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EVOLUTION OF Nb,Ta-OXIDE MINERALS IN THE PRAŠIVÁ GRANITIC PEGMATITES, SLOVAKIA. I. PRIMARY Fe,Ti-RICH ASSEMBLAGE

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Abstract

Accessory Nb,Ta-oxide minerals occur in two narrow veins of relatively poorly fractionated granitic pegmatite that crosscut the parent Hercynian pluton, the Prašivá biotite granodiorite-granite, in central Slovakia. High Ti contents are typical of all members of this magmatic suite, and of their relevant minerals. In the pegmatites, niobian to tantalian rutile (≤24 wt.% Nb_2O_5, ≤30 wt.% Ta_2O_5) and ferrocolumbite are most widespread. Ferrocolumbite (to manganocolumbite) contains 2.5 to 5 wt.% TiO_2, and titanian ixiolite has 11 to 21 wt.% TiO_2. Tiny lamellae of niobian–tantalian armalcolite to pseudobrookite (6 to 10 wt.% Nb_2O_5, 0.5 to 5.5 wt.% Ta_2O_5) exsolved from the rutile matrix; complex exsolution-induced domains of niobian ilmenite rimming intergrowths of ilmenite and titanian hematite are rare. Exsolution of armalcolite – pseudobrookite probably took place at magmatic temperatures, and its subsolidus survival is possibly metastable.

Keywords: ferrocolumbite, titanian ixiolite, rutile, armalcolite, pseudobrookite, ilmenite, hematite, exsolution, granitic pegmatite, Prašivá, Slovakia.

Sommaire

Des oxydes de Nb,Ta forment les minéraux accessoires dans deux veines étroites de pegmatite granitique peu évoluée qui recoupent le pluton parental de Prašivá, en Slovaquie centrale, d'âge hercynien, contenant granite à biotite et granodiorite. Des teneurs élevées en Ti sont typiques de tous les membres de cette suite magmatique et les minéraux constituants. Dans les pegmatites, le rutile enrichi en Nb et Ta (≤24% Nb_2O_5, ≤30% Ta_2O_5, par poids) et la ferrocolumbite sont les plus répandus. La ferrocolumbite (zonée vers la manganocolumbite) contient de 2.5 à 5% TiO_2 en poids, et l'ixiolite titanifère peut en contenir de 11 à 21%. D'infimes lamelles d'exsolution d'armalcolite en solution solide vers la pseudobrookite, riche en Nb et Ta (6 à 10% Nb_2O_5, 0.5 à 5.5% Ta_2O_5, en poids) se trouvent dans une matrice de rutile. De rares lamelles complexes d'ilménite niobifère recouvrent une intercroissance d'ilménite et de hématite titanifère. L'exsolution dans l'armalcolite – pseudobrookite a probalement eu lieu à un stade magmatique; le fait que cet assemblage ait survécu au stade subsolidus témoignerait d'une métastabilité.

(Traduit par la Rédaction)

Mots-clés: ferrocolumbite, ixiolite titanifère, rutile, armalcolite, pseudobrookite, ilménite, hématite, exsolution, pegmatite granitique, Prašivá, Slovaquie.

Introduction

Nb,Ta-oxide minerals are widespread in rare-element granitic pegmatites, from the moderately fractionated beryl type to the complex Li–Ta–Cs-bearing categories (Černý 1989). Most of the mineralogical data about Nb,Ta-oxide minerals comes from sizeable beryl-bearing and mainly complex pegmatites, such as Tanco and localities in the Black Hills, Yellowknife and other pegmatite fields (Černý & Ercit 1985, 1989). Small and poorly fractionated beryl–columbite pegmatites do not attract much attention because of the negligible extent and grain size of their scarce and economically insignificant rare-element mineralization.

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The Nb,Ta- and Fe,Ti-bearing minerals examined here, extracted from two narrow pegmatite veins in the Prašivá area in Slovakia, clearly belong to the second category. Surprisingly, these poorly fractionated granitic pegmatites contain about twenty Nb,Ta-rich mineral species in two assemblages: (1) primary, with exsolution products, and (2) secondary (hydrothermal). Here we report the mineralogy and discuss some evolutionary aspects of the first assemblage; a separate paper (Uher *et al.* 1998) is devoted to the secondary phases and their derivation.

TABLE 1. ACCESSORY MINERALS, PRAŠIVÁ GRANITIC PEGMATITES (g/tonne)

	S2A	S2B		S2A	S2B
Nb,Ta,Ti-oxides	30	6	Magnetite	600	90
Zircon	50	25	Epidote	100	400
Fluorapatite	1800	6500	Pyrite	15	25
Monazite-(Ce)	tr.	–	Arsenopyrite	20	550
Xenotime-(Y)	tr.	–	Chalcopyrite	1	tr.
Uraninite	tr.	–	Galena	tr.	–

tr.: traces (<1 g/tonne)

The Pegmatites

The minerals described below come from two narrow veins of granitic pegmatites, only 10 to 15 cm thick, emplaced in their parent granitic rocks. The veins, designated S2A and S2B, are located about 200 m apart. They are situated in the Sopotnica Valley, on the southern slope of the westernmost, Prašivá part of the Nízke Tatry (Low Tatra) Mountains in central Slovakia, about 20 km northeast of the town of Banská Bystrica (Fig. 1).

The parent Prašivá-type biotite granodiorite to granite is a medium-grained rock, commonly with pink K-feldspar megacrysts. It belongs to the late-orogenic Hercynian intrusions with calc-alkaline I- or I>S-type characteristics (Lukáčik 1981, Petrík *et al.* 1994), widespread in the Western Carpathians of Slovakia.

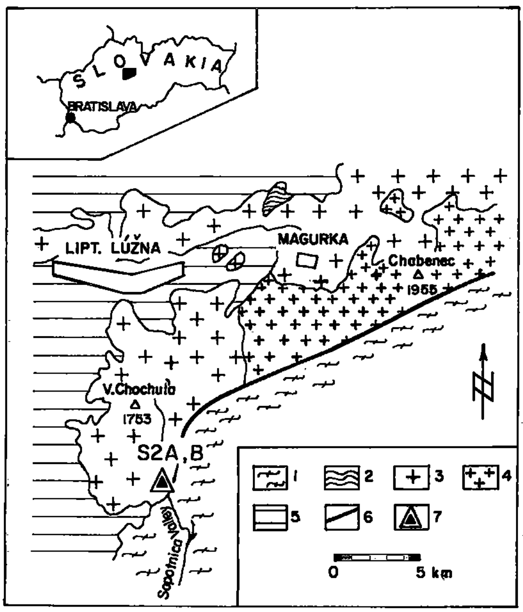

FIG. 1. Location of the Prašivá pegmatites in central Slovakia. Units and features: 1 gneisses, migmatites, 2 phyllites, 3 the Prašivá granodiorites-granites, 4 the Dumbier granodiorites – leucotonalites, 5 Mesozoic sedimentary rocks, 6 fault, 7 pegmatite location.

Both the S2A and S2B pegmatites have very simple bulk mineralogical composition and zoning, similar to hundreds of other small pegmatite veins in the Prašivá granite massif. Most of these pegmatites consist of a homogeneous quartz + K-feldspar + albite–oligoclase + muscovite ± biotite assemblage. Locally they display a subtle zoning, with quartz (+ muscovite) increasing and K-feldspar + plagioclase ± biotite decreasing from border to core. Pegmatites of greater thickness (up to 1 m) are rare; they have well-developed internal zoning, with blocky K-feldspar and quartz (± book muscovite) and locally aplitic albite units (*e.g.*, at the Dúbrava mine) and locally with beryl (Vel'ká Chochul'a hill: Pitoňák & Janák 1983, Uher & Broska 1995; Dúbrava mine).

Határ (1979) first reported accessory minerals from the Prašivá granites, pegmatites and dioritic enclaves. He recognized scarce Nb–Ta minerals (columbite–tantalite and questionable formanite) in the S2A and S2B pegmatites, besides other accessory phases (Table 1).

On the basis of the scarce Nb–Ta mineralization as well as occurrences of beryl, the most evolved Prašivá-type pegmatites belong to the beryl–columbite subtype of rare-element granitic pegmatites (Uher 1994, Uher & Broska 1995).

Experimental Methods

Samples examined in this study come from the original material of Határ (1979). The pegmatite rocks were crushed to about 0.5 mm grain size; accessory minerals were separated in heavy liquids and electromagnetically.

Electron-microprobe analyses were carried out in the wavelength-dispersion mode on a Cameca SX–50 instrument at the Department of Geological Sciences, University of Manitoba, Winnipeg. An accelerating potential of 15 kV and a beam diameter of 1 to 2 μm were used. For Nb, Ta, Ti, Sn, Fe and Mn, a beam current of 20 nA and peak counting time of 20 s were applied; for other elements, 20, 30 or 40 nA and 40 s, respectively. The following standards were used: metallic W or $CaWO_4$ (for W$M\beta$), $MnNb_2O_6$ (Nb$L\alpha$, Mn$K\alpha$), manganotantalite (Ta$M\alpha$), TiO_2 (Ti$K\alpha$), SnO_2

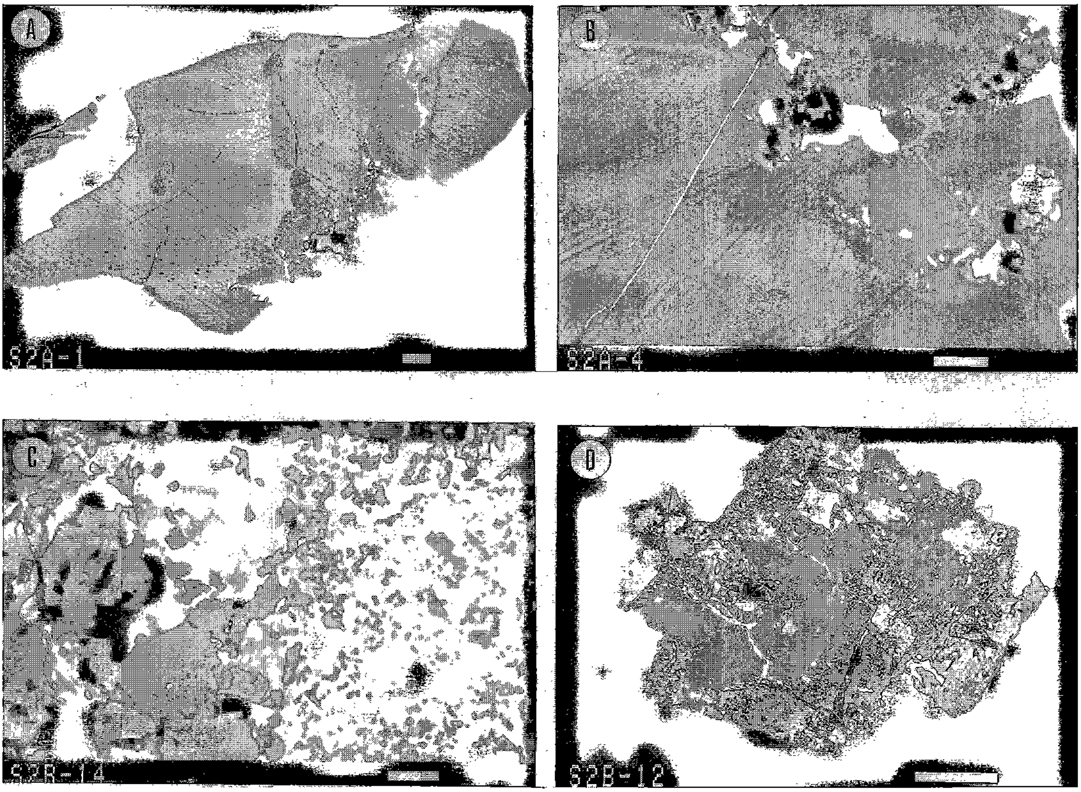

FIG. 2. Back-scattered electron (BSE) micrographs. A, B. Ferrocolumbite (pale grey), titanian ixiolite (dark grey) and secondary microlite (white). C. Ferrocolumbite (pale grey), rutile (dark grey) and secondary hematite (black) and microlite (white). D. Titanian ixiolite (medium grey), rutile (dark grey), fluorapatite (black inclusions) and secondary pyrochlore-group minerals (pale grey to white). Scale bars: 10 μm in A, B and C, 100 μm in D.

(Sn*L*α), ZrO_2 (Zr*L*α), UO_2 (U*M*β), chromite (Cr*K*α), $NaScSiO_4$ (Sc*K*α), YAG (Y*L*α), mimetite (As*L*α), stibiotantalite (Sb*L*α), $BiTaO_4$ (Bi*M*β), $FeNb_2O_6$ (Fe*K*α), $MgNb_2O_6$ (Mg*K*α), $CaNb_2O_6$ (Ca*K*α) and gahnite (Zn*K*α). The overlap correction and PAP routine (Pouchou & Pichoir 1985) were applied.

In columbite, ixiolite, rutile and armalcolite–pseudobrookite, calculation of unit-cell contents was constrained by normalizing to a fixed number of oxygen atoms as well as cations; charge balance was maitained by calculated Fe^{3+} [see Ercit *et al.* (1992) for details].

Titanian ixiolite and rutile also were confirmed by X-ray diffraction (XRD); a Gandolfi camera and Philips PW 1710 diffractometer were used.

Nb,Ta-BEARING OXIDE MINERALS

Ferrocolumbite, titanian ixiolite and niobian–tantalian rutile are the principal primary minerals of Nb, Ta and Ti in both pegmatite bodies examined; rutile dominates over columbite in S2A, but columbite is the most widespread in S2B.

Ferrocolumbite to very rare *manganocolumbite* (in S2B only) could not be verified by X-ray-diffraction methods, but its identity can be safely assumed because of its relatively clean composition (*cf.* Černý *et al.* 1998). It forms discrete tabular crystals (≤0.5 mm in size, locally with inclusions of titanian ixiolite; Fig. 2A, B), or rarely, irregular intergrowths with Nb,Ta-rich rutile (Fig. 2C). Columbite grains are nearly homogeneous, but locally show irregular patchy heterogeneity. Columbite contains elevated Ti (2.5 to 5 wt.% TiO_2), Mg (≤0.4 wt.% MgO) and Sc (≤0.3 wt.% Sc_2O_3), but low Sn and W (≤1 wt.% SnO_2 and WO_3; Table 2, Fig. 3). A relatively moderate fractionation trend is characteristic of the columbite at Prašivá: Mn/(Mn + Fe) in the range 0.18–0.54, Ta/(Ta + Nb) in the range 0.07–0.41 (Fig. 4).

Titanian ixiolite $[(Nb,Ta)>Ti,Fe]_4O_8$ was first recognized by composition and later confirmed by X-ray diffraction as an orthorhombic (or at least

TABLE 2. REPRESENTATIVE COMPOSITIONS OF FERROCOLUMBITE (FC), MANGANOCOLUMBITE (MC), TITANIAN IXIOLITE (IX) AND NIOBIAN, TITANIAN RUTILE (RT), PRAŠIVÁ GRANITIC PEGMATITES

	FC	MC	IX	IX	IX	IX	RT	RT	RT	RT
	A194	B104	A138	A1910	B1214	A1220	A173	A174	B1224	B141
WO_3	0.40	0.26	0.42	0.02	0.37	0.26	0.08	0.09	0.10	0.17
Nb_2O_5	42.79	50.57	28.70	28.10	26.56	25.56	11.29	3.90	23.20	10.91
Ta_2O_5	31.70	26.61	34.31	30.05	30.05	30.00	5.86	16.05	20.91	30.11
TiO_2	5.02	1.71	11.18	16.56	18.90	20.41	76.28	74.48	39.18	47.02
SnO_2	0.34	0.05	1.44	2.17	1.35	1.50	0.11	0.00	1.16	0.85
ZrO_2	0.31	0.12	0.38	0.51	0.27	0.31	0.05	0.00	0.09	0.00
UO_2	0.19	0.02	0.03	0.02	0.12	0.09	0.02	0.00	0.00	0.00
Sc_2O_3	0.12	0.19	0.07	0.05	0.00	0.00	0.00	0.00	0.00	0.00
Sb_2O_3	0.00	0.02	0.00	0.00	0.00	0.02	0.01	0.01	0.00	0.01
Fe_2O_3	3.88	1.39	15.05	15.29	16.75	16.18	3.08	3.06	6.95	4.73
FeO	9.14	7.50	5.31	4.74	3.52	3.65	2.60	2.25	6.43	5.55
MnO	4.80	9.28	0.84	0.62	0.70	0.56	0.00	0.00	0.06	0.15
MgO	0.56	0.13	0.28	0.12	0.22	0.19	0.01	0.00	0.02	0.01
CaO	0.03	0.17	0.00	0.00	0.02	0.02	0.02	0.05	0.04	0.04
Total	99.28	98.02	98.01	98.25	98.83	98.75	99.41	99.89	98.14	99.54
				Formulae based on 24 oxygens and 12 cations						
W^{6+}	0.026	0.017	0.027	0.001	0.022	0.016	0.004	0.004	0.005	0.009
Nb^{5+}	4.859	5.805	3.208	3.008	2.788	2.671	0.892	0.319	2.212	1.034
Ta^{5+}	2.165	1.837	2.307	1.935	1.898	1.886	0.278	0.789	1.199	1.716
Ti^{4+}	0.948	0.327	2.078	2.949	3.301	3.548	10.022	10.122	6.214	7.412
Sn^{4+}	0.034	0.005	0.142	0.205	0.125	0.138	0.008	0.000	0.098	0.071
Zr^{4+}	0.038	0.015	0.046	0.059	0.031	0.035	0.004	0.000	0.009	0.000
U^{4+}	0.011	0.001	0.002	0.001	0.006	0.005	0.001	0.000	0.000	0.000
Sc^{3+}	0.026	0.042	0.015	0.010	0.000	0.000	0.000	0.000	0.000	0.000
Sb^{3+}	0.000	0.002	0.000	0.000	0.000	0.002	0.001	0.001	0.000	0.001
Fe^{3+}	0.734	0.266	2.799	2.725	2.928	2.814	0.405	0.416	1.103	0.746
Fe^{2+}	1.919	1.592	1.098	0.938	0.683	0.706	0.379	0.340	1.134	0.972
Mn^{2+}	1.021	1.996	0.176	0.124	0.138	0.110	0.000	0.000	0.011	0.027
Mg^{2+}	0.210	0.049	0.103	0.042	0.076	0.065	0.003	0.000	0.006	0.003
Ca^{2+}	0.008	0.046	0.000	0.000	0.005	0.005	0.004	0.010	0.009	0.009
Sum	12.000	12.000	12.000	12.000	12.000	12.000	12.000	12.000	12.000	12.00
Mn_{Fe}	0.28	0.52	0.04	0.03	0.04	0.03	0.00	0.00	0.01	0.01
Ta_{Nb}	0.31	0.24	0.42	0.39	0.41	0.41	0.24	0.71	0.35	0,62

Oxides in weight %. Fe_2O_3 and Fe^{3+} calculated by charge-balancing. FC, MC and IX computed per ordered unit cell of columbite, RT per 6 unit cells of rutile (=12 cations) to facilitate mutual comparison. Mn_{Fe}=Mn/(Mn+Fe)at., Ta_{Nb}=Ta/(Ta+Nb)at.

pseudo-orthorhombic) phase (*cf.* Wise & Černý 1986, Černý & Ercit 1989). Cation ordering upon heating was not attempted because the grains examined are intergrown with other potentially reactive phases. The term *titanian ixiolite* is used here because of very high Ti content of this mineral, which may facilitate heating-induced ordering to the titanowodginite structure rather than to that of columbite.

Titanian ixiolite forms nearly euhedral rectangular crystals rimmed and rarely corroded by columbite; in other cases, it occurs as irregular patches in columbite (Figs. 2A, B, D). In contrast to columbite, titanian ixiolite contains 11 to 21 wt.% TiO_2 and 1.2 to 2.2 wt.% SnO_2, is enriched in Fe (~20 wt.% Fe_2O_3 + FeO), and is very poor in Mn (0.7 to 0.9 wt.% MnO; Table 2). The titanian ixiolite displays intermediate overall composition between rutile and columbite (Fig. 3), but shows the lowest Fe^{2+}/Fe^{3+}. Relative to the columbite, characterized in the preceding paragraph, titanian ixiolite shows higher Ta/(Ta + Nb) but clearly lower Mn/(Mn + Fe) values (Fig. 4): $0.03 < Mn/(Mn + Fe) < 0.05$, $0.35 < Ta/(Ta + Nb) < 0.42$.

Rutile occurs as discrete 0.2 to 0.5 mm crystals, locally also as ≤70 μm irregular inclusions in titanian ixiolite, or as irregular intergrowths with ferrocolumbite and secondary microlite plus hematite (Figs. 2D, 5). Extensive compositional variability is characteristic of the Prašivá rutile, especially in Nb and Ta contents: from Nb- and Ta-poor rutile with 3 wt.% Nb_2O_5 and 0.3 wt.% Ta_2O_5 to very Nb–Ta-rich compositions containing up to 23 and 30 wt.%, respectively (Table 2, Figs. 3, 4). Independent crystals of rutile in S2A are Nb,Ta-poor, whereas in S2B the Nb,Ta-rich rutile occurs only intergrown with grains of columbite or titanian

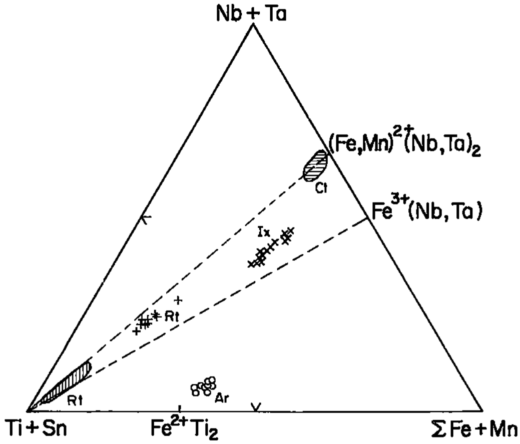

FIG. 3. Compositions of columbite (Ct), titanian ixiolite (Ix), niobian–tantalian rutile (Rt) and armalcolite–pseudobrookite (Ar) in the triangular (Ti + Sn) – (Nb + Ta) – (Fe + Mn) diagram (atomic proportions).

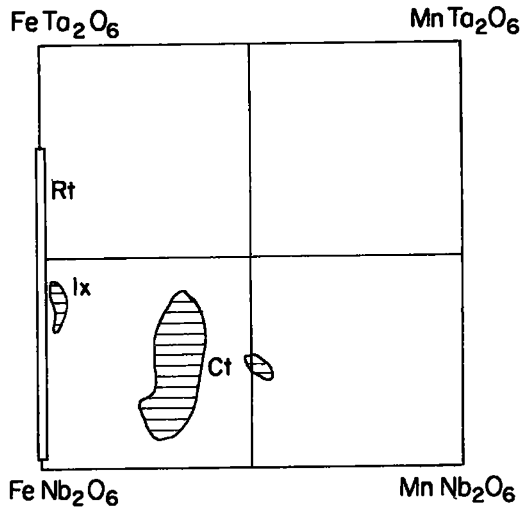

FIG. 4. Compositions of columbite (Ct), titanian ixiolite (Ix) and niobian–tantalian rutile (Rt) in the columbite quadrilateral (atomic proportions).

ixiolite. In the S2A dike, rutile contains numerous trellis-shaped to flame-like exsolution-induced blebs of Nb,Ta-rich armalcolite to pseudobrookite and, rarely, ilmenite + titanian hematite (Fig. 5B).

The presence of *niobian–tantalian armalcolite – pseudobrookite solid solution,* $(Fe,Mn)^{2+}(Ti,Nb,Ta)_2O_5$, could not be verified by XRD or electron diffraction because of its negligible volume in the host rutile and scarcity of material. However, it is homogeneous on back-scattered (BSE) images, and its stoichiometry leaves no doubt about its identity. It forms numerous trellis- to flame-like exsolution lamellae, only 1 to 3 μm thick, in the host Nb,Ta-poor rutile from the S2A dike (Fig. 5). The lamellae form a single system or a network of two intersecting systems. Despite the very small thickness of the lamellae, almost equal to the diameter of the electron beam, the analysis commonly yielded stoichiometric compositions with atomic ratios very close to $A^{2+}B^{4+,5+}{}_2O_5$ (Table 3).

The overall composition indicates that this mineral should be considered armalcolite to very Fe^{3+}-poor pseudobrookite, in all cases very close to the formula of "ferropseudobrookite", $Fe^{2+}Ti^{4+}{}_2O_5$. However, high content of Nb (6 to 10 wt.% Nb_2O_5) and Ta (0.5 to 5.5 wt.% Ta_2O_5) and, in some cases, substantial Mn (0.2 to 6.4 wt.% MnO) deviate from compositions of these minerals established to date (Bowles 1988, Brigatti *et al.* 1993); the high content of these pentavalent cations cannot be accommodated in the IMA-approved diagram of Bowles (1988, Fig. 2).

The unique compositional features of the Prašivá "ferropseudobrookite" are even better expressed in terms of cation proportions: Ti is 10 to 17% lower than the ideal value of 2.00, (Fe^{2+} + Mn) commonly exceed 1.00, and (Nb + Ta) constitute 5 to 8% of the sum of cations. The cation content cannot be easily split into two integral populations to satisfy AB_2, although the excess of (Fe^{2+} + Mn) over 1.00 combined with the total of (Nb + Ta) comes close to complementing Ti to 2.00. The excess of (Fe + Mn) evidently contributes to charge-balancing the incorporation of (Nb + Ta), but (Fe^{2+} + Mn)/(Nb + Ta) is between 0.13 and 0.37, lower than 0.5 required by the potential substitution $(Fe,Mn)(Nb,Ta)_2Ti_{-3}$. The cause of this deviation cannot be exactly determined from the available data. Minor beam overlaps with the rutile, if any, would have an opposite effect (*cf.* rutile compositions in Table 2). In any case, the complex nonintegral cation population indicates a high degree of disorder.

Niobian ilmenite forms a narrow (3 to 5 μm thick) rim of a *ca.* 100-μm-long oval exsolution-induced domain of nearly pure *ilmenite* + titanian hematite in one grain of Nb,Ta-poor rutile associated with thinner armalcolite – pseudobrookite lamellae (S2A dike; Fig. 5B). Niobian ilmenite contains up to 7.2 wt.% Nb_2O_5 and 0.74 wt.% Ta_2O_5 (Table 3); these contents possibly are the highest known Nb and Ta concentrations in ilmenite (*cf.* Černý & Ercit 1989). On the other hand, the central part of the above domain consists of nearly pure ilmenite (with only 0.2 wt.% Nb_2O_5 and 0 wt.% Ta_2O_5) and titanian hematite. Both types of ilmenite are enriched in Mn (3 to 6 wt.% MnO).

Titanian hematite forms exsolution-induced lenses in the above-mentioned Nb,Ta-poor ilmenite. The

TABLE 3. REPRESENTATIVE COMPOSITIONS OF ARMALCOLITE (ARM), PSEUDOBROOKITE (PSB), ILMENITE (ILM) AND HEMATITE (HEM), PRAŠIVÁ GRANITIC PEGMATITES

	ARM	ARM	ARM	PSB	PSB	ILM	ILM	ILM	HEM	HEM
	A510	A614	A1613	A104	A166	A65	A63	A68	A64	A66
WO_3	0.00	0.00	0.33	0.00	0.06	0.01	0.00	0.02	0.00	0.00
Nb_2O_5	10.11	8.33	8.92	6.06	6.81	0.22	4.20	7.20	0.13	0.57
Ta_2O_5	4.89	0.46	4.37	3.49	5.15	0.00	0.31	0.74	0.00	0.00
TiO_2	53.55	59.98	56.77	56.84	53.93	52.33	50.02	51.94	12.70	17.71
SnO_2	0.02	0.05	0.00	0.04	0.06	0.04	0.02	0.02	0.00	0.04
ZrO_2	0.03	0.00	0.00	0.00	0.07	0.00	0.02	0.01	0.00	0.00
UO_2	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.00	0.00	0.00
Sc_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sb_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Fe_2O_3	0.00	0.00	0.00	2.20	2.75	0.00	0.00	0.00	73.93	62.34
FeO	24.96	26.76	30.18	30.36	29.92	42.64	37.70	35.41	11.13	15.66
MnO	6.09	3.82	0.33	0.20	0.42	3.02	6.51	4.56	0.36	0.75
MgO	0.06	0.04	0.00	0.01	0.03	0.06	0.06	0.06	0.02	0.07
CaO	0.00	0.00	0.00	0.00	0.00	0.02	0.02	0.02	0.02	0.01
Total	99.71	99.44	100.90	99.20	99.20	98.40	98.86	99.98	98.31	97.16
Formulae based on 5 oxides and 3 cations (ARM, PSB), 18 oxides and 12 cations (ILM, HEM)										
W^{6+}	0.000	0.000	0.003	0.000	0.001	0.000	0.000	0.001	0.000	0.000
Nb^{5+}	0.188	0.150	0.162	0.112	0.127	0.015	0.291	0.487	0.009	0.042
Ta^{5+}	0.055	0.005	0.048	0.039	0.058	0.000	0.013	0.030	0.000	0.000
Ti^{4+}	1.658	1.794	1.719	1.740	1.676	6.036	5.768	5.840	1.530	2.149
Sn^{4+}	0.000	0.001	0.000	0.001	0.001	0.002	0.001	0.001	0.000	0.003
Zr^{4+}	0.001	0.000	0.000	0.000	0.001	0.000	0.001	0.001	0.000	0.000
U^{4+}	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.000
Sc^{3+}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sb^{3+}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000
Fe^{3+}	0.000	0.000	0.000	0.067	0.085	0.000	0.000	0.000	8.912	7.572
Fe^{2+}	0.859	0.890	1.016	1.034	1.034	5.470	4.835	4.428	1.491	2.114
Mn^{2+}	0.212	0.129	0.011	0.007	0.015	0.392	0.846	0.577	0.049	0.103
Mg^{2+}	0.004	0.002	0.000	0.001	0.002	0.014	0.014	0.013	0.005	0.017
Ca^{2+}	0.000	0.000	0.000	0.000	0.000	0.003	0.003	0.003	0.003	0.002
Sum	2.977	2.971	2.959	3.000	3.000	11.936	11.773	11.381	12.000	12.00
Mn_{Fe}	0.20	0.13	0.01	0.01	0.01	0.07	0.15	0.12	0.00	0.01
Ta_{Nb}	0.23	0.03	0.23	0.26	0.32	0.00	0.04	0.06	0.00	0.00

Oxides in weight %. Fe_2O_3 and Fe^{3+} calculated by charge-balance. ARM and PSB computed per one formula unit (1/2 unit cell), ILM and HEM per unit cell. Mn_{Fe}=Mn/(Mn+Fe)at., Ta_{Nb}=Ta/(Ta+Nb)at.

individual particles are only 6 × 2 μm in size (Fig. 2B). The compositions are relatively Ti-rich, containing up to 36 mole % $FeTiO_3$, but very Nb,Ta-poor (Table 3).

Associated Phases

Magnetite forms crystals in association with feldspars, up to 1 mm in size, separate from the Nb, Ta-bearing minerals. *Uraninite* rarely occurs in the S2A dike as an overgrowth *ca.* 100 μm thick on zircon, associated with ferrocolumbite. *Zircon* was found in both dikes as prismatic pale brown crystals 200 to 400 μm long or tiny ~10 μm inclusions in magnetite. Zircon displays moderate hafnium contents, 3 to 7 wt.% HfO_2, and is metamict. *Fluorapatite* is relatively common, in the form of irregular inclusions (<50 μm) in columbite or titanian ixiolite.

Discussion

Petrogenetic considerations and geochemical signature

Both the S2A and S2B dikes at Prašivá belong to poorly fractionated rare-element granitic pegmatites of the beryl type, beryl–columbite subtype of the LCT family according to the classification of Černý (1991). This Prašivá-type pegmatite population (PAOG) is genetically connected with I- to I>S-, allanite-bearing orogenic granodiorites and granites (AOG), in contrast to the Moravany-type pegmatite population (PMOG) of the Western Carpathians, with S>I-type, monazite-bearing orogenic granitic parents (MOG) (Uher 1994, Uher & Broska 1995). The composition of the pegmatite minerals reflects the composition of the parental granitic rocks. Relatively high Ti content (up to 1 wt.% TiO_2) is

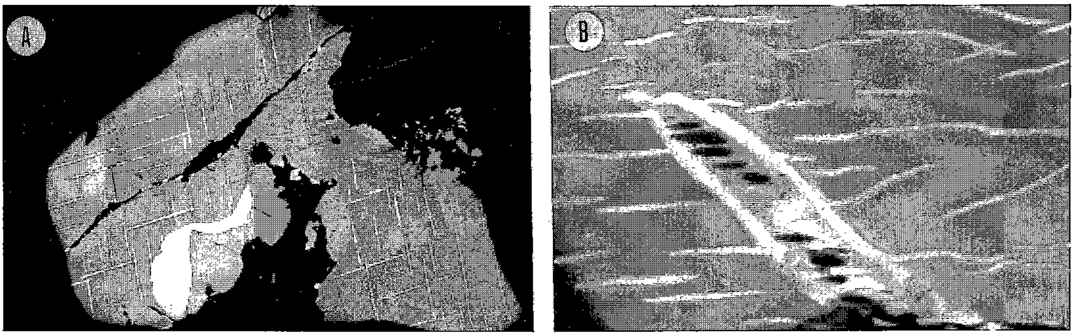

FIG. 5. BSE micrographs. A. Niobian–tantalian rutile (medium to pale grey) with thin lamellae of niobian–tantalian armalcolite – pseudobrookite (white) and the large bleb of Nb,Ta-enriched rutile. B. Niobian–tantalian rutile (grey matrix) with trellis-like exsolution-induced lamellae of niobian–tantalian armalcolite – pseudobrookite (white) and a lenticular aggregate of niobian ilmenite (white) rimming a core of ilmenite (pale grey) intergrown with titanian hematite (white). Scale bars: 10 μm in both cases.

typical in the Prašivá biotite granodiorites and granites (Lukáčik 1981, unpubl. data of the authors); rutile, ilmenite and titanite are three principal titaniferous accessory minerals (Határ 1979). Thus, a titanium-rich oxide assemblage in their pegmatitic differentiates is not surprising. Moreover, the presence of Nb,Ta-bearing minerals, the occurrences of beryl at Vel'ká Chochul'a and Dúbrava dikes, a K/Rb value of 109 to 43 in muscovite from pegmatites in the Dúbrava mine (E. Chovancová, unpubl. data), and 3 to 7 wt.% HfO_2 in the S2A–S2B zircon all indicate a relatively higher level of fractionation of these dikes relative to the other, very primitive and largely barren West-Carpathian AOG pegmatites.

Nevertheless, the Ti,Nb>Ta mineral assemblage, the compositional trend of columbite with low Ta/(Ta + Nb) and Mn/(Mn + Fe) (Fig. 4) and scarcity of Sn imply a generally low level of fractionation in comparison with typical beryl–columbite rare-element pegmatites (*cf.* Černý *et al.* 1986, Černý 1989). The presence of a Nb>Ta, Sn-poor titanian ixiolite also is a feature typical of geochemically primitive systems (*cf.* Ercit 1994), although compositionally similar phases were described in more fractionated beryl pegmatites, such as those at Maršíkov, Czech Republic (Černý *et al.* 1995).

Mineral assemblage and exsolution

The rather indeterminate relationships among ferrocolumbite, titanian ixiolite and niobian rutile suggest more or less simultaneous crystallization of these phases. The distribution of the data in a $M^{4+}O_4 - A^{2+}B_2O_6 - A^{3+}BO_4$ diagram (Fig. 6) closely resembles that obtained for similar aggregates by Ercit (1994). This distribution supports Ercit's view that a large three-phase region may exist in the $TiO_2 - Fe^{2+}Nb_2O_6 - Fe^{3+}NbO_4$ system, although a more-or-less

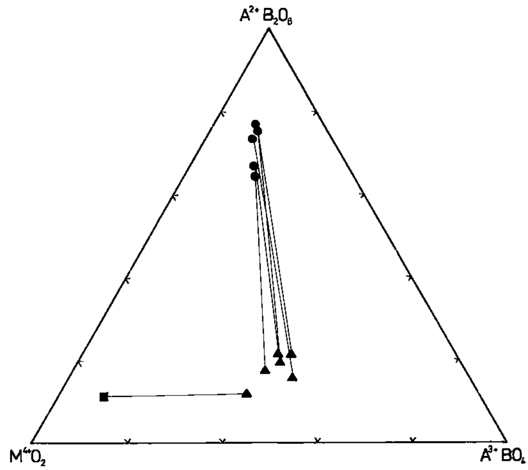

FIG. 6. Coexisting columbite (circles) + titanian ixiolite (triangles) and titanian ixiolite + niobian rutile (square) in the $M^{4+}O_2 - A^{2+}B_2O_6 - A^{3+}BO_4$ diagram (atomic proportions).

pure $Fe^{3+}NbO_4$ phase is not known as a natural mineral, experimental work is not available, and the genetic significance of the Fe^{3+}-rich phase is not known.

Crystals of Nb,Ta-poor rutile in the S2A pegmatite, characterized by numerous armalcolite – pseudobrookite exsolution-induced domains are texturally and compositionally distinctly different from small anhedral inclusions of very Nb- or Ta-rich rutile in the S2B dike (Table 2, Figs. 2, 3, 5). The rutile + armalcolite – pseudobrookite assemblage is the product of subsolidus exsolution of a primary, homogeneous but metastable rutile precursor enriched in Fe, Nb and Ta, which must have contained Fe^{2+} in excess of that required to compensate for Nb and Ta in the columbite – tantalite component.

The exsolved phase lies very close to the $FeTi_2O_5$ member of the pseudobrookite – armalcolite – "anosovite" ($Ti^{3+}{}_2Ti^{4+}O_5$) system (Bowles 1988). The S2A armalcolite is the first occurrence of this mineral noted from a granitic environment in general, and from granitic pegmatites in particular. Armalcolite was primarily described from lunar basalts (Anderson *et al.* 1970), and more recently recognized in terrestrial rocks such as upper mantle xenoliths in kimberlites, lamproites, Ries impact glass, buchite xenoliths, and picrites (Haggerty 1975, 1983, 1991, Velde 1975, Brigatti *et al.* 1993, El Goresy & Chao 1976, Pedersen 1979, Cawthorn & Biggar 1993). The textural pattern of flame to trellis exsolution-induced lamellae in the Prašivá rutile is very similar to that in rutile from metasomatized upper mantle xenoliths in kimberlites from South Africa (Haggerty 1991, Fig. 31b). On the other hand, our armalcolite clearly differs in composition from that found in all other localities, by its high Nb, Ta and locally Mn contents, and very low Mg, Ca, Al, Cr, Zr, and Si (Table 3), which are in turn typical for some lunar as well as other terrestrial occurrences of armalcolite (Haggerty 1991). However, some examples of armalcolite from the xenoliths in kimberlites also are moderately enriched in Nb and Ta, rarely also in Mn (≤3 wt.% Nb_2O_5, ≤0.3% Ta_2O_5 and ≤4% MnO; Haggerty 1983, 1991).

The presence of Fe^{2+} and Ti^{3+}, in the absence of Fe^{3+}, indicates very low oxygen fugacity during precipitation of armalcolite in lunar environments and in some terrestrial environments, such as in association with native iron from the Disko buchite xenolith (Pedersen 1979). On the contrary, Fe^{3+}-bearing armalcolite and pseudobrookite in a Fe^{3+}-rich rutile host in the S2A pegmatite require a more oxidizing environment, possibly between FMQ and NNO buffers (*cf.* Brigatti *et al.* 1993, Cawthorn & Biggar 1993).

Experimental work shows that $Fe^{2+}Ti_2O_5$ decomposes to ilmenite + rutile at and below 1140° ± 10°C. However, the effect of isomorphic substitution of Mg^{2+}, Al^{3+}, Cr^{3+} and Ti^{3+} extends its stability to much lower temperatures, throughout a wide range of geologically feasible pressures (as low as 900–750°C at <100 MPa; Hartzman & Lindsley 1973, Kesson & Lindsley 1975). Although the S2A armalcolite does not contain significant levels of the above elements, it is possible that high Nb^{5+}, Ta^{5+} and locally Mn^{2+} also stabilized armalcolite to temperatures realistic for early stages of pegmatite consolidation. The onset of crystallization of the Prašivá-type pegmatites was estimated at ~600–700°C and ~200–300 MPa on the basis of the estimated minimum temperature of the solidus of the host granite and its emplacement conditions (Uher 1994). The exsolution of armalcolite from rutile could have.proceeded during early stage of pegmatite solidification (*ca.* 700 to 500°C). However, this "extrapolation" from the currently available data could be verified only by further experimental work on minerals of appropriate composition.

In contrast to the exsolution of the very Fe^{2+}-dominant armalcolite, the segregation of the ilmenite-structured phases involves extraction of substantial Fe^{3+} from the host rutile. Exsolution of zoned Nb-rich plus Nb-poor but Fe^{3+}-rich ilmenite suggests disequilibrium, and the breakdown of the latter into ilmenite + titanian hematite indicates its metastability and re-equilibration at lower temperatures. In our case, the exsolution of niobian ilmenite + ilmenite + titanian hematite in rutile from the S2A dike appears to be younger than the armalcolite lamellae (Fig. 3B). It suggests a local excess of Fe in the primary homogeneous rutile, much higher than that generating armalcolite – pseudobrookite. This type of exsolution is apparently very scarce here, as it was encountered only once so far.

Summary

The Hercynian Prašivá S2A and S2B dikes are relatively primitive representatives of the beryl type, beryl – columbite subtype of the LCT rare-element granitic pegmatites. They carry a primary assemblage of Nb,Ta,Ti,Fe-bearing oxide minerals (ferrocolumbite to manganocolumbite, titanian ixiolite, niobian–tantalian rutile, niobian–tantalian armalcolite to pseudobrookite, niobian ilmenite, ilmenite and titanian hematite), associated with minor magnetite, uraninite, zircon and fluorapatite.

The high content of Ti in the accessory minerals reflects the high concentration of Ti encountered in the parent granitic system. Extensive variability in mineral composition, irregular complex textural patterns and lack of oscillatory zoning in Ti,Nb,Ta-minerals indicate rapid precipitation. High-temperature exsolution of armalcolite – pseudobrookite also suggests a metastable composition of some of the primary homogeneous phases. The presence of niobian–tantalian armalcolite – pseudobrookite in granitic pegmatites could imply their stability below 700°C at a relatively high fugacity of oxygen; it indicates the feasibility of their precipitation and at least metastable survival in any case. Later, disequilibrium exsolution of zoned niobian ilmenite and Fe^{3+}-rich ilmenite was followed by re-equilibration of the latter into ilmenite and titanian hematite.

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