

NEW TYPE OF FERRIC IRON TOURMALINE¹CLIFFORD FRONDEL, ALBRECHT BIEDL² AND JUN ITO,
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ABSTRACT

Chemical, optical and x-ray data are given for a tourmaline from Madagascar very low in Al and high in Fe³⁺. This tourmaline represents an intermediate composition, with 23 atomic per cent Fe²⁺ substituting for Al in the Z position, in a series extending toward the idealized end-composition NaMg₃Fe³⁺B₃Si₆O₂₇(OH,F)₄ from dravite, ideally NaMg₃Al₆B₃Si₆O₂₇(OH,F)₄. A tourmaline from Madagascar analyzed by Jannasch and Calb (1889) apparently also is a member of this series, with approximately 14 atomic per cent Fe³⁺ substituting for Al. This type of ferric iron tourmaline differs crystallochemically and in physical properties from the ferric iron tourmaline buergerite, ideally NaFe₃³⁺Al₆B₃Si₆O₃₀(OH,F). A tourmaline from the Urals described by Cossa and Arzruni (1882) may represent the Cr analogue of buergerite.

The generalized formula of tourmaline may be written, following G. Donnay and M. J. Buerger (1950), as XY₃Z₆B₃Si₆O₂₇(OH,F)₄. The X position is occupied by Na, Ca and K chiefly, the Y position by Mg, Fe²⁺, Mn²⁺, Fe³⁺, and LiAl chiefly, and the Z position ordinarily is wholly occupied by Al. The most extensive mutual substitution of cations is found in the Y position, giving rise to two well-defined series in the tourmaline group, as described by Epprecht (1953), between the idealized end-compositions NaMg₃Al₆B₃Si₆O₂₇(OH,F)₄ (dravite) and NaFe₃²⁺Al₆B₃Si₆O₂₇(OH,F)₄ (schorl) and between schorl and Na(Li,Al)₃Al₆B₃Si₆O₂₇(OH,F)₄ (elbaite).

Mason *et al.* (1964) have described a high-iron tourmaline from Mexico, to which the name buergerite has been given (Donnay *et al.*, 1966), that represents a new type of compositional variation. In this tourmaline, the Y position is almost wholly occupied by Fe³⁺, and the composition approaches the idealized formula NaFe₃³⁺Al₆B₃Si₆O₃₀(OH,F). The measured cell contents (150 atoms) are (Na_{2.47}Ca_{0.38}K_{0.05})(Fe_{6.87}³⁺Fe_{0.55}²⁺Ti_{0.21}Mg_{0.10}Mn_{0.06}Al_{0.81})Al₁₈B_{9.27}(Si_{17.55}B_{0.45})(O_{88.78}OH_{1.22}(F_{3.06}OH_{0.16})). Valence compensation for the Fe³⁺ is effected by conversion of hydroxyl to oxygen. It may be termed an oxy-tourmaline analogous to oxyhornblende, oxyannite and other substances in which there is crystallochemical coupling between Fe²⁺Fe³⁺/OH,O or Mn²⁺Mn³⁺/OH,O. Buergerite has abnormal unit-cell constants, optical properties and density, which do not conform to the schorl-dravite series as established by Epprecht (1953). A green tourmaline from the Urals described by Cossa and Arzruni (1882) may represent the Cr analogue of

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buergerite. The analysis is poor, but does indicate that the Z position is wholly occupied by Al with about 49 atomic per cent Cr substituting for (Mg, Fe²⁺) in the Y position.

An additional example of a tourmaline high in ferric iron, that differs from both buergerite and schorl-dravite in its mechanism of compositional variation, may now be described. The specimen is a somewhat rounded waterworn single-crystal, about 560 grams in weight, from an unknown locality in Madagascar. It was obtained from a dealer in Tananarive and attracted attention because of its seemingly monoclinic habit. It is black in color and opaque in small grains. The fine powder is dark gray. The fracture is subconchoidal to irregular. Hardness 7. A complete chemical analysis, cited in Table 1 together with the analysis of

TABLE 1. CHEMICAL ANALYSES OF FERRIC IRON TOURMALINES

1.	Atoms per 31 (O,OH,F)		Cell contents		2.	Buergerite 3.	
			Measured	Theory			
Na ₂ O	1.41	Na 0.464	1.40	2.77	1.92	2.46	
K ₂ O	0.10	K 0.022	0.07		3	0.29	0.07
CaO	2.36	Ca 0.429	1.30			2.03	0.69
MgO	8.69	Mg 2.195	6.64	8.63	6.90	0.13	
MnO	tr	Mn			9		0.13
FeO	4.70	Fe ²⁺ 0.666	2.01			7.99	1.27
Fe ₂ O ₃	10.63	Fe ³⁺ 1.356	4.10	18.06	6.68	17.62	
Al ₂ O ₃	22.12	Al 4.421	13.36		18	25.83	30.79
TiO ₂	1.56	Ti 0.199	0.60			1.22	0.55
B ₂ O ₃	10.42	B 3.048	9.22	9	9.49	10.86	
SiO ₂	34.57	Si 5.864	17.72	18	35.48	33.86	
H ₂ O+	3.55	H 4.01	12.14	93.57	2.58	0.40	
(H ₂ O-	0.12)	O 30.91	93.28				(none)
F	0.18	F 0.09	0.29		93	0.33	1.86
	100.41		150.01	150	100.74	100.69	
F=0	0.08				0.14	0.78	
Total	100.33				100.60	99.91	
S.G.	3.18				3.195	3.31	

1. Madagascar. J. Ito, analyst, 1963. H₂O— disregarded.
2. Madagascar. Jannasch and Calb (1889).
3. Buergerite. Mexico. C.O. Ingamells, analyst, in Donnay *et al.* (1966). Spectrographic analysis (by N. H. Suhr) showed Sr, Ba, Cr, Be, Ni, Co, V less than 0.01, Zn less than 0.1 per cent.

buergerite, corresponds to common types of dravite except for an abnormally low content of Al and a correspondingly high content of Fe^{3+} . The Al content is lower than any yet reported for tourmaline. The Fe^{3+} clearly substitutes for Al, and occupies 23 atomic per cent of the structural position Z. It is apparent from its occupancy of this position that the Fe^{3+} is not secondary and the result of the oxidation of Fe^{2+} . The content of 27 O and 4 (OH,F) indicated by the analysis and unit-cell measurements also indicates the absence of the Fe^{2+} , $\text{Fe}^{3+}/\text{OH},\text{O}$ couple. The measured unit-cell contents are



A semi-quantitative optical spectrographic analysis revealed Mn in the range 0.0X and Cr, V, Ga, Sn and Sr in the range 0.00X.

X-ray precession photographs taken in Mo radiation confirm the rhombohedral symmetry, a point of interest because of the unusual morphological development of the analyzed crystal. The space group is $R\bar{3}m$, $R3m$, $R32$, $R\bar{3}$ or $R3$. The cell dimensions thus obtained (a 15.98, c 7.234 Å) were refined from an *x*-ray powder photograph taken in Fe radiation. The computer program LCLSQ of Burnham (1962) was employed. The indexed pattern and the cell dimensions obtained are given in hexagonal coordinates in Table 2. The unit-cell volume 1612.3 ± 1.1 Å³, is the largest so far found in tourmaline. It contrasts markedly with the relatively small unit-cell volume, 1568.2 Å³, reported for schorl. The larger cell volumes in the tourmaline group are found in schorl. The cell volume calculated for the schorl end-composition, $\text{NaFe}_3^{2+}\text{Al}_6\text{B}_3\text{Si}_6\text{O}_{27} \cdot (\text{OH})_4$, from the cell dimensions as extrapolated by Epprecht (1953) is 1591.3 Å³. There are also marked differences in other properties, as noted beyond. The differences in the cell volumes of these two ferric tourmalines, although the total number of iron atoms in the unit cell is roughly the same, are associated with the substitution of Fe^{3+} for the smaller Al ion in the Z position in the Madagascar material and the substitution of the Fe^{3+} for the larger (Mg, Fe^{2+}) ion in the Y position in buergerite. The cell constants and the axial ratios of these tourmalines both fall far off the plot of axial ratio versus a derived by Epprecht (1953) for the schorl-dravite series and in opposite directions.

The Madagascar material is almost opaque in crushed grains under the microscope. Very small, translucent grains have ϵ $1.656 \pm .002$ (Na) (light olive green). The value of ω (dark olive green) is not measurable accurately because of the strong absorption, but is below 1.70. The birefringence clearly is much less than the extremely high value, 0.080, found in buergerite. In thick grains ϵ is dark olive brown to brown and in the position of ω the grains are opaque. After heating in air for 72 hours at

500° C., the value of ϵ of the Madagascar material increased by about 0.006 while that of buergerite remained essentially unchanged. This increase presumably is the result of oxidation of Fe^{2+} present in the Y position and of conversion of some OH to O. The specific gravity is 3.18 ± 0.01 (meas.), 3.18 (calc.), as compared to 3.31 (meas.) for buergerite.

Morphologically, the crystal has a distinctly monoclinic aspect simu-

TABLE 2. X-RAY POWDER DIFFRACTION DATA

Fe radiation, Mn filter, $\lambda(\text{FeK}\alpha) = 1.9373 \text{ \AA}$. Film pattern; visual intensities. Material of analysis 1. Measured spacings rounded off to 4 figures after refinement. Unit-cell dimensions in hexagonal coordinates: $a = 16.045 \pm 0.012 \text{ \AA}$, $c = 7.238 \pm 0.004$; $a:c = 1:0.4511$. The error range refers to the least squares standard error of the computation.

I	<i>d</i>	hk·l	I	<i>d</i>	hk·l	I	<i>d</i>	hk·l
6	6.44	10.1	1	2.141	30.3	1	1.441	64.2
4	5.01	02.1	1-	2.120	42.2	1-	1.427	01.5
4	4.62	30.0	1-	2.066	22.3	1	1.416	20.5
9	4.245	21.1	3	2.052	15.2	1	1.360	10.0.1
9	4.003	22.0	1-	2.027	16.1	1-	1.347	91.2
9	3.510	01.2	1-	1.998	44.0	1	1.335	92.1
1	3.395	13.1	2+	1.932	34.2	1	1.315	10.1.0
1-	3.025	41.0	1	1.889	41.3	2	1.283	50.5
9+	2.979	12.2	1	1.858	62.1	1	1.267	42.5
1	2.910	32.1	1	1.793	10.4	1	1.242	
1-	2.631	31.2	1-	1.757	02.4	1	1.222	
10	2.586	05.1	1-	1.697	26.2	1	1.208	
1-	2.506	04.2	1+	1.671	60.3	1	1.195	
1-	2.461	24.1	1+	1.650	27.1	1	1.186	
1	2.416	00.3	2	1.603	55.0	1	1.169	
1	2.390	23.2	1-	1.553	46.1	1+	1.156	
1	2.356	51.1	1-	1.539	90.0	1-	1.132	
1-	2.308	60.0	2	1.519	82.0	1+	1.101	
1	2.200	50.2	1-	1.491	24.4	1-	1.087	
1	2.172	43.1	1+	1.467	51.4	1	1.072	

lating class $2/m$, with dominant faces, in this interpretation, of $\{010\}$, $\{100\}$, a prism, and a prominent $\{0kl\}$ form. The crystal could not be visually oriented on hexagonal axes, and the faces finally were identified with the aid of x-ray single-crystal photographs taken of oriented sections and of contact-goniometer measurements. The interfacial angles used for comparison were calculated from the cell constants using the Fortran computer program ANGLE. On hexagonal axes, the crystal is elongated along the direction of the edge between (10.1) and (02.1). The forms present are $r \{10.1\}$, $y \{40.1\}$, $\bar{r} \{01.\bar{1}\}$, $o \{02.1\}$, $m \{10.0\}$ and a

{11.0}. All of these forms are only partially developed, with (10.1) of r ; (40.1) of y ; (01. $\bar{1}$), ($\bar{1}0.\bar{1}$) and ($\bar{1}\bar{1}.\bar{1}$) of \bar{r} ; (02.1) and (22.1) of o ; (10.0) of m ; and (11.0), (21.0), (12.0), and ($\bar{1}\bar{2}.0$) of a . The arrangement and relative size of the more prominent of these faces is such as to produce an apparent plane of symmetry and two-fold axis perpendicular thereto in the malformed and in part broken crystal.

A survey of approximately 80 superior analyses of tourmaline reported in the literature has revealed what may be an additional example of a ferrian tourmaline of the present type. This analysis, by Jannasch and Calb (1889) of material from Tamatave, Madagascar, corresponds rather well to the requirements of the new tourmaline formula-type. On the basis of 31 (O,OH,F) it yields $(\text{Na}_{1.91}\text{Ca}_{.37}\text{K}_{.06})_{1.07} (\text{Mg}_{1.77}\text{Fe}_{1.15}^{2+})_{2.92} \cdot (\text{Al}_{5.23}\text{Fe}_{.86}^{3+})_{6.09} \text{B}_{2.82} (\text{Si}_{6.09}\text{Ti}_{.47})_{6.56} \text{O}_{27} (\text{OH}_{3.82}\text{F}_{.18})_4$ with approximately 14 atomic per cent Fe^{3+} substituting for Al. The only properties given for this tourmaline are the specific gravity (3.195) and the color (black). Tamatave probably is the place where the specimen was obtained in trade rather than the actual mineral locality.

It may be noted that the term ferrian dravite is not applicable to this material because it does not distinguish between the two different structural sites in which the Fe^{3+} can be present, in the Y position or in the Z position.

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