The Canadian Mineralogist
Vol. 36, pp. 659-672 (1998)

NIOBIUM – TANTALUM OXIDE MINERALS FROM COMPLEX GRANITIC PEGMATITES IN THE MOLDANUBICUM, CZECH REPUBLIC: PRIMARY *VERSUS* SECONDARY COMPOSITIONAL TRENDS

MILAN NOVÁK[1]

Department of Mineralogy and Petrography, Moravian Museum, Zelný trh 6, 659 37 Brno, Czech Republic

PETR ČERNÝ[1]

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2

ABSTRACT

Compositional trends of Nb,Ta-oxide minerals in four complex granitic pegmatites (lepidolite and petalite subtypes) in the Moldanubicum, Czech Republic, covering primary (magmatic) and secondary (hydrothermal replacement) stages of crystallization, were investigated. The primary stage is characterized by ferrocolumbite to manganocolumbite, followed after Fe- and Mn-depletion by Ca- or Sb-rich minerals: microlite (Nová Ves), rynersonite (Chvalovice) and stibiotantalite (Dobrá Voda, Laštovičky). Compositional paths in columbite are similar to those of lepidolite pegmatites; the other primary Nb, Ta-oxide minerals exhibit Ta/(Ta+Nb) values significantly higher relative to columbite. Decreasing Nb/Ta and the cation sequence Fe – Mn – (Sb,Ca) are typical of the primary stage. The secondary stage displays a broad spectrum of mainly fracture-filling secondary phases, such as diverse microlite-group minerals, cesstibtantite, manganotantalite, ferrotantalite and ferrotapiolite, which replace stibiotantalite, microlite and rynersonite; columbite in outer pegmatite units remains unaffected. The Ta/(Ta + Nb) values of the secondary phases are comparable to those of their precursors. The general sequence of major *A*-site cations in hydrothermal Nb,Ta-oxide minerals, (Sb) – Ca – Mn – Fe, is reversed relative to that of the primary stage, and it may represent a universal pattern of hydrothermal replacement of primary Nb,Ta-oxide minerals in comparable granitic pegmatites. The composition of microlite-type minerals and textural relations indicate that the secondary hydrothermal stage includes a broad range of P–T–*X* conditions from early subsolidus replacement at ~500–350°C, ~2.5 –2.0 kbar (Nová Ves, Dobrá Voda) to near-surface weathering at ≤100°C (Chvalovice). The likely source of the Sb, Ca, Mn and part of the Fe seems to be the fluid phase exsolved from the residual melt or the replaced primary mineral; the host rock may be a source of Fe (Chvalovice).

Keywords: niobium, tantalum, columbite, microlite, cesstibtantite, rynersonite, stibiotantalite, tantalite, ferrotapiolite, Moldanubicum, Czech Republic.

SOMMAIRE

Nous avons étudié les variations en composition des oxydes de Nb et Ta provenant de quatre massifs de pegmatite granitique complexe (sous-types à lépidolite et pétalite) dans le Moldanubicum, en République Tchèque, tant d'origine primaire (magmatique) que secondaire (remplacement hydrothermal). Le stade primaire a donné la série ferrocolumbite à manganocolumbite, qui a par la suite donné lieu à des minéraux appauvris en Fe et Mn, et riches en Ca et Sb: microlite (Nová Ves), rynersonite (Chvalovice) et stibiotantalite (Dobrá Voda, Laštovičky). Le tracé des compositions de columbite ressemble à celui des pegmatites à lépidolite; les autres oxydes de Nb et Ta du stade primaire ont une valeur Ta/(Ta + Nb) plus élevée que dans la columbite. Au cours du stade primaire, une diminution en Nb/Ta et la séquence d'enrichissement Fe – Mn – (Sb,Ca) sont typiques. Au stade secondaire, nous documentons le remplissage de fissures par plusieurs minéraux secondaires, par exemple les minéraux du groupe du microlite, cesstibtantite, manganotantalite, ferrotantalite et ferrotapiolite, en remplacement de stibiotantalite, microlite et rynersonite; la columbite des zones externes de la pegmatite reste inchangée. Le rapport Ta/(Ta + Nb) des phases secondaires est comparable à celui des précurseurs. En général, la séquence des cations occupant la position *A* dans les minéraux à Nb et Ta d'origine hydrothermale, (Sb) – Ca – Mn – Fe, est renversée par rapport aux minéraux primaires, et pourrait témoigner d'un comportement général suite au ré-équilibrage hydrothermal dans des situations comparables rencontrées dans les pegmatites granitiques. D'après la composition des minéraux du groupe du microlite et les relations texturales, le stade hydrothermal représente un large intervalle de conditions P–T–*X*, en partant du remplacement

---

[1] *E-mail addresses*: mineral@mzm.anet.cz, cernyp@ms.umanitoba.ca

subsolidus précoce à ~500–350°C, ~2.5 –2.0 kbar (Nová Ves, Dobrá Voda), jusqu'à la météorisation près de la surface à une température inférieure ou égale à 100°C (Chvalovice). Les éléments Sb, Ca, Mn et une partie du Fe seraient ajoutés *via* la phase fluide exsolvée du magma résiduel ou viendraient du minéral précurseur. A Chvalovice, la roche-hôte a peut-être été à l'origine du Fe.

(Traduit par la Rédaction)

Mots-clés: niobium, tantale, columbite, microlite, cesstibtantite, rynersonite, stibiotantalite, tantalite, ferrotapiolite, Moldanubicum, République Tchèque.

INTRODUCTION

Compositional trends of primary Nb,Ta-oxide minerals in complex pegmatites are a useful tool for providing information about the degree of melt fractionation. Distinct compositional trends in terms of the Nb–Ta and Fe–Mn fractionation are recognized in columbite-type minerals from individual subtypes of granitic pegmatites (*e.g.*, Černý & Ercit 1985, 1989, Spilde & Shearer 1992, Ercit 1994, Novák & Povondra 1995, Mulja *et al.* 1996). They result from differences in the composition of parent melts, and particularly in the activity of F, P and their complexes (Keppler 1993, Wolf & London 1993, Wolf *et al.* 1994, Linnen & Keppler 1996). Typical cations in the primary Nb, Ta-oxide minerals include Fe and Mn; however, locally Na, Ca, Sb, Bi, Y, Sn and Al may also play a significant role, particularly in diverse minerals of the microlite subgroup, simpsonite and in the stibiotantalite group, all of which are typical of highly fractionated granitic pegmatites (Ercit 1986, Voloshin & Pakhomovskyi 1988).

Secondary (hydrothermal) Nb,Ta-oxide minerals represent a broad spectrum of mineral species, commonly carrying exotic cations: Li, Na, K, Cs, Fe, Mn, Sr, Ba, Pb, Al, Sb, Bi, Sn and U, in addition to abundant and widespread Ca. However, compositional trends evolving during the hydrothermal stage are not understood at a level comparable with those of the primary stage. Diverse views were expressed about the behavior of the ratio Nb/Ta (*cf.* Voloshin 1983, Ercit 1986), and attempts at establishing a general sequence of cations are rather controversial (Voloshin & Pakhomovskyi 1988).

The complex pegmatites in the Bohemian and Moravian part of the Moldanubicum typically contain Nb,Ta-oxide minerals, predominantly manganocolumbite. Other primary minerals include ferrocolumbite, manganotantalite, "wolframoixiolite", ixiolite, wodginite, pyrochlore, microlite, stibiotantalite and rynersonite, but most of them are rare (Novák *et al.* 1992, Černý & Němec 1995, Novák & Diviš 1996, unpubl. data of the authors). The last three minerals were hydrothermally altered at various stages of the subsolidus reconstitution of the pegmatites, producing a variety of secondary minerals such as microlite, stibiomicrolite, cesstibtantite, manganotantalite, ferrotantalite and ferrotapiolite (Staněk 1963, 1973, Ercit *et al.* 1993, Novák & Šrein 1998). However, the available data, scattered in the articles quoted above, are largely restricted to a mere identification. We present here the results of a systematic study of the secondary minerals, remarkable in the uniformity of their evolution in four widely separated pegmatites; in some respects, we significantly depart from the traditional views of the alteration processes.

PEGMATITE BODIES EXAMINED

Complex pegmatites in the Moldanubicum occur in several spatially isolated regions in southern Bohemia and western Moravia (Fig. 1). Pegmatites of the lepidolite subtype predominate over those of the elbaite subtype; several pegmatite dikes of the lepidolite subtype carry variable amounts of petalite and can be designated as transitional to the petalite subtype.

Four bodies of pegmatite are examined here: Nová Ves and Chvalovice (Český Krumlov region, southern Bohemia), and Dobrá Voda and Laštovičky (Velké Meziříčí region, western Moravia) (Fig. 1). The Nová Ves pegmatite belongs to the transitional lepidolite–petalite category, if not to the petalite subtype proper (Staněk 1992). The other three pegmatites are of the lepidolite subtype, locally with abundant elbaite and amblygonite (Novák *et al.* 1992).

All four pegmatites typically form symmetrically zoned dikes (Fig. 2), consisting of the following textural and paragenetic units, from the contacts inward: (1) fine-grained granitic unit, (2) graphic unit, (3) coarse-grained albite – quartz – tourmaline – mica unit, (4) blocky K-feldspar, and (5) lepidolite unit in the center. Amblygonite – montebrasite is commonly found in the lepidolite unit (5) or locally in the coarse-grained albite – quartz – tourmaline – mica unit (3). A blocky petalite unit (6) is developed in the center of the Nová Ves pegmatite (Fig. 2), rare petalite or pseudomorphs of spodumene + quartz after petalite are located in the internal zones of the Chvalovice and Dobrá Voda dikes (Staněk 1965, 1992). Neither petalite nor amblygonite – montebrasite were found at Laštovičky (Staněk 1973). Additional information concerning thickness, host rock and mineral assemblages of the individual pegmatite dikes is given in Table 1.

The pegmatites examined are very similar in their internal structure (Fig. 2) and mineral paragenesis. Petalite is more abundant in localities from southern Bohemia, pollucite was found only at Nová Ves (Teertstra *et al.* 1995). The Dobrá Voda and Laštovičky pegmatites contain small vugs lined with crystals of

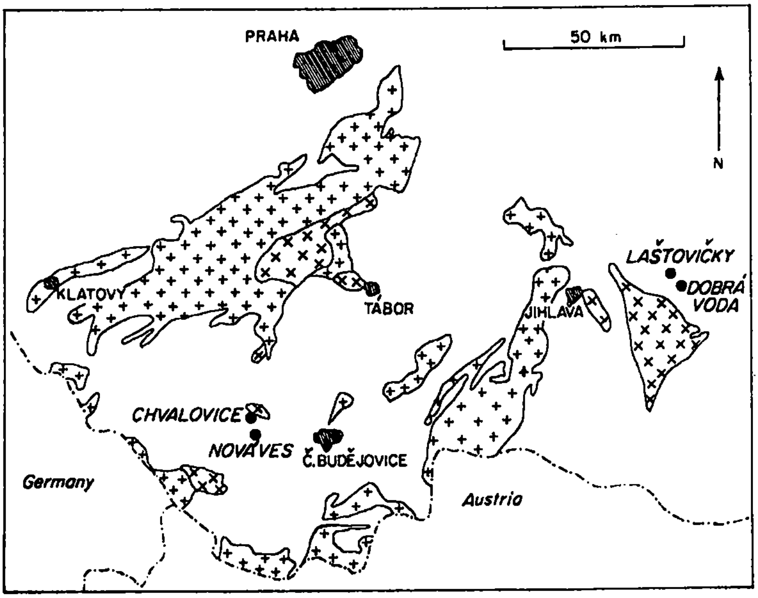

FIG. 1. Locations of complex pegmatites examined (solid dots) in the Moldanubicum. Granitic (crosses) and syenitic (×) intrusions are emplaced into a dominantly gneissic terrane (open).

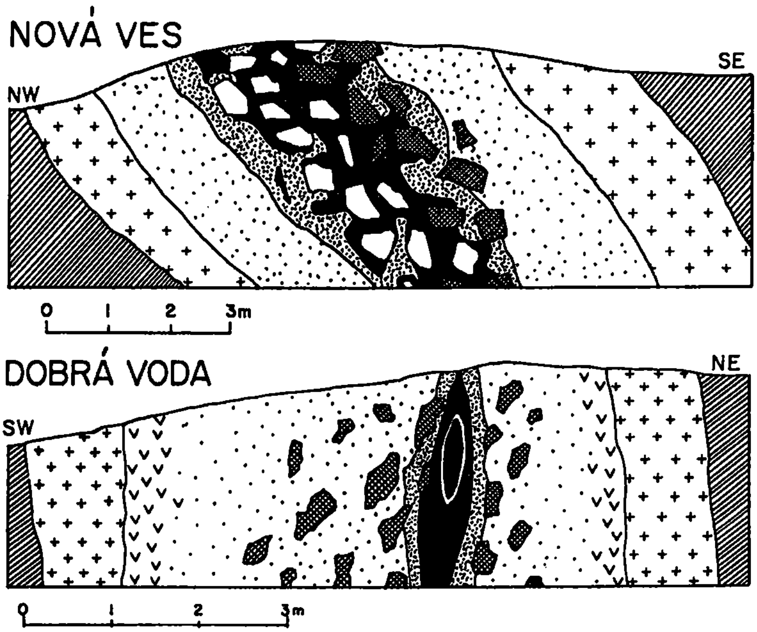

FIG. 2. Sections across the Nová Ves and Dobrá Voda pegmatites. Crosses: fine- to medium-grained granitic unit; check marks: graphic unit, open stipple: coarse-grained albite – quartz – tourmaline – mica unit, cross-hatched: blocky K-feldspar, white: blocky petalite, dense stipple pattern: albite-rich unit, black: lepidolite unit, subdivided into an outer and inner part at Dobrá Voda.

TABLE 1. MINERAL ASSEMBLAGES, HOST ROCK AND THICKNESS OF THE PEGMATITES EXAMINED

	Nová Ves	Chvalovice	Dobrá Voda	Laštovičky
Li-bearing minerals				
lepidolite	■	●	■	♦
petalite	■	+	?	-
spodumene*	♦	•	+	-
elbaite	●	♦	●	♦
amblygonite	♦	♦	♦	-
Nb,Ta-oxide minerals				
primary				
ferrocolumbite	-	-	-	•
manganocolumbite	+	•	+	•
microlite	•	-	-	-
rynersonite	-	+	-	-
stibiotantalite	-	-	+	•
secondary				
microlite	•	•	+	-
cesstibtantite	-	-	•	?
stibiomicrolite	-	-	•	•
manganocolumbite	•	-	-	-
manganotantalite	-	•	+	-
ferrotantalite	-	•	?	-
ferrotapiolite	-	-	?	•
thickness	12	4	8	1
host rock	serpentinite	gneiss	amphibolite	gneiss

Symbols: ■ major, ● common, ♦ minor, + rare, • very rare, ? problematic, – absent, * secondary. Thickness in meters.

quartz, albite, elbaite and lepidolite. The smaller dikes at Chvalovice and Laštovičky are very similar to their larger counterparts at Nová Ves and Dobrá Voda, respectively, but their internal structure and mineral paragenesis are relatively simple.

EXPERIMENTAL METHODS

Electron-microprobe analyses were performed in the wavelength-dispersion mode on a Cameca Camebax SX–50 instrument at the Department of Geological Sciences, University of Manitoba, Winnipeg. A beam diameter of 1–2 μm, accelerating potential of 15 kV, a sample current of 20 mA and a counting time of 20 s were used for Na, Ca, Nb, Ta and F, and 40 mA and 50 s for K, Cs, Sr, Ba, Fe, Mn, Pb, Y, Sb, Bi, Sn, Ti, U, and W. The following standards were used: manganotantalite (Ta$M\alpha$), $MnNb_2O_6$ (Mn$K\alpha$, Nb$L\alpha$), $FeNb_2O_6$ (Fe$K\alpha$), microlite (Na$K\alpha$, F$K\alpha$), $CaNb_2O_6$ (Ca$K\alpha$), SnO_2 (Sn$L\alpha$), rutile (Ti$K\alpha$), $BiTaO_4$ (Bi$M\alpha$), mimetite (Pb$M\alpha$), stibiotantalite (Sb$L\alpha$), $NaScSi_2O_6$ (Sc$K\alpha$), UO_2 (U$M\alpha$), YAG (Y$L\alpha$), $Ba_2NaNb_5O_{15}$ (Ba$L\alpha$), $SrBaNb_4O_{10}$ (Sr$L\alpha$), pollucite (Cs$L\alpha$), orthoclase (K$K\alpha$) and metallic W (W$M\alpha$). Data were reduced using the PAP routine (Pouchou & Pichoir 1985).

Identification of some of the minerals examined was verified by X-ray powder diffraction, using standard procedures on the Philips PW1710 and Siemens D5000 instruments.

TEXTURAL AND PARAGENETIC RELATIONS OF THE Nb,Ta-BEARING PHASES

Primary minerals

Columbite typically forms black blade-like crystals up to 5 mm in size enclosed in the coarse-grained albite – quartz – tourmaline – mica unit (3). It is commonly associated with zoned tourmaline (black schorl to green or pink elbaite), colorless to purple lithian muscovite to lepidolite, and locally with amblygonite. Columbite is exceptionally found in blocky K-feldspar (Nová Ves), in blocky petalite completely converted to quartz + spodumene (Dobrá Voda), and in the medium-grained lepidolite unit (5) (Nová Ves, Dobrá Voda) (Staněk 1963, 1973, 1992, Čech & Staněk 1960). Columbite in the outer units of the pegmatites remains unaffected by any secondary replacement processes.

Beside columbite, stibiotantalite is found at Dobrá Voda and Laštovičky as a primary phase; primary microlite occurs at Nová Ves, and rynersonite at Chvalovice (Table 1). The primary rynersonite deserves special comment, as it is generally known as a secondary mineral. At Chvalovice, however, it occurs in the columbite-free blocky pegmatite unit (4), the medium- to coarse-grained lepidolite unit (5), and inside the columbite-bearing coarse-grained unit (3). It forms subhedral inclusions in amblygonite, feldspars and quartz, and in most cases is extensively replaced by secondary minerals. Extensive depletion of Fe and Mn could have led to the stabilization of an anhydrous Ca,Ta,Nb-oxide mineral as a primary phase.

Secondary assemblages

Late assemblages of secondary minerals form fracture-filling, generally very fine-grained and locally porous aggregates within the replaced primary Nb, Ta-oxide minerals. As some differences were found among individual localities, the conditions of the secondary phases are described separately for each pegmatite.

At *Nová Ves*, primary euhedral to subhedral microlite in a medium-grained "cleavelandite" – lepidolite subunit of the lepidolite unit (5) (Čech & Staněk 1960) exhibits two distinct manifestations of hydrothermal alteration. The first one, more widespread, is represented by secondary microlite penetrating along fractures of the primary phase; such alteration was described in detail from complex pegmatites by Lumpkin & Ewing (1992). The second style is extremely rare: manganocolumbite seems to cement fractured primary microlite. However, the textural relationships are complicated in these cases, and alternative interpretations may be possible.

At *Chvalovice*, primary rynersonite commonly is enclosed in amblygonite. It is almost completely replaced by a mixture of secondary minerals: microlite,

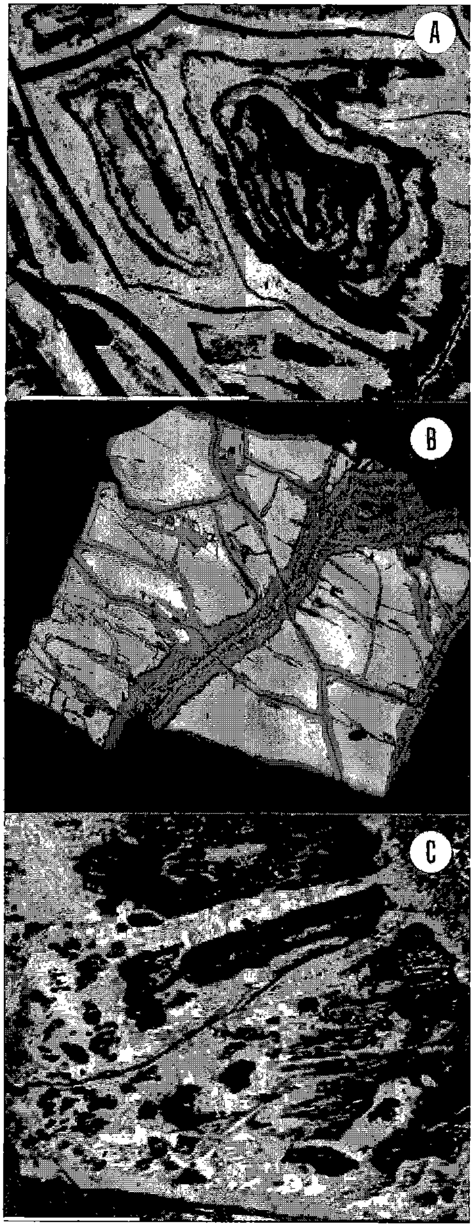

FIG. 3. Back-scattered electron image of secondary Nb,Ta-oxide minerals. A. Onion-skin texture of microlite (bright) and manganotantalite (dark) from Chvalovice. The scale bar is 100 μm long. B. Veins of secondary microlite (gray) and manganotantalite (pale gray) in the center of veins penetrating primary stibiotantalite from Dobrá Voda. The bottom edge of the photograph is 1100 μm long. C. Fine-grained intergrowths of microlite (gray) and manganotantalite (bright) in the center of veins shown in B. Dark poorly polished areas correspond to Fe-rich manganotantalite to ferrotantalite. The scale bar is 80 μm long.

manganotantalite and ferrotantalite. They locally form fracture-filling aggregates; microlite seems to be the earliest to crystallize, followed by Fe-poor manganotantalite. Onion-skin replacement textures consisting of almost alternating monomineralic zones of microlite and manganotantalite also were found (Fig. 3a). Based on EDS-study, poorly polished dark areas in Figure 3a consist largely of manganotantalite . The X-ray powder-diffraction study yielded peaks only of microlite, but none of manganotantalite (F. Veselovský, pers. commun. 1995). A very fine-grained mixture of manganotantalite and ferrotantalite with a random distribution of both minerals also was identified, in which both rynersonite and secondary microlite were completely replaced.

At *Dobrá Voda*, stibiotantalite forms irregular grains or euhedral dipyramidal crystals up to 3 cm in size, enclosed in medium- to coarse-grained albite – "rubellite" subunit of the lepidolite unit (5) (Staněk 1963). It is replaced along fractures by an assemblage of secondary hydrothermal minerals (Fig. 3b). The sequence stibiomicrolite – microlite – manganotantalite is much easier to recognize here than in the Chvalovice pegmatite. However, the last two minerals locally form extremely fine-grained mixtures, situated mainly in the center of veinlets (Fig. 3c). Poorly polished dark areas (Fig. 3c) correspond to Fe-enriched manganotantalite, or perhaps ferrotapiolite. Its presence as a secondary phase is very likely, because a tapiolite-like mineral was detected by X-ray powder diffraction in several samples. Very rare niobian cesstibtantite also was found in the assemblage of secondary minerals (Ercit *et al.* 1993, Novák & Šrein 1998).

At *Laštovičky*, small fragments of compositionally heterogeneous crystals of stibiotantalite, up to 8 mm in size, occur mainly as loose grains in pocket clay, and only exceptionally are enclosed in lepidolite, "rubellite" or quartz. Stibiotantalite is replaced along fractures by very fine-grained ferrotapiolite. Stibiomicrolite and cesstibtantite also were recognized as extremely rare and very small grains in ferrotapiolite; both minerals seem to have formed before ferrotapiolite.

CHEMICAL COMPOSITION

Primary minerals

Ferro- to manganocolumbite from the outer pegmatite units have a very similar composition at all localities examined (Table 2). The composition is characterized by variable Fe contents, but relatively stable and high Nb/Ta values (Fig. 4), decreasing in the late stages of primary crystallization. The relative Mn enrichment is locally extreme, with Mn/(Mn + Fe) very close to 1 except for the Laštovičky pegmatite (Table 2, Fig. 4). Typical minor cations include particularly W [up to 2.88 wt.% WO_3, 0.09 atoms per formula unit (*apfu*)] and Ti (up to 0.65 wt.% TiO_2, 0.06 Ti *apfu*); they are

TABLE 2. REPRESENTATIVE COMPOSITIONS OF PRIMARY MANGANOCOLUMBITE

	1	2	3	4	5	6	7	8	9
WO_3	0.93	0.99	1.38	0.99	2.25	0.48	0.00	1.44	1.15
Nb_2O_5	68.60	68.70	59.70	49.30	65.70	59.10	37.10	63.20	59.80
Ta_2O_5	9.60	9.22	17.70	30.20	11.10	20.10	44.80	14.20	17.80
TiO_2	0.14	0.17	0.27	0.00	0.51	0.04	0.00	0.43	0.16
SnO_2	0.00	0.06	0.00	0.04	0.12	0.09	0.88	0.07	0.00
UO_2	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sc_2O_3	0.00	0.00	0.00	0.05	0.02	0.02	0.05	0.02	0.02
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
CaO	0.02	0.02	0.01	0.03	0.01	0.01	0.03	0.00	0.01
MnO	17.80	17.60	14.20	18.60	11.90	18.00	16.30	9.15	11.80
FeO	2.03	2.44	5.00	0.16	7.79	1.16	0.00	10.20	7.41
Total	99.12	99.26	98.26	99.37	99.44	99.00	99.16	98.71	98.16
					atomic contents				
W^{6+}	0.028	0.030	0.044	0.033	0.069	0.015	0.000	0.045	0.037
Nb^{5+}	3.655	3.655	3.331	2.874	3.526	3.298	2.313	3.455	3.342
Ta^{5+}	0.308	0.295	0.594	1.059	0.358	0.675	1.680	0.467	0.598
Ti^{4+}	0.012	0.015	0.025	0.000	0.046	0.004	0.000	0.039	0.015
Sn^{4+}	0.000	0.003	0.000	0.002	0.006	0.004	0.048	0.003	0.000
U^{4+}	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sc^{3+}	0.000	0.000	0.000	0.006	0.002	0.002	0.006	0.002	0.002
Mg^{2+}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002
Ca^{2+}	0.003	0.003	0.001	0.004	0.001	0.001	0.004	0.000	0.001
Mn^{2+}	1.777	1.754	1.484	2.031	1.197	1.882	1.904	0.937	1.235
Fe^{2+}	0.200	0.240	0.516	0.017	0.773	0.120	0.000	1.031	0.766
$\sum$ cat.	5.985	5.996	5.998	6.028	5.981	6.001	5.958	5.983	6.000

1,2 - Nová Ves, sample VC6; 3,4 - Chvalovice, sample MMC16; 5-7 - Dobrá Voda, 5 - sample MMC39, 6 - sample CDV5, 7 - sample MMC37; 8,9 - Laštovičky, sample VC3. Cation contents normalized to 12 oxygens; 0.00 = below detection limit. Zr,As,Y,Sb and Bi below detection limit. Compositions reported in wt.% oxides.

most abundant in the Dobrá Voda columbite and very low in its Nová Ves counterpart.

Primary microlite from Nová Ves is homogeneous, with Na ≅ Ca; negligible vacancies in the *A* site and high F contents are characteristic (Table 3). The ratio Ta/(Ta + Nb) in two grains varies from 0.73 to 0.90 (Fig. 4), but each individual grain is almost homogeneous.

Rynersonite from Chvalovice is homogeneous, with Ta/(Ta + Nb) in the range 0.68 to 0.71; it displays a relatively simple chemical composition, with W, Pb, Sn, Fe and particularly Mn the typical minor to trace elements detected. Low totals of oxides (about 97 wt.%) and a small excess of R^{2+} cations were observed (Table 4), but cannot be readily explained.

Stibiotantalite from Dobrá Voda is fairly homogeneous, with Ta/(Ta + Nb) between 0.71 to 0.76 (Fig. 4). Except moderate Nb-contents and minor to trace amounts of W, Sn and Bi, it is close to its end-member composition; moderate Y contents (up to 1.13 wt.% Y_2O_3; Table 5) are remarkable. The composition of heterogeneous stibiotantalite in the Laštovičky pegmatite is similar to that from the above locality, except for the Ta/(Ta + Nb) values, which range from 0.68 to 0.95 (Fig. 4, Table 6). Relatively rare Nb-enriched areas are randomly distributed within the stibiotantalite grains.

Primary microlite, rynersonite and stibiotantalite are more evolved relative to the primary columbite. Their Ta/(Ta + Nb) values vary in the broad range from 0.68 to 0.95 (Fig. 4). Except the stibiotantalite from Laštovičky, they are fairly uniform on a single-grain scale, but locally variable among different grains (Fig. 4).

Although not completely developed at all four localities, a general sequence of the *A*-site cations in primary Nb,Ta-oxide minerals can be defined as Fe – Mn – (Ca,Sb).

Secondary minerals

Chemical compositions of secondary minerals are highly variable and complicated compared to the primary minerals, and considerable differences were found among individual localities (Fig. 5). Secondary minerals locally form extremely fine-grained masses; consequently, some microprobe data may represent mixtures of two phases, either microlite with manganotantalite or manganotantalite with ferrotantalite (ferrotapiolite) in a variable ratio.

At *Nová Ves*, secondary microlite was formed during early and late hydrothermal alteration, as described by Lumpkin & Ewing (1992); Na- and F-depletion is typical of early alteration; however, significant Ca-, Na- and F-depletions combined with a considerable increase in U contents (up to 7.11 wt.% UO_2, 0.14 U *apfu*) were found in late secondary microlite (Fig. 5, Table 3). In both types of alteration, the Nb/Ta values remain virtually constant. Late manganocolumbite is Fe-free, locally with minor amount of Ca and F, but it exhibits a significantly depressed Ta/(Ta + Nb), similar to that of the primary manganocolumbite (Fig. 4). The overlap with associated microlite may explain increased Ca and F contents in some compositions. This manganocolumbite may be the only secondary mineral examined to display a change in Nb/Ta relative to its primary precursor.

At *Chvalovice*, highly variable secondary minerals involve mainly Ca-, Na-, F-poor microlite with a high proportion of vacancies in the *A* site; H_2O may be a dominant *A*-site constituent (Ercit *et al.* 1994). A wide spectrum of minor to trace elements W, U, Sn, Bi, Ba, and particularly Pb and K (Table 4) is typical. Pb and K may locally represent dominant *A*-site cations (plumbomicrolite and "kalimicrolite"). Secondary manganotantalite associated with microlite exhibits variable but mostly low Fe- and Ca-contents. Highly heterogeneous ferrotantalite is associated with Fe-rich manganotantalite (Figs. 4, 5, Table 4). Minor to trace amounts of W, Si, Sn, Bi, Ba, Pb, and Ca are typical in both minerals; except Sn and W, the increase in these cations is concomitant with increasing Fe/Mn. Ferrotantalite displays low oxide totals, high excess of R^{2+} (plus R^{3+}) cations, far above the limits of the AB_2O_6 stoichiometry, and appreciable Si (Table 4). Most of the Fe is probably in a trivalent form; however, admixture of Fe-rich hydroxide minerals and quartz in the very fine-grained porous mass is possible.

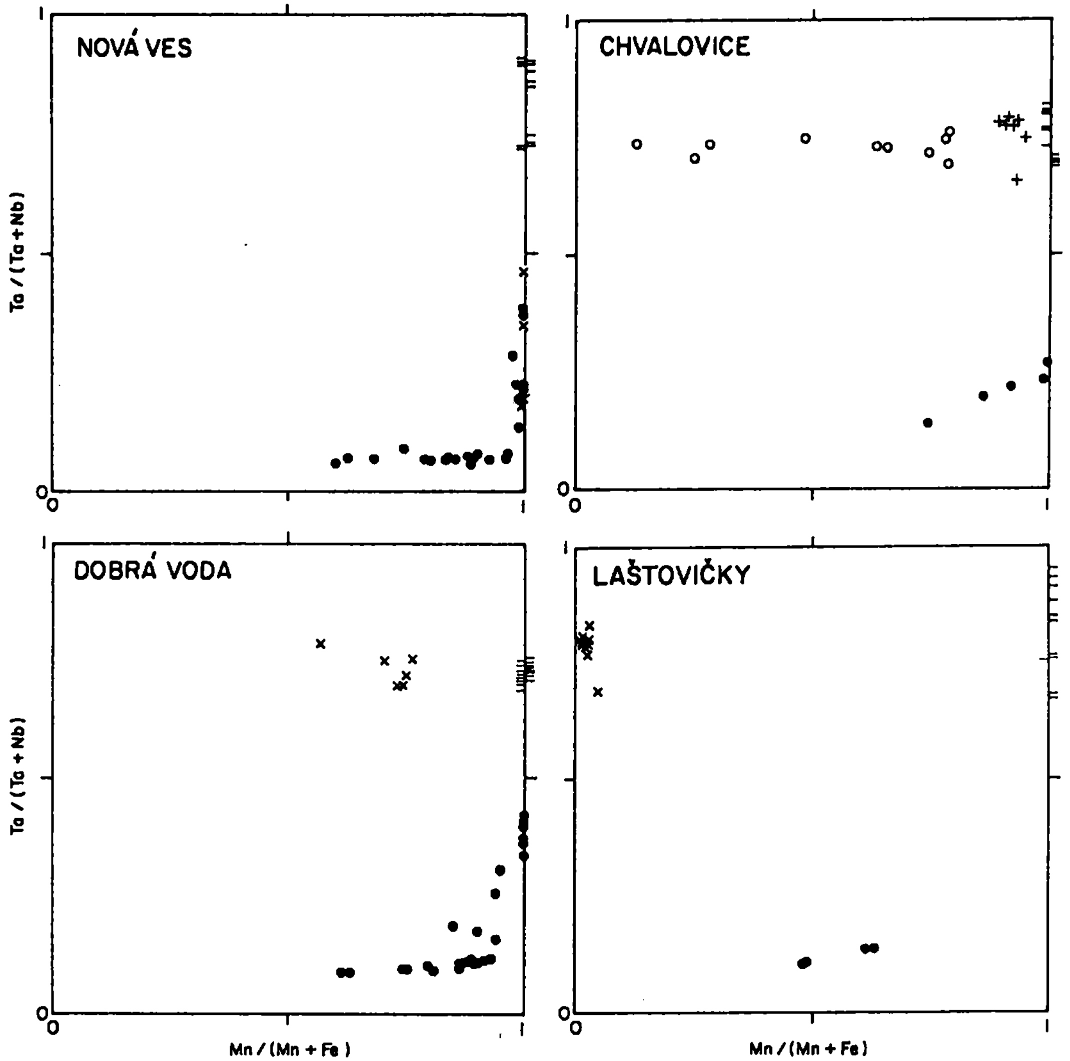

FIG. 4. Compositions of primary and secondary Nb,Ta-oxide minerals in the columbite quadrilateral. Horizontal dashes along the manganoan side of the diagram mark only the Ta/(Ta + Nb) value, and are not related to the Mn/(Mn + Fe) scale. Symbols: ● primary columbite–tantalite, ○ secondary manganotantalite to ferrotantalite, × secondary manganocolumbite – manganotantalite (secondary ferrotapiolite at Laštovičky), + secondary manganotantalite, ⊢ primary stibiotantalite (primary microlite at Nová Ves, primary rynersonite at Chvalovice), ⊣ secondary microlite (stibiomicrolite at Laštovičky).

At *Dobrá Voda*, secondary minerals are highly variable in their chemical composition (Fig. 5, Table 5). Microlite-type minerals vary from stibiomicrolite through Sb- and Sr-enriched microlite varieties to microlite proper. Most of them are Na-, Ca-, and F-poor, with significant vacancies in the *A* site (Table 5, Fig. 6); H_2O may be a dominant constituent in the *A* site (Ercit *et al.* 1994). The minor to trace elements include Sn, Bi, Mn, Fe, Sr, Ba, Na and K. Manganotantalite is dominantly Fe-enriched, with low oxide totals, but stoichiometry close to the AB_2O_6 formula, and low contents of minor elements (Table 5).

At *Laštovičky*, ferrotapiolite is the significantly dominant secondary mineral; cesstibtantite (not analyzed quantitatively because of its small grain-size) and stibiomicrolite (only one spot analyzed, Table 6) are very rare. Two distinct varieties of ferrotapiolite were recognized, Sb-free ferrotapiolite with moderate

TABLE 3. REPRESENTATIVE COMPOSITIONS OF MICROLITE, MANGANOCOLUMBITE AND URANMICROLITE FROM NOVÁ VES

	1	2	3	4	5	6	7
WO_3	0.16	0.00	0.28	0.21	0.04	0.53	0.06
Nb_2O_5	14.10	14.90	49.63	5.30	4.93	5.02	5.02
Ta_2O_5	64.90	63.60	30.45	74.90	75.40	77.90	76.70
TiO_2	0.00	0.00	0.02	0.00	0.00	0.00	0.00
SnO_2	0.05*	0.11*	0.08	0.10*	0.12*	0.08*	0.21*
UO_2	1.19	3.05	0.00	0.00	0.00	4.42	7.11
Sb_2O_3	0.36	0.16	0.00	0.16	0.14	0.00	0.00
Bi_2O_3	0.09	0.00	0.00	0.00	0.07	0.00	0.08
CaO	10.60	9.79	0.05	10.30	10.20	1.35	0.78
MnO	0.00	0.00	15.35	0.01	0.01	0.09	0.73
FeO	0.00	0.00	0.00	0.00	0.01	0.36	0.00
SrO	0.00	0.00	0.00	0.00	0.00	0.00	0.47
BaO	0.00	0.00	0.00	0.00	0.00	0.25	0.40
PbO	0.10	0.14	0.00	0.08	0.13	0.55	0.48
Na_2O	5.09	2.92	0.00	6.04	6.08	0.11	0.00
K_2O	0.00	0.00	0.06	0.01	0.01	0.10	0.15
F	3.01	2.57	0.00	3.18	3.17	0.11	0.00
O = F	-1.27	-1.08	0.00	-1.34	-1.33	-0.05	0.00
Total	98.38	96.16	95.95	98.95	98.98	90.82	91.89
				atomic contents			
W^{6+}	0.003	0.000	0.010	0.005	0.001	0.012	0.001
Nb^{5+}	0.530	0.561	2.983	0.210	0.196	0.192	0.185
Ta^{5+}	1.467	1.439	1.101	1.785	1.803	1.796	1.813
Ti^{4+}	0.000	0.000	0.002	0.000	0.000	0.000	0.000
Sn^{4+}	0.002+	0.004+	0.004	0.004+	0.005+	0.003+	0.008+
U^{4+}	0.022	0.056	0.000	0.000	0.000	0.083	0.138
Sb^{3+}	0.012	0.005	0.000	0.006	0.005	0.001	0.000
Bi^{3+}	0.002	0.000	0.000	0.000	0.002	0.000	0.002
Ca^{2+}	0.944	0.873	0.007	0.967	0.961	0.123	0.073
Mn^{2+}	0.000	0.000	1.728	0.001	0.001	0.006	0.054
Fe^{2+}	0.000	0.000	0.000	0.000	0.001	0.026	0.000
Sr^{2+}	0.000	0.000	0.000	0.000	0.000	0.000	0.024
Ba^{2+}	0.000	0.000	0.000	0.000	0.000	0.008	0.014
Pb^{2+}	0.002	0.003	0.000	0.002	0.003	0.013	0.011
Na^+	0.820	0.471	0.000	1.026	1.037	0.018	0.000
K^+	0.000	0.000	0.010	0.001	0.001	0.011	0.017
F^-	0.791	0.676	0.000	0.881	0.882	0.029	0.000
O^{2-}	6.031	5.903	12.000	6.062	6.063	5.356	5.479
$\sum$ cat.	3.804	3.414	5.850	4.007	4.015	2.292	2.340
$\sum$ an.	6.822	6.579	12.000	6.943	6.945	5.386	5.479

1, 4 and 5 - primary microlite; 2, 6 and 7 - secondary microlite to uranmicrolite; 3 - "secondary" manganocolumbite.
Cation contents normalized to Ta+Nb+Ti+W=2 (microlite #1, 2, 4, 5, 6, 7) and 12 oxygens (manganocolumbite #3). 0.00 = below detection limits; *Sn as SnO, +Sn^{2+}. Cs below detection limit. Compositions reported in wt.% oxides.

inferred Fe^{3+} content (up to 0.25 *apfu*), and a rare Sb-enriched ferrotapiolite (up to 9.76 wt.% Sb_2O_3, 0.67 *apfu*; Table 6, Fig. 5).

General observations

Almost all secondary phases from the localities examined are characterized by a fairly stable Nb/Ta value during all stages of hydrothermal alteration (Fig. 4). The only exception is very rare "secondary" manganocolumbite associated with primary microlite from Nová Ves (Fig. 3). However, textural relations of both minerals are complicated, and this manganocolumbite may in fact be a primary mineral replaced by microlite. Such interpretation also is supported by the very similar composition of primary manganocolumbite at this locality.

The Nb,Ta-oxide minerals from all localities examined exhibit a similar sequence of *A*-site cations, (Sb) – Ca – Mn – Fe, but with significant quantitative variations controlled by the precursors. The secondary phases at the localities with Ca-rich primary minerals (microlite, rynersonite) are characterized by gradual decrease in Ca and increase in Mn, followed at Chvalovice by significant late enrichment in Fe (Fig. 5). The two localities with stibiotantalite exhibit somewhat different evolution. Primary stibiotantalite is initially replaced by stibiomicrolite or Sb-rich microlite, but the subsequent stages of replacement are very similar to

TABLE 4. REPRESENTATIVE COMPOSITIONS OF RYNERSONITE, MICROLITE, MANGANOTANTALITE AND FERROTANTALITE FROM CHVALOVICE

	1	2	3	4	5	6
WO_3	2.10	0.45	0.54	0.53	1.23	0.58
Nb_2O_5	17.00	12.10	10.40	8.43	11.00	16.14
Ta_2O_5	64.90	54.60	58.00	56.70	64.60	59.42
TiO_2	0.00	0.00	0.02	0.00	0.00	0.10
SnO_2	0.48	1.11*	1.10*	1.30*	1.17	0.85
SiO_2	n.d.	n.d.	n.d.	n.d.	n.d.	0.79
UO_2	0.00	2.64	2.57	1.90	0.00	0.00
Sb_2O_3	0.03	0.00	0.00	0.00	0.06	0.12
Bi_2O_3	0.00	0.00	0.10	0.41	0.00	0.33
CaO	12.30	3.20	1.95	1.56	0.67	0.47
MnO	0.35	1.90	0.95	0.66	11.40	10.87
FeO	0.20	1.61	1.35	0.93	0.92	3.08
SrO	0.00	0.27	0.20	0.10	0.00	0.11
BaO	0.00	2.16	1.77	1.08	0.08	0.00
PbO	0.41	0.01	0.04	4.54	2.98	0.37
Na_2O	0.00	0.00	0.00	0.00	0.00	0.00
K_2O	0.00	0.72	1.22	0.30	0.00	0.01
Cs_2O	0.00	0.00	0.18	0.16	0.10	0.00
F	0.00	0.09	0.16	0.00	0.00	0.00
O = F	-0.00	-0.04	-0.07	0.00	0.00	0.00
Total	97.79	80.82	80.46	78.60	94.21	93.24
			atomic contents			
W^{6+}	0.082	0.011	0.014	0.014	0.054	0.024
Nb^{5+}	1.165	0.535	0.456	0.394	0.849	1.181
Ta^{5+}	2.675	1.453	1.530	1.592	3.000	2.615
Ti^{4+}	0.000	0.000	0.000	0.000	0.000	0.012
Sn^{4+}	0.029	0.048+	0.048+	0.060+	0.080	0.055
Si^{4+}	-	-	-	-	-	0.128
U^{4+}	0.000	0.057	0.055	0.044	0.000	0.002
Sb^{3+}	0.002	0.000	0.000	0.000	0.004	0.008
Bi^{3+}	0.000	0.000	0.003	0.001	0.000	0.014
Ca^{2+}	1.997	0.336	0.203	0.173	0.123	0.081
Mn^{2+}	0.045	0.158	0.078	0.058	1.647	0.417
Fe^{2+}	0.025	0.132	0.110	0.080	0.131	0.007
Sr^{2+}	0.000	0.015	0.011	0.006	0.000	1.490
Ba^{2+}	0.000	0.083	0.067	0.044	0.005	0.000
Pb^{2+}	0.017	0.000	0.001	0.126	0.137	0.016
Na^+	0.000	0.000	0.000	0.000	0.000	0.000
K^+	0.000	0.090	0.151	0.040	0.000	0.002
Cs^+	0.000	0.000	0.007	0.007	0.007	0.001
F^-	0.019	0.028	0.049	0.000	0.000	0.000
O^{2-}	11.981	5.903	5.741	5.741	12.000	12.000
$\sum$ cat.	6.037	2.919	2.734	2.648	6.040	6.052
$\sum$ an.	12	5.951	5.743	5.68	12	12

1 - primary rynersonite; 2-4 secondary microlite; 5 - secondary manganotantalite; 6 secondary manganotantalite.
Cation contents normalized to 12 oxygens (rynersonite #1), and Ta+Nb+Ti+W = 2
(microlite #2-4). 0.00 = below detection limit; *Sn as SnO, +Sn^{2+}.
Compositions reported in wt.% oxides.

TABLE 5. REPRESENTATIVE COMPOSITIONS OF STIBIOTANTALITE, STIBIOMICROLITE, MICROLITE AND MANGANOTANTALITE FROM DOBRÁ VODA

	1	2	3	4	5	6	7
WO_3	0.46	0.08	0.00	0.21	0.60	1.23	0.35
Nb_2O_5	9.84	11.10	12.60	13.90	13.60	16.20	11.00
Ta_2O_5	46.80	52.40	62.40	63.20	62.70	63.50	70.90
SnO_2	0.67	1.00*	0.21*	0.59*	0.38*	0.85	0.96
Y_2O_3	1.13	0.47	0.12	0.00	0.02	0.00	0.00
Sb_2O_3	40.60	20.10	7.55	4.41	2.73	0.11	0.00
Bi_2O_3	0.34	1.08	1.00	0.17	0.06	0.00	0.05
CaO	0.00	0.99	6.08	6.45	9.59	0.05	0.13
MnO	0.03	0.16	0.52	0.31	0.530	11.50	8.46
FeO	0.01	0.74	0.27	0.14	0.68	4.10	6.42
SrO	0.10	3.30	1.97	4.00	2.23	0.00	0.00
BaO	0.09	0.72	0.37	0.55	0.38	0.00	0.00
PbO	0.07	0.04	0.09	0.00	0.00	0.00	0.03
Na_2O	0.00	0.52	1.66	0.28	0.90	0.00	0.00
K_2O	0.00	0.18	0.18	0.10	0.03	0.01	0.01
Cs_2O	0.00	0.00	0.10	0.00	0.14	0.00	0.00
F	0.00	0.31	0.47	0.38	0.50	0.00	0.00
O = F	0.00	-0.13	-0.20	-0.16	-0.21	0.00	0.00
Total	100.14	93.06	95.34	94.53	94.86	97.51	97.98
atomic contents							
W^{6+}	0.027	0.002	0.000	0.005	0.013	0.050	0.015
Nb^{5+}	1.014	0.520	0.503	0.534	0.527	1.151	0.805
Ta^{5+}	2.901	1.478	1.497	1.461	1.460	2.713	3.120
Sn^{4+}	0.061	0.046+	0.008+	0.022+	0.015+	0.051	0.041
Sb^{3+}	3.815	0.859	0.275	0.155	0.096	0.007	0.000
Bi^{3+}	0.020	0.029	0.023	0.004	0.001	0.000	0.002
Ca^{2+}	0.000	0.110	0.575	0.588	0.880	0.008	0.023
Mn^{2+}	0.006	0.014	0.039	0.022	0.038	1.530	1.160
Fe^{2+}	0.002	0.064	0.020	0.010	0.049	0.539	0.869
Sr^{2+}	0.013	0.198	0.101	0.197	0.111	0.000	0.000
Ba^{2+}	0.008	0.029	0.013	0.018	0.013	0.000	0.000
Pb^{2+}	0.004	0.001	0.002	0.000	0.000	0.000	0.001
Na^+	0.000	0.105	0.284	0.046	0.149	0.000	0.000
K^+	0.000	0.024	0.020	0.011	0.003	0.002	0.002
Cs^+	0.000	0.000	0.004	0.000	0.005	0.000	0.000
F^-	0.029	0.201	0.131	0.102	0.135	0.000	0.000
O^{2-}	15.971	6.895	6.310	6.097	6.287	12.000	12.000
∑ cat.	8.008	3.506	3.369	3.073	3.362	6.051	6.037
∑ an.	16	6.950	6.432	6.177	6.406	12	12

1 - primary stibiotantalite, 2 - secondary stibiomicrolite, 3-5 - secondary microlite, 6 and 7 - secondary manganotantalite.
Cation contents normalized to 16 anions (stibiotantalite #1),
Ta+Nb+Ti+W = 2 (microlite # 2 to 5), and 12 oxygens (manganotantalite #6,7).
0.00 = below detection limit; *Sn as SnO, + Sn^{2+}. Ti and U below detection limit.
Compositions reported in wt.%.

those given above for Ca-rich primary phases (compare in Fig. 5). No other substantial *A*-site cations participate in the process at the localities examined.

Evident differences exist in the participation of the individual *A*-site cations among the four localities (Fig. 5). In the Nová Ves pegmatite, the early subsolidus phase (secondary microlite) is preserved, indicating high activity of Ca relative to Mn, which is present only in the very rare manganocolumbite of uncertain affiliation and negligible volume. The Laštovičky pegmatite is characterized by high activity of Fe, but very low activities of Ca and Mn, generating abundant ferrotapiolite. Both the Chvalovice and Dobrá Voda pegmatites exhibit a virtually complete replacement sequence, including early Ca(Sb)-rich phases such as stibiomicrolite and microlite, and late Fe-enrichment characterized by presence of Fe-rich manganotantalite (both localities), ferrotantalite (Chvalovice) and probable ferrotapiolite (Dobrá Voda) (see Fig. 5).

Poor polish in some samples, extremely fine grain-size and high porosity of some secondary aggregates, possible presence of very fine-grained admixture of Fe-hydroxides and quartz are typical features of the latest stage of the hydrothermal alteration. They render the study quite difficult, and may obscure some aspects of the mineral assemblages examined. However, the generally stable Nb/Ta values and the sequence of *A*-site cations, (Sb) – Ca – Mn – Fe, characterize the products of hydrothermal alteration of primary Nb,Ta-oxide minerals at the localities examined beyond any doubt (Fig. 5).

TABLE 6. REPRESENTATIVE COMPOSITIONS OF STIBIOTANTALITE, STIBIOMICROLITE AND FERROTAPIOLITE FROM LAŠTOVIČKY

	1	2	3	4	5	6	7
WO_3	0.45	0.31	0.55	1.33	1.12	0.44	0.34
Nb_2O_5	12.80	8.56	3.90	13.05	11.30	9.20	9.41
Ta_2O_5	40.90	48.20	53.70	63.89	70.40	70.80	67.75
SiO_2	0.00	0.00	0.00	n.d.	0.00	0.10	0.04
TiO_2	0.02	0.01	0.02	0.30	0.04	0.02	0.02
SnO_2	0.53	0.52	0.67	0.00	0.39	0.78	0.80
UO_2	0.08	0.00	0.00	0.00	0.00	0.00	0.00
Sb_2O_3	43.00	41.40	40.60	12.82	0.54	4.88	9.87
Bi_2O_3	0.00	0.07	0.37	0.00	0.00	0.00	0.06
CaO	0.00	0.00	0.00	4.28	0.04	0.04	0.00
MnO	0.01	0.00	0.00	0.30	0.35	0.28	0.17
FeO	0.00	0.06	0.00	0.25	13.75	12.49	10.51
Fe_2O_3	0.00	0.00	0.00	0.00	1.06	0.23	0.00
BaO	0.00	0.00	0.19	n.d.	0.18	0.00	0.00
PbO	0.00	0.16	0.00	n.d.	0.00	0.00	0.05
Na_2O	0.00	0.00	0.00	1.10	0.00	0.00	0.00
Total	97.79	99.29	100.00	97.32	99.17	99.26	98.98
atomic contents							
W^{6+}	0.027	0.019	0.034	0.029	0.046	0.019	0.015
Nb^{5+}	1.328	0.900	0.420	0.495	0.814	0.677	0.701
Ta^{5+}	2.553	3.047	3.475	1.457	3.051	3.134	3.037
Si^{4+}	0.000	0.000	0.000	-	0.000	0.016	0.007
Ti^{4+}	0.003	0.002	0.004	0.019	0.005	0.002	0.002
Sn^{4+}	0.049	0.048	0.064	0.000	0.025	0.051	0.053
U^{4+}	0.004	0.000	0.000	0.000	0.000	0.000	0.001
Sb^{3+}	4.068	3.967	3.983	0.443	0.035	0.327	0.671
Bi^{3+}	0.000	0.004	0.023	0.000	0.000	0.000	0.003
Ca^{2+}	0.000	0.000	0.000	0.385	0.007	0.007	0.000
Mn^{2+}	0.002	0.000	0.000	0.021	0.047	0.039	0.024
Fe^{2+}	0.000	0.012	0.000	0.018	1.832	1.700	1.449
Fe^{3+}	0.000	0.000	0.000	0.000	0.127	0.028	0.000
Ba^{2+}	0.000	0.000	0.018	-	0.011	0.000	0.000
Pb^{2+}	0.000	0.010	0.000	-	0.000	0.000	0.002
Na^+	0.000	0.000	0.000	0.179	0.000	0.000	0.000
O^{2-}	16.000	16.000	16.000	6.183	12.000	12.000	12.000
∑ cat.	8.034	8.008	8.020	3.046	6.000	6.000	5.964
∑ an.	16	16	16	6.183	12	12	12

1-3- primary stibiotantalite; 4- secondary stibiomicrolite;
5-7 - secondary ferrotapiolite.
Cation contents normalized to 16 oxygens (stibiotantalite #1-3), Ta+Nb+Ti+W = 2 (stibiomicrolite #4); 12 oxygens and 6 cations (ferrotapiolite #5-7). n.d. - not determined. K, Cs and F below detection limit. Compositions reported in wt.% oxides.

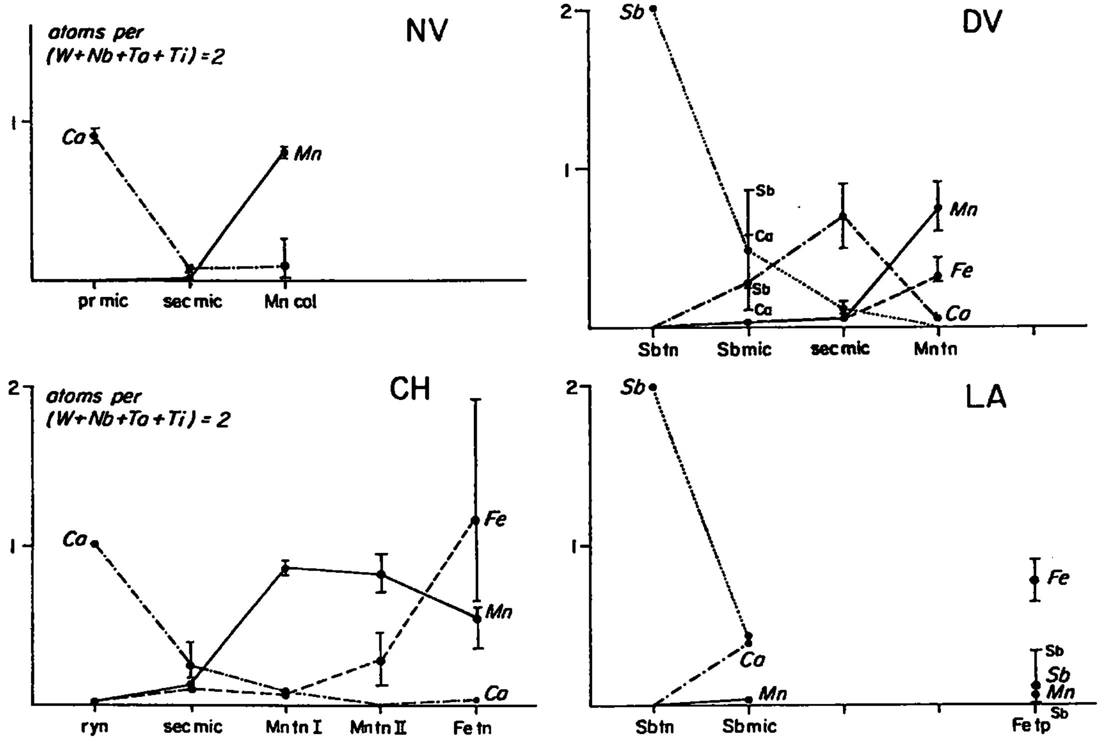

FIG. 5. Variations in the A-site cations Ca, Mn and Fe in primary and secondary Nb,Ta-oxide minerals. All data normalized to Nb + Ta + Ti + W = 2 atoms. Vertical bars: ranges of individual cations. Symbols: NV Nová Ves, CH Chvalovice, DV Dobrá Voda, LA Laštovičky, prmic: primary microlite, secmic: secondary microlite, Mncol: "secondary" manganocolumbite, MntnI: secondary manganotantalite associated with secondary microlite, MntnII: Fe-rich secondary manganotantalite associated with ferrotantalite, Sbtn: primary stibiotantalite, Sbmic: secondary stibiomicrolite, Mntn: secondary manganotantalite, Fetp: secondary ferrotapiolite, Fetn: secondary ferrotantalite.

DISCUSSION

Primary minerals

Compositional trends in columbite and other primary Nb,Ta-oxide minerals (microlite, rynersonite, stibiotantalite) exhibit geochemical signatures typically observed in granitic pegmatites of the lepidolite subtype: in columbite-type minerals, the buildup in Mn over Fe precedes the enrichment in Ta over Nb, and the Mn/(Mn + Fe) values are commonly close to 1; microlite and stibiotantalite represent the most evolved Nb,Ta-oxide minerals (*cf.* Foord 1976, Černý & Ercit 1985, 1989, Černý 1989). Rynersonite from Chvalovice is very likely the first occurrence of this species as a primary mineral in granitic pegmatites. It is generally known as a secondary phase replacing stibiotantalite, bismutotantalite, microlite or other minerals (Foord & Mrose 1978, von Knorring & Fadipe 1981, Černý & Ercit 1985, 1989, Baldwin 1989), or as a late phase in pegmatite pockets (Novák *et al.* 1994). The formation of rynersonite instead of the chemically similar and more abundant microlite may be influenced by low activity of F in the parent medium.

The general sequence of enrichment of the A-site cations in primary minerals, Fe – Mn – Ca – (Sb), is quite common in the Nb,Ta-oxide minerals of moderately to considerably fractionated rare-element pegmatites (as summarized by Černý & Ercit 1985, 1989). Greater complexity is, however, routinely encountered in extremely evolved pegmatites, in which additional cations (such as Li, Na, K, Cs, Pb, Bi, Al, U and Sn) are encountered (Ercit 1986, Voloshin & Pakhomovskyi 1988).

Secondary minerals

Minerals crystallized during the secondary (hydrothermal) stage in the pegmatites examined, including stibiomicrolite, microlite, cesstibtantite, manganotantalite, ferrotantalite and ferrotapiolite, are commonly described from similar mineral assemblages

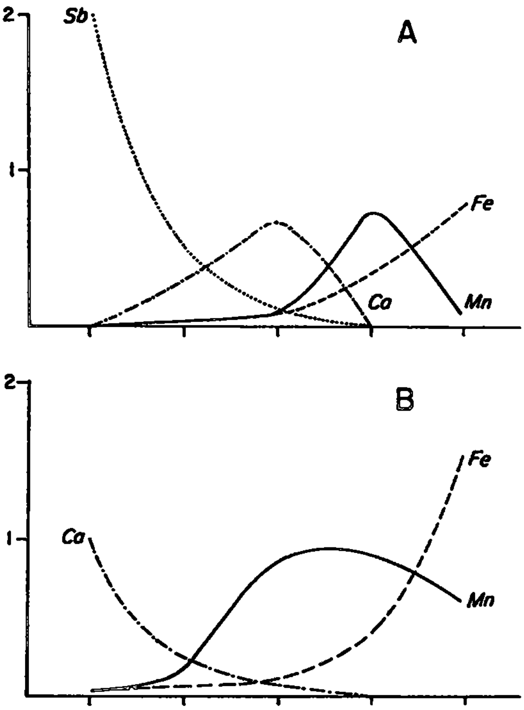

FIG. 6. Generalized trends in the evolution of *A*-site cation abundances at the localities examined, complemented by published observations (see the text for references). A. The Sb – Ca – Mn – Fe sequence. B. The Ca – Mn – Fe sequence in Sb-free assemblages.

considered to be metasomatic, formed at the expense of primary phases analogous to those described here. However, they also replace simpsonite, stibiotantalite, bismutotantalite, holtite and other less common minerals (*e.g.*, Černý & Ercit 1985, Ercit 1986, Voloshin & Pakhomovskyi 1988, Baldwin 1989).

The ratio Nb/Ta in the secondary minerals

A universal decrease in Nb/Ta in not only primary but also secondary minerals was suggested by Voloshin (1983). However, Černý & Ercit (1985), Ercit (1986) and Lumpkin & Ewing (1992) found this ratio in hydrothermally formed late minerals rather stable, and comparable to that of their precursors. Our data are in good agreement with the results of the latter group of authors. Evidently, the mobility of Nb and Ta is about equal during the replacement processes at most localities, and the two metals are incorporated into the metasomatic products in proportions more or less identical to those established in the primary phases.

Sequence of A-site cations in the secondary minerals

The complete sequence of the *A*-site cations (Sb) – Ca – Mn – Fe, as recognized at Chvalovice and Dobrá Voda, has only rarely been recorded in complex granitic pegmatites (Voloshin 1983). However, diverse segments of the sequence, such as Sb – Ca – Mn, Sb – Ca, Ca – Mn and Mn – Fe, are commonly observed at many localities (*e.g.*, Černý & Ercit 1985, 1989, Ercit 1986, Voloshin & Pakhomovskyi 1988, Baldwin 1989). Increased activities of Mn and Fe relative to Ca are also recorded in late varieties of microlite (Wise & Černý 1990, Lumpkin & Ewing 1992). This indicates that the overall sequence documented here, (Sb) – Ca – Mn – Fe (Fig. 6), may represent a universal pattern of hydrothermal replacement of primary Nb,Ta-oxide minerals such as microlite, stibiotantalite, simpsonite and bismutotantalite.

The variable abundance of the individual *A*-site cations may result from the compositions of residual fluids, and from the composition of primary Nb,Ta-oxide minerals. The array of the *A*-site cations is consequently subject to broader variations at individual localities (*e.g.*, Na, Li, K, Cs, Ba, Al, Bi, Sn; Voloshin 1983, Ercit 1986). However, the sequence of (Al) – K, Li – Cs, Na – Ca, derived by Voloshin & Pakhomovskyi (1988), cannot be accepted as a valid generalization. The composition of metamorphic fluids may also have a significant role in the latest stages of the hydrothermal crystallization (as discussed below), and meteoric waters may be involved under conditions of near-surface, low-temperature weathering-induced replacement (*e.g.*, cesstibtantite and kimrobinsonite: Nickel & Robinson 1985).

The suggested sequence of the *A*-site cations in secondary replacement, (Sb) – Ca – Mn – Fe, is reversed from that characteristic of the primary crystallization at the localities examined. However, the mechanism producing such a reversed sequence is not understood at present.

Sources of A-site cations in the secondary phases

The major *A*-site cations in the Nb,Ta-oxide minerals of the secondary stage at the localities studied include Sb, Ca, Mn and Fe (Fig. 5). The likely source of Sb and Ca seems to be the highly evolved fluids exsolved from the residual pegmatite-forming melt, or the replaced primary mineral, or both; elevated Ca-contents were found in the residual melt in the experiments on the Macusani glass (London *et al.* 1989). Infiltration of Ca *via* metamorphic fluids from the host rocks is another possible process, particularly in granitic pegmatites hosted by Ca-rich rocks (London 1990). As Ca participates in very early stages of the hydrothermal replacement of primary Nb,Ta-oxide minerals, possibly before mixing of residual and metamorphic fluids, and as in most cases the host rocks are not Ca-rich (Table

1), this process does not seem to be probable. Release of Ca during hydrothermal alteration of blocky K-feldspar is not likely because of virtual absence of this process at most localities. Highly evolved fluids also are the source of Mn, because high activity of Mn in pore fluids in the host rocks (Table 1) can be ruled out.

High activity of Fe in late stages of the replacement process may have several possible explanations. Iron may have the same residual source as the other *A*-site cations Sb, Ca and Mn; such an idea is supported by late hydrothermal crystallization of Fe-rich tourmaline (foitite) from residual pegmatite-generated fluids uncontaminated by metamorphic fluids, suggested for the Dobrá Voda pegmatite by Novák & Taylor (in prep.). The array of minor *A*-site cations such as Sb, Bi, Sr, Ba, Pb and U recorded at all localities, general lack of columbite alteration in outer pegmatite units, and virtual absence of Mg in most compositions, also point to residual fluids as the main source of all *A*-site cations. On the other hand, some phenomena, such as onion-skin textures, nonstoichiometric compositions of Si-enriched ferrotantalite with a high excess of Fe (Fig. 5), and the chemical composition of most of the secondary microlite (Table 4; *cf.* also Lumpkin & Ewing 1992), recognized particularly at Chvalovice, suggest low-temperature formation, possibly under conditions of near-surface weathering. Consequently, a participation of mixed pegmatite and host-rock-derived fluids in the secondary process at the Chvalovice locality is fairly probable, and the source of Fe may be the host rock.

P–T–X conditions of secondary replacements

The early stage of hydrothermal replacement of the primary Nb,Ta-oxide minerals at the localities studied is represented by the reaction of primary minerals with highly evolved pegmatite-derived fluids soon after crystallization, *i.e.*, at about 500 to 350°C, 2.5–2.0 kbar (typical of low-P, high-T petalite-bearing pegmatites; London 1990). Such fluid has a relatively high pH, high activity of Ca, and low activity of Na, is commonly accompanied and followed by elevated activities of Mn and Fe. Participation of metamorphic fluids released from the host rock is unlikely at this stage. The formation of Fe-rich secondary phases (Fe-rich manganotantalite, ferrotantalite and ferrotapiolite), latest to crystallize in most of the mineral assemblages studied, seems to be more complicated. Veins of ferrotapiolite in stibiotantalite from Laštovičky formed at relatively early stages. However, onion-skin textures and chemical composition of microlite from Chvalovice and in part also from Nová Ves suggest a low temperature of ≤100°C, close to conditions of near-surface weathering (Lumpkin & Ewing 1992). Such conditions would explain the high Fe^{3+} content of secondary tantalite at Chvalovice, and violations of the ferrotapiolite–tantalite gap (Černý *et al.* 1992). However, a total lack of experimental data does not allow realistic estimates of the P–T–*X* conditions of all stages of secondary hydrothermal processes, particularly at the low-temperature end.

CONCLUSIONS

(1) A general sequence of *A*-site cations was established for primary Nb,Ta-oxide minerals in four complex pegmatites in the Bohemian and Moravian Moldanubicum, Fe – Mn – Ca – (Sb) in columbite, microlite, rynersonite and stibiotantalite, with many analogs in similar granitic pegmatites worldwide.

(2) A reversed sequence (Sb) – Ca – Mn – Fe characterizes the products of subsolidus replacement of the primary minerals of Ca and Sb, also with numerous analogies at other localities. It may represent a universal pattern of secondary replacement at the expense of the above primary minerals in moderately to considerably fractionated rare-element pegmatites.

(3) The qualitative and quantitative representation of the *A*-site cations is controlled by the relationships among the primary phases and by the composition of subsolidus fluids. Further complications are encountered in highly fractionated pegmatites, with secondary minerals containing Li, Na, K, Cs, Pb, Al, U or Sn.

(4) The *A*-site cations in the secondary minerals originate mainly from the residual pegmatite-derived fluids and the parent minerals. Early involvement of country-rock-derived solutions is unlikely, but possible locally to explain the pattern of Fe in late stages.

(5) The ratio Nb/Ta decreases during primary crystallization, but the secondary minerals inherit the ratio of their respective precursors.

(6) The P–T conditions of the secondary replacement processes vary from early subsolidus at ~500–350°C, 2.5–2.0 kbar to near-surface weathering.

ACKNOWLEDGEMENTS

This study was supported by the NSERC Research Grants and Major Installation Grant to P.Č., and by NSERC Equipment and Infrastructure Grants to F.C. Hawthorne. A Faculty of Science, University of Manitoba Postdoctoral Stipend supported M.N. Our thanks to to F. Veselovský, P. Korbel and N. Ball for help in X-ray-diffraction work, and to Ron Chapman for assistance during the electron microprobe study. A.U. Falster and W.B. Simmons, Jr. provided thorough reviews which substantially improved the presentation.

REFERENCES

BALDWIN, J.R. (1989): Replacement phenomena in tantalum minerals from rare-metal pegmatites in South Africa and Namibia. *Mineral. Mag.* **53**, 571-581.

ČECH, F. & STANĚK, J. (1960): Microlite from lithium-bearing pegmatite at Nová Ves near Český Krumlov, southern Bohemia. *Čas. Mineral. Geol.* **5**, 235-240 (in Czech).

ČERNÝ, P. (1989): Characteristics of pegmatite deposits of tantalum. *In* Lanthanides, Tantalum and Niobium (P. Möller, P. Černý & F. Saupé, eds). Springer Verlag, New York, N.Y. (195-239).

________ & ERCIT, T.S. (1985): Some recent advances in the mineralogy and geochemistry of Nb and Ta in rare-element granitic pegmatites. *Bull. Minéral.* **108**, 499-532.

________ & ________ (1989): Mineralogy of niobium and tantalum: crystal chemical relationships, paragenetic aspects and their economic implications. *In* Lanthanides, Tantalum and Niobium (P. Möller, P. Černý & F. Saupé, eds). Springer Verlag, New York, N.Y. (27-79).

________, ________ & WISE, M.A. (1992): The tantalite–tapiolite gap: natural assemblages *versus* experimental data. *Can. Mineral.* **30**, 587-596.

________ & NĚMEC, D. (1995): Pristine vs. contaminated trends in Nb,Ta-oxide minerals of the Jihlava pegmatite district, Czech Republic. *Mineral. Petrol.* **55**, 117-130.

ERCIT, T.S. (1986): *The Simpsonite Paragenesis. The Crystal Chemistry and Geochemistry of Extreme Ta Fractionation.* Ph.D. thesis, Univ. of Manitoba, Winnipeg, Manitoba.

________ (1994): The geochemistry and crystal chemistry of columbite-group minerals from granitic pegmatites, southwestern Grenville Province. *Can. Mineral.* **32**, 421-438.

________, ČERNÝ, P. & HAWTHORNE, F.C. (1993): Cesstibtantite – a geologic introduction to the inverse pyrochlores. *Mineral. Petrol.* **48**, 235-255.

________, HAWTHORNE, F.C. & ČERNÝ, P. (1994): The structural chemistry of kalipyrochlore, a "hydropyrochlore". *Can. Mineral.* **32**, 415-420.

FOORD, E.E. (1976): *Mineralogy and Petrogenesis of Layered Pegmatite–Aplite Dikes in the Mesa Grande District, San Diego County, California.* Ph.D. dissertation, Stanford Univ., Stanford, California.

________ & MROSE, M.E. (1978): Rynersonite, $Ca(Ta,Nb)_2O_6$, a new mineral from San Diego County, California. *Am. Mineral.* **63**, 709-714.

KEPPLER, H. (1993): Influence of fluorine on the enrichment of high field-strength trace elements in granitic rocks. *Contrib. Mineral. Petrol.* **114**, 479-488.

VON KNORRING, O. & FADIPE, A. (1981): On the mineralogy and geochemistry of niobium and tantalum in some granite pegmatites and alkali granites of Africa. *Bull. Minéral.* **104**, 496-507.

LINNEN, R.L. & KEPPLER, H. (1996): Columbite solubility in granitic melts: implications for pegmatite genesis. *Geol. Assoc. Can. – Mineral. Assoc. Can., Program Abstr.* **21**, A-57.

LONDON, D. (1990): Internal differentiation of rare-element pegmatites: a synthesis of recent research. *In* Ore-Bearing Granite Systems; Petrogenesis and Mineralizing Processes (H.J. Stein & J.L. Hannah, eds.). *Geol. Soc. Am., Spec. Pap.* **246**, 35-50.

________, MORGAN, G.B., VI & HERVIG, R.L. (1989): Vapor-undersaturated experiments with Macusani glass + H_2O at 200 MPa, and internal differentiation of granitic pegmatites. *Contrib. Mineral. Petrol.* **102**, 1-17.

LUMPKIN, G.R. & EWING, R.C. (1992): Geochemical alteration of pyrochlore group minerals: microlite subgroup. *Am. Mineral.* **77**, 179-188.

MULJA, T., WILLIAMS-JONES, A.E., MARTIN, R.F. & WOOD, S.A. (1996): Compositional variation and structural state of columbite–tantalite in rare-element granitic pegmatites of the Preissac–Lacorne batholith, Quebec, Canada. *Am. Mineral.* **81**, 146-157.

NICKEL, E.H. & ROBINSON, B.W. (1985): Kimrobinsonite, a new tantalum mineral from western Australia, and its association with cesstibtantite. *Can. Mineral.* **23**, 573-576.

NOVÁK, M., ČERNÝ, P., ČECH, F. & STANĚK, J. (1992): Granitic pegmatites in the territory of the Bohemian and Moravian Moldanubicum. *Int. Symp. Mineralogy, Petrology and Geochemistry of Granitic Pegmatites, Lepidolite 200 (Nové Město na Moravě), Field Trip Guidebook*, 11-20.

________ & DIVIŠ, K. (1996): Compositional trends in manganocolumbite from the Puklice I pegmatite, western Moravia, Czech Republic. *J. Czech Geol. Soc.* **41**, 1-6.

________ & POVONDRA, P. (1995): Elbaite pegmatites in the Moldanubicum; a new subtype of complex pegmatites. *Mineral. Petrol.* **71**, 159-176.

________ & ŠREIN, V. (1998): Niobian cesstibtantite from the Dobrá Voda lepidolite pegmatite, western Moravia, Czech Republic. *Neues Jahrb. Mineral., Monatsh.*, in press.

________, STANĚK, J. & ČERNÝ, P. (1994): Incommensurate fractionation trends in the Scheibengraben beryl–columbite pegmatite at Maršíkov, northern Moravia, Czech Republic; the role of $a(F_2)$. *Joint Meeting of German and Czech Geological Societies, Abstr., J. Czech Geol. Soc.* **39**, 78-79.

POUCHOU, J.-L. & PICHOIR, F. (1985): "PAP" procedure for improved quantitative microanalysis. *Microbeam Anal.* **20**, 104-105.

SPILDE, M.N. & SHEARER, C.K. (1992): A comparison of tantalum–niobium oxide assemblages in two mineralogically distinct rare-element granitic pegmatites, Black Hills, South Dakota. *Can. Mineral.* **30**, 719-738.

STANĚK, J. (1963): Minerals of niobium and tantalum from pegmatite in Dobrá Voda, western Moravia. *Acta Mus. Moraviae, Sci. Nat.* **48**, 43-52 (in Czech).

________ (1965): Pegmatite from Dobrá Voda near Velké Meziříčí. *Folia Nat. Fac. UJEP* **6**, 1-39 (in Czech).

________ (1973): Mineral paragenesis of the new lithium-bearing pegmatite at Laštovičky, western Moravia, Czechoslovakia. *Scripta Nat. Fac. UJEP* **3**, 1-14.

________ (1992): Nová Ves near Český Krumlov, a pegmatite dike of the petalite subtype penetrating serpentinite. *Int. Symp. Mineralogy, Petrology and Geochemistry of Granitic Pegmatites, Lepidolite 200 (Nové Město na Moravě), Field Trip Guidebook*, 57-62.

TEERTSTRA, D.K., ČERNÝ, P. & NOVÁK, M. (1995): Compositional and textural evolution of pollucite in pegmatites of the Moldanubicum. *Mineral. Petrol.* **55**, 37-52.

VOLOSHIN, A.V. (1983): Evolution and reaction series of tantalum minerals. *In* New Ideas in Genetic Mineralogy. Nauka, Leningrad, Russia (21-26; in Russ.).

________ & PAKHOMOVSKYI, YA.A. (1988): *Mineralogy of Tantalum and Niobium in Rare-Element Pegmatites.* Nauka, Leningrad, Russia (in Russ.).

WISE, M. & ČERNÝ, P. (1990): Primary compositional range and alteration trends of microlite from the Yellowknife pegmatite field, Northwest Territories, Canada. *Mineral. Petrol.* **43**, 83-98.

WOLF, M.B. & LONDON, D. (1993): Preliminary results of HFS and RE element solubility experiments in 'granites' as a function of B and P. *Eos, Trans. Am. Geophys. Union* **74**, 343 (abstr.).

________, ________ & MORGAN, G.B.,VI (1994): Effects of boron on the solubility of cassiterite and tantalite in granitic liquids. *Geol. Soc. Am., Abstr. Programs* **26**, A-450.

Received September 15, 1996, revised manuscript accepted February 4, 1998.