The Canadian Mineralogist
Vol. 37, pp. 1431-1438 (1999)

THE OCCURRENCE AND CRYSTAL STRUCTURE OF FOITITE FROM A TUNGSTEN-BEARING VEIN AT COPPER MOUNTAIN, TAOS COUNTY, NEW MEXICO

CARL A. FRANCIS[§]

Harvard Mineralogical Museum, Harvard University, 24 Oxford Street, Cambridge, Massachusetts 02138, U.S.A.

M. DARBY DYAR

Department of Geology and Geography, Mount Holyoke College, South Hadley, Massachusetts 01075, U.S.A.

MICHAEL L. WILLIAMS

Department of Geosciences, University of Massachusetts, Amherst, Massachusetts 01003, U.S.A.

JOHN M. HUGHES

Department of Geology, Miami University, Oxford, Ohio 45056, U.S.A.

ABSTRACT

Foitite, an *X*-site-vacant tourmaline, occurs in both cross-fiber and slip-fiber textures with scheelite and wolframite in a quartz vein cutting metaquartzite of the Proterozoic Ortega Formation at the Tungsten (or Wichita) mine on Copper Mountain, Picuris Range, Taos County, New Mexico. The tourmaline is brown, and its indices of refraction $\varepsilon = 1.634(2)$ and $\omega = 1.666(2)$. It is strongly pleochroic, with *E* brown and *O* colorless. The density is 3.17(2) (meas.) and 3.20 g/cm^3 (calc.). Unit-cell parameters refined from powder X-ray data are *a* 15.973(1), *c* 7.137(1) Å, and *V* 1576.8(2) Å^3. The atomic arrangement of the Copper Mountain foitite was refined to $R = 0.018$ using three-dimensional X-ray data. The structural study confirms the low occupancy of the *X* site, and demonstrates that the atomic arrangement is essentially identical to that of the type material from southern California. Mössbauer spectroscopy shows that the iron is entirely ferrous, which indicates that the foitite crystallized at an oxygen fugacity below that of the quartz – fayalite – iron buffer and, perhaps, as low as that of the iron – wüstite buffer.

Keywords: foitite, tourmaline, chemical composition, crystal structure, Copper Mountain, New Mexico.

SOMMAIRE

La foïtite, tourmaline ayant une lacune dans le site *X*, a été signalée en texture fibreuse transversale et longitudinale avec scheelite et wolframite dans une veine de quartz recoupant une métaquartzite de la Formation Ortega, d'âge protérozoïque, à la mine Tungsten (ou Wichita), sur le flanc de la montagne Copper, chaîne de Picuris, comté de Taos, au Nouveau-Mexique. La tourmaline est brune, avec indices de réfraction $\varepsilon = 1.634(2)$ et $\omega = 1.666(2)$. Elle est fortement pléochroïque, avec *E* brun et *O* incolore. La densité est 3.17(2) (mesurée) et 3.20 g/cm^3 (calculée). Les paramètres réticulaires ont été affinés à partir de données sur poudre: *a* 15.973(1), *c* 7.137(1) Å, et *V* 1576.8(2) Å^3. L'agencement des atomes de la foïtite de la montagne Copper a été affinée jusqu'à un résidu $R = 0.018$ en utilisant des données tridimensionnelles. L'étude structurale confirme le faible taux d'occupation du site *X*, et démontre un agencement des atomes quasiment identique à celui de l'échantillon-type, provenant du sud de la Californie. La spectroscopie de Mössbauer indique que le fer y est entièrement sous forme ferreuse, ce qui concorde avec un milieu de cristallisation de la foïtite à faible fugacité d'oxygène, au dessous du tampon quartz – fayalite – fer, et même peut-être aux conditions du tampon fer – wüstite.

(Traduit par la Rédaction)

Mots-clés: foïtite, tourmaline, composition chimique, structure cristalline, montagne Copper, Nouveau-Mexique.

[§] *E-mail address*: francis@eps.harvard.edu

INTRODUCTION

With our improving ability to analyze minerals for boron and the other light elements, there is an increasing interest in minerals of the tourmaline group, the principal carrier of boron in crystalline rocks. A general formula for tourmaline may be written as $XY_3Z_6(BO_3)_3Si_6O_{18}(OH)_3(OH,F)$. As the *Z* site is almost always occupied by aluminum with only minor substitution, it is traditional to subdivide the tourmaline group according to the occupancy of the *X* site into sodic tourmalines, which are the most abundant, and calcic tourmalines, which are found primarily in marble. Tourmaline-group minerals are then assigned to species according to the dominant *Y* cation, either magnesium or iron (or Li + Al for some tourmalines from granitic pegmatites). Foit & Rosenberg (1977) recognized *X*-site vacancies as an important crystal-chemical mechanism ("alkali-defect") to maintain charge balance in tourmalines. Foit *et al.* (1989) described occurrences of alkali-deficient schorl in hydrothermally altered tuffs, and Fuchs & Maury (1995) demonstrated that the presence of an alkali-deficient tourmaline is a characteristic of such deposits. A consequence of the increased attention to tourmaline composition is the recognition that vacancies (represented by $\square$) are not only common, but may dominate in the *X* site, thus leading to an "alkali-deficient" subgroup of the tourmalines.

The species foitite, ideally $\square(Fe^{2+},Al)_3Al_6(BO_3)_3Si_6O_{18}(OH)_3(OH)$, is the alkali-deficient analogue of schorl, the most common member of the tourmaline group. It was formally described and named by MacDonald *et al.* (1993) from isolated crystals in the mineral collection at Dalhousie University, documented only as being from "southern California". The authors logically presumed that it formed in a granitic pegmatite. A second pegmatitic occurrence of foitite was discovered by Pezzotta *et al.* (1996) as the dark gray fibrous tips of elbaite crystals from San Piero in Campo, Elba, Italy. Further investigation by Aurisicchio & Pezzotta (1997) has shown that foitite is widespread in this famous miarolitic pegmatite field. Lyckberg & Hawthorne (1997) reported foitite from the Alabashka pegmatite field in the Ural Mountains, in Russia, and Selway *et al.* (1997) have identified foitite in several rare-element granitic pegmatites of the lepidolite subtype in the Czech Republic. Yavuz *et al.* (1999) reported a hydrothermal vein occurrence near Sebinkarahisar in northern Turkey, where zoned fibers of tourmaline occur in cavities in quartz veins. Although labeled foitite, their material should be considered alkali-deficient schorl, as their electron-microprobe data show Na + Ca greater than 50% of the *X* site.

A specimen labeled merely "Tourmaline, Copper Mt., N.M., #112547" was encountered and initially analyzed in 1988 during an in-house electron-microprobe survey of the Harvard Mineralogical Museum's uncharacterized tourmalines to identify them at the species level. Its low sodium and high aluminum contents identified it as an unusual tourmaline and a candidate for further study. Thus it was included in a suite of 54 tourmaline samples studied by Dyar *et al.* (1994, 1998a, sample 8). Preliminary notice of this new occurrence of foitite was given by Francis *et al.* (1997). Here we describe its geological occurrence, chemical composition, and crystal structure.

GEOLOGICAL SETTING

The Picuris Range of north-central New Mexico is a wedge-shaped Precambrian-cored uplift that forms part of the southern Sangre de Cristo Mountains. The range is dominated by two lithostratigraphic groups. The Vadito Group, the older of the two, consists of metarhyolite, amphibolite, and immature metasediments (Bauer & Williams 1989, Bauer 1993). The Hondo Group consists of a basal 1-km-thick unit of cross-bedded, metamorphosed quartz arenite (Ortega Formation) overlain by a sequence of pelitic schists and quartzites. Metarhyolites from the Vadito Group have been dated at approximately 1.7 Ga (Bauer & Williams 1989, Wingsted 1997). The structure of the Picuris Range is dominated by a single, large, upright synclinal fold, the Hondo syncline (Holcombe & Callender 1982, Bauer 1993) (Fig.1). Metamorphic assemblages are in the amphibolite facies: kyanite, andalusite, and sillimanite coexist in the Ortega Formation; schists contain muscovite, biotite, garnet, and staurolite.

Traditionally, deformation and metamorphism were interpreted to have occurred during the 1.65 Ga Mazatzal orogeny, but recently, investigators have interpreted much of the deformation and metamorphism to have occurred at *ca.* 1.45 Ga in association with the widespread granite plutonism (Williams 1990, Grambling & Dallmeyer 1993, Wingsted 1997). After 1.45 Ga, the rocks apparently remained within the middle crust for several hundreds of Ma (Williams & Karlstrom 1996). Exhumation occurred during the late Proterozoic or even early Paleozoic. Laramide to recent activity was restricted to brittle fracturing (and reactivation of old structures), hydrothermal activity, and uplift to the present 1–2 km elevations.

Foitite occurs on the western slope of Copper Mountain (Fig. 1), in the southern part of the Picuris Range, in a prospect known as the Tungsten mine or Wichita mine (Schilling 1960). Copper Mountain is underlain almost entirely by quartzite of the Ortega Formation, defining the southern limb of the Hondo Syncline. The Tungsten mine is associated with a steeply dipping quartz vein (or vein system) that strikes N10E and is continuous for several km to the north (Bauer & Helper 1994, P.W. Bauer, pers. commun., 1997). Schilling (1960) described the mineralization as consisting of "fibrous, satiny-brown tourmaline and coarse tabular crystals of wolframite, stained green by malachite and chrysocolla." We observed foitite as both cross-fiber and

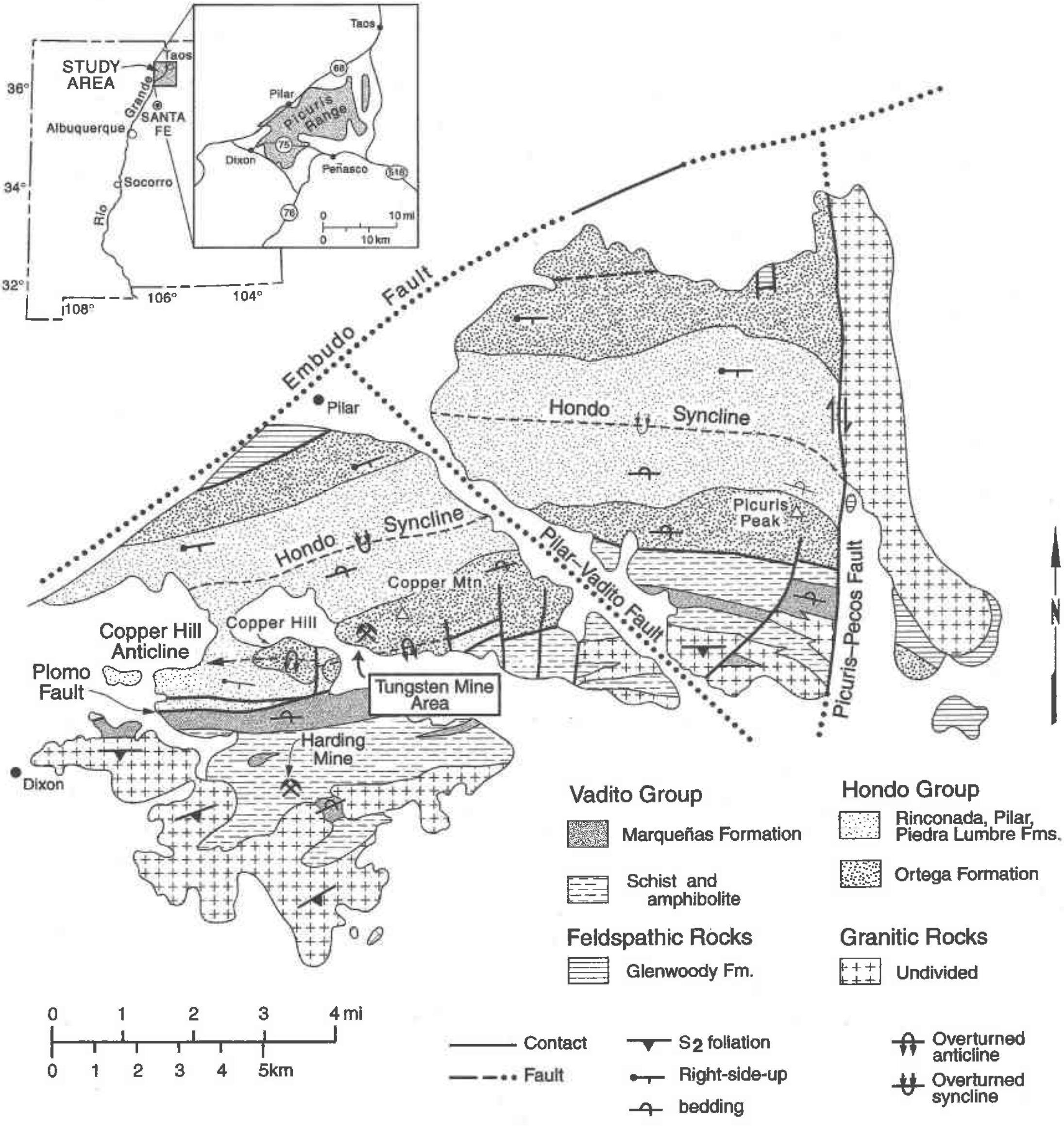

FIG. 1. Generalized geological map of the Picuris Mountains showing major geological units and structural features. Location of the Tungsten mine is shown. Modified from Bauer (1993).

slip-fiber veinlets (1–2 cm wide) in quartz with muscovite, scheelite and wolframite, as well as in minor films and patches of green secondary copper minerals.

Although the distinctive tourmaline–wolframite occurrence has been known for almost 100 years (Lindgren *et al.* 1910), little detailed research has been carried out on the geochemistry or genesis of the deposit. Investigators have tended to associate this mineral occurrence with copper mineralization that occurs predominantly on Copper Hill (Fig. 1) (Schilling 1960, Williams 1982, Williams & Bauer 1995). There, copper minerals are associated with a family of late synmetamorphic, north-striking, vertical quartz veins (several centimeters to one meter thick) that terminate upward against unfractured schists. The copper minerals are interpreted to have been emplaced into the veins and their wall rocks during retrograde metamorphism (*ca.* 1.4 Ga) as the host rocks passed from ductile to brittle behavior (Williams & Bauer 1995). The characteristic orientation of the veins, the presence of kyanite in some vein selvages, and the association with oxidized copper minerals suggest that the foitite and tungsten minerals on Copper Mountain may have a similar late metamorphic age. However, the fact that tungsten minerals are not common in the Copper Hill deposit, and the presence of anomalous brecciation near the Tungsten mine, argue that the tourmaline and tungsten mineralization may be younger, perhaps even Tertiary, in age.

CHEMICAL COMPOSITION

The foitite from Copper Mountain was included in a suite of 54 tourmaline samples characterized by multiple analytical techniques in order to obtain complete chemical compositions (except for oxygen) and to test the effectiveness of new methods for analyzing for light elements (Dyar *et al.* 1994, 1998a). Preference was given to use of microbeam methods where possible, in order to avoid the impurity component in bulk samples. The major-element composition was determined by wavelength-dispersion electron-microprobe analysis. Table 1, column 2 shows the average result of 20 point analyses done as part of a round-robin, interlaboratory comparison study (Dyar *et al.* 1998b). The participating laboratories were the University of Houston, Rice University, Rutgers University, and United States Geological Survey at Reston. Operating conditions typically were: 15 kV accelerating voltage, 20 nA beam current, and 30 s count times, with focused beams. Natural and synthetic mineral standards were used, and ZAF matrix corrections were applied. Analytical errors on all analytical results are estimated to be ±1–2% relative for major elements, ±5–10% relative for minor elements. Chlorine and Cr were also sought, but not observed. Mössbauer analysis, as described in Dyar *et al.* (1998a, sample 8), showed no ferric iron (*i.e.*, <1% of the iron present is ferric), and all of the iron is assigned to the *Y* octahedral site. Analyses for B and Li were made at the University of New Mexico/Sandia National Laboratory SIMS facility using a Cameca IMS 4f ion microprobe, and the same grain mount used for electron-microprobe study. The sample was analyzed twice, and the results averaged to obtain the values reported in Table 1. The concentration of hydrogen was determined by M.D.D. at Southern Methodist University using a uranium extraction method (Dyar *et al.* 1998a) on a sample purified by heavy-liquid methods.

TABLE 1. COMPOSITIONS OF FOITITE

Oxide	1	2	σ	3	4	5	6	7	8
SiO_2 wt.%	36.00	35.41	(0.41)	34.42	35.63	33.97	35.90	36.09	35.51
TiO_2		0.35	(0.18)	0.14	0.03	n.a.	n.a.	0.09	n.a.
B_2O_3	10.43	9.87	(0.34)	*10.30	9.90	*10.36	*10.37	*10.42	*10.20
Al_2O_3	35.63	35.12	(0.45)	35.02	35.77	31.22	34.90	34.91	33.45
Fe_2O_3		n.d.		n.a.	1.85	*5.17	n.a.	n.a.	n.a.
FeO	14.34	12.29	(0.40)	12.36	9.41	*9.89	11.45	10.93	14.47
MnO		0.09	(0.20)	0.03	0.01	0.56	1.71	1.36	0.11
MgO		1.29	(0.21)	1.29	2.16	0.67	0.21	0.33	0.42
CaO		0.01	(0.01)	0.01	0.01	0.00	0.03	0.03	0.00
Na_2O		1.00	(0.16)	1.68	0.95	1.44	0.75	1.11	0.84
K_2O		0.01	(0.01)	0.02	0.02	n.a.	n.a.	n.a.	n.a.
Li_2O		0.01	(0.02)	n.a.	0.00	0.13	*0.31	*0.49	n.a.
H_2O	3.60	3.13	(0.02)	*3.42	3.17	*3.15	*3.56	*3.60	*3.52
F		0.20	(0.04)	0.27	0.08	n.a.	n.a.	n.a.	0.00
-O≡F		–0.08		–0.11	–0.03				–0.00
Total	100.00	98.70		95.43	98.96	97.80	99.19	99.36	98.52

Samples: 1. $\square(Fe^{2+}{}_2Al)Al_6(BO_3)_3Si_6O_{18}(OH)_4$, 2. Copper Mountain, New Mexico #112547, 3. Jack Creek near Basin, Montana (Foit 1989), 4. Jack Creek (Dyar *et al.* 1998a), 5. Cross Lake, Manitoba (Grice & Ercit 1993) (total includes 1.24% ZnO), 6. Southern California (MacDonald *et al.* 1993), 7. San Piero in Campo, Elba (Pezzotta *et al.* 1996). 8. Kazionnitsa pegmatite, Urals (Lyckberg & Hawthorne 1997). * Calculated values; n.a.: not analyzed, n.d.: not detected

Table 1 compares the ideal composition of foitite with the results reported here (column 2) and previously published compositions. The composition of Copper Mountain foitite is very similar to that of the Jack Creek, Montana alkali-deficient schorl (column 3) except for the lower sodium. Another Jack Creek sample supplied by F.F. Foit, Jr. (column 4) was analyzed by the methods employed in this study and is, in fact, foitite with only 0.31 atoms of sodium in the *X* site. The Cross Lake, Manitoba sample, distinctive for its Zn content, is from an unstated paragenesis. It was originally labeled schorl, but with 0.49 Na atoms, it is marginally to be considered foitite. Two samples from granitic pegmatites have distinctly higher Mn, and all three have lower Mg concentrations than the Copper Mountain and Jack Creek samples.

Tourmalines approach the amphiboles in chemical complexity. Calculating a proper formula for a tourmaline is not simple owing to cation disorder as well as to incomplete analyses (*e.g.*, Grice & Ercit 1993). Calculating the formula using only the electron-microprobe data yields:

$$(\square_{0.68}Na_{0.32})(Fe^{2+}{}_{1.71}Al_{0.80}Mg_{0.32}Ti_{0.04}Mn_{0.01})_{\Sigma 2.88}\ Al_6B_3O_9(Si_{5.90}\ Al_{0.10})O_{18}(OH)_3(OH_{1.89}F_{0.11})$$

which is satisfactory in terms of charge balance. However, our study (Dyar *et al.* 1994, 1998a) was predicated on measuring all of the constituents except oxygen to avoid and thereby test the assumptions inherent in the microprobe-based compositions . For example, boron and OH are typically calculated to be stoichiometric. Measurements of boron concentrations made with SIMS are characterized by large errors. Including the observed boron and OH contents yields the formula: $(\square_{0.67}Na_{0.33})(Fe^{2+}{}_{1.74}Al_{1.01}Mg_{0.33}Ti_{0.05}Mn_{0.01})_{\Sigma 3.14}Al_6B_{2.89}O_9Si_{6.00}O_{18}(OH)_3(OH_{0.54}F_{0.11})$. Dyar *et al.*

(1998a) discussed the calculation of tourmaline formulae.

PHYSICAL PROPERTIES

Foitite from Copper Mountain is brown. It is uniaxial negative, with indices of refraction $\varepsilon = 1.634(2)$ and $\omega = 1.666(2)$. It is strongly pleochroic, with *E* brown and *O* colorless. The specific gravity of several fragments was measured in toluene on a Berman balance. The initial trials on cross-fiber material (#112547) ranged from 2.85 to 2.93 g/cm^3, which is much lower than the calculated density of 3.20 g/cm^3. Inspection with an optical microscope showed that the foitite fibers are intimately intergrown with quartz. Subsequently, a more compact slip-fiber specimen (#134242) was collected that yielded a mean of 3.17(2) g/cm^3, in agreement with the calculated value. Gladstone–Dale calculations showed superior compatibility between the physical and chemical measurements.

X-RAY CRYSTALLOGRAPHY

X-ray powder data collected on a Scintag diffractometer ($\lambda = 1.5406$ Å) are a very good match with the data of MacDonald *et al.* (1993) and showed that quartz is present as an impurity. A refinement of the unit cell based on 24 lines in the range 12–70°2θ using the program LCLSQ8 by C.W. Burnham yielded *a* 15.973(1) Å, *c* 7.137(1) Å, and *V* 1576.8(2) Å^3.

CRYSTAL STRUCTURE: EXPERIMENTAL

A crystal of the Copper Mountain foitite (# 112547) was mounted on an Enraf–Nonius CAD4 single-crystal diffractometer; unit-cell parameters were refined without symmetry constraints using diffraction angles from 25 centered reflections (centering four positions for each reflection: $\pm\theta$, $\pm\chi$). X-ray intensity data were collected on the same instrument utilizing graphite-monochromatized Mo$K\alpha$ radiation. The unit cell and crystal data are given in Table 2, with details of data collection and structure refinement.

TABLE 2. CRYSTAL DATA AND CRYSTAL-STRUCTURE RESULTS FOR FOITITE FROM COPPER MOUNTAIN

Crystal size: 0.160 × 0.160 × 0.200 mm		Unit-cell parameters (*R*3*m*)	
		a 15.9633(9) Å	
Data-collection parameters:		c 7.135(1) Å	
$\theta = 0 - 30°$; $+h, \pm k, \pm l$			
≤ 60 seconds, θ–2θ scans			
Results of refinement:			
$R_{merge} = 0.011$;	$R = 0.018$;	$R_w = 0.025$;	$R_{all\ reflections} = 0.020$
GOOF = 0.988;	1020 observations ($I > 4\sigma_I$), 102 variable parameters		
Δρ (max, min), e$^-$/Å^3:	0.43, –0.34;		Refinement on F

The crystallographic package *SDP for Windows* (Frenz 1997) was used for all crystal-structure calculations. Intensity data were reduced to structure factors and corrected for Lorentz and polarization effects. Absorption was corrected using 360° Ψ-scan data for six reflections; after solution, the absorption-surface method as implemented in program DIFABS (Walker & Stuart 1983) was employed. Symmetry-equivalent reflections were averaged; unit weights, $I > 5\sigma_I$ data, and neutral-atoms scattering factors with terms for anomalous dispersion were used throughout structure calculations. The tourmaline starting model was employed, and the atomic arrangement refined routinely. H3, the hydrogen atom associated with the O3 atom, was found to be the highest peak in the difference map, and was subsequently refined using an isotropic temperature-factor. Occupancies of the *X*, *Y*, and *Z* sites were refined by releasing multiplicity factors of Na, Fe, and Al, respectively. The final site-occupancies for the three sites were optimized using the techniques of Foley *et al.* (1998), which, when combined with the chemical data, yield: $(\square_{0.582}Na_{0.414}Ca_{0.002}K_{0.002})$ $(Fe^{2+}{}_{1.64}Al_{1.22}Mg_{0.12}Ti_{0.02})_{\Sigma 3.00}$ $(Al_{5.76}Fe^{2+}{}_{0.06}Mg_{0.18})_{\Sigma 6.00}$ $B_{2.89}O_9Si_{6.00}O_{18}(OH)_3(OH_{0.54}F_{0.11})$.

Table 3 lists refined positional parameters and isotropic thermal parameters, and Table 4 presents selected bond-lengths for atoms in foitite. Table 5 contains anisotropic thermal parameters for the Copper Mountain foitite, and Table 6 contains observed and calculated structure-factors for the phase. Copies of Tables 5 and 6 may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

CRYSTAL STRUCTURE: DESCRIPTION

Foitite was described by MacDonald *et al.* (1993), who refined the crystal structure of the type material from southern California. Their structure analysis confirmed the low occupancy of the *X* site and the dominantly divalent state of the Fe at the *Y* site. The authors noted considerable positional disorder of the occupants of the O1 and O2 sites. They attributed that disorder to variations in bond-valence distribution, with □–Na disorder at the *X* site and Fe^{2+}–Al disorder at the *Y* site.

The atomic arrangement of Copper Mountain foitite is similar to that in the type material from southern California, and the conclusions drawn by MacDonald *et al.* (1993) need not be elaborated. In addition to the atomic parameters of the Copper Mountain material, Table 2 also gives the positional parameters for the foitite of MacDonald *et al.* (1993), cast into orientation of the current crystal (with *z* value of the Si atom in each crystal set equal). The atomic arrangements of the two phases are remarkably similar.

The conclusions of the previous authors for type foitite are valid for the Copper Mountain material. The occupancy of the *X* site, although slightly higher in the

TABLE 3. ATOMIC PARAMETERS FOR COPPER MOUNTAIN FOITITE AND, ON THE SECOND ROW, THOSE OF FOITITE FROM SOUTHERN CALIFORNIA§

Atom	*x*	*y*	*z*	B(Å^2)
Na	0	0	1/4	2.25(8)
	0	0	0.2556	
Fe(*Y*)	0.27106(2)	2*x*	0.31604(8)	0.667(9)
	0.27110	2*x*	0.3146	
Al(*Z*)	0.29835(3)	0.26163(3)	0.63370(9)	0.524(8)
	0.29827	0.26151	0.6341	
Si	0.19193(3)	0.18989(3)	0.02340(8)	0.486(8)
	0.19193	0.18988	0.0234	
B	0.1103(1)	2*x*	0.4778(4)	0.78(5)
	0.11019	2*x*	0.4787	
H3	0.272(4)	2*x*	0.408(6)	1.42(107)*
	N.D.	N.D.	N.D.	
O1	0	0	0.8037(6)	2.57(6)
	0	0	0.8033	
O2	0.06205(7)	2*x*	0.5116(3)	1.28(4)
	0.06224	2*x*	0.5111	
O3	0.2676(2)	½*x*	0.5318(3)	1.03(4)
	0.26854	½*x*	0.5315	
O4	0.09349(7)	2*x*	0.0906(3)	0.88(4)
	0.09369	2*x*	0.0906	
O5	0.1883(2)	½*x*	0.1143(3)	0.84(4)
	0.18904	½*x*	0.1143	
O6	0.19808(8)	0.18743(9)	0.7984(2)	0.78(2)
	0.19831	0.18786	0.7987	
O7	0.28509(9)	0.28589(8)	0.1023(2)	0.72(2)
	0.28512	0.28601	0.1030	
O8	0.21005(8)	0.27082(8)	0.4635(2)	0.81(2)
	0.21049	0.27138	0.4645	

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) * [a^2*\beta(1,1) + b^2*\beta(2,2) + c^2*\beta(3,3) + ab(\cos\gamma)*\beta(1,2) + ac(\cos\beta)*\beta(1,3) + bc(\cos\alpha)*\beta(2,3)]$. N.D.: not determined. § MacDonald *et al.* (1993).

TABLE 4. SELECTED INTERATOMIC DISTANCES IN FOITITE FROM COPPER MOUNTAIN

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Na(*X*) –	O2 (×3)	2.535(2) Å	Fe(*Y*) –	O1	2.044(2) Å
	O4 (×3)	2.8240(8)		O2 (×2)	1.980(1)
	O5 (×3)	2.777(2)		O3	2.148(2)
Mean		2.712		O6 (×2)	2.038(1)
			Mean		2.038
Al(*Z*) –	O3	1.983(1)	Si –	O4	1.621(1)
	O6	1.857(1)		O5	1.634(1)
	O7	1.876(2)		O6	1.610(2)
	O7	1.957(1)		O7	1.612(1)
	O8	1.921(2)	Mean		1.619
	O8	1.881(1)			
Mean		1.913	B –	O2	1.3567(7)
				O8 (×2)	1.382(2)
			Mean		1.374

optimization of the structure than the chemical analysis, clearly demonstrates that the phase has vacancies predominating at the *X* site. Bond lengths of the *Y* site indicate that, in accord with the Mössbauer analyses, the Fe in foitite is divalent. Also in accord with the MacDonald *et al.* (1993) foitite, considerable positional disorder is suggested by the thermal parameters of the O1 and O2 atoms. The isotropic *B* values for O1 and O2 are higher than those for all other atoms, and reflect the different cation occupants in the *X* and *Y* sites, respectively, to which they bond. The *X* site is occupied by Na and □, and the local O1 atom responds to the particular occupant at that site; the refined position and large displacement-parameter represent an average of the O1 positions over the entire crystal. Similarly, the O2 atom bonds to *Y* sites, with (predominantly) Fe^{2+} and Al^{3+} as occupants; the widely disparate bond-lengths from O2 to those occupants yield a large displacement-parameter for O2, modeling the electron density surrounding the average of the O2 positions bonding to Fe^{2+} and Al^{3+}.

DISCUSSION

The physical and chemical properties of Copper Mountain foitite are similar to those of the type material. However, its brown color is unusual. Velickov & Abs-Wurmbach (1997) synthesized the end-member (pure Fe) foitite at varying fugacities of oxygen. Crystals synthesized with the iron–wüstite buffer are colorless. Dichroism (colorless parallel to *c*, blue-green perpendicular to *c*) increases with increasing $f(O_2)$. Increasing Fe^{3+} was observed in their samples by Mössbauer spectroscopy, and the color was attributed to Fe^{2+}– Fe^{3+} spin-pairing in edge-shared octahedra. In contrast, Copper Mountain foitite lacks Fe^{3+}. Its brown color is attributed to intervalence charge-transfer between Fe^{2+} and Ti^{4+} (Rossman 1997).

The complete absence of ferric iron in Copper Mountain foitite has geological significance. Dyar *et al.* (1998a) concluded that Fe^{3+}/Fe^{2+} is controlled by the prevailing oxidation state of the system rather than by crystal-chemical substitutions. Fuchs *et al.* (1998) synthesized mixed-valence tourmalines under a variety of oxidation conditions and concluded that Fe^{3+} in tourmaline is a potential geothermometer and $f(O_2)$ indicator. The data of Fuchs *et al.* (1998) and Velickov & Abs-Wurmbach (1997) indicate that the Copper Mountain foitite crystallized at an oxygen fugacity below that of the quartz – fayalite – iron buffer and, perhaps, as low as that of the iron–wüstite buffer.

SUMMARY

Fibrous brown tourmaline is an abundant gangue mineral in the tungsten-bearing quartz vein that cuts metaquartzite of the Proterozoic Ortega Formation at the Tungsten mine on Copper Mountain in the Picuris Range, Taos County, New Mexico. Analysis shows it to be the species foitite, the recently recognized alkali-deficient analogue of schorl, and the absence of ferric

iron indicates that it crystallized at very low $f(O_2)$. The structural study confirms the low occupancy of the *X* site, and demonstrates that the atomic arrangement of Copper Mountain foitite is essentially identical to that of type foitite from southern California. This well-documented occurrence is of interest as an example of foitite from a hydrothermal vein. Foitite will probably prove to be a common member of the tourmaline group, occurring in low-alkali, iron-rich, boron-bearing hydrothermal systems as well as in granitic pegmatites and piles of hydrothermally altered volcanic rocks.

ACKNOWLEDGEMENTS

We thank R.W. Grant, who collected the initial sample in 1959, and R.S. DeMark and J. Klein, who collected additional samples for our use. We thank David E. Lange for the original electron-microprobe analysis and also Anne McGuire, Virginia Sisson, Jeremy Delaney, and James McGee for the use of their electron-microprobe results. The ion-microprobe data presented here were measured at the SIMS facility of the University of New Mexico/Sandia National Laboratories, a national multi-user facility supported in part by NSF EAR 95–06611. We thank Michael Wiedenbeck and Grant Fowler for doing the analyses. M.D.D. acknowledges support from NSF grants EAR–9527020 and EAR–9909587. J.M.H. acknowledges NSF grants EAR–9804768 and EAR–967222. We thank D. E. Lange, Y. Fuchs, an anonymous reviewer, as well as R.F. Martin, for reviews that improved the manuscript.

REFERENCES

AURISICCHIO, C. & PEZZOTTA, F. (1997): Tourmaline-group minerals of the LCT miarolitic pegmatites of the Elba Island, (Italy): chemical composition and genetic and paragenetic inferences. *In* Tourmaline 1997, Int. Symp. Tourmaline, Abstr., 1.

BAUER, P.W. (1993): Proterozoic tectonic evolution of the Picuris Mountains, northern New Mexico. *J. Geol.* **101**, 483-500.

________ & HELPER, M. A. (1994): Geology of Trampas quadrangle, Picuris Mountains, Taos and Rio Arriba counties, New Mexico. *New Mexico Bur. Mines Mineral Resources, Geol. Map* **71**.

________ & WILLIAMS, M. L. (1989): Stratigraphic nomenclature of Proterozoic rocks, northern New Mexico – revisions, redefinitions, and formalization. *New Mexico Geol.* **11**, 45-52.

DYAR, M.D., FRANCIS, C.A., WISE, M.A., GUIDOTTI, C.V., MCGUIRE, A.V. & ROBERTSON, J.D. (1994): Complete chemical characterization of tourmaline. *Trans. Am. Geophys. Union* **75**, 187 (abstr.).

________, GUIDOTTI, C.V., GREW, E.S., YATES, M., DELANEY, J.S., MCGEE, J.J., MCGUIRE, A.V., PAUL, R.L., ROBERTSON, J.D., CROSS, L., SISSON, V.M., WIEDENBECK, M.W. & FOWLER, G. (1998b): Interlaboratory comparison of tourmaline analyses: major elements including B, Li, and Fe. *Int. Mineral. Assoc., 17th Gen. Meeting, Programme Abstr.*, A101.

________, TAYLOR, M.E., LUTZ, T.M., FRANCIS, C.A., GUIDOTTI, C.V. & WISE, M.A. (1998a): Inclusive chemical characterization of tourmaline: Mössbauer study of Fe valence and site occupancy. *Am. Mineral.* **83**, 848-864.

FOIT, F.F., JR. (1989): Crystal chemistry of alkali-deficient schorl and tourmaline structural relationships. *Am. Mineral.* **74**, 422-431.

________, FUCHS, Y. & MYERS, P.E. (1989): Chemistry of alkali-deficient schorls from two tourmaline–dumortierite deposits. *Am. Mineral.* **74**, 1317-1324.

________ & ROSENBERG, P.E. (1977): Coupled substitution in the tourmaline group. *Contrib. Mineral. Petrol.* **62**, 109-127.

FOLEY, J.A., HUGHES, J. & SCHAEFER, R.L. (1998): Determination of atomic occupancy in multiply- occupied cation and anion sites. *Int. Mineral. Assoc., 17th Gen. Meeting, Programme Abstr.*, A58.

FRANCIS, C.A., DYAR, M.D. & DEMARK, R.S. (1997): A fourth world occurrence of foitite at Copper Mountain, Taos County, New Mexico. *In* 18th New Mexico Mineral. Symp., Abstr., 15.

FRENZ, B.A. (1977): *SDP for Windows Reference Manual.* B.A. Frenz & Associates, Inc., College Station, Texas.

FUCHS, Y., LAGACHE, M. & LINARES, J. (1998): Fe-tourmaline synthesis under different *T* and fO_2 conditions. *Am. Mineral.* **83**, 525-534.

________ & MAURY, R. (1995): Borosilicate alteration associated with U–Mo–Zn and Ag–Au–Zn deposits in volcanic rocks. *Mineral. Deposita* **30**, 449-459.

GRAMBLING, J.A. & DALLMEYER, R.D. (1993): Tectonic evolution of Proterozoic rocks in the Cimarron Mountains, northern New Mexico, U.S.A. *J. Metamorphic Geol.* **11**, 739-755.

GRICE, J.D. & ERCIT, T.S. (1993): Ordering of Fe and Mg in the tourmaline crystal structure: the correct formula. *Neues Jahrb. Mineral., Abh.* **165**, 245-266.

HOLCOMBE, R.J. & CALLENDER, J.F. (1982): Structural analysis and stratigraphic problems of Precambrian rocks of the Picuris Range, New Mexico. *Geol. Soc. Am., Bull.* **93**, 138-149.

LINDGREN, W., GRATON, L.C. & GORDON, C.H. (1910): The ore deposits of New Mexico. *U.S. Geol. Surv., Prof. Pap.* **68**.

LYCKBERG, P. & HAWTHORNE, F.C. (1997): Foitite from the Kazionnitsa pegmatite, Alabashka pegmatite field, Ural Mountains, Russia. *In* Tourmaline 1997, Int. Symp. Tourmaline, Abstr., 52-53.

MACDONALD, D.J., HAWTHORNE, F.C. & GRICE, J.D. (1993): Foitite, $\square[Fe^{2+}_2(Al,Fe)]\ Al_6Si_6O_{18}(BO_3)_3(OH)_4$, a new alkali-deficient tourmaline: description and crystal structure. *Am. Mineral.* **78**, 1299-1303.

PEZZOTTA, F., HAWTHORNE, F.C., COOPER, M.A. & TEERTSTRA, D.K. (1996): Fibrous foitite from San Piero in Campo, Elba, Italy. *Can. Mineral.* **34**, 741-744.

ROSSMAN, G.R. (1997): Color in tourmaline. *In* Tourmaline 1997, Int. Symp. on Tourmaline, Abstr., 1.

SCHILLING, J. (1960): Mineral resources of Taos County, NM. *New Mexico Bur. Mines Mineral Resources, Bull.* **71**.

SELWAY, J.B., NOVÁK, M., ČERNÝ, P. & HAWTHORNE, F.C. (1997): Tourmaline from lepidolite-subtype pegmatites. *In* Tourmaline 1997, Int. Symp. Tourmaline, Abstr., 91-92.

VELICKOV, B. & ABS-WURMBACH, I. (1997): Synthesis and spectroscopic studies (VIS, MS) of alkali free Fe-tourmalines (foitites). *In* Tourmaline 1997, Int. Symp. Tourmaline, Abstr., 109-110.

WALKER, N. & STUART, D. (1983) An empirical method for correcting diffractometer data for absorption effects. *Acta Crystallogr.* **A39**, 158-166.

WILLIAMS, M.L. (1982): *Geology of the Copper Occurrence at Copper Hill, Picuris Mountains, New Mexico.* M.S. thesis, Univ. of Arizona, Tucson, Arizona.

________ (1990): Proterozoic geology of northern New Mexico: recent advances and ongoing questions. *In* Geology of the Southern Rocky Mountains (P.W. Bauer & C.K. Mawer, eds.). *New Mexico Geol. Soc. Guidebook* **41**, 151-159.

________ & BAUER, P.W. (1995): The Copper Hill Cu–Ag–Sb deposit, Picuris Range, New Mexico: retrograde mineralization in a brittle–ductile trap. *Econ. Geol.* **90**, 1994-2005.

________ & KARLSTROM, K.E. (1996): Looping P–T paths, high-T, low-P middle crustal metamorphism: Proterozoic evolution of the southwestern United States. *Geology* **24**, 1119-1122.

WINGSTED, M.B. (1997): *Microstructural History of the Southern Picuris Range, North-Central New Mexico: Implications for the Nature and Timing of Tectonism in the Southwestern United States.* M.S. thesis, Univ. of Massachusetts, Amherst, Massachusetts.

YAVUZ, F., ÇELIK, M. & KARAKAYA, N. (1999): Fibrous foitite from Şebinkarahisar, Giresun Pb–Zn–Cu–(U) mineralized area, northern Turkey. *Can. Mineral.* **37**, 155-161.

Received July 14, 1999, revised manuscript November 21, 1999.