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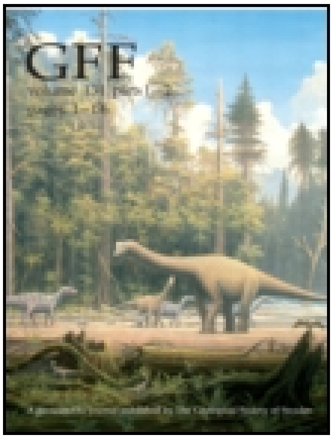

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Compositional evolution of tourmaline in the petalite-subtype Nyköpingsgruvan pegmatites, Utö, Stockholm Archipelago, Sweden

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Compositional evolution of tourmaline in the petalite-subtype Nyköpingsgruvan pegmatites, Utö, Stockholm Archipelago, Sweden

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Abstract: The classic petalite-subtype Nyköpingsgruvan pegmatites are located on the northern part of Utö Island, Stockholm archipelago, Sweden. They consist of two genetically related pegmatite bodies, the southern (minor) and northern (major), transecting the Nyköpingsgruvan iron formation. The pegmatite zones are named according to their most characteristic mineral: (1) spodumene, (2) pink K-feldspar + albite intergrowth, (3) lepidolite, (4) coarse sacchardoidal albite (>1 mm), (5) petalite, and (6) fine saccharoidal albite (<1–2 mm). The internal tourmaline composition evolves through the following crystallization sequence: Al-rich schorl → phases intermediate between schorl and elbaite → "fluor-elbaite" with variable Fe contents → elbaite → phases intermediate between elbaite and rossmanite → Ca-bearing elbaite-rossmanite → Ca-bearing elbaite. The dominant substitutions are Na $\rightleftarrows$ □ (□ = vacancy) with minor Ca variation at the *X* site, and $2Fe^{2+} \rightleftarrows Al + Li$ at the *Y* site. The negative correlation between Fe and (Al + Li) and between Fe and Mn in tourmaline is due to fractionation of the pegmatite melt. The negative correlation between □ at the *X* site and F at the O(1) site is caused by crystal-chemical constraints and controlled by $f(F_2)$. The presence of Ca-bearing elbaite-rossmanite, Ca-bearing elbaite, apatite and microlite in the fractionated pegmatite zones indicates that late-stage Ca-enrichment is probably due to conservation of Ca during consolidation of the pegmatite by Ca-F complexes in the melt. Most tourmaline throughout the pegmatites is veined by cookeite, indicating decreasing salinity and low F-activity in the late low-temperature hydrothermal fluids. In the BIF, the exocontact tourmaline is dominantly schorl-dravite with variable Ca contents and in the aplitic veinlets within the iron formation, the exocontact tourmaline is dominantly (Ca, Mg)-bearing schorl, whereas "fluor-elbaite"-schorl dominates mica schist along the contacts with the pegmatites. In the contaminated, dolomitic-marble-hosted Grundberg outcrop, the endomorphic tourmaline is Li-rich (mainly liddicoatite and elbaite) with (Mg, Fe)-rich fracture-infillings (mainly dravite and schorl).

Keywords: Tourmaline, petalite-subtype pegmatite, fractionation, Utö Island, south-central Sweden

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Petalite-subtype pegmatites are defined as pegmatites with petalite as the dominant Li-bearing mineral (Černý 1991). The petalite-subtype Nyköpingsgruvan pegmatite dykes, located on the northern part of the Utö island, Sweden, were the first recognized lithium pegmatites in the world, and minerals of these pegmatite dykes have been collected and studied since the early 19th century. The dykes are the type locality for spodumene, petalite, manganotantalite and holmquistite (for references see Smeds & Černý 1989). The blue variety of tourmaline was studied and named indicolite by d'Andrada (1800), and a greenish variety was analyzed by Arfwedson (1818). He was the first author to report Li and B in tourmaline. Reddish varieties of tourmaline were recognized by Berzelius (appendix in Arfwedson 1818). The paragenesis and chemistry of tourmaline from this locality were examined by Sjögren (1916). In spite of the early recognition of the tourmaline at Utö, little attention has been paid to them since the early 20th century.

In contrast to the tourmaline from lepidolite-subtype pegmatites (Selway et al. 1999), the chemical evolution of tourmaline from petalite-subtype pegmatites has not been established. The only study of petalite-subtype pegmatite tourmaline is that of Selway et al. (2000a, 2000b) at Tanco, Manitoba, and a brief discussion of tourmaline at Urubu, Brazil by Quéméneur et al. (1993) and Marchetti (1997). For this reason, we undertook a thorough examination of the compositional evolution of tourmaline in the zoned Nyköpingsgruvan pegmatites.

Tourmaline is the most common B-bearing silicate mineral in granitic pegmatites. The tourmaline group has the general formula: $X\,Y_3\,Z_6\,[T_6O_{18}]\,[BO_3]_3\,V_3\,W$, where *X* = Na, K, Ca, □ (vacancy); *Y* = Li, Mg, Fe, Mn, Al, Ti; *Z* = Al, Mg; *T* = Si, Al; *V* = OH, O; *W* = OH, F, O (Hawthorne & Henry 1999). The tourmaline end-members can be divided into three groups based on the occupancy of the *X* site: (1) alkali tourmalines (Na + K dominant), (2) calcic tourmalines (Ca dominant) and (3) *X*-site-vacant tourmalines (□ dominant). This paper will discuss eight tourmaline species which occur within the zoned Nyköpingsgruvan pegmatites and their exocontacts: (1) Alkali tourmalines (X = Na, $Z = Al_6$): dravite ($Y = Mg_3$), schorl ($Y = Fe^{2+}_3$), elbaite ($Y = Li_{1.5}Al_{1.5}$); (2) Calcic tourmalines (X = Ca): uvite ($Y = Mg_3$, $Z = MgAl_6$), feruvite ($Y = Fe^{2+}_3$, $Z = MgAl_6$), liddicoatite ($Y = Li_2Al$, $Z = Al_6$); (3) *X*-site vacant tourmalines (X = □, $Z = Al_6$): foitite ($Y = Fe^{2+}_2Al$), rossmanite ($Y = LiAl_2$). The most common tourmaline species in these pegmatites are schorl and elbaite.

Geology and mineralogy of the Nyköpingsgruvan pegmatites

Geology

The two main lithium pegmatites at Utö transect steeply folded Proterozoic oxide iron formations (BIF) with minor sulphides, skarns, metatuffites, felsic metavolcanics and dolomitic marbles (see Figs. 1 and 2 of Smeds & Černý 1989). The pegmatites have been largely left intact as bridges in the open pits of the Nyköpingsgruvan iron mine, which was mined from the 12th to the 19th century, but are also partly exposed in inaccessible steep walls of flooded open pits with locally flat exposures, and are extensively covered by mine dump material and vegetation. Besides these two lithium pegmatites, there are also aplitic dikes (containing Li minerals) that transect the banded iron formation and have been noted to affect the surrounding rocks by the formation of exocontact holmquistite and tourmaline (Pilava-Podgurski 1956). The age of the dikes has been constrained with a columbite U–Pb age of 1821±16 Ma (Romer & Smeds 1994).

General mineralogy of the pegmatites

The two main Nyköpingsgruvan pegmatites, the major Northern and the minor Southern, have essentially the same mineralogy and degree of fractionation, but differ in zonation pattern (Smeds & Černý 1989). The almost vertical Southern body is essentially symmetrically zoned parallel to its contacts; the Northern body dips 50–60° N and is apparently vertically zoned, in a layered pattern across its altitude.

The Southern Nyköpingsgruvan pegmatite is 5–7 m thick and consists of two zones: (1) an outer zone of abundant greenish K-feldspar (1–5 cm), reddish K-feldspar + albite microintergrowths, spodumene and dark-blue tourmaline, subordinate fine-grained albite, quartz, grey mica and accessory amblygonite, and (2) an inner zone of abundant blocky petalite (10–30 cm), blocky greyish K-feldspar (10–30 cm) and amblygonite, subordinate fine-grained lepidolite, blue apatite and pink tourmaline. Locally, extensive fine-grained saccharoidal-albitic zones occur in this pegmatite.

The Northern Nyköpingsgruvan pegmatite is 18 m thick and 300 m long, and intrudes iron formation, metavolcanics and skarn, except for the western end (including the Grundberg outcrop) which intrudes dolomitic marble (Smeds & Černý 1989). Essentially, the same minerals occur in the Northern Nyköpingsgruvan as in the Southern dike, and six zones, named for their characteristic minerals, can be defined based on the present outcrops and abundant dump material as follows: (1) spodumene, (2) pink K-feldspar + albite intergrowth, (3) lepidolite, (4) coarse saccharoidal albite (>1 mm), (5) petalite, and (6) fine saccharoidal albite (<1-2 mm).

Exocontact phenomena include holmquistite and biotite-phlogopite ± black-blue tourmaline in the mica schist. Dump material also shows some minor (10–20 cm) veinlets of albitic material with black late-stage tourmaline in the iron formation (Langhof & Holtstam 1994; Nysten 1997; Langhof et al. 2000). These veinlets have been interpreted as being genetically related to the main pegmatites.

The spodumene zone (1) contains abundant green spodumene, red K-feldspar + albite intergrowths and amazonite, subordinate black-to-blue tourmaline (2–3 cm long) and arsenopyrite, and accessory albite, brownish mica, quartz, microlite, cassiterite, sphalerite and galena. The spodumene zone (roughly 20 cm wide) is in contact with the galena-bearing iron formation, but available outcrop indicates that it is not in contact with the marbles. Apparently, the green spodumene crystallized due to an influx of Fe from the host rock which expands the stability field of spodumene to pressures lower than established for Fe-free systems (London & Burt 1982). The amazonite and accessory galena crystallized due to an influx of Pb from the host rock (Smeds & Černý 1989).

The pink K-feldspar + albite intergrowth zone (2) contains abundant blocky pink K-feldspar + albite intergrowths (tens of cm), amazonite (5 cm) and petalite (10 cm), subordinate bluish-green apatite, amblygonite, blue tourmaline, white beryl and accessory albite, quartz, lepidolite, white mica, columbite-tantalite, microlite, zircon and cassiterite.

The lepidolite zone (3) contains abundant fine-grained lepidolite, subordinate white mica, blue tourmaline and quartz, and accessory red and blue apatite, albite, petalite, amblygonite, microlite, columbite-tantalite, zircon and cassiterite.

The coarse saccharoidal-albite zone (4) contains abundant albite (rarely cleavelanditic in cm-long plates) and quartz, subordinate corroded petalite, white mica and blue tourmaline, and accessory K-feldspar, lepidolite, amblygonite, microlite and cassiterite.

The petalite zone (5) contains abundant petalite (10–30 cm) and fine-grained lepidolite, subordinate pink, colourless and blue tourmaline and white mica, and accessory quartz, grey blocky K-feldspar, blue apatite, microlite, cassiterite and columbite-tantalite. The petalite zone forms the bulk of the Northern (major) dike (Smeds & Černý 1989).

The fine saccharoidal-albite zone (6) in the Grundberg outcrop contains dominant albite, quartz and K-feldspar, abundant pink tourmaline (3–4 mm long), and accessory pollucite, apatite, potassic to Rb-rich low-temperature K-feldspar (Teertstra et al. 1996, 1998), microlite, niobian calciotantite and plumboan-stannoan cesstibtantite (Smeds et al. 1999). Cesstibtantite forms an overgrowth on zoned niobian calciotantite grains, and both phases are intergrown with skeletal manganocolumbite and cassiterite (Smeds et al. 1999). Diffuse alteration of cesstibtantite spreads out from microfractures to produce veinlets of secondary cesian microlite. These mineral assemblages are partly due to contamination from the host dolomitic marble.

Paragenesis and textural attributes of tourmaline

The tourmaline associated with the Nyköpingsgruvan pegmatites can be divided into three groups: (a) exocontact or in minor aplitic veinlets, (b) endocontact, and (c) internal. (a) Black cm-long needles of tourmaline occur in aplitic veinlets and along the contact or within the BIF. Black-to-navy-blue exocontact tourmaline, which forms 2–15 mm long acicular crystals, occurs in the brown micaceous contact of the pegmatite (spodumene and reddish K-feldspar + albite intergrowth zones) with the host iron formation. (b) Colourless-to-blue endomorphic tourmaline (1–2 mm) occurs at the Grundberg outcrop in fine saccharoidal-albite zone (6) contaminated by dolomitic-marble host rock with local minor disseminations of magnetite.

(c) Internal tourmaline occurs in each of the pegmatite zones. Black-to-navy-blue tourmaline in the spodumene zone (1) forms 1 cm long acicular crystals and may contain veinlets of K-feldspar, quartz and minor galena and sphalerite. Black-to-navy-blue tourmaline in the pink K-feldspar + albite intergrowth zone (2) forms 2–5 mm acicular crystals and may contain K-feldspar and albite inclusions. Blue tourmaline (1–2 mm) in the lepidolite zone (3) may contain lepidolite and pollucite inclusions. Blue tourmaline in the coarse saccharoidal-albite zone (4) forms 1 cm long acicular crystals and may contain lepidolite, Cs-bearing lepidolite, cassiterite and albite inclusions. Green to pink to colourless to minor blue tourmaline in the petalite zone (5) forms 1–2 cm long columnar crystals that may be zoned, with a colourless core and a pink rim, or with a green core and a pink rim. Pink tourmaline is usually associated with quartz (Sjögren 1916). Pink and colourless tourmaline may contain veinlets of apatite and K-feldspar, and inclusions of K-feldspar and quartz. Pink-to-colourless tourmaline forms 5–7 mm crystals in the fine saccharoidal-albite zone (6) in the Grundberg outcrop, and may contain quartz and lepidolite inclusions.

Cookeite veinlets are common in internal tourmaline throughout the Nyköpingsgruvan pegmatites, but are rare in the other pegmatites, e.g., Tanco and lepidolite-subtype pegmatites (Selway et al. 1999, 2000a). Cookeite veinlets commonly form by hydrothermal alteration of Li-rich minerals, such as spodumene, lepidolite and elbaite (Černý et al. 1971; Foord et al. 1986).

Sampling and experimental methods

Tourmalines were sampled in as many varieties and mineral assemblages as possible. Some of the sampled material originates from outcrops of the dykes. However, most of the samples are from the dumps, including the minor aplitic veinlets with black tourmaline, and the coloured elbaites (verdelite, rubellite and indicolite) from the main pegmatites. Most of the rock samples used in this study can be placed into pegmatite zones based on their mineralogy. The labels on the museum samples of Uppsala University do not discriminate between the southern and northern dykes, even though this material was collected in the 1830's to 1870's at the end of active mining in the area, when the exposures should have been of the best quality. However, some of the previously collected samples can not be correlated with the remaining outcrop. Short descriptions of samples are listed in the appendix to aid in identification of Utö samples in museums around the world. Each sample listed in the appendix is a tourmaline-bearing rock. In most samples, each individual tourmaline grain has a range in composition due to the extensive substitutions within its crystal structure.

Electron-microprobe analysis was done at the University of Manitoba 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. The 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. Potassium and P were below detection limits. Count times for peak and background determinations for all elements were 20 and 10 s, respectively. The analytical data were reduced and corrected using the $\varphi(\rho z)$ method (Pouchou & Pichoir 1984, 1985).

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 almost all tourmalines structurally analyzed to date (Hawthorne 1996; Bloodaxe et al. 1999). In the absence of an H_2O analysis, OH + F is assumed to be equal to 4 apfu. Currently, oxygen is dominant in the V and W sites only in end-members with *Y* site = Al^{3+} or Fe^{3+}, i.e., olenite, buergerite and povondraite (Hawthorne & Henry 1999). Lithium is assumed to be present in the tourmaline, as the Nyköpingsgruvan pegmatites are rich in Li, and structural-formula calculation for Li-free compositions produces vacancies at the *Y* site. 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 <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, 2000a, 2000b).

For an individual tourmaline composition, if the ratio of the two end-members is between 4:6 and 6:4 (i.e., close to the 50:50 dividing line), we use both end-member names (e.g. elbaite-schorl), with the first name designating the dominant component. If F > OH at the *W* site, then the prefix "fluor" is used, following Hawthorne & Henry (1999). "Fluor-elbaite" is a hypothetical tourmaline end-member and is not an IMA-approved name (Hawthorne & Henry 1999). Liddicoatite is assumed to have F dominant in the *W* site, following Hawthorne & Henry (1999).

The IMA-approved name for composition 2 in Table 2 is schorl. The name schorl would lead the reader to believe that *Y* = Fe, but actually the *Y* site only contains 1.61 apfu Fe and Al + Li = 1.25 apfu. Thus, the name schorl-elbaite acknowledges that this composition is immediate between schorl and elbaite. The IMA-approved name for compositions 4 and 9 in Table 2 is elbaite, but these two compositions are very different and the name elbaite does not describe the differences between them. Composition 4 has significant Fe contents (0.62 apfu) at the *Y* site and F dominates the *W* site, thus Fe-rich "fluor-elbaite" describes these deviations from the ideal composition. Ideally, elbaite has *X* = Na and rossmanite has *X* = □ (□ = vacancy). Composition 9 is immediate between elbaite and rossmanite, as Na = 0.42 apfu and □ = 0.42 apfu, so the name elbaite-rossmanite is used *not* rossmanite-elbaite, as □ < 0.5 apfu. Composition 9 also has minor Ca contents (0.16 apfu), so the modifier Ca-bearing is added to the name elbaite-rossmanite.

Composition of tourmaline

Exocontact and endomorphic tourmaline

Exocontact tourmaline occurs within the host rock which has been altered by the intruding pegmatite. Black tourmaline occurs in the iron formation and in the aplitic veinlets along the contact with the iron formation, and ranges in composition from uvite-feruvite to phases intermediate between schorl and dravite with elevated Ca contents to Mg-rich schorl-feruvite to schorl with elevated Ca and Mg contents (Fig. 1, Table 1). Navy-blue-to-

Table 1. Representative chemical compositions (wt.%) and unit formulae (apfu) of exocontact and endocontact tourmaline from the Utö pegmatite.

		1	2	3	4	5	6	7	8	9
SiO_2		35.78	35.57	35.02	34.65	37.26	38.00	37.41	36.83	35.40
TiO_2		0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
B_2O_3*		10.36	10.32	10.16	10.64	11.06	11.11	11.06	10.81	10.46
Al_2O_3		26.95	29.22	30.69	39.03	39.79	40.43	40.66	36.21	35.55
MgO		8.79	5.94	1.65	0.04	0.00	0.03	0.03	2.87	0.00
CaO		3.50	2.19	0.90	0.00	2.73	1.33	0.90	1.21	0.87
MnO		0.13	0.13	0.22	0.00	0.43	0.25	0.37	0.20	0.00
FeO		10.32	11.49	15.10	7.80	2.56	1.93	2.73	6.46	12.22
ZnO		0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Li_2O*		0.00	0.13	0.31	1.14	2.19	2.07	1.85	0.99	0.69
Na_2O		1.05	1.61	2.18	2.87	1.29	1.69	1.89	1.68	1.36
H_2O*		3.19	3.27	3.41	3.02	3.21	3.47	3.54	3.46	3.46
F		0.80	0.61	0.20	1.38	1.29	0.76	0.58	0.57	0.32
O=F		–0.34	–0.26	–0.08	–0.58	–0.54	–0.32	–0.24	–0.24	–0.13
Total		100.75	100.22	99.76	99.99	101.27	100.75	100.78	101.05	100.20
Formulae normalized to 31 anions										
T:	Si	6.00	5.99	5.99	5.66	5.85	5.95	5.88	5.92	5.88
	Al	0.00	0.01	0.01	0.34	0.15	0.05	0.12	0.08	0.12
B		3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Z:	Al	5.33	5.79	6.00	6.00	6.00	6.00	6.00	6.00	6.00
	Mg	0.67	0.21	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Y:	Al	0.00	0.00	0.18	1.18	1.22	1.40	1.41	0.78	0.84
	Ti	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Mg	1.53	1.27	0.42	0.01	0.00	0.01	0.01	0.69	0.00
	Mn	0.02	0.02	0.03	0.00	0.06	0.03	0.05	0.02	0.00
	Fe^{2+}	1.45	1.62	2.16	1.06	0.34	0.26	0.36	0.87	1.70
	Zn	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Li	0.00	0.09	0.21	0.75	1.38	1.30	1.17	0.64	0.46
Σ*Y*		3.03	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
X:	Ca	0.63	0.40	0.17	0.00	0.46	0.22	0.15	0.21	0.16
	Na	0.34	0.53	0.72	0.91	0.39	0.51	0.58	0.52	0.44
	□	0.03	0.07	0.11	0.09	0.15	0.27	0.27	0.27	0.40
OH		3.58	3.68	3.89	3.29	3.36	3.62	3.71	3.71	3.83
F		0.42	0.32	0.11	0.71	0.64	0.38	0.29	0.29	0.17

*B_2O_3, Li_2O and H_2O calculated by stoichiometry: B = 3 apfu; Li = 15 – 3*T* + *Z* + *Y*; OH+F = 4 apfu.

Compositions 1–4 from exocontact next to iron formation and compositions 5–9 are endomorphic tourmaline in Grundberg outcrop. 5–7 are main tourmaline grains and 8 and 9 are inclusions. 1, black uvite-feruvite, sample Uto18-3; 2, black Mg-rich schorl-feruvite, sample Uto18-2; 3, black (Ca, Mg)-bearing schorl, sample 17-1; 4, blue "fluor-elbaite"-schorl, sample Uto32-1; 5, colourless Fe-bearing liddicoatite-elbaite, sample Uto 13-1; 6, colourless Ca-rich elbaite, sample Uto 13-1; 7, blue (Ca, Fe)-bearing elbaite, sample Uto 13-2; 8, colourless Ca-rich elbaite-schorl-dravite, sample Uto13-1; 9, blue Ca-bearing schorl-elbaite, sample Uto13-2.

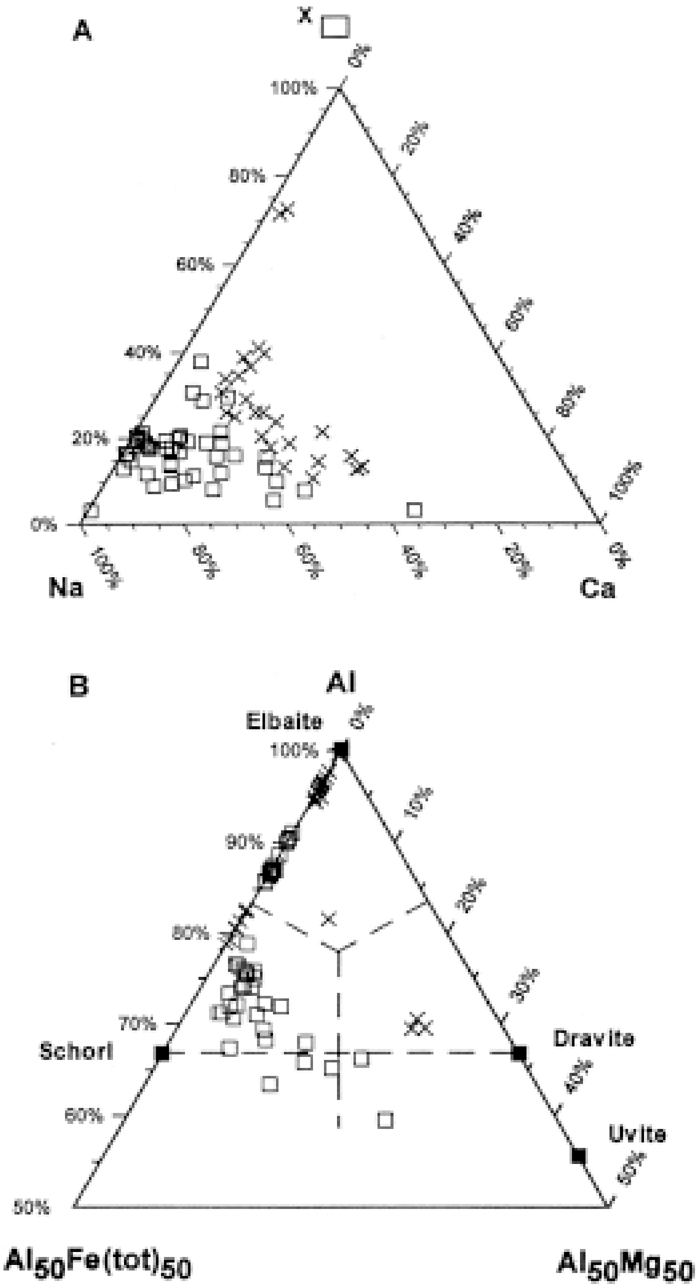

Fig 1. Compositions of exocontact and endocontact tourmaline. **A**. *X*-site vacancy – Na – Ca ternary diagram; **B**. Al – $Al_{50}Fe(tot)_{50}$ – $Al_{50}Mg_{50}$ ternary diagram. ■ = end members, □ = exocontact, × = endocontact tourmaline from the contaminated Grundberg outcrop.

black tourmaline occurs in the mica schist along the contact with the pink K-feldspar + albite intergrowth zone, and ranges in composition from "fluor-elbaite"-schorl to Fe-rich "fluor-elbaite" (Fig. 1, Table 1). Black exocontact tourmaline is (Ca, Fe, Mg)-rich, whereas navy-blue exocontact tourmaline is (Na, Al, Li, F)-rich. The exocontact tourmaline is more (Na, Mg, Fe)-enriched than the (Al, Li)-rich endomorphic tourmaline (Fig. 1).

Endomorphic tourmaline occurs within the pegmatite, close to the contact with the host rock, but its composition is affected by elements from the host rock entering the pegmatite melt. The endomorphic blue tourmaline occurs in fine saccharoidal albite along the contact with the dolomitic marbles, with local minor disseminations of magnetite, of the Grundberg outcrop. The blue-to-colourless tourmaline grains range in composition from liddicoatite-elbaite to elbaite-liddicoatite to elbaite, with minor Fe content in all phases (Fig. 1, Table 1). The (Ca, Li, F)-rich grains are cross-cut and replaced by lepidolite veinlets. The (Ca, Li, F)-rich tourmaline grains contain dark blue elongate (Fe, Mg)-rich fracture-infillings which range in composition from dravite to foitite to schorl-elbaite to elbaite-schorl-dravite, with significant Ca content in all phases.

Table 2. Representative chemical compositions (wt.%) and unit formulae (apfu) of internal tourmaline from the Utö pegmatite.

	1	2	3	4	5	6	7	8	9	10
SiO_2	35.37	36.12	35.49	37.41	38.18	37.57	38.38	39.06	38.95	38.49
TiO_2	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
B_2O_3*	10.35	10.47	10.35	10.99	11.07	11.12	11.27	11.41	11.32	11.28
Al_2O_3	33.53	34.46	32.83	39.53	40.07	41.59	42.88	43.71	42.30	42.38
MgO	0.00	0.33	0.97	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	0.36	0.09	0.56	0.37	0.42	0.40	0.40	0.00	0.98	0.97
MnO	0.22	0.21	0.31	0.29	0.30	0.59	0.30	0.09	0.09	0.12
FeO	14.91	11.60	13.20	4.68	2.81	1.31	0.18	0.00	0.00	0.10
ZnO	0.13	0.17	0.23	0.30	0.19	0.79	0.00	0.00	0.00	0.00
Li_2O*	0.41	0.77	0.54	1.60	1.83	1.78	1.98	1.94	2.19	2.16
Na_2O	1.93	2.31	2.28	2.26	2.00	1.90	1.59	1.52	1.41	1.55
H_2O*	3.18	3.20	3.27	3.20	3.39	3.39	3.51	3.81	3.46	3.48
F	0.82	0.88	0.63	1.24	0.90	0.93	0.81	0.27	0.95	0.87
O=F	–0.35	–0.37	–0.27	–0.52	–0.38	–0.39	–0.34	–0.11	–0.40	–0.37
Total	100.86	100.31	100.39	101.35	100.78	100.98	100.96	101.70	101.25	101.03
Formulae normalized to 31 anions										
T: Si	5.94	5.99	5.96	5.92	6.00	5.87	5.92	5.95	5.98	5.93
Al	0.06	0.01	0.04	0.08	0.00	0.13	0.08	0.05	0.02	0.07
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	0.58	0.73	0.46	1.29	1.41	1.54	1.71	1.80	1.64	1.63
Ti	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.00	0.08	0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.03	0.03	0.04	0.04	0.04	0.08	0.04	0.01	0.01	0.02
Fe^{2+}	2.09	1.61	1.86	0.62	0.37	0.17	0.02	0.00	0.00	0.01
Zn	0.02	0.02	0.03	0.03	0.02	0.09	0.00	0.00	0.00	0.00
Li	0.28	0.52	0.37	1.02	1.16	1.12	1.23	1.19	1.35	1.34
ΣY	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
X: Ca	0.07	0.02	0.10	0.06	0.07	0.07	0.07	0.00	0.16	0.16
Na	0.63	0.74	0.74	0.69	0.61	0.58	0.48	0.45	0.42	0.46
□	0.30	0.24	0.16	0.25	0.32	0.35	0.45	0.55	0.42	0.38
OH	3.56	3.54	3.67	3.38	3.55	3.54	3.61	3.87	3.54	3.54
F	0.44	0.46	0.33	0.62	0.45	0.46	0.39	0.13	0.46	0.46

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

1, black Al-rich schorl, spod. zone, Uto3-2; 2, black schorl-elbaite, spod. zone, Uto3-2; 3, black Ca-bearing schorl-elbaite, K-feldspar zone, Uto14-2; 4, blue Fe-rich "fluor-elbaite", K-feld. zone, Uto1-1; 5, blue Fe-bearing elbaite, lep. zone, Uto7-3; 6, blue elbaite, coarse sac.-albite zone, Uto9-1; 7, colourless elbaite-rossmanite, pet. zone, Uto21-1; 8, colourless rossmanite-elbaite, pet. zone, Uto27; 9, colourless Ca-bearing elbaite-rossmanite, fine sac.-albite zone, Uto31-2; 10, colourless Ca-bearing elbaite, fine sac. albite zone, Uto11-1.

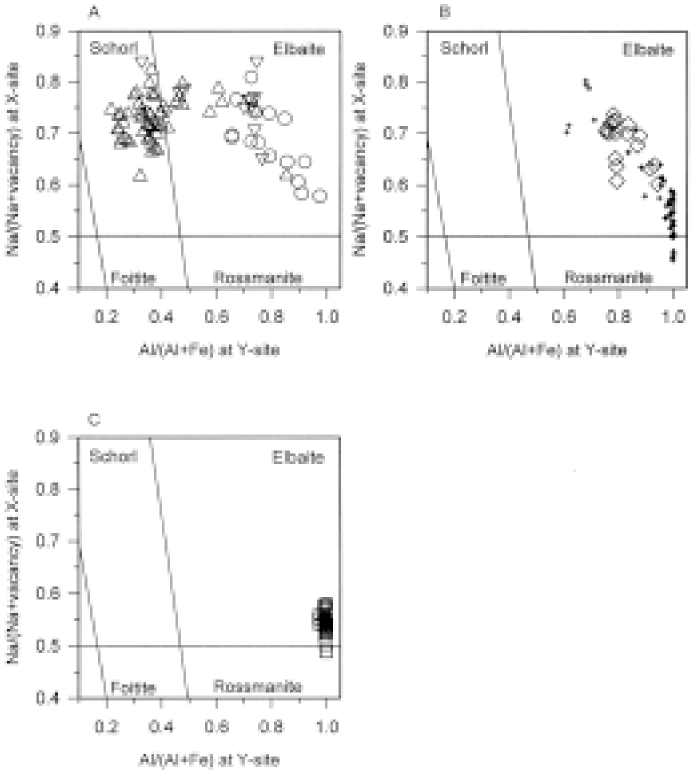

Fig. 2. Compositions of internal tourmaline plotted in Na/(Na + vacancy) at *X*-site vs. Al/(Al + Fe) at *Y*-site. **A**. △ = spodumene zone, ▽ = K-feldspar + albite intergrowth zone, ○ = lepidolite zone; **B**. ◇ = coarse saccharoidal-albite zone, + = petalite zone; **C**. □ = fine saccharoidal-albite zone.

Internal tourmaline

The species of tourmaline examined here are summarized as follows:

(1) Spodumene zone. – Here, the tourmaline species are black to brown to navy-blue Al-rich schorl, schorl-elbaite, ± Ca-bearing schorl, ± elbaite with elevated Fe contents (Fig. 2A). Brown tourmaline has Al-rich schorl cores and schorl-elbaite rims, and schorl-elbaite cores are surrounded by elbaite-schorl and elbaite with variable Fe and F contents rims.

(2) Pink K-feldspar + albite intergrowth zone. – Here, the tourmaline is black to brown ± Ca-bearing schorl, phases intermediate between schorl and elbaite and blue "fluor-elbaite" with elevated Fe contents (Fig. 2A).

(3) Lepidolite zone. – Blue Fe-rich "fluor-elbaite", Fe-bearing elbaite and elbaite (Fig. 2A).

(4) Coarse saccharoidal-albite zone. – Blue "fluor-elbaite" with many phases containing elevated Fe contents (Fig. 2B).

(5) Petalite zone. – Minor blue "fluor-elbaite" with elevated Fe contents and elbaite, and dominant pink, colourless and rare green elbaite, phases intermediate between elbaite and rossmanite which rarely have elevated Ca contents and ± Ca-bearing elbaite (Fig. 2B). Pale-green tourmaline has elbaite-rossmanite cores surrounded by rossmanite-elbaite intermediate zones and elbaite rims due to a Na ⇄ □ (□ = vacancy) substitution. The petalite zone also contains tourmaline with colourless rossmanite-elbaite cores and pink elbaite rims.

(6) Fine saccharoidal-albite zone in the Grundberg outcrop. – Pink-to-colourless elbaite-rossmanite, Ca-bearing elbaite-rossmanite and Ca-bearing elbaite (Fig. 2C).

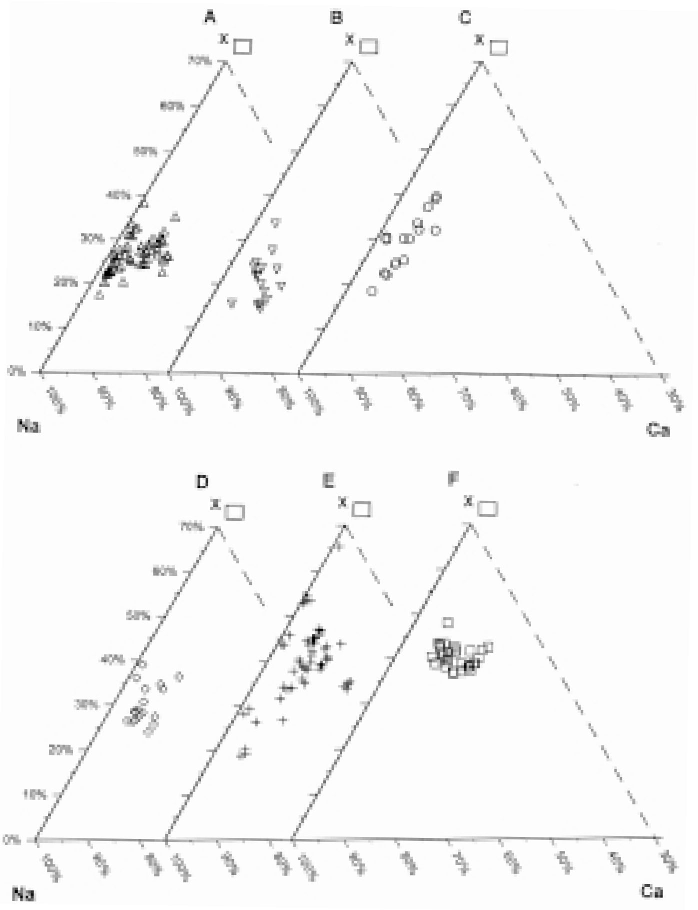

Fig. 3. Compositions of internal tourmaline plotted in *X*-site vacancy - Na - Ca ternary diagrams. **A**. spodumene zone; **B**. K-feldspar + albite intergrowth zone; **C**. lepidolite zone. **D**; coarse saccharoidal- albite zone; **E**. petalite zone. **F**; fine saccharoidal-albite zone.

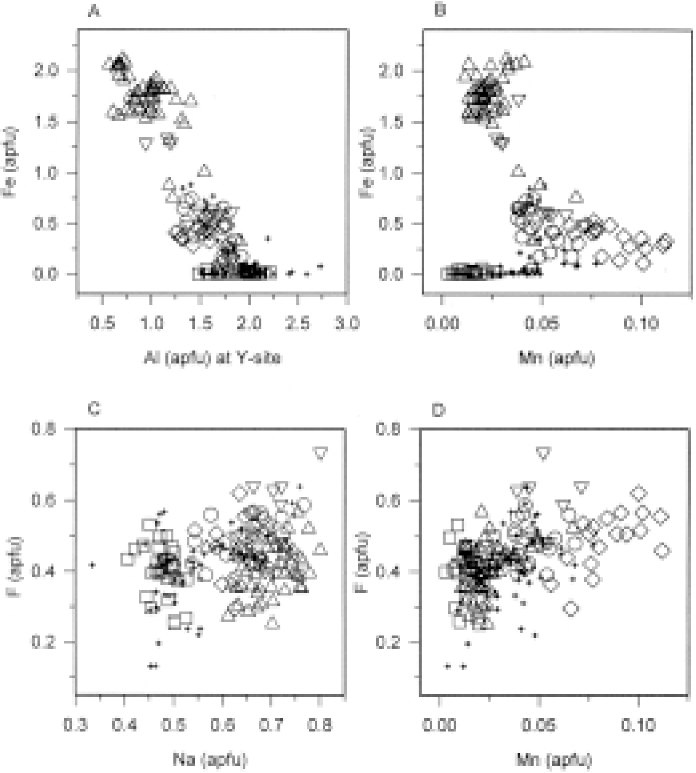

Fig. 4. Compositions of internal tourmaline. **A**. Fe (apfu) vs. Al (apfu) at Y-site; **B**. Fe (apfu) vs. Mn (apfu); **C**. F (apfu) vs. Na (apfu); **D**. F (apfu) vs. Mn (apfu). Symbols as in Fig. 2.

The dominant substitution at the *X* site is Na ⇄ □ with minor Ca variation (Fig. 3). The maximum Na content occurs in schorl-elbaite (up to 0.80 apfu) in the spodumene zone (1). The Na content in the tourmaline is variable throughout the rest of the pegmatite, and is low in the highly fractionated elbaite-rossmanite (minimum of 0.41 apfu Na) in the fine saccharoidal-albite zone (6). The vacancies are moderate at the *X* site in the tourmaline in most of the pegmatite, are elevated in the highly fractionated green, pink and colourless rossmanite-elbaite (up to 0.65 □ apfu) in the petalite zone (5), and are slightly elevated in the colourless Ca-bearing elbaite-rossmanite in the fine saccharoidal-albite zone (6). The Ca content is elevated in the primitive brown Ca-bearing schorl in the spodumene zone (1), is moderate throughout most of the pegmatite, and is elevated again in the highly fractionated pink Ca-bearing elbaite (up to 0.18 apfu Ca) in the petalite zone (5) and colourless Ca-bearing elbaite-rossmanite in the fine saccharoidal-albite zone (6). The fractionation trend is from Na-rich to (□, Ca)-rich.

The dominant substitution at the *Y* site is $2Fe^{2+}$ ⇄ Al + Li (Fig. 4A). The Fe content decreases from Al-rich schorl (with 2.1 apfu Fe) in the spodumene zone (1), Table 2, composition 1, to virtually nil in most elbaite (± rossmanite) of the petalite (5) and fine saccharoidal-albite (6) zones. The negative correlation indicates that primitive tourmaline is Fe-rich and fractionated tourmaline is Al- and Li-rich.

There is a negative correlation between Fe and Mn from Al-rich schorl to schorl-elbaite in the spodumene zone (1) to "fluor-elbaite" with elevated Fe contents in the pink K-feldspar + albite intergrowth (2), lepidolite (3) and coarse saccharoidal-albite (6) zones (Fig. 4B). The maximum of 0.11 apfu Mn occurs in Fe-bearing "fluor-elbaite" in the coarse saccharoidal-albite zone (4). The Fe and Mn contents decrease to nil in elbaite and phases intermediate between elbaite and rossmanite, some of which have elevated Ca in the petalite (5) and the fine saccharoidal-albite (6) zones.

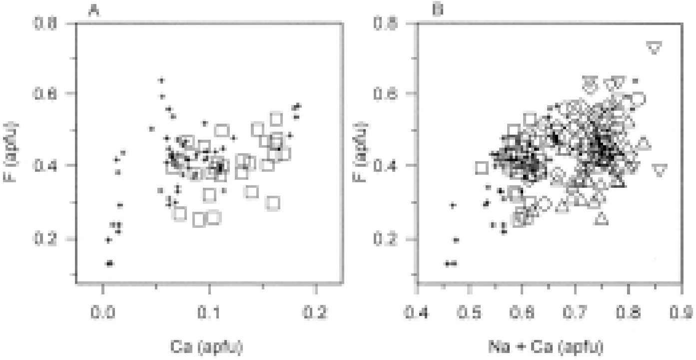

Fig. 5. Compositions of primary tourmaline. **A**. F (apfu) vs. Ca (apfu); **B**. F (apfu) vs. Na + Ca (apfu). Symbols as in Fig. 2.

There is a weak positive correlation between Mn and F in tourmaline (Fig. 4D). The correlation between Na and F is distorted due to the overall enrichment in Ca (Fig. 4C). The Al-rich schorl to Fe-bearing "fluor-elbaite" contains moderate-to-high Na, variable F and low Mn. The maximum Na and F contents of 0.80 apfu Na and 0.74 apfu F occur in Fe-rich "fluor-elbaite" in the K-feldspar + albite intergrowth zone (2). The Fe-bearing "fluor-elbaite" in the coarse saccharoidal-albite zone (4) also contains high Mn and F. The Na, Mn and F contents decrease in tourmaline in the petalite (5) and fine saccharoidal-albite zones (6). The lowest Na and F contents of 0.42 apfu Na and 0.13 apfu F and zero Mn occur in rossmanite-elbaite in the petalite zone (5).

There is a weak positive correlation between Ca and F in the most fractionated tourmaline (Fig. 5A). The correlation between Ca and F is slightly distorted due to elevated Na content, similar to the distortion seen in the Na–F correlation. The Ca content increases from zero Ca and 0.13 apfu F in the Ca-bearing rossmanite-elbaite to 0.18 apfu Ca and 0.57 apfu F in the rare Ca-bearing "fluor-elbaite" in the fractionated petalite (5) and fine saccharoidal-albite (6) zones. A positive correlation exists between (Na + Ca) and F, with high (Na + Ca) and F contents in Fe-rich "fluor-elbaite" in pink K-feldspar + albite intergrowth zone (2) and rarely in the petalite zone (5) and low (Na + Ca) and F contents in rossmanite-elbaite in the petalite zone (5), Fig. 5B.

Most tourmaline contains no Zn, except for ≤0.11 apfu Zn in Fe-bearing "fluor-elbaite" in the coarse saccharoidal-albite zone (4). The Zn enrichment in Fe-bearing elbaite correlates with Mn enrichment. Titanium is absent and Mg only occurs in (Ca, Mg)-bearing Al-rich schorl, with 0.34 apfu Mg in the K-feldspar + albite intergrowth zone (2), and Ca-bearing schorl-elbaite, with 0.19 apfu Mg in the spodumene zone (1).

Discussion

In the iron formation and minor aplitic veinlets within the iron formation, black exocontact tourmaline is enriched in Fe, Mg and Ca relative to internal tourmaline in the pegmatite. The tourmaline composition is strongly influenced by Fe, Mg and Ca in the iron-formation host rock and local lenses of dolomitic marble. Alteration of magnetite to hematite (Pilava-Podgurski 1956) in the iron formation is further evidence of the presence of Fe-rich fluids. The navy-blue-to-black tourmaline in the exocontact mica schist is (Na, Al, Li, F)-rich as it is influenced by an influx of pegmatite fluids into the host rock.

Blue endomorphic tourmaline occurs in the contaminated fine saccharoidal-albite zone in the Grundberg outcrop along the contact with dolomitic marbles. The main tourmaline grains are (Al, Li)-rich liddicoatite or elbaite which crystallized from a fractionated pegmatite melt, whereas the (Fe, Mg)-rich tourmaline within the main grains may have been generated by an influx of Fe and Mg from the dolomitic-marble host-rock which contains local minor disseminations of magnetite. The (Fe, Mg)-rich tourmaline grains are elongate, euhedral and parallel to each other, which suggests that they are late-stage hydrothermal fracture infillings. The presence of accessory calciotantite exclusively in the contaminated Grundberg outcrop is further evidence for an influx of Ca from the marble host-rock.

The internal tourmaline composition in the Nyköpingsgruvan pegmatites evolves through the following crystallization sequence: Al-rich schorl → phases intermediate between schorl and elbaite → "fluor-elbaite" with variable Fe contents → elbaite → phases intermediate between elbaite and rossmanite → Ca-bearing elbaite-rossmanite → Ca-bearing elbaite. The pegmatites are irregularly zoned, and the tourmaline composition is a good way to identify the crystallization sequence of the internal pegmatite zones, as it is the only ferromagnesian mineral that occurs in all of them. It is well known that (Fe, Mg)-rich tourmaline is the most primitive composition and Li-rich tourmaline is the most fractionated in pegmatites (Staatz et al. 1955; Jolliff et al. 1986; Novak & Povondra 1995; Selway et al. 1999). The presence of schorl in the spodumene and the pink K-feldspar + albite intergrowth zones indicates that they are primitive pegmatite zones. The presence of "fluor-elbaite" with variable Fe contents in lepidolite and coarse saccharoidal-albite zones indicates that they are intermediate in the fractionation sequence. Minor amounts of late-stage enriched elbaite in the petalite zone, and common Ca-bearing elbaite-rossmanite and Ca-bearing elbaite in the fine saccharoidal-albite zone indicate that they are the most fractionated pegmatite zones. This overall crystallization sequence of tourmaline is similar to that in the Tanco pegmatite and lepidolite-subtype pegmatites, except for the lack of foitite and the presence of late-stage Ca-enrichment in the Nyköpingsgruvan pegmatites (Selway et al. 1999, 2000a).

The crystallization sequence of internal pegmatite zones can be confirmed by fractionation indicator minerals only for the most primitive spodumene zone and most fractionated fine-grained saccharoidal albite zone. It is conceivable that the spodumene zone (1) is the earliest zone to solidify, as its petrology (green Fe-bearing spodumene) and geochemistry (Pb-bearing amazonite and sulfides) indicate early interaction with the host rocks. The presence of amazonite in the pink K-feldspar + albite intergrowth zone (2), but a lack of green spodumene, indicates reduced influence of the factors affecting zone (1).

The presence of accessory pollucite, potassic to Rb-rich low-temperature K-feldspar and cesstibtantite (Smeds & Černý 1989; Teertstra et al. 1996; 1998; Smeds et al. 1999) in the fine saccharoidal-albite zone (6) of the Grundberg outcrop indicates that it is the most fractioned pegmatite zone.

The negative correlation between Fe and (Al + Li) in tourmaline is due to fractionation of the pegmatite melt. The dominant substitution at the *Y* site is $3Fe^{2+} \rightleftarrows 1.5Al + 1.5Li$, as the most primitive tourmaline is Fe-rich (schorl) and the most fractionated tourmaline is (Al, Li)-rich (elbaite and rossmanite).

The Fe-Mn substitution in minerals is also used to indicate the degree of fractionation in a pegmatite. The fractionation trend in tourmaline is black and brown Al-rich schorl with high Fe and low Mn in the spodumene zone (1) → blue Fe-bearing "fluor-elbaite" with maximum Mn content in the coarse saccharoidal-albite zone (4) → Mn and Fe contents decreasing to nil in pink intermediate phases between elbaite and rossmanite, Ca-bearing elbaite-rossmanite and Ca-bearing elbaite in the petalite (5) and fine saccharoidal-albite zones (6).

The tourmaline composition may also be affected by crystal-chemical constraints, as shown by the correlation between Na at the *X* site and F at the *W* site (Robert *et al.*, 1997), and by $f(F_2)$. The explanation for this correlation is as follows: the OH group at the *W* site is bonded to three *Y* cations and the OH bond is directed along the three-fold axis toward the *X* site in the middle of the (T_6O_{18}) tetrahedral ring. The OH...O interactions between the H atom and the O atoms are weak when a cation occupies the *X* site, and this situation is favourable for F → OH substitution. When the *X* site is occupied by Na and the three *Y* sites are occupied by $2M^{2+} + 1M^{3+}$ (*i.e.*, rossmanite) to produce a 7+ charge environment, F cannot enter the *W* site. A positive correlation between Na and F exists from Al-rich schorl to Fe-bearing "fluor-elbaite" (with maximum Na and F). With increasing Ca content in the tourmaline, this positive correlation is distorted, and the most Ca-rich elbaite-rossmanite plots furthest from the Na-F correlation. A strong positive correlation occurs between Na and F in tourmaline from other Li-rich pegmatites, e.g., the petalite-subtype Tanco pegmatite, Manitoba (Selway et al. 2000a). The positive correlation between (Na + Ca) and F indicates a negative correlation between □ and F, as rossmanite-elbaite in the petalite zone contains low (Na + Ca), high □ and low F contents.

Late-stage enrichment in Ca in the most fractionated pegmatite zones resulted in crystallization of pink-to-colourless Ca-bearing elbaite-rossmanite and Ca-bearing elbaite, which is minor in the petalite zone (5) and common in the fine saccharoidal-albite zone (6). Late-stage Ca-enrichment also resulted in crystallization of calciotantite and alteration of cesstibtantite to cesian microlite in zone (6). Primary accessory Ca- and F-rich minerals (apatite and microlite) in the fractionated pegmatite zones are associated with the Ca-bearing elbaite-rossmanite. Late-stage hydrothermal Ca-rich chiavennite, milarite, apatite and calcite occur in druses or as fissure infillings of albite-rich zones of the two pegmatites (Nysten 1997; Langhof et al. 2000). This late-stage Ca-enrichment is not likely a result of Ca infiltration from the dolomitic marble host rock, as the expected associated Mg- and Fe-enrichment is not present in the tourmaline or in any other minerals within the fractionated, uncontaminated zones of the pegmatite. Calcium-bearing elbaite-rossmanite and Ca-bearing elbaite only occur in samples which also contain microlite which indicates that Ca-enrichment is probably due to conservation of Ca during consolidation of the pegmatite, by sequestering of Ca in the melt as fluoride complexes (Weidner & Martin 1987).

Most tourmaline throughout the Nyköpingsgruvan pegmatites is cross-cut by cookeite veinlets. Cookeite is one of the last minerals to crystallize, and its presence indicates decreasing salinity and low F-activity in the late low-temperature hydrothermal fluids.

Conclusions

In the BIF, the exocontact tourmaline is dominantly black schorl-dravite with variable Ca contents, and in the aplitic veinlets within the iron formation, the exocontact tourmaline is dominantly black (Ca, Mg)-bearing schorl. The tourmaline composition is strongly influenced by (Fe, Mg, Ca)-rich fluids within the iron-formation host rock and local lenses of dolomitic marble. Navy-blue-to-black "fluor-elbaite"-schorl dominates in mica schist along the contacts with the pegmatites. The tourmaline in the exocontact mica schist is (Na, Al, Li, F)-rich, as it is influenced by an influx of pegmatite fluids into the host rock.

Colourless-to-blue endomorphic tourmaline occurs at the Grundberg outcrop in fine saccharoidal-albite zone (6) contaminated by dolomitic-marble host rock with local minor disseminations of magnetite. The endomorphic tourmaline is (Ca, Li, F)-rich (mainly liddicoatite and elbaite with minor amounts of Fe) with (Mg, Fe)-rich fracture-infillings (mainly dravite and schorl with minor amounts of Ca). The main tourmaline grains crystallized from a fractionated pegmatite melt, whereas the tourmaline fracture-infillings may be replacement products due to an influx of Fe and Mg from the dolomitic-marble host-rock.

The crystallization of the internal tourmaline is due to increasing fractionation from Al-rich schorl → phases intermediate between schorl and elbaite → "fluor-elbaite" with variable Fe contents → elbaite → phases intermediate between elbaite and rossmanite → Ca-bearing elbaite-rossmanite → Ca-bearing elbaite. The dominant substitutions are Na ⇄ □ (□ = vacancy) with minor Ca variation at the *X* site, and $2Fe^{2+} \rightleftarrows Al + Li$ at the *Y* site. The negative correlation between Fe and (Al + Li) and between Fe and Mn in tourmaline is due to fractionation of the pegmatite melt. The positive correlation between (Na + Ca) and F indicates a negative correlation between □ and F. The negative correlation between □ at the *X* site and F at the O(1) site is caused by crystal-chemical constraints and controlled by $f(F_2)$. The presence of Ca-bearing elbaite-rossmanite, Ca-bearing elbaite, apatite and microlite in the fractionated pegmatite zones indicates that late-stage Ca-enrichment is probably due to conservation of Ca during consolidation of the pegmatite by Ca-fluoride complexes in the melt.

The crystallization sequence of primary internal tourmaline from the petalite-subtype Nyköpingsgruvan pegmatites differs from that of the lepidolite-subtype pegmatites (Selway et al. 1999). The most primitive tourmaline composition at Nyköpingsgruvan is Al-rich schorl and foitite is not present, whereas in lepidolite-subtype pegmatites, the most primitive tourmaline composition is foitite. The most fractionated tourmaline compositions at Nyköpingsgruvan are Ca-bearing elbaite-rossmanite and Ca-bearing elbaite, whereas in lepidolite-subtype pegmatites, the most fractionated compositions are elbaite-rossmanite and (Fe, Mn)-bearing elbaite. A late-stage enrichment in Ca is common in the tourmaline from Nyköpingsgruvan pegmatites, whereas in lepidolite-subtype pegmatites, the late-stage enrichment in tourmaline is in Fe and Mn.

The crystallization sequence of primary internal tourmaline from the petalite-subtype Nyköpingsgruvan pegmatites is similar to that of the petalite-subtype Tanco pegmatite, Canada (Selway et al. 2000a). The tourmaline compositions from Tanco cover a broader range of compositions, and tourmaline compositions from Nyköpingsgruvan are overall more fractionated. Tourmaline from the border, wall and aplitic albite zones at Tanco is contaminated with Mg and Ti from the host rock, whereas endomorphism is limited to the Grundberg outcrop at Nyköpingsgruvan. Intermediate phases between schorl and foitite, and Mn-bearing elbaite are present at Tanco, but absent at Nyköpingsgruvan. Iron-rich tourmaline is more common at Tanco than Nyköpingsgruvan. “Fluor-elbaite” and phases intermediate between elbaite and rossmanite only occur in the lower and upper intermediate zones (with spodumene + quartz intergrowths) at Tanco, but is more widespread at Nyköpingsgruvan as it occurs in the coarse saccharoidal albite zone (4), petalite zone (5) and fine saccharoidal albite zone (6). The same late-stage Ca enrichment in elbaite occurs at both localities, but it is much more limited at Tanco. Cookeite veinlets are common in internal tourmaline throughout the Nyköpingsgruvan pegmatites, but are rare in Tanco pegmatite.

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References

D’Andrada, J.B., 1800: Kurze Angabe der Eigenschaften und Kennzeichen einiger neuen Fossilien aus Schweden und Norwegen, nebst einigen chemischen Bemerkungen über dieselben. *Allgemeines Journal der Chemie IV(19)*, 28–39.

Arfwedson, A. 1818: Undersökning af några vid Utö Jernmalmsbrott förekommande fossilier och af ett deri funnet eget eldfast alkali. Med tillägg af Berzelius. *Afhandlingar i Fysik, Kemi och Mineralogi 6,* 145–176.

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. *American Mineralogist 84*, 922–928.

Burns, P.C., MacDonald, D.J., & Hawthorne, F.C., 1994: The crystal chemistry of manganese-bearing elbaite. *Canadian Mineralogist 32*, 31–41.

Černý, P., 1991: Rare-element granitic pegmatites. Part I: Anatomy and internal evolution of pegmatite deposits. *Geoscience Canada 18*, 49–67.

Černý, P., Povondra, P. & Staněk, J., 1971: Two cookeites from Czechoslovakia: a boron-rich variety and a II*b* polytype. *Lithos 4*, 7–15.

Foord, E.E., Starkey, H.C. & Taggart, J.E., Jr., 1986: Mineralogy and paragenesis of “pocket” clays and associated minerals in complex granitic pegmatites, San Diego County, California. *American Mineralogist 71*, 428–439.

Hawthorne, F.C., 1996: Structural mechanisms for light-element variations in tourmaline. *Canadian Mineralogist 34*, 123–132.

Hawthorne, F.C. & Henry, D.J., 1999: Classification of the minerals of the tourmaline group. *European Journal of Mineralogy 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. *American Mineralogist 71,* 472–500.

Langhof, J. & Holtstam, D., 1994: Boron-bearing chiavennite and other late-stage minerals of the proterozoic lithium-pegmatites of Utö, Stockholm, Sweden. *Abstracts, International Mineralogical Association, 16th General Meeting, Pisa,* 232.

Langhof, J., Holtstam, D., & Gustafsson, L., 2000: Chiavennite and zoned genthelvite-helvite as late-stage minerals of the Proterozoic LCT pegmatites at Utö, Stockholm, Sweden. *GFF 122*, 207–212.

London, D. & Burt, D.M., 1982: Lithium aluminosilicate occurrences in pegmatites and the lithium aluminosilicate phase diagram. *American Mineralogist 67*, 483–493.

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

Marchetti, A., 1997: *Relazioni composizionali in tourmaline di genesi pegmatitica: La pegmatite di Urubu, MG (Brasile).* [Unpubl. Thesis], Università Degli Studi di Roma “La Sapienza”, Rome, Italy.

Novák, M. & Povondra, P., 1995: Elbaite pegmatites in the Moldanubicum: a new subtype of the rare-element class. *Mineralogy and Petrology 55*, 159–176.

Nysten, P., 1997: Paragenetic setting and crystal chemistry of milarites from Proterozoic granitic pegmatites in Sweden. *Neues Jahrbuch für Mineralogie, Monatshefte 1996, H.12*, 564–576.

Pilava-Podgurski, N., 1956: Nya geologiska undersökningar vid Utö järnmalmsfält. *Sveriges Geologiska Undersökning C541, 1–54.*

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

Pouchou, J.L. & Pichoir, F., 1985: ”PAP” $\varphi(\rho Z)$ procedure for improved quantitative microanalysis. *Microbeam Analysis 1985*, 104–106.

Quéméneur, J., Lagache, M. & Correia Neves, J.M., 1993: La pegmatite d’Urubu, Aracuai, Minas Gerais (Brésil), exemple de pegmatite complexe à pétalite: zonalité minéralogique et géochimie des micas et tourmalines. *Comptes Rendus de l’Académie des Sciences, Série 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 International Symposium on Tourmaline, Abstract volume.* Nové Město na Moravě, Czech Republic, 84–85.

Romer, R.L. & Smeds, S.-A., 1994: Implications of U-Pb ages of columbite-tantalites from granitic pegmatites for the Palaeoproterozoic accretion of 1.90-1.85 Ga magmatic arcs to the Baltic Shield. *Precambrian Research 67, 141–158.*

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

Selway, J.B., Novák, M., Černý, P. & Hawthorne, F.C., 1999: Compositional evolution of tourmaline in lepidolite-subtype pegmatites. *European Journal of Mineralogy 11*, 569–584.

Selway, J.B., Černý, P., Hawthorne, F.C. & Novák, M., 2000a: The Tanco pegmatite at Bernic Lake, Manitoba. XIV. Internal tourmaline. *Canadian Mineralogist 38,* 877–891.

Selway, J.B., Novák, M., Černý, P.& Hawthorne, F.C., 2000b: The Tanco pegmatite at Bernic Lake, Manitoba. XIII. Exocontact tourmaline. *Canadian Mineralogist 38,* 869–871.

Sjögren, H., 1916: The chemical composition of tourmaline from Utö. *Bulletin of the Geological Institute of the University of Uppsala 15*, 317–324.

Smeds, S.-A. & Černý, P., 1989: Pollucite from the Proterozoic petalite-bearing pegmatites of Utö, Stockholm archipelago, Sweden. *Geologiska Föreningens i Stockholms Förhandlingar 111,* 361–372.

Smeds, S.-A. & Černý, P. & Chapman, R., 1999: Niobian calciotantite and plumboanstannoan cesstibtantite from Utö, Sweden. *Canadian Mineralogist 37*, 665–672.

Staatz, M.H., Murata, K.J. & Glass, J.J., 1955: Variation of composition and physical properties of tourmaline with its position in the pegmatite. *American Mineralogist 40,* 789–804.

Taylor, M.C., Cooper, M.A. & Hawthorne, F.C., 1995: Local charge-compensation in hydroxy-deficient uvite. *Canadian Mineralogist 33*, 1215–1221.

Teertstra, D.K., Černý, P., Langhof, J., Smeds, S.-A. & Grensman, F., 1996: Pollucite in Sweden: occurrences, crystal chemistry, petrology and subsolidus history. *GFF 118,* 141–149.

Teertstra, D.K., Černý, P. & Hawthorne, F.C., 1998: Rubidium feldspars in granitic pegmatites. *Canadian Mineralogist* 36, 483–496.

Weidner, J.R. & Martin, R.F.,1987: Phase equilibria of a fluoride-rich leucogranite from the St. Austell pluton, Cornwall. *Geochimica et Cosmochimica Acta* 51, 1591–1597.

Appendix: Descriptions of samples used in this study.

Peg. Zone	sample number	mineral assemblage	description of tourmaline
exo-contact	18 = PN 1	same as PN2, tourmaline with magnetite and biotite, in BIF	black uvite-feruvite, Ca-rich schorl-dravite, Ca-bearing schorl-dravite, schorl-dravite,
	17 = PN 2	dumps, probably minor aplitic dike in BIF, platy albite (3-4 mm), minor greenish beryl, cassiterite (mm), associated with PN1	black (Ca, Mg)-rich schorl to (Ca, Mg)-bearing schorl (2-3 mm) with albite veinlets
	33 = PN 3	in saccharoidal albite, quartz, black tourmaline, [amazonite (3-4 mm)], in aplitic veinlets in contact with and cross-cutting black "mica schist"	black (Ca, Mg)-rich schorl to (Ca, Mg)-bearing schorl to schorl
	32 = UU319/42	"mica schist", brown mica, black tourmaline, [saccharoidal albite]	brown to blue "fluor-elbaite"-schorl
	16 = SAS11	Southern NYK dike, northern contact with Fe-ore, fine-grained albite, amazonite, [brownish mica (mm)]	dark blue to brown "fluor-elbaite"-schorl, blue Fe-rich "fluor-elbaite", in cm clusters
Spod. zone (1)	3 = UU167/122	green spodumene, arsenopyrite (~ 5 vol.%), cassiterite (~ 5 vol.%), quartz, [black tourmaline]	black Al-rich schorl and ± schorl-elbaite; cookeite + K-feldspar veinlets, quartz inclusions
	15 = UU167/122	same as 3	black to brown Al-rich schorl and Ca-bearing schorl, navy blue schorl-elbaite; cookeite, quartz, ± galena, ± sphalerite veinlets
	19 = UU319/62	coarse spodumene, reddish K-feldspar, quartz (2–3 cm), brown tourmaline	brown schorl-elbaite, elbaite-schorl, Fe-rich elbaite, Fe-bearing elbaite (2–3 cm)
	34 = UU319/59	green spodumene, quartz, black tourmaline [reddish K-feldspar + albite intergrowth]	brown Al-rich schorl, blue overgrowth schorl, schorl-elbaite, elbaite-schorl
	20 = UU319/139	quartz, black tourmaline	radiating brown and dark blue schorl-elbaite
pink Kfs zone (2)	14 = SNY-4	Southern dike, amazonite (~ 20 vol.%), sugary albite, cassiterite, [red "K-feldspar", black tourmaline, brown mica, apatite]	black to brown Ca-bearing schorl, (Ca, Mg)-bearing schorl, Ca-bearing schorl-elbaite, Ca-bearing elbaite-schorl, Fe-rich elbaite, Fe-bearing elbaite; K-feldspar and albite inclusions
	1 = LG#20	Northern dike, pink K-feldspar, greyish muscovite, albite, [petalite, blue tourmaline, amblygonite, columbite-tantalite]	pale blue Fe-rich "fluor-elbaite", Fe-bearing "fluor-elbaite" with cookeite veinlets
Lpd zone (3)	7 = UU225/43	lepidolite, green muscovite, quartz, blue tourmaline, K-feldspar, [columbite-tantalite, microlite]	blue Fe-rich "fluor-elbaite", Fe-bearing elbaite
	8 = UU348/36	lepidolite, quartz, muscovite, blue tourmaline	pale blue Fe-bearing elbaite, elbaite; cookeite veinlets; lepidolite and pollucite inclusions
coarse sac. albite zone (4)	9 = LG#33	albite, quartz, blue tourmaline, cassiterite, [lepidolite]	pale blue Fe-bearing "fluor-elbaite", cookeite veinlets; lepidolite and cassiterite inclusions
	10 = UU319/46	albite, quartz, blue tourmaline, muscovite, [Mn-tantalite, cassiterite]	blue to colourless Fe-bearing elbaite; cookeite veinlets; lepidolite, Cs-bearing lepidolite and albite inclusions
petalite zone (5)	6 = UU319/19	white and green mica petalite, quartz, blue tourmaline, [columbite-tantalite]	pale blue Fe-rich "fluor-elbaite" and Fe-bearing "fluor-elbaite" cookeite and apatite veinlets
	21 = UU319/101	petalite, lepidolite (mm), pink tourmaline, [K-feldspar]	colourless elbaite-rossmanite; cookeite and apatite veinlets
	23 = UU319/394	greenish tourmaline in amblygonite, petalite, minor lepidolite	pale green elbaite-rossmanite, rossmanite-elbaite core and elbaite rim
	27 = UU319/Pal	petalite, quartz, lepidolite, pink tourmaline	colourless rossmanite-elbaite core, pink elbaite-rossmanite and elbaite rim
	4 = LG#1	Northern dike, petalite, quartz, pink tourmaline, [lepidolite, microlite]	pink elbaite-rossmanite, Ca-bearing elbaite, ± rossmanite-elbaite; cookeite and apatite veinlets; K-feldspar inclusions
	5 = UU319/Pal	petalite, quartz, pink tourmaline, [yellow microlite]	pink elbaite-rossmanite, Ca-bearing elbaite-rossmanite; cookeite, K-feldspar and apatite veinlets; quartz inclusions
fine sac. albite zone (6)	11 = JL#1	Grundberg outcrop, white albite, quartz, pink tourmaline, microlite	pink to colourless Ca-bearing elbaite, ± elbaite-rossmanite; lepidolite inclusions
	12 = LG#35	Grundberg outcrop, white albite, pink tourmaline, microlite, quartz, [columbite-tantalite, pollucite, apatite, amblygonite, K-feldspar]	pale pink Ca-bearing elbaite-rossmanite; quartz inclusions
	31 = SAS 12	Grundberg outcrop, white albite, pink tourmaline, lepidolite	pale pink elbaite-rossmanite and rossmanite-elbaite, colourless Ca-bearing elbaite-rossmanite
contaminated fine sac. albite	13 = GRB	Grundberg outcrop, white albite, green muscovite, blue tourmaline, [pollucite, yellow microlite, Mn-tantalite]	blue to colourless tourmaline, main grain: liddicoatite to elbaite with variable Fe contents, fracture-infillings: dravite to foitite to schorl-elbaite to elbaite-schorl-dravite with variable Ca contents

Each sample is a tourmaline-bearing rock. Source of samples: UU = Uppsala University, Sweden, SAS = Sten-Anders Smeds' personal collection, PN = Per Nysten's personal collection, LG = Lars Gustafsson's personal collection, SNY = Southern Nyköpingsgruvan pegmatite, Pal = Palmgren 1872, JL = J. Langhof's personal collection, GRB = Grundberg outcrop, [] - rare to minor minerals, Spod = spodumene, Kfs = K-feldspar, Lpd = lepidolite, sac. = saccharoidal