The Canadian Mineralogist
Vol. 42, pp. 1057-1063 (2004)

Fe-RICH OLENITE WITH TETRAHEDRALLY COORDINATED Fe^{3+} FROM EIBENSTEIN, AUSTRIA: STRUCTURAL, CHEMICAL, AND MÖSSBAUER DATA

Andreas ERTL[§] and Franz PERTLIK

Institut für Mineralogie und Kristallographie, Geozentrum, Universität Wien, Althanstraße 14, A-1090 Wien, Austria

M. Darby DYAR

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

Stefan PROWATKE

Mineralogisches Institut, Universität Heidelberg, Im Neuenheimer Feld 236, D-69120 Heidelberg, Germany

John M. HUGHES

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

Thomas LUDWIG

Mineralogisches Institut, Universität Heidelberg, Im Neuenheimer Feld 236, D-69120 Heidelberg, Germany

Heinz-Jürgen BERNHARDT

Institut für Geologie, Mineralogie und Geophysik, Ruhr-Universität Bochum, D-44801 Bochum, Germany

Abstract

A sample of dark green Fe-rich (~7 wt% FeO_{total}) and Mn-bearing olenite from a beryl-bearing granitic pegmatite near Eibenstein, Lower Austria, was chemically and structurally characterized. Electron-microprobe analyses clearly indicate a deficiency in Si. Tetrahedrally coordinated B was not found by chemical analysis (2.98 *apfu* B by SIMS analysis) or structure refinement. A Mössbauer analysis clearly shows that 90% of the total Fe content occurs as $^{[6]}Fe^{2+}$ at the *Y* site (~0.8 *apfu* $^{[6]}Fe^{2+}$), and 10% occurs as Fe^{3+} (~0.1 *apfu* $^{[4]}Fe^{3+}$) at the *T* site. The optimized formula, calculated from chemical and structural data, is $^{X}(Na_{0.52}Ca_{0.01}\square_{0.47})$ $^{Y}(Al_{1.62}Fe^{2+}{}_{0.83}Mn^{2+}{}_{0.42}Li_{0.05}Ti^{4+}{}_{0.03}\square_{0.05})$ $^{Z}(Al_{5.87}Mg_{0.13})$ $^{T}(Si_{5.73}Al_{0.17}Fe^{3+}{}_{0.10})$ O_{18} $(BO_3)_3$ $[(OH)_{3.32}O_{0.54}F_{0.14}]$. The structure refinement [*a* 15.938(1), *c* 7.136(1) Å, *R*3*m*] yielded an *R* value of ~0.022 for 3818 reflections. The observed <*T*–O> bond-length is 1.624 Å, in accord with the assigned site-populations: $(Si_{5.73}Al_{0.17}Fe^{3+}{}_{0.10})$. This is the first example of olenite in which tetrahedrally coordinated Fe^{3+} has been found. The Li content (0.05 *apfu*), which was determined by SIMS analysis, is uncommonly low for an Al-rich, Mg-poor tourmaline (~0.1 *apfu* Mg). The O1 site is occupied by $[O_{0.54}(OH)_{0.32}F_{0.14}]$. We conclude that the Li content in Al-rich and Mg-poor (natural) tourmaline is very low where the O1 site is occupied mainly by O^{2-}.

Keywords: Fe-rich olenite, crystal structure, Mössbauer study, chemical analyses, Eibenstein, Austria.

Sommaire

Nous avons caractérisé la composition et la structure d'un échantillon vert foncé d'olénite riche en fer (environ 7% de FeO, fer total) et porteuse de Mn provenant d'une pegmatite granitique à béryl près de Eibenstein, en Basse-Autriche. Les résultats d'analyses faites avec une microsonde électronique démontrent clairement un déficit en Si. L'échantillon ne contient pas de bore à coordinence tétraédrique, selon une analyse SIMS (2.98 *apfu* B) et un affinement de la structure. Une analyse par spectroscopie de Mössbauer démontre qu'environ 90% de la teneur en fer se trouve sous forme de $^{[6]}Fe^{2+}$ au site *Y* (~0.8 *apfu* $^{[6]}Fe^{2+}$), et 10% se trouve sous forme de Fe^{3+} (~0.1 *apfu* $^{[4]}Fe^{3+}$) au site *T*. La formule optimisée, calculée à partir de données chimiques et

---

[§] *E-mail address*: andreas.ertl@a1.net

structurales, serait $^{X}(Na_{0.52}Ca_{0.01}\square_{0.47})$ $^{Y}(Al_{1.62}Fe^{2+}_{0.83}Mn^{2+}_{0.42}Li_{0.05}Ti^{4+}_{0.03}\square_{0.05})$ $^{Z}(Al_{5.87}Mg_{0.13})$ $^{T}(Si_{5.73}Al_{0.17}Fe^{3+}_{0.10})$ O_{18} $(BO_3)_3$ $[(OH)_{3.32}O_{0.54}F_{0.14}]$. L'affinement de la structure [*a* 15.938(1), *c* 7.136(1) Å, *R*3*m*] mène à un résidu *R* d'environ 0.022 pour 3818 réflexions. La longueur de liaison moyenne <*T*–O> observée est 1.624 Å, ce qui concorde avec la population d'atomes au site *T*, $(Si_{5.73}Al_{0.17}Fe^{3+}_{0.10})$. Il s'agit du premier exemple dans lequel la présence du fer ferrique à coordinence tétraédrique est confirmée. La teneur en Li (0.05 *apfu*), déterminée par analyse SIMS, est inhabituellement faible pour une tourmaline alumineuse à faible teneur en Mg (~0.1 *apfu* Mg). Le site O1 contient la combinaison $[O_{0.54}(OH)_{0.32}F_{0.14}]$. A notre avis, la teneur en Li d'une tourmaline riche en Al et à faible teneur en Mg est apte à être très faible dans les cas où le site O1 contient surtout O^{2-}.

(Traduit par la Rédaction)

Mots-clés: olénite riche en fer, structure cristalline, spectroscopie de Mössbauer, analyse chimique, Eibenstein, Autriche.

INTRODUCTION

Recent work by Ertl *et al.* (1997), Hughes *et al.* (2000, 2004), and Marler *et al.* (2002) has shown that substitution of B for Si at the *T* site in tourmaline results in a modification of bond lengths at this site. A related question is the extent to which substitution of cations larger than Si, such as Fe^{3+}, will be reflected in X-ray parameters. This question can only be addressed with Mössbauer spectroscopy to quantify the amount and site occupancy of Fe^{3+}, in conjunction with accurate refinements of the structure.

Dyar *et al.* (1998) reported on the chemical characterization of a suite of 54 samples of tourmaline. Significant amounts of $^{[4]}Fe^{3+}$ were found in schorl [up to 0.17 atoms per formula unit (*apfu*); sample no. 33] and Fe-bearing dravite (up to 0.17 *apfu*; sample no. 9). The goal of this study is to determine if Fe-rich olenite can also contain some $^{[4]}Fe^{3+}$.

Ertl (1995) determined the chemical composition and unit-cell parameters of Al-rich tourmalines (olenite) from a Moldanubian granitic pegmatite occurring in a quarry near the village of Eibenstein an der Thaya, Lower Austria ("Bunte Serie"). The pegmatite outcrop in this quarry (which exploits marble and amphibolite) existed for a short time only. This granitic pegmatite also contains schorl, quartz, muscovite, beryl (crystals up to 7 cm in length), and apatite (Ertl 1995). Dark green tourmaline [*a* 15.908(3), *c* 7.121(2) Å, determined by X-ray powder diffraction], was originally called elbaite by Ertl (1995), in the absence of chemical data for the light elements. In the present article, we provide results of detailed analyses of this Al-rich tourmaline (Fe-rich olenite) from that pegmatite, with structural, chemical, and Mössbauer data. Note that this locality is quite different from that of the Mn-rich tourmaline described by Ertl *et al.* (2003).

EXPERIMENTAL

Sample selection

Pieces of dark green homogeneous tourmaline (sample OLG) were separated from a euhedral crystal approximately 1 cm in diameter. This crystal is intergrown with quartz and associated with microcline and colorless and blue (Mn-bearing) apatite.

Chemical analysis

This sample of olenite was analyzed with a Cameca SX51 electron microprobe (EMP) equipped with five wavelength-dispersion spectrometers, located at the Mineralogisches Institut, Universität Heidelberg, Germany. We used the following operating conditions: accelerating voltage 15 kV, beam current 20 nA, and beam diameter 5 μm. Peaks for all elements were measured for 10 s, except for Mg (20 s), Cr (20 s), Ti (20 s), Zn (30 s) and F (40 s). Natural and synthetic silicate and oxide standards were used for calibration, and the data were reduced and corrected using the PAP routine (Pouchou & Pichoir 1985). A matrix correction was applied assuming stoichiometry with respect to the O atoms and all non-measured components, such as B_2O_3. The accuracy of the electron-microprobe analysis and the correction procedure was checked by measuring three samples of reference tourmaline (98114: elbaite, 108796: dravite, 112566: schorl; Dyar *et al.* 1998, 2001). Agreement between the published compositions and the measured values was satisfactory.The analytical errors are ±1% for major elements and ±5% for minor elements. Additional chemical analyses of the same olenite crystal were done using wavelength-dispersion spectrometry and a Cameca SX50 electron microprobe at the Ruhr-Universität Bochum, Germany; we used an acceleration voltage of 15 kV, a probe current of 15 nA, and a beam diameter of approximately 5 μm. Natural and synthetic materials were used as standards.

The amounts of H, Be, Li and B were determined by secondary-ion mass spectrometry (SIMS) with a CAMECA ims 3f ion microprobe at the Mineralogisches Institut, Universität Heidelberg, Germany. Primary ions of oxygen were accelerated to 10 keV. The mass spectrometer's energy window was set to 40 eV. An offset of 75 V was applied to the secondary accelerating voltage of 4.5 kV so that secondary ions with an initial energy of 75 ± 20 eV were monitored (energy filtering). This adjustment suppresses effects of light elements related to the matrix (Ottolini *et al.* 1993). For B, Be and Li, the primary current was 20 nA, resulting in a sputtering surface of ~30 μm in diameter. The spectrometer's mass resolution M/ΔM for B, Be and Li was set to ~1100 (10%) to suppress interferences ($^6LiH^+$, $^{10}BH^+$, Al^{3+}). Secondary ions ^7Li, ^9Be and ^{11}B were collected under an ion-imaged field 150 μm in diameter.

For H, the primary beam current was 20 nA and M/ΔM was set to ~400 (10%). To reduce the rate of contamination by H_2O, a smaller field-aperture was chosen, which restricts the analyzed area to 10 μm in diameter in the center of the scanned area. This method reduces the effect of H_2O contamination, which was found to be higher on the edge of the primary beam-spot than in the center (Kalt *et al.* 2001). Contamination by H_2O was further reduced by using a cold trap attached to the sample chamber of the ims 3f, cooled with liquid nitrogen. The count rates of the isotopes analyzed (^1H, ^7Li, ^9Be and ^{11}B) were normalized to the count rate of ^{30}Si.

The relative ion-yield (RIY) for B and H was determined using three different samples of tourmaline as reference material: elbaite (98144), dravite (108796) and schorl (112566), all described and analyzed by Dyar *et al.* (1998, 2001). For Li and Be, the reference material was the SRM610 standard glass of NIST, with concentrations for Li and Be published by Perkins *et al.* (1997). The relative reproducibility (1σ) for the RIY of B, Li and Be was <1%. Matrix effects and the uncertainty of the element concentrations in the reference material limit the accuracy of the analysis. The relative uncertainty is estimated to be <30% for H, <20% for Li and <10% for B. Table 1 contains complete results of the chemical analyses for the Fe-rich olenite (OLG), from Eibenstein, Lower Austria.

Mössbauer analysis

Approximately 50 mg of tourmaline was crushed to a fine powder and mixed with sugar under acetone before mounting in a sample holder confined by "Scotch tape". The resultant thickness of the sample was below the thin-absorber thickness, as approximated by Long *et al.* (1983), but still sufficient for acquisition of a useful spectrum (Fig. 1). A room-temperature Mössbauer spectrum was acquired to determine Fe^{2+} and Fe^{3+} content in the Mineral Spectroscopy Laboratory at Mount Holyoke College. A source of 65 mCi ^{57}Co in Rh was used on a WEB Research Co. spectrometer; run time was two days. Results were calibrated against an α-Fe foil 6 μm in thickness and 99% purity. In the absence of *any* data on recoil-free fractions for Fe in different sites and valences in the tourmaline structure, peak areas were assumed to correspond directly to the abundance of the species in the sample; we recognize that this assumption (and the use of a potentially preferentially oriented absorber) may unavoidably contribute to the overall large errors on the Fe^{3+} and Fe^{2+} distributions in this sample. Thus we estimate that the error on site assignments in this sample is approximately ±5–15%.

The spectrum was fit using the WMOSS software of WEB Research Co., an implementation of the Voigt-based fitting method developed by Rancourt & Ping (1991). This method has been shown to be most appropriate for samples in which the Fe atoms do not have homogeneous environments, but rather have different types of nearest-neighbor and next-nearest-neighbor environments.

Quadrupole-splitting distributions (*QSD*s) were used to represent the contributions of *Y*-site Fe^{2+} and tetrahedral Fe^{3+} in this spectrum (Fig. 1). Following the established conventions for fits using a quadrupole-splitting distribution, γ, the Lorentzian full peak-width and half-maximum intensity was constrained to be 0.20 mm/s, which is roughly the natural linewidth of Fe. The ratio of Lorentzian heights of the two lines in an elemental quadrupole doublet (h_+/h_-) was constrained to be equal to one for all components. The values of δ_0 (the value

TABLE 1. COMPOSITION OF Fe-RICH OLENITE FROM EIBENSTEIN AN DER THAYA, LOWER AUSTRIA

	OLG^1	OLG^3	OLG^5		OLG^3	OLG^5
SiO_2 wt.%	33.87	34.10	34.66	Si *apfu*	5.68	5.73
TiO_2	0.39	0.30	0.24	$^{[4]}Fe^{3+}$	0.09	0.10
B_2O_3	-	10.37^4	10.52^6	$^{[4]}Al$	0.23	0.17
Al_2O_3	39.00	39.36	39.36			
Cr_2O_3	-	0.01	-	Sum *T* site	6.00	6.00
FeO^*	6.23	5.94	6.01			
$Fe_2O_3^*$	0.77	0.73	0.76	$^{[3]}B$	2.98	3.00
MnO	2.80	3.13	3.00			
MgO	0.56	0.55	0.53	Al	7.48	7.49
CaO	0.07	0.05	0.06	Cr	0.00	-
Li_2O	-	0.07^4	0.08	Mn^{2+}	0.44	0.42
Na_2O	1.69	1.55	1.62	Fe^{2+}	0.83	0.83
K_2O	0.02	0.02	-	Mg	0.14	0.13
ZnO	0.03	0.04	-	Zn	0.00	-
F	-	0.27	0.27	Ti^{4+}	0.04	0.03
H_2O	3.01^2	2.97^4	3.00	Li	0.05	0.05
O=F	-	-0.11	-0.11			
				Sum *Y*, *Z* sites	8.98	8.95
Sum	88.44	99.35	100.00			
				Ca	0.01	0.01
				Na	0.50	0.52
				K	0.00	-
				Sum *X* site	0.51	0.53
				Sum cations	18.47	18.48
				OH	3.29	3.31
				F	0.14	0.14
				Sum OH + F	3.43	3.45

Note: ^{1} Average result of 25 EMP analyses (Institut für Geologie, Mineralogie und Geophysik, Ruhr-Universität Bochum). ^{2} The amount of H_2O was determined by U extraction on a bulk sample of this crystal (average result of two analyses). ^{3} Average result of 65 EMP analyses (Mineralogisches Institut, Universität Heidelberg). Cl was not detected. ^{4} Average result of three SIMS analyses for B, H, Li, and Be (5 ppm) (Mineralogisches Institut, Universität Heidelberg). ^{5} Wt. percent calculated from optimal site-occupancies and normalized to 100%. ^{6} B_2O_3 calculated as B = 3.00 *apfu*. Dash: not determined. * FeO and Fe_2O_3 were calculated by Mössbauer spectroscopy (Table 2). The formulae are based on (O + OH + F) = 18 *apfu*.

of isomer shift, δ, where the distributed hyperfine parameter has a value of zero) and δ_1 (the coupling of δ to the distributed hyperfine parameter) were constrained to be the same (but allowed to vary as a group) for the two Fe^{2+} subcomponents, based on the assumption that these both represent atoms at the *Y* site; δ_0 and δ_1 were allowed to vary independently for the Fe^{3+} component. The remaining parameters, including the center of the Gaussian component of the Δ-distribution (Δ_0), the width of the quadrupole-splitting distribution (δ_Δ), and the relative area of the doublets (A), were allowed to vary freely. The isomer shift (δ) is calculated using $\delta = \delta_1 * \Delta_0 + \delta_0$. Details relating to the application of these parameters can be found in Rancourt & Ping (1991). It is important to note that varying combinations of constraints for the parameters of each distribution, as well as additional numbers of subcomponents, were used, but these permutations did not affect the relative peak-areas by more than ±3%, well within the stated errors. *All the models* resulted in a tetrahedral rather than octahedral component for Fe^{3+}, and overall the QSD was found to be extremely stable (Fig. 1). Results are given in Table 2.

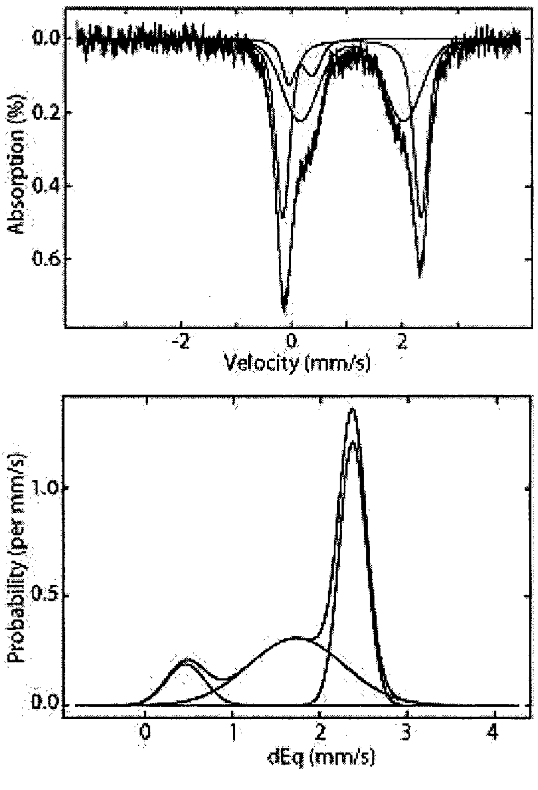

FIG. 1. Room-temperature Mössbauer spectrum of olenite (top), showing one $^{[4]}Fe^{3+}$ doublet and two spectral subcomponents arising from a single Gaussian distribution of the quadrupole splitting from Fe^{2+} at the *Y* site. Below is shown the quadrupole splitting distribution for this fit. Other models with higher numbers of QSD subcomponents were obtained, but the total QSD was essentially the same. This total QSD is well defined and independent of the number of Gaussian subcomponents used.

The parameters of the two modeled Fe^{2+} Gaussian subcomponents (Table 2) correspond to Fe^{2+} at the *Y* site, in keeping with the assignments proposed by Pieczka *et al.* (1997) and used by Dyar *et al.* (1998). Finally, this Mössbauer analysis shows that 90% of the total Fe content occurs as $^{[6]}Fe^{2+}$ at the *Y* site (~0.8 *apfu* Fe^{2+}) and 10% occurs as Fe^{3+} (~0.1 *apfu* $^{[4]}Fe^{3+}$) at the *T* site.

Crystal structure

Crystals of olenite suitable for X-ray work were checked by film methods. A cut chip of this olenite crystal (sample OLG; ~300 μm in diameter) was mounted on a Stoe AED2 diffractometer using graphite-monochromatized Mo*K*α radiation. The structure was refined using the SHELX–76 (Sheldrick 1976) package of programs, with neutral-atom scattering factors. The refinement was done with anisotropic-displacement parameters for all non-H atoms. The *Z* site was modeled using Al scattering factors with fixed occupancy of $Al_{1.00}$, because a released multiplicity showed this site to be essentially fully occupied by Al. Refining the *T* site with Si scattering factors, while fixing the *Z* site at $Al_{1.00}$, showed no significant deviation from a *T* site fully occupied with Si. A *T*-site occupancy of ($Si_{5.73}$ $Al_{0.17}Fe^{3+}_{0.10}$) (derived from the optimized formula) gives 85 *e*, which is not distinctly different from an occupancy of $Si_{6.00}$, which gives 84 *e*. Subsequently, we fixed the *T* site at $Si_{1.00}$, and thus only the *X*-site and *Y*-site occupancies were refined. The occupancy of the *Y* site was modeled with Al and Fe scattering factors, with

TABLE 2. MÖSSBAUER PARAMETERS FOR Fe-RICH OLENITE FROM EIBENSTEIN AN DER THAYA, LOWER AUSTRIA

	$^{Y1}Fe^{2+}$	$^{Y3}Fe^{2+}$	$^{T}Fe^{3+}$
γ (mm/s)	0.20	0.20	0.20
Δ_0 (mm/s)	2.50	1.87	0.43
δ_Δ (mm/s)	0.34	1.30	0.41
δ_0 (mm/s)	1.09	1.09	0.11
δ_1 (mm/s)	0.00	0.00	0.13
δ (mm/s)	1.10	1.09	0.17
A (%)	45	45	10

Note: The reduced X^2 value for this fit is 0.438. Results are given in mm/s relative to the center point of a Fe foil calibration spectrum. The Lorentzian full peak-width (γ) at half maximum intensity is held constant at 0.20 mm/s. The standard error is 0.05 mm/s for all parameters except the peak area, for which standard error is 5–15% absolute. Symbols: Δ_0 is the center of a Gaussian component of the Δ distribution. δ_Δ is the width of the quadrupole splitting distribution. δ_0 is the value of isomer shift, δ, where the distributed hyperfine parameter has a value of zero. A is the relative area of the doublet. δ_1 is the coupling of δ to the distributed hyperfine parameter. The ratio of Lorentzian heights of the two lines in an elemental quadrupole doublet, h_+/h_-, was constrained to have a value of 1 for all three subcomponents.

the assumption that (Al + Fe) = 1. The refinement yields $Na_{0.537}$ for the *X* site, and $(Al_{0.609}Fe_{0.391})$ for the *Y* site. Table 3 lists crystal data, information about the collection of single-crystal X-ray data, and details of structure refinement. Table 4 contains the atom coordinates and anisotropic-displacement factors. Table 5 shows bond lengths and bond angles. Structure factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

Optimization of site occupancies

Using the approach of quadratic programming, Wright *et al.* (2000) described a method of optimizing the site occupancies of cations in minerals. Using that method, the structural formula of this tourmaline sample (OLG) is: $^{X}(Na_{0.52}Ca_{0.01}\square_{0.47})$ $^{Y}(Al_{1.62}Fe^{2+}_{0.83}Mn^{2+}_{0.42}Li_{0.05}Ti^{4+}_{0.03}\square_{0.05})$ $^{Z}(Al_{5.87}Mg_{0.13})$ $^{T}(Si_{5.73}Al_{0.17}Fe^{3+}_{0.10})$ O_{18} $(BO_3)_3$ $[(OH)_{3.32}O_{0.54}F_{0.14}]$

The optimized formula essentially minimizes the differences between the formula obtained from the results of the chemical analysis and that obtained by structure refinement.

TABLE 3. CRYSTAL DATA AND DETAILS OF STRUCTURE REFINEMENT OF Fe-RICH OLENITE FROM EIBENSTEIN AN DER THAYA, LOWER AUSTRIA

Crystal system	trigonal	Reflections, $F_o > 4\sigma(F_o)$	3818
Space group	*R*3*m* (160)	Range of *hkl*	±*h*, *k*, ±*l*
Unit-cell	*a* 15.938(1)	Maximum 2θ value (°)	100
parameters (Å)	*c* 7.136(1)	Absorption correction	ψ-scan data
Cell volume (Å³)	*V* 1569.83	Transmission factors	0.20 to 0.25
T (K)	295(2)	Number of variables	94
Z	3	*R* (F), 3818 data	0.0217
Single crystal (mm³)	0.20 × 0.20 × 0.60	*R*w (F²), 3818 data	0.0547
Diffractometer	Stoe AED 2	$w = 1/[\rho^2(F_o^2) + (0.0296{*}P)^2]$	
Radiation	Mo*K*α	$P = [\max(F_o^2,0) + 2{*}F_c^2]/3$	
Scan mode	ω – 2θ	Extinction coefficient	<0.002
Measured reflections	11281	Max / σ	<0.001
Independent refl.	3933	Difference peaks (e^-/Å³)	+1.02, –0.79
R_{int}	0.0307		

Discussion of the Atomic Arrangement

Hawthorne & Henry (1999) gave the general chemical formula of the tourmaline-group minerals as $X\,Y_3\,Z_6\,[T_6O_{18}]\,(BO_3)_3\,V_3\,W$ (*V* site = O3 site, *W* site = O1 site). Cations in the *T* site include Si, Al (*e.g.*, Grice & Ercit 1993, Hawthorne *et al.* 1993, MacDonald & Hawthorne 1995), B (*e.g.*, Ertl *et al.* 1997, Hughes *et al.* 2000, Schreyer *et al.* 2000, Marler & Ertl 2002), Be (Hughes *et al.* 2004), and Fe^{3+} (Dyar *et al.* 1998). Electron-microprobe analyses of this sample of Fe-rich olenite at two different laboratories clearly revealed a deficiency in Si (Table 1), so there must be other cations present. This is supported by the fact that the measured <*T*–O> bond-length is enlarged to 1.624 Å (Table 5). The ideal <*T*–O> bond length (*T* site fully occupied with Si) has been determined to be ~1.620 Å (MacDonald & Hawthorne 1995, Bloodaxe *et al.* 1999, Ertl *et al.* 2001a, b).

Other *T* cations include B, Al and Fe^{3+}. No evidence of $^{[4]}B$ was found by chemical analysis (2.98 *apfu* B by SIMS analysis) or by structure refinement. Abundant Al is present, in the environment of growth, and it can be responsible for the enlargement of the site. However, our Mössbauer analysis of the Fe-rich olenite shows that 10% of the total Fe content occurs as $^{[4]}Fe^{3+}$ (~0.1 *apfu*). Accordingly, the finally assigned occupants at the *T* site are $(Si_{5.73}Al_{0.17}Fe^{3+}_{0.10})$. The <*T*–O> bond-length (1.624

TABLE 4. STRUCTURAL PARAMETERS OF Fe-RICH OLENITE FROM EIBENSTEIN AN DER THAYA, LOWER AUSTRIA

Atom	Wyckoff	*x*	*y*	*z*	U_{11}/U_{iso}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
X	3a	0	0	0.7798(4)	0.0276(7)	U_{11}	0.0248(9)	0	0	$U_{11}/2$
Y	9b	0.72829(1)	0.45658(1)	0.7055(1)	0.0085(1)	0.0108(1)	0.0172(1)	0.0032(1)	$U_{23}/2$	$U_{22}/2$
Z	18c	0.70225(1)	0.73887(1)	0.3913(1)	0.0082(1)	0.0089(1)	0.0084(1)	0.0007(1)	0.0000(1)	0.0043(1)
T	18c	0.80812(1)	0.81014(1)	0[§]	0.0078(1)	0.0075(1)	0.0089(1)	-0.0005(1)	-0.0002(1)	0.0039(1)
O,F	3a	0	0	0.2269(3)	0.0429(7)	U_{11}	0.0130(5)	0	0	$U_{11}/2$
O1	9b	0.93851(3)	0.87703(5)	0.5124(1)	0.0292(3)	0.0084(2)	0.0156(3)	0.0001(1)	$U_{23}/2$	$U_{22}/2$
O2	9b	0.90588(3)	0.81175(6)	0.9301(1)	0.0102(1)	0.0175(2)	0.0138(2)	-0.0015(2)	$U_{23}/2$	$U_{22}/2$
O3	9b	0.79936(4)	0.59872(7)	0.8258(1)	0.0143(1)	0.0295(4)	0.0099(2)	0.0004(2)	$U_{23}/2$	$U_{22}/2$
O4	9b	0.42739(3)	0.85479(6)	0.5743(1)	0.0108(1)	0.0184(3)	0.0134(2)	-0.0006(2)	$U_{23}/2$	$U_{22}/2$
O5	18c	0.80330(3)	0.81389(4)	0.2260(1)	0.0120(1)	0.0134(1)	0.0088(1)	-0.0004(1)	0.0001(1)	0.0062(1)
O6	18c	0.71398(3)	0.71363(3)	0.9226(1)	0.0091(1)	0.0092(1)	0.0102(1)	-0.0013(1)	-0.0001(1)	0.0030(1)
O7	18c	0.79027(3)	0.72932(3)	0.5615(1)	0.0086(1)	0.0136(1)	0.0126(1)	0.0032(1)	0.0011(1)	0.0060(1)
B	9b	0.88999(3)	0.77998(6)	0.5474(1)	0.0094(2)	0.0093(2)	0.0108(2)	0.0005(2)	$U_{23}/2$	$U_{22}/2$
H	9b	0.793(1)	0.585(2)	0.961(5)	0.0306(8)					

Note: Values of the estimated standard deviation are shown in parentheses. The anisotropic displacement factors (Å²) are defined as $\exp(-2\pi^2 \Sigma^3_{i=1} \Sigma^3_{j=1} U_{ij}\, h_i\, h_j\, \mathbf{a}^*_i\, \mathbf{a}^*_j)$. Wyckoff: number of positions and Wyckoff notation. [§] Fixed.

Å) derived from this crystal-structure refinement is in good agreement with the calculated <*T*–O> bond-length (1.624 Å) by using formula (1) given by Ertl *et al.* (2001a). This formula includes the effective ionic radii and the proportions of the occupants at the *T* site of this sample.

The Li content (0.05 *apfu*), which was determined by SIMS analysis, is uncommonly small for an Al-rich tourmaline, which contains only small amounts of Mg (0.14 *apfu*). This sample from Eibenstein contains only 0.14 *apfu* F. Olenite from the type locality in Russia, reinvestigated by Schreyer *et al.* (2002), contains similar amounts of F (0.08–0.16 *apfu*), but significantly higher amounts of Li (0.45–0.62 *apfu*). This difference may be due to the very small amounts of Fe in that sample of olenite compared to that in the Fe-rich olenite from Eibenstein, and to the low Li content of this granitic pegmatite (Li-enriched minerals are absent). Previous investigations showed that Li and Fe are usually negatively correlated in tourmaline from granitic pegmatites (*e.g.,* Dyar *et al.* 1998, Novák *et al.* 1999, Tindle *et al.* 2002). The O1 site in the olenite from Eibenstein is occupied by $[O_{0.54}(OH)_{0.32}F_{0.14}]$, whereas the O3 site is occupied by $(OH)_3$. Olenite from the type locality shows a different occupancy at the O1 site: $\sim[(OH)_{0.83}F_{0.16}O_{0.01}]$ to $\sim[(OH)_{0.90}F_{0.08}O_{0.02}]$ (Schreyer *et al.* 2002). Manganese-rich olenite (Ertl *et al.* 2003) contains more Li (0.37–0.48 *apfu*) than the Fe-rich olenite investigated here (Li: 0.05 *apfu*). The O1 site of Mn-rich olenite contains between $[F_{0.43}O_{0.32}(OH)_{0.25}]$ and $[F_{0.48}(OH)_{0.33}O_{0.19}]$ (Ertl *et al.* 2003). Taylor *et al.* (1995) and Hawthorne (2002) noted that the anion occupancy of the O1 site is directly dependent on the *Y*-site occupancy because O1 is bonded only to *Y* cations. On the basis of bond-valence arguments, increasing the Al:Li ratio requires O^{2-} at O1, whereas decreasing the ratio leads to a stabilization of $(OH)^-$ and F^- at O1. If we include results of investigations on Al-rich tourmalines (with levels of light elements determined) from various localities by Dyar *et al.* (1998, 2001), Ertl *et al.* (1997), Federico *et al.* (1998), Kalt *et al.* (2001), Novák *et al.* (1999), Prowatke *et al.* (2003), and Selway *et al.* (1998), we conclude that natural samples of Al-rich (Mg-poor) tourmaline contain significant amounts of Li (>0.4 *apfu*) only where the O1 site is occupied primarily by F or [(OH), F], rather than by O^{2-}.

TABLE 5. SELECTED INTERATOMIC BOND-LENGTHS (Å) IN Fe-RICH OLENITE FROM EIBENSTEIN, LOWER AUSTRIA

X	– O1 (×3)	2.554(2)	*T*	– O6	1.617(1)
	– O4 (×3)	2.752(1)		– O5	1.617(1)
	– O2 (×3)	2.811(1)		– O2	1.624(1)
	– O,F	3.191(3)		– O4	1.637(1)
Mean		2.754	Mean		1.624
Y	– O1 (×2)	1.972(1)	B	– O1	1.362(1)
	– O,F	1.992(1)		– O7 (×2)	1.380(1)
	– O5 (×2)	2.018(1)	Mean		1.374
	– O3	2.141(1)			
Mean		2.019			
Z	– O5	1.868(1)			
	– O6	1.879(1)			
	– O7	1.886(1)			
	– O7'	1.918(1)			
	– O6'	1.949(1)			
	– O3	1.980(1)			
Mean		1.913			

ACKNOWLEDGEMENTS

We thank Albert Prayer, Irnfritz, Lower Austria, for providing the tourmaline sample. We are grateful to Andreas Wagner, Vienna, Austria, for preparing the tourmaline crystals for chemical analysis. Special thanks to Kurt Ferguson, Dallas, Texas, U.S.A., for the H_2O determination. This work was supported, in part, by NSF grants EAR–9627222, EAR–9804768, and EAR–0003201 to JMH. We sincerely thank Frank C. Hawthorne and T. Scott Ercit for their careful revision of the manuscript. We thank Associate Editor Franklin F. Foit and Robert F. Martin, who provided invaluable comments on the work.

REFERENCES

BLOODAXE, E.S., HUGHES, J.M., DYAR, M.D., GREW, E.S. & GUIDOTTI, C.V. (1999): Linking structure and chemistry in the schorl–dravite series. *Am. Mineral.* **84**, 922-928.

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

________, WIEDENBECK, M., ROBERTSON, D., CROSS, LR., DELANEY, J.S., FERGUSON, K., FRANCIS, C.A., GREW, E.S., GUIDOTTI, C.V., HERVIG, R.L., HUGHES, J.M., HUSLER, J., LEEMAN, W.P., MCGUIRE, A.V., RHEDE, D., ROTHE, H., PAUL, R.L., RICHARDS, I. & YATES, M. (2001): Reference minerals for the microanalysis of light elements. *Geostandards Newsletter* **25**, 441-463.

ERTL, A. (1995): Elbait, Olenit, Dravit–Buergerit–Mischkristalle, Dravit, Uvit und ein neuer Al-Turmalin (?) von österreichischen Fundstellen. *Mitt. Österr. Mineral. Ges.* **140**, 55-72.

________, HUGHES, J.M. & MARLER, B. (2001a): Empirical formulae for the calculation of <*T*–O> and *X*–O2 bond lengths in tourmaline and relations to tetrahedrally-coordinated boron. *Neues Jahrb. Mineral., Monatsh.*, 548-557.

________, ________, PROWATKE, S., ROSSMAN, G.R., LONDON, D. & FRITZ, E.A. (2003): Mn-rich tourmaline from Austria: structure, chemistry, optical spectra, and relations to synthetic solid solutions. *Am. Mineral.* **88**, 1369-1376.

________, PERTLIK, F. & BERNHARDT, H.-J. (1997): Investigations on olenite with excess boron from the Koralpe, Styria, Austria. *Österr. Akad. Wissensch., Math.-naturw. Kl., Anz. Abt. 1,* **134**, 3-10.

________, ________ & ________ (2001b): Ein hellblauer Olenit–Schörl–Dravit Mischkristall von Ebersdorf, Niederösterreich: Strukturanalyse und Chemie. *Mitt. Österr. Mineral. Ges.* **146**, 75-77.

FEDERICO, M., ANDREOZZI, G.B., LUCCHESI, S., GRAZIANI, G. & CÉSAR-MENDES, J. (1998): Compositional variation of tourmaline in the granitic pegmatite dykes of the Cruzeiro mine, Minas Gerais, Brazil. *Can. Mineral.* **36**, 415-431.

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.

HAWTHORNE, F.C. (2002): Bond-valence constraints on the chemical composition of tourmaline. *Can. Mineral.* **40**, 789-797.

________ & HENRY, D.J. (1999): Classification of the minerals of the tourmaline group. *Eur. J. Mineral.* **11**, 201-215.

________, MACDONALD, D.J. & BURNS, P.C. (1993) Reassignment of cation site-occupancies in tourmaline: Al–Mg disorder in the crystal structure of dravite. *Am. Mineral.* **78**, 265-270.

HUGHES, J.M., ERTL, A., DYAR, M.D., GREW, E.S., SHEARER, C.K., YATES, M.G. & GIUDOTTI, C.V. (2000): Tetrahedrally coordinated boron in a tourmaline: boron-rich olenite from Stoffhütte, Koralpe, Austria. *Can. Mineral.* **38**, 861-868.

________, ________, ________, ________, WIEDENBECK, M. & BRANDSTÄTTER, F. (2004): Structural and chemical response to varying $^{[4]}$B content in zoned Fe-bearing olenite from Koralpe, Austria. *Am. Mineral.* **89**, 447-454.

KALT, A., SCHREYER, W., LUDWIG, T., PROWATKE, S., BERNHARDT, H.-J. & ERTL, A. (2001): Complete solid solution between magnesian schorl and lithian excess-boron olenite in a pegmatite from Koralpe (eastern Alps, Austria). *Eur. J. Mineral.* **13**, 1191-1205.

LONG, G.J., CRANSHAW, T.E. & LONGWORTH, G. (1983): The ideal Mössbauer effect absorber thickness. *Mössbauer Effect Ref. Data J.* **6**, 42-49.

MACDONALD, D.J. & HAWTHORNE, F.C. (1995): The crystal chemistry of Si = Al substitution in tourmaline. *Can. Mineral.* **33**, 849-858.

MARLER, B., BOROWSKI, M., WODARA, U. & SCHREYER, W. (2002): Synthetic tourmaline (olenite) with excess boron replacing silicon in the tetrahedral site. II. Structure analysis. *Eur. J. Mineral.* **14**, 763-771.

________ & ERTL, A. (2002): Nuclear magnetic resonance and infrared spectroscopic study of excess-boron olenite from Koralpe, Styria, Austria. *Am. Mineral.* **87**, 364-367.

NOVÁK, M., SELWAY, J.B., ČERNÝ, P., HAWTHORNE, F.C. & OTTOLINI, L. (1999): Tourmaline of the elbaite–dravite series from an elbaite-subtype pegmatite at Bližná, southern Bohemia, Czech Republic. *Eur. J. Mineral.* **11**, 557-568.

OTTOLINI, L., BOTTAZZI, P. & VANNUCCI, R. (1993): Quantification of lithium, beryllium, and boron in silicates by secondary ion mass spectrometry using conventional energy filtering. *Anal. Chem.* **65**, 1960-1968.

PERKINS, W.T., PEARCE, N.J.G. & WESTGATE, J.A. (1997): The development of laser ablation ICP–MS and calibration strategies; examples from the analyses of trace elements in volcanic glass shards and sulfide minerals. *Geostandards Newsletter* **21**, 115-144.

PIECZKA, A., KRACZKA, J. & ZABINSKI, W. (1997): Mössbauer spectra of Fe^{3+}-poor schorls: reinterpretation of the spectra on a basis of an ordered structure model. *In* Tourmaline '97; Int. Symp. on Tourmaline (Nové Mesto na Morave, Czech Republic), 74-75 (abstr.).

POUCHOU, J.L. & PICHOIR F. (1985): "PAP" procedure for improved quantitative microanalysis. *Microbeam Anal.* **54**, 104-106.

PROWATKE, S., ERTL, A. & HUGHES, J.M. (2003): Tetrahedrally-coordinated Al in Mn-rich, Li- and Fe-bearing olenite from Eibenstein an der Thaya, Lower Austria: a chemical and structural investigation. *Neues Jahrb. Mineral., Monatsh.*, 385-395.

RANCOURT, D.G. & PING, J.Y. (1991): Voigt-based methods for arbitrary-shape static hyperfine parameter distributions in Mössbauer spectroscopy. *Nucl. Instrum. Methods Phys. Res.* **B58**, 85-97.

SCHREYER, W., HUGHES, J.M., BERNHARDT, H.-J., KALT, A., PROWATKE, S. & ERTL, A. (2002): Reexamination of olenite from the type locality: detection of boron in tetrahedral coordination. *Eur. J. Mineral.* **14**, 935-942.

________, WODARA, U., MARLER, B., VAN AKEN, P.A., SEIFERT, F. & ROBERT, J.-L. (2000): Synthetic tourmaline (olenite) with excess boron replacing silicon in the tetrahedral site. I. Synthesis conditions, chemical and spectroscopic evidence. *Eur. J. Mineral.* **12**, 529-541.

SELWAY, J.B., NOVÁK, M., HAWTHORNE, F.C., ČERNÝ, P., OTTOLINI, L. & KYSER, T.K. (1998): Rossmanite, $\square(\mathrm{LiAl_2})\mathrm{Al_6}(\mathrm{Si_6O_{18}})(\mathrm{BO_3})_3(\mathrm{OH})_4$, a new alkali-deficient tourmaline: description and crystal structure. *Am. Mineral.* **83**, 896-900.

SHELDRICK, G.M. (1976): *Program for Crystal Structure Determination*. Univ. of Göttingen, Göttingen, Germany.

TAYLOR, M.C., COOPER, M.A. & HAWTHORNE, F.C. (1995): Local charge-compensation in hydroxyl-deficient uvite. *Can. Mineral.* **33**, 1215-1221.

TINDLE, A.G., BREAKS, F.W. & SELWAY, J.B. (2002): Tourmaline in petalite-subtype granitic pegmatites: evidence of fractionation and contamination from the Pakeagama Lake and Separation Lake areas of northwestern Ontario, Canada. *Can. Mineral.* **40**, 753-788.

WRIGHT, S.E., FOLEY, J.A. & HUGHES, J.M. (2000): Optimization of site occupancies in minerals using quadratic programming. *Am. Mineral.* **85**, 524-531.

Received January 9, 2004, revised manuscript accepted May 16, 2004.