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Original paper

Pegmatitic Nb-Ta oxide minerals in alluvial placers from Limbach, Bratislava Massif, Western Carpathians, Slovakia: compositional variations and evolutionary trend

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Niobium-tantalum mineral assemblage of granitic pegmatite origin was found in alluvial placers near Limbach, the Bratislava granitic massif, Malé Karpaty Mountains, Central Western Carpathians, southwest Slovakia. The most widespread mineral is ferrocolumbite to ferrotantalite, rarely manganocolumbite to manganotantalite I [at. Mn/(Mn + Fe) = 0.17–0.52 and Ta/(Ta + Nb) = 0.19–0.70] shows primary magmatic, fine to coarse, regular oscillatory zoning with an evolutionary trend indicating a moderate degree of fractionation, analogous to beryl–columbite subtype of rare-element granitic pegmatites. On the contrary, irregular oscillatory and patchy zoning of ferrocolumbite to manganotantalite II [Mn/(Mn + Fe) = 0.17–0.66, Ta/(Ta + Nb) = 0.16–0.81] together with precipitation of anhedral Ta-rich intergrowths and inclusions of ferrotapiolite [Mn/(Mn + Fe = 0.05–0.07, Ta/(Ta + Nb) = 0.87–0.93], Ta>Nb-rich rutile [Mn/(Mn + Fe) = 0.02–0.03, Ta/(Ta + Nb) = 0.80–0.86], Sn-rich ixiolite [Mn/(Mn + Ta) = 0.40–0.41, Ta/(Ta + Nb) = 0.81] and uraninite + uranmicrolite [Ta/(Ta + Nb) = 0.81–0.94] indicates their subsolidus origin.

Keywords: columbite–tantalite, ferrotapiolite, ixiolite, Ta-rich rutile, uranmicrolite, pegmatite.
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1. Introduction

Niobium-tantalum oxide minerals, especially columbite and the ixiolite group, the tapiolite series, and Nb, Ta-rich rutile belong to the most characteristic accessory phases of rare-element granitic pegmatites and highly fractionated granites. Their compositional variations within discrete crystals, host-rock zones, localities as well as geological units (provinces) strongly depend on several factors, such as temperature, fractionation level, local composition, pH, fluid activity (especially F, H_2O and B), Nb vs. Ta solubility in melt, and crystallo-chemical properties. Consequently, they can serve as sensitive genetic indicators (e.g. Černý et al. 1985, 1986; Černý and Ercit 1989; Linnen and Keppler 1997; Linnen 1998; Tindle and Breaks 2000; Novák et al. 2000, 2003).

The genetic interpretation of Nb-Ta minerals in secondary geological occurrences (for example in elluvial to alluvial deposits), where information about the parental pegmatite or granite rock are lost, is less straightforward. However, detailed knowledge of characteristic textural, paragenetic, and compositional relations of the Nb-Ta phases in such a secondary geological occurrence could serve as a useful tool for interpretation of the primary character and genetic aspects of their host rocks. Our description of Nb-Ta oxide mineralization in alluvial placers near Limbach in the Bratislava Granitic Massif, Western Carpathians, is one example of such a study.

2. Regional geology

The niobium-tantalum oxide minerals were obtained from the heavy-mineral fraction of recent alluvial placers of the Limbach Brook, at Slnečné Valley in the Malé Karpaty Mountains, 3 km north of the village of Limbach, *c.* 15 km north-northeast of Bratislava. The Limbach Brook and its tributaries drain the Staré Mesto granitic body, a part of the Bratislava Granitic Massif (BGM) and also the surrounding metapelites–metapsammites, an area around 4 km^2 in size (Fig. 1). The BGM represents orogenic, peraluminous calc-alkaline granitic plutonic suite with S-type affinity (e.g. Cambel and Vilinovič 1987; Petrík et al. eds 2001). The age of the BGM is Hercynian, Lower Carboniferous, *c.* 350 Ma on the basis of whole-rock Rb-Sr isochron (Bagdasaryan et al. 1982) and electron-microprobe U-Th-Pb monazite dating (Uher et al. unpublished data). The granitic rocks exhibit distinct intrusive and thermal metamorphic contact with adjacent Lower Paleozoic metapelites to metapsammites

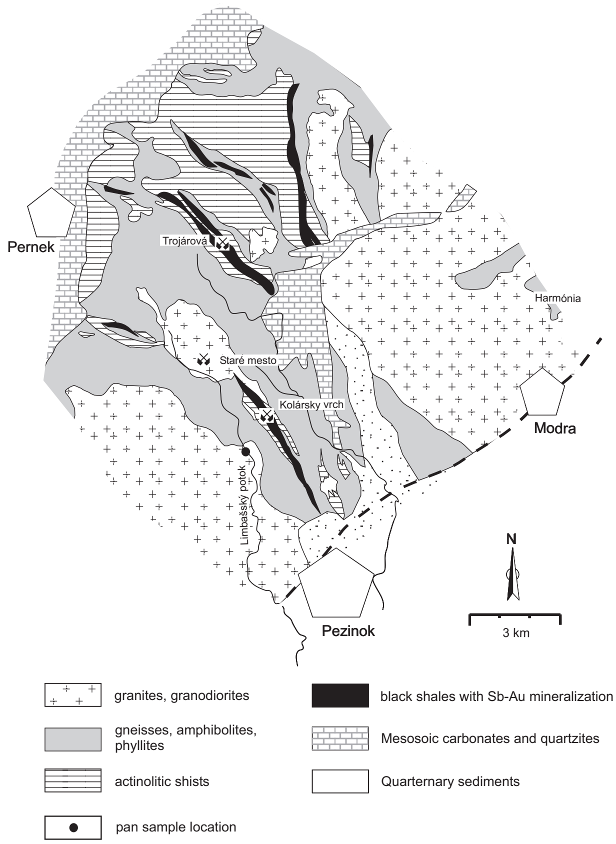

Fig. 1 Generalized geological map of the Limbach area, Malé Karpaty Mountains (modified from Bakos and Chovan eds 2004).

of micaschist to paragneiss character, metamorphosed in amphibolite facies at P ≤ 300–350 MPa and T ≤ 550 °C, which corresponds to a depth of granite emplacement of approximately 12 to 14 km (Korikovsky et al. 1984). Due to the peri-plutonic thermal metamorphism around the BGM, the following metamorphic zones developed in the country-rock metapelites: biotite, garnet, staurolite-chlorite, and staurolite-sillimanite (Korikovsky et al. 1984). The fundamental rock types of the BGM are biotite granodiorites to muscovite-biotite monzogranites, less frequently leucocratic two-mica to muscovite syenogranites and small bodies of biotite-amphibole diorites (Cambel and Vilinovič 1987). The granitic rocks are usually medium-grained and equigranular, rarely porphyritic with K-feldspar phenocrysts. Gold from hydrothermal quartz veins in granites has been exploited from a small deposit in the Staré Mesto area (Bakos and Chovan eds 2004).

Dikes of granitic pegmatites and aplites are widespread in the BGM and also in the Limbach area. The pegmatite dikes, usually up to 1–2 m thick, commonly show zoned internal structure with graphic, blocky K-feldspar, coarse-grained alkali feldspar–quartz–muscovite ± biotite and blocky quartz core zones, locally with late fan-like muscovite and saccharoidal albite-rich replacement zones (Dávidová 1970, 1978). The most fractionated granitic pegmatites of the BGM contain accessory beryl and columbite-tantalite group minerals (Uher et al. 1994) and they could be classified as belonging to the LCT family, beryl-columbite subgroup of the rare-element class of granitic pegmatites (*sensu* Černý and Ercit 2005).

3. Analytical methods

Electron-microprobe analyses of Nb-Ta oxide minerals were carried out in the wavelength-dispersion mode using a Cameca SX-100 instrument at the State Geological Survey of Slovak Republic, Bratislava, with a beam diameter of 1–2 μm and an accelerating voltage of 15 kV, a sample current of 20 nA, and a counting time of 20 to 40 s. The following standards were used: scheelite (W*M*β), $LiNbO_3$ (Nb*L*α), $LiTaO_3$ (Ta*M*α), TiO_2 (Ti*K*α), SnO_2 (Sn*L*α), ZrO_2 (Zr*L*α), UO_2 (U*M*β), $ScPO_4$ (Sc*K*α), YPO_4 (Y*L*α), metallic Sb (Sb*L*α), hematite (Fe*K*α), rhodonite (Mn*K*α), MgO (Mg*K*α), wollastonite (Ca*K*α), willemite (Zn*K*α), and PbS (Pb*M*α). For data processing, PAP corrections were used.

4. Results

The Nb-Ta oxide minerals were identified as rare black prismatic crystals and their broken fragments up to 4 mm in size from the heavy mineral fraction of the sandy alluvium of the Limbach Brook. The crystals are relatively fresh with metallic to semi-metallic luster, without any rounding or other features indicative of a longer transport. The heavy mineral assemblage consists of garnet (almandine–spessartine), staurolite, ilmenite, magnetite, zircon, apatite, monazite and gold.

Minerals of the columbite-tantalite group are the most widespread Nb-Ta phases. Two distinct textural, compositional and genetic types can be distinguished (Figs 2a–f):

(1) Large crystals and fragments (up to 4 mm) with regular fine to coarse oscillatory zoning, locally unzoned or with diffuse zoning (***Ct I***, Fig. 2a). Compositionally they correspond to ferrocolumbite, rarely ferrotantalite, manganocolumbite, and manganotantalite with broad compositional variations (atomic ratios): Mn/(Mn + Fe) = 0.17-0.52 and Ta/(Ta + Nb) = 0.19–0.70 (Tab. 1, Figs 3 and 4). The Ti contents are generally low (0.4–1.3 wt. % TiO_2). Locally, Ct I shows slightly increased Zr concentrations (0.05 to 0.9 wt. % ZrO_2). The contents of other elements (W, Sn, U, Sb and Zn) are negligible.

(2) Zones within columbite-tantalite crystals and their fragments with various irregular zoned textures (Ct II).

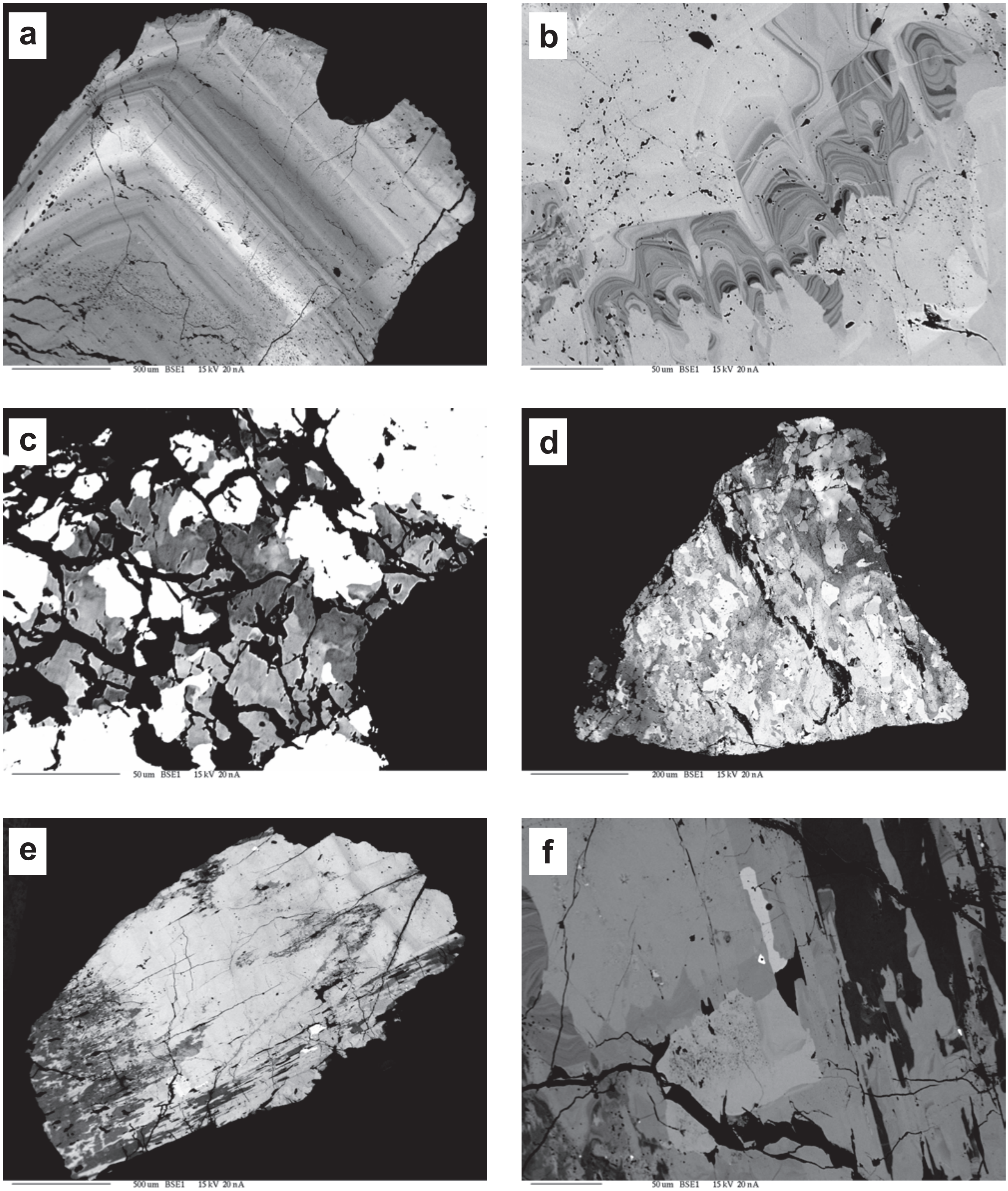

Fig. 2 BSE images of Nb-Ta minerals from Limbach. **a** – Ferrocolumbite (Ct I) with regular fine oscillatory zoning. **b** – Irregular bended fine oscillatory zoning of ferrocolumbite (Ct IIa) replacing surrounding Ct I. **c** – Irregular mosaic-like intergrowths of ferrocolumbite-ferrotantalite (Ct IIb, white) with Ta>Nb-rich rutile (dark grey). **d** – Irregular mosaic-like intergrowths of ferrotantalite-manganotantalite (Ct IIc, grey) with ferrotapiolite (white). **e** – Irregular patchy zoning of ferrocolumbite (Ct IId, dark grey) replacing Ct I (pale grey). **f** – Sn-rich ixiolite (pale grey) and uraninite (white) inclusions in Ct IId (grey).

Tab. 1 Representative compositions of columbite–tantalite (Fe-col: ferrocolumbite, Mn-col: manganocolumbite, Fe-tan: ferrotantalite, Mn-tan: manganotantalite) of type I and IIa to IId, ferrotapiolite (Ft) and Sn-rich ixiolite (Ix) from Limbach (in wt. %).

Mineral	Fe-col	Mn-col	Fe-col	Fe-tan	Mn-tan	Fe-tan	Ft	Ix
Type	Ct I	Ct I	Ct IIa	Ct IIb	Ct IIc	Ct IId		
Anal.#	B6.1	C6.3	B8.10	D1.8	D9b9	C5.12	C5.2	C5.8
WO_3	0.11	0.10	0.00	1.96	0.00	0.26	0.01	0.12
Nb_2O_5	49.58	34.69	42.69	24.96	10.35	28.74	6.08	9.05
Ta_2O_5	28.71	46.21	35.82	52.18	72.85	53.24	77.10	65.19
TiO_2	0.80	0.77	0.82	2.78	1.05	0.30	0.44	0.35
ZrO_2	0.47	0.52	0.19	0.30	0.51	0.09	0.18	1.63
SnO_2	0.03	0.08	0.03	0.10	0.18	0.09	0.80	9.41
UO_2	0.07	0.25	0.05	0.18	0.10	0.03	0.00	0.09
Sc_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Y_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sb_2O_3	0.06	0.03	0.04	0.06	0.06	0.05	0.08	0.09
Fe_2O_3 *calc.*	1.69	1.02	1.91	1.64	0.20	0.87	0.65	1.19
FeO	11.68	7.40	13.29	10.39	4.84	8.29	13.00	6.98
MnO	5.44	8.89	3.01	4.34	9.53	7.66	0.83	5.37
MgO	0.00	0.00	0.01	0.14	0.00	0.00	0.00	0.00
CaO	0.01	0.01	0.00	0.02	0.03	0.01	0.02	0.04
ZnO	0.05	0.00	0.07	0.01	0.00	0.01	0.00	0.05
PbO	0.25	0.11	0.23	0.06	0.02	0.10	0.02	0.04
Total	98.95	100.08	98.16	99.12	99.72	99.74	99.21	99.60
Formulae based on 6 oxygen atoms, 3 cations and Fe^{3+}/Fe^{2+} charge-balancing								
W	0.002	0.002	0.000	0.036	0.000	0.005	0.000	0.002
Nb	1.434	1.076	1.286	0.803	0.370	0.928	0.225	0.322
Ta	0.499	0.862	0.649	1.009	1.566	1.034	1.720	1.396
Ti	0.038	0.040	0.041	0.149	0.062	0.016	0.027	0.021
Zr	0.015	0.017	0.006	0.010	0.020	0.003	0.007	0.063
Sn	0.001	0.002	0.001	0.003	0.006	0.003	0.026	0.296
Sum B	1.989	1.999	1.983	2.010	2.024	1.989	2.005	2.100
U	0.001	0.004	0.001	0.003	0.002	0.000	0.000	0.002
Sc	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Y	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sb	0.002	0.001	0.001	0.002	0.002	0.001	0.003	0.003
Fe^{3+}	0.081	0.053	0.096	0.088	0.012	0.047	0.040	0.071
Fe^{2+}	0.625	0.425	0.741	0.618	0.320	0.495	0.892	0.460
Mn	0.295	0.517	0.170	0.262	0.638	0.464	0.058	0.358
Mg	0.000	0.000	0.001	0.015	0.000	0.000	0.000	0.000
Ca	0.001	0.001	0.000	0.002	0.003	0.001	0.002	0.003
Zn	0.002	0.000	0.003	0.001	0.000	0.001	0.000	0.003
Pb	0.004	0.002	0.004	0.001	0.000	0.002	0.000	0.001
Sum A	1.011	1.003	1.017	0.992	0.977	1.011	0.995	0.901
Sum A+B	3.000	3.002	3.000	3.002	3.001	3.000	3.000	3.001
Mn/(Mn+Fe)	0.29	0.52	0.17	0.27	0.66	0.46	0.06	0.40
Ta/(Ta+Nb)	0.26	0.44	0.34	0.56	0.81	0.53	0.88	0.81

Tab. 2 Representative compositions of Ta>Nb rutile (Rt) from Limbach (in wt. %).

Mineral	Rt	Rt	Rt
Anal.#	D1.4	D1.3	D1.7
WO_3	0.00	0.07	0.05
Nb_2O_5	6.57	4.65	3.86
Ta_2O_5	44.32	42.16	40.86
TiO_2	38.01	43.14	45.46
ZrO_2	0.20	0.05	0.07
SnO_2	0.34	0.24	0.34
UO_2	0.00	0.00	0.02
Sc_2O_3	0.00	0.00	0.00
Y_2O_3	0.00	0.00	0.00
Sb_2O_3	0.06	0.03	0.06
Fe_2O_3 *calc.*	2.39	1.29	2.05
FeO	7.65	7.37	6.56
MnO	0.20	0.15	0.17
MgO	0.00	0.00	0.00
CaO	0.02	0.01	0.02
ZnO	0.00	0.00	0.00
PbO	0.04	0.03	0.01
Total	99.80	99.19	99.53
Formulae based on 2 oxygen atoms, 1 cation and Fe^{3+}/Fe^{2+} charge-balancing			
W	0.000	0.000	0.000
Nb	0.057	0.039	0.032
Ta	0.231	0.215	0.204
Ti	0.547	0.607	0.628
Zr	0.002	0.000	0.001
Sn	0.003	0.002	0.002
U	0.000	0.000	0.000
Sc	0.000	0.000	0.000
Y	0.000	0.000	0.000
Sb	0.000	0.000	0.000
Fe^{3+}	0.034	0.018	0.028
Fe^{2+}	0.122	0.115	0.101
Mn	0.003	0.002	0.003
Mg	0.000	0.000	0.000
Ca	0.000	0.000	0.000
Zn	0.000	0.000	0.000
Pb	0.000	0.000	0.000
Sum	0.999	0.998	0.999
Mn/(Mn+Fe)	0.02	0.01	0.02
Ta/(Ta+Nb)	0.80	0.85	0.86

Tab. 3 Representative compositions of uranmicrolite (Umc) to microlite (Mcr) from Limbach (wt. %).

Mineral	Umc	Umc	Umc	Mcr
Anal.#	B8.1	B8.2	B8.3	D9b10
WO_3	0.00	0.00	0.31	0.00
Nb_2O_5	6.99	6.55	7.77	2.82
Ta_2O_5	61.89	60.19	57.09	70.61
TiO_2	2.51	2.81	2.11	1.52
ZrO_2	0.00	0.12	0.06	0.18
SnO_2	0.14	0.16	0.07	0.17
UO_2	13.05	15.48	19.34	8.63
Sc_2O_3	0.00	0.00	0.00	0.00
Y_2O_3	0.00	0.00	0.00	0.00
Sb_2O_3	0.07	0.06	0.19	0.31
FeO	0.32	0.25	0.43	4.90
MnO	0.11	0.05	0.07	0.46
MgO	0.00	0.00	0.00	0.00
CaO	6.92	6.34	5.69	4.61
ZnO	0.00	0.00	0.00	0.01
PbO	0.23	0.20	0.25	0.20
H_2O *calc.*	1.64	1.61	1.55	1.63
Total	93.87	93.82	94.93	96.05
Formulae based on B = 2 cations and 1 OH anion				
W	0.000	0.000	0.008	0.000
Nb	0.289	0.275	0.339	0.117
Ta	1.538	1.523	1.497	1.770
Ti	0.173	0.197	0.153	0.105
Zr	0.000	0.005	0.003	0.008
Sum *B*	2.000	2.000	2.000	2.000
Sn	0.005	0.006	0.003	0.006
U	0.265	0.320	0.415	0.177
Sc	0.000	0.000	0.000	0.000
Y	0.000	0.000	0.000	0.000
Sb	0.003	0.002	0.008	0.012
Fe^{2+}	0.024	0.019	0.035	0.378
Mn	0.009	0.004	0.006	0.036
Mg	0.000	0.000	0.000	0.000
Ca	0.678	0.632	0.588	0.455
Zn	0.000	0.000	0.000	0.001
Pb	0.006	0.005	0.006	0.005
Sum *A*	0.990	0.988	1.061	1.070
O	6.675	6.715	6.908	6.701
OH	1.000	1.000	1.000	1.000
% U in *A*-site	26.77	32.39	39.11	16.54
Ta/(Ta+Nb)	0.84	0.85	0.82	0.94

Four textural and paragenetic patterns can be distinguished in Ct II (Tab. 1, Figs 2b–f and 3): ***Ct IIa*** forms irregular bended zones of ferrocolumbite (up to 0.3 mm long), with fine oscillatory zoning, which replaces Ct I. The zoning is caused by Nb-Ta variations; Mn/(Mn + Fe) = 0.16–0.19 and Ta/(Ta + Nb) = 0.16–0.34. ***Ct IIb*** occurs as irregular patchy intergrowths of ferrocolumbite–ferrotantalite with Ta-rich rutile (*c.* 1 mm in size); Mn/(Mn + Fe) = 0.19–0.27 and Ta/(Ta + Nb) = 0.49–0.57. Ct IIb shows increased Ti and W contents (up to 2.3 wt. % TiO_2 and 0.7 wt. % WO_3). ***Ct IIc*** forms irregular mosaic intergrowths of ferrotantalite-manganotantalite with ferrotapiolite (*c.* 0.6 mm

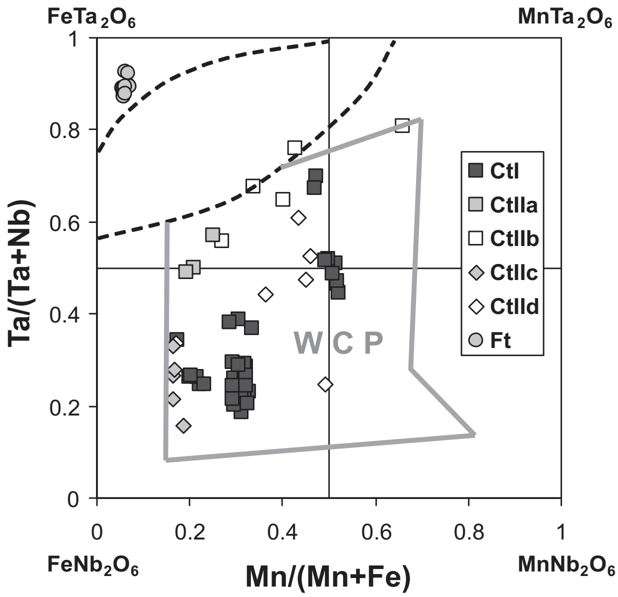

Fig. 3 Quadrilateral diagram (atomic proportions) of columbite-tantalite types (Ct I, Ct IIa to IId) and ferrotapiolite (Ft) from Limbach. Field of columbite–tantalite compositions from the West-Carpathian granitic pegmatites (WCP) is shown for comparison (Uher et al. 1994, 1998; Uher and Benko 1997; Uher 2000; Novák et al. 2000, unpublished data of P. U.).

in size); Mn/(Mn + Fe) = 0.34–0.66 and Ta/(Ta + Nb) = 0.65–0.81. ***Ct IId*** occurs as irregular patchy zones of ferrocolumbite to ferrotantalite (0.2–0.9 mm), mainly along cracks and rims of Ct I; Mn/(Mn + Fe) = 0.43–0.49 and Ta/(Ta + Nb) = 0.24–0.61 (Tab. 1, Figs 3 and 4).

Despite textural variability and locally specific compositions, all types of Ct II show a chemistry generally similar to Ct I with both large variations in Mn/Fe as well as Ta/Nb ratio: Mn/(Mn + Fe) = 0.17–0.66 and Ta/(Ta + Nb) = 0.16–0.81 (Tab. 1, Figs 3 and 4).

Ferrotapiolite forms anhedral to subhedral intergrowths with Ct IIc, 60 to 100 μm in size (Fig. 2d). The ferrotapiolite shows relatively consistent compositions with Mn/(Mn + Fe) = 0.05–0.07 and Ta/(Ta + Nb) = 0.87–0.93. Titanium and Sn contents are relatively low, 0.3 to 1.4 wt. % TiO_2 and 0.3 to 0.8 wt. % SnO_2, respectively (Tab. 1, Figs 3 and 4).

The Ta>Nb-rich rutile (strüverite) occurs as anhedral irregular mosaic intergrowths with Ct IIb, up to 200 μm across (Fig. 2c). Despite their irregular zoning due to some Nb/Ta variations, strüverite is compositionally relatively uniform with Mn/(Mn + Fe) = 0.01–0.03 and Ta/(Ta + Nb) = 0.80–0.84, without increased contents of any other elements (Tab. 2, Figs 3 and 4).

In one case a Sn-rich ixiolite-like phase was found as 110 μm irregular inclusion in Ct IId in vicinity of uraninite inclusion (Fig. 2f). This Sn-rich ixiolite contains 9.4 wt. % SnO_2 (0.3 Sn apfu) with Mn/(Mn + Fe) = 0.40 and Ta/(Ta + Nb) = 0.81. Ixiolite reveals slightly increased Zr contents (1.5–1.6 wt. % ZrO_2), but very low W and Ti concentrations, up to 0.4 wt. % TiO_2 and 0.1 wt. % WO_3, respectively (Tab. 1, Figs 3 and 4).

Rare uranmicrolite to microlite forms anhedral, 5–15 μm thick overgrowths on uraninite in patchy zoned Ct IId (Fig. 5a). Characteristic of this material are Ta/(Ta + Nb) = 0.82–0.94, U = 0.18–0.42 apfu, low contents of Ti (1.5–2.8 wt. % TiO_2, 0.1–0.2 Ti apfu) and Pb (0.2–1 wt. % PbO, 0.005–0.02 Pb apfu); contents of W, Zr, Sn and Sb are negligible (Tab. 3, Figs 3 and 4). Elsewhere, a single anhedral uraninite inclusion was found in Ct II (Fig. 2f).

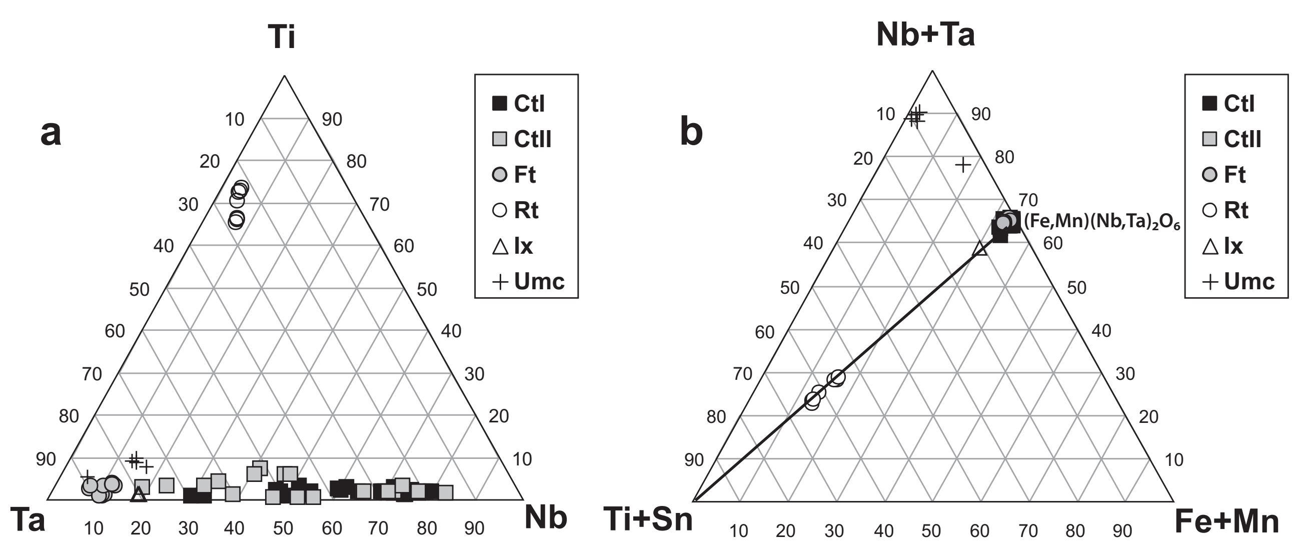

Fig. 4 Triangular diagrams of Nb-Ta minerals from Limbach (atomic proportions). **a** – Ti–Ta–Nb diagram. **b** – (Nb + Ta)–(Ti + Sn)–(Fe + Mn) diagram. CtI: columbite–tantalite I, CtII: columbite–tantalite II, Ft: ferrotapiolite, Rt: rutile, Ix: ixiolite, Umc: uranmicrolite to microlite.

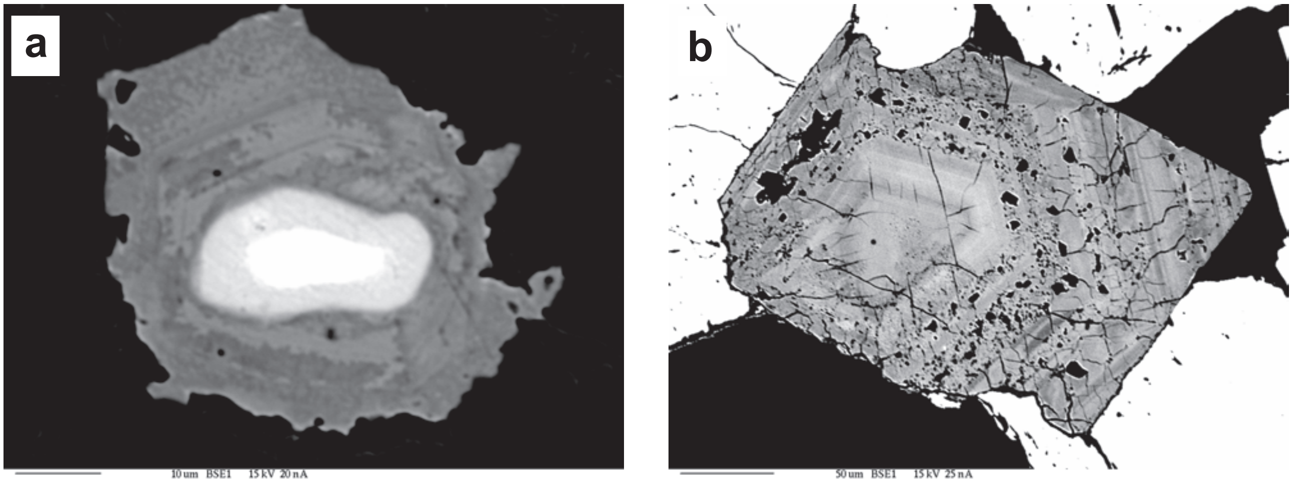

Fig. 5 BSE images of inclusions in columbite–tantalite (Ct IId) from Limbach. **a** – oscillatory to irregular zoned overgrowths of uranmicrolite to microlite (grey) on uraninite (white to pale grey core) in Ct IId (black). **b** – partly metamict zircon with regular oscillatory zoning (grey) in Ct IId (white).

In addition to the above-mentioned Nb-Ta oxide minerals, euhedral to subhedral zircon inclusions *c.* 250 μm in size occur in columbite–tantalite (Ct IId) (Fig. 5b). Zircon exhibits regular fine oscillatory zoning with some probably (partly) metamict zones, rich in cracks. The zircon shows high Hf, U, Th, and P contents (11.6–14.6 wt. % HfO_2, 0.3–2.6 wt. % UO_2, 0.0–3.0 wt. % Y_2O_3, and 0.0–3.6 wt. % P_2O_5, respectively). Locally, anhedral inclusions of quartz and muscovite in columbite–tantalite are also present.

5. Discussion and conclusion

5.1. Comparison to regional Nb-Ta assemblages

The Nb-Ta minerals were found only in recent alluvial placers of the Limbach Brook, not in a primary host-rock *in situ*. Nevertheless, regional geology as well as overall paragenetic, textural, and compositional character of the assemblage suggest rare-element granitic pegmatite(s) as the parental rock of the Nb-Ta mineralization. It is questionable whether the Nb-Ta alluvial minerals originated from one large pegmatite vein or several pegmatite bodies. The Limbach locality is situated in the region of the BGM, Hercynian orogenic S-type granites with numerous dikes of related pegmatites. The granitic rocks alone belong to a common plutonic suite with low to moderate contents of rare lithophile elements (such as Nb, Ta, Sn, Li, Rb, Cs, Be and B), lacking any evidence for extreme magmatic fractionation or possible concentrations of rare-element mineralization (Cambel and Vilinovič 1987; Petrík et al. eds 2001). On the other hand, the most fractionated granitic pegmatites of the BGM contain accessory beryl and Nb-Ta phases, namely ferrocolumbite to ferrotantalite, rarely manganocolumbite. Their chemical composition is similar to the Limbach columbite-tantalite (Bratislava, Kamzík and Bratislava, Patrónka pegmatites; Uher et al. 1994). However, the Limbach locality represents a more fractionated Nb-Ta assemblage with Mn, Ta-rich (manganotantalite, Sn-rich ixiolite) and Ta-rich members (ferrotapiolite, Ta-rich rutile, uranmicrolite to microlite) in comparison to the other known pegmatites of the BGM. Such relatively large variations in Mn/Fe and Ta/Nb ratios with Ta, Mn-dominated members resemble the Moravany nad Váhom, Striebornica granitic pegmatite in the adjacent Bojná Granitic Massif, Považský Inovec Mountains. This is the most fractionated pegmatite body in the Western Carpathians, where columbite–tantalite and ferrotapiolite attain Mn/(Mn + Fe) = 0.18–0.67 and 0.05–0.10, Ta/(Ta + Nb) = 0.09–0.81 and 0.83–0.90, respectively (Uher et al. 1994; Uher and Broska 1995; Novák et al. 2000). Generally, compositional range of columbite–tantalite from the Limbach placers is very similar to granitic pegmatites of the Western Carpathian area (Fig. 3). Analogous columbite–tantalite compositions and fractionation trends with increasing Ta/(Ta + Nb) and low to moderate Mn/(Mn + Ta) ratios exhibit beryl-bearing and Li, F-poor granitic pegmatites, for instance the Greer Lake and PEG Groups, Canada (Černý 1989). On the contrary, the columbite–tantalite fractionation trends commonly reach Mn, Ta-rich members with Ta/(Ta + Nb) and Mn/(Mn + Fe) > 0.8 in the most fractionated beryl-type pegmatites (e.g., Separation Lake, Canada – Tindle and Breaks 2000; Scheibengraben, Maršíkov, Czech Republic – Novák et al. 2003) and Li, F-rich complex-type of the rare-element granitic pegmatites (Černý 1989).

Based on the above-mentioned data, the Nb-Ta oxide minerals from Limbach should have originated in an evolved granitic pegmatite environment, most probably analogous to the rare-element class, LCT family, beryl–columbite subtype (*sensu* Černý and Ercit 2005 classification).

In addition, Hf-rich, partly metamict zircon from Limbach is also characteristic of evolved, rare-element granitic pegmatites and its composition is analogous to zircon from granitic pegmatites of the beryl–columbite subtype from the BGM and other evolved pegmatite populations in the Western Carpathians (Uher and Černý 1998).

5.2. Evolution of Nb-Ta phases

Textural patterns indicate two main crystallization events in the Limbach columbite–tantalite (Fig. 2): (1) older primary magmatic solidification of Ct I with regular fine to coarse oscillatory, rarely diffuse compositional zoning, and (2) post-magmatic recrystallization of Ct II with irregular bended fine-oscillatory, patchy to mosaic zoning (IIa to IId). The regular oscillatory zoning reflects the growth of columbite–tantalite parallel to their crystallographic planes and it is generally considered as a result of magmatic crystallization. On the other hand, irregular, bended, patchy, or mosaic textures with anhedral boundaries indicate non-magmatic, metamorphic or hydrothermal recrystallization, partial leaching and replacement or alteration phenomena (e.g. Lahti 1987; Baldwin 1989; Černý et al. 1992; Tindle and Breaks 1998, 2000). We interpret all these irregular textures of the Limbach columbites–tantalites as products of subsolidus partial leaching and subsequent replacement and recrystallization of the host granitic-pegmatitic rocks during post-magmatic uplift and retrograde fluid overprint. On the basis of textural relations, the origin of the anhedral mosaic of ferrotapiolite, Ta>Nb rutile, Sn-rich ixiolite and uranmicrolite to microlite is closely connected with this subsolidus overprint. However, at least ferrotapiolite and possibly also rutile could have initially originated as primary magmatic phases together with Ct I, but they were probably completely recrystallized during the subsolidus event. On the contrary, euhedral shape and regular oscillation zoning of zircon indicate its primary magmatic origin, possibly with subsequent partial metamictization (Fig. 5b).

The primary evolutional trend of columbite–tantalite (Ct I) reveals a common progression from ferrocolumbite to manganotantalite composition, with relatively continuous increase in both the Mn/Fe and Ta/Nb ratios [Mn/(Mn + Fe) = 0.17 to 0.52 and Ta/(Ta + Nb) = 0.19 to 0.70; Fig. 3]. Such an evolutionary trend indicates a moderate degree of fractionation with low F activity, analogous mainly to the beryl–columbite subtype of rare-element granitic pegmatites (e.g., Černý et al. 1986; Černý 1989; Tindle and Breaks 2000; Novák et al. 2003; Galliski and Černý 2006). In general, the compositional similarity of post-magmatic Ct II and Ct I together with (re)crystallization of Ta-rich phases indicates recrystallization of primary magmatic assemblage without any external influx of metallic ions or different fluids (e.g., F, B and/or P-rich).

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