

## WODGINITE-GROUP MINERALS FROM THE SEPARATION RAPIDS RARE-ELEMENT GRANITIC PEGMATITE GROUP, NORTHWESTERN ONTARIO

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### ABSTRACT

Wodginite (ideally  $\text{MnSnTa}_2\text{O}_8$ ), and the rarer species, ferrowodginite (ideally  $\text{Fe}^{2+}\text{SnTa}_2\text{O}_8$ ) and titanowodginite (ideally  $\text{MnTiTa}_2\text{O}_8$ ), have been discovered in rare-element granitic pegmatites of the complex type, petalite subtype, which occur in the Separation Rapids pegmatite field, northwestern Ontario. Tungsteniferous varieties of wodginite and an unnamed wodginite ("ferrotitanowodginite") are also described from this locality. The pegmatites intrude a metavolcanic (greenstone) belt between the English River and Winnipeg River subprovinces of the Canadian Shield, where they are associated with a  $2643 \pm 2$  Ma rare-element-enriched granitic intrusion, the Separation Rapids pluton. The tungsteniferous wodginite has an excess positive charge at the C site due to substitution of Ta by W, which is balanced by the presence of  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  at the B site via the substitutions:  $^{\beta}[\text{Sn}^{4+}] + ^{\text{C}}[\text{Ta}^{5+}] \leftrightarrow ^{\beta}[\text{Fe}^{3+}] + ^{\text{C}}[\text{W}^{6+}]$ ,  $^{\beta}[\text{Sn}^{4+}] + 2^{\text{C}}[\text{Ta}^{5+}] \leftrightarrow ^{\beta}[\text{Mn}^{2+}] + 2^{\text{C}}[\text{W}^{6+}]$ , and  $2^{\beta}[\text{Sn}^{4+}] + ^{\text{C}}[\text{Ta}^{5+}] \leftrightarrow ^{\beta}[\text{Mn}^{2+}] + ^{\beta}[\text{Ta}^{5+}] + ^{\text{C}}[\text{W}^{6+}]$ . These new schemes of substitution result in hypothetical tungsteniferous end-members  $\text{Mn}^{2+}_4(\text{Fe}^{3+}_2\text{Sn}_2)(\text{W}_2\text{Ta}_6)\text{O}_{32}$ ,  $\text{Mn}^{2+}_4(\text{Mn}^{2+}_2\text{Sn}_2)(\text{W}_4\text{Ta}_4)\text{O}_{32}$ , and  $\text{Mn}^{2+}_4(\text{Mn}^{2+}\text{Sn}_2\text{Ta})(\text{W}\text{Ta}_7)\text{O}_{32}$ . At Separation Rapids, the rare-metal oxides follow two distinct evolutionary paths: (i) ferrocolumbite  $\rightarrow$  ferrocolumbite + ferrowodginite  $\rightarrow$  ferrotantalite + ferrowodginite  $\rightarrow$  microlite-group minerals, and (ii) manganocolumbite  $\rightarrow$  manganocolumbite + wodginite  $\rightarrow$  manganotantalite + wodginite  $\rightarrow$  microlite-group minerals. Sequence (i) is considered to have arisen from a relatively F-poor magma, and sequence (ii), from a magma richer in F, where extreme enrichment in Mn was perhaps achieved through F-complexing. Wodginite-group minerals are most often found in the albite-enriched regions of the pegmatites. Magmatic fractionation is considered to be the major process controlling concentration of the rare elements. Titaniferous wodginite compositions cannot be explained by simple magmatic fractionation (from a Fe- or Mn-rich wodginite starting composition); localized interaction of the pegmatite-forming magma with mafic metavolcanic rocks is proposed for their origin. Of wodginite-group minerals worldwide, only the "giant" Tanco pegmatite at Bernic Lake in Manitoba hosts wodginite with a spread of compositions comparable to that at Separation Rapids. On the basis of a striking similarity in geological setting, mineralogy and age of emplacement with the rare-element pegmatite groups commencing 40 km west in Manitoba (including Tanco), we contend that the Separation Rapids Pegmatite Group constitutes the eastern limit of the Cat Lake – Winnipeg River Pegmatite Field.

**Keywords:** wodginite, ferrowodginite, titanowodginite, granitic pegmatite, tantalum, tin, electron microprobe, Separation Rapids, Ontario.

### SOMMAIRE

Nous documentons la présence de la wodginite (formule idéale  $\text{MnSnTa}_2\text{O}_8$ ) ainsi que des espèces plus rares ferrowodginite (formule idéale  $\text{Fe}^{2+}\text{SnTa}_2\text{O}_8$ ) et titanowodginite (formule idéale  $\text{MnTiTa}_2\text{O}_8$ ) dans un cortège de pegmatites granitiques enrichies en éléments rares, de type complexe, sous-type de la pétalite, à Separation Rapids, dans le nord-ouest de l'Ontario. Une variété tungsténifère de la wodginite et une espèce sans nom ("ferrotitanowodginite") y sont aussi présentes. Les pegmatites ont été mises en place dans une ceinture métavolcanique de roches vertes entre les sous-provinces de English River et Winnipeg River du bouclier canadien, et sont associées au pluton de Separation Rapids ( $2643 \pm 2$  Ma), lui-même enrichi en éléments rares. La wodginite tungsténifère a un excès de charge positive à la position C à cause du remplacement du Ta par W, qui est compensé par la présence de  $\text{Fe}^{3+}$  et de  $\text{Mn}^{2+}$  à la position B selon les substitutions:  $^{\beta}[\text{Sn}^{4+}] + ^{\text{C}}[\text{Ta}^{5+}] \leftrightarrow ^{\beta}[\text{Fe}^{3+}] + ^{\text{C}}[\text{W}^{6+}]$ ,  $^{\beta}[\text{Sn}^{4+}] + 2^{\text{C}}[\text{Ta}^{5+}] \leftrightarrow ^{\beta}[\text{Mn}^{2+}] + 2^{\text{C}}[\text{W}^{6+}]$ , et  $2^{\beta}[\text{Sn}^{4+}] + ^{\text{C}}[\text{Ta}^{5+}] \leftrightarrow ^{\beta}[\text{Mn}^{2+}] + ^{\beta}[\text{Ta}^{5+}] + ^{\text{C}}[\text{W}^{6+}]$ . Ces nouveaux schémas de substitution mènent aux pôles tungsténifères hypothétiques  $\text{Mn}^{2+}_4(\text{Fe}^{3+}_2\text{Sn}_2)(\text{W}_2\text{Ta}_6)\text{O}_{32}$ ,  $\text{Mn}^{2+}_4(\text{Mn}^{2+}_2\text{Sn}_2)(\text{W}_4\text{Ta}_4)\text{O}_{32}$ , et

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$Mn^{2+}_x(Mn^{2+}Sn_xTa)(WTa_7)O_{32}$ . A Separation Rapids, ces oxydes des métaux rares définissent deux lignées évolutives distinctes: (i) ferrocolumbite  $\rightarrow$  ferrocolumbite + ferrowodginite  $\rightarrow$  ferrotantalite + ferrowodginite  $\rightarrow$  minéraux du groupe du microlite, et (ii) manganocolumbite  $\rightarrow$  manganocolumbite + wodginite  $\rightarrow$  manganotantalite + wodginite  $\rightarrow$  minéraux du groupe du microlite. La séquence (i) s'appliquerait à un magma à teneur en F relativement faible, et la séquence (ii), à un magma enrichi en F, dans lequel un enrichissement extrême en Mn aurait peut-être été atteint grâce à une complexation par le fluor. On trouve les minéraux du groupe de la wodginite surtout dans les zones des pegmatites enrichies en albite. Un fractionnement magmatique serait le processus important pour expliquer la concentration des éléments rares. En revanche, les compositions titanifères de la wodginite ne peuvent s'expliquer par fractionnement magmatique simple (à partir d'une wodginite ferrifère ou manganifère); une contamination localisée du magma évolué par les roches métavolcaniques mafiques en serait l'origine. Sur une échelle mondiale, seule la pegmatite "géante" de Tanco, au lac Bernic, au Manitoba, contient des minéraux du groupe de la wodginite avec un éventail de compositions comparable à celui de Separation Rapids. Une ressemblance frappante du contexte géologique, des assemblages de minéraux et du contexte temporel de mise en place des groupes de pegmatites à éléments rares, commençant à 40 km à l'ouest, dans le Manitoba (et comprenant Tanco), nous fait penser que le cortège de pegmatites de Separation Rapids constitue la limite orientale du champ de pegmatites du lac Cat et de la rivière Winnipeg.

(Traduit par la Rédaction)

**Mots-clés:** wodginite, ferrowodginite, titanowodginite, pegmatite granitique, tantalite, étain, microsonde électronique, Separation Rapids, Ontario.

## INTRODUCTION

The Separation Rapids Pegmatite Group in northwestern Ontario (Figs. 1, 2) is the subject of considerable interest since the discovery of cassiterite and petalite ( $LiAlSi_4O_{10}$ ) by Breaks (1993). On a worldwide basis, petalite occurs in only 2% of all lithium-rich rare-element pegmatites (Černý & Ercit 1989) and is a significant indicator of the exploration potential of pegmatites. Following on from this discovery, an investigation was begun to characterize the rare-element assemblage and, in particular, wodginite and other tantalum-bearing oxides (Tindle & Breaks 1998). Wodginite also is of potential importance economically; it is the chief ore mineral of tantalum at the Tanco mine, a globally significant deposit of tantalum.

The name *wodginite* was first proposed by Nickel *et al.* (1963) for a tin-manganese tantalite ( $MnSnTa_2O_8$ ) that had been found in rare-element pegmatites at Wodgina, Australia (Simpson 1909) and Bernic Lake, Manitoba (Hutchinson 1959). The former occurrence had been described as ixiolite ( $Ta,Nb,Sn,Fe,Mn)_4O_8$ , and the latter, as columbite ( $Mn,Fe)(Nb,Ta)_2O_6$ . At Wodgina, the wodginite varies from pale cinnamon brown to dark brown and has a resinous luster. It constituted 28% of the ore, with the remainder being a matrix of granular albite with a little quartz and muscovite. At Bernic Lake, the wodginite occurs in coarse, partially sericitized perthitic microcline and in fine-grained, bluish white aplitic albite, and forms spheroidal or irregular, highly serrated grains commonly associated with ferrotapiolite ( $FeTa_2O_6$ ) and microlite [ $(Na,Ca)_2(Nb,Ta)_2O_6(O,OH,F)$ ]. The mineral assemblages of the pegmatite at Bernic Lake are typical of cesium-lithium deposits worldwide, the principal minerals being quartz, feldspar, lithium micas, spodumene,  $LiAlSi_2O_6$ , pollucite,  $(Cs,Na)[AlSi_2O_6] \cdot H_2O$ , and amblygonite,  $(Li,Na)Al(PO_4)(F,OH)$  (Nickel *et al.* 1963).

This paper is based on results of an electron-microprobe investigation of wodginite-group minerals from Separation Rapids. We discuss the substitution operators described by Ercit *et al.* (1992a), and add three more to account for the variations in tungsten content. We also propose a new substitution scheme for wodginite with excess A-site Mn and outline possible reasons for the variable composition of wodginite-group minerals in the different rare-element pegmatite lithologies at Separation Rapids.

## BACKGROUND INFORMATION

Ercit *et al.* (1992a) described ferrowodginite and titanowodginite ( $MnTiTa_2O_8$ ) as new species and grouped them with wodginite (*sensu stricto*) and lithowodginite ( $LiTaTa_2O_8$ ; Voloshin *et al.* 1990) to define the wodginite group. Excluding the lithian variety, the main wodginite varieties are represented in Figure 3, where ideal compositions occur at the corners of the diagram, and the four quadrants define the boundaries between the wodginite-group minerals shown. This diagram effectively summarizes the main A-site ( $Fe \leftrightarrow Mn$ ) and B-site ( $Ti \leftrightarrow Sn$ ) substitutions. The top left quadrant of Figure 3, equivalent to the end-member  $FeTiTa_2O_8$ , remains unnamed as material available (analyses TSE-82 and -94 from Tanco) was insufficient to characterize the hypothetical species "ferrotitanowodginite" (Ercit *et al.* 1992a). Over 200 unpublished results of analyses (the majority are wodginite *sensu stricto* from Tanco, Manitoba) collected by Ercit *et al.* (1992a) also are plotted in Figure 3. These data include the type compositions for wodginite, ferrowodginite and titanowodginite.

A ferroan "variety" of wodginite was first encountered by Vormá & Stivola (1967) from material found in a granitic pegmatite near Sukula, southwestern Finland. Unfortunately, the samples were collected over 100 years ago, and the exact location is unknown.

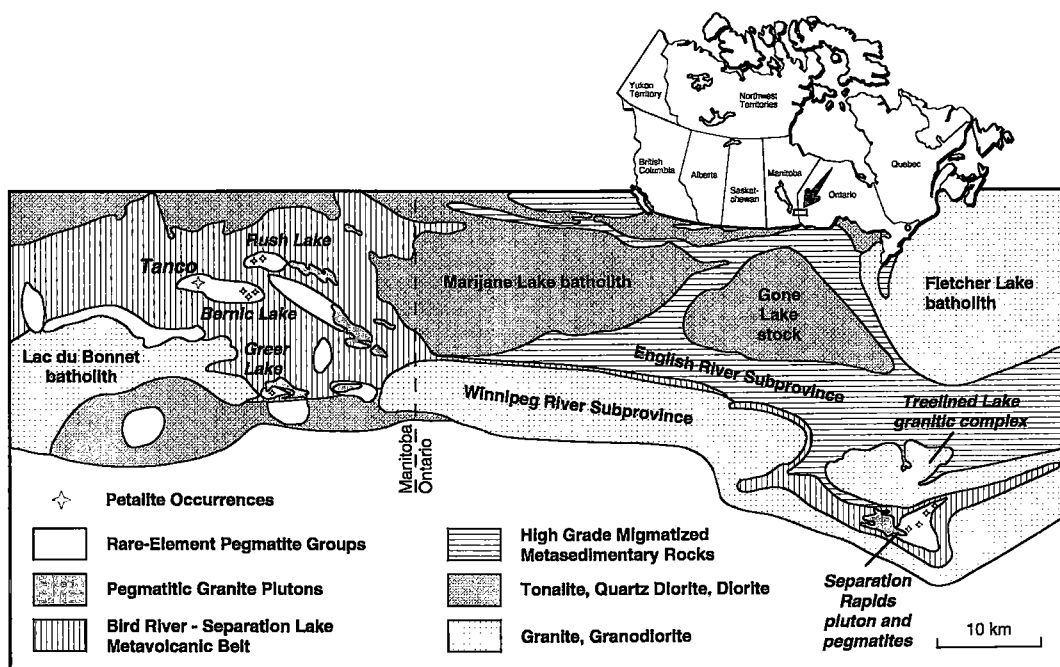


FIG. 1. Regional geology including the location of rare-element pegmatite groups and fertile granite plutons, Bird River - Separation Lake Metavolcanic Belt. Compiled from Breaks *et al.* (1975), Černý *et al.* (1981) and Blackburn & Young (1994a, b).

This material was re-analyzed by Ercit *et al.* (1992b) and is now ascribed to the type ferrowodginite. It occurs as irregular inclusions (0.01–0.2 mm long) together with ferrotapiolite ( $\text{Fe}^{2+}, \text{Mn}^{2+}$ )(Ta,Nb) $_2\text{O}_6$  and native bismuth, in strongly color-zoned tantalian cassiterite. The type ferrowodginite is dark brown to black. Other examples of ferrowodginite have been described from Ankole, Uganda (von Knorring & Fadipe 1981), Muhambe River, Rwanda (Ercit *et al.* 1992a), Tanco, Manitoba (Ercit *et al.* 1992a), Pedro Lavreda, Brazil (Groat *et al.* 1994) and Cap de Creus, Pyrenees, Spain (Abella *et al.* 1995).

The type titanowodginite is from the Tanco pegmatite (Ercit 1986, Ercit *et al.* 1992b) and is found together with microlite and manganocolumbite ( $\text{MnNb}_2\text{O}_6$ ) in the saccharoidal albite and central intermediate units of the pegmatite. It occurs in irregular clusters of crystals and as individual crystals ranging in size from a few mm to 1 cm long. Crystals are dark brown to black and slightly zoned, with rim compositions having higher Mn/Fe and Sn/Ti than in the core. Before our study, titanowodginite had been described only from the Tanco pegmatite.

Compositions (determined by electron microprobe) of wodginite, ferrowodginite and titanowodginite are described here because of their rarity (first occurrences in Ontario) and because of the economic implications

of this mineral group (wodginite is the main ore of Ta at the Tanco mine, Manitoba). The ferrowodginite from Separation Rapids is only the seventh occurrence reported, whereas the titanowodginite is only the second occurrence worldwide. Electron-microprobe data for two other wodginite-group minerals are also presented here, although their strong zonation and limited quantity (they occur mainly as tiny inclusions in cassiterite) preclude a crystallographic study [the same problem was encountered by Ercit *et al.* (1992b) with “ferrotitanowodginite”].

#### THE SEPARATION RAPIDS PLUTON AND PEGMATITE GROUP

The Separation Rapids pluton and Pegmatite Group lie within the Separation Lake metavolcanic belt (Fig. 1), which forms part of the boundary zone between the English River and Winnipeg River subprovinces of the Archean Superior Province, Ontario (Beakhouse 1991, Breaks 1991). The same metavolcanic–metasedimentary belt (termed the Bird River Subprovince) hosts the Greer Lake granite with its rare-element pegmatites (Černý *et al.* 1981, 1986), the Rush Lake pegmatites and the “giant” rare-element pegmatite at Tanco mine, Bernic Lake, 70 km away across the provincial border in Manitoba (Černý 1991). These latter pegmatites and other pegmatites in

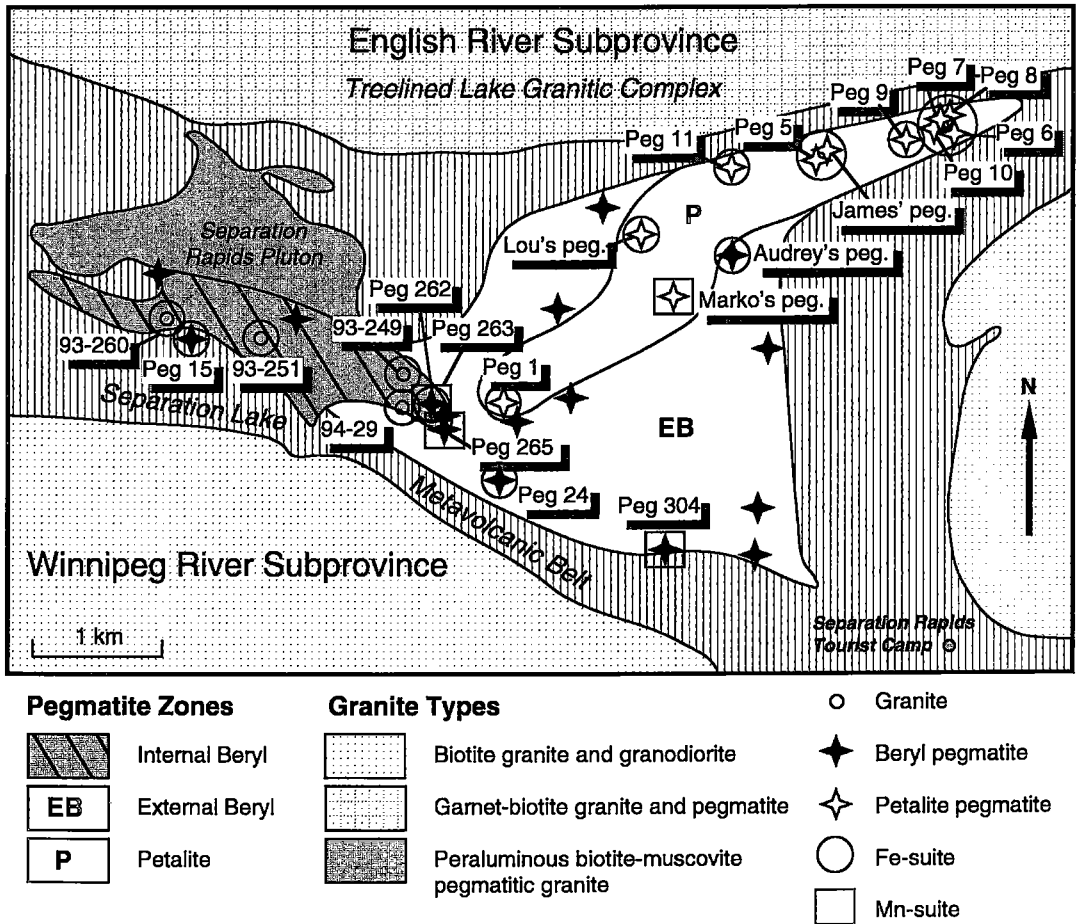


FIG. 2. General geology and location of rare-element mineral occurrences of the Separation Rapids Pegmatite Field. The Fe- and Mn-suite classification is based on columbite–tantalite data from the Separation Rapids pluton and pegmatites, and is discussed at length in Tindle & Breaks (1998).

close proximity from the Cat Lake – Winnipeg River Pegmatite Field.

The  $2643 \pm 2$  Ma (unpubl. U/Pb monazite age; Y. Larbi & R.K. Stevenson, GEOTOP Laboratory, Université du Québec à Montréal) Separation Rapids pluton (4 km<sup>2</sup>) is a fertile, peraluminous S-type granite dominated by distinct units of pegmatitic granite that largely envelop a core of coarse-grained, K-feldspar porphyritic, garnet – muscovite – biotite granite. On the basis of a striking similarity in geological setting, mineralogy and age of emplacement with the various rare-element pegmatite groups commencing 40 km west in Manitoba, we conclude that the Separation Rapids Pegmatite Group constitutes the eastern limits of the Cat Lake – Winnipeg River Pegmatite Field. Striking similarities with the Greer Lake granite include the presence of cordierite, beryl, cassiterite

and ferrocolumbite, the occurrence of primary layering in the pegmatite swarm, and the presence of highly fractionated, rare-element-enriched pods of platy-albite-rich pegmatite. Rare occurrences of gahnite ( $ZnAl_2O_4$ ), cadmium-rich sphalerite, arsenopyrite, löllingite and chalcopyrite are recorded from the Separation Rapids pluton, but wadginite-group minerals are absent (Tindle & Breaks 1998, unpubl. data).

The Separation Rapids pluton and pegmatites are hosted by supracrustal rocks (mafic metavolcanic rocks and banded ironstones) of the Separation Lake greenstone belt (Fig. 2; see also Blackburn *et al.* 1992, Blackburn & Young 1994a, b), which correlates with the 2.74 Ga Bird River greenstone belt of Manitoba (Timmins *et al.* 1985). The southeastern termination of the Separation Rapids pluton and the associated

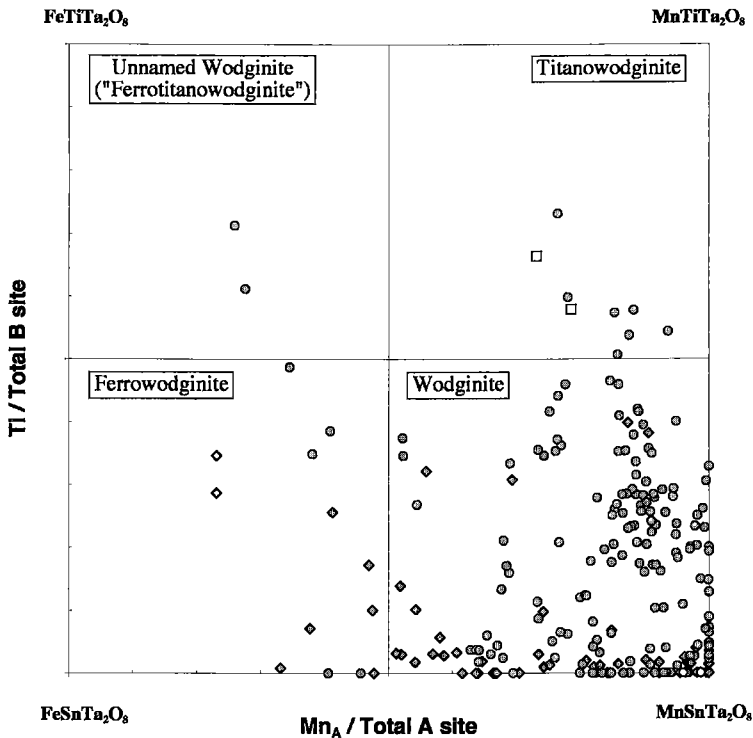


FIG. 3. Classification quadrilateral for wodginite-group minerals. The diagram is based on the columbite–tantallite quadrilateral and illustrates A-site (Mn, Fe<sup>3+</sup>, Li) versus B-site (Sn, Ti, Fe<sup>3+</sup>, Ta, Mn) substitutions. Wodginite data from type localities are highlighted (O: type wodginite, ◇: type ferrowodginite, □: type titanowodginite). World occurrences (shaded diamonds) include Australia, Brazil, China, Canada (Manitoba), Finland, Japan, Namibia, U.S.A. (Connecticut, South Dakota and Virginia) and the former USSR. Data points for Tanco, Manitoba: shaded circles. Data are (mainly) derived from Ercit *et al.* (1992b). Other data from Nickel *et al.* (1963), Dunn *et al.* (1978), Spilde & Shearer (1992), and Groat *et al.* (1994). The diagram does not take C-site (Nb–Ta–W) substitutions into account. Reasons for plotting  $\Delta$ Mn rather than Mn<sub>total</sub> are given in the text.

rare-element pegmatites lie within the core, and along the eastern flanks, of the west-plunging Separation Narrows antiform (Blackburn & Young 1994b). The more deformed pegmatites in the northeastern part of the field are hosted within a 100-meter-wide high-strain zone, which parallels the northern boundary of the Separation Lake metavolcanic belt.

Rare-element pegmatites outcrop to the east of the Separation Rapids pluton over an area of 3 by 7 km. The area contains numerous individual pegmatitic dykes, many of which contain petalite (Breaks & Tindle 1994) and belong to the complex type, petalite subtype of the rare-element pegmatite class (Černý 1991). Three spatially distinct pegmatite zones are recognized in and around the Separation Rapids pluton (Breaks 1993). The first pegmatite zone is internal, of the columbite – cassiterite – beryl (Beryl) type, and occurs within the southern part of the Separation

Rapids pluton. To the east and northeast of the Separation Rapids pluton, there is an outer columbite – cassiterite – beryl (Beryl) zone, which partially envelops a cassiterite – beryl – petalite (Petalite) zone (Fig. 2).

#### *Pegmatites within the Separation Rapids pluton*

Green beryl, garnet (almandine–spessartine solid solution), ferrocolumbite and cassiterite occur sparsely in pegmatitic leucogranite, fine-grained leucogranite and potassic pegmatite units comprising the southern half of the Separation Rapids pluton (Fig. 2), but none contain wodginite-group minerals. However, a trend of increasing magmatic fractionation toward the 200–400-meter-wide southeasternmost margin of the pluton is indicated by increasing levels of Cs and Rb in K-feldspar (Breaks *et al.*, in prep.), a plausible point of

departure for highly evolved batches of residual melt, which may have crystallized as the petalite-bearing rare-element pegmatites.

### Beryl zone

Outside of the Separation Rapids pluton, the first pegmatite zone encountered comprises muscovite- and biotite-muscovite-bearing potassic pegmatites and related aplites (Fig. 2). These pegmatites contain faint green and white beryl, cassiterite, ferrocolumbite, manganocolumbite and, rarely, manganotantalite. Wodginite-group minerals are uncommon in this zone, although some of the highest contents (1–2%) of rare-element oxide minerals (columbite-tantalite and cassiterite) occur in aplite dykes close to the Separation Rapids pluton. Notable in this zone is the presence of 0.5- to 1.0-m-thick topaz- and fluorite-bearing sodic pegmatite and aplite dykes (without wodginite-group minerals) and metasomatic selvages developed in mafic metavolcanic host-rocks containing the highest levels of fluorine of any in the area (5–8.5 wt.% F).

Three occurrences of wodginite-group minerals have been investigated and include (i) ferrowodginite from a dyke of garnetiferous aplite (Peg. 15) close to the margin of the Separation Rapids pluton, (ii) ferrowodginite from a fluorapatite – garnet – biotite – muscovite potassic pegmatite (Audrey's pegmatite) in close proximity to the petalite zone, and (iii) wodginite (*ss*) from a layered 8-m-thick fluorapatite – garnet – biotite – muscovite potassic pegmatite (Peg. 265) containing platy-albite-rich pods with purple lithian muscovite, white beryl, tourmaline, cassiterite, manganocolumbite and (almost end-member) manganotantalite. Wodginite, in appearance similar to cassiterite, forms anhedral or skeletal, dark brown translucent crystals and occurs as inclusions in muscovite. Wodginite crystals can either be isolated or form clusters, and may be partially replaced by bismutomicrolite. A large compositional gap exists between the columbite-tantalite from Peg. 265 and that from the Separation Rapids pluton (which contains ferrocolumbite), and this characteristic has been used to define Fe-suite pegmatites, such as Pegs. 15 and 271, and Mn-suite pegmatites, such as Peg. 265 (Tindle & Breaks 1998).

### Petalite zone

Eleven petalite-bearing pegmatites, within a 0.5 × 5 km elongate zone, mark the compositionally most-evolved part of the pegmatite field (Fig. 2), and it is here that the greatest variety of wodginite-group minerals have been found, with ferrowodginite by far the most widespread. Nine of these pegmatites have been examined. Cassiterite is the oxide mineral most commonly found with the wodginite-group minerals, and in some samples, the wodginite occurs only as

inclusions in cassiterite grains. Columbite and tantalite are also found in most wodginite-bearing samples. In order of increasing rarity, other oxide phases include microlite, uraninite, uranmicrolite, bismutomicrolite, stibiomicrolite and strüverite (tantalian rutile). However, the oxide assemblages are abundant only in primary albite-rich units or secondary beryl – muscovite – albite assemblages that variably replace the central petalite-rich core of some pegmatite bodies. The volume of pegmatite affected by albitization is between 2 and 15%. Concentrations of Nb–Ta–Sn oxides are commonly associated with fluorapatite. Nigerite [(Zn,Fe<sup>2+</sup>)(Sn,Zn)<sub>2</sub>(Al,Fe<sup>3+</sup>)<sub>12</sub>O<sub>22</sub>(OH)<sub>2</sub>], chalcopyrite, arsenopyrite, löllingite, thorium monazite, xenotime and zircon occur less frequently. Tourmaline and garnet may also be present, the latter locally abundant in outer, earlier-crystallized units.

Ferrowodginite is opaque and occurs as isolated grains associated with albite and apatite or as inclusions within cassiterite grains. All ferrowodginite-bearing samples also contain cassiterite. In Figure 4a, ferrowodginite abuts a cassiterite crystal, which itself partially encloses a ferrocolumbite crystal; the ferrowodginite is partially replaced by microlite away from the cassiterite. In a few samples, crystals of ferrowodginite up to 3 mm in length were observed containing uranmicrolite (U,Ca,Ce)<sub>2</sub>(Ta,Nb)<sub>2</sub>O<sub>6</sub>(OH,F) inclusions; in places, the crystals are porous (Fig. 4b). Such pores may represent fluid-inclusion cavities or corrosion pits (Tindle & Webb 1989, Johan & Johan 1994). Ferrowodginite also develops extremely irregular patchy zonation (Figs. 4c, d) and is spatially restricted to seven ferrocolumbite-bearing pegmatites in the northeastern sector of the cassiterite – beryl – petalite zone distal from the Separation Rapids pluton. Three pegmatites also contain wodginite (Marko's, Peg. 5 and Peg. 7) and one, Marko's, also contains titanowodginite and "ferrotitanowodginite" (Ercit *et al.* 1992a). Wodginite was not found in two of the pegmatites examined (Peg. 1 and Peg. 10), but this could simply mean that the duplicate polished sections (or mineral separates) from each pegmatite sample may not have been representative. All samples were examined by electron microprobe.

Marko's pegmatite (Fig. 2) deserves further mention, not only because it is the largest petalite-bearing pegmatite in the Separation Rapids region, but also because it hosts the very rare titaniferous wodginite-group minerals. Marko's pegmatite has a thickness of 8 meters, a minimum length of 130 meters, and contains the greatest amount of petalite of any of the pegmatites in the area (about 40–80% in the westernmost lens and up to 95% in the easternmost lens). Most of the large masses of petalite make up the infill between 1- to 2-m-long blocky crystals of K-feldspar (Fig. 5). In this pegmatite, wodginite (*ss*) occurs either as translucent (dark brown) or opaque

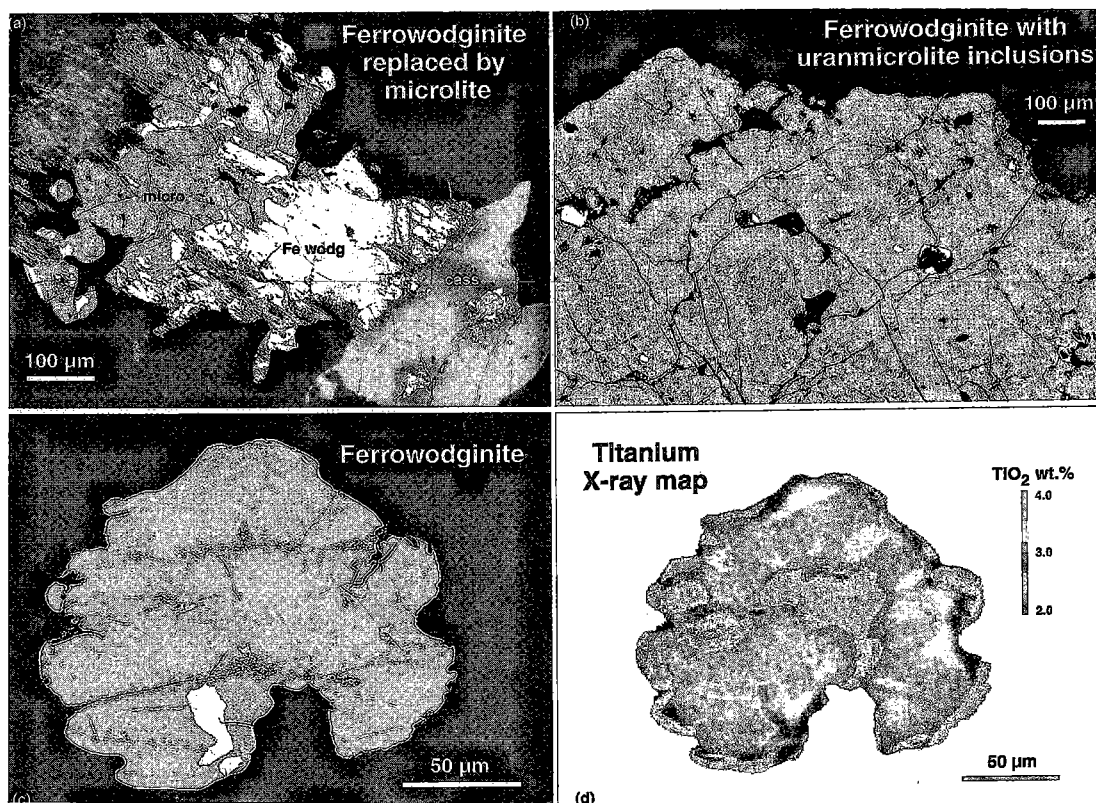


FIG. 4. Internal features of ferrowodginite. (a) Peg 7: ferrowodginite abuts a crystal of cassiterite, which itself partially encloses a crystal of ferrocolumbite. The ferrowodginite is partially replaced by microlite away from the cassiterite [back-scattered electron (BSE) image]. (b) Peg 5: large crystal of ferrowodginite with porous texture and white uranmicrolite inclusions (BSE image). (c) James's pegmatite: complex zonation in ferrowodginite (BSE image). (d) James's pegmatite: X-ray map of Ti distribution in ferrowodginite (calibrated in wt.% oxide units).

crystals. These may be partially altered to microlite (Fig. 6a). Wodginite is better preserved where it occurs as inclusions in cassiterite (Fig. 6b) and in aplitic units (Fig. 6c). It is accompanied by manganocolumbite and manganotantalite. The margin of the pegmatite comprises a muscovite – albite – quartz wall zone that contains metasomatized biotite-rich mafic volcanic selvages. Within the albite, there are rare tabular (pseudocubic) crystals of wodginite up to 2 mm across. The margin of one such crystal displays irregular patchy zonation (Fig. 6d) and has a porous core (Fig. 6e). In the wall zone of this pegmatite, there are large crystals of cassiterite (up to 8.5 mm long) containing inclusions of strüverite, titanowodginite and “ferrotitanowodginite”. Figure 6f shows a titanowodginite inclusion exhibiting oscillatory and truncated zonation. Isolated crystals of grey microlite and yellow-green stibiomicrolite (both considered primary) accompany the cassiterite. Within the wall zone of Marko's pegmatite, columbite–tantalite is rarely found.

#### COMPOSITIONS OF WODGINITE-GROUP MINERALS

Details of an electron-microprobe investigation of wodginite-group minerals from Separation Rapids are presented here. The compositions of selected wodginite-group minerals are given in Table 1. The full dataset (results of approximately 250 analyses) is available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

#### Experimental method and presentation of data

Mineral analyses were obtained at the Open University using a Cambridge Instruments Microscan 9 electron microprobe equipped with two wavelength-dispersion spectrometers. Calibration standards and X-ray lines measured were rutile ( $TiK\alpha$ ), Mn metal ( $MnK\alpha$ ), fayalite ( $FeK\alpha$ ), cassiterite ( $SnL\alpha$ ), synthetic  $FeNb_2O_6$  ( $NbL\alpha$ ), synthetic  $NaTaO_3$  ( $TaM\alpha$ ), synthetic  $WO_3$  ( $WMB$ ) and galena ( $PbM\alpha$ ). Th and U were also

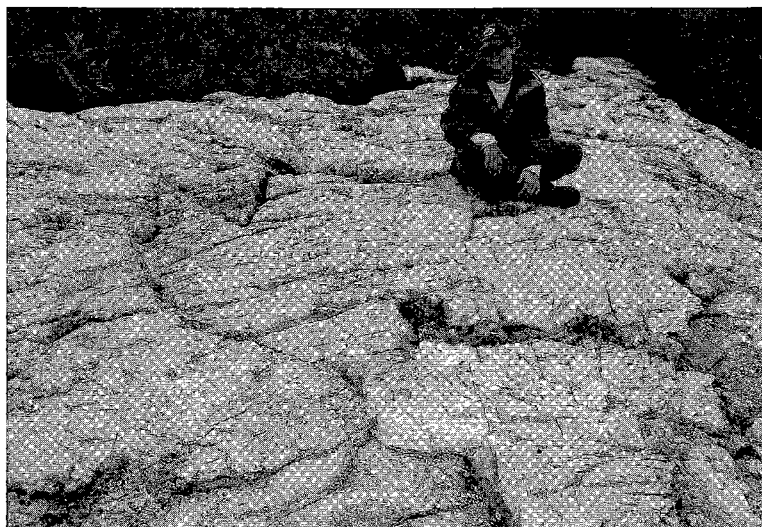


FIG. 5. Core zone of Marko's pegmatite. Field assistant Audrey Robitaille sits on top of a 2-m-long blocky K-feldspar crystal that is cut by a dark micaceous unit. A 3-m-long grey crystal of petalite fills the left-hand edge of the photograph.

measured (using oxide standards and  $M\alpha$  and  $M\beta$  lines, respectively), but usually were not detected. Sc, Sb and Bi were measured in some samples and calibrated against pure metal standards. Although the  $WM\beta$  line has a potential interference from a second-order Sn line, the interference was shown to be insignificant at concentrations of <12%  $SnO_2$ . An operating voltage of 20 kV and probe current of 30 nA (measured on a Faraday cage) were used. Count times varied from 20 to 50 seconds per element.  $Fe^{2+}$  and  $Fe^{3+}$  contents of wodginite-group minerals were calculated following the method of Ercit *et al.* (1992b).

#### *Distribution and occurrence of wodginite-group minerals*

The wodginite-group mineral in beryl and petalite pegmatites belonging to the Fe-suite at Separation Rapids is predominantly ferrowodginite (Fig. 7a, Table 1, anal. 1–4), but it becomes progressively more Mn-rich in the more evolved cores of a few pegmatites (*e.g.*, Table 1, anal. 5).

Pegmatite 265, a beryl pegmatite belonging to the Mn-suite, exhibits extreme Mn-enrichment closely matching end-member wodginite in composition (Table 1, anal. 9). Many of the examples of Mn-rich wodginite are tungsteniferous (Table 1, anal. 10–14), and some have relatively high concentrations of Bi, Pb and U (Table 1, anal. 12, 14). Concentrations of these minor elements are high where alteration of wodginite to microlite occurs (particularly so if bismutomicrolite is the alteration product).

Because of its size and complexity, Marko's pegmatite (a petalite pegmatite belonging to the Mn-suite) has been examined in more detail than the other pegmatites. For clarity, these data are plotted separately, on Figure 7b. The cluster of wodginite data at the bottom right of Figure 7b represents results of 55 analyses from 12 individual samples collected along the outcrop and comprising material from both the primary petalite core region (Table 1, anal. 7) and from the secondary muscovite–albite replacement unit of the pegmatite (Table 1, anal. 8). The layered muscovite – K-feldspar – quartz pegmatite – aplite units from Marko's pegmatite that crystallized early do not contain wodginite.

A second cluster of wodginite-group compositions in Marko's pegmatite have more than 50% of their *B*-site filled with Ti (Table 1, anal. 15–18). They plot in the fields of titanowodginite and the hypothetical "ferrotitanowodginite" (Ercit *et al.* 1992a). These grains all occur in the beryl – muscovite – albite – quartz wall zone and coexist with tourmaline, apatite, microlite, stibiomicrocline, struverite (24–42 wt.%  $Ta_2O_5$ ) and cassiterite (0.1–3.7 wt.%  $Ta_2O_5$ ). All occur as inclusions in cassiterite, and many show zonation (Fig. 6f). Mn/Fe values of individual inclusions within a single crystal of cassiterite may be very variable (44j) or tightly clustered (44m). To date, it has not proved possible to extract homogeneous "ferrotitanowodginite" inclusions for further characterization.

The third group of data points on Figure 7b pertain to a single, relatively large (2 mm across) crystal. The



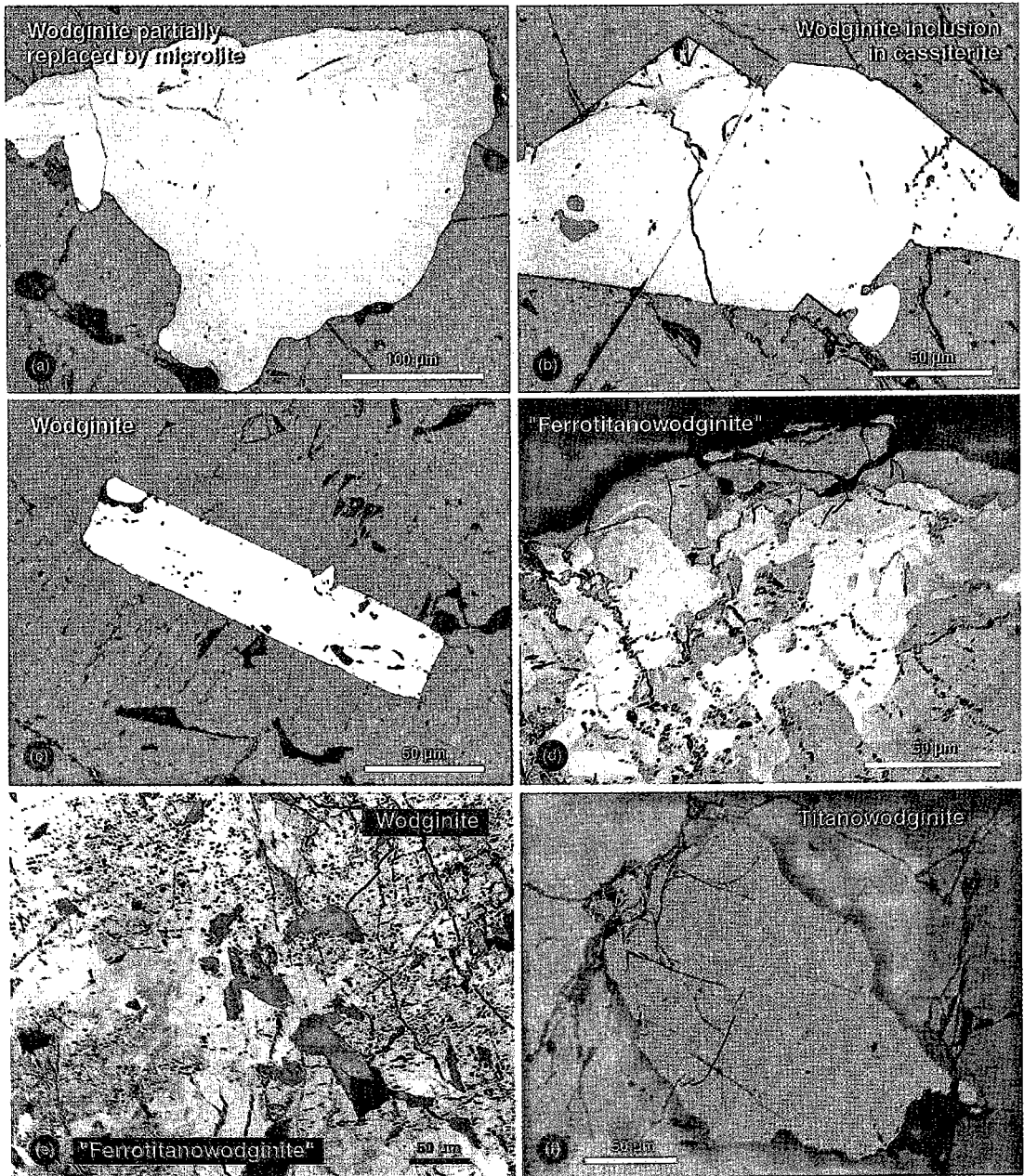


FIG. 6. Internal features of wodginite (*ss*) and titaniferous varieties from Marko's pegmatite. (a) Wodginite partially replaced by microlite (reflected light). (b) Euhedral cassiterite with one "partial" inclusion (white) of wodginite (reflected light). (c) Tabular wodginite in aplitic unit (reflected light). (d) "Ferrotitanowodginite" with complex patchy zoning, margin of 2 mm crystal (BSE image). (e) Porous wodginite core of same crystal as in (d) (BSE image). (f) Zoned inclusion of titanowodginite in cassiterite from wall zone (BSE image). BSE = back-scattered electron.

TABLE 1. COMPOSITION OF WODGINITE-GROUP MINERALS, SEPARATION RAPIDS PEGMATITES

	Ferrowodginite				Wodginite				Tungsteniferous Wodginites (*Wollramwodginites*)										Titanowodginite		*Ferrotitanowodginite*	
	1	2	3	4	5	6*	7S	8†	9*	10	11	12*	13*	13*	14*	15	16	17	18			
	MD	JU	FC	Peg 7B	Peg 7E	93-265P	94-44A	94-44R	93-265A	94-80E	94-80E	93-265A	93-265A	93-265A	93-265A	94-44J	94-44J	94-44M	94-44K2			
				CP	BB	WK	VJ	YA	KB	XC	XL	SL	ZS	ZS	SG	ZX	ZX	LD	CI			
Original data																						
FeO	11.77	12.44	10.29	10.53	6.15	4.92	2.31	2.50	0.47	6.87	9.49	2.32	0.58	1.95	5.83	4.57	12.03	10.86				
MnO	1.89	2.15	3.54	4.61	7.05	9.19	10.12	9.91	12.02	8.55	8.87	16.54	13.36	10.74	7.69	9.49	2.33	2.80				
PbO	0.11	0.03	0.06	0.02	0.03	0.03	0.03	0.05	0.02	0.13	0.05	0.14	0.02	0.99	0.03	0.03	0.08	0.07				
TiO2	1.27	4.17	2.85	1.46	0.48	1.56	1.24	1.13	0.02	1.80	1.50	0.06	0.05	0.08	7.52	9.84	8.61	8.13				
SnO2	18.80	10.45	11.28	11.55	14.03	14.92	15.02	15.05	17.56	4.85	5.66	8.10	14.49	13.75	8.85	6.85	8.32	8.13				
SiO2	0.08	0.46	-	-	0.03	0.02	0.03	0.02	0.00	0.10	0.10	0.02	-	0.03	-	-	0.03	0.06				
Si2O3	-	-	-	-	-	0.02	0.00	0.00	0.00	0.00	0.06	0.02	-	0.08	-	-	0.08	0.08				
Bi2O3	-	-	-	-	-	0.02	-	0.00	0.03	-	-	0.26	-	2.35	-	-	-	-				
ThO2	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.01	0.01	0.01	0.01	0.00				
UO2	0.13	0.00	0.00	0.02	0.08	0.02	0.00	0.06	0.00	0.00	0.02	0.00	0.00	0.43	0.08	0.02	0.03	0.12				
Nb2O5	10.26	17.77	12.33	13.75	5.34	9.03	6.95	5.81	7.20	17.97	15.80	4.00	7.27	7.13	12.92	15.66	11.12	12.82				
Ta2O5	55.08	52.42	57.56	54.35	62.82	59.04	63.06	65.06	61.47	44.55	40.80	34.67	57.51	53.93	56.21	53.86	57.70	56.27				
WO3	1.43	0.00	1.65	3.25	3.82	0.51	0.22	0.25	1.73	12.54	17.36	34.63	7.69	7.82	0.14	0.00	0.00	0.00				
Total	100.64	99.89	99.56	99.62	99.84	99.27	98.98	99.84	100.53	99.36	99.31	100.77	100.97	99.19	99.26	100.16	100.34	99.20				
Recalculated oxides																						
Li2O	0.00	0.00	0.05	0.00	0.10	0.00	0.04	0.05	0.000	0.16	0.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00				
FeO	10.42	10.84	8.12	7.35	3.72	2.81	0.88	1.05	0.000	3.10	3.04	0.00	0.00	0.00	4.86	3.74	10.91	9.86				
MnO	1.69	2.15	3.54	4.61	7.05	9.19	10.12	9.91	12.02	8.55	8.87	16.54	13.36	10.74	7.69	9.49	2.33	2.80				
PbO	0.11	0.03	0.06	0.10	0.03	0.03	0.03	0.05	0.02	0.13	0.05	0.14	0.02	0.99	0.03	0.03	0.08	0.07				
Fe2O3	1.48	1.94	2.38	3.49	2.66	2.33	1.58	1.61	0.52	6.31	7.05	2.58	0.64	2.15	1.07	0.92	1.22	0.88				
TiO2	1.27	4.17	2.85	1.46	0.48	1.56	1.24	1.13	0.02	1.80	1.50	0.06	0.05	0.08	7.52	9.84	8.61	8.13				
SnO2	18.80	10.45	11.28	11.55	14.03	14.92	15.02	15.05	17.56	4.85	5.66	8.10	14.49	13.75	8.85	6.85	8.32	8.13				
SiO2	0.08	0.46	0.00	-	0.03	0.02	0.03	0.02	0.00	0.10	0.10	0.02	-	0.03	-	-	0.03	0.06				
Si2O3	-	-	-	-	-	0.02	0.00	0.00	0.00	0.00	0.06	0.02	-	0.08	-	-	0.08	0.08				
Bi2O3	-	-	-	-	-	0.02	-	0.00	0.03	-	-	0.26	-	2.35	-	-	-	-				
ThO2	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.01	0.01	0.01	0.01	0.00				
UO2	0.13	0.00	0.00	0.02	0.09	0.02	0.00	0.06	0.00	0.00	0.02	0.00	0.00	0.43	0.08	0.02	0.03	0.12				
Nb2O5	10.26	17.77	12.33	13.75	5.34	9.03	6.95	5.81	7.20	17.97	15.80	4.00	7.27	7.13	12.92	15.66	11.12	12.82				
Ta2O5	55.08	52.42	57.56	54.35	62.82	59.04	63.06	65.06	61.47	44.55	40.80	34.67	57.51	53.93	56.21	53.86	57.70	56.27				
WO3	1.43	0.00	1.65	3.25	3.82	0.51	0.22	0.25	1.73	12.54	17.36	34.63	7.69	7.82	0.14	0.00	0.00	0.00				
Total	100.77	100.03	99.81	99.94	100.17	99.49	99.18	100.04	100.58	100.07	100.06	101.03	101.03	99.39	99.36	100.25	100.43	99.27				

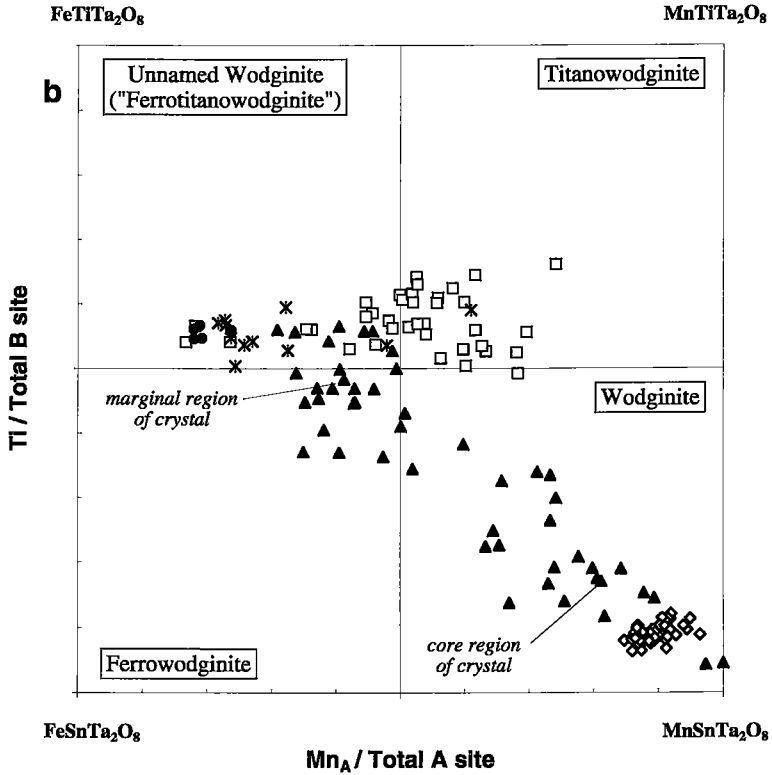
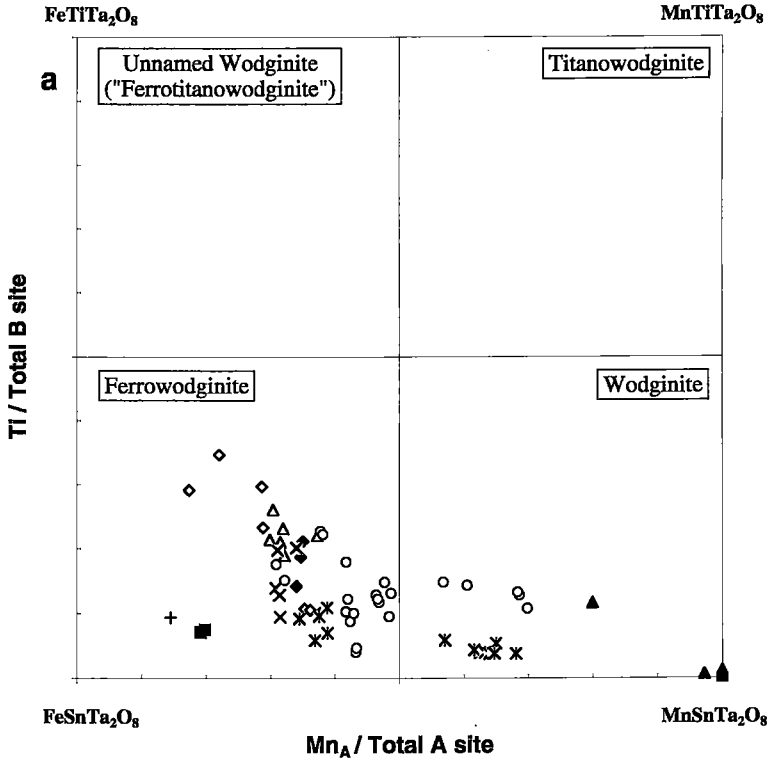
TABLE 1 (continued). COMPOSITION OF WODGINITE-GROUP MINERALS, SEPARATION RAPIDS PEGMATITES

	Ferro-wodginite				Wodginite				Tungsteniferous Wodginites ("Wolffram-wodginites")				Titanowodginite				*Ferro-titanowodginite			
	1	2	3	4	5	6*	7S	8f	9*	10	11	12*	13*	14*	15	16	17	18		
	94-318	95-272E	93-276B	Peg 7B	Peg 7E	93-265P	94-44A	94-44R	93-265A	94-80E	94-50E	93-265A	93-265A	93-265A	94-44J	94-44J	94-44M	94-44K2		
	MD	JJ	FC	CF	BB	WK	VJ	VA	KB	XC	XL	SL	ZS	SS	ZK	ZC	LD	Q		
No. of Oxygens	32	32	32	32	32	32	32	32	32	32	32	32	32	32	32	32	32	32		
<b>A site</b>																				
Li	0.000	0.000	0.080	0.000	0.165	0.000	0.074	0.088	0.000	0.249	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
Fe2+	3.531	3.408	2.717	2.453	1.317	0.970	0.312	0.370	0.000	0.993	0.980	0.000	0.000	0.000	1.565	1.156	3.480	3.170		
Mn A	0.457	0.588	1.197	1.538	2.514	3.028	3.611	3.537	3.988	2.745	2.786	3.985	3.988	3.886	2.435	2.841	0.512	0.823		
Pb	0.012	0.003	0.006	0.011	0.003	0.002	0.003	0.006	0.002	0.013	0.005	0.015	0.002	0.114	0.003	0.003	0.006	0.007		
<b>B site</b>																				
Mn B	0.122	0.106	0.000	0.016	0.000	0.173	0.000	0.000	0.283	0.000	0.000	1.714	0.707	0.004	0.076	0.126	0.241	0.088		
Fe3+	0.452	0.560	0.716	1.048	0.848	0.722	0.502	0.511	0.165	1.819	2.042	0.789	0.202	0.897	0.311	0.255	0.352	0.254		
Ti	0.386	1.196	0.854	0.437	0.152	0.482	0.393	0.358	0.006	0.513	0.430	0.018	0.016	0.026	2.177	2.732	2.466	2.348		
Sn	3.033	1.569	1.784	1.831	2.355	2.446	2.523	2.529	2.944	0.733	0.859	1.314	2.402	2.345	1.356	1.008	1.264	1.245		
Sc	0.028	0.153	0.000	-	0.011	0.007	0.011	0.007	0.000	0.033	0.033	0.007	-	0.011	-	-	0.010	0.020		
Sb	-	-	-	-	-	0.003	0.000	0.000	0.000	0.000	0.009	0.003	-	0.014	-	-	0.013	0.014		
Bi	-	-	-	-	-	0.002	-	0.000	0.003	-	-	0.027	-	0.259	-	-	-	-		
Th	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.001	0.000	0.001	0.001	0.002	0.001	0.000		
U	0.012	0.000	0.000	0.002	0.008	0.002	0.000	0.006	0.000	0.000	0.002	0.000	0.000	0.041	0.007	0.002	0.003	0.010		
Ta B	0.087	0.502	0.637	0.682	0.625	0.335	0.572	0.589	0.587	0.902	0.824	0.222	0.687	0.506	0.146	0.002	0.000	0.108		
<b>C site</b>																				
Nb	1.877	3.064	2.223	2.471	1.016	1.679	1.323	1.107	1.369	3.079	2.686	0.736	1.366	1.379	2.248	2.613	1.915	2.226		
Ta C	5.873	4.936	5.606	5.194	6.567	6.267	6.653	6.866	6.443	3.689	3.601	3.614	5.805	5.755	5.736	5.387	5.978	5.769		
W	0.150	0.000	0.171	0.335	0.417	0.054	0.024	0.027	0.189	1.232	1.713	3.651	0.829	0.867	0.014	0.000	0.000	0.005		
Total	16.122	16.106	16.000	16.016	16.000	16.173	16.000	16.000	15.990	16.000	16.000	16.096	16.024	15.905	16.076	16.126	16.241	16.088		
<b>A site total</b>	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000		
<b>B site total</b>	4.122	4.106	4.000	4.016	4.000	4.173	4.000	4.000	3.990	4.000	4.000	4.096	4.023	3.905	4.076	4.126	4.348	4.088		
<b>C site total</b>	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	7.893	8.000		
MnA/Tot A	0.145	0.174	0.299	0.366	0.628	0.800	0.903	0.884	1.000	0.686	0.689	1.000	0.989	0.973	0.627	0.742	0.188	0.228		
Ti/Tot B	0.094	0.291	0.213	0.109	0.038	0.116	0.098	0.090	0.002	0.128	0.107	0.004	0.004	0.007	0.534	0.662	0.567	0.574		

Comments: \* - Analyses are from cassiterite-beryl-petalite pegmatites except for 6, 9, 12-14 which are from an internal beryl-columbite pegmatite

\$ - petalite core zone

! - Beryl+stibite-muscovite replacement unit



crystal is compositionally zoned from a Mn-rich wodginite core to a Ti-rich "ferrotitanowodginite" rim. The change in composition is not linear, and the crystal has indistinct core and rim features (Figs. 6d, e) most likely of a replacement origin (Lahti 1987).

#### SUBSTITUTION SCHEMES IN WODGINITE

Ferguson *et al.* (1976) gave the ideal formula of wodginite as  $MnSnTa_2O_8$  (where Mn, Sn and Ta occupy A, B and C sites, respectively). For most wodginite-group minerals, variation in the A site is dominated by the 1:1 substitution of Mn by  $Fe^{2+}$  (Table 2, operator 1). Ercit *et al.* (1992a) reported good 1:1 correlation of Mn and Fe, with full site-occupancy, but recorded several compositions with low Fe and Mn, suggesting that other substitutions may operate at the A site. At the B site, the major substitution involves Ti for Sn (Table 2, operator 2), but it is not simply a 1:1 substitution. In all data obtained, constituents other than Sn and Ti are required to fill the B site. At the C site, Nb substitutes for Ta (Table 2, operator 3). However, on the basis of 32 atoms of oxygen, there is an apparent excess of up to 3.7 (Ta + Nb) cations per unit cell. Ercit *et al.* (1992a) showed that the excess was at the B site. Tungsten was considered to behave like  $Nb^{5+}$ , and to occupy the C site. Mössbauer spectroscopy was used to show that Fe at the A site is  $Fe^{2+}$ , and that lesser amounts of  $Fe^{3+}$  reside at the B site (Table 2, operator 4). Voloshin *et al.* (1990) were further able to show that Li can be incorporated into the A site according to the coupled substitution  $Mn^{2+} + Sn^{4+} \Leftrightarrow Li^+ + Ta^{5+}$  (Table 2, operator 6).

On the basis of these site occupancies, Ercit *et al.* (1992a) devised a procedure (set up in a Fortran program) not only to calculate structural formulae, but to infer Li content and  $Fe^{2+}/Fe^{3+}$  from electron-microprobe data. The method involves assigning all the  $Nb^{5+}$  and  $W^{6+}$  to the C site, and filling the remainder with  $Ta^{5+}$ . Excess  $Ta^{5+}$  is allocated to the B site, together with all the  $Sn^{4+}$  and  $Ti^{4+}$ .  $Fe^{3+}$  is estimated by conversion of  $Fe^{2+}$  to occupy available space at the B site, calculated by assuming that the sum of B and C

sites is 12 cations per unit cell. All Mn and the  $Fe^{2+}$  is assigned to the A site. Remaining space at the A site is allocated to Li, but no more than compensates for excess positive charge introduced at the B site by  $Ta^{5+}$  exceeding  $Fe^{3+}$ . A-site vacancies can also occur. It is not clear how the presence of  $W^{6+}$  at C affects this allocation. Ercit *et al.* (1992a) noted that the method can produce significantly low sums for the B site if there are insufficient cations for the sum of B plus C sites to be 12. However, we note that low sums of this kind may be caused by insufficient cations to fill the C site.

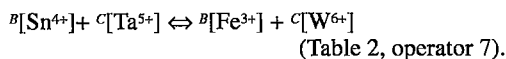
We use an Excel™ 5.0 spreadsheet template that essentially duplicates the procedure of Ercit *et al.* (1992a), but differs slightly in the light of new compositions of wodginite from Separation Rapids (a selection of which are presented in Table 2). Our template calculates proportions of Li,  $Fe^{2+}$  and  $Fe^{3+}$ , structural formulae and classification parameters. It differs from the procedure of Ercit *et al.* (1992a) in dealing with high concentrations of Mn, as some samples from Separation Rapids contain Mn exceeding the full A-site occupancy. This excess Mn generally coincides with vacancies at the B site, *i.e.*,  $Sn + Ti + Fe^{3+} + Ta_B$  is less than 4 (Fig. 8a), and in such cases, all Fe has been converted to  $Fe^{3+}$ . The excess Mn is shown as  $Mn_B$  in Figure 8a, and it commonly produces a full B site. However, where the C site is not completely filled, as may occur with titaniferous wodginite, it is possible to overflow the B site because of the initial "sum to 12" criterion for measuring the deficit in the B site (Fig. 8a).

Most of the A-site variation in wodginite-group minerals at Separation Rapids is a result of  $Fe^{2+}$  substituting for Mn. There is little evidence for Li occupying this site, apart from one cassiterite – beryl – petalite pegmatite (Peg. 5), where Li contents of up to 0.31 wt.%  $Li_2O$  are estimated. Wodginite from this pegmatite is also unusual in its high concentration of W (up to 17.4 wt.%  $WO_3$ ; Table 1, anal. 10, 11), which appears to be charge-balanced by unusually high  $Fe^{3+}$  at the B site. This requires a new substitution to account for the trend labeled "wolframowodginite 1" in Figure 8b:

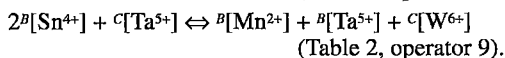
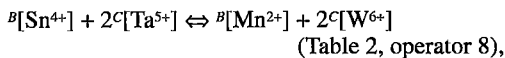
← FIG. 7. Separation Rapids data plotted on the wodginite classification quadrilateral. (a) Wodginite data from three beryl pegmatites (■ Audrey's pegmatite, ◆ pegmatite 15, ▲ pegmatite 265) and six petalite pegmatites (◇ Lou's pegmatite, △ James's pegmatite, ○ pegmatite 5, × pegmatite 6, \* pegmatite 7, + pegmatite 9). (b) Wodginite data from Marko's pegmatite (a petalite pegmatite plotted separately from the others for clarity); □ wall zone, from inclusions in cassiterite 44j, \* wall zone, from inclusions in cassiterite 44k, ● wall zone, from inclusions in cassiterite 44m, ▲ wall zone, from "large" zoned crystal 44i, ◇ petalite core zone and quartz – muscovite – albite replacement unit. Data from a single zoned crystal (44i) extracted from the border zone of the pegmatite defines an apparent continuum from a MnSn-rich core region to a FeTi-rich marginal region.

TABLE 2. SIGNIFICANT SUBSTITUTION OPERATORS IN WODGINITE-GROUP MINERALS FROM SEPARATION RAPIDS

Operators	End-member	Name	Separation Rapids examples	Table 1 analysis
1. $A[Mn^{2+}] \leftrightarrow A[Fe^{2+}]$	$Mn^{2+}_4Sn_4Ta_8O_{32}$	Wodginite	$Fe^{2+}_{0.3}Mn^{2+}_{3.6}(Fe^{3+}_{0.5}Ti_{10.5}Sn_{2.5}Ta_{0.5})(Nb_{0.9}Ta_{7.1})O_{32}$	7
2. $B[Sn^{4+}] \leftrightarrow B[Ti^{4+}]$	$Fe^{2+}_4Sn_4Ta_8O_{32}$	Ferrowodginite	$Fe^{2+}_{3.5}Mn^{2+}_{0.5}(Fe^{3+}_{0.5}Ti_{10.4}Sn_{3.0}Ta_{0.1})(W_{0.2}Nb_{1.9}Ta_{8.9})O_{32}$	1
3. $C[Ta^{5+}] \leftrightarrow C[Nb^{5+}]$	$Mn^{2+}_4Ti_4Ta_8O_{32}$	Titanowodginite	$Fe^{2+}_{1.3}Mn^{2+}_{2.7}(Fe^{3+}_{0.2}Ti_{12.6}Sn_{1.1}Ta_{0.1})(Nb_{2.6}Ta_{8.4})O_{32}$	15
4. $2B[Sn^{4+}] \leftrightarrow B[Fe^{3+}] + B[Ta^{5+}]$	$Mn^{2+}_4(Fe^{3+}_2Ta_2)Ta_8O_{32}$	unnamed	ubiquitous substitution	
5. $A[Mn^{2+}] + B[Sn^{4+}] \leftrightarrow A[Fe^{2+}] + B[Ti^{4+}]$	$Fe^{2+}_4Ti_4Ta_8O_{32}$	"Ferrotitanowodginite"	limited substitution	
6. $A[Mn^{2+}] + B[Sn^{4+}] \leftrightarrow A[Li^{+}] + B[Ta^{5+}]$	$Li_4Ta_4Ta_8O_{32}$	Lithowodginite	$Fe^{2+}_{3.3}Mn^{2+}_{0.7}(Fe^{3+}_{0.3}Ti_{12.3}Sn_{1.3}Ta_{0.1})(Nb_{2.3}Ta_{8.7})O_{32}$	18
7. $B[Sn^{4+}] + C[Ta^{5+}] \leftrightarrow B[Fe^{3+}] + C[W^{6+}]$	$Mn^{2+}_4(Fe^{3+}_2Sn_2)(W_2Ta_2)O_{32}$	"Wollframowodginite 1"	limited substitution	
8. $B[Sn^{4+}] + 2C[Ta^{5+}] \leftrightarrow B[Mn^{2+}] + 2C[W^{6+}]$	$Mn^{2+}_4(Mn^{2+}_2Sn_2)(W_4Ta_4)O_{32}$	"Wollframowodginite 2"	$Li^{+}_{0.2}Fe^{2+}_{1.0}Mn^{2+}_{2.8}(Fe^{3+}_{2.0}Ti_{10.4}Sn_{1.9}Ta_{0.6})(W_{1.7}Nb_{2.7}Ta_{8.6})O_{32}$	11
9. $2B[Sn^{4+}] + C[Ta^{5+}] \leftrightarrow B[Mn^{2+}] + B[Ta^{5+}] + C[W^{6+}]$	$Mn^{2+}_4(Mn^{2+}_2Sn_2Ta)(WTa_7)O_{32}$	"Wollframowodginite 3"	$Mn^{2+}_{4.0}(Mn^{2+}_{0.7}Fe^{3+}_{0.2}Sn_{2.1}Ta_{0.7})(W_{0.8}Nb_{1.7}Ta_{8.9})O_{32}$	12
				13



In one other pegmatite (Peg. 265), tungsteniferous varieties of wodginite containing very high Mn (Table 1, anal. 12, 13) require two further mechanisms of substitution (trends labeled "wolframowodginite 2" and "wolframowodginite 3" on Fig. 8c). These compositions of wodginite have an excess of  $\text{Mn}^{2+}$  from the A site, and the excess positive charge due to W at the C site is balanced by introduction of  $\text{Mn}^{2+}$  at the B site through the following mechanisms (Fig. 8c):



These substitution operators result in the hypothetical end-member compositions  $\text{Mn}^{2+}_4(\text{Fe}^{3+}_2\text{Sn}_2)(\text{W}_2\text{Ta}_6)\text{O}_{32}$ ,  $\text{Mn}^{2+}_4(\text{Mn}^{2+}_2\text{Sn}_2)(\text{W}_4\text{Ta}_4)\text{O}_{32}$ , and  $\text{Mn}^{2+}_4(\text{Mn}^{2+}\text{Sn}_2\text{Ta})(\text{W}\text{Ta}_7)\text{O}_{32}$  respectively. However, as with "ferrotitanowodginite" (Ercit *et al.* 1992b), limited material is available, and the "wolframowodginite" variants must remain hypothetical species until sufficient material is found to characterize them fully.

In ideal wodginite, the B site is filled with 4 Sn cations (based on 32 atoms of oxygen). Both the world dataset (T.S. Ercit, unpubl. data) and our Separation Rapids dataset (particularly that for Marko's pegmatite) show a good correlation of Sn with Ti, but both are displaced below the ideal curve for 1:1 substitution of Ti for Sn, and neither element contributes more than 3 cations to the B site. The remainder of the site may be occupied by  $\text{Fe}^{3+}$ ,  $\text{Ta}^{5+}$ ,  $\text{Mn}^{2+}$  and a number of minor elements (*e.g.*, Sc, Sb, Bi, Th, U). In a few cases, titanowodginite has a high B-site total and a deficiency in the C site (as noted earlier). In most cases, however, wodginite-group minerals have good cation sums and near-ideal site occupancies, especially where minor elements have been determined.

#### EVOLUTION OF RARE-METAL OXIDE ASSEMBLAGES

Although it is not our intention in this paper to discuss in detail the entire oxide assemblage found in the Separation Rapids pegmatites, it is important that other oxides be briefly mentioned here, as they may help our understanding of the processes involved in pegmatite formation. Magmatic fractionation, albitization and reaction with wallrocks are discussed, as these are the likely processes to be involved in the petrogenesis of the Separation Rapids pegmatites and the formation of unusual compositions of wodginite-group minerals.

#### Fractionation and fluorine complexing

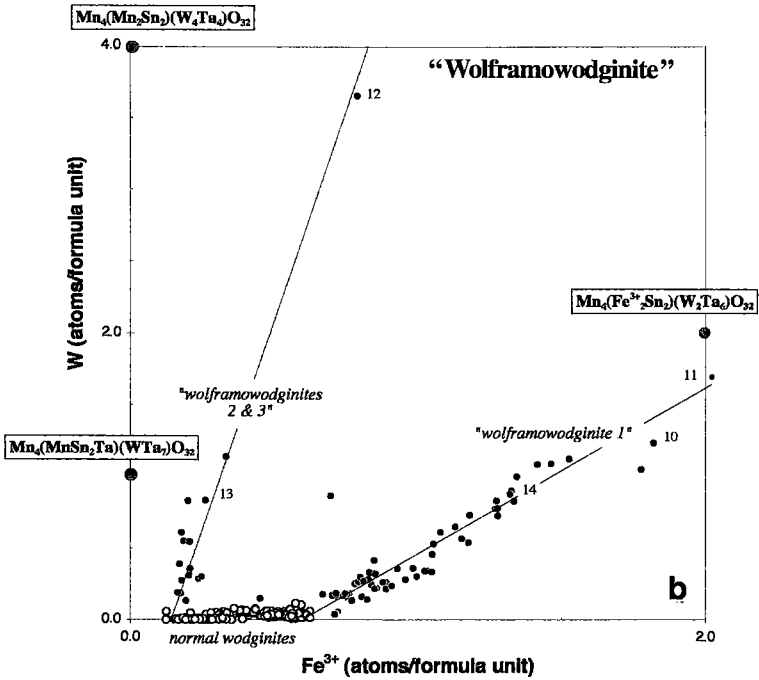
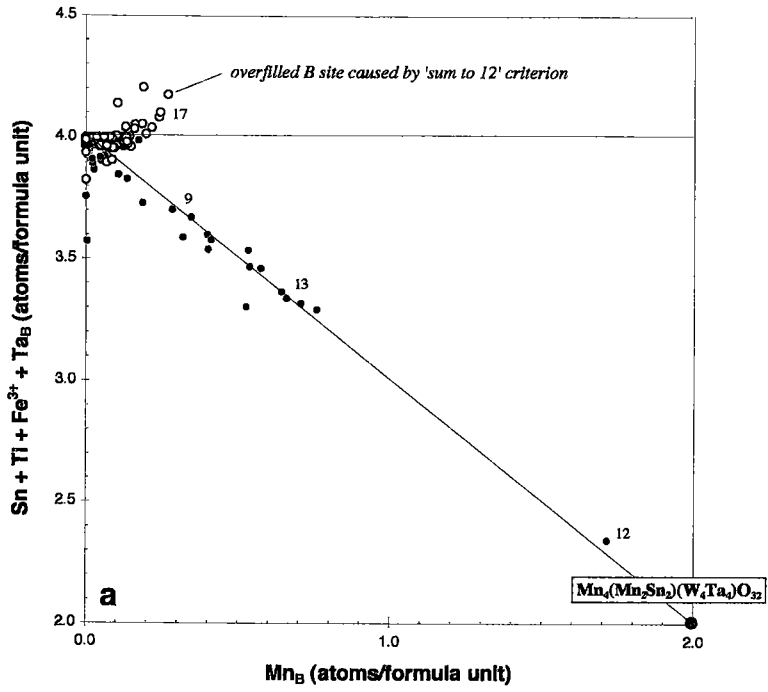
It is commonly accepted that the general sequence ferrocolumbite  $\rightarrow$  manganocolumbite  $\rightarrow$  manganotantalite

$\rightarrow$  microlite represents a trend of primary crystallization of rare-element oxides in many Li-rich pegmatites (Černý & Ercit 1985). This sequence results from progressive Fe  $\rightarrow$  Mn and Nb  $\rightarrow$  Ta substitutions (predominantly in columbite-tantalite) during magmatic fractionation. The final product is quite commonly a Mn-Ta-rich end-member such as manganotantalite. More rarely, wodginite (ss) is that Mn-Ta-rich mineral.

Evolving columbite-tantalite compositions at Separation Rapids do not follow this simple pattern; these are summarized in Figure 9. The most primitive compositions appear to be the ferrocolumbite from the Separation Rapids granite. Together with most of the pegmatites from the beryl and petalite zone, which have the lowest Mn/Fe values, they define an evolutionary sequence (trend 1) from ferrocolumbite  $\rightarrow$  ferrocolumbite + ferrowodginite  $\rightarrow$  ferrotantalite + ferrowodginite  $\rightarrow$  microlite-group minerals, where Fe  $\rightarrow$  Mn fractionation is very limited and Nb  $\rightarrow$  Ta fractionation is dominant. This has been defined as the Fe-suite by Tindle & Breaks (1998) and is illustrated in Figure 9 (left half of diagram) by the ellipse and series of vertical arrows (representing individual samples).

A second suite, referred to as the Mn-suite, follows a different trend that has two distinct parts; the first part, followed by wodginite-free samples, describes a horizontal trend in Figure 9 (trend 2a) and exhibits extensive Fe  $\rightarrow$  Mn fractionation with no Nb  $\rightarrow$  Ta fractionation. It is represented by beryl pegmatites Peg. 304 and Peg. 265, and early crystallized, petalite-free grey granite and layered pegmatite-aplite from Marko's pegmatite. Fractionation involves Mn/Fe only, giving a range of manganocolumbite compositions, all of which are more Mn-rich than any columbite from the Fe-suite. The more evolved parts of these pegmatites (notably the albitized petalite-bearing core zone of Marko's pegmatite and the K-feldspar - platy albite - Li-mica core zone of Peg. 265) follow a fractionation path of manganocolumbite + wodginite  $\rightarrow$  manganotantalite + wodginite  $\rightarrow$  microlite-group minerals, and this results in extreme Mn/Fe and Ta/Nb compositions (trend 2b, the vertical component of the two arrows on the right half of Figure 9).

The columbite-tantalite data, therefore, broadly divide into an Fe-suite that involves ferrowodginite, and a Mn-suite that involves wodginite. Unlike the columbite-tantalite, the wodginite-group minerals show no obvious bimodality (Fig. 9). Instead, a broad trend from ferrowodginite to wodginite is defined, which corresponds to an increase in Sn at the expense of Ti and other B-site cations. However, three wodginite-free beryl pegmatites with low Ta/Nb values (dashed arrows on Fig. 9), having ferrocolumbite compositions intermediate between those of the Separation Rapids pluton and the Mn-suite pegmatites, parallel trend 2a and could represent a Fe-rich precursor to the Mn-suite. They blur the distinction between Fe- and





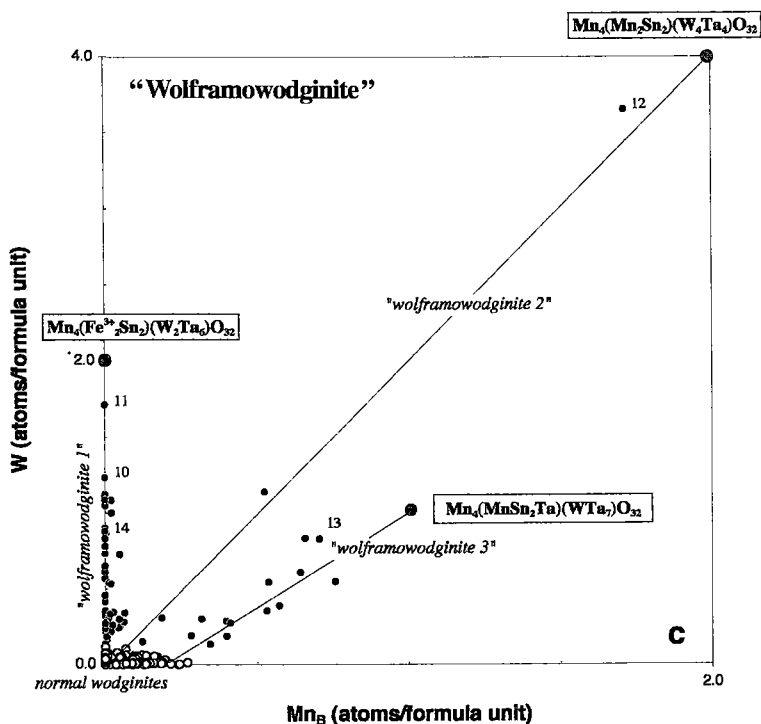


FIG. 8. Substitution relationships in tungsteniferous wodginite from Separation Rapids. (a)  $(\text{Sn} + \text{Ti} + \text{Fe}^{3+} + {}^B\text{Ta})$  and  ${}^B\text{Mn}$ , (b) W and  $\text{Fe}^{3+}$  and (c) W and  ${}^B\text{Mn}$ . Idealized formulae do not take into account other substitutions in A, B and C sites; this is also the reason why correlations do not pass through the origin. Numbers (9, 10–14, 17) refer to compositions of wodginite-group minerals listed in Table 1. Wodginite-group minerals from Marko's pegmatite are not especially tungsteniferous and are plotted with open symbols.

Mn-suites of columbite–tantalite, but offer the possibility of generating both suites from a common parent.

Bimodality of columbite–tantalite is also reported from the Greer Lake pegmatitic granite (Černý *et al.* 1986) although there are one or two samples that appear to bridge the gap, as does material from the associated pegmatitic veins. The extreme compositions of manganocolumbite and wodginite from the internal pods of Li-, Rb-, Cs-, and F-rich assemblages at Greer Lake and the platy albite – Li-mica-rich pods from the pegmatites from Separation Rapids are remarkably similar (apart from the elevated W in wodginite from the latter locality). Fractionation from Fe to Mn compositions in the late stages of pegmatite evolution is particularly conspicuous in F-rich pegmatites. More specifically, extremely Mn-rich garnet, phosphates and Nb–Ta oxides characterize the complex type, lepidolite subtype of rare-element pegmatites with high activity of alkali fluorides (Černý 1992). However, Mn enrichment can also be a primary feature of pegmatite populations, perhaps inherited from a Mn-rich parent,

or by digestion of Mn-rich wallrocks (Harada *et al.* 1976). The garnet from the petalite-zone pegmatites at Separation Rapids, with 24–82 mol.% spessartine (overall mean of 61, and a mean of 73 in Marko's pegmatite), suggests appreciable Mn enrichment. Similarly, metasomatic selvages developed in mafic metavolcanic host-rocks contain up to 8.5 wt.% F adjacent to aplite dykes containing megacrystic topaz and indicate high levels of F. This evidence, coupled with extreme Mn-enrichment of the oxide phases, is consistent with certain pegmatites having had high magmatic F contents (Breaks *et al.*, in prep.). However, ferrocolumbite from the Separation Rapids granite has many similarities with ferrocolumbite in pegmatites from Yellowknife, Northwest Territories, a conspicuously F-poor pegmatite field (Černý & Ercit 1985).

Differences in relative enrichment of Mn and Fe are greatly enhanced by differences in activity of F toward the later stages of granite and pegmatite evolution. Černý *et al.* (1986) suggested that F-based complexing of Mn may explain the development of the sequence

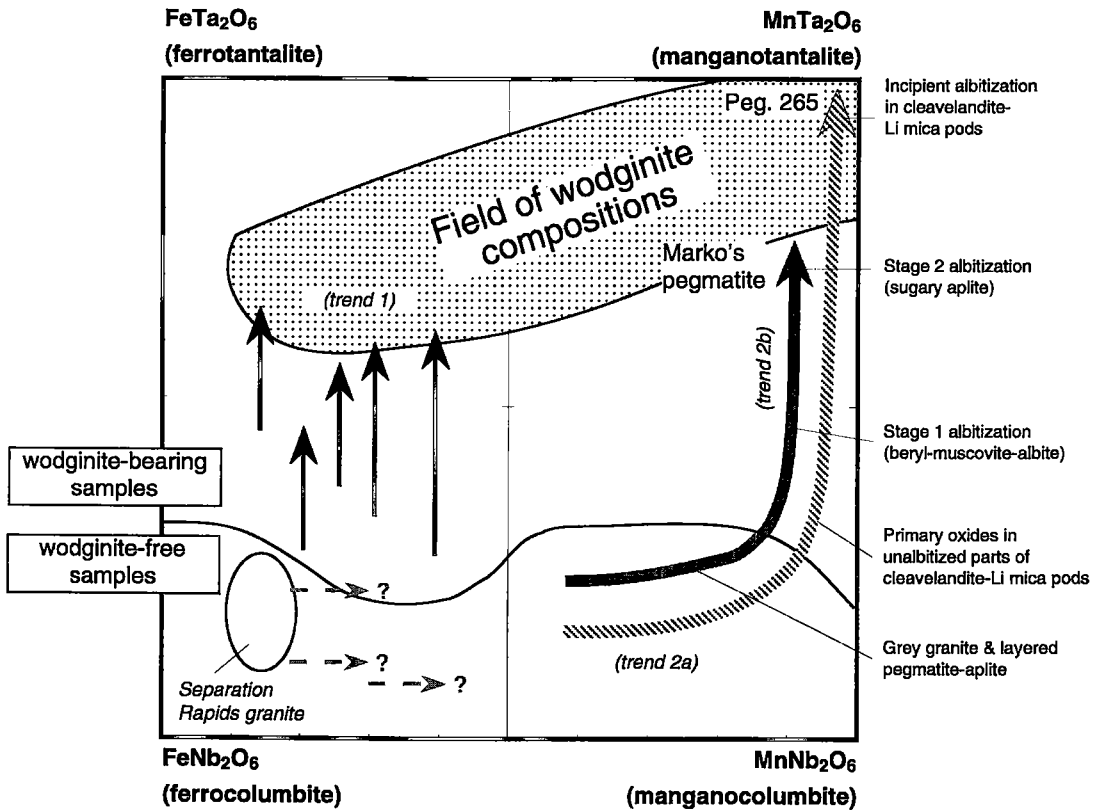


FIG. 9. Columbite-tantalite classification diagram, annotated to show the variation in composition of these minerals in the Separation Rapids pluton and associated pegmatites. Wodginite only occurs in the more evolved pegmatites. Extreme Mn-rich compositions are generally associated with albitized units. See text for further explanation.

manganocolumbite → manganocolumbite + wodginite  
 → manganotantalite + wodginite → microlite-group mineral. Ta/Nb fractionation, however, can proceed with equal ease in both primitive magmas, relatively poor in Li and F, as well as highly fractionated, Li- and F-saturated melts. The high F content of the pegmatite-forming magma was probably also instrumental in concentrating Sn and other rare elements in the pegmatites, as F is an important complexing ligand in such systems (Barnes 1979). A close association of rare-element oxide minerals (particularly cassiterite) with fluorapatite-albite-rich domains in the pegmatites suggests that F also may have played a role in concentrating the rare elements.

The available data on oxide minerals (Tindle & Breaks 1998) and K-feldspar (Breaks *et al.*, in prep.) favor the Separation Rapids pluton as the fertile source of at least the Fe-suite pegmatites. Tindle & Breaks (1998) suggest that the Mn-suite pegmatites may be derived from a separate magma-source with a higher F content.

#### ALBITIZATION

All samples collected for this study were examined for the effects of albitization, as previous studies have indicated a strong correlation between "Na-feldspathization" and rare-element mineralization (Pollard 1983). Where evidence for albitization is lacking, wodginite-group minerals are not found (although columbite-tantalite minerals are present); this includes primary units of the Separation Rapids pluton (aprites, platy-albite-rich units, fine-grained leucogranites, coarser-grained albite-rich units, pegmatitic leucogranites and biotite - muscovite - garnet granites) and early-crystallized zones of some external pegmatites (layered pegmatites, fine-grained granites and some aplite dykes). Excluding the samples described in the following section and some fluorapatite-albite symplectites in a muscovite-quartz unit from Pegmatite 5 (Fig. 2), the only samples containing wodginite-group minerals are those that have been albitized or

belong to the wall zone of Marko's pegmatite. Incipient effects attributed to albitization include albite-rich veins, mica replacement of topaz, masses and veins of apatite-tourmaline-quartz-albite replacing petalite, and "cleavelandite" replacement along margins of blocky K-feldspar crystals. More extensive albitization, best portrayed at Marko's pegmatite, is divided into Stage 1, where beryl - lithian muscovite - albite patches develop, and Stage 2, where sugary aplites are formed (Fig. 9). However, this is not to say that all albite-rich portions of the pegmatites exhibit replacement; in many cases, the albite appears primary.

Clearly, there is a strong correlation between albite content or albitization, and crystallization of wodginite-group minerals; however, because of the way albitization is restricted to particular pegmatite units, it cannot be the reason for the concentration of rare elements. Rather, albitization is seen as a natural result of crystallization of an increasingly sodium- and fluorine-rich pegmatite-forming magma. As with the Beauvoir granite in France (Raimbault *et al.* 1995), rare-element mineralization is considered to have a predominantly magmatic origin. Thus the presence of wodginite indicates advanced magmatic fractionation rather than postmagmatic activity (although appreciable albitization does occur after the main magmatic phase).

#### INTERACTION WITH WALLROCKS

Titaniferous wodginite from the wall zone of Marko's pegmatite and the high tungsten content of certain other wodginite-group minerals still require explanation, as their compositions are not readily explained by the magmatic fractionation model above. It is significant that the high-Ti variants (titanowodginite and "ferrotitanowodginite") display marked zonation and compositional diversity in adjacent crystals. Ercit *et al.* (1992a) suggested that as magmatic fractionation progresses in granitic pegmatites hosting wodginite-group minerals, there is an increase in Sn with respect to Ti prior to an increase in the chemical potential of Ta. In sample 44i, the opposite trend is observed, where in one zoned crystal an early Sn-rich wodginite core is progressively replaced by Ti-rich "ferrotitanowodginite" compositions (see Figs. 6d, e). Similar zonation is reported by Baldwin (1989) and Abella *et al.* (1995) in columbite-tantalite species. Also, in sample 44j, individual inclusions of titanowodginite within a single crystal of cassiterite have compositions that are discrete and with little overlap between inclusions. Both types of variation occur in wall-zone beryl - muscovite - albite pegmatites close to biotite-rich, metasomatized mafic metavolcanic country-rocks. Wodginite away from the wall zone does not show such variations. Pillowed and massive Fe-rich tholeiite flows in the Separation Lake metavolcanic belt range from 0.13 to 2.2 wt.% TiO<sub>2</sub> and could have provided the necessary Ti (and Fe)

through breakdown of ilmenite. Li and K metasomatic alteration by alkali-rich, pegmatite-derived, aqueous fluids can result in instability of plagioclase and ilmenite, and the formation of epidote and titanite in such rocks (Shearer & Papike 1988). Thus, interaction of pegmatite-derived fluids with the country rocks most likely released Ti (and Fe), which contaminated the residual pegmatite-forming melt to produce titanowodginite and "ferrotitanowodginite".

The model is supported by Abella *et al.* (1995), who noted the restriction of rutile to border and wall zones of the Cap de Creus beryl - columbite pegmatites of northern Spain, and suggested that most of the concentration of Ti could be a product of host-rock assimilation. Similarly, Černý *et al.* (1992) reported assimilation of hornblende gneiss at Maršřikov, northern Moravia, Czech Republic, as being responsible for increased levels of Fe, Ti and Mg in beryl - albite - muscovite pegmatites.

The concentration of W in wodginite-group minerals is also problematical, as it does not appear to follow a regular pattern that could be attributed to magmatic fractionation. Rather, the main variation of W content is between pegmatite bodies; Lou and Marko's pegmatites have wodginite with a low W content, whereas others (*e.g.*, Peg. 5 and Peg. 265) have wodginite with a high W content. Even W incorporation in wodginite is not simple; three schemes of substitution have been presented to show this erratic behavior. In addition, there is no correlation of W content of wodginite with pegmatite type, as both high- and low-W types are found in beryl and petalite pegmatites from both Fe- and Mn-suites.

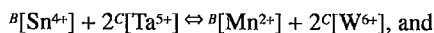
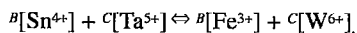
Dynamic, disequilibrium processes are proposed where Ti was introduced into the pegmatite-forming magma as a result of a metasomatic exchange during or after emplacement, and not as a fundamental consequence of fractionation of an uncontaminated primary melt. The complex patchy zoning, porous nature of the wodginite-"ferrotitanowodginite" and "reversed fractionation trend" (Sn → Ti enrichment) are all best explained by replacement of an earlier composition of wodginite rather than by magmatic crystallization, probably by localized reaction with, or incorporation of, adjacent country-rocks. The variable W content of wodginite within individual pegmatites is possibly derived by this process as well.

#### CONCLUSIONS

The Separation Rapids pegmatite field hosts a wide range of wodginite-group minerals. In most cases, the wodginite can be considered to be the highly evolved product of two distinct but possibly related fractionation paths. The Separation Rapids granite and most beryl and petalite pegmatites evolved through the sequence ferrocolumbite → ferrocolumbite + ferrowodginite → ferrotantalite + ferrowodginite →

microlite-group minerals, whereas the more Mn-rich pegmatites, such as Marko's pegmatite, follow an evolutionary trend from manganocolumbite → manganocolumbite + wodginite → manganotantalite + wodginite → microlite-group minerals. The former is consistent with evolution from a relatively F-poor magma, whereas the latter magma was most likely richer in F and led to extreme Mn enrichment, perhaps through F-complexing.

In addition to the substitution operators described by Ercit *et al.* (1992a), three more are described here to account for the variation in wodginite compositions:



These new substitution schemes lead to the hypothetical tungsteniferous end-members  $\text{Mn}^{2+}_4(\text{Fe}^{3+}_2\text{Sn}_2)(\text{W}_2\text{Ta}_6)\text{O}_{32}$ ,  $\text{Mn}^{2+}_4(\text{Mn}^{2+}_2\text{Sn}_2)(\text{W}_4\text{Ta}_4)\text{O}_{32}$  and  $\text{Mn}^{2+}_4(\text{Mn}^{2+}\text{Sn}_2\text{Ta})(\text{WTa}_7)\text{O}_{32}$ .

These "wolframowodginite" variants cannot be defined further until better samples are available and so must remain as hypothetical wodginite-group minerals, along with the "ferrotitanowodginite" described by Ercit *et al.* (1992a).

High Ti contents in zoned "ferrotitanowodginite" and titanowodginite crystals and high W contents are difficult to explain simply by magmatic fractionation. Their origin is more likely to be attributed to localized interaction of the pegmatite-forming magma with titaniferous metavolcanic rocks and banded ironstones.

The Separation Rapids pegmatite field ranks with the most fractionated Li-, Be-, Sn-, Ta-bearing complex type rare-element deposits in the world, belonging to the petalite subtype, which also includes deposits at Tanco, Manitoba (Černý 1982), Bikita, Zimbabwe (Cooper 1964), Varuträsk, Sweden (Quensel 1956), Luolamäki, Finland (Neuvonen & Vesasalo 1960), Londonderry, Australia (McMath *et al.* 1953) and Hirvikallio, Finland (Vesasalo 1959).

Wodginite-group minerals from the Separation Rapids pegmatite field display a wide range of compositions, many of which are matched only at Tanco, a mere 70 km away across the Manitoba border. This fact, together with other mineralogical similarities, strongly suggests a genetic link between the two areas. We speculate that there may be other rare-element deposits of the Tanco type within the metavolcanic belt that extends westward from Separation Lake toward Ryerson Lake and across into Manitoba.

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#### SOFTWARE

A copy of the Excel™ 5.0 template is available from the first author on receipt of a Mac or PC formatted disc, or from the Open University Department of Earth Sciences Web Site at <http://earth2.open.ac.uk/Electron%20Probe/AGTWebPages/AGTSoft.html>

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*Note added in proof*: Since this manuscript was written, a second pegmatite field has been discovered to the southwest of the Separation Rapids pluton. This has been named the Southwestern Pegmatite Sub-Group (Breaks & Tindle 1997, Ontario Geological Survey, Open-File Report). The pegmatites described in this paper are now collectively named the Eastern Pegmatite Sub-Group. An updated version of Figure 2 and further details of the Southwestern Pegmatite Sub-Group can be found in Tindle & Breaks (1998).