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EXSOLUTION AND BREAKDOWN OF SCANDIAN AND TUNGSTENIAN Nb–Ta–Ti–Fe–Mn PHASES IN NIOBIAN RUTILE

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ABSTRACT

Niobian rutile commonly exsolves titanian ferrocolumbite to manganocolumbite or ixiolite with elevated contents of Nb, Mn and Sc, W or Sn, but further breakdown of the exsolved phase has not been reported to date. Niobian rutile from Eptevann, southern Norway, exsolved titanian-scandian phase E1 of the $A^{3+}BO_4$ type, which subsequently broke down to a (Sc,Mn)-enriched and U-depleted phase E2 (11 to 12.8 wt.% Sc_2O_3), a Ti-rich but (Sc,Mn,U)-poor phase E3 , and a (U,Y)-rich but (Ti,Sc,Mn)-depleted, metamict and hydrous phase X (2.5 to 3 wt.% UO_2). Niobian rutile from Ilmen Mountains, Russia, exsolved a (Ti,U)-poor, Mn-rich tungstenian ixiolite (10 to 14 wt.% WO_3), which subsequently broke down into a Ti-poor but W-rich phase (~30 wt.% WO_3) and a U-enriched but W-depleted mineral (~6 wt.% WO_3, 0.7 to 1.5 wt.% UO_2). The second-stage breakdown of the exsolved phases reflects the metastable nature of these minerals, which feature disordered populations of divalent to hexavalent cations in an exclusively octahedral array of oxygen anions, with consequent long-range disorder and local imbalances of electrostatic charges. Under low-temperature conditions, insufficient for further exsolution and ordering, the exsolved phases readily respond to the action of aqueous fluids by breakdown to more cation-selective phases. However, incomplete separation of different categories of cations and non-integral stoichiometries of the products suggest that they did not attain equilibrium.

Keywords: niobian rutile, ixiolite, $A^{3+}BO_4$, scandium, tungsten, granitic pegmatite, exsolution, alteration, Eptevann, Norway, Ilmen Mountains, Russia.

SOMMAIRE

Le rutile niobifère montre couramment des lamelles d'exsolution de ferrocolumbite ou manganocolumbite titanifère ou d'ixiolite contenant des teneurs élevées de Nb, Mn et Sc, W ou Sn, mais une exsolution plus avancée dans ces produits d'exsolution n'a pas été documentée antérieurement. Le rutile niobifère d'Eptevann, dans le sud de la Norvège, a exsolvé la phase E1, de type $A^{3+}BO_4$, enrichie en titane et en scandium; à son tour, la phase E1 s'est décomposée en une phase E2 enrichie en Sc (de 11 à 12.8% Sc_2O_3 en poids) et Mn, et appauvrie en U, une phase E3 riche en titane mais appauvrie en Sc, Mn et U, et une phase X hydratée et métamicte enrichie en U (2.5 à 3% UO_2) et Y, mais appauvrie en Ti, Sc et Mn. Le rutile niobifère des montagnes Ilmen, en Russie, a exsolvé une ixiolite tungstènifère (10 à 14% WO_3) riche en Mn et appauvrie en Ti et U; à son tour, celle-ci s'est déstabilisée en une phase riche en W (~30 wt.% WO_3) et appauvrie en Ti, et une autre enrichie en U (0.7 à 1.5% UO_2) et appauvrie en W (~6% WO_3). Le deuxième stade de déstabilisation des phases exsolvées résulte de la métastabilité de ces minéraux, qui contiennent des populations désordonnées de cations divalents à hexavalents entourés d'atomes d'oxygène dans un agencement exclusivement octaédrique, et donc avec une désordre à longue échelle et des gradients locaux de charges électrostatiques. A faible température, trop faible en fait pour une exsolution plus poussée et une mise en ordre, les phases exsolvées réagissent d'emblée en présence d'une phase aqueuse, pour donner des phases plus sélectives par rapport aux cations. Toutefois, une séparation incomplète des différentes catégories de cations et une stoechiométrie non intégrale des produits font penser qu'ils n'ont pas atteint l'équilibre.

(Traduit par la Rédaction)

Mots-clés: rutile niobifère, ixiolite, $A^{3+}BO_4$, scandium, tungstène, pegmatite granitique, exsolution, altération, Eptevann, Norvège, montagnes Ilmen, Russie.

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INTRODUCTION

Niobian and tantalian rutile, $(Ti,Fe,Nb>Ta)O_2$ and $(Ti,Fe,Ta>Nb)O_2$, respectively, were historically considered rather exotic, identified only as rare accessory minerals in a restricted number of granitic pegmatites. However, in the last forty years, these variants were found in appreciable quantities in peraluminous to peralkaline rare-element granites, and in a variety of styles of hydrothermal mineralization, locally attaining the status of ore minerals of Nb or Ta (*cf.* review by Černý & Ercit 1989). Tantalian rutile is generally known to be homogeneous, but its Nb-dominant counterpart virtually always shows signs of exsolution. The host phase of partially "purified" rutile contains unmixed platelets or coarsened grains of titanian columbite or ixiolite, locally with high contents of Sc, W or Sn (*e.g.*, Černý *et al.* 1964, 1981, 2000a, Sahama 1978). Additional phases form from niobian rutile with about equal amounts of Fe^{2+} and Fe^{3+} (Černý *et al.* 1999: pseudorutile, "ferropseudobrookite", ilmenite) or with dominant Fe^{3+} (Černý *et al.* 2000b: monoclinic derivatives of $Fe^{3+}NbO_4$).

In a given crystal of niobian rutile, the chemical composition of a particular exsolved phase is variable among its different grains, depending on the local degree of equilibration, variable in time. Also, the composition is commonly somewhat variable within the individual grains. However, in all Fe^{2+}- and Fe^{3+}-dominant cases examined to date, the final product of exsolution is a single phase with no indication of further breakdown or alteration. Here, we report the first occurrences of exsolved minerals that underwent low-temperature disintegration into two or more phases, suggestive of inherent metastability of the products of exsolution.

SAMPLES, EXPERIMENTAL METHODS AND DATA TREATMENT

Niobian rutile from the Eptevann pegmatite, in the Evje–Iveland pegmatite field of southern Norway, was examined in a specimen registered as #107439 in the collection of the Mineralogy Museum, Harvard University. The second sample analyzed in the present study has a general label of "Ilmen Mountains", Russia. It was extracted from general-purpose, non-catalogued material stored in the Moravian Museum, Brno, Czech Republic in the early nineteen-sixties.

Chemical compositions were established with a CAMECA SX–50 electron microprobe in wavelength-dispersion mode, under conditions given by Novák & Černý (1998) and Černý *et al.* (2000a). Some of the examined phases were identified by routine X-ray powder diffraction using the Siemens–Nicolet D–5000 instrument in transmission mode.

Niobian rutile, constituting the matrix of both specimens examined, was easy to identify by X-ray powder diffraction. However, the exsolved phases and their alteration products were found to be extremely fine-grained and mutually intergrown. Thus the identification had to be based on chemical composition alone. This was relatively easy in the case of the Eptevann sample, which contains several varieties of phase E, analogous to that characterized by Černý *et al.* (2000b) as a compositional derivative of monoclinic $A^{3+}BO_4$, which is so far not recognized as a mineral species (T.S. Ercit, unpubl. data). The term "wolframoixiolite" was applied to phases encountered in the Ilmen Mts. specimen. However, several minerals of distinctly different properties have been described under this name, and most of them lack crystal-structure definition (Ginsburg *et al.* 1969, Amichba & Dubakina 1976, Borneman-Starynkevich *et al.* 1976, Beddoe-Stephens & Fortey 1981, Konovalenko *et al.* 1982, Wang *et al.* 1988; see also Saari *et al.* 1968, Kluger & Pertlik 1985, Yang *et al.* 1985, and Yamnova *et al.* 1995). The term is used here in the most general sense, indicating a broad compositional relationship but not implying a specific identity with any of the minerals characterized in the literature. Quite a few phases are currently grouped under the umbrella of the ixiolite group, most of them in need of detailed re-examination and reclassification (*e.g.*, Wise & Černý 1986, Černý & Ercit 1989, Černý *et al.* 1998, Wise *et al.* 1998).

To facilitate mutual comparison of chemical composition of rutile, phase E and ixiolite on one hand, and of both of them with columbite-group minerals, atomic contents of all phases are normalized to 8 atoms of oxygen. This gives atomic content per unit cell (*apuc*) for disordered columbite or ixiolite and for $A^{3+}BO_4$, and per 4 unit cells of rutile. The atomic contents equal those per 4 formula units (*ap4fu*), except for phase E (*ap2fu*). Normalization to 8 atoms of oxygen was constrained to a maximum total of 4 cations, maintained by conversion of appropriate amount of Fe^{2+} to Fe^{3+}. The general legitimacy of this procedure was established by Ercit (1986) and Ercit *et al.* (1992a, b).

THE SCANDIUM-RICH ASSEMBLAGE FROM EPTEVANN, NORWAY

Niobian rutile from Eptevann consists of a rutile matrix, with numerous irregular to subgraphic grains of other phases (Fig. 1A). Individual grains are composite mixtures of at least four phases (Fig. 1B). Textural relationships indicate that Sc-poor titanian phase E1 is a relict mineral that yielded three breakdown products: Sc-rich titanian phase E2, Ti-rich phase E3 and (U,Y)-enriched ixiolite-like mineral *X*.

The niobian rutile is compositionally heterogeneous on a fine (microscopic) scale, with an irregular patchy structure in back-scattered electron (BSE) images (Fig. 1A). It has low Mn, Sc and Sn contents, but a prominent content of Fe^{3+}, dominant over Fe^{2+} (Table 1, RA and RB). The early component of the composite grains corresponds to a Sc-poor but Mn-enriched titanian phase

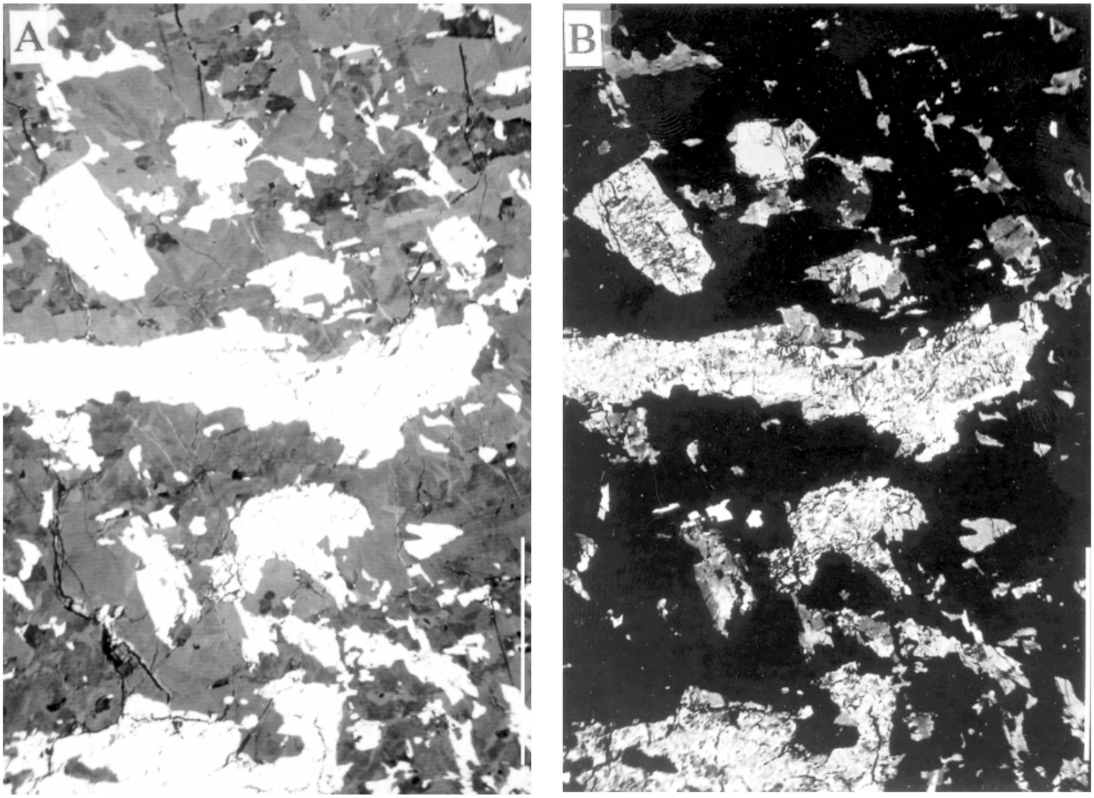

FIG. 1. BSE images of the Eptevann niobian rutile and associated minerals. A. Bright offset with mottled-grey pattern of the rutile matrix indicative of its compositional heterogeneity; all associated minerals are white, displaying the directional controls of their distribution. B. Dark offset revealing heterogeneous composition of the granular material; phases E1 and E2 white, phase E3 medium grey, phase X dark grey, rutile black. Scale bars are 200 μm long.

E1 with a formula indicative of the dominance of the $(Fe,Sc)^{3+}(Nb>Ta)O_4$ component in solid solution, with subordinate TiO_2 and minor $Fe^{2+}(Nb,Ta)O_6$ (Table 1, E1A and E1B). The composition of this phase is very close to that of phase E in niobian rutile from central Iveland (Černý *et al.* 2000b), except for a different value of Nb/Ta.

Among the three decomposition products of the Sc-poor poor titanian phase E1, the phase E2 is the most enriched in Sc (Table 1, E2A and E2B). The Sc_2O_3 content is as high as 12.73 wt.% (0.823 Sc per 8 atoms of oxygen), and it strongly contributes to the dominance of the $(Sc,Fe)^{3+}(Nb>Ta)O_4$ component in the overall composition of this phase. The proportion of the columbite-type component is reduced relative to phase E1, but TiO_2 is about the same.

The second product of breakdown after E1 is the Ti-rich, (Sc,Mn,U)-poor derivative of the $A^{3+}BO_4$ phase, termed E3 (Table 1, E3). In principle, its composition is similar to that of E2; however, the ferric component is much more abundant, Ti is enhanced, Mn is virtually absent, and the scandium component is negligible. The content of the columbite-type component, indicated by the concentration of Fe^{2+}, is about the same as in E2.

The third and least abundant mineral is designated phase X, strongly enriched in Y, U, Ca, Mn relative to total Fe, and poor in Sc, Sn and Ti (Table 1, X). The rare-earth-element (*REE*) contents are very low, at the level of detection limits. The low wt.% total suggests that phase X probably is metamict and hydrated, and consequently dark in BSE images despite its high content of U (Fig. 1B). The composition of this phase cannot be rationalized into any kind of general formula; it distinctly deviates from compositions of ixiolite (Wise & Černý 1986), euxenite, samarskite, fergusonite or formanite.

In the columbite quadrilateral, the rutile matrix shows a strong preference for Ta and Fe, in contrast to the Mn- and Nb-enriched phase E1 (Fig. 2A). Phases E2 and E3 flank the plots of E1 at about the same level

TABLE 1. REPRESENTATIVE COMPOSITIONS OF NIOBIAN RUTILE, EXSOLVED PHASE E AND ITS BREAKDOWN PRODUCTS, EPTEVANN, NORWAY

	RA	RB	E1A	E1B	E2A	E2B	E3	X
WO_3	bdl	0.24	1.68	2.12	0.52	0.25	0.47	0.68
Nb_2O_5	17.40	13.60	42.70	43.10	40.21	39.80	39.70	41.30
Ta_2O_5	12.80	12.60	15.70	15.10	21.28	19.60	13.40	14.08
TiO_2	56.40	61.20	12.30	12.20	11.30	14.80	21.50	8.85
ZrO_2	bdl	bdl	0.37	0.32	0.17	0.39	0.01	bdl
SnO_2	0.41	0.49	1.06	0.82	1.57	1.18	0.90	0.34
ThO_2	bdl	bdl	bdl	0.01	bdl	bdl	0.05	bdl
UO_2	bdl	bdl	0.24	0.22	bdl	0.07	0.03	3.69
Sc_2O_3	0.20	0.01	7.19	7.08	12.73	10.90	1.56	2.03
Y_2O_3	bdl	bdl	0.01	0.06	0.08	0.08	0.03	4.21
As_2O_3	bdl	bdl	bdl	bdl	bdl	0.01	0.02	bdl
Sb_2O_3	0.07	0.01	bdl	0.01	0.02	bdl	bdl	bdl
Bi_2O_3	bdl	0.08	bdl	bdl	bdl	0.04	0.06	bdl
Fe_2O_3	9.90	9.01	11.62	11.19	7.59	6.78	16.09	0.00
FeO	2.19	1.66	4.24	4.83	1.37	2.25	4.93	3.94
MnO	bdl	0.05	1.14	0.94	2.80	2.64	bdl	1.80
CaO	0.01	0.01	0.02	0.03	0.15	0.19	bdl	2.27
MgO	bdl	bdl	0.12	0.03	bdl	0.05	0.03	0.03
ZnO	bdl	bdl	bdl	bdl	0.01	bdl	bdl	bdl
PbO	0.01	bdl	bdl	bdl	bdl	bdl	bdl	0.04
Total	99.39	98.96	98.39	98.14	99.81	99.03	98.78	83.26
				atomic contents				
W	-	0.004	0.032	0.041	0.010	0.005	0.008	
Nb	0.496	0.384	1.439	1.460	1.350	1.327	1.283	
Ta	0.219	0.214	0.689	0.307	0.429	0.393	0.261	
Ti	2.675	2.871	0.321	0.686	0.631	0.821	1.156	
Zr	-	-	0.013	0.012	0.006	0.014	-	
Sn	0.010	0.012	0.031	0.024	0.046	0.035	0.026	
Th	-	-	-	-	-	-	0.001	
U	-	-	0.004	0.004	-	0.001	-	
Sc	0.011	0.001	0.467	0.461	0.823	0.700	0.097	
Y	-	-	-	0.002	0.003	0.003	0.001	
As	-	-	-	-	-	-	0.001	
Sb	0.001	-	-	-	0.001	-	-	
Bi	-	0.001	-	-	-	0.001	0.001	
Fe^{3+}	0.469	0.423	0.652	0.629	0.424	0.376	0.866	
Fe^{2+}	0.116	0.087	0.265	0.302	0.085	0.139	0.295	
Mn	-	0.003	0.072	0.059	0.176	0.165	-	
Ca	0.001	0.001	0.002	0.002	0.012	0.015	-	
Mg	-	-	0.013	0.012	-	0.005	0.003	
Zn	-	-	-	-	0.001	-	-	

R = niobian rutile matrix, E1 = exsolved phase E (derivative of $A^{3+}BO_4$), E2 and E3 = compositionally diversified but related breakdown products of E1, X = hydrous and metamict breakdown product; atomic contents normalized to 8 oxygen atoms and 4 cations (*ap4fu* for rutile, *ap2fu* for phase E).

TABLE 2. REPRESENTATIVE COMPOSITIONS OF NIOBIAN RUTILE, EXSOLVED TUNGSTENIAN IXIOLITE AND ITS BREAKDOWN PRODUCTS, ILMEN MTS., RUSSIA

	RA	RB	WX1A	WX1B	WX2A	WX2B	WX3A	WX3B
WO_3	0.21	0.05	14.50	10.60	30.10	29.80	6.53	6.45
Nb_2O_5	11.80	7.16	47.70	54.50	36.00	35.70	52.40	53.00
Ta_2O_5	11.20	10.60	12.30	11.10	9.40	10.80	12.60	14.00
TiO_2	66.10	73.90	3.71	2.66	2.33	1.91	6.26	5.06
ZrO_2	bdl	bdl	0.05	0.07	0.26	0.14	0.05	bdl
SnO_2	0.02	0.03	0.01	bdl	0.01	bdl	bdl	0.01
UO_2	bdl	bdl	0.22	0.22	0.13	0.19	1.58	1.21
Sc_2O_3	bdl	bdl	0.05	0.03	0.03	0.02	bdl	bdl
Y_2O_3	0.01	bdl	bdl	0.01	bdl	bdl	0.03	0.03
As_2O_3	0.02	0.02	0.01	bdl	0.02	0.01	bdl	0.01
Sb_2O_3	bdl	0.03	bdl	bdl	0.00	0.03	bdl	bdl
Bi_2O_3	0.09	bdl	bdl	bdl	0.02	bdl	0.08	0.03
Fe_2O_3	8.53	7.70	2.46	0.78	1.68	1.39	2.67	1.87
FeO	1.05	0.18	4.04	4.97	3.60	3.36	2.39	2.74
MnO	0.10	bdl	14.00	14.30	16.00	16.40	14.40	14.80
CaO	bdl	0.01	0.02	bdl	bdl	0.02	0.03	0.01
MgO	0.01	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Total	99.18	99.68	99.08	99.24	99.58	99.77	99.02	99.22
				atomic contents				
W	0.003	0.001	0.308	0.223	0.672	0.663	0.135	0.134
Nb	0.325	0.191	1.771	1.996	1.403	1.399	1.889	1.925
Ta	0.186	0.170	0.275	0.245	0.220	0.255	0.273	0.306
Ti	3.029	3.284	0.229	0.162	0.151	0.124	0.375	0.306
Zr	-	-	0.002	0.003	0.011	0.006	0.002	-
Sn	-	0.001	-	-	-	-	-	-
U	-	-	0.004	0.004	0.002	0.004	0.028	0.022
Sc	-	-	0.004	0.002	0.002	0.002	-	-
Y	-	-	-	-	-	-	-	0.001
As	0.001	0.001	-	-	0.001	0.001	-	-
Sb	-	0.001	-	-	-	0.001	-	-
Bi	0.001	-	-	-	-	-	0.003	0.001
Fe^{3+}	0.391	0.342	0.152	0.048	0.109	0.091	0.054	0.113
Fe^{2+}	0.056	0.009	0.278	0.337	0.259	0.243	0.228	0.184
Mn	0.005	-	0.974	0.981	1.168	1.204	0.993	1.007
Ca	-	0.001	0.002	-	-	0.002	-	0.001
Mg	0.001	-	-	-	-	-	-	-

R = niobian rutile, WX1 = exsolved tungstenian ixiolite, WX2 and WX3 = breakdown products of WX1; atomic contents normalized to 8 oxygen atoms and 4 cations (*ap4fu* for rutile, *apfu* for ixiolite).

of Ta/(Ta + Nb), but the locations of phase X are quite random. In the diagram (Ti + Sn) – (Fe_{tot} + Mn + Sc) – (Nb + Ta), the rutile matrix and phases E1, E2 and E3 all follow the same trend of uniform Fe^{2+}/Fe^{3+} value, but phase X defies again any stoichiometric control (Fig. 2B).

TUNGSTEN-RICH ASSEMBLAGE FROM ILMEN MOUNTAINS, RUSSIA

Niobian rutile from the Ilmen Mountains consists of a rutile matrix, strongly heterogeneous in chemical composition and texture. This matrix contains numerous but mostly very small (50 to 300 μm) platy blebs of high electron-density, prominently aligned in two (and only locally three) directions (Fig. 3A). However, as in the preceding case, the platy grains consist of a mixture of several phases (Fig. 3B): Mn-rich "wolframoixiolite" WX1 is predominant and apparently early, corroded and replaced by W-rich "wolframoixiolite" WX2 and W-poor but Ti- and U-enriched "wolframoixiolite" WX3.

The niobian rutile shows a complex pattern of patchy and oscillatory zoning, and has a considerable compositional range. The rutile is fairly rich in Nb and Ta, but W, Zr, U and Mn are negligible to undetectable; Fe^{3+} strongly dominates over Fe^{2+} (Table 2, RA and RB). In contrast, the early and dominant phase in the blebs, WX1, is rich in W, Nb>Ta, Mn and Fe^{2+} dominates over Fe^{3+} (Table 2, WX1A and WX1B).

The two phases that replace WX1 have generally similar compositions, but with significant quantitative differences in the contents of some elements. The WX2 phase is extremely W- and Mn-rich, but poor in Ti and U (Table 2, WX2A and WX2B). In contrast, the WX3 phase is W-poor but enriched in Ti and U, and its Fe^{3+}/Fe^{2+} value is higher (Table 2, WX3A and WX3B).

Figure 4A documents the negligible Mn content of the rutile phase and its higher Ta content relative to the components of the platy blebs. This figure also shows the remarkably constant composition of the bleb components in terms of the columbite quadrilateral, with slight shifts from each other but extensive overlaps. Figure 4B reflects the shift in Fe^{3+}/Fe^{2+} from the high values typical of rutile to the lower values in WX1 and

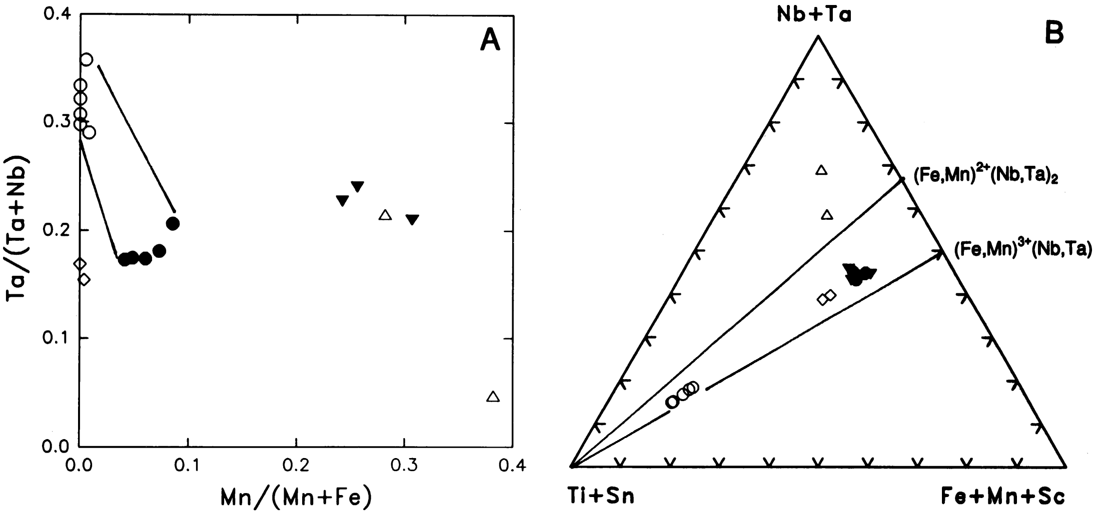

FIG. 2. Compositions of the niobian rutile and associated minerals in the sample from Eptevann, in terms of the columbite quadrilateral (A) and in the (Ti + Sn) – (Fe_{tot} + Mn + Sc) – (Nb + Ta) diagram (B). Open circles: rutile, solid dots: E1, solid triangles: E2, open diamonds: E3, open triangles: phase X. Note the erratic plots of phase X, particularly in B.

WX2. The lowest values of this ratio are actually encountered in WX3, but their effect is masked in this diagram by the extremely high W content, which shifts the points along the columbite–wolframite join.

The relationship among Fe^{3+}, Fe^{2+} and W is better illustrated by the Figure 5A, which show the radical difference between rutile and the WX phases in general, and extensive overlaps among the WX phases but a perceptible drift from WX2 and WX1 to WX3 toward higher Fe^{3+}/Fe^{2+} values. Figure 5B shows the divergence in relative W and Ti contents of the WX2 and WX3 phases, with the early "wolframoixiolite" WX1 intermediate between the two.

DISCUSSION

Textural relationships

The composite grains hosted by the Eptevann niobian rutile are rather evenly distributed in the rutile matrix. The irregular to quasi-graphic shape of these grains, their distribution, and alignment in preferred directions are analogous to those of exsolved titanian ferrocolumbite to manganocolumbite, titanian ixiolite and granular phase E in other occurrences of niobian rutile (*e.g.*, Černý *et al.* 1964, 1981, 2000a, b, Sahama 1978). In the Ilmen Mountains rutile, the shape and distribution of the platy composite grains are perceptibly different. The lamellar pattern resembles the incipient exsolution-induced textures of titanian ferrocolumbite to manganocolumbite in niobian rutile from other localities (*e.g.*, Černý *et al.* 1964) and, to a degree, those exhibited by the initial exsolution of the titanian phase E (Černý *et al.* 2000b).

Texturally, exsolution is indicated, but it seems to be contradicted by the multiphase constitution of the composite grains. This discrepancy is, however, eliminated when we consider the relationships between the host rutile and the early phase of the granular aggregates alone, disregarding its replacement products.

Exsolution products

The niobian rutile matrix in both specimens has all the attributes of a strongly "purified" phase, characteristic of niobian rutile that exsolved substantial quantities of titanian columbite or ixiolite. The composition of rutile in both samples examined is very poor in W, Zr, U, Sc and Mn, and it is enriched in Fe^{3+} and Ta relative to the early components of the multiphase grains, E1 and WX1. In contrast, these two phases are distinctly to prominently enriched in W, Zr, U, Sc and Mn, and they have lower values of Fe^{3+}/Fe^{2+} and Ta/(Ta + Nb). This style of element partitioning is typical of exsolution in niobian rutile, conditioned by crystal-chemical preferences of the tetragonal and orthorhombic (to pseudo-orthorhombic) structures of the exsolution products (*cf.* Černý *et al.* 1964, 1981, 2000a, b, Černý & Ercit 1989). The distribution of rutile and the E1 and WX1 phases in Figures 2A and 4A also is characteristic of exsolution products observed at other localities (references as above).

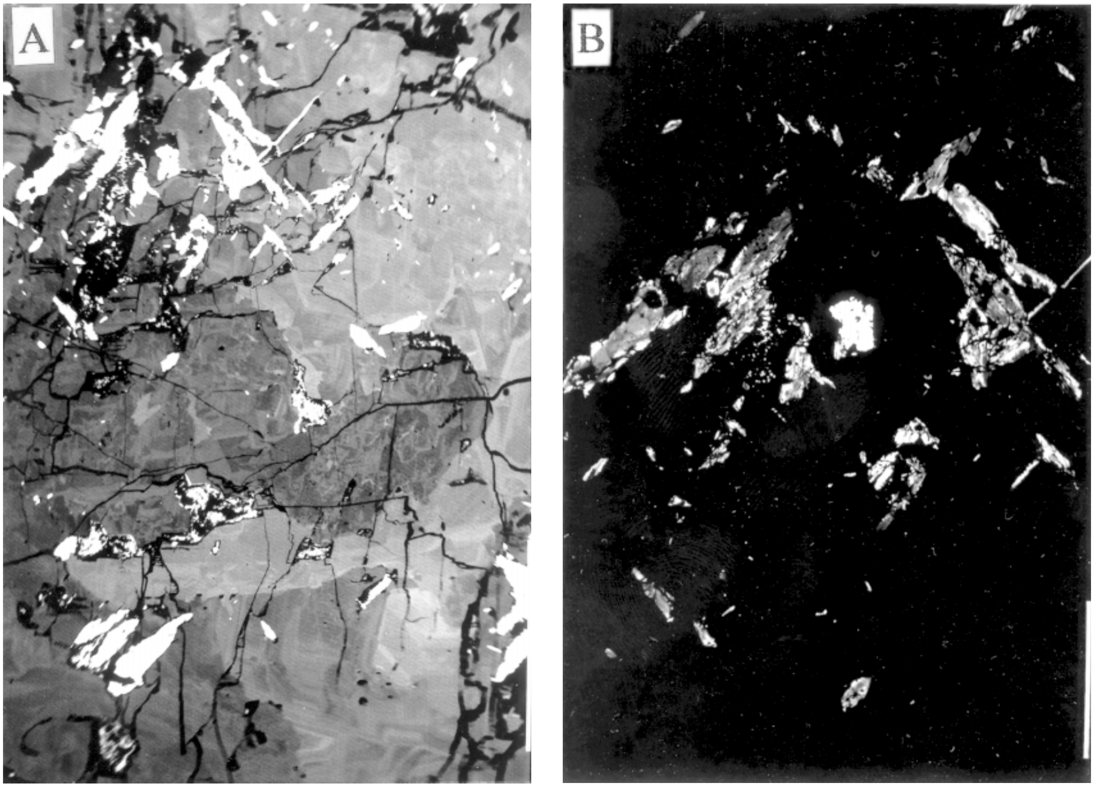

FIG. 3. BSE images of the niobian rutile and associated minerals in the sample from Ilmen Mountains. A. Bright offset revealing complex patchy and oscillatory zoning in (Nb,Ta)-richer and (Nb,Ta)-poorer domains (pale grey and darker grey areas, respectively) in the rutile matrix, and platy to irregular blebs of other minerals (white). Note the two preferred orientations of the platy particles. The scale bar is 500 μm long. B. The upper left quadrant of A at darker offset, showing the heterogeneous nature of the platy blebs. The dominant WX1 is medium grey, the tungsten-rich WX2 is white, and WX3 is dark grey; the rutile matrix is black. The scale bar is 200 μm long.

The Sc and W contents of the exsolved phases E1 and WX1 may seem to be very high and difficult to perceive as generated by exsolution from originally homogeneous niobian rutile alone. However, these elements are known to be almost totally removed from the rutile, and very strongly partitioned into the subordinate volume of exsolution products (*e.g.*, Černý *et al.* 1999, 2000a, b), and homogeneous niobian rutile is known to contain as much as 7 wt.% WO_3 (Urban *et al.* 1992, Michailidis 1997, Rice *et al.* 1998) and 2 wt.% Sc_2O_3 (Voloshin *et al.* 1991). An estimate of ~20 vol.% of E1 in the Eptevann rutile would suggest a maximum of ~2 wt.% Sc_2O_3 in the unexsolved precursor, and ~10 vol% of WX1 in the Ilmen Mountains rutile would correspond to a maximum of ~1.5 wt.% WO_3 in the primary homogeneous rutile. Both these contents are within the empirical "limits" on homogeneous rutile quoted above.

Alteration of the exsolved phase

The $A^{3+}BO_4$ phase E1 and the ixiolite-like phase WX1, exsolved from the specimens of niobian rutile examined here, have presumably simple structures but obviously complex chemical compositions. The crystal structures of minerals of the broader columbite family (including the columbite, ixiolite, tapiolite and wodginite groups, wolframite and $A^{3+}BO_4$ phases) are all based on octahedral coordination alone, and they only differ in styles of linkage among the octahedra, in schemes of cation order, and in variable degrees of cation disorder. Most members of the above groups are compositionaly simple, but considerable complexity is encountered in the wodginite and ixiolite groups.

Wodginite-group minerals, ABC_2O_8, accommodate a variety of divalent to hexavalent cations with relative ease in three highly specialized sites (Ercit *et al.* 1992a, b, Tindle *et al.* 1998, Galliski *et al.* 1999, Masau *et al.*

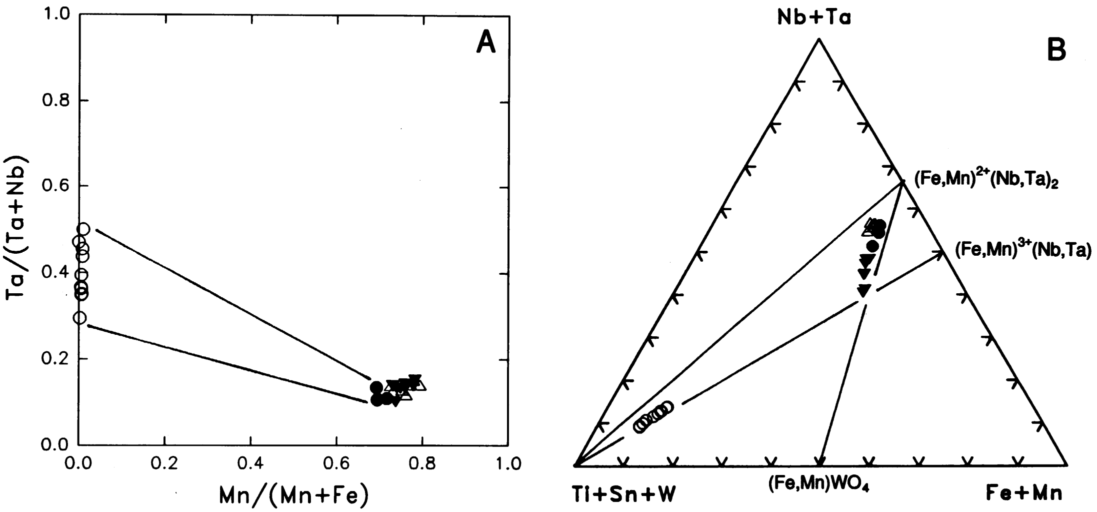

FIG. 4. Compositions of the niobian rutile and associated minerals in the sample from the Ilmen Mountains, in terms of the columbite quadrilateral (A) and in the (Ti + Sn) – (Fe$_{tot}$ + Mn + Sc) – (Nb + Ta) diagram (B). Open circles: rutile, solid dots: WX1, solid triangles: WX2, open triangles: WX3. Note the tight clustering of WX1, WX2 and WX3 in A, and the alignment of WX2 along the columbite–wolframite trend in B.

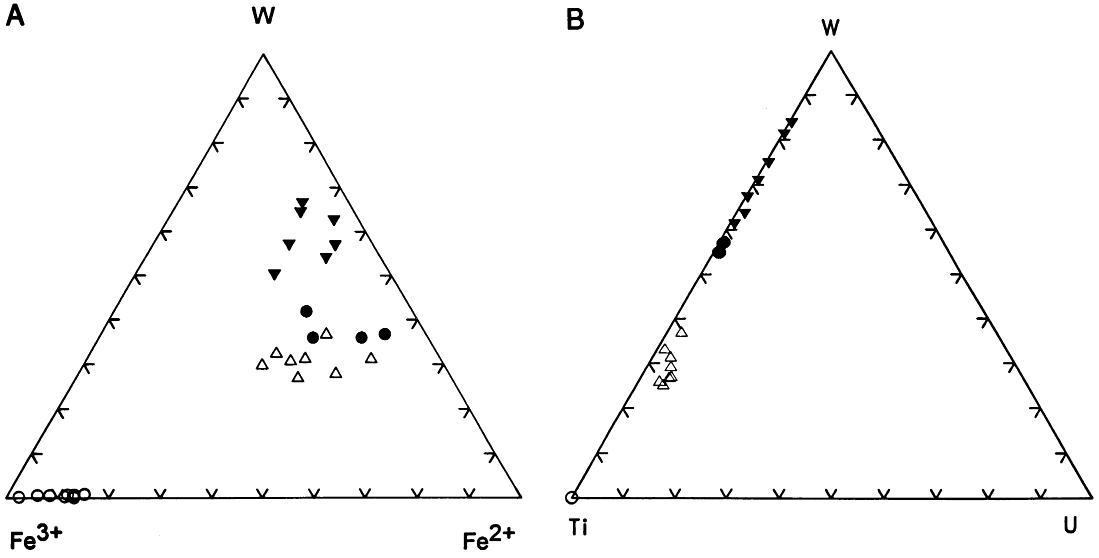

FIG. 5. Compositions of niobian rutile and associated minerals in the sample from the Ilmen Mountains. A. The Fe^{3+} – Fe^{2+} – W diagram shows the Fe^{3+}-rich, W-poor composition of rutile, and the largely overlapping Fe^{3+}/Fe^{2+} ranges and different W contents of WX1, WX2 and WX3; the last phase shows a perceptible preference for Fe^{3+}. B. The Ti – U – W diagram shows the intermediate Ti/W values of WX1 compared to the W-enriched WX2 and Ti-enriched WX3, and the distinctly increased U content of the latter.

2000). The wodginite-group minerals are apparently stable at the time of their crystallization and at lower temperatures. In contrast, their disordered counterparts, *i.e.*, stannian, titanian, tungstenian and scandian ixiolites, commonly display a broader spectrum of cations within the above range of valences (*e.g.*, Wise & Černý 1986, Wise *et al.* 1998, Černý & Ercit 1989, Černý *et al.* 1998), and they probably are metastable. The complex spectrum of heterovalent cations mitigates against any chances of long-range order, and may permit only a short-range order on a local domain-like scale. Local imbalances in bonding should be widespread, and a tendency to break down into two or more compositionally simpler phases with (more closely) integral stoichiometries of a reduced number of cations should be pronounced. Also, alteration and replacement of ixiolite minerals are relatively widespread (*e.g.*, Khvostova *et al.* 1983, Černý *et al.* 1986).

Thus it is not surprising that the exsolved phases E1 and WX1 broke down to three and two phases, respectively, and that the breakdown products show strong preferences in partitioning of cations. The E2, E3 and X phases in the Eptevann sample are distinctly differentiated in terms of their contents of Ti, Zr, Sn, Mn, and particularly U, Sc, Y, Fe_{tot} and Fe^{3+}/Fe^{2+} (Table 1). The WX2 and WX3 phases in the Ilmen Mountains sample also show selectivity in W, Ti, Zr, U and Fe^{3+}/Fe^{2+} (Table 2). However, the breakdown products do not yield simple formulas with integral stoichiometry (whatever may be their crystal structures), and their compositions are still rather complex. Thus it is probable that the breakdown products resulted from arrested reactions, far from having attained chemical and phase equilibrium.

Mechanism of alteration

The compositional complexity and structural disorder *sensu lato* discussed above undoubtedly are significant intrinsic factors contributing to the extensive alteration of the exsolved phases. However, the metastability of compositions cannot be the only factor facilitating the observed disintegration. Breakdown in the solid state is difficult to envisage in the generally low-energy environment of late postmagmatic stages of pegmatite consolidation. Were this not the case, the alteration of exsolution products would have to be much more widespread. Instead, phase E exsolved from the Central Iveland niobian rutile (Černý *et al.* 2000b), which has a composition nearly identical to that of E1 described here, is fresh and intact with no indication of alteration, and the same holds for titanian columbite and ixiolite exsolved from niobian rutile at most localities. However, protracted exsolution, mobilization and redeposition of both rutile and titanian ferrocolumbite at Věžná, Czech Republic (Černý *et al.* 2000b) indicate that aqueous fluids must be involved in reconstitution of the exsolution products after primary niobian rutile. Thus it is probable that the Eptevann and Ilmen Mountains specimens also were exposed to a hydrothermal event, despite the apparently intact state of the exsolution-depleted rutile phase.

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