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Some recent advances in the mineralogy and geochemistry of Nb and Ta in rare-element granitic pegmatites

Petr Černý, T. Scott Ercit

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Abstract

A review of the current understanding of the chemistry and structural properties is provided for columbite-tantalite, ferrotapiolite-manganotapiolite, ixiolite, wodginite, tantalian and niobian rutile, tantalian-niobian cassiterite, and the pyrochlore group. Understanding of the crystal chemistry of some of the most common species appears to be rather spurious.

Paragenetic assemblages of primary Nb, Ta-bearing minerals typical of different classes of rare-element pegmatites are summarized. They show extensive gaps in upgrading old and partly obsolete information. In contrast, a review of recently discovered "exotic" Nb, Ta-bearing minerals is complemented by a summary of late alterations and replacements which is well documented. Extensive variety in fractionation of columbite-tantalite is demonstrated on some pegmatites, pegmatite groups and fields. More data from different pegmatite types are required, in conjunction with experimental work, to understand the factors regulating the course of fractionation.

Compositional and structural stabilities are poorly understood. They require thorough experimental investigation, under conditions comparable to those of crystallizing pegmatite melts and fluids.

Résumé

On a procédé à l'examen des données existantes sur la composition chimique et les propriétés structurales de columbite-tantalite, ferrotapiolite-manganotapiolite, ixiolite, wodginite, rutile tantalifère et niobifère, cassitérite niobo-tantalifère, et du groupe de pyrochlore. La compréhension de la cristallochimie de certaines de ces espèces apparaît quelque peu erronée.

La synthèse des observations sur les paragenèses primaires des minéraux de Nb-Ta, caractéristiques des différents types de pegmatites à éléments rares, met en évidence des lacunes considérables lorsque l'on réinterprète les anciennes données partiellement désuètes. Par contre, les données sur les minéraux "exotiques" niobo-tantalifères, récemment découverts, sont complétées par un résumé bien documenté des phénomènes de remplacement et d'altérations tardives.

On met en évidence des variations considérables du fractionnement chimique de la columbite-tantalite dans certaines pegmatites et districts pegmatitiques. Afin de comprendre les facteurs qui président à ce fractionnement, il est indispensable d'acquérir les données supplémentaires sur différents types de pegmatites, complétées par des études expérimentales.

Les conditions de stabilité chimique et structurale sont mal connues. Leur compréhension nécessite une étude expérimentale détaillée, menée dans des conditions comparables à celles de la cristallisation des bains et fluides pegmatitiques .

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Some recent advances in the mineralogy and geochemistry of Nb and Ta in rare-element granitic pegmatites

by PETR ČERNÝ and T. SCOTT ERCIT

Department of Earth Sciences, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2.

Abstract. — A review of the current understanding of the chemistry and structural properties is provided for columbite-tantalite, ferrotapiolite-manganotapiolite, ixiolite, wodginite, tantalian and niobian rutile, tantalian-niobian cassiterite, and the pyrochlore group. Understanding of the crystal chemistry of some of the most common species appears to be rather spurious.

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Compositional and structural stabilities are poorly understood. They require thorough experimental investigation, under conditions comparable to those of crystallizing pegmatite melts and fluids.

Key words : niobium, tantalum, mineralogy, geochemistry, pegmatites.

Progrès récents dans la minéralogie et la géochimie du Nb et du Ta dans les pegmatites granitiques à éléments rares.

Résumé. — On a procédé à l'examen des données existantes sur la composition chimique et les propriétés structurales de columbite-tantalite, ferrotapiolite-manganotapiolite, ixiolite, wodginite, rutile tantalifère et niobifère, cassitérite niobo-tantalifère, et du groupe de pyrochlore. La compréhension de la cristallochimie de certaines de ces espèces apparaît quelque peu erronée.

La synthèse des observations sur les paragenèses primaires des minéraux de Nb-Ta, caractéristiques des différents types de pegmatites à éléments rares, met en évidence des lacunes considérables lorsque l'on réinterprète les anciennes données partiellement désuètes. Par contre, les données sur les minéraux "exotiques" niobo-tantalifères, récemment découverts, sont complétées par un résumé bien documenté des phénomènes de remplacement et d'altérations tardives.

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Les conditions de stabilité chimique et structurale sont mal connues. Leur compréhension nécessite une étude expérimentale détaillée, menée dans des conditions comparables à celles de la cristallisation des bains et fluides pegmatitiques.

Mots-clés : niobium, tantale, minéralogie, géochimie, pegmatites.

INTRODUCTION

It might be considered superfluous to review the niobium- and tantalum-bearing minerals occurring in granitic pegmatites, when a mere two years has elapsed since this subject was dealt with so competently by Foord (1982). However, there are two compelling reasons for a new look at this mineral family : its systematics have been expanded by several additions and corrections, and its paragenetic, geochemical and stability relationships were not a primary subject of the above paper. Thus the present review provides a brief account of the Nb, Ta-bearing species discovered since the nineteen sixties, and of new developments concerning some of the well-established mineral groups. Nb, Ta-bearing mineral assemblages in the different pegmatite types of the rare-element class are then reviewed. Complexity of geochemical fractionation trends

and variations in structural state are demonstrated on the example of the columbite-tantalite group and some closely related species. Problems of stability and equilibrium are considered in the concluding section.

Rarely is a comprehensive treatment attempted in this paper. Original sources are referenced whenever a substantial progress has been recently achieved ; otherwise, this study focusses on those twilight areas which remain largely unexplored and require our attention in the future.

SYSTEMATICS AND CRYSTAL CHEMISTRY

New exotica

Behierite, $TaBO_4$ (Mrose and Rose, 1961), a tetragonal mineral with zircon-type structure, was the first species to suggest that, given suitable compositional and physical parameters of parental fluids, more minerals of Nb and Ta with "unorthodox" composition may be expected in granitic pegmatites. The discovery of a variety of new mineral species, found particularly in late replacement and alteration assemblages, began shortly afterwards.

Rankamaite (v. Knorring *et al.*, 1969*d*) replaces simpsonite in alluvial pebbles from Kivu, Zaire. It was assigned the formula $(Na,K,Pb,Li)_6(Ta,Nb,Al)_{22}(O,OH)_{60}$, and orthorhombic symmetry. A (K>Na)-bearing, Sb-enriched analogue from the Kola Peninsula was named *sosedkoite* $(K,Na,Ca)_5Al_2(Ta,Nb,Sb)_{22}O_{60}$, and the structures of both species were likened to that of synthetic $K_3Li_2Ta_5O_{15}$ (Voloshin *et al.*, 1982*a*). Voloshin *et al.* also reanalyzed rankamaite and proposed the formula $(Na,K,Pb)Al_2(Ta,Nb,Fe)_{22}(O,OH)_{60}$. Unfortunately, the mineral was far too fibrous for single-crystal examination, and even general aspects of its structural chemistry are still unknown.

Holtite was another pegmatite mineral found first in alluvial pebbles, associated with stibiotantalite and tantalite (Pryce, 1971). Its structure and complex chemical composition, essentially an (Al,Ta,Nb,Sb)-borosilicate, are related to those of dumortierite. This relationship was confirmed by Voloshin *et al.* (1977) who proposed a formula $XY_{6-n}[\{(Al,As)_kSi_{1-k}\}O_4]_3[B_{1-m}O_3](O,OH)_{2-3}$, where $X = R^{5+}$ (Ta,Nb, Sb),Al,Fe^{3+},R^{2+} ; Y = Al ; $m+n < 1$, and $k \simeq (m+n)/3$.

A series of late Ta-rich minerals from Kola Peninsula was described during the past 4 years by Voloshin *et al.* *Alumotantite*, $AlTaO_4$, described by Voloshin *et al.* (1981*a*) as orthorhombic and related to the stibiotantalite-bismutotantalite group, was re-oriented and found to be orthorhombic (*Pbcn*) with a different structure type, new among the (Al,Ga)(Nb,Ta)O_4 compounds (Ercit *et al.*, 1985*d*).

Natrotantite was originally assigned the formula of $NaTa_3O_8$ and monoclinic symmetry *C*2/*c* (Voloshin *et al.*, 1981*a*). However, an excellent match was found later between the natural natrotantites from Kola and Brazil and the synthetic hexagonal ($R\bar{3}c$) compound $Na_2Ta_4O_{11}$ (Ercit *et al.*, 1984 and 1985*e*). Deviations from this ideal composition could be due to the substitution of $Na^{1+} + O^{2-}$ by $\square + (OH)^{1-}$.

The structure of natrotantite is also related to those of synthetic $Na_2Nb_4O_{11}$ and $CaTa_4O_{11}$ (Ercit *et al.*, 1985*e*). The natural analogue of the latter compound was discovered by Voloshin *et al.* (1982*b*) and named *calciotantite*.

Lithiotantite, $Li(Ta,Nb)_3O_8$, (Voloshin *et al.*, 1983*b*) is monoclinic, $P2_1/c$, by analogy of its X-ray powder diffraction pattern with synthetic, low-temperature polymorphs of $LiTa_3O_8$ (Gatehouse and Leverett, 1972). It is noteworthy that there is another monoclinic, intermediate-temperature polymorph of $LiTa_3O_8$ which is isostructural with wodginite (Gatehouse *et al.*, 1976) ; so far it has no natural counterpart.

Tantite, Ta_2O_5 (Voloshin *et al.*, 1983*a*) occurs in association with microlite, stibiotantalite, holtite and a $CaTa_4O_{11}$ phase (which seems to be distinctly different from calciotantite). The X-ray powder diffraction pattern of tantite was interpreted as reasonably close to that of the triclinic polymorph of Ta_2O_5.

Among the complex, (Ca,REE,U,Th)-bearing and mostly metamict minerals with the aeschynite structure, three new species were recently discovered : *rynersonite*, $Ca(Ta,Ti,Nb)_2O_6$ (Foord and Mrose, 1978), its Nb-rich counterpart *vigezzite*, $(Ca,Ce)(Nb,Ta,Ti)_2O_6$ (Graeser *et*

al., 1979), and *tantalaeschynite* (Ca,Y,Ce,Th,U)(Ta,Ti,Nb)$_2$O$_6$ (Adusumili *et al.*, 1974). Vigezzite seems to be a polymorph of orthorhombic fersmite which has the same composition but a columbite-type structure.

Petscheckite, $U^{4+}Fe^{2+}(Nb,Ta)_2O_8$ and *liandratite*, $U^{6+}(Nb,Ta)_2O_8$, were found by Mücke and Strunz (1978) near Berere, Madagascar. Recrystallization of these metamict minerals restores structures resembling synthetic $U^{6+}Ta_2O_8$.

Although not a separate mineral species, the *niobian wolframite* from Mozambique should be mentioned because of its high Nb_2O_5 content (Saari *et al.*, 1968).

The first and so far only phosphate with Nb and Ta was found in the Black Hills of South Dakota : *olmsteadite* has the formula $K_2Fe_2^{2+}[Fe_2^{2+}(Nb,Ta)_2O_4(H_2O)_4(PO_4)_4]$, and is structurally related to montgomeryite and vauxite (Moore *et al.*, 1976).

The most recent discoveries include zimbabweite, $(Na,K)_2PbAs_4(Ta,Nb,Ti)_4O_{18}$ from Zimbabwe (Gaines *et al.*, 1984, and Foord *et al.*, 1985) and a mineral which seems to be, on the basis of semiquantitative estimate of chemical composition, its phosphate analogue (unpublished data of the authors).

The "classic" species

Columbite-tantalite group

This orthorhombic group encompasses ferrocolumbite, $Fe_4Nb_8O_{24}$, manganocolumbite, $Mn_4Nb_8O_{24}$, manganotantalite, $Mn_4Ta_8O_{24}$, and ferrotantalite compositions, $(Fe>Mn)_4(Ta>Nb)_8O_{24}$, with the structure highly ordered (as described by Sturdivant, 1930) up to essentially disordered (as described by Nickel *et al.*, 1963*a*, for "pseudo-ixiolite"). Disordered members of the columbite-tantalite group, $(Fe,Mn,Nb,Ta)_4O_8$ with $a \simeq 4.71$-4.76, $b \simeq 5.75$, $c \simeq 5.12$-5.16 Å, develop an ordered structure on heating at about 1000°C : $(Fe,Mn)_4(Nb,Ta)_8O_{24}$ with $a \simeq 14.26$-14.43 (3×4.7 Å), $b \simeq 5.75$, $c \simeq 5.05$-5.08 Å. The structures of both ordered and disordered phases tolerate minor quantities of Fe^{3+}, Sc^{3+}, Ti^{4+} and Sn^{4+}.

A new magnesian end member was added by Matias *et al.* (1963) and re-investigated by Kornetova *et al.* (1971) : magnocolumbite was described from pegmatites crosscutting dolomitic marbles in southwest Pamir, and from a second occurrence in Siberia (Nedashkovskyi *et al.*, 1967). Magnocolumbite evidently forms under the very unusual conditions of Mg saturation and virtual absence of Fe. At the type locality, its parent pegmatites also carry spinel, anthophyllite, cordierite and dravite, all of them extremely magnesian. Thus it is not surprising that it has been found in only two localities.

Most descriptions of the (Fe,Mn)-based minerals of this group found in the older literature are inadequate for quantitative characterization of structural state and chemistry. We have started a study aimed at expanding the existing data base and properly defining the compositional and order-disorder ranges. Preliminary results are shown in figure 1A, based on the data by Haapala *et al.* (1967), Černý and Turnock (1971), Zelt (1975), Foord (1976), Černý *et al.* (1979), Sahama (1980), Wang *et al.* (1981), Ucakuwun (1981), v. Knorring and Fadipe (1981), Černý *et al.* (1981*b*, 1985*a*,*b*,*c*), Ferreira (1984), Anderson (1984), Wise and Černý (1984), Ercit (1985), Paul (1984), Wise (1985), and much unpublished data. The samples come from many pegmatite fields in Africa, notably Mozambique, Zimbabwe and Uganda ; from California, Arizona, New Mexico, Virginia, New England States and South Dakota in the United States ; Ontario, Manitoba, the Yellowknife field and Baffin Island in Canada ; and from several localities in France, Finland, Germany, Czechoslovakia, Brazil and China. The data set may show some bias in terms of geographic distribution, geological age, pegmatite type and degree of fractionation. Nevertheless, the sample population seems to be large and diversified enough to draw several conclusions.

Columbite-tantalite shows only a few data in the $Nb_{2.0}$ to $(Nb_{1.90}Ta_{0.10})$ region of the compositional quadrilateral (Figure 1A), and only two points inside the $Fe_{1.0}$ to $(Fe_{0.9}Mn_{0.1})$ area. This is a geochemical feature, as synthetic compounds of these compositions can be readily produced. The gap between the (Fe,Ta)-rich compositions in the ferrotantalite quadrangle and the field of tetragonal tapiolite, $FeTa_2O_6$, is broader than shown in the reviews of pre-1970 literature (*e.g.*, Kuznetsov, 1956 ; Moreau and Tramasure, 1965 ; Gouder de Beauregard *et al.*,

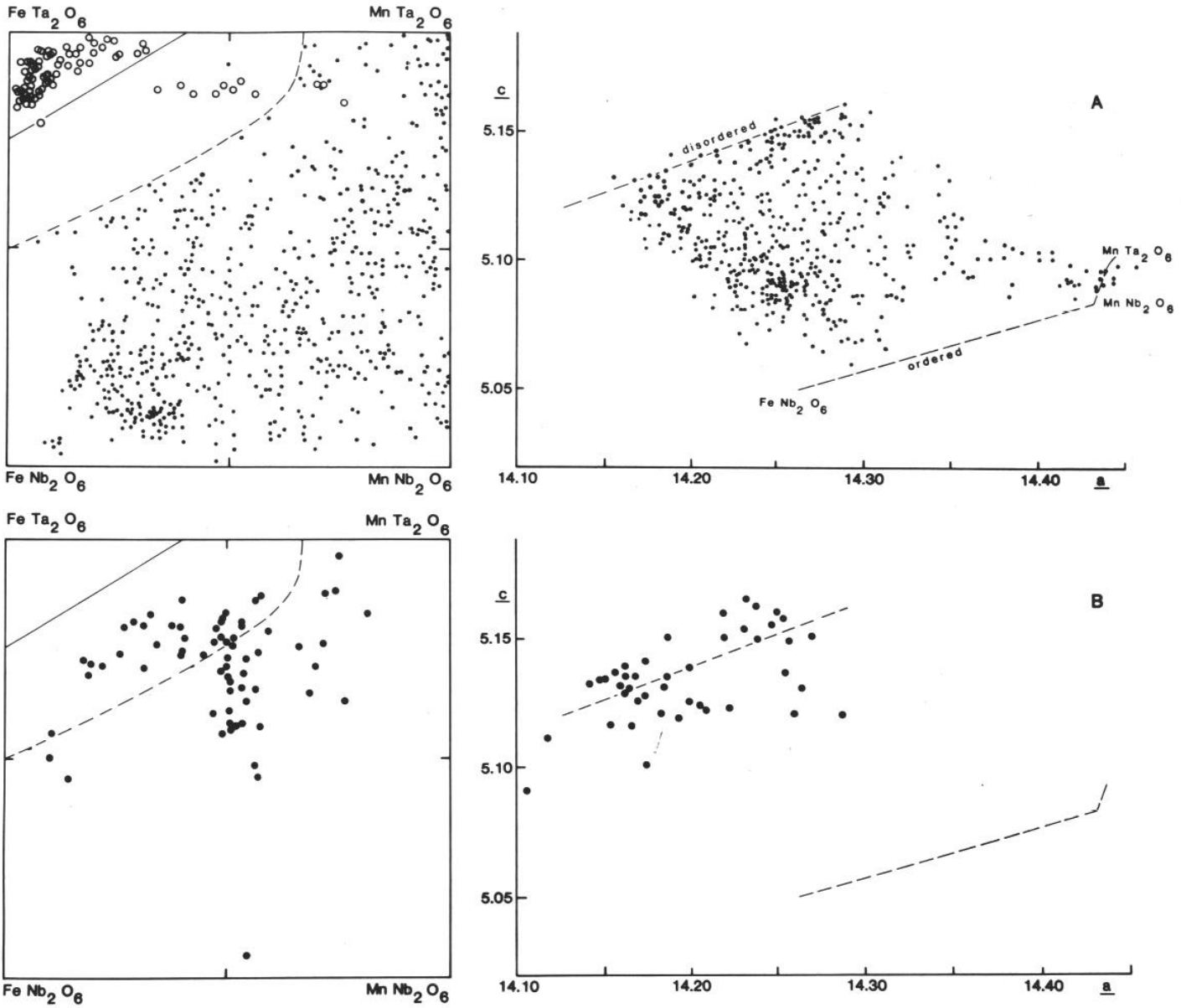


FIG. 1. — *Compositional fields (left) and structural states (right) of columbite-tantalite (●) and tapiolite (o) (A), and ixiolite (B).* See text for sources of data.

Domaines de composition (à gauche) et états structuraux (à droite) de : columbo-tantalite (●), tapiolite (o) (A) et ixiolite (B). Voir le texte pour la source des données.

1967). Older data sets are obviously plagued by analyses of columbite-tapiolite mixtures and/or errors in Nb and Ta determination.

The *a*/*c* ratio of columbite-tantalite was found a suitable order-disorder indicator by Komkov (1970) ; the unit cell expands along *c* and contracts along *a* with increasing disorder. Černý and Turnock (1971) introduced the *a* (3*a* for disordered phases) vs. *c* plot as a convenient graphic representation of the degree of ordering. This plot also indicates the approximate Fe/Mn ratio but it is relatively insensitive to changes in Nb/Ta.

In its present modification shown in figure 1A, the *a* vs. *c* diagram is based on new unit cell dimensions determined for Turnock's (1966) synthetic ordered $Fe_6Nb_8O_{24}$, $Mn_4Nb_8O_{24}$ and $Mn_4Ta_8O_{24}$ (M.A. Wise, pers. comm. 1984). The bounding cell dimensions in the disordered $(Mn,Ta)_4O_8$ corner were selected from the extreme values for natural phases approaching this composition. The $(Fe,Nb)_4O_8$ corner was approximated as an intersection of the empirical borderline for the ($Fe \gtrless Mn$, $Nb \gtrless Ta)_4O_8$ compositions (''disordered'' line in figure 1A) with the average slope of tielines

joining natural disordered minerals and their heated counterparts, drawn from the ordered $Fe_4Nb_8O_{24}$ corner.

Moreau and Tramasure (1965, run No. 201) happened to synthesize disordered columbite-tantalite, but there has been no systematic effort to grow disordered phases, and the data of the above authors cannot be considered as representative. Disordered structural end-members were undoubtedly grown by Komkov and co-authors at several occasions, but the unit cell dimensions were not published.

The columbites-tantalites examined so far exhibit a wide range of order-disorder, and they confirm the opinions of Giese (1975) and Sahama (1980) that disordered phases may be widespread in this group (Figure 1A). The dense cluster of data at about $a = 14.24$ and $c = 5.08$ Å probably reflects a sampling bias, in part corresponding to the cluster in the ferrocolumbite quadrangle of the compositional diagram (Figure 1A). The vacant region between the ferroan extremes of the order-disorder field is related to the lack of extremely ferroan compositions among natural minerals, as commented on earlier. Otherwise, the data indicate an almost uniform distribution of all degrees of order except the more or less completely ordered state close to the synthetic phases. There also seems to be a low population density in the structurally intermediate region at the Mn-rich side of the diagram, at about $a = 14.34$ and $c = 5.125$ Å, with an apparent bimodal distribution close to the extremes of order and disorder. More data should be collected for this compositional range to clarify this pattern.

Ferrotapiolite-manganotapiolite

The tetragonal tapiolite was thoroughly re-investigated by Clark and Fejer (1978), but the present nomenclature is based on the recent study of Lahti *et al.* (1983). Tapiolite is a group name covering two end-member species, ferrotapiolite $Fe_2Ta_4O_{12}$ and manganotapiolite $Mn_2Ta_4O_{12}$.

Limited compositional variation in the tapiolite group was confirmed by the above authors within the previously recognized range, and substitution of Sn and Ti was found to be very restricted. As shown by Khvostova and Archangelskaya (1970), Fe^{3+} is also an important component of some tapiolites.

In figure 1A, Clark and Fejer's (1978) data are complemented by those of Černý and Harris (1973), v. Knorring and Fadipe (1981), Ferreira (1984), Wise (1984), Ercit (1985) and Černý *et al.* (1985*a*,*c*). All of these data fit into the experimentally established tapiolite field of Moreau and Tramasure (1965). However, some analyses obtained by Lahti *et al.* (1983) on a small zoned crystal cross the compositional gap into the columbite-tantalite field (Figure 1A). The most Mn-rich of these correspond to the new species manganotapiolite.

Clark and Fejer (1978) confirmed the existence of disordered, monorutile-type tapiolites, $(Fe,Ta)_2O_4$ ($a \simeq 4.755$, $c \simeq 3.095$ Å ; *cf.* Hutton, 1958) and intermediate structural states transitional to ordered trirutile-type tapiolite, $Fe_2Ta_4O_{12}$ ($a \simeq 4.755$, $c \simeq 9.22 \simeq 3 \times 3.07$ Å). They also recognized the influence of Nb, Ti and Mn substitutions on the unit cell dimensions. These are also affected by the incorporation of Fe^{3+}, and their variations with diverse compositional substitutions are currently being re-examined (Wise, 1985).

The persistent differences in chemical composition, symmetry and structure between tapiolite and columbite-tantalites have been known for a long time (*e.g.*, Permingeat, 1955). It was only recently that Weitzel (1976) provided a plausible explanation. According to him, the polarizing effect of Ta^{5+} on the surrounding oxygens, weaker in comparison with that of Nb^{5+}, favours the rutile structure for $FeTa_2O_6$. However, the ionic radius of Mn^{2+} is too large for the rutile structure, and $MnTa_2O_6$ crystallizes with the orthorhombic columbite structure. Thus it is not surprising that recent re-examination of the alleged Nb-dominant numbers of the tapiolite group, mossite (Brøgger, 1897) and manganomossite (Bowley, 1923) has led to their discreditation (Ewing, 1976 ; Dunn *et al.*, 1979).

Ixiolite

As defined by Nickel *et al.* (1963*a*), ixiolite is a complex oxide with the formula $(Ta,Nb,Sn,Fe,Mn,Ti)_4O_8$ and an orthorhombic unit cell corresponding to that of disordered columbite-tantalite (*Pbcn* ; $a \simeq 4.78$, $b \simeq 5.76$, $c \simeq 5.16$ Å). In contrast to disordered columbite-tantalite ("pseudo-ixiolite"), heating promotes ordering into the wodginite structure rather than the columbite structure. [The heating

product of Nickel's *et al.* (1963*a*) ixiolite was likened to "olovotantalite" of Matias (1961), which can be interpreted as a pseudo-orthorhombic, disordered wodginite. Heating of the type Skogsböle ixiolite under somewhat more extreme conditions (1000°C/16 hrs.) than those used by Nickel *et al.* (1963*a*) produces a definite wodginite pattern (M.A. Wise, pers. comm. 1984), comparable to others obtained by us on other ixiolites from diverse localities.]

An expanded application of the term ixiolite was proposed by Graham and Thornber (1974*a*) for all phases that have the small cell of the columbite-tantalite substructure, including disordered columbites-tantalites ("pseudo-ixiolites"). In our opinion, this is an overgeneralization which obscures the fundamental structural and compositional differences between "pseudo-ixiolites" as disordered counterparts of columbite-tantalite, with only minor contents of Sn,Ti, etc., and true ixiolites with major contents of Sn,Ti,Fe^{3+},Sc,W, etc., that have no compositional or heating-product relationship to ordered columbite-tantalite but produce their own ordered analogues on heating.

Even after eliminating disordered columbite-tantalite from consideration, ixiolite represents quite a spectrum of compositional varieties. Besides the type chemistry rich in Sn, varieties with substantial Sc^{3+}, Fe^{3+}, W^{6+}, Ti^{4+}, U and Nb > Ta have been discovered during the last 15 years.

Scandian ixiolite with over 10 wt.% Sc_2O_3 and Fe_2O_3 > FeO, (Nb ≷ Ta,Fe^{3+},Fe^{2+},Sc,Ti, Zr,Sn,Mn,REE)$_4O_8$, was described from Mozambique and Madagascar by v. Knorring *et al.* (1969*b*) and Borisenko *et al.* (1969). Heating of this mineral produces a phase with the wolframite $Fe^{3+}NbO_4$-type structure.

Wolframoixiolite, (Nb,W,Fe,Mn,Ta,Zr,U, Ca,Mg,Ti)$_4O_8$, was reported from an unknown locality, possibly a pegmatite (Ginsburg *et al.*, 1969). It is associated with microcline, fluorite, quartz and secondary wolframite, and it contains very fine plates of ilmenite. On heating, it forms an ordered columbite-tantalite-type phase and a UTa_2O_8-type phase. Other W-rich phases such as the wolframian columbite and ixiolite described by Konovalenko *et al.* (1982) have not been sufficiently characterized, or they represent mixtures of orthorhombic phases with wolframite (*cf.* Fleischer, 1984). Similar problems are encountered in "wolframoixiolites" of non-pegmatitic origin (Amichba and Dubakina, 1976*a*,*b*). However, some W-rich "columbites" from wolframite-bearing quartz veins are homogeneous on electron microprobe scale (Beddoe-Stephens and Fortey, 1981 ; E.E. Foord, pers. comm. 1983) and may also occur in W-bearing pegmatites. Columbite-tantalite with low but persistent W content is widespread in the pegmatitic cupola of the Beauvoir granite at Echassières (Kosakevitch, 1976).

Titanian ixiolite (Ta,Ti,Nb,Mn,Fe,Sn)$_4O_8$, which forms a wodginite phase on heating, is known to contain up to 15.8 wt.% TiO_2 in the Tanco pegmatite (unpublished data of the authors). The titanian "columbite" described from alkalic pegmatites of the Ural Mountains and Siberia (Sveshnikova *et al.*, 1965) may also belong to this ixiolite variety, as it contains 10.57 to 12.82 wt.% TiO_2. It has the ixiolite-type cell in natural state but its behaviour on heating is not known. A similar case is probably represented by the "Ti-columbite" of v. Knorring and Fadipe (1981 ; table 1, anal. 9 ; 6.97 wt.% TiO_2 and 1.74 wt.% SnO_2).

Ashanite, (Nb,Ta,U,Fe,Mn)$_4O_8$, was described by Zhang *et al.* (1980) as a Nb-dominant member of the ixiolite group with substantial U content. However, several properties of this mineral are questionable (Foord, 1982) : discrepancies occur between unit cell dimensions and X-ray powder diffraction data, the mineral's response to heating was not tested, and the mineral was reported as non-metamict despite its content of 23.8 wt.% U_3O_8. Examination of a specimen of supposed ashanite given to R.V. Gaines showed at least seven different phases, but no ashanite (E.E. Foord, pers. comm. 1983).

Only the data on reliably identified and characterized ixiolites are shown in figure 1B, as extracted from Nickel *et al.* (1963*a*), v. Knorring *et al.* (1969*a* and *b*), Borisenko *et al.* (1969), Anderson (1984) and Wise (1985), together with unpublished data of the authors. The chemical compositions plotted on the columbite-tantalite quadrilateral show Ta > Nb for almost all samples, and show quite a few data falling between the tapiolite and columbite-tantalite fields of figure 1A. The (Sn+Ti)-(Nb+Ta)-(ΣFe+Mn) plot of figure 2 shows that the R^{4+}

content of ixiolites can reach 26 %. The presence of Fe^{3+} in some specimens is suggested by an excess of cations over 4.00 per 8 oxygens in the formula unit, and by their tendency to plot on the (Fe+Mn) side of the (Fe,Mn)(Ta,Nb)$_2$-(Sn,Ti) join. The overall scatter of points in figure 2 is probably the result of other substitutions involving Sc^{3+}, W^{6+} and U.

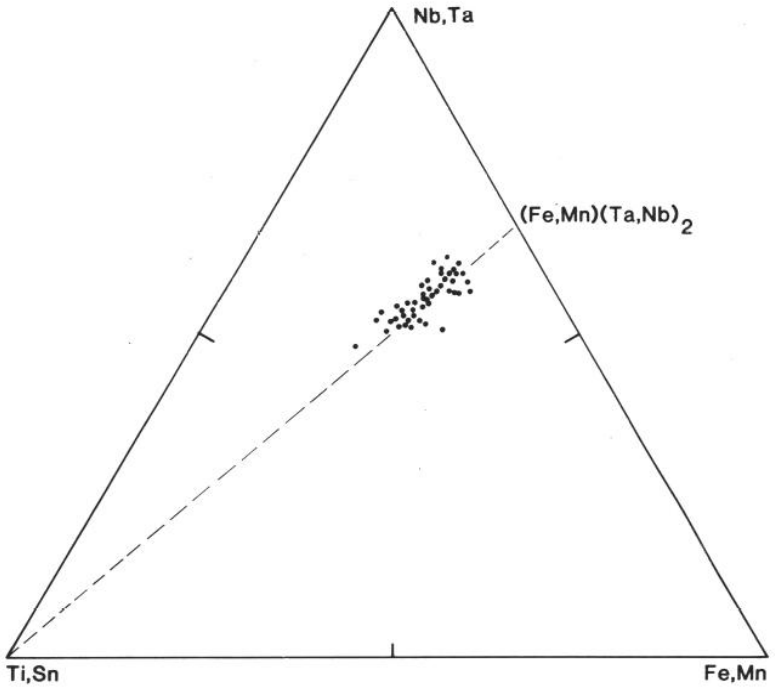


FIG. 2. — *Composition of ixiolite in the (Ti,Sn)-(Nb,Ta)-(Fe,Mn) diagram.* See text for sources of data.
Composition de l'ixiolite dans le plan (Ti,Sn)-(Nb,Ta)-(Fe,Mn). Voir le texte pour la source des données.

In the *a-c* diagram of figure 1B, the data are scattered above, below and to the left of the empirical limit for disordered columbite-tantalite. This could be due to the compositional variations among the samples, and to the possibility that some of these ixiolites are actually monoclinic phases (as discussed in the second next section).

Wodginite group

Wodginite was first described by Nickel *et al.* (1963*b*) as a monoclinic mineral with a unit cell content of (Ta,Mn,Sn,Nb,Fe,Ti)$_{16}$O$_{32}$. Its unit cell ($a \simeq 9.52$, $b \simeq 11.47$, $c \simeq 5.10$ Å, $\beta \simeq 91°$) was found to be related to that of disordered columbite-tantalite, with doubled *a* and *b* parameters. Progressive improvement of the structure refinement (Grice, 1973 ; Graham and Thornber, 1974*b* ; Ferguson *et al.*, 1976) confirmed the space group *C*2/*c* and the general formula $A_4C_4B_8O_{32}$, where A = Mn,Fe^{2+} ; C = Sn,Ti,Fe^{3+},Ta, and B = Ta,Nb.

Wodginites found in an increasing number of pegmatites have mostly been close to the manganoan, tin-rich and tantalian compositions of the type specimens (*e.g.*, Graham and Thornber, 1974*b*). A few samples have been described with elevated Fe^{2+} contents, some of them with Fe > Mn (Vorma and Siivola, 1967 ; v. Knorring *et al.*, 1969*a* ; Burke *et al.*, 1970). It was only recently that more extensive substitutions were recognized, involving both the A and C sites (Ercit, 1985).

Figure 3 illustrates variations in the main cation contents of the A and C sites as shown by electron microprobe analysis. A-site substitutions for Mn can involve considerable Fe^{2+} and vacancies. C-site substitutions for Sn mainly involve Ti, but substitution by Ta can also be substantial ; those involving Fe^{3+} tend to be less important. As with the pyrochlore group, Ta $\rightleftharpoons$ Ti isomorphism is limited, severely so in the absence of Sn (Figure 3B).

Three new end-members with the wodginite structure were approved by the International Mineralogical Association, Commission on New

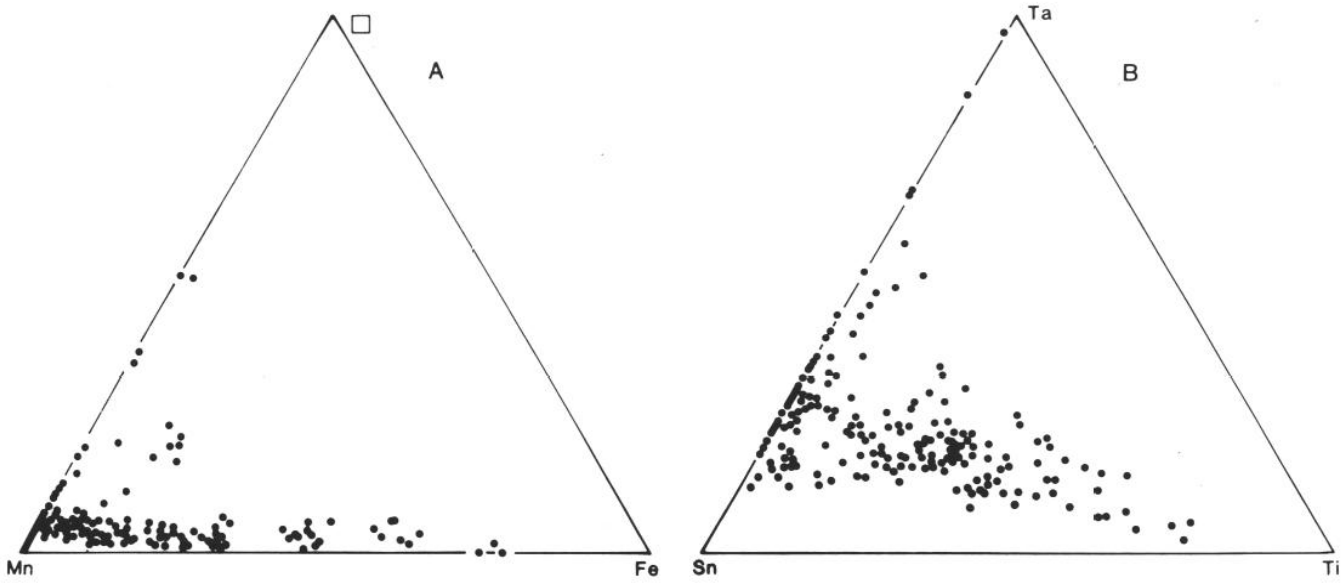


FIG. 3. — *Populations of the main cations (and vacancies) in the A-sites (A) and C-sites (B) of wodginite* (Ercit *et al.*, 1985*b*).

Distribution des cations majeurs (et lacunes) dans les sites A (A) et C (B) de la wodginite (Ercit *et al.*, 1985*b*).

Minerals and Mineral Names : ferrowodginite $Fe_4Sn_4Ta_8O_{32}$, titanowodginite $Mn_4Ti_4Ta_8O_{32}$, and tantalowodginite $(Mn_2\square_2)_{\Sigma 4}Ta_4Ta_8O_{32}$ (Ercit *et al.*, 1985*a*). The existence of a natural analogue to Turnock's (1966) synthetic Fe^{3+}-based phase is suggested by a mineral described by Kornetova *et al.* (1978), which may be interpreted as close to $(Fe,Mn)_4(Fe^{3+} > [Ti,Ta,Sn])_4(Ta,Nb)_8O_{32}$. However, this mineral occurs in an intimate intergrowth with a Sn-rich phase, and the X-ray powder diffraction data of the mixture suggest the presence of a columbite-type phase. Thus it is not possible to unambiguously assign symmetry and a cell to the above composition.

Partial disorder in wodginite was suggested by, *e.g.*, Khvostova *et al.* (1966) because of variable β, occasionally approaching 90°. Complementary effects of compositional factors must also be considered when assessing order-disorder by means of unit cell parameters, *e.g.* substitution of Mn by Fe and of Sn by Ti (v. Knorring *et al.*, 1969*a* ; Graham and Thornber, 1974*b*, unpublished data of the authors). A detailed report on the crystal chemistry of the wodginite group is in preparation (Ercit *et al.*, 1985*b*).

Ixiolite-wodginite transition

Several minerals were recorded in the literature, and more of them were found in our work, that show properties transitional between the ixiolite and wodginite structures. Compositionally, all of them are close to the Sn(±Ti)-rich chemistry of wodginite, with variable Fe/Mn ratios. However, structurally they can be characterized as either monoclinic ixiolites, or as pseudo-orthorhombic wodginites with strong ixiolite-type subcells and β only slightly larger than 90°. Polyakov and Cherepivskaya (1981) provided a detailed description of what seems to be a monoclinic ixiolite. Specimens studied by Lahti (1982) and Wise (1985), and some of our Fe,Ti-enriched wodginites from the Tanco pegmatite (Ercit *et al.*, 1985*a*,*b*) represent the pseudo-orthorhombic case. "Olovotantalite" of Matias (1961), interpreted by Nickel *et al.* (1963*b*) as a possibly orthorhombic phase with wodginite cell, probably belongs with these as well.

In view of the compositional similarities between wodginites and ixiolites, and of the total cation disorder in ixiolite (A_4O_8) as compared to the well-ordered wodginite ($A_4C_4B_8O_{32}$), it is possible that the transitional structural forms may well represent intermediate ordering states (Maksimova and Khvostova, 1970). Ordering may even follow different paths, *e.g.* via a reasonably gradual transition from ixiolite to wodginite with no new intermediate forms, or the same path but involving intermediate states.

These may be represented by, *e.g.*, a monoclinic $(A,C)_8B_8O_{32}$ type (Polyakov and Cherepivskaya, 1981) with no suggestion of the wodginite supercell, or an "early" pseudo-orthorhombic type but with a wodginite supercell indicated (such as "olovotantalite"). Nothing less than complete structure refinements are required for a series of these transitional phases of different compositions to clarify these relationships which have been referred to as "polymorphism" by Nickel *et al.* (1963*b*), order-disorder by Gorzhevskaya and Sidorenko (1974) and high-T vs. low-T phases by Černý (1975).

Tantalian and niobian rutile

These varieties of rutile (also known as strüverite and ilmenorutile, respectively), were characterized by Černý *et al.* (1964) and reviewed more recently by Černý *et al.* (1981*a*). Compositionally, they are interpreted as solid solutions of rutile, TiO_2, and "mono-tapiolite", $(Fe > Mn)(Nb \geqslant Ta)_2O_6$. However, they invariably show a slight to considerable excess of (Fe > Mn) over the 1:2 ratio to (Nb ≧ Ta). This ratio varies from the ideal value of 0.5 to as high as 2.10. This may be caused by the incorporation of either the rutile-type compound $Fe^{3+}NbO_4$ (Langhof *et al.*, 1980), or Fe alone, independent of the substitutions involving (Nb ≧ Ta). Cation totals normalized to 4 oxygens usually exceed the ideal value of 2.00, when all Fe is calculated as Fe^{2+}. The range of the totals is 1.97 to 2.16. Oxygen deficiency (Bursill and Blanchin, 1984), the incorporation of hydroxyl, and/or substitutions of the $Ti^{4+} \rightleftharpoons 2Fe^{2+}$ or $3Ti^{4+} \rightleftharpoons 4Fe^{3+}$ type may be responsible. Compositions containing substantial Fe^{3+}, occasionally to the exclusion of Fe^{2+} are well documented (Gordiyenko and Kulchitskaya, 1962 ; Lugovskoi and Stolyarova, 1969). Another compensating factor may be the presence of Ti^{3+} or Ti^{2+}, induced by the entrance of Fe^{2+} or Fe^{3+}, as proposed for Sn in cassiterite by Clark *et al.* (1976).

Figure 4A shows the bulk compositions of niobian and tantalian rutiles based on the data collected by Černý *et al.* (1981*b*), and complemented by those of Lebedeva (1968), Sahama (1978), Černý *et al.* (1985*b*), and by unpublished data of the authors. It is evident that the incorporation of cations other than Ti^{4+} can reach 67 at.%.

Most phases with compositions showing appreciable substitution and Nb predominant over Ta are heterogeneous, containing an exsolved columbite phase or, rarely, ilmenite (Figure 4B,C). In contrast, Ta-dominant compositions are homogeneous. Exceptions to this behaviour are very rare. The Nb/Ta and Mn/Fe ratios of the exsolved columbite are invariably higher than those of the parent (as well as exsolved) rutile phase, in keeping with the preference of Nb and Mn for the orthorhombic structure in co-existing columbite-tapiolite pairs. If W or Sc are present in the rutile phase, they also become preferentially concentrated into the exsolved columbite (Sahama, 1978 ; unpublished data of P. Černý and W.B. Simmons). As shown in figure 4B, the columbite phase is invariably enriched in Ti (2.5 to 8.0 wt.% TiO_2, 4-16 at.% Ti).

Structurally, all specimens examined to date have monorutile unit cells. The trirutile and birutile X-ray powder diffraction patterns reported by Flinter (1959) actually represent monorutile + columbite and monorutile + ilmenite mixtures, respectively (Černý *et al.*, 1964 ; Flinter, 1964). The structural state of the columbite phase seems to be disordered (Černý *et al.*, 1981*b*), and the exsolved phase rich in Ti may actually be ixiolite. However, the ordering style on heating was not examined to date.

Variation of unit cell dimensions with increasing substitution by the "mono-tapiolite" component was reported by Černý *et al.* (1964) and Sahama (1978). However, a re-examination of this relationship is desirable.

In conclusion, the occurrence of W-, Fe- and Sb-enriched rutile from a pegmatite in the Murchison Gold Fields, Western Australia should be mentioned (Graham and Morris, 1973). The composition does not provide a clue for the substitution mechanism.

Tantalian-niobian cassiterite

Cassiterite displays incorporation of a "monotapiolite" component in much the same manner as rutile. However, no systematic study has been so far attempted. Figure 4D shows a random collection of compositions from the literature (Clark *et al.*, 1976 ; Dunn *et al.*, 1978 ;

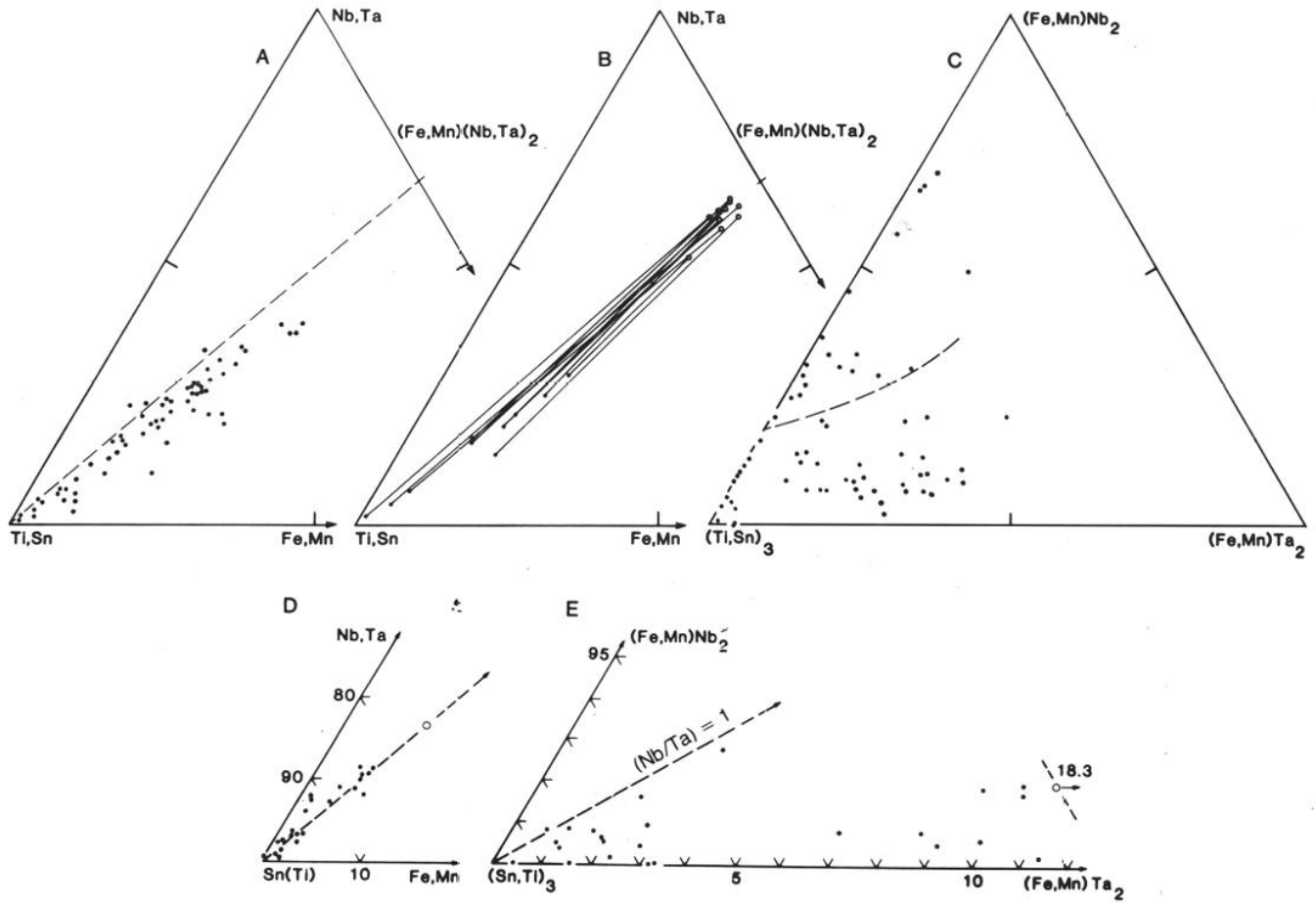


FIG. 4. — *Crystallochemical relationships in niobian-tantalian rutile and cassiterite :* bulk compositions (A), compositions of exsolved phases (B ; open circles designate columbite-tantalite) and bulk compositions of predominantly homogeneous and exsolved phases (C ; below and above dashed line, respectively) for rutile ; bulk compositions in two "systems" (D,E) for cassiterite (open circle denotes staringite).

Corrélations cristallochimiques pour le rutile niobo-tantalifère et la cassitérite : compositions globales (A), compositions des phases exsolvées (B ; les cercles vides représentent la columbotantalite), et compositions globales des phases en majorité homogènes et des phases en exsolution (C ; respectivement en-dessous et au-dessus de la ligne pointillée) dans le rutile ; compositions globales représentées dans les deux "systèmes" de la cassitérite (D, E ; cercle vide = staringite).

Černý *et al.*, 1981*b*, 1985*a,b,c*) and from our unpublished data. In contrast to niobian-tantalian rutiles, cassiterite compositions plot well along the Sn-(Fe,Mn)(Ta,Nb)$_2$ join. However, in the (Sn,Ti)-Nb-Ta diagram, cassiterite from a variety of pegmatite types shows a distinct preference for Ta over Nb, as opposed to the wide Nb $\gtrless$ Ta range of rutile (Figure 4E ; *cf.* 4B).

Much has been written about the form of Fe, Ta and Nb "impurities" in cassiterite. Maximyuk and Lebedeva (1968) concluded, for example, that the limit of incorporation of Ta and Nb into the cassiterite structure is 0.1 wt.% (Ta,Nb)$_2$O$_5$, any excess being concentrated in submicro- and micro-inclusions of columbite-tantalite and tapiolite. Similarly, Fe accepted into the Sn^{4+} sites is considered very limited ; inclusions of Fe-hydroxy-stannates and Fe-stannates (giving magnetite and hematite on oxidation) are considered responsible for most of the Fe content (Grubb and Hannaford, 1966 ; Voronina *et al.*, 1979).

This is in contrast with the observation that unit cell dimensions of cassiterite (and particularly *c*) are inversely proportional to the sum of their Fe, Nb, Ta and Ti contents (as determined by electron microprobe ; Clark *et al.*, 1976). This is also supported by the existence of "staringite", (Fe,Mn)$_{0.5}$(Ta,Nb)$_{1.0}$(Sn,Ti)$_{4.5}$O$_{12}$, a phase corresponding to a cassiterite$_{0.75}$-"tapiolite"$_{0.25}$ solid solution (Burke *et al.*, 1969). This

phase, well documented as it is compositionally, should be re-examined from the structural viewpoint. It was assigned the trirutile structure on the basis of X-ray powder diffraction data but its stoichiometry seems to preclude any periodicity of site populations that might lead to tripling of the *c* parameter. It should be also noted that *c*/3 of staringite as given by Burke *et al.* (1969 ; 3.178 Å) equals the *c* of a rather pure cassiterite (3.18 Å).

It should be pointed out in this respect that the Siberian and Kazakhstan "staringites" of Khvostova *et al.* (1974, 1983) show variable ratios of Sn^{4+} to other substituting cations, and that they have not been examined by X-ray diffraction. Also, the "ainalites" of Khvostova *et al.* (1983) are claimed to possess the trirutile structure only by analogy to the "ainalite" examined almost half a century ago by Åmark (1941). These and similar applications of the names "staringite" and "ainalite" are confusing and should be avoided at present. The true nature of these questionable species should be established first, by coupled microprobe analysis and X-ray diffraction of pure phases on identical grains. If the existence of either of the two species turns out to be justified, its new occurrences should be documented by both compositional and structural data.

Inclusions abound in some pegmatitic cassiterites, and they are present in most of them in at least small quantities. Electron microprobe analyses identify them as tapiolite and columbite-tantalite. No systematic study has so far been performed to correlate the element partitioning among these phases, and to distinguish primary inclusions from products of exsolution and late-stage segregation.

The pyrochlore-microlite-betafite group

Minerals of this group are possibly the second most abundant phases concentrating Nb and Ta in granitic pegmatites, after the columbites-tantalites. Nevertheless, it is only since the nineteen sixties that the extensive compositional variability of this group has been recognized, specifically in its microlite subgroup. New members are being defined all the time, despite the restrictions imposed by the (simple and logical) recommandations of the I.M.A. Commission on New Minerals and Mineral Names (Hogarth, 1977).

The general formula of the group is $A_{2-m}B_2O_6(O,OH,F)_{1-n}.pH_2O$, with the current limits of m = 0-2, n = 0-1, and p = 0-? (Foord, 1982 ; Groult *et al.*, 1982). Only microlite, the tantalum-dominant (Na,Ca)-based species, and uranmicrolite (originally djalmaite), the U-enriched derivative, were known before 1960. Plumbomicrolite (Safiannikof and van Wambeke, 1961), bismutomicrolite (originally westgrenite ; v. Knorring and Mrose, 1962), bariomicrolite (originally rijkeboerite ; v. d. Veen, 1963), and stannomicrolite (originally sukulaite ; Vorma and Siivola, 1967) were then discovered.

Eid and v. Knorring (1976) reported the first microlite compositions with low Cs from several African localities. These signalled the latest additions to the microlite subgroup, cesstibtantite and natrobistantite, found in Kola Peninsula (Voloshin *et al.*, 1981*b*, 1983*c*). Voloshin *et al.* claim a special status for these minerals within the subgroup ; some of their samples display a R^+/R^{3+} ratio of 1.0 in the A-group of cations, suggesting a formula of $(R^+)_{0.5}(R^{3+})_{0.5}(Ta, Nb)_2O_6$ However, minerals closely related to cesstibtantite and natrobistantite found at the type and other localities have the same gross composition but deviate randomly from such a stoichiometry of A-cations (Eid and v. Knorring, 1976 ; Ercit and Černý, 1982 ; Černý, 1982*b* ; unpublished data of the authors ; E.H. Nickel, pers. comm. 1983). A structure analysis of cesstibtantite is underway (Ercit, 1985).

A rhombohedral derivative of the microlite sub-group with a composition close to $BaTa_4O_8(OH)_6$ was found associated with simpsonite from the Alto do Giz pegmatite, Brazil. A mineral with similar stoichiometry but so far uncertain structural properties occurs with simpsonite in alluvial pebbles at Kivu, Zaire. The distortion of the cubic symmetry is probably due to the size of the Ba^{2+} cation and to ordering of A-site vacancies. From this viewpoint, it appears that the structure of bariomicrolite (rijkeboerite) requires close examination.

Occurrences of pyrochlores, marked by Nb-dominated B-group of cations, are rather limited in granitic pegmatites. However, the typical pyrochlore of geochemically primitive paragenesis, uranpyrochlore (formerly hatchettolite) may be joined by some other species such as plumbopyrochlore and yttropyrochlore, so far known only from non-pegmatitic environments.

Betafite, with over 33 wt.% Ti in the B-group of cations and rich in U, was until recently the only representative of its subgroup in granitic pegmatites. New species found in granitic pegmatites include stibiobetafite (Černý *et al.*, 1979) and yttrobetafite (Kalita, 1957).

EVOLUTION OF Nb-Ta MINERAL ASSEMBLAGES

Paragenesis of Nb-Ta in rare-element pegmatites

The general features of Nb-Ta mineralogy in different types of granitic pegmatites have been understood since the nineteen thirties, within the limits of contemporary pegmatite classifications. Although not explicitly stated, it was realized that euxenite, fergusonite, yttrotantalite, samarskite, etc., occur predominantly in the Y, REE, Ti-rich pegmatites poor in rare alkalis. Progressive fractionation of Nb/Ta and Fe/Mn was recognized in pegmatite sequences marked by increasing enrichment in Li, Rb and Cs. The rarity and paragenesis of minerals such as stibiotantalite, thoreaulite and simpsonite indicated that they may be restricted only to pegmatites of the highest overall fractionation level.

Further progress was made in the fifties and sixties when several papers were published that summarized the considerable information accumulated during pegmatite exploration in the USSR (Ginsburg, 1955, 1956, 1960). Although meager in specific documentation, these and related generalizing publications improved our understanding of the Nb, Ta mineralogy in granitic pegmatites by an order of magnitude. Since then, it has been mainly (v. Knorring, 1965, 1966, 1967, 1968, 1973, 1974 ; v. Knorring and Mrose, 1962 ; v. Knorring and Sahama, 1979 ; v. Knorring *et al.*, 1969*a,b,c,d*) who has furthered our knowledge of Nb-Ta mineral assemblages. Ercit and Černý (1982), Voloshin and Pakhomovskyi (1983) and Voloshin (1983) dealt mainly with the secondary phases formed in the late stages of replacement, at the expense of pre-existing Ta-oxide minerals.

The present situation is affected by several factors. On the positive side, the geological, paragenetic and geochemical classification of rare-element pegmatites has been considerably improved (Rudenko *et al.*, 1975 ; Ginsburg *et al.*, 1979 ; Černý, 1982*a*, 1985). Also, the mineralogy of Nb and Ta in granitic pegmatites has been considerably expanded, as discussed in the preceding chapter. However, documentation of the complete paragenesis of Nb-Ta minerals in a given pegmatite or pegmatite group, in the detail required by the present level of crystal chemistry, is so far rather rare. Moreover, vital information is commonly missing in much of the literature. Topographical and geological settings, reviews of overall pegmatite paragenesis, and listing of complete paragenetic sequences of Nb, Ta-bearing minerals from the whole pegmatite are persistently missing in many papers (*e.g.*, Ginsburg *et al.*, 1969 ; Voloshin *et al.*, 1981*a,b*, 1982*a,b*, 1983*a,b*).

Thus it is rather difficult to develop an improved general paragenetic scheme of the Nb,Ta-bearing species at the present time. Table I includes information of highly variable quality. On one hand, recent data collected by electron microprobe, X-ray fluorescence, and single-crystal plus powder X-ray diffraction on complete Nb,Ta-mineral suites are included for some localities (Shatford Lake, Plex, Yellowknife, Věžná, Greer Lake, Peerless, Viitaniemi, Mongolian Altai #3, Tanco, Himalaya). On the other side of the spectrum are the data based on largely out-dated work (Ytterby, Evje-Iveland, Georgia Lake) and incomplete studies (Etta, Harding, Varuträsk, Greenbushes, Bikita, Kamativi, Kings Mountain). Abundance or scarcity of different species is rarely documented in a given deposit or pegmatite group ; thus even the attempt to emphasize the most abundant phases in table I is occasionally bordering on guesswork.

The examples of Nb,Ta-bearing assemblages in individual pegmatites and pegmatite groups, as assembled in table I, do not include all the different mineral species known from granitic pegmatites. A more complete list for each pegmatite type within the rare-element class follows :

Gadolinite type : aeschynite, niobo-aeschynite, samarskite, fergusonite, formanite, (yttrocolumbite), yttratantalite, polymignite, euxenite, polycrase, ferrocolumbite, (ixiolite), niobian rutile, ilmenite, (pyrochlore), betafite, microlite, fersmite, (rynersonite).

	Be, Y, REE, Nb > Ta, U, Th	Be, Nb ≳ Ta (Sn) (±B, P)	Li, Be, Ta ≳ Nb (Rb, Sn) (±B, P)	Li, Rb, Cs, Ta > Nb, Sn, (B, P)	Li, Be, Sn, Ta ≳ Nb, (±B, P)	F, Li, Rb, Be, Ta > Nb, (Cs, Sn) (±B, P)
Locality	Shatford Lake, Man. Evje-Ireland, N. Ytterby, Sweden Barringer Hill, Tex.	Plex, N.W.T. Peg group, N.W.T. Věžná, Czech. Greer Lake, Man.	Yellowknife, N.W.T. Etta, S.D. Peerless, S.D. Harding, N.M.	Viitaniemi, Finland Mong. Altai #3 Varuträsk, Sweden Odd West, Man. Greenbushes, Austr. Bikita, Zimbabwe Tanco, Man.	Kamativi, Zimb. King Mountain, N.C. Georgia Lake, Ont. São João, Brazil	Dobrá Voda, Czech. Brown Derby, Colo. Muiane, Mozambique Himalaya, Calif.
Aeschynite	?					?
Samarskite	•					
Fergusonite	●					
Yttrotantalite	●					•
Euxenite	•					
Polycrase	•					
Fersmite	•					• •
Rynersonite	?					• •
Ferrocolumbite	● ● •	● ● • ●	●	• •	| |	● • • ●
Manganocolumbite	• ? |	● ● •	● ● ● ●	• ● • • ● •	| |	•
Manganotantalite	• • |	•	● ● ●	● ● • • ● ● ●	| |	• ●
Ferrotantalite		•	•	•		
Tapiolite		•	● •	• • • •		•
Ixiolite	●		•	● • •		
Wodginite			• ●	• • • ●		
Niobian rutile	• •	• •		?		
Tantalian rutile		•	• —	?		
Ilmenite	• • •	•		?	•	
Cassiterite	• •	• • •	• • • •	• • • ● ● • ●	• • • •	• ? •
Betafite	•					
Stibiobetafite	•	•				
Microlite	• • •	? • •	• • ●	• ● ● • • ● ●	•	• ● ● ●
Stannomicrolite*		•				
Bismutomicrolite*		•		•		•
Uranmicrolite*			●	• •		● • •
Cesstibtantite*				•		
Antimonian microlite				• • •		
Bariomicrolite*				•	•	
Bismutotantalite				•		
Stibiocolumbite						•
Stibiotantalite				• • ● ?		• • • •
Simpsonite				• ●		
Alumotantite				•		
Holtite				•		

Extracted from Björlykke (1935), Brotzen (1959), Brookins et al. (1979), Černý (1965), Černý et al. (1964), Černý and Turnock (1971), Černý and Harris (1973), Černý et al. (1979), Černý et al. (1981a,b), Černý et al. (1985a,b,c), Crook (1977), Cotelo Neiva and Correia Neves (1960), Ehlmann et al. (1964), Ercit (1985), Ercit et al. (1985), Foord (1976), Frigstad (1968), Grice et al. (1972), Hatcher and Bolitho (1982), Heinrich (1964, 1967), Hutchinson (1955), Jahns and Ewing (1976), v. Knorring (1974), I. Kunasz (pers. comm., 1984), Lahti (1981 and pers. comm., 1984), Landes (1932, 1928), MacGregor (1946), Nordenskjöld (1906), Pye (1965), Paul (1984), Quensel (1956), Rijks and v.d. Veen (1972), Schneiderhöhn (1961), Staněk (1963), Wang et al. (1981), White (1981), Wise (1985) and unpublished data of the authors.

Large dot represents a particularly abundant mineral.
Vertical line marks an uncertainty about composition in a mineral group.
Question mark signifies uncertain identification or paragenetic affiliation.
*Includes microlite with elevated contents of the typical A-cations.

TABLE I. — *Paragenesis of Nb, Ta-bearing minerals in selected rare-element pegmatites.*
Paragenèses des minéraux de Nb-Ta dans quelques pegmatites choisies à éléments rares.

Beryl-columbite type : ferrocolumbite, manganocolumbite, (ferrotantalite), ixiolite, tapiolite, niobian rutile, cassiterite, microlite (also with U, Bi, Sn), (stibiobetafite).

Complex (Li,Be,Ta $\geqslant$ Nb) : fersmite, (rynersonite), manganocolumbite, manganotantalite, (ferrotantalite), tapiolite, ixiolite, (wodginite), tantalian rutile, cassiterite, (staringite), thoreaulite, microlites (also with U, Sb, Sn).

Complex (Li,Rb,Cs,Ta > Nb) : manganocolumbite, manganotantalite, tapiolite, (ixiolite), wodginite, (tantalian rutile), cassiterite, microlites (also with U, Bi, Sb, Cs, Pb, Ba), cesstibtantite, natrobistantite, stibiotantalite, (bismutotantalite), simpsonite, alumotantite, natrotantite, calciotantite, lithiotantite, tantite, sosedkoite, rankamaite, holtite, behierite.

Spodumene type : columbite-tantalite, cassiterite, (microlite).

Lepidolite type : manganocolumbite, (manganotantalite), microlites (also with Bi, U), stibiotantalite.

It should be emphasized, of course, that the above list and the examples given in table I are meant to be typical cases ; exceptions to the rule should be expected. For example, the Muiane deposit in Mozambique and several others in its area are evidently highly fractionated in terms of Ta, Mn, Li and F concentrations, but also enriched in Y (Cotelo Neiva and Correia Neves, 1960). The same holds for the Høydalen pegmatite at Tørdal, Telemark, southern Norway (Oftedal, 1942 ; Bergstøl *et al.*, 1977 ; R. Kristiansen, pers. comm., 1980). This pegmatite represents the only Norwegian occurrence of lepidolite, associated with cassiterite and tantalite. However, it also carries gadolinite, yttrotantalite, fergusonite, xenotime and other Y-bearing species. Evidently a strong Y, REE signature of the whole pegmatite district persists through advanced fractionation into the Li, F-enriched, lepidolite-bearing pegmatite type.

Extensive influence of individual cations on mineral paragenesis is also demonstrated by some of the more common, "rock-forming" elements. For example, activity of Ca^{2+} was recognized already by Björlykke (1935, 1937) as a significant factor. Even in the less fractionated gadolinite-type pegmatites, high vs. low activity of Ca generates considerably different mineral assemblages : betafite + fergusonite (+ hellandite), as compared with fergusonite + euxenite ± columbite (± thalenite).

Variability in the chemical composition of individual species must also be kept in mind when considering Nb, Ta-bearing parageneses. For example, fersmite is very close to $CaNb_2O_6$ in some localities (*e.g.*, Himalaya, Huron Claim) but it may carry up to 24 wt.% RE_2O_3 and abundant TiO_2 (Ewing, 1974). Thus the geochemical significance of a given mineral species should be considered with reference to its observed chemistry in each particular occurrence.

There is a clear need for detailed studies of Nb,Ta-mineral assemblages in a diversity of pegmatite types, to complement existing information and to allow a general scheme to be formulated.

Late secondary assemblages of Nb,Ta-minerals

Some of the most common reactions among the Nb,Ta-bearing minerals have been known since the nineteen thirties. For example, replacement of columbite-tantalite by microlite is a very common process (*e.g.*, Bowley, 1939 ; Ginsburg, 1956), and the breakdown of stibiotantalite to microlite has been considered typical of the species (Ginsburg, 1956). However, it was only during the last 20 years that detailed studies of late alterations revealed their diversity in terms of both processes and products.

Table II presents a literature survey of mineral sequences, including alteration, metasomatism and pseudomorphism for a diversity of cases. For ease of reference, the mineral associations are grouped by the parent phases. To condense the information from the literature, it was occasionally necessary to interpret the original statements into a more explicit form ; thus some minor inaccuracies could have been introduced. On the other hand, in some cases of repetitive publication it is difficult to differentiate between rewording of an earlier statement, complementing earlier observations by new facts, and/or correcting the original data. Thus it is possible, *e.g.*, that the multiplicity of reactions and assemblages quoted from the papers of Voloshin and associates is exaggerated.

columbite-tantalite ← microlite	
columbite ← fersmite	Černý and Turnock, 1971
manganotantalite + wodginite - microlite - calciotantite	Voloshin et al., 1982b
manganotantalite + wodginite - microlite + calciotantite	Voloshin et al., 1982b
tantalite ← stibiotantalite	Pryce, 1971
tantalite ← holtite	Pryce, 1971
columbite ← plumbopyrochlore ← plumbomicrolite	Voloshin, 1983
columbite ← plumbomicrolite	Voloshin, 1983
columbite + niobian rutile ← stibiobetafite	Černý et al., 1979
tapiolite ← microlite	Pough, 1945, Eid and v. Knorring, 1976
wodginite ← ixiolite + manganotantalite + microlite	Voloshin et al., 1983c
stibiotantalite ← microlite	Ginsburg, 1956
stibiotantalite ← antimonian microlite + antimony	Quensel, 1956
stibiotantalite ← antimonian microlite	v. Knorring and Hornung, 1963; Černý and Harris,1973
stibiotantalite ← microlite+ antimony	Voloshin, 1983
stibiotantalite ← antimonian microlite - manganotantalite	Staněk, 1963
stibiotantalite ← rynersonite ← fersmite + stannian microlite	Foord, 1976
stibiotantalite + simpsonite ← cesstibtantite + microlite	Voloshin et al., 1981b
stibiotantalite ← cesstibtantite ± sosedkoite	Voloshin et al., 1982a
stibiotantalite ← sosedkoite cesstibtantite	Voloshin and Pakhomovskyi, 1983
stibiotantalite + simpsonite + microlite - sosedkoite + natrotantite + alumotantite	Voloshin et al., 1982a
bismutotantalite ← bismutomicrolite	v. Knorring and Mrose, 1962
bismutotantalite ← Ca, Bi-microlite	Voloshin et al., 1983a
bismutotantalite ← bismutomicrolite ← rynersonite	v. Knorring and Sahama, 1979
bismutotantalite ← natrobistantite (+ bismuthinite) manganotantalite	Voloshin et al., 1983a
bismutotantalite ← (natrobistantite ± antimonian bismutotantalite) Cs,Ca,(Sb)-microlite	Voloshin et al., 1983a
thoreaulite ← cassiterite ← rankamaite; lithiotantite; rankamaite	Voloshin et al., 1983b
simpsonite ← microlite	Bowley, 1939
simpsonite ← rankamaite	v. Knorring et al., 1969d
simpsonite ← stibiotantalite + microlite (+ cassiterite)	Voloshin and Pakhomovskyi, 1983
simpsonite ← wodginite + microlite	Voloshin, 1983
simpsonite ← wodginite + microlite + tantalite (± tapiolite, cassiterite)	Voloshin, 1983, Voloshin and Pakhomovskyi, 1983
simpsonite ← ixiolite	Voloshin et al., 1983c
simpsonite - natrotantite (+ cesstibtantite + microlite)-alumotantite	Voloshin et al., 1981a
simpsonite ← alumotantite + microlite	MacGregor, 1946; Voloshin and Pakhomovskyi, 1983
simpsonite ← cesstibtantite + alumotantite + natrotantite + sosedkoite	Voloshin, 1983
simpsonite ← alumotantite + Al-hydroxides, or silicates	Ercit et al., 1985a
simpsonite ← tapiolite	Ercit and Černý, 1982
microlite ← other microlite compositions	
microlite-tantite + unknown $CaTa_4O_{11}$	Voloshin et al., 1983a
microlite ← stibiotantalite + holtite	Voloshin et al., 1983a
holtite ← stibiotantalite + arsenic ← microlite	Voloshin et al., 1977
holtite I ← stibiotantalite ← holtite II	Voloshin, 1983

← replacement of the left-hand phase
– crystallization after the left-hand phase
+ more or less simultaneous crystallization
± right-hand phase locally missing
( ) minor quantity

TABLE II. — *Precipitation, replacement and alteration sequences of late Nb, Ta-bearing minerals in rare-element pegmatites.*

Ordre de cristallisation, de remplacement et d'altération des minéraux tardifs de Nb-Ta dans les pegmatites à éléments rares.

In general, of course, the multitude of processes and products should not be surprising. Each parent phase containing yet another element in addition to Nb and Ta (such as Sn, Ca, Al, Sb, Bi) generates on its breakdown a new multicomponent system with the potential to generate new

daughter compounds. Also, each cation and/or anion active in the late fluids may promote precipitation of a different replacement product from a single precursor. Mutual interplay of these two factors leads inevitably to great diversity.

Ionic abundances and activities may be conditioned by the gross geochemical features of the parent pegmatites. For example, the drastic difference between the fluorine activities in the spodumene- and lepidolite-type pegmatites is prominently reflected in the primary assemblages of Nb,Ta-bearing minerals and their chemistry (Table I). However, on the small scale of late hydrothermal stages, relatively slight variations in P,T-conditions can dramatically shift the course of low-temperature metasomatism even in the same pegmatite.

For example, Voloshin *et al.* (1981*a,b*, 1982*a,b*) correlate the formation of natrotantite, alumotantite, cesstibtantite, calciotantite and sosedkoite with late K-metasomatism. This process is expressed, i.a., by replacement of lepidolite and other minerals by orthoclase, and alteration of pollucite ; it probably corresponds to the stage of adularia crystallization (Černý and Chapman, 1984). Experimental evidence shows that significant change in the activities of Na^+ and K^+ may be produced by mere shifts in P and/or T, with a consequent reversal from albitization to K-metasomatism and *vice versa* (Lagache and Weisbrod, 1977). It is conceivable that the chemical potential of other components (*e.g.*, Fe, Mn, Al) may also be influenced by such a variation in physical parameters, either directly or via changing alkali activities. Thus it is not surprising that mineral precipitation may be oscillatory or cyclic (Ercit and Černý, 1982 ; Voloshin and Pakhomovskyi, 1983).

Voloshin (1983) advocated a universal increase in Ta and reduction of Nb/Ta with progressive alteration of Nb,Ta-bearing minerals. This is undoubtedly true in most instances, and it apparently holds for the bulk of secondary reaction products even if it does not apply to individual phases. For example, stibiotantalite from the Himalaya district of California (Foord, 1976) is replaced first by rynersonite (showing a decrease in Nb/Ta), which is in turn replaced by fersmite + stannian microlite. Fersmite shows Nb/Ta higher than rynersonite, but the bulk composition of fersmite + stannian microlite is probably enriched in Ta relative to rynersonite. Another example of such a case are the Ta-poorer tantalite and wodginite formed after simpsonite (Ercit and Černý, 1982) ; these minerals are associated with tapiolite and with abundant microlite.

In some cases, however, there is no doubt that the Nb/Ta ratio of the parent phase is preserved in the replacement product. In the Huron Claim pegmatite of southeastern Manitoba, fersmite shows the same Nb/Ta range as its columbite precursor (Paul, 1984). Thus, it is understandable that Voloshin and Pakhomovskyi (1983) do not consider the Nb/Ta ratio to be determined by the paragenetic position of any given mineral.

In conclusion, a comment is required on compositional complexity vs. simplicity in late metasomatic Ta-bearing minerals. Voloshin (1983) postulated that progressively younger phases are increasingly "purified" of substituting elements prominent in their precursors. This may apply to some processes listed in table II, but reactions such as stibiotantalite ← holtite, simpsonite ← rankamaite, tantalite ← holtite, stibiotantalite ← cestibtantite + sosedkoite, or bismutotantalite ← bismutomicrolite represent reverse trends.

GEOCHEMICAL TRENDS IN Nb, Ta MINERALS

The chemistry of an individual mineral species evolves in multigeneration sequences within a single pegmatite, in a sequence of pegmatites belonging to the same type, and even more prominently in zoned pegmatite groups and fields consisting of two or more types.

A series of examples introduced below demonstrates the variability in the geochemical evolution (and structural state) of the columbite-tantalite, the most ubiquitous mineral group encountered in all types of rare-element pegmatites. In some cases, closely related species such as ixiolite, tapiolite and wodginite are also included to complement the data. For convenience of correlation with figures 1A and 1B, atomic ratios Mn/(Mn+Fe) and Ta/(Ta+Nb) are plotted in figures 5 to 8, instead of the weight ratios commonly used in geochemistry.

Fractionation trends in individual pegmatites

The *Huron Claim* pegmatite (Paul, 1984) is a member of the gadolinite-type Shatford Lake group in the Cat Lake-Winnipeg River field of southeastern Manitoba, in the western part of the Archean Superior province of the Canadian Shield (Černý *et al.*, 1981*b*). An apparently single generation of columbite-tantalite is widely dispersed in the pegmatite, following its albite-rich segments and penetrating along fractures into the blocky K-feldspar and quartz. Columbite-tantalite is extensively replaced by fersmite and an unknown Ca, Ta, Nb, Ti-bearing phase, and is also closely associated with microlite and an euxenite-like phase. Most of the columbite-tantalite mineral corresponds to ferrocolumbite but both Mn and Ta become locally enriched enough to approach the compositions of manganocolumbite and ferrotantalite (Figure 5A). Most of the specimens examined have an intermediate structural state but the overall range is extensive.

The *Plex* pegmatite, centrally located on Baffin Island, N.W.T. in a Proterozoic metamorphic terrane, can be classified as the beryl-columbite type. Two generations of columbite show well-defined differences in composition : columnar ferrocolumbite is associated with zircon and gigantic tourmaline in the quartz core, whereas smaller equant grains of manganocolumbite occur in large pods of medium-grained muscovite (Figure 5B). Intermediate to high degrees of disorder are typical of both generations, the ferrocolumbite showing a greater range of structural states (unpublished data of P. Černý and D.L. Trueman).

The *Moose* pegmatite is located at the southeastern extremity of the Yellowknife pegmatite field, N.W.T. (Meintzer *et al.*, 1984). It belongs to the Li, Be, Nb ≷ Ta subtype of complex pegmatites, with abundant spodumene and amblygonite. Three paragenetic and morphological varieties of columbite-tantalite are found in this deposit (Wise, 1985). However, the platy, tabular and blocky habit is not correlated with the associated cleavelandite + quartz, cleavelandite + amblygonite, or (sporadic) cleavelandite + lithian muscovite assemblages. There also seems to be no correlation with the location within the pegmatite. Despite the above morphological and paragenetic diversity, the chemistry and structural state are essentially uniform (Figure 5C) : the ferrocolumbite composition shows a very narrow Mn/(Mn+Fe) range and only a slight spread of Ta/(Ta+Nb) values. The variation in the generally intermediate structural state is also limited.

The *Peerless* pegmatite at Keystone, South Dakota is another example of the Li, Be, Nb ≷ Ta subtype of complex rare-element pegmatites, in this case a member of the Proterozoic pegmatite field of the southern Black Hills. In contrast to the Moose pegmatite, the Peerless is P-rich, with abundant triphylite, amblygonite and only traces of spodumene, and it also contains a centrally located unit of lithian muscovite. The minerals shown in figure 6A represent the Nb-Ta phase population of only the innermost units adjacent to the quartz core. They are, from outside toward the core, thin plates of ferrocolumbite-manganocolumbite, brick-shaped crystals of manganocolumbite-manganotantalite, and columnar wodginite. Compositions of associated cassiterite and tapiolite (and exsolutions of columbite and tapiolite in cassiterite) are given in Černý *et al.* (1985*c*). The fractionation range of Nb and Ta is remarkable, all the more that the examined specimens come from only a single unit out of the total of 7 units composing the pegmatite.

The *Tanco* deposit is among the most fractionated complex pegmatites of the world (Černý, 1982*b*). Abundant petalite and (secondary) spodumene, amblygonite, triphylite-lithiophilite, lepidolite, pollucite, tantalum mineralization, tourmaline and beryl mark it as a Li, Rb, Cs, Be, Ta, B, F and P-rich body. The Ta-mineralization is extensive, distributed over 5 units of the pegmatite, and mineralogically diverse (Grice *et al.*, 1972 ; Ercit, 1985). Figure 6B presents the compositions of ferrocolumbite-manganocolumbite from the saccharoidal albite unit of the eastern flank of the pegmatite, and of manganotantalite typical of the same unit in the western and northwestern extremities of the deposit. Intermediate between these two populations are the manganocolumbites-manganotantalites and ixiolites of the petalite-rich zones. Tapiolites are Nb-poor and Mn-enriched. It should be noted, however, that wodginites and microlite varieties (including cestibtantite and Sb, Sn, U, Pb-enriched types) are the predominant minerals of Ta in Tanco,

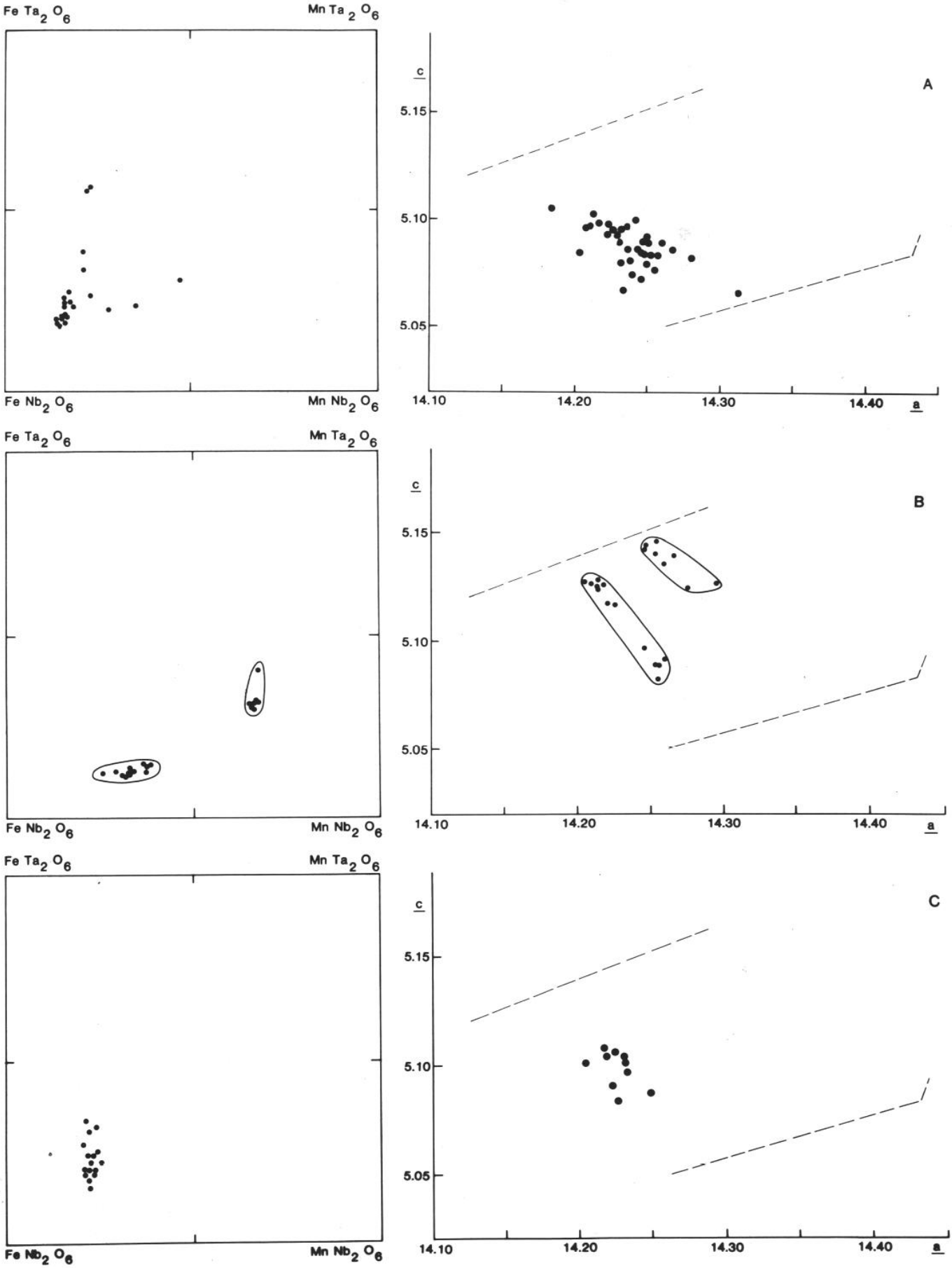


FIG. 5. — *Compositional fields (left) and structural states (right) of columbite-tantalite from the Huron Claim (A), Plex (B) and Moose (C) pegmatites*. See text for sources of data.

Domaines de composition (à gauche) et états structuraux (à droite) de la columbo-tantalite provenant des pegmatites de : Huron Claim (A), Plex (B) et Moose (C). Voir le texte pour la source des données.

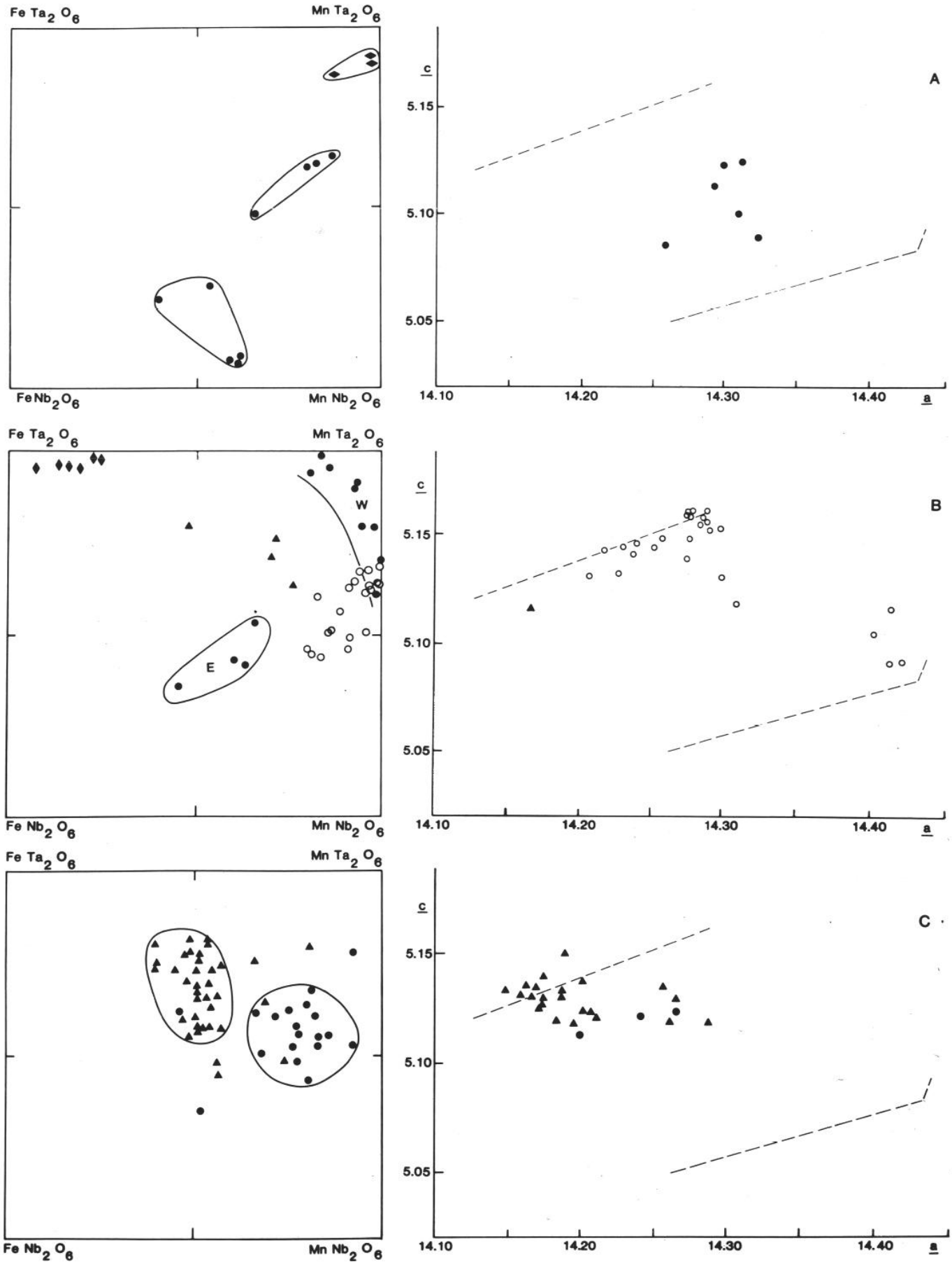


FIG. 6. — *Compositional fields (left) and structural states (right) for columbite-tantalite (●, o) from the Peerless (A), Tanco (B) and Lower Tanco (C) pegmatites.* Includes tapiolite (vertical diamonds), wodginite (horizontal diamonds), and ixiolite (▲). See text for sources of data.

Domaines de composition (à gauche) et états structuraux (à droite) de la columbo-tantalite (●, o) provenant des pegmatites de Peerless (A), Tanco (B) et Lower Tanco (C). Egalement tapiolite (losanges verticaux), wodginite (losanges horizontaux) et ixiolite (triangles pleins). Voir le texte pour la source des données.

and simpsonite abounds in the western parts. On the average, these minerals are much more extreme in terms of both Ta-(and Mn-)enrichment than the broad field of the orthorhombic phases shown in figure 6B. Most of the orthorhombic phases are highly disordered ; a wide gap separates the disordered phases from the few manganotantalites with largely ordered structures.

The Ta-mineral assemblage of the *Lower Tanco* pegmatite is entirely different. This pegmatite is parallel with, and closely underlying the Tanco deposit. It shows a similar degree of Li, Rb, Cs enrichment but a very low F and P content, as reflected in its lack of amblygonite, scarcity of apatite, and negligible development of lepidolite (Ferreira, 1984). Only a part of the pegmatite was studied so far, selected for its high concentration of Ta, Nb and Sn. The mineral assemblage carrying these elements is dramatically different from that encountered in Tanco (Figure 6C). In its outer parts, Lower Tanco contains ixiolite with numerous exsolution lamellae of cassiterite. In the inner units, the Mn and Ta in ixiolite are higher, exsolution of cassiterite is virtually nonexistent and separate grains of disordered (manganocolumbite)-manganotantalite are commonly associated with ixiolite. Tapiolite and wodginite are extremely rare, and uranian microlite was found only once. The structural state of the manganocolumbite (which could be cleanly separated from ixiolite only in a few cases) is highly disordered (Figure 6C).

The above examples of fractionation trends in individual pegmatites demonstrate several noteworthy facts. First of all, the two columbite generations of the Plex pegmatite are compositionally in accord with what is considered "standard" in this particular pegmatite type. The more extensive and non-uniform fractionation of ferrocolumbite within the Huron Claim pegmatite may be in part influenced by (potentially) coexisting phases, but its overall extent is again within the expected limits (Figure 5A, B).

In contrast, the extremely uniform ferrocolumbite chemistry in the Moose deposit is rather unique for such a Li,P,F-enriched complex body in general, and in particular for a pegmatite with columbite-tantalite of diversified morphology and association (Figure 5C). The wide range of columbite-tantalite-wodginite (-microlite) compositions in the Peerless pegmatite (Figure 6A) is probably at the other extremity of the scale, but more in line with the Nb,Ta-mineral fractionation known for this pegmatite type (*e.g.*, Ginsburg, 1956).

For a pair of cogenetic, closely adjacent, and otherwise very similar pegmatites, the Tanco and Lower Tanco bodies display a dramatic contrast in mineral assemblages and mineral chemistries (Figure 6B, C). There seems to be no doubt that the much lower F-concentration is behind the lower degrees of Fe/Mn and Nb/Ta fractionation in Lower Tanco, and its lack of F-bearing Nb,Ta species. Otherwise, no unambiguous clues are so far available for explaining the differences in the respective mineral assemblages.

Fractionation trends in pegmatite groups and fields

The *Cross Lake* field is located along the northwestern margin of the Archean Superior province in Manitoba, close to the Churchill province boundary in the Canadian Shield. Two pegmatite groups carry Nb,Ta-mineralization in this field (Anderson, 1984). The southern group ranges from biotite + peristerite-bearing pegmatites with ferrocolumbite to highly fractionated (but F-poor) spodumene-rich complex dykes with manganocolumbite-manganotantalite and rare ixiolite (Figure 7A). The northern group is predominantly of the beryl-columbite type, very poor in Li but F-enriched. Manganocolumbite and manganotantalite predominate, but uranian microlite also occurs in the most fractionated members of the group. (The few points outside the fields outlined in Figure 7A represent Ti-enriched ferrotantalites, some of which are associated with tapiolite and/or tantalian rutile.) Columbite-tantalite of the southern group ranges from disordered to intermediate in structural state (Figure 7A).

The *Greer Lake pegmatite group* belongs to the same pegmatite field as the Tanco pegmatite discussed above (Černý *et al.*, 1981*b*, 1985*b*). Its pegmatites span the whole range of the beryl-columbite type, from Y, REE, Ti-enriched bodies to dykes with pods of lithian muscovite. Columbite-tantalite shows an extensive compositional spread over all four quadrants of the diagram (Figure 7B). The most fractionated

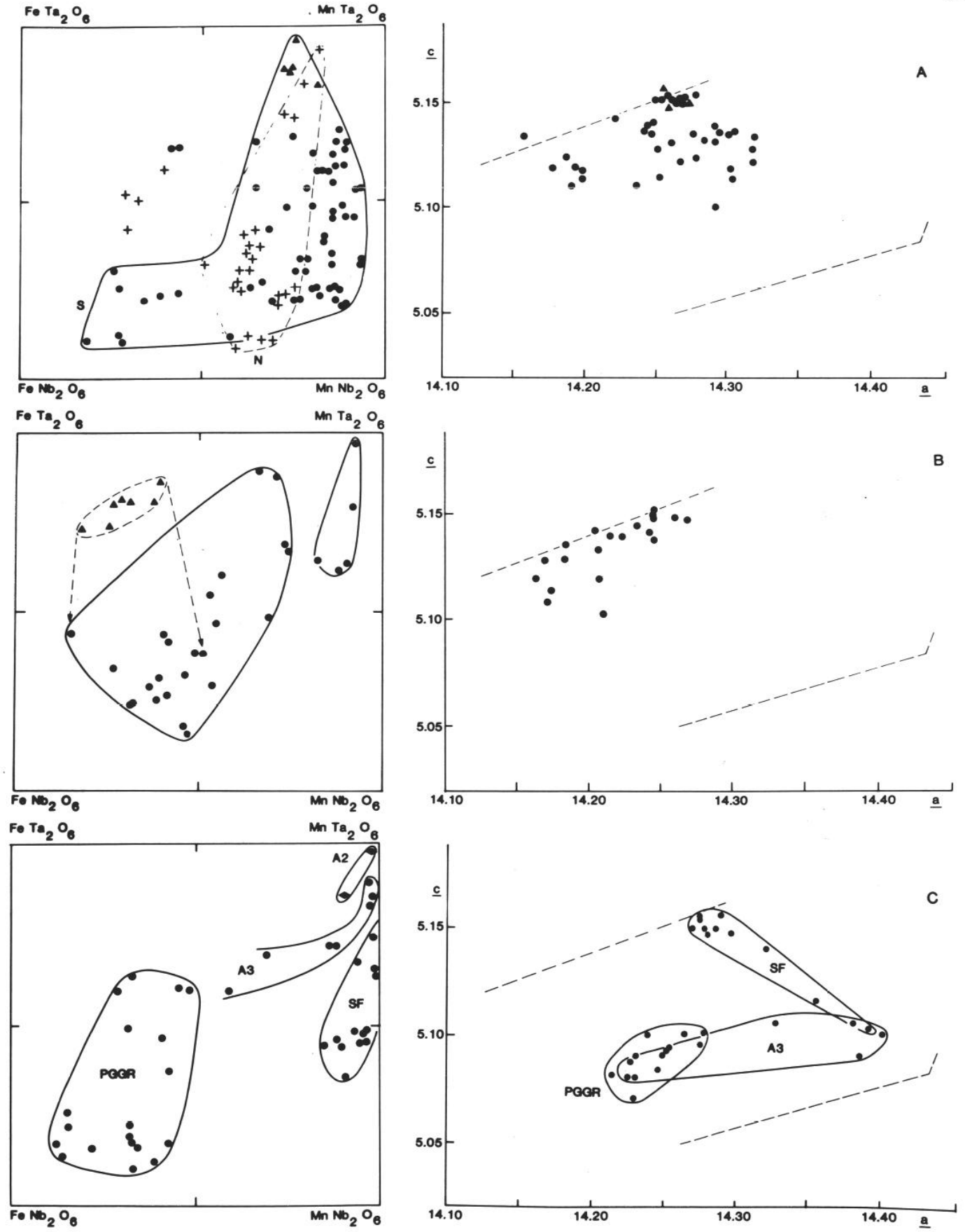


FIG. 7. — *Compositional fields (left) and structural states (right) of columbite-tantalite (●, +) from the Cross Lake field (A), Greer Lake group (B) and Greer Lake pegmatitic granite (C).* Includes wodginite (diamonds) and ixiolite (▲).

Domaines de composition (à gauche) et états structuraux (à droite) de la columbo-tantalite (●, +) des districts de Cross Lake (A), Greer Lake (B) et du granite pegmatitique de Greer Lake (C). Egalement wodginite (losanges) et ixiolite (triangles pleins). Voir le texte pour la source des données.

manganotantalite composition, typical of the pegmatites carrying lithian muscovite, is somewhat separated from the others. Sn- and Ti-rich ixiolite typically occurs in the least-fractionated pegmatites, commonly associated with niobian rutile and several varieties of microlite. However, it is never found in close association with columbite-tantalite. The structural states of most orthorhombic phases are extremely disordered (Figure 7B).

Nb,Ta-bearing minerals of the *Greer Lake pegmatitic granite* (parental to the pegmatite group discussed in the preceding paragraph) show a similar but more extreme diversity in composition, and more complex structural relationships (Figure 7C ; Goad and Černý, 1981 ; Černý *et al.*, 1981*a*). Columbite laths associated with green beryl in potassic pegmatite layers of the average pegmatitic granite are predominantly ferrocolumbites. Internal pods of Li, Rb, Cs, F-rich assemblages (A2, A3) and the Silverleaf pegmatitic offshoot of similar composition (SF) show extreme enrichment in Mn, and partly also Ta, in their manganocolumbites-manganotantalites and wodginite. Several crystals of manganotantalite collected in the immediate vicinity of A3 show intermediate compositions bridging the gap to the ferrocolumbites-ferrotantalites (Figure 7C). Structurally, the columbites-tantalites of the ordinary pegmatitic granite and internal lepidolite pods are intermediate to considerably ordered, but those from the Silverleaf offshoot show an extensive range similar to that found in the Tanco pegmatite, including a hint of bimodal distribution.

The Proterozoic pegmatite field of southern *Black Hills*, South Dakota, has a population of about 22,000 pegmatites (Norton, 1975). Most of them are barren, but rare-element-enriched bodies abound as well, ranging from poorly mineralized beryl-columbite type through spodumene-bearing complex bodies to a single pollucite-bearing locality. The Li, Be, Nb ≷ Ta subtype ranges from a spodumene-amblygonite-triphylite assemblage to bodies with considerable accumulation of lithian micas. The data collected so far on the columbite-tantalite, wodginite and ixiolite of this field are rather sporadic, but they cover all the pegmatite types encountered (Figure 8A). The broad scatter of compositions through the ferrocolumbite, manganocolumbite and manganotantalite quadrants attests to the paragenetic and geochemical diversity of this field. The structural state of the orthorhombic oxide minerals displays a distinct correlation with their Mn content : with increasing Mn, the range of order-disorder shrinks to the more ordered part of the diagram (Figure 8A).

The Archean *Yellowknife* field, N.W.T., is also composed of a variety of rare-element pegmatite types, from barren and beryl + columbite-bearing to the Li, Be, Nb ≷ Ta complex subtype (Meintzer *et al.*, 1984). Amblygonite is locally abundant but Li, F-rich micas are virtually absent. The data shown in figure 8B are incomplete but they encompass all the pegmatite types and topographic series present ; additional work (in progress : Wise, 1985) is not expected to change the overall population spread. Thus, the restriction of columbite-tantalite to the Fe-rich half of the quadrilateral seems to be real, as well as the rarity of ixiolite, the high Nb but low Mn of tapiolite and the absence of other Nb,Ta-bearing minerals except cassiterite (Wise, 1985). The structural state of the columbite-tantalite is predominantly intermediate ; the highly disordered specimens are mainly those enriched in Fe (Figure 8B).

In contrast to the Yellowknife pegmatites, compositional data collected for the pegmatite field of *Mongolian Altai* (Wang *et al.*, 1981) populate the Mn-rich half of the diagram (Figure 8C). The pegmatites range from the beryl-columbite type to extremely fractionated, pollucite-bearing complex bodies (*cf.* also Kuzmenko *et al.*, 1976). These latter pegmatites also carry bismutotantalite, microlite, bismutomicrolite, uranomicrolite, and extensive lepidolite-rich units.

Finally, Figure 8D shows first data from pegmatites of the *lepidolite type* (or carrying extensive Li, F-mica units), collected on samples from the Himalaya District, California (Foord, 1976) ; the Brown Derby swarm, Colorado ; Rožná, Czechoslovakia, and several localities in Arizona. Extreme manganocolumbite compositions are typical, but the bulk composition of the Nb,Ta-mineralization has Ta definitely predominant over Nb ; for example, microlite and uranian microlite are the overwhelmingly predominant species in the Brown Derby pegmatites (Staatz and Trites, 1955).

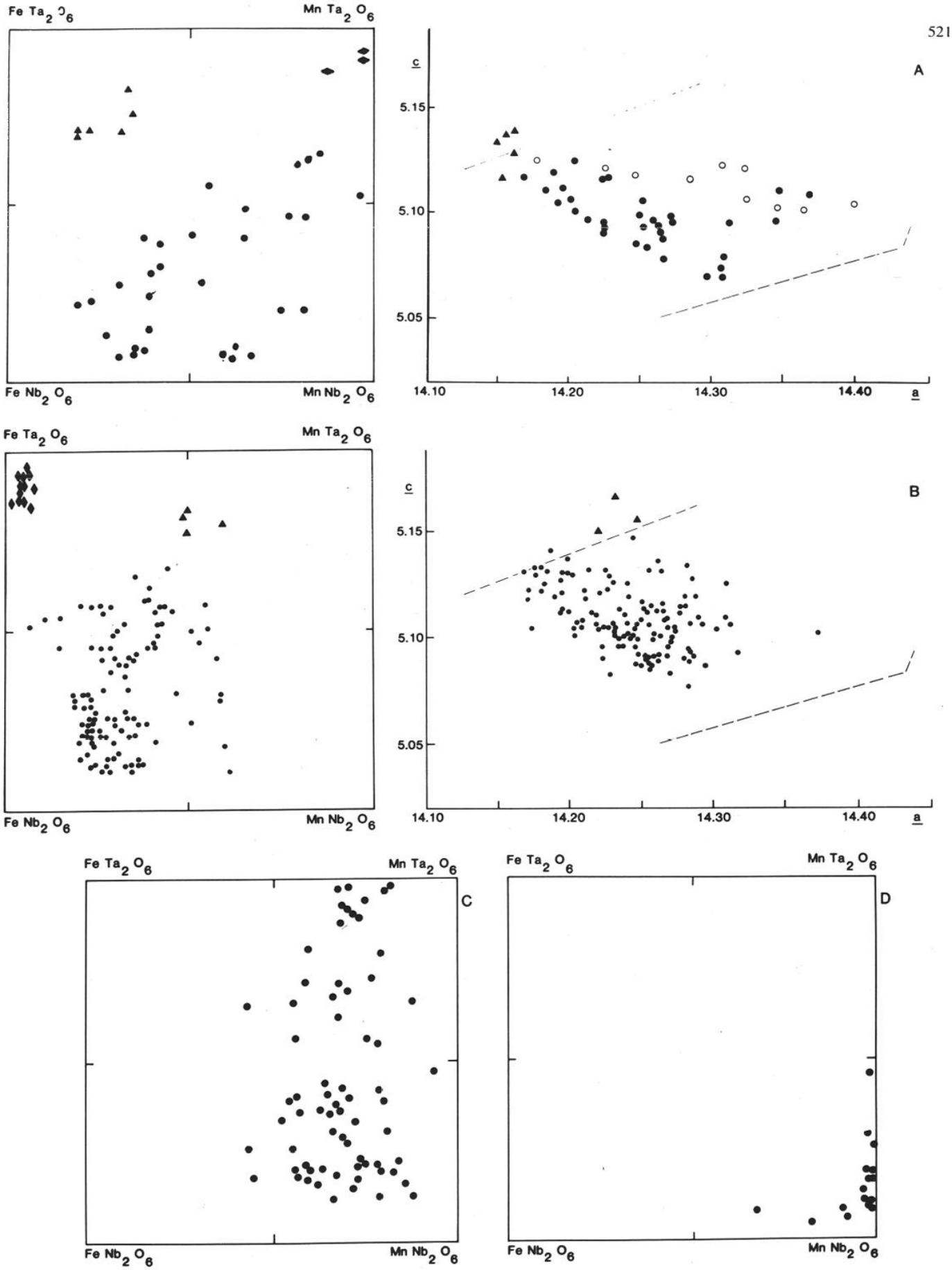


FIG. 8. — *Compositional fields (left) and structural states (right) for columbite-tantalite* (●, o) from the Black Hills field (A), Yellowknife field (B), Mongolian Altai field (C) and lepidolite-type pegmatites (D). Includes tapiolite (vertical diamonds), wodginite (horizontal diamonds) and ixiolite (▲). See text for sources of data.

Domaines de composition (à gauche) et états structuraux (à droite) de la columbo-tantalite (●, o) *de : champ de Black Hills (A), champ de Yellowknife (B), champ de l'Altai Mongolien (C) et pegmatites à lépidolite (D).* Egalement tapiolite (losanges verticaux), wodginite (losanges horizontaux) et ixiolite (triangles pleins). Voir le texte pour la source des données.

In summary, the data in figures 7 and 8 both confirm *and* contradict some of the widely accepted generalizations about Nb,Ta-minerals in granitic pegmatites, and expand some of the "anomalies" shown in examples of individual pegmatites bodies :

(i) The columbite-tantalite compositions partly agree with the thesis that Mn-enriched species are typical of Li-rich pegmatites (Cross Lake south, Mongolian Altai, lepidolite-type pegmatites). On the other hand, the Li-rich pegmatites of the Yellowknife field carry minerals with Fe > Mn (Figures 5C, 8B), and in contrast, the extremely Li-depleted pegmatites of the northern Cross Lake group do not differ in the Nb-Ta range (and are only slightly Mn-poor), compared to the Li-rich part of the nearby southern group (Figure 7A).

(ii) It appears from figures 6A, 7B, 7C and 8D that F-enrichment conducive to late Li-mica formation is promoting not only Nb/Ta fractionation, but may also be responsible for extreme Mn-enrichment. The data shown in the above figures strongly suggest that most of the Mn-enrichment actually precedes the Nb/Ta fractionation effect. Such a sequence is demonstrated by Foord (1976) on the zoning patterns of the Himalaya manganocolumbites (included in figure 8D). On a regional scale, the Yellowknife field (with an overall Fe > Mn signature ; figure 8B) is conspicuously F-poor (except some early amblygonite-montebrasite) as compared to the Mongolian Altai pegmatites (Figure 8C).

(iii) Important as the role of fluorine is, it cannot be the total and exclusive answer to the diversity of fractionation patterns shown in figures 5 to 8. Initial abundances of Fe,Mn,Nb,Ta (and Sn,Ti) in the metamorphic protoliths, chemistry and accessory mineralogy of the parent granites, assimilation of country rocks, and influence of other complexing anions such as Cl^-, CO_3^{2-}, BO_3^{3-} etc. are just a few additional factors affecting the course of fractionation.

(iv) Besides geochemical variables, another aspect of the course of fractionation and crystallization is the possible influence of pressure. Rare-element pegmatite groups and entire fields are found emplaced at depths ranging from about 12 to 5 km (~ 4 to 2 kbar), and the miarolitic class is distinctly shallow-seated to subvolcanic. Possible changes in Nb-Ta mineralogy with pressure have not been examined to date, mainly because of lack of sufficient data.

(v) Considering the subject of emplacement depth, a severe constraint on our data collecting must be kept in mind. In large pegmatite groups and particularly fields, understanding of the geochemistry and fractionation paths is restricted to the level of surface exposure and mine depth. At present, no detailed data are available from mountainous terranes. These would add a sorely needed degree of vertical dimension to our data sets, which so far come almost exclusively from flat subhorizontal sections through 3-dimensional pegmatite populations.

STABILITY AND EQUILIBRIA

These are the least known aspects of the pegmatite story of Nb and Ta, and consequently the following section is brief and questioning rather than expository.

Compositional phase stabilities

Burt and London (1982) emphasized that the crystal chemistry of the Nb-Ta-Ti-Sn oxide minerals is poorly understood, and consequently our knowledge of phase relations lags far behind. They pointed out a few compositional degeneracies, such as

$$A^{3+}B^{5+}O_4 + B^{4+}O_2 \rightarrow A^{3+}(B^{4+}B^{5+})O_6$$

where A^{3+} = Y, REE ; B^{5+} = Nb,Ta ; and B^{4+} = Ti,Sn. Polycrase, euxenite, samarskite and aeschynite can be considered stable intermediates between REE-minerals of the fergusonite-formanite type, and cassiterite or rutile. Another relationship of widespread significance is

$$AB_2O_6 + Na(F,OH) \rightarrow \text{pyrochlore group minerals}$$

e.g., fersmite producing pyrochlore on Na/F-metasomatism.

Similar models can be written for some wodginite species :

$$A^{2+}B_2^{5+}O_6 + C^{4+}O_2 \rightarrow ACB_2O_8$$

where A^{2+} = Fe,Mn ; B^{5+} = Ta,Nb ; and C^{4+} = Sn,Ti. A modification of the above, with the same symbols, would apply to ixiolites :

$X(A^{2+}B_2^{5+}O_6) + Y(C^{4+}O_2) \rightarrow$
$Z(A^{2+},B^{5+},C^{4+})_4O_8$

However, in this case the stability of ixiolite as an intermediate between columbite-tantalite-tapiolite and cassiterite-rutile is questionable, and the number of additional substitutions involving R^{3+} and R^{6+} is considerably complicating the issue.

Thermodynamic modelling is a matter of future research. Detailed anatomy of crystal structures and experimental definition of compositional stability fields must come first, and in this latter respect the available information is extremely limited. Starting with the pioneering studies of Brandt (1943), all experimental work on Nb/Ta-bearing systems has concentrated on dry synthesis at atmospheric pressure and temperatures above 700, if not 1000 or 1200°C (*e.g.*, Moreau and Tramasure, 1965 ; Schröcke, 1966 ; Shabynin, 1981). The only work involving controlled oxygen fugacity was also done under these conditions (*e.g.*, Turnock, 1966 ; Komkov and Dubik, 1974). Some other studies were aimed at Fe^{3+}- and $Mn^{3+,4+}$-bearing compounds that have extremely limited representations among natural minerals (*e.g.*, Gorzhevskaya *et al.*, 1967 ; Sidorenko *et al.*, 1974).

Laboratory synthesis under geologically reasonable conditions (600-200°C, 750-3000 bars $P(H_2O)$, aqueous Na,K,F,Cl,CO_2-bearing fluids) is also being reported. Some of these studies have been aimed much more at the nature of transporting fluids and precipitation mechanisms than the compositional stabilities of solid phases (*e.g.*, Alexandrov and Trusikova, 1973 ; Wang *et al.*, 1982), but the latter subject is also drawing more attention.

For the present, even some of the simplest systems are poorly understood. For example, Moreau and Tramasure (1965) obtained a wide two-phase region (columbite-tantalite + tapiolite) between the single-phase fields of the columbite-tantalite-tapiolite quadrilateral (dry system at 1050°C/ 1 atm./50 hrs.). Schröcke's (1966) results suggest that this 2-phase region may even expand at lower temperatures. However, long experimental runs of Turnock (1966) that probably approach equilibrium more closely contradict the results of the above authors. Metastability may also plague the experimental data of Komkov and Dubik (1974, 1983), despite their attempt to correlate stability shifts with changes in structural states. In general, none of the experimentally derived two-phase fields approaches the corresponding field of figure 1A, representative of natural compositions and very close to the field defined by co-existing tantalites + tapiolites (Černý *et al.*, 1984). So far the question remains unanswered whether it is some of the experimental results or the natural field boundaries that represent true equilibria. In the first case, most "ferrotantalites" and neighbouring compositions or orthorhombic phases would be metastable.

Some information may be gleaned from textural relationships of natural assemblages. For example, the manganotapiolites of Lahti *et al.* (1983) are fine-grained and intergrown with antimony, cassiterite, silicates and "exsolutions" of microlite on the scale of 0.02 mm. In contrast, large and homogeneous tapiolites coexisting with tantalites which have grown in Mn-rich environments (*e.g.*, Černý *et al.*, 1984 ; Ercit, 1985) do not show the degree of Mn-enrichment displayed by the manganotapiolites. It is very probable that the Finnish manganotapiolites are a product of metastable crystallization, facilitated by fast nucleation rates and quenching.

The same is suggested for the Greer Lake ixiolites that occur in fine-grained blebs, intergrown with niobian-tantalian rutile, cassiterite, ilmenite and microlite (Černý *et al.*, 1985*b*). In contrast, separate occurrences of coarser-grained aggregates contain disordered columbite-tantalite as the only orthorhombic phase. However, this model cannot be extrapolated to other ixiolite occurrences, where the mineral forms large crystals (Helen Beryl, Tanco, Lower Tanco, Skogsböle and other localities). Only experimental work can answer the question whether ixiolites are metastable "wastebaskets" in general, or orthorhombic phases stabilized in the 2-phase region by their (R^{3+}, R^{4+}) content (Figure 1B).

Experimental modelling is also required in the TiO_2-$(Fe,Mn)Ta_2O_6$-$(Fe,Mn)Nb_2O_6$ system. Compositions of unmixed niobian-tantalian rutile + columbite-tantalite pairs suggest an asymmetric solvus, steep on the columbite-tantalite side but rather shallow towards the rutile phase (Figure 4C). However, the scatter of data shows that the paired compositions are probably out of

equilibrium. Similarly, the SnO_2-(Fe,Mn)Ta_2O_6-(Fe,Mn)Nb_2O_6 system has not been experimentally investigated to date ; the questionable existence of "staringite" makes it particularly attractive.

Structural aspects

The stability of ordered vs. disordered structural states of diverse Nb,Ta-bearing minerals is virtually unknown. This is not surprising in view of the fact that crystal structure refinements so far cover only a haphazard collection of species and groups ; systematic work on material representative of order-disorder sequences is lacking.

A classic example is the relationship between disordered-ordered columbite-tantalite, and ixiolite-wodginite. Since the first recognition of quasi-"polymorphic" relationships among these minerals by Nickel *et al.* (1983*b*), distinctive compositional differences between the above pairs have been confirmed requiring separate treatment of the two series (*e.g.*, Gorzhevskaya and Sidorenko, 1974 ; Černý, 1975 ; *cf.* p. 501-507).

Several recent structure refinements were done on ordered columbites-tantalites (Grice *et al.*, 1976 ; Foord, 1976 ; Weitzel, 1976), but only one was done on a largely disordered tantalite ("ixiolite" of Grice *et al.*, 1976). Synthesis of disordered columbite-tantalite happened to have been performed only twice under geologically unrealistic conditions (Schröcke, 1961 ; Moreau and Tramasure, 1965) but it was achieved more systematically under supercritical conditions (Komkov and Dubik, 1974, 1983). Possible compositional controls on the order-disorder in natural minerals, demonstrated on synthetic Co- and Ni-based tapiolites and columbites-tantalites (Felten, 1967), were only qualitatively outlined by Gorzhevskaya and Sidorenko (1974) in terms of Nb_2O_5/Ta_2O_5 and FeO/MnO ratios. The possible influence of low Ti,Sn, etc. substitutions has not been examined.

Giese (1975) showed that the electrostatic energies of the 495 different distributions of 8 Nb and 4 Mn over the cation sites in manganocolumbite are close to the energy of ordered $Mn_4Nb_8O_{24}$. He concluded that disordered structures can form as easily as the ordered one. Our data seems to support this idea (Figure 1A). Nevertheless, the striking differences among the structural state populations from different localities suggest that some factors operative in geological environments do enhance specific order-disorder states (*cf.* figure 7C ; compare figures 7B vs. 7C, 5C vs. 7B, etc.). It should be also noted that synthetic phases tend to crystallize disordered, and to reach increasing order upon extended heating (Komkov and Dubik, 1974, 1983).

As suggested earlier (p. 503), there seems to be a bimodal tendency suggested for largely ordered vs. largely disordered manganotantalite compositions. This tendency is even more pronounced than suggested in figure 1A because most of the truly intermediate-state plots at the Mn-rich side of the diagram belong to extreme manganocolumbites. Such a tendency is also shown by the Tanco plots (Figure 6B) and suggested by the SF data distribution (Figure 7C). Further structural data for extremely manganoan compositions are required to test this observation.

It is also noteworthy that in several groups of cogenetic columbites-tantalites with variable composition and structural state, the degree of ordering increases with enrichment in Mn. This trend is observed in several pegmatite series of the Yellowknife field (Wise, 1985), in the A3 specimens from Greer Lake (Černý *et al.*, 1985*b* ; figure 7C), and partly in the Huron Claim pegmatite (Paul, 1984 ; figure 5A). Of the pegmatites in the Black Hills of South Dakota, the Tin Mountain columbites-tantalites best express this trend (Figure 8A).

As mentioned earlier in this paper, wodginites show variable degrees of order (Ercit, 1985) and may be transitional into ixiolites in more than one manner. However, only one refinement of a wodginite structure is available (Ferguson *et al.*, 1976), and none for ixiolite or partially ordered wodginite. Experimental work on the ixiolite-wodginite stability is non-existent, which is all the more disconcerting in view of the compositional variability of both species (p. 503-506).

Another example of structurally underexplored minerals is the microlite subgroup of the cubic $A_{2-m}B_2O_6(O,OH,F)_{1-n}$ oxide minerals (p. 509-510). To the best of our knowledge, no structure refinement is available for natural microlite, which is totally out of balance with the dramatic compositional diversity of this sub-

group. A systematic program of structure refinement is warranted (and currently in progress in our laboratory), all the more that new species are being defined on the basis of hypothetical cation stoichiometries and/or distributions (Voloshin *et al.*, 1981*b*, 1983*a*).

CONCLUDING REMARKS

Despite the recent progress in our understanding of Nb,Ta-bearing minerals in granitic pegmatites, and partly because of this progress, many fundamental problems remain unresolved, and new ones are coming to our attention. To make substantial inroads into the areas of our ignorance, five principal approaches should be followed :

(i) paragenetic, compositional and quantitative structural documentation of *all* members of natural Nb,Ta-mineral sequences from geologically interpreted and classified pegmatites, pegmatite groups and fields, to improve the existing data base ;

(ii) structure refinements of all new minerals, and systematic structure refinements in all compositional and/or order-disorder series and groups, to understand the crystallochemical state and potential of individual species and their relationships ;

(iii) experimental definition of compositional and structural stability relationships under geologically realistic conditions, to interpret the natural assemblages of Nb,Ta-bearing species ;

(iv) geochemical studies of the assemblages and associations carrying Nb,Ta-minerals, in terms of bulk composition, trace element distributions, stable and radiogenic isotope fractionation, and fluid inclusion characteristics, to establish constraints on their mode(s) of formation ; and

(v) experimental modelling of Nb,Ta migration and precipitation in granitic melts, co-existing supercritical fluids and postmagmatic solutions, to verify the interpretation of natural fractionation products.

The above program is a tall order indeed, but most of its components are already pursued in many institutions around the world, and substantial advances in our knowledge of Nb,Ta mineralogy should be forthcoming in the foreseeable future.

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