$(OH)_3$	O
[2.1a]	□	Al_3	Al_5Mg	(Si_6O_{18})	$(BO_3)_3$	$(OH)_3$	O
[2.2]	□	$Li_{0.5}Al_{2.5}$	Al_6	(Si_6O_{18})	$(BO_3)_3$	$(OH)_3$	O
[2.3]	□	Al_3	Al_6	(Si_6O_{18})	$(BO_3)_3$	$O_2(OH)$	(OH)
[2.4]	□	Al_3	Al_6	(Si_6O_{18})	$(BO_3)_3$	$(OH)_2O$	O
				Alkali tourmalines			
[2.5]	Na	Mg_2Al	Al_6	(Si_6O_{18})	$(BO_3)_3$	$(OH)_3$	O
[2.5a]	Na	Al_3	Al_4Mg_2	(Si_6O_{18})	$(BO_3)_3$	$(OH)_3$	O
[2.6]	Na	$LiAl_2$	Al_6	(Si_6O_{18})	$(BO_3)_3$	$(OH)_3$	O
[2.7]	Na	Al_3	Al_6	(Si_6O_{18})	$(BO_3)_3$	O_3	(OH)
				Calcic tourmalines			
[2.8]	Ca	$LiMg_2$	Al_6	(Si_6O_{18})	$(BO_3)_3$	$(OH)_3)$	(OH)
[2.9]	Ca	Mg_3	Al_6	(Si_6O_{18})	$(BO_3)_3$	$(OH)_3$	O
[2.9a]	Ca	Al_3	Al_3Mg_3	(Si_6O_{18})	$(BO_3)_3$	$(OH)_3$	O
[2.10]	Ca	$Li_{1.5}Al_{1.5}$	Al_6	(Si_6O_{18})	$(BO_3)_3$	$(OH)_3$	O
[2.11]	Ca	$MgAl_2$	Al_6	(Si_6O_{18})	$(BO_3)_3$	O_3	(OH)
[2.11a]	Ca	Al_3	Al_5Mg	(Si_6O_{18})	$(BO_3)_3$	O_3	(OH)
[2.12]	Ca	Al_3	Al_6	(Si_6O_{18})	$(BO_3)_3$	O_3	O

Bond Valence and the Tourmaline Structure

The bond-valence table for a sample of dravite is shown in Table 4. One of the important aspects of a bond-valence table (which is not apparent from a table of bond lengths) is the coordination of the anions. Inspection of Table 4 shows that the O(2), O(4), O(5), O(6), O(7) and O(8) anions link to at least one *T* or *B* cation. As the typical *T*–O and *B*–O bond-valences are ~1 *vu*, and the O(2), O(4), O(5), O(6), O(7) and O(8) anions also bond strongly to *X*, *Y* and *Z* cations, these anion sites cannot be occupied by monovalent anions. This is not the case for the O(1) and O(3) sites. As discussed by Hawthorne (1996), both the O(1) and O(3)

TABLE 3. POTENTIAL END-MEMBER COMPOSITIONS OF TOURMALINE INVOLVING Al AT THE *T* SITE

	X	*Y*	*Z*	*T*	*B*	O(3)	O(1)
				***X*-site-vacant tourmalines**			
[3.1]	□	Al_3	Al_6	$(Si_4Al_2O_{18})$	$(BO_3)_3$	$(OH)_3$	(OH)
[3.2]	□	Al_3	Al_6	(Si_5AlO_{18})	$(BO_3)_3$	$(OH)_3$	O
				Alkali tourmalines			
[3.3]	Na	Al_3	Al_6	$(Si_3Al_3O_{18})$	$(BO_3)_3$	$(OH)_3$	OH
[3.4]	Na	Al_3	Al_6	$(Si_4Al_2O_{18})$	$(BO_3)_3$	$(OH)_3$	O
				Calcic tourmalines			
[3.5]	Ca	Al_3	Al_6	$(Si_2Al_4O_{18})$	$(BO_3)_3$	$(OH)_3$	(OH)
[3.6]	Ca	Al_3	Al_6	$(Si_3Al_3O_{18})$	$(BO_3)_3$	$(OH)_3$	O
[3.7]	Ca	Al_3	Al_6	(Si_5AlO_{18})	$(BO_3)_3$	O_3	(OH)

sites can be occupied by both monovalent and divalent anions. Inspection of Table 4 shows that the O(1) anion is coordinated by three *Y* cations. Hence the occupancies of the *Y* and O(1) sites are strongly constrained by the valence-sum rule. The O(3) site is surrounded by one *Y* and two *Z* sites (Table 4): $Y + 2Z$; hence the occupancies of *Y*, *Z* and O(3) are also strongly constrained by the valence-sum rule. Although all site-occupancies are constrained by the valence-sum rule to some extent, the O(1) and O(3) sites are particularly important in this regard as they are not coordinated by cations at the *T* or *B* sites, and hence have much greater potential variability in the possible arrangements of incident bond-valences.

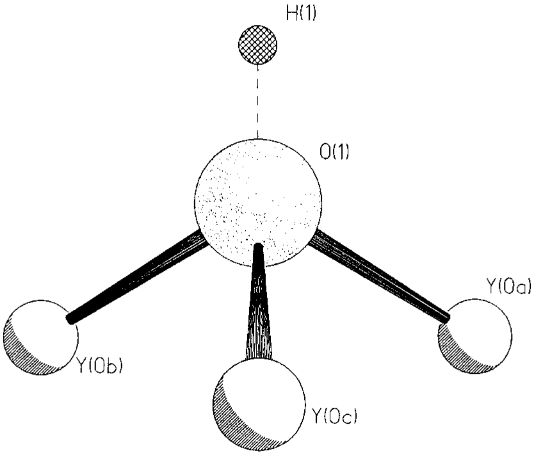

FIG. 1. The local environment of the O(1) oxygen atom (random-dot-shaded circle); O(1) is linked to three *Y* cations (highlighted circle), and the H(1) site is occupied where O(1) = OH.

TABLE 4. EMPIRICAL BOND-VALENCES IN DRAVITE (HAWTHORNE *et al.* 1993)

	X	*Y*	*Z*	*T*	B	Σ
O(1)		0.481$^{\times3}$→				1.443
O(2)	0.134$^{\times3}$↓	0.429$^{\times2}$↓→			1.018	2.010
O(3)		0.331	0.405$^{\times2}$→			1.141
O(4)	0.076$^{\times3}$↓			0.989$^{\times2}$→		2.054
O(5)	0.089$^{\times3}$↓			0.941$^{\times2}$→		1.971
O(6)		0.442$^{\times2}$↓	0.49	1.043		1.975
O(7)			0.444 0.497	1.046		1.987
O(8)			0.473 0.507		1.009	1.989
Σ	0.897	2.554	2.816	4.019	3.036	
Σ*	(0.846)	(2.542)	(2.847)			

* sum of charge at site from unit formula

Coordination of the O(1) site

The O(1) site occurs on the three-fold axis passing through the origin of the unit cell, and is surrounded by three *Y* sites (Fig. 1). The three O(1)–*Y* bonds are crystallographically (*i.e.*, long-range) equivalent, and must satisfy the bond-valence requirements of the O(1) anion. From a long-range perspective, there are two distinct situations: (1) where O(1) = OH or F, the O(1)–*Y* bond has a bond valence, *s*, of ~0.33 *vu*; (2) where O(1) = O^{2-}, the O(1)–Y bond has a bond valence of ~0.67 *vu*. Where the *Y* site has mixed occupancy (*e.g.*, Mg, Al), the three *Y* cations surrounding any specific O(1) anion are not necessarily the same species, and the local O(1)–*Y* bonds may be of very different lengths and bond valence. However, the valence-sum rule must still hold locally, and hence there is a local constraint on occupancies of the O(1) and three *Y* sites. As the bulk (*i.e.*, long-range) situation is the sum of the local (*i.e.*, short-range) situations, these local constraints must be reflected in the bulk characteristics of the crystal.

Where O(1) = F, $\sum_{i=1}^{3} s_i\,[\mathrm{O}(1) - Y]$ is 1.0 *vu*; where O(1) = O^{2-}, the incident bond-valence sum is 2.0 *vu*. However, where O(1) = OH, the situation is somewhat more complicated: the sum of the incident bond-valence can vary between a lower limit of 1.0 *vu* and an upper limit that is defined by the strength of any hydrogen bond formed. From the infrared spectra of many tourmalines (Robert *et al.* 1997), it is clear that the principal OH-stretching frequency of OH at O(1) is higher than that of OH at O(3). Although there is (as yet) no well-developed relation between principal OH-stretching frequency and the bond-valence of the associated hydrogen-bond, one can estimate an upper limit to the strength of any hydrogen bond involving OH at O(1), and hence to the bond-valence incident at O(1) from the *Y* cations. As shown below, the bond valence incident at O(3) [not including any contribution from H(3)] is ~1.15 *vu*. As the principal stretching frequency of the O(3)–H bond is lower than that of the O(1)–H(1) bond, the bond valence incident at O(1) [not including any contribution from H(1)] must lie between 1.0 and 1.15 *vu*. The value 1.05 *vu* will be used here; minor variations in this value do not materially affect the values calculated or the resultant conclusions.

For specific occupancies of the O(1) site, possible bond-valences for the associated O(1)–*Y* bonds can be proposed according to the valence-sum rule. The bond lengths corresponding to these specific bond-valences and a particular set of cation occupancies of the *Y* sites can be calculated from the bond-valence curves of Brown & Shannon (1973) and Brown & Altermatt (1985). If the calculated bond-lengths fall within the range of observed bond-lengths for that specific cation–anion pair, then that local arrangement is possible. If the calculated bond-lengths do not fall within the range of observed bond-lengths, then the local arrangement is not possible. These values are calculated for occupancy of the O(1) site by OH, F and O^{2-}, and occupancy of the *Y* site by Li, Mg and Al; the results are listed in Table 5, together with an evaluation of the stability of each arrangement (*i.e.*, *yes* or *no*) from the perspective of bond-valence theory and stereochemistry. This evaluation is, in some cases, somewhat speculative, as the limits of stability of specific bonds are not known. Where the examples are extreme, there is no problem: thus one does not expect an $^{[6]}$Al–O distance of 1.70 Å. Where the examples are less extreme, it is less easy to evaluate the probable stability (occurrence) of such a configuration: thus an $^{[6]}$Al–O distance of 1.75 Å may not be stable, but this evaluation is less definite than that for an $^{[6]}$Al–O distance of 1.70 Å. However, this is not a major setback; arrangements involving bond lengths at the extreme range of their distribution will be energetically unfavorable relative to arrangements with more common bond-lengths, and thus one still has a basis for assessing the relative likelihood of local arrangements.

TABLE 5. LOCAL CATION AND BOND-VALENCE ARRANGEMENTS (*vu*) AND PREDICTED LOCAL BOND LENGTHS (Å) AROUND THE O(1) SITE IN THE TOURMALINE STRUCTURE

	Anion	Bond-valence sum at O(1)	3*Y*	Bond valences at O(1)	*Y*–(OH,O)		*Y*–F		Stable
(1.1)	OH, F	1.00	3Mg	0.33 x 3	Mg: 2.10	–	Mg: 1.98	–	yes
	OH, F	1.05	3Mg	0.35 x 3	Mg: 2.07	–	Mg: 1.96	–	yes
(1.2)	OH, F	1.00	2Mg + Al	0.28 x 2 + 0.44	Mg: 2.18	Al: 1.96	Mg: 2.06	Al: 1.86	yes
	OH, F	1.05	2Mg + Al	0.30 x 2 + 0.45	Mg: 2.15	Al: 1.95	Mg: 2.03	Al: 1.85	yes
(1.3)	OH, F	1.00	Mg + 2Al	0.25 + 0.38 x 2	Mg: 2.24	Al: 2.03	Mg: 2.12	Al: 1.92	no
	OH, F	1.05	Mg + 2Al	0.26 + 0.39 x 2	Mg: 2.22	Al: 2.02	Mg: 2.10	Al: 1.91	no
(1.4)	OH, F	1.00	3Al	0.33 x 3	–	Al: 2.10	–	Al: 1.98	no
	OH, F	1.05	3Al	0.35 x 3	–	Al: 2.07	–	Al: 1.96	no
(2.1)	O	2.00	3Al	0.67 x 3	Al: 1.78	–	Al: 1.68	–	yes
(2.2)	O	2.00	2Al + Mg	0.75 x 2 + 0.50	Al: 1.73	Mg: 1.91	Al: 1.64	Mg: 1.80	yes
(2.3)	O	2.00	Al + 2Mg	0.86 + 0.57 x 2	Al: 1.68	Mg: 1.85	Al: 1.59	Mg: 1.75	no
(2.4)	O	2.00	3Mg	0.67 x 3	–	Mg: 1.78	–	Mg: 1.68	no
(3.1)	OH, F	1.00	3Li	0.33 x 3	–	Li: 1.81	–	Li: 1.71	no
	OH, F	1.05	3Li	0.35 x 3	–	Li: 1.78	–	Li: 1.69	no
(3.2)	OH, F	1.00	2Al + Li	0.43 x 2 + 0.14	Al: 1.97	Li: 2.24	Al: 1.87	Li: 2.13	yes
	OH, F	1.05	2Al + Li	0.45 x 2 + 0.15	Al: 1.95	Li: 2.20	Al: 1.81	Li: 2.09	yes
(3.3)	OH, F	1.00	Al + 2Li	0.60 + 0.20 x 2	Al: 1.83	Li: 2.05	Al: 1.73	Li: 1.95	yes
	OH, F	1.05	Al + 2Li	0.63 + 0.21 x 2	Al: 1.81	Li: 2.02	Al: 1.67	Li: 1.92	yes
(3.4)	OH, F	1.00	3Al	0.33 x 3	Al: 2.10	–	Al: 1.98	–	no
	OH, F	1.05	3Al	0.35 x 3	Al: 2.07	–	Al: 1.96	–	no
(4.1)	O	2.00	3Li	0.67 x 3	–	Li: 1.52	–	Li: 1.43	no
(4.2)	O	2.00	2Al + Li	0.80 x 2 + 0.40	Al: 1.71	Li: 1.73	Al: 1.61	Li: 1.63	no
(4.3)	O	2.00	Al + 2Li	1.20 + 0.40 x 2	Al: 1.55	Li: 1.73	Al: 1.47	Li: 1.63	no
(4.4)	O	2.00	3Al	0.67 x 3	Al: 1.78	–	Al: 1.68	–	yes
(5.1)	OH, F	1.00	3Li	0.33 x 3	–	Li: 1.81	–	Li: 1.71	no
	OH, F	1.05	3Li	0.35 x 3	–	Li: 1.78	–	Li: 1.69	no
(5.2)	OH, F	1.00	Mg + 2Li	0.50 + 0.25 x 2	Mg: 1.91	Li: 1.94	Mg: 1.80	Li: 1.84	yes
	OH, F	1.05	Mg + 2Li	0.53 + 0.26 x 2	Mg: 1.88	Li: 1.92	Mg: 1.78	Li: 1.82	yes
(5.3)	OH, F	1.00	2Mg + Li	0.40 x 2 + 0.20	Mg: 2.01	Li: 2.05	Mg: 1.90	Li: 1.95	yes
	OH, F	1.05	2Mg + Li	0.42 x 2 + 0.21	Mg: 1.99	Li: 2.02	Mg: 1.88	Li: 1.92	yes
(5.4)	OH, F	1.00	3Mg	0.33 x 3	Mg: 2.10	–	Mg: 1.98	–	yes
	OH, F	1.05	3Mg	0.35 x 3	Mg: 2.07	–	Mg: 1.96	–	yes

Coordination of the O(3) site

The O(3) site is coordinated by one *Y* cation and two *Z* cations, the four sites forming a triangular pyramidal arrangement (Fig. 2). Although the local arrangement is similar to that of the O(1) site, there are some important differences: (1) the bond-valence constraints around the *Z* site are different from those around the *Y* site; (2) the strength of the hydrogen bond involving OH at O(3) is stronger than the strength of the hydrogen bond involving OH at O(1). In regard to the first point, it is useful to inspect the bond-valence pattern shown in Table 4. The O(7) and O(8) anions are coordinated by $2Z + T$ and $2Z + B$ cations, respectively. The *T*–O and *B*–O bond valences are ~1.0 *vu*, and hence the incident bond-valence from the two *Z* cations has to sum to ~1.0 *vu*. In regard to the second point, the hydrogen bonding to O(5) requires that the sum of the bond valence incident at O(3) from the *Y* and *Z* cations must significantly exceed 1.0 *vu*; hence F cannot occur at the O(3) site. Following the discussion of the O(1) site, the range of incident bond-valence at O(3) is estimated at 1.15 *vu*. Following the same procedure as for the O(1) site, the bond-valence, bond-length and cation arrangements around O(3) are shown in Table 6, together with evaluations of their probable stability.

IS THERE Al–Mg ORDER–DISORDER OVER THE *Y* AND *Z* SITES?

Consider composition [2.1] in Table 2; this has $Y = Mg_2Al$ and $Z = Al_6$ *apfu*. In principle, Mg could occur also at the *Z* site, producing the arrangement $Y = Al_3$, $Z = Al_5Mg$ for the same chemical composition. Thus there is the potential for an order–disorder series for this chemical composition, represented by the exchange ${}^{Y}Al + {}^{Z}Mg \rightleftharpoons {}^{Y}Mg + {}^{Z}Al$. Does this type of variation in order occur in tourmaline? Yes, it does. Hawthorne *et al.* (1993) showed that Al and Mg occur at both the *Y* and *Z* sites in several refined structures of tourmaline. Taylor *et al.* (1995) showed that disorder of Al and Mg over the *Y* and *Z* sites in a calcic tourmaline occurs in tandem with significant O^{2-} at the O(1) site. Hawthorne (1996) suggested that the occurrence of O^{2-} at O(1) is associated with Al–Mg disorder over the *Y* and *Z* sites. Extending this argument to chemical compositions such as [2.1] and [2.11] (Table 2) produces two different possible *ordered* arrangements for the same chemical composition, *i.e.*, two distinct end-member structural arrangements. These are listed in Table 2 as arrangements [2.xa], where [2.x] corresponds to compositions in which the *Y* site contains two cations, and [2.xa] corresponds to compositions in which the *Z* site contains two cations.

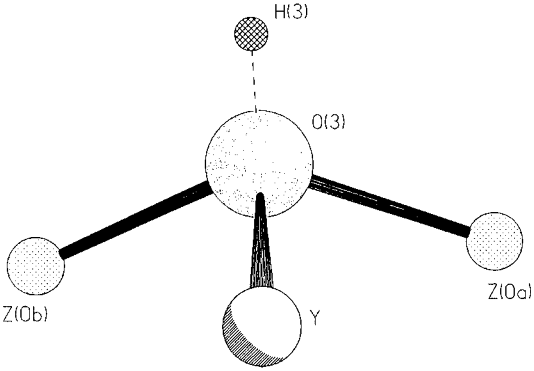

FIG. 2. The local environment of the O(3) oxygen atom (random-dot-shaded circle); two *Z* cations (regular-dot-shaded circle) and a *Y* cation (highlighted circle) bond to one side of O(3), and the *H*(3) site is occupied where O(3) = OH.

IS THERE Al–Li DISORDER OVER THE *Y* AND *Z* SITES?

Although it has not been suggested that Li occurs at the *Z* site in tourmaline, it is just as well to formally examine the bond-valence implications of that possibility. Of particular interest in this regard are the O(7) and O(8) anions. As noted above, the O(7) and O(8) anions receive ~1 *vu* from the *T* and *B* cations, respectively, and hence they each need to receive ~1 *vu* from the two coordinating *Z* cations. If Li were to occur at one of the two coordinating *Z* sites (the other being occupied by Al), the resulting bond-valences required for satisfaction of the valence-sum principle are 0.25 (Li) + 0.75 (Al). These bond valences correspond to Li–O = 1.938 Å and Al–O = 1.937 Å. The value for Al–O is reasonable, but the value for Li–O is far too short, and hence one can conclude that Li cannot occur at the *Z* site.

STABILITY OF POTENTIAL END-MEMBERS OF THE TOURMALINE GROUP

It is now possible to calculate whether the potential end-members listed in Tables 2 and 3 are intrinsically unstable or not, based on bond-valence criteria.

Tourmaline with $T = Si_6$

X-site vacant tourmaline: Composition [2.1] (Table 2) has arrangement (2.2) (Table 5) around O(1), and arrangement {2.3} (Table 6) around O(3); the calculated bond-lengths seem reasonable for Mg–O and Al–O bonds, and this composition should be stable from a bond-valence perspective. Composition [2.1a] (Table 2) has arrangement (2.1) (Table 5) around O(1) and arrangement {2.2} (Table 6) around O(3); the calculated distances seem at the lower end of allowable Mg–O and Al–O distances, and thus the composition and arrangement should be stable. Composition [2.2] is

TABLE 6. LOCAL CATION AND BOND-VALENCE ARRANGEMENTS (*vu*) AND BOND LENGTHS (Å) AROUND THE O(3) SITE IN THE TOURMALINE STRUCTURE

		Y + 2*Z*	Bond-valence at O(3)	Σ O(3)	*Y*–(OH,O)	*Z*–(OH,O)		Stable
{1.1}	OH, F	Li + 2Al	0.17 + 0.49 x 2	1.15	Li–O: 2.13	Al–O: 1.92		yes
{1.2}	OH, F	Mg + 2 Al	0.23 + 0.46 x 2	1.15	Mg–O: 2.28	Al–O: 1.94		yes
{1.3}	OH, F	Al + 2Al	0.38 + 0.38 x 2	1.15	Al–O: 2.03	Al–O: 2.03		yes
{2.1}	O	Li + 2Al	0.29 + 0.86 x 2	2.00	Li–O: 1.87	Al–O: 1.68		no
{2.2}	O	Mg + 2Al	0.50 + 0.75 x 2	2.00	Mg–O: 1.91	Al–O: 1.73		no
{2.3}	O	Al + 2 Al	0.67 + 0.67 x 2	2.00	Al–O: 1.78	Al–O: 1.78		yes
{3.1}	OH, F	Al + Mg + Al	0.46 + 0.23 + 0.46	1.15	Al–O: 1.94	Mg–O: 2.28	Al–O: 1.94	yes
{3.2}	OH, F	Al + 2Mg	0.49 + 0.33 x 2	1.15	Al–O: 1.92	Mg–O: 2.10		yes
{3.3}	OH, F	Mg + Mg + Al	0.33 + 0.33 + 0.49	1.15	Mg–O: 2.10	Mg–O: 2.10	Al–O: 1.92	yes
{3.4}	OH, F	Li + Mg + Al	0.19 + 0.38 + 0.57	1.15	Li–O: 2.07	Mg–O: 2.03	Al–O: 1.85	yes
{3.5}	OH, F	Li + 2Mg	0.23 + 0.46 x 2	1.15	Li–O: 1.98	Mg–O: 1.94		no
{4.1}	O	Al + 2Al	0.67 + 0.67 x 2	2.00	Al–O: 1.78	Al–O: 1.78		yes
{4.2}	O	Al + Mg + Al	0.75 + 0.50 + 0.75	2.00	Al–O: 1.73	Mg–O: 1.91	Al–O: 1.73	yes

forced to have some Li present at *Y*, coordinating O^{2-} at O(1). As indicated by arrangements (4.1) and (4.2), the required bond-lengths are not chemically reasonable; the Al–O and Li–O distances are much shorter than observed in real structures, and hence end-member composition [2.2] is not stable. Composition [2.3] is not stable, as arrangement (1.4) requires chemically unreasonable Al–O distances. Composition [2.4] has a stable arrangement (2.1) around O^{2-} at the O(1) site, and has a disordered occupancy of the O(3) site. Where O(3) is occupied by O^{2-} or OH, it is coordinated to three atoms of Al (*i.e.*, *Y* = Al, 2*Z* = 2Al).

Alkali tourmaline: Composition [2.5] has arrangement (2.3) (Table 5) around O(1) and arrangement {2.1} (Table 6) around O(3), and is thus unlikely to be stable. Composition [2.5a] has arrangement (2.4) around O(1) and {2.2} around O(3), and this also is unlikely to be stable. Composition [2.6] has arrangement (4.2) around O(1) and will not be stable. Composition [2.7] has arrangement (1.4) around O(1) and thus will not be stable. However, note that if composition [2.7] is modified such that O(3) = $O_2(OH)$ and O(1) = O, the olenite structure is obtained.

Calcic tourmaline: Composition [2.8] has arrangement (5.3) around O(1) and arrangement {2.3} around O(3), and hence is stable. Composition [2.9] has arrangement (2.4) around O(1) and hence is unstable; composition [2.9a] has arrangement {2.1} around O(1) and arrangement {3.1} around O(3), and hence is stable. Composition [2.10] has arrangements (4.2) and (4.3) around O(1) and hence is not stable. Composition [2.11] has arrangement (1.3) around O(1) and hence is not stable; composition [2.11a] has arrangement (1.4) around O(1), and also is not stable. Composition [2.12] has arrangement (2.1) around O(1) and arrangement {4.1} around O(3), and hence seems stable from a bond-valence perspective; it is notable that this is the only tourmaline composition that could be H-free.

TABLE 7. EMPIRICAL BOND-VALENCES IN UVITE T78 OF MACDONALD & HAWTHORNE (1995)

	X	*Y*	*Z*	*T*	*B*	Σ
O(1)*		$0.309^{\times3}\downarrow$				0.927
O(2)	$0.238^{\times3}\downarrow$	$0.377^{\times2}\downarrow\rightarrow$			1.018	2.010
O(3)		0.309	$0.420^{\times2}\rightarrow$			1.149
O(4)	$0.122^{\times3}\downarrow$			$0.967^{\times2}\rightarrow$		2.056
O(5)	$0.146^{\times3}\downarrow$			$0.920^{\times2}\rightarrow$		1.986
O(6)		$0.395^{\times2}\downarrow$	0.546	1.043		1.984
O(7)			0.451 0.514	1.027		1.992
O(8)			0.476 0.518		$1.000^{\times2}\downarrow$	1.994
Σ	1.518	2.162	2.925	3.957	3.018	
Σ**	(1.750)	(2.046)	(2.933)	(3.919)	(3.000)	

* O(1) = 0.81 F + 0.19 (OH)

Tourmaline with T = (Si,Al)

MacDonald & Hawthorne (1995) showed that there can be significant (>0.20 *apfu*) Al at the *T* site in tourmaline. A bond-valence table for their most $^{[4]}$Al-rich structure is given in Table 7. The anions directly affected by local replacement of Si by Al are O(4), O(5), O(6) and O(7), which will receive ~0.75 *vu* each instead of the usual ~1.00 *vu*. It is immediately apparent why the $^{[4]}Al \rightleftharpoons Si$ substitution occurs primarily in calcic tourmaline. The bond valence incident at O(4) and O(5) is

~0.75 + 1.00 ≡ 1.75 *vu*, requiring ~0.25 vu to be contributed from the *X* cation. Where *X* = Ca, the resultant bond-valence is ~2/9 = 0.22 vu, as required, although the fact that the *X*–O(2) distance is usually much less than the *X*–O(4) and *X*–O(5) distances suggests that the local *X*–O(4) and *X*–O(5) distances may result in bond-valence contributions somewhat less than ideal. Nonetheless, this argument provides the reason for more extensive $^{[4]}$Al $\rightleftharpoons$ Si substitution in calcic tourmaline than in alkali and *X*-site-vacant tourmalines.

The situation *vis-à-vis* short-range bond-valence requirements is somewhat more complicated for the O(6) and O(7) anions. These anions each bond to one *T* cation, and (*Y* + *Z*) and (2*Z*) cations, respectively. Where *T* = Al, this cation will contribute ~0.75 *vu* to both O(6) and O(7). Inspection of bond-valence tables for many tourmaline structures shows that the bond valences contributed to O(6) and O(7) average ~1.05 *vu*; accordingly, I assume that, where *T* = Al, the *T* cation will contribute ~0.80 *vu* to both the O(6) and O(7) anions. With these preliminary considerations settled, I will now examine the potential end-member compositions listed in Table 3.

X-site-vacant tourmaline: Composition [3.1] has arrangement (1.4) around O(1), and hence is not stable. Composition [3.2] has arrangement (2.1) around O(1) and arrangement {2.3} around O(3), and both of these arrangements are stable from a bond-valence perspective. However, one also needs to examine the situation with regard to the O(4) and O(5) anions. As noted above, Al and Si at the two adjacent *T* sites contribute ~1.70 *vu* to each of these anions, leaving ~0.30 *vu* to be contributed by the *X* cation. If *X* = □, this situation is obviously not feasible, and hence $^{[4]}$Al will not occur in *X*-site-vacant tourmaline. Thus composition {3.4} is not stable.

Alkali tourmaline: Composition [3.3] has arrangement (1.4) around O(1), and hence is not stable. Composition [3.4] has arrangement (2.1) around O(1) and arrangement {2.3} around O(3), and both of these arrangements are stable from a bond-valence perspective. However, as before, one now needs to consider the arrangements around O(4) and O(5). These anions receive a contribution of ~1.70 *vu* from the bonded *T* cations, requiring ~0.30 *vu* from the *X* cation. The *X*-site is [9]-coordinated, and the *X*–O(4) and *X*–O(5) bonds are significantly longer than the *X*–O(2) bond; thus the bond valence associated with the *X*–O(4) and *X*–O(5) bonds for *X* = Na are less than 1/9 = 0.11 *vu*. Hence significant $^{[4]}$Al $\rightleftharpoons$ Si substitution is not expected to be a common feature in alkali tourmaline, as this would decrease the bond-valence incident at the O(4) and O(5) sites.

Calcic tourmaline: Composition [3.5] has arrangement (1.4) around O(1) and hence is not stable. Composition [3.6] has arrangement (2.1) around O(1) and arrangement {2.3} around O(3), and both of these arrangements are stable from a bond-valence perspective. The O(4) and O(5) anions receive ~1.70 *vu* from the *T* cations, and can be satisfied by Ca at the *X*-site. Each of the O(6) and O(7) cations receives ~0.80 *vu* from Al at the *T* site. The relevant bond-valences and bond lengths about these anions are 0.60 *vu* and Al–O = 1.827 Å. These are reasonable, and composition [3.6] is reasonable from a bond-valence perspective. However, there could be stereochemical problems linking the structure together as the [T_6O_{18}] ring is large (T_6 = Si_3Al_3) and the cluster of octahedra [Al_3] is small, and hence this arrangement may not be stable for reasons other than short-range bond-valence requirements. Composition [3.7] has arrangement (1.4) around O(1) and hence is not stable.

STABILITY OF POTENTIAL NEW SPECIES OF TOURMALINE

Just because an end-member composition is not stable for reasons of local bond-valence does not necessarily mean that the species is not stable for cases where the end-member composition involves more than one cation at one of the sites in the structure. This possibility arises because the range of possible chemical compositions of a specific species may allow a complete set of stable short-range-ordered configurations, whereas the end-member composition may not be compatible with the requirements of short-range order.

Consider the composition given below:

$$(Na_{0.6}\square_{0.4})\ (Li_{0.8}Al_{2.2})\ (Al_{5.6}Mg_{0.4})\ (Si_6O_{18})$$
$$(BO_3)_3\ (OH)_3\ O_{0.6}\ (OH)_{0.4}$$

The contents of the *Y* site, ($Li_{0.8}Al_{2.2}$), can be written as $(Li_2Al)_{0.4}$ + $(Al_3)_{0.6}$. If the former is associated with $(OH)_{0.4}$ at the *W* site and the latter is associated with $O_{0.6}$ at the *W* site, then these local arrangements [(3.3) and (4.4) in Table 5] are stable. Hence this composition should be stable. The end member corresponding to this composition is Na ($LiAl_2$) Al_6 (Si_6O_{18}) $(BO_3)_3$ $(OH)_3$ O. This is composition [2.6] of Table 2; this end-member composition is not stable as it requires ($LiAl_2$) coordinating O at the *W* site [*i.e.*, arrangement (4.2) of Table 5], but compositions within the compositional field associated with this end member may be stable. Thus, even though an end-member may not be stable from the viewpoint of local bond-valence requirements, this does not necessarily mean that compositions within the compositional field analogous to the end-member are not stable.

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