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THE TANTALITE–TAPIOLITE GAP: NATURAL ASSEMBLAGES VERSUS EXPERIMENTAL DATA

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ABSTRACT

Compositions of 45 ferrotapiolite–tantalite pairs from 12 granitic pegmatites were analyzed by electron microprobe to establish empirically the shape, extent and position of the two-phase field in the columbite quadrilateral. The field is perceptibly broader than that defined earlier on the basis of single-phase samples. The compositions of single phases located within the boundaries based on coexisting minerals are, under the conditions of crystallization, probably metastable. The two-phase field derived from coexisting minerals approximates an isothermal section through a pseudoquaternary solvus in the columbite quadrilateral through most of the course of its boundaries, as defined by primary Nb-enriched ferrotapiolite – tantalite pairs from blocky zones and albitic units of their parent pegmatites. Extremely fractionated mineral pairs most enriched in Mn and Ta come from late associations replacing simpsonite; they crystallized at distinctly lower temperatures. Boundaries of the two-phase field are controlled by temperature, $f(O_2)$, structural state, impurities disturbing the AB_2O_6 stoichiometry, and probably pressure. All these factors require thorough experimental reinvestigation.

Keywords: tantalite, tapiolite, columbite, miscibility gap, metastability, granitic pegmatites.

SOMMAIRE

La composition chimique de 45 paires ferrotapiolite + tantalite provenant de douze pegmatites granitiques a été déterminée par analyse à la microsonde électronique afin de déterminer la forme, la portée et la position du domaine à deux phases dans le quadrilatère de la columbite. Ce domaine est plus large que celui qui est déjà établi à partir des échantillons monophasés. La composition de ceux-ci qui sont situés à l'intérieur des limites du domaine à deux phases serait due à un phénomène de cristallisation métastable dans le milieu pegmatitique. Le domaine à deux phases qui respecte la composition des minéraux coexistants simule une section isothermale d'un solvus pseudo-quaternaire dans le quadrilatère de la columbite, telle que définie par des paires ferrotapiolite enrichie en Nb + tantalite provenant des zones à grains grossiers et des unités albitiques des pegmatites. Un fractionnement extrême, avec enrichissement en Mn et Ta, caractérise les paires d'une association tardive qui remplace la simpsonite, et qui s'est formée à une température nettement plus faible. Les limites du domaine à deux phases dépendent de la température, $f(O_2)$, le degré d'ordre, le niveau d'impuretés qui affectent la stoechiométrie AB_2O_6, et tout probablement la pression. Tous ces facteurs devront faire l'objet d'une étude expérimentale.

(Traduit par la Rédaction)

Mots-clés: tantalite, tapiolite, lacune de miscibilité, métastabilité, pegmatites granitiques.

INTRODUCTION

Extensive confusion reigned in the initial studies of the Fe, Mn, Nb, Ta oxide minerals, but the compositional difference between tetragonal ferrotapiolite $FeTa_2O_6$ and orthorhombic tantalite $(Fe \lesseqgtr Mn)(Ta > Nb)_2O_6$ was recognized rather early (*e.g.*, Ford 1932; see Černý *et al.* 1989a for nomenclature). However, the existence of a compositional gap between ferrotapiolite and tantalite was recognized only much later. Since the 1960s, published compilations of columbite–tantalite and ferrotapiolite compositions, combined with sets of new data, have demonstrated this gap rather clearly. Nevertheless, the extent and shape of the two-phase region differ somewhat from author to author, and are more often than not violated by a few data-points.

Surprisingly, experimental work performed to date has not substantially improved our understanding of the two-phase region. Experiments conducted under geologically realistic conditions are extremely scarce, and field boundaries established by various researchers under comparable conditions are considerably different.

In the course of study of several pegmatite localities and pegmatite fields, we have collected data on coexisting ferrotapiolite and tantalite from a variety of pegmatite types (Černý *et al.* 1984, 1987). Aware of an emerging pattern, internally consistent but perceptibly different from previous experience, we have complemented these data by examining additional pairs of ferrotapiolite + tantalite, and by critically evaluating data from the literature for reliability. The present paper summarizes all acceptable results; we evaluate the data characterizing the natural pairs of ferrotapiolite + tantalite, compare them to the experimental results, and suggest a course of action for further studies.

PREVIOUS WORK

Natural assemblages

Figures 1A to 1E show the columbite quadrilateral, with diverse compilations of data on the composition of columbite–tantalite and tapiolite minerals as they were published, and in part already mutually combined, by Moreau & Tramasure (1965), Zelt (1975), Sahama (1980), Foord (1976), von Knorring & Fadipe (1981) and Voloshin & Pakhomovskyi (1988). None of these authors mentioned coexisting tapiolite + columbite–tantalite minerals. Thus it can be assumed that most data points on these diagrams represent single-phase compositions. With the exception of the von Knorring & Fadipe data, the two-phase region separating tapiolite from tantalite is not well expressed, and it is violated even in their diagram.

Single-phase tapiolite and columbite–tantalite also constitute the data points of Figure 1F, based on Černý & Ercit (1985, 1989). However, this diagram summarizes only reliable modern data acquired since 1970, and additional unpublished compositions collected by the present authors since 1980. The two-phase field is rather sharply defined here, violated only by the ferrotapiolite–manganotapiolite sequence from the Tiainen pegmatite (Lahti *et al.* 1983), which is so far unique in the world and most probably metastable (Černý & Ercit 1985). For this reason, this sequence will be disregarded in our forthcoming considerations.

Note that the "gaps" adjacent to the $FeNb_2O_6$–$FeTa_2O_6$ and $FeNb_2O_6$–$MnNb_2O_6$ joins of Figure 1F are geochemical rather than crystallochemical. The data shown in Figure 1F refer exclusively to columbite–tantalite from granitic pegmatites that invariably show at least an incipient fractionation of Mn from Fe and Ta from Nb. The apparent gaps would be significantly reduced were any data for columbite from alkaline, peralkaline and carbonatite rocks included. However, such data are not readily available in the literature and, in any case, they are not relevant to the problem at hand because of low levels of Ta fractionation from Nb in these environments; tapiolite is not known, and even tantalite is extremely unlikely to occur.

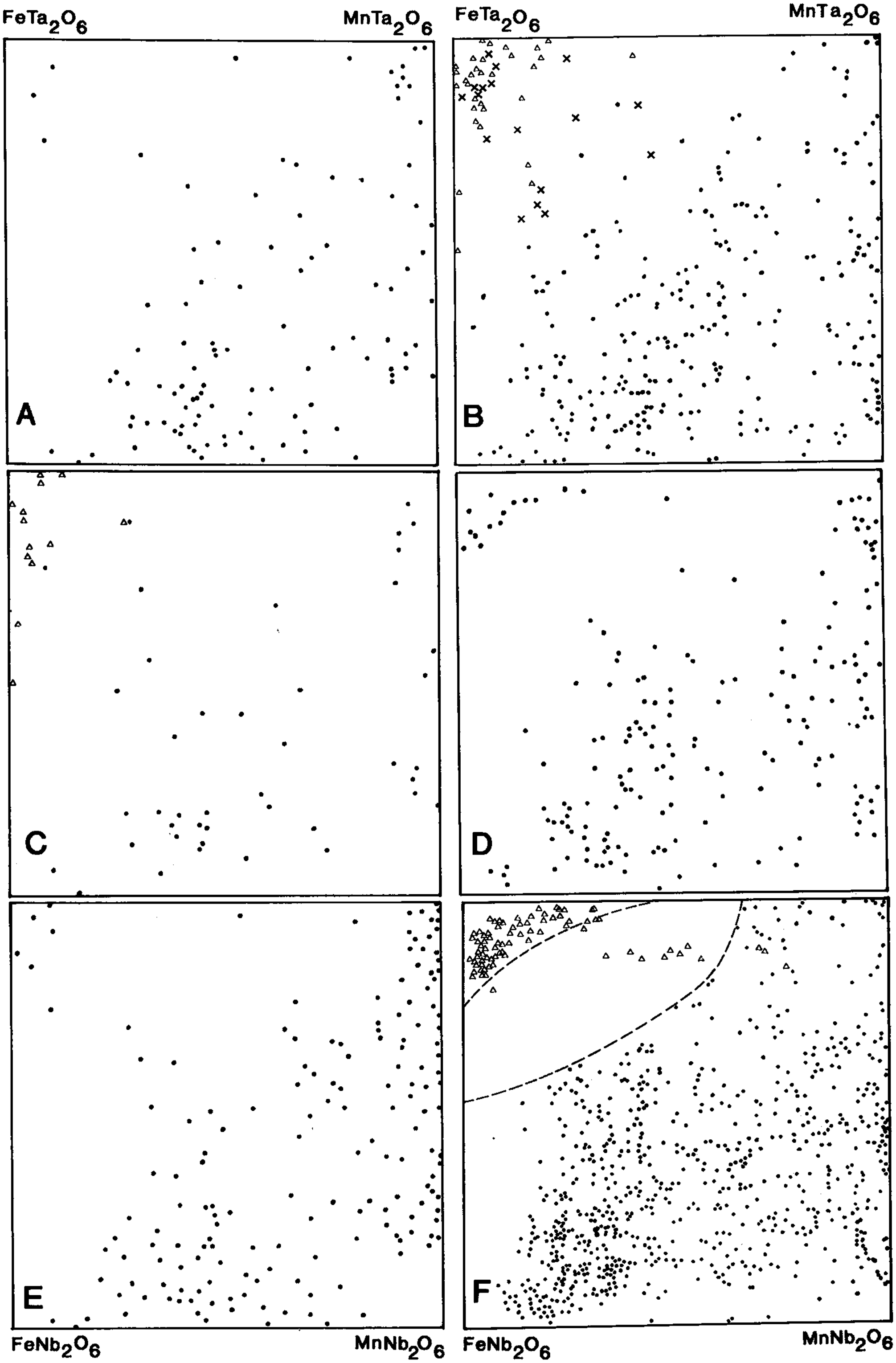
Several reasons undoubtedly account for the differences in the shape and "purity" of the ferrotapiolite–tantalite gap in Figures 1A–E and 1F. Analytical separation of Nb and Ta was notoriously difficult until the 1960s; the phase composition of the analyzed material was also potentially questionable before the advent of the electron microprobe, unless checked by X-ray diffraction. Impurities that become prominent in ixiolite compositions (Sn, Ti, W, Sc, Fe^{3+}) expand the columbite–tantalite field, and their contents increase with the decreasing degree of cation order in columbite–tantalite (Černý *et al.* 1984, Černý & Ercit 1985, 1989). Last, but not least, metastable precipitates may also constitute some of the phases shown in Figures 1A–E that violate the two-phase region of Figure 1F (Graham & Thornber 1974, 1975).

Synthetic phases

Figure 2 summarizes the results of experimental work by Schröcke (1966), Moreau & Tramasure (1965), Komkov (1973) and Komkov & Dubik (1974a, b, 1983). In addition to these studies covering the entire quadrilateral, Turnock (1966) examined the $MnTa_2O_6$–$FeTa_2O_6$ edge of the quadrilateral in his synthesis of wodginite, with results closely matching those of Komkov & Dubik (1974a) under comparable conditions. However, the results of Tanaka *et al.* (1988) on the binary systems $FeTa_2O_6$–$MnTa_2O_6$ and $MnNb_2O_6$–$MnTa_2O_6$ differ from all other data. Tokizaki *et al.* (1986) were the only authors to systematically examine the influence of oxygen fugacity on the stability of orthorhombic and tetragonal phases.

Most of the two-phase field boundaries were determined in dry systems at high temperatures (900–1100°C) and atmospheric pressure. Results obtained by Moreau & Tramasure (1965) and Komkov (1973) at 1050–1100°C are roughly comparable, but the 1100°C boundaries of Schröcke (1966) differ distinctly, and an attempted interpolation to 1050°C would differ even more. The fields determined by Komkov & Dubik

FIG. 1. Compositions of natural columbite–tantalite and tapiolite minerals in the columbite quadrilateral, as compiled and analyzed by Zelt (1975) and Sahama (1980) (A), Foord (1976; B), Moreau & Tramasure (1965; C), von Knorring & Fadipe (1981; D), Voloshin & Pakhomovskyi (1988; E) and Černý & Ercit (1985, 1989; F). The original figures for A, D and E do not distinguish plots of tetragonal (triangles) and orthorhombic phases (dots). In B, X marks compositions of unknown symmetry. The two-phase field derived from data in F marks approximate extent of single-phase compositions.


$FeTa_2O_6$
$MnTa_2O_6$
$FeTa_2O_6$
$MnTa_2O_6$
A
B
C
D
E
F
$FeNb_2O_6$
$MnNb_2O_6$
$FeNb_2O_6$
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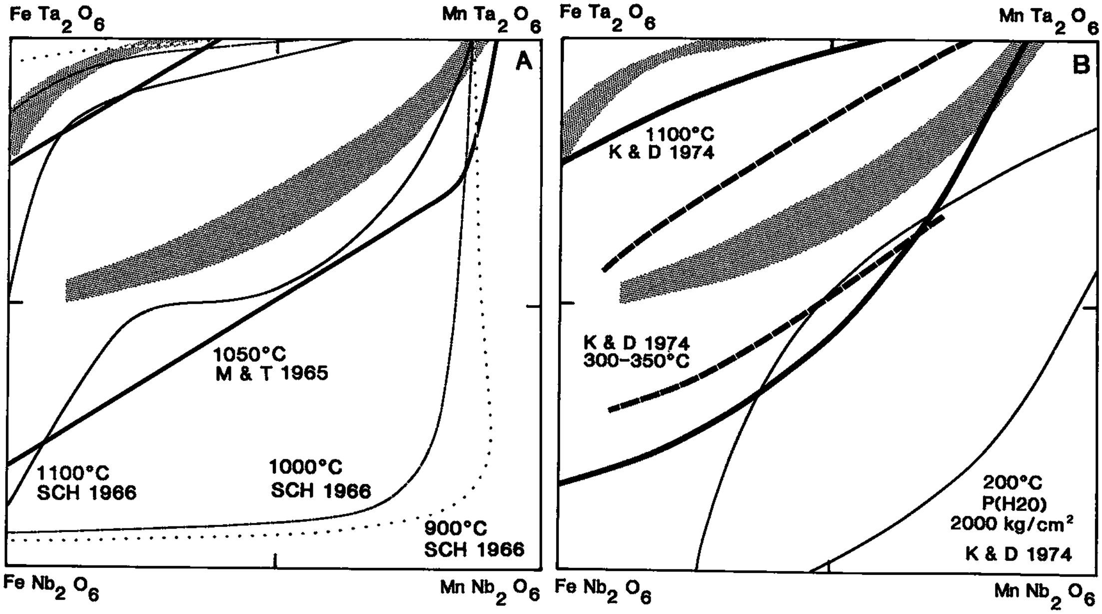

FIG. 2. Two-phase regions in the columbite quadrilateral, as interpreted from experimental work. A: Moreau & Tramasure (1965; heavy solid line) and Schröcke (1966; thin solid, dashed and dotted lines) in dry systems at 1 atm.; B: Komkov & Dubik (1974) in hydrothermal systems at 200°C and 300–350°C, and on dry heating at 1100°C. Patterned belts from Figure 4B are shown for comparison.

(1974a) in hydrothermal experiments at 300–350°C are the only ones that somewhat approach the boundaries defined by natural assemblages in Figure lF; however, the shift of their two-phase field at 200°C into the Mn,Nb-dominant part of the system is rather unexpected.

A review of the available experimental data suggests that an insufficient control over intensive variables involved in examining the columbite quadrilateral, the small number of experiments in some cases, incomplete equilibration of reaction products (most evident in the work of Tanaka *et al.* 1988), and differences in phase equilibria between ordered and disordered phases may be responsible for the discrepancies among the results obtained by different authors. General lack of correspondence between the boundaries defined by natural assemblages shown in Figure lF and those defined experimentally stems primarily from the experimental conditions, which are largely not comparable to the P–T regime of pegmatite consolidation at the stages of crystallization of the Nb,Ta oxide minerals.

SPECIMENS, METHODS AND RESULTS

Table 1 summarizes the specimens used for the present study, or sources of data. In the case of the Yellowknife pegmatite field, tantalite and ferrotapiolite crystals are rarely in contact, but close to each other within fist-sized hand specimens. In other cases, the two minerals were found to be in direct contact, and locally also intimately intergrown, or only a few mm apart but of the same generation. Although we do not claim that we have exhausted all possible sources, our study seems to indicate that the coexistence of tantalite + ferrotapiolite is not common in nature.

Electron-microprobe analyses of the tantalite and ferrotapiolite phases were performed in part on a MAC-5 electron microprobe in the energy-dispersion mode, in part on the CAMECA SX–50 electron microprobe. Table 2 shows compositions representative of coexisting tantalite and ferrotapiolite from some of the twelve localities examined in this study, and the analytical conditions. Figure 3 shows all data obtained for the individual localities as tie-lines connecting coexisting phases in the columbite quadrilateral. Figures 4A and 4B summarize data from all localities in the form of individual data-points.

X-ray powder diffraction was used to verify the identity of individual minerals, and to check the degree of structural order. The conditions of X-ray diffraction study are quoted by Ercit (1986), Jutz (1986), Wise (1987) and Černý *et al.* (1989a, b).

TABLE 1. SPECIMENS EXAMINED

Locality	Description	Parent pegmatite*	Reference/source
Spittal a.d. Drau, Austria	primary (or exsolution?) intergrowth recrystallized on deformation	beryl-columbite subtype	Černý et al. (1989b)
Upper Bear Gulch, South Dakota	inclusions of ferrotantalite in ferrotapiolite	beryl-columbite subtype	Harvard Mineralogy Museum #102894
Yellowknife field, NWT	individual grains several centimetres apart	beryl-columbite (-phosphate) subtypes	Wise (1987)
Nyanga, Uganda	exsolution intergrowth	beryl-columbite subtype	Černý et al. (1989a)
Muhembe, Rwanda	adjacent grains in an aggregate with wodginite and cassiterite	(Li-bearing)	Ercit (1986)
Moss, Norway	intimate granular intergrowth	gadolinite subtype	Ecole des Mines, Paris
Finnis River, Australia	intimate lamellar intergrowths within small grains	spodumene to amblygonite subtype	Jutz (1986)
Bulema, Uganda	adjacent grains associated with microlite	?	O. von Knorring
Scheibengraben, Czechoslovakia	adjacent grains	beryl-columbite subtype	Moravian Museum
Tanco, Manitoba	crystals 0.5 to a few mm apart, and a microcrystalline intergrowth	petalite subtype (with pollucite)	Ercit (1986)
Alto do Giz, Brasil	crystals 2 mm apart, both replacing simpsonite, associated with alumotantite	spodumene subtype, miarolitic	Ercit (1986)
Bikita, Zimbabwe	crystals a few mm apart, both replacing simpsonite	petalite subtype (with pollucite)	Ercit (1986)

*See Černý (1990, 1992) for pegmatite classification.

TABLE 2. CHEMICAL COMPOSITION OF REPRESENTATIVE PAIRS OF FERROTAPIOLITE + TANTALITE

	Spittal		Upper B. Gulch		Nyanga		Muhembe		Moss		Bulema		Scheibengraben		Tanco		Alto do Giz		Bikita	
	FTP	FTN	FTP	FTN	FTP	FTN	FTP	FTN	FTP	FTN	FTP	MTN	FTP	MTN	FTP	MTN	FTP	MTN	FTP	MTN
Ta_2O_5 wt.%	75.0	56.5	77.3	58.0	76.5	55.8	76.0	57.9	76.3	58.7	80.8	73.6	82.7	78.1	83.8	81.7	86.0	86.2	83.7	84.4
Nb_2O_5	8.5	26.8	7.6	25.5	7.0	27.3	6.2	24.8	7.4	25.2	3.6	10.8	1.0	5.0	1.4	3.2	-	0.3	0.2	0.2
TiO_2	1.0	0.6	0.3	0.3	0.4	0.7	1.3	0.4	0.3	-	0.1	0.1	0.5	0.6	0.1	-	-	-	-	-
SnO_2	0.6	-	0.4	0.1	0.5	0.2	0.9	0.3	0.9	-	0.4	-	-	-	0.7	0.4	-	-	1.0	0.6
Fe_2O_3	0.5	-	-	-	-	-	0.8	-	-	-	-	-	-	-	-	-	0.5	-	-	-
FeO	14.0	12.9	13.4	11.5	13.3	12.2	12.8	9.7	14.0	8.3	13.4	4.4	10.7	3.6	12.1	2.8	9.5	1.6	9.2	1.5
MnO	0.5	3.3	1.0	4.4	0.9	4.3	0.9	6.7	0.5	7.7	0.5	10.3	2.9	10.6	2.3	11.5	4.3	12.1	4.4	12.8
	100.1	100.1	100.0	99.6	98.6	100.5	98.7	99.8	99.4	99.9	99.0	99.2	97.8	98.9	100.2	99.6	100.3	100.2	98.5	99.0
Ta	1.62	1.11	1.70	1.15	1.71	1.09	1.69	1.15	1.70	1.17	1.85	1.60	1.94	1.77	1.42	1.86	1.99	1.99	1.97	1.97
Nb	0.30	0.87	0.28	0.84	0.26	0.88	0.23	0.82	0.27	0.83	0.14	0.39	0.04	0.18	0.05	0.12	-	0.01	0.01	0.01
Ti	0.06	0.03	0.02	0.02	0.02	0.03	0.07	0.02	0.02	-	0.01	0.01	0.03	0.04	0.01	-	-	-	-	-
Sn	0.02	-	0.01	-	0.02	0.01	0.03	0.01	0.03	-	0.01	-	-	-	0.02	0.01	-	-	0.04	0.02
Fe^{3+}	0.03	-	-	-	-	-	0.05	-	-	-	-	-	-	-	-	-	0.03	-	-	-
Fe^{2+}	0.93	0.78	0.91	0.70	0.91	0.73	0.87	0.59	0.95	0.51	0.94	0.29	0.77	0.25	0.85	0.19	0.67	0.11	0.66	0.11
Mn	0.03	0.20	0.07	0.27	0.06	0.26	0.06	0.42	0.04	0.48	0.04	0.70	0.21	0.75	0.16	0.81	0.31	0.87	0.33	0.89
	2.99	2.99	2.99	2.98	2.98	3.00	3.00	3.01	3.01	2.99	2.99	2.99	2.99	2.99	3.01	2.99	3.00	2.98	3.01	3.00
Ta/(Ta+Nb)	0.84	0.56	0.86	0.58	0.87	0.55	0.88	0.59	0.86	0.58	0.93	0.80	0.98	0.90	0.97	0.94	1.00	0.99	0.99	0.99
Mn/(Mn+Fe)	0.03	0.20	0.07	0.28	0.06	0.26	0.06	0.41	0.04	0.49	0.04	0.70	0.22	0.75	0.16	0.81	0.30	0.88	0.33	0.90

FTP - ferrotapiolite, FTN - ferrotantalite, MTN - manganotantalite; atomic contents calculated on the basis of 6 oxygen atoms per formula unit. Conditions of analysis (all data except Scheibengraben): MAC-5 electron microprobe in energy dispersion mode, accelerating potential 20kV, sample current 5nA measured on ZnS, counting 200s live time; standards used were cassiterite (SnLα), titanite (TiKα), manganotantalite (MnKα, TaLα, Mα), $Ba_2NaNb_5O_{15}$ and $CaNb_2O_6$ (NbLα); data were collected with a KEVEX Model 7000 ED spectrometer and were reduced with KEVEX software, utilizing the program MAGIC V (Colby 1980). Peak-overlap problems were resolved by stripping techniques involving library spectra. Compositions calculated with total Fe as FeO were adjusted by converting appropriate amount of Fe^{2+} to Fe^{3+}, if total of cations exceeded structurally available sites. Conditions of analysis (Scheibengraben): Cameca CAMEBAX SX50 electron microprobe in wavelength dispersion mode, accelerating potential 15kV, sample current 20 nA measured on Faraday cup, counting time 20s; standards used were manganotantalite (TaMα), $FeNb_2O_6$ (FeKα), $MnNb_2O_6$ (NbLα, MnKα), SnO_2 (SnLα) and rutile (TiKα). Data were reduced using the PAP routine of Pouchou & Pichoir (1985).

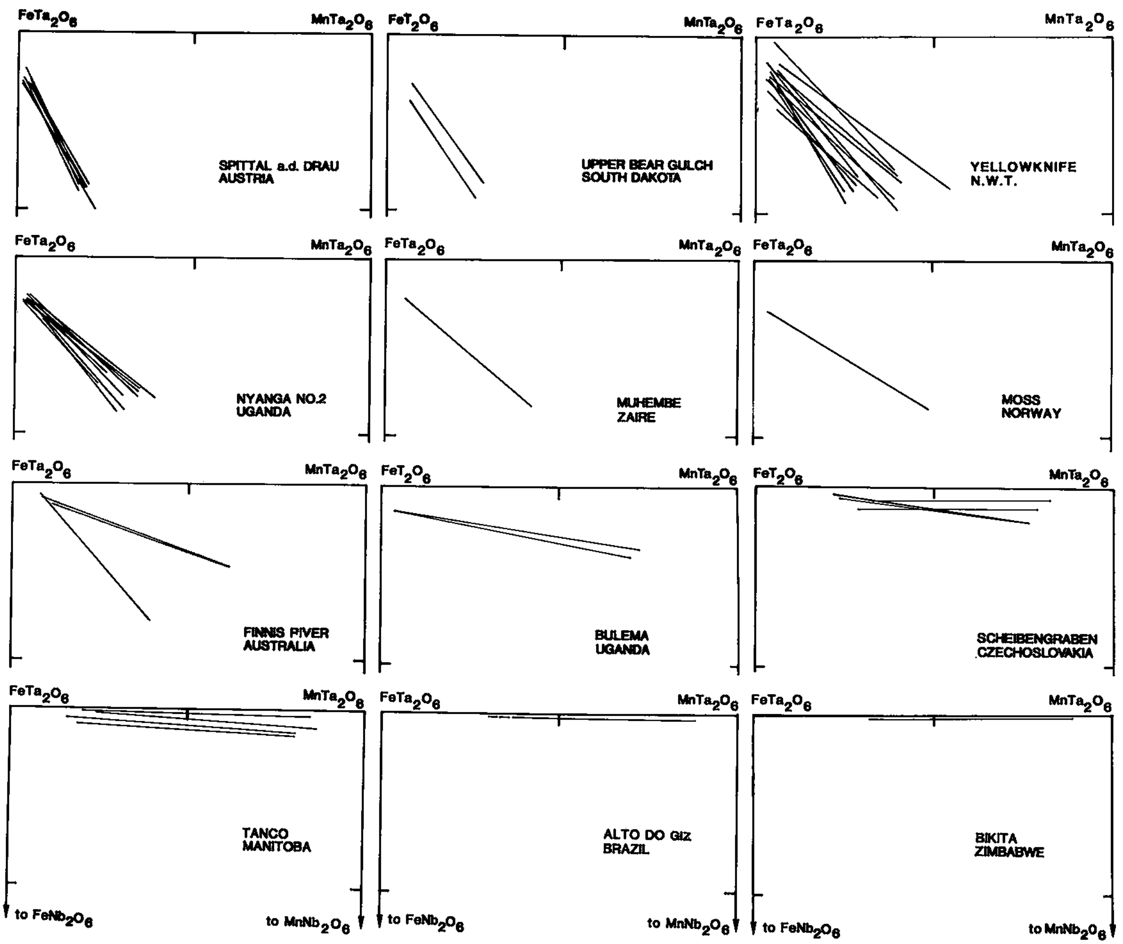

FIG. 3. Pairs of coexisting (or associated) natural ferrotapiolite and tantalite from the twelve localities examined in the present study; see text and Table 1 for descriptive comments.

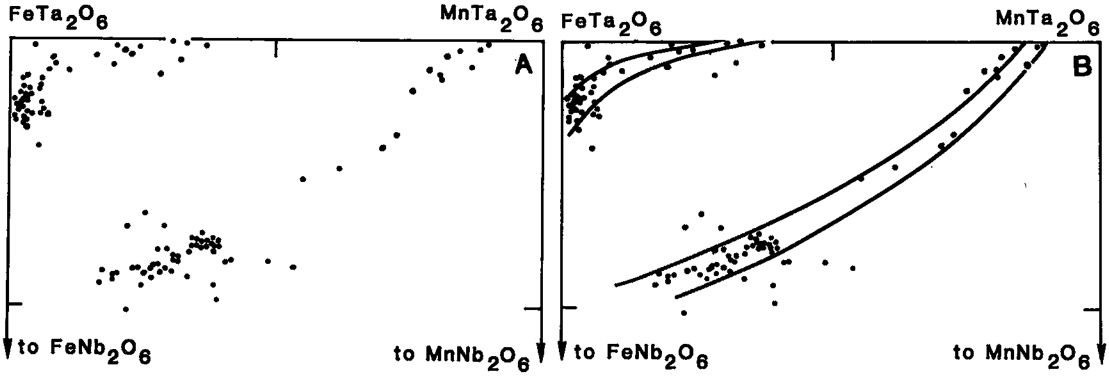

FIG. 4. Summary of data points shown in individual parts of Figure 3 (A), and position of data bands encompassing 80% of the examined ferrotapiolite and tantalite compositions (B).

DISCUSSION

Character of the data on individual localities

It is evident from Figure 3 that the tie-lines linking coexisting grains of ferrotapiolite and tantalite sweep across the length of a two-phase region that is similar to that shown in Figure lF. However, the nature of the data varies widely among the individual localities. The best internal consistency is shown by the Spittal data-set, obtained on material recrystallized (and presumably re-equilibrated) during Alpine regional deformation imposed on the Hercynian pegmatite host (Černý *et al.* 1989b). Similar consistency is suggested by most of the data pairs from Nyanga #2, except those with Ta-enriched compositions of tantalite; these are relics from one of the precursor phases identified in this exsolution intergrowth (Černý *et al.* 1989a). Compositions of the late ferrotapiolite + tantalite pairs that replace or postdate simpsonite at Tanco, Bikita and Alto do Giz are very close, indicating analogous conditions of crystallization (Ercit 1986).

In contrast, the data obtained on the Finnis River specimens (Jutz 1986) are considerably divergent, strongly suggestive of disequilibrium. The Yellowknife set is particularly disturbed: it represents a summary of data obtained on specimens found in a broad range of pegmatites (which accounts for the wide range of Fe/Mn values). Also, as already stressed above, the minerals are separated by silicate matrix and consequently are not truly coexisting (which accounts for some of the scatter in Nb/Ta values). Moreover, the presence of crossing tie-lines suggests that the associated phases did not reach equilibrium. The same applies to the Scheibengraben compositions, with slopes of two tie-lines opposite to those from other localities.

The structural state of the minerals examined is variable. A structurally uniform suite of mineral pairs could not be assembled because of the general scarcity of coexisting tantalite and tapiolite. Both phases show a high degree of order at Spittal a.d. Drau, Tanco, Alto do Giz and Bikita, but intermediate disorder at Upper Bear Gulch, Yellowknife, Muhembe, Moss, Bulema and Scheibengraben. The Nyanga ferrotantalite is moderately disordered, but the coexisting tapiolite is highly ordered. No data are available for the Finnis River minerals.

General trend of coexisting phases

Despite the diversified provenance of the above data sets and their variable quality, most of the compositions are well aligned across the quadrilateral (Figs. 4B, 5). Relatively narrow belts are defined by 80% of all the data points, most of the remaining compositions belonging to the collection of the most disturbed Yellowknife pairs. These belts can be considered general empirical boundaries of the two-phase field for natural minerals in the columbite quadrilateral.

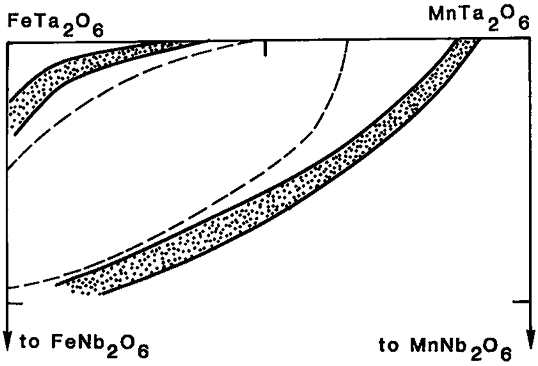

FIG. 5. Comparison of the bands of coexisting (or associated) ferrotapiolite and tantalite compositions of Figure 4B (dotted) with the two-phase field outlined by singular data in Figure lF (dashed).

Based on compositions of coexisting phases, these belts define the two-phase region much better than the margins of compositional fields of single phases shown in Figure lF. This is supported by the fact that the belts of coexisting compositions are situated within the fields defined by single phases. This strongly suggests that individual tantalite and ferrotapiolite compositions inside the two-phase field defined by coexisting compositions may well be metastable, prone to unmix under suitable conditions (*cf.* Černý *et al.* 1989a; see also Graham & Thornber 1974).

It must be stressed again that the boundaries derived from the data are strictly empirical, characterizing natural ferrotapiolite–tantalite compositions coexisting in granitic pegmatites. The relationship of these boundaries to specific values of diverse physical and chemical parameters cannot be quantitatively defined at present. Nevertheless, the qualitative appraisal that follows suggests a more or less pronounced sensitivity of the boundaries to conditions of crystallization.

Factors controlling the two-phase region

Figure 6 schematically demonstrates shifts in the boundaries of the two-phase field as they are known, or suspected, at present.

Temperature is probably the most effective modifier of the ferrotapiolite–tantalite gap, but the experimental evidence is contradictory. Schröcke's (1966) results indicate that the two-phase field broadens as temperature decreases from 1100 to 900°C, whereas Komkov's & Dubik's (1974a) experiments at 1100–300°C in the system $FeNb_2O_6$–$FeTa_2O_6$ suggest the opposite. Within the quadrilateral, Komkov & Dubik (1974a) claimed broadening of the tapiolite field from 1100 to 200°C,

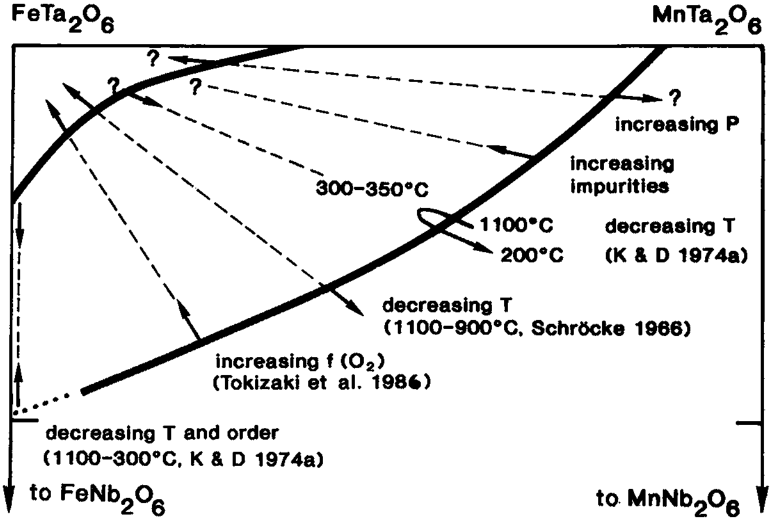

FIG. 6. Schematic illustration of shifts in the two-phase field boundaries induced by variations in temperature, pressure, oxygen fugacity, structural state and heterovalent substitutions.

whereas the columbite–tantalite field initially expands somewhat (to 300–350°C) and dramatically shrinks on further cooling (at 200°C; *cf.* Fig. 2B). In view of the above inconsistencies, there is no straightforward answer available at present to the question of the temperature factor.

The fugacity of oxygen also is a potentially important variable, as shown by Komkov & Dubik (1974a) and Tokizaki *et al.* (1986). According to the latter authors, increasing $f(O_2)$ favors the orthorhombic structure, at least for the $FeNb_2O_6$ composition.

Structural state was reported by Komkov & Dubik (1974a) to affect the field boundaries. Increased degree of order of synthetic phases at higher temperatures is claimed to be responsible for the widening gap between orthorhombic and tetragonal structures in the system $FeNb_2O_6$–$FeTa_2O_6$ (Komkov & Dubik 1974a, Fig. 5).

Impurities that disturb the simple AB_2O_6 stoichiometry of the tetragonal and orthorhombic phases were not examined experimentally. However, compositions of natural ixiolite with substantial proportions of Sn, Ti, Sc, Fe^{3+} or W are known to populate most of the two-phase region in the columbite quadrilateral. Although the effect of the above cations on the field of ferrotapiolite is not known, they do expand the columbite–tantalite field, and thus reduce the width of the two-phase region.

Pressure effects are not known at present. We can only speculate that increasing pressure may expand the two-phase field at the expense of both ferrotapiolite and columbite–tantalite regions.

In view of the above variables, it is rather surprising that the scatter in the compositions that empirically define the boundaries is so limited. If we eliminate the extreme data from the Yellowknife field as caused by disequilibrium (Figs. 4B, 5), we may conclude that the belts closely approximate an isothermal section through a pseudoquaternary solvus. This is probably true for the boundaries in the Fe > Mn part of the quadrilateral, defined by primary ferrotapiolite–ferrotantalite pairs from blocky zones and albitic units: the boundaries indicate *essentially uniform conditions of their crystallization.* However, the uppermost segments of the boundaries, close to the ferrotapiolite–manganotantalite edge of the quadrilateral, are defined by late associates of simpsonite. These ferrotapiolite–manganotantalite pairs undoubtedly precipitated at temperatures *distinctly lower* than did the primary Nb-enriched pairs.

SUMMARY

Empirical boundaries of the ferrotapiolite–tantalite gap, based on pairs of coexisting or associated minerals, approach equilibrium conditions much more closely than those separating compositions of isolated ferrotapiolite and tantalite, as established earlier (Černý & Ercit 1985, 1989). Single-phase compositions located inside the two-phase field defined by coexisting minerals are metastable. This is demonstrated by the relict character of their representatives, which are otherwise largely equilibrated into ferrotapiolite–tantalite pairs (Černý *et al.* 1989a).

The shape, extent and location of the two-phase region are controlled by temperature, $f(O_2)$, structural state of the coexisting phases, impurities that affect their stoichiometry, and probably also by pressure. In spite of the experimental work performed to date, the quantitative role of these variables is poorly understood, and in some cases even the qualitative sense of changes induced by the above factors is not reliably established.

Experimental determination of binary and pseudo-quaternary solvi is required, separately for disordered and ordered phases, through geologically realistic ranges of temperature and pressure. Modifications of these solvi by impurities (Sn, Ti, W, Sc, Fe^{3+}) and geochemically feasible changes in $f(O_2)$ should then be examined. Such a systematic study is the only approach that will result in proper understanding of natural conditions of ferrotapiolite + tantalite crystallization. At present, we can only stress that these conditions must be considerably uniform at different localities, and uniformly changing from primary to late secondary assemblages in the course of pegmatite consolidation.

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