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FOITITE: FORMATION DURING LATE STAGES OF EVOLUTION OF COMPLEX GRANITIC PEGMATITES AT DOBRÁ VODA, CZECH REPUBLIC, AND PALA, CALIFORNIA, U.S.A.

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ABSTRACT

Zoned crystals of tourmaline (elbaite–foitite) were found in pockets of the lepidolite-subtype granitic pegmatites at Dobrá Voda, western Moravia, Czech Republic, and the White Queen mine, Pala, San Diego County, California. Zoned crystals consist of pale pink, colorless and greenish Fe-poor elbaite, blue, violet or green Fe-rich elbaite, and dark violet to black foitite. Elbaite–foitite is associated with quartz, cookeite, albite and apatite at Dobrá Voda, and with albite, quartz, K-feldspar, beryl, and muscovite at the White Queen mine. Chemical compositions of foitite and associated Fe-poor to Fe-rich elbaite are similar at both localities, and exhibit an *X*-site vacancy (≤0.78 *apfu*, in foitite), and variable amounts of Ca (≤0.05 *apfu*), Mn (≤0.47 *apfu*) and F (≤0.75 *apfu*, in elbaite), in contrast to foitite that in many cases is F-free. Two distinct stages of late Fe-enrichment in tourmaline were recognized, in contrast to Fe-depletion, noted in many granitic pegmatites. The first stage is generally characterized by increasing Fe and Na, and decreasing Al and Li contents; three substages show the following substitutions: (i) $R_2(\text{LiAl})_{-1}$, $\text{Na}R_2(\text{OH})(^{X}\square\text{Al}_2\text{O})_{-1}$ and $(\text{OH})\,\text{F}_{-1}$ for elbaite containing <0.3 Fe *apfu* at Dobrá Voda ($R = \text{Fe}_{\text{tot}} + \text{Mn} + \text{Mg} + \text{Zn}$); (ii) $\text{Na}\,R_2(\text{OH})(^{X}\square\text{Al}_2\text{O})_{-1}$ or $\text{NaR}\,(^{X}\square\text{Al})_{-1}$ and $\text{F}\,(\text{OH})_{-1}$ for Fe-rich elbaite with 0.5–1.0 Fe *apfu*; (iii) $\text{AlO}_2\,[\text{Li}(\text{OH})_2]_{-1}$ and $(\text{OH})\,\text{F}_{-1}$, perhaps combined with $R_2\,(\text{LiAl})_{-1}$ for Fe-rich elbaite with 1.0–1.3 Fe *apfu* at the White Queen mine. The second stage involves formation of foitite *via* the $^{X}\square R(\text{NaLi})_{-1}$ exchange and, at White Queen, also the substitution $(\text{OH})\,\text{F}_{-1}$. Foitite at Dobrá Voda crystallized from Fe-rich fluids at temperatures below ~400°C (as low as 300°C), on the basis of observed mineral assemblages, textural relations and results of experimental studies. Iron enrichment during the late stages of pegmatite crystallization recorded in Fe-rich elbaite, foitite, schorl and other minerals [micas, (Nb,Ta)-oxides] appears to be a widespread but volumetrically negligible process in complex granitic pegmatites. However, the source of Fe has not been sufficiently explained.

Keywords: tourmaline, foitite, elbaite, electron microprobe, compositional evolution, paragenesis, Fe-enrichment, complex granitic pegmatite, Dobrá Voda, Czech Republic, White Queen mine, California.

SOMMAIRE

Nous décrivons des cristaux zonés de tourmaline (elbaïte–foïtite) prélevés de poches dans des pegmatites granitiques à lépidolite à Dobrá Voda, en Moravie occidentale, en République Tchèque, et à la mine White Queen, à Pala, comté de San Diego, en Californie. Les cristaux zonés contiennent une elbaïte rose pâle, incolore ou verdâtre à faible teneur en fer, une elbaïte bleue, violacée ou verte riche en fer, et une foïtite violette foncé ou noire. Les cristaux d'elbaïte–foïtite montrent une association avec quartz, cookeïte, albite et apatite à Dobrá Voda, et avec albite, quartz, feldspath potassique, béryl, et muscovite à la mine White Queen. Les compositions chimiques de la foïtite et de l'elbaïte riche ou pauvre en Fe des deux endroits se ressemblent, et font preuve de lacunes dans le site *X* (≤0.78 *apfu*, dans la foïtite), et de teneurs variables en Ca (≤0.05 *apfu*), Mn (≤0.47 *apfu*) et F (≤0.75 *apfu*, dans l'elbaïte), ce qui contraste avec la foïtite, qui dans plusieurs cas est sans fluor. Nous distinguons deux stades distincts d'enrichissement tardif en fer, ce qui contraste avec l'appauvrissement en fer qui est signalé dans plusieurs massifs de pegmatite granitique. Le premier stade se distingue par une augmentation en Fe et Na, et une diminution en Al et Li; trois subdivisions de ce stade montrent les substitutions suivantes: (i) $R_2(\text{LiAl})_{-1}$, $\text{Na}R_2(\text{OH})(^{X}\square\text{Al}_2\text{O})_{-1}$ et $(\text{OH})\text{F}_{-1}$ dans le cas de l'elbaïte contenant moins de 0.3 Fe *apfu* à Dobrá Voda ($R = \text{Fe}_{\text{tot}} + \text{Mn} + \text{Mg} + \text{Zn}$); (ii) $\text{Na}\,R_2(\text{OH})(^{X}\square\text{Al}_2\text{O})_{-1}$ ou $\text{NaR}(^{X}\square\text{Al})_{-1}$ et $\text{F}(\text{OH})_{-1}$ dans le cas de l'elbaïte riche en fer avec entre 0.5 et 1.0 Fe *apfu*; (iii) $\text{AlO}_2[\text{Li}(\text{OH})_2]_{-1}$ et $(\text{OH})\text{F}_{-1}$, possiblement en combinaison avec $R_2\,(\text{LiAl})_{-1}$ dans le cas de l'elbaïte riche en fer contenant entre 1.0 et 1.3 Fe *apfu* à la mine White Queen. Le deuxième stade implique la formation de la foïtite *via* le mécanisme d'échange $^{X}\square R(\text{NaLi})_{-1}$ et, à la mine White Queen, la substitution $(\text{OH})\text{F}_{-1}$ en plus. La foïtite à Dobrá Voda a cristallisé à partir d'une phase fluide riche en fer à une température

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inférieure à environ 400°C (même possiblement 300°C), compte tenu des assemblages de minéraux observés, des relations texturales et des résultats d'études expérimentales. L'enrichissement en fer signalé aux stades tardifs de cristallisation, que témoignent l'elbaïte riche en Fe, la foïtite, le schorl et les autres minéraux [micas, oxydes de (Nb,Ta)], semble répandu, mais il affecte un volume infime d'une pegmatite granitique complexe. Toutefois, la provenance du fer n'est pas expliquée de façon satisfaisante.

(Traduit par la Rédaction)

Mots-clés: tourmaline, foïtite, elbaïte, microsonde électronique, évolution en composition, paragenèse, enrichissement en fer, pegmatite granitique complexe, Dobrá Voda, République Tchèque, mine White Queen, Californie.

INTRODUCTION

The physical and optical properties, chemical composition and crystal structure of foitite, $\square(Fe^{2+}{}_2Al)Al_6Si_6O_{18}(BO_3)_3(OH)_4$, are well described, but the type locality is known only as "southern California" (MacDonald *et al.* 1993; redescribed by Hawthorne & Henry 1999). Although the holotype specimen of foitite is a single crystal removed from its matrix, one can assume that the type locality is one of southern California's many complex rare-element granitic pegmatites.

Since the initial description, foitite has been found at a number of localities and in various rocks, chiefly granitic pegmatites (Dutrow & Henry 2000, and references therein). Foitite was found in pockets from several pegmatite dikes from Elba, Italy (Aurisicchio *et al.* 1999) as dark violet to black terminations on zoned crystals of elbaite. It also occurs there as gray, hair-like clusters within small vugs spatially associated with sekaninaite aggregates from the Filone Rosina dike, San Piero in Campo, Elba (Pezzotta *et al.* 1996). Dutrow & Henry (2000) described complexly zoned fibrous tourmaline (foitite – Fe-rich elbaite – Li-rich schorl – "fluor-elbaite") hosted by elbaite from the Cruzeiro mine, Minas Gerais, Brazil. Black tourmaline from less fractionated, outer units of lepidolite- and petalite-subtype pegmatites also locally exhibit a slight predominance of the foitite component over schorl (Novák & Selway 1997, Selway *et al.* 1999, 2000). Foitite was also found in pseudomorphs after sekaninaite associated with cookeite, albite and muscovite at pegmatite from Dolní Bory (unpubl. data of MN).

During a systematic study of tourmalines from complex rare-element granitic pegmatites in the Bohemian Massif, Czech Republic and the Peninsular Ranges batholith, southern California, paragenetically late foitite was discovered in two similar lepidolite-subtype pegmatites: Dobrá Voda near Velké Meziříčí, western Moravia, and the White Queen mine, Pala, San Diego County, California. In this paper, we describe the paragenesis of foitite and associated elbaite, and discuss the mechanisms of substitution, alkali depletion and Fe-enrichment of tourmaline during late stages of crystallization of complex granitic pegmatites.

GEOLOGICAL SETTING AND INTERNAL STRUCTURE OF PEGMATITES

Dobrá Voda

This pegmatite is a symmetrically zoned, steeply dipping dike, up to 6 m in width and about 100 m in length, emplaced in amphibolite and gneiss (Staněk 1965, Černý *et al.* 1995, Novák & Staněk 1999). It consists of (1) a volumetrically dominant marginal granitic unit, (2) a graphic unit, (3) a coarse-grained albite unit with blocks of K-feldspar, which is subdivided into three subunits: (3a) muscovite–albite, (3b) outer lepidolite–albite, and (3c) inner lepidolite–albite. Subunit 3c is adjacent to (4) a lepidolite unit in the central part of the dike. Amblygonite–montebrasite and pseudomorphs of spodumene + quartz intergrowths after petalite occur in subunits (3b) and (3c). Typical accessory minerals include andalusite, dumortierite, (Nb,Ta)-oxide minerals (manganocolumbite, stibiotantalite, microlite, manganotantalite), apatite, zircon and cassiterite (Novák & Staněk 1999).

Three types of pockets, each with a distinctive location in the dike and distinct mineral assemblages, were found (Novák & Staněk 1999; see Table 1). (5) Pink elbaite-bearing pockets in the lepidolite unit (4) are up to 10 cm across, equidimensional in shape, and lined with crystals of smoky quartz, homogeneous Fe-free, *X*-site-deficient elbaite, and lepidolite. (6) Green elbaite-bearing pockets are similar in shape and size, and occur in the inner lepidolite–albite subunit (3c). Elbaite is zoned from (pink) Fe-free elbaite to (dark green) Fe-rich elbaite to rare (bluish black) foitite. (7) Cookeite-

TABLE 1. MINERAL ASSEMBLAGES IN POCKETS FROM DOBRÁ VODA, CZECH REPUBLIC

Type of pocket	Tourmaline and common minerals	Rare minerals
(5) pink elbaite	elbaite, quartz, lepidolite	
(6) green elbaite	elbaite → Fe-rich elbaite → foitite, quartz	lepidolite or cookeite
(7) cookeite	elbaite → Fe-rich elbaite → foitite, quartz, cookeite	albite, apatite, cassiterite

bearing pockets are more common; they are elongate, flat pockets, up to 20 cm in length and 5 cm in width, and occur in the outer albite–lepidolite subunit (3b) close to the contact with, or locally in, subunit (3c) and unit (4). The host rock of the cookeite-bearing pockets consists primarily of albite, quartz, lepidolite and (pink) elbaite, and locally massive pale gray to colorless lepidolite with subordinate elbaite. Those pockets are lined with crystals of quartz, tourmaline longitudionally zoned from (pink) Fe-free elbaite to (green) Fe-rich elbaite to (bluish black) foitite, albite, late apatite, and cookeite. No textural or paragenetic evidence was found to indicate pocket rupture in any pocket.

White Queen mine

Although gem-quality pink beryl ("morganite") was mined at this locality for many years, few data on the internal structure and mineralogy of the pegmatite were published (*cf*. Jahns & Wright 1951, Foord *et al.* 1991). The pegmatite is an asymmetrically zoned dike, up to 5 m in thickness and several hundreds m in length, emplaced in gabbro. The dike exhibits a zonal pattern typical of the more fractionated pegmatites in the Pala pegmatite district: (1) a fine-grained, layered aplite footwall, (2) a graphic hanging wall unit, and centrally located (3) blocky K-feldspar + quartz unit, (4) bladed albite, and (5) massive fine-grained lepidolite units. Pockets occur near the center within the units (4) and (5), and are lined with crystals of quartz, albite, K-feldspar, muscovite, and minor beryl and tourmaline. Typical accessory minerals include almandine–spessartine, spodumene, lithiophilite, beryl and manganocolumbite.

TOURMALINE DESCRIPTION AND PARAGENESIS

Dobrá Voda

Tourmaline typically is subordinate to minor in all units and subunits. It varies in composition from (black) foitite–schorl to schorl–foitite in the outer units through (black) schorl to (blue and green) Fe-rich elbaite in the subunit (3a), (commonly pink) Fe-free elbaite and very rare (pink) rossmanite in units and subunits (3b, 3c, 4) (Selway *et al.* 1999, Novák & Staněk 1999). In general, the sequence of tourmaline crystallization and its compositional evolution in massive pegmatite units (tourmalines from pockets are discussed in the next paragraph) are comparable with those described in other complex pegmatites, particularly those of the lepidolite subtype (*e.g.,* Jolliff *et al.* 1986, Novák & Povondra 1995, Selway *et al.* 1999).

Elbaite–foitite occurs as elongate columnar crystals, subparallel intergrowths, with striated prisms, up to 15 × 5 mm in size in the green elbaite-bearing and cookeite-bearing pockets (Table 1). Early-formed pale green to pink or nearly colorless elbaite grades to semifibrous bluish black foitite at crystal terminations ≤ 0.1 mm thick. The change of color in elbaite is continuous, with small oscillations in early stages, but a sharp boundary separates pale green elbaite from light violet Fe-rich elbaite and violet Fe-rich elbaite from bluish black foitite (Fig. 1a) (see also Staněk 1963). Dark violet Fe-rich elbaite and bluish black foitite exhibit strong pleochroism: O blue, E pale pink and O deep blue, E pale violet, respectively.

White Queen mine

Tourmaline is a minor constituent of the pegmatite, and black schorl apparently predominates in massive units. Foitite occurs as terminations and rarely as a rim on solitary, striated columnar crystals of (dark blue to green) elbaite to Fe-rich elbaite, up to 25 × 5 mm in

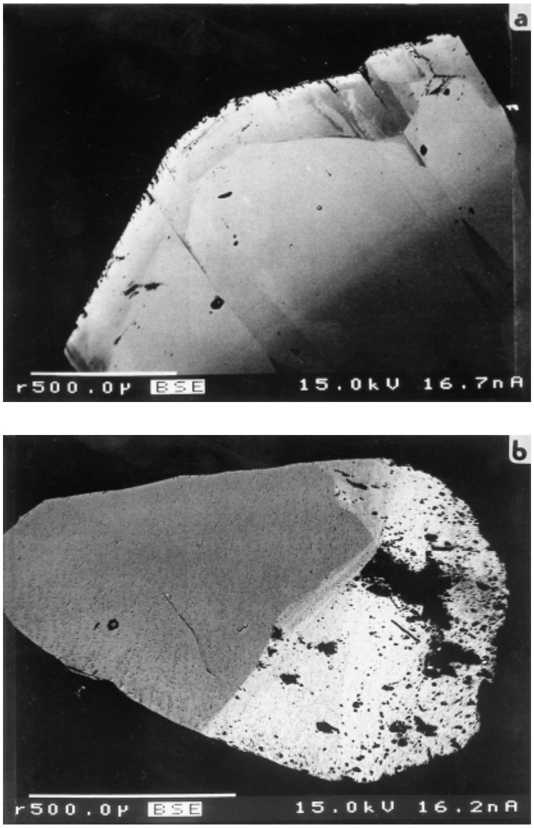


FIG. 1. Back-scattered electron image of elbaite–foitite crystals. a) Foitite termination of the crystal; note some oscillatory zoning in the intermediate zone between elbaite (dark) and foitite (bright), sectorial zoning of elbaite and semifibrous termination, Dobrá Voda. b) Foitite termination of the crystal; note porous and semifibrous texture of foitite and zoning between homogeneous elbaite (dark) and foitite, White Queen mine.

size. The prisms are associated with tabular crystals of beryl, albite, microcline, ordered orthoclase, muscovite and rare elbaite to Fe-rich elbaite exclusively in pockets. A sharp boundary between the early-crystallized (dark violet) Fe-rich elbaite and (bluish black) foitite terminations of crystals is typical. Foitite also forms porous semi-fibrous terminations, up to 0.5 mm thick, on Fe-rich elbaite crystals (Fig. 1b); elbaite–foitite crystals show local sector zoning.

ANALYTICAL METHODS

Three solitary crystals of elbaite–foitite from the green elbaite- and cookeite-bearing pockets at Dobrá Voda and two solitary crystals from pockets at White Queen were studied with an electron microprobe; the total amount of spot analyses is 29 at Dobrá Voda and 58 at White Queen.

Electron-microprobe analysis was performed in wavelength-dispersion mode on a Cameca Camebax SX–50 instrument with a beam diameter of 4–5 μm and an accelerating potential of 15 kV. A sample current of 20 nA measured on a Faraday cup was used for Si, Al, Ti, Fe, Mn, Mg, Ca, Na and K, and a current of 40 nA was used for Zn, F and P. Counting time for all elements was 20 seconds. The following standards were used ($K\alpha$ X-ray lines): diopside (Si, Ca), kyanite (Al), fayalite (Fe), rutile (Ti), pyrope (Mg), spessartine (Mn), albite (Na), orthoclase (K), fluorapatite (P, F) and gahnite (Zn). Data were reduced on-line using the PAP routine (Pouchou & Pichoir 1984, 1985).

Chemical formulae were calculated from stoichiometry constraints (*e.g.,* Hawthorne 1996) using the method of Dutrow & Henry (2000), on the basis of the following assumptions: (i) Si = 6 *apfu* (atoms per formula unit), (ii) B = 3 *apfu*, (iii) Li = 3 – ^{Y}Al – Fe$_{tot}$ – Mn – Mg – Zn, (iv) Fe$_{tot}$ is assumed to be essentially Fe^{2+}; see the discussion in Dutrow & Henry (2000) and Henry & Dutrow (1996).

RESULTS

Chemical composition

The chemical compositions of elbaite–foitite from both localities are similar (Tables 2, 3). Apart from the major elements (Si, Al, Fe and Na), minor elements include Mn (≤0.15 and ≤0.47 *apfu*), Ca (≤0.05 and ≤0.03 *apfu*, commonly in elbaite), and F (≤0.70 and ≤0.75 *apfu*, in elbaite) at the Dobrá Voda and White Queen pegmatites, respectively. Low Zn contents (≤0.06 *apfu*) were found in elbaite at the White Queen mine. Magnesium is below or close to the detection limit in all cases at both localities. Calculated cation charges are less than 58 in all cases (Table 2, 3) and indicate presence of Fe^{3+}, which is also supported by the wet-chemical analytical data on elbaite (Table 2) from a green elbaite-bearing pocket at Dobrá Voda (Povondra *et al.* 1985), polarized absorption spectra (Platonov *et al.* 1995), and the strong pleochroism of foitite.

Foitite from southern California (MacDonald *et al.* 1993), foitite from the Elban localities (Pezzotta *et al.* 1996, Aurisicchio *et al.* 1999) and foitite from the Cruzeiro mine, Minas Gerais, Brazil (Dutrow & Henry 2000) show very similar compositions relative to the foitite studied here, but they also contain higher Mg contents [≤0.23 *apfu*; locality Grotta d'Oggi, San Piero in Campo: Aurisicchio *et al.* (1999)] and traces of Ti (≤0.02 *apfu*).

Compositional variations in the elbaite–foitite series from pockets

Distinct compositional trends were found in the early-crystallized elbaite and late foitite, respectively (Figs. 2, 3, 4). The chemical composition of very early elbaite has a significant deficiency in the *X* site, up to

TABLE 2. REPRESENTATIVE CHEMICAL COMPOSITIONS OF ELBAITE FROM DOBRÁ VODA AND WHITE QUEEN MINE

	DV 5023	DV 5024	DV 5022	DV 1012	4/75[b]	WQ 226	WQ 220	WQ 219	WQ 435
P_2O_5 wt%	0.04	0.00	0.00	0.07	0.03	0.00	0.00	0.00	0.00
SiO_2	39.39	38.81	38.62	37.29	37.59	39.00	38.30	37.90	36.70
Al_2O_3	42.10	40.13	38.35	37.32	36.79	41.10	39.00	37.40	35.90
MgO	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.01	0.03
MnO	0.14	0.46	1.14	1.13	1.20	0.53	0.71	1.07	1.27
FeO	0.03	1.36	3.41	3.99	3.73	0.20	3.01	4.61	7.13
ZnO	0.01	0.01	0.02	0.04	n.d.	0.06	0.23	0.23	0.24
CaO	0.02	0.04	0.15	0.38	0.29	0.02	0.04	0.04	0.14
Na_2O	1.93	2.03	2.30	2.48	2.52	1.83	1.96	2.23	2.52
K_2O	0.01	0.01	0.01	0.00	0.05	0.00	0.01	0.03	0.04
F	0.55	0.30	0.85	1.00	1.56	0.20	0.53	0.80	0.99
B_2O_3[a]	11.41	11.24	11.19	10.80	10.80	11.30	11.09	10.98	10.63
Li_2O[a]	2.32	2.33	2.21	1.90	1.75	2.33	2.04	1.95	1.36
O=F	–0.23	–0.13	–0.36	–0.42	–0.66	–0.08	–0.22	–0.34	–0.42
total	97.71	96.60	97.89	95.98	99.35	96.49	96.70	96.91	96.54
P *apfu*	0.005	0.000	0.000	0.010	–	0.000	0.000	0.000	0.000
Si	6.000	6.000	6.000	6.000	6.168	6.000	6.000	6.000	6.000
^{Z}Al	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000
^{Y}Al	1.558	1.312	1.022	1.077	1.116	1.452	1.201	0.978	0.917
Mg	0.000	0.000	0.000	0.000	0.007	0.000	0.000	0.002	0.007
Mn	0.018	0.060	0.150	0.154	0.167	0.069	0.094	0.143	0.176
Fe^{2+}	0.004	0.176	0.443	0.537	0.512	0.026	0.394	0.610	0.975
Zn	0.001	0.001	0.002	0.005	–	0.007	0.027	0.027	0.029
Li	1.419	1.451	1.381	1.227	1.157	1.444	1.284	1.239	0.896
Ca	0.003	0.007	0.025	0.066	0.051	0.003	0.007	0.007	0.025
Na	0.570	0.608	0.693	0.774	0.803	0.546	0.595	0.684	0.799
K	0.002	0.002	0.002	0.000	0.011	0.000	0.002	0.006	0.008
$^{X}\square$	0.425	0.383	0.280	0.160	0.135	0.451	0.396	0.303	0.168
F	0.265	0.147	0.418	0.509	0.812	0.097	0.263	0.401	0.512
Cation charge	57.743	57.483	57.390	57.081	–	57.567	57.525	57.445	57.878

[a] calculated from stoichiometry (see explanation in the text); [b] green elbaite, data obtained by wet-chemical analysis (Povondra *et al.* 1985); the elbaite contains: Fe_2O_3 0.39 wt.%, 0.048 *apfu* Fe^{3+}; H_2O 2.92 wt.%, 3.198 *apfu* H^{+}. Ti is below the detection limit of EMP. n.d.: not determined.

TABLE 3. REPRESENTATIVE CHEMICAL COMPOSITIONS OF FOITITE FROM DOBRÁ VODA AND WHITE QUEEN MINE

	DV 509	DV 508	DV 504	WQ 705	WQ 403	WQ 404	WQ 406	WQ 405
SiO_2 wt%	37.20	37.50	37.10	36.70	36.90	36.70	36.70	36.50
Al_2O_3	36.00	35.90	35.70	35.40	36.20	35.50	35.20	35.50
MgO	0.00	0.00	0.00	0.04	0.06	0.04	0.03	0.03
MnO	0.58	0.68	0.25	2.01	3.43	3.25	2.72	2.64
FeO	11.10	10.80	13.10	10.50	8.39	9.10	10.00	10.20
ZnO	0.00	0.00	0.00	0.27	0.21	0.16	0.35	0.26
Na_2O	1.25	1.26	0.72	1.05	0.85	0.87	0.74	0.72
K_2O	0.02	0.01	0.00	0.00	0.02	0.01	0.00	0.01
F	0.00	0.06	0.03	0.16	0.00	0.10	0.00	0.00
B_2O_3[a]	10.78	10.86	10.75	10.63	10.69	10.63	10.63	10.57
Li_2O[a]	0.89	1.08	0.60	0.64	0.63	0.66	0.64	0.47
O=F	0.00	-0.03	-0.01	-0.07	0.00	-0.04	0.00	0.00
total	97.82	98.12	98.24	97.34	97.38	96.98	97.01	96.90
Si *apfu*	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000
^{Z}Al	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000
^{Y}Al	0.843	0.770	0.805	0.821	0.937	0.840	0.782	0.878
Mg	0.000	0.000	0.000	0.010	0.015	0.010	0.007	0.007
Mn	0.079	0.092	0.034	0.278	0.472	0.450	0.377	0.368
Fe^{2+}	1.497	1.445	1.772	1.436	1.141	1.244	1.367	1.402
Zn	0.000	0.000	0.000	0.033	0.025	0.019	0.042	0.032
Li_{calc}	0.58	0.693	0.389	0.423	0.410	0.437	0.422	0.314
Na	0.391	0.391	0.226	0.333	0.268	0.276	0.235	0.229
K	0.004	0.002	0.000	0.000	0.004	0.002	0.000	0.002
$^{X}\square$	0.605	0.607	0.774	0.667	0.728	0.722	0.765	0.769
F	0.000	0.030	0.015	0.083	0.000	0.052	0.000	0.000
Cation charge	57.662	57.468	57.643	57.737	57.800	57.682	57.606	57.794

[a] calculated from stoichiometry (see explanation in the text). P, Ca and Ti were found to be below the detection limits of electron microprobe.

about 0.45 *apfu* (Fig. 2a). Elbaite to Fe-rich elbaite from Dobrá Voda and the White Queen mine show generally an increase in Fe and Na, a decrease in Al and Li (Figs. 2, 3 and 4, Table 2), and evident oscillatory behavior of F with progressive crystallization (Fig. 2c). However, the behavior of Mn differs at each locality; in the White Queen mine, Mn increases from early to late stages of the elbaite–foitite series, whereas in the Dobrá Voda foitite, Mn shows oscillatory zoning and lower concentrations (Table 3).

Late foitite is characterized by an entirely different compositional trend relative to the Fe-enrichment in elbaite; moreover, there is a distinct compositional gap between early-crystallized Fe-rich elbaite and late foitite (Fig. 2), particularly at Dobrá Voda. The compositional evolution of foitite is very similar at both localities: each has relatively constant Al content, increasing Fe, and decreasing Na, Li and F. Foitite from the White Queen pegmatite is apparently Mn-enriched (Figs. 2, 3, 4, Table 3).

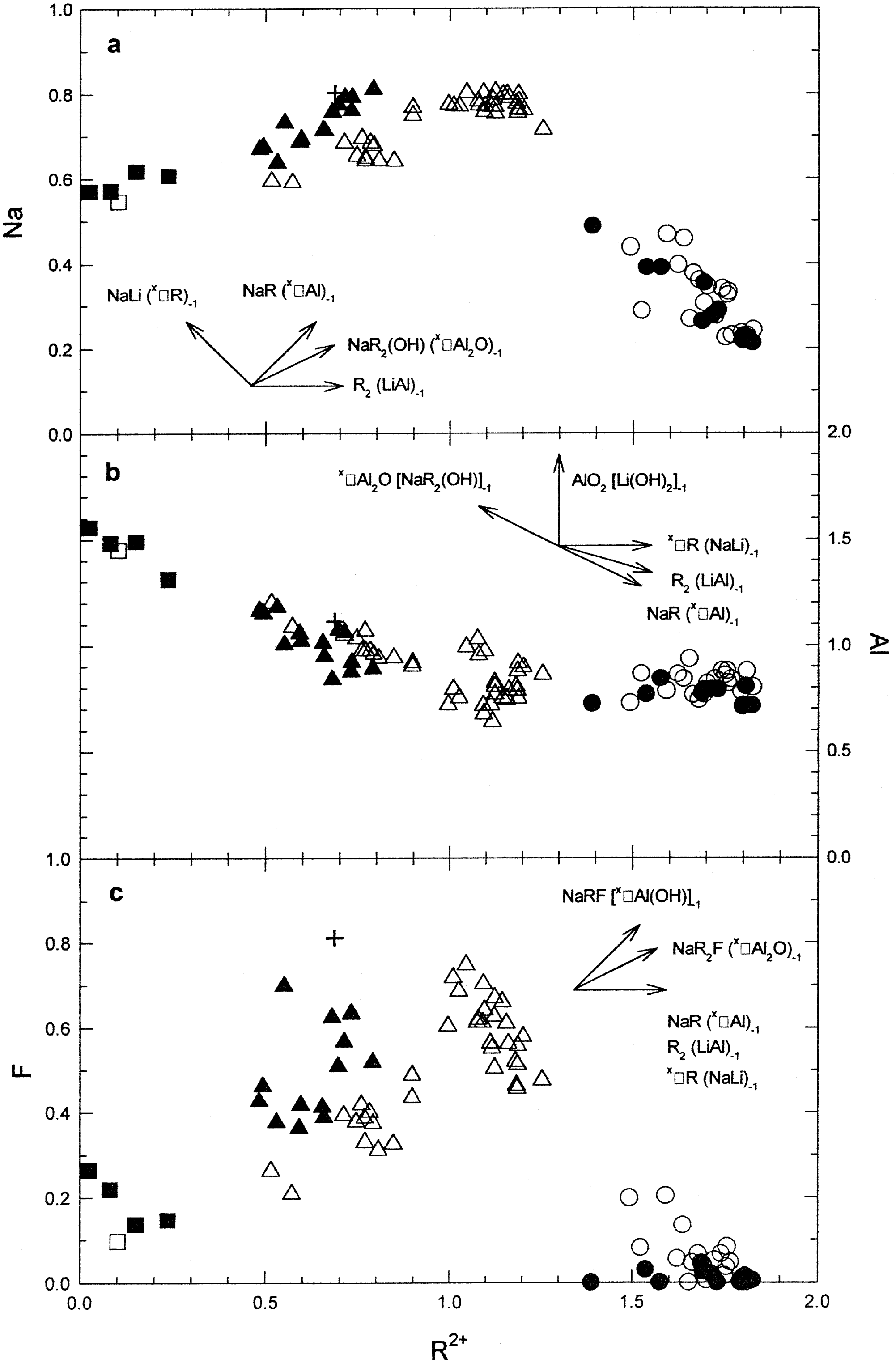
The compositional evolution from elbaite to foitite exhibits two distinct stages (Figs. 2, 3, 4, Tables 2, 3), which can be expressed using complex exchange-operators (Burt 1989), where $R = \mathrm{Fe_{tot}} + \mathrm{Mn} + \mathrm{Mg} + \mathrm{Zn}$. The first stage has three rather distinct substages (Fig. 2): (i) elbaite with <0.3 Fe *apfu* from Dobrá Voda exhibits the substitutions $R_2\,(\mathrm{LiAl})_{-1}$, $\mathrm{Na}R_2(\mathrm{OH})\,(^{X}\square\mathrm{Al_2O})_{-1}$ and $(\mathrm{OH})\,\mathrm{F}_{-1}$; (ii) the compositional trend of Fe-rich elbaite with 0.5–1.0 Fe *apfu* from both localities suggests participation of the substitutions $\mathrm{Na}R_2(\mathrm{OH})\,(^{X}\square\mathrm{Al_2O})_{-1}$ or $\mathrm{Na}R(^{X}\square\mathrm{Al})_{-1}$, and $\mathrm{F}\,(\mathrm{OH})_{-1}$; (iii) rather complicated evolutionary trends in Fe-rich elbaite with 1.0–1.3 Fe *apfu* from White Queen (Figs. 2b, 3) indicate the exchange operators $\mathrm{AlO_2}\,[\mathrm{Li(OH)_2}]_{-1}$ and $(\mathrm{OH})\,\mathrm{F}_{-1}$, perhaps combined with $R_2\,(\mathrm{LiAl})_{-1}$ exchange. In the second stage, evolutionary trends of foitite can be expressed by the exchange-operator $^{X}\square R\,(\mathrm{NaLi})_{-1}$ and, exclusively at White Queen, also by the substitution $(\mathrm{OH})\,\mathrm{F}_{-1}$. Other operators also may participate, but the presence of Fe^{3+} inferred from the sum of cation charges less than 58 (Tables 2, 3), results of a wet-chemical analysis of Fe-rich elbaite (Povondra *et al.* 1985) and the strong pleochroism of foitite do not allow a reliable derivation of more complicated exchange-operators, particularly those involving substitutions in the *W* site of tourmaline (*e.g.,* Dyar *et al.* 1998, Aurisicchio *et al.* 1999, Hawthorne & Henry 1999).

DISCUSSION

P–T conditions of the foitite formation at Dobrá Voda

The overgrowth of foitite on elbaite is a late pocket mineral associated with quartz and commonly with cookeite, albite and apatite at Dobrá Voda. Textural relations indicate cookeite to be later than elbaite and foitite. On the basis of the experimental data of Vidal & Goffé (1991), the assemblage cookeite + quartz, commonly present in the cookeite-bearing pockets at the Dobrá Voda pegmatite, is stable between 380 and 280°C at $P(H_2O) = 2$ kbar. This is a reasonable pressure for this locality, in view of the presence of primary petalite, now replaced by the spodumene + quartz intergrowths (Novák & Staněk 1999). The shape and appearance of the cookeite-bearing pockets (elongate, flat pockets developed through different textural and paragenetic units) indicate them to be products of a subsolidus reaction. Therefore, a temperature of formation below ~450°C (London *et al.* 1989, London 1992) seems likely. On the basis of observed mineral assemblages, textural relations and results of experimental studies (Vidal & Goffé, 1991, London *et al.* 1989), we conclude that foitite and associated minerals (elbaite, cookeite, quartz, albite, apatite) precipitated from a hydrothermal fluid medium below ~400°C, possibly as low as 300°C.

Cookeite was not found in the foitite-bearing pockets at the White Queen mine. In view of the recent find of petalite in the Pala district (Taylor & Wise 1998), the P–T conditions of consolidation of the Pala and related pegmatites (including overall conditions of pocket for-


a
b
c
Na
Al
F
R^{2+}
0.0
0.2
0.4
0.6
0.8
1.0
0.5
1.5
2.0
$\mathrm{NaLi}\,({}^{x}\square\mathrm{R})_{-1}$
$\mathrm{NaR}\,({}^{x}\square\mathrm{Al})_{-1}$
$\mathrm{NaR_2(OH)}\,({}^{x}\square\mathrm{Al_2O})_{-1}$
$\mathrm{R_2}\,(\mathrm{LiAl})_{-1}$
${}^{x}\square\mathrm{Al_2O}\,[\mathrm{NaR_2(OH)}]_{-1}$
$\mathrm{AlO_2}\,[\mathrm{Li(OH)_2}]_{-1}$
${}^{x}\square\mathrm{R}\,(\mathrm{NaLi})_{-1}$
$\mathrm{R_2}\,(\mathrm{LiAl})_{-1}$
$\mathrm{NaR}\,({}^{x}\square\mathrm{Al})_{-1}$
$\mathrm{NaRF}\,[{}^{x}\square\mathrm{Al(OH)}]_{-1}$
$\mathrm{NaR_2F}\,({}^{x}\square\mathrm{Al_2O})_{-1}$
$\mathrm{NaR}\,({}^{x}\square\mathrm{Al})_{-1}$
$\mathrm{R_2}\,(\mathrm{LiAl})_{-1}$
${}^{x}\square\mathrm{R}\,(\mathrm{NaLi})_{-1}$
0.0
0.5
1.0
1.5
2.0

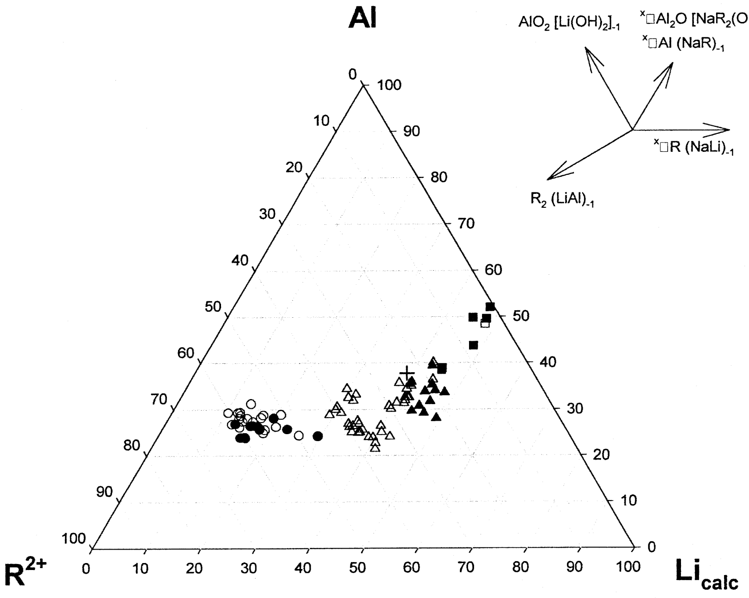


FIG. 3. Al – R^{2+} – Li_{calc} triangle. Arrows labeled with the exchange vectors represent directions of the vector but not the magnitude. Same symbols as in Figure 2. Dispersion of the data within Fe-rich elbaite at White Queen is almost parallel with the vector $AlO_2[Li(OH)_2]_{-1}$.

mation at the White Queen mine) could have been similar to those outlined for the Dobrá Voda.

Fe-enrichment during crystallization in complex granitic pegmatites

Iron depletion (*e.g.,* in tourmaline and other minerals) is generally developed in the late stages of pegmatite crystallization in complex pegmatites (*e.g.,* Černý & Ercit 1985, Jolliff *et al.* 1986, Federico *et al.* 1998); however, Fe-enrichment of tourmaline in the late stages of pegmatite crystallization also is documented. The Fe-enrichment has two distinct stages. (i) The formation of Fe-rich elbaite (green, blue, violet) characterizes the first stage, and such a rather weak Fe-enrichment in tourmaline has been documented at many localities in so-called "watermelon" elbaite (*e.g.,* Foord 1976, Althaus 1979, Dietrich 1985, Zagorskyi & Peretiazko 1992, Selway 1999). (ii) This stage is followed by the formation of foitite *via* Na- and F-depletion and strong Fe-enrichment; it occurs almost exclusively in pockets, and is known from several localities (*e.g.,* Pezzotta *et al.* 1996, Novák & Taylor 1996, Dutrow & Henry 2000). The distinct compositional gap between early Fe-rich elbaite and late foitite found in all localities (Fig. 2; see also Aurisicchio *et al.* 1999, Dutrow & Henry 2000) may be an indication of different conditions of crystallization during early and late stages of the tourmaline precipitation in pockets (*e.g.,* decreased temperature or decreased activity of F and Na), although high activities of Fe and B are maintained throughout the process. However, a crystal-chemical control may also be responsible for such a compositional gap; F cannot enter the O(1) (*V* site) site, and the *X* site is expected to be vacant if three *Y* sites are occupied by $2M^{2+}$ + $1M^{3+}$ and produce a seven-charge environment in foitite (Hawthorne 1996, Robert *et al.* 1997), whereas Fe-rich elbaite with $1M^{+}$ + $1M^{2+}$ + $1M^{3+}$ in the *Y* site produces a six-charge envi-

FIG. 2. $Na^+ – R^{2+}$, $Al – R^{2+}$ and $F – R^{2+}$ plots of elbaite–foitite series from pockets at Dobrá Voda and White Queen mine. Arrows labeled with the exchange vectors represent directions of the vector but not the magnitude; $R^{2+} = Fe_{tot} + Mn + Mg + Zn$. a) Na^+ *versus* R^{2+}. Note three rather distinct substages in the elbaite – Fe-rich elbaite series. b) Al *versus* R^{2+}. Dispersion of the data within Fe-rich elbaite with 1.0–1.3 Fe *apfu* at White Queen is roughly parallel with the exchange vector $AlO_2[Li(OH)_2]_{-1}$. c) F *versus* R^{2+}. Note oscillatory behavior of F. Symbols used for Figures 2, 3 and 4: square: early elbaite (<0.3 Fe *apfu*), triangle: Fe-rich elbaite (>0.5 Fe *apfu*), circle: foitite; Dobrá Voda: solid symbols; White Queen: open symbols; cross: Fe-rich elbaite from Dobrá Voda (Povondra *et al.* 1985).

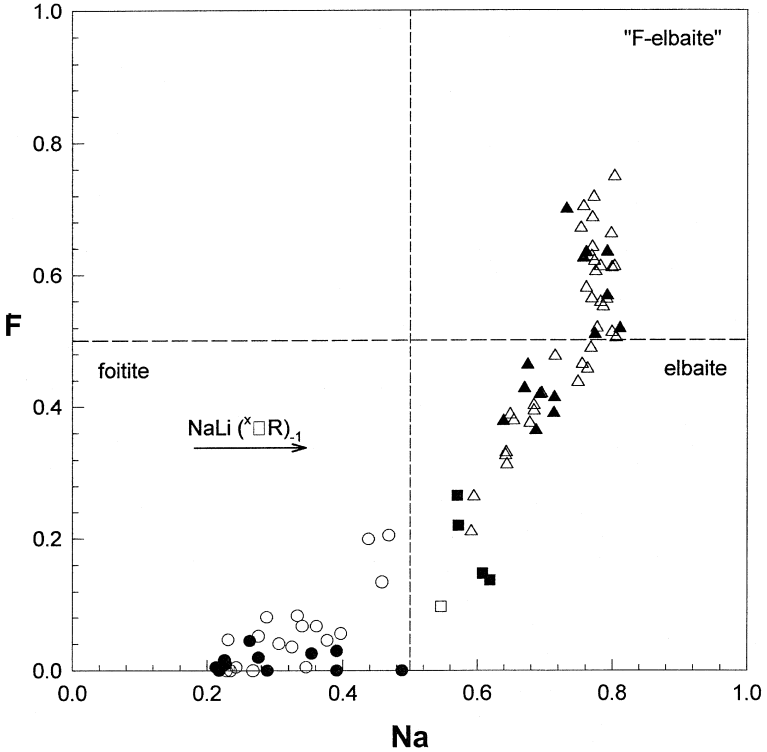


FIG. 4. Na – F plot of the elbaite–foitite series. Same symbols as in Figure 2.

ronment suitable for incorporation of F and Na into the structure (Table 2, anal. 4/75 and WQ435).

In addition to the trend displayed by late Fe-rich elbaite, schorl and foitite (*e.g.*, Tonarini *et al.* 1998, Aurisicchio *et al.* 1999, Selway 1999, Dutrow & Henry 2000, Novák *et al.* 2000), several other examples of late Fe-enrichment are known in complex pegmatites: late Fe-enrichment in some (Nb,Ta)-oxide minerals (Ercit 1986, Novák & Černý 1998a, 2001), and Fe-rich elbaite + Fe-rich lepidolite to zinnwaldite subsolidus reaction-rims around Mn-rich garnet (Němec 1983, Novák & Černý 1998b).

Pocket rupture, which may be associated with an influx of Fe-rich fluids from the host rock and the formation of Fe-rich tourmaline overgrowths, is the frequently cited cause of the Fe-enrichment during late stages of pegmatite evolution (*e.g.*, Foord 1976, Tonarini *et al.* 1998, Aurisicchio *et al.* 1999, Selway 1999). Magnesium is commonly below the detection limit of the electron microprobe in late foitite (or schorl) at the localities studied and other occurrences (*e.g.*, Aurisicchio *et al.* 1999, Dutrow & Henry 2000, Novák *et al.* 2000). As some of the above-mentioned pegmatite dikes are located in Mg-rich rocks (*e.g.*, serpentinite, dolomitic marble), Fe is unlikely to have infiltrated into the pegmatite from host rocks, unless Mg is totally immobile. It does not appear that infiltration from the host rocks can explain the enrichment in Fe.

Aurisicchio *et al.* (1999) described two distinct parageneses of late Fe-rich tourmalines from pockets in the pegmatites on Elba. (i) In the foitite-bearing pockets, replacement of biotite and sekaninaite by white mica and circulation of Fe-enriched fluids through the pegmatite are considered to make Fe available for incorporation into foitite, but the system (pocket environment) is closed relative to the host rock (Aurisicchio *et al.* 1999). As both biotite and sekaninaite carry subordinate amounts of Mg (Orlandi & Pezzotta 1993), such process would increase the availability of Mg, but foitite is commonly Mg-free. (ii) In the schorl-bearing pockets on Elba, Fe-rich fluids were probably expelled during a hydrothermal pulse related to the latest stages of the Mt. Capanne pluton, and the system (pocket environment) is open relative to the host rock. The only example of apparent late Mg-enrichment was found in foitite from the Grotta d'Oggi, San Piero in Campo, with up to 0.23 *apfu* Mg (Aurisicchio *et al.* 1999).

The Fe-enrichment in the late stages of the pegmatite crystallization seems to be a relatively widespread but volumetrically negligible process in complex granitic pegmatites, although its details differ in individual pegmatites. An external source of Fe seems improbable in the case where the host rocks are Mg-rich (amphibolite, gabbro, dolomitic marble), and Mg is below the limit of detection in late Fe-rich tourmaline and in other late Fe-rich minerals [micas, (Nb,Ta)-oxides]. Thus an internal source of Fe must be sought; the origin of Fe in late stages of such complex granitic pegmatites remains unknown.

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REFERENCES

ALTHAUS, E. (1979): Wassermelonen und Möhrenkopfe. *Lapis* **4**, 8-11.

AURISICCHIO, C., OTTOLINI, L. & PEZZOTTA, F. (1999): Electron- and ion-microprobe analyses, and genetic inferences of tourmalines of the foitite–schorl solid solution, Elba Island (Italy). *Eur. J. Mineral.* **11**, 217-225.

BURT, D.M. (1989): Vector representation of tourmaline compositions. *Am. Mineral.* **74**, 826-839.

ČERNÝ, P. & ERCIT, T.S. (1985): Some recent advances in the mineralogy and geochemistry of Nb and Ta in rare-element granitic pegmatites. *Bull. Minéral.* **108**, 499-532.

________, STANĚK, J., NOVÁK, M., BAADSGAARD, H., RIEDER, M., OTTOLINI, L., KAVALOVÁ, M. & CHAPMAN, R. (1995): Geochemical and structural evolution of micas in the Rožná and Dobrá Voda pegmatites, Czech Republic. *Mineral. Petrol.* **55**, 177-201.

DIETRICH, R.V. (1985): *The Tourmaline Group*. Van Nostrand, New York, N.Y.

DUTROW, B.L. & HENRY, D.J. (2000): Complexly zoned fibrous tourmaline, Cruzeiro mine, Minas Gerais, Brazil: a record of evolving magmatic and hydrothermal fluids. *Can. Mineral.* **38**, 131-143.

DYAR, M.D., 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. (1998): Interlaboratory comparison of tourmaline analyses: major elements including B, Li and Fe. *Int. Mineral Assoc., 17th Gen. Meeting* (*Toronto*), *Programme Abstr.*, A101.

ERCIT, T.S. (1986): *The Simpsonite Paragenesis. The Crystal Chemistry and Geochemistry of Extreme Ta Fractionation.* Ph.D. thesis, Univ. Manitoba, Winnipeg, Manitoba.

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.

FOORD, E.E. (1976): *Mineralogy and Petrogenesis of Layered Pegmatite–Aplite Dikes in the Mesa Grande District, San Diego County, California*. Ph.D. thesis, Stanford Univ., Stanford, California.

________, LONDON, D., KAMPF, A.R., SHIGLEY, J.E. & SNEE, L.W. (1991): Gem-bearing pegmatites of San Diego County, California. *In* Geological Excursions in Southern California and Mexico (M.J. Walawender & B.B. Hanan, eds.). *Geol. Soc. Am., Field Trip Guidebook*, 128-146.

HAWTHORNE, F.C. (1996): Structural mechanisms for light-element variations in tourmaline. *Can. Mineral.* **34**, 123-132.

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

HENRY, D.J. & DUTROW, B.L. (1996): Metamorphic tourmaline and its petrologic applications. *In* Boron: Mineralogy, Petrology and Geochemistry (E.S. Grew & L.M. Anovitz, eds.). *Rev. Mineral.* **33**, 503-557.

JAHNS, R.H. & WRIGHT, L.A. (1951): Gem- and lithium-bearing pegmatites of the Pala district, San Diego County, California. *Calif. Dep. Nat. Resources, Div. Mines, Spec. Rep.* **7-A**.

JOLLIFF, B.L., PAPIKE, J.J. & SHEARER, C.K. (1986): Tourmaline as a recorder of pegmatite evolution: Bob Ingersoll pegmatite, Black Hills, South Dakota. *Am. Mineral.* **71**, 472-500.

LONDON, D. (1992): The application of experimental petrology to the genesis and crystallization of granitic pegmatites. *Can. Mineral.* **30**, 499-540.

________, MORGAN, G.B., VI & HERVIG, R.L. (1989): Vapor-undersaturated experiments with Macusani glass + H_2O at 200 MPa, and the internal differentiation of granitic pegmatites. *Contrib. Mineral. Petrol.* **102**, 1-17.

MACDONALD, D.J., HAWTHORNE, F.C. & GRICE, J.D. (1993): Foitite, $\square[Fe^{2+}_2(Al,Fe^{3+})]\ Al_6Si_6O_{18}(BO_3)_3(OH)_4$, a new alkali-deficient tourmaline: description and crystal structure. *Am. Mineral.* **78**, 1299-1303.

NĚMEC, D. (1983): Zinnwaldit in Moldanubischen Lithium-Pegmatiten. *Chem. Erde* **42**, 197-204.

Novák, M. & Černý, P. (1998a): Niobium-tantalum oxide minerals from complex pegmatites in the Moldanubicum, Czech Republic: primary *versus* secondary compositional trends. *Can. Mineral.* **36**, 659-672.

________ & ________ (1998b): Abundances and fractionation trends of Rb and Cs in micas from lepidolite- and elbaite-subtype pegmatites in the Moldanubicum, Czech Republic. *Acta Univ. Carol., Geol.* **42**, 86-90.

________ & ________ (2001): Distinctive compositional trends in columbite-tantalite from two segments of the lepidolite pegmatite at Rožná, western Moravia, Czech Republic. *J. Czech Geol. Soc.* (in press).

________ & Povondra, P. (1995): Elbaite pegmatites in the Moldanubicum; a new subtype of the rare-element class. *Mineral. Petrol.* **55**, 159-176.

________ & Selway, J.B. (1997): Rožná near Bystřice nad Pernštejnem, Hradisko Hill. *In* Field trip guidebook, Tourmaline 1997 Symposium (M. Novák & J.B. Selway, eds.). Nové Město na Moravě, Czech Republic (23-38).

________, ________, Černý, P., Chapman, R.C. & Masau, M. (2000): Correlation between Mn content in tourmaline and garnet abundance in two elbaite-subtype pegmatites: Dolní Rožínka and Pikárec, Czech Republic. *Geol. Assoc. Can. – Mineral. Assoc. Can., Abstr.*

________ & Staněk, J. (1999): Lepidolite pegmatite from Dobrá Voda near Velké Meziříčí, western Moravia. *Acta Mus. Moraviae, Geol. Sci.,* **84**, 3-44 (in Czech with English summary).

________ & Taylor, M.C. (1996): New occurrences of foitite and its position in pegmatite evolution. *Geol. Assoc. Can. – Mineral. Assoc. Can., Program Abstr.* **21**, A70.

Orlandi, P. & Pezzotta, F. (1993): La sekaninaite dei filoni pegmatitici elbani. *Atti Soc. Tosc. Sci. Nat. Mem., Ser.* **A 100**, 85-91.

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.

Pouchou, J.L. & Pichoir, F. (1984): A new model for quantitative analysis. I. Application to the analysis of homogeneous samples. *La Recherche Aérosp.* **3**, 13-38.

________ & ________ (1985): "PAP" procedure for improved quantitative microanalysis. *Microbeam Anal.* **20**, 104-105.

Povondra, P., Čech, F. & Staněk, J. (1985): Crystal chemistry of elbaites from some pegmatites of the Czech Massif. *Acta Univ. Carol., Geol.* **1**, 1-24.

Robert, J.-L., Gourdant, J.-P., Linnen, R.L., Rouer, O. & Benoist, P. (1997): Crystal-chemical relationships between OH, F and Na in tourmaline. *In* Tourmaline 1997, Int. Symp. on Tourmaline (Nové Město na Moravě, Czech Republic), Abstract Vol., 84-85.

Selway, J.B. (1999): *Compositional Evolution of Tourmaline in Granitic Pegmatites*. Ph.D. thesis, Univ. Manitoba, Winnipeg, Manitoba.

________, Černý, P., Hawthorne, F.C. & Novák, M. (2000): The Tanco pegmatite at Bernic Lake, Manitoba. XIV. Internal tourmaline. *Can. Mineral.* **38**, 1103-1117.

________, Novák, M., Černý, P. & Hawthorne, F.C. (1999): Compositional evolution of tourmaline in lepidolite-subtype pegmatites. *Eur. J. Mineral.* **11**, 569-584.

Staněk, J. (1963): Tourmalines from pegmatite at Dobrá Voda near Velké Meziříčí. *Folia Univ. Purkyn. brun., Geol.* **4**, 13-28 (in Czech with German summary).

________ (1965): Pegmatite from Dobrá Voda near Velké Meziříčí. *Folia Univ. Purkyn. brun., Geol.* **6**, 1-39 (in Czech with English summary).

Taylor, M.C. & Wise, M.A. (1998): Primary petalite + spodumene assemblages in rare-element pegmatites of the Peninsular Ranges batholith, southern California. *Int. Mineral. Assoc., 17th Gen. Meeting (Toronto), Programme Abstr.*, A152.

Tonarini, S., Dini, A., Pezzotta, F. & Leeman, W.P. (1998): Boron isotopic composition of zoned (schorl–elbaite) tourmalines, Mt. Capanne Li–Cs pegmatites, Elba (Italy). *Eur. J. Mineral.* **10**, 941-951.

Vidal, O. & Goffé, B. (1991): Cookeite $LiAl_4(Si_3Al)O_{10}(OH)_8$: experimental study and thermodynamical analysis of its compatibility relations in the $Li_2O–Al_2O_3–SiO_2–H_2O$ system. *Contrib. Mineral. Petrol.* **108**, 72-81.

Zagorskyi, V.E. & Peretiazhko, I.C. (1992): *Pegmatites with Gemstones of Central Transbaikalia*. Nauka, Novosibirsk, Russia (in Russ.).

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