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Refinement of the Crystal Structure of Buergerite and the Absolute Orientation of Tourmalines*

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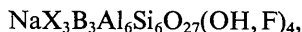
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The crystal structure of buergerite from Mexico has been refined by least-squares by use of single-crystal X-ray intensity data collected by counter diffractometry. Buergerite, ideally $\text{NaFe}_3^{3+}\text{B}_3\text{Al}_6\text{Si}_6\text{O}_{30}\text{F}$, crystallizes in $R3m$; the hexagonal cell dimensions for the specimen used are: $a = 15.869 \pm 2$, $c = 7.188 \pm 1 \text{ \AA}$ at 21°C . $D_m = 3.30 \pm 1$ at 23°C ; with $Z = 3$, $D_x = 3.29 \text{ g.cm}^{-3}$. Of 3909 independent reflections measured, 3121 were observed; the residual R for the observed reflections is 0.046. The structure is very similar to the refined dravite structure of Buerger, Burnham & Peacor (*Acta Cryst.* (1962), **15**, 583) which was used as the starting model. Refinement of the (Fe^{3+} , Al) distribution shows that some ferric iron replaces octahedral aluminum in the 18(c) position, a substitution not required by the chemical analysis. The absolute orientation of the crystal structure with respect to the macroscopic polar properties of tourmaline was determined by anomalous dispersion, mostly due to iron, under copper radiation. The SiO_4 tetrahedra point toward the analogous pole of the c axis, the pole that becomes positively charged on heating.

Introduction

The extensive chemical substitution observed in tourmaline makes this mineral group a natural laboratory for the study of solid solution and the variation of structure with chemical composition. Three principal species are recognized: dravite, schorl, and elbaite, for which, in the idealized formula



X stands for Mg, Fe^{2+} , and (Li, Al), respectively.

Epprecht (1953) combined cell dimensions and published chemical analyses to show that two series of tourmalines can be distinguished (Fig. 1), and by extrapolation he derived ideal cell dimensions for the three end-members (Table 1). The dravite-schorl and schorl-elbaite series are virtually immiscible, and it was later suggested that they might represent distinct sub-phases, separated by a compositional transition of first or higher order (Donnay, Wyart & Sabatier, 1959).

Table 1. *Extrapolated cell dimensions (Epprecht, 1953)*

End-member	a (Å)	c (Å)	c/a
Elbaite	15.842	7.099	0.4481
Schorl	16.032	7.149	0.4459
Dravite	15.942	7.225	0.4522

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These conclusions were prompted by two published tourmaline structures which, although similar in bonding patterns, were different in detail, particularly in the configuration of the Si₆O₁₈ ring: the first structure (Donnay & Buerger, 1950), that of a dravite, contained a ditrigonal ring, whereas the second (Ito & Sadanaga, 1951), reportedly an elbaite, contained an exactly hexagonal ring. However, the probability that this difference did not represent any real variation in structure as a function of chemical composition was established by the refinement of dravite (Buerger, Burnham & Peacor, 1962), which showed the Si₆O₁₈ ring to be nearly, though not exactly, hexagonal.*

A new species of iron tourmaline was described by Mason, Donnay & Hardie (1964). It is distinguished by an unusual combination of cell dimensions: *c* is too large for the small value of *a*, and *a* is too low for the rather high value of *c* (Fig. 1). It has a density higher than any found in other tourmalines, and it shows a good, though difficult, cleavage which no other tourmaline species show. As it is also characterized by high refractive indices and extreme birefringence, it was thought to contain a high proportion of ferric iron. This presumption was later confirmed by chemical analysis, spectroscopic study, and the synthesis of ferric tourmaline with similar cell dimensions. The new species was named buergerite (Donnay, Ingamells & Mason, 1966). It has the idealized formula NaFe₃³⁺-B₃Al₆Si₆O₃₀F.

* This refinement also revealed as incorrect a third and somewhat different version of the tourmaline structure proposed by Belov & Belova (1949).

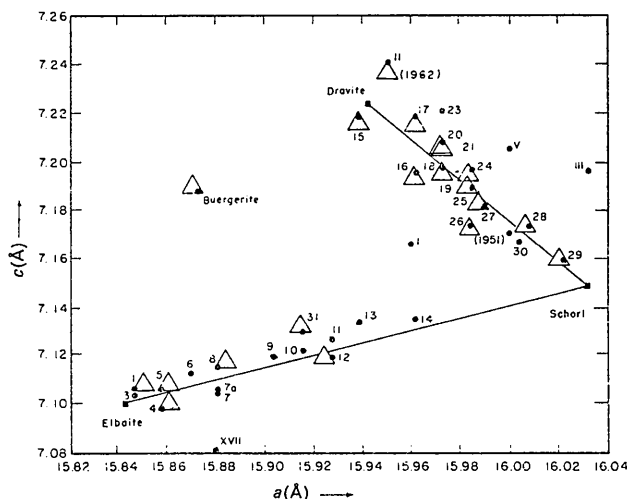


Fig. 1. Cell dimensions of tourmalines, after Mason *et al.* (1964). Literature data and reference numbers from Epprecht (1953). Composition, when known, is shown by the position of the point inside the triangle: elbaite (lower left), schorl (lower right), dravite (upper corner).

Since buergerite apparently conforms with neither tourmaline series, its structure might show some interesting differences in detail from that of dravite. Furthermore, a good chemical analysis, necessary for detailed structure work, is available and consequently a structure refinement has been undertaken.

Chemical composition and crystal data

The buergerite crystals used in this work come from the same specimen as the material already described (Mason, Donnay & Hardie, 1964). The formula given by Donnay *et al.* (1966) is: (Na_{2.47}K_{0.05}Ca_{0.38}□_{0.10}) (Fe_{6.87}³⁺Fe_{0.55}²⁺Ti_{0.21}Mg_{0.10}Mn_{0.06}Al_{0.81}□_{0.40})Al_{18.00}B_{9.27} · · (Si_{17.55}B_{0.45}) (O_{88.78}OH_{1.22}) (F_{3.05}OH_{0.16}) for the hexagonal cell. □ is a vacant site.

This formula contains a puzzling excess of boron which cannot be physically accommodated in the structure. Recently Ingamells (private communication) suggested a possible explanation: the buergerite specimen which he analyzed contained, as an intergrowth, a white impurity which was later identified as quartz. If this impurity had not been completely removed prior to the analysis, buergerite would appear to contain excess silicon. If 0.96 wt.% SiO₂ (*i.e.* 3% of the silica present) is discarded as impurity, the 'excess' boron can be accommodated in the tetrahedral position primarily occupied by silicon. The value of 0.96% for the amount of impurity is chosen to make the ratio (Si + B):(O + OH + F) equal to 27:93 as demanded by the tourmaline structure. In addition to accommodating the excess boron, this correction slightly improves the agreement between calculated and observed densities and reduces the number of vacancies in the other cation sites.

Thus the buergerite structural formula adopted at this stage is: (Na_{2.49}K_{0.05}Ca_{0.39}□_{0.07}) (Fe_{6.93}³⁺Fe_{0.56}²⁺Ti_{0.22}Mg_{0.10}Mn_{0.06}Al_{0.97}□_{0.16})Al_{18.00}B_{9.08}(Si_{17.20}B_{0.80}) (O_{88.63}OH_{1.39}F_{0.08})F_{3.00}.

Single-crystal photographs show diffraction symmetry consistent with the space group *R3m* found for all tourmalines. All observed reflections are sharp; no diffuse scattering was observed on precession photographs. Cell dimensions were obtained from a back-reflection Weissenberg photograph taken about the *a* axis of the specimen used for intensity collection (with Cu *Kα* radiation, * $\lambda(K\alpha_1) = 1.54056$, $\lambda(K\alpha_2) = 1.54440$ Å). The cell constants were refined by use of the computer program *LCLSQ* (Burnham, 1962), and the final values thus obtained are $a = 15.869 \pm 2$, $c = 7.188 \pm 1$ Å, $V = 1567.5 \pm 6$ Å³ at 21 °C.

The average density of several buergerite specimens measured on the Berman balance is $D_m = 3.30 \pm 1$ g.cm⁻³ at 23 °C. The density calculated from the refined cell constants and the given chemical composition is $D_x = 3.29$ g.cm⁻³.

* The numerical values of all X-ray wavelengths used are those of Bearden (1964), rounded to five decimals.

Data collection

Integrated intensities were measured on a General Electric XRD-5 diffractometer, by use of a scintillation counter, balanced Zr-Y filters, Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), and the moving-crystal, moving-counter technique.

Instrumental settings were obtained by the computer program *GSET 4* (Prewitt, 1964), but each reflection was centered prior to measurement. A standard reflection (90.0) was measured frequently. Short term variations were consistent with counting statistics, but a long range variation was observed, and all intensities were later normalized by a scale factor (varying from 1.000 to 1.099).

The point group of tourmaline is $3m$; thus the asymmetric unit occupies a 60° wedge of reciprocal space defined by the a_1^* , a_2^* , c^* , and $-c^*$ axes. All reflections in this wedge having $2\theta < 100^\circ$ were measured. The total number measured was 4098, but the 189 $hk.0$ reflections were measured twice, once in each of two crystal settings; thus the independent set used in the refinement contains 3909 reflections.

Integrated intensities were converted to structure factors by correcting for filter imbalance, for Lorentz and polarization factors, and for the scale factor derived from the standard reflection. Finally, the intensities were corrected for absorption through the computer program *ACACA* of Prewitt (1965) wherein the shape of the crystal is described by a collection of analytic functions. For buergerite the linear absorption coefficient is 26.1 cm^{-1} ; the specimen used was roughly equant, with dimensions $0.021 \times 0.017 \times 0.024 \text{ cm}$, and the computed transmission factors varied between 0.638 and 0.718.

The 189 duplicate measurements provide a check on their reproducibility. For the 166 pairs whose intensities were measurable above background, the quantity

$$\frac{\sum_i |F'_i - F''_i|}{\sum_i \frac{1}{2} |F'_i + F''_i|}$$

has the value 0.034. (The two members of the i th pair are indicated by the signs ' and ''.)

Structure refinement

Structure refinement was carried out on an IBM 7094 computer using *SFLS 5*, a full-matrix least-squares program written by Prewitt (1962). Scattering factors for Na^+ , Ca^+ , K^+ , Fe^{2+} , Ti^{3+} , Mg^{2+} , Mn^{2+} , Al^{2+} , B^{2+} , Si^{3+} , O^- , and F^- are those of Hanson, Herman, Lea & Skillman (1964). Anomalous dispersion corrections were made by use of the coefficients of Cromer (1965).

Observed structure factors were weighted in inverse proportion to their variance for the least-squares refinement. Estimates of σF_o based on counting statistics were obtained from the following relation:

$$\text{SD} = \frac{|F_o|}{2 \text{CN}} \times \text{SF} \times \left[\frac{I_o + \text{BG}}{10} \right]^{1/2}$$

I_o = observed intensity;

BG = background;

CN = observed intensity corrected for filter imbalance;

SF = scale factor based on standard reflection;

$|F_o|$ = observed structure factor, absolute value;

$\text{SD} \propto \sigma |F_o|$.

Intensities were regarded as unobservable if $\text{CN} < 5.0$; for such reflections, I_o was reset to 2.0 and SD to $0.75 \times \text{SF}$. Of the 3909 independent reflections, 788 were unobserved.

Least-squares refinement started with transformed coordinates based on the refined dravite model (Buerger, Burnham & Peacor, 1962) and the revised buergerite formula. Using the 'inner set' of 1180 reflections having $2\theta < 60^\circ$, the structure converged after two cycles of refining the atom positions, isotropic temperature factors (starting with $B_{\text{cation}} = 0.5$, $B_{\text{anion}} = 1.0$), a scale factor, and the secondary extinction parameter B_0 . This was followed by three cycles of anisotropic refinement, varying β_{ij} of the metals only during the first cycle and all β_{ij} 's thereafter. At this stage the residual R had the value 0.066 and the weighted residual R_w had the value 0.049.

The structure factors and residuals were now calculated from parameters from the latest cycle of anisotropic refinement, but for $B_0 = 0$. Comparison of structure factors from the last two runs indicated that correction for secondary extinction was unnecessary for the 'outer' reflections ($60^\circ < 2\theta < 100^\circ$). Thus the observed structure factors for the inner reflections were adjusted for secondary extinction according to the formula (after Zachariasen, 1963):

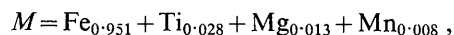
$$F_{\text{obs}'} = F_{\text{obs}} \times (1.0 + I_o \times \beta \times B_0)$$

and all subsequent refinement proceeded with $B_0 = 0$.

The parameters β for these reflections had been calculated by the computer program *ACACA* (Prewitt, 1965) and varied from 0.87 to 1.31. For the specimen used the final value of B_0 was $(1.87 \pm 21) \times 10^{-6}$. The largest change produced by this correction was 5.3% for $(05.1)-(50.1)$; the largest change among those reflections not corrected for secondary extinction would have been 0.15%.

Following the extinction correction, two cycles of isotropic refinement were carried out for the full set of 3909 reflections, varying positional parameters, the scale factor, and all temperature factors. A low value for the temperature factor of Al (0.27) and a high value for that of Fe (1.04) suggested a redistribution of some portion of these ions.

For the purpose of refining the octahedral occupancy, the participating ions were combined into a statistical ion



and the occupancy factor for M in the 9(b) position was the only occupancy parameter allowed to vary. The occupancies of Al in the 9(b) and 18(c) positions and of

M in the 18(*c*) position were reset after each cycle according to the constraints of chemical analysis and an arbitrary distribution of one-third of the octahedral vacancy in 9(*b*) and two-thirds in 18(*c*). In four cycles of isotropic refinement with the inner set of reflections the occupancy converged, accompanied by a change in the temperature factors which became 0.73 for iron and 0.67 for aluminum.

The full set of reflections was used in the following two cycles of isotropic refinement, in which atomic coordinates, scale factor, *M*-Al distribution, and all temperature factors were allowed to vary; at this stage the residual *R* reached the value 0.102 and *R_w* was equal to 0.041, both for all reflections.

Finally, three cycles of anisotropic refinement with the inner set and two cycles with the full set were carried out with varying occupancy, scale factor, positional parameters, and all anisotropic temperature factors throughout. The final residuals were 0.065 for all 3909 reflections and 0.046 for the 3121 observed reflections used in the refinement. The least-squares minimized the function

$$\left[\frac{\sum_i w(|F_o| - |F_c|)^2}{\sum_i wF_o^2} \right]^{1/2}$$

down to a value of 0.028 for all reflections.

The final observed structure factors (Table 2) contain corrections for absorption, secondary extinction, Lorentz and polarization factors, and a scale factor.

The calculated structure factors have been multiplied by the least-squares scale factor (0.7583).

Discussion of the structure

The characteristics of the tourmaline structure (six-membered Si rings, Fe-Mg octahedra, B triangles; structural units linked together by Al octahedra) have already been discussed at length in the references cited.

Table 2. *Observed and calculated structure factors*

hk.0 reflections
 column 1 = running index;
 column 2 = 10|*F_o*|;
 column 3 = 10|*F_c*|;
 column 4 = phase angle in millicycles.

The intensities of reflections (*hk.l*) and (*kh.l*) are related by a pseudo-center of symmetry for X-rays: in the absence of anomalous dispersion they are equal. Corrected here for anomalous dispersion, they are approximately equal and are presented side by side to demonstrate the magnitude of the effect in this work.

hk.l reflections, *l* ≠ 0
 column 1 = running index for both entries;
 column 2 = 10|*F_o*|;
 column 3 = 10|*F_c*|;
 column 4 = phase angle in millicycles; } *hk.l*
 column 5 = 10|*F_o*|;
 column 6 = 10|*F_c*|;
 column 7 = phase angle in millicycles. } *kh.l*

Unobserved reflections are designated with an asterisk.*

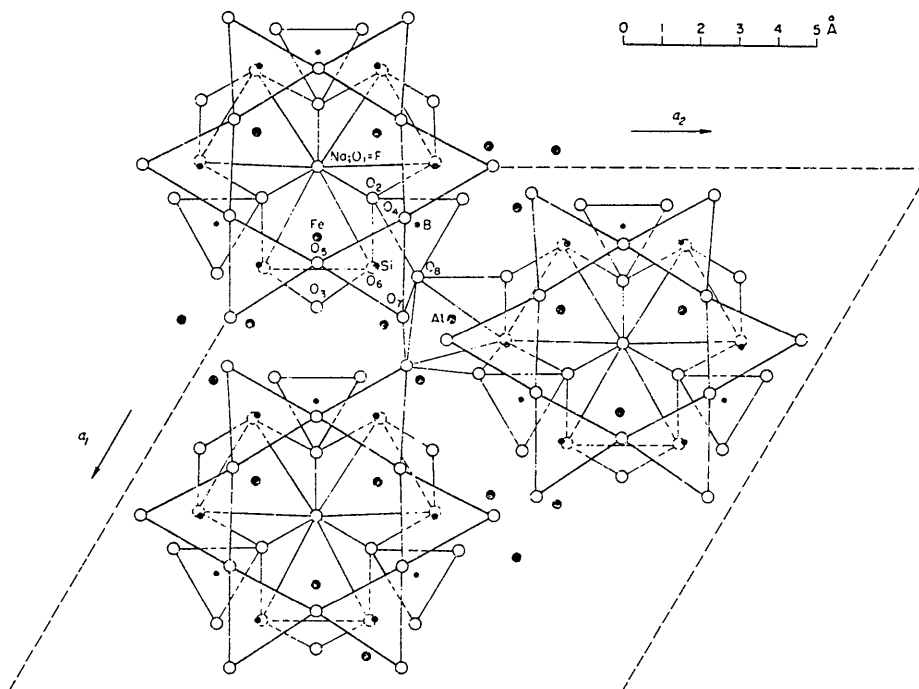


Fig. 2. Projection of buergerite structure on (0001). Repeats at 0,0,0; 2/3, 1/3, 1/3; 1/3, 2/3, 2/3.

Table 2 (cont.)

Table with multiple columns of numerical data and labels (e.g., h, k, l, F, etc.) representing crystal structure refinement parameters.

Table 2 (cont.)

Table with multiple columns containing numerical data and alphanumeric codes. The table is organized into several vertical sections, each starting with a header row of numbers and codes. The data consists of rows of numbers, some with associated codes, arranged in a structured grid.

The final atomic coordinates (Table 3) show that the buergerite structure is very similar to the refined dravite structure (Buerger *et al.*, 1962); only in fine details are they different.

In the present refinement, as in that of dravite, the z coordinate of Si was held constant throughout; its value is arbitrary since the origin along the c axis is not fixed by symmetry. The z coordinates for the other twelve atoms in the asymmetric unit shifted both up and down with respect to Si by as much as 0.019 (Table 3). As to x and y parameter shifts, however, only Fe, Al, O(3), and O(7) show changes exceeding three (dravite) standard deviations.

Interatomic distances and bond angles (Tables 5 and 6), uncorrected for the effects of thermal motion, were computed by the program *ORFFE* (Busing, Martin & Levy, 1964). As compared with dravite, the 9(*b*) octa-

hedra in buergerite have been flattened parallel with the basal plane and are less regular. Bond distances (for $M_{6.30}Al_{2.65}$) vary between 1.942 and 2.111 Å in buergerite *vs.* 2.023 and 2.116 Å for magnesium octahedra in dravite.

The SiO_4 tetrahedra are more regular in buergerite; bond angles vary between 104.0° and 112.0°. The generalization of Clark & Papike (1967), that non-bridging Si-O bonds are shorter than bridging ones, which was proposed for chain and framework silicate structures, but was not verified in double chains, holds only partially in the present case of buergerite although it is obeyed in dravite – both of which have ring structures. The non-bridging Si-O(7) bond (1.602 Å) is significantly shorter than the bridging Si-O(4) (1.620 Å) and Si-O(5) (1.626 Å) bonds, but Si-O(6) (1.620 Å) is also a non-bridging bond. In dravite the Si-O(6) and Si-O(7)

Table 3. Final coordinates of buergerite with transformed coordinates of dravite (Buerger, Burnham & Peacor, 1962) for comparison

Buergerite above, dravite below.								
	Position	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B
Na	3a	0	—	0	—	0.21338	0.00041	2.328
		0	—	0	—	0.2324	0.0010	0.688
B	9b	0.10992	0.00025	0.21984	0.00050	0.45182	0.00046	0.467
		0.1103	0.0007	0.2206	0.0015	0.4538	0.0020	-0.229
Fe	9b	0.13320	0.00008	0.06660	0.00004	0.62072	0.00010	0.848
Mg		0.1270	0.0005	0.0635	0.0002	0.6282	0.0007	0.327
Si	18c	0.19156	0.00004	0.19065	0.00004	0	—	0.306
		0.1922	0.0003	0.1898	0.0003	0	—	0.201
Al	18c	0.29880	0.00004	0.25887	0.00004	0.60437	0.00010	0.587
		0.2976	0.0003	0.2615	0.0003	0.6138	0.0006	0.167
O(1)=F	3a	0	—	0	—	0.76698	0.00051	2.130
		0	—	0	—	0.7783	0.0022	-0.678
O(2)	9b	0.06056	0.00015	0.12112	0.00029	0.48607	0.00029	0.789
		0.0609	0.0005	0.1218	0.0010	0.4787	0.0013	0.378
O(3)	9b	0.26450	0.00034	0.13225	0.00017	0.52094	0.00030	0.756
		0.2680	0.0010	0.1340	0.0005	0.5145	0.0014	0.548
O(4)	9b	0.09478	0.00015	0.18956	0.00030	0.07532	0.00028	0.741
		0.0935	0.0005	0.1870	0.0010	0.0724	0.0014	0.526
O(5)	9b	0.18258	0.00033	0.09129	0.00016	0.08388	0.00028	0.785
		0.1812	0.0010	0.0906	0.0005	0.0888	0.0012	-0.040
O(6)	18c	0.19314	0.00011	0.18680	0.00011	0.77481	0.00018	0.622
		0.1952	0.0006	0.1866	0.0007	0.7789	0.0009	0.178
O(7)	18c	0.28670	0.00010	0.28580	0.00010	0.07445	0.00018	0.573
		0.2844	0.0007	0.2851	0.0006	0.0810	0.0010	0.301
O(8)	18c	0.20894	0.00010	0.26941	0.00010	0.43778	0.00020	0.628
		0.2085	0.0007	0.2698	0.0007	0.4445	0.0011	0.694

Table 4. Anisotropic temperature factor coefficients for buergerite

$$\exp[-(h^2\beta_{11} + \dots + 2hk\beta_{12} + \dots)]$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na	0.00302 ± 14	0.00302 ± 14	0.01172 ± 58	0.00151 ± 7	0	0
B	0.00062 ± 16	0.00062 ± 16	0.00263 ± 40	0.00038 ± 10	0.00005 ± 17	-0.00005 ± 17
Fe	0.00072 ± 3	0.00072 ± 3	0.00544 ± 10	0.00003 ± 2	0.00087 ± 4	-0.00087 ± 4
Si	0.00040 ± 2	0.00038 ± 2	0.00152 ± 8	0.00018 ± 2	0.00003 ± 4	-0.00008 ± 4
Al	0.00064 ± 2	0.00086 ± 3	0.00286 ± 9	0.00034 ± 2	-0.00007 ± 4	0.00035 ± 4
O(1)	0.00378 ± 24	0.00378 ± 24	0.00328 ± 66	0.00189 ± 12	0	0
O(2)	0.00103 ± 14	0.00103 ± 14	0.00516 ± 36	0.00077 ± 8	0.00009 ± 14	-0.00009 ± 14
O(3)	0.00082 ± 12	0.00082 ± 12	0.00367 ± 33	0.00014 ± 8	0.00008 ± 15	-0.00008 ± 15
O(4)	0.00093 ± 13	0.00093 ± 13	0.00330 ± 33	0.00033 ± 8	-0.00005 ± 15	0.00005 ± 15
O(5)	0.00095 ± 13	0.00095 ± 13	0.00330 ± 32	0.00024 ± 8	-0.00012 ± 15	0.00012 ± 15
O(6)	0.00088 ± 6	0.00073 ± 6	0.00274 ± 20	0.00032 ± 5	0.00005 ± 10	-0.00002 ± 9
O(7)	0.00081 ± 6	0.00069 ± 6	0.00237 ± 20	0.00028 ± 5	-0.00017 ± 9	-0.00023 ± 9
O(8)	0.00062 ± 5	0.00087 ± 6	0.00381 ± 22	0.00040 ± 5	-0.00001 ± 9	0.00023 ± 9

bonds are both shorter than Si-O(4) and Si-O(5) (1.603 and 1.606 Å vs. 1.639 and 1.635 Å).

In the configuration of the Si₆O₁₈ ring buergerite and dravite maintain their similarity. Let ditrigonality be

defined as $\delta = (r_l - r_s)/r_s$,

where r_l and r_s are the longer and shorter distances,

Table 5. *Interatomic distances (Å) in cation coordination polyhedra in buergerite*

Silicon - oxygen tetrahedron	
Si-O(4) = 1.620 ± 2	O(6)-O(4) = 2.678 ± 3
Si-O(5) = 1.626 ± 3	O(6)-O(5) = 2.647 ± 3
Si-O(6) = 1.620 ± 2	O(6)-O(7) = 2.642 ± 2
Si-O(7) = 1.602 ± 2	O(4)-O(5) = 2.559 ± 3
	O(4)-O(7) = 2.638 ± 3
Mean Si-O = 1.617	O(5)-O(7) = 2.676 ± 3
Mean O-O = 2.640	
Boron - oxygen triangle	
B-O(2) = 1.379 ± 4	(2) O(8)-O(2) = 2.379 ± 3
(2) B-O(8) = 1.364 ± 4	O(8)-O(8') = 2.356 ± 3
Mean B-O = 1.369	
Mean O-O = 2.371	
Iron-oxygen octahedron	
Fe-O(1) = 2.111 ± 4	(2) O(1)-O(2) = 2.617 ± 4
(2) Fe-O(2) = 2.003 ± 2	(2) O(1)-O(6) = 3.016 ± 4
Fe-O(3) = 1.942 ± 3	(2) O(3)-O(2) = 3.162 ± 3
(2) Fe-O(6) = 1.989 ± 2	(2) O(3)-O(6) = 2.518 ± 3
	(2) O(2)-O(6) = 2.762 ± 3
Mean Fe-O = 2.006	O(2)-O(2') = 2.883 ± 5
Mean O-O = 2.825	O(6)-O(6') = 2.864 ± 3
Aluminum-oxygen octahedron	
Al-O(3) = 1.897 ± 3	O(3)-O(6) = 2.518 ± 3
Al-O(6) = 1.924 ± 2	O(3)-O(8) = 2.791 ± 3
Al-O(7) = 1.979 ± 2	O(3)-O(7') = 2.903 ± 3
Al-O(7') = 1.888 ± 2	O(3)-O(8') = 2.820 ± 3
Al-O(8) = 1.931 ± 2	O(7)-O(6) = 2.751 ± 2
Al-O(8') = 1.893 ± 2	O(7)-O(8) = 2.396 ± 2
	O(7)-O(7') = 2.723 ± 3
Mean Al-O = 1.919	O(7)-O(8') = 2.845 ± 2
Mean O-O = 2.711	O(6)-O(8) = 2.705 ± 2
	O(6)-O(8') = 2.817 ± 2
	O(7')-O(8) = 2.868 ± 2
	O(7')-O(8') = 2.396 ± 2
Sodium-oxygen polyhedron	
(3) Na-O(2) = 2.571 ± 4	
(3) Na-O(4) = 2.788 ± 4	
(3) Na-O(5) = 2.676 ± 4	
Mean Na-O = 2.678	

Table 6. *Selected bond angles in buergerite*

Silicon tetrahedron		Boron triangle	
O(6)-Si-O(4) = 111.5°		O(8)-B-O(8') = 119.4°	
O(6)-Si-O(5) = 109.2		(2) O(2)-B-O(8) = 120.3	
O(6)-Si-O(7) = 110.1			
O(5)-Si-O(4) = 104.0		Aluminum octahedron	
O(5)-Si-O(7) = 112.0		O(3)-Al-O(6) = 82.4°	
O(4)-Si-O(7) = 109.9		O(3)-Al-O(7') = 100.1	
		O(3)-Al-O(8) = 93.6	
		O(3)-Al-O(8') = 96.2	
Iron octahedron		O(7)-Al-O(6) = 89.6	
(2) O(1)-Fe-O(6) = 94.7°		O(7)-Al-O(7') = 89.5	
(2) O(1)-Fe-O(2) = 79.0		O(7)-Al-O(8) = 94.3	
(2) O(3)-Fe-O(6) = 79.7		O(7)-Al-O(8') = 76.4	
(2) O(3)-Fe-O(2) = 106.5		O(6)-Al-O(8) = 89.1	
(2) O(2)-Fe-O(6) = 87.6		O(6)-Al-O(8') = 95.1	
O(2)-Fe-O(2') = 92.1		O(7')-Al-O(8) = 77.7	
O(6)-Fe-O(6') = 92.1		O(7')-Al-O(8') = 97.6	

respectively, between the vertices and the center of gravity of the ditrignon. The ditrignality δ has the value 0 for a hexagonal ring and approaches the value 1.0 as the six-membered ring approaches the configuration of an equilateral triangle. In tourmaline r_1 and r_2 are the distances from O(4) and O(5), respectively, to the threefold axis.

The original Donnay & Buerger (1950) dravite structure had $\delta=0.20$, while the structure of Ito & Sadanaga (1951) had $\delta=0$ (hexagonal ring). The refined dravite (Buerger *et al.*, 1962) gives $\delta=0.032 \pm 7$. Buergerite gives $\delta=0.038 \pm 2$. Within the limits of error, buergerite and dravite thus have the same ditrignality for their Si_6O_{18} rings.

The final values of the occupancies of the M -Al positions [9(b) and 18(c)] (Table 7) represent a marked improvement in the agreement between observed and calculated structure factors: R_w went from 0.045 to 0.031.* Although the mutual substitution of M and Al in two different positions is not extensive, it is nevertheless remarkable; there was no reason to expect this kind of replacement as there was sufficient Al to fill its own position.

The equivalent isotropic temperature factors (Hamilton, 1959) for buergerite are, in general, more reasonable than those for dravite, three of which have negative values (Table 3). The high value for Na is

* The refinement was originally carried out to completion by use of the formula of Donnay *et al.* (1966). The formula revision suggested by Ingamells necessitated extensive re-computation; the results reported in this paper are, of course, based on the revised analysis. However, it is worth noting that the formula revision caused no essential change in the crystal structure (no parameter changed more than one standard deviation) but had a significant effect on the M -Al distribution: the occupancy factor for M in 9(b) was lowered from 0.7826 ± 23 to 0.7039 ± 23 . Moreover, the residual R for all 3909 reflections (anisotropic temperature factors) changed from 0.047 to 0.046, the weighted residual R_w from 0.030 to 0.028.

probably due to positional disordering off the threefold axis. The thermal ellipsoid for Na is nearly spherical; thermal vibrations of all other atoms are significantly anisotropic. The ellipsoid of F is an oblate spheroid with its short axis along c ; B and O(2) are approximately oblate spheroids. The thermal ellipsoids for Fe, Al, O(4), O(5), and O(6) are approximately prolate spheroids, with that of iron extremely prolate.

In conclusion, the near-identity of the fractional atomic coordinates of the refined buergerite and dravite structures, surprising in view of their differences in composition, cleavage, and cell dimensions, show that the tourmaline structure is, apparently, virtually independent of chemical substitutions. In other words, the present refinement would appear to reconfirm the idea of a single tourmaline structure.

Such a conclusion is inconsistent with the absence of solid solution between elbaite and dravite; however, there is now reason to question whether an elbaite specimen has indeed been studied. Although Ito & Sadanaga (1951) stated that they used a rubellite (lithian tourmaline, *i.e.* an elbaite) from Brazil, they gave no chemical analysis for the actual crystal used, and the cell dimensions they reported ($a=16.0$, $c=7.17 \text{ \AA}$) place their specimen in the dravite-schorl series (Fig. 1). In all probability their idealized chemical composition, taken from Dana (Sadanaga, private communication) does not apply to the crystal studied. Thus, the details of the structure of members of the elbaite-schorl series may still be an open question. To resolve this confusion, the refinement of a well-analyzed elbaite specimen is in progress.

The absolute orientation of tourmalines

The absolute orientation of the tourmaline structure has been determined by the use of anomalous scattering (Barton & Donnay, 1966). Tourmaline is non-

Table 7. Occupancy parameters for M and Al in 9(b) and 18(c)

	M	Al
9(b)	0.704	0.296
18(c)	0.087	0.913

$$M = \text{Fe}_{0.951} + \text{Ti}_{0.028} + \text{Mg}_{0.013} + \text{Mn}_{0.008}$$

Final formula for buergerite

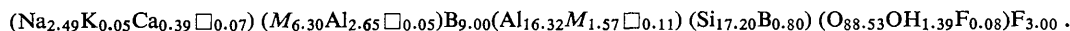


Table 8. Polar properties of tourmaline

Polar property	Antilogous pole (+c)	Analogous pole (-c)
Crystal habit: typical form	{10 $\bar{1}$ 1}	{10 $\bar{1}$ $\bar{2}$ }
Pyroelectricity: charge on cooling	Positive	Negative
Piezoelectricity: charge on compression along c	Positive	Negative
Crystal structure: SiO_4 tetrahedra point	Away from it	Toward it

centrosymmetric and polar, and exhibits well marked polar properties (Table 8).

Taking the antilogous pole as the positive end of the c axis, as is traditional in morphological descriptions, the upper pyramids are steeper than the lower pyramids (analogous pole) (Dana, 1892). Tourmalines commonly occur with only a single termination, and a survey of such specimens at the U.S. National Museum reveals that the analogous end occurs in about 80% of the cases (G. Donnay, private communication, 1966); likewise, large crystals of tourmaline, grown from spherical seeds by hydrothermal synthesis, develop only their analogous ends (Voskresenskaya, private communication, 1966). Furthermore, the magnitude of the piezoelectric effect is such that tourmalines have found use as hydrostatic pressure gauges (Fron del, 1948).

In the six-membered ring of silicon-oxygen tetrahedra, all six tetrahedra point in the same c direction, each having a face nearly parallel to the (0001) plane, and so it is convenient to refer the orientation of the structural unit to the direction in which these tetrahedra point.

Buergerite is a particularly suitable tourmaline for this determination: the high iron content gives rise to large anomalous dispersion effects under Cu $K\alpha$ radiation. However, the determination preceded the refinement of the buergerite structure, so that the 1962 dravite model (Buerger *et al.*, 1962) was used. Because the structure was already approximately known, the sense of the inequality for one reflection and its inverse was sufficient.

Two different specimens were used in the actual determination: one, a ferrous-magnesium tourmaline (dravite) from Brazil, cut in the form of a plate perpendicular to the c axis, on which a pyroelectric test was made to determine which end was the antilogous pole and which the analogous; the other, a buergerite crystal, on which both a pyroelectric test and a morphological examination were performed.

For both crystals precession films showed the 41·0 reflection to be more intense than the $\bar{4}\bar{1}\cdot\bar{0}$, and the $\bar{5}\bar{1}\cdot\bar{1}$ more intense than the 51·1. On another buergerite crystal, diffractometer measurements of the six symmetry-related reflections of {41·0} and their inverse reflections gave an average $I\{41\cdot0\}/I\{\bar{4}\bar{1}\cdot\bar{0}\}$ ratio of 1·93.

Calculated intensities based on the coordinates of Buerger *et al.* (1962) give opposite inequalities. Thus, these coordinates have to be transformed to make the SiO_4 tetrahedra point in the opposite direction, *i.e.* toward the analogous pole. With transformed coordinates, the calculated value of the ratio $F^2(41\cdot0)/F^2(\bar{4}\bar{1}\cdot\bar{0})$ is 2·01. Subsequent refinement of buergerite gives a new calculated ratio of 2·03.

The absolute orientation could have been obtained by the separate refinement of the two possible orientations. Once the intensity data for buergerite were collected and the refinement was complete, this approach was tested.

For the 1103 observed inner reflections and starting with the 1962 dravite coordinates (untransformed, *i.e.* wrong orientation), the structure converged after six cycles (isotropic temperature factors) of least-squares to $R=0\cdot056$, $R_w=0\cdot043$. The same operation, starting with transformed 1962 dravite coordinates (correct orientation), converged to $R=0\cdot046$, $R_w=0\cdot033$. By application of the significance test of Hamilton (1965) to these results, the incorrect orientation can be strongly rejected at the 0·005 level.

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