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TWO-STAGE EXSOLUTION OF A TITANIAN $(Sc,Fe^{3+})(Nb,Ta)O_4$ PHASE IN NIOBIAN RUTILE FROM SOUTHERN NORWAY

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ABSTRACT

Niobian rutile from Håverstad and an unspecified locality in central Iveland, southern Norway, displays a novel two-stage exsolution of phase E, corresponding to titanian $(Sc,Fe^{3+})(Nb>Ta)O_4$, not yet characterized as a mineral species. In general, rutile retains Ti, Fe^{3+} (relative to Fe^{2+}), ΣFe (relative to Mn) and Ta (relative to Nb), whereas the exsolved phase E concentrates Nb, Ta, ΣFe, Sc, W, Zr, Mg and U. In the first stage, phase E forms platelets averaging ~20 × 2 μm; their orientation is controlled by the structure of the host rutile. The platelets contain ≤30.40 wt.% TiO_2 and Sc_2O_3 as low as 3.37 wt.%, whereas the rutile retains ≤24.00 wt.% Nb_2O_5, ≤8.15 wt.% Ta_2O_5 and ≤1.61 wt.% Sc_2O_3. In the second stage, coarsening of phase E produces irregular subround blebs 10 to 30 μm in size. Exsolution is advanced during this stage, increasing the Sc content of phase E up to 10.06 wt.% Sc_2O_3 and reducing its Ti content to as low as 11.90 wt.% TiO_2, whereas the rutile matrix is depleted in Nb, Ta and Sc to as low as 21.30, 7.61 and 0.52 wt.% of the respective oxides. The average $Fe^{3+}:Fe^{2+}$ ratio of rutile is 3.51, whereas it decreases to 3.18 in platelets of phase E, and it drops to 2.60 in the blebs of the second-generation phase E. The platelet stage might prove to be typical of exsolution of phase E from niobian rutile with high $(Sc,Fe)^{3+}/Fe^{2+}$, in contrast to the much more widespread granular exsolution of titanian ixiolite or titanian ferrocolumbite from Sc-poor niobian rutile with Fe^{3+}/Fe^{2+} much less than 1.

Keywords: niobian rutile, exsolution, scandian-ferrian niobate, granitic pegmatite, Norway.

SOMMAIRE

Le rutile niobifère provenant de Håverstad et d'une localité inconnue dans l'Iveland central, dans le secteur sud de la Norvège, fait preuve de deux stades d'exsolution d'une phase appelée E, qui correspond à $(Sc,Fe^{3+})(Nb>Ta)O_4$ titanifère, non encore caractérisé comme nouvelle espèce minérale. En général, le rutile retient Ti, Fe^{3+} (relativement au Fe^{2+}), ΣFe (relativement au Mn) et Ta (relativement au Nb), tandis que la phase exsolvée E concentre Nb, Ta, ΣFe, Sc, W, Zr, Mg et U. Au cours du premier stade, la phase E forme des plaquettes mesurant ~20 × 2 μm en moyenne; leur orientation est régie par la structure du rutile, le minéral hôte. Les plaquettes contiennent ≤30.40% (poids) de TiO_2 et aussi peu que 3.37% de Sc_2O_3, tandis que le rutile retient ≤24.00% de Nb_2O_5, ≤8.15% de Ta_2O_5 et ≤1.61% de Sc_2O_3. Au cours du deuxième stade d'exsolution, le grossissement de la phase E produit des taches irrégulières plus ou moins rondes mesurant de 10 à 30 μm. L'exsolution, avancée à ce stade, mène à une augmentation de la teneur en Sc de la phase E, jusqu'à 10.06% de Sc_2O_3, et une réduction de sa teneur en Ti, jusqu'à même11.90% de TiO_2, tandis que la matrice de rutile est appauvrie en Nb, Ta and Sc, jusqu'à 21.30, 7.61 et 0.52% des oxydes respectifs. Le rapport moyen $Fe^{3+}:Fe^{2+}$ du rutile est 3.51, tandis qu'il diminue à 3.18 dans les plaquettes de la phase E, et à 2.60 dans les taches de la deuxième génération de la phase E. Le stade de formation des plaquettes de la phase E pourrait s'avérer typique de l'exsolution d'un rutile niobifère ayant un rapport $(Sc,Fe)^{3+}/Fe^{2+}$ élevé, par opposition à l'exsolution en granules beaucoup plus répandue, impliquant l'ixiolite titanifère ou la ferrocolumbite titanifère formée à partir du rutile niobifère à faible teneur en Sc, et ayant un rapport Fe^{3+}/Fe^{2+} nettement inférieur à 1.

(Traduit par la Rédaction)

Mots-clés: rutile niobifère, exsolution, niobate scandifère et ferrifère, pegmatite granitique, Norvège.

INTRODUCTION

Niobian and tantalian rutile, originally known only as rarities in granitic pegmatites under the respective names ilmenorutile and strüverite, gained prominence in the past three decades as an accessory mineral in peraluminous to peralkaline granitic rocks, and as a substantial component of hydrothermal assemblages associated with alkaline intrusions. Both varieties attained the status of ore minerals of Nb and Ta in several types of lithophile rare-element mineralization (Černý & Ercit 1989). Despite the paragenetic, geochemical and eco-

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[§] *E-mail address*: p_cerny@umanitoba.ca nomic significance of these minerals, our understanding of their crystal chemistry and phase composition is still rather sketchy.

In contrast to tantalian rutile, which is homogeneous in virtually all of its occurrences, niobian rutile with substantial contents of Fe and Nb commonly contains exsolved grains of titanian columbite or ixiolite (*e.g.*, Černý *et al.* 1964, 1981, 2000, Černý & Ercit 1989). The columbite or ixiolite phase forms irregular, subround grains 10 to 500 μm across, and rarely up to a few mm in size. These grains tend to be aligned and elongate parallel to the *c* axis of the host rutile, but the morphology and distribution of the coarse blebs seem to lack any textural relationship to the rutile matrix.

Here we describe the first cases of a two-stage exsolution and coarsening of a titanian niobate of scandium and ferric iron from a niobian rutile with an exceptionally low proportion of Fe^{2+} to Fe^{3+}. So far, the exsolved phase (termed phase E in this paper) has not been fully characterized as a new mineral, but it was identified by Ercit (1994) as a Sc-poor phase associated with niobian rutile and titanian columbite in granitic pegmatites of the Grenville Province; it was mislabeled titanian ixiolite by Černý *et al.* (1995) in a Moravian locality, but correctly recognized by Uher *et al.* (1998) in Slovak pegmatites.

SAMPLES EXAMINED, EXPERIMENTAL METHODS AND TREATMENT OF DATA

One of the samples examined here is labeled "Ilmenorutile, Håverstad, Norway", and was obtained from the Mineralogical and Geological Museum of the University of Oslo. The second sample, "Ilmenorutile, central Iveland, Norway", was donated by the late Prof. Paul Ramdohr from his collection of polished sections. The phase assemblages, textural relationships and chemical compositions of individual mineral constituents are virtually identical in both samples. It is quite possible that they come from the same pegmatite, at Håverstad in southern Norway. Consequently, the phase relationships in the two samples are treated jointly, although specific examples of compositional relationships are referred to individual samples.

Chemical compositions were established using the Cameca CAMEBAX SX–50 electron microprobe in wavelength-dispersion mode, under conditions given by Novák & Černý (1998a). Unit-cell dimensions were refined from X-ray powder-diffraction data collected using a Siemens D–5000 instrument, with NIST silicon 640b as an internal standard [*a* 5.430940(35) Å]. To facilitate mutual comparison of chemical composition of rutile and phase E on one hand, and of both of them with columbite-group minerals, the atomic contents of both phases are normalized to eight atoms of oxygen. This approach gives atomic content per unit cell for disordered columbite or ixiolite and for $A^{3+}BO_4$, and per four unit cells of rutile. The atomic contents equal those per four formula units (*ap4fu*), except for phase E (*ap2fu)*. Normalization to eight atoms of oxygen was constrained to a maximum total of four 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.* (1992). In the present case, the calculated results were confirmed by identification of the $A^{3+}BO_4$ phase.

PHASES AND TEXTURES

Phase composition

The samples examined consist of a matrix of niobian rutile that hosts phase E. Identity of both phases was confirmed by electron-microprobe analysis and by X-ray powder diffraction. Despite the high level of diversified substitution for Ti, the niobian rutile has the monorutile structure, with no indication of a tapiolite-like or related supercell: *a* 4.648(2), *c* 2.991(1) Å. Diffraction maxima attributed to phase E are scarce, as the rutile host is volumetrically greatly predominant (~90 vol.% of the aggregates; Fig. 1A). Nevertheless, the observed maxima closely correspond to those of a monoclinic Ti^{4+},Fe^{2+}-bearing $Fe^{3+}NbO_4$ phase, which is not yet established as a natural mineral, and is currently examined by T.S. Ercit (pers. commun., 1998) in samples from other localities. The Håverstad sample yielded the following diffraction-maxima in addition to those of rutile [*d in* Å (I)]: 3.59 (3), 2.93 (10), 2.82 (1), 2.51 (1), 2.18 (0.5), 1.98 (0.5), 1.71 (~2, shoulder on a rutile peak), 1.52 (0.5), 1.44 (1). The intensities are related to the strongest peak at 2.93 Å, which was arbitrarily assigned an intensity of 10. However, this peak would correspond to an *I* of 0.5 on a scale based on *I* of the strongest peak of rutile taken as 10.

Texture and products of early exsolution

In the first stage of breakdown of the rutile samples examined, microscopic platelets of phase E exsolved from the rutile matrix. The platelets are flat and lenticular in shape, 5 to 30 μm long and ≤5 μm thick. In any single grain of rutile, the platelets show up to four different orientations, evidently controlled by the structural elements of the parent phase (possibly corresponding to {100} and {110} of rutile; Fig. 1A).

The rutile matrix retains a high proportion of substituting cations at this stage. The least exsolved rutile from the Håverstad sample yields the formula $(Ti_{2.313}Nb_{0.741}Fe^{3+}_{0.518}Ta_{0.161}Fe^{2+}_{0.141}Sc_{0.091}Sn_{0.015}W_{0.006}Mn_{0.004}Zr_{0.003}Mg_{0.002}U_{0.001})_{\Sigma 3.998}O_8$, and its counterpart from the central Iveland sample is very similar in the content of major components (Table 1, #H1 and CI1). The platelets of phase E are very rich in Ti and poor in Mn (Table 1, #H2 and CI2; Figs. 2A, B). The composition with the highest proportion of Ti, *i.e.*, CI2, gives the formula $[(Fe^{3+}_{0.694}Sc_{0.195}Fe^{2+}_{0.189}Mn_{0.028}Mg_{0.010}Sb_{0.001}$

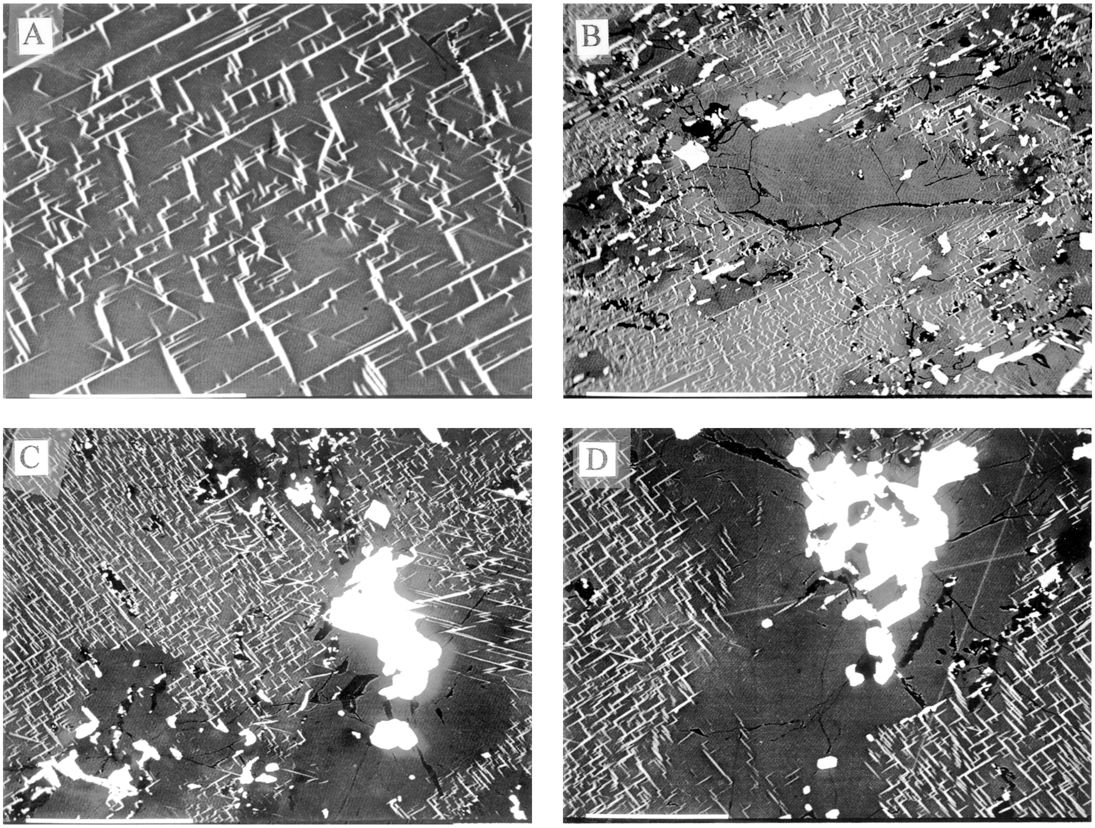

FIG. 1. Back-scattered-electron images of exsolution in niobian rutile from Håverstad (A, B) and central Iveland (C, D). (A) The early stage of exsolution of platelets of the E-phase (white), with $Fe^{3+} < Sc$, from the matrix of niobian rutile (black). (B) The early platelet-exsolution stage as in (A), followed by the second-stage coarsening and continued exsolution along microfractures; note the orientation of the coarse domains of phase E generally parallel with the ENE-trending set of early platelets. (C) Coarsening of phase E; note the continuity of platelets into the right-hand side of the large grain of phase E, and orientation of the grain boundaries parallel with the platelets at that site but otherwise largely random. (D) Coarsening of phase E; some margins of the large grain are parallel to the ENE-trending platelets but others are randomly oriented. Scale bars for (A), (B), (C) and (D) are 100, 500, 100 and 100 μm long, respectively.

$Ca_{0.000})_{\Sigma 1.085}$ $(Ti_{1.523}Sn_{0.019}Zr_{0.010})_{\Sigma 1.552}$ $(Nb_{1.169}Ta_{0.149}W_{0.012})_{\Sigma 1.330}]_{\Sigma 3.967}O_8$. The cation content of this formula is segmented to emphasize the prominent role of the tetravalent cations relative to the trivalent and pentavalent ones.

Texture and products of second-stage exsolution and coarsening

In the second stage, subround grains of phase E develop by coarsening and segregation of the first-stage platelets (Figs. 1B, C, D). The coarsening seems to be particularly well developed along microfractures cross-cutting the products of early exsolution. Locally, direct transition from the platelets into the granular segregations can be observed (Fig. 1C), and some of the boundaries of the coarsened grains remain parallel to the orientation of the platelets (Figs. 1B, C). With progressive coarsening and segregation, however, the morphological link between the platelets and granular aggregates becomes obscured (Figs. 1C, D).

Relative to the host of the platelets, the chemical composition of rutile associated with granular phase E shows lower contents of Fe, Mn, Nb and Ta. The most strongly exsolved rutile from the Håverstad sample has the formula $(Ti_{2.575}Nb_{0.609}Fe^{3+}_{0.469}Ta_{0.155}Fe^{2+}_{0.134}Sc_{0.032}Sn_{0.015}W_{0.005}Mn_{0.001})_{\Sigma 3.996}O_8$, but its central Iveland counterpart retains somewhat higher contents of Nb, Ta and Fe (Table 1, #H3 and CI3). The composition of the granular phase E shows Ti lower than the platelets, but the contents of Nb, Ta, Sc, Mn and Fe are much higher, as exemplified by the Håverstad composition H4:

TABLE 1. REPRESENTATIVE COMPOSITIONS OF NIOBIAN RUTILE AND PHASE E FROM HÅVERSTAD AND CENTRAL IVELAND, NORWAY

	H1	H2	H3	H4	CI1	CI2	CI3	CI4
WO_3	0.34	1.42	0.30	1.67	0.49	0.69	0.09	1.00
Nb_2O_5	25.62	40.00	21.56	50.21	24.23	38.80	23.85	48.72
Ta_2O_5	9.26	8.46	9.14	9.97	8.23	8.27	8.01	9.86
TiO_2	48.03	26.90	54.77	12.42	51.39	30.40	53.41	13.92
ZrO_2	0.08	0.50	0.01	0.78	0.04	0.32	bdl	0.93
SnO_2	0.58	0.79	0.60	1.10	0.56	0.74	0.54	1.00
UO_2	0.09	0.10	bdl	0.20	0.13	0.02	bdl	0.20
Sc_2O_3	1.62	4.26	0.61	10.06	0.64	3.37	0.21	8.90
Y_2O_3	bdl	bdl	0.01	0.17	bdl	bdl	bdl	0.05
Sb_2O_3	bdl	bdl	bdl	bdl	bdl	0.02	bdl	bdl
Bi_2O_3	bdl	0.04	bdl	bdl	0.01	0.02	bdl	0.04
Fe_2O_3	10.76	12.34	9.98	6.08	10.80	13.84	11.04	10.35
FeO	2.63	4.19	2.56	6.03	2.80	3.34	2.40	3.79
MnO	0.07	0.41	0.01	1.19	0.03	0.50	0.04	1.56
CaO	0.02	bdl	bdl	0.25	bdl	0.02	0.01	bdl
MgO	0.06	0.12	0.01	0.07	0.01	0.10	0.02	0.16
ZnO	bdl	0.03	bdl	bdl	bdl	bdl	bdl	bdl
$\sum$	99.37	99.57	99.61	100.2	99.37	100.4	100.0	100.7
				atomic contents				
W	0.006	0.025	0.005	0.031	0.008	0.012	0.001	0.018
Nb	0.741	1.234	0.609	1.624	0.692	1.169	0.671	1.550
Ta	0.161	0.157	0.155	0.194	0.141	0.149	0.136	0.189
Ti	2.312	1.380	2.575	0.661	2.442	1.523	2.499	0.736
Zr	0.003	0.017	-	0.027	0.001	0.010	-	0.032
Sn	0.015	0.021	0.015	0.031	0.014	0.019	0.013	0.028
U	0.001	0.002	-	0.003	0.002	-	-	0.003
Sc	0.091	0.253	0.032	0.627	0.035	0.195	0.022	0.559
Y	-	-	-	0.007	-	-	-	0.002
Sb	-	-	-	-	-	0.001	-	-
Bi	-	0.001	-	-	-	-	-	0.001
Fe^{3+}	0.518	0.630	0.469	0.328	0.514	0.694	0.528	0.548
Fe^{2+}	0.141	0.239	0.134	0.361	0.148	0.189	0.125	0.223
Mn	0.004	0.024	0.001	0.072	0.002	0.028	0.002	0.093
Ca	-	-	-	0.019	-	0.001	0.001	-
Mg	0.002	0.012	0.001	0.008	0.001	0.010	0.002	0.017
Zn	-	0.002	-	-	-	-	-	-

H = Håverstad, CI = central Iveland; 1 = rutile matrix of phase E platelets, 2 = platelets of phase E, 3 = rutile matrix of granular phase E, 4 = granular phase E; bdl = below detection limit. Atomic contents normalized for 8 oxygen atoms and 4 cations (*apfu* for phase E, *ap4fu* for rutile).

$[(Sc_{0.627}Fe^{3+}_{0.328}Fe^{2+}_{0.361}Mn_{0.072}Ca_{0.019}Mg_{0.008}Y_{0.007})_{\Sigma 1.422}$ $(Ti_{0.661}Sn_{0.031}Zr_{0.027}U_{0.003})_{\Sigma 0.722}$ $(Nb_{1.624}Ta_{0.194}W_{0.031})_{\Sigma 1.849}]_{\Sigma 3.993}$ O_8 (*cf.* Table 1, #H4 and CI4; Figs. 2A, B).

DISCUSSION

Exsolution of phase E

Exsolution in niobian rutile normally produces titanian columbite or titanian ixiolite (*e.g.*, Černý *et al.* 1964, 1981, 2000, Černý & Ercit 1989). The intergrowths described above are the first documented case of exsolution of a Ti-rich $(Fe^{3+},Sc)(Nb,Ta)O_4$ phase with a subordinate columbite component. Judging by the lamellar texture of the intergrowth, very analogous to that observed in our samples, it is possible that a similar phase was exsolved from niobian rutile described by Yeremenko *et al.* (1996) from granitic pegmatites of the Kirovograd segment of the Ukrainian Shield. However, the authors only presented ranges of wt.% concentration of individual oxide component, and reported Fe as FeO; these data are insufficient for unambiguous interpretation of the nature of the exsolved phase.

The exsolution of phase E in our samples also represents the first case of a two-step process: differences in texture and grain size of the exsolved phase clearly indicate structurally controlled, solid-state exsolution of phase E (with $Fe^{3+} > Sc$) in the first stage, followed by coarsening and extended exsolution to a product with $Sc > Fe^{3+}$ along microfractures, presumably assisted by a fluid phase. The widespread exsolution of titanian ferrocolumbite and ixiolite at other localities commonly displays extensive variation in grain size and in the apparent degree of crystallographic control; however, textural and compositional data indicate a protracted single event rather than a multistage sequence (*e.g.*, Černý *et al.* 1964, Sahama 1978). The only possible exception, described by Černý *et al.* (2000), is suggested by the trimodal statistics of chemical composition of the exsolved titanian ferrocolumbite.

Element partitioning

In general, the distribution of cations during the exsolution follows the pattern established in previous studies of niobian rutile (*e.g.*, Černý *et al.* 1964, 1981, Sahama 1978) and titanian columbite and ixiolite (Černý *et al.* 1998). The parent rutile retains Ti, but all other cations, *i.e.*, Mg, Mn, Fe^{2+}, Fe^{3+}, Sc, Zr, U, Nb, Ta and W, become concentrated in the exsolved phase, which is evidently more flexible and accommodating for a greater variety of cation radii, bond types and charge compensations. In terms of *relative* proportions, rutile shows Fe^{3+}/Fe^{2+}, Fe/Mn and Ta/Nb values higher than those of the exsolved product.

Crystal chemistry of rutile and phase E

The Nb, Ta and Fe contents of the niobian rutile examined fall within the range established from other occurrences of this mineral (*e.g.*, Černý *et al.* 1964, Černý & Ercit 1989). However, the high Fe^{3+}/Fe^{2+} ratio is very unusual; it was so far observed only in a few specimens analyzed by classic wet methods (Gordiyenko & Kulchitskaya 1962, Lugovskoy & Stolyarova 1969).

A high proportion of Fe^{3+} also characterizes phase E, although average Fe^{3+}/Fe^{2+} values decrease from niobian rutile (3.51; *N* = 22) through the platelets (3.18; *N* = 18) to the granular form of phase E (2.60; *N* = 19). However, Sc is very effectively accumulated in phase E, and its crystal-chemical role in this phase is clearly identical to that of Fe^{3+}. Considering the trivalent cations collectively, the $(Fe^{3+} + Sc)(Nb,Ta)O_4$ component is distinctly dominant in phase E over TiO_2 and the columbite-type component $(Fe,Mn)^{2+}(Nb,Ta)_2O_6$ (Fig. 3A): for example, the composition CI4 of granular phase E in Table 1 shows 56.5, 19 and 24.5 mole % of the three respective components. However, individual

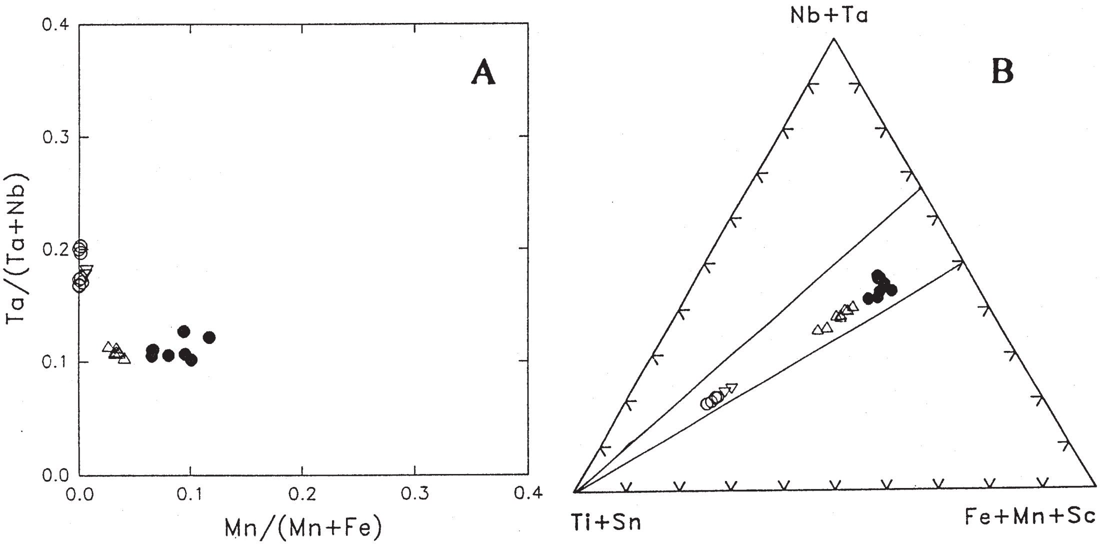

FIG. 2. Matrix and exsolution products in niobian rutile from Håverstad, in the columbite quadrilateral (A) and the (Nb + Ta) – (Ti + Sn) – (Fe + Mn + Sc) triangular diagram (B) (in atomic proportions). Symbols used in Figures 2 and 3: ▽: rutile matrix of platelets of phase E; △, ○: rutile matrix of coarsened granular phase E (●).

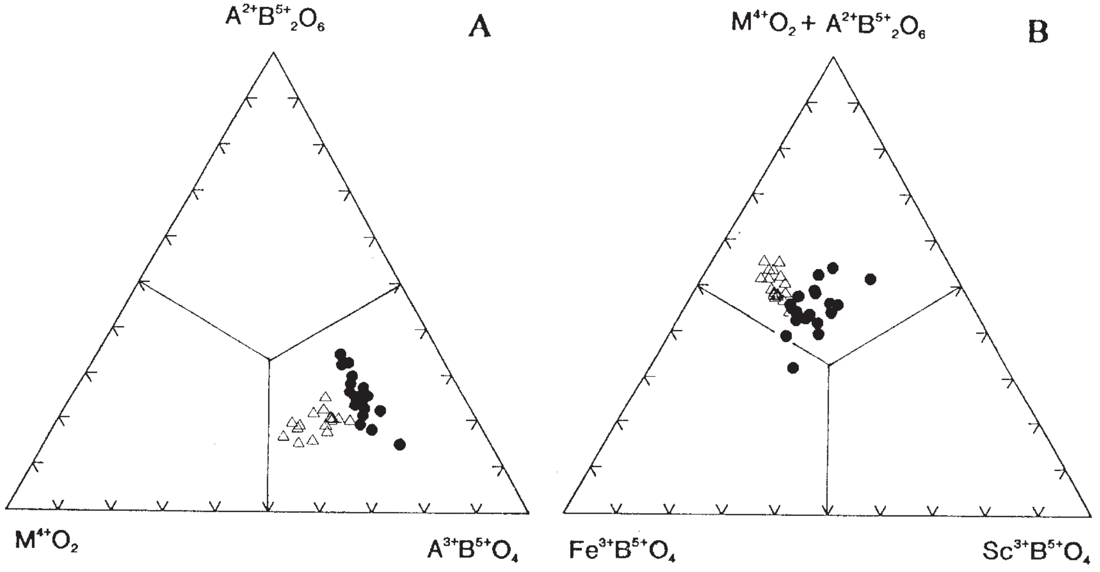

FIG. 3. Compositional relations of phase E, from the Håverstad and central Iveland samples combined, in triangular diagrams $(Ti,Sn)O_2$ – $(Fe,Mn)^{2+}(Nb,Ta)_2O_6$ – $(Fe,Sc)^{3+}(Nb,Ta)O_4$ (A) and $[(Ti+Sn) + (Fe,Mn)^{2+}(Nb,Ta)_2O_6]$ – $Fe^{3+}(Nb,Ta)O_4$ – $Sc(Nb,Ta)O_4$ (B). Note the dominance of the coupled (Fe^{3+},Sc) component in (A), but the subordinate roles of both if separated, as in (B).

ferric and scandian components are, with negligible exceptions, subordinate to the sum of the columbite-type and rutile components (Fig. 3B).

The Sc content of the granular phase E does not attain the maximum values established for *primary* scandian columbite and ixiolite (as reviewed by Wise *et al.* 1998). However, it is distinctly higher than that of Fe^{2+}-dominant ixiolite or ferrocolumbite *exsolved* from niobian rutile at other localities; from such occurrences, Sahama (1978) reported 3.40, Nekrasov *et al.* (1986), 4.40, Voloshin *et al.* (1991), 2.18, and Novák & Černý (1998b), 4.62 wt.% Sc_2O_3.

In general, the high Sc content of the oxide minerals examined here should not be surprising, as they come from a pegmatite population that includes the type locality of thortveitite, the Ljosland pegmatite, and at least six other occurrences including Håverstad (Bjørlykke 1935, Neumann 1961). Niobian rutile was actually considered an indicator of the probable occurrence of thortveitite by Norwegian researchers (Bjørlykke 1935).

Concluding note

Studies of niobian rutile were so far limited to samples from peraluminous granitic pegmatites of the LCT family, related to peraluminous, largely S-type granitic parents. The only exception is the material studied by Černý *et al.* (1999) from the NYF-family pegmatites of the South Platte district, Colorado. The affiliation of the Fe^{3+}-rich samples examined by Gordiyenko & Kulchitskaya (1962) and Lugovskoy & Stolyarova (1969) cannot be ascertained. The samples of niobian rutile examined here come from granitic pegmatites of the NYF family, related to *A*-type, subaluminous to metaluminous granites in dominantly anorogenic settings (*cf.* Černý 1991). These pegmatites are commonly characterized by a somewhat higher $f(O_2)$ during their consolidation than their peraluminous LCT-family counterparts (as shown by the compositions of biotite and zinnwaldite; Černý & Burt 1984, Foord *et al.* 1995, Kile & Foord 1998). The Fe^{3+}/Fe^{2+} of the examined niobian rutile evidently reflects this overall high $f(O_2)$. Further studies of niobian rutile from this environment are evidently required, as the behavior of this mineral under subsolidus conditions in NYF pegmatites is evidently different, and could be more diversified, than that of its LCT-family analogs (*cf.* Černý *et al.* 1999).

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