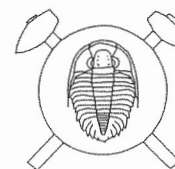# Potassium-bearing, fluorine-rich tourmaline from metamorphosed fluorite layer in leucocratic orthogneiss at Nedvědice, Svratka Unit, western Moravia

Draslík obsahující a fluorem bohatý turmalín z metamorfované fluoritové polohy v leukokratní ortorule z Nedvědice, svratecké krystalinikum (Czech summary)

(3 text-figs., 2 photos)

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Three tourmaline parageneses occur in orthogneiss and associated rocks at Nedvědice: (i) columns of black tourmaline, locally corroded, show patchy zoning with schorl > dravite rims and dravite > schorl cores, and occur in a metamorphosed fluorite layer; (ii) black columnar crystals of accessory to subordinate homogeneous schorl from leucocratic orthogneiss are locally concentrated in thin bands or in elongated clusters with quartz and muscovite; (iii) black columnar tourmaline crystals with schorl > dravite rims and dravite > schorl cores are heterogeneous in thin section and BSE images, and occur in muscovite >> biotite schists. Tourmaline from all three parageneses is characterized by high F (up to 0.77 apfu) and K (up to 0.09 apfu) in tourmaline from the metamorphosed fluorite layer. Two dominant substitutions were recognized in tourmaline: (1) Fe <-> Mg substitution in schorl-dravite from mica schists and metamorphosed fluorite layer; and (2) OH <-> F substitution typical for tourmaline from all rock types. Potassium rarely substitutes for Na at the X-site in the tourmaline structure. The chemical compositions suggest that K <-> Na, KFe^{3+} <-> NaAl and/or $NaFe^{2+}OH$ <-> $KFe^{3+}O$ substitutions may be responsible for K in tourmaline from Nedvědice.

Key words: tourmaline, electron microprobe, metamorphosed fluorite layer, orthogneiss, mica schist, Nedvědice, Svratka Unit, Czech Republic

Introduction

Compositional variation of the X-site cations in tourmaline has previously focused on Na and Ca. Only recently, the abundance of significant vacancies in the X-site was recognized with the identification of two new X-site deficient tourmalines - foitite $\square$ $(Fe_2Al)Al_6(BO_3)_3Si_6O_{18}(OH)_4$ (MacDonald et al. 1993) and rossmanite $\square$ $(Al_2Li)Al_6(BO_3)_3Si_6O_{18}(OH)_4$ (Selway et al. 1997). Similarly, K was previously considered to be a rare cation at the X-site in the tourmaline group minerals. Wet-chemical analyses with K contents up to 0.80 wt.% K_2O, were sporadically reported (e.g., Deer et al. 1986). However, electron microprobe study (unpubl. data of the authors) of K-bearing tourmalines from the Czech Republic (Povondra 1981, Povondra et al. 1985, Němec 1989) indicated that high K contents are likely due to microscopic impurities (e.g., mica or K-feldspar). So far, the highest K content determined by electron microprobe occur in povondraite (formerly known as ferridravite) and particularly in the K-dominant tourmaline from Alto Chapare, Bolivia, with up to 0.98 to 2.35 wt.% K_2O (Walenta - Dunn 1979, Grice et al. 1993, Žáček et al. 1998). Other K-enriched tourmalines known to date include dravite-buergerite (up to 0.31 wt.% K_2O) from the Bottino mining district, Apuane Alps, Italy (Benvenuti et al. 1991) and dravite-schorl (up to 0.35 wt.% K_2O) from tourmalinite at Pernštejn, Czech Republic (Houzar et al. 1997).

A systematic study of tourmaline from various rock types in Czech Republic (Novák - Selway 1997, author's unpubl. data) agree with the previous report that K is a very rare cation in tourmaline and it is commonly below the detection limit of the electron microprobe. Remarkably high K contents (K_2O = 0.27-0.43 wt.%) in F-rich tourmaline from a metamorphosed fluorite layer in a leucocratic orthogneiss at Nedvědice are discussed in this paper.

Geological setting and occurrence

Medium- to coarse-grained lepidoblastic schists are typical rocks in the Svratka Unit. They are interlayered with fine-grained two-mica paragneiss, rare marbles, Fe-skarns, amphibolites and tourmalinites. Numerous bodies of various types of orthogneiss also occur in this region (Němec 1980). A tourmaline-bearing muscovite > biotite orthogneiss constitutes a distinct variety of these rocks, forming a well-defined discontinuous belt separated into discrete bodies, along the eastern border of the southern part of the Svratka Unit (Němec 1980, Melka et al. 1992). Leucocratic orthogneiss at Nedvědice forms a N-S trending elongate body about 100 m thick and up to 1 km long, enclosed in mica schists. The foliation of the orthogneiss is continuous with, and parallel to, the foliation of the host rocks. The P-T conditions of the regional medium grade metamorphism have not been studied in detail. They may be similar to the metamorphic conditions of the metapelites at Pernstejn, situated about 2 km SW of Nedvědice (Pertoldová et al. 1987), with T = 600-750 °C and P ~ 5 kbar.

The protolith of the Nedvědice orthogneiss is a highly evolved, leucocratic, peraluminous granite. It is depleted in Sr, Zr, Cr and REE, but is distinctly enriched in Rb (300-400 ppm), K/Rb = 84-114, and in Ga (about 25 ppm). A negative Eu-anomaly and HREE > LREE are typical. Němec (1986) reported 0.52 to 0.69 wt.% F in orthogne-

iss from Nedvědice, and the muscovite is extremely F-rich (Němec 1979). Abundant primary fluorite and tourmaline indicate elevated F and B activities in the original melt (London et al. 1996).

A regionally metamorphosed fluorite layer with abundant tourmaline is up to 3 cm thick and several m long. Its foliation is comparable to that of the host rock; however, tourmaline crystals enclosed in fluorite exhibit a low degree of preferred orientation, similar to tourmaline from the coarse-grained pegmatitic pods locally present in the orthogneiss body (Novák et al. 1997). This fluorite layer is distinct from dark violet fluorite crystals occurring on tourmaline-free fissures penetrating discordantly the orthogneiss.

Petrography of the metamorphosed fluorite layer and associated rock

Metamorphosed fluorite layer

The fluorite layer contains abundant columnar black tourmaline, muscovite and rare quartz are concentrated along the contact with the surrounding orthogneiss. Fine- to coarse-grained fluorite is violet to pink-violet. Based on mineral composition and textures, the fluorite layer may represent a hydrothermal vein which underwent regional metamorphism. The tourmaline is completely surrounded by fluorite grains and is locally corroded. Black columnar crystals of tourmaline, up to 2 cm long, show strong pleochroism O = dark greenish to bluish grey, E = colourless to pale bluish green; this is different from the tourmalines with brown pleochroism in other parageneses at Nedvědice. Tourmaline from the fluorite layer also exhibits widespread patchy zoning with Mg-enriched domains (Photo 1) which is unknown in the other parageneses.

Orthogneiss

Leucocratic, medium-grained muscovite to muscovite > biotite orthogneiss, locally with accessory to minor tourmaline. The average modal composition is (in vol.%) 40.0 quartz, 27.7 K-feldspar, 17.8 plagioclase, 9.3 muscovite, 3.7 biotite and 1.5 tourmaline (Němec 1979); accessory minerals include apatite, zircon, rutile and fluorite. Tourmaline is locally concentrated in very thin bands or elongated clusters along schistosity planes with abundant quartz and flakes of F-rich muscovite. The feldspar-rich bands are relatively poor in tourmaline. Coarse-grained pegmatitic pods with coarse-grained K-feldspar and tourmaline, and poorly developed foliation of tourmaline locally present within the orthogneiss body. Tourmaline from the leucocratic orthogneiss forms black columnar crystals, commonly about 1 cm long, but up to 3 cm long in the coarse-grained pegmatitic variety. It is homogeneous with strong pleochroism: O = dark brown, E = pale yellowish brown.

Photo 1. BSE image of tourmaline from metamorphosed fluorite layer. Euhedral crystal of tourmaline contains small fluorite inclusions (bright). Dravite-schorl domains (dark) within the Mg-rich schorl crystal

Intercalations of mica schist

Two types of mica schists were recognized: (i) Medium-grained two-mica (muscovite >> biotite) quartz-rich schist with abundant columnar crystals of tourmaline is the most widespread type. Black columnar tourmaline crystals, up to 1 cm long, are similar in appearance to those from the orthogneiss, but exhibit increased preferred orientation (i.e., foliation and lineation). Tourmaline is heterogeneous in thin section and BSE images show Fe-enriched rims. It shows strong pleochroism: the core has O = dark yellowish brown, E = pale yellowish brown, and the rim has O = dark brown, E = pale brown. (ii) Rare, fine-grained muscovite schist with abundant fine-grained tourmaline resembles, in hand specimen, tourmaline-rich muscovite-bearing quartzite from Pernštejn (Houzar et al. 1997).
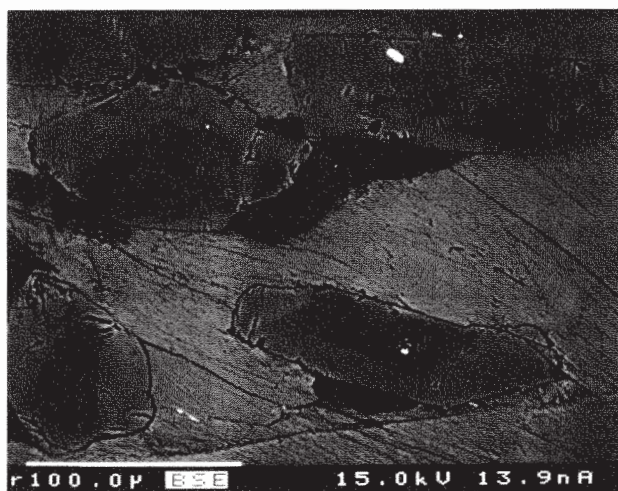

Photo 2. BSE image of tourmaline from medium-grained mica schist. Zoned crystals are enclosed in K-feldspar (bright) and quartz (black). Dravite core (dark) is rimmed and locally cut by schorl-dravite (intermediate bright)

Tourmaline grains are locally zoned with Fe-enriched rims (Photo 2) and have the pleochroism as tourmaline in two-mica schist. Notice fine patchy or vein-like zoning in all samples examined (Photos 1 and 2). It is typical for tourmaline crystallized from hydrothermal fluids.

Chemical composition

Electron-microprobe analysis was done in WDS (wavelength-dispersive) mode on a Cameca SX-50 instrument, Department of Geological Sciences, University of Manitoba, Winnipeg, with a beam diameter of 1 μm and accelerating potential of 15 kV. A beam current of 20 nA was used for Si, Al, Fe, Mg, Ca and Na, and a current of 40 nA for P, Ti, Mn, Zn, F and K; the counting time for all elements was 20 s. The detection limit of 3 sigma for K_2O is 0.027 wt.% which was calculated using L.D. = [3(wt.% oxide)(Rb/tb)1/2]/(Rp-Rb), where Rb = background count-rate (counts/s), tb = background count-time (s), Rp = peak count-rate (counts/s). The following standards were used for K_α X-ray lines: Si, Ca-diopside; Al-kyanite; Fe-fayalite; Ti-rutile; Mg-pyrope; Mn-spessartine; Na-albite; K-orthoclase; P-apatite; F-fluor-riebeckite and Zn-gahnite. Data were reduced using the PAP routine (Pouchou - Pichoir 1985).

Tourmaline has the general formula $X\ Y_3\ Z_6\ (BO_3)_3$ T_6O_{18} (O, OH)$_3$ (OH,F)$_1$, where X = Na, Ca, vacancy and K; Y = Li, Fe^{2+}, Mg, Mn, Zn, Al, Cr^{3+}, V^{3+}, Fe^{3+}, Ti; Z = Al, Mg, Fe^{3+}, Cr^{3+}, V^{3+}; and T = Si, Al. The structural formulae were calculated on the basis of 31 anions assum OH + F = 4, and B = 3 atoms per formula units (apfu). These recalculated compositions have oxide totals of approximately 100 wt.% and the Y-site totals are close to the ideal value of 3.0 apfu.

The three paragenetic types of tourmaline from Nedvědice have quite different chemical compositions (Tables 1, 2). Fluorite layers contain K-bearing schorl-dravite rims and dravite-schorl cores; orthogneiss contains schorl; the mica schist contains schorl-dravite rims and dravite-schorl cores.

T-site and Z-site

Tourmaline from all paragenetic types commonly have a T-site fully occupied by Si. The slight Si excess (up to 0.14 apfu) may suggest that OH + F < 4 (Taylor et al. 1995). The Z-site is occupied mostly by Al in tourmaline from all paragenetic types. However, some tourmaline compositions, particularly from mica schists have Al < 6 with up to 5.75 apfu total Al, hence Mg very likely enters the Z-site (Fig. 1a; Tables 1, 2).

Table 1. Representative compositions (wt.% and apfu) of tourmaline from metamorphosed fluorite layer

	1	2	3	4	5	6	7	8	9
SiO_2	34.70	35.00	35.80	35.10	35.10	35.50	35.30	35.30	35.80
TiO_2	0.40	0.33	0.24	0.23	0.27	0.27	0.09	0.10	0.10
B_2O_3 *	10.20	10.21	10.32	10.13	10.16	10.24	10.39	10.34	10.56
Al_2O_3	31.30	31.00	30.50	30.00	30.10	30.20	32.00	31.60	32.30
MgO	2.95	3.05	4.29	3.99	4.22	4.01	5.89	5.49	6.39
CaO	0.16	0.16	0.08	0.07	0.07	0.05	0.06	0.04	0.06
MnO	0.10	0.12	0.07	0.01	0.06	0.01	0.00	0.04	0.06
FeO **	13.40	13.50	12.30	12.70	12.40	13.00	9.15	9.71	8.91
ZnO	0.10	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
Na_2O	2.59	2.48	2.50	2.48	2.46	2.56	2.50	2.56	2.69
K_2O	0.09	0.07	0.40	0.35	0.43	0.31	0.34	0.34	0.38
F	1.19	1.18	1.28	1.21	1.13	1.24	1.31	1.18	1.36
H_2O *	2.96	2.96	2.95	2.92	2.97	2.95	2.96	3.01	3.00
O=F	-0.50	-0.50	-0.54	-0.51	-0.48	-0.52	-0.55	-0.50	-0.57
TOTAL	99.64	99.58	100.20	98.69	98.90	99.82	99.45	99.21	101.03
T-Si	5.91	5.96	6.03	6.02	6.00	6.02	5.91	5.94	5.90
Al	0.09	0.04	-	-	-	-	0.09	0.06	0.10
Z-Al	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
Y-Ti	0.05	0.04	0.03	0.03	0.04	0.03	0.01	0.01	0.01
Al	0.19	0.18	0.06	0.06	0.07	0.04	0.22	0.20	0.17
Mg	0.75	0.77	1.08	1.02	1.08	1.01	1.47	1.38	1.57
Mn^{2+}	0.01	0.02	0.01	0.00	0.01	0.00	0.00	0.01	0.01
Fe^{2+}	1.91	1.92	1.73	1.82	1.77	1.85	1.28	1.37	1.23
Zn	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ΣY	2.92	2.93	2.91	2.93	2.97	2.93	2.98	2.97	2.99
X-Ca	0.03	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Na	0.86	0.82	0.82	0.83	0.82	0.84	0.81	0.84	0.86
K	0.02	0.02	0.09	0.08	0.09	0.07	0.07	0.07	0.08
ΣX	0.91	0.87	0.92	0.92	0.92	0.92	0.89	0.92	0.95
F-	0.64	0.64	0.68	0.66	0.61	0.67	0.69	0.63	0.71
OH-	3.36	3.36	3.32	3.34	3.39	3.33	3.31	3.37	3.29

* - calculated from stoichiometry. ** total Fe as FeO.
Sample T41-1, from rim to core; 1, 2 - narrow outer rim; 3-6 - dominant intermediate zone; 7-9 - patchy zoned core

Table 2. Representative compositions (wt.% and apfu) of tourmaline from orthogneiss and mica schists

	1	2	3	4	5	6	7	8
SiO_2	35.07	33.70	34.60	34.80	35.10	35.20	36.30	36.10
TiO_2	0.74	0.94	0.21	0.21	1.46	0.93	0.68	0.48
B_2O_3*	10.07	9.98	10.08	10.03	10.09	10.18	10.46	10.52
Al_2O_3	29.59	30.10	30.90	30.50	28.40	29.30	30.70	31.80
Fe_2O_3	0.36	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MgO	2.01	1.45	0.56	0.30	3.39	4.31	5.37	6.68
CaO	0.36	0.21	0.10	0.08	0.31	0.53	0.25	0.03
MnO	0.13	0.08	0.07	0.08	0.05	0.10	0.08	0.12
FeO**	14.47	16.30	17.30	17.40	13.90	12.50	10.30	7.30
ZnO	n.d.	0.13	0.05	0.00	0.06	0.00	0.00	0.00
Li_2O	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Na_2O	2.24	2.52	2.39	2.46	2.60	2.43	2.58	2.75
K_2O	0.20	0.12	0.07	0.04	0.09	0.09	0.06	0.06
F	2.06	0.99	1.23	1.14	1.00	1.25	1.17	1.28
H_2O*	2.57	2.98	2.89	2.92	3.01	2.92	3.05	3.02
O=F	-0.87	-0.42	-0.52	-0.48	-0.42	-0.53	-0.49	-0.54
TOTAL	100.86	99.09	99.94	99.48	99.04	99.22	100.51	99.58
T-Si	5.98	5.87	5.97	6.03	6.04	6.01	6.03	5.97
Al	0.02	0.13	0.03	-	-	-	-	0.03
Z-Al	5.94	6.00	6.00	6.00	5.76	5.89	6.00	6.00
Mg	-	-	-	-	0.24	0.11	-	-
Fe^{3+}	0.06	-	-	-	-	-	-	-
Y-Ti	0.10	0.12	0.03	0.03	0.19	0.12	0.09	0.06
Al	-	0.05	0.25	0.23	-	-	0.01	0.19
Fe^{3+}	0.17	-	-	-	-	-	-	-
Mg	0.55	0.38	0.14	0.08	0.63	0.99	1.33	1.65
Mn^{2+}	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.02
Fe^{2+}	2.06	2.37	2.50	2.52	2.00	1.78	1.43	1.01
Zn	0.00	0.02	0.01	0.00	0.01	-	-	-
Li	-	-	-	-	-	-	-	-
ΣY	2.90	2.95	2.94	2.87	2.84	2.90	2.91	2.93
X-Ca	0.07	0.04	0.02	0.02	0.06	0.10	0.05	0.01
Na	0.74	0.85	0.80	0.83	0.87	0.80	0.83	0.88
K	0.04	0.03	0.02	0.01	0.02	0.02	0.01	0.01
ΣX	0.93	0.92	0.84	0.86	0.95	0.92	0.89	0.90
F^-	1.11	0.55	0.67	0.63	0.55	0.68	0.62	0.67
OH^-	2.92	3.45	3.33	3.37	3.45	3.32	3.38	3.33

*calculated from stoichiometry; **total Fe as FeO except the analysis No. 1.

1-4 - orthogneiss, 1 - Povondra (1981); 5, 6 - mica schist; 7, 8 - fine-grained mica schist

Y-site

In the fluorite layer, tourmaline shows a wide variation in Fe (1.23-1.94 apfu) and Mg (0.76-1.60 apfu) (Fig. 1b). The slightly elevated Al contents at the Y-site typically range from 0.00 to 0.54 apfu (Fig. 1a). The Ti contents are low (Ti < 0.05 apfu) and increase from core to rim (Table 1); there is a good negative correlation of Ti with Mg (Fig. 1c).

The almost pure schorl from orthogneiss is rather homogeneous with a narrow range in Fe and Mg (Fig. 1b). Low Al contents at the Y-site (0.00-0.33 apfu), are typical (Fig. 1a). The Ti contents are usually low to moderate, from 0.03 up to 0.17 apfu (Fig. 1c).

Tourmaline from mica schists shows a wide variation in Fe and Mg contents and a moderate range in Al content (Fig. 1a,b). Titanium contents are low to moderate, from 0.05 up to 0.19 apfu (Fig. 1c). Titanium and particularly Fe are enriched in the rims, whereas Mg is enriched in the cores of crystals, and there is a good negative correlation of Ti to Mg (Fig. 1c). All tourmaline samples from Nedvědice have Mn and Zn usually below the detection limits of the electron microprobe (Tables 1, 2).

X-site

Tourmaline in the fluorite layer has relatively low X-site vacancies ranging (Fig. 2). The K contents vary from 0.06 to 0.09 apfu (up to 0.43 wt.% K_2O) (Figs. 1d,e; 3). A narrow K-depleted outer zone with up to 0.07 wt.% K_2O was found in one crystal (Table 1).

Schorl from orthogneiss is characterized by low but variable vacancies at the X-site (Fig. 2). Slightly elevated K contents, up to 0.04 apfu, were detected in most analyses (Fig. 1d,e).

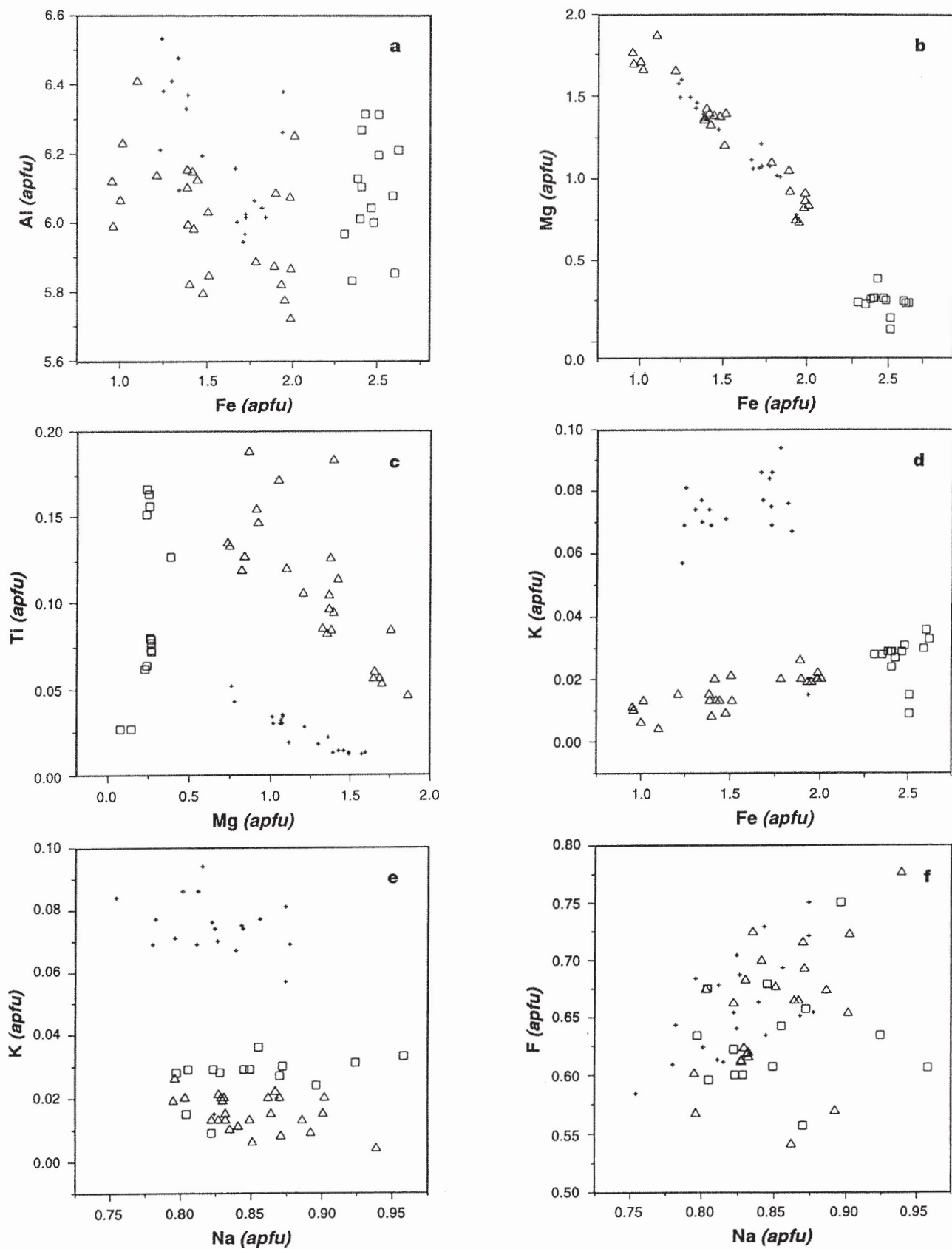Tourmaline in mica schists has Ca ranging from 0.02 to 0.12 apfu, but a lower X-site vacancy (Fig. 2).

Fig. 1. Composition of tourmaline from fluorite layer, orthogneiss and mica schists given in atoms per formula unit (apfu) tourmaline from fluorite layer - *crosses;* tourmaline from othogneiss - *squares;* tourmaline from mica schist - *triangles.* a - Al_{tot} versus Fe_{tot}; b - Mg versus Fe; c - Ti versus Mg; d - K versus Fe; e - K versus Na; f - F versus Na

Fig. 2. Composition of tourmaline from fluorite layer, orthogneiss and mica schists in the X-site vacancy-Na-Ca diagram. Same symbols in Fig. 1.
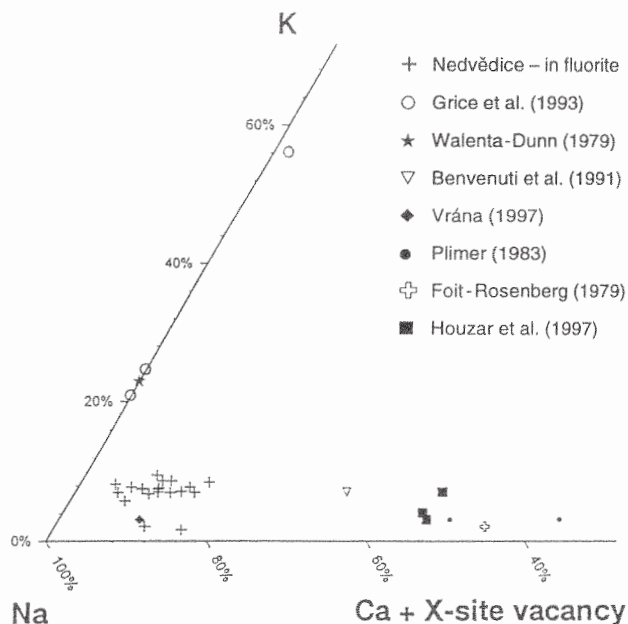
Fig. 3. Composition of K-bearing tourmalines in the K-Na-(Ca + X-site vacancy) diagram

Monovalent anions

Variable moderate-to-high F contents are typical for all paragenetic types of tourmaline at Nedvědice. All tourmalines share a similar range in F contents: the fluorite layer - 0.58 to 0.75 apfu, the orthogneiss - 0.55 to 0.73 apfu and the mica schists - 0.53 to 0.77 apfu F. A positive correlation between Na and F occurs in all paragenetic types (Fig. 1f).

Discussion

Tourmaline from the individual parageneses have different chemical compositions, reflecting their different premetamorphic origins.

Schorl from orthogneiss exhibits chemical characteristics (Fe >> Mg, high F) typical of tourmaline from Li-poor pegmatites and granites (Povondra 1981, Manning 1982, Henry - Guidotti 1985, London - Manning 1995). Consequently, the schorl very likely crystallized from a highly evolved B- and F-rich granitic melt. Wet-chemical analysis of schorl from the orthogneiss (Povondra 1981) yielded an extremely high F content - 2.06 wt.% F or 1.11 apfu F (Table 2, anal. no 1). Such high F-content is in contradiction with the experimental data which limit F contents in tourmaline up to 1.00 apfu (Robert et al. 1997). Extremely high F and elevated Ca contents in the wet-chemical analysis (Table 2) may be caused by fluorite impurities.

Heterogeneous schorl-dravite from mica schists exhibits the compositional characteristics (variable Fe/Mg ratio, relatively low Al contents) typically of in tourmaline from metapelites when not coexisting with an Al-saturating phase (Henry - Guidotti 1985). However, the very high F-content is remarkable; this tourmaline probably formed by reaction of B- and F-rich fluids released from the granite with the metapelite envelope. There are no other known localities of metamorphosed fluorite + tourmaline layers to compare with Nedvědice. The Ca content in the tourmaline is very low, whereas the F content is high and similar to that in tourmaline from the mica schists and orthogneiss (Fig. 1f). Assuming Ca- and F-saturation conditions during tourmaline precipitation, Ca and F were significantly preferentially partitioned into fluorite over tourmaline. Subsequent recrystallization during medium-grade regional metamorphism probably did not change the primary composition of the tourmaline. Only the narrow K-depleted rims around tourmaline grains from the fluorite layer (similar in composition to rims around tourmaline grains from mica schists) may be a product of regional metamorphism.

Several substitution mechanisms occur in tourmaline from all three parageneses. Homogeneous schorl from the orthogneiss has a narrow range in Fe, Mg and Al contents, and possibly a weak heterovalent substitution Na for vacancy at the X-site (Fig. 2). Heterogeneous schorl-dravite from the mica schists and from the metamorphosed fluorite layer is characterized by the dominant homovalent substitution Fe $\leftrightarrow$ Mg. A weak substitution Ca $\leftrightarrow$ Na also occurs in tourmaline from mica schists. Moderate to high F contents ranging from 0.71 to 1.43 wt.% F are typical for all tourmalines at Nedvědice (Němec 1979, Novák et al. 1997).

Potassium in tourmaline

Relatively low K content and the absence of Fe^{3+}/Fe^{2+} and H_2O determinations for the K-bearing tourmaline from the fluorite layer make it difficult to predict a reliable substitution mechanism for K at the X-site. There is a weak positive correlation between K and Fe (Fig. 1d) and a weak negative correlation between Na and K (Fig. 1e), and bet-

ween Al and Fe (Fig. 1a) in tourmaline from fluorite layer. These correlations suggest the following substitutions: K <-> Na, KFe^{3+} <-> NaAl and/or $KFe^{3+}O$ <-> $NaFe^{2+}OH$.

Comparison of the chemical composition of K-enriched tourmalines from Nedvědice with those in the literature (Fig. 3) show two different compositional types: (i) K- and Fe-rich, Al-poor tourmalines with very low vacancies at the X-site or a slight surplus of X-site cations (Walenta - Dunn 1979, Benvenuti et al. 1991, Grice et al. 1993, Vrána 1997, Žáček et al. 1998). Some of these compositions are extremely Fe-rich, with up to 6.84 apfu total Fe (Fe^{3+} > Fe^{2+}), and Al-poor, up to 0.2 apfu Al total (Grice et al. 1993). (ii) Al-rich dravite to schorl, commonly with high vacancies at the X-site (Foit - Rosenberg 1979, Plimer 1983, Houzar et al. 1997), only a minor amount of K and unknown Fe^{3+}/Fe^{2+} ratios. Both types are Li-poor, with highly variable F content and Fe/Mg ratios.

Structural data of Grice et al. (1993) indicate that K enters the X-site in the tourmaline structure. Expansion of the Z-site octahedron due to Fe^{3+} for Al substitution (Grice et al. 1993) and the accompanying expansion of the X-site polyhedron is likely responsible for the large K cation entering the X-site. Potassium substitutes for Na in povondraite and associated K-dominant tourmaline (Grice et al. 1993), and in rock-forming minerals (e.g., amphiboles). Good negative correlation K-Al and K-Na in povondraite (Žáček et al. 1998) indicates the substitution KFe^{3+} <-> NaAl a dominant mechanism. However, there is only a slight negative correlation between Na and K in K-bearing tourmaline from Nedvědice, suggesting a more complex substitution mechanism.

Conclusions

Three paragenetic types of tourmaline occur in Nedvědice: heterogeneous schorl-dravite from metamorphosed hydrothermal fluorite layer, homogeneous schorl from leucocratic orthogneiss and heterogeneous schorl-dravite from mica schists. Tourmaline from all three parageneses is characterized by high F (up to 0.77 apfu) low Al at the Y-site and elevated K (up to 0.09 apfu) in the tourmaline from fluorite layer.

Following substitutions occur: dominant Fe <-> Mg substitution occurs in schorl-dravite from mica schists and the metamorphosed fluorite layer, and significant OH <-> F substitution is typical of all tourmaline types. Subsequent recrystallization during regional metamorphism likely did not change the primary composition of the tourmaline from all paragenetic types. Only the narrow K-depleted rims around tourmaline grains from the fluorite layer (similar in composition to rims around tourmaline grains from mica schists) may be a product of regional metamorphism.

Two different compositional types of K-enriched tourmaline were recognized in the literature; (i) Fe-rich, Al-poor tourmalines with very low vacancies at the X-site or a slight surplus of X-site cations, and (ii) relatively Al-rich dravite-to-schorl with high vacancies at the X-site. The substitution KFe^{3+} <-> NaAl is likely responsible for the K substitution into povondraite and K-dominant tourmaline (Grice et al. 1993, Žáček et al. 1998), but more complex coupled substitution may be responsible for the K in tourmaline from Nedvědice.

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Draslík obsahující a fluorem bohatý turmalín z metamorfované fluoritové polohy v leukokrátní ortorule z Nedvědice, svratecké krystalinikum

Tři odlišné parageneze turmalínu byly zjištěny v nedvědické ortorule a horninách v ní uložených. (i) V metamorfované fluoritové poloze se vyskytují sloupce černého zonálního turmalínu s dravitem bohatým jádrem a skorylem bohatým okrajem. (ii) Černé, chemicky homogenní, sloupcovité krystaly skorylu se objevují v leukokratní ortorule a jsou většinou koncentrovány do tenkých poloh bohatých křemenem a muskovitem. (iii) Černá zrna zonálního turmalínu s dravitem bohatými jádry a skorylem bohatými okraji se vyskytují v muskovitickém svoru se vzácným biotitem. Turmalín ze všech paragenezí je bohatý fluorem (až 0,77 apfu F), turmalín z fluoritové polohy je bohatý draslíkem (až 0,09 apfu K). V turmalínu se uplatnily dvě hlavní substituce: 1. Fe<->Mg ve skoryl-dravitu z metamorfované fluoritové polohy a ze svoru, 2. substituce OH<->F ve všech typech turmalínu. Komplikované chemické složení turmalínu z Nedvědice naznačuje, že K může zastupovat Na podle následujících substitucí K<->Na, KFe^{3+}<->NaAl a/nebo $NaFe^{2+}OH$<->$KFe^{3+}O$.