The Canadian Mineralogist
Vol. 38, pp. 869-876 (2000)

THE TANCO PEGMATITE AT BERNIC LAKE, MANITOBA. XIII. EXOCONTACT TOURMALINE

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ABSTRACT

The petalite-subtype Tanco granitic pegmatite, southeastern Manitoba, intrudes an amphibolite (metagabbro), which is metasomatically altered to tourmaline and magnesian annite close to the contact. The composition of exocontact tourmaline depends on the composition of the host rock and on the composition and amount of fluid injected from the pegmatite-forming melt into the host rock. Two compositional groups of tourmaline occur in the exocontacts at Tanco: (1) common feruvite – schorl – dravite (Ca- and Mg-rich), and (2) rare intermediate ternary tourmaline: elbaite – schorl – dravite (Na-, Al- and Li-rich). The Ca, Mg and Ti contents of group-1 tourmaline increase with distance from the contact between the pegmatite and the host rock. Group-1 and -2 tourmalines crystallize as a result of Na-, Al-, Li- and B-rich pegmatite-derived fluids infiltrating the Ca-, Mg- and Fe-rich host amphibolite, or as a chemical reaction between the pegmatite-forming melt and the host rock. The exocontact tourmaline is zoned, with a (Fe, Mg)-rich group-1 core and a Li-rich group-2 rim. Early consumption of Ca, Mg and Fe by crystallization of feruvite – schorl – dravite increased the chemical potential of Na, Al and Li in the fluid and promoted crystallization of elbaite – schorl – dravite. The rare ternary tourmaline of group 2 crystallized in the tourmaline aureole from fluids with high chemical potential of B, Al, Na and Ca, which are major constituents in tourmaline, but absent or minor in holmquistite. The influx of B-rich acidic fluids promoted crystallization of tourmaline and prevented crystallization of holmquistite.

Keywords: tourmaline, exocontact, metasomatism, granitic pegmatite, Tanco, Manitoba.

SOMMAIRE

La pegmatite granitique de Tanco, dans le sud-est du Manitoba, du sous-type à pétalite, a été mis en place dans une amphibolite (métagabbro) altérée par métasomatose en un assemblage de tourmaline et d'annite magnésienne près du contact. La composition de la tourmaline dans l'exocontact dépend de la composition de la roche hôte et de la composition et la quantité de la phase fluide qui s'est infiltrée à partir du magma responsable de la pegmatite. Deux groupes distincts de tourmaline se trouvent dans la zone d'exocontact à Tanco: (1) feruvite – schorl – dravite (tourmaline enrichie en Ca et Mg), commune, et (2) tourmaline ternaire intermédiaire, plus rare, de type elbaïte – schorl – dravite (tourmaline enrichie en Na, Al et Li). Les teneurs de la tourmaline du premier groupe en Ca, Mg et Ti augmentent avec la distance du contact entre la roche hôte et la pegmatite. Les tourmalines des deux groupes cristallisent suite à l'introduction de fluides porteurs de Na, Al, Li et B dérivés de la pegmatite dans la roche hôte riche en Ca, Mg et Fe, ou bien à une réaction chimique entre le magma et l'encaissant. La tourmaline de l'exocontact est zonée, avec un noyau riche en Fe et Mg, et donc du groupe 1, entouré d'une bordure riche en Li, et donc du groupe 2. L'élimination précoce de Ca, Mg et Fe par cristallisation de tourmaline de type feruvite – schorl – dravite augmenta localement le potentiel chimique de Na, Al et Li dans la phase fluide et a provoqué la cristallisation d'une tourmaline de type elbaïte – schorl – dravite. La tourmaline plus rare du groupe 2 a cristallisé dans l'auréole là où il y avait un potentiel élevé de B, Al, Na et Ca dans la phase fluide; ces éléments constituent des éléments majeurs dans la tourmaline, mais sont absents ou accessoires dans la holmquistite. L'infiltration de fluides borifères acides est responsable de la cristallisation de la tourmaline au détriment de la holmquistite.

(Traduit par la Rédaction)

Mots-clés: tourmaline, exocontact, métasomatose, pegmatite granitique, Tanco, Manitoba.

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INTRODUCTION

Recent studies show that the black tourmaline found in the exocontacts of rare-element granitic pegmatites is not just schorl – dravite, but may be far more diverse in composition (Selway *et al*. 1999a). For example, meta-andesite and metabasalt host-rocks surrounding the lepidolite pegmatites at Red Cross Lake, Manitoba, contain exocontact feruvite, uvite, schorl and dravite (Selway *et al.* 1998); biotite-bearing gneissic host-rocks at Stak Nala, Pakistan, contain exocontact schorl, dravite and elbaite – dravite – schorl (Laurs *et al*. 1998); dolomite – calcite marble host-rocks at Bližná, Czech Republic, contain exocontact uvite, dravite and Mg-rich elbaite (Novák *et al*. 1999). In this paper, we record the diverse chemical compositions of exocontact tourmaline at the Tanco pegmatite, Manitoba, and address the conditions of crystallization of feruvite – schorl – dravite and elbaite – schorl – dravite. This is one of the few reported occurrences of feruvite in the exocontacts of a rare-element granitic pegmatite.

BACKGROUND INFORMATION

Feruvite has been described in the amphibolite exocontacts of the lepidolite pegmatites at Red Cross Lake, Manitoba (Selway *et al.* 1998) and the olivine gabbro exocontacts of the elbaite-subtype pegmatite at Belo Horizonte, California (Selway *et al*. 1999a). Ternary elbaite – schorl – dravite compositions are another relatively rare exocontact tourmaline at Tanco; their occurrence has significant implications for the crystal chemistry of the tourmaline group and for the character of exocontact metasomatism. Intermediate schorl – elbaite – dravite has been observed in exocontacts of granitic pegmatites intruding amphibolite and amphibole–biotite gneisses from Mozambique (Sahama *et al*. 1979, Duda 1987), and in the tourmaline-rich metapelite enclaves and the exocontacts of the lepidolite- to amblygonite-subtype Bob Ingersoll I pegmatite, South Dakota (Jolliff *et al*. 1986). Intermediate elbaite – schorl – dravite occurs in metapelite enclaves of the lepidolite-subtype Rožná–Hradisko pegmatite, Czech Republic (Novák & Selway 1997), the tourmaline-rich gneiss exocontacts of the spodumene-subtype White Picacho granitic pegmatite, Arizona (Novák *et al*. 1999), and in the tourmaline-rich biotite granodiorite gneiss exocontacts of the miarolitic pegmatites at Stak Nala, Pakistan (Laurs *et al*. 1998).

GENERAL GEOLOGY

The Tanco granitic pegmatite is located on the northwest shore of Bernic Lake, Manitoba, about 180 km east–northeast of Winnipeg, close to the Manitoba–Ontario boundary. It is a member of the Bernic Lake pegmatite group, in the Bird River Greenstone Belt of the Superior Province. The geology of the Tanco pegmatite, a zoned petalite-subtype pegmatite 1990 × 1060 × 100 m in size (Stilling 1998), has been described in detail by Černý *et al.* (1998) and in publications cited therein. It is classified as a petalite-subtype pegmatite because the abundance of spodumene + quartz intergrowths formed by the breakdown of petalite indicates that petalite was the dominant Li-bearing mineral in the pegmatite. Within the Tanco pegmatite, the pegmatite zones are assigned numbers (10), (20), (30), *etc.* following the system of Stilling (1998) to correspond to the numbering system used by the Cabot Corporation, which operates a mine at Tanco.

The unaltered amphibolite host-rock consists of 54 vol.% ferrohornblende, 37% plagioclase (An_{38}), 4% ilmenite, 1% apatite and 4% quartz, plus minor biotite, epidote, titanite, almandine and chlorite (Morgan & London 1987). The texture of the unaltered amphibolite ranges from medium-grained and weakly foliated to very fine-grained, strongly foliated and locally banded. The precursor of the amphibolite was gabbro, coeval with basaltic flows of the Bernic Lake Formation (Trueman 1980, Černý *et al*. 1981). The amphibolite attained its present composition and fabric during the peak of regional metamorphism, which predated emplacement of the Tanco pegmatite (Černý 1982).

Metasomatism of the wallrocks at Tanco has been studied in detail by Morgan & London (1987). The four types of alteration of the host rocks surrounding the Tanco pegmatite are (in chronological order) as follows: (1) textural recrystallization, (2) B (±Li) metasomatism, (3) K–Rb–Cs–F (±Li) metasomatism, and (4) propylitic alteration with concomitant influx of Li and CO_2. Holmquistite is present in all three metasomatic assemblages and, along with biotite and tourmaline, served as a sink for Li. All types of metasomatic alteration occurred within greenschist-facies conditions ($T \leq 500$–550°C, $P \leq 3$ kbar) (Morgan & London 1987). The overall similarity of recrystallized and unaltered amphibolite suggests that recrystallization occurred during the regional metamorphism preceding pegmatite emplacement. Textural recrystallization is here characterized by coarsening of hornblende and plagioclase, and loss of foliation.

Boron (±Li) metasomatism is characterized by alteration of hornblende + plagioclase ± biotite ± apatite to tourmaline + quartz ± titanite ± apatite ± calcite ± holmquistite (Morgan & London 1987). The tourmaline alteration aureole is dominated by tourmaline (90–95 vol.%), and holmquistite is rare (<< 1 vol. %) (Morgan & London 1989). The tourmaline-bearing aureole at Tanco is 7 to 10 mm wide at the pegmatite–amphibolite contact, but locally extends up to 3 m into the host rock along fractures or small apophyses of pegmatite. Small rafts of amphibolite, along with biotite, are engulfed by the pegmatite. Tourmalization is most pervasive in the footwall, where the voluminous aplitic albite zone (30) occurs in the pegmatite near the lower wall-zone (20) and in the hanging wall above the pollucite zone (80).

The common coexistence of metasomatic biotite and tourmaline, and the complex cross-cutting relations between the two metasomatic assemblages, indicate that B (±Li) metasomatism and K–Rb–Cs–F (±Li) metasomatism may have occurred nearly simultaneously. Garnet–biotite geothermometry on metasomatic biotite adjacent to apparently primary metamorphic garnet in the altered host-rock indicates that the temperature of K–Rb–Cs–F metasomatism was approximately 450°C (Morgan & London 1987).

K–Rb–Cs–F (±Li) metasomatism is characterized by alteration of hornblende ± plagioclase ± apatite to magnesian annite (FeO >> MgO) ± apatite ± holmquistite; arsenopyrite and monazite are common accessory minerals (Morgan & London 1987). The biotite aureole is typically less than 3 m thick, but locally extends up to 4.5 m into host rock along fractures and foliation. Conversion to biotite is most pervasive in the host rock where the microcline-rich central intermediate zone (60) and lower intermediate zone (40) occur next to the wall zone (20).

Propylitic alteration, with concomitant influx of Li and CO_2, is characterized by alteration of hornblende + plagioclase to epidote + chlorite + titanite + calcite + clay ± holmquistite, and forms an aureole 2–9 m wide (Morgan & London 1987). All major phases in the propylitic assemblage, including holmquistite, are poor in Na, K, Rb, Cs and F.

EXPERIMENTAL METHODS

Analyses were done on a CAMECA SX–50 electron microprobe operating in wavelength-dispersion mode; the beam voltage for all elements was 15 kV, and the spot diameter was ~1–2 μm. Data were collected with a beam current of 20 nA for Na, Fe, Ca, Al, Si and Mg, and 30 nA for F, Mn, Zn, K, Ti and P. Count times for peak and background determinations for all elements were 20 and 10 s, respectively. Analytical data were reduced and corrected using the $\phi(\rho z)$ method (Pouchou & Pichoir 1984).

Structural formulae were calculated on the basis of 31 anions, assuming stoichiometric amounts of H_2O as $(OH)^-$ (*i.e.*, OH + F = 4 *apfu*; atoms per formula unit), B_2O_3 [as (BO_3)], and Li_2O (as Li) (MacDonald *et al.* 1993, Burns *et al.* 1994). Crystal-structure refinement and bond-valence calculations indicate that B = 3 *apfu* in virtually all tourmalines structurally analyzed to date (Hawthorne 1996, Bloodaxe *et al*. 1999). Lithium is assumed to be present as (1) normalization for Li-free compositions produce apparent vacancies at the *Y* site, and (2) the Tanco pegmatite is known to be rich in Li (Černý *et al*. 1998). The amount of Li assigned to the *Y* site is equal to the ideal sum of the *T*, *Z* and *Y* sites minus the amount of other cations occupying those sites [Li = 15 – (Si + Al + Ti + Mg + Fe + Mn)], and the calculation was iterated to self-consistency (Burns *et al.* 1994). If OH + F is less than 4 *apfu*, then the estimated Li content will be too high (Taylor *et al.* 1995). All Mn and Fe are assumed to be divalent, as crystal-structure studies have shown that this is the most common valence state of Mn and Fe in tourmaline (Burns *et al.* 1994, Bloodaxe *et al.* 1999). Each of the compositions of tourmaline listed in Table 1 represents the result of a single point-analysis on a tourmaline grain, and the entire list of compositions represents the variation in composition that occurs in the Tanco exocontact.

In order to describe the composition of tourmaline-group minerals in more detail, a combination of end-member names and adjectives is used, following the method of Selway & Novák (1997) and Selway *et al.* (1999b). If F is greater than OH at the *W* site, then the prefix "fluor" is used, following Hawthorne & Henry (1999). The composition that the authors have labeled feruvite – schorl – uvite (Table 1, composition 1) would be renamed "hydroxy-feruvite" if the nomenclature of Hawthorne & Henry (1999) was used, according to the assumption that OH exceeds F at the *W* site. However, use of the name "hydroxy-feruvite" requires direct determination of H_2O, so the IMA-approved name feruvite

TABLE 1. REPRESENTATIVE COMPOSITIONS OF EXOCONTACT TOURMALINE AT TANCO, MANITOBA

	1	2	3	4	5	6	7	8	9
SiO_2,wt%	35.70	35.40	35.50	35.70	36.80	37.10	35.70	36.50	36.60
TiO_2	1.28	0.76	0.56	0.72	0.71	0.18	0.54	0.48	0.25
B_2O_3*	10.35	10.21	10.12	10.36	10.56	10.66	10.51	10.59	10.76
Al_2O_3	27.10	27.80	27.80	29.60	30.20	33.30	34.20	34.90	36.80
MgO	7.23	5.48	4.14	5.82	6.81	4.53	1.66	2.12	2.06
CaO	3.05	2.29	0.83	1.77	0.69	0.46	1.07	0.12	0.15
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.17	0.00
FeO	10.80	12.30	14.20	10.40	8.39	6.66	9.85	7.40	6.27
Li_2O*	0.22	0.27	0.29	0.23	0.35	0.87	0.88	0.97	1.09
Na_2O	1.15	1.48	2.24	1.58	2.31	2.43	1.89	2.38	2.47
H_2O*	3.35	3.31	3.14	3.04	3.18	3.05	3.27	3.28	3.19
F	0.47	0.45	0.75	1.13	0.97	1.33	0.76	0.79	1.10
O=F	-0.20	-0.19	-0.32	-0.48	-0.41	-0.56	-0.32	-0.33	-0.46
Total	100.50	99.56	99.25	99.87	100.56	100.01	100.11	99.37	100.28
Formulae normalized to 31 anions									
T: Si, *apfu*	6.00	6.02	6.10	5.99	6.06	6.05	5.90	5.99	5.91
Al	0.00	0.00	0.00	0.01	0.00	0.00	0.10	0.01	0.09
B	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Z: Al	5.36	5.58	5.63	5.84	5.86	6.00	6.00	6.00	6.00
Mg	0.64	0.42	0.37	0.16	0.14	0.00	0.00	0.00	0.00
Y: Al	0.00	0.00	0.00	0.00	0.00	0.40	0.56	0.74	0.92
Ti	0.16	0.10	0.07	0.09	0.09	0.02	0.07	0.06	0.03
Mg	1.17	0.97	0.69	1.29	1.53	1.10	0.41	0.52	0.49
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.00
Fe^{2+}	1.52	1.75	2.04	1.46	1.15	0.91	1.36	1.02	0.85
Li	0.15	0.18	0.20	0.16	0.23	0.57	0.59	0.64	0.71
$\sum Y$	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
X: Ca	0.55	0.42	0.15	0.32	0.12	0.08	0.19	0.02	0.03
Na	0.37	0.49	0.75	0.51	0.74	0.77	0.61	0.76	0.77
□	0.08	0.09	0.10	0.17	0.14	0.15	0.20	0.22	0.20
OH	3.75	3.76	3.59	3.40	3.50	3.31	3.60	3.59	3.44
F	0.25	0.24	0.41	0.60	0.50	0.69	0.40	0.41	0.56

* B_2O_3, H_2O and Li_2O calculated by stoichiometry; B = 3 *apfu*, OH + F = 4 *apfu* and Li = 15 - $\sum(T + Z + Y)$.

Compositions 1-5 are from group 1 and 6-9 are from group 2. (1) black feruvite-schorl-uvite, sample TTC22-1; (2) black schorl-feruvite-dravite, sample TT2; (3) black Ca-bearing Mg-rich schorl, sample TT26; (4) brown Ca-rich "fluor-schorl"-dravite core, sample TTC37-2; (5) brown Ca-bearing dravite-schorl, sample TTC29-2; (6) brown "fluor-dravite"-elbaite-schorl, sample TT21; (7) brown (Ca, Mg)-bearing schorl-elbaite, sample TT23; (8) brown elbaite-schorl-dravite rim, sample TTC37-1; and (9) "fluor-elbaite"-schorl-dravite, sample TT24.

is used. The name feruvite for this composition would lead the reader to believe that *X* = Ca and *Y* = Fe, but actually the composition is intermediate between feruvite and schorl, as it contains 0.55 *apfu* Ca and 0.37 *apfu* Na, and it is intermediate between feruvite and uvite, as it contains 1.52 *apfu* Fe and 1.17 *apfu* Mg at the *Y* site. Thus, using the 50% rule of Nickel (1992), it should be called feruvite, but the nomenclature of Selway & Novák (1997) more completely describes its composition by using the name feruvite – schorl – uvite.

The IMA-approved name of composition 3 in Table 1 is schorl. The name schorl would lead the reader to believe that *X* = Na and *Y* = Fe, but actually the composition has minor amounts of Ca at the *X* site (0.15 *apfu*) and significant amounts of Mg at the *Y* site (0.69 *apfu*). The more descriptive name of Ca-bearing Mg-rich schorl, according to the nomenclature of Selway & Novák (1997), acknowledges these deviations from the ideal composition.

Paragenetic and Textural Attributes of Exocontact Tourmaline

At Tanco, black-to-brown euhedral tourmaline occurs in the metasomatized amphibolite exocontacts and xenoliths, which are characterized by the dominance of tourmaline and biotite. In the exocontact, tourmaline is more abundant than biotite, whereas in the xenoliths, biotite is more abundant than tourmaline, and arsenopyrite is common. The xenoliths also contain minor calcite, K-feldspar, albite, quartz and apatite. In the exocontact, tourmaline ranges from fine- to coarse-grained (0.3–2.0 cm long) and occurs as radiating needles perpendicular to the pegmatite contact. In xenoliths, coarse-grained tourmaline occurs as columns (1.0–2.5 cm long) perpendicular to the pegmatite contact and enclosed in very fine-grained brown biotite. The tourmaline grains may be homogeneous or zoned, and may be cut by carbonate veinlets.

Chemical Composition of the Exocontact Tourmaline

Tourmalines in the exocontacts at Tanco comprise two different compositional groups: (1) common feruvite – schorl – dravite [(Ca, Mg)-rich, Al-poor], and (2) rare elbaite – schorl – dravite [(Na, Al, Li)-rich] (Table 1). Tourmalines of both groups are similar in appearance and texture. Typically, tourmalines of group 1 and group 2 occur in separate hand-specimens. Rarely, individual hand-specimens contain zoned tourmaline with a group-1 core and group-2 rim. Zoned brown tourmaline in sample TTC37 has a Ca-rich "fluor-schorl" – dravite core, a "fluor-feruvite" – schorl zone, a Ca-bearing "fluor-schorl" – dravite zone and a Ca-bearing "fluor-elbaite" – schorl – dravite rim. This zoned crystal shows decreasing Ca, Fe and Mg and increasing Na, Al and Li from core to rim.

Tourmaline grains of the feruvite – schorl – dravite group 1 (Fig. 1a) are Ca-rich with up to 0.55 *apfu* Ca at the *X* site (Table 1, composition 1). Group-1 compositions are Al-poor, commonly with <6.0 *apfu* total Al (Fig. 1b), and have up to 0.64 *apfu* Mg at the *Z* site in feruvite – schorl and rare feruvite – uvite. Schorl is the dominant component in group-1 compositions, which range from feruvite – schorl to schorl – feruvite to Ca-rich schorl – dravite to Ca-bearing schorl – dravite to (Ca, Mg)-rich schorl to Ca-bearing dravite – schorl (Fig. 2a). There are positive correlations among Ca, Mg and Ti in group-1 tourmaline: tourmaline far from the contact with the pegmatite is Ca-, Mg- and Ti-rich,

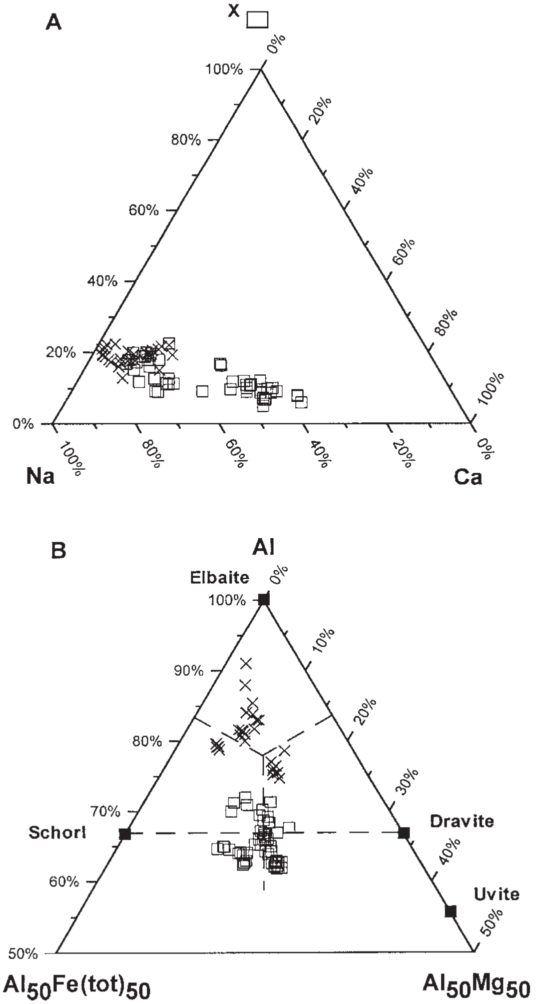

FIG. 1. Tourmaline compositions from the exocontacts at Tanco. A. $^{X}\square$–Na–Ca diagram. B. Al–Fe–Mg diagram. ■: end members; □: group-1 tourmaline; ×: group-2 tourmaline.

whereas the tourmaline close to the contact is Ca-, Mg- and Ti-poor. Calcium, Mg, and Ti decrease from Ti-bearing feruvite–schorl (≤0.18 *apfu* Ti) to Ca-rich "fluor-schorl" – dravite (>0.02 *apfu* Ti) (Figs. 2b, c).

Tourmaline of the elbaite – schorl – dravite group 2 is Na-rich (≤0.79 *apfu* Na), Ca-poor (≤0.19 *apfu* Ca), and Al-rich (≤7.43 *apfu* total Al) (Fig. 1). These tourmaline compositions plot close to the center of elbaite – schorl – dravite diagram, and range from intermediate "fluor-dravite" – schorl – elbaite to (Ca, Mg)-bearing schorl–elbaite to "fluor-elbaite" – schorl – dravite (Fig. 1b). All of these compositions plot in what was previously thought to be a compositional gap (*e.g.*, Foit & Rosenburg 1979, Dietrich 1985, Henry & Dutrow 1996).

DISCUSSION

Stability of tourmaline

The composition of the exocontact tourmaline at Tanco depends on the composition of the host rock and the pegmatite-derived fluids. The host-rock composition is considered to control the populations of the *X* and *Y* sites: at Tanco, the amphibolite wallrock is the source of Ca, Mg, Fe and Ti in tourmaline. Factors that enhance tourmaline stability during conversion of amphibolite to "tourmalinite" are: (1) the abundance of Fe and Mg produced by the breakdown of hornblende + plagioclase, (2) the neutralization of the acidic fluid by Na ± Ca produced by the breakdown of hornblende + plagio-

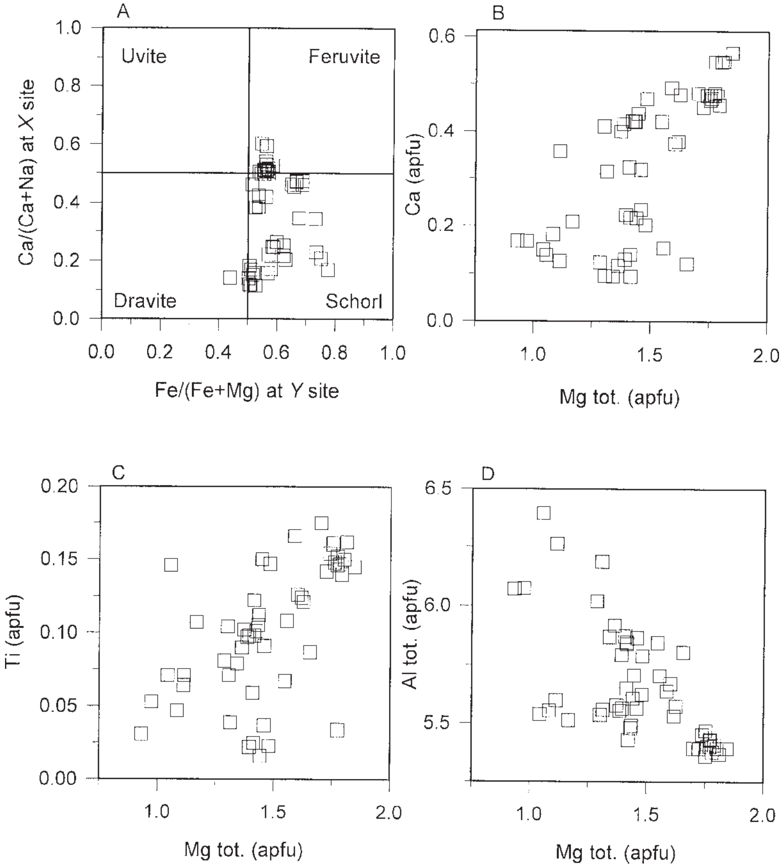

FIG. 2. Group-1 tourmaline compositions from the exocontacts at Tanco. A. Ca/(Ca + Na) at the *X* site *versus* Fe/(Fe + Mg) at the *Y* site. Quadrants are labeled according to the dominant tourmaline end-members. B. Ca *versus* total Mg (*apfu*). C. Ti *versus* total Mg (*apfu*). D. Total Al *versus* total Mg (*apfu*).

clase, (3) an influx of B, Al, Li and F from the pegmatite-forming melt, and (4) the acidity of the aqueous fluid (pH < 6) (Morgan & London 1989).

Almost 90 mol% of Fe in the amphibolite at Tanco is conserved by tourmaline formation (Morgan & London 1989). Morgan & London (1989) showed experimentally that ferromagnesian tourmaline is unstable in fluids with pH above 6.5 (*i.e.*, alkaline fluids), and in systems that lack ferromagnesian components, tourmaline is unstable regardless of pH, pressure, temperature and B content. Once Fe and Mg in the fluids are depleted, there may be no crystallization of tourmaline until the abundance of Li increases in the late fluids *via* fractional crystallization in a closed system (London 1999).

Morgan & London (1989) concluded that only about 60% of the B lost from the pegmatite is conserved as tourmaline in the wallrocks, and that the pegmatite-forming magma lost about 70% of its original B content. Aluminum is particularly soluble in B-rich aqueous fluids, and an influx of Al (in addition to B) is necessary to convert amphibolites to “tourmalinites” (Morgan & London 1989).

The acidic B- and F-rich fluids required for tourmalinization probably emanate from the aplitic albite zone (30), as the tourmaline aureole at Tanco is thickest and replacement is most complete adjacent to albitic bodies (Morgan & London 1987). These residual fluids also caused alteration of microcline to white mica within the lower intermediate zone (40), and the microcline-rich central intermediate zone (60) is the probable source of alkalis for alteration of the wallrock to biotite. The widespread distribution of holmquistite and Li-enriched tourmaline and biotite throughout the entire metasomatic aureole suggests that Li was released more or less continuously during a hydrothermal stage associated with the pegmatite, and probably had multiple sources: (1) the “primary” Li content of the exsolved supercritical fluid, and (2) Li mobilized during low-temperature breakdown of Li-aluminosilicates and phosphates (such as petalite, spodumene and amblygonite–montebrasite) to Li-poor or Li-free phases (Černý *et al*. 1998).

The overall mineralogy of alteration products in the exocontact indicates high activities of B, F, Li, Rb and Cs. Whereas B is virtually exclusively bound in tourmaline, F and (to a degree) Li are shared among tourmaline, biotite and holmquistite (as discussed later), whereas K, Rb plus Cs are incorporated almost solely in the mica. Morgan & London (1987) recorded ≤0.22 wt% Rb_2O and ≤0.42 wt% Cs_2O in exocontact tourmaline; the ionic radii of Rb and Cs are apparently too large to allow their extensive incorporation at the *X* site in tourmaline, and Rb and Cs are preferentially partitioned into mica over tourmaline. Metasomatic biotite close to the pegmatite contacts contains ≤4.6 wt% Rb_2O and ≤5.0 wt% Cs_2O (Morgan & London 1987), a phenomenon also observed at numerous other localities (*cf.* Černý & Burt 1984).

Increase in μ(HF) (acidity) also corresponds to an increase in the extent of the exchange $F(OH)_{-1}$, leading to replacement of OH by F in minerals such as micas and amphiboles (Burt 1981). The magnesian biotite that is close to the pegmatite contact at Tanco contains intermediate F contents (1.18 *apfu* F) (Morgan & London 1987). The presence of biotite with moderate F contents indicates that it crystallized under high μ(HF) (acidity) and μ(KF) (salinity) (Burt 1981).

Crystallization of tourmaline versus holmquistite

The tourmaline aureole at Tanco contains abundant tourmaline, but we did not find holmquistite. Group-2 elbaite – schorl – dravite crystallized (rather than holmquistite) because of the high chemical potential of B, Na and Ca in the fluids; all of these are major constituents of tourmaline but are absent in holmquistite. The fluids were also Al-rich, as tourmaline is significantly more Al-rich (~27–36 wt% Al_2O_3) than holmquistite (~12 wt% Al_2O_3) at Tanco (Morgan & London 1987).

Conversion of hornblende to schorl or dravite may be schematically represented by increasing chemical potential of Al and B, as expressed by the exchange operator $AlB(Fe^{2+},Mg)_{-3}$, but application of this component depends on the Al content of the hornblende and the oxidation state of Fe (Fig. 2 of London 1986). Conversion of hornblende to elbaite involves two exchange operators: $AlB(Fe^{2+},Mg)_{-3}$ and $LiAl(Fe^{2+},Mg)_{-2}$ at a 1:1 ratio (London 1986). Therefore, both group-1 and group-2 tourmalines require an influx of Al and B, but tourmaline of group 2 also requires an influx of Li from the pegmatite-forming melt into the host rock. Conversion of hornblende to holmquistite only involves the exchange vector $LiAl(Fe^{2+},Mg)_{-2}$ (London 1986). Thus, influx of B-rich fluids promotes the crystallization of tourmaline and prevents the crystallization of holmquistite.

The altered amphibolite host-rock surrounding the spodumene-rich Edison pegmatite, Black Hills, South Dakota, has alteration assemblages similar to those at Tanco: a biotite assemblage and a hornblende–holmquistite assemblage (Shearer & Papike 1988). The biotite assemblage occurs closest to the pegmatite contact and formed before the hornblende–holmquistite assemblage (Shearer & Papike 1988). Alteration of the amphibolite host-rock was caused by influx of K and Li from the pegmatite-derived aqueous fluids (Shearer & Papike 1988). There is one significant difference between the exocontacts of the Tanco and Edison pegmatites. At Tanco, the exocontact is tourmaline-rich, whereas at Edison, it is holmquistite-rich and tourmaline-free; this difference is due to the abundance of B in the pegmatite-derived fluid at Tanco and to its virtual absence at Edison.

Exocontact tourmaline at Tanco

There are positive correlations among Ca, Mg and Ti in the group-1 feruvite – schorl – dravite in the exocontacts at Tanco. The Ca, Mg and Ti contents of exocontact tourmaline increase with distance from the contact between pegmatite and host rock. Group-1 and group-2 tourmaline crystallized both as a result of the Na-, Al- and B-rich pegmatite-generated fluid infiltrating the Ca-, Mg- and Fe-rich host amphibolite, and by chemical reaction between the pegmatite-forming melt and the host rock.

Holmquistite is widespread in the biotite-rich and propylitic assemblages in the aureole at Tanco (Morgan & London 1987), but our observations indicate that holmquistite does not occur in the tourmaline-rich aureole. Thus group-2 Li-rich tourmaline crystallized in preference to holmquistite owing to the abundance of B, Al and Na in the fluid. Novák *et al*. (1999) concluded that dravite–elbaite and Mg-bearing elbaite compositions have a similar origin in the holmquistite-free exocontacts of the elbaite-subtype pegmatite at Bližná, Czech Republic.

The exocontact tourmaline at Tanco is zoned, with (Fe, Mg)-rich group-1 cores and Li-rich group-2 rims, but G.B. Morgan VI (pers. commun.) observed the reverse of this zonation. The normal zonation reflects the fact that Fe- and Mg-rich tourmaline usually crystallizes before Li-rich tourmaline in pegmatites. Foit & Rosenberg (1979) noted that Fe and Mg preferentially partitioned (relative to Li) into the *Y* site in tourmaline. Early consumption of Ca, Mg and Fe by crystallization of feruvite – schorl – dravite increased the chemical potential of Na, Al and Li in the fluid and promoted crystallization of elbaite – schorl – dravite. Tourmaline and biotite in the exocontact crystallized simultaneously, but group-2 Li-rich tourmaline tends to be more F-rich than (Fe, Mg)-rich group-1 tourmaline, which indicates that group-2 tourmaline crystallized at a higher μ(HF) than group-1 tourmaline.

ACKNOWLEDGEMENTS

The authors thank Bob Martin and the reviewers, G.B. Morgan, VI and R.V. Dietrich, for their helpful comments, which substantially improved the manuscript. This work was supported by NSERC Research, Equipment and Major Installation Grants to FCH and PC, a Faculty of Science Postgraduate Student Fellowship from the University of Manitoba to JBS, and a Faculty of Science (University of Manitoba) Postdoctoral Fellowship to MN. Sampling was facilitated by P. Vanstone of the Tantalum Mining Corporation of Canada Ltd. at Bernic Lake.

REFERENCES

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

BURNS, P.C., MACDONALD, D.J. & HAWTHORNE, F.C. (1994): The crystal chemistry of manganese-bearing elbaite. *Can. Mineral.* **32**, 31-41.

BURT, D.M. (1981): Acidity–salinity diagrams – application to greisen and porphyry deposits. *Econ. Geol.* **76**, 832-843.

ČERNÝ, P. (1982): The Tanco pegmatite at Bernic Lake, southeastern Manitoba. *In* Granitic Pegmatites in Science and Industry (P. Černý, ed.). *Mineral. Assoc. Can., Short Course Handbook* **8**, 527-543.

________ & BURT, D.M. (1984): Paragenesis, crystallochemical characteristics, and geochemical evolution of micas in granitic pegmatites. *In* Micas (S.W. Bailey, ed.). *Rev. Mineral.* **13**, 257-297.

________, ERCIT, T.S. & VANSTONE, P.J. (1998): Mineralogy and petrology of the Tanco rare- element pegmatite deposit, southeastern Manitoba. *Int. Mineral. Assoc., 17th Gen. Meet.* (*Toronto*), *Field Trip Guidebook* **B6**.

________, TRUEMAN, D.L., ZIEHLKE, D.V., GOAD, B.E. & PAUL, B.J. (1981): The Cat Lake – Winnipeg River and the Wekusko Lake pegmatite fields, Manitoba. *Manitoba Dep. Energy and Mines, Mineral Resources Div., Econ. Geol. Rep.* **ER80-1**.

DIETRICH, R.V. (1985): The tourmaline group: a résumé. *Mineral. Rec.* **16**, 339-351.

DUDA, J. (1987): The Muiane pegmatite deposit in Mozambique. *Čas. Mineral. Geol.* **32**, 79-86 (in Czech).

FOIT, F.F., JR. & ROSENBERG, P.E. (1979): The structure of vanadium-bearing tourmaline and its implications regarding tourmaline solid solution. *Am. Mineral.* **64**, 788-798.

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.

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.

Laurs, B.M., Dilles, J.H., Wairrach, Y., Kausar, A.B. & Snee, L.W. (1998): Geological setting and petrogenesis of symmetrically zoned, miarolitic granitic pegmatites at Stak Nala, Nanga Parbat – Haramosh massif, northern Pakistan. *Can. Mineral.* **36**, 1-47.

London, D. (1986): Holmquistite as a guide to pegmatite rare metal deposits. *Econ. Geol.* **81**, 704-712.

________ (1999): Stability of tourmaline in peraluminous granite systems: the boron cycle from anatexis to hydrothermal aureole. *Eur. J. Mineral.* **11**, 253-262.

MacDonald, D.J., Hawthorne, F.C. & Grice J.D. (1993): Foitite, $\square\,[Fe^{2+}_2(Al,Fe^{3+})]\,Al_6\,Si_6O_{18}\,(BO_3)_3\,(OH)_4$, a new alkali-deficient tourmaline: description and crystal structure. *Am. Mineral.* **78**, 1299-1303.

Morgan, G.B., VI & London, D. (1987): Alteration of amphibolitic wallrocks around the Tanco rare-element pegmatite, Bernic Lake, Manitoba. *Am. Mineral.* **72**, 1097-1121.

________ & ________ (1989): Experimental reactions of amphibolite with boron-bearing aqueous fluids at 200 MPa: implications for tourmaline stability and partial melting in mafic rocks. *Contrib. Mineral. Petrol.* **102**, 281-297.

Nickel, E.H. (1992): Solid solutions in mineral nomenclature. *Can. Mineral.* **30**, 231-234.

Novák, M. & 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., Hawthorne, F.C. & Ottolini, L. (1999): Tourmaline of the elbaite–dravite series from an elbaite-subtype pegmatite at Bližná, southern Bohemia, Czech Republic. *Eur. J. Mineral.* **11**, 557-568.

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.

Sahama, T.G., von Knorring, O. & Tornroos, R. (1979): On tourmaline. *Lithos* **12**, 109-114.

Selway, J.B., Černý, P. & Hawthorne, F.C. (1998): Feruvite from lepidolite pegmatites at Red Cross Lake, Manitoba. *Can. Mineral.* **36**, 433-439.

_________, _________, ________ & Novák, M. (1999a): Exocontact tourmaline rimming pegmatites. *Geol. Assoc. Can. – Mineral. Assoc. Can., Abstr. Vol.* **24**, A-112.

________ & Novák, M. (1997): Experimental conditions, normalization procedures and used nomenclature for tourmaline. *In* Tourmaline 1997 International Symposium on Tourmaline, Field Trip Guidebook (M. Novák & J.B. Selway, eds.). Nové Město na Moravě, Czech Republic, 19-21.

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

Shearer, C.K. & Papike, J.J. (1988): Pegmatite–wallrock interaction: holmquistite-bearing amphibolite, Edison pegmatite, Black Hills, South Dakota. *Am. Mineral.* **73**, 324-337.

Stilling, A. (1998): *Bulk Composition of the Tanco Pegmatite at Bernic Lake, Manitoba, Canada*. M.Sc. thesis, Univ. of Manitoba, Winnipeg, Manitoba.

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

Trueman, D.L. (1980): *Stratigraphy, Structure and Metamorphic Petrology of the Archean Greenstone Belt at Bird River, Manitoba*. Ph.D. thesis, Univ. of Manitoba, Winnipeg, Manitoba.

Received October 22, 1999, revised manuscript accepted June 16, 2000.