Fe-BEARING OLENITE WITH TETRAHEDRALLY COORDINATED Al FROM AN ABYSSAL PEGMATITE AT KUTNÁ HORA, CZECH REPUBLIC: STRUCTURE, CRYSTAL CHEMISTRY, OPTICAL AND XANES SPECTRA

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ABSTRACT

The pale blue rim of olenite on a black crystal of olenite–schorl tourmaline from an abyssal pegmatite at the locality Kuklík, near Kutná Hora, Czech Republic, has been chemically and structurally characterized. The optimized formula, calculated using chemical and structural data, is ^{X}(Na$_{0.54}$Ca$_{0.14}$K$_{0.01}$□$_{0.31}$) ^{Y}(Al$_{2.15}$Fe$^{2+}_{0.78}$Mn$^{2+}_{0.06}$Ti$^{4+}_{0.01}$) ^{Z}(Al$_{5.90}$Mg$_{0.10}$) ^{T}(Si$_{5.60}$Al$_{0.40}$) B$_3$ O$_{27}$ ^{V}[(OH)$_{2.49}$O$_{0.51}$] ^{W}(O$_{0.99}$F$_{0.01}$), with a 15.8838(3), c 7.1056(2) Å and R = 0.017. The relatively short <Y–O> bond-length, 1.992 Å, confirms the high content of Al at the Y site (~2.1 atoms per formula unit, *apfu*). It is similar to that of olenite from the type locality, though the olenite from Kuklík contains significant amounts of Fe at the Y site, and significant amounts of $^{[4]}$Al (~0.4 *apfu*) instead of $^{[4]}$B in the T site. This finding is supported by results of the structure determination, which show an enlarged <T–O> bond-length of ~1.626 Å. This sample of olenite shows that nonstoichiometric content of Si does not always imply $^{[4]}$B in aluminous tourmaline. No H could be found at the O1 site by refinement, and the spherical distribution of electron density in the difference-Fourier map around the O1 site supports the conclusion that this site is only or mainly occupied by O and not by OH. On a bond-angle distortion (σ_{oct}^2 of the ZO$_6$ octahedron) – <Y–O> distance diagram, the olenite from Kuklík lies between compositions containing 3 (OH) at the V site, and natural buergerite, which contains 0.3 (OH) and 2.7 O at the V site (O3 site). The (OH) content with ~2.5 (OH) *pfu*, which was calculated for a charge-balanced formula, is in a good agreement with these findings and with the integrated intensity of the OH overtones in the 7000 cm^{-1} region (690 cm^{-2} per cm thickness), which is one of the lowest measured to date for tourmaline. The OH seems to be ordered strongly at the O3 site. The composition of this sample of olenite shows a trend toward the proposed olenite end-member formula, which contains only 1 OH group. The low content of F (0.01 *apfu*) is uncommon for natural Al-rich and Mg-poor tourmaline from granitic pegmatites. Synchrotron micro-XANES was used to detect the valence state of Fe in this crystal; it was found to have 93 ± 10% of the total Fe as Fe^{2+}. Optical absorption spectra show that the blue color is derived primarily from a combination of $^{[6]}$Fe^{2+}, together with $^{[6]}$Fe^{2+} interaction with a minor amount of $^{[6]}$Fe^{3+}.

Keywords: Fe-bearing olenite, chemical analyses, crystal structure, optical absorption spectra, Kuklík, Kutná Hora, Czech Republic.

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Sommaire

La bordure bleu pâle d'olénite sur un cristal noir de tourmaline de type olénite–schorl, provenant d'une pegmatite abyssale à Kuklík, près de Kutná Hora, en République Tchèque, a fait l'objet d'une caractérisation chimique et structurale. La formule optimisée, calculée à partir des données chimiques et structurales, est $^X(Na_{0.54}Ca_{0.14}K_{0.01}\square_{0.31})$ $^Y(Al_{2.15}Fe^{2+}_{0.78}Mn^{2+}_{0.06}Ti^{4+}_{0.01})$ $^Z(Al_{5.90}Mg_{0.10})$ $^T(Si_{5.60}Al_{0.40})$ B_3 O_{27} $^V[(OH)_{2.49}O_{0.51}]$ $^W(O_{0.99}F_{0.01})$, avec a 15.8838(3), c 7.1056(2) Å et $R = 0.017$. La longueur de la liaison Y–O relativement courte, 1.992 Å, confirme la teneur élevée de Al au site Y (~2.1 $apfu$). Ce résultat est semblable au cas de l'olénite de la localité-type, quoique l'olénite de Kuklík contient des teneurs importantes de Fe au site Y, et une proportion importante de $^{[4]}$Al (~0.4 $apfu$) au lieu de $^{[4]}$B sur le site T. Cette situation est confirmée par les résultats de l'ébauche de la structure, qui montre un allongement de la liaison T–O, jusqu'à ~1.626 Å. Cet échantillon d'olénite montre qu'un écart de la teneur stoechiométrique en Si ne veut pas nécessairement indiquer la présence de $^{[4]}$B dans une tourmaline alumineuse. Nous n'avons pu déceler aucun H sur le site O1 par affinement; la distribution sphérique des nuages d'électrons autour du site O1 sur la carte de différence-Fourier concorderait avec la conclusion que ce site est entièrement ou surtout occupé par l'oxygène et non l'hydroxyle. En termes de distorsion des angles entre les liaisons (σ_{oct}^2 de l'octaèdre ZO_6) *versus* la distance Y–O, l'olénite de Kuklík se situe entre les compositions contenant 3 (OH) sur le site V et la buergerite naturelle, qui contient 0.3 (OH) et 2.7 O au site V (site O3). La teneur en (OH), ~2.5 (OH) pfu, calculée pour une formule à charges balancées, concorde bien avec nos mesures et avec l'intensité intégrée des overtones OH dans la région de 7000 cm^{-1} (690 cm^{-2} par cm d'épaisseur), qui en fait une des plus faibles mesurées sur une tourmaline. Le groupe OH semble fortement ordonné sur le site O3. La composition de cet échantillon d'olénite montre une tendance vers la composition proposée du pôle olénite, qui ne contient qu'un seul groupe OH. La faible teneur en F (0.01 $apfu$) est inhabituelle pour une tourmaline riche en Al et pauvre en Mg provenant d'une pegmatite granitique. Nous nous sommes servi de spectres micro-XANES obtenus avec rayonnement synchrotron pour documenter la valence du fer; ce cristal contient 93 ± 10% du fer à l'état ferreux. Les spectres d'absorption optique montrent que la couleur bleue est surtout due au $^{[6]}Fe^{2+}$, avec une légère interaction avec la petite quantité de $^{[6]}Fe^{3+}$.

(Traduit par la Rédaction)

Mots-clés: olénite riche en Fe^{2+}, analyses chimiques, structure cristalline, spectres d'absorption optique, Kuklík, Kutná Hora, République Tchèque.

Introduction

Recent investigations of tourmaline show the high degree of chemical complexity in this group of minerals. In aluminous tourmalines, there are questions about the role of Al, Li and B as well as about the role of O and OH in the V and W sites. To help address these issues, specific types of aluminous tourmaline have recently been studied: Fe-bearing olenite to lithian olenite with tetrahedrally coordinated B (Ertl *et al.* 1997, Hughes *et al.* 2000, 2004, Kalt *et al.* 2001), lithian olenite with tetrahedrally coordinated B from the type locality of olenite (Schreyer *et al.* 2002), elbaite–rossmanite with tetrahedrally coordinated B (Tagg *et al.* 1999, Hughes *et al.* 2001) and synthetic olenite (Wodara & Schreyer 2001, Marler *et al.* 2002). However, questions still exist about the role of B in tourmaline, and in particular in aluminous tourmaline.

Cempírek & Novák (2003) pointed out that the chemical composition of Fe-bearing olenite from Kuklík, near Kutná Hora, Czech Republic, represents a special example of aluminous tourmaline. This sample contains a stoichiometric amount of B and negligible Li content. Hence it is an ideal specimen for further study of the role of Al in the tourmaline structure. Here we provide detailed chemical, structural and spectroscopic analyses of this aluminous tourmaline from an abyssal pegmatite at the Kuklík locality.

Occurrence and Paragenesis

Cempírek (2003) and Cempírek & Novák (2003) provided results of chemical analyses of different samples of aluminous tourmaline from small bodies of abyssal pegmatite located in the eastern part of the Moldanubicum (Gföhl Unit), Bohemian Massif, Czech Republic. The Kuklík pegmatite is the most evolved pegmatite in the region. Losert (1956) described the internal structure of the pegmatite and its mineral assemblages. The border zone consists of coarse-grained quartz + oligoclase + K-feldspar + tourmaline (I) + muscovite. The core zone is enriched in quartz and black to dark green tourmaline (I), commonly rimmed by pale blue (Kelley & Judd 1976) tourmaline (II) (Fig. 1), which also can form small individual crystals, together with abundant colorless to green dumortierite. It represents the latest primary (Al, B)-rich phase in the pegmatite (Cempírek 2003, Cempírek *et al.*, in prep.). The average composition of the black tourmaline (I) is close to $^X(Na_{0.5}Ca_{0.1}\square_{0.4})$ $^Y(Al_{1.6}Fe_{1.2}Mg_{0.1}Mn_{0.1})$ $^Z(Al_6)$ $^T(Si_{5.8}Al_{0.2})$ B_3O_{27} $[(OH)_{2.9}O_{1.1}]$, which belongs to the "oxy-schorl" – "oxy-foitite" series, in terms of the proposed classification (Hawthorne & Henry 1999). The rim of pale blue tourmaline (II) is even more enriched in Al, and it is the subject of our study.

EXPERIMENTAL

Sample selection

Pieces of the pale blue tourmaline (II), intergrown with quartz, were separated from a black to dark green euhedral crystal of tourmaline (I) found in the core zone (Fig. 1) [~8 mm in diameter, 2 cm in length; sample "Kuklík-2 (714)" of Cempírek 2003]. This material was used for chemical analysis, structure refinement, XANES spectra, and optical absorption spectra. The sample is deposited in the Moravian Museum, Brno, Czech Republic, no. a 301/1954.

Chemical analysis

The tourmaline crystals were analyzed with the Cameca SX100 electron microprobe at the Slovak Geological Survey, Bratislava, Slovakia, in the wavelength-dispersion mode (Table 1). Accelerating voltage was 15 kV, beam current 20 nA, and spot size 5 μm. We used the following standards: Na: albite, Ca, Si: wollastonite, K: orthoclase, Mg: MgO, Fe: Fe_2O_3, Mn: rhodonite, Cr: chromite, Al: Al_2O_3, Ti: TiO_2, Cl: NaCl, F: BaF_2. Counting time for all elements was 20 seconds. Data were reduced using the PAP routine.

The boron content was determined on a Cameca SX100 instrument at the Institute of Mineralogy, University of Hanover (accelerating voltage 10 kV, beam current 200 nA, spot size 10 μm; the amount of boron was established with a PC3 crystal, and borosilicate glass Verre 4 was used as standard). The boron content of the tourmaline was found to be stoichiometric (Table 1) and homogeneous within both black and blue types of tourmaline (Fig. 1).

The amount of B_2O_3 was calculated in the optimized formula as B = 3.00 *apfu* by assuming that there is no [4]B in this tourmaline sample; this assumption is confirmed by the structure refinements and a <*T*–O> distance of ~1.626 Å (see below). The ideal <*T*–O> bond-length (*T* site fully occupied by Si) has been determined to be ~1.620 Å in various structural studies (MacDonald & Hawthorne 1995, Bloodaxe *et al.* 1999, Ertl *et al.* 2001a, b).

The Li content was assumed to be insignificant because of the pegmatite's primitive signature, the absence of Li-enriched minerals, and the low contents of Li (<0.03 *apfu*) in black tourmaline from cogenetic abyssal pegmatites of the Kutná Hora region (Povondra 1981). A low level of Li is also indicated by an uncommonly low fluorine content (0.01 *apfu* F; Table 1); Li and F are usually positively correlated in aluminous tourmaline (*e.g.,* data in Dyar *et al.* 1998).

XANES spectroscopy

XANES (X-Ray Absorption Near-Edge Structure) measurements were made at the synchrotron X-ray microprobe (beamline X26A at the National Synchrotron Light Source of Brookhaven National Laboratory, N.Y.). The incident-beam energy was tuned using a Si(111) channel-cut monochromator that was scanned across the Fe *K* edge from low to high energy. This monochromatic beam is collimated to 350 μm diameter and then focused using a set of mutually orthogonal Kirkpatrick–Baez mirrors to a roughly 8 × 10 μm size. The structure of the Fe *K* absorption edge was scanned over the region from 7090 to 7200 eV. The incident X-ray energy was incremented in 0.3 eV steps over the most critical range in energy, –10 to +30 eV relative to the energy of the main absorption. Collection times of 10 live seconds per step were used (depending on Fe abundance). Peak energies were corrected using the position of the centroid of a magnetite standard from the National Museum of Natural History (Bajt *et al.* 1994), which is known to have an energy of 7113.25 eV (Petit *et al.* 2001, Wilke *et al.* 2001).

Optical absorption spectra

A fragment of the crystal containing a prism face was oriented and prepared as a 2.7 × 1.0 × 0.182 mm polished slab. The optical quality of the slab was poor owing to numerous fractures and inclusions. A comparatively clear region of the pale blue material measuring 0.1 × 0.1 mm was selected for the spectroscopic measurement. Polarized optical absorption spectra in the 380–1100 nm range were obtained at about 1 nm resolution with a locally built microspectrometer system

TABLE 1. CHEMICAL COMPOSITION OF OLENITE FROM KUKLÍK, KUTNÁ HORA, CZECH REPUBLIC

	olenite[1]	olenite[2]		olenite[1]	olenite[2]
SiO_2 wt.%	33.56	34.18	Si *apfu*	5.56	5.60
TiO_2	0.07	0.08	[4]Al	0.44	0.40
B_2O_3	10.42[3]	10.61			
Al_2O_3	43.44	43.76	Sum *T* site	6.00	6.00
FeO[#]	5.70	5.69			
MnO[#]	0.38	0.43	[3]B	2.98	3.00
MgO	0.40	0.41			
CaO	0.69	0.80	Al	8.05	8.05
Na_2O	1.63	1.70	Mg	0.10	0.10
K_2O	0.03	0.05	Ti^{4+}	0.01	0.01
F	0.02	0.02	Fe^{2+}	0.79	0.78
H_2O[d]	2.38	2.28	Mn^{2+}	0.05	0.06
O≡F	-0.01	-0.01			
			Sum *Y*, *Z* sites	9.00	9.00
Sum	98.71	100.00	Ca	0.12	0.14
			Na	0.53	0.54
			K	0.01	0.01
			Sum *X* site	0.66	0.69
			Sum cations	18.64	18.69
			OH	2.63	2.49
			F	0.01	0.01
			Sum OH + F	2.64	2.50

Note: [1] Average result of 15 EMP analyses. [2] Composition calculated from optimal site-occupancies and normalized to 100%. [3] Average result of 10 EMP spot-analyses. [4] H_2O was calculated for a charge-balanced formula, on the basis 15 *apfu* (*T* + *Y* + *Z*). [#] Total Fe and total Mn calculated as FeO (see text) and MnO. Cr and Cl are below the detection limit.
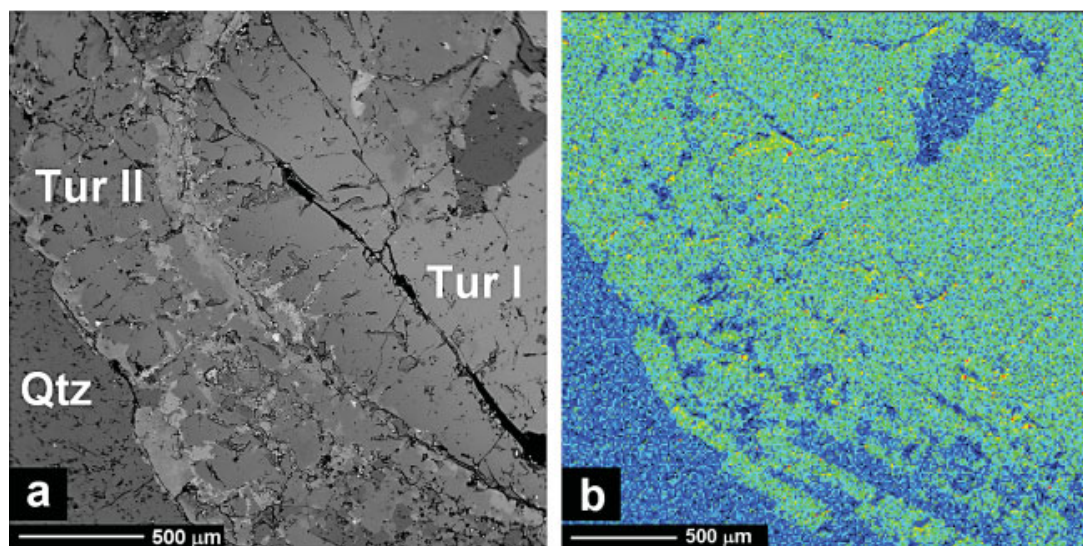
FIG. 1. a) Back-scattered-electron (BSE) image of tourmaline (I) with rim of tourmaline (II) from the coarse zone of the Kuklík pegmatite, Czech Republic. Brighter areas between tourmaline (I) and tourmaline (II) and within tourmaline (II) are secondary muscovite, dark areas are quartz. b) Map of boron distribution of approximately the same part of the sample.

at Caltech, consisting of a 1024-element Si diode – array detector coupled to a grating spectrometer system *via* fiber optics to a highly modified NicPlan infrared microscope containing a calcite polarizer. Pairs of conventional 10× objectives were used as objectives and condensers. One hundred scans were averaged for the optical spectrum. The near-infrared extension of the spectrum was obtained on a Nicolet Magna 860 FTIR with a silica beam-splitter, MCT–A detector, tungsten lamp, and $LiIO_3$ polarizer at 2 cm^{-1} resolution.

Crystal structure

Crystal KUK2RB (~100 μm in diameter) of the pale blue tourmaline (II) was mounted on a Bruker Apex CCD diffractometer employing graphite-monochromated Mo$K\alpha$ radiation. Redundant data were collected for an approximate sphere of reciprocal space, and were integrated and corrected for Lorentz and polarization

TABLE 2. CRYSTAL DATA AND RESULTS OF STRUCTURE REFINEMENT FOR OLENITE FROM KUKLÍK, CZECH REPUBLIC

Space group:	R3m
Unit-cell parameters (Å):	a 15.8838(3), c 7.1056(2)
Frame width, scan time:	0.20°, 15 s
number of frames, detector distance:	4500, 5 cm
Measured reflections, full sphere:	11,345
Unique reflections; refined parameters:	1,104; 94
R1, all data:	0.0169
Difference peaks (+, –):	0.31, 0.29
Goodness-of-fit:	1.082

factors using the Bruker program SAINTPLUS (Bruker AXS Inc. 2001).

The structures were refined using the Bruker SHELXTL V. 6.10 package of programs, with neutral-atom scattering factors and terms for anomalous dispersion. The refinement was done with anisotropic thermal parameters for all non-hydrogen atoms. Table 2 lists crystal data and details of structure refinement for the tourmaline sample. Table 3 contains the atom coordinates, equivalent-isotropic displacement parameters, and site occupancies. Table 4 contains selected bond-lengths. 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 quadratic programming methods, Wright *et al.* (2000) described a method of optimizing the site occupancies of cations in minerals with multiply occupied cation-sites. Using this method with structure refinement and chemical data obtained in this study, the structural formula of tourmaline sample KUK2RB is: $^X(Na_{0.54}Ca_{0.14}K_{0.01}\square_{0.31})$ $^Y(Al_{2.15}Fe^{2+}_{0.78}Mn^{2+}_{0.06}Ti^{4+}_{0.01})$ $^Z(Al_{5.90}Mg_{0.10})$ $^T(Si_{5.60}Al_{0.40})$ B_3 O_{27} $^V[(OH)_{2.49}O_{0.51}]$ $^W(O_{0.99}F_{0.01})$. The optimized formula minimizes the differences between the formula obtained by chemical analysis and that obtained by structure refinement. Even though XANES and optical spectroscopy indicate that there is a minor amount of Fe^{3+}, Fe^{2+} is used in the formula above. The absolute

uncertainty in the proportions of Fe^{3+} and Fe^{2+} is large, so it is impossible to accurately evaluate the proportion of Fe^{2+} and Fe^{3+}.

TABLE 3. ATOM POSITIONS AND EQUIVALENT-ISOTROPIC U IN OLENITE FROM KUKLÍK, CZECH REPUBLIC

Atom	x	y	z	U_{eq}	Occupancy
Na	0	0	3/4	0.0206(8)	0.729(9)
Si	0.80806(3)	0.81011(3)	0.9667(4)	0.00628(14)	0.960(4)
B	0.89037(9)	0.78075(18)	0.5162(5)	0.0094(4)	1.00
^{Y}Al	0.87802(4)	0.93901(2)	0.3328(4)	0.00940(17)	1.223(5)
^{Z}Al	0.70287(3)	0.73930(3)	0.3595(4)	0.00786(11)	1.00
O1	0	0	0.1965(5)	0.0226(6)	1.00
O2	0.93921(6)	0.87843(12)	0.4794(4)	0.0164(4)	1.00
O3	0.73841(14)	0.86921(7)	0.4605(4)	0.0142(3)	1.00
O4	0.90572(6)	0.81145(13)	0.8948(4)	0.0141(3)	1.00
O5	0.81252(13)	0.90626(7)	0.8717(4)	0.0147(3)	1.00
O6	0.80460(8)	0.81545(8)	0.1944(4)	0.0110(2)	1.00
O7	0.71296(8)	0.71324(7)	0.8910(4)	0.00969(19)	1.00
O8	0.79067(8)	0.72982(8)	0.5309(4)	0.0107(2)	1.00
H3	0.741(3)	0.8703(17)	0.580(7)	0.059(15)	1.00

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) FOR OLENITE FROM KUKLÍK, CZECH REPUBLIC

X-	O2 (×3)	2.548(3)	T-	O4	1.6232(7)	Z-	O3	1.982(1)
	O4 (×3)	2.789(2)		O5	1.6395(8)		O6	1.869(1)
	O5 (×3)	2.721(2)		O6	1.624(1)		O7	1.878(1)
Mean		2.686		O7	1.618(1)		O7'	1.933(1)
			Mean		1.626		O8	1.913(1)
							O8'	1.885(1)
Y-	O1	1.937(2)	B-	O2	1.367(3)	Mean		1.910
	O2 (×2)	1.974(1)		O8 (×2)	1.376(2)			
	O3	2.123(2)	Mean		1.373			
	O6 (×2)	1.973(1)						
Mean		1.992						

RESULTS AND DISCUSSION OF THE ARRANGEMENT OF ATOMS

XANES spectroscopy

The Fe XANES spectrum of the Kuklík olenite is shown in Figure 2. The Fe^{3+} content of the sample was determined through use of a calibration line relating pre-edge energy to % Fe^{3+}, utilizing three tourmaline standards from Dyar *et al.* (2001): schorl (18% Fe^{3+}), (Fe-bearing) dravite (54% Fe^{3+}), and (Fe-bearing) elbaite (0% Fe^{3+}). The resultant regression line has an R^2 value of 0.984. Different grains with random orientations were used to avoid the effects of preferred orientation (*cf.* Stein *et al.* 2004), except in the case of the unknown itself, for which we had only a single grain. The calculated % Fe^{3+} for the Kuklík olenite is 7 ± 10% using our estimated errors of ±10% absolute.

Optical spectra

The weak band near 430 nm (Fig. 3) is in the general region where Fe^{2+}–Ti^{4+} intervalence charge transfer is found in tourmalines (Smith 1977) and other minerals (Mattson & Rossman 1988). The bands near 715 nm (E ⊥ c), 780 nm (E ∥ c), and 1100 nm (E ⊥ c, E ∥ c) are typical of Fe^{2+} in tourmalines (Mattson & Rossman 1987). Other sharper features near 1450 and above 2200 nm are mostly due to vibrations of OH groups.

There is no direct evidence for ferric iron in this olenite from the optical spectrum because the characteristic Fe^{3+} bands are not evident. However, the spectrum provides clear, indirect evidence for a minor amount of Fe^{3+} from the unequal intensities of the Fe^{2+} bands in
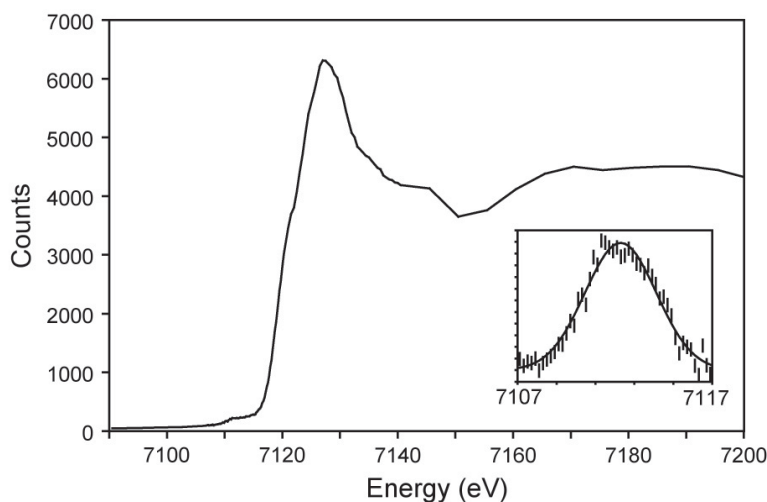

FIG. 2. Fe XANES spectrum of the Kuklík olenite, showing main edge-region and extracted pre-edge (inset).

the $E \perp c$ and $E \parallel c$ directions. Mattson & Rossman (1987) showed that where Fe^{3+} is absent in tourmaline, these bands have essentially equal intensity. Where the $E \parallel c$ direction has greater intensity than the $E \perp c$ direction, Fe^{3+} is present and is interacting with the Fe^{2+}. There are major quantitative differences between the spectra of tourmalines where a minor quantity of Fe^{3+} interacts with Fe^{2+} and those with much of the Fe^{3+} interacting with Fe^{2+}. From the best fit to Figure 6 in Mattson & Rossman (1987), the intensity of the Fe^{2+} band at 1100 nm in the olenite indicates that only ~1.2% of the Fe^{2+} in this olenite is interacting with Fe^{3+} in an adjacent Y site.

In principle, it should be possible to determine the concentration of Fe^{2+} from the bands in the $E \parallel c$ direction of the optical spectrum. Unfortunately, an absolute value of the molar absorption coefficient of Fe^{2+} for various species of tourmalines is not known. Mattson & Rossman (1987) showed in their Figure 5 that the value of this coefficient is usually less than 10. The calculated molar absorption coefficient of Fe^{2+} in olenite, 7.8, based on the 1100 nm band ($E \parallel c$), is consistent with Fe present mainly as $^{[6]}Fe^{2+}$ and with only a minor amount of $^{[6]}Fe^{3+}$. This is certainly consistent with the $7 \pm 10\%$ Fe^{3+} (relative to total Fe) found in the XANES analysis.

Crystal structure

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]. Grice & Ercit (1993), Hawthorne *et al.* (1993), and MacDonald & Hawthorne (1995) described significant amounts of Al at the T site in tourmaline. Our chemical analysis suggests that the olenite from Kuklík also contains $^{[4]}$Al (~0.4 *apfu*). This finding is supported by the structure refinement, which shows an enlarged $<T$–O$>$ bond-length of ~1.626 Å. The measured $<T$–O$>$
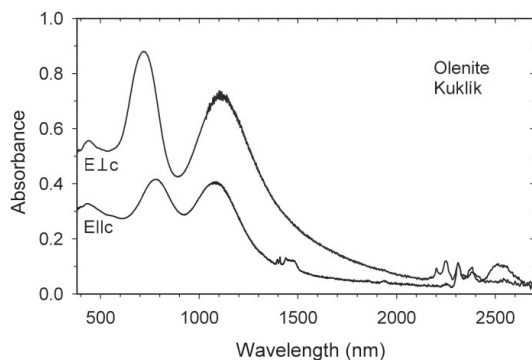

FIG. 3.   Optical absorption spectra of a single-crystal fragment of a blue, Fe-bearing olenite from Kuklík, Czech Republic. Sample thickness: 0.182 mm.

bond-length, ~1.626 Å (Table 4), is in very good agreement with the calculated $<T$–O$>$ bond-length of ~1.625 Å obtained by using formula (1) of Ertl *et al.* (2001a). Refinement of the T site with Si scattering factors, while fixing the Z site at $Al_{1.00}$, indicated that there was no significant deviation from a T site fully occupied with Si. Small amounts of Mg (0.10 *apfu*) were assigned to the Al-dominant Z site, because the $<Z$–O$>$ bond-length, 1.910 Å, is slightly enlarged compared to that in Fe-bearing olenite with similar Fe content (Hughes *et al.* 2004), which contains essentially no Mg ($<Z$–O$>$ = 1.907 Å).

The ~2.5 (OH) *pfu* content of the olenite from Kuklík, which was calculated for a charge-balanced formula, is distinctly lower than the usual 3 (OH) *pfu* at the O3 site of most tourmaline samples. Small amounts of Fe^{3+}, as were indicated by the XANES spectra (Fig. 2) and by optical absorption spectra (Fig. 3), require a decreased OH content to produce a charge-balanced formula. The integrated intensity of the OH overtones in the 7000 cm^{-1} region (690 cm^{-2} per cm thickness) in Figure 3 is one of the lowest measured to date for tourmaline. With the exception of buergerite, no other tourmaline has shown such a low intensity. "Oxy-rossmanite", the tourmaline richest in Al known to date, is occupied by $\sim OH_{2.80}$ (850 cm^{-2} per cm thickness) at the O3 site (Ertl *et al.* 2005). Note that Al- and B-rich olenite from Koralpe, Styria, Austria, which contains ~3.3 OH (Ertl *et al.* 1997, Hughes *et al.* 2000, Kalt *et al.* 2001), has an integrated intensity of 1030 cm^{-2} (Ertl *et al.* 2005). Although the rigorous calibration of this method of OH analysis is still in progress, this result suggests that the olenite from Kuklík has about 60 to 70% of the amount of OH normally found in common tourmalines of elbaite–schorl type in pegmatites.

In the absence of sufficient material, we were unable to undertake an analysis for H_2O by U-extraction, and because of relatively large errors on SIMS analytical procedures (and the lack of appropriate standards), we characterized the occupancy of OH by structural methods, which have the advantage that they are not influenced by fluid inclusions.

No H could be found at the O1 site by refinement, and the essentially spherical electron-density in the difference-Fourier map around the O1 site supports the conclusion that this site is only or mainly occupied by O and not by OH. On a bond-angle distortion (σ_{oct}^2 of the ZO_6 octahedron) – $<Y$–O$>$ distance diagram (Fig. 4), olenite from Kuklík lies between the tourmaline samples containing 3 (OH) at the V site, and natural buergerite, which contains 0.3 (OH) and 2.7 O at the V site (O3 site) (Dyar *et al.* 1998). Qualitatively, we can conclude that the amount of H3 is smaller than for a fully occupied H3 site. As a result, we have an OH content of < 3.0 OH *pfu* at the O3 site. The O1 site (W site) is occupied by $\sim(O_{0.99}F_{0.01})$. Such a very low fluorine content is uncommon for a natural aluminous
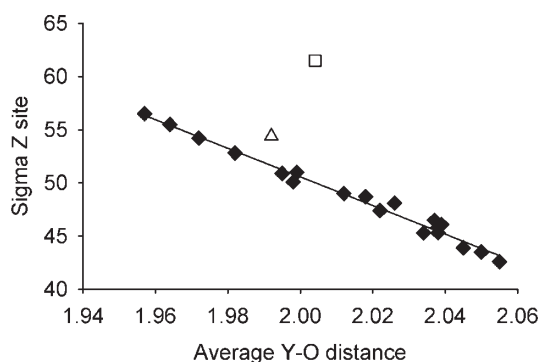
FIG. 4. Relationship between bond-angle distortion σ_{oct}^2 of the ZO_6 octahedron and the average Y–O distance [modified from Figure 3 from Ertl *et al.* (2002) (including the structural data from Hughes *et al.* 2004)]; diamonds: tourmalines with full *V*-site occupancy, open triangle: olenite from Kuklík (~2.5 OH at *V* site), open square: buergerite (0.3 OH at the *V* site). Regression line: $R^2 = 0.983$ (for all samples with 3 OH *pfu* at the *V* site).

and Mg-poor tourmaline found in granitic pegmatites (Novák *et al.* 2004).

Hawthorne & Henry (1999) cited the ideal formula of olenite as $NaAl_3Al_6[Si_6O_{18}](BO_3)_3O_3(OH)$, to produce a proper end-member. The occupancy of the O3 and O1 sites was modified by Hawthorne (2002) as $^{O3}[O_2(OH)]^{O1}(O)$. Because the strength of the hydrogen bond involving OH at O3 is stronger than the strength of the hydrogen bond involving OH at the O1 site (Hawthorne 2002), hydrogen atoms in tourmaline are strongly ordered at the O3 site (see also Taylor *et al.* 1995).

The relatively small <Y–O> bond-length, 1.992 Å, confirms the high content of Al at the Y site (~2.1 *apfu*); it is similar to that in olenite from the type locality (Schreyer *et al.* 2002). Sokolov *et al.* (1986) did not recognize that their most Al-rich olenite from the type locality contains significant amounts of Li, [IV]B and ~4(OH), as was shown by Schreyer *et al.* (2002). In contrast to olenite from the type locality, Olenii Range, Kola Peninsula, Russia, the olenite from Kuklík does not contain [IV]B or Li, and the (OH) content is less than 3 *pfu*.

This Fe-bearing olenite shows a trend toward the olenite end-member formula with only one OH group, as proposed by Hawthorne & Henry (1999), and $NaAl_3Al_6[Si_6O_{18}](BO_3)_3{}^V(O_2OH)^WO$, as modified by Hawthorne (2002). The results of this study should encourage further investigations into the possibility that there are olenite samples even more enriched in Al than our sample from Kuklík, possibly with a composition close to the proposed end-member formula of olenite with 1 OH group, as given by Hawthorne & Henry (1999) and Hawthorne (2002). Also, this tourmaline is a good example of ordering of OH groups at the O3 (*V*) site driven by bond-valence constraints.

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