SCHORL REFINEMENT SHOWING COMPOSITION DEPENDENCE OF THE TOURMALINE STRUCTURE

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ABSTRACT

The structure of an Andreasberg schorl tourmaline, with hexagonal cell content $(Na_{2.63} \, Ca_{0.34} \, K_{0.03})$ $(Fe^{2+}_{4.92} \, Al_{1.33} \, Fe^{3+}_{1.25} \, \square \, _{0.52} \, Mg_{0.32} \, Ca_{0.21} \, Ti^{4+}_{0.20}$ $Li_{0.20} \, Mn^{2+}_{0.05})$ $(Al_{16.82} \, Fe^{3+}_{1.18})$ $B_{9.00} \, Si_{18.00} \, O_{81.89}$ $(F, OH)_{11.11}$ has been refined to $R = 3.4\%$ for the 3961 observed reflections. A comparison of schorl with the other three tourmaline species, dravite, buergerite and elbaite, shows significant differences in atomic coordinates (up to 53σ). Thus the crystal structure of a solid solution will generally be composition-dependent, provided only that not all atomic positions are parameterless.

INTRODUCTION

Structure refinements of dravite (Donnay & Buerger 1950; Buerger *et al.* 1962), buergerite (Barton 1969; Tippe & Hamilton 1971) and elbaite (Donnay & Barton 1972) have preceded the present schorl refinement. This is astounding in a way, as the Andreasberg schorl was the first tourmaline to be studied by *x*-ray analysis on this continent. This work was begun in the thirties by William Parrish, it was taken up again by H. T. Evans Jr. in the forties, both times under the direction of M. J. Buerger at the Massachusetts Institute of Technology. We kept searching for a ferrous-iron tourmaline closer in composition to the end-member than the Andreasberg material, but this search was unsuccessful. Pure schorl has not been found in nature, and has not been synthesized as yet (Barton 1967). The conditions that prevail during the growth of terrestrial schorl are evidently not sufficiently reducing to prevent partial oxidation of iron from the ferrous to ferric state. Non-terrestrial tourmaline has not as yet been reported; perhaps some day we shall find lunar ferrous tourmaline with F^- instead of OH^-.

The reason for the four successive tourmaline refinements is the following. Since 1912 mineralogists have assumed that a crystal structure, no matter how wide a range of chemical composition it may cover, will not show any measurable variation in fractional coordinates with composition. Since the concept of mineral species has been tied to a crystal structure, such a species is thus supposed to remain "isostructural" (also spoken of as isomorphic) throughout any range of solid solution not interrupted by a first-order transition. Compositional changes do, of course, lead to changes in cell geometry, cell volume and density. Just why the fractional coordinates should remain constant, has not, to our knowledge, been discussed in any mineralogical or crystallographic paper or textbook and one of us has indeed, for the last 25 years, harbored the suspicion that this assumption is one of convenience or, rather, of practical necessity. How could mineralogical crystallographers claim to be doing useful work, if the atomic coordinates they obtain at the end of a lengthy and expensive mineral structure refinement were valid only for the particular specimen mounted on the goniometer head? Tourmaline, which is famous as one of nature's catch-all or garbage-can minerals (Bragg 1937), seemed as good a species as any on which to test the assumption. Donnay, Wyart & Sabatier (1959) suggested variability of atomic coordinates with composition in silicates, which was misconstrued as a suggestion of tourmaline polymorphism by Buerger *et al.* (1962).

CRYSTAL CHEMISTRY

The shiny black Andreasberg crystal we used came from the above-mentioned hand-specimen No. 246 of the Institute of Mineralogy of the Technical University of Berlin. An irregular fragment, 0.4 mm in its largest dimension, was used for intensity collection. Another fragment from the same crystal was used for an electron microprobe analysis carried out by Professor W. H. MacLean (Table 1). All elements except B and Li were determined directly with an estimated accuracy of 2 wt % of the amount present for Si, Al, Fe, and about 5 wt % of the amount present for Na, Ca, Ti, Mg, Mn, K. Boron was assumed to fill completely its position ($9b$) since it is the only cation to be expected in regular triangular coordination. The analysis was converted from weight per cent oxides to chemical formula on the basis of 18 Si per hexagonal cell. The subsequently refined mean ^{iv}Si-^{iii}O distance

TABLE 1. ELECTRON PROBE ANALYSIS* OF ANDREASBERG TOURMALINE
ON A FRAGMENT FROM CRYSTAL USED IN STRUCTURE REFINEMENT

Oxides	Wt %	Element	Ions present referred to 18 Si
+SiO$_2$	36.04	Si	18.00
Al$_2$O$_3$	30.83	Al	18.15
FeO, Fe$_2$O$_3$	17.59	Fe^{2+}	6.099**
		Fe^{3+}	1.240**
+B$_2$O$_3$	10.43	B	9.000
Na$_2$O	2.72	Na	2.63
CaO	1.01	Ca	0.543
TiO$_2$	0.54	Ti	0.201
MgO	0.42	Mg	0.415
MnO	0.11	Mn	0.048
K$_2$O	0.05	K	0.033
total	99.74		56.359

*W.H. MacLean, analyst. **From Mössbauer results (Hermon
et al. 1972). +Amounts of cations per cell have been assumed

of 1.620(1)*Å agrees with the one predicted
from effective ionic radii for $^{IV}Si^{4+}$ and $^{III}O^{2-}$
(Shannon & Prewitt 1969), namely 0.26Å +
1.36Å = 1.62Å. From Mössbauer data (Hermon
et al. 1972), which gave the Fe^{2+}/Fe^{3+} ratio
(4.89) and which also led to the percentages of
total iron present as Fe^{2+} in Y (67%) and in Z
(16%) and as Fe^{3+} in Y (17%), we deduced the
cell-content formula. On the basis of 93 anions
per cell, the balanced formula can be written
X_3 Y_9 Z_{18} B_9 Si_{18} $O_{81.89}$ (F, OH)$_{11.11}$, with $3X$
= Na$_{2.36}$ Ca$_{0.34}$ K$_{0.03}$, $9Y$ = Fe$^{2+}_{4.92}$ Al$_{1.33}$
Fe$^{3+}_{1.25}$ □ $_{0.53}$ Mg$_{0.32}$ Ca$_{0.20}$ Ti$^{4+}_{0.20}$ Li$_{0.20}$ Mn$^{2+}_{0.05}$
and $18Z$ = Al$_{16.82}$ Fe$^{2+}_{1.18}$.

CELL DATA

The cell dimensions (Table 2) are based on
the least-square refinement of twelve accurate-
ly measured general reflections with 2θ values
greater than 50°. These reflections, like all our
data, were collected on an automated 4-circle
Picker diffractometer, using graphite-mono-
chromated MoKα_1 radiation (λ = 0.70926Å).
The θ - 2θ scan method was used and the crystal
was turned through the angle θ at the rate
of 0.5°/minute.

TABLE 2. CELL DATA

$R3m$ a=15.992(2)Å c= 7.190(1) V=1592.4Å^3	Formula weight of cell-content (Z=1): 3111.40 Density (calc.): 3.244 g/cm^3 Density (meas.): 3.20(2) g/cm^3 Linear absorption coefficient for MoKα: 25.6 cm^{-1}

*The number in parenthesis following a numerical
value gives the standard deviation referred to the
last-given decimal place as calculated by the least-
square program.

EXPERIMENTAL PROCEDURE

The crystal fragment was mounted randomly
on a Eulerian cradle. From the minimum 2θ
value of 5.084° (for reflection 11.0) up to 2θ =
30°, all six symmetry-related reflections were
measured; for 30° < 2θ ⩽ 80°, only two, $hk.l$
and $\overline{kh}.l$, were used; for 80° < 2θ ⩽ 115.43°,
only one, $hk.l$, was measured. The indices h and
k ranged from −34 to +34, l ranged from −17
to +17. Of the 4101 symmetry-independent re-
flections contained in the molybdenum sphere,
3961 had integrated intensities that were at least
2σ above background intensity. The intensities
of symmetry-related reflections showed a mean
per cent deviation of 3.8%, so that we felt justi-
fied in neglecting absorption corrections.

STRUCTURE DETERMINATION

From the X-RAY '72 programs (Stewart et
al. 1972) we chose the "DATRDN" program to
correct intensities for Lorentz and polarization
factors and the "CRYLSQ" program to carry
out a full-matrix least-square refinement of the
Andreasberg structure, beginning with the buer-
gerite coordinates of Barton (1969). Atomic
scattering factors for neutral atoms were taken
from Hanson et al. (1964). Anomalous disper-
sion corrections were introduced for Fe, Mn,
Ca, K, Al, Si, Ti, (Internat. Tables III, p. 215,
1962). Observed Fs were weighted in inverse
proportion to their variance in the refinement
calculations, where the values of σ F_{obs} were
based on counting statistics. Employing aniso-
tropic temperature factors, the refinement ter-
minated with an unweighted residual R of 3.4%
and a weighted one, R_w, of 5.4%. The residual
of the "less-than-2σ reflections" alone is 13%.
The "less-than" reflections for which $|F_{calc}|$ is
greater than $|F_{obs}|$ are included in the refinement
calculations. Table 3 lists $|F_{obs}|$, $|F_{calc}|$ and the
calculated phase angles.*

The absolute orientation of the structure was
determined by carrying out separate refinements
for the two possible orientations, as Barton
(1969) had previously done for buergerite. The
unweighted residual for the alternate orientation

*Table 3 has been deposited with the Depository of
Unpublished Data. Copies may be obtained on re-
quest to: Depository of Unpublished Data, National
Science Library, National Research Council of Can-
ada, Ottawa, Ontario, Canada.

is found to be about 6%. In schorl, as in buergerite (Barton & Donnay 1966), the SiO_4 tetrahedra point towards the analogous pole, *i.e.* toward the negative end of the z-axis of the morphological description (Dana 1892). The final atomic coordinates (Table 4) and their anisotropic temperature factors (Table 5) refer, of course, to the traditional mineralogical orientation, in which the antilogous pole defines the positive end of the z-axis.

DISCUSSION

Bond lengths and bond valences (Table 6) yield satisfactory agreement between calculated and ideal anionic valence sums (Donnay & Allmann 1970), with a discrepancy value $\Delta v_{rms} = 0.040$ v.u., as compared with 0.049 v.u. for elbaite (Donnay & Barton 1972), 0.081 v.u. for buergerite (Barton 1969) and 0.034 v.u. for dravite (Buerger *et al.* 1962)**.

The ditrigonality δ of the Si_6O_{18} ring was defined by Barton (1969) as the ratio of the difference between the longer and the shorter distance from the center of gravity of the ditrigon to its vertices, divided by the shorter distance. In schorl, the silicon ring deviates the least from hexagonal symmetry, $\delta = 0.005$, in elbaite the value is 0.009, in dravite it is considerable, namely 0.032, and in buergerite even more so, $\delta = 0.038$.

The interbond angles and the interatomic approaches under 3.2Å in length are listed in Table 7. The edges of coordination polyhedra, which can be readily computed from the bond lengths given in Table 6 and the interbond angles in Table 7, are not explicitly listed. No major topological differences between the four species are evident. Nevertheless, highly significant differences appear between the fractional atomic coordinates of the four species (Table 8), bearing out the suspicion that led to this series of structure refinements. The observed differences in refined crystal structure with composition should generally apply to mineral structures that cover large compositional ranges and in which not all atomic positions are invariant.

**Dravite, unfortunately, was not refined accurately enough, nor was the chemical composition determined for the specimen used, so that its low bond-valence discrepancy value is not as meaningful as it looks.

It follows that, for any such mineral, careful decisions have to be made before chemical or physical properties (cation occupancy, in particular) can be meaningfully correlated with the crystal structure.

TABLE 4.. ATOMIC COORDINATES OF ANDREASBERG SCHORL

Position	Chemical atom	x	y	z
(3a)	X	Na..	0	0	0.22353(43)
(9b)	Y	Fe^{2+},Fe^{3+},Al..	0.12566(2)	x/2	0.62792(6)
(18c)	Z	Al,Fe^{2+}..	0.29883(3)	0.26171(3)	0.61158(6)
(9b)	B	B	0.11029(6)	2x	0.45461(24)
(18c)	Si	Si	0.19177(2)	0.18986(2)	0
(3a)	01	OH,0	0	0	0.78366(29)
(9b)	02	0	0.06154(5)	2x	0.48301(24)
(9b)	03	OH,0	0.27060(12)	x/2	0.51146(18)
(9b)	04	0	0.09278(5)	2x	0.06907(17)
(9b)	05	0	0.18566(12)	x/2	0.09037(17)
(18c)	06	0	0.19772(7)	0.18787(7)	0.77785(11)
(18c)	07	0	0.28462(7)	0.28518(7)	0.07966(11)
(18c)	08	0	0.20985(7)	0.27048(8)	0.44247(15)

TABLE 5. ANISOTROPIC TEMPERATURE FACTORS OF ANDREASBERG SCHORL

	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Na	0.0226(6)	0.0226(6)	0.0275(9)	0.0113(3)	0	0
Fe,Al..	0.0046(1)	0.0046(1)	0.0107(1)	0.0011(1)	0.0016(1)	-0.0016(1)
Al,Fe..	0.0034(1)	0.0038(1)	0.0044(1)	0.0016(1)	0.0001(1)	0.0007(1)
B	0.0043(4)	0.0043(4)	0.0081(4)	0.0021(4)	0.0007(2)	-0.0007(2)
Si	0.0034(1)	0.0031(1)	0.0052(1)	0.0016(1)	-0.0002(1)	-0.0005(1)
01	0.0514(13)	0.0514(13)	0.0087(4)	0.0257(7)	0	0
02	0.0165(5)	0.0165(5)	0.0128(4)	0.0147(5)	0.0006(1)	-0.0006(1)
03	0.0104(3)	0.0104(3)	0.0067(3)	0.0019(4)	-0.0009(2)	0.0009(2)
04	0.0094(2)	0.0094(2)	0.0086(3)	-0.0007(3)	-0.0006(1)	0.0006(1)
05	0.0058(3)	0.0058(3)	0.0086(3)	-0.0002(3)	-0.0005(1)	0.0005(1)
06	0.0080(3)	0.0083(3)	0.0049(2)	0.0041(2)	0.0002(2)	-0.0007(2)
07	0.0054(2)	0.0045(2)	0.0077(2)	0.0010(2)	-0.0011(2)	-0.0011(2)
08	0.0042(3)	0.0094(3)	0.0112(2)	0.0035(2)	0.0012(2)	0.0027(2)

The components u_{ij} represent the tensor that expresses the ellipsoid of mean-square amplitude of the vibration of the atom:

$$\exp. [-2\pi^2 (h^2a^{*2}u_{11} + ... + 2kl\ b^*c^*\ u_{23})]$$

TABLE 6. BOND LENGTHS AND BOND VALENCES IN ANDREASBERG SCHORL

Cation Anion	Multi-plicity	X	Y	Z	B	Si	Σv	Anion Occupancy	$|\Delta v|$
01	3		3^{+} $1^{\dagger\dagger}$ 2.070(1)Å 0.394(0)v.u.				1.182(0)	$(OH)^-_{0.82}O^{2-}_{.18}$	0.002
02	9	1 3 2.527(3) 0.173(1)	2 2.013(1) 0.452(1)		1 1.366(1) 1.022(2)		2.100(2)	O^{2-}	0.100
03	9		1 1 2.175(1) 1.974(1) 0.293(0) 0.416(1)				1.125(1)	$(OH)^-_{0.96}O^{2-}_{.04}$	0.003
04	9	1 3 2.800(2) 0.091(0)				2 1 1.627(1) 0.987(1)	2.065(1)	O^{2-}	0.065
05	9	1 3 2.744(1) 0.106(0)				2 1 1.640(1) 0.962(1)	2.029(1)	O^{2-}	0.029
06	18		1 2 2.044(1) 1.876(1) 0.419(1) 0.557(1)			1 1 1.605(1) 1.031(2)	2.007(2)	O^{2-}	0.007
07	18		1 1 1.891(1) 0.533(1)			1 1 1.610(1) 1.021(2)	1.977(2)	O^{2-}	0.023
			1 1 1.969(1) 0.423(1)						
08	18		1 1 2 1.891(1) 1.382(1) 0.533(1) 0.989(2)				1.999(2)	O^{2-}	0.001
			1 1 1.930(1) 0.477(1)						
L(MEAN)		2.690	2.060	1.922	1.377	1.620			
L(MAX)		3.145	2.478	2.276	1.870	2.130			
p(EXP)		5.917	4.926	5.426	2.791	3.181			
V(Σ)		1.11/9	2.43/6	2.94/6	3.00/3	4.00/4			
NORM.F.		0.971	0.997	0.997	1.000	1.000			
Σ^v		1.110	2.430	2.940	3.000	4.000		$\Delta v_{rms} = .040$ v.u.	

†Number of bonds received by anion   ††Number of bonds emanating from cation

TABLE 7. INTERBOND ANGLES AND INTERIONIC APPROACHES BETWEEN IONS OF THE SAME POLARITY LESS THAN 3.20Å APART

Silicon tetrahedron

04 - Si - 05 = 104.05(5)°	
04 - Si - 06 = 111.69(7)°	
04 - Si - 07 = 110.40(6)°	
05 - Si - 06 = 110.64(7)°	
05 - Si - 07 = 110.20(6)°	
06 - Si - 07 = 109.74(4)°	

Z octahedron

03 - Z - 06 = 84.45(5)°
03 - Z - 07' = 94.21(4)°
03 - Z - 08 = 92.60(5)°
03 - Z - 08' = 94.53(5)°
06 - Z - 07 = 92.13(4)°
06 - Z - 08 = 90.64(5)°
06 - Z - 08' = 94.15(5)°
07 - Z - 07' = 90.70(3)°
07 - Z - 08 = 95.68(5)°
07 - Z - 08' = 77.47(3)°
07' - Z - 08 = 78.45(5)°
07' - Z - 08' = 96.89(5)°

03 - 04 = 3.0189(13)Å
04 - 08 = 3.1646(16)Å
Y - Y = 3.0143(5)Å*
Y - Z = 2.9985(6)Å
Y - B = 2.9322(12)Å
Z - Z = 2.9491(7)Å*
Z - B = 2.9986(14)Å
Z - B = 2.9689(10)Å
Z - Si = 3.1755(6)Å
Z - Si' = 3.1841(6)Å
Si - Si' = 3.0059(6)Å*
Si - Si'' = 3.0972(6)Å*

B Triangle

2x 02 - B - 08 = 120.26(7)°	
08 - B - 08' = 119.46(7)°	

X polyhedron

3x 02 - X - 02' = 71.48(8)°
3x 02 - X - 04 = 70.96(4)°
6x 02 - X - 04' = 127.05(5)°
3x 02 - X - 05 = 152.84(11)°
6x 02 - X - 05' = 86.65(4)°
3x 04 - X - 04' = 105.31(7)°
3x 04 - X - 05 = 136.21(12)°
6x 04 - X - 05' = 55.35(3)°
3x 05 - X - 05' = 108.50(7)°

Y octahedron

2x 01 - Y - 02 = 84.78(5)°
2x 01 - Y - 06 = 97.25(5)°
02 - Y - 02' = 94.31(5)°
2x 02 - Y - 03 = 102.00(4)°
2x 02 - Y - 06 = 88.67(4)°
2x 03 - Y - 06 = 75.62(3)°
06 - Y - 06' = 88.30(2)°

*error shown may be a fraction of true value

TABLE 8. COMPARISON OF ATOMIC FRACTIONAL COORDINATES OF SCHORL WITH THOSE OF ELBAITE, DRAVITE AND BUERGERITE

Posi-tion	Spec-ies*	Chemical data	x	$\frac{|\Delta x|}{(\sigma_s^2+\sigma_i^2)^{\frac{1}{2}}}$ i=e,d,b	y	$\frac{|\Delta y|}{(\sigma_s^2+\sigma_i^2)^{\frac{1}{2}}}$	z	$\frac{|\Delta z|}{(\sigma_s^2+\sigma_i^2)^{\frac{1}{2}}}$
(3a) x	s	Na,Ca,..	0	–	0	–	.2235(4)	–
	e	Na,..	0	–	0	–	.2347(9)	11
	d	Ca,..	0	–	0	–	.2324(10)	8
	b	Na,Ca,..	0	–	0	–	.2134(4)	18
(9b) y	s	Fe²⁺,..	.1257(1)	–	x/2		.6279(1)	–
	e	Al,Li,..	.1234(1)	16	x/2		.6348(5)	14
	d	Mg,Fe,..	.1270(5)	3	x/2		.6282(7)	0
	b	Fe³⁺,..	.1332(1)	53	x/2		.6207(1)	51
(18c) z	s	Al,Fe²⁺	.2988(1)	–	.2617(1)	–	.6116(1)	–
	e	Al	.2964(1)	17	.2598(1)	13	.6105(3)	3
	d	Al,Mg,..	.2976(3)	4	.2615(3)	1	.6138(6)	4
	b	Al,Fe	.2988(1)	0	.2589(1)	20	.6044(1)	51
(9b) B	s	B	.1103(1)	–	2x		.4546(2)	–
	e	B	.1092(3)	3	2x		.4548(10)	0
	d	B	.1103(7)	0	2x		.4538(20)	0
	b	B	.1099(2)	2	2x		.4518(5)	5
(18c) Si	s	Si	.1918(1)	–	.1899(1)	–	0	–
	e	Si,B	.1917(1)	1	.1896(1)	2	0	–
	d	Si,Al	.1922(3)	1	.1898(3)	3	0	–
	b	Si	.1916(1)	1	.1907(1)	6	0	–
(3a) O 1	s	F,O	0	–	0	–	.7837(3)	–
	e	F,O	0	–	0	–	.7794(18)	2
	d	OH	0	–	0	–	.7783(21)	2
	b	F	0	–	0	–	.7670(5)	29
(9b) O 2	s	O	.0615(1)	–	2x		.4830(2)	–
	e	O	.0614(2)	0	2x		.4868(7)	5
	d	O	.0609(5)	1	2x		.4787(13)	3
	b	O	.0606(1)	6	2x		.4861(3)	9
(9b) O 3	s	OH,O	.2706(1)	–	x/2		.5115(2)	–
	e	OH,O	.2676(2)	13	x/2		.5069(7)	6
	d	OH,F,O	.2680(10)	3	x/2		.5145(14)	2
	b	O,OH,F	.2645(3)	19	x/2		.5209(3)	26
(9b) O 4	s	O	.0928(1)	–	2x		.0691(2)	–
	e	O	.0937(2)	4	2x		.0729(6)	6
	d	O	.0935(5)	1	2x		.0724(14)	2
	b	O	.0948(2)	9	2x		.0753(3)	17
(9b) O 5	s	O	.1857(1)	–	x/2		.0904(2)	–
	e	O	.1858(2)	0	x/2		.0937(6)	5
	d	O	.1812(10)	4	x/2		.0888(12)	1
	b	O	.1826(3)	10	x/2		.0839(3)	18
(18c) O 6	s	O	.1977(1)	–	.1879(1)	–	.7774(1)	–
	e	O	.1966(2)	5	.1859(2)	9	.7746(4)	7
	d	O	.1952(6)	4	.1866(7)	2	.7789(9)	2
	b	O	.1931(1)	33	.1868(1)	8	.7748(2)	12
(18c) O 7	s	O	.2846(1)	–	.2852(1)	–	.0797(1)	–
	e	O	.2863(2)	8	.2859(2)	3	.0783(4)	3
	d	O	.2844(7)	0	.2851(6)	0	.0810(10)	1
	b	O	.2867(1)	15	.2858(1)	4	.0745(2)	23
(18c) O 8	s	O	.2099(1)	–	.2705(1)	–	.4425(1)	–
	e	O	.2092(2)	3	.2693(2)	5	.4397(4)	7
	d	O	.2085(7)	2	.2698(7)	1	.4445(11)	2
	b	O	.2089(1)	7	.2694(1)	8	.4378(2)	21

* s=schorl, e=elbaite, d=dravite, b=buergerite

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