

Original paper

Complex magmatic and subsolidus compositional trends of columbite–tantalite in the beryl–columbite Šejby granitic pegmatite, Czech Republic: role of crystal-structural constraints and associated minerals

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The simply zoned Šejby pegmatite of beryl–columbite subtype is enclosed in migmatitized gneisses – country rocks of the southern part of the Central Moldanubian Plutonic Complex, Bohemian Massif, Czech Republic. The columbite-group minerals (CGM) occur mostly in blocky K-feldspar unit. Primary magmatic CGM [columbite-(Fe)–tantalite-(Fe)], show an interesting compositional and textural evolution. Subhomogeneous cores of columbite-(Fe)–tantalite-(Fe) (A) are surrounded by heterogeneous intermediate zones (B) and (C) with irregular to oscillatory zoning and mutually comparable compositions. Zone (B) contains grains of tapiolite-(Fe) and inclusions of pyrite decomposed into a mixture of secondary jarosite-group minerals. In the next zone (C), irregular Mn-enriched patches occur and in the outermost thin zone (D) CGM exhibit fine oscillatory zoning typically developed at crystal terminations. The late, subsolidus CGM include patchy-zoned Mn-enriched columbite-(Fe) and late columbite-(Fe) veinlets both formed at the expense of their magmatic precursors in the zone C; the veinlets are also present in the zone D. Similar but fine patches and veinlets are developed around jarosite pseudomorphs after pyrite. The compositional evolution of CGM shows a slight increase in Ta/Nb and Mn/Fe in the zones A and B followed by a reverse trend to elevated Nb and Fe in the zone C and, in particular, in the zone D. Complex subsolidus fluid–melt interactions that generated patches and veinlets caused only minor changes in Ta/Nb and slight Mn-enrichment. Tantalum depletion in veins close to jarosite pseudomorphs after pyrite indicates higher mobility of Ta in acidic low-temperature fluids.

Keywords: columbite-group minerals, tapiolite, compositional trends, Nb–Ta and Fe–Mn fractionation, granitic pegmatite

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1. Introduction

Columbite-group minerals (CGM) belong to the most widespread niobium and tantalum phases in geochemically highly evolved rocks, in particular leucogranites and granitic pegmatites. As mafic minerals, they represent also essential carriers of Fe and Mn, and in specific cases also Mg and Ti in the host rocks of distinctly leucocratic character.

Compositional variations of CGM, especially Nb–Ta and Fe–Mn pairs, are sensitive indicators of magmatic to subsolidus evolution of the parental rock. During primary magmatic crystallization, they commonly show a progressive increase in one or both of the Ta/(Ta + Nb) and Mn/(Mn + Fe) ratios, as illustrated by distinct evolutionary trends in the columbite quadrilateral diagram (e.g., Černý and Ercit 1985, 1989; Černý et al. 1986; Lahti 1987, 2000; Spilde and Shearer 1992; Mulja et al. 1996; Tindle and Breaks 2000; Galliski and Černý 2006; Beurlen et al. 2008; Badanina et al. 2015; Melcher et al. 2015). Based on numerous empirical observations of

mineral assemblages in the host granites or pegmatites, these trends commonly show a positive relationship to the activity of F in a parent medium, manifested by the abundance of lepidolite and other F-rich minerals (e.g. Černý 1992; Novák et al. 2003).

Results of experimental works signify the activity of volatiles, chiefly F and P, in melt (Linnen and Cuney 2005; Aseri et al. 2015). Solubility of individual CGM in melt (Linnen and Keppler 1997; Bartels et al. 2010) and activity of Li (Linnen 1998; Chevychev et al. 2010; Bartels et al. 2011; Chevychev 2014) were used to explain these compositional trends. However, an influence of associated Fe, Mn-bearing minerals such as micas, garnets, primary Fe, Mn-phosphates or tourmalines was discussed only exceptionally (e.g. Mulja et al. 1996; Van Lichtervelde et al. 2006, 2007; Stepanov et al. 2014). Behaviour of the relevant elements (Nb–Ta, Fe–Mn) is thus not satisfactorily resolved. Because the Ta/Nb ratio is an important indicator of fractionation degree in parental magmatic rocks (Černý et al. 1985; Raimbault 1998; Barth et al. 2000; Černý and Ercit 2005; Melcher et al.

2015), a study of behaviour of both Nb and Ta in distinct geological environments, at variable P–T–X conditions and in various mineral assemblages is long overdue.

Simply zoned beryl–columbite pegmatite from Šejby near Nové Hradý, southern Bohemia, Czech Republic is a unique example of highly leucocratic, Li, F, B-poor but P- and Nb,Ta-moderately rich system. The almost complete absence of Fe, Mn-bearing silicate or phosphate minerals makes the assemblage CGM + ferrotapiolite + pyrite (completely replaced by secondary jarosite-group minerals) an excellent case study of Nb–Ta and Fe–Mn fractionation trends from primary magmatic, through early subsolidus to late-veining stages not influenced by associated Fe, Mn-bearing minerals. Our contribution is focused on a detailed study of textural zoning, compositional variations and trends of columbite-group minerals and tapiolite-(Fe) as tools for understanding the complex magmatic to subsolidus evolution on the example of the Šejby beryl–columbite-subtype pegmatite.

2. Regional geology and pegmatite characterization

Leucogranites, marginal pegmatites (stockscheider) and pegmatite dikes are common in the southern part of the Central Moldanubian Plutonic Complex, particularly at the Homolka, Nakolice and Šejby occurrences (Breiter 1998; Heřmánek et al. 1998). In this region, the Central Moldanubian Plutonic Complex is built by the Weinsberg biotite granite (331–323 Ma; Gerdes 2001; Gerdes et al. 2003), Eisgarn two-mica granites (328–326 Ma; Klötzli 1999; Gerdes 2001; Gerdes et al. 2003; Žák et al. 2011)

Tab. 1. Analytical conditions for the EPMA measurement of Nb–Ta minerals

Element	Line	Calibrant	Detection limits*
W	L_{α}	W	2490–2639
Nb	L_{α}	columbite “Ivigut”	1337–1530
Ta	M_{α}	CrTa ₂ O ₆	842–880
Ti	K_{α}	TiO ₂	465–493
Zr	L_{α}	zircon	666–711
Sn	L_{α}	Sn	1021–1089
U	M_{β}	U	1123–1154
Sc	K_{α}	ScVO ₄	341–384
Y	L_{α}	YPO ₄	745–806
As	L_{α}	lammerite	608–673
Sb	L_{β}	Sb	1852–1906
Bi	M_{β}	Bi	1235–1403
Fe	K_{α}	hematite	541–574
Mn	K_{α}	Mn ₂ SiO ₄	467–501
Mg	K_{α}	MgAl ₂ O ₄	192–202
Ca	K_{β}	titanite	205–213
Pb	M_{β}	vanadinite	882–943

* Detection limits (3 σ) are in ppm

and leucogranites (319±2 Ma; Breiter and Scharbert 1998).

At Šejby, N–S trending dikes of albite–muscovite pegmatitic granite with accessory biotite, topaz, garnet, fluorapatite and columbite–tantalite cut the Weinsberg granite and the surrounding migmatized paragneisses (Matějka and Klečka 1994; Breiter and Scharbert 1998). The exposed pegmatites form zoned N- to S-trending dikes, up to 3 m thick and ~50 m long, cutting migmatized paragneiss close to the granite exocontact (Welser and Zikeš 2013). Going inwards, it consists of a thin border granitic zone (Kfs + Ab + Qz + Bt), a graphic zone (Kfs + Qz), a blocky K-feldspar zone, an albite unit, a coarse-grained muscovite-rich unit and a quartz core (Pavliček et al. 2009; Welser and Zikeš 2013). At the contact of the blocky K-feldspar zone with the quartz core occur columnar crystals of beryl, up to 15 cm long, associated with albite, coarse-flaked muscovite and accessory zircon, fluorapatite and Nb–Ta oxide minerals. Single euhedral columnar to tabular crystals and aggregates of CGM, up to 15 mm in size, were found in the blocky K-feldspar zone, muscovite-rich portions and are closely associated with beryl. Hafnium-rich zircon (5 to 10 wt. % HfO₂) contains tiny inclusions of uraninite (Pavliček et al. 2009). Moreover, primary Be-phosphates [hurlbutite, (hydroxyl)herderite] along with rare secondary crandallite-group minerals and strengite have been identified (Welser and Zikeš 2013). However, magmatic Fe, Mn-bearing minerals typical of granitic pegmatites, such as garnet, tourmaline or triplite, have not been described in this pegmatite, except accessory Mn-rich fluorapatite (Pavliček et al. 2009) and very rare biotite in the outermost granitic zone (Welser and Zikeš 2013).

Cassiterite, CGM, and other associated Ta, Nb, Ti-oxide minerals were found in fine-grained leucogranites and in coarse-grained pegmatites as well as in placers of this region (Breiter 1998). Chemical compositions of CGM, rare ferrotapiolite and ilmenite from leucogranites, granitic pegmatites and placers were studied by several authors (Novák et al. 1994; Frýda and Breiter 1995; Uher 1998; Pavliček et al. 2009; Welser and Zikeš 2013). All these minerals show similar compositional characteristics: significant Nb/Ta fractionation but rather constant and mostly low Fe/Mn ratio.

3. Methods

The Cameca SX-100 electron microprobe at the Laboratory of Electron Microscopy and Microanalysis, the joint facility of the Masaryk University and Czech Geological Survey in Brno, was used to determine the chemical composition of minerals. The wavelength-dispersion mode and the following analytical conditions were applied: an

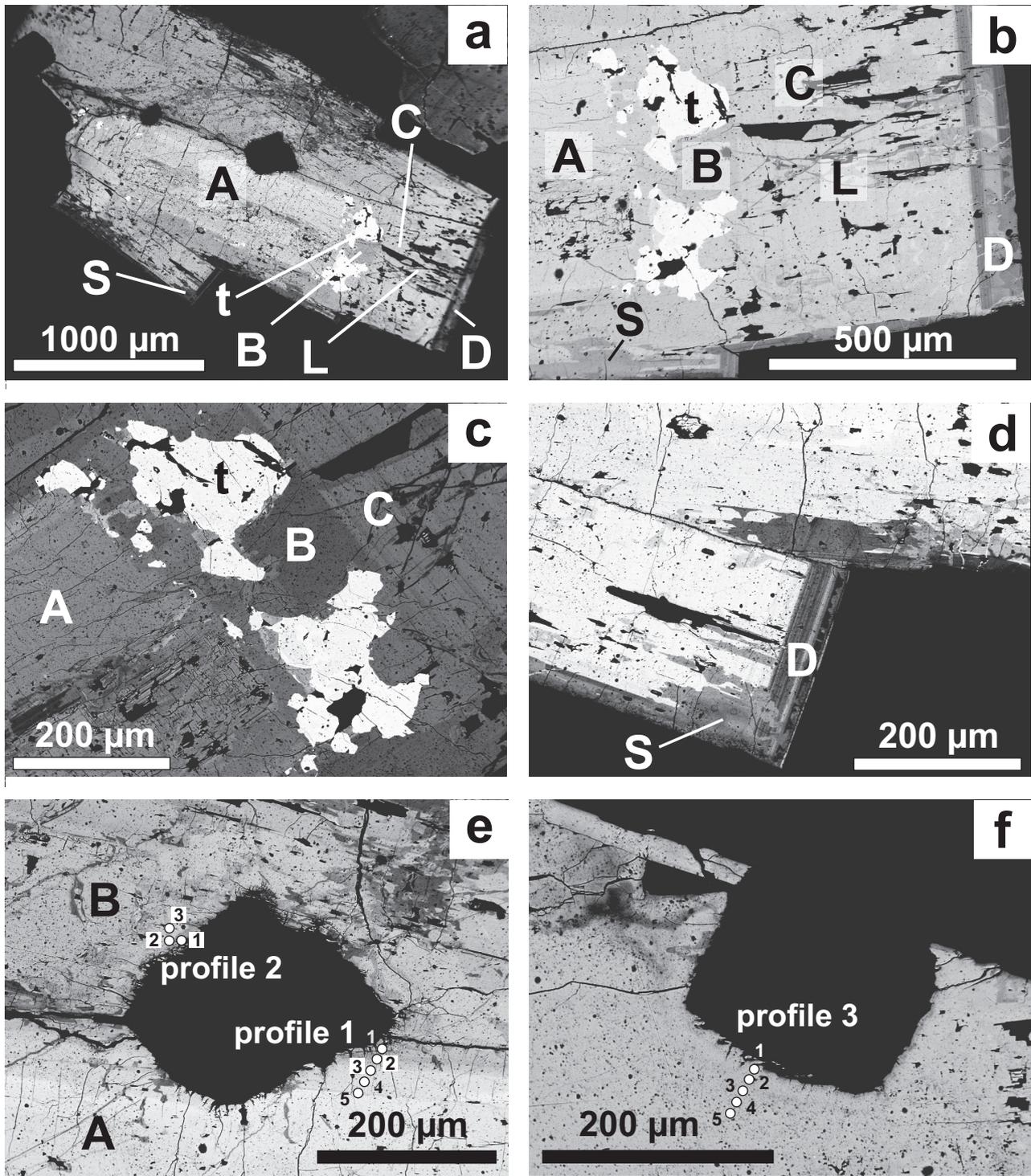


Fig. 1 Back-scattered electron (BSE) images of Nb–Ta minerals from the Šejby pegmatite. **a** – Columbite-(Fe) to tantalite-(Fe) showing distinct textural variations: central zone (A), irregular intermediate zone B with anhedral bright ferrotapiolite grains, oscillatory-zoned intermediate zone C and thin outer zone (D) showing oscillatory zoning. These primary zones are distinctly replaced by subsolidus patches (S) and late veinlets (L). Dark inclusions are pyrite replaced by a mixture of secondary jarosite-group minerals. The following figures are details of the Fig. 1a: **b** – The intermediate zone B with anhedral bright inclusions of tapiolite-(Fe) and other primary zones, note the significant replacement of border zones by subsolidus patchy portions (S) and late veining (L); **c** – Central zone (A) and adjacent irregular textures of intermediate zone B with anhedral bright inclusions of ferrotapiolite. Adjacent oscillatory-zoned intermediate zone C contains pyrite decomposed into mixture of secondary jarosite-group minerals (dark inclusions); **d** – Thin outer zone (D); note that primary oscillatory zoning in crystal rim succumbed to alteration of subsolidus patchy portions (S); **e** – Dark inclusion of pyrite totally decomposed into a mixture of secondary jarosite-group minerals, situated at the contact of the central (A) with the intermediate zone B, including profiles 1 and 2; **f** – Crystal rim with marked position of the profile 3 and a dark inclusion of decomposed pyrite.

acceleration voltage of 15 kV, a beam current of 20 nA, and a beam diameter of 2 μm . The data were reduced using the PAP routine of Pouchou and Pichoir (1985). The remaining analytical details are given in Tab. 1.

4. Results

4.1. Textural relations and internal zoning of Nb, Ta-oxide minerals

The examined CGM were found on a loose fragment of massive quartz in contact with blocky K-feldspar close to outcrops of pegmatite dikes (see Welser and Zikeš 2013). The CGM exhibit complex internal growth zoning; the following primary zones were distinguished from centre to rim of columbite–tantalite crystals (Fig. 1a–d). **Central zone (A)** is slightly heterogeneous, showing locally fine oscillatory zoning. Adjacent heterogeneous **intermediate zone (B)** is developed particularly on (001) plane of the (A), whereas on prismatic planes of (A) only narrow and discontinuous zone (B) is present (Fig. 1a–b). The zone (B) consists of heterogeneous columbite–tantalite with irregular to patchy zoning in intergrowths with common anhedral tapiolite-(Fe) grains, up to 200 μm in diameter (Fig. 1a–c). The next **intermediate zone (C)** is moderately heterogeneous, locally with oscillatory zoning (Fig. 1c) and rare inclusions of jarosite. Very thin **outer zone (D)** is seen chiefly on (001) plane and shows fine but contrasting oscillatory zoning relative to the other units (Fig. 1b, d). **Subsolidus patchy portions**, up to 300 μm in size, are evident particularly within the (C) and (D) zones, respectively (Fig. 1b, d). **Late veinlets** are observed especially in the (C) and (D) zones (Fig. 1b, 2a–b). Similar subsolidus but finer patches and veinlets (Fig. 2a, e, g) also occur close to jarosite pseudomorphs after pyrite.

Hexahedral or irregular inclusions occur in central–outer parts of the CGM crystals. They reveal a K–Na–Pb sulphate composition of the jarosite-group minerals and apparently represent pseudomorphs after primary pyrite. Two morphological types of pyrite pseudomorphs were distinguished in all primary zones of the columbite–tantalite except for the outer one (D). Large subhedral to euhedral grains of pyrite, up to 250 μm across, occur on the contact of central zone A or intermediate C zone of columbite–tantalite (Fig. 1a, e–f, 2a). These large grains of pyrite were completely altered to jarosite-group minerals (Fig. 1d). Small elongated grains of pyrite, ~ 20 μm long and also completely altered to jarosite-group minerals, are commonly oriented along the *c* axis of CGM. They are present chiefly within the intermediate zone C (Figs 1b, 2b), less commonly also in the central zone (A) and intermediate zone (B) (Fig. 1b–c). No changes in

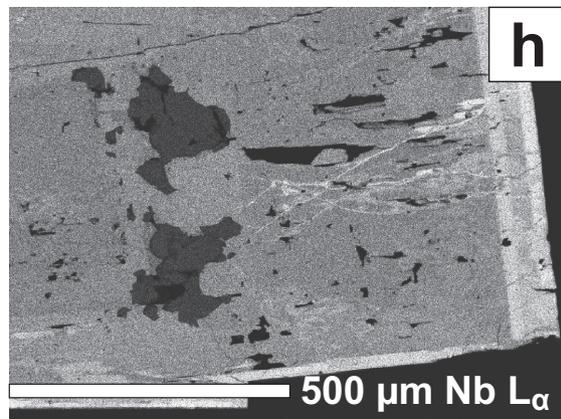
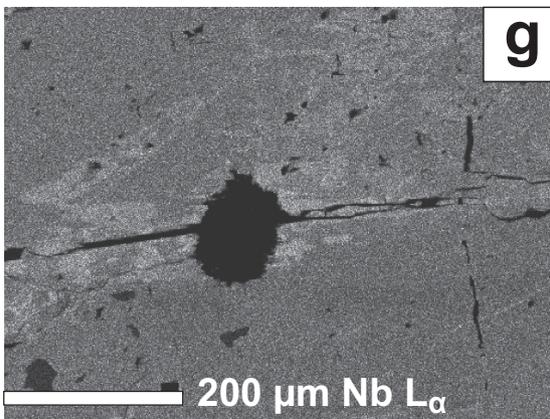
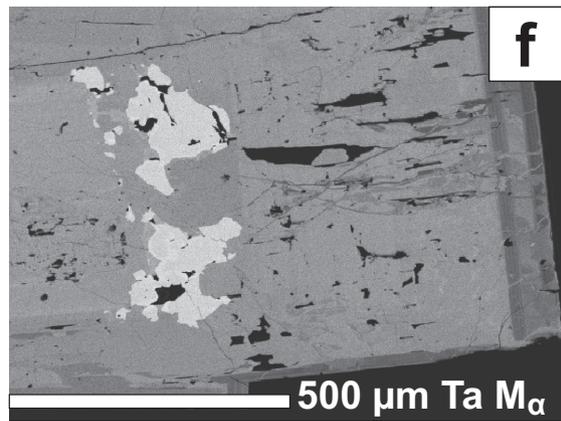
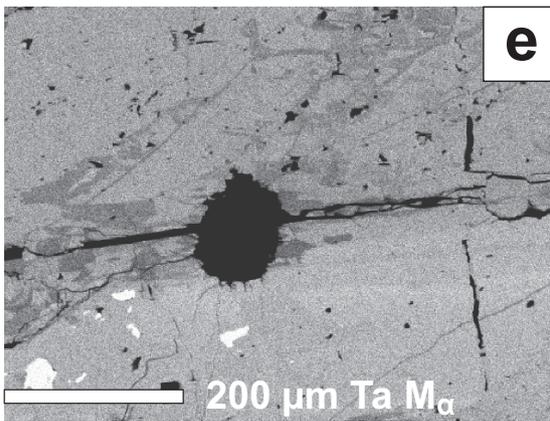
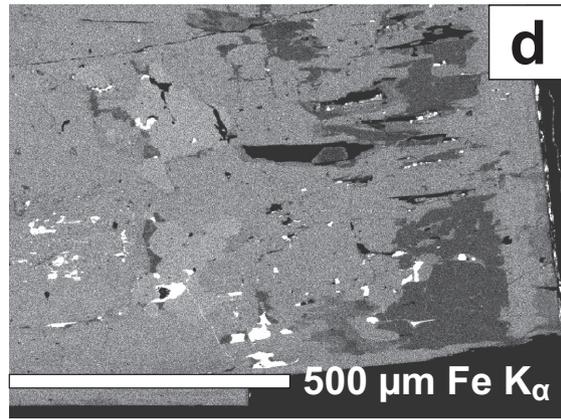
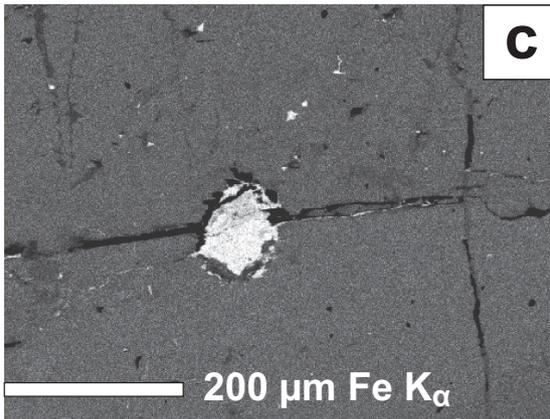
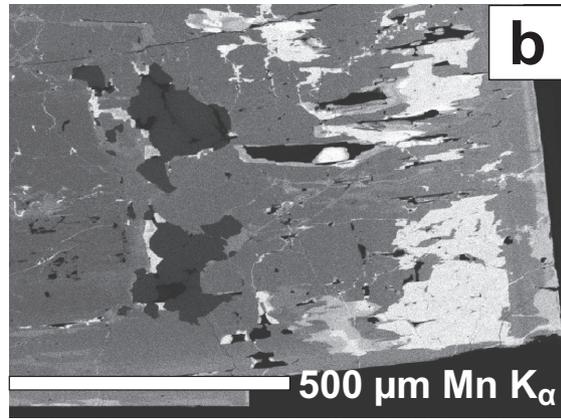
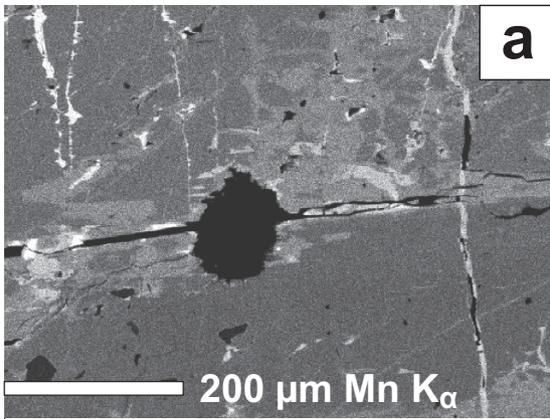
primary composition of adjacent columbite–tantalite were recorded directly at the contacts of former pyrite in BSE images (Fig. 1e). However, element mapping revealed several irregular patches of Mn-enriched and Ta-depleted columbite–tantalite (≤ 100 μm) close to them (Fig. 2a) as well as a complex network of slightly Mn, Nb-enriched veinlets of CGM. They occur directly next to the pyrite grains and continue mainly into the intermediate zone C and less commonly also into the central zone (A) (Fig. 2a–b). Moreover, rare small inclusions of zircon and a Fe, Al-phosphate mineral (strengite?) are present within the intermediate B zone (Fig. 1b–c).

4.2. Mineral composition

The central zone (A) of the columbite–tantalite grains is characterized by slightly heterogeneous columbite-(Fe) to tantalite-(Fe) with $\text{Mn}/(\text{Mn} + \text{Fe}) = 0.12\text{--}0.22$ and $\text{Ta}/(\text{Ta} + \text{Nb}) = 0.44\text{--}0.59$ (Fig. 3a; Tab. 2). Heterogeneous tantalite-(Fe) from the intermediate zone B exhibits $\text{Mn}/(\text{Mn} + \text{Fe})$ of 0.15–0.39 and $\text{Ta}/(\text{Ta} + \text{Nb})$ of 0.50–0.62 (Fig. 3a); associated ferrotapiolite is also relatively heterogeneous [$\text{Mn}/(\text{Mn} + \text{Fe}) = 0.03\text{--}0.05$, $\text{Ta}/(\text{Ta} + \text{Nb}) = 0.79\text{--}0.92$] (Fig. 3a). Columbite-(Fe) to tantalite-(Fe) from the intermediate zone C is rather homogeneous [$\text{Mn}/(\text{Mn} + \text{Ta}) = 0.16\text{--}0.21$, $\text{Ta}/(\text{Ta} + \text{Nb}) = 0.49\text{--}0.54$] (Fig. 3a). Columbite-(Fe) from the outer zone (D) is homogeneous in $\text{Mn}/(\text{Mn} + \text{Fe})$ (0.19–0.22) but it shows wide variations in $\text{Ta}/(\text{Ta} + \text{Nb})$ ratios (0.25 to 0.41) (Fig. 3a). Columbite-(Fe) to tantalite-(Fe) patches adjacent to small grains of the former pyrite are enriched in Mn [$\text{Mn}/(\text{Mn} + \text{Fe}) = 0.39\text{--}0.42$], whereas the $\text{Ta}/(\text{Ta} + \text{Nb})$ ratios of 0.48–0.51 are similar to those of host tantalite-(Fe) of the intermediate zone C (Fig. 3b). Columbite-(Fe) of the late veinlets is slightly Nb-enriched [$\text{Ta}/(\text{Ta} + \text{Nb}) = 0.39\text{--}0.46$], whereas its $\text{Mn}/(\text{Mn} + \text{Fe})$ of 0.16–0.26 is comparable to the host primary columbite–tantalite (Fig. 3a). Other detected cations in CGM include Ti (≤ 3.3 wt. % TiO_2 ; 0.17 apfu), W (≤ 2.8 wt. % WO_3 ; 0.045 apfu) and Zr (≤ 0.8 , mostly ~ 0.3 wt. % ZrO_2 ; 0.011 apfu). Only trace amounts of Sn (≤ 0.3 wt. % SnO_2) and Pb (≤ 0.2 wt. % PbO) were found. Tapiolite-(Fe) compositions show typically very low and nearly constant $\text{Mn}/(\text{Mn} + \text{Fe})$ but very high and slightly variable $\text{Ta}/(\text{Ta} + \text{Nb})$ atomic ratios: 0.02 to 0.04 and 0.79 to 0.91, respectively (Tab. 3). In tapiolite-(Fe), W is mostly below the detection limit of EMPA, whereas the concentrations of ZrO_2 and SnO_2 both attain up to 0.3 wt. % (≤ 0.01 Zr or Sn apfu), and are in general comparable to columbite–tantalite (Tab. 3).

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Fig. 2 The X-ray elemental maps of columbite-group minerals from the Šejby pegmatite (details of Fig. 1a–b). Inclusion in Fig. 2a, c, e and f is decomposed pyrite.



Tab. 2. Representative chemical compositions (in wt. %) and mineral formulae (in apfu) of CGM from the Šejby pegmatite

Zone	(A)	(A)	(B)	(B)	(C)	(C)	(D)	(D)	(S)	(S)	(L)	(L)
Analysis #	1	9	14	24	35	37	41	43	51	67	76	83
WO ₃	0.32	1.47	1.10	0.90	0.83	0.95	1.03	1.76	1.02	1.58	1.00	1.23
Nb ₂ O ₅	25.65	33.71	28.09	26.78	27.05	27.42	37.05	46.70	28.58	29.40	34.20	38.70
Ta ₂ O ₅	55.57	43.98	50.94	52.26	51.46	50.05	41.14	31.00	51.40	49.40	44.72	40.60
TiO ₂	0.95	2.18	1.90	1.70	2.04	2.40	1.10	1.46	1.33	1.44	1.23	1.06
ZrO ₂	0.34	0.32	0.42	0.21	0.45	0.43	0.12	0.00	0.31	0.02	0.17	0.00
SnO ₂	0.04	0.22	0.16	0.21	0.17	0.20	0.09	0.08	0.06	0.09	0.10	0.05
UO ₂	0.09	0.10	0.18	0.08	0.05	0.09	0.04	0.03	0.08	0.05	0.02	0.08
Y ₂ O ₃	0.06	0.03	0.01	0.04	0.05	0.09	0.07	0.00	0.13	0.02	0.11	0.01
Sb ₂ O ₃	0.00	0.01	0.09	0.00	0.00	0.00	0.00	0.00	0.13	0.09	0.00	0.00
Fe ₂ O ₃	0.42	0.96	0.49	0.44	0.99	1.32	1.15	0.00	0.58	1.14	1.14	0.30
FeO	13.84	12.58	13.39	12.82	12.68	11.77	13.01	14.40	9.03	8.62	13.11	13.93
MnO	1.97	3.56	2.50	2.89	2.71	3.33	3.37	3.53	6.82	7.05	3.04	3.26
PbO	0.12	0.16	0.12	0.13	0.08	0.12	0.14	0.00	0.13	0.01	0.15	0.00
Total	99.35	99.27	99.40	98.44	98.55	98.15	98.31	96.96	99.60	98.90	98.99	99.22
W ⁶⁺	0.006	0.026	0.020	0.017	0.015	0.018	0.018	0.035	0.019	0.029	0.018	0.022
Nb ⁵⁺	0.844	1.043	0.900	0.873	0.873	0.882	1.147	1.368	0.916	0.938	1.067	1.182
Ta ⁵⁺	1.095	0.818	0.981	1.025	0.999	0.969	0.765	0.546	0.990	0.948	0.839	0.746
Ti ⁴⁺	0.052	0.112	0.101	0.092	0.109	0.128	0.057	0.073	0.071	0.078	0.064	0.059
Zr ⁴⁺	0.012	0.011	0.014	0.007	0.016	0.015	0.004	0.000	0.011	0.001	0.006	0.000
Sn ⁴⁺	0.001	0.006	0.005	0.006	0.005	0.006	0.003	0.002	0.002	0.003	0.003	0.001
Sum B	2.010	2.016	2.021	2.020	2.017	2.017	1.994	2.024	2.009	1.996	1.997	2.009
U ⁴⁺	0.001	0.002	0.003	0.001	0.001	0.001	0.001	0.000	0.001	0.001	0.000	0.001
Y ³⁺	0.002	0.001	0.000	0.002	0.002	0.003	0.002	0.000	0.005	0.001	0.004	0.000
Sb ³⁺	0.000	0.000	0.003	0.000	0.000	0.000	0.000	0.000	0.004	0.006	0.000	0.000
Fe ³⁺	0.024	0.049	0.026	0.024	0.056	0.071	0.060	0.000	0.033	0.060	0.060	0.015
Fe ²⁺	0.839	0.720	0.793	0.773	0.757	0.701	0.745	0.780	0.538	0.600	0.758	0.787
Mn ²⁺	0.122	0.206	0.152	0.177	0.165	0.200	0.195	0.194	0.407	0.419	0.178	0.187
Pb ²⁺	0.002	0.003	0.002	0.002	0.002	0.002	0.003	0.000	0.003	0.000	0.003	0.000
Sum A	0.990	0.981	0.979	0.979	0.983	0.979	1.006	0.974	0.991	1.086	1.003	0.990
Sum of cations	3.000	3.000	3.000	3.000	3.000	3.000	3.000	2.998	3.000	3.000	3.000	2.999
Mn/(Mn + Fe)	0.127	0.222	0.161	0.186	0.179	0.222	0.207	0.199	0.431	0.411	0.190	0.192
Ta/(Ta + Nb)	0.565	0.440	0.522	0.540	0.534	0.523	0.400	0.285	0.519	0.503	0.440	0.387

Mineral formulae based on 3 cations and valence calculation

(A) central zone, (B) intermediate zone B, (C) intermediate zone C, (D) outer zone, (S) subsolidus patches, (L) late veins

5. Discussion and conclusions

5.1. Compositional evolution of columbite–tantalite + ferrotapiolite

The examined grains of columbite–tantalite + ferrotapiolite show quite complex primary compositional trends (Fig. 3), disregarding simple internal structure of the pegmatite, and simple mineral assemblages almost free of Fe, Mn, Mg-bearing primary minerals. The central zone (A) of complexly zoned CGM crystals yielded rather homogeneous columbite-(Fe) to tantalite-(Fe) compositions that straddle the boundary of the tapiolite–tantalite immiscibility field (Černý et al. 1992). The CGM of the intermediate zone B (“tapiolite zone” of Fig. 3) generally reveal higher Ta/(Ta + Nb) = 0.50–0.62 and Mn/(Mn + Fe) = 0.15–0.39 than the previous (A) zone (Fig. 3). The composition of the tapiolite–tantalite pair is very

similar to that from the Moravany nad Váhom pegmatite, Slovakia (Novák et al. 2000). The next intermediate zone C has tantalite-(Fe) of an almost identical composition and only columbite-(Fe) from the outer zone (D) exhibits evident decrease in Ta/(Ta + Nb) whereas Mn/(Mn + Fe) is comparable to the other zones. Chiefly in the intermediate zones B and C are present several remarkable Mn-enriched patches (or veinlets) of columbite-(Fe) to tantalite-(Fe) with Mn/(Mn + Fe) of 0.39–0.42, i.e. distinctly higher than in any other zones (Fig. 2a–b). They may represent products of early subsolidus reactions, evidently preceding late veinlets present in all zones and showing only minor Mn enrichment (Fig. 3).

Such a complicated zoning of Nb–Ta oxide minerals in relatively simple pegmatite seems to reflect not only changes in P–T conditions (mainly decrease in temperature) but also crystal-structural constraints of the relevant minerals. The existence of the tapiolite–tantalite immisci-

bility field (Černý et al. 1992) resulted in the formation of the tantalite-(Fe) + ferrotapiolite pair instead of a single CGM during increasing Ta/(Ta + Nb) in the parental pegmatite melt. This demonstrates a significant role of crystal-structural constraints on the chemical composition of the oxide minerals in the system Fe–Mn–Nb–Ta \pm Ti, W, Sn.

The melt that produced the Šejby granitic pegmatite was relatively rich in Ta at initial magmatic stage, as indicated by the crystallization of the Ta-rich central (A) and the intermediate (B) zones. However, columbite-(Fe) to tantalite-(Fe) from intermediate zone (C) shows a relatively slight decrease in Ta and this trend is intensified by the crystallization of columbite-(Fe) from the outer zone (D). Moreover, the late patchy parts and veinlets show lower Ta/(Ta + Nb) than the most evolved magmatic CGM from the zone (B). These late domains were probably connected with late-magmatic or early subsolidus stage of the Šejby pegmatite evolution.

The observed decrease in Ta/(Ta + Nb) of the CGM is opposite to common magmatic trend, whereby this value increases due to extended fractionation and precipitation of more incompatible and soluble Ta-rich compositions (Černý et al. 1985, 1986; Černý 1989; Linnen and Keppler 1997; Linnen 1998). However, comparable evolution has been observed in some granitic pegmatites, commonly associated with late-magmatic or early subsolidus

albitization and with partial dissolution–reprecipitation of early Nb–Ta oxide minerals (e.g. Uher et al. 1994; Wang et al. 1997; Tindle and Breaks 2000; Novák et al. 2003; Rao et al. 2009; Chudík et al. 2011; Neiva et al. 2015). This Nb-enrichment and reversal of Nb/Ta values of CGM can be attributed to the late-magmatic addition of relatively Nb-rich melt or complex fluid–melt interactions (Černý et al. 1986; London 2008). Alternatively, the reverse compositional trend can be explained by crystallization of CGM from a late-magmatic Na-rich

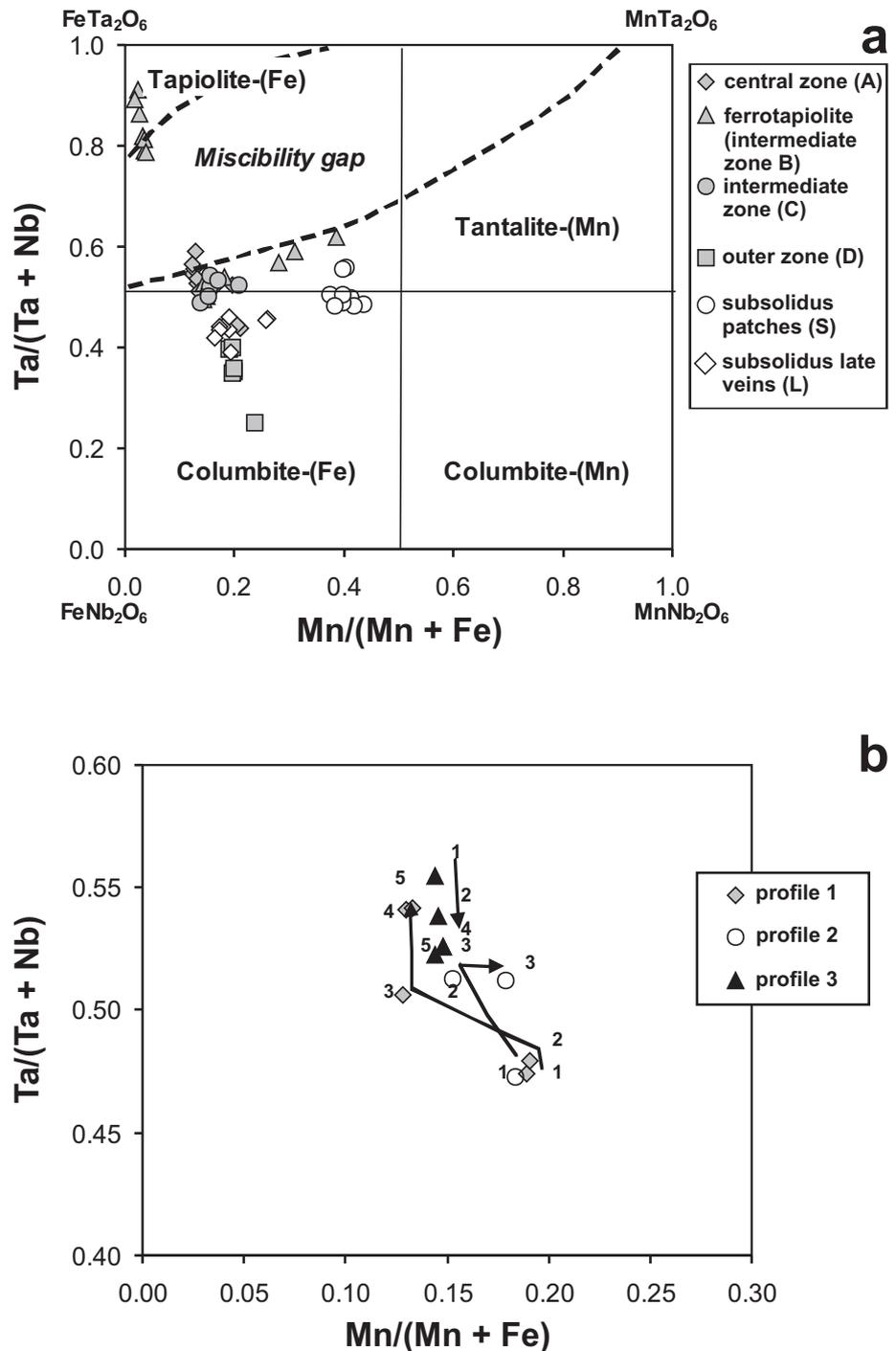


Fig. 3 Composition and evolutionary trends of Nb–Ta oxide minerals from the Šejby pegmatite. **a** – The columbite quadrilateral diagram showing compositional variations of various CGM primary zones (A to D) and secondary domains (S and L) and associated tapiolite-(Fe); **b** – Representative compositional profiles reflecting Mn/(Mn + Fe) and Ta/(Ta + Nb) ratios in the studied CGM. Positions of the point analyses in the profiles are illustrated in Fig. 1e (profiles 1 and 2) and 1f (profile 3).

Tab. 3. Representative chemical compositions (in wt. %) and mineral formulae (in apfu) of tapiolite-(Fe) from the Šejby pegmatite

Analysis #	1	2	3	4	5
WO ₃	0.14	0.21	0.00	0.02	0.02
Nb ₂ O ₅	11.40	10.10	7.20	5.71	4.65
Ta ₂ O ₅	70.74	73.10	74.87	77.59	78.15
TiO ₂	1.86	1.26	1.71	1.66	1.69
ZrO ₂	0.24	0.00	0.09	0.09	0.08
SnO ₂	0.28	0.22	0.31	0.25	0.18
UO ₂	0.04	0.02	0.00	0.00	0.00
Sc ₂ O ₃	0.04	0.05	0.00	0.04	0.02
Y ₂ O ₃	0.04	0.00	0.07	0.00	0.09
As ₂ O ₃	0.01	0.00	0.02	0.03	0.00
Sb ₂ O ₃	0.09	0.00	0.00	0.00	0.06
Bi ₂ O ₃	0.00	0.00	0.04	0.00	0.00
Fe ₂ O ₃	0.68	0.06	0.38	0.46	0.72
FeO	13.66	14.15	13.54	13.65	13.27
MnO	0.54	0.42	0.37	0.25	0.31
MgO	0.02	0.03	0.00	0.01	0.00
CaO	0.01	0.00	0.00	0.00	0.00
PbO	0.03	0.00	0.00	0.00	0.03
Total	99.83	99.62	98.60	99.76	99.26
W ⁶⁺	0.003	0.004	0.000	0.000	0.000
Nb ⁵⁺	0.400	0.362	0.263	0.208	0.172
Ta ⁵⁺	1.495	1.575	1.648	1.705	1.735
Ti ⁴⁺	0.109	0.075	0.104	0.101	0.104
Zr ⁴⁺	0.009	0.000	0.003	0.004	0.003
Sn ⁴⁺	0.009	0.007	0.010	0.008	0.006
U ⁴⁺	0.001	0.000	0.000	0.000	0.000
Sc ³⁺	0.003	0.003	0.000	0.003	0.001
Y ³⁺	0.002	0.000	0.003	0.000	0.004
As ³⁺	0.001	0.000	0.001	0.002	0.000
Sb ³⁺	0.003	0.000	0.000	0.000	0.002
Bi ³⁺	0.000	0.000	0.001	0.000	0.000
Fe ³⁺	0.040	0.003	0.023	0.028	0.044
Fe ²⁺	0.888	0.937	0.917	0.923	0.906
Mn ²⁺	0.035	0.028	0.025	0.017	0.021
Mg ²⁺	0.002	0.004	0.000	0.001	0.000
Ca ²⁺	0.001	0.000	0.000	0.000	0.000
Pb ²⁺	0.001	0.000	0.000	0.000	0.001
Sum of cations	3.000	3.000	3.000	3.000	3.000
Mn/(Mn + Fe)	0.037	0.029	0.026	0.018	0.022
Ta/(Ta + Nb)	0.789	0.813	0.862	0.891	0.910

Mineral formulae based on 3 cations and valence calculation

Contents of P, Th and Zn were below detection limits

melt, significantly depleted in Ta with the respect to Nb after crystallization of a relatively large amount of Ta-rich CGM, tapiolite-(Fe) and ferrowodginite of the first magmatic generation (Chudík et al. 2011).

5.2. Role of associated minerals

Only a few authors have reported chemical influences of various Fe- and Mn-bearing minerals on the composition of the associated CGM. Mulja et al. (1996) explained a progressive increase in Ta/(Ta + Nb) at a constant Mn/

(Mn + Fe) by the contemporaneous crystallization of CGM with garnet at the Lacorne pegmatites, Quebec (Canada). In the Tanco pegmatite deposit, Manitoba, Canada, the Fe–Mn composition of the melt was controlled by the co-precipitation of Fe-rich tourmaline (schorl to elbaite) with CGM, which led to an increase of Mn/(Mn + Fe) ratio in associated columbite–tantanite (Van Lichtervelde et al. 2006). Crystallization of abundant Mn-rich fluorapatite could have depleted the melt in Mn and prevent substantial increase of the Mn/(Mn + Fe) ratio in associated columbite–tantanite in highly fractionated, P, F-rich granite at Podlesí, Czech Republic (Breiter et al. 2007).

Although the above-mentioned Fe, Mn-bearing minerals may play a significant role in Fe–Mn fractionation, the assemblage CGM + pyrite does not appear to have any influence on Fe–Mn fractionation during primary crystallization of the Šejby pegmatite. The Mn/Fe ratio of the Nb–Ta minerals did not change significantly due to the general scarcity of other Mn-bearing minerals such as garnet, tourmaline or phosphates. Only Mn-rich fluorapatite with up to 6.6 wt. % MnO (≤ 0.46 apfu Mn; Pavlíček et al. 2009) could theoretically have influenced the Mn/Fe ratio of Nb–Ta phases. However, direct (or close) paragenetic relationships between apatite and Nb–Ta oxide minerals have not been observed and apatite is rather rare. Such a conclusion is supported by negligible compositional changes during magmatic CGM growth (Figs 2–3); even their primary oscillatory zoning was not disrupted (Fig. 1). Moreover, results of the chemical analyses in profiles close to pyrite grains show that there is no extensive enrichment in Mn, which would indicate preferential partitioning of Fe into pyrite over CGM (Fig. 2a, c). Consequently, crystallization of pyrite did not cause any noticeable Mn-enrichment disregarding expected strong Fe-partitioning into pyrite over CGM.

Late enrichment in Nb is evident in late veinlets in primary columbite–tantanite from both zones (Fig. 1b, 2a–b). Textural features show that the formation of veinlets and their fillings by the latest generation of CGM was the terminating event in the evolution of the Nb–Ta oxide minerals in the Šejby pegmatite. Very low pH of fluids is required for the origin of jarosite-group minerals (e.g. Welch et al. 2008). Thin veinlets and fillings located close to the jarosite pseudomorphs (Fig. 2c) may be related to the pyrite replacement by jarosite and indicate higher mobility of Ta relative Nb at such acidic conditions. However, the role of pH in low-T fluids for CGM compositions is worthy of future study (Wood 2005).

5.3. Comparison to other granitic pegmatites of the Moldanubian Zone

Mineral assemblages of Nb–Ta–Sn–Ti oxide minerals from two major leucogranite–pegmatite occurrences (Ho-

molka, Šejby) and adjacent placers in the Moldanubian Zone of the southern Bohemian Massif are rather variable (Novák et al. 1994; Frýda and Breiter 1995; Uher 1998; Pavlíček et al. 2009).

A more primitive, Nb, Ta-poor and Ti-rich mineral assemblage including cassiterite, niobian and tantalite rutile, ilmenite, pseudobrookite and pseudorutile was described in the Homolka leucogranites and marginal pegmatites (Novák et al. 1994; Uher 1998). Ixiolite is present only as inclusions in niobian rutile whereas individual grains of columbite-(Fe) to tantalite-(Fe) are rare and more evolved CGM members (columbite-(Mn) and tantalite-(Mn)) and tapiolite-(Fe) are absent.

Conversely, chemical composition of CGM and tapiolite-(Fe) from the examined Šejby pegmatite documented in previous papers (Novák et al. 1994; Frýda and Breiter 1995; Pavlíček et al. 2009; Welser and Zikeš 2013) and especially in this study (Fig. 3a) shows distinct Nb, Ta-enrichment and higher fractionation degree of the beryl–columbite granitic pegmatites in comparison to the leucogranites and their marginal pegmatite facies. The only similar beryl–columbite pegmatite related to the Eisgarn granite with primary magmatic hurlbutite [$\text{CaBe}_2(\text{PO}_4)_2$] is known from Kostelní Vydří near Telč (Novák 1994; Cempírek et al. 1999). Here, columbite-(Fe) shows Nb/Ta fractionation [$\text{Ta}/(\text{Ta} + \text{Nb}) = 0.27\text{--}0.37$] but almost constant Mn/(Mn + Fe) ratio (0.07–0.10) resembling the studied Šejby pegmatite.

By comparison, compositional trends in columbite–tantalite and associated Nb, Ta-oxide minerals from tourmaline-rich pegmatites of the Moldanubian Zone varying from beryl (beryl–columbite subtype) to complex (lepidolite, elbaite, petalite subtype) types, are entirely different (see Novák and Černý 1998, 2001). Less evolved beryl–columbite pegmatites with niobian (tantalite) rutile and columbite exhibit significant Fe/Mn fractionation, whereas Ta/(Ta + Nb) are low and rather constant (e.g., Černý et al. 2000, 2007). Complex pegmatites typically contain columbite-(Mn) with very high Mn/(Mn + Fe) but commonly low Ta/(Ta + Nb) (Novák and Černý 1998, 2001). Significant role of associated abundant tourmaline (schorl–foitite–dravite) controlling the activity of Fe is evident because it was preferentially incorporated into tourmaline and associated CGM are typically Mn-rich (e.g., London et al. 2001; Van Lichtervelde et al. 2006).

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