

## THE TANCO PEGMATITE AT BERNIC LAKE, MANITOBA. XIV. INTERNAL TOURMALINE

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### ABSTRACT

The zoned petalite-subtype Tanco granitic pegmatite, located about 180 km east-northeast of Winnipeg, near the Manitoba–Ontario border, intrudes amphibolite. Tourmaline is not abundant, but is widespread in most of the pegmatite zones. Tourmaline is black, brown or rarely green in the border zone (10), wall zone (20), aplitic albite zone (30) and central intermediate zone (60); it is pink and rarely green in the petalite-bearing lower and upper intermediate zones (40) and (50). On the basis of paragenesis and compositional zoning within individual tourmaline crystals, tourmaline at Tanco is characterized by the following sequence of crystallization: foitite – schorl → (± schorl – foitite) → Al-rich schorl (±Mg) → schorl (±Mg) → schorl – elbaite (±Mg) → “fluor-elbaite” – schorl (±Mg) → Fe-rich “fluor-elbaite” → Mn-bearing “fluor-elbaite” → rossmanite – elbaite → elbaite – rossmanite → (± Ca-bearing “fluor-elbaite”, Ca-bearing “fluor-elbaite” – rossmanite). The dominant substitution at the X site is  $\text{Na} \rightleftharpoons \square$ , and there is a positive correlation between proportions of Na and F. The dominant substitution at the Y site is  $3\text{Fe}^{2+} \rightleftharpoons 1.5\text{Al} + 1.5\text{Li}$ , which is controlled by fractionation of the pegmatite-forming melt. Magnesium and Ti incorporated from the host amphibolite into the pegmatite-forming melt generated endomorphic Mg-bearing schorl to Al-rich Mg-bearing schorl to Mg-bearing schorl – elbaite to Mg-bearing elbaite – schorl in zones (10), (20) and (30). Sodium, Mn and F all increase from foitite – schorl to “fluor-elbaite” – schorl and Fe-rich “fluor-elbaite” in zones (10), (20), (30) and (60). In late-stage tourmaline, Ca and F increase from rossmanite–elbaite to Ca-bearing “fluor-elbaite” – rossmanite to Ca-bearing “fluor-elbaite” in zones (40) and (50). Late Ca-enrichment is due to sequestering of Ca in the melt as fluoride complexes. This is the first occurrence of foitite, rossmanite and late-stage Ca-enrichment in tourmaline reported a petalite-subtype pegmatite.

*Keywords:* tourmaline, foitite, rossmanite, granitic pegmatite, petalite subtype, Tanco, Manitoba.

### SOMMAIRE

La pegmatite granitique de Tanco, zonée, située environ 180 km à l'est-nord-est de Winnipeg, près de la frontière Manitoba–Ontario, a été mise en place dans une amphibolite. La tourmaline n'est pas abondante, mais elle est répandue dans la plupart des zones de cette pegmatite. Elle est noire, brune ou, plus rarement, verte dans la zone de bordure (10), la zone de paroi (20), la zone à albite aplitique (30) et le centre de la zone intermédiaire (60); elle est rose ou, plus rarement, verte, dans les parties inférieure et supérieure (à petalite) de la zone intermédiaire, (40) et (50), respectivement. À la lumière de la paragenèse et de la zonation des cristaux individuels, la tourmaline à Tanco suit la séquence de cristallisation suivante: foitite – schorl → (± schorl – foitite) → schorl alumineux (±Mg) → schorl (±Mg) → schorl – elbaite (±Mg) → “fluor-elbaite” – schorl (±Mg) → “fluor-elbaite” enrichi en Fe → “fluor-elbaite” manganifère → rossmanite – elbaite → elbaite – rossmanite → (± “fluor-elbaite” et “fluor-elbaite” – rossmanite calcifères). La substitution dominante au site X serait  $\text{Na} \rightleftharpoons \square$ , et il y a une corrélation positive entre les proportions de Na et de F. La substitution dominante au site Y serait  $3\text{Fe}^{2+} \rightleftharpoons 1.5\text{Al} + 1.5\text{Li}$ , qui témoigne du fractionnement du magma. Le Mg et le Ti, incorporés dans le magma par contamination avec l'encaissant amphibolitique, a généré une croissance endomorphique de schorl magnésien à schorl magnésien alumineux à schorl–elbaite magnésien à elbaite – schorl magnésien dans les zones (10), (20) et (30). Le Na, Mn et F augmentent dans la séquence foitite – schorl à “fluor-elbaite” – schorl à “fluor-elbaite” ferreuse des zones (10), (20), (30) et (60). Dans la tourmaline tardive, la concentration en Ca et F augmente dans la séquence rossmanite – elbaite à “fluor-elbaite” – rossmanite calcifère à “fluor-elbaite” calcifère des zones (40) et (50). L'enrichissement tardif en Ca serait dû à la présence de Ca dans le bain fondu sous forme de complexe fluoré. Il s'agit du premier exemple de foitite, rossmanite et d'enrichissement tardif en Ca d'une tourmaline à être signalé dans une pegmatite granitique du sous-type à pétalite.

(Traduit par la Rédaction)

*Mots-clés:* tourmaline, foitite, rossmanite, pegmatite granitique, sous-type à pétalite, Tanco, Manitoba.

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## INTRODUCTION

Tourmaline is a useful petrochemical indicator because it shows extensive substitutions that are controlled by the environment in which it crystallized. In granitic pegmatites, changes in tourmaline composition can be related to the bulk composition of each pegmatite zone and the compositions of the coexisting minerals (Jolliff *et al.* 1986, Laurs *et al.* 1998, Selway *et al.* 1999). The Tanco granitic pegmatite, in southeastern Manitoba, is extensively exposed owing to underground mining operations, and is one of the few petalite-subtype pegmatites that has been studied in detail (Černý *et al.* 1998). These attributes make it an excellent candidate for a detailed study of the compositional variation in tourmaline in petalite-subtype pegmatites. Previously, the tourmaline compositions from only one petalite-subtype pegmatite (Urubu, Brazil) have been discussed briefly in the literature (Quémeñeur *et al.* 1993, Marchetti 1997).

Here, we discuss the compositional evolution of tourmaline and explain the origin of various correlations in tourmaline of the Tanco granitic pegmatite.

## GENERAL GEOLOGY

The zoned petalite-subtype Tanco pegmatite intrudes amphibolite, and is located on the northwestern shore of Bernic Lake, about 180 km east–northeast of Winnipeg, near the Manitoba–Ontario border. It is a member of the Bernic Lake pegmatite group, and is located in the Bird River Greenstone Belt of the Superior Province.

The geology of the Tanco pegmatite has been summarized by Černý *et al.* (1998, and references cited therein). The subhorizontal Tanco pegmatite, 1990 × 1060 × 100 m in size (Stilling 1998), consists of an exomorphic halo and nine pegmatite zones: (10) border zone, (20) wall zone, (30) aplitic albite zone, (40) lower intermediate zone, (50) upper intermediate zone, (60) central intermediate zone, (70) quartz zone, (80) pollucite zone and (90) lepidolite zone. In contrast to previous papers on Tanco, in which the above pegmatite zones were numbered (1) up to (9), we use the (10) to (90) designation to correspond to the system used by the Cabot Corporation, which operates the mine at Tanco (*cf.*, Stilling 1998). The Tanco pegmatite consists of nine pegmatite zones, *not* ninety, as the numbering system may imply. The border zone (10) is dominantly an assemblage of saccharoidal albite and quartz along the pegmatite–wallrock contact, and is <30 cm thick. The wall zone (20) consists dominantly of giant columnar microcline perthite (≤3 m) in a matrix of quartz, medium-grained albite and tabular greenish muscovite (≤10 cm). The aplitic albite zone (30) consists mainly of fine-grained undulating layers of saccharoidal albite and quartz with significant Ta–Nb mineralization. The lower intermediate zone (40) consists of two main assemblages: (1) large crystals of microcline perthite and spodumene + quartz pseudomorphs after petalite (≤2 m)

embedded in medium-grained quartz, albite and micas; (2) quartz pods (0.5–2.0 m) with amblygonite–montebrasite and aggregates of spodumene + quartz. The lower intermediate zone (40) grades gradually into the upper intermediate zone (50), characterized by gigantic crystals (*e.g.*, amblygonite to 2 m, microcline perthite to 10 m, petalite to 13 m long). The central intermediate zone (60) consists mainly of microcline perthite, quartz (5–40 cm) and fine-grained greenish muscovite with significant amounts of Ta–Nb oxide minerals, beryl and hafnian zircon. The quartz, pollucite and lepidolite zones (70), (80) and (90) are monomineralic. The Tanco pegmatite is mined for Ta (wodginite and tantalite), Cs (pollucite), Rb (lepidolite) and ceramic-grade spodumene.

## EXPERIMENTAL METHODS

Electron-microprobe analyses were done on a CAMECA SX–50 instrument in wavelength-dispersion mode; the beam voltage for all elements was 15 kV, and the spot diameter was 1 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, 1985).

Structural formulae were calculated on the basis of 31 anions, under the assumption of stoichiometric amounts of H<sub>2</sub>O as (OH)<sup>−</sup> (*i.e.*, OH + F = 4 *apfu*, atoms per formula unit), B<sub>2</sub>O<sub>3</sub> [as (BO<sub>3</sub>) with B = 3 *apfu*], and Li<sub>2</sub>O (as Li) (MacDonald *et al.* 1993, Burns *et al.* 1994). Lithium is assumed to be present, as (1) calculations of structural formulae for Li-free compositions produce 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 taken to be 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). In order to describe the tourmaline composition in more detail, a combination of end-member names and adjectives is used, following the method of Selway & Novák (1997) and Selway *et al.* (1999). If F is greater than OH at the W site, then the prefix “fluor” is used, following Hawthorne & Henry (1999).

## CRYSTALLIZATION SEQUENCE OF THE TANCO PEGMATITE

Textural evidence indicates that consolidation of the pegmatite proceeded from the border zone (10) and wall

zone (20) to the lower and upper intermediate zones (40) and (50) (Černý *et al.* 1998). Zones (40) and (50) crystallized inward in their footwall and hanging-wall segments, forming a shell-like concentric zone. The central intermediate zone (60), aplitic albite zone (30), lepidolite zone (90) and most of the quartz bodies (70) crystallized within this innermost concentric shell, the upper parts of which contain the pollucite zone (80) as a late but integral part (for a map of Tanco, see Fig. 5 of Černý 1991, Stilling 1998). The pressure and temperature conditions of solidification, based on experimental studies of the Li-aluminosilicates (London 1984, 1986) and on studies of the fluid inclusions (London 1986, Morgan & London 1987, Thomas & Spooner 1988a, b, Thomas *et al.* 1988, 1990), support this sequence of crystallization.

The presence of petalite, amblygonite, Rb-rich and Cs-bearing lepidolite, pink elbaite, manganotantalite and lithiophilite (81–92 mol.% of the end-member) in the lower and upper intermediate zones (40) and (50) indicates that these zones are Li-rich and highly fractionated (Černý *et al.* 1998). There is a notable lack of Li-bearing minerals in the central intermediate zone (60), which is enclosed in the concentric shell consisting of zones (40) and (50). The presence of greenish (Rb, Cs, Li)-poor muscovite, black schorl, ferrotapiolite and lithiophilite (77 mol.% of the end-member) in central intermediate zone (60) indicates that it is Fe-enriched and, in some respects, less fractionated than lower and upper intermediate zones (40) and (50).

In the eastern lobe of the pegmatite, the aplitic albite zone (30) either forms sheet-like layers along the contacts of the wall zone (20) with overlying the central intermediate zone (60) and quartz zone (70), or grades into the central intermediate zone (60) (Černý *et al.* 1998). In the western lobe, the aplitic albite zone (30) is dispersed as a network within the central intermediate zone (60) and along the contacts between the wall zone (20) and lower intermediate zone (40) (see Fig. 8 of Černý *et al.* 1998). Some of the minerals in aplitic albite zone (30) (*i.e.*, greenish muscovite, curvilamellar lithian muscovite to lepidolite, black and green tourmaline) are slightly more fractionated than those in the central intermediate zone (60), whereas the oxide minerals in zone (60) are more fractionated than those in zone (30). Rare apatite, cassiterite, ilmenite, zircon and sulfides occur in zones (30) and (60).

#### PARAGENETIC AND TEXTURAL ATTRIBUTES OF TOURMALINE

Tourmaline at Tanco occurs in the exocontact and in the pegmatite. The exocontact tourmaline is discussed by Selway *et al.* (2000). The internal tourmaline occurs in the border zone (10), wall zone (20), lower and upper intermediate zones (40) and (50), central intermediate zone (60) and aplitic albite zone (30).

#### Border zone (10)

Fine needles of tourmaline range from black to brown to green, and are commonly zoned (but may be homogeneous). The tourmaline is enclosed in aplitic albite and quartz, and may contain albite + quartz inclusions. Tourmaline and minor green prismatic beryl are arranged perpendicular to the pegmatite contact with the host amphibolite.

#### Wall zone (20)

Black to brown tourmaline occurs in “leopard rock” (round brown quartz enclosed in a network of pink albite of the “cleavelandite” habit) and in an albite + K-feldspar + quartz matrix. Euhedral tourmaline ranges in size from medium (<3 mm) to comb-textured and very coarse ( $\leq 24 \times 4$  cm), and is commonly compositionally zoned perpendicular to its length. The coarse to very coarse prismatic tourmaline may be cross-cut by veinlets of K-feldspar + quartz. Tourmaline commonly contains albite inclusions.

Fine (<1 mm) to coarse (<5 mm) needles of green tourmaline occur in aplitic albite pods in wall zone (20), and may be zoned with a brown core and a green rim.

#### Lower and upper intermediate zones (40) and (50)

The accessory tourmaline is commonly euhedral, zoned and pink, and rarely has a green core and a pink rim. Pink tourmaline ranges from coarse to very coarse columnar to fibrous (1–18 cm long) and is commonly zoned with a cloudy pale-pink core and a transparent pink rim. Pink tourmaline (50 vol.%) enclosed in albite forms parallel aggregates of very coarse columnar crystals (6–18 cm  $\times$  2–5 mm) surrounded by coarse (1–3 cm long) radiating needles of tourmaline and minor 1.5 cm pods of fine-grained lepidolite. Tourmaline enclosed in purple curvilamellar (Cs, Rb)-bearing lepidolite is dark pink to red. Zoned pink tourmaline enclosed in pollucite is columnar (6  $\times$  1 cm) and contains K-feldspar + pollucite veinlets. Pink patchily zoned tourmaline enclosed in amblygonite is associated with fine-grained, almost end-member topaz ( $\text{Al}_{2.00}\text{Si}(\text{F}_{1.96}\text{OH}_{0.04})\Sigma_{2.00}$  by electron-microprobe analysis), to date the only occurrence of topaz at Tanco.

Pink tourmaline in the lower and upper intermediate zones (40) and (50) is commonly altered to mica. Tourmaline enclosed in fine-grained white muscovite is commonly completely replaced by medium-grained pale purple lepidolite, with the basal plane of lepidolite perpendicular to the *c* axis of tourmaline. Some very coarse columns of tourmaline ( $\leq 12$  cm long) are zoned parallel to the *c* axis and consist of pink tourmaline at one end, a narrow zone of very fine-grained green muscovite, a narrow zone (2 mm) of blue tourmaline and very fine-grained green muscovite at the other end.

### Central intermediate zone (60)

The central intermediate zone (60) contains very coarse ( $\leq 4$  cm long) black to brown tourmaline with an occasional thin green rim.

### Aplitic albite zone (30)

Black-to-brown and green zoned prisms of tourmaline occur in the aplitic albite zone (30). They are enclosed in albite and form medium (1–3 mm long) needles, whereas tourmaline crystals in contact with coarse-grained K-feldspar are slightly longer (5 mm long).

## COMPOSITION OF THE TOURMALINE

On the basis of compositional zoning within individual crystals of tourmaline (Table 1), tourmaline at Tanco evolved through the following sequence of crystallization from the border zone (10) to the wall zone (20), to the lower intermediate zone (40) and upper intermediate zone (50): ( $\pm$  foitite – schorl, schorl – foitite)  $\rightarrow$  Al-rich schorl ( $\pm$  Mg)  $\rightarrow$  schorl ( $\pm$  Mg)  $\rightarrow$  schorl – elbaite ( $\pm$  Mg)  $\rightarrow$  “fluor-elbaite” – schorl ( $\pm$  Mg)  $\rightarrow$  Fe-rich “fluor-elbaite”  $\rightarrow$  Mn-bearing “fluor-elbaite”  $\rightarrow$  rossmanite – elbaite  $\rightarrow$  elbaite – rossmanite  $\rightarrow$  ( $\pm$  Ca-bearing “fluor-elbaite”, Ca-bearing “fluor-elbaite” – rossmanite) (Fig. 1, Tables 2, 3, 4). Rossmanite is a recently described X-site-vacant, (Al, Li)-rich tourmaline end-member that is common in lepidolite-subtype pegmatites (Selway *et al.* 1998, 1999). This is the first re-

ported occurrence of rossmanite, foitite and late-stage Ca-enrichment in tourmaline in a petalite-subtype pegmatite. A similar sequence of crystallization occurs from central intermediate zone (60) to aplitic albite zone (30): foitite – schorl  $\rightarrow$  ( $\pm$  schorl – foitite)  $\rightarrow$  schorl – elbaite  $\rightarrow$  “fluor-elbaite” – schorl ( $\pm$  Mg)  $\rightarrow$  Fe-rich “fluor-elbaite” (Fig. 1e, Table 5).

This sequence of crystallization is also seen in the tourmaline compositions for each pegmatite zone (Fig. 1). Endomorphic tourmaline occurs within the pegmatite, close to the contact with the host amphibolite or a biotite-enriched xenolith, and the tourmaline’s composition reflects an influx of Mg and Ti from the amphibolite into the pegmatite-forming melt. Magnesium-rich endomorphic tourmaline cores are surrounded by Mg-poor or Mg-free rims (Fig. 2). Black-to-brown endomorphic tourmaline in border zone (10) is zoned according to the sequence: Al-rich Mg-bearing schorl  $\rightarrow$  Mg-bearing schorl  $\rightarrow$  Mg-bearing schorl – elbaite  $\rightarrow$  Mg-bearing elbaite – schorl [*e.g.*,  $\leq 0.44$  apfu Mg and 0.10 apfu Ti occurs in black Mg-bearing schorl in fine-grained albite in border zone (10)]. Black-to-brown endomorphic tourmaline in the wall zone (20) is Mg-bearing schorl and Mg-bearing elbaite – schorl [*e.g.*,  $\leq 0.37$  apfu Mg and  $\leq 0.09$  apfu Ti occurs in black Mg-bearing schorl in the granitic parts of wall zone (20)]. The source of Mg and Ti (and to a degree, Fe) is the host amphibolite. Calcium infiltrating from the amphibolite was preferentially partitioned into plagioclase over tourmaline, as andesine (An<sub>30</sub>) occurs in border zone (10) (Černý *et al.* 1998). The plagioclase in the rest of the pegmatite is almost pure albite (An<sub>1–3</sub>).

Black-to-brown and green tourmalines in the border zone (10) and wall zone (20) have a similar compositional range, from foitite – schorl to Fe-rich “fluor-elbaite”, with or without Mg (Figs. 1a, b, c). Black-to-brown tourmaline in the granitic part of the wall zone (20) is foitite – schorl to “fluor-elbaite” – schorl, whereas green tourmaline in aplitic pods in the wall zone (20) is slightly more fractionated: “fluor-elbaite” – schorl to Fe-rich “fluor-elbaite”. Pink and rare green tourmalines in the lower and upper intermediate zones (40) and (50) are more fractionated than those in the rest of the pegmatite, with a compositional range from Fe-rich elbaite to Ca-bearing “fluor-elbaite” – rossmanite (Fig. 1d).

Endomorphic tourmaline also occurs in the aplitic albite zone (30), as the tourmaline’s composition reflects the influx of Mg and Ti from the host amphibolite. Endomorphic tourmaline in the aplitic albite zone (30) is Mg-bearing elbaite – schorl with  $\leq 0.40$  apfu Mg and  $\leq 0.09$  apfu Ti, associated with biotite. Zoned endomorphic tourmaline in zone (30) has a Mg-bearing elbaite – schorl core and an elbaite – schorl rim (Fig. 2c). Tourmaline in the central intermediate zone (60) has a compositional range from black foitite – schorl to schorl – elbaite, and in the aplitic albite zone (30), it has a range from black-to-brown and green schorl – elbaite to Fe-rich “fluor-elbaite” (Fig. 1e), similar to the composi-

TABLE 1. COMPOSITIONAL ZONING IN TOURMALINE AT TANCO

pegmatite zone	compositional zones
zones	brown Al-rich schorl core, schorl–elbaite zone, elbaite–schorl zone, Fe-rich elbaite rim
(10) + (20)	brown schorl–elbaite core, green elbaite–schorl rim
	brown primary Mg-bearing elbaite–schorl core, elbaite–schorl rim
zones	green elbaite–schorl core, pink Mn-bearing elbaite rim
	cloudy pale pink rossmanite–elbaite core, clear dark pink elbaite–rossmanite rim
(40) + (50)	pink rossmanite–elbaite core, Ca-bearing elbaite–rossmanite rim
	patchy pink rossmanite–elbaite base, blue Fe-rich elbaite cap, above cap: fine-grained green muscovite
zone (60)	black foitite–schorl core, schorl–elbaite rim
zone (30)	brown primary Mg-bearing elbaite–schorl core, schorl–elbaite zone, elbaite–schorl rim

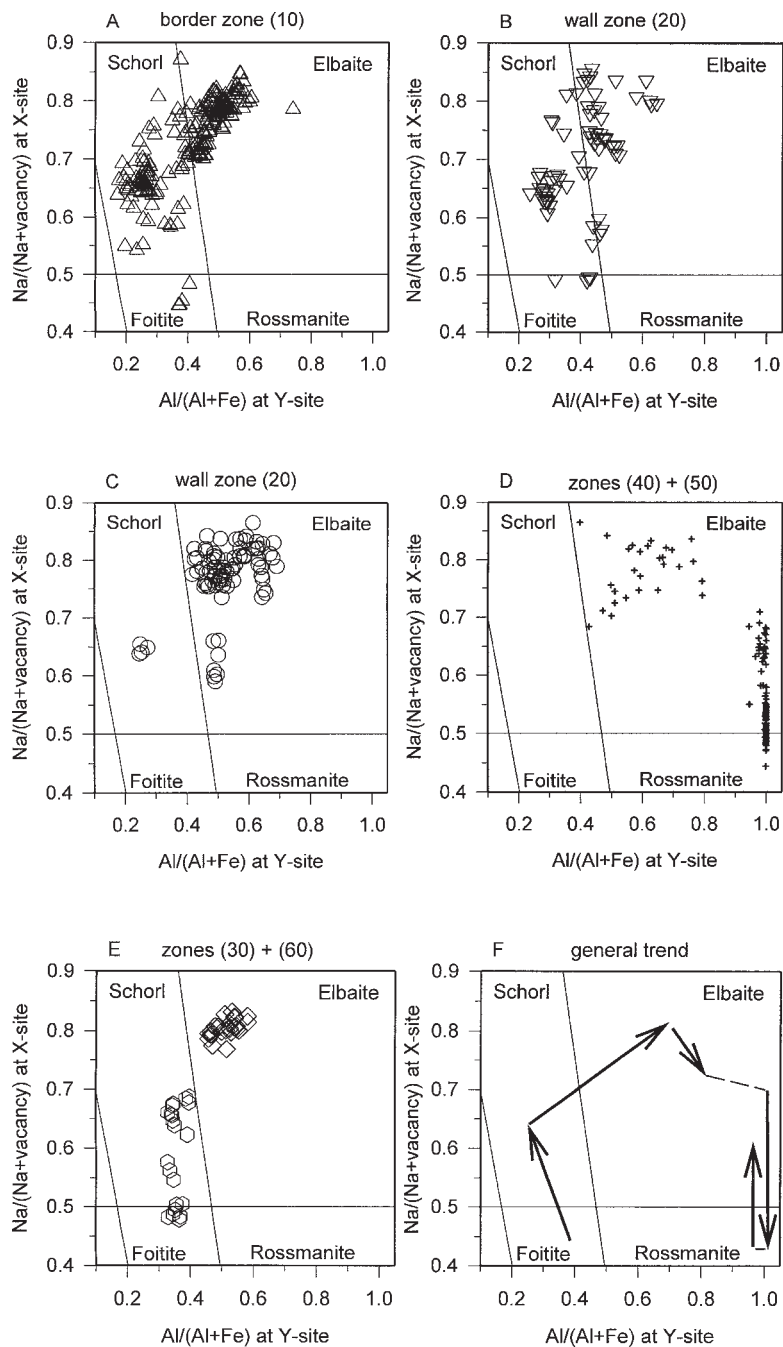


FIG. 1. Tourmaline compositions from the Tanco pegmatite. A. Black-to-brown, ± green tourmaline from the border zone (10). B. Black-to-brown tourmaline from the wall zone (20). C. Green tourmaline from the wall zone (20). D. Pink tourmaline from the lower intermediate zone (40) and upper intermediate zone (50). E. Diamonds: black-to-brown and green tourmaline from the aplitic albite zone (30), hexagons: black-to-brown tourmaline from central intermediate zone (60). F. General trend of fractionation of tourmaline at Tanco.

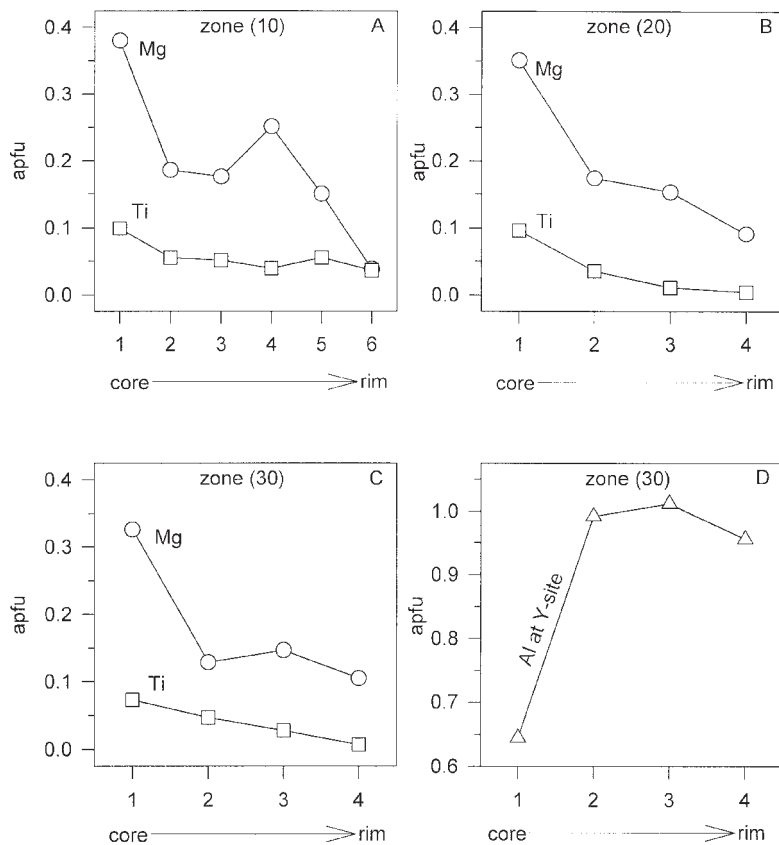


FIG. 2. Mg and Ti core-to-rim variation in endomorphous tourmaline at Tanco. A. Brown tourmaline with a Mg-bearing elbaite – schorl core and an “fluor-elbaite” – schorl rim from the border zone (10). B. Dark brown tourmaline with a Mg-bearing elbaite – schorl core and an “fluor-elbaite” – schorl rim from the wall zone (20). C, D. Brown tourmaline with a Mg-bearing elbaite – schorl core, a schorl – elbaite zone and an “fluor-elbaite” – schorl rim from the aplitic albite zone (30).

tional range of foitite – schorl to Fe-rich “fluor-elbaite” in the border zone (10) and wall zone (20).

In the Tanco tourmaline, the dominant substitution at the X site is  $\text{Na} \rightleftharpoons \square$  ( $\square$ : vacancy) (Fig. 3). Tourmaline in the border zone (10) and black-to-brown tourmaline in the wall zone (20) have a similar wide range in Na content (from 0.44 to 0.87 apfu Na); green tourmaline in the wall zone (20) is slightly more Na-enriched (with 0.60 to 0.84 apfu Na). In lower and upper intermediate zones (40) and (50), vacancy-rich tourmaline (elbaite – rossmanite and rossmanite – elbaite) is abundant, but with a wide range in Na content (0.45 to 0.86 apfu Na). Most tourmaline at Tanco contains almost no Ca, except in the lower and upper intermediate zones (40) and (50) where late-stage “fluor-elbaite” – rossmanite and “fluor-elbaite” contain up to 0.16 apfu

Ca at the X site (Table 4, composition 8). The fractionation trend from the border zone (10) to wall zone (20) to the lower and upper intermediate zones (40) and (50) is from vacancy-rich (foitite – schorl) to Na-rich (“fluor-elbaite” – schorl and Fe-rich “fluor-elbaite”) to vacancy-rich (rossmanite – elbaite) to (Na,  $\square$ )-rich (elbaite – rossmanite), with slight late-stage Ca-enrichment in Ca-bearing “fluor-elbaite” – rossmanite (Table 1, Fig. 3). Tourmaline in the central intermediate zone (60) and aplitic albite zone (30) has a narrow range in Na content, with 0.48 to 0.68 apfu Na in zone (60) and 0.67 to 0.82 apfu Na in zone (30). The fractionation trend from the central intermediate zone (60) to the aplitic albite zone (30) is from vacancy-rich (foitite – schorl) to Na-rich (“fluor-elbaite” – schorl and Fe-rich “fluor-elbaite”) (Table 1, Fig. 3e).



TABLE 2. REPRESENTATIVE CHEMICAL COMPOSITIONS OF TOURMALINE IN ZONE (10) OF THE TANCO PEGMATITE

	1	2	3	4	5	6	7	8	9
SiO <sub>2</sub> , wt%	34.30	36.70	35.60	35.60	34.80	35.60	35.00	37.20	36.50
TiO <sub>2</sub>	0.75	0.68	0.17	0.27	0.40	0.73	0.43	0.31	0.14
B <sub>2</sub> O <sub>3</sub> *	10.16	10.62	10.40	10.30	10.21	10.30	10.34	10.62	10.61
Al <sub>2</sub> O <sub>3</sub>	32.10	34.30	35.20	33.20	33.20	32.30	34.50	35.00	36.60
MgO	1.73	1.55	0.04	0.37	0.24	0.45	0.62	0.20	0.18
CaO	0.13	0.08	0.00	0.00	0.05	0.06	0.08	0.00	0.06
MnO	0.18	0.36	0.55	0.31	0.35	0.28	0.29	0.11	0.74
FeO	13.40	8.94	11.80	13.80	13.60	14.10	11.50	8.03	6.03
ZnO	0.20	0.24	0.50	0.30	0.39	0.31	0.34	0.00	0.33
Li <sub>2</sub> O*	0.23	0.94	0.45	0.36	0.38	0.44	0.56	1.60	1.40
Na <sub>2</sub> O	2.17	2.43	1.36	1.65	1.91	1.93	1.99	2.78	2.63
H <sub>2</sub> O*	3.25	3.24	3.45	3.37	3.26	3.35	3.22	3.18	3.04
F	0.54	0.89	0.30	0.39	0.56	0.43	0.74	1.03	1.31
O=F	-0.23	-0.37	-0.13	-0.16	-0.24	-0.18	-0.31	-0.43	-0.55
Total	98.91	100.60	99.69	99.76	99.11	100.10	99.30	99.63	99.02
Formulae normalized to 31 anions									
T: Si <i>apfu</i>	5.87	6.01	5.95	6.01	5.93	6.01	5.88	6.09	5.98
Al	0.13	0.00	0.05	0.00	0.07	0.00	0.12	0.00	0.02
B	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Z: Al	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
Y: Al	0.34	0.62	0.88	0.60	0.59	0.43	0.71	0.75	1.05
Ti	0.10	0.08	0.02	0.03	0.05	0.09	0.05	0.04	0.02
Mg	0.44	0.38	0.01	0.09	0.06	0.11	0.16	0.05	0.04
Mn	0.02	0.05	0.08	0.04	0.05	0.04	0.04	0.01	0.10
Fe <sup>2+</sup>	1.92	1.22	1.65	1.95	1.94	1.99	1.62	1.10	0.83
Zn	0.03	0.03	0.06	0.04	0.05	0.04	0.04	0.00	0.04
Li	0.15	0.62	0.30	0.25	0.26	0.30	0.38	1.05	0.92
ΣY	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
X: Ca	0.02	0.01	0.00	0.00	0.01	0.01	0.01	0.00	0.01
Na	0.72	0.77	0.44	0.54	0.63	0.63	0.65	0.88	0.84
□	0.26	0.22	0.56	0.46	0.36	0.36	0.34	0.12	0.15
OH	3.71	3.54	3.84	3.79	3.70	3.77	3.61	3.47	3.32
F	0.29	0.46	0.16	0.21	0.30	0.23	0.39	0.53	0.68

\* The proportion of B<sub>2</sub>O<sub>3</sub>, Li<sub>2</sub>O and H<sub>2</sub>O is calculated by stoichiometry; B = 3 *apfu*, Li = 15 - Σ(T + Z + Y), and OH + F = 4 *apfu*. Samples: (1) black Mg-bearing schorl, sample TTC26-1; (2) brown Mg-bearing elbaite-schorl core, sample TTC36-1; (3) black foitite-schorl, sample TTC6-1; (4) dark green schorl-foitite, sample TTC30-2; (5) brown Al-rich schorl core, sample TTC31-3; (6) dark green schorl, sample TTC30-2; (7) brown schorl-elbaite, sample TTC34-3; (8) brown "fluor-elbaite"-schorl, sample TTC31-2; (9) brown Fe-rich "fluor-elbaite", sample TTC36-2.

The negative correlation between Fe and Al at the Y site indicates that the dominant substitution in tourmaline at Tanco is  $3\text{Fe}^{2+} \rightleftharpoons 1.5\text{Al} + 1.5\text{Li}$  (Figs. 4a, 5a, 6a, 7a, 8a). Tourmaline in the border zone (10) and black-to-brown tourmaline in the wall zone (20) have similar wide ranges in Fe and Al at the Y site, but green tourmaline in the wall zone (20) is slightly more Al-rich (Figs. 4a, 5a, 6a). Most of the tourmaline in the lower and upper intermediate zones (40) and (50) is devoid of Fe (Fig. 7a). Tourmaline in the central intermediate zone (60) is more Fe-enriched than tourmaline in the aplitic albite zone (30) (Fig. 8a). This negative correlation indicates that the primitive tourmaline is Fe-rich, and the fractionated tourmaline is Al-rich at the Y site (Table 1).

There is a negative correlation between Fe and Mn from schorl - foitite and schorl (Fe-rich, Mn-poor) to Fe-rich "fluor-elbaite" (moderate Fe and Mn) in the

border zone (10) and black-to-brown tourmaline in the wall zone (20) (Figs. 4b, 5b). Green tourmaline in the wall zone (20) is slightly more Fe- and Mn-enriched, with  $\leq 0.27$  *apfu* Mn in Fe-rich "fluor-elbaite" (Fig. 6b). Most tourmaline in lower and upper intermediate zones (40) and (50) is devoid of Fe and has variable Mn content; Mn content decreases from Mn-bearing "fluor-elbaite" (with  $\leq 0.39$  *apfu* Mn) to undetectable Mn in rossmanite - elbaite and elbaite - rossmanite,  $\leq 0.07$  *apfu* Mn in Ca-bearing "fluor-elbaite" - rossmanite (Table 4, composition 7) and  $\leq 0.20$  *apfu* Mn in Ca-bearing "fluor-elbaite" (Table 4, composition 8) (Fig. 7b). Foitite-schorl and schorl - elbaite in the central intermediate zone (60) contains high Fe and low Mn, whereas "fluor-elbaite" - schorl and Fe-rich "fluor-elbaite" in the aplitic albite zone (30) contain moderate Fe and Mn (Fig. 8b).

There is a positive correlation between Na and F and a weak positive correlation between Mn and F in tourmaline in the border zone (10) and wall zone (20), from foitite - schorl (low Na, Mn and F) to "fluor-elbaite" - schorl and Fe-rich "fluor-elbaite" (high Na and F) (Figs. 4c, d, 5c, d, 6c, d). The maximum F content occurs in Fe-rich "fluor-elbaite" in the border zone (10), with  $\leq 0.72$  *apfu* F and  $\leq 0.80$  *apfu* Na, and the maximum Mn content occurs in green Fe-rich "fluor-elbaite" in the wall zone (20). Most tourmaline in the lower and upper intermediate zones (40) and (50) plots above that in the border zone (10) and wall zone (20) because of high Ca and vacancy contents (Fig. 7c). The composition that plots furthest from the trend is Ca-bearing "fluor-elbaite" - rossmanite, with  $\leq 0.11$  *apfu* Ca,  $\leq 0.49$  *apfu* Na and  $\leq 0.60$  *apfu* F (Table 4, composition 7). There is a positive correlation between Ca and F in late-stage tourmaline, as these elements increase from rossmanite - elbaite  $\rightarrow$  Ca-bearing "fluor-elbaite" - rossmanite  $\rightarrow$  Ca-bearing "fluor-elbaite". Tourmaline in the lower and upper intermediate zones (40) and (50) shows a wide range in Mn and F contents, from Mn-bearing "fluor-elbaite" (high Mn and F) to rossmanite - elbaite (no Mn and very low F) to elbaite - rossmanite (no Mn and low F) to Ca-bearing "fluor-elbaite" - rossmanite (very low Mn and high F) and Ca-bearing "fluor-elbaite" (low Mn and high F) (Figs. 7c, d).

Tourmaline in the central intermediate zone (60) and aplitic albite zone (30) also shows a positive correlation between Na and F from foitite - schorl (low Na, Mn and F) in zone (60) to "fluor-elbaite" - schorl (high Na and F and low Mn) (Table 5, composition 6), and Fe-rich "fluor-elbaite" (high Na and F, moderate Mn) in zone (30) (Figs. 8c, d).

Most tourmaline at Tanco is very poor in Zn, which is commonly below its detection limit ( $\leq 0.10$  wt% Zn). The only exceptions are  $\leq 0.11$  *apfu* Zn in dark green Fe-rich "fluor-elbaite" in the lower and upper intermediate zones (40) and (50) and  $\leq 0.09$  *apfu* Zn in green and dark brown elbaite - schorl in the wall zone (20).

## SUBSOLIDUS ALTERATION

Tourmaline appears as an alteration product, and it becomes altered itself to low-temperature mineral phases. In the wall zone (20) and aplitic albite zone (30), orange lithiophilite is rimmed by blue tourmaline as a consequence of local replacement. The tourmaline ranges in composition from  $\pm$ schorl – elbaite to “fluor-elbaite” – schorl to Fe-rich “fluor-elbaite” to  $\pm$ Fe-bearing elbaite. In the wall zone (20), green-to-brown (Fe, Mg)-rich lithiophilite (Černý *et al.* 1998) is rimmed by (Fe, Mg)-rich blue tourmaline, which ranges in composition from schorl – elbaite, with up to 0.24 *apfu* Mg, to “fluor-elbaite” – schorl. This blue tourmaline locally

replaces lithiophilite, but its compositional range is similar to that of primary tourmaline in the same pegmatite zone.

Crystals of pink tourmaline in the lower and upper intermediate zones (40) and (50) are commonly altered along the rim and cracks, or completely replaced by pink (Rb, Cs)-bearing lepidolite. Sample TTC50–3 is a zoned crystal 11 cm long consisting of patchy pink rossmanite–elbaite at one end, a zone of fine-grained green muscovite, narrow blue Fe-rich “fluor-elbaite” (Table 4, composition 3) + relict rossmanite – elbaite (2 mm long), and fine-grained green muscovite at the other end. The blue tourmaline zone is optically continuous with the pink rossmanite – elbaite zone, and the fine-grained

TABLE 3. REPRESENTATIVE CHEMICAL COMPOSITIONS OF TOURMALINE IN ZONE (20) AT TANCO

	1	2	3	4	5	6	7	8	9	10
SiO <sub>2</sub> , wt%	35.10	36.70	36.10	35.90	34.60	35.30	36.70	37.30	37.20	36.20
TiO <sub>2</sub>	0.72	0.78	0.20	0.25	0.22	0.16	0.28	0.23	0.11	0.37
B <sub>2</sub> O <sub>3</sub> *	10.19	10.54	10.56	10.53	10.26	10.35	10.57	10.74	10.75	10.69
Al <sub>2</sub> O <sub>3</sub>	31.40	33.90	36.10	36.10	34.10	34.60	35.50	36.40	37.10	37.40
MgO	1.45	1.44	0.01	0.02	0.17	0.19	0.03	0.18	0.13	0.00
CaO	0.08	0.00	0.00	0.00	0.09	0.07	0.00	0.00	0.25	0.15
MnO	0.21	0.14	0.56	0.44	0.31	0.29	0.10	0.58	1.38	1.01
FeO	14.00	8.54	10.60	10.20	13.50	11.90	7.97	7.07	4.96	5.92
ZnO	0.16	0.19	0.54	0.56	0.35	0.35	0.26	0.00	0.00	0.47
Li <sub>2</sub> O*	0.29	1.12	0.64	0.72	0.38	0.60	1.42	1.46	1.58	1.38
Na <sub>2</sub> O	2.14	2.42	1.52	1.70	1.95	1.96	2.69	2.55	2.56	2.62
H <sub>2</sub> O*	3.32	3.23	3.48	3.38	3.25	3.25	3.11	3.20	3.10	3.18
F	0.41	0.86	0.35	0.54	0.62	0.67	1.14	1.06	1.29	1.08
O=F	-0.17	-0.36	-0.15	-0.23	-0.26	-0.28	-0.48	-0.45	-0.54	-0.45
total	99.30	99.50	100.51	100.11	99.54	99.41	99.29	100.32	99.87	100.02
Formulae normalized to 31 anions										
T: Si	5.98	6.05	5.94	5.93	5.86	5.93	6.03	6.04	6.01	5.89
Al	0.02	0.00	0.06	0.07	0.14	0.07	0.00	0.00	0.00	0.11
B	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Z: Al	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
Y: Al	0.29	0.59	0.95	0.95	0.67	0.77	0.88	0.94	1.07	1.05
Ti	0.09	0.10	0.02	0.03	0.03	0.02	0.03	0.03	0.01	0.04
Mg	0.37	0.35	0.00	0.00	0.04	0.05	0.01	0.04	0.03	0.00
Mn	0.03	0.02	0.08	0.06	0.05	0.04	0.01	0.08	0.19	0.14
Fe <sup>2+</sup>	2.00	1.18	1.46	1.41	1.91	1.67	1.10	0.96	0.67	0.81
Zn	0.02	0.02	0.07	0.07	0.04	0.04	0.03	0.00	0.00	0.06
Li	0.20	0.74	0.42	0.48	0.26	0.41	0.94	0.95	1.03	0.90
$\Sigma Y$	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
X: Ca	0.02	0.00	0.00	0.00	0.02	0.01	0.00	0.00	0.04	0.03
Na	0.71	0.77	0.49	0.54	0.64	0.64	0.86	0.80	0.80	0.83
□	0.27	0.23	0.51	0.46	0.34	0.35	0.14	0.20	0.16	0.14
OH	3.78	3.55	3.82	3.72	3.67	3.64	3.41	3.46	3.34	3.45
F	0.22	0.45	0.18	0.28	0.33	0.36	0.59	0.54	0.66	0.55

\*B<sub>2</sub>O<sub>3</sub>, Li<sub>2</sub>O and H<sub>2</sub>O calculated by stoichiometry; B = 3 *apfu*, Li = 15 –  $\Sigma(T + Z + Y)$  and OH + F = 4 *apfu*.

Compositions 1–8 are black to brown, and 9–10 are green tourmaline. (1) black Mg-bearing schorl, sample TTC16–1; (2) dark brown Mg-bearing elbaite–schorl core, sample TTC8–2; (3) brown foitite–schorl, sample TTC25–1; (4) brown schorl–foitite, sample TTC25–1; (5) brown Al-rich schorl core, sample TTC24–2; (6) brown schorl–elbaite core, sample TTC11–1; (7) brown “fluor-elbaite” – schorl, sample TTC24–3; (8) green “fluor-elbaite” – schorl rim, sample TTC11–1; (9) black Fe-rich “fluor-elbaite”, sample TTC10–2; (10) green Fe-rich “fluor-elbaite”, sample TTC21–2.



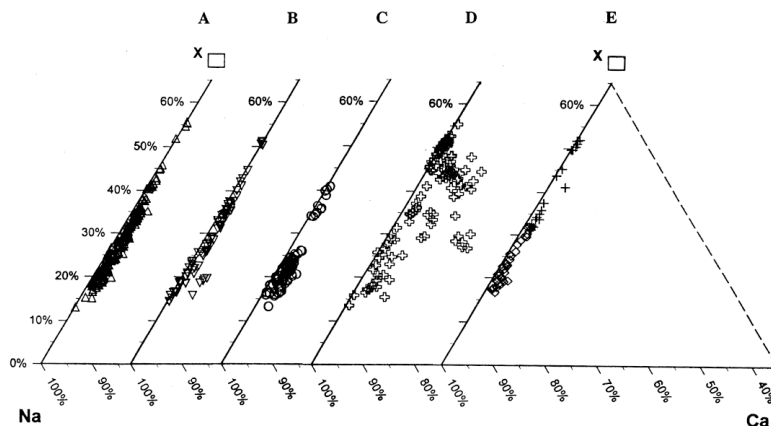


FIG. 3. X-site contents in tourmaline at Tanco. A. Black-to-brown,  $\pm$  green tourmaline from the border zone (10). B. Black-to-brown tourmaline from the wall zone (20). C. Green tourmaline from the wall zone (20). D. Pink tourmaline from the lower and upper intermediate zones (40) and (50). E. Diamonds: black-to-brown and green tourmaline from the aplitic albite zone (30), crosses: black-to-brown tourmaline from the central intermediate zone (60).

TABLE 4. REPRESENTATIVE CHEMICAL COMPOSITIONS OF TOURMALINE IN ZONES (40) AND (50) AT TANCO

	1		2		3		4		5		6		7		8
	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	
SiO <sub>2</sub> , wt%	36.20	38.00	38.39	38.30	38.30	39.40	38.80	38.10							
TiO <sub>2</sub>	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00							
B <sub>2</sub> O <sub>3</sub> *	10.48	11.11	10.97	11.24	11.20	11.32	11.21	11.07							
Al <sub>2</sub> O <sub>3</sub>	35.50	41.10	38.14	43.30	42.50	41.90	41.50	40.50							
MgO	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00							
CaO	0.05	0.13	0.20	0.00	0.22	0.44	0.65	0.94							
MnO	0.64	2.52	0.40	0.00	0.18	0.29	0.52	1.51							
FeO	9.04	0.11	4.22	0.00	0.00	0.00	0.00	0.00							
ZnO	0.41	0.00	0.00	0.00	0.00	0.00	0.00	0.00							
Li <sub>2</sub> O*	0.98	1.80	1.98	1.91	2.02	2.23	2.16	2.09							
Na <sub>2</sub> O	2.11	2.06	2.38	1.54	1.77	1.53	1.63	1.78							
H <sub>2</sub> O*	3.06	3.33	3.26	3.60	3.65	3.43	3.29	3.32							
F	1.18	1.06	1.11	0.59	0.46	1.01	1.22	1.05							
O=F	-0.50	-0.45	-0.47	-0.25	-0.19	-0.43	-0.51	-0.44							
Total	99.26	100.77	100.58	100.23	100.11	101.12	100.47	99.92							

Formulae normalized to 31 anions

T: Si	6.00	5.94	6.09	5.92	5.94	6.05	6.02	5.98
Al	0.00	0.06	0.00	0.08	0.06	0.00	0.00	0.02
B	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Z: Al	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
Y: Al	0.94	1.52	1.13	1.81	1.72	1.58	1.58	1.48
Ti	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.09	0.34	0.05	0.00	0.02	0.04	0.07	0.20
Fe <sup>2+</sup>	1.25	0.01	0.56	0.00	0.00	0.00	0.00	0.00
Zn	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Li	0.65	1.13	1.26	1.19	1.26	1.38	1.35	1.32
$\Sigma Y$	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
X: Ca	0.01	0.02	0.03	0.00	0.04	0.07	0.11	0.16
Na	0.68	0.63	0.73	0.46	0.53	0.46	0.49	0.54
$\square$	0.31	0.35	0.24	0.54	0.43	0.47	0.40	0.30
OH	3.38	3.48	3.44	3.71	3.77	3.51	3.40	3.48
F	0.62	0.52	0.56	0.29	0.23	0.49	0.60	0.52

\*B<sub>2</sub>O<sub>3</sub>, Li<sub>2</sub>O and H<sub>2</sub>O calculated by stoichiometry; B = 3 *apfu*, Li = 15 -  $\Sigma(T + Z + Y)$  and OH + F = 4 *apfu*.

(1) green "fluor-elbaite" - schorl core, sample TTC40-2; (2) pink Mn-bearing "fluor-elbaite" rim, sample TTC40-1; (3) blue Fe-rich "fluor-elbaite" rim, sample TTC50-3; (4) cloudy pale pink rossmanite-elbaite core, sample TTC44; (5) clear dark pink elbaite-rossmanite rim, sample TTC44; (6) green rossmanite-elbaite core, sample TTC39-2; (7) pink Ca-bearing "fluor-elbaite" - rossmanite rim, sample TTC39-1; (8) pink to purple Ca-bearing "fluor-elbaite" core, sample TTC41-3.

TABLE 5. REPRESENTATIVE CHEMICAL COMPOSITIONS OF TOURMALINE IN ZONES (60) AND (30) AT TANCO

	zone (60)			zone (30)			
	1	2	3	4	5	6	7
SiO <sub>2</sub> , wt%	35.50	35.60	35.20	36.00	36.30	36.90	37.00
TiO <sub>2</sub>	0.19	0.29	0.43	0.58	0.36	0.05	0.00
B <sub>2</sub> O <sub>3</sub> *	10.40	10.43	10.36	10.45	10.56	10.73	10.72
Al <sub>2</sub> O <sub>3</sub>	35.10	34.90	34.90	33.70	34.90	36.90	37.20
MgO	0.03	0.05	0.02	1.60	0.50	0.20	0.00
CaO	0.00	0.00	0.06	0.05	0.09	0.07	0.07
MnO	0.43	0.34	0.41	0.14	0.28	0.29	1.11
FeO	12.20	12.50	11.10	10.10	11.00	7.62	5.93
ZnO	0.53	0.30	0.51	0.19	0.27	0.12	0.00
Li <sub>2</sub> O*	0.44	0.50	0.67	0.74	0.76	1.29	1.44
Na <sub>2</sub> O	1.45	1.66	1.86	2.37	2.09	2.59	2.59
H <sub>2</sub> O*	3.53	3.41	3.41	3.13	3.38	3.20	3.18
F	0.12	0.39	0.35	1.00	0.56	1.07	1.09
O=F	-0.05	-0.16	-0.15	-0.42	-0.24	-0.45	-0.46
Total	99.87	100.21	99.13	99.63	100.81	100.58	99.87

Formulae normalized to 31 anions

T: Si	5.93	5.93	5.91	5.99	5.97	5.98	6.00
Al	0.07	0.07	0.09	0.01	0.03	0.02	0.00
B	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Z: Al	6.00	6.00	6.00	6.00	6.00	6.00	6.00
Y: Al	0.84	0.79	0.81	0.59	0.74	1.02	1.11
Ti	0.02	0.04	0.05	0.07	0.05	0.01	0.00
Mg	0.01	0.01	0.01	0.40	0.12	0.05	0.00
Mn	0.06	0.05	0.06	0.02	0.04	0.04	0.15
Fe <sup>2+</sup>	1.70	1.74	1.56	1.40	1.52	1.03	0.80
Zn	0.07	0.04	0.06	0.02	0.03	0.01	0.00
Li	0.30	0.33	0.45	0.50	0.50	0.84	0.94
$\Sigma Y$	3.00	3.00	3.00	3.00	3.00	3.00	3.00
X: Ca	0.00	0.00	0.01	0.01	0.02	0.01	0.01
Na	0.47	0.54	0.61	0.76	0.67	0.81	0.81
$\square$	0.53	0.46	0.38	0.23	0.31	0.18	0.18
OH	3.94	3.79	3.81	3.47	3.71	3.45	3.44
F	0.06	0.21	0.19	0.53	0.29	0.55	0.56

\*B<sub>2</sub>O<sub>3</sub>, Li<sub>2</sub>O and H<sub>2</sub>O calculated by stoichiometry; B = 3 *apfu*, Li = 15 -  $\Sigma(T + Z + Y)$  and OH + F = 4 *apfu*.

(1) black foitite-schorl core, sample TTC3-3; (2) black schorl-foitite, sample TTC2-2; (3) black schorl-elbaite rim of (1), sample TTC3-3; (4) green Mg-bearing "fluor-elbaite" - schorl core, sample TTC19-3; (5) brown schorl-elbaite, sample TTC19-1; (6) black "fluor-elbaite" - schorl, sample TTC20-1; (7) green and brown Fe-rich "fluor-elbaite", sample TTC1-2.

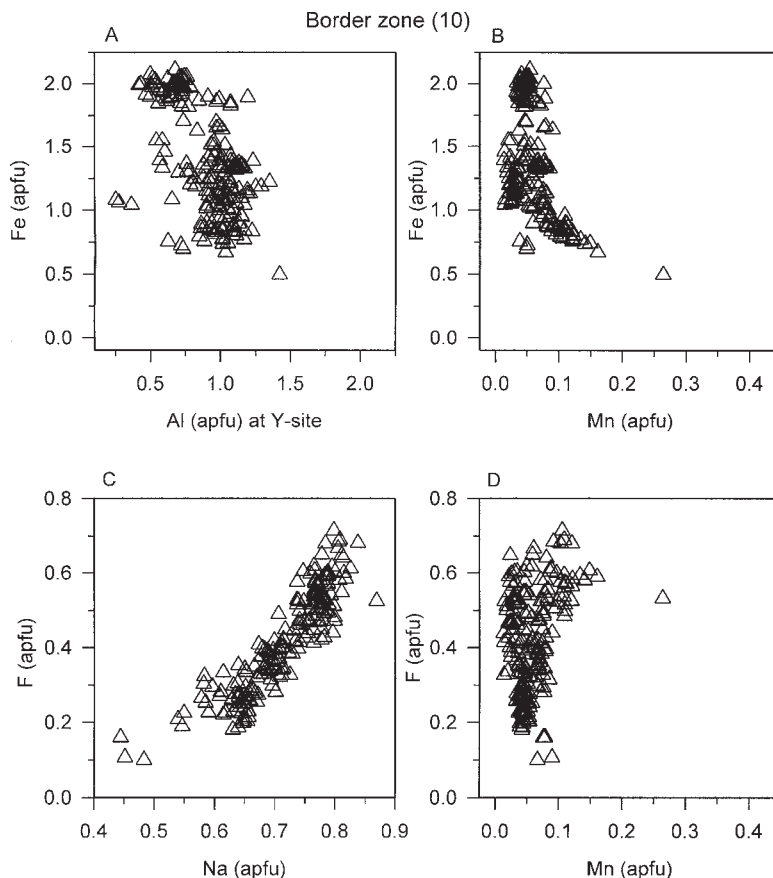


FIG. 4. Tourmaline compositions from the border zone (10) at Tanco.

green muscovite forms a complete pseudomorph of the pink tourmaline. The fine-grained green muscovite and Fe-rich “fluor-elbaite” are products of subsolidus alteration of the pink elbaite – rossmanite.

#### SUMMARY

On the basis of compositional zoning within individual crystals (Table 1), the tourmaline at Tanco evolves through the following sequence: foitite – schorl → ( $\pm$  schorl – foitite) → Al-rich schorl ( $\pm$ Mg) → schorl ( $\pm$ Mg) → schorl – elbaite ( $\pm$ Mg) → “fluor-elbaite” – schorl ( $\pm$ Mg) → Fe-rich “fluor-elbaite” → Mn-bearing “fluor-elbaite” → rossmanite – elbaite → elbaite – rossmanite → ( $\pm$  Ca-bearing “fluor-elbaite”, Ca-bearing “fluor-elbaite” – rossmanite) (Fig. 1f). This is the first reported occurrence of foitite, rossmanite and late-stage Ca-enrichment in tourmaline in a petalite-subtype pegmatite.

Endomorphic tourmaline occurs in the border zone (10), wall zone (20) and aplitic albite zone (30), and ranges in composition from Mg-bearing schorl to Al-rich Mg-bearing schorl to Mg-bearing schorl – elbaite to Mg-bearing elbaite – schorl. The source of Mg and Ti in the tourmaline is the host-rock amphibolite.

The dominant substitution at the X site is  $\text{Na} \rightleftharpoons \square$ , which is closely connected with the F content. There is a positive correlation between Na and F and a weak positive correlation between Mn and F from foitite – schorl to “fluor-elbaite” – schorl and Fe-rich “fluor-elbaite” in the border zone (10), wall zone (20), aplitic albite zone (30) and central intermediate zone (60). The correlation between Na at the X site and F at the O(1) site is caused by crystal-chemical constraints (Gebert & Zemann 1965, Robert *et al.* 1997). Where the X site is occupied by Na and the three Y sites are occupied by  $3M^{2+}$  or  $1.5M^+ + 1.5M^{3+}$  (as in schorl and elbaite), F can replace OH in this six-charge environment. The

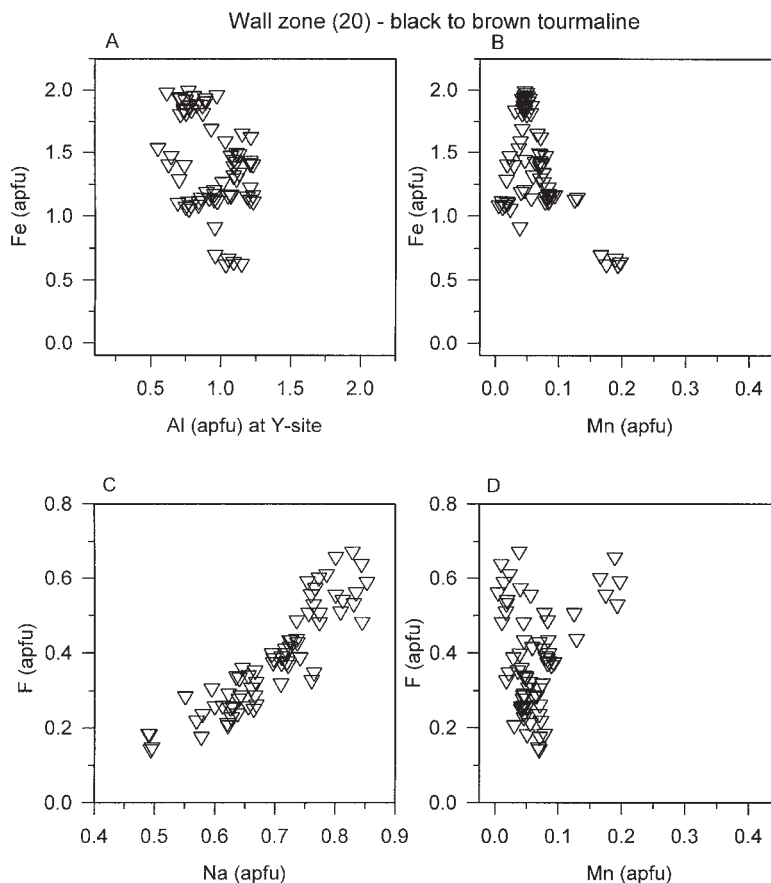


FIG. 5. Compositions of black to brown tourmaline from the wall zone (20) at Tanco.

positively charged  $H^+$  at the O(1) site is repulsed by the positively charged  $Na^+$  at the X site. Where the X site is empty and the three Y sites are occupied by  $2M^{2+} + 1M^{3+}$  or  $1M^+ + 2M^{3+}$  (as in foitite and rossmanite) to produce a seven-charge environment, F cannot enter the O(1) site. There is a similar positive correlation between Na and F in tourmaline from lepidolite-subtype pegmatites (Selway *et al.* 1999).

The dominant substitution at the Y site at Tanco is  $3Fe^{2+} \rightleftharpoons 1.5Al + 1.5Li$ , which is controlled by fractionation of the pegmatite-forming melt. This compositional trend is also shown by coexisting micas, which progress from rare biotite to muscovite and lithian muscovite to lepidolite (Černý *et al.* 1998), parallel to the evolution of tourmaline.

The concentrations of Ca and F are positively correlated in late-stage tourmaline in the lower and upper intermediate zones (40) and (50). This late-stage Ca-enrichment is not attributed to Ca infiltration from the host rock, as the expected associated Mg-enrichment is

not present in the tourmaline nor in any other minerals within zones (40) and (50). The presence of albite (An<sub>1-3</sub>), fluorapatite (0.1–0.2 vol.%), F-rich microlite (0.02 vol.%) and very rare, almost end-member, topaz associated with the Ca-bearing “fluor-elbaite” – rossmanite (Černý *et al.* 1998, Stilling 1998) indicates that the late Ca-enrichment is due to conservation of Ca during consolidation of the pegmatite by sequestering as fluoride-bearing complexes, such as was suggested by Weidner & Martin (1987).

The lower and upper intermediate zones (40) and (50) crystallized under conditions of high salinity ( $\mu$ KF) (London 1982), as indicated by the abundance of blocky microcline perthite (24–25 vol.%) (Stilling 1998). These petalite-bearing zones also contain rare lepidolite (0.1–0.5 vol.%) (Stilling 1998), indicating intermediate acidity ( $\mu$ HF), and high Li-activity (London 1982). Very rare, almost end-member topaz associated with ambygonite in zones (40) and (50) indicates a brief period of high acidity (London 1982).

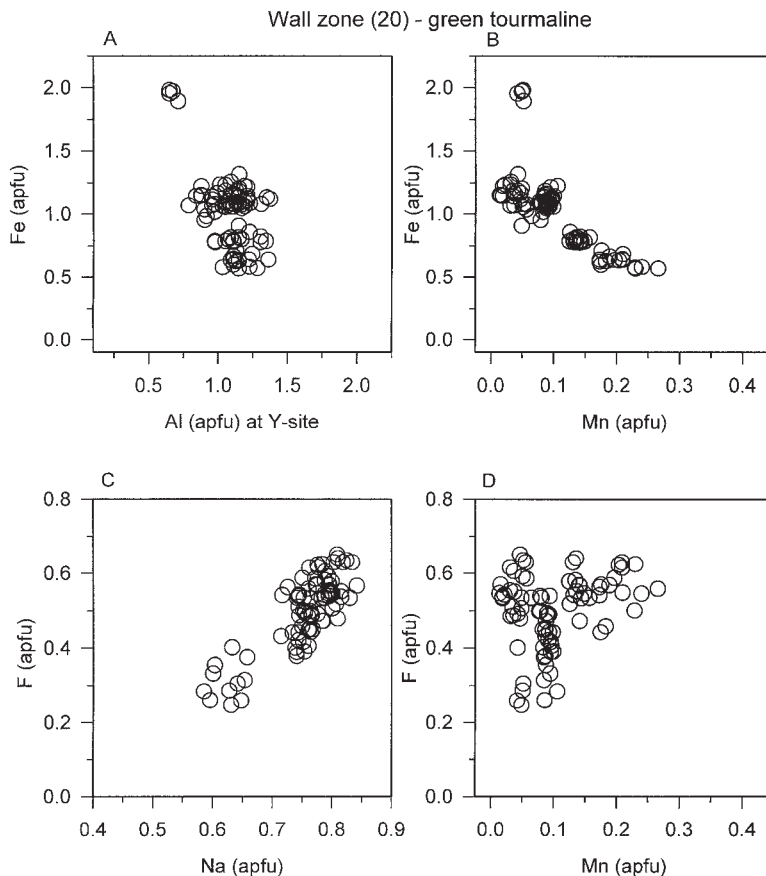


FIG. 6. Compositions of green tourmaline from the wall zone (20) at Tanco.

Pink tourmaline in lower and upper intermediate zones (40) and (50) is commonly replaced by a pink (Rb, Cs)-bearing lepidolite and muscovite. The source of the Rb and Cs is probably K-feldspar and pollucite in the upper intermediate zone (50). Both are commonly affected by incipient conversion to clay minerals and white mica, and veined by muscovite + spodumene  $\pm$  sanidine (variety "adularia").

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#### 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.
- ČERNÝ, P. (1991): Rare-element granitic pegmatites. I. Anatomy and internal evolution of pegmatite deposits. *Geosci. Can.* **18**, 49-67.
- \_\_\_\_\_, ERCIT, T.S. & VANSTONE, P.J. (1998): Mineralogy and petrology of the Tanco rare-element pegmatite deposit, southeastern Manitoba. *Int. Mineral. Assoc., 17<sup>th</sup> Gen. Meet. (Toronto), Field Trip Guidebook B6*.

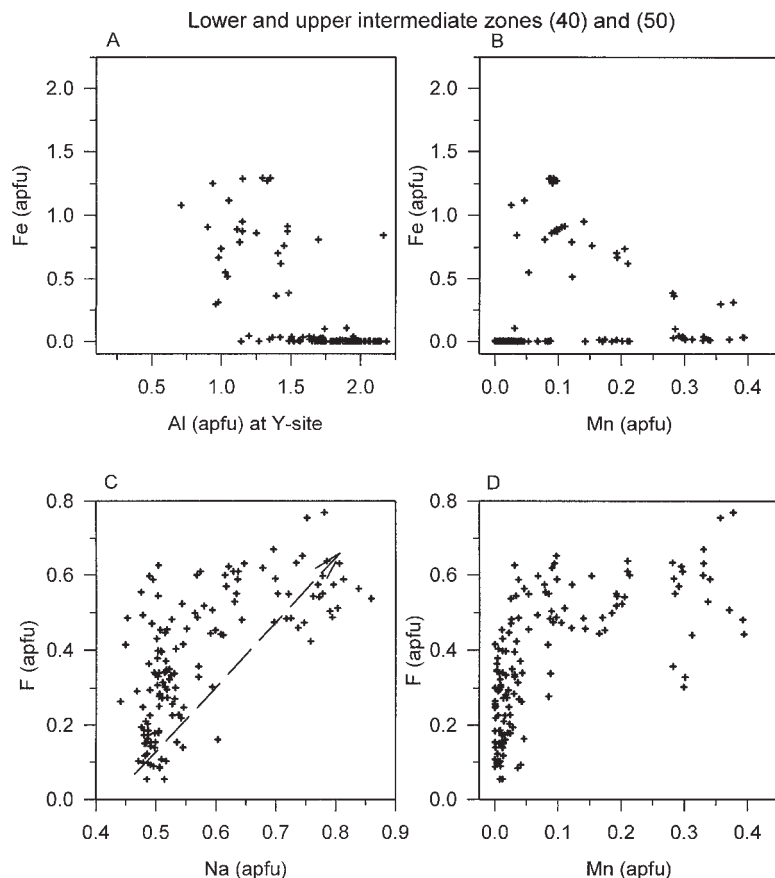


FIG. 7. Tourmaline compositions from the lower and upper intermediate zones (40) or (50). C. The arrow indicates the positive correlation between Na and F in tourmaline in the other Tanco pegmatite zones.

- GEBERT, W. & ZEMANN, J. (1965): Messung des Ultrarot-Pleochroismus von Mineralen. II. Der Pleochroismus der OH-Streckfrequenz in Turmalin. *Neues Jahrb. Mineral., Monatsh.*, 232-236.
- HAWTHORNE, F.C. & HENRY, D.J. (1999): Classification of the minerals in the tourmaline group. *Eur. J. Mineral.* **11**, 201-215.
- 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., WAIRACH, 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. (1982): Stability of spodumene in acidic and saline fluorine-rich environments. *Carnegie Inst. Wash., Geophys. Lab. Year Book* **81**, 331-334.
- \_\_\_\_\_ (1984): Experimental phase equilibria in the system  $\text{LiAlSiO}_4\text{-SiO}_2\text{-H}_2\text{O}$ : a petrogenetic grid for lithium-rich pegmatites. *Am. Mineral.* **69**, 995-1004.
- \_\_\_\_\_ (1986): Magmatic-hydrothermal transition in the Tanco rare-element pegmatite: evidence from fluid inclusions and phase equilibrium experiments. *Am. Mineral.* **71**, 376-395.
- MACDONALD, D.J., HAWTHORNE, F.C. & GRICE J.D. (1993): Foitite,  $\square[\text{Fe}^{2+}_2(\text{Al,Fe}^{3+})]\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_4$ , a new alkali-deficient tourmaline: description and crystal structure. *Am. Mineral.* **78**, 1299-1303.



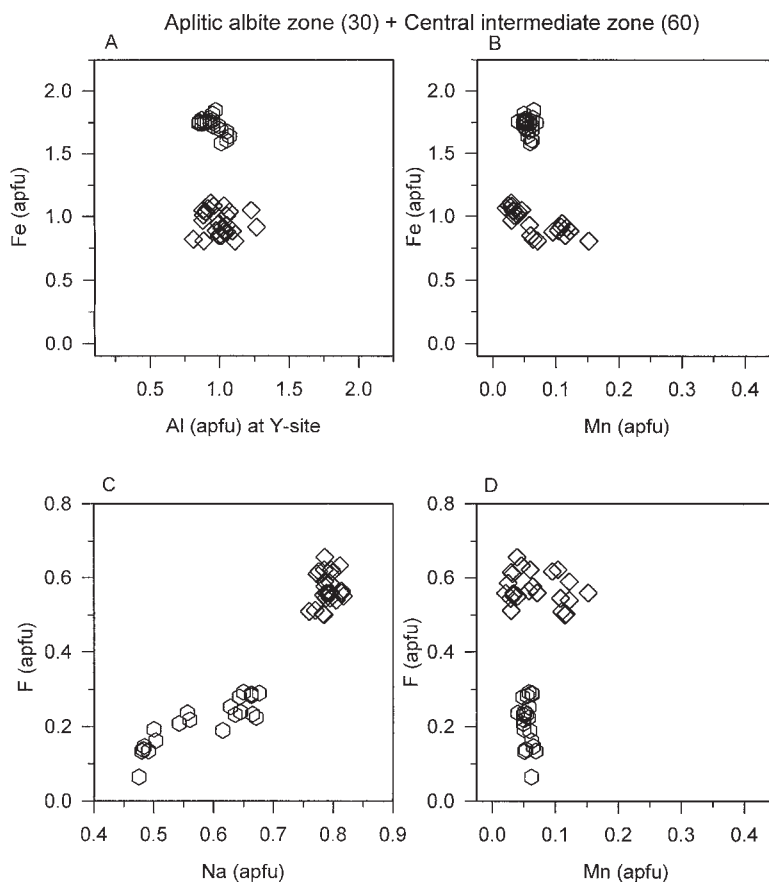


FIG. 8. Tourmaline compositions at Tanco. Diamonds: aplitic albite zone (30), hexagons: central intermediate zone (60).

MARCHETTI, A. (1997): *Relazioni composizionali in tormaline di genesi pegmatitica: la pegmatita di Urubu, MG (Brasile)*. Thesis, Università degli Studi di Roma "La Sapienza", Rome, Italy.

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.

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

\_\_\_\_\_ & \_\_\_\_\_ (1985): "PAP"  $\phi(\rho Z)$  procedure for improved quantitative microanalysis. In *Microbeam Analysis - 1985*. San Francisco Press, San Francisco, California (104-106).

QUÉMÉNEUR, J., LAGACHE, M. & CORREIA NEVES, J.M. (1993): La pegmatite d'Urubu, Araçuaí, Minas Gerais (Brésil), exemple de pegmatite complexe à péralite: zonalité

minéralogique et géochimie des micas et tourmalines. *C.R. Acad. Sci., Sér. II*, **317**, 1425-1431.

ROBERT, J.-L., GOURDANT, J.-P., LINNEN, R.L., ROUER, O. & BENOIST, P. (1997): Crystal-chemical relationships between OH, F and Na in tourmaline. *Tourmaline 1997, Int. Symp. on Tourmaline (Nové Město na Moravě), Abstr. Vol.*, 84-85.

SELWAY, J.B. & NOVÁK, M. (1997): Experimental conditions, normalization procedures and used nomenclature for tourmaline. *Tourmaline 1997, Int. Symp. on Tourmaline (Nové Město na Moravě), Field Trip Guidebook* (M. Novák & J.B. Selway, eds.), 19-21.

\_\_\_\_\_, \_\_\_\_\_, ČERNÝ, P. & HAWTHORNE, F.C. (1999): Compositional evolution of tourmaline in lepidolite-subtype pegmatites. *Eur. J. Mineral.* **11**, 569-584.

\_\_\_\_\_, \_\_\_\_\_, \_\_\_\_\_ & \_\_\_\_\_ (2000): The Tanco pegmatite at Bernic Lake, Manitoba. XIII. Exocontact tourmaline. *Can. Mineral.* **38**, 869-876.

- \_\_\_\_\_, \_\_\_\_\_, HAWTHORNE, F.C., ČERNÝ, P., OTTOLINI, L. & KYSER, T.K. (1998): Rossmanite,  $\square(\text{LiAl}_2)\text{Al}_6(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_4$ , a new alkali-deficient tourmaline: description and crystal structure. *Am. Mineral.* **83**, 896-900.
- 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.
- THOMAS, A.V., BRAY, C.J. & SPOONER, E.T.C. (1988): A discussion of the Jahns–Burnham proposal for the formation of zoned granitic pegmatites using solid – liquid – vapour inclusions from the Tanco pegmatite, S.E. Manitoba, Canada. *Trans. R. Soc. Edinburgh: Earth Sci.* **79**, 299-315.
- \_\_\_\_\_, PASTERIS, J.D., BRAY, C.J. & SPOONER, E.T.C. (1990):  $\text{H}_2\text{O}-\text{CH}_4-\text{NaCl}-\text{CO}_2$  inclusions from the footwall contact of the Tanco granitic pegmatite: estimates of internal pressure and composition from microthermometry, laser Raman spectroscopy, and gas chromatography. *Geochim. Cosmochim. Acta* **54**, 559-573.
- \_\_\_\_\_ & SPOONER, E.T.C. (1988a): Fluid inclusions in the system  $\text{H}_2\text{O}-\text{CH}_4-\text{NaCl}-\text{CO}_2$  from metasomatic tourmaline within the border unit of Tanco zoned granitic pegmatite, S.E. Manitoba. *Geochim. Cosmochim. Acta* **52**, 1065-1075.
- \_\_\_\_\_ & \_\_\_\_\_ (1988b): Occurrence, petrology and fluid inclusion characteristics of tantalum mineralisation in the Tanco granitic pegmatite, S.E. Manitoba. *In Recent Advances in the Geology of Granite-Related Mineral Deposits* (R.P. Taylor & D.F. Strong, eds.). *Can. Inst. Mining Metall., Spec. Vol.* **39**, 208-222.
- WEIDNER, J.R. & MARTIN, R.F. (1987): Phase equilibria of a fluorine-rich leucogranite from the St. Austell pluton, Cornwall. *Geochim. Cosmochim. Acta* **51**, 1591-1597.

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