

EVOLUTION OF Nb,Ta-OXIDE MINERALS IN THE PRAŠIVÁ GRANITIC PEGMATITES, SLOVAKIA. II. EXTERNAL HYDROTHERMAL Pb,Sb OVERPRINT

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ABSTRACT

Titanite, fersmite, pyrochlore-group minerals and roméite in two small dikes of relatively poorly fractionated pegmatite, located in the parent Hercynian Prašivá biotite granodiorite-granite, in central Slovakia, were generated by hydrothermal alteration of primary columbite, titanian ixiolite and niobian-tantalum rutile. The early titanite has elevated contents of Nb, Ta, Al and Fe, and the fersmite is very REE-poor. Pyrochlore, microlite, betafite, uranpyrochlore, uranmicrolite, stibiomicrolite, stibiobetafite, plumbomicrolite and several transitional compositions were identified in the next generation, most of them Si-bearing. The late roméite is considerably enriched in Nb, Ta, U and Si. The hydrothermal fluids mobilized Nb, Ta, Ti, U, Fe, Si, and probably also Ca and Na from the primary minerals of the pegmatite, but Sb and Pb must have been imported from an external source. The hydrothermal overprint is attributed to the same metamorphic – magmatic solutions that caused the nearby Sb ± Au and Pb–Zn–Sb sulfide deposits.

Keywords: titanite, fersmite, pyrochlore, microlite, betafite, uranpyrochlore, uranmicrolite, stibiomicrolite, stibiobetafite, plumbomicrolite, roméite, granitic pegmatite, Prašivá, Slovakia.

SOMMAIRE

L'assemblage de titanite, fersmite, minéraux du groupe du pyrochlore et roméite dans deux petits filons de pegmatite granitique peu évoluée, liés au pluton granitique et granodioritique hercynien de Prašivá, en Slovaquie centrale, résulte de l'altération hydrothermale de la columbite, l'ixiolite titanifère et le rutile niobifère et tantalifère primaires. La titanite précoce possède des teneurs élevées en Nb, Ta, Al et Fe, et la fersmite contient très peu de terres rares. Nous avons identifié pyrochlore, microlite, bétafite, uranpyrochlore, uranmicrolite, stibiomicrolite, stibiobétafite, plumbomicrolite, et plusieurs compositions transitionnelles dans la seconde génération de minéraux, dans la plupart des cas avec une teneur mesurable de Si. La roméite tardive est considérablement enrichie en Nb, Ta, U et Si. La phase fluide hydrothermale responsable de ces transformations a mobilisé le Nb, Ta, Ti, U, Fe, Si, et probablement aussi le Ca et Na à partir des minéraux primaires de la pegmatite, mais dans le cas de Sb et Pb, la source a dû être externe à la pegmatite. La modification hydrothermale aurait été effectuée par les mêmes infiltrations de fluide métamorphique et magmatique que celles qui sont à l'origine des gisements avoisinants de sulfures de Sb ± Au et Pb–Zn–Sb.

(Traduit par la Rédaction)

Mots-clés: titanite, fersmite, pyrochlore, microlite, bétafite, uranpyrochlore, uranmicrolite, stibiomicrolite, stibiobétafite, plumbomicrolite, roméite, pegmatite granitique, Prašivá, Slovaquie.

INTRODUCTION

Two narrow (≤15 cm thick), homogeneous and generally primitive granite-pegmatite veins in the Sopotnica Valley, Prašivá massif, central Slovakia

contain scarce Ti,Nb,Ta-minerals. The geological conditions and mineralogical characterization of both S2A and S2B pegmatite dikes, as well as their primary Nb,Ta-rich oxide minerals and products of their exsolution (ferrocolumbite, manganocolumbite, titanian

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ixiolite, Nb,Ta-rich rutile, armalcolite and ilmenite) were described in the companion paper (Uher *et al.* 1998).

In this paper, we characterize the secondary hydrothermal assemblage of the Prašivá S2A and S2B pegmatites. Besides fersmite, Nb,Ta-rich titanite and a rather unusual Nb,Ta,U,Si-rich roméite, a surprisingly broad spectrum of pyrochlore-group minerals was identified here, including U,Pb and Sb-bearing members. We also argue that the secondary assemblage was generated by hydrothermal fluids from an external, *i.e.*, non-pegmatite source.

EXPERIMENTAL METHODS

The experimental methods are the same as those in Uher *et al.* (1998); however, some of the conditions of electron-microprobe analysis differ in detail. A Cameca SX-50 electron microprobe at the Department of Geological Sciences, University of Manitoba was used. The same analytical conditions and standards were used for fersmite as for the primary Nb,Ta-minerals.

The pyrochlore-group minerals and roméite were analyzed using an accelerating potential of 15 kV, beam current 20 kV (Nb, Ta, Si, Ti, U, Sb, Fe, Mn, Ca, Pb, Na, F) or 40 kV (Sn, Zr, Y, As, Bi, Sr, Ba, K, Cs), counting time 20 s, beam diameter 1–2 μm . The following standards were used: MnNb_2O_6 (for NbL α , MnK α), manganotantalite (TaM α), diopside (SiK α), TiO_2 (TiK α), SnO_2 (SnL α), ZrO_2 (ZrL α), UO_2 (UM β), YAG (YL α), mimetite (AsL α), stibiotantalite (SbL α), BiTaO_4 (BiM β), microlite (NaK α , FK α), orthoclase (KK α), and pollucite (CsL α). For titanite, additional elements were calibrated with zircon (SiK α) and kyanite (AlK α) standards at 15 kV, 20 nA and 20 s counting time. The overlap correction and PAP routine programs of Pouchou & Pichoir (1985) were applied.

Nb,Ta-BEARING MINERALS

Paragenetic relationships

The textural relationships clearly show that all of the pyrochlore-group minerals studied, as well as titanite, fersmite and roméite, replaced primary columbite, titanian ixiolite and, locally, Nb,Ta-rich rutile and uraninite. This replacement occurred along fractures, contacts and rims of the primary phases (Fig. 1 to 3).

Niobian–tantalian titanite and *fersmite* belong to the earliest of the secondary minerals. Titanite replaces niobian rutile and ferrocolumbite, and is in turn replaced by plumbomicrolite (Fig. 1). Fersmite extensively replaces ferrocolumbite beginning at the outer surface of the grains, or forms complete pseudomorphs after a primary Nb,Ta-mineral, probably columbite or ixiolite (Figs. 2A, B). It rarely occurs as discrete (*ca.* 10 μm) grains in Nb,Ta-rich rutile and is itself replaced by stibioan microlite (Fig. 2B).

Minerals of the *pyrochlore group* are the most widespread and the most diversified among the secondary Nb,Ta-minerals in both pegmatite bodies studied. They replace mainly ferrocolumbite, rarely titanian ixiolite, Nb,Ta-rich rutile, as well as titanite and fersmite, and appear as irregular microscopic veinlets, fissure fillings and along boundary zones (Figs. 1, 2). All recognized species and compositional varieties of this mineral group described below crystallized virtually simultaneously. For example, titanian ixiolite in grain #12 from the S2B pegmatite is replaced by Sb,U-rich pyrochlore to microlite, uranmicrolite, nearly pure end-member microlite, stibiobetafite and stibiomicrolite (Fig. 2D). No systematic age relationship can be discerned among these phases, and growth features of individual grains, compositionally heterogeneous at the 1–100 μm scale, do not provide clues for the direction of compositional change with time.

Niobian–tantalian roméite was recognized in only a single case, as a late fracture filling of primary uraninite but younger than adjacent crystals of betafite (Fig. 3). This relationship classifies roméite as one of the last secondary minerals to form, and probably the latest.

Chemical composition

Titanite contains appreciable Nb, Ta, Al and Fe (presumed trivalent). Predictably, the atomic sum of these elements closely matches the deficit of Ti in all compositions (Table 1). The dominant mechanism of substitution $(\text{Al,Fe})^{3+}(\text{Nb,Ta})^{5+}\text{Ti}^{4+}_{-2}$ (Fig. 4) is accompanied in most cases by $(\text{Al,Fe})^{3+}(\text{F,Cl,OH})-(\text{Ti}^{4+}\text{O}^{2-})_{-1}$. If real, this would be a novel substitution in addition to those listed by Bernau & Franz (1987) and Černý *et al.* (1995). A number of compositions in addition to those represented in Table 1 show an excess of cations at both the Ti and Si sites, combined with deficiency in the Ca site, if recalculated on either five anions or three cations; the Ca deficiency increases with normalization on a total of 2 Ti + Si sites. This strongly suggests partial leaching of Ca from this earliest member of the secondary assemblage during hydrothermal events subsequent to the crystallization of titanite.

In the pegmatite samples studied, the *fersmite* is a Ca-rich, rare-earth-element-poor variety, with <0.5 wt.% Y_2O_3 (Table 1). The Ti content can be relatively high, up to 0.26 atoms per formula unit, but negligible in other cases. Excess of cations in the Ca site, very common in other occurrences and so far unexplained, is not in evidence at Prašivá.

Minerals of the *pyrochlore group* $\text{A}_{2-m}\text{B}_2\text{X}_6\text{Y}_{1-n} \cdot p\text{H}_2\text{O}$, where $X = \text{O}^{2-}, \text{F}^-, \text{OH}^-$ and $Y = \text{OH}^-, \text{F}^-, \text{O}^{2-}$, are very diversified in terms of both A and B cations, as illustrated by representative compositions in Table 2. In terms of mineral species, eight members were identified: pyrochlore, microlite, betafite, uranpyrochlore,

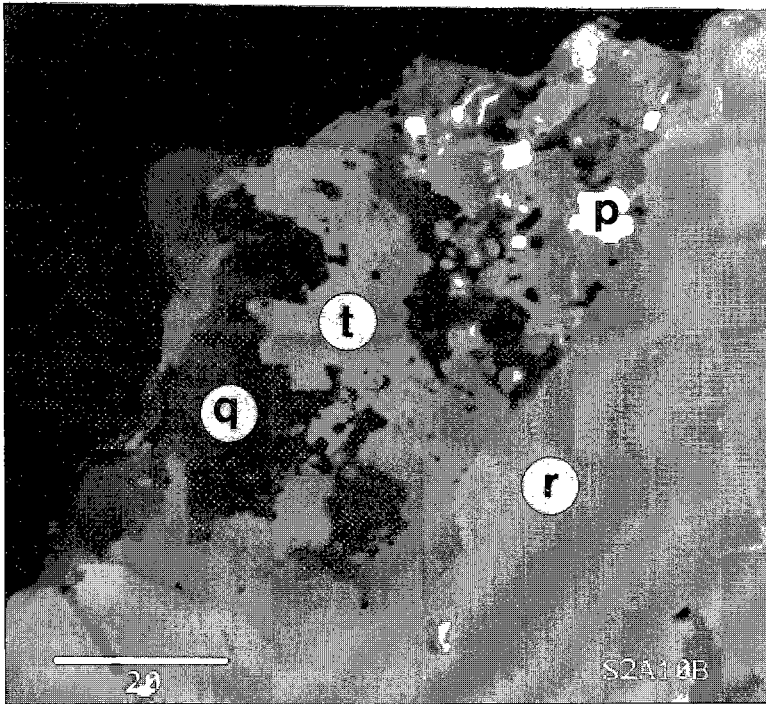


FIG. 1. Replacement of niobian rutile (r) by quartz (q), niobian-tantalum titanite (t) and the latest plumbomicrolite (p). Back-scattered electron (BSE) microphotograph. Scale bar: 20 μm .

uranmicrolite, plumbomicrolite, stibiomicrolite and stibiobetafite. In addition, many transitional varieties were found, such as stiboan pyrochlore-to-microlite, uranoan-stiboan microlite, uranoan-plumboan microlite, and others. The mutual relationships of all species and varieties recognized at Prašivá are illustrated in the Nb – Ti – Ta diagram for the *B* site (Fig. 5A), and in the (U,Pb) – Sb – (Ca,Na) diagram (Fig. 5B), which shows at least some of the relations among the *A* cations. The Ca,Na-rich compositions are generally enriched in Ta, and the U,Pb,Sb-rich members are more Nb-rich (Fig. 6).

The compositional complexity of most phases, and the fact that the electron microprobe was the only means of study, led us to express the anion content in the simplest terms of oxygen equivalents plus F.

A significant feature of most of the compositions is an elevated content of Si. The amount of Si is negligible in a single Sb-rich phase analyzed for this element, it is subordinate in microlite (<1 wt.% SiO_2), but quite substantial in most U- and U,Pb-rich phases (2.8 to 9.5 wt.% SiO_2). Subramanian *et al.* (1983) and Johan & Johan (1994) documented the entry of Si into the *B* site, but the charge-balancing mechanism in natural

minerals is uncertain. Our data suggest a correlation of Si with U similar to that shown by Johan & Johan (1994), but any mechanism of compensation involving these cations is undoubtedly insufficient to account for all the Si present. Normalization to the sum of *B* cations, which is the only realistic approach to the pyrochlore-type minerals (Ercit *et al.* 1993), generates oxygen equivalents much below the ideal $\text{O}_6(\text{O},\text{OH},\text{F})$ in *X* and *Y* sites, and actually less than O_6 , because of a high proportion of otherwise uncompensated Si^{4+} . Vacancies in the *X* site, extensive (OH)-for-O substitution in the *X* site, or a combination of both features, may be involved to accommodate the Si. Low analytical totals indicate high H_2O contents, and recent refinements of crystal structures of cesstibantite, the so-called kalipyrochlore, and related ferritungstite (Ercit *et al.* 1993, 1994, Ercit & Robinson 1994) show that (OH) can extensively enter the *X* site, and molecular H_2O can be accommodated in both the *A* and *Y* sites.

Another characteristic feature of the Prašivá pyrochlore-group minerals is the variable but generally high Ti content. It is rather low in microlite proper, but it increases in the Sb(U)-enriched compositions, and culminates in the U-rich minerals, betafite and stibiobetafite (Fig. 5A).

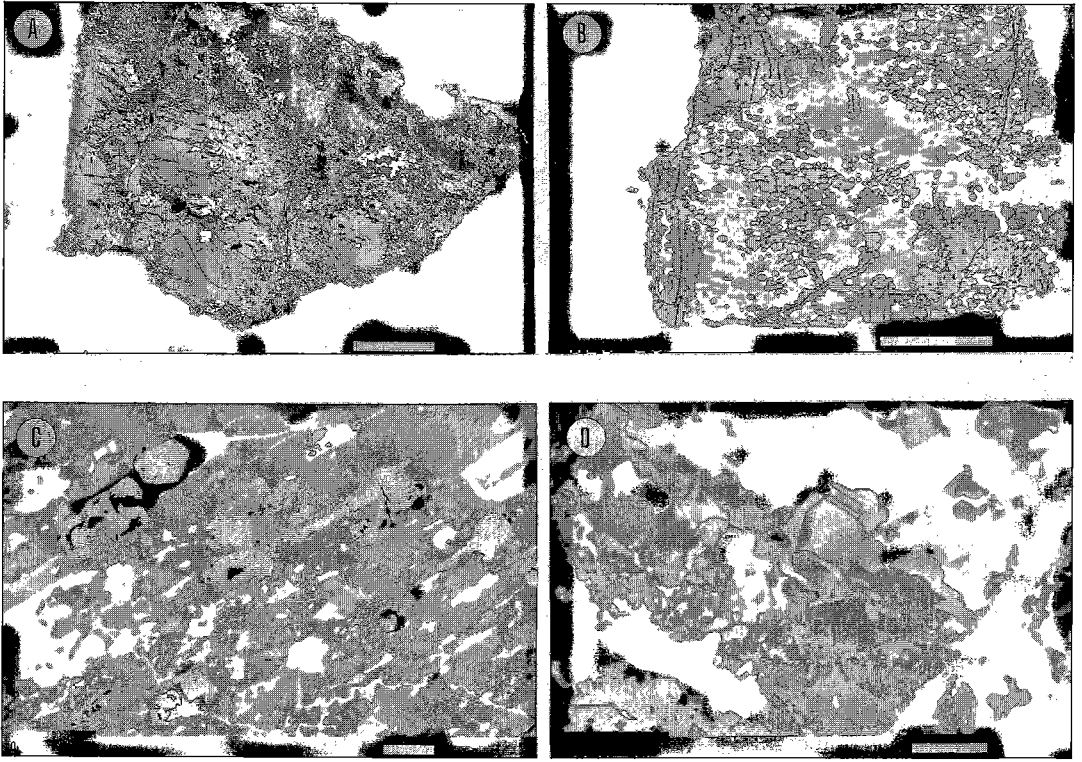


FIG. 2. A. Ferromicrite (dark grey) replaces ferrocolumbite (light grey), and microlite (white) replaces both minerals. B. Stibioan-uranoan microlite (white) replaces ferromicrite pseudomorph after columbite or ixiolite (dark grey). C. Inclusions of uranoan-stibioan microlite and uranoan plumbomicrolite (white) in ferrocolumbite (grey). D. Stibioan microlite to stibomicrolite (grey) and microlite (white) replace titanian ixiolite (dark grey, upper right corner). BSE microphotographs. Scale bars: 100 μm in A and B, 10 μm in C and D.

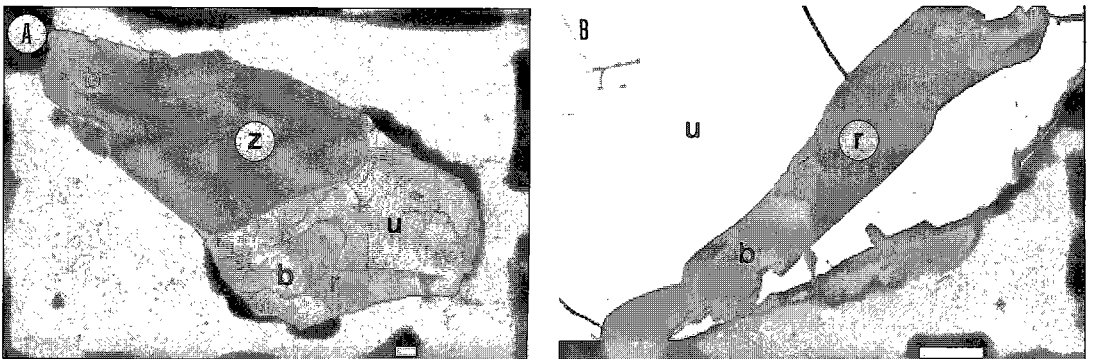


FIG. 3. A, B. Betafite (b) and niobian-tantalian-uranoan roméite (r) replace zircon (z) and uraninite (u). Scale bar: 10 μm in each case.

The composition A8.5 represents a curiosity from the viewpoint of the currently accepted classification (Table 2). This composition, referred to here as "plumbo-uranmicrolite", qualifies for the status of both

plumbomicrolite and uranmicrolite (*cf.* Hogarth 1977), with virtually equal atomic contents of Pb and U. Similar compositions are known from the Sahatany field, Madagascar (Yeremenko *et al.* 1987).

TABLE 1. REPRESENTATIVE COMPOSITIONS OF TITANITE (TTN) AND FERSMITE (FER), PRAŠIVÁ GRANITIC PEGMATITES

	TTN B1T1	TTN A1O16	TTN A1O12	TTN A1O17	TTN A1O13	FER B28.1	FER A9.1
Nb ₂ O ₅	2.46	2.88	1.13	1.76	1.15	70.96	61.90
Ta ₂ O ₅	1.91	3.04	1.30	2.93	5.59	11.21	16.71
SiO ₂	30.30	30.16	30.84	28.89	30.33	n.a.	n.a.
TiO ₂	33.69	32.50	32.82	36.16	34.48	0.39	6.35
SnO ₂	0.06	0.03	0.00	0.02	0.05	0.04	0.00
UO ₂	0.00	0.00	0.00	0.00	0.00	0.09	0.28
Al ₂ O ₃	1.71	0.83	2.51	1.03	1.41	n.a.	n.a.
Y ₂ O ₃	0.07	0.03	0.00	0.00	0.00	0.08	0.41
Fe ₂ O ₃	3.10	2.72	2.17	1.80	0.81	n.a.	n.a.
FeO	n.a.	n.a.	n.a.	n.a.	n.a.	0.38	0.25
MnO	0.31	0.00	0.02	0.01	0.03	0.11	0.00
CaO	25.81	26.65	27.42	25.61	26.81	16.73	15.45
Na ₂ O	0.00	0.16	0.00	0.17	0.11	0.02	0.00
F	0.16	0.19	0.13	0.29	0.00	0.06	0.07
O=F	-0.07	-0.08	-0.05	-0.12	0.00	-0.03	-0.03
Total	99.51	99.11	98.29	98.55	100.77	100.04	101.39

Formulae based on 5 anions (TTN), 3 cations (FER)

Si ⁴⁺	1.009	1.018	1.030	0.975	1.012	n.a.	n.a.
Nb ⁵⁺	0.037	0.044	0.017	0.027	0.017	1.781	1.543
Ta ⁵⁺	0.017	0.028	0.012	0.027	0.051	0.170	0.252
Ti ⁴⁺	0.844	0.825	0.824	0.918	0.865	0.016	0.264
Sn ⁴⁺	0.001	0.000	0.000	0.000	0.001	0.004	0.000
Al ³⁺	0.067	0.033	0.099	0.041	0.055	n.a.	n.a.
Fe ³⁺	0.078	0.069	0.055	0.046	0.020	n.a.	n.a.
ΣB	1.044	0.999	1.007	1.059	1.009	1.971	2.059
U ⁶⁺	0.000	0.000	0.000	0.000	0.000	0.001	0.004
Y ³⁺	0.001	0.001	0.000	0.000	0.000	0.003	0.012
Fe ²⁺	n.a.	n.a.	n.a.	n.a.	n.a.	0.018	0.012
Mn ²⁺	0.009	0.000	0.001	0.000	0.001	0.005	0.000
Ca ²⁺	0.921	0.964	0.981	0.926	0.958	1.000	0.913
Na ⁺	0.000	0.010	0.000	0.011	0.007	0.002	0.000
ΣA	0.931	0.965	0.982	0.937	0.966	1.029	0.941
Σ(A+B)	1.975	1.964	1.989	1.996	1.975	3.000	3.000
F ⁻	0.017	0.020	0.014	0.031	0.000	0.011	0.012
Ta ₉₆	0.32	0.39	0.41	0.50	0.75	0.09	0.14

Oxides in wt. %. ΣB=Nb+Ta+Ti+Sn+Al+Fe³⁺; ΣA=U+Y+Fe²⁺+Mn+Ca+Na. Ta₉₆=Ta/(Ta+Nb)at.

Niobian-tantalian roméite could not be verified by X-ray diffraction, but the formula calculated on the basis of (Sb⁵⁺, Nb⁵⁺, Ta⁵⁺, Si⁴⁺, Ti⁴⁺, Sn⁴⁺) = 2 does not leave much doubt about its identity (Table 3): it closely matches the general formula (Ca, Fe²⁺, Mn²⁺, Na)₂(Sb, Ti)₂O₆(O, OH, F) (Fleischer & Mandarino 1995). Besides the presence of Nb and Ta (≤10 and 4 wt.% of the oxides, respectively), the content of SiO₂ (≤5 wt. %) also is noteworthy, in keeping with the above-mentioned recent discoveries of Si in the isostructural minerals of pyrochlore group. Other features include high level of U (≤8 wt.% UO₂) and of F (≤3.5 wt.%). In view of the low analytical totals (90 to 94 wt.%), high contents of H₂O are undoubtedly present, probably in both hydroxyl and molecular form. Calculated oxygen equivalents are much more conformable with the ideal formula, although largely lower than 6; the analogous X-site oxygen deficiency is documented also by Brugger *et al.* (1997), and the same arguments apply here as in the case of silicic members of the isostructural pyrochlore group, discussed above.

DISCUSSION

An extensive replacement of primary ferrocolumbite, titanian ixiolite and Nb, Ta-rich rutile by a variety of calcium-rich secondary products characterizes both of the Prašivá pegmatite dikes. Such replacement

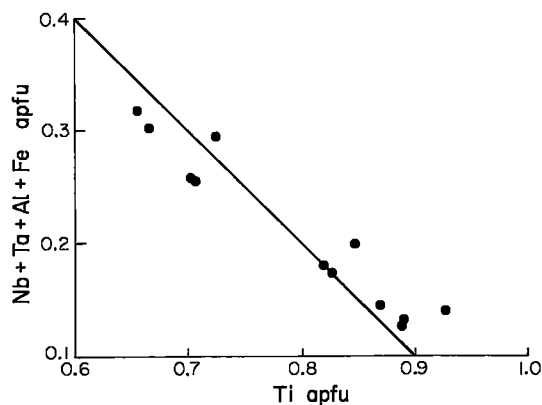


FIG. 4. (Nb + Ta + Al + Fe) versus Ti diagram of niobian-tantalian titanite, in atoms per formula unit.

of primary Nb, Ta-oxide minerals is widespread in pegmatite environments, generally considered as a postmagmatic, subsolidus overprint in a closed system (Černý & Ercit 1985, Voloshin & Pakhomovsky 1988).

Niobian and tantalian titanite was described as a secondary mineral in the Huron Claim and Irgon Claim pegmatites, Manitoba, and in the Maršíkov pegmatite, Czech Republic (Paul *et al.* 1981, Groat *et al.* 1985, Černý *et al.* 1995). However, titanite from both Manitoba localities occurs only in mirolitic cavities in albite (± quartz), separate from other Nb, Ta-bearing minerals. On the contrary, the Maršíkov titanite fills fissures dispersed in tantalian rutile, in close analogy to the Prašivá titanite penetrating Nb, Ta-bearing rutile or ferrocolumbite (Fig. 1).

Fersmite is commonly documented as a product of secondary alteration of columbite-tantalite minerals in rare-element granitic pegmatites (Černý & Ercit 1989). The composition of the Prašivá fersmite, with Ca much in excess over Y, REE, is comparable to that of fersmite from other granitic pegmatites (Voloshin & Pakhomovsky 1988, Černý & Ercit 1989); the locally elevated Ti content of the fersmite examined here (6 to 9 wt.% TiO₂) is comparable to that from the Maršíkov pegmatite (4 to 13 wt.% TiO₂; Černý *et al.* 1995).

TABLE 2. REPRESENTATIVE COMPOSITIONS OF PYROCHLORE-GROUP MINERALS, PRAŠIVÁ GRANITIC PEGMATITES

wt. %	MIC A13.5	UPY B1.2	UMC A3.13	BET B14.2	PUM A8.5	PMC A8.2	PMC A10.1	PMC B2.1	USM B2.15	USM A15.11	SMC B9.6	STM B12.5	STM B12.16	STB B12.7
WO ₃	0.21	0.28	0.12	n.a.	0.02	0.12	0.09	n.a.	0.02	0.03	n.a.	n.a.	n.a.	n.a.
Nb ₂ O ₅	15.77	19.62	13.30	14.52	14.76	12.41	7.65	18.24	12.98	17.96	19.26	19.16	18.88	21.28
Ta ₂ O ₅	55.28	28.33	27.73	28.05	27.03	25.05	35.36	35.21	41.29	40.46	50.61	32.29	33.83	29.04
SiO ₂	0.74	0.12	2.83	n.a.	8.78	8.86	9.49	n.a.	8.59	0.06	n.a.	n.a.	n.a.	n.a.
TiO ₂	2.26	9.35	10.90	12.60	6.36	5.19	6.44	5.28	4.35	7.21	4.09	11.24	11.05	12.48
SnO ₂	0.44	0.05	1.09	0.77	0.11	0.11	0.07	0.09	0.11	0.13	0.22	0.32	0.28	0.27
ZrO ₂	n.a.	n.a.	n.a.	0.00	n.a.	n.a.	n.a.	0.58	n.a.	n.a.	0.00	0.07	0.03	0.00
UO ₂	0.69	18.81	22.31	26.64	11.82	8.28	8.36	8.87	10.45	4.84	0.97	3.02	1.64	0.53
Sb ₂ O ₃	1.00	0.21	1.15	0.00	1.28	1.35	0.63	1.85	2.24	7.14	3.34	13.50	14.06	17.12
Bi ₂ O ₃	0.09	0.00	0.07	0.00	0.00	0.12	0.00	0.00	0.00	0.08	0.00	0.00	0.09	0.02
FeO	0.19	1.38	1.78	0.32	1.48	1.31	2.65	1.75	2.72	0.50	0.10	0.52	0.69	0.62
MnO	0.07	0.40	0.31	0.26	0.35	0.23	0.20	0.26	0.22	0.35	0.28	0.26	0.15	0.33
CaO	14.72	12.18	5.99	9.91	3.33	3.10	5.26	6.75	4.98	13.22	16.61	15.25	14.28	15.82
SrO	0.12	0.13	0.16	0.06	0.56	0.24	0.07	0.30	1.05	0.10	0.02	0.07	0.14	0.07
BaO	0.00	0.00	0.00	0.00	0.67	0.10	0.00	0.62	0.90	0.00	0.00	0.00	0.00	0.00
PbO	0.03	0.09	0.09	0.19	10.09	18.97	12.92	15.20	1.52	0.00	0.06	0.08	0.37	0.15
Na ₂ O	2.77	2.25	0.00	2.97	0.13	0.28	0.27	0.63	0.02	1.38	0.57	0.26	0.23	0.14
K ₂ O	0.01	0.07	0.11	0.09	0.38	0.40	0.22	0.33	0.25	0.04	0.03	0.04	0.08	0.00
F	2.00	0.85	0.17	0.43	0.02	0.04	0.00	0.43	0.06	0.94	0.66	0.37	0.37	0.28
O=F	-0.84	-0.36	-0.07	-0.18	-0.01	-0.02	0.00	-0.18	-0.03	-0.40	-0.28	-0.16	-0.16	-0.12
Total	95.55	93.76	88.04	96.63	87.16	86.14	89.68	96.21	91.72	94.04	96.54	96.29	96.01	98.04

Formulae based on $\Sigma B=2$.

W ⁶⁺	0.004	0.006	n.a.	n.a.	0.000	0.002	0.002	n.a.	0.000	0.001	n.a.	n.a.	n.a.	n.a.
Nb ⁵⁺	0.574	0.745	0.512	0.548	0.483	0.444	0.252	0.756	0.405	0.658	0.679	0.666	0.653	0.712
Ta ⁵⁺	1.211	0.647	0.837	0.636	0.532	0.539	0.700	0.877	0.774	0.892	1.074	0.675	0.703	0.585
Si ⁴⁺	0.060	0.010	n.a.	n.a.	0.635	0.701	0.691	n.a.	0.592	0.005	n.a.	n.a.	n.a.	n.a.
Ti ⁴⁺	0.137	0.590	0.603	0.790	0.346	0.309	0.353	0.364	0.226	0.440	0.240	0.650	0.635	0.695
Sn ²⁺	0.014	0.002	0.048	0.026	0.003	0.003	0.002	0.003	0.003	0.004	0.007	0.010	0.009	0.008
Zr ⁴⁺	n.a.	n.a.	0.000	0.000	n.a.	n.a.	n.a.	0.026	n.a.	n.a.	0.000	0.003	0.001	0.000
U ⁴⁺	0.012	0.351	0.483	0.495	0.190	0.146	0.135	0.181	0.160	0.087	0.017	0.057	0.028	0.009
Sb ³⁺	0.033	0.007	0.000	0.000	0.038	0.044	0.019	0.070	0.064	0.239	0.107	0.428	0.443	0.523
Bi ³⁺	0.002	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.002	0.000	0.000	0.002	0.000
Fe ²⁺	0.013	0.097	0.037	0.022	0.090	0.087	0.161	0.134	0.157	0.034	0.007	0.033	0.044	0.038
Mn ²⁺	0.005	0.028	0.019	0.018	0.021	0.015	0.012	0.020	0.013	0.024	0.019	0.017	0.010	0.021
Ca ²⁺	1.270	1.096	0.889	0.886	0.258	0.263	0.410	0.663	0.368	1.149	1.389	1.256	1.170	1.255
Sr ²⁺	0.006	0.006	0.008	0.003	0.024	0.011	0.003	0.016	0.042	0.005	0.001	0.003	0.006	0.003
Ba ²⁺	0.000	0.000	0.000	0.000	0.019	0.003	0.000	0.022	0.024	0.000	0.000	0.000	0.000	0.000
Pb ²⁺	0.001	0.002	0.004	0.004	0.197	0.404	0.253	0.375	0.028	0.000	0.001	0.002	0.008	0.003
Na ⁺	0.433	0.366	0.492	0.480	0.018	0.043	0.038	0.112	0.003	0.217	0.086	0.039	0.034	0.020
K ⁺	0.001	0.007	0.007	0.010	0.035	0.040	0.020	0.039	0.022	0.004	0.003	0.004	0.008	0.000
ΣA	1.776	1.960	1.939	1.918	0.890	1.058	1.051	1.658	0.881	1.761	1.630	1.837	1.754	1.872
F	0.509	0.226	0.133	0.113	0.005	0.010	0.000	0.125	0.013	0.241	0.163	0.090	0.089	0.066
O ²⁻	6.230	6.719	6.780	6.703	5.578	5.676	5.647	6.578	5.644	6.512	6.450	6.708	6.617	6.748
Σan	6.739	6.945	6.913	6.816	5.583	5.686	5.647	6.703	5.657	6.753	6.613	6.798	6.706	6.814
Ta _{Nb}	0.68	0.46	0.62	0.54	0.52	0.55	0.74	0.54	0.66	0.58	0.61	0.50	0.52	0.45

 $\Sigma B=W+Nb+Ta+Si+Ti+Sn$; $\Sigma A=Zr+U+Sb+Bi+Fe+Mn+Ca+Sr+Ba+Pb+Na+K$; $\Sigma an=F+O$; $Ta_{Nb}=Ta/(Ta+Nb)at$.

Symbols: MIC microlite, UPY uranoan pyrochlore, UMC uranmicrolite, BET betafite, PUM "plumbo-uranmicrolite", PMC plumbomicrolite, USM uranoan-stibioan microlite, SMC stibioan microlite, STM stibiomicrolite, and STB stibiobetafite.

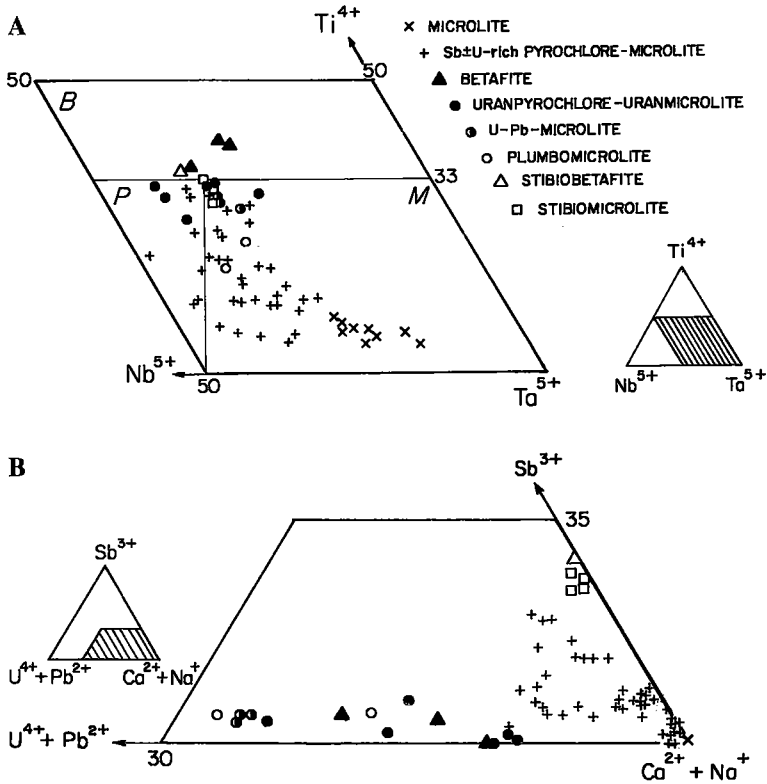


FIG. 5. Nb - Ti - Ta (A) and (U + Pb) - Sb - (Ca + Na) (B) diagrams for the pyrochlore-group minerals. *B*: betafite, *P*: pyrochlore, *M*: microlite; atomic proportions.

Roméite is considered as a mineral formed at different P-T-X conditions in two contrasting geological environments: (1) in metamorphosed deposits of Mn ± Fe during retrograde metamorphism, and (2) in hydrothermal, mainly Sb-deposits during late hydrothermal stages or during weathering (Brugger *et al.* 1997). The Nb,Ta,U,Si-rich variety of roméite in the Prašivá pegmatite is a product of specific conditions of high activity of Sb and high fugacity of oxygen at a low temperature, operating during alteration of the primary Nb,Ta-bearing oxides. This environment is not to be confused with the supergene oxidation of stibnite on the dumps of the nearby Dúbrava Sb-deposit, where roméite also is found (Bernard 1981). Compared to the recent data on roméite (Brugger *et al.* 1997), the Prašivá roméite is the first Nb-, Ta- and Si-rich variety of this mineral and the first documented find of roméite in a granite pegmatite environment.

The abundance and diversified compositions of the pyrochlore-group minerals are a striking feature of both the S2A and S2B dikes. Besides the common and

nearly pure calcian pyrochlore to microlite, U,Pb- and Sb-bearing varieties are widespread here. Uranium-rich members (uranpyrochlore, uranmicrolite and betafite) are locally among the common accessory phases of granitic pegmatites; at many localities, they belong to assemblages that replace primary columbite-tantalite and other early minerals (Černý & Ercit 1985, 1989, Wise & Černý 1990).

Plumbomicrolite, and especially stibiomicrolite and stibiobetafite, also are typical late or secondary minerals in granitic pegmatites, but they are relatively rare, related to specific environments. Pb-rich pyrochlore and microlite are rarely associated with other Nb, Ta-minerals in highly fractionated granites, such as the Beauvoir granite, France (Ta, Nb, Sn, Li, F: Ohnenstetter & Piantone 1992) or at Cínovec, Czech Republic (Sn, W, Li, F: Johan & Johan 1994). However, the vast majority of Pb- and Pb,U-rich microlite to plumbomicrolite (rarely plumbopyrochlore and plumbobetafite) occur in amazonite-bearing and locally lithium-rich rare-element pegmatites, such as

TABLE 3. REPRESENTATIVE COMPOSITIONS OF ROMÉITE, PRAŠIVÁ GRANITIC PEGMATITES

	A3.6	A3.9	A3.11	A3.5
Sb ₂ O ₅	57.95	55.58	50.66	39.29
Nb ₂ O ₅	5.03	6.49	7.34	9.47
Ta ₂ O ₅	1.20	1.93	2.28	4.20
SiO ₂	3.04	3.33	3.89	5.00
TiO ₂	2.24	2.26	2.78	4.19
SnO ₂	0.56	0.44	0.66	0.63
UO ₂	1.57	2.59	4.00	8.26
FeO	1.64	1.94	2.28	3.34
MnO	0.08	0.09	0.11	0.16
CaO	14.41	14.10	13.34	11.11
SrO	0.09	0.18	0.15	0.42
PbO	0.16	0.00	0.55	2.74
Na ₂ O	3.16	2.86	2.39	0.82
K ₂ O	0.04	0.02	0.05	0.07
F	1.37	3.21	2.41	1.29
O=F	-0.58	-1.35	-1.01	-0.54
Total	91.96	93.67	91.88	90.45

Formulae based on $\Sigma(\text{Sb}+\text{Nb}+\text{Ta}+\text{Si}+\text{Ti}+\text{Sn})=2$

Sb ⁵⁺	1.481	1.409	1.298	1.027
Nb ⁵⁺	0.156	0.200	0.229	0.301
Ta ⁵⁺	0.022	0.036	0.043	0.080
Si ⁴⁺	0.209	0.227	0.268	0.352
Ti ⁴⁺	0.116	0.116	0.144	0.222
Sn ⁴⁺	0.015	0.012	0.018	0.018
U ⁴⁺	0.024	0.039	0.061	0.129
Fe ²⁺	0.094	0.111	0.131	0.197
Mn ²⁺	0.005	0.005	0.006	0.010
Ca ²⁺	1.062	1.031	0.986	0.838
Sr ²⁺	0.004	0.007	0.006	0.017
Pb ²⁺	0.003	0.000	0.010	0.052
Na ⁺	0.421	0.378	0.320	0.112
K ⁺	0.004	0.002	0.004	0.006
ΣA	1.617	1.573	1.524	1.361
F ⁻	0.298	0.693	0.526	0.287
O ²⁻	6.109	5.899	5.946	5.991
Σan	6.407	6.592	6.472	6.278
Ta _{Nb}	0.12	0.15	0.16	0.21

Oxides in wt. %. ΣA=U+Fe+Mn+Ca+Sr+Pb+Na+K; Σan=F+O. Ta_{Nb}=Ta/(Ta+Nb)at.

those in the Sahatany field, Madagascar (Yeremenko *et al.* 1987), Utö, Sweden (Smeds & Černý 1989), Mumba, Democratic Republic of Congo, or the Keivy Range, Russia (Stepanov *et al.* 1982, Voloshin *et al.* 1993). Sb-rich microlite, stibiomicrolite and other Sb-bearing niobium-tantalum minerals (stibiotantalite, cesstibtantite, holtite) so far have been reported only from highly fractionated complex rare-element granitic pegmatites, such as Varuträsk, Sweden, Alto do Giz, Brazil, Lshaia, Russia, western Moravia, Czech Republic, and Tanco, Manitoba (Groat *et al.* 1987, Ercit

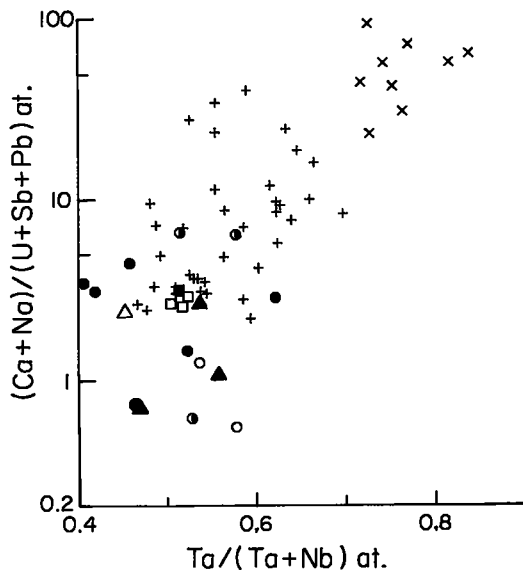


FIG. 6. $(\text{Ca} + \text{Na})/(\text{U} + \text{Sb} + \text{Pb})$ versus $\text{Ta}/(\text{Ta} + \text{Nb})$ diagram for the pyrochlore-group minerals, atomic proportions. Symbols as in Figure 5.

et al. 1993, Černý *et al.* 1996). The type stibiobetafite was described as a late metasomatic phase from a moderately fractionated pegmatite at Věžná, Czech Republic (Černý *et al.* 1979) which is, however, closely related to a nearby pollucite-bearing dike (Teertstra *et al.* 1995).

In contrast, the Prašivá pegmatites belong to a rather poorly fractionated population, with only rare-element mineralization of the beryl-columbite subtype, without Li-bearing phases. Thus, the presence of the Pb- and Sb-rich pyrochlore-group minerals and roméite is at odds with the overall character of the parent pegmatites. An external source of these elements, and a low-temperature process that would introduce them into the pegmatites and trigger reactions with the primary Nb, Ta-bearing phases, should be considered. Such a source and process are readily available in the region.

We propose that Pb and Sb come from postmagmatic fluids, which generated numerous hydrothermal Sb, Sb-Au-(As-W) or Sb-Pb-Zn sulfide veins in the Nízke Tatry Mountains (Fig. 7). Such vein-type mineralization can be found directly in the Prašivá granodiorite-granite, in the Dumbier granodiorite-leucotonalite, as well as in adjacent para- and orthogneisses and migmatites. The age of these sulfide assemblages is considered also to be Variscan, but clearly younger than the pegmatites; a stibnite-bearing vein clearly cuts through a granitic pegmatite at the Dúbrava mine (M. Chovan, pers.

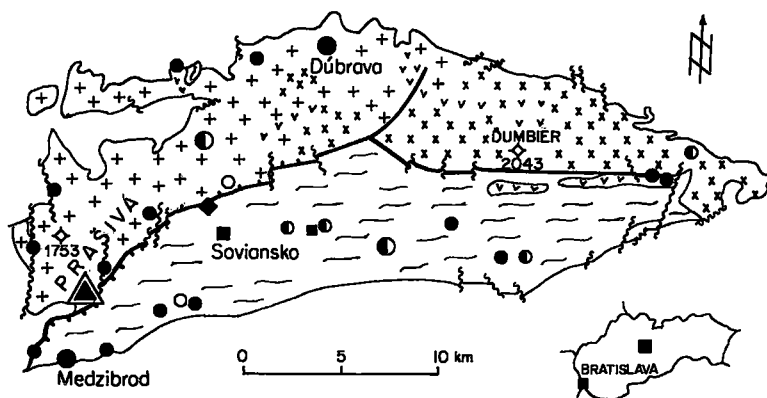


FIG. 7. Geological map of the Nízke Tatry Mountains (simplified after unpubl. data of M. Chovan). Shown are the Prašivá granodiorites – granites (+), the Dumbier leucotonalites – granodiorites (x), leucogranites (v), metamorphic rocks (~), tectonic boundaries: faults (—), strike slips (---), overthrusts (|||), the S2A, S2B pegmatite dikes (large triangle), Sb (solid circles), Sb–Au (half-open circles), Pb–Zn–Ag (full square) and scheelite (full diamond) hydrothermal occurrences.

commun., 1995). Fluid-inclusion and oxygen isotope data indicate a CO_2 -rich aqueous metamorphic–magmatic fluid with an isotopically lighter, meteoric water component as the solution parental to the Dúbrava Sb-bearing sulfide deposit (Chovan *et al.* 1995). Deposition of the main Sb and Sb–Pb stage, with dominant stibnite and zinkenite, as well as of the younger tetrahedrite-dominant stage, was connected with the circulation of fluids of moderate to low salinity (15.5 to 23.5, and *ca.* 10 wt.% NaCl equiv., respectively), both at epithermal conditions of about 170–105°C (Chovan *et al.* 1995).

In addition to the presence of the Pb- and Sb-rich niobian tantalum minerals, the possibility of an external hydrothermal overprint in the Prašivá pegmatites is supported by (1) stibnite veins cutting and locally reacting with an older Prašivá pegmatite vein at the Dúbrava mine, (2) accessory galena and chalcocopyrite dispersed in the S2A and S2B dikes (Uher *et al.* 1998), and (3) hydrothermal alteration of the S2A, S2B pegmatites; widespread epidote and fine-grained mica (muscovite, illite?) replace plagioclase, the biotite is chloritized, and fine-grained second-generation quartz locally fills fractures in the feldspars.

Thus, the primary magmatic ferrocolumbite and titanite ixiolite could also be altered along microfissures and contacts by the external hydrothermal solutions and replaced by secondary titanite, fersmite, pyrochlore-group minerals and roméite. The early secondary phases, titanite and fersmite, are exclusively Ca-bearing. The later minerals are moderately Ca-,

Na-, U-, Pb- and Sb-bearing (≤ 17 wt.% Sb_2O_3), and the youngest roméite is the most Sb-rich phase (39 to 58 wt.% Sb_2O_5).

In contrast to Pb and Sb, uranium probably was extracted from primary magmatic uraninite, a low-abundance but widespread accessory phase in the Prašivá pegmatites [S2A: Uher *et al.* (1998), Dúbrava mine: unpubl. data of P. Uher, M. Chovan and Š. Dávidová]. The Si, Ca, Na and F of the secondary Nb,Ta-assembly could be mobilized from the altered plagioclase and micas of the pegmatite veins.

CONCLUSIONS

The S2A and S2B granitic pegmatite dikes in the Variscan Prašivá granodiorites–granites, central Slovakia, contain scarce but diversified Nb, Ta-bearing oxide minerals. A primary assemblage, mainly ferrocolumbite, titanite ixiolite and niobian–tantalum rutile, was extensively hydrothermally overprinted, and a secondary assemblage of Nb,Ta-minerals was generated.

Niobian–tantalum titanite and fersmite belong to the earliest secondary phases, which are solely Ca-bearing. A variety of later silica-bearing pyrochlore-group minerals constitutes the bulk of the secondary assemblage. In addition to Ca-dominant pyrochlore to microlite, the primary minerals were replaced by (Sb \pm U \pm Pb)-rich pyrochlore, microlite and Na-enriched betafite, uranpyrochlore–uranmicrolite, plumbomicrolite and stibiobetafite. Finally, Nb,Ta,U,Si-rich roméite filled fissures in uraninite.

We propose that the hydrothermal overprint of the Prašivá pegmatites was caused by external, low-temperature ($\leq 170^\circ\text{C}$) CO_2 -rich aqueous solutions of magmatic–metamorphic origin (Chovan *et al.* 1995), which generated Sb- and Pb-bearing sulfide mineralization near the pegmatites examined, and contributed these metals to the secondary Nb,Ta-bearing minerals in the pegmatite dikes. In contrast, Nb, Ta, Ti, U, Fe, Si, Na, Ca and F were mobilized from the primary accessory and rock-forming minerals of the granitic pegmatites.

ACKNOWLEDGEMENTS

This study was supported by a NSERC Research Grant and a Major Installation Grant to PČ, by a University of Manitoba Post-Doctoral Fellowship to PU, and by the Scientific Grant Agency (VEGA) grant #4078, the Ministry of Education of the Slovak Republic and the Slovak Academy of Sciences, to Igor Petrík (Geological Institute, Slovak Academy of Sciences, Bratislava). We also thank to Martin Chovan (Comenius University, Bratislava) for unpublished data on sulfide mineralization in the Nízke Tatry Mountains. Reviews by A. Falster, M. A. Wise and W. B. Simmons are gratefully acknowledged.

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Received May 29, 1996, revised manuscript accepted January 15, 1998.