

## FERUVITE, A NEW MEMBER OF THE TOURMALINE GROUP, AND ITS CRYSTAL STRUCTURE

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### ABSTRACT

Feruvite, ideally  $\text{CaFe}_3(\text{Al,Mg})_6(\text{BO}_3)_3\text{Si}_6\text{O}_{18}(\text{OH})_4$ , is a new tourmaline species that is associated with quartz, microcline, chlorapatite and pyrite in a tourmalinized rock at Cuvier Island, New Zealand. Feruvite forms dark brown-black, equant grains up to 2 mm in diameter. The mineral is brittle, H about 7, conchoidal fracture, optically uniaxial negative with  $\omega$  1.687(1),  $\epsilon$  1.669(1). It is trigonal, space group  $R\bar{3}m$ ,  $a$  16.012(2),  $c$  7.245(2) Å and  $Z = 3$ . The strongest X-ray-diffraction lines in the powder pattern [ $d$  in Å ( $hkl$ )] are: 6.43(40)(101), 4.24(60)(211), 4.00(60)(220), 3.50(60)(012), 2.979(80)(122), 2.586(100)(051), 2.051(50)(152), 1.928(40)(342), 1.600(40)(550) and 1.439(40)(740). Results from an electron-microprobe analysis gave:  $\text{SiO}_2$  33.33,  $\text{TiO}_2$  2.19,  $\text{B}_2\text{O}_3$  (calc.) 9.93,  $\text{Al}_2\text{O}_3$  23.38,  $\text{FeO}$  11.26,  $\text{Fe}_2\text{O}_3$  (calc.) 2.56,  $\text{MgO}$  7.80,  $\text{MnO}$  0.07,  $\text{CaO}$  3.30,  $\text{Na}_2\text{O}$  1.16,  $\text{K}_2\text{O}$  0.05,  $\text{H}_2\text{O}$  (calc.) 3.8, sum 98.45 wt.%, corresponding to  $(\text{Ca}_{0.62}\text{Na}_{0.39}\text{K}_{0.01})_{\Sigma 1.02}(\text{Fe}^{2+}_{1.53}\text{Mg}_{1.21}\text{Ti}_{0.29}\text{Mn}_{0.01})_{\Sigma 3.04}(\text{Al}_{4.72}\text{Mg}_{0.82}\text{Fe}_{0.34}\text{Fe}^{3+}_{0.12})_{\Sigma 6.00}(\text{BO}_3)_3(\text{Si}_{5.83}\text{Al}_{0.10})_{\Sigma 5.93}\text{O}_{18}(\text{OH})_4$ .  $D_{\text{calc}}$  3.21,  $D_{\text{meas}}$  3.207(9) g/cm<sup>3</sup>. The structure, which is that of the tourmaline group, refined to an  $R$  of 1.6%.  $Y$  and  $Z$  site occupancies refined to those in the formula above. The rarity of the species is attributed to its unique paragenesis. Feruvite is named as the Fe-analog of uvite (Ca-analog of schorl).

**Keywords:** feruvite, new mineral species, tourmaline group, Cuvier Island, New Zealand, structure refinement, tourmalinization.

### SOMMAIRE

La feruvite, de formule idéale  $\text{CaFe}_3(\text{Al,Mg})_6(\text{BO}_3)_3\text{Si}_6\text{O}_{18}(\text{OH})_4$ , est un pôle nouveau de la famille de la tourmaline. Elle est associée à quartz, microcline, chlorapatite et pyrite dans une roche tourmalinisée prélevée sur l'île de Cuvier, en Nouvelle-Zélande. Les cristaux brun foncé à noir et équidimensionnels atteignent 2 mm en diamètre. C'est un minéral cassant, ayant une dureté de 7 et une fracture conchoïdale. La feruvite est uniaxe négative,  $\omega$  1.687(1),  $\epsilon$  1.669(1); elle est rhomboédrique, groupe spatial  $R\bar{3}m$ ,  $a$  16.012(2),  $c$  7.245(2) Å,  $Z = 3$ . Les dix raies les plus intenses du cliché de poudre [ $d$  en Å ( $hkl$ )] sont: 6.43(40)(101), 4.24(60)(211), 4.00(60)(220), 3.50(60)(012), 2.979(80)(122), 2.586(100)(051), 2.051(50)(152), 1.928(40)(342), 1.600(40)(550) et 1.439(40)(740). Une analyse à la microsonde électronique a donné  $\text{SiO}_2$  33.33,  $\text{TiO}_2$  2.19,  $\text{B}_2\text{O}_3$  (calc.) 9.93,  $\text{Al}_2\text{O}_3$  23.38,  $\text{FeO}$  11.26,  $\text{Fe}_2\text{O}_3$  (calc.) 2.56,  $\text{MgO}$  7.80,  $\text{MnO}$  0.07,  $\text{CaO}$  3.30,  $\text{Na}_2\text{O}$  1.16,  $\text{K}_2\text{O}$  0.05,  $\text{H}_2\text{O}$  (calc.) 3.8, total 98.45% (en poids), ce qui correspond

à  $(\text{Ca}_{0.62}\text{Na}_{0.39}\text{K}_{0.01})_{\Sigma 1.02}(\text{Fe}^{2+}_{1.53}\text{Mg}_{1.21}\text{Ti}_{0.29}\text{Mn}_{0.01})_{\Sigma 3.04}(\text{Al}_{4.72}\text{Mg}_{0.82}\text{Fe}_{0.34}\text{Fe}^{3+}_{0.12})_{\Sigma 6.00}(\text{BO}_3)_3(\text{Si}_{5.83}\text{Al}_{0.10})_{\Sigma 5.93}\text{O}_{18}(\text{OH})_4$ .  $D_{\text{calc}}$  3.21,  $D_{\text{meas}}$  3.207(9) g/cm<sup>3</sup>. La structure, qui est celle des membres de la famille de la tourmaline, a été affinée jusqu'à un résidu  $R$  de 1.6%. La répartition des cations des sites  $Y$  et  $Z$  a aussi été affinée (résultats cités ci-haut). Cette espèce est rare à cause de sa paragenèse unique. Son nom indique qu'elle est l'équivalent ferrique de l'uvite (ou l'équivalent calcique du schorl).

(Traduit par la Rédaction)

**Mots-clés:** feruvite, nouvelle espèce minérale, groupe de la tourmaline, île de Cuvier, Nouvelle-Zélande, affinement de la structure, tourmalinisation.

### INTRODUCTION

In a systematic search for the iron analog of uvite, the authors found several tourmalines whose chemical composition suggests an end member in which Ca and Fe dominate, but subsequent crystal-structure determinations proved that not to be the case, as there are multiple site-occupancies by iron, magnesium and aluminum atoms. Tourmaline compositions may be expressed by the general formula  $\text{XY}_3\text{Z}_6(\text{BO}_3)_3\text{Si}_6\text{O}_{18}(\text{O,OH,F})_4$ , where  $X$  is commonly Na, Ca or K;  $Y$  is Al,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , Li, Mg or  $\text{Mn}^{2+}$ , and  $Z$  is Al, Mg,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$  or  $\text{V}^{3+}$ . In feruvite,  $X$ ,  $Y$  and  $Z$  must be dominated by Ca, Fe and Al, respectively.

Black (1971) reported the occurrence of a Ca-Fe tourmaline from Cuvier Island, New Zealand. Subsequent investigation of this material has shown that it contains the new species feruvite, the iron analog of uvite (calcium analog of schorl). Feruvite seems to be a relatively scarce mineral in spite of the global abundance of iron-bearing uvite (Dunn *et al.* 1977).

Both the new mineral and its name have been approved by the IMA Commission on New Minerals and Mineral Names. The name was chosen because of the mineral's crystal-chemical similarity to uvite. The holotype specimen is deposited in the National Mineral Collection at the National Museum of Natural Sciences, Ottawa (53776).

### OCCURRENCE AND PARAGENESIS

Feruvite occurs in a pegmatitic, tourmalinized rock

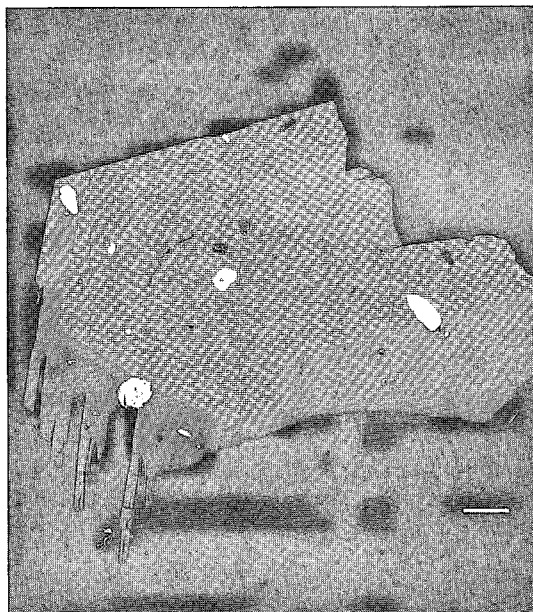


FIG. 1. Backscattered-electron image of a typical zoned feruvite–dravite crystal in quartz. The lighter grey core is feruvite, and the darker rim and overgrowths consist of dravite. The white grains are chlorapatite. Bar scale: 100  $\mu\text{m}$ .

from Cuvier Island, New Zealand. These rocks were described by Black (1971), who attributed their origin to hydrothermal replacement of the aluminous and ferromagnesian host-rock silicates by tourmaline and tourmaline–quartz vein sequences. The compositions of the tourmaline are thought to be at least partly derived from the host rock by such tourmalinization. The actual process probably was complex, as demonstrated by the compositional zoning within individual feruvite–dravite crystals and later overgrowths of schorl–dravite upon them (Fig. 1). Associated species include quartz, microcline, chlorapatite and pyrite.

#### PHYSICAL AND OPTICAL PROPERTIES

Feruvite occurs as dark brown-black, subhedral to anhedral, equant grains that attain 2 mm in diameter. The mineral is aggregated into dark patches that compose approximately 30% of the fine-grained tourmalinized rock. Some individual grains have an acicular, lighter-colored dravite overgrowth on one pole. Feruvite has a grey streak, vitreous to dull luster, and shows no fluorescence. It has a Mohs hardness of  $\sim 7$ , is brittle, and has a conchoidal fracture. The density, measured in methylene iodide, is 3.207(9)  $\text{g}/\text{cm}^3$ , which agrees well with the calcu-

lated density of 3.21  $\text{g}/\text{cm}^3$  based on the observed empirical formula and unit-cell volume.

Optically, feruvite is strongly pleochroic, with *O* light brown and *E* very dark brown. It is uniaxial negative, with  $\omega$  1.687(1) and  $\epsilon$  1.669(1), measured with sodium light (590 nm). No variation in optical properties consistent with the chemical zoning noted in the following section was observed within individual grains. Although variation in the ratio Fe:Mg is significant, it does not affect color except in the polar overgrowths as noted above.

#### CHEMICAL COMPOSITION

Several feruvite–dravite crystals were mounted in epoxy, polished flat, and coated with a vacuum-evaporated layer of carbon for microprobe analysis with a JEOL Superprobe 733. Because of strong compositional zoning, backscattered-electron images coupled with qualitative energy-dispersion analyses were used to locate zones of interest for subsequent wavelength-dispersion analyses, which were done using an operating voltage of 15 kV, a beam current of 25 nA measured on a Faraday cup, and a beam diameter of 10  $\mu\text{m}$  to minimize volatilization. The following standards were used: almandine (Mg, Fe, Si), gehlenite (Ca, Al), sanidine (K), albite (Na), tephroite (Mn) and titanite (Ti). The data were reduced utilizing the Tracor Northern 5600 computer program TASK, which employs a conventional ZAF correction routine. Chlorine and fluorine also were sought, but neither was detected.

Boron also was determined by wavelength-dispersion analysis with operating conditions of 5 kV and 100 nA, using elbaite as a standard. Data for boron were reduced with the Tracor Northern 5600 program  $\phi\rho Z$ . An average of five analyses done on the crystal used for the structure determination gave:  $\text{SiO}_2$  33.33(18),  $\text{TiO}_2$  2.19(3),  $\text{B}_2\text{O}_3$  11.25(60),  $\text{Al}_2\text{O}_3$  23.38(13), total iron expressed as FeO 13.56(13), MgO 7.80(5), MnO 0.07(2), CaO 3.30(3),  $\text{Na}_2\text{O}$  1.16(2),  $\text{K}_2\text{O}$  0.05(1),  $\text{H}_2\text{O}(\text{calc.})$  3.48, sum 99.57. The strongly zoned crystals did not permit meaningful determinations of the ratio of ferrous to ferric iron, but bond-valence calculations based on the crystal-structure data indicate the presence of both ferrous and ferric iron. There is, however, no structural evidence supporting an excess of boron; although the microprobe-determined value is within two standard deviations of the calculated value, it is considered to be too high.

If the above considerations are taken into account, and the proportion of FeO,  $\text{Fe}_2\text{O}_3$ ,  $\text{B}_2\text{O}_3$  and  $\text{H}_2\text{O}$  calculated by stoichiometry assuming 19.0 cations and 31.0 anions, which is consistent with the structure refinement, the analytical results may be rewritten as:  $\text{SiO}_2$  33.33,  $\text{TiO}_2$  2.19,  $\text{B}_2\text{O}_3$  9.93,  $\text{Al}_2\text{O}_3$  23.38,  $\text{Fe}_2\text{O}_3$  2.56, FeO 11.26, MgO 7.80, MnO

0.07, CaO 3.30, Na<sub>2</sub>O 1.16, K<sub>2</sub>O 0.05, H<sub>2</sub>O 3.43, sum 98.45. With the site occupancies for Mg and Fe determined by the structure refinement, the resulting formula is: (Ca<sub>0.62</sub>Na<sub>0.39</sub>K<sub>0.01</sub>)<sub>Σ1.02</sub>(Fe<sup>2+</sup><sub>1.53</sub>Mg<sub>1.21</sub>Ti<sub>0.29</sub>Mn<sub>0.01</sub>)<sub>Σ3.04</sub>(Al<sub>4.72</sub>Mg<sub>0.82</sub>Fe<sup>3+</sup><sub>0.34</sub>Fe<sup>2+</sup><sub>0.12</sub>)<sub>Σ6.00</sub>(BO<sub>3</sub>)<sub>3</sub>(Si<sub>5.83</sub>Al<sub>0.10</sub>)<sub>Σ5.93</sub>O<sub>18</sub>(OH)<sub>4</sub>, or more simply (Ca,Na)(Fe,Mg,Ti)<sub>3</sub>(Al,Mg,Fe)<sub>6</sub>(BO<sub>3</sub>)<sub>3</sub>Si<sub>6</sub>O<sub>18</sub>(OH)<sub>4</sub>. Because Fe<sup>2+</sup> and Fe<sup>3+</sup> contents were not determined directly, it is impossible to verify with certainty how much of each is present in both Y and Z. Nevertheless, the assignment of the 0.34 Fe<sup>3+</sup> cations (calculated by stoichiometry) to the Z site makes sense from a crystal-chemical viewpoint, and is consistent with the bond lengths and octahedral distortions observed. The allotment of 0.10 Al to the Si site is similar to the amounts of Al found by Buerger *et al.* (1962) to substitute for Si in uvite from Dekalb, New York.

X-RAY CRYSTALLOGRAPHY

X-ray precession photographs show feruvite to be trigonal with possible space-group choices *R*3̄*m*, *R*3*m* and *R*32. Results of the crystal-structure refinement, presented below, confirm the noncentrosymmetric space-group found in all tourmalines, *R*3̄*m*. Unit-cell parameters were refined from X-ray powder-diffraction data obtained with a 114.6-mm-diameter Gandolfi camera with FeKα(Mn-filtered) radiation (Table 1). The refined unit-cell parameters are: *a* 16.012(2), *c* 7.245(2) Å, *V* 1606.6(4) Å<sup>3</sup>, and *Z* = 3.

REFINEMENT OF THE CRYSTAL STRUCTURE

Experimental

The grain chosen for the crystal-structure determination was that analyzed by electron microprobe. The grain was ground to a sphere, 0.27 mm in diameter, which not only facilitated the absorption correction but also removed an outer zone of the crystal that is poorer in Fe and Ca. Intensity data were collected on a fully automated Nicolet *R*3̄*m* four-circle diffractometer using the method of Grice & Ercit (1986). The data relevant to the structure refinement are given in Table 2.

Structure refinement

The structure refinement of feruvite was essential for the definition of the species. From the chemical data given above, the number of Fe and Mg atoms is almost equal, 1.99 and 2.03, respectively. The distribution of these cations in the Y and Z sites determines the species. Simply stated, if all the Mg is in Y then the species would be uvite, but with a predominance of Fe in Y it is the new species feruvite.

For the structural refinement of feruvite, the

TABLE 1. FERUVITE: X-RAY-DIFFRACTION DATA

<i>hkl</i>	<i>d</i> calc	<i>d</i> obs	<i>I</i> obs	<i>hkl</i>	<i>d</i> calc	<i>d</i> obs	<i>I</i> obs
110	8.00	8.00	1	342	1.929	1.928	4
101	6.42	6.43	4	701	1.911	1.907	<1
021	5.01	5.02	2	413	1.888	1.886	1
300	4.62	4.63	2	621	1.859	1.857	2
211	4.25	4.24	6	333	1.791	1.791	1
220	4.00	4.00	6	024	1.752	1.752	<1
012	3.50	3.50	6	072	1.738	1.739	<1
131	3.40	3.39	<1	262	1.698	1.698	<1
410	3.026	3.028	<1	603	1.670	1.669	3
122	2.980	2.979	8	271	1.650	1.649	2
321	2.913	2.909	1	550	1.601	1.600	4
312	2.637	2.636	1	461	1.554	1.553	<1
051	2.590	2.586	10	722	1.535	1.537	1
042	2.505	2.503	<1	054	1.516	1.517	3
241	2.464	2.462	<1	244	1.490	1.490	<1
003	2.415	2.416	1	514	1.465	1.465	3
232	2.390	2.388	1	740	1.438	1.439	4
511	2.355	2.353	2	205	1.418		
600	2.311	2.308	<1	434	1.418	1.417	2
502	2.202	2.200	2	633	1.416		
431	2.175	2.172	2	1001	1.362	1.363	2
303	2.141	2.141	2	912	1.349	1.350	<1
422	2.123	2.124	<1	704	1.337	1.336	3
223	2.068	2.068	1	553	1.334		
152	2.052	2.051	5	1010	1.316	1.317	2
161	2.030	2.028	<1	903	1.299	1.299	<1
440	2.001	2.000	<1	505	1.284	1.283	3

Mn-filtered FeKα radiation; *a* 16.012(2), *c* 7.245(2)

TABLE 2. FERUVITE: STRUCTURE-REFINEMENT DATA

Ideal Formula:	CaFe <sub>3</sub> Al <sub>6</sub> (BO <sub>3</sub> ) <sub>3</sub> Si <sub>6</sub> O <sub>18</sub> (OH) <sub>4</sub>	<i>a</i> (Å):	16.000(2)
Space Group:	<i>R</i> 3̄ <i>m</i>	<i>a</i> (Å):	7.248(1)
<i>Z</i> :	3	<i>V</i> (Å <sup>3</sup> ):	1606.8(3)
Radiation/Mono.:	Mo/graphite	No. of Fo:	1161
<i>μ</i> :	23.9 cm <sup>-1</sup>	No. of Fo>2.5σ( <i>I</i> ):	1154
Min. transmission:	0.652	Final <i>R</i> :	1.60%
Max. transmission:	0.676	Final <i>R</i> <sub>w</sub> :	1.63%
<i>R</i> = Σ( Fo  -  Fc ) / Σ Fo			
<i>R</i> <sub>w</sub> = {Σw( Fo  -  Fc ) <sup>2</sup> / Σw Fo  <sup>2</sup> } <sup>1/2</sup> , w = σ <sup>-2</sup> (Fo)			

atomic coordinates of buergerite (Barton 1969) were used. Barton (1969) did not have any H atomic positions in his structure. Refinement of positional, isotropic thermal parameters and the occupancy factors of Fe and Mg in the Y and Z sites gave a residual index *R* = 2.8%. Within the Y site, Ti was assigned (Povondra 1981), Mn was assigned (Nuber & Schmetzer 1984), Fe refined to 1.54(3) atoms, and Mg refined to 1.17(3) atoms. Within the Z site, Al was assigned, Mg refined to 0.80(3) atoms, and Fe refined to 0.48(3) atoms. Two H atoms were located with a Δ*F* synthesis and added to the refinement, with anisotropic thermal parameters for all other atoms. The final residual index *R* was 1.60%; with a weighting scheme incorporating an isotropic, primary-extinction correction, an *R*<sub>w</sub> of 1.63% was obtained. The H3 atomic site agrees within 1σ of the one hydrogen atom found in the neutron-diffraction study of buergerite (Tippe & Hamilton 1971).

Bond-valence sums for O1 and O3 are 1.00 and 1.12 v.u., respectively, which support our proton assignments, yet the O1-H1 bond length of 0.41(6)

$\Delta$  is too short. The O3-H3 bond length of 0.74(3) Å is more reasonable. The final positional parameters and equivalent isotropic temperature-factors are given in Table 3, and the anisotropic temperature-factor coefficients are given in Table 4. Bond lengths and angles are given in Table 5. The observed and calculated structure-factors have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

## DISCUSSION

Dietrich (1985) alluded to the probable existence of the "Ca-analog of schorl" (feruvite) and showed a few compositions on a plot of  $Mg/(Mg + Fe^{2+})$  versus  $Ca/(Ca + Na)$  in  $X$ , that fall within the quadrant of  $Fe > Mg$  and  $Ca > Na$ . Neither the provenance of these analytical data nor the designation of sites for Mg and Fe is given, but the rarity of such a phase is evident. Mittwede (1984) reported a Ca-Fe tourmaline, which he found to be calcian schorl, from a pegmatite dyke containing calcic plagioclase in Cherokee County, South Carolina. Brown & Ayuso (1985) reported on the presence of a Ca-Fe tourmaline from a tourmalinite breccia in St. Lawrence

TABLE 3. FERUVITE: POSITIONAL AND THERMAL PARAMETERS

SITE	x	y	z	$U(eq) \times 10^4 \text{ \AA}^2$
Ca(X)	0	0	0.2222(2)	177(4)
Fe(Y)	0.12299(4)	0.06149(2)	0.63661(9)	95(2)
Al(Z)	0.29832(3)	0.26167(4)	0.61132(10)	65(2)
B	0.11001(11)	0.22003(21)	0.45175(38)	84(8)
S1	0.19151(3)	0.18985(3)	0	60(2)
O1	0	0	0.7812(5)	190(9)
O2	0.0607(1)	0.1214(1)	0.4764(3)	116(6)
O3	0.2660(2)	0.1330(1)	0.5125(3)	141(6)
O4	0.0919(1)	0.1838(1)	0.0710(3)	114(6)
O5	0.1814(1)	0.0907(1)	0.0902(3)	111(6)
O6	0.1953(1)	0.1862(1)	0.7789(2)	98(5)
O7	0.2842(1)	0.2835(1)	0.0789(2)	105(5)
O8	0.2088(1)	0.2695(1)	0.4411(2)	123(5)
H1	0	0	0.725(9)	100(0)
H3	0.258(3)	0.129(1)	0.412(4)	100(0)

X =  $(Ca_{0-0.02}Na_{0-0.01}K_{0-0.01})$   
 Y =  $(Fe_{1-0.03}Mg_{1-0.11}Ti_{0-0.02}Mn_{0-0.01})$   
 Z =  $(Al_{1-0.02}Mg_{0-0.02}Fe_{0-0.06})$

TABLE 4. FERUVITE: ANISOTROPIC TEMPERATURE-FACTORS ( $\times 10^4 \text{ \AA}^2$ )

SITE	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U(eq)$
Ca(X)	167(4)	167(4)	197(6)	0	0	84(2)	177(4)
Fe(Y)	102(2)	73(2)	119(2)	-22(1)	-44(2)	51(1)	95(2)
Al(Z)	63(2)	66(2)	65(2)	8(2)	1(2)	31(2)	65(2)
B	83(8)	95(12)	79(10)	-6(9)	-3(4)	47(6)	84(8)
S1	57(2)	55(2)	67(2)	-5(2)	-3(2)	26(2)	60(2)
O1	201(11)	201(11)	169(7)	0	0	100(5)	190(9)
O2	119(6)	65(8)	147(9)	20(6)	10(3)	32(4)	116(6)
O3	215(10)	166(7)	58(7)	9(4)	19(7)	108(5)	141(6)
O4	88(6)	168(9)	114(8)	-12(7)	-6(3)	84(5)	114(6)
O5	158(9)	83(6)	118(8)	8(3)	15(7)	79(5)	111(6)
O6	114(6)	107(6)	80(5)	-16(4)	-7(5)	61(5)	98(5)
O7	91(6)	76(6)	117(6)	-7(4)	-29(5)	18(5)	105(5)
O8	69(6)	110(6)	184(6)	20(5)	6(5)	41(5)	123(5)

TABLE 5. FERUVITE: SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°)

Na (X-site) polyhedron					
Ca-O2	2.496(2)	x3			
Ca-O4	2.775(2)	x3			
Ca-O5	2.692(2)	x3			
mean	2.654				
Fe (Y-site) octahedron					
Fe-O1	2.002(2)		O1-Fe-O2	86.5(1)	x2
Fe-O2	2.055(1)	x2	O1-Fe-O6	98.9(1)	x2
Fe-O3	2.177(2)		O2-Fe-O6	90.0(1)	x2
Fe-O6	2.021(1)	x2	O2-Fe-O2	90.4(1)	
mean	2.055		O2-Fe-O3	98.6(1)	x2
			O3-Fe-O6	76.1(1)	x2
			O6-Fe-O6	89.2(1)	
			mean	90.0	
Al (Z-site) Octahedron					
Al-O3	1.990(1)		O3-Al-O6	83.1(1)	
Al-O6	1.915(1)		O3-Al-O7b	95.3(1)	
Al-O7b	1.923(1)		O3-Al-O8	91.1(1)	
Al-O7c	1.982(1)		O3-Al-O8	95.4(1)	
Al-O8	1.942(2)		O6-Al-O7c	92.0(1)	
Al-O8	1.913(2)		O6-Al-O8	90.8(1)	
mean	1.944		O6-Al-O8	94.4(1)	
			O7-Al-O7	90.8(1)	
			O7-Al-O8	78.8(1)	
			O7-Al-O8	96.1(1)	
			O7-Al-O8	95.9(1)	
			O7-Al-O8	78.1(1)	
			mean	90.2	
Boron triangle					
B-O2	1.380(3)		O2-B-O8	120.2(1)	x2
B-O8	1.372(2)		O8-B-O8	119.6(2)	
mean	1.374		mean	120.0	
Silicon tetrahedron					
Si-O4	1.632(1)		O4-Si-O5	101.3(1)	
Si-O5	1.649(1)		O4-Si-O6	111.5(1)	
Si-O6	1.607(1)		O4-Si-O7	111.3(1)	
Si-O7	1.598(1)		O5-Si-O6	110.4(1)	
mean	1.622		O5-Si-O7	111.1(1)	
			O5-Si-O7	110.9(1)	
			mean	109.4	

County, New York, but the species was not determined.

Considering the Ca-Fe-rich skarn assemblages and pegmatites of the Grenville Province a likely environment to host such a tourmaline, the authors began a systematic search for the Ca-Fe-Al member of the group in these rocks, but dozens of analyses yielded mostly dravite and uvite in the nepheline syenites and skarn assemblages, and schorl in the pegmatites. The apparent presence of such a member of the group only in the tourmalinized rocks of Cuvier Island, New Zealand, attests to the unique geochemical environment of this locality.

Several authors have proposed various distortion parameters to explain adjustments within the tourmaline structure to compensate for the variety of cation substitutions in the X, Y and Z sites. The fundamental topological unit within tourmaline is the hexagonal ring of  $SiO_4$  tetrahedra. Barton (1969) proposed the ditrigonal distortion index,  $\sigma$ , and Gorskaya *et al.* (1982) proposed the  $\Delta z$  index to numerically describe the distortion of this ring. Schmetzer *et al.* (1979) and Nuber & Schmetzer (1984) tabulated mean cation-oxygen bond lengths for the Y and Z sites. Gorskaya *et al.* (1982) calculated  $\psi$ , the distortion of the Y- and Z-site octahedra. No satisfactory correlation between any of the above parameters

explains the distortion of the tetrahedral or octahedral rings in terms of cation substitutions.

In feruvite, notable distortions in its topology can always be related to the O3 site (an OH species). In the SiO<sub>4</sub> tetrahedron the bond angle O4-Si-O5 is 101.3°, which is considerably smaller than the ideal tetrahedral angle of 109.4°. This angular change occurs in response to elongation of the Si-O5 bond length due to the hydrogen bond with O3 (O3-O5 = 3.28 Å and H3-O5 = 2.56 Å). The effect of this hydrogen bond influences both the Y- and Z-site octahedra by extending one bond length in each, as shown in Table 5.

Although the above discussion of distortions in the feruvite structure is helpful in explaining the structural response to the large Ca and Fe<sup>2+</sup> cation substitutions, it does not answer the question of rarity of the species. In general, it would seem that Ca-dominant tourmalines are much rarer than Na-dominant tourmalines owing to early fractionation of calcium minerals in magmatic processes. Thus Ca-Fe silicates probably crystallize in igneous rocks long before a Ca-Fe tourmaline would form. The most likely geological process that would produce such a unique chemical species is that exemplified on Cuvier Island: tourmalinization of rocks rich in Ca, Fe and Al.

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