

Ferridravite, a new mineral of the tourmaline group from Bolivia

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Abstract

Ferridravite, a new member of the tourmaline group, occurs at the San Francisco mine, near Villa Tunari (Alto Chapare), Bolivia, as a rare coating on the schistose country rock. The observed forms are a {11 $\bar{2}$ 0}, r {10 $\bar{1}$ 1}, and \bar{o} { $\bar{2}$ 02 $\bar{1}$ }. Ferridravite has no cleavage and an uneven fracture. The measured density of 3.26(3) g/cm³ is in good agreement with the calculated value of 3.33 g/cm³. The color is black; the streak is brown. The luster is resinous, more or less splendent. Ferridravite is uniaxial (-) with refractive indices $\epsilon = 1.743(3)$ and $\omega = 1.800(3)$. Crystallographically, ferridravite is rhombohedral, $R3m$, with unit-cell parameters $a = 16.20(2)$, $c = 7.47(1)A$, $a:c = 1:2.1687$, $Z = 3$. The strongest lines in the X-ray diffraction pattern are (d in A , I , hkl): 6.63, 9, 10 $\bar{1}$ 1; 4.05, 9, 22 $\bar{4}$ 0; 3.05, 9, 41 $\bar{5}$ 0, 12 $\bar{3}$ 2; 2.63, 10, 05 $\bar{5}$ 1. The chemical formula is $(Na_{0.80}K_{0.24})(Mg_{1.58}Fe_{2.15}^{2+})(Fe_{3.49}^{3+}Al_{0.51})Si_6B_3(O,OH)_{30}(OH,F)$ or ideally $NaMg_3Fe_6^{2+}B_3Si_6(O,OH)_{30}(OH,F)$.

Introduction

During a visit to La Paz, Bolivia, in September 1976, the senior author received a small sample of an unidentified black mineral from Dr. W. Wetzenstein of La Paz. The mineral originated from the San Francisco mine, near Villa Tunari in Alto Chapare (Province of Aranibar, Dept. Cochabamba), Bolivia. An examination indicated that this unknown mineral was a member of the tourmaline group but possessed unusual properties. Chemical analysis confirmed that the high refractive indices and distinct X-ray pattern were due to a high ferric iron content.

The name is for the composition and relationship to dravite. The mineral and the name were approved by the Commission on New Minerals and Mineral Names, IMA, prior to publication. Type material is preserved at the Institut für Mineralogie und Kristallchemie at the University of Stuttgart, and at the National Museum of Natural History, Smithsonian Institution (#144478).

Occurrence

Ferridravite occurs in black euhedral crystals which coat the country rock at the San Francisco

mine. The San Francisco mine exploits crocidolite on a small scale. The country rock is a schist composed of quartz, potassium feldspar, alkali amphibole, and muscovite. In addition, schorl tourmaline is present in varying amounts. The schists belong to the Cristalmayu formation, a series of more or less metamorphosed sedimentary rocks (including economically important magnesite) probably of Cambrian age (Franz *et al.*, 1979). The new mineral, ferridravite, may be limited in its occurrence to younger fissures and cavities within the country rock, as is the case with the original sample. The authors were not able to visit the locality, but further investigation is under way with Dr. Wetzenstein, and we hope to obtain further data about the occurrence. Our attempts to obtain additional samples for study were unsuccessful; the samples sent from Bolivia contained only schorl. Hence, ferridravite must be considered a rare mineral, even at the type locality.

Morphology

Ferridravite crystals are intergrown with one another, in part forming subparallel aggregates. The maximum crystal size is several mm. The crystals are

predominantly misshapen and their habit is such that the mineral is not easily recognized as a member of the tourmaline group. Recognition is further complicated by the fact that crystals are not elongated along the c axis as is most tourmaline, but are more equant in habit, similar to some uvites (Dunn *et al.*, 1977a). Nonetheless the morphology of the crystals is simple. The crystals are comprised of the second-order hexagonal prism, a $\{11\bar{2}0\}$ and the trigonal pyramids, r $\{10\bar{1}1\}$ and \bar{o} $\{20\bar{2}1\}$. A somewhat idealized crystal is depicted in Figure 1, in which two faces of the prism, a , and the two pyramids, r and \bar{o} , meet at one coign.

Physical and optical properties

As for most members of the tourmaline group, except buergerite, ferridravite shows no cleavage. The fracture is distinct but uneven. The Mohs hardness is approximately 7. The density, determined by heavy-liquid techniques, is 3.26(3) g/cm³, in satisfactory agreement with the calculated density of 3.33 g/cm³. Optically, ferridravite crystals are black in color and appear opaque; light is transmitted only in thin splinters. The streak is brown, and the luster resinous, more or less splendent. The refractive indices are $\epsilon = 1.743(3)$, $\omega = 1.800(3)$, and ferridravite is uniaxial negative. The mineral is strongly pleochroic with $E =$ light brown and $O =$ dark brown, blackish brown to opaque. The determination of the refractive indices by immersion was somewhat impeded by the fact that even thin fragments become dark brown to opaque in the position of stronger absorption. In addition, the refractive indices are slightly variable within the same crystal fragment, probably as a result of small differences in the Fe:Al ratio. The observed maximum value of ω is about 1.82, and it corresponds to the highest Fe content.

X-ray crystallography

The X-ray powder diffraction data given in Table 1 were used for calculating the unit-cell parameters.

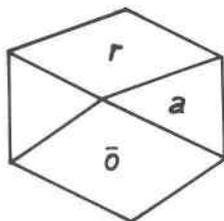


Fig. 1. Idealized sketch of ferridravite crystal showing the prism, a , and the trigonal pyramids, r and \bar{o} .

Table 1. X-ray powder diffraction data for ferridravite

d (obs.)	I/I ₀	d (calc.)	hkl	d (Obs.)	I/I ₀
6.63	9	6.59	10 $\bar{1}$ 1	1.554	4b
5.13	7	5.11	02 $\bar{2}$ 1	1.528	1
4.71	7	4.68	30 $\bar{3}$ 0	1.502	2
4.32	7	4.32	21 $\bar{3}$ 1	1.479	2
4.05	9	4.05	22 $\bar{4}$ 0	1.458	3
3.61	8	3.61	01 $\bar{1}$ 2	1.447	3
3.46	2	3.45	13 $\bar{4}$ 1	1.382	1
3.28	1	3.30	20 $\bar{2}$ 2	1.370	1
3.18	1/2	3.17	40 $\bar{4}$ 1	1.355	1
3.05	9	3.06	41 $\bar{5}$ 0	1.335	2
2.96	1	3.05	12 $\bar{3}$ 2	1.320	2
2.69	1	2.96	32 $\bar{5}$ 1	1.299	1
		2.70	33 $\bar{6}$ 0	1.260	1vd
		2.69	31 $\bar{4}$ 2	1.205	2
2.63	10	2.63	05 $\bar{5}$ 1	1.175	2
2.56	1/2	2.56	04 $\bar{4}$ 2	1.161	1d
2.49	2	2.49	0003	1.152	1d
2.44	3	2.44	24 $\bar{6}$ 1	1.131	1vd
2.39	2	2.39	51 $\bar{6}$ 1	1.105	1d
2.34	1	2.34	60 $\bar{6}$ 0	1.093	1vd
2.24	3	2.24	50 $\bar{5}$ 2	1.052	4vd
2.20	3	2.20	43 $\bar{7}$ 1, 30 $\bar{3}$ 3	1.036	1vd
2.15	1/2	2.16	42 $\bar{6}$ 2	1.018	2vd
2.11	1/2	2.12	22 $\bar{4}$ 3	1.004	1d
2.09	7	2.09	15 $\bar{6}$ 2		
2.06	1/2	2.06	16 $\bar{7}$ 1		
2.02	1/2	2.03	44 $\bar{8}$ 0		
1.961	5	1.962	34 $\bar{7}$ 2		
1.929	2	1.932	41 $\bar{5}$ 3		
1.884	1	1.883	62 $\bar{8}$ 1		
1.802	1/2	1.805	02 $\bar{2}$ 4		
1.770	1/2	1.766	53 $\bar{8}$ 2		
1.702	4	1.705	60 $\bar{6}$ 3		
1.670	3				
1.620	4				

Abbreviations: b = broad, d = diffuse, vd = very diffuse. This pattern obtained with FeK α X-radiation using a camera of 57.3 mm diameter. Intensities visually estimated. Spacings corrected for shrinkage.

These are $a = 16.20(2)$; $c = 7.47(1)\text{Å}$; $a:c = 1:2.1687$; $V = 1697.8\text{Å}^3$; $Z = 3$. The powder data show that the conditions limiting reflections are the same as those of all other members of the tourmaline group, confirming the rhombohedral symmetry and space group $R3m$. Ferridravite is easily identified by its X-ray powder diffraction pattern; the replacement of Al by Fe³⁺ causes a marked increase in the cell dimensions and hence of the d values.

Chemistry

Due to the paucity of material, a wet-chemical analysis was not possible. Ferridravite was chemically analyzed on an ARL-SEM-Q electron microprobe. The standards used were: hornblende for Si, Al, K, and Na; buergerite for Fe; uvite for Mg. The data were corrected with Bence-Albee factors. There was inadequate material for the direct quantitative determination of boron, but spectrographic analysis

indicated the presence of boron in large amounts. H₂O determined by ignition loss is 3.5% ($\pm 0.5\%$). The imprecision in this figure is due to the extremely small amount of material available for analysis.

The empirical formula for ferridravite was calculated on the basis of six silicon atoms, inasmuch as the silicon content of tourmalines is almost always constant at six atoms per formula unit, and there is no known solid solution between Si and Al in tourmalines. The resultant formula, after calculation of Fe³⁺ to compensate for the deficiency of Al, is: (Na_{0.80}K_{0.24}) (Mg_{1.58}Fe_{1.15}²⁺) (Fe_{5.49}Al_{0.51})Si₆B₃(O,OH)₃₀(OH,F). Although boron was not determined quantitatively, this is not a serious shortcoming because the boron content of tourmalines, like the silicon content, varies little; almost all tourmalines have 3 boron atoms per formula unit. Slight deviations from this stoichiometry of silicon and boron are uncommon. Barton (1969) suggested that any "excess" boron over three atoms substitutes for silicon. No chemical inhomogeneity was noted. However, variations in refractive indices do suggest some Al/Fe variation, and no firm statement concerning chemical zoning is possible due to the paucity of material. An interesting characteristic of ferridravite is the moderately high amount of potassium. Very little potassium substitutes for sodium in tourmalines, and this is quite uncommon. However, it may be explained by the fact that in view of the increased size of the Z octahedra as a result of the larger cell dimensions there is also greatly increased room available to the X ions. In addition to those elements reported in Table 2, spectrographic analysis revealed the presence of small amounts of Cu, Pb, and Sn.

Crystal chemistry

Ferridravite, ideally NaMg₃Fe₆³⁺B₃Si₆(O,OH)₃₀(OH,F), is the ferric iron analog of dravite, NaMg₃Al₆B₃Si₆(O,OH)₃₀(OH,F). Ionic substitution is common in the X, Y, and Z sites of most tourmalines, all of which conform to the general formula, XY₃Z₆B₃Si₆(O,OH)₃₀(OH,F). The seven known members of the tourmaline group are listed in Table 3. Ferric iron is known to be essential in only one other tourmaline, buergerite. However, in buergerite there is a full complement of aluminum in the Z site and the ferric iron occupies the Y site.

Ferridravite is unique in that it is essentially the only non-aluminous tourmaline. Because there is little aluminum in this tourmaline, the ferric iron must occupy the Z site, substituting for aluminum.

Table 2. Electron microprobe analysis of ferridravite

	Theory***	Analysis
SiO ₂	31.08 %	31.58 %
Al ₂ O ₃	2.25	2.30
Fe ₂ O ₃	37.74	38.37
FeO	7.80	7.25
MgO	5.94	5.57
K ₂ O	0.97	0.98
Na ₂ O	2.13	2.18
B ₂ O ₃	8.98	8.98*
H ₂ O	3.11	3.5 **
	100.00 %	100.71 %

Results of ARL-SEMQ electron microprobe, 15 kV, sample current 0.15 μ A.

Accuracy of data: 3 % of the amount present.

* theoretical B₂O₃ from formula

** from weight loss on ignition.

*** theoretical composition for the empirical formula.

F, Ca, Mn, Ti and Cr are absent or present only as traces.

Ferric iron exists in many tourmalines, including magnesium tourmalines such as dravite and uvite from near Pierrepoint, New York (Dunn *et al.*, 1977a). A large number of analyses of schorl tourmalines (by PJD) suggested that most schorl contains some Fe³⁺ in substitution for Al, and that most schorl has an excess of 5 atoms of Al per formula unit. Limited substitution of Fe³⁺ for Al in position Z is also shown by Mössbauer studies of dravite-schorl tourmalines (Hermon *et al.*, 1973).

A magnesium tourmaline rich in Fe³⁺ from Madagascar was noted by Frondel *et al.* (1966). This ferric iron, magnesium tourmaline contained in excess of four atoms of aluminum per formula unit and did not qualify for species status. It is a ferric dravite and is a mid-member in a solid solution series between dravite and ferridravite.

Although tourmalines form under a wide range of geochemical conditions, the presence of abundant silicon and aluminum is essential to their formation. Indeed, SiO₂ and Al₂O₃ comprise more than 70

Table 3. Theoretical idealized formulae, unit-cell dimensions, and refractive indices for the members of the tourmaline group

General Formula	X	Y ₃	Z ₆	B ₃	Si ₆	(O,OH) ₃₀	(OH,F)	a ₀	c ₀	n _ε	n _ω
FERRIDRAVITE	Na	Mg	Fe ³⁺ ₆	B ₃	Si ₆	(O,OH) ₃₀	(OH,F)	16.20	7.47	1.743	1.800(-1.820)
DRAVITE	Na	Mg ₃	Al ₆	B ₃	Si ₆	(O,OH) ₃₀	(OH,F)	15.94-15.98	7.19-7.23	1.610-1.632	1.635-1.661
UVITE *	Ca	Mg ₃	Al ₅ Mg ₁	B ₃	Si ₆	(O,OH) ₃₀	(OH,F)	15.98	7.21	1.619-1.620	1.634-1.638
ELBAITE	Na	Al,Li	Al ₆	B ₃	Si ₆	(O,OH) ₃₀	(OH,F)	15.84-15.93	7.10-7.13	1.615-1.620	1.640-1.655
LIDDICOATITE**	Ca	Li,Al	Al ₆	B ₃	Si ₆	(O,OH) ₃₀	(OH,F)	15.87	7.14	1.621	1.637
SCHORL	Na	Fe ²⁺	Al ₆	B ₃	Si ₆	(O,OH) ₃₀	(OH,F)	15.93-16.03	7.12-7.19	1.625-1.650	1.655-1.675
BUERGERITE	Na	Fe ³⁺ ₃	Al ₆	B ₃	Si ₆	(O,OH) ₃₀	(OH,F)	15.87	7.19	1.655	1.735

* Dunn et al. (1977a)

** Dunn et al. (1977b)

weight percent of most tourmalines. The occurrence of ferridravite in association with aluminum-rich phases such as muscovite and potassium feldspars is a problem for which we have no answer at this time. Ferridravite may form only under extraordinary circumstances, hence its rarity.

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