Original paper Chemical composition of tourmalines from the Manjaka pegmatite and its exocontact, Sahatany Valley, Madagascar

Petr GADAS^{1*}, Milan NOVÁK¹, Michaela VAŠINOVÁ GALIOVÁ^{2,3}, Federico PEZZOTTA⁴

¹ Department of Geological Sciences, Faculty of Science, Masaryk University, Kotlářská 2, CZ-611 37 Brno, Czech Republic; pgadas@sci.muni.cz

² Institute of Chemistry and Technology of Environmental Protection, Faculty of Chemistry, Brno University of Technology, Purkyňova 118, 612 00 Brno, Czech Republic

³ BIC Brno, Purkyňova 125, 612 00, Brno, Czech Republic

⁴ Mineralogy Department, Museo di Storia Naturale, Corso Venezia 55, I-20121 Milan, Italy

*Corresponding author



Chemical compositions and mineral assemblages of tourmalines from the elbaite-subtype Manjaka pegmatite in the Sahatany Valley, central Madagascar, and its exocontact were examined using EPMA and LA-ICP-MS. Several textural, compositional and paragenetic types of tourmalines were recognized in the individual pegmatite units and in the zones located towards the host rock in the order: wall pegmatite unit \rightarrow border pegmatite unit \rightarrow contact zone \rightarrow recrystallization zone; the latter zone evidently originated after the host Mg-rich calc-silicate rock (Di+Tr+Qz>Pl+Kfs>Phl+Dol>Cal). Zoned prismatic crystals from the border unit evolved from the core Tur Ia (dravite < Fe-rich elbaite), Tur Ib (Mn,Fe-rich to Mn-rich fluor-elbaite > elbaite), to the crystal rims Tur II (elbaite > darrellhenryite) via the substitutions: (1) $2^{y}R^{2+} = {}^{y}LiAl, (2) {}^{y}Mn^{w}F = {}^{y}Fe^{2+w}OH, (3) {}^{y}Li_{0,5}{}^{w}OH = {}^{y}Al_{0,5}{}^{w}O, and (4) {}^{y}Li^{T}Al^{w}OH_{3} = {}^{y}Al^{T}Si^{w}O_{3}.$ The contact zone, ~ 2 mm thick, contains abundant Tur IV (Li,Fe,Al-enriched dravite > oxy-dravite), and the recrystallization zone, ~ 1.5 cm thick, common Tur V (fluor-uvite > dravite > fluor-dravite, magnesio-lucchesiite, uvite) via the substitutions: (1) $2^{\gamma}R^{2+}$ = "LiAl and (5) " $R^{2+W}OH$ = "Al"O, (6) "Na"OH = "Ca"O and (7) "Na"Al = "Ca" R^{2+} . The chemical compositions of the individual types of tourmalines suggest that the mobility of elements between calc-silicate rock and pegmatite was low. Only weak influx of Mg, V and Cr into pegmatite and Li and Al from the pegmatite to the host rock - recrystallization zone, respectively, were observed. The existence of thin B-rich contact zone with dominant Tur IV suggests low influx of B into the host rock in early magmatic stage. High contents of F in Tur V from the recrystallization zone were very likely triggered by influx of B,F-enriched residual pegmatite fluids. Very high $a(B_2O_2)$, but low $a(H_2O)$ and a(F) in the pegmatite melt constrained very low degree of external contamination of the pegmatite. Compositional evolution in tourmalines from Manjaka was compared with the pegmatites and their exocontact at Stoffhütte, Koralpe, Austria, and Bližná I, Moldanubian Zone, Czech Republic.

Keywords: Tourmaline, granitic pegmatite, exocontact, mobility of elements, Manjaka, Madagascar Received: 5 January 2023, accepted: 17 April 2023; handling editor: J. Cempírek

1. Introduction

Tourmaline is widely used as an excellent petrogenetic indicator of a variety of geological processes due to its ability to incorporate a large number of elements, negligible diffusion up to high temperatures, stability in a wide range of *PT*-conditions, and refractory behaviour (e.g., van Hinsberg et al. 2011; Dutrow and Henry 2011). Chemical composition of tourmalines is constrained by chemical composition of the system, *PTX*-conditions, effect of associated minerals as well as by crystal-structural constraints (e.g., Hawthorne 1996, 2002; Ertl et al. 2002; Bosi 2011, 2018).

Tourmalines from exocontacts of granitic pegmatites, typically developed around fractionated Li-rich pegmatites, were studied in numerous papers (e.g., Jolliff et al. 1986; Shearer et al. 1986; Morgan and London 1987; Selway et al. 1998, 2000, 2002; Tindle et al. 2002, 2005; Zhang et al. 2008). These fractionated pegmatites with tourmaline exocontacts can be also rather small Li-bearing or even Li-poor pegmatites (e.g., Laurs et al. 1998; Novák et al. 1999b, 2012; Kalt et al. 2001). The authors above revealed high compositional variations including mobility of individual elements in contact with a variety of silicate- or carbonate-dominant rocks. However, compositional trends and behaviour of Li in tourmalines from different pegmatite zones towards the exocontact were examined only sporadically (Novák et al. 1999b; Kalt et al. 2001).

The Manjaka pegmatite, Sahatany Valley (Ranorosoa 1986; Pezzotta 2005; Novák et al. 2015; Cempírek et al. 2016) is an excellent example of Li-bearing pegmatite enclosed in compositionally contrasting Mg-rich calc-silicate rock where tournaline is commonly developed

in the pegmatite body as well as in the exo/endocontact rocks. We examined chemical compositions and mineral assemblages of tournalines from the border zone of pegmatite and adjacent exocontact to reveal parameters which controlled the chemical composition of tournalines. They include external contamination of the pegmatite by the host rocks with contrasting chemical compositions, infiltration of fluids from the crystallizing Li-bearing pegmatite to the host rock as well as the role of associated minerals and crystal-structural constraints in tournaline.

2. Geological setting

The Manjaka pegmatite occurs in the Sahatany Valley pegmatite field, located in the north-eastern part of the Itremo Region in central Madagascar (Fig. 1). The area comprises low- to medium-grade metamorphic rocks of the Proterozoic Itremo Complex (e.g., Cox et al. 1998). This region is characterized by numerous occurrences of Li-enriched, gem-bearing pegmatites (e.g., Ranorosoa 1986; Pezzotta 2005), occasionally with large pockets lined with attractive gem quality crystals of elbaite–liddicoatite, hambergite such as pegmatites from Estatoby and Tsarafara villages surroundings (Pezzotta and Praszkier 2013; Buřival and Novák 2018) located about 2 km north of the studied Manjaka pegmatite.



The mineral assemblages with elbaite-liddicoatite, the most common Li-bearing mineral along with locally abundant spodumene and minor lepidolite, indicate the dominance of elbaite-subtype pegmatites over spodumene subtype in this pegmatite field. Occurrences of borates (hambergite, béhierite, and rhodizite-londonite) or borosilicates (danburite, manandonite, dumortierite, boralsilite, and vránaite; Ranorosoa 1986; Ranorosoa et al. 1989; Simmons et al. 2001; Novák et al. 2015; Cempírek et al. 2016) as well as the scarcity of primary micas strongly corroborate their elbaite-subtype affinity (Novák and Povondra 1995; Černý and Ercit 2005; Černý et al. 2012). However, in contrast to the classical elbaite-subtype pegmatites in the Moldanubian Zone, Czech Republic, and some other regions (e.g., Zagorskyi and Peretyazko 1992; Novák and Povondra 1995; Laurs et al. 1998; Novák et al. 1999b, 2012; Ercit et al. 2003; Novotný et al. 2019), graphic intergrowths (Kfs+Qz and Tur + Oz) are scarce.

The Manjaka locality exhibits pegmatite dikes variable in shape, size, geological position and mineral assemblages. Two major types were recognized. (A) Rare, E–W-trending dikes, up to ~ 2 m thick, are usually short with numerous apophyses and discordant or parallel to the foliation of the layered and heterogeneous calc-silicate rock. (B) Very common elongated dikes, from 2 to ~ 20 cm thick, are typically concordant

with the foliation of the host calc-silicate rocks (Figs 2, 3). The type (A) is located in the northern part whereas the type (B) typically in southern part of the locality. Contacts with host rock are usually sharp; only locally a narrow reaction zone, up to $\sim 2 \text{ mm}$ thick, with abundant tourmaline and minor quartz is developed. The following pegmatite textural-paragenetic units were recognized in the outcrops of the (A) type pegmatite accessible in 1980^s to 2010^s (Ranorosoa 1986; Novák et al. 2015): (1) a medium-grained aplitic unit with black tourmaline, rare garnet, and fluorapatite mostly developed in apophyses; (2) a medium- to coarse-grained

Fig. 1 Schematic map of the Sahatany Valley pegmatite district. Symbols: white square – the location of the area shown; yellow star – Manjaka pegmatite occurrence; black triangles – mountain peaks; white circles – larger towns in the area.





Fig. 2 Photographs of \mathbf{a} – the pegmatite outcrop with apophyses (light rock) and \mathbf{b} – polished section of pegmatite contact showing ductile behaviour of the host rock; thin reaction rim (the contact zone) of tourmaline is marked by arrows, and the host rock also includes the recrystallization zone of unknown thickness.

wall zone with black, brown, pink to red tourmaline; (3) a rare spodumene-bearing unit with prismatic grains of spodumene, up to 5 cm long, where small crystals of black, brown to red tourmaline are locally present. The individual units are irregularly distributed within the pegmatite body and may occur in a direct contact with the host rock or its xenoliths including the spodumenebearing unit where tourmaline-rich contact zone is typically absent. Textural units typical for granitic pegmatites, such as graphic intergrowths of Kfs+Qz, blocky K-feldspar and quartz core were not observed in the accessible outcrops. The abundant pegmatite dikes type (B) are coarse-grained, subhomogeneous, and elongated tourmaline grains often crystallized from the contact inwards. Locally, small pockets with crystals of albite and red tourmaline are developed. The major to minor minerals in the (A) and (B) types are similar and include albite > quartz ~ K-feldspar > tourmaline (black, brown, yellow, red, pink) >> spodumene (colourless to pinkish; Novák et al. 2015; Cempírek et al. 2016), and numerous accessory minerals, e.g., fluorapatite, Cs-rich beryl (Novák et al. 2013a), columbite-tantalite, rhodizite-lon-



Fig. 3a, b - Two thin sections of the contact between the pegmatite and the host rock including the contact zone with Tur IV, and the recrystallization zone with Tur V.

donite, lithiophyllite. However, primary micas are absent (Novák et al. 2015) and tourmaline is the only common hydrous mineral in the pegmatites. In the (A) type, dark tourmaline (black, brown) mostly significantly predominates over pink to red tourmaline located in the central parts of the pegmatite. In contrast, in the (B) type pink to red tourmaline significantly predominates and locally grows directly from the contact.

3. Analytical methods and samples

The chemical compositions of tourmalines and other rock-forming minerals were determined using a CAM-ECA SX100 electron-microprobe analyser (EMPA) at the Joint Laboratory of Electron Microscopy and Microanalysis, Department of Geological Sciences, Masaryk University, Brno and Czech Geological Survey (operator P. Gadas). Operating conditions for analyses were as follows: an accelerating voltage of 15 kV, a beam current of 10 nA and beam diameter of 5 μ m. The element concentrations in silicate minerals were analysed using the following reference materials and X-ray lines: K_{α} lines – andradite (Si, Al, Fe), albite (Na), sanidine (K), pyrope (Mg), wollastonite (Ca), spessartine (Mn), titanite (Ti), chromite (Cr), fluorapatite (P), topaz (F), vanadinite (Cl), Ni₂SiO₄ (Ni), gahnite (Zn), ScVO₄ (Sc); L_{α} lines – SrSO₄ (Sr), baryte (Ba), Rb-leucite (Rb), pollucite (Cs). For oxides, the following reference materials and X-ray lines were used: K_{α} lines – TiO (Ti), MgAl₂O₄ (Mg, Al), hematite, columbite (Fe), chromite (Cr), wollastonite (Ca), Ni₂SiO₄ (Ni), ScVO₄ (V), titanite (Si), Mn₂SiO₄ (Mn), gahnite (Zn); K_{α} line – ScVO₄ (V); L_{α} lines – zircon (Zr), gahnite (Zn), columbite (Nb), Sn (Sn), W (W). The peak counting times were 10–20 s for major and 20–120 s for minor and trace

elements. The raw data were processed using the X– φ or PAP matrix correction routine (Pouchou and Pichoir 1985; Merlet 1994). Based on the counting statistics, the measurement error expressed as 2σ is approximately less than 1 rel. % for concentrations around 20 wt. %, less than 5 rel. % for concentrations around 5 wt. % and less than 15 rel. % for concentrations around 1 wt. %. Formulae were calculated from the EMP data on the basis of 15 T+Z+Y cations, including ^{*v*}Li, the values of which were obtained from LA-ICP-MS, assuming B = 3 *apfu* (atoms per formula unit) with no B at the *T*-site, and all Fe and Mn assumed as Fe²⁺ and Mn²⁺. The H₂O contents were calculated as OH = (4–^{*v*,*w*}O–F).

Tab. 1 Mineral assemblages and abundances in the individual rock types. A – abundant, C – common, R – rare, VR – very rare. Based on the data of Novák et al. (2015), Cempírek et al. (2016) and this work.

Rock type		Host rock			Pegm	atite
textural-petrographic	host rock	host rock	recrystallization zone	contact zone	border unit	wall unit
unit/zone	carbonate-rich	silicate-rich				
tourmaline type	absent	absent	Tur V	Tur IV	Tur I, II	Tur III
fluor-uvite			С			
uvite			VR			
magnesio-lucchesiite			VR			
fluor-dravite			VR			
dravite			R	А	R	
oxy-dravite				R		
elbaite					С	С
fluor-elbaite					R	С
darrellhenryite					R	
diopside	А	А	А	R		
plagioclase	С	С	С			
phlogopite	С	С	С			
Cs-phlogopite			С	R		
tremolite	С	С	С	VR		
dolomite	С	R				
calcite	С					
danburite		VR	VR			
K-feldspar	R	R	С		А	С
quartz		R	R	С	А	А
albite					А	А
beryl			R	R	С	С
spodumene					R	С
fluorapatite		VR	R	R	С	R
boralsilite						VR
vránaite						VR
rhodizite-londonite					VR	VR
pollucite						VR
chrysoberyl						VR
phenakite						VR
rodochrosite						VR
lithiophyllite						VR
native bismuth						VR
columbite-(Mn)			VR	VR	VR	R
microlite/pyrochlore			VR			VR
Ta-titanite			R	VR		
rutile		VR	VR			
zircon		VR	VR	VR	VR	VR



Fig. 4 Images of cross-section through the recrystallization zone, the contact zone, and the border unit; a – optical microscope, b – BSE.

The contents of trace elements in tourmaline samples were analysed using LA-ICP-MS consisting of quadrupole based ICP-MS (Agilent 7900) connected to ArF* excimer laser ablation system Analyte Excite+ (Teledyne CETAC Technologies) at the shared laboratories of BIC Brno and Faculty of Chemistry, Brno University of Technology. The laser ablation system emits the laser beam at a wavelength of 193 nm and is equipped with 2-Volume Cell HelEx II. The ablated material was carried by He flow (0.5 and 0.3 $1 \cdot \text{min}^{-1}$) and mixed with Ar (~1 $1 \cdot \text{min}^{-1}$) prior to entering the ICP mass spectrometer. The sample surface of individual spots was ablated for 25 s using laser beam of a 50 μ m- diameter with a fluence of 5 J·cm⁻², 10 Hz repetition rate and 60 s washout time. The following isotopes were monitored: ^{6,7}Li⁺, ⁹Be⁺, ^{10,11}B⁺, ²³Na⁺, ${}^{27}\breve{A}l^+,\ {}^{28,29}Si^+,\ {}^{39}K^+,\ {}^{43,44}Ca^+,\ {}^{45}Sc^+,\ {}^{47,49}Ti^+,\ {}^{51}V^+,\ {}^{52,53}Cr^+,$ $^{55}Mn^{\scriptscriptstyle +},\ ^{56,57}Fe^{\scriptscriptstyle +},\ ^{60}Ni^{\scriptscriptstyle +},\ ^{66,68}Zn^{\scriptscriptstyle +},\ and\ ^{69,71}Ga^{\scriptscriptstyle +}.$ ICP-MS was tuned using SRM NIST 612 with respect to the sensitivity, and minimal doubly charged ions, oxide formations $(^{248}\text{ThO}^{+}/^{232}\text{Th}^{+} < 1\%)$ and mass response $^{238}\text{U}^{+}/^{232}\text{Th}^{+} \sim 1$. The potential interferences were minimized via collision cell (He 1 ml·min⁻¹). The elemental contents were calibrated using artificial glass reference materials SRM NIST 610 and 612, and EPMA-determined Al contents were used as internal reference element after baseline correction and integration of the peak area.

The abbreviations of minerals given in the text and figures are used according to Warr (2021).

4. Results

4.1. Description of the individual tourmaline--bearing units/zones and the host rock

We studied fragments of the pegmatite body transitional between (A) and (B) type in its size and internal structure, and abundant black to brown tourmaline predominates over minor red to pink tourmaline. The pegmatite is characterized by subhomogeneous internal structure; from its contact with the host rock, we distinguished the **border unit** (outer medium- to coarse-grained unit with abundant tourmaline, *ca* 1–10 cm thick), which is directly adjacent to the contact zone (former host rock); and the **wall unit** (inner coarse-grained unit) which is developed in central parts of the pegmatite. Contacts between both units are transitional.

The **border unit** contains locally very abundant black, brown, yellow, red to pink tournaline. Zoned prismatic crystals of tournaline typically crystallized from the contact with the host rock (contact zone) into the pegmatite (Figs 3, 4, 5a). The thickness of this unit varies from 1 to \sim 10 cm. It locally contains accessory minerals (Tab. 1) including common subhedral to euhedral grains of blue fluorapatite (Figs 4, 5c), rare spodumene, colourless Cs-enriched beryl (Novák et al. 2013a), and tabular crystals of columbite-(Mn) (Fig. 4b). In the **wall unit**, the orientations of elongated crystals of tournaline and spodumene are random. Tournaline is locally absent in spodumene-rich parts of the pegmatite including those situated in a direct contact with the host rock where tournaline-rich contact zone is typically not developed.



Fig. 5 BSE images of the individual types of tournalines. **a** – cross-section through the border unit, the contact zone and part of the recrystallization zone; **b**, **c** – zoned tournalines Ia, Ib and II; **d** – the contact zone with zoned subhedral grains of tournaline IV and anhedral grain of beryl; **e**, **f** – the recrystallization zone, note subhedral grain of danburite. Scale bar is 200 μ m long; figures **b** to **f** are details from Fig. 4b.

In the host rock, a narrow tourmaline-rich **contact zone**, typically ~ 2 mm thick (Figs 3, 4, 5a), is developed at the contact of the tourmaline-bearing border unit with the partially recrystallized host calc-silicate rock, as well as along thin ductile bands and xenoliths enclosed in the border

unit (Fig. 3b). It is formed by the assemblage tourmaline > quartz (Figs 4b, 5d); rare, zoned crystals of Cs-rich beryl are locally present (Fig. 5d). No textural or mineralogical indications of the original border between exocontact after host rock and endocontact after pegmatite were observed.

The recrystallization zone, up to ~1.5 cm thick, adjacent to the contact zone, is very similar to the host calc-silicate rock in a hand specimen as well as in its texture and mineral assemblages observed in thin sections. It is locally porous, mostly close to the contact zone (Figs 4b, 5a), and exhibits a zoned distribution of newly-formed minerals. The presence of small anhedral to euhedral grains of tourmaline is a typical feature along with several rare accessory minerals such as Ta-enriched titanite and Cs-enriched phlogopite (Tab. 1). The presence of tourmaline marks the extent of the recrystallization zone into the host calc-silicate rock whereas nodular aggregates of Cs-rich phlogopite and anhedral to subhedral oscillatory-zoned grains of Cs,Mg-rich beryl (Fig. 5e; Novák et al. 2013a) are present typically close to the contact zone. Also, the modal abundance of tourmaline increases towards the contact zone (Fig. 4b). Rare danburite (Fig. 5f) associated with more abundant tourmaline occurs within the same unit; however, its rarity does not allow to recognize its textural relationship to tourmaline.

Host calc-silicate rock is highly heterogeneous and consists of compositionally different layers comprising abundant carbonate-poor layers (Di+Tr+Qz>Pl+Kfs>Phl>Dol>Cal) and rather sporadic carbonate-enriched layers (Di>Tr+Cal+Dol+Phl). The rock-forming minerals of both layers are Mg- and/or Ca-rich and their chemical compositions are similar to those measured in the recrystallization zone: diopside (Di₉₄₋₁₀₀Hd₀₋₄Jhn₀₋₄), plagioclase (An₂₆₋₃₂), Ba-enriched K-feldspar (Kfs₇₃₋₉₆Ab₁₋₁₀Cls₀₋₂₆), tremolite and Ti-rich phlogopite both close to the ideal endmembers. The accessory minerals comprise e.g., rare zircon and titanite (Tab. 1).

4.2. Textural and paragenetic types of tourmalines

The applied simplification of the complex internal structure of the pegmatite and zoned rocks at its contact with the host rock (distinguishing the inner wall unit, outer border unit, contact zone and recrystallization zone), allows us to establish the crystallization history of the various paragenetic, textural, and compositional types of tourmalines.

Tourmaline from the border unit typically crystallized from the contact inwards and is closely adjacent to the contact zone (Figs 3, 4, 5a). It forms zoned, black, brown, yellow to red prismatic crystals, up to ~ 2 cm long (Figs 3, 4a), with obvious zoned structure formed by bright core and dark rims in the BSE images (Figs 3b, 5b, 5c). It is subdivided in detail on early basal part of the core Tur Ia (adjacent to the Tur IV from contact zone) and on upper part of the core Tur Ib (Fig. 5b); the discontinuity at the transition from Tur Ia and Tur Ib visible at BSE image (Fig. 5b) suggests that Tur Ib overgrows and partially replaces the Tur Ia. Dark rims of Tur II around Tur Ia or Tur Ib form irregular zones apparently replacing the early Tur Ia and Ib (Figs 5b, 5c). Zoned Tur I+Tur II are locally volumetrically dominant minerals in the border unit along with albite and less common quartz and K-feldspar.

In the wall unit, two textural types of pink to red Tur III commonly associated with spodumene were studied in detail by Novák et al. (2015). They include simply zoned euhedral to subhedral, crystals of tourmaline (Fe,Mn-enriched fluor-elbaite to elbaite) and oscillatory zoned tourmaline (Fe,Mn-enriched elbaite); the latter often frequently enclosed in spodumene, both are Ca- and Mg-poor ($\leq 0.14 \ apfu$, $\leq 0.11 \ apfu$, respectively). Tur III is not discussed in detail in this work.

In the contact zone, dark brown to yellow Tur IV forms subhedral to euhedral equigranular grains, up to 0.3 mm in size. The grains are subhomogeneous (Fig. 5d), and apparent concentric zoning is rare. The contact zone is rather heterogeneous; the part adjacent to the pegmatite has larger tourmaline grains and contains more common fluorapatite (Fig. 4b). The contact between Tur Ia from the border unit and Tur IV in the contact zone is rather transitional (Figs 4b, 5a). The recrystallization zone contains rare, slightly heterogeneous, subhedral to euhedral grains of Tur V, ~0.2 mm in size, rather randomly distributed within matrix composed of diopside, plagioclase, tremolite, phlogopite, quartz, and K-feldspar (Figs 5e, 5f) show insignificant modal increase towards the contact zone (Fig. 4b).

4.3. Chemical composition

We examined in detail a single cross section, ~ 2 cm long (Fig. 4), through the recrystallization zone, contact zone and border unit of the Manjaka pegmatite using EPMA and LA-ICP-MS (Tab. 2). It represents a typical example of the contact between the pegmatite dike with multicoloured tourmalines in the border unit and its host rock.

4.3.1. EMPA

The zoned Tur Ia+Ib+II from the border unit (Figs 4, 5a, 5b, 5c) exhibit rather complicated compositional evolution (Figs 6, 7) although variations at the X-site (Na, Ca, X-site vacancy) are moderate to small in the individual types of tournaline (Figs 6a, 7a). Variations in the Y-site are more pronounced, with an obvious decrease of Mg from 1.01 *apfu* in Tur Ia adjacent to the contact zone (single spot; Fig. 7) to the values close to or below the detection limit of Mg in Tur Ib and II (Fig. 7d). Also, an increase of Al is apparent from mod-

Fig. 6 Discrimination diagrams for tourmalines (Henry et al. 2011) a - X-site occupancy, b - W-site occupancy, c - Y-site occupancy.

rocks.

erate Al_{tot} of approximately 6.91 *apfu* in Tur Ia close to the contact zone to higher values of 7.11–7.49 *apfu* in Tur Ia and Ib and particularly in Tur II with highly variable $Al_{tot} = 7.47-8.11$ *apfu* (Fig. 7d). Variations in Fe and Mn in Tur Ia and Ib are very large; Fe – moderate to high (0.32–0.66 *apfu*) in Tur Ia, low to moderate (0.10–0.45) *apfu* in Tur Ib and low (0.10–0.14 *apfu*) in Tur II; Mn – low (0.18–0.36 *apfu*) in Tur Ia, high (0.48–0.66 *apfu*) in Tur Ib and low (≤ 0.25 *apfu*) in Tur II (Fig. 7b), respectively. The contents of Ti are very low, decreasing from Tur Ia and Ib with ~0.03 *apfu* to the values close to or below the detection limit in Tur II. Fluorine is strikingly different in each type; it is very high (0.70–0.77 *apfu*) in the Mn-rich Tur Ib but low (0.09–0.24 *apfu*) in Tur Ia and II (Figs 6b, 7c).

Tur IV from the contact zone is similar to Tur V only in its rather low Fe and Mn contents and high Mg, otherwise, its composition is transitional between Tur Ia and Tur V. It is enriched in Na (0.68–0.77 *apfu*), Al_{tot} (6.21–6.61 *apfu*) and slightly in Fe and Mn (Figs 6a, 7a, 7b, 7d) but depleted in F (0.14–0.32 *apfu*), Ca (0.15–0.23 *apfu*) and (Mg 1.86–2.46 *apfu*) relative to Tur V (Figs 6b, 7c). Tur V from the recrystallization zone is highly variable at the *X*-site: Ca (0.28–0.66 *apfu*), Na (0.31–0.68 *apfu*), and rather low *X*-site vacancy mostly \leq 0.1 pfu (Figs 6a, 7a). Concentrations of F are also rather high and quite variable (0.30–0.56 *apfu*) (Figs 6c, 7c). Cations at the *Y*+*Z* sites are rather variable: Al_{tot} (5.52–6.05 *apfu*), Mg (2.77–3.14 *apfu*), Ti (0.03–0.20 *apfu*), Fe ~0.12 *apfu* (Figs 7b, 7d).

4.3.2. LA-ICP-MS

The LA-ICP-MS study was focused chiefly on the concentrations of Li and several trace elements compatible in the tourmaline structure – V, Cr, Ni, Zn and Ga (Figs 7e, 7f; Tab. 2) to illustrate mobility of these elements in

easy comparison with the EPMA data provided above.
Zoned tourmalines Tur Ia+Ib+II from border unit show
a slight increase of Li from Tur Ia to Tur Ib and equal to

higher Li in Tur II (Fig. 7d). Very large variations in Li contents are typical for the individual tourmaline types Tur Ia (0.61–1.43 *apfu*), Tur Ib (0.78–1.54 *apfu*) and Tur II (0.91–1.86 *apfu*) (Fig. 7d, Tab. 2). Lithium is low in Tur V from the recrystallization zone ($\leq 0.13 apfu$) and slightly higher in Tur IV from the contact zone with values $\leq 0.29 apfu$ (Fig. 7d).

the contact of the granitic pegmatite with the calc-silicate

rock and to reveal potential mass transfer between these

Concentrations of Li are given in apfu (Fig. 7d) for

Determination of Li using LA-ICP-MS enabled more reliable allocation to the nomenclature (Henry et al. 2011) of the examined tourmalines in comparison with use of calculated Li by empirical methods (Pesquera et al. 2016 and references therein). The concentrations of Li, up to 1.86 apfu in Tur II, are very high in comparison to Li-tourmalines described elsewhere (e.g., Povondra et al. 1985; Ertl et al. 2006, 2010; Novák et al. 2013b; Bosi et al. 2021). The formula calculations also yielded up to 1.77 pfu OH along with 0.13 apfu F in the *W*-site plus $V(OH)_2$ (analyses No 45; Tab. 2). Overestimation of Li using LA-ICP-MS may be an explanation of these very high values. However, a more detailed study of small-sized rims Tur II very rich in Li (Figs 5c, 5d) to reveal an Li-rich tourmaline with Li close to 2 apfu is desirable. Tur I varies from Li, Fe, Al-enriched dravite (one spot) to Mg-poor, Fe-enriched elbaite in Tur Ia, and Mn,Fe-rich to Mn-rich fluor-elbaite or elbaite in Tur Ib, respectively. Tur II has variable Li/Al ratios but is otherwise rather homogeneous in Na, Ca and R²⁺ (Figs 6a, 6c, 7a, 7b, 7d); the compositions correspond to elbaite > darrellhenryite. Tur IV is heterogeneous in Mg, Al and Li and the analyses fall within the field of Li-

Fig. 7 Diagrams showing compositional evolution of tourmalines based on the EPMA and LA-ICP-MS data from the recrystallization zone, the contact zone and the border unit. $\mathbf{a} - X$ -site (EPMA), $\mathbf{b} - Y$ -site (Mn, Fe, Ti – EPMA), $\mathbf{c} - W$ -site (F – EPMA, O, OH – calculated), $\mathbf{d} - Y$ -site (Li – LA-ICP-MS, Al, Mg – EPMA), $\mathbf{e} - Y$ -site (V, Cr, Ni – LA-ICP-MS), $\mathbf{f} - Y$ -site (Zn,Ga – LA-ICP-MS).

,Fe-,Al-enriched dravite > oxy-dravite. Tur V is rather homogeneous in X_{Mg} (Figs 7b, 7d); but high variations at the X-site and W-site generated the five tourmaline species: fluor-uvite > dravite > magnesio-lucchesiite, fluor-dravite and uvite.

The examined trace elements compatible in tourmalines (Cr, V and Ni) exhibit similar compositional evolutions. Their concentrations are close to almost zero in Tur I+II from the border unit (Tab. 2, Fig. 7e), moderate in the Tur V from the recrystallization zone (Cr \leq 149, V \leq 78, and Ni \leq 19 µg/g), and the highest in the Tur IV from the contact zone (Cr \leq 277 µg/g; V \leq 182 µg/g; Ni \leq 24 µg/g). In the recrystallization zone, V and Cr exhibit gradual increase of concentrations towards the contact zone (Fig. 7e). The positive correlations between the concentrations of V and Cr in most analysed spots (Fig. 7e) are typical.

The highest concentrations of Zn, up to 2170 μ g/g, were found in Fe-rich Tur Ia and then its contents drop down via Tur Ib (309–1900 μ g/g) to Tur II with 329–791 μ g/g (Fig. 7f). Zinc has the lowest concentrations in Tur V from the recrystallization zone ($\leq 101 \ \mu$ g/g) but in Tur IV its contents increase (up to 934 μ g/g). Behaviour of Ga is rather simple; the highest contents were found in Tur Ia and Ib (133–422 μ g/g). It slightly falls to 102–289 μ g/g in Tur II and in Tur IV $\leq 205 \ \mu$ g/g whereas the Tur V from the recrystallization zone yielded $\leq 75 \ \mu$ g/g Ga only (Fig. 7f).

			TU Ia			TU Ib			TU	П		-	TU IV					TU V			
Analysis 1	Vo.	29	33	35	36	38	41	45	47	48	51	23	24	27	3	6	10	14	17	19	21
SiO_2	wt. %	36.47	34.94	35.91	36.36	36.11	36.75	35.57	35.91	35.69	35.60	36.90	37.00	36.37	36.66	37.15	36.61	37.06	36.38	36.83	36.63
TiO_2		0.27	0.86	0.23	0.25	0.25	0.23	0.00	0.00	0.00	0.00	0.40	0.35	0.29	1.03	0.14	0.22	0.41	0.93	1.66	0.87
Al_2O_3		36.40	38.47	38.88	37.18	38.02	38.82	42.40	41.16	42.35	42.35	32.46	35.07	34.44	29.41	31.02	30.15	31.26	29.48	28.70	29.57
$B_2O_3^*$		10.78	10.91	10.62	10.55	10.75	10.80	11.25	10.87	10.80	10.83	10.71	10.87	10.77	10.72	10.79	10.68	10.73	10.56	10.66	10.71
$\mathrm{FeO}_{\mathrm{tot}}$		2.82	4.34	4.82	3.27	1.39	0.74	0.94	0.79	0.80	0.77	0.99	1.58	0.91	1.01	1.08	0.98	0.93	0.92	0.66	0.76
MgO		4.22	0.62	0.16	0.22	0.00	0.00	0.00	0.00	0.00	0.00	10.16	7.80	8.97	12.83	12.00	12.47	11.83	12.40	12.46	12.94
MnO		1.32	1.78	2.06	3.41	4.54	4.21	1.59	1.35	1.51	1.33	0.42	0.64	0.45	0.00	0.21	0.00	0.00	0.10	0.21	0.07
ZnO		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO		0.30	0.53	0.36	0.24	0.36	0.55	0.75	0.82	0.93	0.76	0.97	0.89	1.33	3.36	2.41	3.61	1.58	3.75	3.66	3.13
Na_2O		2.34	2.08	2.05	2.58	2.36	2.69	2.00	1.92	2.07	2.14	2.43	2.20	2.31	1.21	1.64	1.09	2.16	1.18	0.99	1.31
К,Õ		0.06	0.04	0.00	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.05	0.05	0.05	0.00
$Li_2O^{\#}$		0.93	1.78	0.94	1.18	1.67	1.58	2.34	1.90	1.40	1.55	0.15	0.44	0.33	0.13	0.09	0.11	0.00	0.00	0.19	0.09
F		0.17	0.35	0.32	1.40	1.50	1.37	0.26	0.31	0.28	0.27	0.62	0.28	0.32	0.99	0.58	0.97	0.68	0.90	0.81	0.93
H_2O^*		3.66	4.30	3.10	2.62	3.22	2.85	4.63	3.72	3.06	3.29	3.12	3.42	3.27	3.04	3.30	2.97	3.09	2.64	2.92	3.09
O=F		-0.08	-0.15	-0.14	-0.60	-0.64	-0.58	-0.12	-0.14	-0.12	-0.12	-0.27	-0.12	-0.14	-0.42	-0.25	-0.41	-0.29	-0.38	-0.35	-0.39
Total		98.89	98.99	99.62	99.61	98.46	100.47	101.14	99.65	100.70	98.66	99.33 1	00.41	99.82 1	00.11 1	00.33	99.67	99.82	99.51	99.78	98. <i>6</i> 6
$^{\mathrm{T}}\mathrm{Si}$	apfu	5.876	5.565	5.873	5.988	5.835	5.912	5.494	5.736	5.743	5.707	5.987	5.912	5.864	5.938	5.980	5.955	6.001	5.986	6.003	5.938
$^{T}A1$		0.123	0.434	0.126	0.011	0.164	0.087	0.505	0.263	0.256	0.292	0.000	0.087	0.135	0.061	0.019	0.044	0.000	0.013	0.000	0.061
В		3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000
$I M^2$		5.967	5.897	5.971	5.968	5.969	5.972	6.000	6.000	6.000	6.000	5.950	5.958	5.964	5.553	5.864	5.737	5.950	5.703	5.515	5.589
${}^{\rm Z}M{}^{\rm Z}$		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.322	0.120	0.237	0.000	0.183	0.283	0.306
$^{\gamma}$ Al		0.820	0.890	1.395	1.237	1.105	1.300	1.212	1.487	1.774	1.711	0.257	0.559	0.445	0.000	0.000	0.000	0.016	0.000	0.000	0.000
$^{\gamma}Mg$		1.014	0.147	0.038	0.053	0.000	0.000	0.000	0.000	0.000	0.000	2.458	1.857	2.156	2.775	2.761	2.788	2.856	2.859	2.746	2.824
Τi		0.033	0.103	0.029	0.032	0.031	0.028	0.000	0.000	0.000	0.000	0.050	0.042	0.036	0.125	0.016	0.026	0.050	0.114	0.202	0.105
$\mathrm{F}\mathrm{e}^{2+}$		0.379	0.577	0.658	0.449	0.187	0.100	0.121	0.106	0.107	0.103	0.134	0.211	0.122	0.137	0.145	0.133	0.125	0.126	0.090	0.103
${ m Mn}^{2+}$		0.180	0.241	0.285	0.476	0.622	0.574	0.209	0.183	0.206	0.181	0.059	0.087	0.062	0.000	0.029	0.000	0.000	0.014	0.030	0.010
Zn		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Li		0.606	1.144	0.623	0.785	1.086	1.025	1.458	1.225	0.913	1.005	0.103	0.285	0.215	0.087	0.065	0.079	0.000	0.000	0.131	0.063
Y-site		2.999	2.999	2.999	3.000	3.000	2.999	3.000	3.001	3.000	3.000	3.011	2.999	3.000	2.999	3.000	3.000	2.997	2.999	2.997	3.000
X Ca		0.052	0.090	0.063	0.044	0.062	0.095	0.124	0.141	0.159	0.131	0.169	0.153	0.230	0.582	0.417	0.630	0.275	0.660	0.640	0.544
Na		0.730	0.642	0.650	0.825	0.738	0.838	0.599	0.594	0.647	0.666	0.766	0.680	0.722	0.382	0.512	0.342	0.678	0.377	0.313	0.412
К		0.013	0.008	0.000	0.000	0.010	0.000	0.000	0.000	0.000	0.000	0.011	0.000	0.000	0.000	0.000	0.000	0.009	0.009	0.009	0.000
X vac.		0.205	0.260	0.287	0.131	0.190	0.067	0.277	0.265	0.194	0.203	0.054	0.167	0.048	0.036	0.071	0.028	0.038	0.000	0.038	0.044
HO_M		0.942	1.577	0.383	0.000	0.475	0.061	1.775	0.966	0.288	0.524	0.386	0.646	0.524	0.293	0.546	0.230	0.345	0.000	0.182	0.349
F		0.086	0.178	0.168	0.730	0.767	0.696	0.129	0.159	0.140	0.135	0.320	0.140	0.166	0.505	0.296	0.500	0.351	0.466	0.419	0.475
0		0.000	0.000	0.449	0.384	0.000	0.243	0.000	0.000	0.572	0.341	0.294	0.214	0.310	0.202	0.158	0.270	0.304	0.627	0.399	0.176
	(LOD)						1					0								0	
Lı (ppm)	(1.20)	4320	8269	4366	5481	7758	7340	10870	8826	6503	7200	696	2044	1533	603	418	511	0	0	882	418
>	(0.04)	LL	1	0	0	0	0	0	0	0	0	27	53	43	35	26	25	7	0	47	22
Cr	(0.63)	277	0	0	0	1	1	0	0	0	0	18	×	18	34	29	28	ŝ	1	68	20
Ni	(0.49)	10	1	0	0	0	0	1	7	0	1	11	10	4	14	10	12	0	1	14	S
Zn	(1.32)	934	2170	1670	1900	547	309	767	791	624	355	256	483	196	27	33	28	с	31	118	54
Ga	(0.02)	199	422	210	190	133	221	279	264	233	131	153	200	135	86	108	99	-	29	83	112

5.1. Mineral assemblages and textures of the individual types of tourmalines

The mineral assemblages and textures of the individual tourmaline types defined above are distinct. The zoned, prismatic Tur Ia+Ib+II from the border unit as well as Tur III from the wall unit are enclosed in albite > quartz > K-feldspar; Tur III is occasionally enclosed also in spodumene (Novák et al. 2015). Consequently, the mineral assemblages of tourmalines from the border and wall units are rather simple and similar (Tab. 1). The main difference is the abundance of tourmalines and common fluorapatite in the border unit.

The origin of these tourmaline-rich assemblages is facilitated by high content of B in the parental rock units manifested by the occurrence of further B-rich minerals in both border and wall units (Novák et al. 2015; Cempírek et al. 2016; see Tab. 1). The absence of Limicas, locally common spodumene, rare lithiophyllite altered to rhodochrosite (Tab. 1), and mostly low concentrations of F in tourmalines support low $a(H_2O)$, a(F)and elevated $a(CO_2)$ in the parental rock units. It is also manifested by almost total absence of hydrous minerals disregarding tourmalines, and origin of the assemblage - anhydrous borosilicates (boralsilite and vránaite)+ albite after spodumene (Novák et al. 2015; Cempírek et al. 2016). Similar tourmaline-rich assemblages with additional B-rich minerals (hambergite, tusionite, B-rich polylithionite, boromuscovite, danburite, datolite, axinite) are typical for the majority of elbaite-subtype pegmatites (e.g., Zagorskyi and Peretyazko 1992; Novák and Povondra 1995; Laurs et al. 1998; Novák et al. 1998, 1999a, b; 2012, 2013c; Ercit et al. 2003; Flégr 2016). However, the Manjaka pegmatite differs principally from other localities in the absence of micas and graphic textures, a predominance of albite over K-feldspar, and the low F contents in the majority of Li-bearing tourmalines. The distinct composition of Tur II with low concentration of F along with no Mg and Ti and low Mn, Fe suggests that it formed by a different process compared to the Tur Ia + Ib.

Tur IV and Tur V exhibit distinct mineral assemblages and textures. Tur IV is a dominant mineral in the locally almost monomineralic contact zone along with less common quartz, accessory fluorapatite and rare oscillatory-zoned Cs-enriched beryl (Novák et al. 2013a; Figs 4b, 5d). The recrystallization zone has a rather sharp contact with the adjacent contact zone and exhibits a texture very similar to its calc-silicate rock precursor. Rock-forming minerals significantly prevail over newly-formed minerals – anhedral to euhedral grains of Tur V and Cs-enriched phlogopite along with several rare accessory minerals (Tab. 1). A very high $X_{M\sigma}$ of the

host silicate rock documented by the compositions of rock-forming minerals is distinct from most exocontact tourmaline-bearing zones studied to date (e.g., Jolliff et al. 1986; Morgan and London 1987; Laurs et al. 1998; Selway et al. 1998, 2000, 2002; Novák et al. 1999b, 2012; Kalt et al. 2001; Tindle et al. 2002, 2005; Zhang et al. 2008). Also, the occurrence of Cs(Rb)-enriched trioctahedral micas is typical in exocontacts of most pegmatite localities described by the authors above except for the Bližná I pegmatite, Moldanubicum, Czech Republic (Novák et al. 1999b). This pegmatite is enclosed in silicates-rich dolomite marble with high $X_{M_{P}}$ (Novák et al. 2012), where micas are absent in the pegmatite as well as in its exocontact zone; common axinite-(Fe)+ fluorite + pyrite are associated with dominant tourmalines (fluor-uvite, fluor-dravite, Li,F-rich dravite, Mg-bearing elbaite, Mg-bearing fluor-liddicoatite; Novák et al. 1999b, 2012; Krmíček et al. 2021). They manifest higher Ca, F and Li in tourmalines from the Bližná I exocontact compared to the Manjaka pegmatite. Also, the presence of the tourmaline-dominant zone in direct contact with the pegmatite (contact zone) in the Manjaka pegmatite is rather unusual. A similar tourmaline-dominant zone at exocontact is known only from the Stoffhütte pegmatite at the Koralpe in Austria (Kalt et al. 2001) and the Bližná I pegmatite (Novák et al. 1999b).

5.2. Compositional evolution of tourmalines and substitution mechanisms

The individual types of tourmalines exhibit generally three distinct compositions (Figs. 6, 7, 8, 9): heterogeneous Ca-poor, Mg-free and Al,Li-rich Tur Ia+Ib+II with high variability in F, Fe, Mn, Al and Li; heterogeneous Tur IV with high and variable Mg, slightly elevated Al+Li but low Ca and F; heterogeneous, Ca,Mg-rich, Al-poor and F-enriched Tur V with variable contents of Na, Ca and F.

The compositional trend of Tur I shows a gradual increase of Fe, up to 0.66 *apfu*, in Tur Ia followed by an increase in Mn to 0.66 *apfu*, in Tur Ib towards the pegmatite center (Fig. 7b). Low concentration of Ca \leq 0.09 *apfu* and almost absent Mg except for two spots in the base of Tur Ia (Figs 7a, 7d) are rather unusual in the face of the Ca,Mg-rich host rock with minor dolomite and calcite. In summary, the compositional trend of Tur I and II from the pegmatite is similar to the trends typically observed in elbaite-subtype pegmatites which were not externally contaminated (e.g., Novák and Povondra 1995; Novák 2000; Novák et al. 2012, 2013c; Laurs et al. 2009; Novotný et al. 2019; Flégr 2016).

The overall compositional evolution in the Tur Ia, Ib, and Tur II from border unit (Figs 7, 8a) suggests the dominant heterovalent substitution (1) $2^{y}R^{2+} = {}^{y}LiAl$ (Fig. 8a)

Fig. 8 Diagrams of chemical composition of tournalines: $\mathbf{a} - \text{Li} \text{ vs. } \text{Al}_{\text{tot}}$, $\mathbf{b} - \text{Si} \text{ vs. } \text{Al}_{\text{tot}}$, $\mathbf{c} - \text{Mn}_{\text{tot}}$ vs. F, $\mathbf{d} - \text{Ca} + \text{R}^{2+}$ vs. Na+Al_{tot}, $\mathbf{e} - \text{Li} \text{ vs. }^{T}\text{Al}$, $\mathbf{f} - \text{Ca} \text{ vs. } \text{F}$.

from core to rim in Tur Ia and Ib. The high variation in Li versus Al_{tot} (Fig. 8a) chiefly in Tur II showing negative correlation of Li/Al with 1.7 to 0.7 *apfu* Li versus 1.5 to 2.3 *apfu* Al (Fig. 7d) combined with rather stable contents of F, Ca, Na and R²⁺ (see Figs 6a, 7b, 7d) indicate the significant participation of substitution (2) $^{Y}\text{Li}_{0.5}^{W}\text{OH} = ^{Y}\text{Al}_{0.5}^{W}\text{O}$ (Fig. 7a) especially in Tur II. However, the positive correlation ^{Y}Li versus ^{T}Al (Fig. 8e) in Tur Ia, Ib and

II with a slope close to 1/2 suggests at least minor participation of the substitution (3) ${}^{y}Li^{T}Al^{W}(OH)_{3} = {}^{y}Al^{T}Si^{W}O_{3}$ along with substitution (1). The high variation in Mn, Fe and F and a positive correlation Mn vs. F (Fig. 8c) imply minor substitution (4) ${}^{y}Mn^{W}F = {}^{y}Fe^{2+W}OH$ in Tur Ib.

Tur IV and also Tur V reflect the composition of the host rock; the effect of fluids released from the adjacent pegmatite is evident mainly in the composition of Tur IV. In comparison with Tur I and II, they differ significantly at the X-site as well as at the Y-site and W-site occupancy (Figs 6a, 6b, 7). Tur V shows high variations in Na and Ca, but X-site vacancy is mostly low (Figs 6a, 7a, 7c). It has a very high and constant content of Mg, low to very low Fe and Mn contents and a moderate to high Ti content (Figs 7b, 7d; Gadas et al. 2019); however, Al_{tot} varies from 5.5 to 6.1 *apfu* (Fig. 7d) and typically is higher in dravite. The absence of a compositional gradient in Tur V towards the contact zone and the sharp contact between these two zones are rather uncommon.

The composition of Tur IV with high Mg and low to moderate Ca in the contact zone is rather unusual. It is similar to dravite and fluor-uvite from an exocontact of the Bližná I pegmatite (Novák et al. 1999b) and some tourmalines from calc-silicate rocks (Povondra and Novák 1986; Bačík et al. 2012; Krmíček et al. 2021); however, it differs from other tourmalines in exocontacts of granitic pegmatites examined to date particularly by very high X_{Mg} (see Laurs et al. 1998; Selway et al. 1998, 2000, 2002; Kalt et al. 2001). The composition of Tur V with high Ca, Mg and typically high F is similar to tourmalines from metacarbonates (e.g., Povondra and Novák 1986; Krmíček et al. 2021). The substitutions (1) $2^{Y}R^{2+} = {}^{Y}LiAl$ and (5) ${}^{Y}R^{2+W}OH = {}^{Y}Al^{W}O$ are dominant in Tur IV although the minor substitutions (6) $^{X}Na^{W}OH =$ ^{*X*}Ca^{*W*}O and (7) ^{*X*}Na^{*Y*}Al = ^{*X*}Ca^{*Y*}R²⁺ may participate. Moderate variations in the X-site and the Y-site in Tur V (Figs. 6a, 6c, 8d) suggest the dominant substitution (7) $^{X}Na^{Y}Al$ $= {}^{X}Ca^{Y}R^{2+}$. A positive correlation of Ca and F (Fig. 8f) indicates a modification of the substitution (7) to (7a) ^xNa^yAl^wOH = ^xCa^yR^{2+w}F. Also, minor substitution (6) $^{X}Na^{W}OH = ^{X}Ca^{W}O$ participated.

High variability in tourmaline compositions is also highlighted by the behaviour of trace elements (Figs 7e, 7f). Vanadium, Cr and Ni contents are high in Tur V and even higher in Tur IV (Fig. 7e), but very low in Tur I and II from the border unit. Zinc exhibits a sharp increase starting in Tur IV and culminating in Fe-rich core Tur Ia. Concentrations of Ga are in general positively correlated with Al, and higher in Tur I and II from the pegmatite. Behaviour of Zn in Tur I and II is comparable to ordinary tourmalines from Li-rich pegmatites (Jolliff et al. 1986; Tindle et al. 2002, 2005).

The diagram in Fig. 9 illustrates the compositional evolution of tourmalines from the host rock to the pegmatite at two pegmatite dikes, which were studied in detail to date including concentrations of Li: Lipoor Stoffhütte pegmatite, Koralpe, Austria (Kalt et al. 2001) and Li-bearing Manjaka pegmatite. Both studied localities differ significantly from each other due to the following reasons: Li-poor versus Li-bearing pegmatite and mica schist versus Fe-poor Mg-rich calc-silicate as host rocks, respectively. The tourmalines evolved from the host rock to border unit of the pegmatite (Fig. 9): Stoffhütte – Mg-rich schorl \rightarrow Al-rich schorl \rightarrow olenite with low Li and F contents and an increase of Ca, ^TB and ^{*T*}Al; Manjaka – fluor-uvite \rightarrow dravite \rightarrow elbaite \rightarrow fluor-elbaite \rightarrow darrellhenryite/elbaite with highly variable F and Ca contents and an increase of Fe, Mn, Al_{tot}, Li and ^TAl contents. Tourmaline from Stoffhütte rather exhibits continuous evolution of the individual elements whereas in Manjaka isolated compositional fields for the individual types are typical. Also, zoning in the individual tourmaline grains is developed mainly in the Stoffhütte pegmatite (Kalt et al. 2001). These differences may be facilitated by the distinct compositions of granitic pegmatites and their host rocks; however, they also differ in geological environment although it was not specified in detail at either locality. At Stoffhütte, the host mica schists experienced high-pressure metamorphism (Kalt et al. 2001), whereas at the region around the Manjaka pegmatite low- to medium-grade metamorphism has been proposed (Cox et al. 1998); nevertheless, a discussion

Fig. 9 Diagram Li–Al– R^{2+} at Y-position. R^{2+} – divalent cations.

of these geological implications would require a more detailed study at both localities.

5.3. Mobility of elements between the granitic pegmatite and the host calc-silicate rock

The compositional contrast between the Fe-poor but Mg-rich calc-silicate rock and the Li-bearing pegmatite with the simple and dominant mineral assemblage albite+ tourmaline+quartz+K-feldspar in border unit makes the locality a suitable setting for the study of mobility of the individual elements between the pegmatite and its host rock (e.g., Novák 2013; Novák et al. 2017; Čopjaková et al. 2021). We discussed the behaviour of the individual elements in tourmalines starting from (Mg, Ca) typical for the host calc-silicate rock followed by (Al, Li, B, F) typical for granitic pegmatites. Some elements (K, Na) are less suitable for such a discussion due to the common abundance of K-feldspar, phlogopite and plagioclase (An_{26-32}) in the host rock. Also, the occurrence of very rare danburite associated with Tur V (Tab. 1; Fig. 5f) complicates the discussion about the behaviour of B; it is not clear whether it is a newly formed mineral, as is Tur V, or it existed in the host rock before the intrusion/ onset of the pegmatite.

Magnesium is the most reliable cation in tourmalines from evolved granitic pegmatites which verifies external contamination by the host rock in distinct stages of pegmatite evolution (e.g., Novák et al. 2013c, 2017; Čopjaková et al. 2021). Concentrations of Mg in Tur V ~3.00 *apfu* Mg (Fig. 7d) drop down to 2.46–1.86 *apfu* within Tur IV and to 1.02 *apfu* in a single spot from core Tur Ia closely adjacent to the contact zone. It is in contrast with very low concentrations of Mg in cores of zoned Tur Ia closely adjacent to the contact zone and the concentrations of Mg below the detection limit in Tur Ib and Tur II (Fig. 6). Behaviour of Mg manifests that the pegmatite was not or only slightly contaminated by the host rock *in situ* during or after pegmatite magma emplacement (Novák 2013; Novák et al. 2013c).

Compositional evolution of Ca in tourmalines is more complicated (Figs. 6a, 7a). Moderate to high contents of Ca 0.28–0.68 *apfu* were found in Tur V, then Ca drops down to 0.23–0.15 *apfu* in Tur IV and to \leq 0.1 *apfu* in Tur Ia and Ib; Ca is slightly higher 0.12–0.16 *apfu* in rim Tur II. The low Ca content in Tur I is consistent with the low degree of external contamination manifested by the low contents of Mg in Tur Ia. However, abundant fluorapatite in the border unit (Figs 3, 4b) may have consumed part of Ca from the parental medium and constrained rather low Ca in Tur Ia.

High concentrations of Fe (and Zn) in Tur Ia and low contents in Tur V and Tur IV as well as high X_{Mg} in the associated rock-forming minerals manifest that Fe

could not have been supplied from the host rock. This compositional trend with increase of Fe followed by Zn and Mn during tourmaline crystallization is known from numerous pegmatites of the elbaite subtype (e.g., Novák and Povondra 1995; Morgan and London 1999; Laurs et al. 2009) and was proposed by Jolliff et al. (1986) as an ideal covariation on the *Y*-site in response to decreasing temperature and increasing fractionation of parental melt. This trend confirms the B-rich pegmatite melt as a source of Fe in the pegmatite hosted in an extremely Fe-poor but Mg-rich host rock. Tur I is the first phase that crystallized on the liquidus (Benard et al. 1985) from uncontaminated melt rather than a product of mixing of externally derived Mg,Fe-bearing fluids with B-rich melt (London et al. 1996).

Low contents of Li and Al in Tur V and Tur IV (Fig. 7d) are triggered by low Li in the host pegmatite and particularly by a small amount of Li in acidic B,F-rich fluids escaping from the pegmatite into the host rock. This fact is also supported by the absence of holmquistite in the recrystallization zone, a typical exocontact mineral in many large and mainly Li-rich pegmatites with spodumene (e.g., London 1986, 2008; Shearer and Papike 1988; Selway et al. 1998; Tindle et al. 2005).

The behaviour of volatiles (F, B) is more complex. Tur V is F-enriched (0.30-0.56 apfu F) relative to Tur IV (0.14-0.32 apfu) and Tur Ia and II (0.09-0.24 and 0.10-16 apfu F; Fig. 7c). In contrast, the Mn-rich Tur Ib is strongly F-enriched (0.70-0.77 apfu) and show a strong positive correlation of Mn and F (Fig. 8c), which is typical in tourmalines from some elbaite-subtype pegmatites (e.g., Novák et al. 1999b, 2012; Morgan and London 1999). High contents of F in Tur V and rather low in Tur IV may be explained as a result of two distinct processes. The Tur IV in the contact zone crystallized during magmatic stage of pegmatite crystallization rather contemporary with Tur Ia which exhibits similar low concentrations of F. In contrast, origin of Tur V was facilitated by F,B-enriched residual fluids escaping from the pegmatite after crystallization of F-rich Tur Ib. High F in Mn-rich fluor-elbaite Tur Ib may be product of magmatic fractionation but also triggered by crystal-structural constraints. The configuration ^{*X*}Na ^{*Y*}(LiR²⁺Al) ^{*W*}F is very common in primary tourmalines (blue, green) from most lepidolite- or elbaite-subtype pegmatites. The tourmaline compositions close to: X-site - Na, Y-site - LiR²⁺Al and W-site – F (OH) are quite common in Li-bearing pegmatites as green or blue Fe-rich fluor-elbaite and pink to yellow Mn-rich fluor-elbaite to elbaite (e.g., Povondra et al. 1985; Morgan and London 1999; Simmons et al. 2011). Moreover, similar configuration ^yLi-Mg-Al and W(OH,F) is considered stable by Hawthorne (2002). The existence of the B-rich contact zone with dominant Tur IV compositionally and texturally similar to Tur Ia shows an influx of B from the pegmatite outwards in an early magmatic stage; however, it is limited chiefly to the contact zone. A weak modal gradient in subordinate Tur V from the recrystallization zone suggests moderate influx of B,F-enriched residual fluids derived from the pegmatite into the host rock.

6. Conclusions and summary

The mineral assemblages in the Manjaka pegmatite with abundant tourmalines (dravite, elbaite, fluor-elbaite and darrellhenryite) common mainly in the border unit, the complete absence of micas, the occurrence of minor spodumene and the abundance of B-rich minerals (borates, anhydrous borosilicates) manifest a very high activity of B, and a moderate activity of Li, but low activities of F and H₂O (see Novák et al. 2015; Cempírek et al. 2016). The observed mineral assemblages and compositional trends in tourmalines are typical for elbaite-subtype pegmatites. However, the abundance of tourmalines in the border unit as well as the occurrence of B-rich minerals in the entire pegmatite body are exceptional. These compositional and paragenetic features make the Manjaka pegmatite a unique example of a B-rich, and H₂O- and F-poor elbaite-subtype pegmatite.

The exocontact tourmaline mineralizations can be divided according to their parental granitic pegmatites into two main categories: large, highly fractionated, and complexly zoned Li-rich pegmatite bodies (e.g., Tanco, Manitoba; Utö, Sweden; Harding, New Mexico; Kotkotay, northwestern China) and rather small pegmatites (up to 5 m thick) mostly of elbaite-subtype (e.g., Bližná I, Manjaka). The mineral assemblages of the host Mg-rich calc-silicate rock at Manjaka differ from most exocontact zones examined to date by very high X_{Mg} in the dominant rock-forming minerals (diopside, tremolite, phlogopite) as well as by the chemical composition of tourmalines (fluor-uvite>dravite>magnesio-lucchesiite, fluor-dravite, uvite) in the recrystallization zone.

The overall mobility of elements between the Manjaka pegmatite and its host calc-silicate rock was low; a weak influx of Mg into the pegmatite is manifested solely on the compositions of Tur IV and the Tur Ia closely adjacent to contact zone. An influx of Ca into pegmatite was negligible to non-existed and detected only in the composition of Tur IV from the thin contact zone. A negligible influx of Li and Al into the host rock is evident from their slightly elevated contents in Tur IV from the contact zone and Tur V in the adjacent recrystallization zone. Tur V manifests an influx of B,F-enriched fluids from the pegmatite to the host rock.

A very low degree of external contamination of the relatively small Li-bearing Manjaka pegmatite cutting compositionally contrasting host rocks is similar to some small Li-bearing pegmatites (London 2008) but unique compared to the contaminated pegmatites of comparable size, degree of fractionation, and Mg-rich host rock e.g., dolomite marble at the pegmatite Bližná I (Novák et al. 1999b, 2012) or serpentinite at the pegmatite Věžná I (Novák et al. 2017; Čopjaková et al. 2021). This is very likely a consequence of the fluid/melt composition at the Manjaka pegmatite with very high $a(B_2O_3)$, but low $a(H_2O)$ and a(F) indicated by the absence of hydrous phases (micas) except for tourmalines, and the abundance of anhydrous minerals (Novák et al. 2015; Cempírek et al. 2016). Also, the dominance of less soluble silicates (diopside > tremolite, plagioclase) in the host rock from Manjaka compared to carbonates and hydrous Mgsilicates in the host rocks of the Bližná I and Věžná I pegmatites may have played a role.

Acknowledgements: The authors appreciate constructive reviews and comments by anonymous reviewer and A. Müller, and the Associate Editors H. Marschall and J. Cempírek. This work was supported by the research project GAČR P210/19/05198S to Petr Gadas and Milan Novák and financially supported by the EXPRO 2019 project of the The Czech Science Foundation (no. 19-29124X) to Michaela Vašinová Galiová.

References

- BAČÍK P, UHER P, CEMPÍREK J, VACULOVIČ T (2012) Magnesian tourmalines from plagioclase–muscovite–scapolite metaevaporite layers in dolomite marble near Prosetín (Olešnice Unit, Moravicum, Czech Republic). J Geosci 57(3): 143–153
- BENARD F, MOUTOU P, PICHAVANT M (1985) Phase relations of tourmaline leucogranites and the significance of tourmaline in silicic magmas. J Geol 93(3): 271–291
- Bosi F (2011) Stereochemical constraints in tourmaline: from a short-range to a long-range structure Canad Mineral 49(1): 17–27
- Bosi F (2018) Tournaline crystal chemistry. Amer Miner 103(2): 298–306
- BOSI F, CELATA B, SKOGBY H, HÅLENIUS U, TEMPESTA G, CIRIOTTI ME, BITTARELLO E, MARENGO A (2021) Mn-bearing purplish-red tourmaline from the Anjanabonoina pegmatite, Madagascar. Mineral Mag 85(2): 242–253
- BUŘIVAL Z, NOVÁK M (2018) Secondary blue tourmaline after garnet from elbaite-subtype pegmatites; implications for source and behaviour of Ca and Mg in fluids. J Geosci 63(2): 111–122
- Cempírek J, Grew ES, Kampf AR, Ma C, Novák M, Gadas P, Škoda R, Vašinová Galiová M, Pezzotta F, Groat

LA, KRIVOVICHEV SV (2016) Vránaite, ideally $Al_{16}B_4$ Si_4O_{38} , a new mineral related to boralsilite, $Al_{16}B_6Si_2$ O_37 , from the Manjaka pegmatite, Sahatany Valley, Madagascar. Amer Miner 101: 2108–2117

- ČERNÝ P, ERCIT TS (2005) The classification of granitic pegmatites revisited. Canad Mineral 43: 2005–2026
- ČERNÝ P, LONDON D, NOVÁK M (2012) Granitic pegmatites as reflection of their sources. Elements 8: 289–294
- ČОРЈАКОVÁ R, PROKOP J, NOVÁK M, LOSOS Z, GADAS P, ŠKODA R, HOLÁ M (2021) Hydrothermal alteration of tourmaline from pegmatitic rocks enclosed in serpentinites: Multistage processes with distinct fluid sources. Lithos 380: 105823
- Cox R, ARMSTRONG RA, ASHWAL LD (1998) Sedimentology, geochronology and provenance of the Proterozoic Itremo Group, central Madagascar, and implications for pre-Gondwana palaeogeography. J Geol Soc 155(6): 1009–1024
- DUTROW BL, HENRY DJ (2011) Tourmaline: a geologic DVD. Elements 7(5): 301–306
- ERCIT TS, GROAT LA, GAULT RA (2003) Granitic pegmatites of the O'Grady batholith, N.W.T., Canada: A Case study of the evolution of the elbaite subtype of rare-element granitic pegmatite. Canad Mineral 41: 117–137

ERTL A, HUGHES JM, PERTLIK F, FOIT JR FF, WRIGHT SE, BRANDSTÄTTER F, MARLER B (2002) Polyhedron distortions in tourmaline. Canad Mineral 40(1): 153–162

ERTL A, HUGHES JM, PROWATKE S, LUDWIG T, PRASAD PS, BRANDSTÄTTER F, KÖRNER W, SCHUSTER R, PERTLIK F, MARSCHALL H (2006) Tetrahedrally coordinated boron in tourmalines from the liddicoatite–elbaite series from Madagascar: Structure, chemistry, and infrared spectroscopic studies. Amer Miner 91(11–12): 1847–1856

ERTL A, ROSSMAN GR, HUGHES JM, LONDON D, WANG Y, O'LEARY JA, DYAR D, PROWATKE S, LUDWIG T, TILL-MANNS E (2010) Tournaline of the elbaite-schorl series from the Himalaya Mine, Mesa Grande, California: A detailed investigation. Amer Miner 95(1): 24–40

FLÉGR T (2016) Vývoj chemického složení turmalínů z elbaitového pegmatitu Řečice [online]. Brno. Available from: https://is.muni.cz/th/c6tqv/. Master's thesis. Masaryk University, Faculty of Science. 1–68

GADAS P, NOVÁK M, ŠKODA R, CEMPÍREK J, ZACHAŘ A, FLÉGR T, PEZZOTTA F (2019) Titanium in tourmalines from granitic pegmatites and their exocontacts. Canad Mineral 57(5): 745–747

- HAWTHORNE FC (1996) Structural mechanisms for lightelement variations in tourmaline. Canad Mineral 34(1): 123–132
- HAWTHORNE FC (2002) Bond-valence constraints on the chemical composition of tourmaline. Canad Mineral 40(3): 789–797

HENRY D, NOVÁK M, HAWTHORNE FC, ERTL A, DUTROW B, UHER P, PEZZOTTA F (2011) Nomenclature of the tourmaline-group minerals. Amer Miner 96: 895–913

- VAN HINSBERG VJ, HENRY D J, DUTROW BL (2011) Tourmaline as a petrologic forensic mineral: A unique recorder of its geologic past. Elements 7(5): 327–332
- JOLLIFF BL, PAPIKE JJ, SHEARER CK (1986) Tourmaline as a recorder of pegmatite evolution; Bob Ingersoll pegmatite, Black Hills, South Dakota. Amer Miner 71(3–4): 472–500
- KALT A, SCHREYER W, LUDWIG T, PROWATKE S, BERNHARDT HJ, ERTL A (2001) Complete solid solution between magnesian schorl and lithian excess-boron olenite in a pegmatite from the Koralpe (eastern Alps, Austria). Eur J Mineral 13(6): 1191–1205
- KRMÍČEK L, NOVÁK M, TRUMBULL RB, CEMPÍREK J, HOUZAR S (2021) Boron isotopic variations in tourmaline from metacarbonates and associated calc-silicate rocks from the Bohemian Massif: Constraints on boron recycling in the Variscan orogen. Geosci Front 12: 219–230
- LAURS BM, DILLES JH, WAIRRACH Y, KAUSAR AB, SNEE LW (1998) Geological setting and petrogeneseis of symmetrically zoned, miarolitic granitic pegmatites at Stak Nala, Nanga-Parbat – Haramosh massif, northern Pakistan. Canad Mineral 36: 1–47
- LAURS BM, SIMMONS WB, FALSTER AU, ANCKAR B (2009) Genesis of yellow manganese-rich elbaite from the Canary mining area, Lundazi, Zambia. Appl Geochem 24(6): 1113–1124
- LONDON D (1986) Holmquistite as a guide to pegmatitic rare metal deposits. Econ Geol 81(3): 704–712
- LONDON D (2008) Pegmatites. Canad Mineral, Special Publication 10: 1–347
- LONDON D, MORGAN GB, WOLF MB (1996) Boron in granitic rocks and their contact aureoles. Rev Mineral Geochem 33: 299–330
- MERLET C (1994) An Accurate Computer Correction Program for Quantitative Electron Probe Microanalysis. Microchim Acta (114/115): 363–376
- MORGAN GB VI, LONDON D (1987) Alterations of amphibolitic wallrocks around the Tanco rare-element pegmatite, Bernic Lake, Manitoba. Amer Miner 72: 1097–1121
- MORGAN GB VI, LONDON D (1999) Crystallization of the Little Three layered pegmatite–aplite dike, Ramona District, California. Contrib Mineral Petrol 136 (4): 310–330
- Novák M (2000) Compositional pathways of tourmaline evolution during primary (magmatic) crystallization in complex (Li) pegmatites of the Moldanubicum, Czech Republic. Mem Soc Ital Sci Nat Mus Civ Stor Nat Milano 30: 45–56
- NOVÁK M (2013) Contamination processes in in complex granitic pegmatites. In: SIMMONS WB, WEBBER KL, FALSTER AU, RODA-ROBLES E, HANSON SL, MÁRQUEZ-ZAVALÍA MF, GALLISKI MÁ (EDS) PEG 2013 – contributions to the 6th International symposium on granitic pegmatites, 100–103
- NOVÁK M, POVONDRA P (1995) Elbaite pegmatites in the Moldanubicum: a new subtype of the rare-element class. Mineral Petrol 55: 159–176

- NOVÁK M, BURNS PC, MORGAN GB VI (1998) Fluorine variation in hambergite from granitic pegmatites. Canad Mineral 36(2): 441–446
- NOVÁK M, ČERNÝ P, COOPER M, HAWTHORNE FC, OT-TOLINI L, XU Z, LIANG JJ (1999a) Boron-bearing 2M1 polylithionite and 2M1 + 1M boromuscovite from an elbaite pegmatite at Řečice, western Moravia, Czech Republic. Eur J Mineral 11(4): 669–678
- NOVÁK M, SELWAY JB, ČERNÝ P, HAWTHORNE FC (1999b) Tourmaline of the elbaite–dravite series from an elbaitesubtype pegmatite at Bližná, southern Bohemia, Czech Republic. Eur J Mineral 11(4): 557–568
- NOVÁK M, ŠKODA R, GADAS, P, KRMÍČEK, L, ČERNÝ, P (2012) Contrasting origins of the mixed (NYF+LCT) signature in granitic pegmatites, with examples from the Moldanubian Zone, Czech Republic. Canad Mineral 50: 1077–1094
- Novák M, Gadas P, Galiová Vašinová M, Pezzotta F (2013a) Compositional variations in Cs,Li,Mg-rich beryl from exocontact of the complex Manjaka pegmatite, Sahatany Valley, Madagascar. In: SIMMONS WB, WEBBER KL, FALSTER AU, RODA-ROBLES E, HANSON SL, MÁRQUEZ-ZAVALÍA MF, GALLISKI MÁ (EDS) PEG 2013 – Contrib 6th International Symposium on Granitic Pegmatites. 100–103
- NOVÁK M, ERTL A, POVONDRA P, GALIOVÁ VAŠINOVÁ M, ROSSMAN GR, PRISTACZ H, PREM M, GIESTER G, GADAS P, ŠKODA R (2013b) Darrellhenryite, Na(LiAl₂) Al₆ (BO₃)₃ Si₆O₁₈(OH)₃O, a new mineral from the tourmaline supergroup. Amer Miner 98(10): 1886–1892
- NOVÁK M, KADLEC T, GADAS P (2013c) Geological position, mineral assemblages and contamination of granitic pegmatites in the Moldanubian Zone, Czech Republic; examples from the Vlastějovice region. J Geosci 58: 21–47
- NOVÁK M, CEMPÍREK J, GADAS P, ŠKODA R, VAŠINOVÁ-GALIOVÁ M, PEZZOTTA F, GROAT LA (2015) Boralsilite and Li, Be-bearing "boron mullite" Al₈B₂Si₂O₁₉, breakdown products of spodumene from the Manjaka pegmatite, Sahatany Valley, Madagascar. Canad Mineral 53: 357–374
- NOVÁK M, PROKOP J, LOSOS Z, MACEK I (2017) Tourmaline, an indicator of external Mg-contamination of granitic pegmatites from host serpentinite; examples from the Moldanubian Zone, Czech Republic. Mineral Petrol 111: 625–641
- NOVOTNÝ F, NOVÁK M, CEMPÍREK J (2019) Chemical composition of tourmaline from the Dolní Rožínka elbaite pegmatite. Bull Mineral Petrolog Odd Nár Muz 27 (1): 38–45 (in Czech with English abstract)
- PESQUERA A, GIL-CRESPO P P, TORRES-RUIZ F, TORRES-RUIZ J, RODA-ROBLES E (2016) A multiple regression method for estimating Li in tournaline from electron microprobe analyses. Mineral Mag 80(6): 1129–1133
- PEZZOTTA F (2005) First attempt to the petrogenesis and the classification of granitic pegmatites of the Itremo

Region (central Madagascar). International Meeting on Crystallization processes in granitic pegmatites. Elba, May 2005

- PEZZOTTA F, PRASZKIER T (2013) Giant liddicoatites from Madagascar. Minerals 6: 13–17
- POUCHOU JL, PICHOIR F (1985) "PAP" (frZ) procedure for improved quantitative microanalysis. In: ARMSTRONG JT (ED) Microbeam Analysis. San Francisco Press, San Francisco: 104–106
- POVONDRA P, NOVÁK M (1986) Tournalines from metamorphosed carbonate rocks from western Moravia. Neu Jb Mineral, Mh 6: 273–282
- POVONDRA P, ČECH F, STANĚK J (1985) Crystal chemistry of elbaites from some lithium pegmatites of the Czech massif. Acta Univ Carol Geol (1): 1–24
- RANOROSOA N (1986) Etude minéralogique et microthermométrique des pegmatites du champ de la Sahatany
 Madagascar. – PhD Thesis, University Paul Sabatier, Toulouse. 1–223
- RANOROSOA N, FONTAN F, FRANSOLET A-M (1989) Rediscovery of manandonite in the Sahatany Valley, Madagascar. Eur J Mineral 1: 633–638
- SELWAY JB, ČERNÝ P, HAWTHORNE FC (1998) Feruvite from lepidolite pegmatites at Red Cross lake, Manitoba. Canad Mineral 36(2): 433–439
- SELWAY JB, NOVÁK M, ČERNÝ P, HAWTHORNE FC (2000) The Tanco pegmatite at Bernic Lake, Manitoba. XIII. Exocontact tourmaline. Canad Mineral 38(4): 869–876
- SELWAY JB, SMEDS SA, ČERNÝ P, HAWTHORNE FC (2002) Compositional evolution of tourmaline in the petalitesubtype Nyköpingsgruvan pegmatites, Utö, Stockholm Archipelago, Sweden. GFF 124(2): 93–102
- SHEARER CK, PAPIKE, JJ (1988) Pegmatite–wallrock interaction; holmquistite-bearing amphibolite, Edison Pegmatite, Black Hills, South Dakota. Amer Miner 73(3–4): 324–337
- SHEARER CK, PAPIKE, JJ, SIMON SB, LAUL JC (1986) Pegmatite–wallrock interactions, Black Hills, South Dakota; interaction between pegmatite-derived fluids and quartz-mica schist wallrock. Amer Miner 71(3–4): 518–539
- SIMMONS WB, PEZZOTTA F, FALSTER AU, WEBER KL (2001) Londonite, a new mineral species: the Cs-dominant analogue of rhodizite from Antadrokomby granitic pegmatite, Madagascar. Canad Mineral 39: 747–755
- SIMMONS WB, FALSTER AU, LAURS BM (2011) A survey of Mn-rich yellow tournaline from worldwide localities and implications for the petrogenesis of granitic pegmatites. Canad Mineral 49(1): 301–319
- TINDLE AG, BREAKS FW, SELWAY JB (2002) Tourmaline in petalite subtype granitic pegmatites: evidence of fractionation and contamination from the Pakeagama lake and Separation Lake areas of northwestern Ontario, Canada. Canad Mineral 40: 753–788

- TINDLE AG, SELWAY JB, BREAKS FW (2005) Liddicoatite and associated species from the McCombe spodumene-subtype rare-element granitic pegmatite, northwestern Ontario, Canada. Canad Mineral 43(2): 769–793
- WARR LN (2021) IMA-CNMNC approved mineral symbols. Mineral Mag 85, 291–320
- ZAGORSKYI VE, PERETYAZHKO IC (1992) Pegmatites with gemstones of Central Transbaikalia. Nauka, Novosibirsk. (in Russian). 1–222
- ZHANG AC, WANG RC, JIANG SY, HU H, ZHANG H (2008) Chemical and textural features of tourmaline from the spodumene-subtype Koktokay No. 3 pegmatite, Altai, northwestern China: a record of magmatic to hydrothermal evolution. Canad Mineral 46(1): 41–58