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COMPOSITIONAL, STRUCTURAL AND PHASE RELATIONSHIPS IN TITANIAN IXIOLITE AND TITANIAN COLUMBITE – TANTALITE

PETR ČERNÝ[1]

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

T. SCOTT ERCIT

Research Division, Canadian Museum of Nature, Ottawa, Ontario K1P 6P4

MICHAEL A. WISE

Department of Mineral Sciences, Smithsonian Institution, Washington, D.C. 20560, U.S.A.

RON CHAPMAN AND HARVEY M. BUCK

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

ABSTRACT

Titanium-enriched members of the columbite family (orthorhombic) commonly contain exsolved niobian–tantalian rutile, or are aggregated with a coprecipitated rutile phase. This assemblage is the Fe,Mn,Nb,Ta-rich counterpart of the Ti-dominant niobian rutile + exsolved titanian columbite pair. The rutile phase is enriched in Fe^{2+}, Ta, Fe^{3+} and Sn, whereas the orthorhombic phase favors Mn, Nb, Sc, W and Zr. Most samples of the orthorhombic phase are defined as titanian columbite – tantalite; they have low to moderate Ti content, moderately to considerably disordered structure, and convert to highly ordered columbite – tantalite on heating. A minor number of samples of the orthorhombic phase develops the highly ordered structure of wodginite on heating, which identifies them as titanian ixiolite, the disordered counterpart of titanowodginite. These samples are highly disordered in the natural state. They are Ti-rich, with Mn > Fe and Ta > Nb; these features correspond to the composition of natural titanowodginite and of the only titanowodginite synthesized to date. However, subordinate but significant Sn seems to be present in all samples of titanian ixiolite as well as natural titanowodginite, and it may affect the path of ordering. Excess of Ta over the $(Fe, Mn)(Nb, Ta)_2$ stoichiometry of columbite, characteristic of most compositions of wodginite, may play a significant role. Ordered nuclei potentially present in the bulk of natural disordered phases also may be important.

Keywords: titanium, columbite, tantalite, ixiolite, order–disorder, exsolution.

SOMMAIRE

Les membres du groupe de la columbite (orthorhombique) qui sont enrichis en titane possèdent généralement des domaines de rutile enrichi en Nb et Ta dus à l'exsolution, ou bien des agrégats de rutile coprécipité. Il s'agit de l'assemblage contenant Fe, Mn, Nb et Ta qui est la contrepartie de l'association rutile niobifère + columbite titanifère exsolvée. La phase rutile est enrichie en Fe^{2+}, Ta, Fe^{3+} et Sn, tandis que la phase orthorhombique favorise Mn, Nb, Sc, W et Zr. Dans la plupart des cas, la phase orthorhombique fait partie de la série columbite – tantalite titanifère; elle possède une teneur faible à modérée en Ti et une structure relativement désordonnée, et se transforme en columbite – tantalite bien ordonnée en chauffant. Dans un nombre restreint de cas, la phase orthorhombique se transforme en wodginite bien ordonnée en chauffant, ce qui les identifie comme ixiolite titanifère, la contrepartie désordonnée de la titanowodginite. Ces échantillons sont fortement désordonnés à l'état naturel. Ils sont riches en Ti, avec Mn > Fe et Ta > Nb; ces caractéristiques correspondent à la composition de la titanowodginite naturelle et du seul exemple qui en ait été synthétisé jusqu'à maintenant. Toutefois, il semble que des quantités non négligeables d'étain soient présentes dans tous les échantillons d'ixiolite titanifère et de titanowodginite naturelle, et ceci pourrait influencer la mise en ordre. Un excédent de Ta par rapport à la stoechiométrie $(Fe,Mn)(Nb,Ta)_2$ de la columbite, qui caractérise la plupart des compositions de wodginite, pourrait aussi jouer un rôle important. Les domaines ordonnés potentiellement présents dans les phases naturelles désordonnées pourraient aussi être importants.

(Traduit par la Rédaction)

Mots-clés: titane, columbite, tantalite, ixiolite, ordre–désordre, exsolution.

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[1] *E-mail address*: cernyp@ms.umanitoba.ca

INTRODUCTION

Ixiolite was redefined by Nickel *et al.* (1963) as a complex oxide of the $(A,B)O_2$ type, a Sn-substituted, cation-disordered derivative of the AB_2O_6 columbite structure (in which A = Fe, Mn, Mg, and B = Nb, Ta). More specifically, ixiolite was assigned the composition $(Ta,Nb,Sn,Fe,Mn)O_2$, with an orthorhombic unit-cell corresponding to that of disordered columbite; on heating, it was reported to transform into a presumably orthorhombic "olovotantalite"-like phase.

"Olovotantalite" (Matias 1961) was later identified with monoclinic wodginite (Gorzhevskaya *et al.* 1974), and further study of samples of Sn-rich ixiolite from numerous localities established its ordering upon heating to wodginite as a typical feature (Wise & Černý 1986, Wise 1987). The presence of a slight monoclinic distortion in samples of natural (pseudo)orthorhombic ixiolite, indicative of incipient ordering, was detected by the above authors, apparently converging with highly disordered pseudo-orthorhombic wodginite (Lahti 1982, Wise 1987, Ercit 1986, Ercit *et al.* 1992a). Thus, stannian ixiolite is established as a disordered counterpart of the ordered wodginite.

Compositional variations led to recognition of additional varieties of ixiolite, namely titanian ixiolite, scandian ixiolite and "wolframo-ixiolite" (Černý & Ercit 1985, 1989, Wise & Černý 1986). Whereas the crystal-chemical and structural behavior of scandian ixiolite and "wolframo-ixiolite" remained essentially uncharted, titanian ixiolite was generally considered a close analog of its Sn-rich countepart (*e.g.*, Černý & Ercit 1985, 1989). However, significant differences were subsequently found in the response of Ti-rich samples to heating; widespread presence of associated rutile was noticed, and the need for a systematic study was recognized.

Here we present a review of data from the literature and our new observations, as a first step toward proper characterization and definition of titanian derivatives of the columbite – tantalite and ixiolite minerals, and of their relation to the wodginite and rutile groups of minerals in the system $TiO_2 - (Fe,Mn)^{2+}(Nb,Ta)^{5+}{}_2O_6 - Fe^{3+}(Nb,Ta)O_4$.

PREVIOUS WORK

Information on the Ti-enriched members of the family of columbite minerals *sensu lato* (ordered to disordered columbite group, ixiolite, wodginite group) is so far rather meager, dispersed in papers describing individual occurrences, and is in most cases incomplete. Data on chemical composition are commonly not accompanied by structural characteristics (Černý *et al.* 1981a, Zagorskyi & Peretyazhko 1992, Johan & Johan 1994); this is due in part to a fine grain-size of the samples and dispersal in and intimate intergrowth with other phases (Černý *et al.* 1986, Černý & Němec 1995). Unit-cell dimensions are provided for the natural phase by Sveshnikova *et al.* (1965) and Černý *et al.* (1979), and are complemented by data on heated material by Paul (1984), Ferreira (1984) and Černý *et al.* (1989).

The above sources suggest that the Ti-enriched orthorhombic minerals of the AB_2O_6 or $(A,B)O_2$ types are either homogeneous, or closely associated with a rutile phase. They show variable degrees of cation disorder, and attain on heating either an ordered columbite structure or a wodginite structure. However, the data are too limited for any attempts to quantify and generalize these relationships and their controls.

SAMPLES EXAMINED

Table 1 provides condensed information on the sources of data from the literature, and on the samples examined during our current work. The table also presents the acronyms used to designate localities in most of the figures and some of the tables below. In total, data on titanian columbite – tantalite and ixiolite from four localities were extracted from the literature, besides those from five localities examined in our laboratories and published over the last 17 years. Some of these data were in part complemented during the current work, which covered samples from 11 additional localities.

A broad compositional range is covered by the selected samples, with the TiO_2 content of the orthorhombic phase variable from ~2 to ~20 wt.%. Both homogeneous minerals and exsolved intergrowths with rutile are represented, as well as orthorhombic phases associated with rutile in a texturally non-replacive and unexsolved, but side-by-side coexisting manner. In some cases, the orthorhombic phase and rutile are dispersed in the parent rock, but not in mutual contact; in others, rutile is absent.

Care was taken to select samples of reasonably simple compositions, free of substantial quantities of other components that may influence the structural behavior or phase relationships of the orthorhombic mineral on heating. In this respect, the most significant element is Sn, which also is the most common one in the minerals examined. Only samples that show Ti/Sn (at.) greater than 2 were used here; unfortunately, Ti-rich specimens truly poor in Sn are quite rare. Scandian ixiolite, notorious for its high Ti content, was not employed.

EXPERIMENTAL METHODS

Chemical composition was established by means of electron-microprobe analysis. Some of the data were obtained using the MAC–5 instrument in energy-dispersion mode, under conditions given in Černý *et al.* (1986). The other data were generated in wavelength-dispersion mode on the CAMECA SX–50 apparatus, using the same analytical conditions and standardization

TABLE 1. LIST OF EXAMINED SAMPLES

Locality	Comp. #	Association[1]	Source/Reference[2]
Central Transbaikalia, Russia	ZAG-1 to -2	hom, nor	Zagorskyi & Peretyazhko (1992)
Cínovec, Czech Republic	JOH-3 to -4	hom, sep	Johan & Johan (1994)
Tanco, Manitoba	TRT-5 to -29	coex	research coll. PČ
Věžná IIst, Czech Republic	VZS-30 to -31	coex	Černý *et al.* (1979)
Siberia and Urals, Russia	SVE-32 to -33	hom, nor	Sveshnikova *et al.* (1965)
North Star, Texas, USA	NST-34 to -66	hom & exs	research coll. PČ
Weinebene, Austria	BRD-67 to -94	exs	res. coll. PČ; Černý *et al.* (1989)
Unknown	NN-95 to -96	coex	research coll. PČ
Canyon City, Colorado, USA	CCC-97 to -98	exs	USNM #124389
La Modera, New Mexico, USA	LMN-99 to -100	exs	USNM #102118
Guffey, Colorado, USA	GUC-101 to -102	exs	USNM #96418
Norway	NOR-103 to -104	exs	USNM # 107397
Ambatofotsikely, Madagascar	AMB-105 to 1020	exs	USNM #107397
Huron Claim, Manitoba	HUC-121 to -124	hom, sep	Paul (1984)
Muskox Lake, NWT	MSX-125 to -136	exs	research coll. PČ
Greer Lake, Manitoba	GL-137 to -140	coex	Černý *et al.* (1986)
Věžná II, Czech Republic	KVV-141 to -154	exs	research coll. PČ
K-1, Manitoba	K-1-188 to -183	exs	research coll. PČ
Bradlo, Czech Republic	JIH-185 to -186	hom, sep	Černý & Němec (1995)
Lower Tanco, Manitoba	LOT-187 to -226	exs, hom	Ferreira (1984) and this study
Irgon Claim, Manitoba	IRA-227 to -229	coex	research coll. PČ

[1] hom - homogeneous orthorhombic phase; exs - orthorhombic phase with exsolved rutile; coex-orthorhombic phase with coprecipitated rutile in mutual contact; sep - dispersed separate grains of orthorhombic phase and rutile; nor - no rutile associated with the orthorhombic phase.

[2] Sources quoted for samples investigated during the present study, references given for data taken from the literature.

as Uher *et al.* (1998), except that a 50 s counting time for minor elements was used, and ThO_2 glass for $ThM\alpha$. Formula contents were calculated on the basis of 24 atoms of oxygen and 12 cations per unit cell of ordered columbite – tantalite. This might seem misleading for both the disordered orthorhombic phases (8 atoms of oxygen per unit cell) and rutile (4 atoms of oxygen per unit cell), but it facilitates direct comparison of cation abundances and proportions in all minerals analyzed in this study. Apparently cation-excess results were accommodated by converting as much of Fe^{2+} to Fe^{3+} as required to satisfy the second limitation above; for the legitimacy of this procedure in minerals of the columbite family, see Ercit *et al.* (1992a).

X-ray powder-diffraction data were collected on two powder diffractometers. A Philips PW 1710 instrument was used with experimental conditions and processing as reported in Černý *et al.* (1986). A Siemens D 5000 diffractometer was employed recently in transmission mode, with a primary beam monochromator ($CuK\alpha_1$) and calibration with annealed CaF_2 internal standard, $a = 5.465397(4)$ Å. Unit-cell dimensions were calculated with the program CELREF (Appleman & Evans 1973).

Phase Composition

As shown in Table 1, Ti-rich orthorhombic phases at most of the localities examined contain exsolved

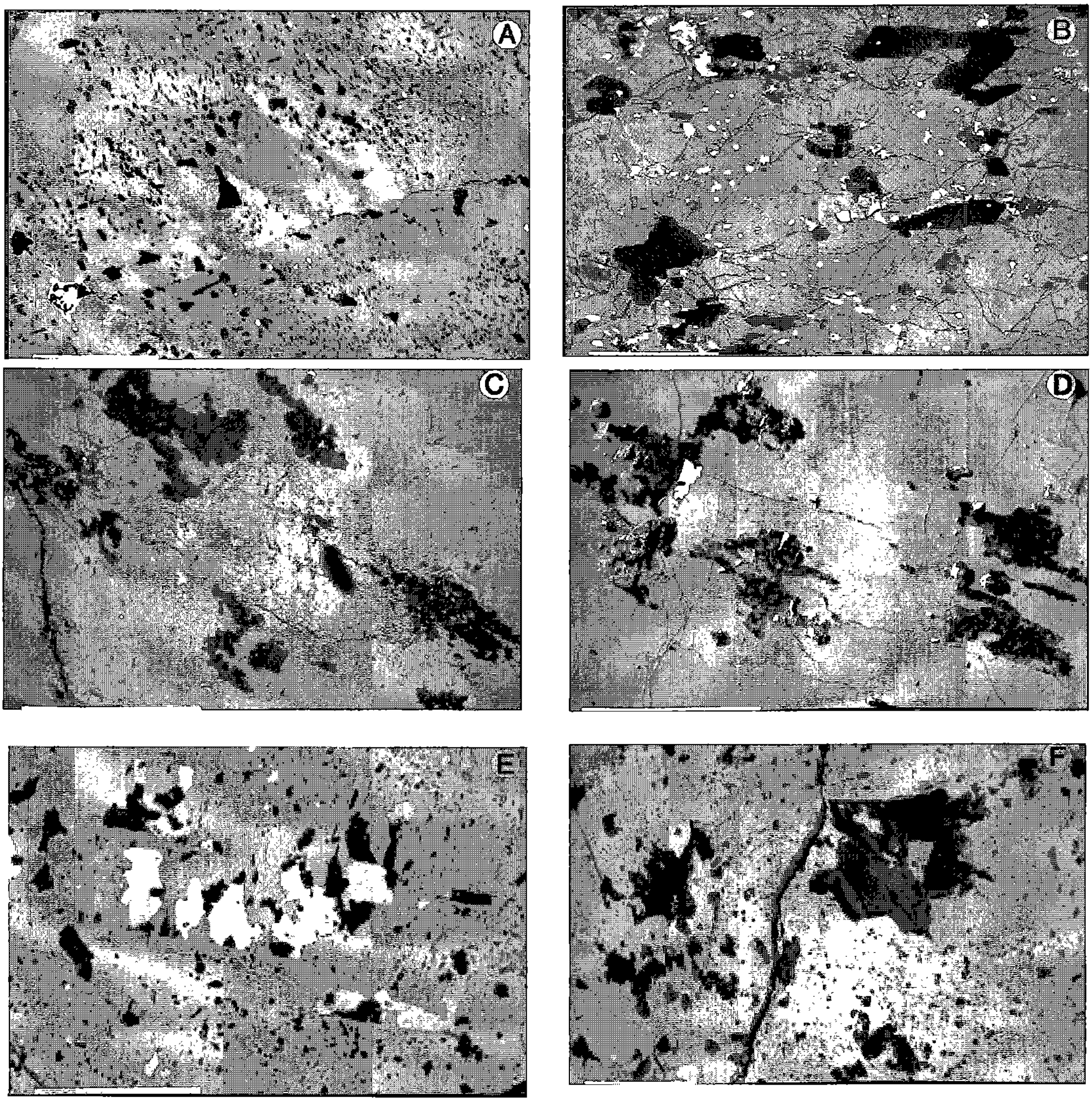

FIG. 1. Typical textural relationships of the orthorhombic and rutile phases in back-scattered electron (BSE) images. A. Exsolution-induced droplets of niobian rutile (black) and cassiterite (white) in slightly heterogeneous orthorhombic phase (mottled grey), Weinebene, Austria. B. Exsolution-induced blebs of niobian rutile (black) and droplets of cassiterite (white) in near-homogeneous orthorhombic phase (pale grey), Muskox Lake, N.W.T. C. Dendritic to mossy segregations of niobian rutile (black to dark grey) in an orthorhombic phase (grey), Věžná, Czech Republic. D. Joint-related exsolution of rutile (dark shades of grey) and cassiterite (white) in an orthorhombic phase (pale grey), K–1, Manitoba. E. Fine-grained exsolution-induced domains of tantalian rutile (dark grey) in an orthorhombic phase (pale grey), but coarsening along contacts with inclusions of microlite (white), Lower Tanco, Manitoba. F. Heterogeneous exsolution-induced domains of tantalian rutile (mottled dark grey), in part associated with a microfracture, in an orthorhombic phase (pale grey) with a few inclusions of microlite (white), Lower Tanco, Manitoba. Scale bars are 100 μm long, except 50 μm for F.

niobian or tantalian rutile. A small number of occurrences shows these two phases in mutual contact, but seemingly not exsolved. At some localities, the rutile phase is either absent or not related to the orthorhombic mineral.

Examples of typical exsolution-induced textures are shown in Figure 1. Blebby, amoeboid outlines of the rutile phase, the density of its distribution inversely proportional to its grain size, and local crystallographic control on the distribution and shape of its grains, all strongly indicate an exsolution origin. This conclusion is also supported by the commonly low Ti content of the orthorhombic phase in areas containing dense accumulations or relatively large grains of rutile, in contrast to neighboring patches of homogeneous orthorhombic phase, which are routinely Ti-rich. However, primary inclusions of rutile are suspected in cases of compositionally homogeneous orthorhombic host.

At some localities, granular aggregates of the orthorhombic phase show no textural evidence of exsolution, and no features suggestive of replacement. In their present state, they represent products of more-or-less simultaneous coprecipitation with the rutile phase.

The ZAG and SVE samples of homogeneous orthorhombic minerals are the only ones that are probably totally free of any form of associated rutile. A part of the NST samples also is homogeneous, but most of its grains are exsolved. Some of the LOT crystals are homogeneous and not accompanied by rutile of any kind. The JOH phases are associated with niobian rutile dispersed in a granitic rock, but are not in mutual contact. The same relationship applies to the JIH and HUC pegmatites, in which rutile is very scarce.

CHEMICAL COMPOSITION

All compositions obtained during the present study and extracted from the literature are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2. Table 2 shows selected representative data. The diagrams used here do not show all data as collected in the deposited table; numbers of compositions were reduced for some samples to minimize locality bias.

Figure 2 illustrates the composition of all analyzed minerals in the columbite quadrilateral, and in the diagram (Ti + Sn) – (Ta + Nb) – (Mn + Fe). In the quadrilateral, the rutile compositions are restricted to the Mn-poor part of the diagram, whereas the orthorhombic phase covers the full range of the Mn/(Mn + Fe) values. In contrast, both minerals extend over most of the Ta/(Ta + Nb) range, except the most Ta-enriched part of the diagram. In the triangular plot, most of the data populate the (Ti,Sn) – $(Fe,Mn)^{2+}(Nb,Ta)^{5+}{}_2$ – $Fe^{3+}(Nb,Ta)^{5+}$ triangle; the orthorhombic phase and rutile are distinctly separated.

The orthorhombic phase

The composition of the orthorhombic phase seems to cover about the same range in both homogeneous minerals and those associated with rutile (Figs. 3A, B). In the latter case, Nb- and Fe-rich compositions seem to be preferred in many samples, but not to the exclusion of Ta- and Mn-rich phases (Figs. 3A, B).

Orthorhombic minerals paired with rutile extend over a slightly broader range of Ti (+Sn) contents than the rutile-free phases (Figs. 3C, D). A significant proportion of the data fall above the (Ti + Sn) – $(Fe,Mn)^{2+}(Nb,Ta)^{5+}{}_2$ tie line, indicating a surplus of (Nb,Ta) over the stoichiometry of columbite.

Besides the main components (Nb_2O_5, Ta_2O_5, FeO, Fe_2O_3, MnO, TiO_2), the orthorhombic phase commonly contains subordinate SnO_2 (≤6.65 wt.%, but in most cases in the 0.X–~2 wt.% range), minor ZrO_2 (≤1.30 wt.%), WO_3 (≤3.88 wt.%), CaO and MgO [≤1.15 and ≤1.41 wt.% respectively, as reported by Sveshnikova *et al.* (1965), but negligible in most cases], and Sc_2O_3 (≤2.02 wt.%). The contents of UO_2, ThO_2, Bi_2O_3, and PbO are very low and in most cases below detection limits. As could be expected, the abundances of minor elements show remarkable differences among individual localities, controlled by the overall geochemistry of the parent mineral assemblages.

Besides the homovalent substitutions in the *A* and *B* sites (Fe, Mn, Mg, Ca and Nb, Ta, respectively), which are common to all members of the columbite family, the heterovalent mechanism introducing Fe^{3+} and most probably also Sc^{3+} is widespread: $(Fe,Sc)^{3+}{}_3Nb^{5+}{}_{-1}Fe^{2+}{}_{-2}$. The entry of Ti and Sn is facilitated mainly by $(Ti,Sn)^{4+}{}_3(Fe,Mn)^{2+}{}_{-1}(Nb,Ta)^{5+}{}_{-2}$ and possibly also by $(Ti,Sn)^{4+}{}_2Fe^{3+}{}_{-1}(Nb,Ta)^{5+}{}_{-1}$. In the JOH samples, which contain appreciable W, this element is incorporated *via* the substitution $W^{6+}(Ti,Sn)(Nb,Ta)^{5+}{}_{-2}$ (Johan & Johan 1994). The contents of the other minor elements are too low to decipher their mode(s) of substitution, as the relevant calculations operate close to the limits of analytical error.

Rutile

The rutile phase shows extensive solid-solution of both the columbite – tantalite and $Fe^{3+}(Nb,Ta)O_4$ components (Fig. 2). In addition to the dominant components (TiO_2, Nb_2O_5, Ta_2O_5, FeO, Fe_2O_3), rutile routinely contains minor MnO (≤0.95 wt.%) and SnO_2 (≤2.40 wt.%). The contents of WO_3 (≤0.17 wt.%), Sc_2O_3 (0.17 wt.%), ZrO_2 (≤1.30 wt.%), CaO (≤0.20 wt.%) and MgO (0.10 wt.%) are sporadic and largely below the detection limits.

In addition to the homovalent substitution of Ti^{4+} by Sn^{4+} (and probably minor Zr^{4+}), the same heterovalent mechanisms are involved in rutile as those affecting the orthorhombic phase above, but in reversed sense: $(Fe,Mn)^{2+}(Nb,Ta)^{5+}{}_{+2}Ti^{4+}{}_{-3}$ and $(Fe,Sc)^{3+}(Nb,Ta)^{5+}Ti^{4+}{}_{-2}$.

TABLE 2. REPRESENTATIVE COMPOSITIONS OF THE ORTHORHOMBIC PHASE AND ASSOCIATED RUTILE

	K-1		Muskox L.		North Star		Věžná II.		Weinebene		Ambatofotsikely		Lower Tanco		Tanco	
	157X	158R	132X	133R	62X	61R	149X	145R	80X	79R	120X	119R	221X	223R	16X	15R
WO_3	1.18	0.00	1.20	0.22	1.36	0.00	2.02	0.20	1.16	0.16	0.14	0.00	0.00	0.00	0.00	0.00
Ta_2O_5	24.23	13.42	9.84	8.55	11.86	11.31	11.67	11.29	13.42	13.73	5.20	6.51	63.10	27.44	51.14	27.40
Nb_2O_5	50.39	7.64	65.59	10.75	61.82	10.35	59.37	16.75	60.35	17.50	68.05	19.38	9.53	1.50	26.92	2.26
UO_2	0.28	0.00	0.00	0.00	0.37	0.00	0.19	0.00	0.29	0.00	0.00	0.00	0.00	0.00	0.43	0.00
ZrO_2	0.27	0.00	0.00	0.00	0.23	0.00	0.85	0.00	0.54	0.00	0.59	0.00	0.00	0.00	0.46	0.00
SnO_2	0.61	0.30	0.15	1.08	0.06	0.69	1.08	2.82	0.90	3.18	0.41	1.78	3.68	0.92	0.92	1.14
TiO_2	2.88	69.85	2.29	74.14	2.94	67.60	6.64	59.67	4.63	57.19	5.22	59.85	10.45	64.32	3.53	62.34
Bi_2O_3	0.18	0.00	0.00	0.00	0.00	0.00	0.14	0.00	0.00	0.00	0.00	0.12	0.00	0.14	0.00	0.00
Sb_2O_3	0.00	0.00	0.00	0.00	0.08	0.00	0.00	0.29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Y_2O_2	0.00	0.00	0.00	0.00	0.22	0.00	0.00	0.00	0.00	0.00	0.23	0.00	0.00	0.00	0.00	0.00
Sc_2O_3	0.00	0.00	0.22	0.00	0.00	0.00	0.85	0.08	0.28	0.00	1.70	0.04	0.47	0.00	0.69	0.00
Fe_2O_3	1.95	6.99	1.39	3.21	2.10	7.82	0.90	4.92	0.43	1.58	1.06	10.64	0.00	0.88	0.09	0.19
FeO	8.81	1.02	9.75	2.79	2.30	0.80	13.15	3.41	12.13	6.16	9.96	1.29	1.90	4.33	3.16	4.79
MnO	7.77	0.08	9.07	0.09	15.45	0.31	1.43	0.06	6.15	0.14	7.49	0.18	9.91	0.12	11.88	0.17
CaO	0.20	0.00	0.02	0.03	0.06	0.00	0.03	0.28	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00
MgO	0.05	0.00	0.00	0.00	0.00	0.00	1.72	0.15	0.09	0.00	0.17	0.00	0.00	0.00	0.00	0.01
total	98.80	99.30	99.52	100.86	98.85	98.88	100.04	99.92	100.36	99.64	100.22	99.79	99.06	99.65	99.22	98.30
W^{6+}	0.076	0.000	0.072	0.010	0.083	0.000	0.119	0.010	0.070	0.008	0.008	0.000	0.000	0.000	0.000	0.000
Ta^{5+}	1.646	0.664	0.623	0.409	0.762	0.562	0.723	0.576	0.851	0.718	0.315	0.324	4.965	1.461	3.900	1.487
Nb^{5+}	5.692	0.629	6.907	0.854	6.607	0.855	6.114	1.420	6.363	1.521	6.847	1.604	1.247	0.133	3.413	0.204
U^{4+}	0.016	0.000	0.000	0.000	0.019	0.000	0.010	0.000	0.015	0.000	0.000	0.000	0.000	0.000	0.027	0.000
Zr^{4+}	0.033	0.000	0.000	0.000	0.027	0.000	0.094	0.000	0.061	0.000	0.064	0.000	0.000	0.000	0.063	0.000
Sn^{4+}	0.061	0.022	0.014	0.076	0.006	0.050	0.098	0.211	0.084	0.244	0.036	0.130	0.425	0.072	0.103	0.091
Ti^{4+}	0.541	9.560	0.401	9.798	0.523	9.287	1.137	8.412	0.812	8.268	0.874	8.239	2.274	9.469	0.744	9.358
Bi^{3+}	0.012	0.000	0.000	0.000	0.000	0.000	0.008	0.000	0.000	0.000	0.000	0.006	0.000	0.007	0.000	0.000
Sb^{3+}	0.000	0.000	0.000	0.000	0.008	0.000	0.000	0.022	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Y^{3+}	0.000	0.000	0.000	0.000	0.028	0.000	0.000	0.000	0.000	0.000	0.027	0.000	0.000	0.000	0.000	0.000
Sc^{3+}	0.000	0.000	0.045	0.000	0.000	0.000	0.169	0.013	0.057	0.000	0.330	0.006	0.119	0.000	0.169	0.000
Fe^{3+}	0.367	0.957	0.244	0.425	0.374	1.075	0.155	0.695	0.075	0.228	0.177	1.465	0.000	0.130	0.019	0.028
Fe^{2+}	1.840	0.156	1.899	0.410	0.455	0.123	2.505	0.535	2.365	0.990	1.854	0.198	0.460	0.708	0.741	0.800
Mn^{2+}	1.644	0.012	1.790	0.013	3.094	0.048	0.276	0.010	1.215	0.023	1.412	0.028	2.429	0.020	2.822	0.029
Ca^{2+}	0.054	0.000	0.005	0.006	0.015	0.000	0.007	0.056	0.000	0.000	0.000	0.000	0.006	0.000	0.000	0.000
Mg^{2+}	0.019	0.000	0.000	0.000	0.000	0.000	0.584	0.042	0.031	0.000	0.056	0.000	0.000	0.000	0.000	0.003

X - orthorhombic phase, R - rutile

Atomic contents based on 24 oxygen atoms and 12 cations of the ordered columbite cell, to facilitate mutual comparison; Fe_2O_3 calculated to eliminate cation surplus over 12.000 (*cf. Ercit et al.* 1992a).

Scarcity and low concentration of the minor elements do not permit meaningful interpretation of their entry into the structure of the rutile examined.

Element partitioning between the orthorhombic phase and rutile

The orthorhombic-phase and rutile populations are separated by their Ti contents (Fig. 2B), and by the strong tendency of rutile to exclude Mn (Figs. 2A, 4). The preference of the orthorhombic phase for Mn and Nb, and the affinity of Fe and Ta for rutile, are expressed in all mineral pairs examined, disregarding what may be the specific values of Mn/(Mn + Fe) and Ta/(Ta + Nb) of the minerals, the exsolved or coprecipitated nature of their association, their relative abundances, or their provenance (Fig. 4). Strong preferences also are shown by the distribution of subordinate and minor components (Table 2). The orthorhombic phase invariably concentrates WO_3, Sc_2O_3 and ZrO_2, commonly to their virtual exclusion from rutile. In contrast, the SnO_2 and Fe_2O_3 contents of

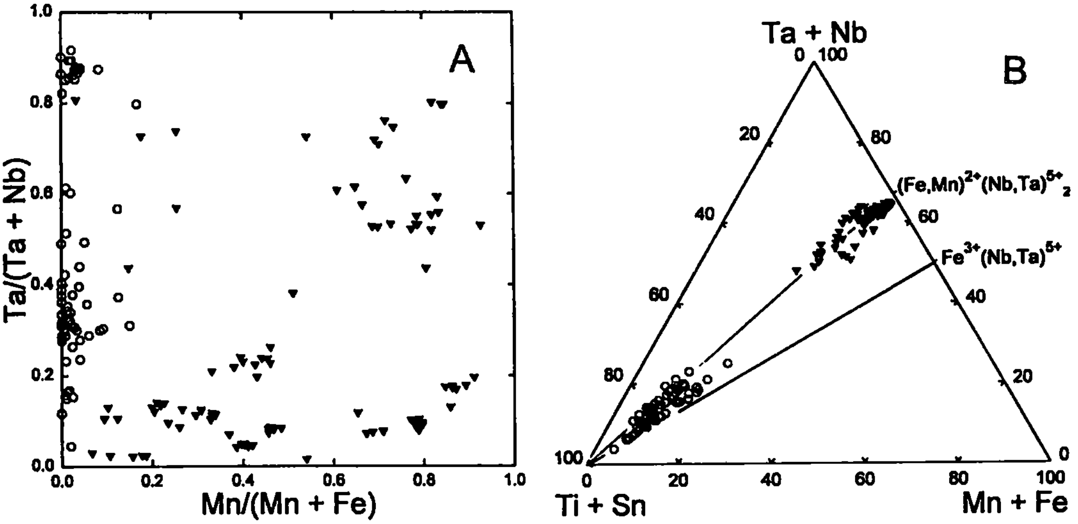

FIG. 2. Summary of all data collected for this study, expressed in terms of atomic proportions in the columbite quadrilateral (A), and in the triangular plot (Ta + Nb) – (Ti + Sn) – (Mn + Fe) (B). Triangles: the orthorhombic phase, circles: rutile.

rutile are considerably higher than those of the orthorhombic phase, with only a few exceptions.

Figure 5 illustrates the compositions of coexisting orthorhombic and rutile phases at individual localities. It is evident that the extent of solid solution of TiO_2 in the orthorhombic phase increases concomitantly with that of the $(Fe{>>}Mn)^{2+}(Nb,Ta)_2O_6$ and $Fe^{3+}(Nb,Ta)O_4$ components in the rutile phase. It also is evident that the solid solution is in all cases slightly to distinctly more extensive in the rutile phase than in the orthorhombic mineral.

STRUCTURAL STATE

The orthorhombic phase in natural state

Unit-cell dimensions of samples represented in Table 2 are listed in Table 3. Figure 6 summarizes the available data on unit-cell dimensions of the orthorhombic phase in the *a versus c* diagram of Černý & Turnock (1971), as progressively modified by Wise *et al.* (1985) and Ercit *et al.* (1995). This diagram shows the variations induced by the Fe–Mn substitution (subparallel to *a*), and by the transition from ordered *A*-site (Fe,Mn) + *B*-site $(Nb,Ta)_2$ distribution of cations to disordered population of all cations in a single octahedral site (in diagonal direction).

It is evident that the data cover almost the full span of structural states, except the region of highly ordered structures. Comparison with chemical compositions shows that most of the data in the lower half of the diagram, indicative of moderate to considerable degree of order, belong to phases with low to moderate Ti contents (*e.g.*, the NST compositions 43–49 and 53–58, 60, 62, BRD 67–74, CCC, LMN and GUC 97, 99 and 101, respectively). These phases extend into the most disordered region of the diagram, which also contains the Ti-rich samples (TRT 5–7, 16, LOT 187–191, 221). The only exceptions to the above distribution are the Ti-rich samples examined by Sveshnikova *et al.* (1965; 32 and 33), which display *a* and *c* values indicative of a considerable to high degree of order. However, the magnitude of standard error, the age and the single-crystal method used in the above study do not encourage confidence in the quality of these data.

The *a* – *c* plots are generally shifted from the region outlined by ordered and disordered columbite – tantalite *sensu stricto* toward lower values of *c* and particularly *a*. This is in agreement with the results of Ercit *et al.* (1995), who quantified such an effect of Ti substitution on the unit-cell dimensions of the columbite – tantalite minerals.

The orthorhombic phase after heating

Heating promotes the ordering of cations in columbite-type minerals, and standard conditions of 1000°C for 16 hours were adopted by Černý & Turnock (1971) to facilitate mutual comparisons. These conditions are sufficient to effect virtually complete ordering in natural samples of diverse structural state, including those with total disorder of the cations. Heating of granular (~1–2 mm) material in air produces effects indistinguishable from those achieved in an oxidation-suppressing atmosphere of $CO + CO_2$.

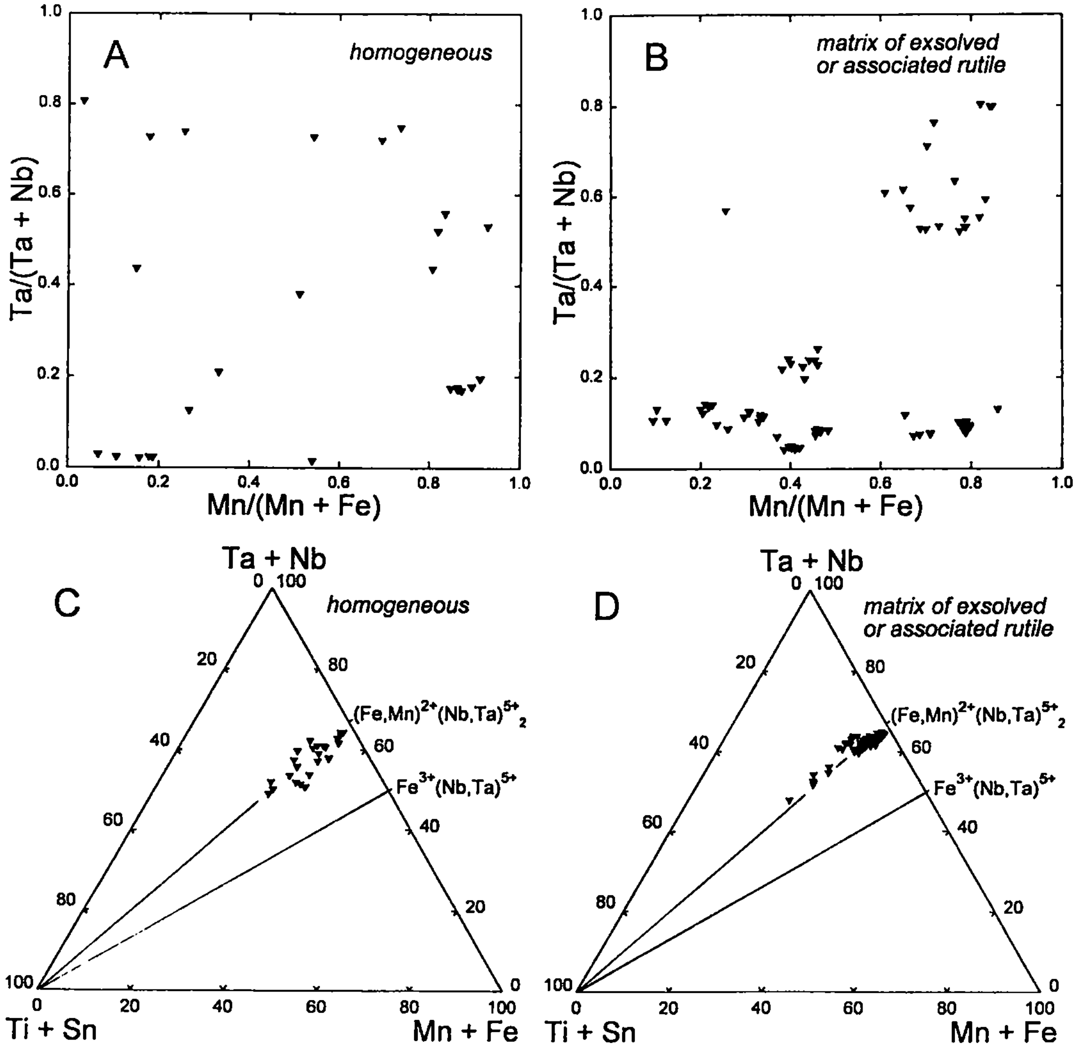

FIG. 3. Composition of the homogeneous orthorhombic phase (A, C) and of the orthorhombic phase with exsolved or associated rutile (B, D) in the columbite quadrilateral and in the (Ta + Nb) – (Ti + Sn) – (Mn + Fe) system (atomic proportions).

Of the samples subjected to heating, those with low to moderate contents of Ti and low to moderate disorder were converted to more or less fully ordered columbite – tantalite (Fig. 6). However, samples with high Ti (and Mn) content and high degree of disorder in the natural state (TRT 5, 6, 7, 16 and LOT 187–191, 221, italicized in Figure 6) developed the wodginite structure (Fig. 7, Table 3).

Rutile

Because of its subordinate quantities in exsolution-induced intergrowths and aggregates with the orthorhombic phase, rutile usually generates only a few individualized X-ray powder-diffraction maxima. Refinement of its unit-cell dimensions is not feasible in most cases. However, diffraction maxima indicative of

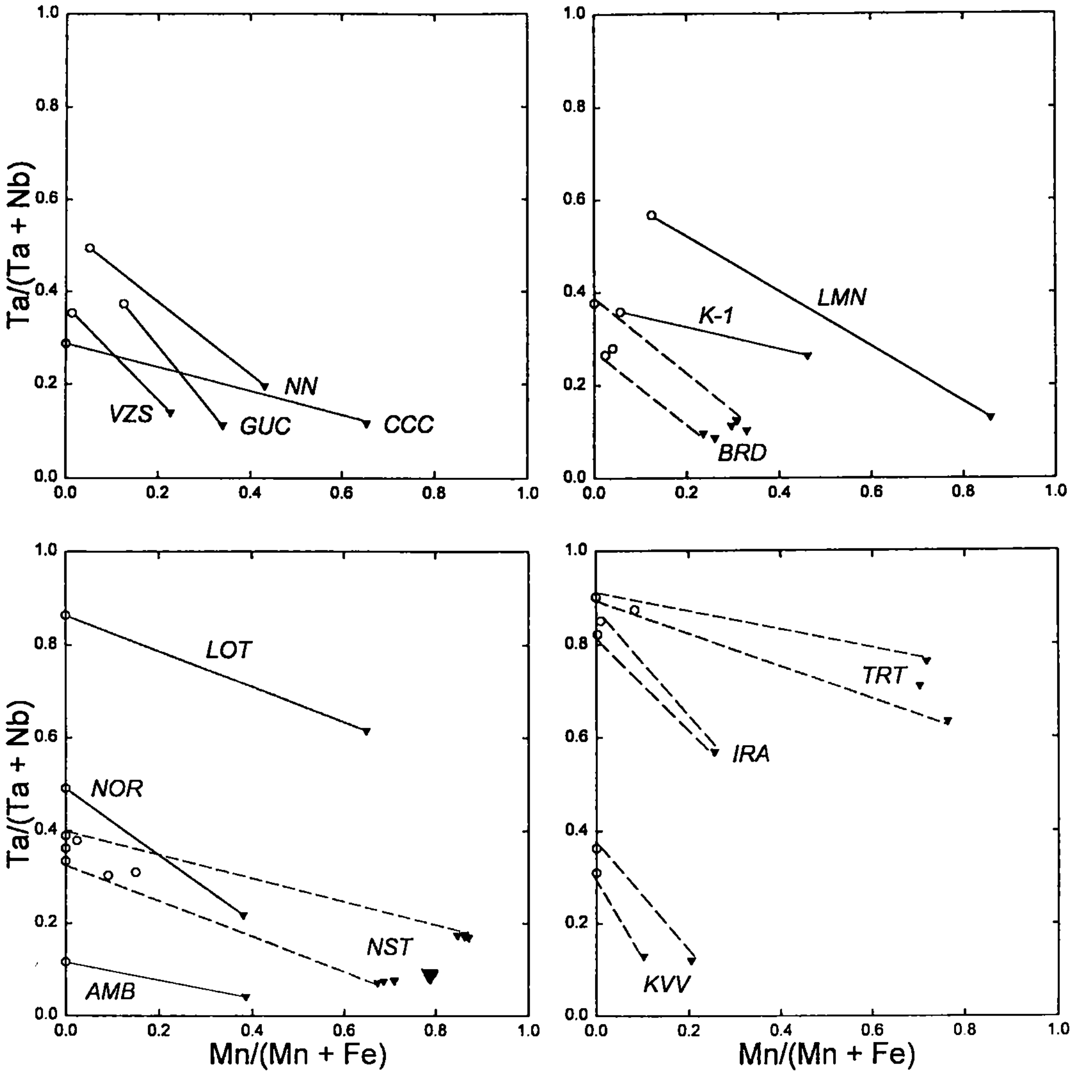

FIG. 4. Compositions of exsolved or associated pairs of the orthorhombic and rutile phases in the columbite quadrilateral (atomic proportions). Symbols as in Figure 2. Locality acronyms as listed in Table 1.

a trirutile superstructure were never observed. Thus it is possible to assume that the structure corresponds to that of pure rutile, with disordered distribution of non-integral quantities of substituting elements over octahedral positions representing a single cation site.

After heating, the diffraction maxima of rutile display about the same intensities as those generated by the natural phase. This finding indicates that dissolution of rutile in the orthorhombic phase must have been minimal.

DISCUSSION

Phase relationships

In most samples examined, the Ti-enriched orthorhombic phase contains exsolved rutile; in many others, the orthorhombic phase is associated with rutile in aggregates suggesting simultaneous crystallization. In a few other instances, the orthorhombic phase is dispersed among rock-forming silicates along with

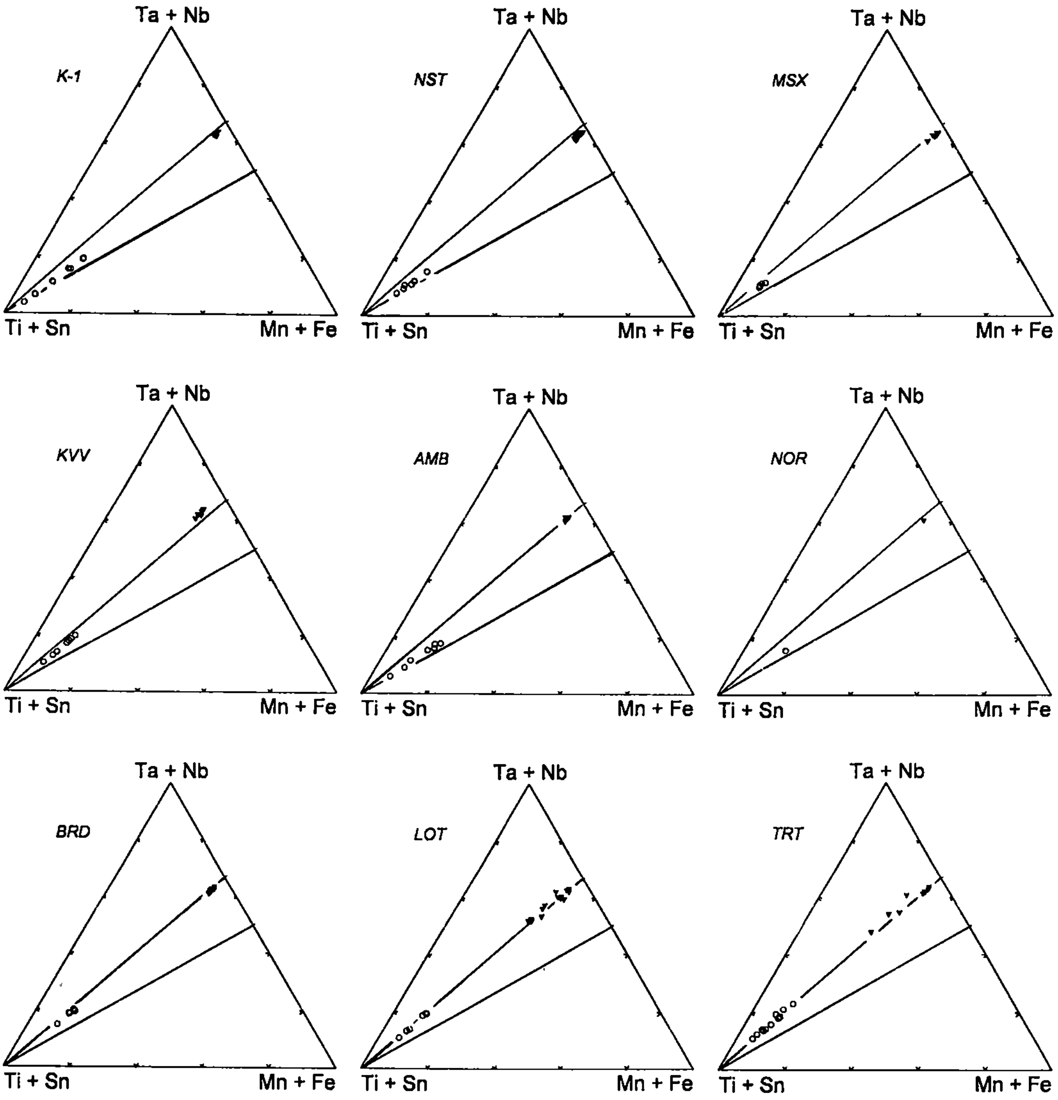

FIG. 5. Compositions of the orthorhombic phase and exsolved or associated rutile at individual localities, in the (Ta + Nb) – (Ti + Sn) – (Mn + Fe) system. Symbols as in Figure 2, locality acronyms listed in Table 1.

rutile, but not in mutual contact. Occurrences of a homogeneous orthorhombic phase devoid of any association with rutile seem to be very rare.

In many cases, the orthorhombic phase evidently crystallized as a metastable, homogeneous, disordered mineral with a tendency to exsolve rutile on cooling, and only rarely was it preserved in the original homogeneous state. In this respect, the examined exsolution-induced intergrowths are a counterpart of those exhibited by niobian (and, to a degree, tantalian) rutile, which commonly exsolves an orthorhombic phase (*e.g.*, Lebedeva 1968, Sahama 1978, Černý *et al.* 1964, 1981b, 1986). The difference between the two cases is in the bulk composition and structure of the homogeneous precursor; the roles of the host mineral and the exsolved phase are reversed.

In contrast to niobian–tantalian rutile, which exsolves titanian columbite if Nb-dominant but remains in most cases homogeneous if its original composition is Ta-dominant (Černý & Ercit 1989), there seems to be

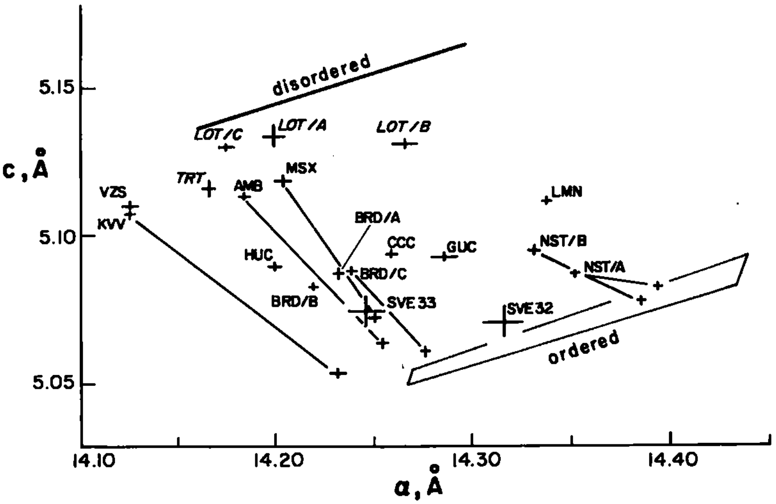

FIG. 6. The $a - c$ plot of unit-cell dimensions for the orthorhombic phase, with a expressed in values corresponding to the ordered columbite superstructure to facilitate comparison. Data for end-member compositions from Ercit *et al.* (1995). Data for compositions that order to the wodginite structure upon heating are labeled in italics; other samples develop the ordered columbite superstructure with unit-cell dimensions marked at the unnumbered ends of the tie lines. Crosses indicate standard deviations of 1σ.

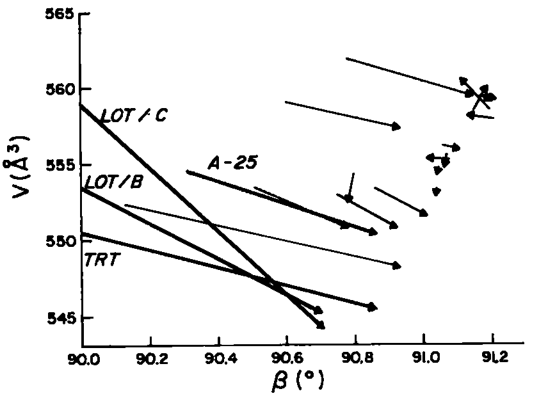

Fig. 7. The β *versus* unit-cell volume diagram for the wodginite-group minerals (after Ercit *et al.* 1992a). The ordering observed upon heating is proportional to the length of vectors, which go from the data-points for natural minerals (tail-end of arrows) to those for heated samples (arrowheads). Thin lines: wodginite from the above study; heavy lines: orthorhombic phases from the present work, except A–25, which corresponds to type titanowodginite (from Ercit *et al.* 1992b).

no such compositional control on the exsolution behavior of the titanium-rich orthorhombic phase: the ZAG and homogeneous NST samples are Mn- and Nb-rich; the two SVE specimens are extremely Nb-rich and highly variable in Mn, and both apparently contain a remarkably high percentage of Fe^{3+}. In contrast, the homogeneous LOT samples are Mn- and Ta-rich, and the HUC samples are Fe- and Nb-dominant (Tables 2, 3).

Assemblages of a cocrystallized orthorhombic mineral and rutile may represent either primary coprecipitation under temperature conditions lower than those generating the homogeneous precursor of the exsolution-induced intergrowths, or a product of recrystallization of the exsolved aggregates. Low-temperature conditions of cocrystallization also are sugested by the high Ti content of any orthorhombic phase that did not undergo exsolution (*e.g.*, some of the LOT samples); metastable crystallization and preservation in a low-energy environment may have been the cause.

Chemical composition

The orthorhombic phase and the exsolved rutile show the same compositional features as their analogs in rutile-hosted intergrowths (*e.g.*, Sahama 1978, Černý *et al.* 1981b, 1986, unpubl. data of PČ). The

TABLE 3. UNIT-CELL DIMENSIONS OF THE ORTHORHOMBIC PHASE

	K-1	MSX	NST/A	NST/B	KVV	BRD/C	AMB	LOT/A	LOT/B	LOT/C	TRT
					Natural Samples						
a	4.752(1)	4.735(1)	4.784(1)	4.777(1)	4.709(1)	4.746(1)	4.728(1)	4.733(3)	4.755(3)	4.725(1)	4.722(1)
[a]	[14.259]	[14.205]	[14.352]	[14.330]	[14.127]	[14.238]	[14.184]	[14.199]	[14.265]	[14.175]	[14.166]
b	5.730(1)	5.728(1)	5.742(1)	5.740(1)	5.712(1)	5.728(1)	5.709(2)	5.717(3)	5.728(4)	5.710(1)	5.703(2)
c	5.095(1)	5.120(1)	5.088(1)	5.095(1)	5.107(1)	5.088(1)	5.113(1)	5.133(5)	5.131(2)	5.130(1)	5.116(2)
V	138.73(5)	138.76(3)	139.76(3)	139.68(5)	137.35(3)	138.32(4)	138.03(5)	138.36(9)	139.74(9)	138.42(4)	137.76(5)
[V]	[416.2]	[416.49]	[419.28]	[419.05]	[412.05]	[414.96]	[414.09]	[415.08]	[419.22]	[415.26]	[413.28]
					Heated at 1000°C/16 hours in air						
a	14.284(2)	14.261(2)	14.378(2)	14.370(2)	14.233(3)	14.269(3)	14.255(3)	9.426(2)	9.418(2)	9.433(3)	9.435(12)
b	5.733(1)	5.731(2)	5.742(1)	5.748(1)	5.720(1)	5.722(1)	5.713(1)	11.386(3)	11.382(2)	11.384(3)	11.395(6)
c	5.072(1)	5.072(1)	5.081(1)	5.074(1)	5.506(1)	5.060(1)	5.065(1)	5.081(1)	5.076(1)	5.077(1)	5.078(3)
β	-	-	-	-	-	-	-	90.72(1)°	90.70(1)°	90.70(3)°	90.86(6)°
V	415.30(8)	414.53(9)	419.47(7)	419.10(7)	416.12(8)	413.12(9)	412.49(8)	545.2(2)	544.0(2)	545.2(2)	545.9(2)

All data in Å units; data in square brackets tripled for direct comparison with ordered cell dimensions of heated samples; NST/A corresponds to compositions 53-58, 60, 62; NST/B 43 to 49; BRD/C 73, 74, 80; LOT/A 187; LOT/B 189, 221; LOT/C 191; TRT 5, 6, 7, 16.

crystal-chemical constraints regulating the chemical composition of the two exsolved phases are identical in both cases.

The orthorhombic phase occasionally incorporates Ti to a degree closely approaching the stoichiometry of wodginite ABC_2O_8 or, more specifically, that of ideal titanowodginite, (Mn,Fe)(Ti>Sn,Ta)$(Ta,Nb)_2O_8$ (Ercit *et al.* 1992b). For example, composition TRT 7 can be interpreted as $(Mn_{2.65}Fe^{2+}_{1.05}Ca_{0.17})_{\Sigma 3.87}$ $(Ti_{2.44}Sn_{0.97}Ta_{0.43}Sc_{0.17})_{\Sigma 4.01}(Ta_{6.01}Nb_{2.00})_{\Sigma 8.01}O_{32.00}$. Many compositions analyzed in the TRT and LOT samples approach this type of formula (Table 3), characterized by (Nb,Ta)/Fe,Mn) > 2 typical of the wodginite group (Ercit *et al.* 1992a). However, in most compositions, the (Mn,Fe) population of the *A* site would be excessive, and the excess could not be incorporated into the *B* site of the ordered wodginite structure, despite the deficiency in Ti and Sn.

The rutile phase shows a broad range of substitution by the $(Fe{>}{>}Mn)^{2+}(Nb,Ta)_2O_6$ and $Fe^{3+}(Nb,Ta)O_4$ components, with widely variable Nb/Ta values. The proportions of TiO_2 and the above components are randomly non-integral, and they do not approximate any potential formulas with simple stoichiometry.

As shown in Figure 5, the extent of mutual solid-solution residual in the two exsolved phases is highly variable but positively correlated, with a distinct tendency for rutile to retain a higher percentage of the orthorhombic component than the TiO_2 content of the associated orthorhombic phase. The crest of a potential solvus between the orthorhombic phase and rutile is evidently shifted off-center, closer to the (Fe,Mn) – (Nb,Ta) sideline. This again agrees with the observations on niobian rutile with exsolved titanian columbite – tantalite (Černý *et al.* 1981b, Černý & Ercit 1985, 1989).

Structural state of natural phases

The degree of cation disorder in the orthorhombic phase tends to increase with increasing Ti content, but the trend is disturbed by some highly disordered Ti-poor samples and the highly ordered Ti-rich minerals of Sveshnikova *et al.* (1965). Metastable crystallization of disordered and compositionally complex orthorhombic minerals can be expected to generate disordered phases, which would undergo variable degrees of ordering in the solid state, commonly in conjunction with exsolution of the main substituents or with recrystallization.

The rutile phase has the monorutile structure in accordance with its complex and variable composition, which precludes long-range ordering into tapiolite-like or other superstructures.

Response of the orthorhombic phase to heating

For most samples of the orthorhombic phase with low to moderate Ti content, heating produces the ordered columbite structure. Only a minority of the samples examined develop the monoclinic structure of wodginite. Which factors favor ordering to the wodginite structure?

(1) The Ti content of the samples that adopt the wodginite pattern of order is among the highest encountered in our study (1.56 to 4.21 Ti, 2.02 to 4.71 Ti + Sn atoms per 32 atoms of oxygen), as compared to the specimens that order to columbite – tantalite (0.28 to 1.45 Ti, 0.28 to 1.58 Ti + Sn atoms per 32 atoms of oxygen). This is in considerable contrast to stannian ixiolite, which orders to wodginite for Sn contents as low as 1.40 (Sn + Ti 1.82) atoms per 32 atoms of oxygen (unpubl. data of PČ), and to the Sn-based natural

wodginite *sensu stricto*, which has Sn and (Sn + Ti) as low as 1.06 atoms per 32 atoms of oxygen (Ercit *et al.* 1992a).

(2) The rather substantial presence of Sn may play a role, as Sn^{4+} does not fit the orthorhombic columbite structure as easily as Ti^{4+}. Orthorhombic minerals may allocate their moderate Ti contents on ordering in the ratio of the most common mechanism of substitution, $Ti^{4+}{}_3(Fe,Mn)^{2+}{}_{-1}(Nb,Ta)^{5+}{}_{-2}$, *i.e.*, one third into the *A* site and two thirds into the *B* site. As shown above in (1), Sn^{4+} readily segregates into its own site, rendering the structure monoclinic, at distinctly lower formula contents than does Ti. As shown in Tables 3 and 4, most of the samples that adopted the monoclinic structure upon heating contain substantial Sn, and even those that are Sn-poor in the two-dimensional surfaces of polished sections may be Sn-richer in the bulk of their volumes used for XRD study. Considerable variation of the Ti/Sn value was found in individual grains closely related to the LOT samples (Ferreira 1984). It should be noted in this respect that the type titanowodginite and all other compositions so far analyzed (Ercit *et al.* 1992a, b) also contain appreciable Sn.

(3) The path of ordering could be predetermined by the presence of structural nuclei with short-range order in the natural minerals. Such a possibility must be considered all the more because the monoclinic-ordering samples happen to be restricted to two closely related pegmatite bodies, the Tanco and Lower Tanco deposits (Table 1). Conditions favorable for incipient wodginite-type order in the orthorhombic (or pseudo-orthorhombic?) natural phases could have been realized in such a restricted environment but absent at other localities.

(4) The dominance of Ta over Nb, and Mn over Fe, may be significant in developing the wodginite structure on heating the Ti-rich orthorhombic phases. The TRT and LOT samples are the only ones with both Ta/(Ta + Nb) and Mn/(Mn + Fe) greater than 0.50 (Table 3, Fig. 4). This is a feature of virtually all compositions of the classic Sn-based wodginite and stannian ixiolite [Černý & Ercit (1989, Figs. 4 and 9), Ercit *et al.* (1992a, Table 2), and deposited data]. It is significant in this respect that Ercit *et al.* (1992a) successfully synthesized titanowodginite $MnTiTa_2O_8$, but phases with the wodginite structure were not generated in any previous or present studies of the $FeNb_2O_6 - TiO_2$ and $FeTa_2O_6 - TiO_2$ systems (*cf.* Wise *et al.* 1998).

(5) Last but far from least, the presence of "excess" Ta over and above the stoichiometry of tantalite, $(Mn,Fe)Ta_2O_6$, may condition ordering to the wodginite structure. Wodginite $A_4B_4C_8O_{32}$ routinely contains (Ta>Nb) > 8 on the basis of 32 atoms of oxygen, with all Nb in the *C* site and the "excess" Ta incorporated at the *B* site (Ercit *et al.* 1992a). It is noteworthy that the compositions #6 and 7 (TRT) and 187, 189, 191 (LOT), which order upon heating to the monoclinic structure, all contain (Ta>Nb) > 8 and (Nb,Ta)/(Fe,Mn) > 2. However, a better statistical base is required to verify the role of this factor.

Implications for mineral systematics

As stated in the Introduction, stannian and titanian ixiolite are defined by high contents of these respective metals and by ordering to monoclinic wodginite on heating, in contrast to disordered stannian and titanian columbite – tantalite, which orders to an orthorhombic supercell. It is evident from the preceding sections that true Ti-dominant ixiolite seems to be an exception rather than a rule among the Ti-enriched orthorhombic phases, and titanian columbite – tantalite is quite widespread. As in the case of the classic Sn-based ixiolite, chemical composition does not seem to be at present a reliable indicator of the mineral species, *i.e.*, disordered titanian columbite – tantalite *versus* titanian ixiolite; path of ordering upon heating is the only unambiguous criterion for identification.

CONCLUSIONS

(1) Titanium-enriched members of the orthorhombic columbite family of minerals typically contain exsolved niobian–tantalian rutile, whereas homogeneous phases are much less common. Some homogeneous phases are aggregated with a coprecipitated rutile phase, some occur in a general association, but not in contact with rutile. Rutile-absent occurrences are extremely rare.

(2) The bulk of the exsolved or coprecipitated orthorhombic phase + rutile pairs is the Fe,Mn,Nb, Ta-rich counterpart of the Ti-dominant pairs of niobian rutile + exsolved titanian columbite. In both assemblages, the rutile phase is enriched in Fe^{2+}, Ta, Fe^{3+} and Sn, whereas the orthorhombic phase favors Mn, Nb, Sc, W and Zr.

(3) The orthorhombic phase has in most cases the disordered structure typical of ixiolite and disordered columbite – tantalite. The degree of disorder tends to increase with increasing Ti content. On heating, most samples of the orthorhombic phase develop the ordered columbite superstructure, with Ti probably stoichiometrically distributed between the *A* (Fe,Mn) and *B* $(Nb,Ta)_2$ cation sites. In contrast to these titanian varieties of true columbite – tantalite, some specimens are transformed into the ordered monoclinic structure of wodginite, which identifies them as titanian ixiolite, the disordered counterpart of titanowodginite.

(4) The development of the wodginite structure on heating is facilitated by high Ti contents and by dominance of Mn and Ta over Fe and Nb, respectively. Both these features are in agreement with the characteristics of natural titanowodginite and with the Mn,Ta-based composition of the only titanowodginite synthesized to date. However, "programming" of the path of ordering by the presence of wodginite-type or ordered

columbite-type nuclei may play a role, as may the presence of appreciable Sn. Also, "excess" Ta in the disordered phase, over and above the (Fe,Mn) $(Nb,Ta)_2$ stoichiometry of columbite, may turn out to be significant.

(5) Further heating and XRD experiments are required on natural samples of homogeneous Ti-rich orthorhombic phases with negligible Sn content, and the synthesis of titanowodginite with substantial Fe and Nb contents should be attempted, to verify the potential controls given in (4). Also, HRTEM work is desirable on natural orthorhombic phases to check on the possible presence of ordered nuclei, and on the details of the exsolution history of individual samples (*cf.* staringite: Groat *et al.* 1994). Crystal structures of the heat-induced ordered orthorhombic phases should be refined to verify the distribution of Ti.

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