

STRUCTURAL MECHANISMS FOR LIGHT-ELEMENT VARIATIONS IN TOURMALINE

FRANK C. HAWTHORNE*

CNR Centro di Studio per la Cristallografia e la Cristallografia, via Abbiategrosso, 209, I-27100 Pavia, Italy

ABSTRACT

It is now well known that Si, B and OH + F are variable components of tourmaline, and yet the stereochemical details of their variation in the tourmaline structure are still not well characterized or understood. Application of the valence-sum rule of bond-valence theory to questions of *short-range* atomic arrangements shows that there are considerable stereochemical constraints associated with the variation of Si, B and OH + F in the tourmaline structure. The occurrence of a trivalent cation (Al, B) at the *T* site must be *locally* associated with the occurrence of trivalent cations (Al, Fe³⁺) at the neighboring *Y* and *Z* sites, and possibly with Ca at the neighboring *X* site. In Li-free tourmaline, the occurrence of O²⁻ at O(1) (*i.e.*, OH + F < 4 *apfu*) must be locally associated with 3Al or 2Al + Mg (or the Fe²⁺-Fe³⁺ analogues) at the adjacent 3*Y* sites in order for the valence-sum rule to be satisfied on a local scale. In Li-bearing Mg-free tourmaline, O²⁻ at O(1) must be locally associated with 3Al at the adjacent 3*Y* sites. These requirements provide stringent constraints on the possible substitution schemes whereby additional O²⁻ (*i.e.*, a deficiency in OH + F) is incorporated into tourmaline.

Keywords: tourmaline, ordering, short-range order, chemical substitutions, bond-valence.

SOMMAIRE

Il est maintenant bien établi que Si, B et OH + F sont des composants variables de la tourmaline, quoique les détails stéréochimiques de leur variation dans la structure ne sont pas encore bien documentés ou compris. L'application de la règle d'additivité des valences de liaison aux questions de mise en ordre des atomes à courte échelle montre qu'il y a des contraintes stéréochimiques considérables associées aux variations des teneurs en Si, B et OH + F dans la structure de la tourmaline. La présence d'un cation trivalent (Al, B) au site *T* doit nécessairement engendrer la présence locale de cations trivalents (Al, Fe³⁺) aux sites *Y* et *Z* adjacents, et peut-être de Ca dans les sites *X* adjacents. Dans la tourmaline sans lithium, la présence de O²⁻ à O(1) (*i.e.*, OH + F < 4 atomes par unité formulaire) doit nécessairement être associée à 3Al ou 2Al + Mg (ou les analogues Fe²⁺ - Fe³⁺) aux sites *Y* adjacents afin de satisfaire la somme des valences de liaison locales. Dans le cas de la tourmaline contenant du lithium mais sans Mg, la présence de O²⁻ à O(1) doit nécessairement être associée à 3Al aux sites *Y* adjacents. Ces exigences imposent des contraintes fermes concernant les schémas de substitution possibles dans lesquels un excédent d'atomes O²⁻ (*i.e.*, un déficit dans la somme OH + F) est incorporé dans la tourmaline.

(Traduit par la Rédaction)

Mots-clés: tourmaline, mise en ordre, ordre à courte échelle, substitutions chimiques, valences de liaison.

INTRODUCTION

Tourmaline is one of the last common silicates to be well understood in terms of both structure and chemistry, and significant aspects of its character and behavior still remain obscure. Although the tourmaline minerals are structurally and chemically complicated, they pale in comparison to amphiboles and micas. Nevertheless, our understanding of tourmaline lags behind that of the latter two groups of

minerals. This is probably due to two factors: (1) for a long time, tourmaline was regarded as an "odddity", occurring in strange rocks (pegmatites), and it is only relatively recently that its importance as a petrogenetic indicator has been demonstrated in common rocks (Henry & Guidotti 1985, Povondra & Novák 1986); (2) tourmalines contain essential and variable contents of light lithophile elements (H, Li, B), and it is (again) only relatively recently that the role of variable levels of light lithophile elements in common silicate minerals has been investigated in detail (see review by Hawthorne 1995). However, tourmaline is now under intense investigation (Foit 1989, Grice & Robinson 1989, Grice & Ercit 1993, Grice *et al.* 1993, Hawthorne *et al.* 1993, MacDonald *et al.* 1993, Burns

* Now permanently incarcerated in the Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2.

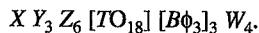
et al. 1994, MacDonald & Hawthorne 1995a, b, Dyar *et al.* 1994, Taylor *et al.* 1995), and our understanding of this group should soon be commensurate with that of other common silicate minerals.

Site nomenclature in tourmaline

With the increase in amount of structural and compositional data for tourmaline, it has become apparent that there is significant occupancy of the Si site by cations other than Si. This being the case, it is awkward to use an atom designation for this site. I propose that this site be labeled as *T*; thus *Si*(old) = *T*(new), where *T* carries the connotation of tetrahedral coordination.

DETERMINATION OF CHEMICAL COMPOSITION AND SITE POPULATIONS

The chemical formula of tourmaline may be written as



This is written in a more general way than is usually the case to allow for substitutions that are possible (but not necessarily proven as yet). It must be emphasized that this formula corresponds to the sites identified by crystal-structure refinement as being occupied or partly occupied; it makes no assignment of chemical species to specific sites except for the identification of the anions O(2) and O(4)–O(7) as (formally) O²⁻. Chemical analysis indicates what elements (and in which valence states) are present, but does not tell us where these elements are located in the structure. Although this distinction might seem somewhat over-pedantic, it is of significance in tourmaline, as incorrect assignment of elements to specific sites can lead to incorrect chemical formulae and mineral names (e.g., Grice *et al.* 1993). As part of crystal-structure refinement, site-scattering refinement (SREF) gives the number of electrons (i.e., the site-scattering power) at a site; it is necessary to emphasize that it does not indicate directly what elements are present at that site.

In combination, SREF and chemical analysis can, in many cases, indicate which scattering species occupy which sites, provided the number of scattering species at each site does not exceed two and provided that the species have significantly different scattering powers. Again, use of these methods alone can lead to erroneous assignment of cations to specific sites (e.g., see discussion by Hawthorne *et al.* 1993). It is necessary to combine crystal-chemistry analysis with SREF and chemical analysis (and possibly spectroscopic methods) to arrive at a correct structure and formula. Mean bond-length *versus* ionic radius relations and bond-valence theory (Brown 1981) are of particular importance in this regard. It is necessary to stress these points, as several conclusions and proposals of previous work can be shown to be

untenable when all aspects (crystal structure, crystal chemistry and chemical composition) of the problem are considered.

We may interpret the above formula of tourmaline in the following way: *X* = Ca, Na, K, □ (vacancy); *Y* = Li, Mg, Fe²⁺, Mn²⁺, Al, Cr³⁺, V³⁺, Fe³⁺, Ti⁴⁺; *Z* = Mg, Al, Fe³⁺, V³⁺, Cr³⁺; *T* = Si, Al, (B); *B* = B, (□); ϕ = O²⁻, (OH)⁻; *W* = OH⁻, F⁻, O²⁻; where the species in parentheses are, as yet, not directly proven to occur at these sites.

CRYSTAL-CHEMICAL ASPECTS OF CHEMICAL SUBSTITUTIONS AND MECHANISMS OF SUBSTITUTION

There are two important crystal-chemical principles that pertain to the derivation of site populations and mechanisms of substitution in crystals, one involving mean bond-lengths and the other involving local bond-valence restrictions.

Variation in mean bond-lengths

It is well known that atoms in specific formal valence-states can be assigned radii such that the sum of radii reproduce observed mean bond-lengths to within ± 0.02 Å (Shannon & Prewitt 1969, Shannon 1976). Furthermore, for a given structure-type, observed mean bond-lengths are a linear function of the radii of the constituent cations to within $\pm 0.00x$ Å (where *x* is small for accurately refined structures). There are two ways of representing this type of relation: (1) mean bond-length as a function of site population for a binary solid-solution; (2) mean bond-length as a function of mean constituent-cation radius for ternary and more complex solid-solutions. For most complex silicate minerals, type-(2) representation is often necessary; indeed, deviation from a type-(1) relationship is often indicative of additional components at the site under examination.

A further constraint, not usually considered, is the fact that the variation in mean bond-length as a function of constituent-cation radius must have a slope close to 1.0 (the *hard-sphere model*). Significant deviations from the hard-sphere model can indicate the presence of an additional undetected component at the site examined. Significant deviations from a hard-sphere model do occur for some structure types [e.g., the *M*(2) site in amphiboles], but occur across such a wide range of composition that they are known to be structurally, rather than compositionally, related. As will be shown later, observed variations in mean bond-lengths in tourmaline provide significant information on site populations.

Local bond-valence restrictions

Bond-valence theory is described by Brown (1981,

1992), and aspects relating to the behavior of H in minerals are developed by Hawthorne (1992, 1994). Of particular importance in the present context is the valence-sum rule: *the sum of the bond-valence incident at an atom is approximately equal to the formal valence of that atom*. This rule puts great constraints on mechanisms of substitution in crystals, and any proposed mechanism must conform to this rule.

VARIATION IN B CONTENT

There are several recent indications that B can be a variable component in tourmaline (Povondra 1981, Povondra & Novák 1986, Dyar *et al.* 1994). From a crystal-chemical viewpoint, the conditions $B < 3 \text{ apfu}$ (atoms per formula unit) and $B > 3 \text{ apfu}$ are quite distinct, and these will be considered separately.

B less than 3 apfu

If B is less than 3 *apfu*, □ (vacancies) must be present at the B site. Is it possible to detect the presence of such vacancies *via* crystal-structure refinement, what crystal-chemical ramifications are there to this substitution, and can this substitution be detected *directly* (*i.e.*, by a physical technique)?

Crystal-structure refinement: The substitution of □ for B at the B site would decrease the scattering from the B site. However, B ($Z = 5$) is a light element, and hence scatters X rays quite weakly. Is a moderate amount of □ \rightleftharpoons B substitution detectable? A 10% vacancy at the B site ($\rightleftharpoons B_{2.7}\square_{0.3}$) would decrease the aggregate charge at this site *pfu* by 1+, and would decrease the scattering at this site from 5e to 4.5e; this is a fairly marginal change in terms of site-scattering refinement. Hence, the detection of vacancies at or below the 10% level is uncertain by X-ray scattering.

Will there be a change in the $\langle B-O \rangle$ distance? We cannot answer this question at present, as the only way we can assess the "size" of a vacancy at a site in a structure is to obtain mean bond-lengths for structures of known vacancy content; in the present case, this is obviously not applicable to tourmaline as there are no data of this type currently available.

Bond-valence considerations: Where the B site is occupied by B, the central cation contributes $\sim 1.0 \text{ vu}$ (valence units) to each of the coordinating O atoms [O(2) and O(8), Fig. 1]. Substitution of a vacancy at the B site means that each of the coordinating O atoms is deficient in incident bond-valence by $\sim 1.0 \text{ vu}$. This situation could possibly be compensated by bonding H atoms to each of the coordinating O atoms to produce OH groups. From a chemical and a mechanistic viewpoint, this may be written directly as

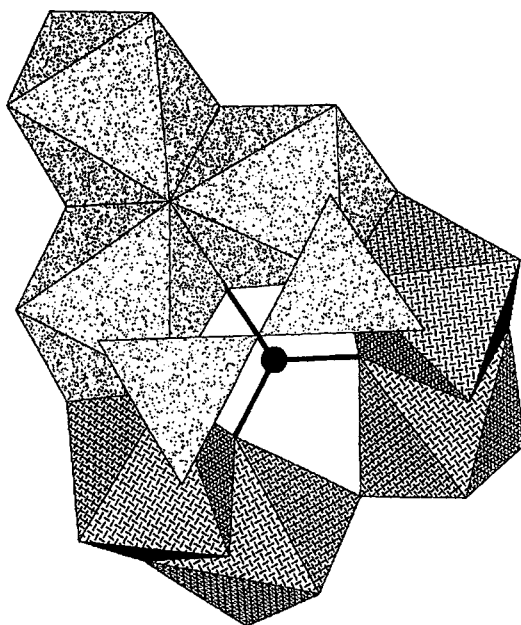
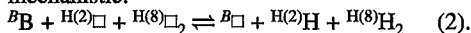


FIG. 1. The local environment of the B site (black circle) in the tourmaline structure; random-dot-shaded tetrahedra coordinate the T site, random-dot-shaded octahedra coordinate the Y site and orthogonal-dash-shaded octahedra coordinate the Z site.

mechanistic:



This seems an adequate chemical mechanism for the occurrence of a deficiency of B in tourmaline; however, it is stereochemically possible? Geometrically, the simplest way to bond H atoms to the O(2) and O(8) anions (those coordinating B in the tourmaline structure) is to place them at the same x and y coordinates as the oxygen anions, but with the z coordinate $\pm 0.98 \text{ \AA}$. However, this produces unacceptably small H-Y or H-Z distances ($1.5\text{--}1.7 \text{ \AA}$) in all cases except one, where a H atom at $x \approx 0.94$, $y \approx 0.06$, $z \approx 0.72$ can bond to O(2) if the X site is vacant. Possibly H atoms could bond to the O(8) anions in some sort of skew arrangement, but the tourmaline structure is quite crowded around the (BO_3) group, and it is not clear if there is enough space for such an arrangement to occur.

Detection of a $3H \rightleftharpoons B$ substitution: The presence of such a substitution will give rise to an additional band (or bands if fine-structure is also present) in the fundamental OH-stretching region of the infrared, and hence is, in principle, detectable by infrared spectroscopy.

B greater than 3 apfu

It seems straightforward that excess B should occur at the *T* site, as B has never been observed in octahedral coordination by O. However, this substitution cannot be assumed; it must be proven. In the analogous situation in vesuvianite, it was long assumed that B substituted directly for Si at the tetrahedrally coordinated *Z* sites. Direct investigation (Groat *et al.* 1994, 1995) showed this not to be the case: B is actually incorporated into vesuvianite *via* two new sites in the structure.

Crystal-structure refinement. The X-ray scattering for B ($Z=5$) and Si ($Z=14$) is sufficiently different that SREF is sensitive to $B \rightleftharpoons Si$ substitution and can be used as an accurate determinative method for B (Hawthorne *et al.* 1995). Thus $T = Si$ gives a site-scattering value of $14 \times 6 = 84$ *epfu* (electrons per formula unit), whereas $T = Si_{0.9}B_{0.1}$ ($\equiv Si_{5.4}B_{0.6}$ *apfu*) gives a site-scattering value of $5.4 \times 14 + 0.6 \times 5 = 78.6$ *epfu*. Such a difference is easily detectable by SREF, and the derived B value should be accurate to within the level of the assigned precision *if* the X-ray intensity data are free from systematic error. Thus SREF should be able to detect $B \rightleftharpoons Si$ substitution at the *T* site directly.

As B ($r = 0.11$ Å) is significantly different in size from Si ($r = 0.26$ Å), any $B \rightleftharpoons Si$ substitution should be reflected in variation in the $\langle T-O \rangle$ distance. However, the situation is complicated by the fact that significant Al also occurs at the *T* site in some species of tourmaline (Foit 1989, MacDonald & Hawthorne 1995). However, as Al ($r = 0.39$ Å) is larger than Si ($r = 0.26$ Å), it is possible to distinguish the effects of $Al \rightleftharpoons Si$ and $B \rightleftharpoons Si$ substitutions, even where they occur simultaneously (Cooper & Hawthorne, *in prep.*). The situation for some published structures of tourmaline is shown in Figure 2, where the $\langle T-O \rangle$ bond-length is plotted against the Si content. For $T = Si$, the $\langle T-O \rangle$ distance is approximately equal to 1.616 Å. The ideal variation in $\langle T-O \rangle$ with $Al \rightleftharpoons Si$ and $B \rightleftharpoons Si$ substitution for a hard-sphere model is shown by the lines in Figure 2. The $Al \rightleftharpoons Si$ substitution results in an increase in $\langle T-O \rangle$, whereas a $B \rightleftharpoons Si$ substitution results in a decrease in $\langle T-O \rangle$. Combined substitution will result in $\langle T-O \rangle$ distances between these two lines; indeed, in principle, it is possible to deduce the Al and B contents of the *T* site, given the $\langle T-O \rangle$ distance and the Si content (provided that the hard-sphere model holds). The data shown in Figure 2 follow the hard-sphere model for $Al \rightleftharpoons Si$ substitution. This indicates that $B \rightleftharpoons Si$ substitution is negligible to nonexistent in these particular tourmaline structures.

A composition of $Si_{5.4}B_{0.6}$, easily detectable by SREF, would produce a $\langle T-O \rangle$ distance of 1.612 Å; this is significantly different from the $\langle T-O \rangle$ distance

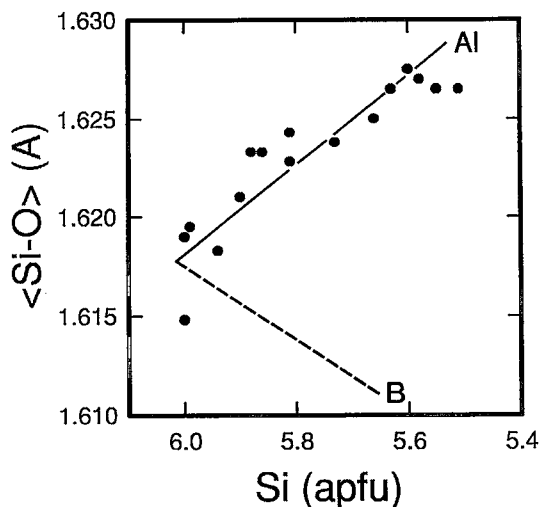


Fig. 2. Variation in $\langle T-O \rangle$ as a function of Si content; the data are taken from Burns *et al.* (1994), MacDonald & Hawthorne (1995) and Taylor *et al.* (1995). The full line is a least-squares fit to the data, the full line shows a hard-sphere model for $Si \rightleftharpoons Al$ substitution, and the broken line shows a hard-sphere model for $Si \rightleftharpoons B$ substitution.

for complete Si occupancy of the *T* sites, and hence this amount of substitution should be apparent in the observed stereochemistry. However, it must be realized that mean bond-lengths also are influenced by chemical variations at other sites in the structure; for example, in silicate garnets, the $\langle Si-O \rangle$ distance is strongly influenced by the type of X cation present (Novak & Gibbs 1971, Merli *et al.* 1995, Ungaretti *et al.* 1995). Thus one has to be careful in assigning small variations in mean bond-lengths to changes in site populations. In this regard, I find the arguments of Grice & Ercit (1993) concerning the substitution ($Ti, B \rightleftharpoons Si$) unconvincing. The total variation in $\langle T-O \rangle$ exhibited by their data is 1.6205 ± 0.0025 Å. Now each $\langle T-O \rangle$ distance has a standard deviation in the range 0.0010–0.0015 Å, and thus the total range of the data is, at most, ± 2 standard deviations. This is neither statistically significant *nor* crystal-chemically significant if one considers possible inductive effects from other parts of the structure. In this regard, SREF seems more sensitive than variation in $\langle T-O \rangle$ distance to small amounts of $B \rightleftharpoons Si$ substitution.

Bond-valence considerations: Substitution of a trivalent cation (Al, B) for Si at the *T* site reduces the bond valence incident to the coordinating anions around the *T* site. This must be compensated in some fashion by increasing the incident bond-valence from other cations. This situation is shown in Table 1, which suggests a bond-valence distribution that is compatible with the occurrence of Al at *T* and yet satisfies the

TABLE 1. PROPOSED LOCAL (SHORT-RANGE) BOND-VALENCE ARRANGEMENTS AROUND A T SITE OCCUPIED BY A TRIVALENT CATION (A1,B) IN TOURMALINE

X_{Ca^*}	Y_{Al}	Z_{Al}	$T_{T^{3+}}$	H(3)	Σ
O(3)	0.40	0.40 ²⁻		0.80	2.00
O(4)	0.30		0.80 ²⁻		1.90
O(5)	(0.15 ²⁻)		0.78 ²⁻	0.20	2.00
O(6)	0.65	0.50	0.75		1.90
O(7)		0.65	0.70		2.00
		0.65			
Σ	(2.00)	(3.00)	(3.00)	3.00	1.00

* Ca at X is disordered off the 3-fold axis such that it forms one short (strong) bond and two longer bonds to the three 'equivalent' anions: e.g. $X-O(4) = 0.30 + 2 \times 0.15 \nu$ instead of $3 \times 0.20 \nu$ as required by the long-range symmetry of the structure.

bond-valence requirements of the associated anions (and cations); it should be emphasized that Table 1 describes a *short-range* feature around a single T site occupied by Al, not an arrangement in a long-range average structure. In order to satisfy the bond-valence requirements of the anions, note that the Y and Z sites must be (locally) occupied by Al, and that it is an advantage if the X site is occupied by Ca. Thus it is to be expected that calcium-bearing tourmaline compositions will show significant M^{3+} -for-Si substitution, as the composition allows local (short-range) satisfaction of anion bond-valence requirements in the presence of relatively weak ($\sim 0.75 \nu$) T-O bonds. Note that this argument makes no distinction between Al and B as the substituent cation at the T site, as the average $^{[4]}Al-O$ and $^{[4]}B-O$ bond-valences are the same. However, there are presumably more subtle steric effects (associated with the different sizes of these two cations) that also will affect these substitutions.

VARIATION OF OH + F IN TOURMALINE

For most tourmaline compositions, it is usually assumed that $OH + F = 4 \text{ apfu}$; from a structural viewpoint, this means that $O(1) = O(3) = (OH,F)$. Grice & Ercit (1993) showed F to be ordered at the O(1) position *via* a bond-valence argument, and MacDonald & Hawthorne (1995) arrived at the same conclusion by direct site-scattering refinement. This pattern of ordering is in accord with the observation that F does not exceed 1 *apfu* in tourmaline, as the O(1) and O(3) sites occur in the ratio 1:3. Careful analytical (Povondra 1981, Povondra & Novák 1986, Dyar *et al.* 1994) and statistical (Foit & Rosenberg 1977) work has shown that the assumption that $OH + F = 4 \text{ apfu}$ is not of general validity. This fact has significant structural implications, as the occurrence of a deficiency or an excess of monovalent anions in the structure requires major re-arrangements of bond valence around the structural sites involved in this behavior.

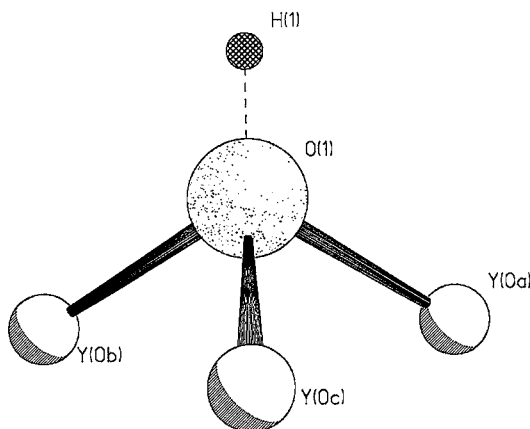


FIG. 3. The local environment of the O(1) oxygen atom (random-dot-shaded circle); O(1) is linked to three Y cations (highlighted circle), and the H(1) site is occupied where $O(1) = OH$.

Monovalent-anion deficiency at O(1)

The O(1) site is located on the 3-fold axis passing through the origin of the unit cell, and is surrounded by three Y sites (Fig. 3), such that the O(1)-Y bonds are crystallographically (*i.e.*, long-range) equivalent. The local bond-valence arrangement for a uvite crystal with O(1) occupied predominantly by F [$O(1) = 0.92F + 0.08(OH \text{ or } O)$; T77 of MacDonald & Hawthorne 1995] is shown in Table 2. The calculated Y-O(1) bond-valence is 0.306ν , and the sum of the bond-valence incident at O(1) is 0.918ν , close to the ideal value of 1ν for occupancy of O(1) by a monovalent anion (F^-).

In a tourmaline deficient in monovalent anions at the O(1) site, the valence-sum rule (Brown 1981) requires that the sum of the bond-valences incident at O(1)

TABLE 2. BOND-VALENCE TABLE FOR UVITE* WITH F AT O(1)

X	Y	Z	T	B	H(1)	H(3)	Σ
O(1)	0.306 ²⁻				-		0.918
O(2)	0.229 ²⁻	0.375 ²⁻		1.030			2.009
O(3)	0.312	0.417 ²⁻				0.9	2.046
O(4)	0.121 ²⁻		0.969 ²⁻				2.059
O(5)	0.143 ²⁻		0.929 ²⁻			0.1	2.101
O(6)	0.392 ²⁻	0.539	1.041				1.972
O(7)		0.451	1.024				1.990
		0.515					
O(8)		0.476		1.000 ²⁻			1.991
		0.515					
Σ	1.479	2.230	2.913	3.963	3.030		

* data from T77 of MacDonald & Hawthorne (1995)

match the formal valence of the anion(s) at O(1). Thus in those *short-range* configurations that have O^{2-} at O(1), the sum of the bond valences incident at O(1) must be $\sim 2 \nu u$; in those short-range configurations that have OH^- or F^- at O(1), the sum of the incident bond-valences at O(1) must be $\sim 1 \nu u$. Using the bond-valence curves of Brown (1981), one can calculate the bond lengths corresponding to any particular arrangement of bond valences to check whether the resulting bond-lengths are realistic (*i.e.*, fall within the range observed for that specific cation-anion pair). In this regard, the universal curves of Brown (1981) are particularly useful as each one applies to an iso-electronic series of cations with the same core-electron configuration (*e.g.*, Na, Mg, Al, Si, P, S).

Li-free tourmaline: First, I will consider tourmaline in which Y is occupied dominantly by (Mg, Al); similar arguments apply to their (Fe^{2+}, Fe^{3+}) analogues.

Where O(1) is a monovalent anion, the incident bond-valence requirements at O(1) are satisfied by arrangement (1.1) (Table 3), in which there are three identical bonds; the corresponding distance of 2.096 Å is typical for Mg–(O, OH) bonds. Although this seems a very reasonable arrangement, it cannot be tested at the moment because there is no accurate refinement available for an Fe-free and Li-free tourmaline with OH known to be approximately 4 *apfu*. However, consider the F-equivalent problem; this is shown in Table 3, arrangement (1.3). The calculated Y–O(1) [F] distance is 1.980 Å; this agrees reasonably well with the corresponding Y–O(1) distance of 2.03 Å in F-bearing uvite (MacDonald & Hawthorne 1995), with $O(1) = 0.92F + 0.08(O, OH)$. Are other local configurations possible for O(1) as a monovalent anion?

TABLE 3. LOCAL (SHORT-RANGE) BOND-VALENCE ARRANGEMENTS, BOND-LENGTHS AND CATION ARRANGEMENTS THAT SATISFY LOCAL ANION BOND-VALENCE REQUIREMENTS AROUND THE O(1) SITE IN THE TOURMALINE STRUCTURE; BOND LENGTHS ARE GIVEN FOR $O(1) = [OH]^-$, O^{2-} AND $O(1) = F^-$; FOR $O(1) = OH^-$ OR F^- , THE SUM OF THE BOND VALENCES IS $1 \nu u$; FOR $O(1) = O^{2-}$, THE SUM OF THE BOND VALENCES IS $2 \nu u$

	Bond valence (νu)	$Y-O^{OH}[OH, O]$ (Å)	$Y-O^{OH}[F]$ (Å)	local arrangement
(1.1)	$0.33 \times 3 = 1.0$	Mg: 2.096	Mg: 1.983	3Mg
(1.2)	$0.44 + 0.28 \times 2 = 1.0$	Mg: 2.182 Al: 1.964	Mg: 2.061 Al: 1.845	Al+2Mg
(2.1)	$0.67 \times 3 = 2.0$	Al: 1.783	–	3Al
(2.2)	$0.75 \times 2 + 0.50 = 2.0$	Al: 1.734 Mg: 1.906	–	2Al+Mg
(2.3)	$0.80 + 0.60 \times 2 = 2.0$	Al: 1.709 Mg: 1.827	–	Al+2Mg
(3.1)	$0.40 \times 2 + 0.20 = 1.0$	Al: 2.008 Li: 2.047	Al: 1.887 Li: 1.946	2Al+Li
(3.2)	$0.60 + 0.20 \times 2 = 1.0$	Al: 1.827 Li: 2.047	Al: 1.726 Li: 1.946	Al+2Li
(3.3)	$0.33 \times 3 = 1.0$	Li: 1.806	Li: 1.708	3Li
(4.1)	$0.80 \times 2 + 0.40 = 2.0$	Al: 1.709 Li: 1.726	–	2Al+Li

Arrangements (1.2) of Table 3 involves one short Y–O(1) bond and two long Y–O(1) bonds, with corresponding bond-valences of 0.45 and $2 \times 0.28 \nu u$; the corresponding distances are reasonable for $3Y = Al + 2Mg$, and this configuration also may be possible.

Where O(1) is a divalent anion, the incident bond-valence requirements at O(1) are satisfied by arrangements (2.1) and (2.2) of Table 3. Solution (2.1) has three Y–O(1) distances and is possible for $3Y = 3Al$. Solution (2.2) has two short Y–O(1) distances and one longer distance, and is possible for $3Y = 2Al + Mg$. Solution (2.3) has one short Y–O(1) distance and two longer Y–O(1) distances, but the distances are not reasonable for $Y = Al + 2Mg$. Thus only the local arrangements $3Y = 3Al$ and $3Y = 2Al + Mg$ are compatible with the occurrence of a divalent anion at O(1).

Li-bearing tourmaline: Where O(1) is a monovalent anion, bond-valence arrangements (3.1) and (3.2) (Table 3) are possible, and correspond to the local arrangements $3Y = 2Al + Li$ and $3Y = Al + 2Li$. In ideal end-member elbaite, both arrangements (3.1) and (3.2) must occur in equal amounts to be compatible with the bulk chemical composition. In ideal end-member liddicoatite, arrangement (3.2) is forced by the chemical composition, and arrangement (3.1) will not occur.

Where O(2) is a divalent anion, can Y be locally occupied by Li, *i.e.*, can a coordination of $2Al + Li$ deliver an incident bond-valence of $2 \nu u$ at O(1)? The necessary arrangement is shown as (4.1) in Table 3; the Li–O and Al–O bond-lengths are too short to be realistic, and hence Li cannot be involved in local coordination to O^{2-} at O(1) in the tourmaline structure. Does this mean that liddicoatite and elbaite cannot have O^{2-} at the O(1) site? In a tourmaline with $Y = (Li, Al)$, O^{2-} can be incorporated at the O(1) site only in local association with the arrangement $3Y = 3Al$. End-member liddicoatite has the composition $Y = Li_2Al$, and if local arrangements of the form $3Y = 3Al$ were to occur, the bulk composition of the crystal would require a corresponding number of local arrangements of the form $3Y = 3Li$. The required bond-lengths for this latter configuration fall outside the range of Li–O and Li–F bond-lengths normally observed in inorganic structures, and this arrangement is hence forbidden. If $3Y = 3Li$ cannot occur in end-member liddicoatite, the arrangement $3Y = 3Al$ cannot occur either, and hence end-member liddicoatite cannot have O^{2-} at the O(1) site. This is not the case for ideal end-member elbaite. For a bulk composition $Y = Al_{1.5}Li_{1.5}$, the local arrangement $3Y = 3Al$ and $3Y = Al + 2Li$ are possible in the ratio 1:3, and hence end-member elbaite (*i.e.*, $Y = Al_{1.5}Li_{1.5}$) can incorporate 0.25 O^{2-} at the O(1) site provided the additional negative charge introduced by the additional O^{2-} is compensated by cation variation at a site other than

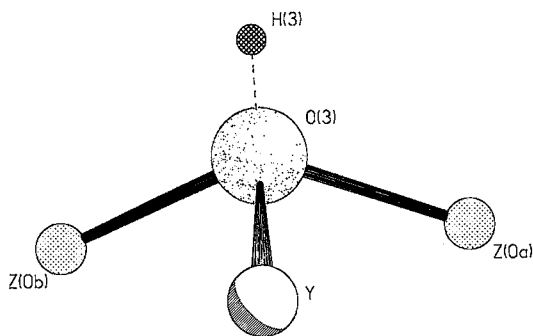


FIG. 4. The local environment of the O(3) oxygen atom (random-dot-shaded circle); two Z cations (regular-dot-shaded circle) and a Y cation (highlighted circle) bond to one side of O(3), and the H(3) site is occupied where O(3) = OH.

the Y site. These constraints on the O^{2-} content of liddicoatite and elbaite are obviously relaxed by the incorporation of divalent cations at the Y site.

Monovalent anion deficiency at O(3)

The O(3) site is coordinated by one Y cation and two Z cations (Fig. 4). In most tourmaline end-members, the O(3) site is occupied by $(OH)^-$, and the sum of the incident bond-valences is close to 1.0 *vu* if the associated H atom is excluded. However, in buergerite, ideally $NaFe_3^{3+}Fe_6^{2+}(Si_6O_{18})(BO_3)_3O_3F$, the O(3) site is occupied by O^{2-} . Hence the tourmaline structure *must* be capable of supplying an incident bond-valence of 2.0 *vu* to the O(3) site; how this is done is shown in Table 4 for the buergerite structure of Grice &

TABLE 4. BOND-VALENCE TABLE FOR BUERGERITE* WITH (O^{2-}, OH) AT O(3) AND (F, OH) AT O(1)

	X	Y	Z	T	B	Σ
O(1)		0.300 ^{ca} -				0.900
O(2)	0.136 ^{ca}	0.476 ^{ca} -			0.977	2.065
O(3)		0.554	0.524 ^{ca} -			1.602
O(4)	0.093 ^{ca}			1.003 ^{ca} -		2.096
O(5)	0.111 ^{ca}			0.987 ^{ca} -		2.085
O(6)		0.497 ^{ca}	0.488	1.005		1.990
O(7)			0.539	1.038		2.009
			0.432			
O(8)			0.490		1.024 ^{ca}	2.049
			0.535			
Σ	1.020	2.800	3.008	4.033	3.025	

* calculated from the structural parameters of Grice & Ercit (1993)

TABLE 5. PROPOSED LOCAL (SHORT-RANGE) BOND-VALENCE ARRANGEMENT IN BUERGERITE WITH O^{2-} AT O(3)

	X	Y	Z	T	B	Σ
O(1)		0.33 ^{ca} -				1.00
O(2)	0.14 ^{ca}	0.43 ^{ca} -			1.00	2.00
O(3)		0.66	0.67 ^{ca} -			2.00
O(4)	0.09 ^{ca}			0.96 ^{ca} -		2.01
O(5)	0.10 ^{ca}			0.96 ^{ca} -		2.02
O(6)		0.58 ^{ca}	0.40	1.01		1.99
O(7)			0.52	1.07		2.00
			0.41			
O(8)			0.48		1.00 ^{ca}	2.00
			0.52			
Σ	0.99	3.01	3.00	4.00	3.00	

Ercit (1993) with O^{2-} dominating at O(3) and O(1) = $F_{0.74}(OH)_{0.36}$. The sum of the bond valences incident at O(3) is 1.602 *vu*, indicating occupancy of O(3) by both O^{2-} and OH. Where O(3) is occupied by $(OH)^-$, the local (short-range) bond-valence arrangement will resemble that in other tourmaline structures (e.g., Table 2). Where O(3) is occupied by O^{2-} , the local bond-valence arrangement must resemble that shown in Table 5; the sum of the bond-valences incident at O(3) is 2.00 *vu*, and the rest of the structure can adjust to accommodate these changes in the O(3)-Y and O(3)-Z bond-valences while maintaining the bond-valence requirements at other sites in the structure. Are the analogous bond-lengths physically reasonable? A bond-valence of 0.67 *vu* corresponds to an Fe^{3+} -O bond-length of 1.91 Å, a reasonable value. The same argument applies to the structure of olenite, $NaAl_3Al_6(Si_6O_{18})(BO_3)_3O_3(OH)$, the bond-lengths given for Al in Table 3 being applicable to this species.

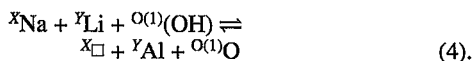
Constraints on mechanisms of substitution imposed by requirements of short-range order

Many algebraic substitutions have been written involving $O^{2-} \rightleftharpoons (OH)^-$ variation in tourmaline. However, many of these are *not* independent of other substitutions, as, by themselves, they do not satisfy the compositional constraints imposed by the requirements of short-range order arising from local bond-valence requirements. As an example, consider the substitution of O^{2-} into elbaite *via*

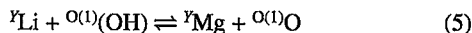


This conserves charge, and hence satisfies the electroneutrality requirement. Application of this substitution to end-member elbaite $Na(Li_{1.5}Al_{1.5})$

$\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{OH})$ produces the composition $\text{Na}(\text{LiAl}_2)\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3\text{O}$. Now consider the replacement of $(\text{OH})^-$ by O^{2-} at O(1) from the constraints imposed by the local incident bond-valence requirements of O^{2-} at the O(1) site. Each O^{2-} atom at O(1) must be locally associated with 3Al at the three adjacent Y sites, and hence $\text{O}(1) = \text{O}_{1.0}^{2-}$ requires that $Y = \text{Al}_3$ rather than $Y = \text{LiAl}_2$, which is produced by substitution (3). Substitution (3) can produce the local arrangement $3Y = 3\text{Al}$ and $3Y = \text{Al} + 2\text{Li}$ in the ratio 1:2, allowing an O(1) composition of $\text{O}_{0.33}(\text{OH})_{0.67}$ only. This situation may be alleviated by combining substitution (3) with another substitution that also increases the amount of Al at the Y site:

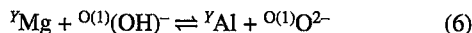


Fifty % substitution into end-member elbaite would produce a composition of $\text{Na}_{0.5}(\text{Li}_1\text{Al}_2)\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{OH})_{0.5}\text{O}_{0.5}$. This O(1) composition of $(\text{OH})_{0.5}\text{O}_{0.5}$ would require local arrangements $3Y = 3\text{Al}$ (for O^{2-}) and $3Y = \text{Al} + 2\text{Li}$ (for OH) in the ratio 1:1, which is compatible with the Y composition of LiAl_2 . A substitution of the form

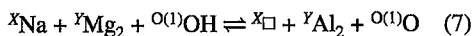


if acting on the elbaite end-member, will produce a composition $\text{Na}(\text{Li}_{0.5}\text{MgAl}_{1.5})\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{OH})_3\text{O}$. However, the requisite local bond-valence requirements around O at O(1) cannot be satisfied because of the presence of Li at the Y site. The substitution can go up to 50% to produce the site composition $Y = \text{LiMg}_{0.5}\text{Al}_{1.5}$ and $\text{O}(1) = (\text{OH})_{0.5}\text{O}_{0.5}$; in this case, the Y-site composition allows the local configurations $3Y = 2\text{Al} + \text{Mg}$ [for $\text{O}(1) = \text{O}^{2-}$] and $3Y = \text{Al} + 2\text{Li}$ [for $\text{O}(1) = \text{OH}$] in the ratio 1:1.

The corresponding situation is similar in other species of tourmaline. Consider the substitution



in dravite, $\text{Na}(\text{Mg}_3)\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{OH})$; this will produce a tourmaline of composition $\text{Na}(\text{Mg}_2\text{Al})\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3\text{O}$. Inspection of Table 3 shows that the occurrence of O^{2-} at O(1) requires a local configuration of $3Y = 2\text{Al} + \text{Mg}$ (or $3Y = 3\text{Al}$). The composition $Y = \text{Mg}_2\text{Al}$ can produce local arrangements $3Y = 2\text{Al} + \text{Mg}$ and $3Y = 3\text{Mg}$ in the ratio 1:1, compatible with an O(1) composition of $\text{O}_{0.5}(\text{OH})_{0.5}$ only. Again, the algebraic substitution is not compatible with short-range order arising from local bond-valence requirements. However, as above, substitution (6) may be combined with other substitutions that increase the amount of Al at the Y site and allow complete occupancy of O(1) by O^{2-} :



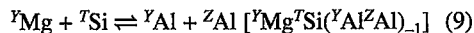
produces the composition $Y = \text{MgAl}_2$ and $\text{O}(1) = \text{O}^{2-}$, compatible with local ordering of $3Y = 2\text{Al} + \text{Mg}$ around O^{2-} at the O(1) site. It may be significant that application of substitution (7) to dravite to the extent of 50% gives the composition $\text{Na}_{0.5}(\text{Mg}_2\text{Al})\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{OH})_{0.5}\text{O}_{0.5}$, more similar to many compositions of dravite (Foit & Rosenberg 1977) than the ideal end-member composition.

O^{2-} at O(1): A CAUSE OF Mg–Al DISORDER IN TOURMALINE

Several end-member compositions have Al at the Y site or Mg at the Z site. However, none have Al at the Y site and Mg at the Z site! The reason for this is quite straightforward: if one writes the chemical formula of a tourmaline in the most ordered form possible, one will never obtain a formula with Al at Y and Mg at Z. Thus the occurrence of this type of arrangement in tourmaline (Hawthorne *et al.* 1993, Grice & Ercit 1993, Taylor *et al.* 1995) is due to disorder rather than differences in chemical composition, and we can write an order–disorder reaction of the form



What drives this reaction? Above, we have seen that the substitution ${}^{T(1)}\text{Al} \rightarrow {}^{T(1)}\text{Si}$ locally requires Al at the Y site. However, this can be associated with a substitution of the form

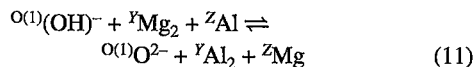


that does not introduce Mg at the Z site and hence does not cause any Mg–Al disorder over the Y and Z sites. *This disorder is driven by the short-range requirement of O^{2-} at the O(1) site to be associated with $2\text{Al} + \text{Mg}$ (and perhaps 3Al) configurations at the coordinating Y sites so as to satisfy the bond-valence requirements of O^{2-} at the O(1) site.* The amount of Mg–Al disorder is actually quantified by the amount of Mg at the Z site in cases where there is Al in excess of ${}^z\text{Mg}$ at the Y site, or the amount of Al at the Y site where there is Mg in excess of ${}^y\text{Al}$ at the Z site. Of course, Al may be introduced into the Y site as long-range compensation of charge for the replacement of OH^- by O^{2-} at the O(1) site; indeed, Foit & Rosenberg (1977) suggested this as the most important heterovalent substitution in alkali tourmalines:



However, this substitution only produces one Al per O^{2-} at O(1), and this is insufficient to form any

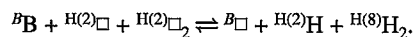
of the local arrangements of Table 3 that satisfy the local bond-valence requirements of O^{2-} at O(1). This substitution *must* be accompanied by the disordering substitution (9) in an equal amount to produce a local arrangement of the type Al_2Mg (Table 3):



This combination describes both the chemical substitution and the concomitant disordering reaction; in the absence of any other substitution, the smaller of the two values ${}^Y Al/2$ and ${}^Z Mg$ should indicate the divalent anion content of the O(1) site. This prediction may be tested with the data of Taylor *et al.* (1995) on OH-deficient uvite. In this crystal, the (Al + Cr³⁺) content of the Y site is 1.30 *apfu*, and the Mg content of the Z site is 0.78 *apfu*. These values predict an O^{2-} content at O(1) of $1.30/2 = 0.65$ *apfu*, in good agreement with the observed content of 0.69 O^{2-} *apfu* at O(1). A good test of this hypothesis will be its ability to predict ordering in other well-refined tourmaline structures of known H content.

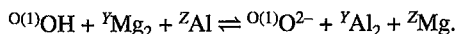
SUMMARY AND CONCLUSIONS

1. The tetrahedrally coordinated site, occupied primarily by Si, but also by Al and perhaps B, should be labeled the *T* site (rather than the *Si* site as it is at present).
2. It may be possible that vacancies can be incorporated at the *B* site *via* the mechanism



3. Boron in excess of 3 *apfu*, incorporated into the tourmaline structure *via* the substitution ${}^T Si \rightleftharpoons {}^T B$, should lead to significant decrease in the effective X-ray scattering from the *T* site and in the $\langle T-O \rangle$ bond-length. This substitution may be more effective in calcic tourmaline (or be locally coupled to Ca at the *X* site) because of local bond-valence requirements.
4. Short-range bond-valence considerations indicate that the occurrence of divalent anions at O(1) is associated with local clusters of the type $2Al + Mg$ and $3Al$ at the trimer of *Y* sites coordinating the O(1) anion.
5. The short-range order associated with O^{2-} at the O(1) site places significant stoichiometric constraints on the possible substitutions involved in incorporating O^{2-} at O(1).
6. Point 5 may be extended to show that Mg-Al disorder over the *Y* and *Z* sites is driven by the short-range bond-valence requirements of O^{2-} at O(1).
7. This argument may be further extended to show that the O^{2-} content of O(1) may be predicted as the smaller of the two quantities ${}^Y Al/2$ and ${}^Z Mg$.

8. An important mechanism for the incorporation of O^{2-} at the O(1) site is



ACKNOWLEDGEMENTS

I thank Don Peacor, an anonymous reviewer and Associate Editor Phil Rosenberg for their comments on this manuscript. I thank the CNR Centro di Studio per la Cristallografia e la Cristallografia, Pavia, for the peace and quiet needed to write this paper. Financial support was provided by the Natural Sciences and Engineering Research Council of Canada.

REFERENCES

- BROWN, I.D. (1981): The bond-valence method: an empirical approach to chemical bonding and structure. *In* Structure and Bonding in Crystals II (M. O'Keeffe and A. Navrotsky, eds.). Academic Press, New York, N.Y. (1-30).
- _____ (1992): Chemical and steric constraints in inorganic solids. *Acta Crystallogr.* **B48**, 553-572.
- BURNS, P.C., MACDONALD, D.J. & HAWTHORNE, F.C. (1994): The crystal chemistry of manganese-bearing elbaite. *Can. Mineral.* **32**, 31-41.
- DYAR, M.D., FRANCIS, C.A., WISE, M.A., GUIDOTTI, C.V., MCGUIRE, A.V. & ROBERTSON, J.D. (1994): Complete chemical characterization of tourmaline. *Trans. Am. Geophys. Union* **75**, 187 (abstr.).
- FOTT, F.F., JR. (1989): Crystal chemistry of alkali-deficient schorl and tourmaline structural relationships. *Am. Mineral.* **74**, 422-431.
- _____ & ROSENBERG, P.E. (1977): Coupled substitutions in the tourmaline group. *Contrib. Mineral. Petrol.* **62**, 109-127.
- GRICE, J.D. & ERCIT, T.S. (1993): Ordering of Fe and Mg in the tourmaline crystal structure: the correct formula. *Neues Jahrb. Mineral. Abh.* **165**, 245-266.
- _____, _____ & HAWTHORNE, F.C. (1993): Povondraite, a redefinition of the tourmaline ferridravite. *Am. Mineral.* **78**, 433-436.
- _____ & ROBINSON, G.W. (1989): Feruvite, a new member of the tourmaline group, and its crystal structure. *Can. Mineral.* **27**, 199-203.
- GROAT, L.A., HAWTHORNE, F.C. & ERCIT, T.S. (1994): The incorporation of boron into the vesuvianite structure. *Can. Mineral.* **32**, 505-523.
- _____, _____, ROSSMAN, G.R. & ERCIT, T.S. (1995): The infrared spectroscopy of vesuvianite in the OH region. *Can. Mineral.* **33**, 609-626.

- HAWTHORNE, F.C. (1992): The role of OH and H₂O in oxide and oxysalt minerals. *Z. Kristallogr.* **201**, 183-206.
- _____ (1994): Structural aspects of oxide and oxysalt crystals. *Acta Crystallogr.* **B50**, 481-510.
- _____ (1995): Light lithophile elements in metamorphic rock-forming minerals. *Eur. J. Mineral.* **7**, 607-622.
- _____, COOPER, M., BOTTAZI, P., OTTOLINI, L., ERCIT, T.S. & GREW, E.S. (1995): Micro-analysis of minerals for boron by SREF, SIMS and EMPA: a comparative study. *Can. Mineral.* **33**, 389-397.
- _____, MACDONALD, D.J. & BURNS, P.C. (1993): Reassignment of cation site occupancies in tourmaline: Al/Mg disorder in the crystal structure of dravite. *Am. Mineral.* **78**, 265-270.
- HENRY, D.J. & GUIDOTTI, C.V. (1985): Tourmaline as a petrogenetic indicator mineral: an example from the staurolite-grade metapelites of NW Maine. *Am. Mineral.* **70**, 1-15.
- MACDONALD, D.J. & HAWTHORNE, F.C. (1995a): Cu-bearing tourmaline from Paraiba, Brazil. *Acta Crystallogr.* **C51**, 555-557.
- _____ & _____ (1995b): The crystal chemistry of Si \rightleftharpoons Al substitution in tourmaline. *Can. Mineral.* **33**, 849-858.
- _____, _____ & GRICE, J.D. (1993): Foitite, $\square[\text{Fe}_2^{2+}(\text{Al}, \text{Fe}^{3+})]\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_4$, a new alkali-deficient tourmaline: description and crystal structure. *Am. Mineral.* **78**, 1299-1303.
- MERLI, M., CALLEGARI, A., CANNILLO, E., CAUCIA, F., LEONA, M., OBERTI, R. & UNGARETTI, L. (1995): Crystal-chemical complexity in natural garnets: structural constraints on chemical variability. *Eur. J. Mineral.* **7**, 1239-1249.
- NOVÁK, G.A. & GIBBS, G.V. (1971): The crystal chemistry of the silicate garnets. *Am. Mineral.* **56**, 791-825.
- POVONDRÁ, P. (1981): The crystal chemistry of tourmalines of the schorl-dravite series. *Acta Univers. Carol. Geol.* **3**, 223-264.
- _____ & NOVÁK, M. (1986): Tourmalines in metamorphosed carbonate rocks from western Moravia, Czechoslovakia. *Neues Jahrb. Mineral., Monatsh.*, 273-282.
- SHANNON, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* **A32**, 751-767.
- _____ & PREWITT, C.T. (1969): Effective ionic radii in oxides and fluorides. *Acta Crystallogr.* **B25**, 925-946.
- TAYLOR, M.C., COOPER, M.A. & HAWTHORNE, F.C. (1995): Local charge-compensation in hydroxyl-deficient uvite. *Can. Mineral.* **33**, 1215-1221.
- UNGARETTI, L., LEONA, M., MERLI, M. & OBERTI, R. (1995): Non-ideal solid-solution in garnet: crystal-structure evidence and modelling. *Eur. J. Mineral.* **7**, 1299-1312.

Received June 16, 1995, revised manuscript accepted November 2, 1995.