Distinctive compositional trends in columbite-tantalite from two segments of the lepidolite pegmatite at Rožná, western Moravia, Czech Republic

Různé trendy ve složení columbit-tantalitu ve dvou částech lepidolitového pegmatitu v Rožné, západní Morava (Czech summary)

(3 fgs)

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The Fe-Mn and Nb-Ta fractionation trends were studied in columbite-group minerals from two spatially separated segments of the zoned lepidolite pegmatite dike at Rožná. In both segments, Hradisko and Borovina, columbite-tantalite occurs exclusively in the lepidolite subunit and in the adjacent quartz core. Manganocolumbite from Hradisko is largely homogeneous and displays extreme values of Mn/ (Mn+Fe) 0.99–1.00, but commonly low Ta/(Ta+Nb) = 0.05–0.10, rarely up to 0.44. Manganocolumbite to manganotantalite from Borovina is heterogeneous and exhibits moderate to high Mn/(Mn+Fe) = 0.48–0.97, as well as Ta/(Ta+Nb) = 0.43–0.89. Columbite-tantalite contains low concentrations of W and Ti in both segments, slightly higher in Hradisko. Rare, late, oscillatory zoned columbite veinlets in manganocolumbite from quartz core at Hradisko display highly variable Mn/(Mn+Fe) of 0.08–0.98, but Ta/(Ta+Nb) = 0.10–0.23 which is slightly higher than that of the primary host manganocolumbite. Columbite-tantalite is largely highly ordered, but intermediate disorder was found in some samples from Hradisko. Different compositional trends in columbite-tantalite from both segments were compared with parent mineral assemblages and with composition of associated lepidolite and elbaite. Both lepidolite and elbaite are Fe-enriched in Borovina relative to the Hradisko segment. The advanced Fe-Mn fractionation in Hradisko is very likely related to high activity of F and alkali fluorides inferred from the abundance of lepidolite and topaz; whereas the Nb-Ta fractionation is probably controlled by a different factor: Compositional homogeneity of manganocolumbite from Hradisko suggests equilibrium crystallization; however, high heterogeneity in columbite-tantalite from Borovina indicates disequilibrium conditions.

Key words: columbite-tantalite, fractionation, structural state, lepidolite pegmatite, Rožná, Czech Republic

Introduction

Compositional trends of primary Nb,Ta-oxide minerals in complex pegmatites and leucocratic granites are useful indicators of fractionation. Distinct compositional trends, in terms of Fe-Mn and Nb-Ta fractionation, were recognized in the columbite-group minerals from individual subtypes of rare-element granitic pegmatites (Černý – Erict 1985, 1989, Černý 1991). In lepidolite-subtype pegmatites, high activity of alkali fluorides seems to promote extensive Mn-enrichment preceding the bulk of the Nb-Ta fractionation (Černý – Erict 1985). In contrast, ambygonite, spodumene and petalite pegmatites characterized by relatively low F-activity display more or less simultaneous Fe-Mn and Nb-Ta fractionation, or a significant Nb-Ta fractionation is accompanied by only a slight Mn-enrichment (e. g., Černý et al. 1985, 1998, Špildev – Shearer 1992, Novák – Povondra 1995, Mulja et al. 1996, Novák – Černý 1998).


Geological setting

The pegmatite dike is located along the contact of the Strážek Moldanubicum with the Svrata Unit at the eastern border of the Bohemian massif and is hosted by a rock sequence consisting of dominant leucocratic biotite gneiss with intercalations of hornblende gneiss (Sekanina 1946). The metamorphic complex exhibits multistage evolution; a MP-HT regional metamorphism of staurolite-kyanite type was locally overprinted by a LP-HT cordierite-sillimanite metamorphic event. No granitic rocks have been observed in the pegmatite vicinity, except for numerous dikes of barren pegmatites situated E and NE of the lepidolite pegmatite dike (Novák 1992). Černý et al. (1995) gave Rb-Sr age for lepidolite from pegmatites at Rožná 323 ± 4 Ma, however, it seems to be too low and very likely indicates resetting of the isotopic system in micas during hydrothermal stage of the pegmatite development.

The pegmatite dike, about 1 km long and about 35 m wide, is oriented parallel to the NWN-trending strike of
the foliation of the host gneiss, and dips about 60° WSW (Fig. 1). Contact with the host gneiss is commonly sharp, but scarce metapelite enclaves situated in the upper part of the dike (Fig. 1) contain abundant hydrothermal tourmaline (dravite-schorl-elaite; Novák – Selway 1997). The Rožná pegmatite was mined particularly in an old quarry on the Hradisko hill, where the most differentiated central part of the dike is exposed with a voluminous albite + lepidolite assemblage. The second main exposure, a small open pit in the Borovina hill about 150 m SE of the top of the Hradisko hill, exposes what might be a different erosion level of the main dike. The albite + lepidolite unit is less common unit here, and Li-minerals are less abundant. However, the Borovina pegmatite may also represent an independent and geochemically distinct segment of the main dike characterized by different geochemical evolution. Current exposures do not allow unequivocal interpretation.

The pegmatite

Internal structure of the pegmatite dike at Rožná, in the Hradisko and Borovina outcrops, is close to symmetric, consisting of the several textural-paragenetic units (see Fig. 1). (i) very rare, coarse-grained biotite-bearing wall zone; (ii) abundant coarse-grained schorl-bearing intermediate zone, locally transitional to a (iii) graphic unit; masses (veins?) of (iv) fine- to medium-grained granitic unit; relatively rare (v) blocky core-margin zone (K-feldspar + quartz + amblygonite) and (vi) quartz core. This last unit is surrounded and in part penetrated by (vii) albite + lepidolite complex with locally abundant elbaite and rare amblygonite-montebrazite (Novák 1992).

The albite + lepidolite complex is very heterogeneous in its texture and mineral composition, and consists of an outer albite subunit and an inner lepidolite subunit (Fig. 1). The complex shows noticeable differences between the Hradisko and Borovina outcrops.

The albite subunit situated in the outer part of the complex contains dominant albite, quartz, subordinate greenish to colorless muscovite to lithian muscovite, black to green or blue tourmaline, and accessory cassiterite, fluorapatite and amblygonite-montebrazite. No major differences are observed between the albite subunits in Hradisko and Borovina; however, primary phosphates including amblygonite-montebrazite and triplite are more abundant in the Borovina hill.

In contrast, the lepidolite subunits are distinctive in each outcrop. In the Hradisko hill, massive lepidolite is dominant in the inner part of the unit besides locally abundant albite, and it contains relatively widespread pink, red, green, and rare blue, gray to colorless elbaite and exceptionally rossmanite (Novák – Selway 1997, Selway et al. 1998, 1999). Accessory minerals include fluorapatite, amblygonite-montebrazite, topaz, beryl, cassiterite and manganocolumbite. The lepidolite subunit in the Borovina hill is volumetrically quite negligible; widespread but diversified albite + lepidolite + elbaite + quartz assemblages predominate over massive lepidolite, typical in the Hradisko hill. The massive lepidolite is main-

![Fig. 1 Vertical section through the Hradisko and Borovina segments of the Rožná pegmatite. According to Novák (1992). A – Hradisko, B – Borovina. 1 – coarse-grained biotite-bearing unit (quartz + K-feldspar + plagioclase + biotite); 2 – coarse-grained schorl-bearing unit zone (quartz + K-feldspar + plagioclase + schorl + muscovite); 3 – graphic unit (K-feldspar + quartz ± albite, schorl, muscovite); 4 – granitic unit (quartz + K-feldspar + albite + schorl + muscovite); 5 – albite-lepidolite unit (black: lepidolite subunit); 6 – quartz core; 7 – host rocks and enclaves; 8 – level of mining.](image-url)
ly green or grey, in contrast to the dominant purple (and minor green or grey) lepidolite at Hradisko (Černý et al. 1995). The Borovina elbaite is typically blue, other coloured varieties are rare. Accessory minerals — fluorapatite, amblygonite-montebrazsite, beryl, cassiterite and manganocolumbite-manganotantalite — are comparable to those in the Hradisko outcrop. However, they also include ixiolite, zircon and pseudomorphs of hydroxylyherderite after an unknown mineral.

The quartz core adjacent to the lepidolite subunit commonly contains lepidolite, elbaite and albite in veinlets or irregular masses in both outcrops. Masses of late fine-grained greenish-grey muscovite and clay minerals locally, with aggregates of hematite, are typical of both segments. Despite of an extensive study, no other Nb, Ta-oxide minerals such as microlite or wodginite were found in the Rožná pegmatite.

Textural and paragenetic relations of columbite-tantalite

In the two pegmatite segments, columbite-tantalite associates with different minerals, it shows different shape and size of crystals, and has different compositional zoning (Table 1).

Hradisko

Manganocolumbite typically forms black, euhedral to subhedral grains, up to 2 cm in size, with good cleavage and strong submetallic lustre. It occurs only in the lepidolite subunit, mainly close to the quartz core, or within the quartz core closely adjacent to the lepidolite subunit. Columbite seems to be absent in the albite subunit, which is otherwise a typical columbite-bearing assemblage in most other lepidolite pegmatites in the Moldanubicum (e.g., Novák — Diviš 1996, Novák — Černý 1998, 1999). Several distinct paragenetic types of manganocolumbite were distinguished: (i) large manganocolumbite grains in fine-grained purple lepidolite + albite, mostly located close to or penetrating quartz core (paragenetic type of lepidolite — F9; all paragenetic types of lepidolite from Černý et al. 1995); (ii) large manganocolumbite grains in massive quartz of the quartz core, locally associated with cassiterite and purple lepidolite (type F9); (iii) rare, large subhedral grain of manganocolumbite in green lepidolite (type H4); (iv) very rare, anhedral manganocolumbite grains in massive, fine- to medium-grained grey lepidolite (type H6).

All manganocolumbite samples of paragenetic types (i), (ii) and (iii) are homogeneous, except very rare late veins of oscillatory zoned manganocolumbite to ferrocolumbite found in two samples from the quartz core (Table 1). Manganocolumbite (vi) from grey lepidolite is heterogeneous in terms of Nb/Ta with a simple progressive zoning, locally with sharp borders between individual zones.

Borovina

Columbite-tantalite forms rare black subhedral grains, ~1 mm in size, exceptionally up to 3 mm. It occurs in the lepidolite subunit and in the adjacent quartz core, and it seems to be absent in the albite subunit. Two distinct paragenetic types of columbite-tantalite were distinguished: (i) in a medium-grained green lepidolite + blue elbaite + albite assemblage; and (ii) in massive quartz of the quartz core with blue elbaite and rare late muscovite. The examined grain of manganotantalite of the latter type has a narrow rim of Sn,W-rich ixiolite-like mineral. All samples display random patchy zoning particularly in Nb and Ta.

### Table 1 Description of columbite-tantalite samples examined from Rožná

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Explanations: lpd — lepidolite; ab — albite; cas — cassiterite; elb — elbaite; qtz — quartz; ap — apatite; msc — muscovite.

Experimental

Electron-microprobe analyses of columbite-tantalite were carried out on a Cameca SX-50 instrument in the wavelength-dispersion mode with beam diameter of 1–2 μm, accelerating potential of 15 kV, and sample current of 20 (40) nA measured on Faraday cup. Counting times of 20 (40) s were used for Fe, Mn, Sn, Ti, Nb, Ta (and for Mg, Ca, Sb, As, Bi, Sc, Zr, U and W), respectively. The following standards were used: manganotantalite (TaMo), FeNaO₆ (FeKα), MnNaO₆ (NbLa, MnKα), SnO₂ (SnLα), rutile (TiKα), ZrO₂ (ZrLα), NaSO₄ (ScKα), MgNaO₆ (MgKα), BiTaO₆ (BiMα), mimetite (AsLα), CaNaO₆ (CaKα), stibiotantalite (SbLα), UO₂ (UMα) and tungsten metal (Wα). Data were reduced using the PAP routine of Pouchou — Pichoir (1985). The normalization on 12 cations and 24 anions per formula unit was used to calculate Fe³⁺.

Unit-cell dimensions of columbite-tantalite were refined using the CELREF least-squares program (Appelman — Evans 1973) from data obtained on the Philips
PW1710 automated powder diffractometer with graph-lite-monochromatized CuKα radiation at 40 kV and 40 mA. Annealed CaF₂, with a = 5.46379(4) Å was used as an internal standard.

**Compositional trends in columbite-tantalite**

In each of the two outcrops, columbite-tantalite exhibits distinct chemical compositions and compositional trends. Apparent differences within the individual paragenetic types also were observed. Consequently, columbite-tantalite from the Hradisko and Borovina segments is discussed separately.

**Hradisko**

A typical feature of manganocolumbite from the pink lepidolite + albite assemblage, green lepidolite and massive quartz is a virtually homogeneous chemical composition. The Mn/[(Mn+Fe)] values are very close to 1 (0.99–1.00) in all samples, and Ta/[(Ta+Nb)] vary within the very narrow range of 0.06–0.10. The sample MM 56 from grey lepidolite exhibits

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<td>3.904</td>
<td>0.004</td>
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* = late columbite; Zr, U, As, Bi, Sc and Sb - below detection limits (0.02–0.05 wt. %).

**Fig. 2** Compositions of Nb, Ta-oxide minerals from Hradisko and Borovina in the columbite quadrilateral. The two-phase field marks the approximate extent of single-phase, non-paired tapiolite and columbite-tantalite (Wise – Černý 1996). Hradisko: solid circles – primary manganocolumbite, open circles – secondary columbite; Borovina: crosses – manganotantalite-manganocolumbite, solid triangles – ixiolite. About 30 point analyses are confined to the area bounded by Mn/(Mn+Fe) = 0.99–1.00 and Ta/(Ta+Nb) = 0.06–0.10.
identical Mn/(Mn+Fe) ratios, but a broader range of Ta/(Ta+Nb) of 0.25–0.44 (Fig. 2, Table 2); Ta increases from core to rim. Late oscillilolitely zoned columbite from samples RZN and MM 35 exhibits low Ta/(Ta+Nb) of 0.10–0.23, comparable or slightly elevated relative to those of the associated primary manganocolumbite, but it shows extensive variation in Mn/(Mn+Fe) from 0.08 to 0.98 (Fig. 2).

Minor elements include particularly W, which is present in moderate amounts in all samples examined in up to 0.15 apfu (atoms per formula unit). Titanium is very low, only locally up to 0.18 but mostly below 0.05 apfu (Table 2). The lowest contents of minor elements are typically found in sample MM 56 with the highest Ta/(Ta+Nb) value. Trace amounts of Sn, Ca, Sc and Mg also were found, but the two latter elements only in the late oscillilolitely zoned ferrocolumbite-manganocolumbite.

**Borovina**

Compared to the Hradisko minerals, columbite-tantalite exhibits here a distinctive fractionation trend in terms of both Fe-Mn and Nb-Ta pairs. All grains examined are strongly heterogeneous, and their overall variations in Fe-Mn and Nb-Ta are similar: Mn/(Mn+Fe) = 0.48–0.97 and Ta/(Ta+Nb) = 0.43–0.89 (Fig. 2). However, the individual grains vary particularly in Fe-Mn; e.g., the sample MM 176 has Mn/(Mn+Fe) of 0.57–0.85 but Ta/(Ta+Nb) only 0.43–0.57. Minor cations include particularly W, up to 0.09 apfu, but largely below 0.02. Only trace amounts of Ti and Sn were found (Table 3).

Sample MMC 33 from the quartz core yielded Mn/(Mn+Fe) of 0.48–0.76 but Ta/(Ta+Nb) of 0.69–0.88. An associated ixiolite-like mineral shows a smaller range of fractionation of major elements, Mn/(Mn+Fe) of 0.70–0.72 and Ta/(Ta+Nb) of 0.91, which is on average higher than in the associated tantalite. However, ixiolite is characterized by high contents of Sn, up to 1.36 apfu, and W, up to 0.57 apfu. Minor amounts of Zr (up to 0.05 apfu) are typical; other elements are below the detection limits (Table 3).

**Structural state**

The cell parameters a and c (Table 4) are plotted in Fig. 3. The manganocolumbite from Hradisko exhibits an intermediate to highly ordered structure. Variation in the cation order is remarkable in view of the almost identical chemical composition (including minor elements) of all samples examined. Columbite-tantalite from Borovina has on average a more ordered structure. This may reflect the lower concentration of most minor to trace elements relative to the Hradisko samples. However, the cause-and-effect of cation substitutions on the structural state of columbite-tantalite is not sufficiently understood (Ercit et al. 1995) and in any case the concentrations of minor elements are very low in both types (Table 2 and 3).

**Paragenesis and chemistry of associated minerals**

In order to find an explanation for the distinctive compositional trends in columbite-tantalite from the Hradisko and Borovina segments, some paragenetic and compositional aspects of columbite-tantalite and associated phases must be examined in detail.

Manganocolumbite from Hradisko is mainly associated with medium-grained purple lepidolite, pink elbaite, albite and quartz (samples MM 13, MM 50, MMC 174), or it is enclosed in massive quartz of the quartz core.

**Table 3** Representative compositions of columbite-tantalite from Borovina (EMPA data).

<table>
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<tr>
<th>WO₃</th>
<th>Nb₂O₅</th>
<th>Ta₂O₅</th>
<th>TiO₂</th>
<th>SnO₂</th>
<th>ZrO₂</th>
<th>UO₂</th>
<th>Sc₂O₃</th>
<th>As₂O₃</th>
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<th>Fe₂O₃</th>
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<tr>
<td>0.09</td>
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Formulate calculated on 12 cations and 24 oxygens.

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<tr>
<td>Mg</td>
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U, Bi, Sb, Ca and Mg – below detection limits (0.02–0.05 wt. %).
Table 4 Unit-cell dimensions of columbite-tantalite from Rožná.

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
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<tr>
<td>Hradisko</td>
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<tr>
<td>MM 13</td>
<td>14.417(5)</td>
<td>5.758(2)</td>
<td>5.089(2)</td>
<td>422.5(2)</td>
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<td>MM 50</td>
<td>14.349(7)</td>
<td>5.747(6)</td>
<td>5.107(4)</td>
<td>423.1(4)</td>
</tr>
<tr>
<td>MM 12</td>
<td>14.379(1)</td>
<td>5.750(1)</td>
<td>5.107(1)</td>
<td>422.9(1)</td>
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<tr>
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<td>5.760(1)</td>
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<tr>
<td>Borovina</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>MMC 176</td>
<td>14.390(4)</td>
<td>5.753(2)</td>
<td>5.080(1)</td>
<td>420.5(2)</td>
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<td>BORX</td>
<td>14.364(5)</td>
<td>5.751(3)</td>
<td>5.074(2)</td>
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</tr>
<tr>
<td>MMC 33</td>
<td>14.371(9)</td>
<td>5.757(4)</td>
<td>5.082(3)</td>
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</table>

(samples MM 12, RZN), locally associated with minor purple lepidolite (sample MM 35). The purple lepidolite associated with these samples displays Rb/Cs = 52.3, Fe/Mn = 0.03, Fe = 0.004 and Mn = 0.158 apfu (Černý et al. 1995), pink elbaite shows Fe/Mn = 0.18, Fe = 0.024 and Mn = 0.131 (Novák – Selway 1997). Green lepidolite (sample RZ HX) has Rb/Cs = 1.6, significantly elevated Fe and reduced F contents, Fe/Mn = 6.7, Fe = 0.31 and Mn = 0.046 apfu. Grey lepidolite containing manganocolumbite with elevated Ta/(Ta+Nb) ratios (sample MM 56) has somewhat more evolved geochemical characteristics relative to purple lepidolite (Černý et al. 1995): elevated content of the polythionite component, Rb/Cs = 1.9, Fe/Mn = 0.34, Fe = 0.024 and Mn = 0.071 apfu.

At Borovina, green lepidolite associated with columbite-tantalite (samples MMC 30, MMC 48, MMC 176) is characterized by Rb/Cs = 2.5, Fe/Mn = 3.90, Fe = 0.187 and Mn = 0.048 apfu (unpubl. data of the authors). Associated blue elbaite exhibits Fe/Mn = 1.11, Fe = 0.103 and Mn = 0.093 apfu. Columbite-tantalite from the quartz core (MMC 33) is associated with blue Fe-enriched elbaite with Fe/Mn = 8.77, Fe = 0.816 and Mn = 0.093 apfu, and late greenish muscovite with Rb/Cs = 3.39 and Fe/Mn = 6.0.

Generally, a progressive Rb-Cs fractionation in lepidolite is evident in both pegmatite segments. Behavior and concentrations of Fe, Mn and F are rather irregular. Increasing Fe/Mn ratio in lepidolite and elbaite is typical in both segments, and columbite-tantalite bearing assemblages at Borovina, particularly the sample from the quartz core, are evidently Fe-enriched and F-poor relative to those from Hradisko. No other minerals were found in the columbite-bearing samples except quartz, albite, rare cassiterite and late muscovite in both segments (Table 1).

Discussion

Columbite-tantalite phases from the Hradisko and Borovina outcrops of the Rožná pegmatite dike differ in their Fe-Mn and Nb-Ta fractionation trends (Fig. 2). However, they are remarkably similar in the concentrations of minor element, slightly lower as they are in columbite-tantalite from Borovina (Table 2 and 3). The compositional trend of manganocolumbite from Hradisko characterized by Mn/(Mn+Fe) of 0.99–1.00 and Ta/(Ta+Nb) of 0.06–0.10 (rarely up to 0.44) is very similar to those typical of the lepidolite pegmatites, where columbite typically occurs in a massive lepidolite or a lepidolite-rich unit (e. g., Meldon, Cornwall, UK; v. Knorring – Condiffe 1984; Chédéville, France; Raimbault 1998; Drahoš-nín I, Ti Studně and Opatov in Moldanubicum, Czech Republic; unpublished data of the authors). However, it is rather distinctive from the pegmatites with columbite enclosed in less fractionated, albite-dominated, commonly lepidolite- or lithium-muscovite-bearing units (e. g., Jihlava district, Puklice, Dobrá Voda and Nová Ves near Český Krumlov in Czech Republic; Černý – Némec 1995, Novák – Diviš 1996, Novák – Černý 1998, 1999, Novák – Staněk 1999; Larmont Group, Chédéville, France, Raimbault 1998). They exhibit a similar range of low Ta/(Ta+Nb) (0.1 to 0.2, rarely up to 0.5 or more), but the span of the Mn/(Mn+Fe) ratios is much broader (0.5 to 1.0, mainly 0.8 to 1.0).

Columbite-tantalite from Borovina exhibits a compositional pattern entirely different from those found in the other lepidolite pegmatites of the Moldanubicum (Novák – Černý 1999) and elsewhere (as referenced above).

![Fig. 3 Unit-cell dimensions of columbite-tantalite from Hradisko and Borovina in the a–c diagram for columbite group minerals (Ercit et al. 1995).](image-url)
Experimental studies of columbite-tantalite solubility in granitic melts revealed strong influence of A. S. I. (aluminum saturation index), P. Li and particularly F on the Nb-Ta fractionation, whereas the B content has almost no effect (e.g., Keppler 1993, Wolf – London 1993, Wolf et al. 1994, Linnen – Keppler 1995, 1997, Linnen 1998). In peraluminous melts rich in F, expected in many highly evolved pegmatite magmas, the solubility of MnTaO₄ is increased relative to that of MnNb₂O₆ (Linnen – Keppler 1997).

The Hradisko outcrop with abundant Fe-poor but F-rich lepidolite and elbaite and accessory topaz is characterized by columbite exhibiting extreme Fe-Mn fractionation, but the Nb-Ta fractionation is low to moderate; in the Borovina outcrop with Fe-rich but F-poor lepidolite and Fe-rich elbaite, columbite-tantalite displays moderate to high Fe-Mn but advanced Nb-Ta fractionations (Fig. 2). Thus the Nb-Ta fractionation trends in columbite-tantalite from both outcrops are not consistent with experiments (Keppler 1993, Linnen 1998). The activity of F and Li in Hradisko seems to have been higher than in Borovina, but the Nb-Ta fractionation is evidently restricted. The difference between actual Nb-Ta fractionation trends in columbite and F and Li activities in pegmatite melt inferred from mineral assemblages (abundant F-rich lepidolite, accessory topaz) indicate that the abundance of lepidolite in a pegmatite does not simply reflect the effective activities of F and Li in the melt.

High activity of alkali fluorides may be responsible for the extreme Mn-enrichment, which actually precedes Nb-Ta fractionation in lepidolite pegmatites (e.g., Černý – Erct 1985, 1989); however, experiments with Fe-Mn fractionation in columbite have not been performed to date. The Fe-Mn fractionation in columbite-tantalite from both outcrops seems to be evidently more related to high alkali-fluoride activity inferred from the abundance of lepidolite in the Hradisko and Borovina segments than the Nb-Ta fractionation. Raimbuft (1998) explained changes in Fe/Mn ratio in columbite from Chédeville pegmatites due to precipitation of Fe-bearing minerals; however, no Fe-bearing minerals are associated with manganocolumbite in Hradisko. The higher solubility of MnTaO₄ compound in highly evolved peraluminous melt (Linnen – Keppler 1997) or possible differences in thermal stabilities of Nb- and Ta-based complexes may have caused the Nb-Ta separation.

Composition of late oscillatory zoned columbite from Hradisko with Mn/(Mn+Fe) of 0.08–0.98 and Ta/(Ta+Nb) of 0.10–0.23 indicates elevated activity of Fe in fluids, but the Nb-Ta ratio remains almost constant relative to the primary columbite, as is typical for subsolidus replacement of Nb,Ta-oxide minerals (Novák – Černý 1998).

Homogeneity of most manganocolumbite samples from Hradisko is remarkable. During the crystallization of large grains, up to 2 cm in size, in purple lepidolite, green lepidolite or massive quartz, the Mn/(Mn+Fe) and Ta/(Ta+Nb) ratios remained almost constant. Homogeneity of associated minerals (lepidolite, elbaite) and manganocolumbite suggest local equilibrium crystallization in this assemblage. Evident heterogeneity in Nb/Ta found in manganocolumbite from gray lepidolite (Hradisko) and particularly from all samples in Borovina is quite contrasting and disequilibrium crystallization is indicated.

Conclusions

Distinctly different compositional trends in Fe-Mn and Nb-Ta fractionation were found in columbite-tantalite from spatially separated segments of the large lepidolite pegmatite dike in Rožná. Manganocolumbite from Hradisko displays extreme fractionation in Mn/(Mn+Fe) (0.99–1.00), but low values of Ta/(Ta+Nb) (0.06–0.10, only sporadically up to 0.44); manganocolumbite to manganotantalite from Borovina exhibits moderate to high Mn/(Mn+Fe) (0.48–0.97) and Ta/(Ta+Nb) (0.43–0.89). Both types contain low concentrations of W and Ti. Columbite-tantalite is rather highly-ordered, but moderate degree of disorder was found in some samples from Hradisko.

Different compositional trends in columbite-tantalite in the two segments of the Rožná lepidolite pegmatite cannot be satisfactorily explained. The Fe-Mn fractionation is very likely related to high activity of alkali fluorides and HF inferred from the abundance of lepidolite and topaz in Hradisko. In contrast, the Nb-Ta fractionation must be controlled by factors other than the activities of F and Li inferred from mineral assemblages. Differences in solubilities of columbitetantalite in melts, or in stabilities of Nb, Ta-complexes may control Nb-Ta fractionation.

Compositional homogeneity of most manganocolumbite samples and associated lepidolite and elbaite from Hradisko suggests local equilibrium crystallization in this columbite-bearing assemblage. In contrast, due to extensive heterogeneity of columbite-tantalite grains from Borovina, disequilibrium crystallization is indicated.

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References