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Linking structure and chemistry in the Schorl-Dravite series

**ERICH S. BLOODAXE,[1] JOHN M. HUGHES,[1,*] M. DARBY DYAR,[2] EDWARD S. GREW,[3]
AND CHARLES V. GUIDOTTI[3]**

[1]Department of Geology, Miami University, Oxford, Ohio 45056, U.S.A.
[2]Department of Geography and Geology, Mount Holyoke College, South Hadley, Massachusetts 01075, U.S.A.
[3]Department of Geological Sciences, University of Maine, Orono, Maine 04469-5711, U.S.A.

ABSTRACT

Nine tourmaline crystals for which major and minor element composition data are available have been examined by single-crystal X-ray structure refinement. The single crystals were then analyzed for major elements (by electron microprobe methods), Fe^{3+}/Fe^{2+} (by synchrotron micro-X-ray absorption near-edge spectroscopy), B and Li (by secondary ion mass spectrometry), and bulk H content (by uranium extraction). Despite recent claims based on chemical analyses, structure analysis suggests that no B exists in tetrahedral coordination in these samples. Analysis of cation ordering between the Y and Z octahedral sites suggests that the occurrence of an Fe^{2+} atom on a Y octahedral site may be locally associated with the absence of Mg at both of the neighboring Z sites, as substitutions of Fe^{2+} on Y and Mg on Z require antithetic shifts of the O6 anion.

INTRODUCTION

Recently, tourmaline has been the subject of many papers dealing mostly with a specific site or substitution pair in an attempt to complete the understanding of the structure of the phase (Grice and Ercit 1993; Hawthorne et al. 1993; Hawthorne 1996). For an understanding of the tourmaline atomic arrangement, accurate chemical analyses of the sample are necessary. However, common methods of chemical analysis such as electron microprobe analysis (EMPA) cannot determine B with sufficient accuracy to ensure stoichiometry, nor the amount of Li present or the oxidation state of Fe; consequently, most crystal structure work on tourmalines begins with incomplete compositional data. In addition, analytically obtained H-O balances typically have been ignored in tourmalines, which has resulted in assumptions about the numbers of oxygen atoms and hydroxyls in the O1 and O3 sites.

It has been suggested recently (Dyar et al. 1994; Wodara and Schreyer 1998) that the amount of boron in tourmalines is not fixed at the putative stoichiometric values of 3.0 atoms per formula unit (apfu), but is in fact variable. The tourmaline crystals for this study were obtained from a larger suite characterized in Dyar et al. (1998); this subset is one in which preliminary PIGE (proton-induced Gamma-ray emission) data suggested marked variations in the amount of B. Consequently, one rationale for undertaking structural analysis was to assess B stoichiometry in tourmaline belonging to the most widespread species, namely schorl, dravite, and elbaite (MacDonald and Hawthorne 1995).

THE TOURMALINE STRUCTURE, $XY_3Z_6B_3Si_6O_{27}(O,OH,F)_4$

The tourmaline structure is covered in detail in Henry and Dutrow (1996) and Foit (1989); here we briefly summarize details of the Y and Z octahedral sites. The Y site in tourmaline is octahedrally coordinated, with three octahedra sharing edges around the threefold axis. The Y site bonds to one central O atom (O1) along the threefold axis, two O atoms (O6) from the apices of the silicon tetrahedral ring below, two corner O atoms (O2) of the B triangles above, and another O atom (O3) that bonds to Z sites.

The Z site is a smaller, slightly distorted octahedron arranged around the Y octahedra such that each Y octahedron shares two O3-O6 edges with Z octahedra. Of the O atoms connected to a Z site cation, two O8 atoms are shared with B triangles from different “islands,” three O atoms (O6, O7, O7) are shared with tetrahedra from three different silicate rings, and the last is an O3, which is the O atom not part of either a silicate tetrahedron or a B triangle.

PREVIOUS WORK

Boron has generally been presumed to be present in stoichiometric amounts of 3.0 apfu filling the B trigonal planar site. If the possibility of B in amounts > 3.0 apfu is to be considered, B would most likely be present on the T site (Grice and Ercit 1993). Hawthorne (1996) argued persuasively that electron occupancy would be more sensitive than bond lengths to the presence of B on the T site. He pointed out that the variation in bond lengths presented by Grice and Ercit (1993), in which they argue for B, Ti, and Si occupancy, is not statistically significant.

Grice and Ercit (1993) proposed a somewhat complex scheme for the ordering of Fe and Mg between the Y and Z octahedral sites. At the same time, Hawthorne et al. (1993) were approaching the problem of disordering Mg from a different direction. They noted that in many previously published tourmaline structures, site occupancies can be linked more easily to the octahedral sizes exhibited by the two sites if Mg is

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*E-mail: hughesjm@muohio.edu

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partially disordered onto the Z site, even if Al is present in sufficient amounts to occupy Z completely.

It also should be noted that, although H measurements were performed for the present study, no new relationships based upon amounts of F, OH, and O on O1 and O3 were discovered. Taylor et al. (1995) and Grice and Ercit (1993) covered the relationships of anion substitution to structure with associated coupled cation substitutions.

EXPERIMENTAL METHODS

Single crystals were isolated from mineral separates prepared for Dyar et al. (1998). The suite of nine samples included samples collected for that study (DLux1, O-T16-92, SmFalls, Ru-T17-92, and Ru-T18-92), as well as samples from previous work of other investigators (HP 2-1 from Rockhold et al. 1987 and no. 32008 from Grice and Ercit 1993) and from the Harvard Mineralogical Museum (108749 and LCW2356). Additional information about the samples is given in Dyar et al. (1998).

The samples of this study had been chemically analyzed in bulk samples via electron microprobe methods, Mössbauer spectroscopy, PIGE, and hydrogen extraction. For this study, new chemical data were collected on the nine crystals on which single crystal work was performed; these microanalyses were conducted via EMPA, SIMS (secondary ion mass spectroscopy), and SmX (synchrotron micro-X-ray absorption near-edge spectroscopy). Thus, the only compositional variable that was measured on bulk, rather than single-crystal samples, was H. The individual elements analyzed by each method are noted in Table 1. The methods of these analyses are discussed in detail in Dyar et al. (1998).

Where sufficient material existed (7 samples), single crystals were ground to spheres with diameters ranging from 100 to 160 μm. Two samples were not amenable to such preparation, but were instead cut to roughly equant shapes. X-ray intensity data for the tourmalines were collected on an Enraf-Nonius CAD-4 diffractometer utilizing graphite-monochromatized Mo$K\alpha$ radiation for a hemisphere of reciprocal space. Psi-scan absorption corrections were applied in each instance. Unit-cell parameters were refined using diffraction angles from 25 automatically centered reflections. The starting model for all refinements was taken from the dravite structure in Grice and Ercit (1993). Details of data collection and structure refinement are provided in Table 2, and Table 3 provides positional parameters and equivalent isotropic thermal parameters for the structures.

All structures were refined with anisotropic thermal parameters (Table 4[1]) and, initially, with all cation multiplicities released. When the refinements had converged and the correct enantiomer was determined, bond lengths (Table 5) and electron occupancies of each site were used as the basis for site assignment as detailed below. Table 6 lists final site assingments.

CHEMICAL FORMULAE

All tourmaline compositions were normalized to 31 O atoms, minus the applicable number of halogen ions, following the method of Deer et al. (1992) for clinohumite analysis (Table 1). This procedure subtracts the oxygen equivalent of F from the total oxide percentages, and also subtracts half the fluorine contents from the atom proportion total. This procedure is necessary to have formulas that charge balance to neutrality because the more commonly used method of simply subtracting twice the weight percent of F from the number of normalizing oxygens does not yield electronically neutral formulas. However, in some samples this method results in stoichiometries in which the sum of cations in the sites that are known to be full from XRD data (i.e., the T, B, Y, and Z sites) is greater than the stoichiometric 18 cations. Dyar et al. (1998) have shown that such "nonstoichiometry" cannot be correlated with any particular analytical variables, and it is the result of random analytical errors propagated from the oxide measurements.

SITE ASSIGNMENT

It has been shown previously that all of the non-oxygen (OH, F) anions occur at the O1 and O3 sites in tourmaline. Chlorine contents provided by chemical analyses are negligible (<0.004 apfu) and thus ignored in site assignments. Previous work on other types of tourmaline (Hawthorne 1996; Grice and Ercit 1993) suggested that hydroxyls would occupy O3, and other monovalent anions preferentially occupy O1. Bond-valence calculations performed for the samples of this study agreed with this suggestion.

Among the cations, the bond lengths and chemical analyses in all but sample 108749 show the T site to be fully occupied with Si; Si ranges from 5.93(6)–6.15(3) apfu. Thus, in all samples other than 108749, Si was assigned at 6 apfu. In sample 108749, a marked silicon deficiency [Si = 5.66(7) apfu] is indicated by the chemical analysis, and an excess of Al exists over that necessary to fill the octahedral sites. As no vacancies are expected on the T site, the excess aluminum from the octahedral sites was assigned to the T site along with additional Si (0.167 apfu) above the analyzed amount to balance the bond lengths and electron occupancy at the site. B ranges from 3.01(8)–3.22(4) apfu by chemistry within the sample set. Bond lengths at the site are compatible with full occupancy by boron, and thus B was assigned at 3 apfu.

Hawthorne et al. (1993) assigned Al and Mg to the Y and Z sites such that linear relationships were obtained between mean bond lengths and constituent cation radii. In our study, every crystal possessed an electron occupancy at the Z site between 12 and 13 e^-, consistent with these sites being filled with Mg and Al; thus Z was modeled exclusively with a mixture of Al and Mg.

For final refinement, the aggregate Y and Z occupants were normalized to nine cations. One sample (32008) yielded 8.67 atoms in octahedra before normalization; we attribute this 3.7% cation deficiency to accumulated analytical error. For final refinement, the Hawthorne et al. (1993) method of ordering Mg and Al between the two octahedra by minimizing the errors between grand mean octahedral bond length and bond lengths

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[1] For a copy of Table 4, Document AM-99-012, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the *American Mineralogist* web site at http://www.minsocam.org.

TABLE 1. Chemical compositions of tourmaline crystals*

	32008	O-T16-92	Ru-T17-92	Ru-T18-92	SmFalls	DLux1	LCW2356	HP 2-1	108749
SiO_2	36.92(18)	36.26(32)	36.40(46)	36.38(24)	36.38(22)	35.14(28)	36.51(33)	35.63(37)	34.08(43)
Al_2O_3	26.74(23)	33.16(31)	33.64(20)	32.24(25)	33.14(20)	32.62(20)	31.75(21)	33.49(30)	35.85(36)
TiO_2	0.27(13)	0.56(14)	0.67(15)	0.99(21)	0.20(13)	0.64(24)	0.30(13)	0.07(9)	0.39(11)
FeO_{total}‡	8.31(27)	7.42(27)	7.54(12)	5.73(34)	7.62(24)	12.40(29)	2.43(16)	12.01(33)	8.89(25)
FeO‡	2.10	5.68	4.94	3.83	6.69	11.07	2.25	8.77	7.60
Fe_2O_3‡	6.90	1.93	2.89	2.11	1.03	1.47	0.19	3.60	1.43
MgO	8.89(20)	5.47(13)	4.97(19)	6.99(22)	5.21(15)	2.06(14)	10.50(16)	2.52(15)	3.41(33)
MnO	0.09(6)	0.05(4)	0.02(3)	0.05(3)	0.13(6)	0.10(6)	0.02(3)	0.09(6)	0.02(3)
Cr_2O_3	0.02(4)	0.06(5)	0.01(3)	0.04(7)	0.00(1)	0.01(2)	0.08(8)	0.01(3)	0.03(4)
V_2O_3	0.01(1)	0.04(6)	0.11(8)	0.07(12)	0.05(7)	0.03(4)	0.06(11)	0.04(7)	0.05(5)
CaO	2.06(5)	0.88(11)	0.10(2)	0.35(14)	0.09(1)	0.17(1)	2.10(5)	0.15(1)	0.56(7)
Na_2O	1.46(17)	1.08(27)	1.66(17)	1.96(16)	2.14(15)	1.84(18)	1.31(20)	1.67(16)	2.21(19)
K_2O	0.14(17)	0.07(7)	0.19(24)	0.15(20)	0.07(9)	0.14(14)	0.13(23)	0.12(15)	0.20(22)
B_2O_3	10.61(39)	10.96(17)	10.59(58)	11.31(13)	11.07(22)	10.28(36)	10.69(39)	10.71(43)	10.51(29)
Li_2O	0.03(3)	0.00(0)	0.00(0)	0.01(0)	0.01(0)	0.03(1)	0.01(0)	0.00(0)	0.01(0)
F	0.94(11)	0.11(6)	0.20(8)	0.64(10)	0.58(6)	0.66(8)	0.26(10)	0.39(7)	0.58(6)
Cl	0.01(1)	0.00(1)	0.00(1)	0.00(0)	0.00(0)	0.01(1)	0.00(1)	0.01(1)	0.00(0)
H_2O	2.72	2.80	2.75	2.44	2.94	2.82	2.75	3.06	3.13
%Fe^{3+}‡	74.7	23.4(9.6)	34.5(7.5)	33.1	12.2	10.7	7.2	27.0(6.2)	14.5
SUM	99.92	99.11	99.13	99.54	99.73	99.11	98.92	100.34	100.06
Si	6.146(30)	6.006(53)	6.035(76)	5.991(40)	6.000(36)	5.977(48)	6.007(54)	5.929(62)	5.657(71)
Al	5.245(45)	6.473(61)	6.573(39)	6.257(49)	6.442(39)	6.540(40)	6.156(41)	6.568(59)	7.014(70)
Ti	0.034(16)	0.070(18)	0.083(19)	0.122(26)	0.025(16)	0.082(31)	0.037(16)	0.009(12)	0.049(14)
Fe^{2+}	0.293	0.787	0.685	0.528	0.922	1.575	0.310	1.220	1.055
Fe^{3+}	0.864	0.241	0.361	0.261	0.128	0.189	0.024	0.450	0.179
Mg	2.207(50)	1.350(32)	1.230(47)	1.717(54)	1.282(37)	0.523(36)	2.576(39)	0.626(37)	0.844(82)
Mn	0.012(8)	0.007(6)	0.003(5)	0.006(4)	0.018(8)	0.015(9)	0.003(5)	0.013(9)	0.003(5)
Cr	0.003(6)	0.008(7)	0.002(6)	0.005(9)	0.001(1)	0.002(4)	0.010(10)	0.002(6)	0.003(4)
V	0.001(1)	0.006(9)	0.014(10)	0.010(17)	0.007(10)	0.004(5)	0.008(15)	0.005(9)	0.007(7)
Ca	0.368(9)	0.156(20)	0.017(3)	0.061(24)	0.016(2)	0.031(2)	0.370(9)	0.027(2)	0.100(13)
Na	0.471(55)	0.348(87)	0.533(55)	0.626(51)	0.684(48)	0.608(59)	0.418(64)	0.540(52)	0.711(61)
K	0.029(35)	0.015(15)	0.040(51)	0.031(41)	0.015(19)	0.030(30)	0.027(48)	0.025(31)	0.043(47)
B	3.048(112)	3.133(49)	3.030(166)	3.215(37)	3.151(63)	3.019(106)	3.035(111)	3.076(123)	3.011(83)
Li	0.018(18)	0.001(1)	0.001(1)	0.006(3)	0.006(3)	0.020(7)	0.005(2)	0.002(2)	0.006(3)
F	0.495(58)	0.060(33)	0.106(42)	0.331(52)	0.301(31)	0.355(43)	0.134(52)	0.204(37)	0.302(31)
Cl	0.004(4)	0.001(1)	0.001(1)	0.001(1)	0.000(1)	0.003(3)	0.001(1)	0.002(2)	0.001(1)
H	3.020	3.094	3.041	2.681	3.234	3.200	3.018	3.396	3.466

* All analyses except wt% H_2O (est. error <0.1 wt%) were done on the exact crystals used for the single crystal XRD refinements. Methods used included EPMA for Si, Al, Ti, total Fe, Mg, Mn, Cr, V, Ca, Na, K, F, and Cl; SIMS for B and Li, and SmX for %Fe^{3+}.

† Errors are the standard deviation of repeat analyses on the individual crystals by the applicable analytical technique. For EPMA, these represent standard deviations on at least 10 analyses per crystal; for SIMS, 2–4 analyses per crystal, and for SmX, 2 analyses per crystal. If no error is tabulated here, only one analysis was obtained.

‡ The SmX method yields data on the percentage of the total Fe that is Fe^{3+}. Accuracy is believed to be ±5–10%. These values were used to recalculate the total FeO determined by EPMA.

TABLE 2. Crystal data

	108749	DLux1	LCW2356	HP 2-1	O-T16-92	SmFalls	Ru-T17-92	Ru-T18-92	No. 32008
Unit cell									
a	15.939(1)	15.963(1)	15.915(1)	15.946(1)	15.935(1)	15.934(1)	15.935(1)	15.945(1)	15.965(1)
c	7.146(1)	7.154(1)	7.187(1)	7.157(1)	7.160(1)	7.167(1)	7.164(1)	7.169(1)	7.199(1)
Scan type	θ/2θ	θ/2θ	θ/2θ	θ/2θ	θ/2θ	θ/2θ	θ/2θ	θ/2θ	θ/2θ
Scan times (s)	≤60	≤60	≤60	≤60	≤60	≤60	≤60	≤60	≤60
θ limits (°)	0.1–30	0–30	0.1–30	0.1–30	0–30	0–30	0–30	0–30	0-30
Data collected	3150	3167	3164	3163	3163	3165	3161	3176	3197
R_{merge}	0.012	0.022	0.023	0.018	0.028	0.022	0.027	0.024	0.025
No. observations (3σ)	1092	969	939	1057	870	948	901	960	984
No. variable parameters	88	88	88	88	88	88	88	88	88
R	0.017	0.021	0.027	0.021	0.022	0.022	0.027	0.022	0.025
Rw	0.024	0.028	0.034	0.030	0.027	0.028	0.032	0.026	0.033
Goodness-of-Fit	0.911	0.829	1.004	0.969	0.731	0.826	0.878	0.737	0.907
Difference Peaks (e/Å^3)									
(+)	0.926	0.898	1.100	0.920	0.872	0.838	0.860	0.895	0.878
(-)	0.574	0.740	0.749	0.615	0.684	0.530	0.847	0.591	0.800

TABLE 3. Positional parameters and equivalent isotropic temperature factors

Site	*X*	*y*	*z*	B(Å²)
Sample 108749				
X	0	0	1/4	1.67(3)
Y	0.27140(2)	2*x*	0.32225(8)	0.818(9)
Z	0.29802(3)	0.26158(3)	0.63386(7)	0.386(7)
T	0.19205(3)	0.19007(3)	0.02373(7)	0.427(6)
B	0.10995(9)	2*x*	0.4766(3)	0.57(4)
O1	0	0	0.7984(5)	1.68(4)
O2	0.06111(6)	2*x*	0.5082(2)	1.06(3)
O3	0.2660(1)	1/2*x*	0.5326(2)	1.00(3)
O4	0.09313(7)	2*x*	0.0940(2)	0.88(3)
O5	0.1858(1)	1/2*x*	0.1168(2)	0.87(3)
O6	0.19696(7)	0.18640(8)	0.7984(2)	0.72(2)
O7	0.28589(8)	0.28604(7)	0.1022(2)	0.68(2)
O8	0.20956(7)	0.27008(7)	0.4632(2)	0.71(2)
DLux1				
X	0	0	1/4	1.72(6)
Y	0.27084(3)	2*x*	0.3124(1)	0.89(1)
Z	0.29845(5)	0.26173(5)	0.6288(1)	0.31(1)
T	0.19187(4)	0.18987(5)	0.0179(1)	0.42(1)
B	0.1103(2)	2*x*	0.4716(6)	0.65(7)
O1	0	0	0.7972(8)	2.07(8)
O2	0.0617(1)	2*x*	0.5035(4)	1.18(6)
O3	0.2681(2)	1/2*x*	0.5275(4)	0.98(6)
O4	0.0928(1)	2*x*	0.0864(4)	0.85(6)
O5	0.1866(2)	1/2*x*	0.1081(4)	0.72(5)
O6	0.1976(1)	0.1871(1)	0.7931(3)	0.73(3)
O7	0.2852(1)	0.2860(1)	0.0969(3)	0.68(3)
O8	0.2099(1)	0.2703(1)	0.4586(3)	0.72(3)
LCW2356				
X	0	0	1/4	1.06(4)
Y	0.27101(5)	2*x*	0.3202(2)	0.31(2)
Z	0.29800(6)	0.26160(6)	0.6316(2)	0.51(1)
T	0.19181(5)	0.19005(6)	0.0197(1)	0.51(1)
B	0.1094(2)	2*x*	0.4720(7)	0.64(9)
O1	0	0	0.7958(8)	0.98(7)
O2	0.0606(1)	2*x*	0.5019(5)	1.12(7)
O3	0.2633(3)	1/2*x*	0.5307(4)	1.17(7)
O4	0.0928(1)	2*x*	0.0902(4)	0.91(7)
O5	0.1831(3)	1/2*x*	0.1120(5)	0.95(7)
O6	0.1957(2)	0.1860(1)	0.7969(3)	0.80(4)
O7	0.2852(1)	0.2846(1)	0.0994(3)	0.78(4)
O8	0.2092(1)	0.2700(2)	0.4606(3)	0.84(3)
HP 2-1				
X	0	0	1/4	1.40(5)
Y	0.27130(2)	2*x*	0.3159(1)	0.91(1)
Z	0.29822(4)	0.26160(4)	0.6299(1)	0.31(1)
T	0.19184(3)	0.18982(4)	0.0193(1)	0.401(9)
B	0.1104(1)	2*x*	0.4741(5)	0.66(6)
O1	0	0	0.7957(7)	1.78(6)
O2	0.06144(9)	2*x*	0.5064(3)	1.17(5)
O3	0.2665(2)	1/2*x*	0.5288(3)	1.02(5)
O4	0.09323(9)	2*x*	0.0880(3)	0.82(5)
O5	0.1868(2)	1/2*x*	0.1109(3)	0.76(4)
O6	0.1968(1)	0.1864(1)	0.7949(2)	0.72(3)
O7	0.2853(1)	0.2856(1)	0.0981(2)	0.68(3)
O8	0.2099(1)	0.2703(1)	0.4597(2)	0.75(3)
O-T16-92				
X	0	0	1/4	1.50(6)
Y	0.27168(4)	2*x*	0.3238(2)	0.86(2)
Z	0.29797(5)	0.26147(5)	0.6356(1)	0.41(1)
T	0.19180(5)	0.18986(5)	0.0255(1)	0.45(1)
B	0.1100(2)	2*x*	0.4778(6)	0.71(8)
O1	0	0	0.8000(9)	1.50(8)
O2	0.0614(1)	2*x*	0.5108(4)	1.02(6)
O3	0.2652(2)	1/2*x*	0.5348(4)	1.10(7)
O4	0.0930(1)	2*x*	0.0955(4)	0.84(6)
O5	0.1860(2)	1/2*x*	0.1178(4)	0.77(6)
O6	0.1965(1)	0.1859(1)	0.8003(3)	0.75(4)
O7	0.2851(1)	0.2855(1)	0.1035(3)	0.73(4)
O8	0.2094(1)	0.2702(1)	0.4648(3)	0.70(4)
SmFalls				
X	0	0	1/4	1.94(6)
Y	0.27098(3)	2*x*	0.3130(1)	0.82(2)
Z	0.29811(5)	0.26160(5)	0.6279(1)	0.40(1)
T	0.19185(4)	0.18983(5)	0.0170(1)	0.45(1)
B	0.1096(2)	2*x*	0.4704(6)	0.63(7)
O1	0	0	0.7915(8)	1.52(7)
O2	0.0616(1)	2*x*	0.5035(4)	1.12(6)
O3	0.2651(2)	1/2*x*	0.5271(4)	1.04(6)
O4	0.0931(1)	2*x*	0.0863(4)	0.85(6)
O5	0.1861(2)	1/2*x*	0.1087(4)	0.79(5)
O6	0.1967(1)	0.1862(1)	0.7925(3)	0.75(3)
O7	0.2853(1)	0.2857(1)	0.0954(3)	0.70(3)
O8	0.2097(1)	0.2701(1)	0.4572(3)	0.76(3)
Ru-T17-92				
X	0	0	1/4	1.40(8)
Y	0.27150(4)	2*x*	0.3176(2)	0.84(2)
Z	0.29790(6)	0.26149(6)	0.6301(2)	0.42(1)
T	0.19178(5)	0.18978(6)	0.0198(1)	0.42(1)
B	0.1103(2)	2*x*	0.4733(7)	0.61(9)
O1	0	0	0.7949(9)	1.60(9)
O2	0.0615(1)	2*x*	0.5078(5)	1.02(7)
O3	0.2645(3)	1/2*x*	0.5281(5)	1.06(7)
O4	0.0931(1)	2*x*	0.0891(4)	0.87(7)
O5	0.1865(3)	1/2*x*	0.1120(5)	0.77(7)
O6	0.1961(2)	0.1857(2)	0.7951(3)	0.82(4)
O7	0.2849(1)	0.2854(1)	0.0978(3)	0.73(4)
O8	0.2097(2)	0.2701(2)	0.4597(3)	0.81(4)
Ru-T18-92				
X	0	0	1/4	1.46(5)
Y	0.27103(3)	2*x*	0.3151(1)	0.82(1)
Z	0.29813(4)	0.26166(4)	0.6300(1)	0.45(1)
T	0.19181(4)	0.18982(4)	0.0188(1)	0.457(9)
B	0.1102(1)	2*x*	0.4733(5)	0.61(6)
O1	0	0	0.7954(7)	1.25(6)
O2	0.06143(9)	2*x*	0.5041(4)	0.98(5)
O3	0.2660(2)	1/2*x*	0.5283(3)	1.02(5)
O4	0.0931(1)	2*x*	0.0888(3)	0.85(5)
O5	0.1859(2)	1/2*x*	0.1106(3)	0.78(5)
O6	0.1966(1)	0.1864(1)	0.7947(2)	0.73(3)
O7	0.2851(1)	0.2854(1)	0.0979(2)	0.68(3)
O8	0.2097(1)	0.2705(1)	0.4596(2)	0.72(3)
No. 32008				
X	0	0	1/4	0.74(3)
Y	0.27140(4)	2*x*	0.3223(2)	1.01(2)
Z	0.29804(5)	0.26164(5)	0.6346(1)	0.28(1)
T	0.19175(5)	0.18997(5)	0.0223(1)	0.40(1)
B	0.1102(2)	2*x*	0.4745(6)	0.61(8)
O1	0	0	0.8001(8)	0.83(7)
O2	0.0609(1)	2*x*	0.5005(4)	0.81(6)
O3	0.2678(2)	1/2*x*	0.5338(4)	0.82(6)
O4	0.0922(1)	2*x*	0.0931(4)	0.76(6)
O5	0.1835(2)	1/2*x*	0.1133(4)	0.72(6)
O6	0.1960(1)	0.1866(1)	0.7997(3)	0.65(4)
O7	0.2847(1)	0.2846(1)	0.1027(3)	0.74(4)
O8	0.2097(1)	0.2702(1)	0.4639(3)	0.73(4)

Note: Anisotropically refined atoms are given in the form of their isotropic equivalent displacement parameter defined as: $(4/3) * [a^2*\beta_{11} + b^2*\beta_{22} + c^2*\beta_{33} + ab(\cos\ \gamma)*\ \beta_{12} + ac(\cos\ \beta)*\beta_{13} + bc(\cos\ \alpha)*\ \beta_{23}]$.

TABLE 5. Selected bond lengths (Å)

Bond	108749	Dlux1	LCW2356	HP 2-1	O-T16-92	SmFalls	Ru-T17-92	Ru-T18-92	No. 32008
X-O2 ×3	2.500(1)	2.490(2)	2.464(3)	2.499(2)	2.521(2)	2.488(2)	2.509(3)	2.490(2)	2.467(2)
X-O4 ×3	2.802(1)	2.819(1)	2.803(1)	2.824(1)	2.796(1)	2.826(1)	2.817(1)	2.818(1)	2.789(1)
X-O5 ×3	2.736(2)	2.772(3)	2.711(4)	2.765(3)	2.736(3)	2.761(3)	2.758(3)	2.755(3)	2.722(3)
Mean	2.679	2.694	2.659	2.696	2.684	2.692	2.695	2.688	2.659
Y-O1	1.991(2)	2.040(3)	1.999(3)	2.009(3)	1.986(3)	2.011(3)	1.994(4)	2.018(3)	2.004(3)
Y-O2 ×2	1.999(1)	1.996(2)	2.015(3)	1.988(2)	1.995(2)	1.993(2)	1.987(2)	1.997(2)	2.032(2)
Y-O3	2.150(2)	2.152(3)	2.106(4)	2.147(3)	2.146(3)	2.118(3)	2.133(4)	2.134(3)	2.174(3)
Y-O6 ×2	2.006(1)	2.026(2)	1.997(2)	2.016(2)	2.005(2)	2.011(2)	2.004(2)	2.015(2)	2.018(2)
Mean	2.025	2.039	2.022	2.027	2.022	2.023	2.018	2.029	2.046
Z-O3	1.985(1)	1.981(2)	1.991(3)	1.983(1)	1.985(2)	1.986(3)	1.991(2)	1.988(1)	1.984(2)
Z-O6	1.866(1)	1.864(2)	1.885(2)	1.873(2)	1.873(2)	1.872(2)	1.879(2)	1.875(2)	1.884(2)
Z-O7	1.882(1)	1.880(2)	1.902(3)	1.885(2)	1.891(2)	1.890(2)	1.892(3)	1.891(2)	1.902(2)
Z-O7'	1.946(1)	1.954(2)	1.956(2)	1.955(2)	1.955(2)	1.951(2)	1.957(2)	1.956(2)	1.967(2)
Z-O8	1.920(1)	1.922(3)	1.927(3)	1.920(2)	1.925(2)	1.922(2)	1.918(3)	1.922(2)	1.927(2)
Z-O8'	1.889(1)	1.886(2)	1.894(2)	1.887(2)	1.890(2)	1.889(2)	1.892(2)	1.889(2)	1.895(2)
Mean	1.915	1.915	1.926	1.917	1.920	1.918	1.922	1.920	1.927
T-O4	1.627(1)	1.624(2)	1.623(2)	1.623(2)	1.624(2)	1.623(2)	1.622(2)	1.625(2)	1.629(2)
T-O5	1.642(1)	1.634(2)	1.643(2)	1.636(2)	1.639(2)	1.636(2)	1.637(2)	1.638(2)	1.643(2)
T-O6	1.615(1)	1.613(2)	1.605(2)	1.610(2)	1.617(2)	1.613(2)	1.615(3)	1.611(2)	1.606(2)
T-O7	1.614(1)	1.615(2)	1.601(2)	1.611(1)	1.606(2)	1.609(2)	1.605(2)	1.609(1)	1.606(1)
Mean	1.625	1.622	1.618	1.620	1.622	1.620	1.620	1.621	1.621
B-O2	1.367(1)	1.363(1)	1.361(1)	1.372(1)	1.363(1)	1.348(1)	1.368(1)	1.364(1)	1.376(1)
B-O8 ×2	1.378(2)	1.380(3)	1.378(3)	1.378(2)	1.375(3)	1.384(3)	1.376(3)	1.378(3)	1.378(3)
Mean	1.374	1.374	1.372	1.376	1.371	1.372	1.373	1.373	1.377

TABLE 6. Final assigned site occupancies

Sample	Assigned occupants
	X site
108749	$Ca_{0.100}Na_{0.711}K_{0.043}\square_{0.146}$
DLux1	$Ca_{0.031}Na_{0.608}K_{0.030}\square_{0.331}$
LCW2356	$Ca_{0.370}Na_{0.418}K_{0.027}\square_{0.185}$
HP 2-1	$Ca_{0.027}Na_{0.540}K_{0.025}\square_{0.408}$
O-T16-92	$Ca_{0.156}Na_{0.348}K_{0.015}\square_{0.481}$
SmFalls	$Ca_{0.016}Na_{0.684}K_{0.015}\square_{0.285}$
Ru-T17-92	$Ca_{0.017}Na_{0.533}K_{0.040}\square_{0.410}$
Ru-T18-92	$Ca_{0.061}Na_{0.626}K_{0.031}\square_{0.282}$
No. 32008	$Ca_{0.368}Na_{0.471}K_{0.029}\square_{0.132}$
	Y site
108749	$Al_{1.284}Mg_{0.407}Fe^{2+}_{1.055}Fe^{3+}_{0.179}Ti_{0.049}V^{3+}_{0.007}Li_{0.006}Zn_{0.007}$
DLux1	$Al_{1.103}Fe^{2+}_{1.575}Fe^{3+}_{0.189}Ti_{0.082}Li_{0.020}Mn_{0.015}$
LCW2356	$Al_{1.092}Mg_{1.517}Fe^{2+}_{0.310}Fe^{3+}_{0.024}Ti_{0.037}V^{3+}_{0.008}Li_{0.005}Cr_{0.010}$
HP 2-1	$Al_{1.197}Mg_{0.077}Fe^{2+}_{1.220}Fe^{3+}_{0.450}Ti_{0.009}V^{3+}_{0.005}Mn_{0.013}Zn_{0.006}$
O-T16-92	$Al_{1.217}Mg_{0.656}Fe^{2+}_{0.787}Fe^{3+}_{0.241}Ti_{0.070}V^{3+}_{0.006}Cr_{0.008}Mn_{0.007}$
SmFalls	$Al_{1.270}Mg_{0.603}Fe^{2+}_{0.922}Fe^{3+}_{0.128}Ti_{0.025}V^{3+}_{0.007}Li_{0.006}Mn_{0.018}$
Ru-T17-92	$Al_{1.253}Mg_{0.594}Fe^{2+}_{0.685}Fe^{3+}_{0.361}Ti_{0.083}V^{3+}_{0.014}$
Ru-T18-92	$Al_{0.954}Mg_{1.099}Fe^{2+}_{0.528}Fe^{3+}_{0.261}Ti_{0.122}V^{3+}_{0.010}Li_{0.006}Cr_{0.005}Mn_{0.006}$
No. 32008	$Al_{0.350}Mg_{1.379}Fe^{2+}_{0.293}Fe^{3+}_{0.864}Ti_{0.034}Li_{0.018}Mn_{0.012}$
	Z site
108749	$Al_{5.563}Mg_{0.437}$
DLux1	$Al_{5.474}Mg_{0.526}$
LCW2356	$Al_{4.977}Mg_{1.023}$
HP 2-1	$Al_{5.444}Mg_{0.556}$
O-T16-92	$Al_{5.297}Mg_{0.703}$
SmFalls	$Al_{5.296}Mg_{0.704}$
Ru-T17-92	$Al_{5.354}Mg_{0.646}$
Ru-T18-92	$Al_{5.365}Mg_{0.635}$
No. 32008	$Al_{5.090}Mg_{0.910}$
	O1 site
108749	$O^{2-}_{0.233}OH_{0.465}F_{0.302}$
DLux1	$O^{2-}_{0.445}OH_{0.200}F_{0.355}$
LCW2356	$O^{2-}_{0.848}OH_{0.018}F_{0.134}$
HP 2-1	$O^{2-}_{0.400}OH_{0.396}F_{0.204}$
O-T16-92	$O^{2-}_{0.846}OH_{0.094}F_{0.060}$
SmFalls	$O^{2-}_{0.465}OH_{0.234}F_{0.301}$
Ru-T17-92	$O^{2-}_{0.853}OH_{0.041}F_{0.106}$
Ru-T18-92	$O^{2-}_{0.669}F_{0.331}$
No. 32008	$O^{2-}_{0.485}OH_{0.020}F_{0.495}$
	T site
108749	$Si_{5.834}Al_{0.166}$
All other samples	Si_6
	B site
All samples	B_3
	O3 site
Ru-T18-92	$O^{2-}_{0.319}OH_{2.681}$
All other samples	$(OH)_3$

Note: Elements present in amounts less than 0.004 atoms by chemistry omitted.

calculated from constituent cation radii was implemented. As a minimum total error over both sites can be reached by assignments that include shifting almost all of the error to one site or the other, the final assignment was made by minimizing the difference between the error on Y and that on Z.

RESULTS

The combination of X-ray structure data and complete major-element chemical analyses allows us to address questions regarding tourmaline crystal chemistry. First, given chemical analyses indicating >3 apfu B in the samples, will structure refinement verify this proposed B excess? Second, do the site refinements yield information regarding site assignments on Y and Z?

The absence of tetrahedral boron

Although most of the chemical analyses do show Si ≈ 6 apfu, the analysis of sample 108749 shows Si = 5.66(7) apfu by chemistry, Si = 5.83(1) apfu by refinement, allowing us to address the question of tetrahedral substitutions raised by a half-dozen authors over the last two decades (for example, Wodara and Schreyer 1998; Hawthorne 1996). Bond valence sums and bond lengths provided a mechanism to confirm that Al^{3+} was the substituent.

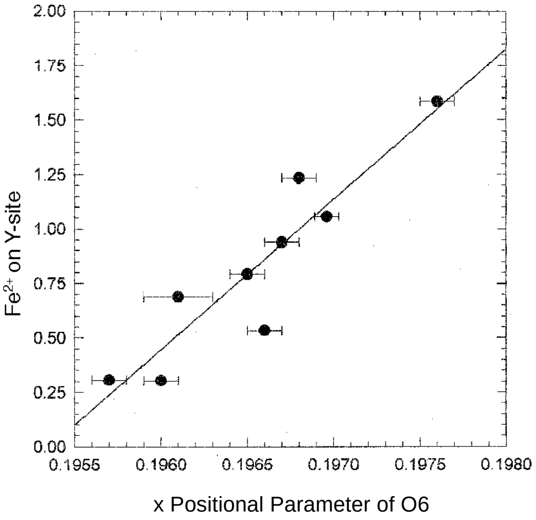

FIGURE 1. The x positional parameter of O6 vs. Fe^{2+} on Y.

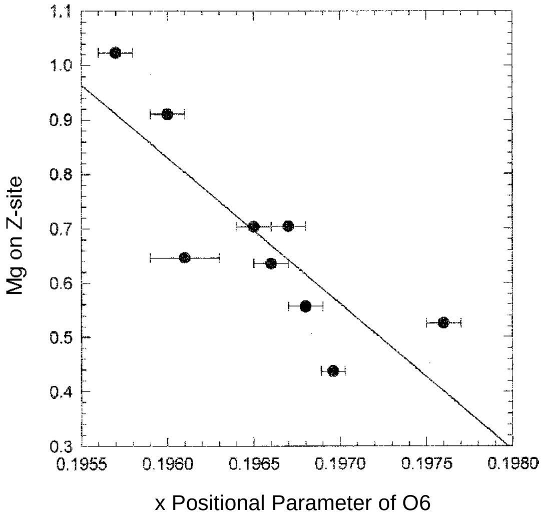

FIGURE 2. The x positional parameter of O6 vs. Mg on Z.

The tetrahedral substitution $3Si^{4+} = 2Al^{3+} + B^{3+}$ with an unspecified coupled substitution for charge balance **{Auth: ok?}** preserves the putative Si-O bond length, and can be considered in samples that yield an Si deficiency. Thought was given to placing excess B on the T site in sample 108749, but of the nine samples, this one had the lowest amount of excess B (0.011 excess B apfu). Despite the apparent presence of B in amounts >3 apfu in all samples as given by chemical analyses, structural refinement did not verify the existence of tetrahedral B in any sample.

This study does not rule out the *possibility* of B substituting on the T site if Si deficiencies exist (Wodara and Schreyer 1998), but in the absence of such deficiencies on the T site coupled with excess B in amounts greater than those observed in this study, we believe there is no compelling evidence for B > 3.0 apfu, thus confirming the conclusions of MacDonald and Hawthorne (1995). As Dyar et al. (1998) conclude, this apparent nonstoichiometry is most likely the result of systematic analytical errors propagated from the oxide measurements.

Constraining Mg and Fe^{2+} ordering

Grice and Ercit (1993) suggested ordering of Fe and Mg between the Y and Z sites, but made several assumptions because of incomplete chemical analyses. As a result, they presented a fairly complex method for modeling this ordering. With Fe valence-state data available, the ordering can be explained more simply.

Each Y octahedron shares two O3-O6 edges with Z octahedra, and thus substitution on a Y site directly affects two Z sites. In addition to joining a Y and Z site, O6 is the apical oxygen of a neighboring silicate tetrahedron; therefore, shifts in O6 positions are constrained by the silicate ring as well.

There is a positive correlation (r = 0.921; Fig. 1) between Fe^{2+} on Y and the *x* positional parameter of O6 and a negative correlation ($r = -0.827$; Fig. 2) between Mg on Z and the x positional parameter of O6. Substitution of Fe^{2+} on Y and Mg on Z thus require antithetic displacements of the O6 atom, apparently diminishing the probability of such substitutions in adjacent sites.

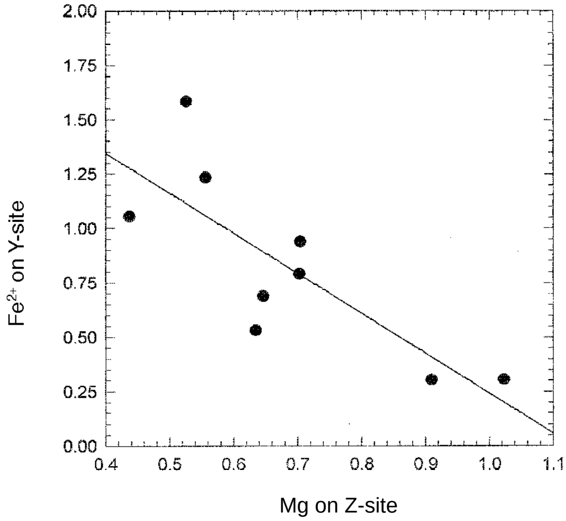

FIGURE 3. Mg on Z vs. Fe^{2+} on Y, depicting the negative correlation between Fe^{2+} on the Y site and Mg on Z.

Fe^{2+} is the largest of the cations occupying Y and Mg the larger of the two cations occupying Z. Therefore, the presence of Fe^{2+} on a given Y site may preclude the presence of Mg^{2+} on either of the two adjacent Z sites. This limitation is suggested when Fe^{2+} on Y is plotted against Mg on Z ($r = -0.796$; Fig. 3), which illustrates that with increasing substitution of Fe^{2+} on Y there is decreasing substitution of Mg on Z. The relationship has a slope of nearly –2 (actually –1.84), suggesting that occupancy of one Y site by Fe^{2+} precludes occupancy of the two adjacent Z octahedra by Mg. It may be noted that an inverse relationship between total Mg and Fe^{2+} exists; this is to be expected from the substitution of one divalent cation for another in the structure. The inverse relationship between Fe^{2+} on Y and Mg on Z points to a structural rather than a partitioning causative agent, which might be expected to displace Mg from Y to Z, resulting in a positive correlation between Fe^{2+} on Y and Mg on Z.

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