Eur. J. Mineral.
1999, **11**, 557-568

This paper was presented at the Tourmaline 97
meeting (Czech Republic)

Tourmaline of the elbaite-dravite series from an elbaite-subtype pegmatite at Bližná, southern Bohemia, Czech Republic

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Abstract: The elbaite-subtype pegmatite at Bližná, near Černá v Pošumaví in southern Bohemia, Czech Republic, intrudes dolomite-calcite marble. It can be divided into two distinct units, unit A and unit B, and has a narrow exocontact zone along the edge of the pegmatite. The crystallization sequence of tourmaline from unit A is Ca-rich schorl-elbaite → Ca-rich elbaite-schorl-dravite → Mn-rich elbaite → Mn-rich liddicoatite → liddicoatite-elbaite, typical of tourmaline from elbaite-subtype pegmatites. The crystallization sequence of tourmaline from unit B is Na-rich uvite → Ca-rich schorl-elbaite-dravite → Ca-rich Mg-bearing elbaite → (Ca, Mn)-rich elbaite → Mn-rich liddicoatite-elbaite → Na-rich liddicoatite. Tourmaline from the exocontact ranges from Na-rich uvite → Ca-rich dravite → dravite-elbaite → Ca-rich Mg-bearing elbaite → liddicoatite-elbaite. The intermediate elbaite-schorl-dravite from unit A and schorl-elbaite-dravite from unit B are characterized by low F, moderate Mn and high Ti and Ca contents. The Mg-bearing elbaite from unit B and the exocontact is characterized by low Fe, moderate Ti, and high Ca and F contents. The dravite-elbaite from the exocontact is characterized by low Fe, Mn, Ti, Ca and F contents. The intermediate elbaite-schorl-dravite and elbaite-dravite solid-solutions crystallized as a result of mixing of (Ca, Mg)-rich fluids from the dolomite-calcite marble host-rock and exsolved (Na, Al, Li, F, B)-rich pegmatitic fluids. The factors controlling formation of elbaite-dravite in rocks may be summarized as follows: high activities of Li, Mg, Al and B, high Li/Mg ratio in the parent medium, acidic conditions with pH $< \sim 6$, and lack of holmquistite. Consequently, elbaite-dravite solid-solutions should occur in highly contaminated elbaite-subtype pegmatites penetrating marble and in holmquistite-free contact aureoles around complex LCT pegmatites.

Key-words: elbaite-dravite series, EMPA, SIMS, elbaite-subtype pegmatite, Bližná.

Introduction

Tourmaline compositions intermediate between elbaite and dravite have not been reported previously (Dietrich, 1985; Deer *et al.*, 1986), but the reason for this is not well-established. Most authors have explained this gap as a consequence of extreme relative fractionation of Mg relative to Li during most geological processes (*e.g.*, Staatz *et al.*, 1955; Foit & Rosenberg, 1979; Deer *et al.*, 1986; Werding & Schreyer, 1996; Henry & Dutrow, 1996). Donnay & Barton (1972) and Hermon *et al.* (1973) suggested that (Al, Li) and Mg cannot mutually substitute at the *Y*-site because this substitution will not allow the required O(3)-O(6) adjustments between the Y and Z octahedra. However, Foit & Rosenberg (1979) noted that there is no distinct coupling between the sizes of the Y and Z octahedra, and concluded that there is no obvious structural reason why dravite-elbaite solid-solution should not be more extensive.

Some compositions of tourmaline from exocontact zones adjacent to, or from enclaves enclosed in, complex pegmatites show high Al, Li,

0935-1221/99/0011-0557 $ 3.00

Fe and Mg contents, corresponding to tourmaline intermediate between elbaite, schorl, and dravite (Sahama *et al.*, 1979; Jolliff *et al.*, 1986; Němec, 1989; Novák & Selway, 1997a; Laurs *et al.*, 1998). Such compositions occur within the compositional gap described by Henry & Guidotti (1985). However, these compositions are transitional between elbaite and schorl, with only a minor dravite component. Relatively abundant tourmaline of the elbaite-dravite series with substantial uvite and liddicoatite components was recently found in the elbaite-subtype pegmatite and its exocontact at Bližná, southern Bohemia (Novák & Selway, 1997b; Novák *et al.*, 1997); a detailed chemical study of these tourmalines is reported here.

Occurrence, mineral assemblages and textural relations

The elbaite-subtype pegmatite at Bližná, near Černá v Pošumaví, is located in the southern part of the Český Krumlov unit of the Moldanubicum in southern Bohemia, Czech Republic. It is about 4 m thick and intrudes dolomite-calcite marble. The contact with the host rock is generally sharp, without any visible reaction rim; however, a tourmaline-rich exocontact zone is developed locally along the pegmatite margin.

There are two distinct units in the pegmatite: unit A and unit B (Novák *et al.*, 1997). The volumetrically dominant unit A (Fig. 1) is commonly coarse-grained and consists of grey to bluish-grey perthitic microcline and subordinate quartz and albite. Minor zoned tourmaline ranges from black schorl-elbaite through brown-to-yellow Mn-rich elbaite to pink Mn-rich elbaite to pink liddicoatite in the most evolved regions. Accessory minerals include oligoclase-andesine, diopside, datolite, titanite, zircon, bastnaesite-(Ce), hydroxylbastnaesite-(Ce), allanite-(Ce), apatite, microlite-pyrochlore and manganaxinite. There is a weakly developed textural differentiation within unit A, caused by a moderate increase in grain size from 2 cm to almost 10 cm in randomly distributed patches. These assemblages and textures are similar to those characteristic of elbaite-subtype pegmatites from Moldanubicum (Novák & Povondra, 1995).

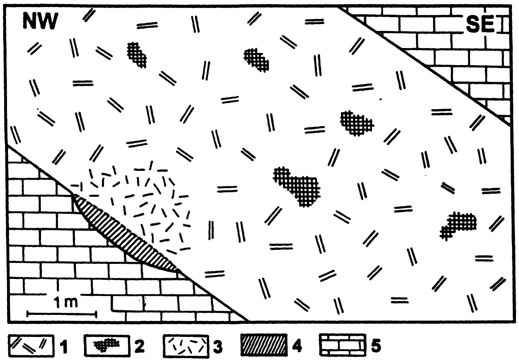

Fig. 1. Vertical section through the Bližná pegmatite (Novák *et al.*, 1997). 1 - pegmatite unit A with schorl; 2 - pegmatite unit A with Li-rich tourmalines; 3 - pegmatite unit B; 4 - exocontact; 5 - dolomite-calcite marble.

Unit B is limited spatially to a 1.5 × 1.0 m zone along the footwall of the pegmatite (Fig. 1). It consists of coarse- to locally medium-grained white-to-beige microcline, quartz, tourmaline and albite. Olive-green subhedral Ca-rich Mg-bearing elbaite is volumetrically dominant over early dark-brown uvite and schorl-elbaite, and late pink Mn-rich elbaite and liddicoatite.

The boundary between unit A and unit B is transitional over a distance of about 5 cm. Through this transition zone, K-feldspar changes from grey or bluish-grey in unit A to white or beige in unit B, and tourmaline changes from black in unit A to dominantly olive green in unit B.

A reaction zone, 1.5 m long and up to 15 cm thick, is developed along the contact between unit B and the host marble (Fig. 1). About 75 volume% of the zone consists of fine-grained aggregates of tourmaline. The tourmaline varies from dark- to pale-brown uvite to dravite (in the outermost part) to olive green Ca-rich Mg-bearing elbaite to liddicoatite (along the contact with unit B). Minor quartz, accessory calcite, fluorite, titanite, pyrite and magnesioaxinite occur in the exocontact zone.

The abundance of tourmaline increases from the centre of the pegmatite toward the contact with the host rock. Small veinlets of late hydrothermal blue-to-colourless dravite penetrate and replace early-crystallized uvite and Ca-rich Mg-bearing elbaite in unit B. Blue dravite is occasionally associated with calcite (Novák, 1998).

The Ca-rich Mg-bearing elbaite and dravite-elbaite from Bližná typically is olive green to greenish brown, and is concentrated in unit B and the innermost part of the exocontact zone. It forms randomly distributed, subhedral columnar crystals (<1 cm) in unit B. The crystals are locally zoned with dark-brown uvite cores, a narrow heterogeneous intermediate zone of Ca-rich schorl-elbaite, and volumetrically dominant Ca-rich Mg-bearing elbaite (Fig. 2a), locally with patches of Ca-rich Mn-bearing dravite-elbaite (Fig. 2b,c). Highly heterogeneous elbaite-dravite is sporadically rimmed by, or associated with, pink Mg-free Mn-rich elbaite to liddicoatite (Fig. 2c). Homogeneous Mg-bearing elbaite also forms fine-grained quartz-tourmaline intergrowths concentrated in the outer part of unit B, and fine-grained aggregates in the exocontact zone adjacent to the pegmatite contact. Tourmaline from the exocontact zone is highly heterogeneous and its composition varies irregularly within small patches <0.05 mm.

Experimental

EMPA

Electron-microprobe analysis was done in wavelength-dispersion mode on a Cameca SX 50 instrument with a beam diameter of 1–3 μm and an accelerating voltage of 15 kV. A beam current of 20 nA was used for Si, Al, Ti, Fe, Mn, Mg, Ca and Na, and 40 nA for Zn, F, K and P; the counting time for all elements was 20 s. The following standards were used for *K*α X-ray lines: Si,Ca: diopside, Al: kyanite, Fe: fayalite, Ti: rutile or titanite, Mg: pyrope or olivine, Mn: spessartine, Na: albite, K: orthoclase, P: apatite, F: apatite or fluororiebeckite, and Zn: gahnite. Data were reduced using the PAP routine of Pouchou & Pichoir (1985).

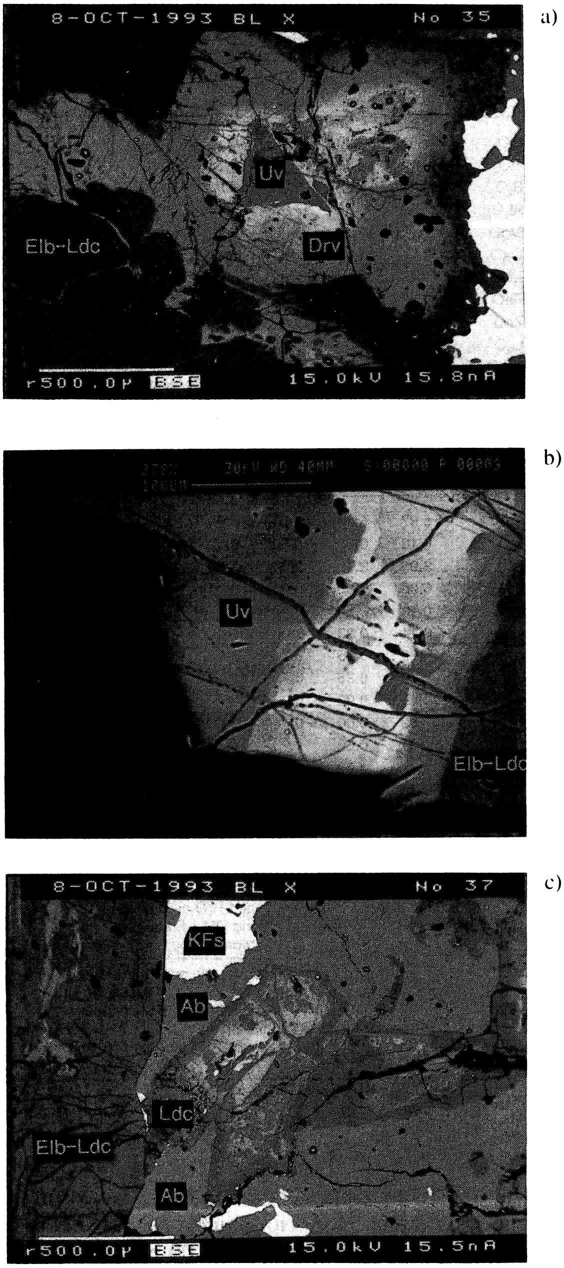

Fig. 2. Back-scattered-electron images of tourmaline from pegmatite unit B. (a) Zoned crystal of tourmaline enclosed in K-feldspar (white) with Na-rich uvite core (Uv), heterogeneous Ca-rich schorl-elbaite intermediate zone I (bright), Ca-rich dravite intermediate zone II (Drv) and homogeneous Mg-rich elbaite-liddicoatite (Elb-Ldc) outer zone. (b) Fragment of zoned crystal analysed using SIMS consisting from left to right of Na-rich Fe-bearing uvite core (Uv) (Table 2, comp. 1), Ca-rich Mn-bearing schorl-elbaite-dravite intermediate zone I (bright) (Table 2, comp. 7, 8, 9), heterogeneous Ca-rich Mg-bearing elbaite intermediate zone II (grey) with a small patch of Ca-rich Mn-bearing dravite-elbaite (dark) (Table 2, comp. 4) at contact between zone I and II, and homogeneous Mg-bearing elbaite-liddicoatite (Elb-Ldc) outer zone (Table 2, comp. 3). Late veinlets of blue dravite (dark) penetrate all zones. (c) Large grain of homogeneous Mg-bearing elbaite-liddicoatite (Elb-Ldc) on left and small highly heterogenous crystals consisting from core to rim of Ca-rich Mn-bearing elbaite-dravite-schorl core (bright), intermediate zone of Mn-rich elbaite-liddicoatite (grey) both zones contain abundant patches of elbaite-dravite-schorl (grey) and Mg-bearing liddicoatite-elbaite (dark), and Na-rich liddicoatite rim (Ldc). Associated minerals: albite (Ab) and K-feldspar (Kfs).

Table 1. Representative compositions of tourmaline from pegmatite unit A, Bližná.

	1	2	3	4	5	6	7
SiO_2	35.01	35.20	36.01	36.57	35.50	37.12	37.00
TiO_2	1.11	1.83	0.65	0.13	0.34	0.00	0.05
B_2O_3*	10.36	10.52	10.80	10.82	10.84	10.94	10.88
Al_2O_3	32.67	33.56	37.80	37.84	38.30	38.57	38.52
MgO	0.92	1.83	0.00	0.01	0.05	0.00	0.00
CaO	1.43	1.59	2.31	2.21	2.58	3.00	3.20
MnO	2.26	2.57	5.29	5.01	4.62	3.48	2.32
FeO	10.29	6.68	0.25	0.53	0.14	0.03	0.00
ZnO	0.18	0.00	0.00	0.00	0.00	0.00	0.00
Li_2O*	0.76	1.04	1.85	1.84	1.66	2.21	2.37
Na_2O	1.58	1.58	1.54	1.55	1.39	1.22	1.14
H_2O*	3.46	3.42	3.38	3.37	3.07	3.33	3.26
F	0.25	0.44	0.72	0.77	1.13	0.93	1.04
O=F	–0.11	–0.19	–0.30	–0.32	–0.48	–0.39	–0.44
total	100.17	100.07	100.30	100.33	99.14	100.44	99.34
Unit formula normalized to 31 anions							
T: Si	5.87	5.82	5.80	5.88	5.77	5.90	5.91
Al	0.13	0.18	0.20	0.12	0.23	0.10	0.09
B	3.00	3.00	3.00	3.00	3.04	3.00	3.00
Z: Al	6.00	6.00	6.00	6.00	6.00	6.00	6.00
Y: Al	0.33	0.35	0.97	1.04	1.10	1.12	1.16
Ti	0.14	0.23	0.08	0.02	0.04	0.00	0.01
Mg	0.23	0.45	0.00	0.00	0.01	0.00	0.00
Mn	0.32	0.36	0.72	0.68	0.64	0.47	0.31
Fe^{2+}	1.45	0.92	0.03	0.07	0.02	0.00	0.00
Zn	0.02	0.00	0.00	0.00	0.00	0.00	0.00
Li	0.51	0.69	1.20	1.19	1.08	1.41	1.52
ΣY	3.00	3.00	3.00	3.00	2.89	3.00	3.00
X: Ca	0.26	0.28	0.40	0.38	0.45	0.51	0.55
Na	0.52	0.51	0.48	0.48	0.44	0.38	0.35
□	0.22	0.21	0.12	0.14	0.11	0.11	0.10
OH	3.87	3.77	3.63	3.61	3.33	3.53	3.47
F	0.13	0.23	0.37	0.39	0.58	0.47	0.53

All compositions, except 5: B_2O_3, Li_2O and H_2O calculated by stoichiometry; B = 3 *apfu*, Li = 3 – ΣY and OH + F = 4 *apfu*. Composition 5: B_2O_3, Li_2O and H_2O determined by SIMS.

(1) black Ca-rich Mn-bearing schorl-elbaite, sample 210; (2) black Ca-rich (Mg, Mn)-bearing elbaite-schorl, sample 326; (3) yellow Mn-rich elbaite-liddicoatite, sample 327; (4) yellow Ca-rich Mn-rich elbaite, sample 213; (5) pink Mn-rich liddicoatite-elbaite, sample 10-1-3; (6) pink Na-rich Mn-bearing liddicoatite, sample 246; (7) pink Na-rich Mn-bearing liddicoatite, sample 54.

SIMS

Lithium, B and H in tourmaline were measured with a Cameca IMS 4f ion microprobe at C.N.R.-CSCC, Pavia. High-energy (~ 100 ± 25 eV) $^{7}Li^{+}$, $^{11}B^{+}$, $^{1}H^{+}$ and $^{30}Si^{+}$ secondary ions (Si was used as the matrix reference-element) were monitored under steady-state sputtering conditions. The quantification of secondary-ion signal to elemental concentration was done using calibration curves derived from well-characterized tourmaline crystals. As the compositional range of these standard crystals is different from that of the samples, and as Fe and Mn seem to affect Li ionization (Ottolini *et al.*, 1993), we used the procedure described in Ottolini & Hawthorne (1999) that takes into account variation in Li-ion yield relative-to-Si as a function of (Fe + Mn) (cat %) content of the sample; the overall accuracy of Li in SIMS analysis is estimated to be of the order of ~15–20% rel. (Ottolini & Hawthorne, 1999). Quantification of H was done using the working curve of Ottolini & Hawthorne (1999): under the present experimental conditions, we estimate an overall accuracy as ~10% rel. for this element. For B, we used a regression line IY(B/Si) *vs.* (Fe + Mn) (cat %) [where IY(B/Si) represents the ion yield of B relative-to-Si] as was done for Li. This calibration procedure should allow an accuracy for B of about 3% rel.

The lack of Mg-rich tourmaline standards did not allow us to examine the role of Mg in the ionization of H, Li and B. Preliminary SIMS analysis on these crystals confirms the presence of matrix effects for Li/Si ionization: however, we could not calibrate them adequately, and thus the Li content was not derived by SIMS in uvite and Li-bearing dravite.

Chemical composition

Structural formulae were calculated on the basis of 31 (O, OH, F). When SIMS data are available, SIMS-determined Li_2O, H_2O and B_2O_3 are used; when SIMS data are not available, stoichiometric amounts of H_2O as $(OH)^-$ [*i.e.* OH + F = 4 atoms per formula units (apfu)], B_2O_3 as $(BO_3)^{3-}$ (*i.e.* B = 3 apfu), and Li = 3 – ΣY apfu are assumed. The nomenclature of tourmaline (*e.g.*, Ca-rich Mg-bearing elbaite) used is that of Selway *et al.* (1999).

Boron concentrations determined by SIMS range from 2.98 to 3.05 apfu, essentially corresponding to ideal stoichiometry. The (OH + F) contents vary from 3.58 to 4.00 apfu, indicating considerable O^{2-} at O(1) in some samples; however, O^{2-} never becomes dominant at O(1) in any of the samples analyzed.

Tourmaline from unit A

The tourmalines of unit A are typical of elbaite-subtype pegmatites, particularly those intruding Ca-rich rocks (Novák & Povondra, 1995), and range from Ca dominant to Na dominant with minor *X*-site vacancies (Fig. 3A); thus the dom-

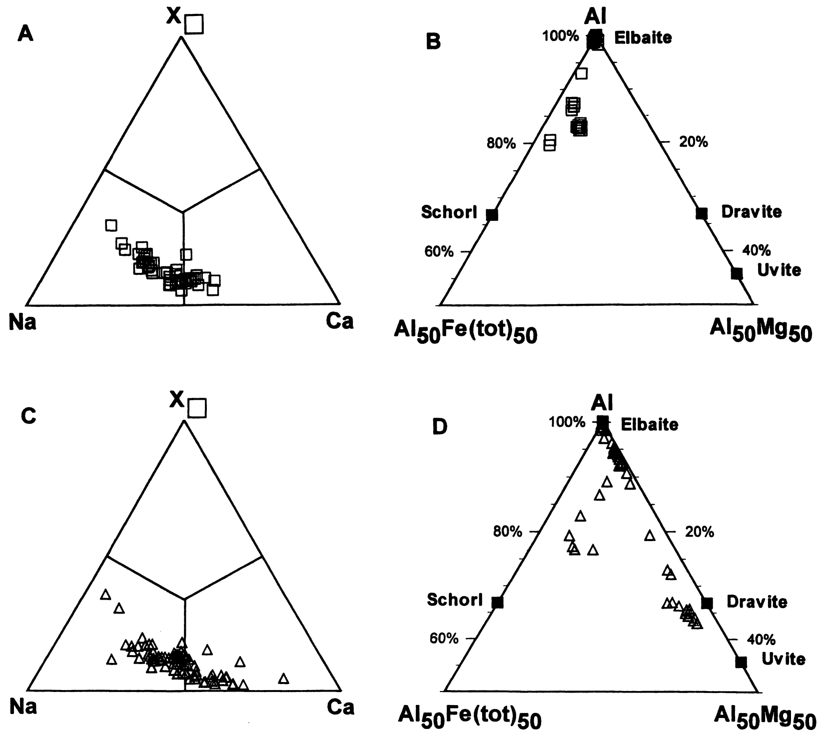

Fig. 3. Compositional variation of tourmaline from the Bližná pegmatite: (A) Ca–Na–□ in unit A; (B) Al_{tot}–Fe_{tot}–Mg_{tot} in unit A; (C) Ca–Na–□ in unit B; (D) Al_{tot}–Fe_{tot}–Mg_{tot} in unit B.

inant substitution at the *X*-site is Ca ↔ Na. Fig. 3B indicates that the dominant substitution at the *Y*-site is Fe ↔ (Al + Li). Zoned tourmaline crystals indicate that the sequence of crystallization is ± black Ca-rich Mn-bearing schorl-elbaite → black to dark brown Ca-rich Mn-bearing elbaite-schorl-dravite → yellow Mn-rich elbaite-liddicoatite → pink Mn-rich elbaite-liddicoatite → pink Mn-rich liddicoatite-elbaite → pink Mn-bearing liddicoatite-elbaite (Table 1). The Mn content in these tourmalines increases with increasing fractionation from schorl-elbaite → elbaite-schorl-dravite → elbaite-liddicoatite, and then decreases in late-stage liddicoatite-elbaite (Fig. 5A). The Fe-rich tourmalines have a relatively low Mn content, whereas the (Al + Li)-rich tourmalines have high Mn (Fig. 5C). The Ti content in the tourmaline decreases with increasing fractionation, so that the primitive elbaite-schorl-dravite contains relatively high Fe, Mg and Ti, and elbaite and liddicoatite contain almost no Ti (Fig. 6A). There are positive correlations between F and Ca, and between F and Mn, indicating that F increases with increasing fractionation; the fractionated Mn-bearing liddicoatite-elbaite contains the maximum F content (Fig. 7A,C). With increasing fractionation, the tourmaline in unit A becomes enriched in Ca, (Al + Li), Mn and F, and depleted in Fe, Mg and Ti. The presence of elbaite-schorl-dravite and rare dravite represents an influx of Mg-rich fluids from the dolomite-calcite marble host, whereas the schorl-elbaite, elbaite and liddicoatite crystallized directly from the pegmatitic melt.

Tourmaline from unit B

The tourmaline compositions range from Ca dominant to Na dominant with minor *X*-site vacancies (Fig. 3C); the dominant substitution at the *X*-site is Ca ↔ Na, and the dominant substitution at the *Y*-site is Mg ↔ (Al + Li) (Fig. 3D). Zoned tourmaline crystals indicate that the sequence of crystallization is dark brown Na-rich Fe-bearing uvite → dark brown Ca-rich Mn-bearing schorl-elbaite-dravite → abundant olive green Ca-rich Mg-bearing elbaite → pink (Ca, Mn)-rich elbaite → pink Mn-rich liddicoatite-elbaite → pink Na-rich liddicoatite (Table 2). The compositions of Mg-bearing tourmaline, the Mg-free elbaite and liddicoatite (Table 2) are similar to compositions listed in Table 1.

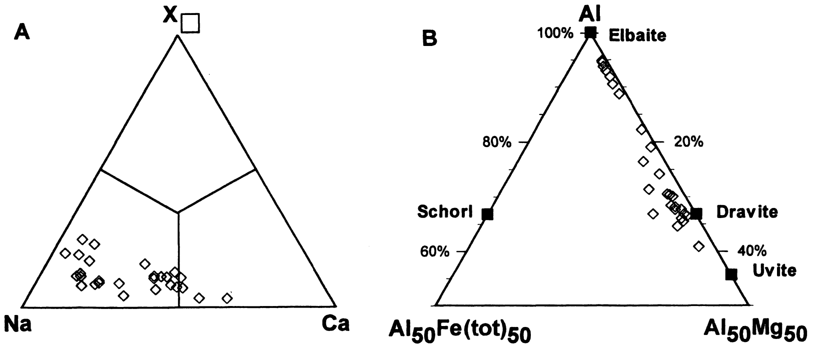

Fig. 4. Compositional variation of tourmaline in the exocontact of the Bližná pegmatite: (A) Ca–Na–□; (B) Al_{tot}–Fe_{tot}–Mg_{tot}.

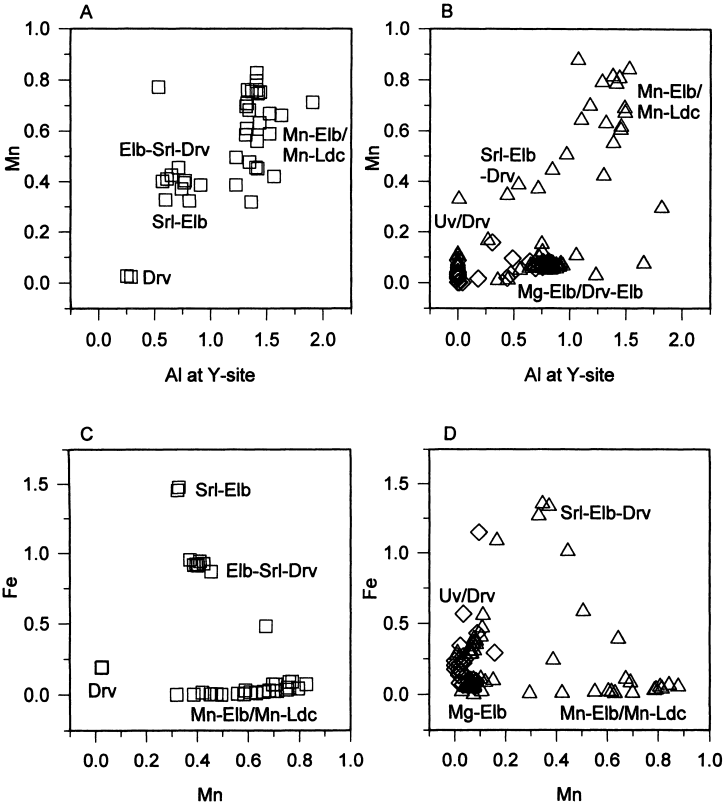

Fig. 5. (A) Mn *vs.* Al at the *Y*-site for pegmatite unit A; (B) Mn *vs.* Al at the *Y*-site for pegmatite unit B (Δ) and exocontact (◊); (C) Fe *vs.* Mn for pegmatite unit A; (D) Fe *vs.* Mn for pegmatite unit B (Δ) and exocontact (◊). Labels: Uv - uvite, Drv - dravite, Srl - schorl, Elb - elbaite and Ldc - liddicoatite.

Generally, the Mn contents are low in Mg-rich tourmaline (*i.e.*, uvite and Mg-bearing elbaite), intermediate in Fe-rich tourmaline (*i.e.*, schorl-elbaite-dravite) and high in Mg-free (Al + Li)-rich tourmaline (*i.e.*, elbaite, liddicoatite-elbaite and liddicoatite) (Fig. 5B, D). The Ti contents are low in uvite, reach a maximum in schorl-elbaite-dravite, and decrease from Mg-elbaite to elbaite to liddicoatite (Fig. 6B). There is a positive correlation between F and Ca and between F and Mg, as indicated by the increase in F content from Fe-rich tourmaline (*i.e.*, schorl-elbaite-dravite) to (Al + Li)-rich tourmaline (*i.e.*, Mn-rich elbaite and liddicoatite) to Mg-rich tourmaline (*i.e.*, Mg-bearing elbaite and uvite) (Fig. 7B). In contrast to tourmaline in unit A, there is no positive correlation between F and Mn in tourmaline from unit B (Fig. 7D). With increasing fractionation, the tour-

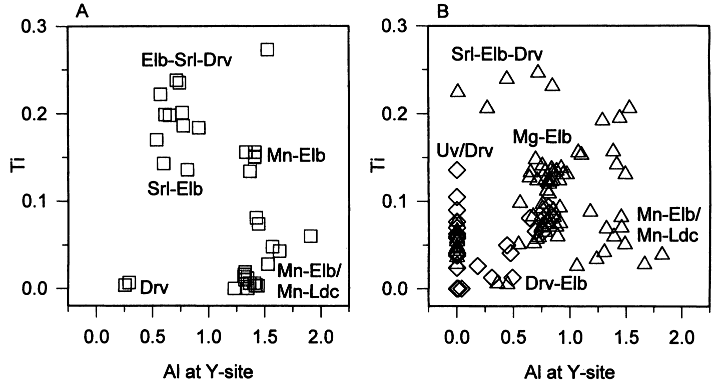

Fig. 6. (A) Ti *vs.* Al at the *Y*-site for pegmatite unit A; (B) Ti *vs.* Al at the *Y*-site for pegmatite unit B (Δ) and exocontact (◊). Labels same as in Fig. 5.

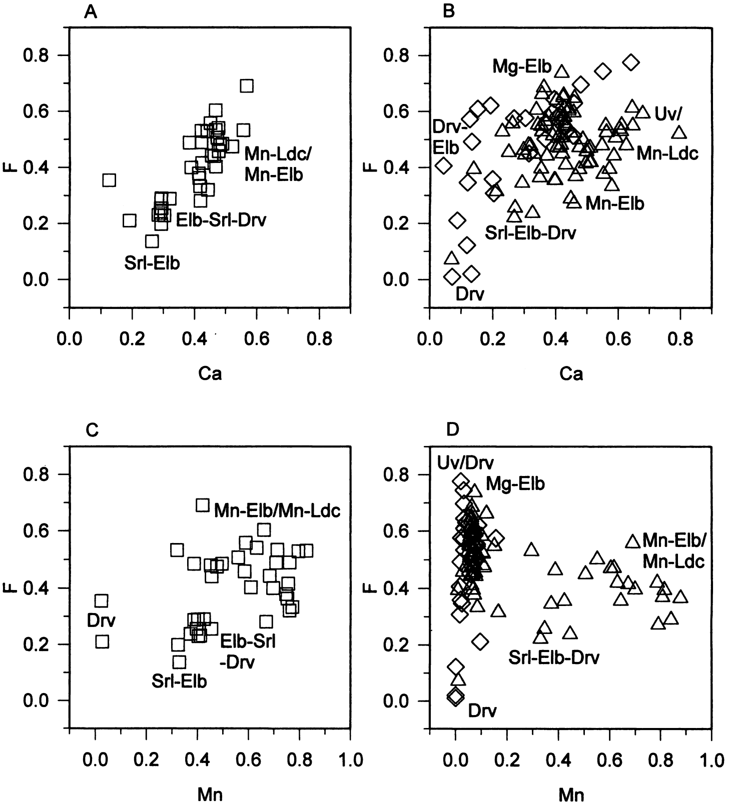

Fig. 7. (A) F *vs.* Ca for pegmatite unit A; (B) F *vs.* Ca for pegmatite unit B (Δ) and exocontact (◊); (C) F *vs.* Mn for pegmatite unit A; (D) F *vs.* Mn for pegmatite unit B (Δ) and exocontact (◊). Labels same as in Fig. 5.

maline in unit B increases in (Al + Li), Mn and decreases in Mg. The most primitive uvite and most fractionated liddicoatite contain high Ca and F. Intermediate schorl-elbaite-dravite contains high Fe and Ti.

In unit B, Mg-rich tourmaline (*i.e.*, uvite) crystallized dominantly from (Ca, Mg)-rich fluids from the dolomite-calcite marble host-rock, the (Mg, Al, Li)-rich tourmalines (*i.e.*, schorl-elbaite-dravite and Mg-bearing elbaite) crystallized from a mixture of fluids from the dolomite-calcite marble and the pegmatitic melt, and the Mg-free (Al + Li)-rich tourmaline (*i.e.*, elbaite and liddicoatite) crystallized from the uncontaminated (Na, Al, Li, B)-rich pegmatitic melt. The late hydrothermal blue dravite in fissures cross cuts pegmatite unit B and replaces Mg-bearing elbaite (Table 3, composition 7).

Table 2. Representative compositions of tourmaline from pegmatite unit B, Bližná.

	1	2	3	4	5	6	7	8	9
SiO_2	36.60	36.00	37.50	36.10	38.51	38.45	36.10	34.50	34.10
TiO_2	0.44	1.79	1.09	0.41	0.93	1.08	1.65	1.77	1.86
B_2O_3*	10.67	10.51	10.96	10.60	11.18	10.88	10.56	10.43	10.30
Al_2O_3	28.70	30.60	36.80	33.40	37.03	36.79	32.00	33.40	32.40
MgO	12.20	2.30	1.38	5.97	1.44	1.35	3.36	1.62	1.67
CaO	3.67	1.50	2.48	1.67	2.33	2.60	1.18	1.75	1.55
MnO	0.46	2.34	0.49	2.75	0.44	0.48	1.18	3.02	2.49
FeO	2.22	9.09	0.39	1.73	0.40	0.39	7.82	6.95	9.07
ZnO	0.00	0.25	0.00	0.10	0.00	0.00	0.13	0.24	0.12
Li_2O*	0.05	0.69	2.13	0.78	2.46	2.47	0.86	0.96	0.73
Na_2O	1.06	1.66	1.53	1.81	1.65	1.48	2.09	1.62	1.58
H_2O*	2.81	3.00	2.95	3.25	2.95	3.12	3.36	3.40	3.26
F	1.06	0.42	1.30	0.88	1.35	1.16	0.60	0.43	0.62
O=F	–0.45	–0.18	–0.55	–0.37	–0.57	–0.49	–0.25	–0.18	–0.26
total	99.49	99.97	98.45	99.08	100.10	99.76	100.64	99.91	99.49
Unit formula normalized to 31 anions									
T: Si	6.01	6.05	6.02	5.91	6.07	6.08	5.94	5.75	5.75
Al	0.00	0.00	0.00	0.09	0.00	0.00	0.06	0.25	0.25
B	3.02	3.05	3.04	2.99	3.04	2.97	3.00	3.00	3.00
Z: Al	5.56	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
Mg	0.44	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Y: Al	0.00	0.06	0.96	0.35	0.88	0.86	0.14	0.31	0.20
Ti	0.05	0.23	0.13	0.05	0.11	0.13	0.20	0.22	0.24
Mg	2.54	0.58	0.33	1.46	0.34	0.32	0.82	0.40	0.42
Mn	0.06	0.33	0.07	0.38	0.06	0.07	0.17	0.43	0.36
Fe^{2+}	0.31	1.28	0.05	0.24	0.05	0.05	1.08	0.97	1.28
Zn	0.00	0.03	0.00	0.01	0.00	0.00	0.02	0.03	0.01
Li	0.04	0.47	1.38	0.51	1.56	1.57	0.57	0.64	0.49
$\sum Y$	3.00	2.98	2.92	3.00	3.00	3.00	3.00	3.00	3.00
X: Ca	0.65	0.27	0.43	0.29	0.39	0.44	0.21	0.31	0.28
Na	0.34	0.54	0.48	0.57	0.50	0.45	0.67	0.52	0.52
□	0.01	0.19	0.09	0.14	0.11	0.11	0.12	0.17	0.20
OH	3.08	3.36	3.16	3.55	3.10	3.29	3.69	3.77	3.67
F	0.55	0.22	0.66	0.46	0.67	0.58	0.31	0.23	0.33
Σ	3.63	3.58	3.82	4.01	3.77	3.87	4.00	4.00	4.00

*Composition 1, 4–6: B_2O_3 and H_2O determined by SIMS and Li_2O calculated by stoichiometry, Li = 3 – ΣY. Composition 2, 3: B_2O_3, Li_2O and H_2O determined by SIMS. Composition 7–9: B_2O_3, Li_2O and H_2O calculated by stoichiometry; B = 3 *apfu*, Li = 3 – ΣY and OH + F = 4 *apfu*.

(1) brown Na-rich Fe-bearing uvite, sample 8-2-1; (2) dark brown Ca-rich (Mg, Li, Mn)-bearing schorl, sample 8-1-1; (3) olive green Mg-bearing elbaite-liddicoatite, sample 8-2-9; (4) Ca-rich Mn-bearing dravite-elbaite patch, sample 8-2-12; (5) olive green Ca-rich Mg-bearing elbaite rim, sample 9-3-1; (6) olive green Mg-bearing elbaite-liddicoatite core of (5), sample 9-3-2; (7) dark brown Ca-rich schorl-dravite-elbaite, sample 8-2-6; (8) dark brown Ca-rich Mn-bearing schorl-elbaite-dravite, sample 8-2-4; (9) dark brown Ca-rich Mn-bearing schorl-elbaite-dravite, sample 8-2-5.

Tourmaline from the exocontact

The exocontact is also characterized by the abundance of elbaite-dravite solid-solution. Tourmaline compositions range from Ca-rich to Na dominant with minor *X*-site vacancies (Fig. 4A), indicating that the dominant substitution at the *X*-site is Ca $\leftrightarrow$ Na; the dominant substitution at the *Y*-site is Mg $\leftrightarrow$ (Al + Li) (Fig. 4B). Tourmaline varies from dark to pale brown Na-rich uvite $\rightarrow$ Ca-rich Fe-bearing dravite $\rightarrow$ Ca-bearing dravite (in the outermost part of the exocontact) to olive green Ca-bearing dravite-elbaite $\rightarrow$ (Ca, Mg)-rich elbaite $\rightarrow$ Ca-rich Mg-bearing elbaite (along the contact with unit B) $\rightarrow$ ± Mg-bearing liddicoatite-elbaite (Table 3). Tourmaline from the exocontact contains very low Mn and Ti (<0.16 apfu Mn and <0.14 apfu Ti) with no systematic trends (Fig. 5B,D, 6B); Ti is preferentially partitioned into the associated titanite. There is a positive correlation between F and Ca with increasing F content from dravite to dravite-elbaite to Mg-bearing elbaite to uvite, with a maximum of 0.78 apfu F (Fig. 7B). With increasing fractionation, tourmaline in the exocontact increases in (Al + Li) and decreases in Mg and Fe. The most primitive Na-rich Fe-bearing uvite has the highest Ca and F. Exocontact tourmaline crystallizes from a mixture of (Ca, Mg)-rich fluids from the dolomite-calcite marble host rock and (Na, Al, Li, F, B)-rich pegmatitic fluids.

Discussion

Chemical composition of intermediate elbaite-schorl-dravite and elbaite-dravite

At Bližná, dark brown to black elbaite-schorl-dravite from unit A and dark brown schorl-elbaite-dravite from unit B are characterized by relatively low F (average 0.27 apfu), moderate Mn (average 0.38 apfu), high Ti (average 0.22 apfu), and high Ca (average 0.29 apfu) contents. Intermediate elbaite-schorl-dravite compositions from other localities are shown in Fig. 8. They occupy part of the elbaite-dravite gap described by Henry & Guidotti (1985). Intermediate schorl-elbaite-dravite compositions occur in the contact zones of granitic pegmatites intruding amphiboles and amphibole-biotite gneisses from Mozambique (Sahama *et al.*, 1979; Duda, 1987), and in tourmalinized metapelite enclaves and the exocontact of the lepidolite- to amblygonite-subtype Bob Ingersol I pegmatite, Keystone, S. Dakota (Jolliff *et al.*, 1986). Intermediate elbaite-schorl-dravite occurs in metapelite enclaves of the lepidolite-subtype Rožná-Hradisko pegmatite, Czech Republic (Novák & Selway, 1997a), the tourmalinized gneiss exocontact of spodumene-subtype White Picacho pegmatite, Arizona (D. London, pers. comm.), and in the tourmalinized biotite-granodiorite-gneiss exocontact of the miarolitic pegmatites at Stak Nala, Pakistan (Laurs *et al.*, 1998). Intermediate elbaite-schorl-dravite also occurs in contaminated elbaite-subtype pegmatites at Sahatany Valley, Madagascar, intruding dolomite marble (Bloomfield, 1997).

The major element and Ti contents of schorl-elbaite-dravite and elbaite-schorl-dravite from the literature are very similar to those from units A and B at Bližná. The intermediate-tourmaline compositions from Bližná have higher Mn contents than those from the literature, as Mn-rich tourmaline is characteristic of elbaite-subtype pegmatites (Novák & Povondra, 1995, Aurisicchio & Freda, 1992, Taylor *et al.*, 1997). The intermediate tourmaline compositions from Bližná also have high Ca content, similar to those from the pegmatite at Sahatany Valley, due to interaction with Ca-rich fluids from their dolomite marble host rocks.

Table 3. Representative compositions of tourmaline from exocontact and fissures, Bližná.

	1	2	3	4	5	6	7
SiO_2	37.37	37.56	37.31	37.25	38.28	38.43	38.33
TiO_2	1.13	0.34	0.87	0.11	0.56	0.80	0.08
B_2O_3*	10.78	10.79	10.67	10.78	11.00	11.05	11.00
Al_2O_3	27.52	29.74	29.69	33.24	36.25	36.99	33.80
MgO	13.14	11.19	9.31	6.95	3.30	1.36	9.04
CaO	3.72	2.80	0.88	1.55	1.87	2.72	0.57
MnO	0.15	0.24	0.25	1.15	0.43	0.57	0.13
FeO	1.62	1.69	4.23	2.17	0.68	0.46	1.54
Li_2O*	0.36	0.56	0.49	0.85	1.97	2.51	0.54
Na_2O	1.06	1.46	2.47	2.07	1.74	1.45	1.95
H_2O*	2.99	3.07	3.11	3.18	3.36	3.32	3.69
F	1.53	1.38	1.20	1.13	0.91	1.04	0.21
O=F	-0.64	-0.58	-0.51	-0.48	-0.38	-0.44	-0.09
total	100.73	100.24	99.97	99.95	99.97	100.26	100.79
Unit formula normalized to 31 anions							
T: Si	6.03	6.05	6.08	6.01	6.05	6.05	6.06
Z: Al	5.23	5.65	5.70	6.00	6.00	6.00	6.00
Mg	0.77	0.35	0.30	0.00	0.00	0.00	0.00
Y: Al	0.00	0.00	0.00	0.32	0.75	0.86	0.30
Ti	0.14	0.04	0.11	0.01	0.07	0.09	0.01
Mg	2.39	2.34	1.96	1.67	0.78	0.32	2.13
Mn	0.02	0.03	0.03	0.16	0.06	0.08	0.02
Fe^{2+}	0.22	0.23	0.58	0.29	0.09	0.06	0.20
Li	0.23	0.36	0.32	0.55	1.25	1.59	0.34
ΣY	3.00	3.00	3.00	3.00	3.00	3.00	3.00
X: Ca	0.64	0.48	0.15	0.27	0.32	0.46	0.10
Na	0.33	0.46	0.78	0.65	0.53	0.44	0.60
□	0.03	0.06	0.07	0.08	0.15	0.10	0.30
OH	3.22	3.30	3.38	3.42	3.54	3.48	3.89
F	0.78	0.70	0.62	0.58	0.46	0.52	0.11

*B_2O_3, Li_2O and H_2O calculated by stoichiometry; B = 3 *apfu*, Li = 3 – ΣY and OH + F = 4 *apfu*.

Compositions 1-6 from the exocontact, composition 7 from fissures. (1) brown Na-rich uvite, sample 177; (2) light brown Li-bearing uvite-dravite, sample 491; (3) brown (Ca, Fe, Li)-bearing dravite, sample 595; (4) brown Ca-rich (Li, Fe)-bearing dravite, sample 593; (5) olive green (Ca, Mg)-rich elbaite, sample 6100; (6) olive green Mg-bearing liddicoatite-elbaite, sample R309; (7) (Ca, Li)-bearing dravite, sample 134.

At Bližná, olive green Ca-rich Mg-bearing elbaite from unit B and the exocontact are characterized by relatively low Fe (<0.11 apfu), low Mn (<0.15 apfu), moderate Ti (<0.15 apfu), high Ca (average 0.38 apfu), and high F contents (average 0.55 apfu). Minor olive green dravite-elbaite from the exocontact has significantly more Mg than the Ca-rich Mg-bearing elbaite, and similar low Fe (<0.18 apfu), lower Mn (<0.03 apfu), Ti (<0.05 apfu), Ca (average 0.10 apfu), and F (average 0.49 apfu) contents.

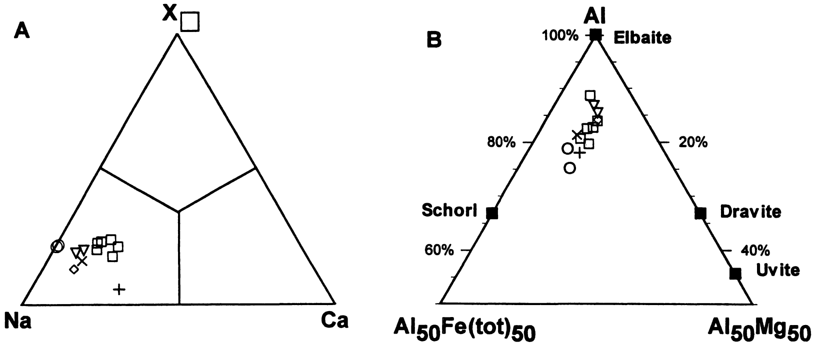

Fig. 8. Compositional variation of intermediate elbaite-schorl-dravite from pegmatite exocontacts or enclaves in the literature; (A) Ca–Na–□; (B) Al_{tot}–Fe_{tot}–Mg_{tot}. + - Mozambique, Sahama *et al.* (1979); o - Bob Ingersol I pegmatite, Jolliff *et al.* (1986); ▽ - Rožná pegmatite, Novák & Selway (1997a); □ - Sahatany Valley pegmatite, Bloomfield (1997); ◊ - Stak Nala, Pakistan, Laurs *et al.* (1998); x - White Picacho pegmatite, Arizona (this work).

Potential geological environments for elbaite-dravite solid-solution

The occurrence of intermediate elbaite-dravite compositions at Bližná refutes the suggestion that (Al,Li) and Mg cannot mutually substitute at the *Y*-site because of crystal-chemical restrictions. Hence the scarcity of elbaite-schorl-dravite and elbaite-dravite compositions in nature *must* be a consequence of extreme fractionation of Li from Mg in most geological processes (Dietrich, 1985; Henry & Dutrow, 1996). However, there are geological environments with potentially high activities of Li, B and Mg. Elbaite-dravite(-uvite) compositions occur in tourmaline from unit B and the adjacent exocontact reaction zone at Bližná. Formation of uvite and dravite in the outer exocontact zone suggests dominance of (Ca,Mg)-rich fluids and decreasing activity of Li outward away from the pegmatite. In contrast, tourmaline from the volumetrically dominant unit A evolves from schorl-elbaite to elbaite-schorl-dravite to Mn-rich elbaite to liddicoatite (Novák *et al.*, 1997), typical for elbaite-subtype pegmatites intruding Ca-rich rocks in the Moldanubicum (Novák & Povondra, 1995). This sequence of tourmaline compositions illustrates the fractionation of Li relative to Mg in the melt that formed unit A.

So what suppressed this mechanism in unit B and led to the crystallization of elbaite-dravite solid-solution? At a late stage of evolution of the pegmatite melt, there will be exsolution of an (H_2O, F, B, Li)-rich fluid. However, the host rock is a dolomite-calcite marble which will coexist with a (Ca, Mg, CO_2)-rich fluid. In the exocontact zone and unit B, these two fluids mixed and allowed crystallization of (Li, Mg)-rich tourmaline (elbaite-dravite) in unit B and the exocontact. The (Ca, Mg, CO_2)-rich host-rock fluid did not penetrate unit A of the pegmatite, and hence unit A shows the typical schorl-elbaite-liddicoatite compositions.

Most Li-rich complex (elbaite-, lepidolite-, spodumene- and petalite-subtype) pegmatites have dravite-schorl-uvite tourmaline in their tourmalinized exocontact zones. These pegmatites frequently intrude amphibolites, and the presence of an exsolved (H_2O, F, B, Li)-rich fluid, together with the bulk composition of the country rock, leads to the formation of holmquistite as the principal Li-bearing phase in the exocontact (London, 1986). LCT pegmatites intruded into metapelites lack the necessary host-rock composition for the formation of holmquistite, and hence may form elbaite-schorl-dravite tourmalines in the exocontact (*e.g.*, Rožná-Hradisko, Novák & Selway, 1997a). Similarly, elbaite-schorl-dravite tourmaline occurs along the contact of lepidolite-subtype pegmatites hosted by Mg-rich syenites (durbachites) from the Jihlava pegmatite district, Moldanubicum, Czech Republic (Němec, 1989).

Thus the key condition for the formation of elbaite-dravite and elbaite-schorl-dravite is the mixing of an exsolved (Li, B, H_2O)-rich pegmatite fluid with an Mg-rich (Fe-poor) host-rock fluid under pH conditions (<6) suitable for the crystallization of tourmaline. Another important aspect is the absence of holmquistite in the tourmalinized exocontacts.

Summary

(1) Tourmaline of the elbaite-dravite series occurs in the elbaite-subtype pegmatite penetrating dolomite-calcite marble at Bližná, southern Bohemia. There are three compositional trends in tourmaline from Bližná: (a) Ca-rich Mn-bearing schorl-elbaite → Ca-rich Mn-bearing elbaite-schorl-dravite → Mn-rich elbaite-liddicoatite → Mn-rich liddicoatite-elbaite → Mn-bearing liddicoatite-elbaite in the dominant unit A; (b) Na-rich Fe-bearing uvite → Ca-rich Mn-bearing schorl-elbaite-dravite → volumetrically dominant Ca-rich Mg-bearing elbaite with patches of Ca-rich Mn-bearing dravite-elbaite → (Ca, Mn)-rich elbaite → Mn-rich liddicoatite-elbaite → Na-rich liddicoatite in the pegmatite unit B; (c) Na-rich uvite → Ca-rich Fe-bearing dravite → Ca-bearing dravite → Ca-bearing dravite-elbaite (Ca, Mg)-rich elbaite → Ca-rich Mg-bearing elbaite → Mg-bearing liddicoatite-elbaite from host marble to pegmatite in the exocontact zone.

(2) The intermediate elbaite-schorl-dravite and elbaite-dravite solid-solution series from unit B of the pegmatite and from the exocontact zone are a result of the interaction between (B, F, Li)-rich pegmatite fluid and (Ca, Mg)-rich fluids from the host marble.

(3) The factors controlling formation of elbaite-dravite in rocks may be summarized as follows: high activities of Li, Mg, Al and B and a high Li/Mg ratio in the parent medium, acidic conditions with pH $<\sim 6$, and lack of holmquistite. Consequently, tourmaline of elbaite-dravite series may be expected particularly in highly contaminated elbaite-subtype pegmatites penetrating marble and in holmquistite-free contact aureoles around complex LCT pegmatites.

Acknowledgements: We thank Carlo Aurisicchio and Reto Gieré for comments that substantially improved this manuscript, and Dave London for supplying a sample of the tourmalinized exocontact from White Picacho pegmatite. This work was supported by Natural Sciences and Engineering Research Council Major Installation, Major Equipment and Research Grants to FCH and PČ, a University of Manitoba Fellowship to JBS, and a Faculty of Science (University of Manitoba) Postdoctoral Fellowship and Granting Agency of the Czech Republic, Grant No. 205/96/0855, to MN.

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Received 2 June 1998
Accepted 6 January 1999