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

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The crystal structure of buergerite from Mexico has been refined by least-squares by use of singlecrystal X-ray intensity data collected by counter diffractometry. Buergerite, ideally NaFe₃³⁺B₃Al₆Si₆O₃₀F, crystallizes in R3m; the hexagonal cell dimensions for the specimen used are: $a = 15 \cdot 869 \pm 2$, $c = 7 \cdot 188 \pm 1$ Å at 21°C. $D_m = 3 \cdot 30 \pm 1$ at 23°C; with Z=3, $D_x = 3 \cdot 29$ 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 (Fe³⁺, 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 SiO₄ 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

 $NaX_3B_3Al_6Si_6O_{27}(OH, F)_4$, X stands for Mg, Fe²⁺, 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 schorlelbaite 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	0.4532

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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 exactyl, 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 $NaFe_3^{3+}$ -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: $(Na_{2\cdot47}K_{0\cdot05}Ca_{0\cdot38}\square_{0\cdot10})$ $(Fe_{0\cdot57}^{3+}Fe_{0\cdot55}^{5}Ti_{0\cdot21}Mg_{0\cdot10}Mn_{0\cdot06}Al_{0\cdot81}\square_{0\cdot40})Al_{18\cdot00}B_{9\cdot27} \cdots$ $(Si_{17\cdot55}B_{0\cdot45})$ (O_{88\cdot78}OH_{1\cdot22}) (F_{3\cdot05}OH_{0\cdot16}) for the hexagonal cell. \square 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: $(Na_{2\cdot49}K_{0\cdot05}Ca_{0\cdot39}\Box_{0\cdot07})$ $(Fe_{0\cdot3}^{3+}Fe_{0\cdot56}^{2+}Fi_{0\cdot22}Mg_{0\cdot10}Mn_{0\cdot06}Al_{0\cdot97}\Box_{0\cdot16})Al_{18\cdot00}B_{4\cdot06}(Si_{17\cdot20}B_{0\cdot80})$ $(O_{88\cdot63}OH_{1\cdot39}F_{0\cdot08})F_{3\cdot00}$.

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 $K\alpha$ 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 + 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 ($\lambda = 0.71073$ Å), 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 $26 \cdot 1 \text{ cm}^{-1}$; the specimen used was roughly equant, with dimensions $0.021 \times 0.017 \times 0.024$ 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

$$\sum_{i} |F'_{i} - F''_{i}| / \sum_{i} \frac{1}{2} |F'_{i} + F''_{i}|$$

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⁺, Fe²⁺, Ti³⁺, Mg²⁺, Mn²⁺, Al²⁺, B²⁺, Si³⁺, 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:

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

 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;

 $SD \propto \sigma |F_o|$.

Intensities were regarded as unobservable if CN < 5.0; for such reflections, I_o was reset to 2.0 and SD to $0.75 \times SF$. 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):

$$F_{\text{obs}'} = F_{\text{obs}} \times (1 \cdot 0 + I_o \times \beta \times B_0)$$

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

 $M = Fe_{0.951} + Ti_{0.028} + Mg_{0.013} + Mn_{0.008} ,$

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

$$\begin{bmatrix} \sum_{i} w(|F_o| - |F_c|)^2 \\ \vdots \\ \sum_{i} wF_o^2 \end{bmatrix}^{1/2}$$

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 (sixmembered 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.

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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.

$$\begin{array}{l} hk.l \text{ reflections, } l \neq 0 \\ \text{column } 1 = \text{running index for both entries;} \\ \text{column } 2 = 10|F_o|; \\ \text{column } 3 = 10|F_c|; \\ \text{column } 4 = \text{phase angle in millicycles;} \end{array} \right\} hk.l \\ \text{column } 5 = 10|F_o|; \\ \text{column } 6 = 10|F_c|; \\ \text{column } 7 = \text{phase angle in millicycles.} \end{array} \right\} kh.l$$

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Unobserved reflections are designated with an asterisk.*



Fig. 2. Projection of buergerite structure on (0001). Repeats at $0,0,0; \frac{2}{3}, \frac{1}{3}, \frac{1}{3}; \frac{2}{3}, \frac{2}{3}, \frac{2}{3}$.

Table 2 (cont.)

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12 14. 44 450 15 21. 14 744 18 77 76 262	42 14 147 21+ 14 155 70 71 748	20 30 72 50 23 244 30 447	40 72 988 244 36 385 218-7	5 100 106 742 6 83 84 900 9 45 45 285 12 85 82 585	102 274 77 74 108 52 48 764 89 82 426	22 24. 25 240 m,2,7	201 - 20	5 91 91 940 8 59 65 531 11 44 53 981	103 100 64 67 67 482 39 49 31	······································	10,8,-11 72 85 97	7 75 67 122 10 106 108 575 13 66 66 568	47 44 843 44 108 434 254 46 455
A 72 73 33	1 1 17 11 11	0 197 195 565 5 166 166 682 6 97 90 159 8 62 60 115	101 105 446 157 149 121 97 08 455	15 185 186 46 18 73 79 545 21 59 57 2 24 244 41 328	140 173 467 81 74 475 744 54 447 244 40 720	2 19 15 427 5 98 91 474 8 51 54 643 11 54 29 189	48 14 762 82 88 741 76 62 176 48 24 618	17 24- 11 717 20 34 36 213	25- 27 294	5 25+ 29 110 6 92 96 112 9 24+ 40 868 12 24+ 25 927	40 31 401 86 49 412 43 16 181 244 24 118	#.4.13 2 244 25 661 5 61 60 162	4.413 25+ 17 372 25+ 37 640
4 216 217 546 7 151 124 817 10 125 127 510	228 227 459 130 121 200 122 125 482	12 145 141 104 15 70 75 492 18 95 95 852	144 138 705 66 71 576 94 107 187	1 109 107 357	2.44 111 99 670	14 22+ 48 451 17 75 78 120 20 45 51 325	41 56 567 75 75 685 47 53 781		5,4,-10 21+ 21 875 138 127 613 206 203 958	11.11 1 23+ 47 432 4 107 117 143	24+ 38 394 122 120 878	11 37 60 483 H. 5, 13	45 55 29 5.413
13 120 125 415 16 89 98 951 19 86 89 582 22 71 89 917	107 108 67 102 93 440 67 84 93	34 344 44 448 	244 45 116 1484-17	7 40 41 131 10 74 81 147 19 144 147 788	57 55 676 81 82 620 146 147 224	0 1/8 1 14 391	131 140 414	12 95 101 45 15 76 77 787	145 119 60 121 96 969 61 66 225 67 76 629	10 121 133 912 13 23- 13 628	11 14 107	5 43 54 100 6 157 167 11 9 78 79 877	25- 15 918
25 99 100 189	105 49 632	· //· /·· ···		22 70 71 11	: :: ::)	6 51 64 227 79 77 267 12 104 108 302	62 49 764 61 71 745 118 111 710	H.6.10 1 45 53 803	6,6,-10 46 46 206	H.12.11	12.411 87 90 936 254 12 869 254 17 976	12 53 60 617	6.413 23- 1- Con
5 Jac 341 882 8 74 78 445 11 106 105 151 14 72 85 166	116 125 126 88 78 575 118 118 858 72 77 861	10 50 57 107 10 50 57 51 10 50 35 517 77 50 61 515	47 54 485 744 51 585 50 50 505	2 101 101 001 5 101 101 007 8 00 00 010	191 188 359 173 168 350 194 41 479		71 44 502 40 54 551	7 100 114 104 10 141 155 934 11 49 67 446	100 111 504 130 155 84 57 84 548	11 12 44 217	11.111.	1 200 22 018 7 200 22 018 10 00 73 900	25+ 125 +55 25+ 19 +12 41 +6 +8
17 49 59 902 20 111 130 897 23 244 14 875		H.4.7 2 84 73 826 3 170 90 188	4.27 40 40 100 40 37 855	11 72 73 441 14 91 97 444 17 53 65 484 20 70 64 709	16 78 521 87 90 515 62 62 516 73 72 510			10 30 35 170 m. /. 10	14 19 861 7.810	1 21+ 12 108 4 91 90 479 9 21+ 35 441	23+ 32 904 40 41 540 24+ 40 344	**************************************	7.813 137 139 435 25+ 27 494
H.6.6 0 411 416 7 3 104 102 820	4,0 422 4 106 100 148 213 208 218	11 126 127 476 14 260 256 571 17 61 65 576	127 130 41 270 258 441 58 51 444	21 24 27 40 0 49 72 42	1 12 100	10 21- 55 50 11 106 108 617 16 124 127 30 19 28 97 661	106 107 166 119 122 986 96 100 558	5 15 40 491 6 79 84 718 11 23- 10 268	10 15 224 10 17 757	1 23+ 26 770 5 38 34 50+	14.411 250 30 276 67 66 557	1 23 17 234	20 6 61 1.119
12 12 10 107 13 124 147 15 124 147 31	60 52 552 65 50 675 152 167 988 151 126 580	20 130 131 425 23 44 47 131	41 45 701	4 215 217 648 6 211 207 467 9 171 167 507 17 214 9 250	240 279 551 212 206 46 179 174 508 220 18 656		4.44 61 67 477 67 69 48	·····	74. 15 354 8.410		13.411	1 15 10 17	46 51 502 254 55 578 45 53 337
21 244 45 828	244 46 191 7.56	0 113 109 734 5 168 184 455 6 266 258 247	105 103 102 145 143 558 262 265 765		61 65 679 240 44 640 90 94 992		78 86 157 252 241 971 92 84 114 121 124 996	1 21.0 3 147 4 220 11 484 7 41 30 215	220 4 731 230 7 196 61 46 795	4 /3+ 10 164 #.14.11	244 26 627 14,4,-11	···· *.13 1 6* 76 *35 4 76 80 333	9.413 63 69 77 65 79 688
7 206 200 192 10 70 67 179	42 44 282 203 203 610 70 72 640	12 10 110 21 15 192 141 421 16 76 67 741		1 271 273 144	7.8.1.8 287 288 840 297 287 840	20 57 60 790	24+ 53 500	12 74 81 187 15 39 40 587 #.9.10	70 70 625 230 60 660 9,4,-10	0 81 106 484 3 60 67 525 6 23+ 30 637	63 69 63 59 67 692 266 10 605	7 244 34 388 m,10,11 2 48 35 725	25+ 37 640 10+#+-13 +4 56 280
10 21- 14 740 10 47 43 719 22 244 17 300		1	4. 4. · · / 60 •1 /11	10 112 144 458 11 50 48 801 14 114 124 57		5 134 136 712 6 101 108 973 9 127 116 261	131 131 240 102 100 22 140 198 777	1 102 102 452 4 141 155 445 7 70 45 475 10 47 43 135	101 100 40 157 155 574 76 69 544 93 86 840	· · · · · · · · · · · · · · · · · · ·	17.811 25+ 19 867 67 66 475	· /›· ·/ //	50 52 544 54 47 234
2 202 200 471 3 10 13 6	203 199 542	10 221 275 447				15 162 165 485	10 10 10	15 240 11 241 16 61 77 39	25- 12 754 55 70 444	, 74, 24, 717	18,8,-11 29+ 22 812	0 127 139 957 5 244 67 607 6 67 56 6	25+ 35 +75
11 200 16 220 16 220 18 200 17 83 87 352	21.0 27 721 22.0 97 732 72 87 440		2. 7 %	6 144 114 710 1 146 144 710 1 19 67 10		1 100 % 1/8 5 10 18 534 7 130 147 455	*** *** *** 16 *** *** 146 1** 146		87 84 101 65 69 115	0 40 15 147 1 51 49 197	44 57 979 46 53 612 20.613	1 24 12 12	25+ 12 502 25+ 57 837
0 10 10 10 10	9.86 210 204 967		40 40 444 44 44 863 126 115 403	17 75 76 161	11 14 17	10 700 70 017 10 700 10 71 10 11 71 300	244 10 344 41 35 803 45 71 438	1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1	45 80 261	1 41 45 96	86 49 918 0.817	240 10 484	13.813 25+ 11 450
5 154 120 000 6 76 72 965 9 244 247 631 12 119 121 713		14 105 102 419 17 81 87 444 20 44 47 354	101 104 141 84 85 518 58 50 676	0 56 67 517 5 66 66 691 6 197 191 501	55 61 502 59 51 319 187 184 500	2 160 197 160 5 216 19 298	100 130 031	1 107 110 404 5 54 61 706 70 71 714	113 104 408 54 58 313 61 71 746	1 42 36 162 6 138 146 66 9 146 140 907	47 40 877 141 146 995 135 135 111	0 244 16 680 3 214 29 387	250 20 295
	67 68 713 79 67 911	0 111 111 545 5 105 105 51	8.47 119 121 424 109 103 471	17 22- 14 145 15 140 10 711 18 14 15 15 147	/3+ 1/ 4C5 /4 85 780 +1 47 111		10 14 174 744 76 764 47 63 471	******	101 111 51	1 3 2 3	40 57 748 53 62 377	1 92 100 76	41 101 446
1 348 340 412 4 97 103 112 7 59 44 214	251 247 600 94 99 917 67 61 866	12 17 16 140 15 70 76 855	84 83 747 59 40 672 75 79 148	1 1 1 1 1	100 11 17			7 230 22 440 7 230 22 440 10 41 44 18	44 45 440 /44 /4 551	1 60 61 640	40 54 177 114 110 894 84 85 547	5 106 106 45 8 240 26 454 11 160 154 979	118 116 965 25- 25 316 155 156 36
10 120 127 444 15 22- 20 483 16 44 50 19 19 19 48 999	73+ 18 5+3 49 55 972 58 49 55	21 80 78 624	10 17 34 Mart 1	/ 111 110 407	120 117 004	· 194 190 493	207 145 561 260 26 561 102 91 823		11.410	1 2.3 %	23. 21. 132	0 70 84 975 3 244 44 441	1.814 75 76 81 25+ 42 565
	11,4,-6. 121 129 186 110 111 21	4 297 231 343 7 116 117 746 10 81 74 107	108 115 271 40 75 752		240 24 164		10.84 10.84		2· 1 22	2 72 48 595	67 72 467 50 58 779 109 105 478	12 43 49 477	44 49 785 31 34 310
8 20- 28 840 11 78 80 911 15 85 91 454 17 256 26 457	21- 25 192 73 76 111 88 91 567 259 25 565	10 86 82 200 16 91 86 20 19 86 76 972	41 82 744 42 40 444 79 78 452	2 % 10% #17 5 71 76 16 8 76 81 601	** ** /0* *1 #* **0 #1 #* *01	4 125 123 452 7 154 152 458 10 104 110 428 15 14 44 477	110 122 64 131 137 54 95 102 161 255 52 523	1 23+ 21 810 1 23+ 21 810 1 126 128 457 4 39 44 842	41 28 167 151 128 150 61 46 186		23. 21 33.	1 44 62 621 4 744 14 774 7 50 70 591	34 45 383 25+ 10 270 44 74 419
20 33 64 18 m.12.4 0 60 75 3	53 70 15 12,4,-6 90 77 985		10.47 50 55 27 97 105 987 91 100 717	··· 10.*	250 11 511	2 38 63 338	11, 1, 1 11, 1, 1 12, 1, 1	+ 1+2 1 +4 +01 12 +7 +1 112 +- 13-10	15, R 10	· · · · · · · · · · · · · · · · · · ·	45 48 521 236 22 348 246 27 334	2 41 58 275	244 17 744 3.814 254 52 735
1 54 10 348 6 75 71 404 9 155 156 718	42 32 640 84 67 613 156 167 297 239 23 603		15 71 115 67 64 11	0 44 36 751 1 100 101 396 6 175 176 364	11 51 514 96 99 620 185 185 967	5 287 296 6 8 230 10 604 11 70 78 851	/ 10 / 10 / 1 / 10 / 1 445	1 111 114 116 4 52 40 802 7 56 57 846 10 44 60 801	120 122 402 61 42 236 44 54 176 48 57 207	1/ 48 61 19/ 15 91 99 651	57 55 618 97 96 368	5 240 29 338 8 240 39 588	25+ 33 675 25+ 41 416
13 33 39 114	41 40 471 41 56 474		11.4 124 226 33 91 42 236	12 133 140 444	140 142 47 244 24 131 41 27 488	······································	12.0.0	4.10.10 2 21- 10 150 3 13- 151 902	16.810 43 40 858 140 150 19		4,8,-12 50 40 83 244 14 453 244 33 354	0 61 61 690 1 66 67 592 6 57 59 909 9 269 36 362	51 70 418 49 55 102 245 13 495
1 114 104 542 4 112 110 196 7 88 86 419	115 113 457 116 104 614 89 86 600 36 49 951	4 48 45 410 12 41 85 479 15 117 128 59	104 94 614		11+4	6 67 % 170 9 62 39 668 12 26 70 666	101 68 618	• 13 41 473 +,17,10 0 39 41 817	43 43 544 17.810 53 47 134	12 33 43 42 13 24- 13 465 16 44 48 7			5.424 128 116 92 102 96 225
	244 27 411 244 36 115	1 111 122 22	13 11 19	10 164 171 13 11 62 60 658 16 101 105 60	175 172 6 260 57 559 49 97 962		11,6,	· • • • • • • • • • • • • • • • • • • •	25+ 12 41 +1 +0 #10	7 71- 13 591 7 71- 13 591 7 81 8- 701	5.412 24+ 17 418 106 42 805	7 49 59 815	53 58 202 6.K14 34 49 367
2 40 45 770	81 94 249 99 90 460 38 51 655		22+ 41 211 21+ 40 444	2 46 50 655 2 46 50 655 3 216 50 142	12.8 44 56 556 61 56 887 210 21 100	1 62 62 180 17 746 5 386 13 716 11 515	40 18 694 244 15 497 244 10 620	1 124 118 461 6 246 27 466 7 216 48 686	126 120 557 256 27 70 256 57 509		111 124 405		50 57 173 58 57 576 74815
17 175 191 728	12.12.11	2 31 34 14	14.4			H,14,9 2 76 72 549 3 42 16 149	** ** ***	2 84 80 404 2 84 80 404 3 104 130 207	ND 61 410	0 82 44 880 3 45 77 526 4 42 51 123	82 93 139 76 77 495 90 96 682	0 41 35 148 3 244 52 826 6 40 42 45	25+ 34 859 25+ 29 177 48 38 914
0 162 162 420 3 225 234 410 6 42 45 22	155 151 47 225 216 579 55 55 969	1 52 61 214 11 56 51 52 16 57 24 57	62 65 775 66 51 6C1 76 76 670	0 270 22 414 1 210 42 434	21.0.25 140 21.0.25 140 35 10 575	11 24+ 51 90	244 44 711	0 44 70 404 3 70 48 173	20.810 67 65 88 36 34 686	12 41 44 156	00 64 679 7,6,-17	H.B.14 1 58 63 526 5 52 62 535	8,8,-14 68 60 586 59 68 371
12 10 10 10 15 75 11 797	41 65 957 71 78 225	0 14 24 250	14.4.17		244 16 P67 68 61 520 85 85 110	1 210 13 456 6 110 126 88 1 65 60 742	/** 10 550 11/ 115 4/1 76 67 /65	. 77 1. 15	/1	· · · · · · · · · ·		······································	7.814 23. 50 337 24. 8 203
1 190 18- AA1 4 57 60 416 7 44 77 404	100 101 150 70 55 538 67 77 607	6 22+ 26 A18 9 171 173 585 12 24+ 42 717	224 1A 197		14,4,-4 47 106 /12 441	1 21 2 2		2 111 106 111 2 111 106 111 4 11 42 125 4 87 82 420	107 108 685 107 100 641 81 78 587	· · · · · · · · · · · · · · · · · · ·	8.412 2.4.4.8.12	0 111 114 14 3 /3• 7 /7	10.814 138 126 985 254 3 639
10 121 129 992 13 AN 54 535 He17c6	12.13.43	1 105 07 150 1 105 109 274	10 107 /47	10 53 70 354	60 65 AV4	7 244 24 54	/** /\$ 480	14 145 144 882 17 244 11 27 20 244 12 697	148 143 134 744 73 10 744 73 10	8 24+ 23 546 11 51 50 505	25+ 25 +52	*.11,14 1 244 38 123	41.414 254 43 878
2 210 21 961 5 220 10 655 0 114 112 617 11 66 66 651	210 3 540 110 107 565 240 17 565	4 1/6 1/5 741 7 60 65 8 10 /16 17 977 11 /46 44 545		2 110 111 4/7	110 113 84 210 34 000 21 47 776	2 88 96 361 5 244 41 164 8 244 10 727	66 100 446 /44 11 /71		1.611 170 170 150 101 41 610	· ····································	65 56 672 111 113 670 62 55 657	0 1/0 131 84 3 31 53 111 6 107 104 806	153 157 031 /** 3/ 005 115 109 130
14 / 14 16 817 0 41 77 117	18. 17 711 18	2 N/ 10 407	16.87 87 94 605 141 207 918	14 102 82 750	101 25 211	······································	14.64 47 75 467 740 37 608	4 37 61 745 4 46 76 168 12 42 44 16 15 244 18 888	102 98 ATA 102 98 ATA 102 525	12 47 13 28	10141-12	· · · · · · · · · · · · · · · · · · ·	1.413 23. 36 73 24. 36 73
3 143 115 789 6 45 40 597 7 744 47 90 17 234 72 34	1/4 118 721 5/ 46 411 744 50 941 744 74 750	11 100 117 444 15 210 42 213	740 57 161 74 111 60 740 48 871	5 774 38 701 5 774 38 701 5 81 47 418 5 744 17 114	124 122 977 47 14 115 70 45 71 50 41 707	6 116 108 546 9 60 59 867 8,19,4	100 107 424	18 65 56 367 1 63 67 361	11 - 11 - 11 	1 100 196 71 4 71 20 868 7 744 51 797 10 714 18 414		· ····································	2.415 254 61 432 244 25 707
4.17.6 1 124 117 945 4 35 94 417	14,4,16 111 124 12 20 24 187		1/14.1/ 2/4 5/ 565 54 53 418 244 27 615	17 234 17 407	17.5.5.5 17.5.5.5 37 17 365	1 740 18 934 7 740 103 465 7 710 12 551		4 54 51 702 7 22+ 10 53 10 23+ 17 454 13 73 65 515	210 7 100 210 7 16 230 11 300 01 73 000	· · · · · · · · · · · · · · · · · · ·	11.412 11.412 21.42 21.		3.815 25- 44 761 25- 13 805
1 55 61 616 10 88 88 88 905	14 65 404 76 87 676 70.4. 6	12 23. 20 265	244 13 707 244 13 731	1 105 115 576 10 744 48 173	108 117 428	/ 1/ 01 000 / 1/ 01 000	20,4,-7 47 59 50 760 13 705	10 71 72 407 10 71 72 407	2* 2 22 3.811	# 60 A6 557	60 64 457 12.617 234 17 648	1 71 70 743	N.K15 13 40 213
7 73+ 10 747 5 67 76 711 8 84 76 450	14 14 4/ /44 64 105 70 /5 571 40 44 641	1 74 72 614 6 216 27 965 7 64 75 506 10 26 22 71	10 12 411 46 16 16 49 10 564 744 21 212	H,18,8 / 6/ 58 /19 5 61 58 146 5 71 58 146	18.2,-4 77 61 782 62 49 253 744 16 551	0 168 168 444 1 /10 3/ 619	21.8.1.9 178 177 74 1.51 59 181	2 105 100 291 5 86 90 518 8 210 19 667	10 10 177 10 10 101 11 10 101	1 46 18 628 6 246 27 241 9 68 64 101		2 242 12 117	25. 4 22.
	(1.5	2 66 54 541	11. 6. 651	0 25 35 411	17.4* 4/ 45 541	1 16 11 11	24.4.1.N 254.57.947	14 37 31 845 17 744 25 178	14 14 170 75• 77 ×71	1 74 14 4/1	61 68 591	0 23- 20 101	6.815 25- 19 Pee

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.

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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 $M_{6\cdot30}Al_{2\cdot65}$) vary between 1.942 and 2.111 Å in buergerite vs. 2.023 and 2.116 Å for magnesium octahedra in dravite.

The SiO₄ tetrahedra are more regular in buergerite; bond angles vary between $104 \cdot 0^{\circ}$ and $112 \cdot 0^{\circ}$. 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 coordina	tes of bue	rgerite wi	th transf	ormed	coordinates
of dra	avite (Buerger,	Burnham	& Peacon	r, 1962) j	for con	nparison

Buergerite above, dravite below.

		-	,				
Position	x	$\sigma(x)$	У	$\sigma(y)$	z	$\sigma(z)$	В
3a	0	-	0		0.21338	0.00041	2.328
	0		0	_	0.2324	0.0010	0.688
9 <i>b</i>	0.10992	0.00025	0.21984	0.00020	0.45182	0.00046	0.467
	0.1103	0.0007	0.2206	0.0012	0.4538	0.0020	-0.229
9 <i>b</i>	0.13320	0.00008	0.06660	0.00004	0.62072	0.00010	0.848
	0.1270	0.0002	0.0635	0.0002	0.6282	0.0007	0.327
18c	0.19156	0.00004	0.19065	0.00004	0	_	0.306
	0.1922	0.0003	0.1898	0.0003	0		0.201
18 <i>c</i>	0.29880	0.00004	0.25887	0.00004	0.60437	0.00010	0.587
	0.2976	0.0003	0.2615	0.0003	0.6138	0.0002	0.167
F 3a	0		0	<u> </u>	0.76698	0.00021	2.130
	0	<u> </u>	0		0.7783	0.0022	-0.678
9 <i>b</i>	0.06026	0.00012	0.12112	0.00029	0.48607	0.00029	0.789
	0.0609	0.0005	0.1218	0.0010	0.4787	0.0013	0.378
9 <i>b</i>	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
9 <i>b</i>	0.09478	0.00012	0.18956	0.00030	0.07532	0.00028	0.741
	0.0935	0.0002	0.1870	0.0010	0.0724	0.0014	0.526
9 <i>b</i>	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
18 <i>c</i>	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
18 <i>c</i>	0.28670	0.00010	0.28580	0.00010	0.07445	0.00018	0.573
	0.2844	0.0302	0.2821	0.0006	0.0810	0.0010	0.301
18 <i>c</i>	0.20394	0.00010	0.26941	0.00010	0.43778	0.00020	0.628
	0.2085	0.0302	0.2698	0.0002	0.4445	0.0011	0.694
	Position 3a 9b 9b 18c 18c 18c 9b 9b 9b 18c 18c 18c 18c	$\begin{array}{c cccc} {\rm Position} & x \\ & 3a & 0 \\ & 0 \\ & 0 \\ 9b & 0 \cdot 10992 \\ & 0 \cdot 1103 \\ 9b & 0 \cdot 13320 \\ & 0 \cdot 1270 \\ 18c & 0 \cdot 19156 \\ & 0 \cdot 1922 \\ 18c & 0 \cdot 29880 \\ & 0 \cdot 2976 \\ F & 3a & 0 \\ & 0 \\ 9b & 0 \cdot 06056 \\ & 0 \cdot 0609 \\ 9b & 0 \cdot 06056 \\ & 0 \cdot 0609 \\ 9b & 0 \cdot 06056 \\ & 0 \cdot 0609 \\ 9b & 0 \cdot 06056 \\ & 0 \cdot 0609 \\ 9b & 0 \cdot 06056 \\ & 0 \cdot 0609 \\ 9b & 0 \cdot 06056 \\ & 0 \cdot 0609 \\ 9b & 0 \cdot 06056 \\ & 0 \cdot 02880 \\ 0 \cdot 09478 \\ & 0 \cdot 0935 \\ 9b & 0 \cdot 18258 \\ & 0 \cdot 1812 \\ 18c & 0 \cdot 19314 \\ & 0 \cdot 1952 \\ 18c & 0 \cdot 28670 \\ & 0 \cdot 2844 \\ 18c & 0 \cdot 20894 \\ & 0 \cdot 2085 \\ \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				

Table 4. Anisotropic temperature factor coefficients for buergerite

exp	[]	h ² B	11	+				+	2hk	:B	12	+			.`)1		
Unp		$\mu \mu$			٠	٠	٠			μ	12	1	٠	٠	•	, 1	٠	

	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
В	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 defi and 1.606 Å vs. 1.639 and 1.635 Å).

defined as

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

In the configuration of the Si_6O_{18} ring buergerite and dravite maintain their similarity. Let ditrigonality be

where r_l and r_s are the longer and shorter distances,

Silicon – oxygen tetrahedron	
Si-O(4) = 1.620 + 2	$O(6) - O(4) = 2 \cdot 678 + 3$
$Si-O(5) = 1.626 \pm 3$	$O(6) - O(5) = 2.647 \pm 3$
$Si-O(6) = 1.620 \pm 2$	$O(6) - O(7) = 2.642 \pm 2$
$Si-O(7) = 1.602 \pm 2$	$O(4) - O(5) = 2.559 \pm 3$
	$O(4) - O(7) = 2 \cdot 638 \pm 3$
Mean $Si - O = 1.617$	$O(5) - O(7) = 2.676 \pm 3$
Mean $0-0=2.640$	
Boron – oxygen triangle	
$B-O(2) = 1.379 \pm 4$	(2) $O(8)-O(2) = 2.379 \pm 3$
(2) $B-O(8) = 1.364 \pm 4$	$O(8) - O(8') = 2.356 \pm 3$
Mean $B-O = 1.369$	
Mean $O - O = 2.371$	
Iron-oxygen octahedron	
$Fe-O(1) = 2 \cdot 111 \pm 4$	(2) $O(1)-O(2) = 2.617 \pm 4$
(2) Fe-O(2) = 2.003 ± 2	(2) $O(1)-O(6) = 3.016 \pm 4$
$Fe-O(3) = 1.942 \pm 3$	(2) $O(3)-O(2) = 3.162 \pm 3$
(2) Fe-O(6) = 1.989 ± 2	(2) $O(3)-O(6) = 2.518 \pm 3$
	(2) $O(2)-O(6) = 2.762 \pm 3$
Mean $Fe-O = 2.006$	$O(2) - O(2') = 2 \cdot 883 \pm 5$
Mean $0-0=2.825$	$O(6) - O(6') = 2.864 \pm 3$
Aluminum-oxygen octahedron	
$AI-O(3) = 1.897 \pm 3$	$O(3) - O(6) = 2.518 \pm 3$
$Al-O(6) = 1.924 \pm 2$	$O(3) - O(8) = 2.791 \pm 3$
$AI-O(7) = 1.979 \pm 2$	$O(3) - O(7') = 2.903 \pm 3$
$AI - O(7) = 1.888 \pm 2$	$O(3) - O(8') = 2.820 \pm 3$
$AI - O(8) = 1.931 \pm 2$	$O(7) - O(6) = 2.751 \pm 2$
$AI = O(8) = 1.893 \pm 2$	$O(7) - O(8) = 2.396 \pm 2$ $O(7) - O(7') - 2.723 \pm 3$
Mean A1- $\Omega = 1.919$	O(7) - O(8') = 2.845 + 2
Mean $O - O = 2.711$	$O(6) - O(8) = 2 \cdot 705 + 2$
	$O(6) - O(8') = 2.817 \pm 2$
	$O(7') - O(8) = 2 \cdot 868 \pm 2$
	$O(7') - O(8') = 2 \cdot 396 \pm 2$
Sodium-oxygen polyhedron	
(1) $N_{1} = O(2) = 2.571 + 4$	

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

(3) Na-O(2) = $2 \cdot 571 \pm 4$ (3) Na-O(4) = $2 \cdot 788 \pm 4$ (3) Na-O(5) = $2 \cdot 676 \pm 4$

Mean Na-O = 2.678

(2) (2) (2) (2) (2)

Silicon tetrahedron	Boron triangle
$O(6)-Si-O(4) = 111.5^{\circ}$	$O(8)-B-O(8') = 119.4^{\circ}$
$O(6) - Si - O(5) = 109 \cdot 2$	(2) $O(2)-B-O(8) = 120.3$
$O(6)-Si-O(7)=110\cdot 1$	
$O(5) - Si - O(4) = 104 \cdot 0$	Aluminum octahedron
$O(5) - Si - O(7) = 112 \cdot 0$	$O(3) - Al - O(6) = 82.4^{\circ}$
O(4) - Si - O(7) = 109.9	O(3) - Al - O(7') = 100.1
×	O(3) - Al - O(8) = 93.6
Iron octahedron	O(3) - Al - O(8') = 96.2
$O(1)$ -Fe- $O(6) = 94.7^{\circ}$	O(7) - Al - O(6) = 89.6
O(1)-Fe- $O(2) = 79.0$	O(7) - Al - O(7') = 89.5
O(3)-Fe- $O(6) = 79.7$	O(7) - Al - O(8) = 94.3
O(3)-Fe- $O(2) = 106.5$	O(7) - Al - O(8') = 76.4
O(2)-Fe- $O(6) = 87.6$	O(6) - Al - O(8) = 89.1
O(2)-Fe- $O(2') = 92.1$	O(6) - A - O(8') = 95.1
O(6)-Fe- $O(6') = 92.1$	O(7') - AI - O(8) = 77.7
	O(7) - AI - O(8) = 97.6

Table 6. Selected bond angles in buergerite

respectively, between the vertices and the center of gravity of the ditrigon. The ditrigonality 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_l and r_s 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 ditrigonality for their Si₆O₁₈ 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 recomputation; 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 \pm 23 to 0.7039 \pm 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 Å)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

 $M = Fe_{0.951} + Ti_{0.028} + Mg_{0.013} + Mn_{0.008}$.

Final formula for buergerite

 $(Na_{2.49}K_{0.05}Ca_{0.39}\Box_{0.07})\ (\textit{M}_{6.30}Al_{2.65}\Box_{0.05})B_{9.00}(Al_{16.32}\textit{M}_{1.57}\Box_{0.11})\ (Si_{17.20}B_{0.80})\ (O_{88.53}OH_{1.39}F_{0.08})F_{3.00}\ .$

Polar property Crystal habit: typical form	Antilogous pole (+c) $\{10\overline{1}1\}$	Analogous pole (-c) $\{10\overline{12}\}$
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

Table 8. Polar properties of tourmaline

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 (Frondel, 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 $\overline{41}.0$, and the $\overline{51}.\overline{1}$ 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 $I\{41.0\}/I\{\overline{41}.0\}$ 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 SiO₄ tetrahedra point in the opposite direction, *i.e.* toward the analogous pole. With transformed coordinates, the calculated value of the ratio $F^2(41\cdot0)/F^2(\overline{41}\cdot0)$ 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=0.056, $R_w=0.043$. The same operation, starting with transformed 1962 dravite coordinates (correct orientation), converged to R=0.046, $R_w=0.033$. 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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