

Reassignment of cation site occupancies in tourmaline: Al-Mg disorder in the crystal structure of dravite

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ABSTRACT

The crystal structure of a dravite (tourmaline) sample from Osarara, Narok District, Kenya, $a = 15.947(2)$, $c = 7.214(1)$ Å, $V = 1589.0(6)$ Å³, $R3m$, has been refined to an R index of 2.0% based on 1136 reflections measured with $\text{MoK}\alpha$ X-radiation. Electron microprobe analysis, site-scattering refinement, electronic absorption (published), stereochemical analysis, and Mössbauer spectra show the structural formula to be $^{+}(\text{Na}_{0.814}\text{Ca}_{0.009}\text{K}_{0.014}\text{□}_{0.163})^{+}(\text{Mg}_{1.301}\text{Mn}_{0.003}\text{Fe}_{0.051}^{2+}\text{Fe}_{0.560}^{3+}\text{Cr}_{0.006}\text{Ti}_{0.030}\text{Al}_{0.985})^{+}(\text{Al}_{5.090}\text{Mg}_{0.910})(\text{BO}_3)_3\text{Si}_6\text{O}_{18}^{+}(\text{O},\text{OH})_4$. Of particular interest is the assignment of significant Mg to the Z site and Al to the Y site. For published structural refinements of tourmaline, the grand mean size of the Y and Z polyhedra is a linear function of the constituent cation radii. That is not the case for the Y and Z sites individually. However, greatly improved linearity occurs if significant Mg is assigned to the Z site for some compositions when $\text{Al} > 6.0$ atoms pfu; this indicates that the usual assumption that Al completely occupies the Z site before occupying any other site is not universally correct.

INTRODUCTION

Tourmaline is a common mineral in igneous, sedimentary, and metamorphic environments and is very useful as an indicator mineral (e.g., Henry and Dutrow, 1990; Henry and Guidotti, 1985). There has been considerable work on general variations in tourmaline compositions (e.g., Foit and Rosenberg, 1977; Benvenuti et al., 1991; Povondra, 1981) and extensive examination of polyhedral rotations as a function of chemical composition. However, compared with other silicate minerals, there has not been any detailed examination of structural variations (particularly changes in polyhedral sizes) as a function of constituent-site chemistry, and few structures have been refined.

Tourmaline is a very difficult mineral to characterize with respect to its chemistry. Many significant components (i.e., H, Li, $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{Mn}^{3+}/\text{Mn}^{2+}$) cannot be studied by electron microprobe analysis, there is often significant zonation, and crystals are difficult to dissolve for wet-chemical analysis. Crystal structure refinement can be a powerful technique for determination of chemical composition through definition of stereochemical relationships and refined site-scattering values (Hawthorne and Grice, 1990; Ungaretti, 1980; Ungaretti et al., 1983). Here we present a crystal structure refinement of dravite and examine mean bond-length constituent-cation radius relationships in published tourmaline structures.

EXPERIMENTAL

The sample used in this work was supplied by George R. Rossman, California Institute of Technology. Mössbauer and polarized electronic absorption spectra are re-

ported by Mattson and Rossman (1984, Sample 1, from Osarara, Narok District, Kenya, archival code NMNH no. 126030 from the U.S. National Museum of Natural History).

X-ray data collection

A crystal fragment was ground to a sphere in an air-driven crystal grinder and mounted on a Nicolet R3m automated four-circle diffractometer. Twenty-five reflections were centered using graphite-monochromated $\text{MoK}\alpha$ X-radiation, and the cell dimensions and orientation matrix were derived from the resulting setting angles. A total of 1136 reflections were measured ($2\theta = 3\text{--}60^\circ$) with index ranges $0 \leq h \leq 19$, $0 \leq k \leq 19$, $-11 \leq l \leq 11$. Two standard reflections were measured every 48 reflections; no significant changes in their intensities were observed during data measurement. A ψ -scan absorption correction was applied, together with the usual geometrical corrections, and the data were reduced to structure factors. Numerical details are given in Table 1.

Structure refinement

Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from Cromer and Mann (1968) and Cromer and Liberman (1970), respectively. The Siemens SHELXTL Plus (PC version) system of programs was used for all calculations.

The structure was refined in space group $R3m$ using the coordinates of feruvite (Grice and Robinson, 1989) as an initial model. Refinement with all variable positional parameters, anisotropic displacement factors, site occupancies for the X, Y, and Z sites, an empirical isotropic ex-

TABLE 1. Miscellaneous information concerning data measurement, data reduction, and crystal structure refinement of dravite

<i>a</i> (Å)	15.947(2)	Crystal size (mm)	0.23 sphere
<i>c</i>	7.214(1)	Rad/Mon	Mo/Gr
<i>V</i> (Å ³)	1589.0(6)	Total $ F_o $	1136
Space group	<i>R3m</i>	<i>R</i> _{azimuthal} (%)	0.80 → 0.77
<i>Z</i>	3	<i>R</i> _{obs} (%)	2.00
		<i>R</i> _w	2.34

$$R = \sum (|F_o| - |F_c|) / \sum |F_o|$$

$$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}, w = 1/(\sigma^2 F_o + gF_o^2)$$

tion parameter, and weights given as in Table 1 with *g* as a refinable parameter converged to an *R* index of 2.0%. Refined positional and displacement parameters are given in Table 2, observed and calculated structure factors in Table 3¹, and selected interatomic distances and angles in Table 4.¹

Electron microprobe analysis

Subsequent to the X-ray data measurement, the crystal used to collect the intensity data was mounted in epoxy, then ground, polished, and C coated for electron microprobe analysis. The analysis was done on a Cameca SX-50 instrument in the wavelength-dispersive mode, with an excitation voltage of 15 kV, a beam current of 20 nA, and a beam diameter of 1 μm. Counting times for peaks and backgrounds were 20 and 10 s, respectively. The analysis (mean of 12 points) is given in Table 5; the formula unit was calculated on the basis of Mg + Fe²⁺ + Fe³⁺ + Ti + Mn + Al + Si = 15 with the Fe³⁺/Fe²⁺ ratio taken from Mattson and Rossman (1984). B₂O₃ and H₂O contents were calculated stoichiometrically. There was a slight deficiency in the Y-site sum; however, the refined site scattering value was not compatible with any vacancy or Li at the Y site, and thus the Y-site contents were normalized to full occupancy.

¹ To obtain a copy of Tables 3 and 4, order Document AM-93-522 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

RESULTS

Mattson and Rossman (1984) reported the Mössbauer spectrum and polarized electronic absorption spectra of this dravite. From these data, they gave the Fe³⁺/Fe²⁺ ratio as 0.915:0.085; this value was used in calculating the formula unit (Table 5).

A comparison of the refined site scattering factors and the occupancies assigned from the electron microprobe analysis is given in Table 6. As is apparent, the agreement is very good, with a weighted deviation of 0.07 e (electrons) per site; this is of the same order as the standard deviation of each method, and thus suggests that the results are accurate to the level of their precision. Note that the relative distribution of Al (*Z* = 13) and Mg (*Z* = 12) does not materially affect this comparison because of the similarity in X-ray scattering powers. This also means that the site-scattering results do not contain any information as to the relative distribution of Mg and Al over the Y and *Z* sites.

DISCUSSION

The site-scattering results indicate that there is no significant transition-metal occupancy of the *Z* site (Table 6). In all previous work on tourmaline, it has been customary to assign all available Al to the *Z* site. Al in excess of that necessary to fill *Z* is assigned to Y. When the amount of Al is insufficient to fill *Z*, the deficiency can be made up by transition metals (e.g., Fortier and Donnay, 1975; Nuber and Schmetzer, 1979) and Mg (Grice and Robinson, 1989).

In most structure types with extensive solid solution, there are well-developed linear relationships between the sizes (mean bond length) of the coordination polyhedra and the mean empirical radii of the constituent cations (and anions if variable). These relationships have been important in assigning site occupancies and cation valence states in complex minerals (e.g., amphiboles: Ungaretti, 1980; Hawthorne, 1983; pyroxenes: Ribbe and Prunier, 1977; Cameron and Papike, 1981; garnets: Novak and Gibbs, 1971; Hawthorne, 1981). Thus it seems worthwhile to develop such relationships for the tourmaline structures, as they should be of use in deriving transition-

TABLE 2. Final parameters for the crystal structure of dravite

Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} [*]	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
X	0	0	0.15920	211(8)	227(9)	227(9)	177(9)	0	0	114(5)
Y	0.93867(3)	0.06133(3)	0.5643(4)	112(3)	90(3)	90(3)	137(4)	-17(1)	17(1)	30(3)
Z	0.73849(4)	0.70217(4)	0.5386(4)	71(2)	73(3)	69(3)	69(3)	-2(2)	-10(2)	35(2)
Si	0.81018(3)	0.80835(3)	0.9280(4)	61(2)	56(2)	54(3)	69(2)	4(2)	6(2)	25(2)
B	0.11000(9)	0.89000(9)	0.3819(5)	83(8)	86(8)	86(8)	82(9)	-4(4)	4(4)	45(9)
O1	0	0	0.6989(5)	124(7)	128(8)	128(8)	118(9)	0	0	64(4)
O2	0.06109(7)	0.93891(7)	0.4156(4)	123(6)	138(7)	138(7)	122(9)	-5(3)	5(3)	91(7)
O3	0.86947(8)	0.13053(8)	0.4381(5)	140(6)	139(6)	139(6)	71(8)	1(3)	-1(3)	17(8)
O4	0.09300(8)	0.90601(8)	0.9989(5)	119(6)	101(6)	101(6)	115(8)	10(4)	-10(4)	19(7)
O5	0.90733(8)	0.09267(8)	0.0212(4)	114(6)	97(6)	97(6)	106(8)	11(3)	-11(3)	17(7)
O6	0.81568(9)	0.80578(9)	0.7059(4)	99(5)	119(6)	110(6)	74(6)	8(4)	12(4)	63(5)
O7	0.71512(9)	0.71494(9)	0.0059(4)	99(5)	76(6)	86(6)	112(6)	21(5)	27(5)	22(5)
O8	0.73016(9)	0.79077(9)	0.3674(4)	107(5)	98(6)	62(6)	159(6)	-17(5)	-34(4)	38(5)

* *U*_{ij} = *U*_{ij} × 10⁴.

TABLE 5. Electron microprobe analysis and formula unit* for dravite

SiO ₂	37.19	Si	6.080
Al ₂ O ₃	31.53	Al	6.075
TiO ₂	0.25	Ti	0.030
Cr ₂ O ₃	0.05	Cr	0.006
Fe ₂ O ₃	4.43	Fe ³⁺	0.560
FeO	0.37	Fe ²⁺	0.051
MgO	9.07	Mg	2.211
MnO	0.02	Mn	0.003
CaO	0.05	Ca	0.009
Na ₂ O	2.57	Na	0.814
K ₂ O	0.07	K	0.014
F	0.01	F	0.005
B ₂ O ₃	(10.78)	B	3
H ₂ O	(3.72)	OH	3.995
Total	100.10		

* Calculated as discussed in text.

metal valence states, light element (e.g., Li) contents, and aspects of ordering that are ambiguous with regard to X-ray scattering (e.g., Mg/Al, Fe/Mn ordering).

The available data are summarized in Table 7 and graphically displayed in Figure 1. There are no well-developed linear relationships. The best-behaved trend is for the Z site (Fig. 1a). Six structures define a linear trend with a slope that is close to unity, the ideal value for a hard-sphere model. Two structures depart significantly (~0.008 Å) from this trend, having longer Z–O distances than expected for the assigned site population. It is notable that the dravite structure refined here (circled star in Fig. 1a) has a ⟨Z–O⟩ distance of 1.936 Å, no transition metals at the Z site, and more than sufficient Al to fill the Z site. If we assign full Al occupancy to the Z site, this dravite will deviate from the line in Figure 1a by ~0.03 Å. This suggests that the constituent cations occupying the Z site have a larger aggregate radius than Al. This may be the case if significant Mg replaces Al at the Z site, and this replacement can occur without perturbing the agreement between the chemical populations and the refined site-scattering values given in Table 6.

The data for the Y site (Fig. 1b) show far more scatter; indeed, one even questions whether a linear relationship exists. However, all other structure types show well-behaved relationships of this type, and there is no apparent reason why tourmaline should not do so as well. Consequently we will examine the factors that could perturb such relationships in tourmaline. There are three obvious factors: (1) wrong assignment of cations between the Y and Z sites; (2) variable OH and F contents and possible order-disorder over O1 and O3; and (3) incorrect assignment of valence states for the transition metals. The discussion given above for the Z-site behavior indicates that point 1 is definitely a factor in this situation. However, in order to make better site-population assignments, points 2 and 3 must be dealt with first, as reassignment of such atom pairs as Al–Mg and Fe–Mn must depend on stereochemical rather than scattering data. Errors in assignment of cations between the Y and Z polyhedra may be by-

TABLE 6. Comparison of formula unit site assignments with refined site-scattering results and final site assignments

Site		Electron microprobe	Structure refinement	Stereochemical criteria
X	Na	0.814		0.814
	Ca	0.009		0.009
	K	0.014		0.014
	e	9.40	9.27	—
	Ti	0.030		0.030
Y	Cr	0.006		0.006
	Fe ³⁺	0.560		0.560
	Fe ²⁺	0.051		0.051
	Mn	0.003		0.003
	Mg	2.273		1.349
	Al	0.077		1.001
Z	e	15.01	15.15	—
	Al	6.00		5.076
	Mg	—		0.924
	e	13.00	13.03	—

Note: Refined site-scattering results are in electrons.

passed by considering the aggregate behavior of the Y and Z polyhedra as a function of their aggregate chemistry. Figure 2 shows the variation of the weighted mean size of the Y and Z polyhedra [$(3\langle Y-O \rangle + 6\langle Z-O \rangle)/9$] as a function of the mean radius of the Y and Z cations. There is greatly improved linearity over the individual relationships shown in Figure 1; this indicates that wrong cation assignment to the Y and Z sites is a significant factor in the nonlinearity exhibited by Figure 1a and 1b.

However, there is still some scatter in Figure 2, indicating that variations in OH and F contents or oxidation states of Fe and Mn are also significant factors affecting ⟨Y–O⟩ and ⟨Z–O⟩. Let us first examine OH and F contents as a possible factor. The tourmaline structure shows considerable variation in total monovalent anion content, from 1 atom pfu in such compositions as buergerite to 4 atoms pfu in uvite; in addition, there may be significant F ≈ OH variation. As there are significant differences in the radii of these three anions (³¹O = 1.36; ³¹OH = 1.34;

TABLE 7. Anion contents of the O1 and O3 sites in refined tourmaline structures

Name	OH	F	O	⟨r⟩(Å)*	Reference
Buergerite	0.46	1.03	2.51	1.342	(1)
Feruvite	4.00	0.00	0.00	1.340	(2)
Elbaite	2.87	0.60	0.53	1.337	(3)
Chromium tourmaline	1.62	—	2.38	1.352	(4)
Aluminum dravite	3.72	—	0.28	1.341	(5)
Vanadium dravite	2.58	0.32	1.10	1.342	(6)
Uvite	3.29	0.44	0.27	1.337	(5)
□-schorl	3.86	0.14	—	1.339	(7)
Aluminum elbaite	2.44	0.09	1.47	1.346	(8)

Note: Anion contents in atoms pfu.

References: (1) Barton, 1969; (2) Grice and Robinson, 1989; (3) Donnay and Barton, 1972; (4) Nuber and Schmetzer, 1979; (5) Schmetzer et al., 1979; (6) Foit and Rosenberg, 1979; (7) Foit, 1989; (8) Gorskaya et al., 1982.

* Calculated with the radii of Shannon (1976).

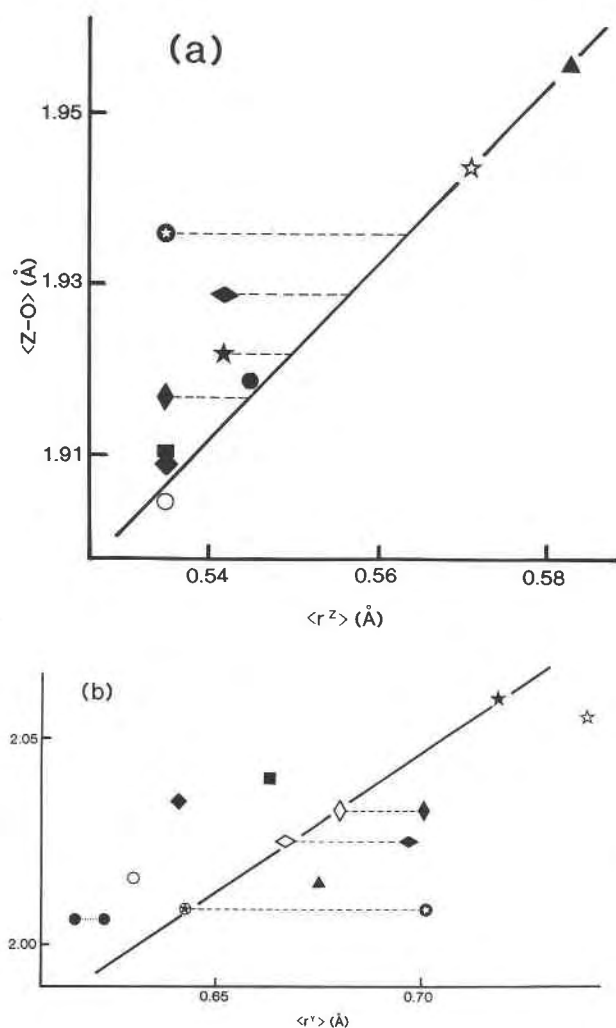


Fig. 1. Relationships between mean bond length and constituent ionic radius in refined tourmaline structures: (a) the Z site; (b) the Y site. The horizontal dashed lines show the revised constituent cation radii for the reassigned populations. Buergerite: solid circle; feruvite: open star; schorl: solid star; liddicoatite: inclined solid square; elbaite: open circle; tsilaisite: solid square; chromium tourmaline: triangle; vanadium dravite: horizontal solid diamond; □-schorl: vertical solid diamond; dravite: circled stars.

$^{13}\text{F} = 1.30 \text{ \AA}$; Shannon, 1976), such variations can cause significant differences in mean bond lengths around the cations to which they are coordinated. The situation is not straightforward here, as the monovalent anions occupy two distinct sites, O1 and O3, and thus the individual mean bond lengths can be affected by monovalent anion ordering over O1 and O3 for a fixed anion composition. To some extent, this latter difficulty also may be bypassed for the moment by considering the grand mean bond length of the Y and Z polyhedra, as in Figure 2. The anion contents of the crystals used for the X-ray structure refinement are given in Table 7.

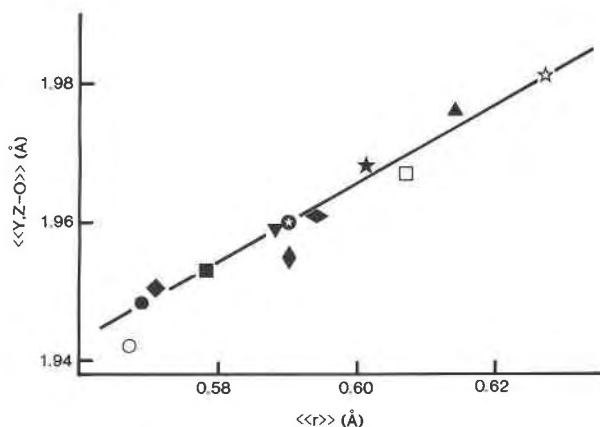


Fig. 2. Weighted-mean bond length of the Y and Z polyhedra as a function of constituent cation radius in tourmalines. The squares show the data points in three F-rich tourmalines corrected for their F content. Legend as in Fig. 1 plus aluminum dravite: solid inverted triangle; uvite: open square.

In terms of possible anion variations and anion size, the extreme end-members are $(\text{OH})\text{O}_3$ and F_4 , with mean anion radii of 1.355 and 1.300 Å, respectively. This range would produce a maximum variation of 0.012 Å in terms of the weighted mean bond lengths of the Y and Z polyhedra and a much larger possible variation in the individual mean bond lengths if there is significant anion order over the O1 and O3 sites. However, the variation in anion chemistry shown in Table 7 can only produce a variation of 0.003 Å in the grand mean X and Y bond lengths; nevertheless, the structures with smaller anion radii do move closer to the general trend (Fig. 2) with these small corrections. The aluminum elbaite of Gorskaya et al. (1982) seems to have an anomalously small grand mean bond length for the Y and Z polyhedra, and the large mean anion radius of the O1 and O3 sites further increases the deviation from the general trend in Figure 2; the origin of this is not yet clear and needs further investigation.

The data of Figure 2, when corrected for minor variations in anion content, are fairly linear, suggesting that there are no major errors in the assignment of transition-metal oxidation states. We may thus conclude that the crystallographic data are broadly consistent with the reported composition of the samples and that the poorly developed correlations between $\langle \text{Y-O} \rangle$ and $\langle \text{Z-O} \rangle$ are due to wrongly assigned cation and anion site populations.

Reconsideration of site populations in tourmaline

The Z site. Some of the data in Figure 1a do define a linear trend with a slope of unity, consistent with the hard-sphere model. However, there are significant deviations from this trend, always to the larger bond-length side (except for aluminum elbaite, which seems anomalous in all regards, see Fig. 2). It has generally been assumed that the Z site is completely occupied by Al when allowed by the constituent chemistry of the crystal, unless transition-metal cations have been detected here by site occupancy

TABLE 8. Empirical bond valence table for dravite

	X	Y	Z	Si	B	Σ
O1		0.481 ^{x3}				1.443
O2	0.134 ^{x3}	0.429 ^{x2-}			1.018	2.010
O3		0.331	0.405 ^{x2}			1.141
O4	0.076 ^{x3}			0.989 ^{x2}		2.054
O5	0.089 ^{x3}			0.941 ^{x2}		1.971
O6		0.442 ^{x2}	0.490	1.043		1.975
O7			0.444	1.046		1.987
			0.497			
O8			0.473		1.009	1.989
			0.507			
TOTAL	0.897 (0.846)	2.554 (2.542)	2.816 (2.847)	4.019	3.036	

refinement. The data of Figure 1a suggest that this assumption is wrong. The occurrence of some Mg at the Z site would maintain the same scattering from this position in the structure while increasing the size of the Z octahedron relative to those structures in which Z is completely occupied by Al. Of particular note in this regard are the V-bearing tourmaline (horizontal solid diamond: Foit and Rosenberg, 1979), schorl (solid star: Fortier and Donnay, 1975), and the alkali-deficient schorl (vertical solid diamond: Foit, 1989). For the schorl, setting the Z-site Fe^{3+} to Fe^{2+} moves this point to the ideal trend, and hence this is possible, particularly as the Y polyhedron in schorl is well-behaved in this regard. If the site populations of these crystals are adjusted such that they agree with the general trend of Figure 1a, the resultant change in Y-site populations has a significant effect on the analogous Y-site relationship.

The Y site. As noted above, changing the population of the Z site has a significant effect on the assigned population of the Y site, particularly as the multiplicity of the former is twice that of the latter. As can be seen in Figure 1b, the four tourmalines with divalent Z-site cations are shifted considerable distances (0.055 Å for dravite) to become linear with some of the other structures. This improvement reinforces the correctness of the reassignments based on the Z-site relationship alone.

However, there are still structures that deviate from linearity, and it is notable that for most of them, the Y octahedron is larger than the mean radius of the assigned constituent cations would suggest. Of particular note in this regard are buergerite (solid circle: Barton, 1969; Tippe and Hamilton, 1971), elbaite (open circle: Donnay and Barton, 1972), liddicoatite (inclined solid square: Nuber and Schmetzer, 1981), and tsilaisite (solid square: Nuber and Schmetzer, 1984). One can suggest that the Fe at Y in buergerite is partly Fe^{2+} , and this could bring this sample into line with the general trend. However, the same argument cannot be used for the other three crystals, as these are virtually Fe-free; hence the deviations cannot be the result of errors in assignment of cation population (presuming the analyses to be correct and representative of the crystal used in the X-ray intensity data collection). In addition, the variations in anion occupancies are not

sufficient to account quantitatively for these deviations. Hence complete resolution of this matter must await additional data, and we are planning further work on this point.

Bond-valence calculations for dravite

The site populations used in the calculation of bond valences are obviously of importance. Here we calculate the bond-valence distribution in dravite using the universal curves of Brown (1981). Each universal curve works for all cations of a specific isoelectronic series; in the case of dravite, the curve for the (Na···S)-O series is of importance, as this single relationship describes the relationship of bond valence to bond length for Na-O, Mg-O, Al-O, Si-O, P-O, and S-O bonds. Thus any disorder involving these cations (e.g., Mg/Al, Al/Si) need not be specified in the site populations used for bond-valence calculations as the relationship used is the same for both cations. Thus in the calculation of the bond-valence table for dravite (Table 8), both sets of site populations in Table 6 give the same result.

The valence-sum rule (Brown, 1981) states that the sum of the bond valences at each atom is equal to the formal valence of the atom. Therefore, when averaged over the whole structure, the sum of the bond valences incident to a site is equal to the average atom valence at that site. Thus when there is polyvalent cation substitution (e.g., $\text{Mg} \rightleftharpoons \text{Al}$) at a specific cation site, the sum of the incident bond valence at that site gives an estimate of the amount of such substitution, and this estimate is independent of the assumed site populations if the substituting cations belong to the same isoelectronic series. Let us focus on the bond-valence sums at the X, Y, and Z sites in Table 8. The values in parentheses are the mean valences of the cation site populations of Table 6; as assigned by stereochemical criteria, they agree closely with the bond-valence sums at these three sites. The corresponding values for the site populations as conventionally assigned from the electron microprobe analysis are 2.23 and 3.00 for the Y and Z sites, respectively, in conspicuous disagreement with the bond-valence sums. Thus the bond-valence sums at the Y and Z sites confirm the stereochemically assigned site populations of Table 6.

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