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POLYHEDRON DISTORTIONS IN TOURMALINE

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Abstract

Distortion parameters [Δ, σ^2, DI(Y–O), DI(O–Y–O), DI(O–O)] have been calculated for cation polyhedra in tourmalines of different chemical compositions. Tourmalines with greater amounts of small, highly charged ions in the YO_6 octahedron display greater bond-length distortion in Y. The size and charge of the occupants at the Y site have been included in an empirically determined formula intended to evaluate the bond-length distortion of the YO_6 octahedron. This equation demonstrates that the bond-length distortion in the YO_6 octahedron is a function of the size and charge of the Y-site occupants, and is predictable from those occupants (r = 0.972 for observed *versus* calculated distortion). The distortion of the Z octahedron in a tourmaline is largely a function of the <Y–O> of that tourmaline [r = –0.985 for all tourmalines where O3 is occupied by 3 (OH) *apfu*], although the occupant of the O3 site also affects that distortion. The bond-length distortion of the TO_4 tetrahedron is small, but examination of the angle distortion of the tetrahedron demonstrates a strong covariance with the charge at the X site (r = 0.892). Finally, distortions in the XO_9 polyhedron were found to correlate with the charge of the occupants at the Y site and the fluorine content (r = 0.881).

Keywords: tourmaline, crystal structure, polyhedron distortion.

Sommaire

Les paramètres de distorsion [Δ, σ^2, DI(Y–O), DI(O–Y–O), DI(O–O)] ont été évalués pour les polyèdres de coordinence dans les tourmalines de compositions diverses. Les tourmalines possédant une quantité importante d'ions à petit rayon et à charge élevée dans l'octaèdre YO_6 montrent une distorsion plus importante dans les longueurs de liaisons. Nous avons donc inclus la charge et la taille des occupants au site Y site dans une formule empirique prévue pour évaluer la distorsion des longueurs de liaisons dans l'octaèdre YO_6. L'équation démontre que cette distorsion dépend de la taille et de la charge des occupants du site Y, et est prévisible pour le cas de ces occupants (r = 0.972 pour la distorsion observée *versus* la distorsion calculée). La distorsion

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associée à l'octaèdre *Z* de la tourmaline est largement fonction de la longueur moyenne <*Y*–O> de cette tourmaline [$r = -0.985$ pour tous les exemples dans lesquels trois groupes (OH) occupent le site O3 par unité formulaire], quoique l'occupant du site O3 site peut aussi influencer la distorsion. L'écart des longueurs de liaison du tétraèdre TO_4 est petit, mais l'écart dans les angles montre une covariance marquée avec la charge au site *X* ($r = 0.892$). De plus, les distorsions du polyèdre XO_9 montrent une corrélation avec la charge des occupants du site *Y* et de la teneur en fluor ($r = 0.881$).

(Traduit par la Rédaction)

Mots-clés: tourmaline, structure cristalline, distorsion des polyèdres.

INTRODUCTION

As part of a study of vanadium-bearing tourmaline, Foit & Rosenberg (1979) examined polyhedron distortions of different members of the tourmaline group. Although based on a limited number of extant structures, the work was the first to suggest several correlations between substituents in one site and the distortions of neighboring sites as the tourmaline structure accommodated the substituents.

Because of the recent proliferation of high-quality structure refinements of tourmalines with a great variety of substituents, we again examine polyhedron distortions in the atomic arrangement of tourmalines. Part of the impetus for this work was the recent discovery of significant amounts of tetrahedrally coordinated boron in natural and synthetic Al-rich tourmaline samples (Ertl *et al.* 1997, Ertl & Hughes 2002, Hughes *et al.* 2000, 2001, Marler & Ertl 2002, Schreyer *et al.* 2000, 2002, Tagg *et al.* 1999, Wodara & Schreyer 1997, 2001), a discovery that invited re-examination of earlier principles of tourmaline crystal chemistry. Like the $^{[4]}$B-bearing tourmalines, the data presented below were chosen to represent a wide range in chemical composition in the tourmaline structure.

Throughout this work, we will use the site nomenclature proposed in the definitive work of Hawthorne & Henry (1999), who give the general chemical formula of the tourmaline-group minerals as $X\ Y_3\ Z_6\ [T_6O_{18}]\ (BO_3)_3\ V_3\ W$. The data are all from published structures except those for the Cu-bearing elbaite from Paraíba, Brazil. Those data are from our recent refinement of Paraíba material; the optimization (Wright *et al.* 2000) from that structure refinement ($R = 0.016$), and the chemical data (electron-microprobe analysis, EMPA) gives the structural formula of this copper-bearing elbaite (*ca.* 1 wt.% CuO) as: $^{X}(\mathrm{Na}_{0.54}\mathrm{Ca}_{0.11}\square_{0.35})\ ^{Y}(\mathrm{Al}_{1.62}\mathrm{Li}_{1.13}\mathrm{Cu}^{2+}_{0.11}\ \mathrm{Mn}^{3+}_{0.08}\square_{0.06})\ ^{Z}(\mathrm{Al}_{5.91}\square_{0.09})\ \mathrm{B}_{3.00}{}^{T}(\mathrm{Si}_{5.74}\mathrm{B}_{0.26})\ \mathrm{O}_{27}\ [(\mathrm{OH})_3\ (\mathrm{F}_{0.39}(\mathrm{OH}_{0.61}))]$. We exclude Li from the *Z* site of the optimized formula because Hawthorne (2002) showed by application of bond-valence theory that Li cannot occur at the *Z* site in tourmaline. The refinement shows small amounts of $^{[4]}$B in this Al-rich, Cu-bearing elbaite from Paraíba. Structural and chemical data are not listed here, as the data are similar to those of the Cu-bearing elbaite structures determined by MacDonald & Hawthorne (1995).

DISCUSSION OF THE DISTORTION PARAMETERS

Robinson *et al.* (1971) first proposed using angle variance as a measure of distortion, and it has proved to be an effective method for evaluating relationships between polyhedron properties and chemical substituents. The definitions and values for all distortion parameters [Δ, σ^2, DI(*Y*–O), DI(O–*Y*–O), DI(O–O)] are listed in Table 1–4 for the *Y*, *Z*, *T*, and *X* sites respectively. Table 1 contains information on various distortion parameters; the distortion indices (DI), originally defined by Baur (1974) for tetrahedra, were adapted for octahedra by Wildner (1992) (*Y* site, Table 1; *Z* site, Table 2). The distortion indices for the *T* site (Table 3) were taken from the original work of Baur (1974), and were adapted for the polyhedron of the *X* site in this work (Table 4).

Polyhedron distortion can result from factors internal to a polyhedron, in which incorporation of cations of differing size and charge induce distortions in that polyhedron. It can also result from factors external to a polyhedron, wherein adjacent polyhedra induce distortions by expansions or contractions that propagate to the polyhedron in question. For tourmaline, we present the calculated distortion-parameters of samples covering a wide range in chemical composition, and also speculate on the sources of the distortion.

Distortion of the YO_6 octahedron

The *Y* octahedron is connected through oxygen atoms to the *X* sites (2×), the *T* sites (2×), the *Z* sites (3×), the *W* site [(O1): OH, F, O], the *V* site [(O3): OH, O], and the *B* sites (×2). Table 1 shows that tourmalines with Al as the main octahedrally coordinated cation, but also with significant amounts of Li at the *Y* site, have the highest bond-length distortion in the YO_6 octahedron [$\Delta_{\mathrm{oct}} \times 10^3$: 1.0–1.2; DI(*Y*–O): 0.024–0.025]. MacDonald & Hawthorne (1995) observed significant disorder at the O1 and O2 positions in Cu-bearing tourmaline, as indicated by relatively high U_{eq} values at those two sites (in the Cu-bearing tourmaline sample examined here, those sites also possess the largest *U*eq values among the oxygen atoms). They also noted that high U_{eq} values are common in many tourmaline structures, and suggested that the values result from local positional disorder induced by occupancy of the *X* and *Y* sites by cations of very different size and charge. In

TABLE 1. THE EXTENT OF DISTORTION IN $Y\mathrm{O}_6$ OCTAHEDRA OF VARIOUS TOURMALINES

Type	*a* [Å]	*c* [Å]	*Y* site (main elements)	F (*apfu*)	Δ_{oct} ×10^3	σ_{oct}^2	DI (*Y*–O)	DI (O–*Y*–O)	DI (O–O)	<*Y*-O> [Å]
Elbaite (Cu)[1]	15.831(3)	7.0957(8)	$\mathrm{Al_{1.62}Li_{1.13}Cu^{2+}{}_{0.11}Mn^{3+}{}_{0.08}}$	0.4	1.04	80.6	0.024	0.081	0.067	1.998
Elbaite[2]	15.822(2)	7.0949(5)	$\mathrm{Al_{1.63}Li_{1.37}}$	0.5	1.13	79.6	0.025	0.080	0.066	1.995
Liddicoatite[3]	15.875	7.126	$\mathrm{Al_{1.60}Li_{1.40}}$	0.9	1.15	72.6	0.025	0.071	0.060	2.034
Olenite ($^{[4]}$B)[4]	15.731(3)	7.0638(9)	$\mathrm{Al_{2.42}Li_{0.36}\square_{0.22}}$	0.1	1.17	73.8	0.024	0.078	0.065	1.957
Olenite-schorl[5]	15.935(3)	7.164(2)	$\mathrm{Al_{1.36}Fe^{2+}{}_{1.01}Mg_{0.62}}$	0.0	0.56	83.6	0.017	0.086	0.068	2.012
Olenite-schorl[6]	15.935(1)	7.160(1)	$\mathrm{Al_{1.22}Fe^{2+}{}_{0.79}Mg_{0.66}Fe^{3+}{}_{0.24}}$	0.1	0.75	82.5	0.020	0.083	0.067	2.022
Schorl[6]	15.963(1)	7.154(1)	$\mathrm{Fe^{2+}{}_{1.79}Al_{1.10}Ti_{0.08}Li_{0.02}}$[6]	0.4	0.67	85.2	0.018	0.085	0.068	2.039
Schorl ($^{[4]}$B)[7]	15.951(2)	7.164(2)	$\mathrm{Fe^{2+}{}_{1.72}Al_{1.08}Ti_{0.11}\square_{0.06}}$	0.1	0.98	80.8	0.023	0.080	0.064	2.038
Foitite[8]	15.9633(9)	7.135(1)	$\mathrm{Fe^{2+}{}_{1.64}Al_{1.22}Mg_{0.12}Ti_{0.02}}$	0.1	0.75	90.0	0.019	0.089	0.070	2.038
Buergerite[9]	15.874(3)	7.196(2)	$\mathrm{Fe^{3+}{}_{2.12}Al_{0.82}}$[14]	0.8	0.57	91.8	0.016	0.085	0.067	2.004
Povondraite[10]	16.186(2)	7.444(1)	$\mathrm{Fe^{3+}{}_{2.28}Mg_{0.53}Fe^{2+}{}_{0.27}}$	0.0	0.67	54.7	0.021	0.066	0.054	2.037
Feruvite[11]	16.012(2)	7.245(2)	$\mathrm{Fe^{2+}{}_{1.53}Mg_{1.21}Ti_{0.29}}$	0.0	0.80	66.0	0.020	0.066	0.055	2.055
Uvite[9]	15.973(3)	7.213(2)	$\mathrm{Mg_{3.0}}$	0.6	0.33	71.2	0.011	0.072	0.059	2.050
Dravite[12]	15.9459(3)	7.1723(3)	$\mathrm{Mg_{2.46}Al_{0.54}}$	0.1	0.36	77.4	0.014	0.078	0.063	2.045
Dravite (V,Cr)[13]	15.967(2)	7.191(1)	$\mathrm{Mg_{2.05}V^{3+}{}_{0.76}Cr^{3+}{}_{0.19}}$[13]	0.3	0.67	75.6	0.018	0.077	0.062	2.026

Note: [1] This work (Paraíba, Brazil). [2] Sample SS15 (Brown Derby pegmatite, Colorado, U.S.A.) with *ca.* 0.2 $^{[4]}$B *apfu* from Hughes *et al.* (2001). [3] Liddicoatite from Nuber & Schmetzer (1981). [4] Hughes *et al.* (2000), olenite (Koralpe, Styria, Austria) with *ca.* 1 $^{[4]}$B *apfu*. [5] Olenite – schorl – dravite (Ebersdorf, Lower Austria) from Ertl *et al.* (2001b). [6] Schorl (Dlux1; North Windham, Oxford County, Maine, U.S.A.) and olenite – schorl – dravite (O–T16–92; Rangeley, Oxford County, Maine, U.S.A.) from Bloodaxe *et al.* (1999). Dyar *et al.* (1998) reported for sample Dlux1 (schorl) all iron as Fe^{2+} by Mössbauer study. [7] Al-rich schorl (Koralpe, Styria, Austria) with *ca.* 0.2 $^{[4]}$B *apfu* from Ertl & Hughes (2002). [8] Foitite from Francis *et al.* (1999); site occupancies from optimized formula (chemical data in combination with refinement of the site scattering). [9] Uvite (52210; Gouverneur, St. Lawrence County, New York, U.S.A.) and buergerite (43293; Mexquitic, San Luis Potosí, Mexico) from Grice & Ercit (1993). [10] Povondraite from Grice *et al.* (1993). [11] Feruvite from Grice & Robinson (1989). [12] Dravite from the "Friesacher Marmor" [Zadorlaky-Stettner (1961), Pertlik *et al.* (in prep.)], Carinthia, Austria. [13] V- and Cr-rich dravite (Silver Knob, Mariposa County, California, U.S.A.) from Foit & Rosenberg (1979); Dyar *et al.* (1998) reported only $^{[4]}\mathrm{Fe}^{3+}$ but no $^{[6]}$Fe in this sample by Mössbauer study. [14] Dyar *et al.* (1998) reported for sample 43293 (buergerite) all iron as $^{[6]}\mathrm{Fe}^{3+}$ by Mössbauer study. General: Hawthorne & Henry (1999) described Ti at the *Y* site in the general formula of tourmaline as Ti^{4+}.

Distortion parameters:

Bond-length distortion: $\Delta_{oct} = \frac{1}{6}\sum_{i=1}^{6}\left[(d_i - d_m)/d_m\right]^2$, where d_i = (*Y*–O) bond-length, d_m = <*Y*–O> bond-length.

Bond-angle distortion: $\sigma_{oct}^2 = \frac{1}{11}\sum_{i=1}^{12}(\alpha_i - 90)^2$, where α = bond-angle (O–*Y*–O).

Bond-length distortion: $DI(Y-O) = \left(\sum_{i=1}^{6}|d_i - d_m|\right)\Big/6 * d_m$.

Bond-angle distortion: $DI(O-Y-O) = \left(\sum_{i=1}^{12}|\alpha_i - \alpha_m|\right)\Big/12 * \alpha_m$, where α_m = average bond-angle.

Edge-length distortion: $DI(O-O) = \left[\sum_{i=1}^{12}|(O-O)_i - (O-O)_m|\right]\Big/12 * (O-O)_m$.

For the calculations of DI(O–O), DI(O–*Y*–O), and σ_{oct}^2, only (O–O) distances (respectively corresponding angles) between neighboring atoms are taken into account (i = 12 instead of i = 15).

tourmalines with the *Y* site occupied principally by monovalent Li and trivalent Al, such disparities lead to the largest bond-length distortions among *Y* octahedra in tourmaline.

No obvious relation is observed between the bond-length distortion of the *Y* octahedron and the F contents at the *W* site in the investigated structures of tourmaline (Table 1). Comparison of the two Cu-bearing and Cu-free elbaites reveals no obvious distortions that result from the Jahn–Teller element substituents.

Mg-rich tourmalines (dravite and uvite) have the lowest values of bond-length distortion in the $Y\mathrm{O}_6$ octahedron of all investigated tourmalines [$\Delta_{oct} \times 10^3$: 0.33–0.36; DI(*Y*–O): 0.011–0.014; Table 1], and also a low edge-length distortion [DI(O–O): 0.059–0.063]. Povondraite and feruvite have the lowest bond-angle

TABLE 2. THE EXTENT OF DISTORTION IN ZO_6 OCTAHEDRA OF VARIOUS TOURMALINES

Type	*a* [Å]	*c* [Å]	*Z* site (main elements)	Δ_{oct} ×10³	σ_{oct}^2	DI (Z–O)	DI (O–Z–O)	DI (O–O)	<Z-O> [Å]
Elbaite (Cu)[1]	15.831(3)	7.0957(8)	$Al_{5.91}\square_{0.09}$	0.35	50.1	0.016	0.062	0.049	1.905
Elbaite[2]	15.822(2)	7.0949(5)	$Al_{5.93}Li_{0.07}$	0.34	50.9	0.016	0.062	0.050	1.905
Liddicoatite[3]	15.875	7.126	Al_6	0.40	45.3	0.017	0.058	0.047	1.909
Olenite ($^{[4]}$B)[4]	15.731(3)	7.0638(9)	$Al_{5.92}\square_{0.08}$	0.32	56.5	0.015	0.066	0.053	1.902
Olenite-schorl[5]	15.935(3)	7.164(2)	$Al_{5.35}Mg_{0.60}Fe^{2+}_{0.05}$	0.42	49.0	0.017	0.061	0.048	1.922
Olenite-schorl[6]	15.935(1)	7.160(1)	$Al_{5.30}Mg_{0.70}$	0.42	47.4	0.018	0.060	0.049	1.920
Schorl[6]	15.963(1)	7.154(1)	$Al_{5.47}Mg_{0.53}$	0.48	46.1	0.020	0.059	0.048	1.915
Schorl ($^{[4]}$B)[7]	15.951(2)	7.164(2)	$Al_{5.70}Mg_{0.20}Fe^{2+}_{0.08}$	0.43	45.8	0.019	0.058	0.047	1.919
Foitite[8]	15.9633(9)	7.135(1)	$Al_{5.76}Mg_{0.18}Fe^{2+}_{0.06}$	0.56	45.3	0.034	0.058	0.048	1.913
Buergerite[9]	15.874(3)	7.196(2)	$Al_{5.50}Fe^{3+}_{0.50}$	0.29	61.5	0.014	0.068	0.052	1.919
Povondraite[10]	16.186(2)	7.444(1)	$Fe^{3+}_{4.29}Mg_{1.36}Al_{0.32}$	0.22	46.5	0.012	0.062	0.048	2.007
Feruvite[11]	16.012(2)	7.245(2)	$Al_{4.72}Mg_{0.82}Fe^{3+}_{0.34}Fe^{2+}_{0.12}$	0.26	42.6	0.014	0.056	0.046	1.944
Uvite[9]	15.973(3)	7.213(2)	$Al_{5.46}Mg_{0.50}$	0.37	43.5	0.016	0.057	0.046	1.929
Dravite[12]	15.9459(3)	7.1723(3)	$Al_{5.64}Mg_{0.36}$	0.43	43.9	0.018	0.057	0.047	1.918
Dravite (V,Cr)[13]	15.967(2)	7.191(1)	$Al_{5.56}V^{3+}_{0.38}$	0.37	48.1	0.016	0.060	0.048	1.929

Note: [1] This work (Paraíba, Brazil). [2–13] See Table 1. Distortion parameters: see Table 1 (for the formulae, take *Z* instead of *Y* for the bond lengths and bond angles).

distortion [σ_{oct}^2: 54.7–66.0; DI(O–*Y*–O): 0.066]. These tourmalines with the largest lattice constants contain Fe^{2+}, Fe^{3+}, Mg, and (feruvite) Ti, but no significant amounts of Al at the *Y* site. These tourmalines also have the lowest edge-length distortion [DI(O–O): 0.054–0.055]. Buergerite, with *ca.* ($Fe^{3+}{}_2$Al) at the *Y* site [and only $\Sigma(OH)_{0.3}$], has the highest bond-angle distortion (σ_{oct}^2 = 91.8; Table 1).

Foit & Rosenberg (1979) cautiously noted that the bond-angle distortion of the YO_6 octahedron and the <*Y*–O> (average *Y*–O distance) appear to be negatively correlated, although the paucity and poor quality of the data prevented definitive conclusions on their part. In this work, with higher-quality data now available, we also note the low correlation (r^2 = 0.05), but also note the low value of the variance.

Several possible causes can contribute to the distortion of a polyhedron, and it is difficult to separate the effects of size and charge of the central cation substituents, as well as distortions induced from neighboring polyhedra. In tourmaline, the YO_6 octahedron is the more distorted of the two octahedral sites (Tables 1, 2), and also the octahedron that incorporates a wider variety of substituents. Figure 1 illustrates the variation of the bond-length distortion parameter for the *Y* octahedron (Table 1) with the amount of (Al + Ti) per three *Y* sites. Among the octahedrally coordinated occupants, Al and Ti are the smallest of the occupants (Ti is present only in minor amounts in the octahedra) and also among those with the highest charges.

As noted in Figure 1, the octahedra with greater amounts of the (Al + Ti) occupants display greater bond-length distortion. Such a relationship suggests that although some of the bond-length distortion of the *Y* site in tourmaline may be induced by adjacent polyhedra, a portion of the distortion is induced by incorporation of cations of higher charge, which are typically the smaller cations. Although this relationship exists for bond-length distortion parameters, it does not exist for bond-angle distortion, nor does it allow separation of the effects of cation charge and cation size. In examining the tourmalines listed for variations in bond-length distortion in the octahedra, the above observation regarding the relationship between occupants of the *Y* site and distortion of the YO_6 polyhedra was explored.

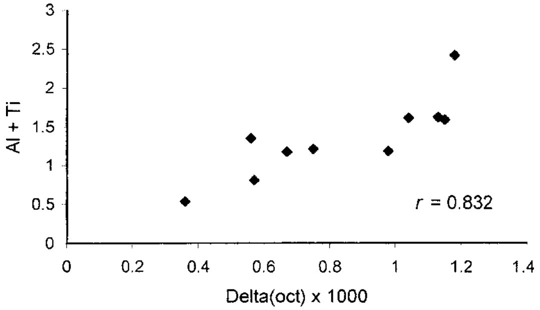

FIG. 1. Relationship between octahedral bond-length distortion (Δ_{oct} × 1000) and sum of (Al + Ti) octahedrally coordinated occupants per three *Y* sites. Only samples with Al on the *Y* site are plotted.

TABLE 3. THE EXTENT OF DISTORTION IN TO_4 TETRAHEDRA OF VARIOUS TOURMALINES

Type	*a* [Å]	*c* [Å]	*T* site (main elements)	Δ_{tet} $\times 10^3$	σ_{tet}^2	DI (*T*–O)	DI (O–*T*–O)	DI (O–O)
Elbaite (Cu)[1]	15.831(3)	7.0957(8)	$Si_{5.74}B_{0.26}$	0.05	6.87	0.006	0.016	0.009
Elbaite[2]	15.822(2)	7.0949(5)	$Si_{5.57}B_{0.22}Al_{0.22}$	0.05	6.86	0.006	0.016	0.009
Liddicoatite[3]	15.875	7.126	$Si_{6.0}$	0.11	12.85	0.010	0.022	0.012
Olenite ($^{[4]}B$)[4]	15.731(3)	7.0638(9)	$Si_{4.86}B_{1.06}Al_{0.08}$	0.02	7.32	0.004	0.016	0.010
Olenite-schorl[5]	15.935(3)	7.164(2)	$Si_{6.0}$	0.05	4.73	0.006	0.013	0.007
Olenite-schorl[6]	15.935(1)	7.160(1)	$Si_{6.00}$	0.05	7.33	0.006	0.016	0.010
Schorl[6]	15.963(1)	7.154(1)	$Si_{5.98}$	0.03	6.11	0.005	0.015	0.010
Schorl ($^{[4]}B$)[7]	15.951(2)	7.164(2)	$Si_{5.76}B_{0.24}$	0.06	7.12	0.007	0.016	0.010
Foitite[8]	15.9633(9)	7.135(1)	$Si_{6.00}$	0.04	3.43	0.005	0.011	0.007
Buergerite[9]	15.874(3)	7.196(2)	$Si_{5.83}B_{0.10}$	0.02	8.93	0.003	0.018	0.011
Povondraite[10]	16.186(2)	7.444(1)	$Si_{5.96}$	0.07	6.80	0.008	0.016	0.008
Feruvite[11]	16.012(2)	7.245(2)	$Si_{5.83}Al_{0.10}$	0.16	16.07	0.012	0.025	0.014
Uvite[9]	15.973(3)	7.213(2)	$Si_{5.99}$	0.13	15.19	0.011	0.024	0.014
Dravite[12]	15.9459(3)	7.1723(3)	$Si_{6.00}$	0.15	11.61	0.011	0.021	0.011
Dravite (V,Cr)[13]	15.967(2)	7.191(1)	$Si_{5.65}Fe^{3+}_{0.17}Al_{0.18}$[14]	0.07	9.61	0.008	0.019	0.011

Note: [1] This work (Paraíba, Brazil). [2–13] See Table 1. [14] Dyar *et al.* (1998) reported only $^{[4]}Fe^{3+}$ in this sample (Silver Knob) by Mössbauer spectroscopy.

Distortion parameters:

Bond-length distortion: $\Delta_{tet} = \frac{1}{4}\sum_{i=1}^{4}\left[(d_i - d_m)/d_m\right]^2$, where d_i = (*T*–O) bond-length, d_m = <*T*–O> bond-length.

Bond-angle distortion: $\sigma_{tet}^2 = \frac{1}{5}\sum_{i=1}^{6}(\alpha_i - 109.4712)^2$, where α = bond-angle (O–*T*–O), α_m = average bond-angle.

Bond-length distortion: $DI(T-O) = \left(\sum_{i=1}^{4}|d_i - d_m|\right)\Big/4*d_m$.

Bond-angle distortion: $DI(O-T-O) = \left(\sum_{i=1}^{6}|\alpha_i - \alpha_m|\right)\Big/6*\alpha_m$.

Edge-length distortion: $DI(O-O) = \left[\sum_{i=1}^{6}|(O-O)_i - (O-O)_m|\right]\Big/6*(O-O)_m$.

As noted previously, MacDonald & Hawthorne (1995) suggested that local positional disorder, common in many tourmaline structures, is induced by occupancy of the *X* and *Y* sites by cations of very different size or charge. Such an observation is supported by the observation of high distortion of (Li, Al)-occupied YO_6 octahedra, and suggests that distortion of the *Y* octahedron may be related to the size and charge of the occupying cations.

To test the relationship between site distortion and properties of the substituent cations, the size (effective ionic radius) and charge of the occupants at the *Y* site have been included in an empirically determined formula for the bond-length distortion (Δ_{calc}) of the YO_6 octahedron (Formula 1). The influence of every occupant against each of the others from the *Y* site is considered in this formula. In the case of the bond-length distortion, there are several candidates for an idealized occupancy at the *Y* site. Consequently, all parameters appearing in Formula (1) were optimized in a nonlinear least-squares fit between the "observed" ($\Delta_{oct} \times 10^3$; Table 1) and "calculated" values [Δ_{calc}; Formula (1)] of bond-length distortion for the samples listed in Table 1. The optimization was initialized with the heuristically determined values (0.34, 1.00, 1.50, –0.50) in place of the values (0.3683, 0.8926, 1.4227, –0.6212) shown in Formula (1).

$$\Delta_{calc} = A + B * \sum_{1 \le i < j \le n} x_j * \left|\alpha_i * r_i^C - \alpha_j * r_j^C\right| \quad (1)$$

In the above expression,

TABLE 4. THE EXTENT OF DISTORTION IN XO_9 POLYHEDRA OF VARIOUS TOURMALINES

Type	*a* [Å]	*c* [Å]	*X* site (main elements)	Δ_X ×10³	DI (*X*–O)	DI (O–*X*–O)	DI (O–O)	<*X*-O> [Å]
Elbaite (Cu)[1]	15.831(3)	7.0957(8)	$Na_{0.54}Ca_{0.11}\square_{0.35}$	3.50	0.055	0.151	0.124	2.671
Elbaite[2]	15.822(2)	7.0949(5)	$Na_{0.52}Ca_{0.09}\square_{0.39}$	3.32	0.053	0.151	0.124	2.670
Liddicoatite[3]	15.875	7.126	$Ca_{0.65}Na_{0.35}$	4.47	0.062	0.156	0.120	2.645
Olenite ($^{[4]}$B)[4]	15.731(3)	7.0638(9)	$Na_{0.40}Ca_{0.29}\square_{0.31}$	1.04	0.028	0.150	0.125	2.647
Olenite-schorl[5]	15.935(3)	7.164(2)	$Na_{0.50}Ca_{0.02}\square_{0.48}$	2.46	0.046	0.152	0.126	2.713
Olenite-schorl[6]	15.935(1)	7.160(1)	$Na_{0.35}Ca_{0.16}K_{0.02}\square_{0.48}$	1.91	0.040	0.147	0.122	2.684
Schorl[6]	15.963(1)	7.154(1)	$Na_{0.61}Ca_{0.03}K_{0.03}\square_{0.33}$	1.33	0.031	0.156	0.126	2.694
Schorl ($^{[4]}$B)[7]	15.951(2)	7.164(2)	$Na_{0.64}Ca_{0.10}K_{0.06}\square_{0.20}$	1.84	0.040	0.146	0.121	2.686
Foitite[8]	15.9633(9)	7.135(1)	$\square_{0.58}Na_{0.41}$	2.19	0.044	0.148	0.121	2.712
Buergerite[9]	15.874(3)	7.196(2)	$Na_{0.86}Ca_{0.04}K_{0.02}\square_{0.07}$	1.18	0.028	0.158	0.130	2.675
Povondraite[10]	16.186(2)	7.444(1)	$Na_{0.80}K_{0.26}$	1.52	0.035	0.168	0.141	2.74
Feruvite[11]	16.012(2)	7.245(2)	$Ca_{0.62}Na_{0.39}K_{0.01}$	1.97	0.040	0.150	0.122	2.654
Uvite[9]	15.973(3)	7.213(2)	$Ca_{0.56}Na_{0.33}\square_{0.11}$ [14]	3.06	0.050	0.155	0.119	2.651
Dravite[12]	15.9459(3)	7.1723(3)	$Na_{0.66}Ca_{0.18}\square_{0.16}$	2.07	0.041	0.149	0.118	2.664
Dravite (V,Cr)[13]	15.967(2)	7.191(1)	$Na_{0.37}Ca_{0.33}K_{0.03}\square_{0.27}$ [14]	1.46	0.034	0.146	0.120	2.673

Note: [1] This work (Paraíba, Brazil; optimized occupancy). [2–13] See Table 1. [14] *X*-site occupancy (samples Silver Knob and 52210) from Dyar *et al.* (1998).

Distortion parameters:

Bond-length distortion: $\Delta_X = \frac{1}{9}\sum_{i=1}^{9}\left[(d_i - d_m)/d_m\right]^2$, where d_i = (*X*–O) bond-length, d_m = <*X*–O> bond-length.

Bond-length distortion: $DI(X-O) = \left(\sum_{i=1}^{9}|d_i - d_m|\right)\Big/ 9 * d_m$.

Bond-angle distortion: $DI(O-X-O) = \left(\sum_{i=1}^{18}|\alpha_i - \alpha_m|\right)\Big/ 18 * \alpha_m$, where α_i = bond-angle (O–*X*–O), α_m = average bond-angle.

Edge-length distortion: $DI(O-O) = \left[\sum_{i=1}^{18}|(O-O)_i - (O-O)_m|\right]\Big/ 18 * (O-O)_m$.

For the calculations of DI(O–O) distances, and DI(O–*X*–O) between neighboring atoms are taken into account (i = 18 instead of i = 30).

Δ_{calc} = calculated bond-length distortion for the YO_6 octahedron

A = 0.3683 (constant)

B = 0.8926 (constant)

C = 1.4227 (constant)

i, *j* = elements (*e.g.*, Li, Mg,...) at 3 *Y* sites

n = number of main elements (>0.01 atoms per formula unit, *apfu*) at 3 *Y* sites

x_i, x_j = concentration (*apfu*) of element *i*, *j*, or of vacancies at 3 *Y* sites; it is important that $x_i > x_j$ wherever $i < j$

α_i, α_j = charge of element *i*, *j* (*e.g.*, 1+, 2+,...), and

r_i, r_j = effective ionic radius (IR) of atom $^{[6]}i$, $^{[6]}j$, from Shannon (1976).

For vacancies ($\square$), the value –0.6212 should be employed for ($\alpha_\square * r_\square^C$).

Figure 2 shows a high positive correlation ($r = 0.972$) between the observed bond-length distortion (Δ_{oct}) and the calculated bond-length distortion (Δ_{calc}). Hence we conclude that the influence of the adjacent polyhedra on *Y* site-distortion is not large, and the distortion of the *Y* octahedron can be almost completely explained by the occupants. Equation (1) above demonstrates that the bond-length distortion in the YO_6 polyhedron results from the size and charge of the occupants at the *Y* site. Such a relationship may be useful in examining distortions in other chemically complex minerals.

Distortion of the ZO_6 *octahedron*

The *Z* octahedron is connected through oxygen atoms to the *T* sites (3×), the *Y* sites (2×), the *B* sites (2×), and the *V* site. The calculated values of the distortion parameters of the ZO_6 octahedra in tourmalines display a very small variation as compared to the YO_6 octahedron.

Foit & Rosenberg (1979) previously demonstrated that the angular distortion of the *Z* octahedron appears to be negatively correlated to <*Y*–O> (smaller size of *Y* producing greater *Z* distortion) for various tourmaline samples (aluminous dravite, buergerite, dravite, elbaite, schorl, uvite, vanadian dravite). Our data from high-quality refinements show a very high negative correlation (Fig. 3; $r = -0.985$) between bond-angle distortion (σ_{oct}^2) of the *Z* octahedron and <*Y*–O> for all tourmalines where O3 (*V* site) is occupied by 3 (OH) *pfu* (Dyar *et al.* 1998, Ertl *et al.* 1997, 2001b, Ertl & Hughes 2002, Grice & Ercit 1993, Grice *et al.* 1993, Grice & Robinson 1989, Hughes *et al.* 2000, 2001, Nuber & Schmetzer 1981). Thus, the occupancy of the *Y* site greatly influences the distortion of the *Z* site with which it shares edges. Only the data for buergerite, where O3 is occupied mainly by O^{2-} and only by 0.29 (OH) *pfu* (Dyar *et al.* 1998), do not fit this linear correlation. O3 is also connected with the *Z* site, suggesting that the occupancy at the *V* site is responsible for the difference in this sample and not the occupancy at the *Y* and *Z* site. A line parallel to the correlation from Figure 3 through the data point for buergerite possibly shows the correlation for chemically different tourmaline samples with only (or mainly) O^{2-} at the *V* site. Hence it may be possible to distinguish between *ca.* 0, 1, 2 or 3 (OH) *pfu* at the *V* site in tourmaline structures by calculating the bond-angle distortion σ_{oct}^2 of the *Z* polyhedron and by applying Figure 3.

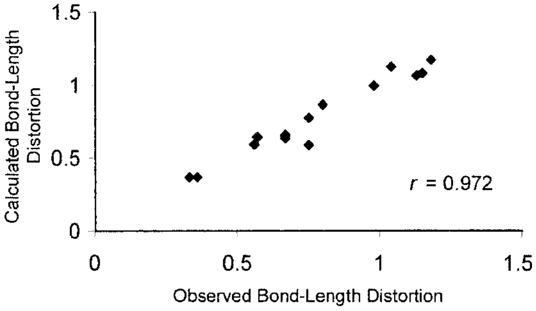

FIG. 2. Relationship between observed bond-length distortion (Δ_{oct} × 1000) and calculated bond-length distortion (Δ_{calc}) of the YO_6 octahedron.

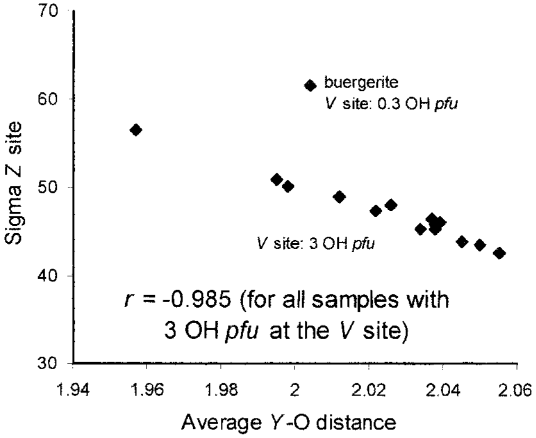

FIG. 3. Relationship between octahedron-distortion parameter σ_{oct}^2 and the average *Y*–O distance.

Distortion of the TO_4 *tetrahedron*

The *T* tetrahedron is connected through oxygen atoms to the *X* sites (2×), the *Y* site, and the *Z* sites (2×). The calculated values for the bond-length distortion for the TO_4 tetrahedron are the smallest of all polyhedra, which is not unexpected for such a rigid polyhedron. In tourmaline, the values of the bond-length distortion from the smallest to the largest polyhedra generally increase as *T* site < *Z* site < *Y* site < *X* site. Tourmalines with a *T* site fully occupied by Si have tetrahedral bond-length distortion ($\Delta_{oct} \times 10^3$) values in the range 0.03–0.15 (Table 3). Surprisingly, olenite with *ca.* one B *apfu* at the *T* site has a very low bond-length distortion in the tetrahedra ($\Delta_{oct} \times 10^3$: 0.02; Table 3).

Although the distortion of the *T* site is not large, Foit & Rosenberg (1979) noted a correlation between the size of the occupants of the *X* site and the distortion of the *T* site. We can improve that correlation by plotting the charge of the *X* site *versus* the bond-angle distortion of the tetrahedron. In the atomic arrangement of a tourmaline, six of the nine *X*-site ligands are shared with tetrahedrally coordinated cations; indeed, O4 and O5 bond only to tetrahedron occupants and *X*-site occupants. The angle distortion of the tetrahedra demonstrates a strong covariance with the charge of the *X* site (Fig. 4; $r = 0.892$). As the *X*-site occupants are typically Na, Ca, K and □, there is a wide range in site charge, with the samples in Table 4 spanning the range 0.52–1.65 valence units, *vu*, inducing a range of angular distortion in the TO_4 tetrahedra from 4.73 to 16.07 (σ_{tet}^2; Table 3). The positive correlation of the *T*-site distortion with both the size and charge of *X*-site occupants is not unexpected: size and charge themselves commonly are correlated among the typical occupants of the *X* site in tourmaline.

Distortion of the XO_9 polyhedron

In tourmaline, the values of the bond-angle distortions generally increase as *T* site < *Z* site < *Y* site < *X* site. The bond-angle distortion [DI(O–*X*–O)] in the XO_9 polyhedra is relatively constant at *ca.* 0.15–0.16 [except for povondraite, with *ca.* $Na_{0.80}K_{0.26}$ at the *X* site, wherein DI(O–*X*–O) is 0.17; Table 4]. The *X* site in the tourmaline structure is connected through oxygen atoms to *T* sites (6×), *Y* sites (3×), and *B* sites (3×). The *B* site is always fully occupied with boron and has little influence on the variations of the distortion in the XO_9 polyhedra [although Clark & Hawthorne (2001) have demonstrated that variations in *B*-site geometry result from the occupants of adjacent polyhedra].

The cause of bond-length distortion in the *X* site is not immediately clear, but several observations relating to composition of the *X*, the *Y*, and *W* sites can be made. Tourmalines with high Li and Al contents (>1 Li *apfu*), and relatively high fluorine contents have the highest bond-length distortion in the XO_9 polyhedron [$\Delta_x \times 10^3$: 3.3–4.5; DI(*X*–O): 0.053–0.062; Table 4]. The highest Δ_x of all investigated tourmalines is found in liddicoatite, with large amounts of Li (1.40 Li *apfu*) and Al, and a very high fluorine content (0.9 F *apfu*) [$\Delta_x \times 10^3$: 4.47; DI(*X*–O): 0.062]. The lowest Δ_x of all investigated samples is B-rich olenite (with only 0.36 Li *apfu*) with *ca.* 1.0 $^{[4]}$B *apfu,* and a very low fluorine content [$\Delta_x \times 10^3$: 1.04; DI(*X*–O): 0.028].

Hence a relationship among site distortion of the *X* site and the charge of the occupants at the *Y* site and the fluorine content was sought. The relationship is revealed by an empirically determined formula for the bond-length distortion (Δ_{calc}) of the XO_9 polyhedron (Formula 2). The influence of the fluorine content and of the *Y*-site occupants (each cation against the others) are considered in this formula. All parameters appearing in Formula (2) were optimized in a nonlinear least-squares fit between the "observed" ($\Delta_X \times 10^3$; Table 4) and "calculated" values [$\Delta_{calc} \times 10^3$; Formula (2)] of bond-length distortion for the samples listed in Tables 1 and 4. The optimization was initialized with heuristically determined values in place of the values shown in Formula (2).

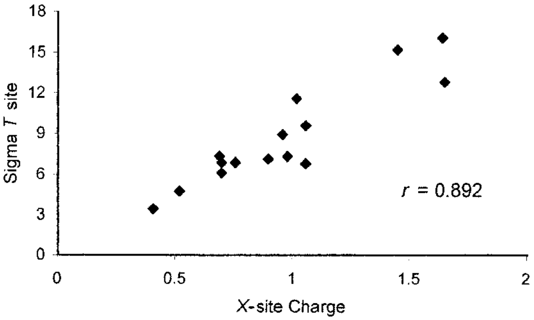

FIG. 4. Relationship between tetrahedron-distortion parameter σ_{tet}^2 and *X* site charge.

$$\Delta_{calc} * 10^3 = A + B * \sum_{1 \le i < j \le n} x_i * \alpha_i + C * F + D * \sum_{1 \le i < j \le n} x_j * \left| \alpha_j - \alpha_i \right| \qquad (2)$$

In this formula,

Δ_{calc} = calculated bond-length distortion for the XO_9 polyhedron

A = 5.4763 (constant)

B = 0.5891 (constant)

C = 1.1199 (constant)

D = 0.4326 (constant)

F = fluorine content (*apfu*) (Table 1)

i, j = elements (*e.g.*, Li, Mg,...) at 3 *Y* sites

n = number of main elements (>0.01 *apfu*) at 3 *Y* sites

x_i, x_j = concentration (*apfu*) of element *i, j* at 3 *Y* sites; it is important that $x_i > x_j$ wherever $i < j$, and

α_i, α_j = charge of element *i, j* (*e.g.*, 1+, 2+,...).

Figure 5 shows a high positive correlation (*r* = 0.881) between the observed bond-length distortion (Δ_X) and the calculated bond-length distortion (Δ_{calc}). Hence we conclude that the influence of the occupants of the *X* site is not great, and the occupants of the *Y* site and the fluorine content can mainly explain the distortion of the *X* polyhedron. The relationship with fluorine content is made clear through crystal-chemical reasoning. The O1 site (*W* site), located on the three-fold axis central to the pseudohexagonal ring of tetrahedra, is bonded to three *Y*-site cations. Where OH occupies the *W* site, the H points toward the *X* site. Experimental and crystallographic studies as well as extensive analytical data on tourmaline establish that F is found also (only) at the *W* site (as summarized by Henry & Dutrow 1996). The presence or absence of the fluorine immediately adjacent to the polyhedron thus effects the distortion of the XO_9 polyhedron.

The size of the cations at the *X* site (and also appreciable amounts of $^{[4]}$B) correlate with the *X*–O2 distance, as was shown by Ertl *et al.* (2001a). Hence these factors may also have some influence on the distortion of the XO_9 polyhedron.

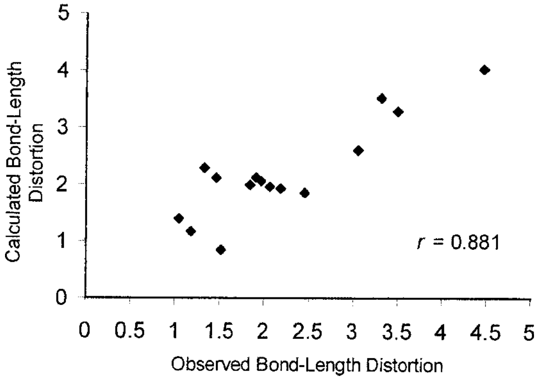

FIG. 5. Relationship between observed bond-length distortion ($\Delta_{oct} \times 1000$) and calculated bond-length distortion ($\Delta_{calc} \times 1000$) of the XO$_9$ polyhedron.

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