

Povondraite, a redefinition of the tourmaline ferridravite

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ABSTRACT

Povondraite, previously the tourmaline ferridravite, is redefined. It is rhombohedral, $R3m$, with $a = 16.186(2)$ and $c = 7.444(1)$ Å. The new chemical formula, derived by crystal structure analysis, is $(\text{Na}_{0.80}\text{K}_{0.26})_{\Sigma 1.06}(\text{Fe}_{2.28}^{3+}\text{Fe}_{0.27}^{2+}\text{Mg}_{0.53})_{\Sigma 3.08}(\text{Fe}_{4.29}^{3+}\text{Mg}_{1.36}\text{Al}_{0.32})_{\Sigma 5.97}\text{B}_3\text{Si}_{5.96}\text{O}_{27.88}(\text{OH})_{3.12}$ and the ideal end-member formula is $\text{NaFe}_3^{3+}\text{Fe}_6^{3+}(\text{BO}_3)_3(\text{Si}_6\text{O}_{18})_4(\text{O},\text{OH})_4$.

INTRODUCTION

During the investigation of a series of tourmaline crystal structures with varying contents of Fe and Mg (Grice and Ercit, 1990, 1993) the "ferridravite" structure was refined. It was discovered that the formula proposed by Walenta and Dunn (1979) for the species ferridravite was incorrect. They adopted the standard scheme for assignment of cations to the X, Y, and Z sites, i.e., with Fe^{3+} and Al^{3+} assigned to the Z site and Mg^{2+} and Fe^{2+} to the Y site, yielding the empirical formula $(\text{Na}_{0.80}\text{K}_{0.24})_2(\text{Mg}_{1.58}\text{Fe}_{1.15}^{2+})(\text{Fe}_{3.49}\text{Al}_{0.51})_2\text{Si}_6\text{B}_3(\text{O},\text{OH})_{30}(\text{OH},\text{F})$. As with the structure refinement of feruvite (Grice and Robinson, 1989), it became evident that the assumed site assignments of Mg^{2+} and Fe^{3+} were incorrect. The crystal structure refinement of "ferridravite" yielded a new empirical formula that bears no resemblance to "the ferric analog of dravite" (Walenta and Dunn, 1979); therefore renaming of the species was required. The new name, povondraite, is in recognition of the extensive work on the chemistry of the tourmaline group by Dr. Pavel Povondra, Karlovy University. The data and new name for this redefined species were approved by the Commission on New Minerals and Mineral Names, I.M.A. Type material for povondraite is preserved at the National Museum of Natural History, Smithsonian Institution (no. 144478) and at the Royal Ontario Museum (no. M35899).

PHYSICAL AND CHEMICAL DATA

The two samples used in this study (Royal Ontario Museum no. M35899 and Smithsonian Institution no. 144478) are both type material of "ferridravite" from the San Francisco mine, near Villa Tunari, Bolivia. The mineral is described (Walenta and Dunn, 1979) as occurring in metamorphosed sedimentary rocks. The schist is composed of quartz, potassium feldspar, alkali amphibole, muscovite, and tourmaline (schorl and povondraite).

Povondraite is strongly pleochroic with O yellow-brown and E dark red-brown. It is uniaxial negative with $\omega = 1.820(5)$ and $\epsilon = 1.751(3)$, measured with Na light (590

nm). These values are greater than those given by Walenta and Dunn (1979).

Povondraite was chemically analyzed using a Jeol model 733 electron microprobe. Wavelength-dispersion analyses used an operating voltage of 15 kV, a beam current of 25 nA measured with a Faraday cup, and a beam diameter of 10 μm . The following standards were used: synthetic gehlenite (Al), almandine (Si, Mg), synthetic fayalite (Fe), microcline (K), sodic amphibole (Na), VP_2O_7 (V), and titanite (Ti). The elements F, Mn, and Ca were sought but not detected. Data reduction was performed with a conventional ZAF routine in the Tracor Northern Task series of programs. The analyses of the single crystals used in the crystal structure refinements are given in Table 1, along with the chemical data of Walenta and Dunn (1979), which agree very well with the present analyses. Also in Table 1 are analyses of K-dominant tourmaline that forms a thin (10 μm) outer rim on a portion of the Royal Ontario Museum sample no. M35899. Unfortunately, there is not sufficient material to properly characterize the K-dominant tourmaline as a new species, but its presence is very germane from a crystal-chemical viewpoint.

Chemical zoning of povondraite and its potassic rim is shown in Figure 1. There is a sharp discontinuity in the ratio K:Na between povondraite and the K-rich tourmaline at the rim; however, chemical trends established within povondraite continue into the rim tourmaline. For the entire system, Fe_{tot} and $\text{K}/(\text{Na} + \text{K})$ increase, whereas Al, Ti, and V decrease with crystallization.

CRYSTAL STRUCTURE REFINEMENT

Initially the crystal structure of povondraite was refined using a crystal fragment supplied by the Royal Ontario Museum (sample no. M35899). The quality of intensity data from this crystal was such that it was evident there was a problem with the empirical formula given by Walenta and Dunn (1979), but a better crystal structure refinement was desirable. Five grains were obtained from

TABLE 1. Electron microprobe analyses of povondraite

	Structure 144478	Structure 35899	K-rich tourm. 35899	Walenta and Dunn
SiO ₂	30.7	31.1	29.6	31.58
TiO ₂	0.0	0.1	0.0	—
Al ₂ O ₃	1.4	4.2	0.8	2.30
V ₂ O ₃	trace	0.1	0.0	—
Fe ₂ O ₃ *	45.0	42.1	45.6	38.37
FeO*	1.7	0.7	0.9	7.25
MgO	6.5	6.9	6.3	5.57
K ₂ O	1.0	0.9	2.2	0.98
Na ₂ O	2.1	2.2	1.1	2.18
B ₂ O ₃ **	9.0	9.1	8.7	8.98
H ₂ O†	2.4	2.5	2.3	3.5
TOTAL	99.8	99.0	97.5	100.71
Number of cations on the basis of O = 31				
Si	5.96	5.92	5.91	6.02
Ti	0.00	0.01	0.00	—
Al	0.32	0.95	0.20	0.52
V	0.01	0.02	0.00	—
Fe ³⁺	6.57	6.04	6.87	5.51
Fe ²⁺	0.27	0.11	0.15	1.16
Mg	1.89	1.95	1.87	1.58
K	0.26	0.21	0.56	0.24
Na	0.80	0.80	0.42	0.81
B	3	3	3	3
H	3.12	3.12	3.12	3.5

* Fe³⁺/Fe²⁺ calculated by stoichiometry.** B₂O₃ from B = 3 atoms in formula.† H₂O from bond valence sum H = 3.12 except for Walenta and Dunn L.O.I.

the Smithsonian Institution (sample no. 144478) and the best of these crystals, as determined by the quality of reflections on precession films, was used to measure a second data set. Intensity data were obtained on a fully automated Nicolet R3m four-circle diffractometer using the method of Grice and Ercit (1986). The data relevant to the structure refinement are given in Table 2. No X-ray powder diffraction data are listed here, as there is no change from that presented by Walenta and Dunn (1979).

The structure refinement of povondraite was essential for the definition of the species. From the chemical data given in Table 1, the number of Fe and Mg atoms are known to be 6.84 and 1.89, respectively. The distribution of these cations in the Y and Z sites determines the species. The atomic coordinates of feruvite (Grice and Robinson, 1989) were used to begin the structure refinement of povondraite. Refinement of positional and anisotropic thermal parameters and the occupancy factors of Fe and Mg in the Y and Z sites gave a residual index $R = 5.06$ and $R_w = 5.07\%$. For the Y site, refinement gave 2.52(7) Fe atoms, and 0.48(7) Mg atoms. All Al was assigned to

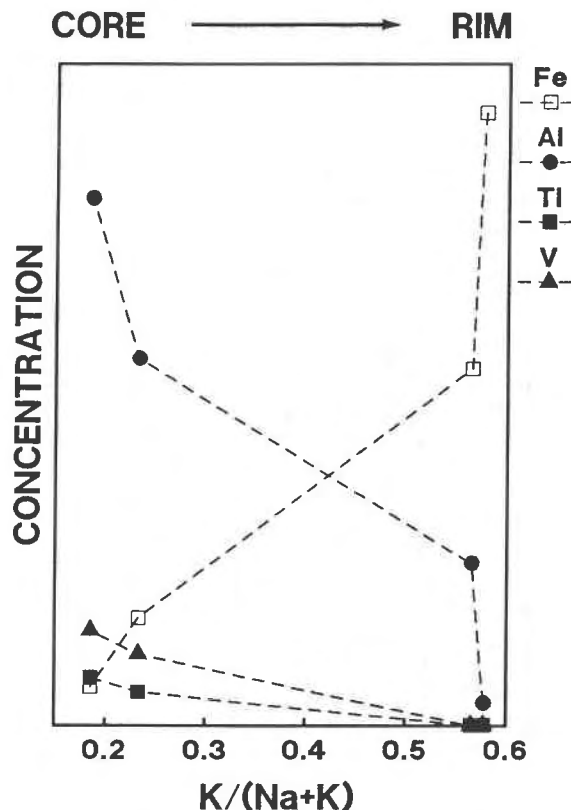


Fig. 1. Chemical zoning in povondraite (core) and K-rich tourmaline (rim), Royal Ontario Museum sample no. M35899. There is a sharp discontinuity in the ratio K:Na (dashed line) between povondraite and the K-rich tourmaline. Scales are relative.

the Z site, and refinement gave occupancy factors corresponding to 3.84(12) Fe atoms and 1.86(12) Mg atoms. These refined values agree within 3σ of the electron microprobe analysis of this crystal.

We have found that the residual index R for a tourmaline crystal structure refinement usually falls between 2 and 3%. The R index in this experiment is controlled primarily by the poorer quality of povondraite crystals, which tend to have a large mosaic spread. This gives rise to larger standard errors in observed structure factors and thus to larger uncertainties in structure parameters. Although the standard deviations of Fe and Mg occupancies in the Y and Z sites is rather large, there is no doubt about the partitioning preference of these elements be-

TABLE 2. Structure refinement data for povondraite

Ideal formula:	NaFe ₃ ⁺ Fe ₃ ²⁺ B ₃ Si ₆ O ₂₈ (O,OH) ₃	$a = 16.186(2) \text{ \AA}$
Space group:	$R3m$	$c = 7.444(1) \text{ \AA}$
Z:	3	$V = 1688.9(3) \text{ \AA}^3$
Radiation/Mono:	Mo/graphite	1214
μ :	47.9 cm ⁻¹	717
Min. transmission:	0.463	Final R :
Max. transmission:	0.552	Final R_w :
$R = \frac{\sum (F_o - F_c)}{\sum F_o }$		5.06%
$R_w = \frac{[\sum w(F_o - F_c)^2]^{1/2}}{[\sum w F_o ^2]^{1/2}}$, $w = \sigma^{-2}(F_o)$		5.07%

TABLE 3. Positional and anisotropic thermal parameters ($\times 10^3 \text{ \AA}^2$) for povondraite

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Na(X)	0	0	0.228(2)	17(3)	17(3)	34(6)	0	0	8(1)	23(3)
Fe(Y)	0.1224(2)	0.0612(1)	0.6429(5)	4(1)	4(1)	12(1)	-1(1)	-1(1)	2.2(6)	6.5(8)
Fe(Z)	0.2987(1)	0.2626(1)	0.6124(5)	4(1)	4(1)	9.1(8)	10(7)	5(6)	2.2(7)	5.8(7)
B	0.1097(7)	0.219(1)	0.456(2)	12(6)	4(7)	7(6)	1(6)	0(3)	2(3)	9(5)
Si	0.1892(2)	0.1876(2)	0	5(1)	4(1)	9(1)	-1(1)	-1(1)	3(1)	6(1)
O1	0	0	0.772(3)	7(5)	8(5)	7(9)	0	0	4(3)	7(4)
O2	0.0610(4)	0.1220(8)	0.490(2)	10(4)	4(4)	13(5)	2(4)	1(2)	2(2)	10(3)
O3	0.2578(8)	0.1289(4)	0.512(1)	12(5)	7(3)	9(5)	-1(2)	-3(4)	6(3)	9(3)
O4	0.0924(4)	0.1848(8)	0.069(2)	8(3)	16(6)	12(4)	-2(4)	-5(9)	8(3)	11(3)
O5	0.1827(8)	0.0913(3)	0.086(1)	10(5)	4(3)	18(5)	0(2)	0(4)	5(2)	10(3)
O6	0.1922(6)	0.1829(5)	0.784(1)	12(4)	7(3)	8(3)	-2(3)	0(3)	6(3)	8(3)
O7	0.2811(5)	0.2814(5)	0.075(1)	8(4)	7(4)	12(3)	0(3)	0(3)	2(3)	10(3)
O8	0.2069(5)	0.2678(6)	0.442(1)	5(3)	10(4)	17(4)	6(3)	4(3)	5(3)	10(3)
H3	0.24(1)	0.120(7)	0.41(3)	20						

tween the two sites. Only one H atom could be located with certainty from a ΔF synthesis. Refining the structure of the other enantiomorph gave an R index of 5.8%, verifying the correct choice of enantiomorph.

Bond-valence sums for each atomic site are $X = 1.03$, $Y = 2.71$, $Z = 2.87$, $B = 2.94$, $Si = 4.10$, $O1 = 1.65$, $O2 = 1.98$, $O3 = 1.17$, $O4 = 2.09$, $O5 = 2.04$, $O6 = 2.01$, $O7 = 2.02$, and $O8 = 2.02$ vu. This confirms that O3 is

an OH molecule. As far as we can determine, there is little if any occupancy of the H site often associated with O1. Final atomic and thermal vibration parameters are given in Table 3. Selected interatomic distances and angles are given in Table 4. The observed and calculated structure factors are deposited as Table 5.¹

DISCUSSION

The most important point in this paper is the illustration of the need for crystal structure analysis of minerals whose species status is dependent on the grouping of elements within the empirical formula according to their ordering within the crystal structure. The data for the description of "ferridravite" presented by Walenta and Dunn (1979) were correct, but the formula was in error because of assumptions made on assignment of cations to various sites. The data presented here are but a small portion of those presented in Grice and Ercit (1993), which clarifies the relationships of Fe and Mg substitution in the Y and Z sites. The proportion of Mg in the Y site decreases linearly with the fraction $Fe/(Fe + Mg)$, where Fe and Mg are numbers of atoms. This simple relationship should help petrologists and mineralogists determine the correct formula and species name as well as help reveal the many errors that presently exist in the literature. With the present crystal-chemical model it may be possible to better interpret Mössbauer spectra. Unfortunately there is insufficient povondraite for such studies at present. Also there are many possibilities for studying the additional complexity of this scheme when significant amounts of Ti, V, Mn, or Cu are included in the crystal structure.

In the tourmaline group there are presently ten species (Table 6), and povondraite is unique among these as the species with the largest unit cell. The large cell volume of povondraite is primarily due to the large average bond length of the Z polyhedron (2.007 Å) and to a lesser ex-

TABLE 4. Selected interatomic distances (Å) and angles (°) for povondraite

Na (X site) polyhedron			
Na-O2	2.60(1) × 3		
O4	2.85(1) × 3		
O5	2.77(1) × 3		
Average	2.74		
Fe1 (Y site) octahedron			
Fe1-O1	1.97(1)	O1-O2	84.5(4) × 2
O2	2.055(8) × 2	O1-O6	99.8(5) × 2
O3	2.13(1)	O2-O6	89.3(4) × 2
O6	2.007(8) × 2	O2-O2	92.3(5)
Average	2.037	O2-O3	97.0(3) × 2
		O3-O6	78.7(3) × 2
		O6-O6	88.8(5)
		Average	90.0
Fe2 (Z site) octahedron			
Fe2-O3	2.061(6)	O3-O6	80.3(4)
O6	2.009(8)	O3-O7	95.2(4)
O7	1.991(8)	O3-O8	87.7(4)
O7'	2.022(7)	O3-O8	97.2(4)
O8	1.99(1)	O6-O7'	93.3(4)
O8'	1.97(1)	O6-O8	90.7(3)
Average	2.007	O6-O8'	93.9(4)
		O7-O7'	91.7(1)
		O7-O8'	96.1(3)
		O7-O8'	79.2(3)
		O7-O8	79.5(3)
		O7'-O8	96.4(3)
		Average	90.1
B triangle			
B-O2	1.39(2)	O2-O8	120.2(8) × 2
O8	1.37(1) × 2	O8-O8'	120(2)
Average	1.38	Average	120.1
Si tetrahedron			
Si-O4	1.628(5)	O4-O5	104.2(6)
O5	1.640(5)	O4-O6	111.4(5)
O6	1.614(8)	O4-O7	109.9(6)
O7	1.603(6)	O5-O6	109.6(5)
Average	1.621	O5-O7	110.5(5)
		O6-O7	111.0(4)
		Average	109.4

¹ A copy of Table 5 may be ordered as Document AM-93-518 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

TABLE 6. Tourmaline group: compositions, cell dimensions, bond lengths

Species	X	Y ₃	Z ₆	a (Å)	c (Å)	V (Å ³)	X-O (Å)	Y-O (Å)	Z-O (Å)	Ref.*
Povondraite	Na	Fe ³⁺	Fe ³⁺	16.186	7.444	1689	2.738	2.037	2.007	1
Buergerite	Na	Fe ³⁺	Al	15.874	7.196	1570	2.706	2.004	1.919	2
Schorl	Na	Fe ²⁺	Al	15.990	7.195	1593	2.690	2.045	1.924	2
Feruvite	Ca	Fe ²⁺	Al	16.012	7.245	1607	2.654	2.055	1.944	3
Uvite	Ca	Mg	Al	15.973	7.231	1594	2.651	2.050	1.928	2
Dravite	Na	Mg	Al	15.941	7.201	1585	2.681	2.019	1.928	2
Chromdravite	Na	Mg	Cr	16.11	7.27	1634	—	—	—	4
Olenite	Na	Al	Al	15.802	7.086	1532	2.677	1.936	1.898	5
Elbaite	Na	Al, Li	Al	15.838	7.103	1543	2.670	2.002	1.905	2
Liddicoatite	Ca	Li	Al	15.875	7.126	1555	2.645	2.038	1.909	6

* References: 1 = present study; 2 = Grice and Ercit, 1993; 3 = Grice and Robinson, 1989; 4 = Rumantseva, 1983; 5 = Gorskaya et al., 1982; 6 = Nuber and Schmetzer, 1981.

tent the X polyhedron (2.738 Å), both of which exceed the average bond lengths for all other tourmaline species. Foit (1989) has shown that there is a very high linear correlation ($r = 0.98$) between cell volume and the weighted mean octahedral bond length. The Z-site octahedron of povondraite is considerably larger than that of other tourmaline because of substitution of Fe³⁺ for Al³⁺. Chromdravite is the only other species of the tourmaline group that does not have Al³⁺ as the principal Z-site cation. With Cr³⁺ in this site the Z-O distance should be quite large. Although the crystal structure of chromdravite has not been refined, that of Cr-rich dravite has (Nuber and Schmetzer, 1979). Nuber and Schmetzer (1979) have assigned Al_{4.06}Cr_{2.48}Fe_{0.24} to the Z site and determined the average Z-O distance as 1.956 Å, which, as predicted, is larger than for the Al³⁺ species. In povondraite the ninefold X site is exceptionally large because of the unique presence of K (to the extent of approximately one quarter of the site occupancy). For all of the other tourmalines listed in Table 6, the large cation K is absent.

The unique geochemistry responsible for the formation of povondraite (an Al-poor and K- and Fe-rich environment) explains its rarity. The possibility of a K end-member tourmaline should encourage investigators to look further for sufficient material to characterize the species.

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