A COMPARISON OF TANTALUM–NIOBIUM OXIDE ASSEMBLAGES IN TWO MINERALOGICALLY DISTINCT RARE-ELEMENT GRANITIC PEGMATITES, BLACK HILLS, SOUTH DAKOTA

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ABSTRACT

A comparison is made between Ta–Nb mineral assemblages of two Li-enriched but mineralogically distinct rare-element granitic pegmatites in the Black Hills, South Dakota. The Bob Ingersoll No. 1 pegmatite is lepidolite-bearing, whereas the Tin Mountain pegmatite is spodumene-bearing. Both pegmatites display a diverse assemblage of Ta–Nb minerals. A general paragenetic sequence of the Ta–Nb mineral species in these pegmatites is represented by: ferrocolumbite → manganocolumbite → manganotantalite → microlite + tapiolite (+ wodginite). In both pegmatites, the Ta/(Ta + Nb) ratio of the columbite-tantalite (CT) increases systematically from the wall zone to the core. The systematic increase of Ta at the expense of Nb in the pegmatites correlates with a sequence of crystallization determined by other mineral indicators (*i.e.*, tourmaline, K-feldspar, mica). The wall zone, which crystallized first, contains CT with the lowest Ta/(Ta + Nb) ratios. The intermediate zones crystallized simultaneously and show an overlap in Ta/(Ta + Nb) values. The core contains the highest levels of Ta and was the last unit to consolidate. In addition, the Mn/(Mn + Fe) ratio in the CT increases from wall zone to core. An early Mn-enrichment of the CT occurs in the wall zone of the lepidolite-bearing pegmatite, and may parallel an early F-enrichment of the crystallizing melt. The difference in F content between the two pegmatites also influenced the differences in Sn mineralization. Microlite and tapiolite in each pegmatite have the highest Ta/Nb of the Ta – Nb oxides. In the core of the Tin Mountain, microlite, tapiolite, and wodginite are associated with albite–mica replacement of spodumene + quartz. The microlite contains evidence of hydrothermal alteration following crystallization. An increase in $f(O_2)$ during crystallization may be indicated by Fe^{3+} in the wodginite and microlite.

Keywords: granitic pegmatite, columbite, tantalite, Black Hills, South Dakota.

SOMMAIRE

Nous comparons les assemblages de minéraux de Ta–Nb de deux pegmatites granitiques enrichies en éléments rares et en lithium mais à caractères minéralogiques distincts, situées dans les Black Hills, Dakota du Sud. La pegmatite Bob Ingersoll No. 1 contient de la lépidolite, tandis que la pegmatite de Tin Mountain contient du spodumène. Les deux contiennent un assemblage de divers minéraux de Ta–Nb. Une séquence paragénétique générale de ces minéraux serait ferrocolumbite → mangonocolumbite → manganotantalite → microlite + tapiolite (+ wodginite). Dans les deux cas, le rapport Ta/(Ta + Nb) de la columbite-tantalite (CT) augmente systématiquement à partir de la bordure du complexe vers le coeur. L'augmentation systématique du Ta aux dépens du Nb comme indicateur de l'évolution du complexe concorde avec les autres indicateurs (*i.e.*, tourmaline, feldspath potassique, mica). La zone près de la paroi, première à cristalliser, contient les exemples de CT ayant les plus faibles valeurs du rapport Ta/(Ta + Nb). Les zones intermédiaires ont cristallisé de façon simultanée, et montrent un chevauchement dans leurs valeurs de ce rapport. Le coeur contient les concentrations de Ta les plus élevées, et a cristallisé en dernier. De plus, le rapport Mn/(Mn + Fe) dans la CT augmente de la bordure vers le coeur des complexes. Nous trouvons un enrichissement précoce en Mn près de la paroi dans la pegmatite à lépidolite, qui pourrait accompagner un enrichissement parallèle en F dans le magma. La différence dans la teneur en F dans les deux venues magmatiques a aussi influencé les différences en Sn. Microlite et tapiolite dans chaque pegmatite contiennent le rapport Ta/Nb le plus élevé des oxydes Ta–Nb. Dans le coeur de la pegmatite de Tin Mountain, microlite, tapiolite et wodginite sont associées à un assemblage d'albite et de mica développé aux dépens de spodumène + quartz. La microlite montre de l'évidence d'une altération hydrothermale suite à la cristallisation. La présence de Fe^{3+} dans la wodginite et la microlite pourrait indiquer une augmentation en $f(O_2)$ au cours de la cristallisation.

(Traduit par la Rédaction)

Mots-clés: pegmatite granitique, columbite, tantalite, Black Hills, Dakota du Sud.

INTRODUCTION

The columbite group is one of many species of compositionally diverse Ta–Nb minerals that occur in granitic pegmatites throughout the world. Recent work on Ta- and Nb-bearing minerals has centered on chemical and structural variations (Foord 1976, Černý & Ercit 1985), and on fractionation of Ta–Nb minerals in rare-element pegmatites (*e.g.*, Černý & Turnock 1971, Grice *et al.* 1972, Černý *et al.* 1985, Lumpkin *et al.* 1986, von Knorring & Condliffe 1984, Černý 1989, Wise 1987, Ercit 1986). This paper addresses the paragenetic and geochemical evolution of Ta–Nb mineralization as related to the crystallization of pegmatites having contrasting assemblages of lithium aluminosilicates. The goals of this research are: 1) to examine the textural, chemical, and structural characteristics of Ta, Nb, and Sn minerals in two contrasting, but highly evolved pegmatites in South Dakota, and 2) to relate the compositional variability of cassiterite, columbite–tantalite and other Ta–Nb minerals to pegmatite composition and to the zones within the individual pegmatites.

The two pegmatites selected for study contain contrasting lithium-mineral assemblages: the Bob Ingersoll No. 1 dike is a lepidolite- and lithian muscovite-bearing pegmatite, and the Tin Mountain is a spodumene-bearing pegmatite. The difference in Li minerals reflects differences in H_2O/F ratios of the crystallizing melt (Munoz 1971, London & Burt 1982b). In addition to this influence on the assemblage of lithium aluminosilicates, the abundance of F as a volatile in the granitic melt also may affect the history of crystallization of the Ta–Nb oxides (Černý *et al.* 1986a, b, Černý 1989, Černý & Ercit, 1985).

GEOLOGY OF THE HARNEY PEAK GRANITE AND PEGMATITES

Regional geology

The Harney Peak Granite (Fig. 1), a classic example of a granite surrounded by a pegmatite field, contains over 20,000 individual pegmatite dikes and sills (Redden *et al.* 1982). Riley (1970) obtained a Rb-Sr isochron age of 1709 ± 12 Ma (recalculated from Riley's original data by Walker *et al.* 1986a). Metamorphism peaked at the high sillimanite grade near the main body of granite. Both pegmatites examined in this paper lie on the staurolite side of the staurolite – low sillimanite isograd (Fig. 1). The granite and associated pegmatite field exhibit a regional pattern of mineralogical and geochemical zonation (Norton 1975, Shearer *et al.* 1987, 1992).

The Bob Ingersoll No. 1 dike

The Bob Ingersoll No. 1 dike (referred to in the remainder of the text as the Bob Ingersoll pegmatite) is located 3.2 km northwest of Keystone, in Pennington County, approximately 2 km northeast of the Harney Peak Granite (Fig. 1). It is one of several dikes located on the Bob Ingersoll prospect. The Bob Ingersoll pegmatite is a large, zoned, lepidolite-bearing pegmatite, enriched in Li, F, B, Be, U, Ta, Nb, and Sn. The deposit was extensively mined for lepidolite, beryl, and amblygonite prior to 1945, and has been mined intermittently since that time. The No. 1 dike is a steeply plunging, funnel-shaped body with a vertical depth of at least 76 m. A vertical cross-section through the dike is represented in Figure 2. The pegmatite consists of six zones: (1) quartz – albite – muscovite (border zone), (2) albite – quartz – muscovite (wall zone), (3) perthite – quartz – albite (first intermediate zone), (4) quartz – albite – amblygonite (second intermediate zone), (5) quartz – albite (third intermediate zone), and (6) quartz – albite – lepidolite (core). The approximate modal mineralogy of the individual zones is given in Table 1. A complete description of each of the zones is found in Jolliff *et al.* (1986).

The Tin Mountain Pegmatite

The Tin Mountain pegmatite is a spodumene – amblygonite – pollucite-bearing pegmatite located 10 km west of Custer, in Custer County and 16 km southwest of the main body of the Harney Peak Granite (Fig. 1). Like the Bob Ingersoll pegmatite, it is enriched in Li, P, Cs, Be, U, Rb, Ta, and Nb (minor Sn) compared to the majority of pegmatites associated with Harney Peak Granite. The pegmatite forms an L-shaped body. The upper limb, plunging gently to the east, is 90 m in length, and the lower limb, plunging fairly steeply to the northwest, is at least 100 m long and 25 m wide. The thickness of both limbs is about 30 m. A cross-section along the length of the lower limb is shown in Figure 2. The five zones that comprise the pegmatite are: (1) albite – quartz – muscovite (border and wall zones), (2) perthite – quartz – albite (first intermediate zone), (3) perthite (second intermediate zone), (4) albite – quartz – spodumene (third intermediate zone), and (5) quartz – spodumene – mica (core). Table 1 lists the approximate modal mineralogy of the zones. A detailed description of the individual zones is presented by Walker *et al.* (1986b).

Sequence of crystallization

A sequence of crystallization has been proposed for the Bob Ingersoll pegmatite by Jolliff *et al.*
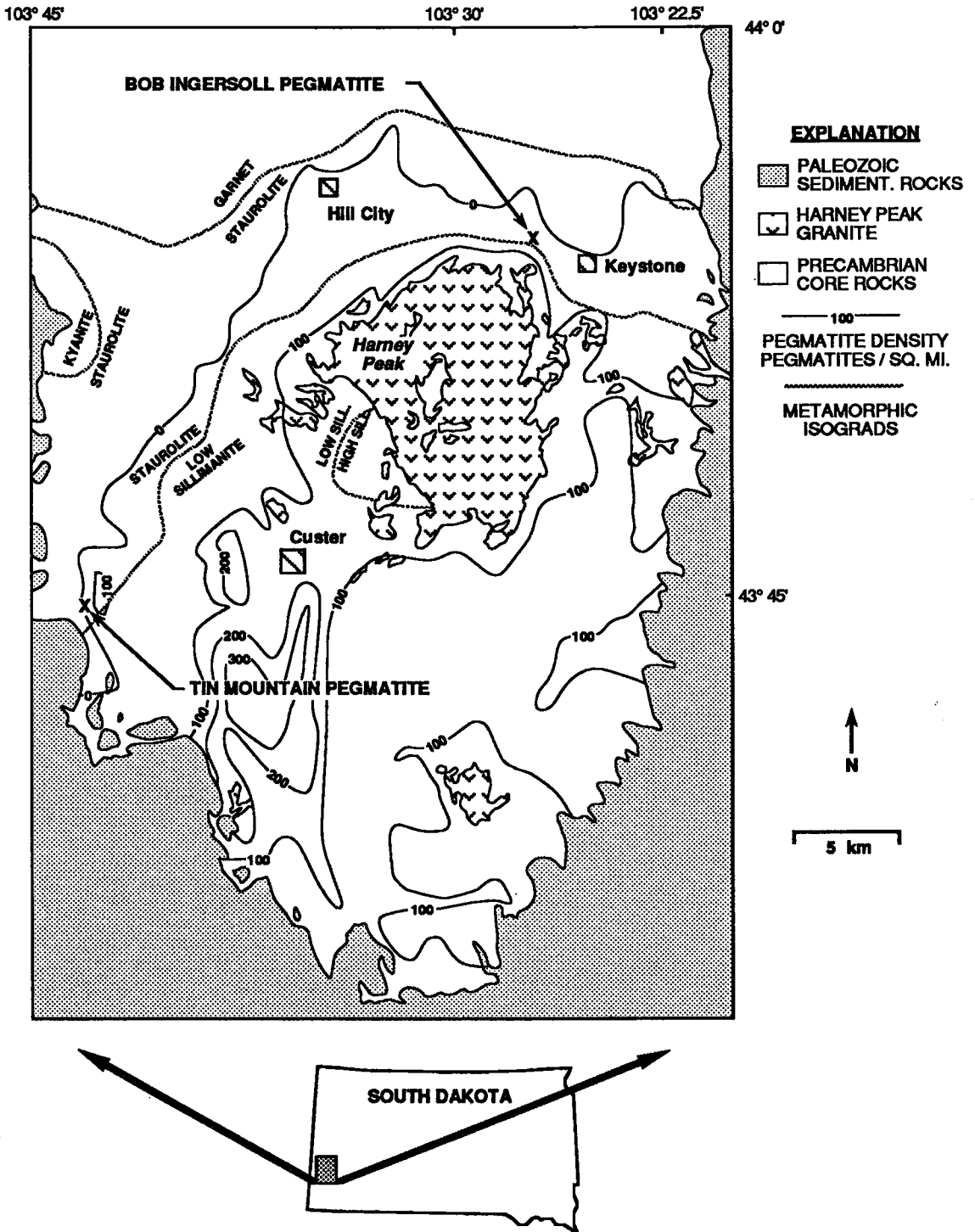
FIG. 1. Location and geological setting of the Bob Ingersoll and Tin Mountain pegmatites, southern Black Hills, South Dakota (after Redden *et al.* 1982).
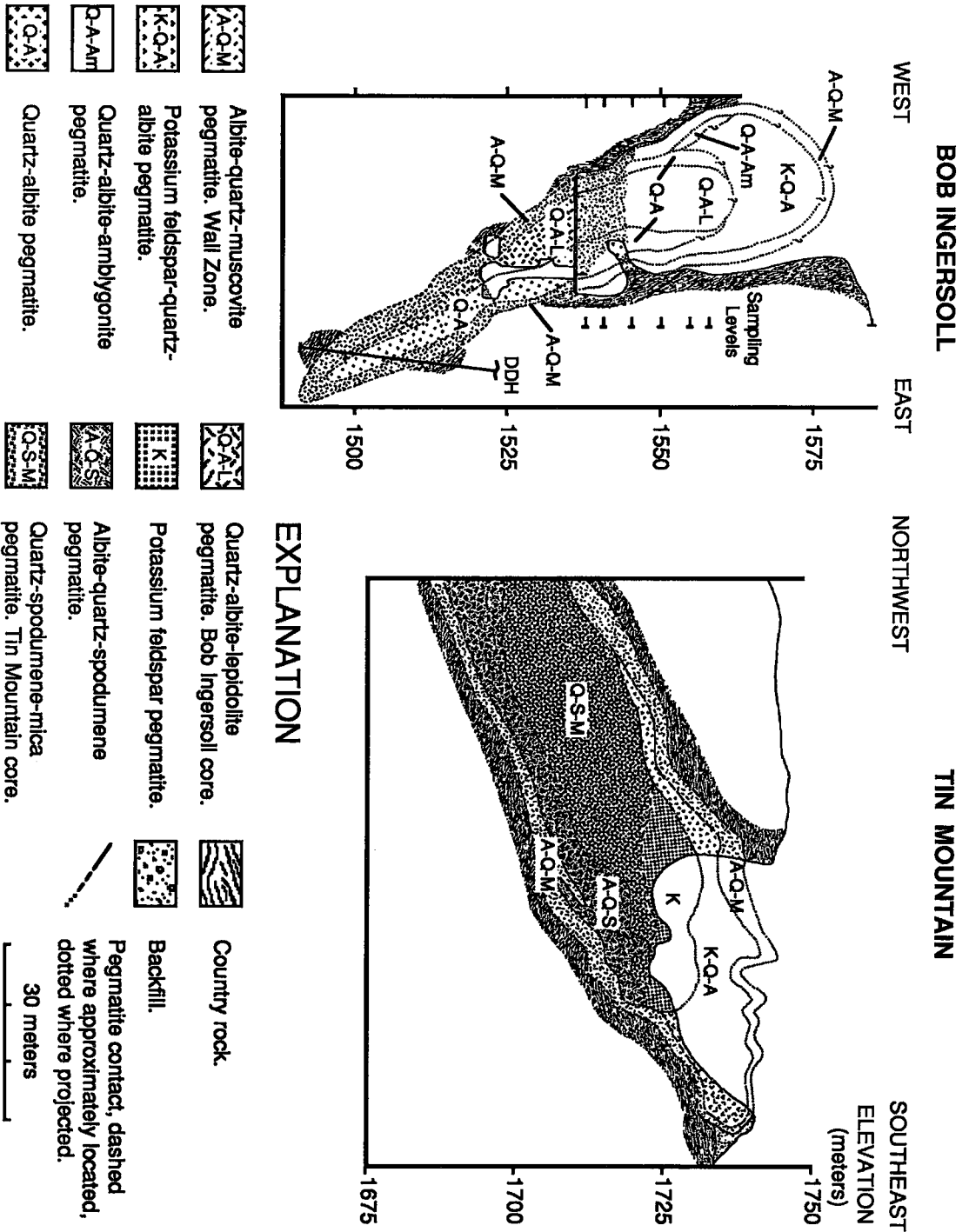
FIG. 2. Schematic geological cross-section of the Bob Ingersoll No. 1 Dike (from Jolliff *et al.* 1986), and of the Tin Mountain pegmatite (through the lower limb); cross-section is oriented N2°W (from Walker *et al.* 1986, Fig. 2, section E–E′).

TABLE 1. MODAL MINERALOGY OF THE BOB INGERSOLL
PEGMATITE AND THE TIN MOUNTAIN PEGMATITE *

	Wall Zone	First	Second	Third	Core
BOB INGERSOLL					
Quartz	29	29	40	65	28
Albite	58	9	31	32	36
K-spar	Tr	62	Tr	Tr	Tr
Mica[1]	13	Tr	Tr	3	36
Amb[2]	Tr	Tr	29	Tr	Tr
Accessory minerals	ap, ct, tur	ap, lt, tur	ap, brl, cst	ap, brl, cst ct, tur	ap, brl, cst mic, tur
TIN MOUNTAIN					
Quartz	34	33	7	27	55
Albite	54	10	2	43	6
K-spar	Tr	50	89	Tr	Tr
Mica	12	7	1	2	15
Amb	Tr	Tr	Tr	1	0.5
Spodumene	Tr	Tr	1	26	23
Beryl	Tr	Tr	Tr	1	0.5
Accessory Minerals	ap, cst ct, tur	cst, lt, tur	ap, ct, lt	ap, cst	ap, cst ct, mic

[1] Mica includes muscovite, transitional lithium-mica, and lepidolite.
[2] Abbreviations: amb, amblygonite-montebrasite; ap, apatite; brl, beryl; cst, cassiterite; ct, columbite-tantalite; lt, lithiophilite-triphylite; mic, microlite; tur, tourmaline.

* Jolliff et al. (1986), Staatz et al. (1963).

(1986) based on variations in the *Y*-site chemistry for tourmaline, and trace-element chemistry of sheet silicates and feldspar. Likewise, a scheme of crystallization has also been postulated by Walker *et al.* (1986b) for the Tin Mountain pegmatite, based on trace element data. A detailed discussion of the supporting evidence is available in Jolliff (1985) and Walker (1984).

Jolliff (1985) postulated the following sequence of crystallization for the Bob Ingersoll pegmatite. The border zone of the Bob Ingersoll pegmatite crystallized initially as a "quenched margin" owing to the loss of volatiles to the country rock. The pegmatite crystallized inward from the outer margin of the albite – quartz – muscovite wall zone. The crystallization of tourmaline removed boron from the melt, resulting in an increase in H_2O–silicate immiscibility (London 1986) and the exsolution of an aqueous fluid. The aqueous fluid served as a medium of transport for several constituents. K-feldspar-enriched units in the upper portion of the pegmatite crystallized as a result of upward transport of K. The transport of K and crystallization of K-feldspar in the upper portion of the pegmatite resulted in an increased abundance of albite in the inner wall zone. Furthermore, removal of K shifted the composition of the residual melt from the minimum melt position and forced simultaneous crystallization of the quartz–albite zone. Fractionation increased the Li and B components in the melt, resulting in renewed crystallization of tourmaline in the inner albite–

quartz zone. The residual melt had reached a point of Li-saturation as lepidolite began to crystallize from the melt in an F-rich environment (Munoz 1971). The quartz – albite – lepidolite core was then the last zone to form.

The following sequence of crystallization was proposed by Walker (1984) and Walker *et al.* (1986b) to have occurred at the Tin Mountain pegmatite. The albite – quartz – muscovite wall zone was the first to crystallize, as indicated by low Rb and Cs and high Sr and Ba relative to other mineral assemblages in the pegmatite. Feldspar geothermometry and positive Eu anomalies in the feldspars are evidence that the perthite – quartz – albite zone also formed early. However, feldspar geothermometry indicates a cooling trend between the two perthite zones. The concentrations of Rb and Sr in the feldspars (Walker 1984, unpubl. data of C.K. Shearer) and *REE* patterns in other coexisting minerals suggest that the lower perthite zone, the quartz – albite – spodumene zone and the quartz – spodumene – lithian muscovite core crystallized simultaneously, and that the direction of crystallization was toward the center of the pegmatite.

London's experimental studies (1990, 1991) suggest that a dynamic model of crystallization involving disequilibrium fractional crystallization may be responsible for the mineralogical zonation observed in these pegmatites. In contrast to the models proposed by Walker *et al.* (1986b), and Jolliff *et al.* (1986) for the Black Hills pegmatites and by Jahns & Burnham (1969) for zoned pegmatites in general, London (1990, 1991) suggested that aqueous vapor has a minimal effect on the redistribution of components during pegmatite crystallization. Nevertheless, these studies do not contradict the sequence of crystallization of assemblages suggested by Jolliff (1985), Walker (1984) and Walker *et al.* (1986b).

The trace-element concentrations in the K-feldspar have been used to interpret petrogenetic relationships among pegmatites (Shearer *et al.* 1985, 1992, Černý 1982). According to one criterion of Černý *et al.* (1986b), Černý (1989) and Shearer *et al.* (1985, 1992), the substantially lower K/Rb ratio of the K-feldspar suggests that the Tin Mountain pegmatite is the "more evolved" of the two pegmatites. The slight enrichment in Cs of the Tin Mountain pegmatite, compared to the Bob Ingersoll pegmatite, supports this conclusion.

TEXTURAL RELATIONSHIPS AND MINERAL CHEMISTRY

Analytical methods

Each deposit has been the site of detailed geochemical investigations into the evolution and

crystallization of pegmatites (Jolliff *et al.* 1986, 1987, Walker *et al.* 1986b). Every sample was located within the pegmatite by plane-table survey techniques. Twenty-one samples containing Sn-, Ta-, and Nb-oxides were collected from all zones of the Bob Ingersoll pegmatite, and 19 samples were collected from all but the perthite zone of the Tin Mountain pegmatite. The oxide minerals were analyzed for major and minor elements on an automated MAC electron microprobe at the South Dakota School of Mines and Technology. Analyses were conducted at an accelerating voltage of 15 kV and a beam current of 20 nA. Standards used for microprobe analysis include spessartine (Mn), chromite (Fe, Mg), titanite (Ca, Ti), scheelite (W), cassiterite (Sn), pollucite (Cs), monazite (Ce), zircon (Y), albite (Na), $LiTaO_3$ (Ta$M\alpha$), uranium (U) and $LiNbO_3$ (Nb$L\alpha$). Beam diameter was approximately 3 μm. To avoid volatilization of Na by heating due to the electron beam, a beam diameter of 12 μm was used on microlite. Each element was counted for 20 seconds or 40,000 counts. ZAF corrections were applied using the program MAGIC IV (Colby 1968).

The concentration of fluorine in 16 samples of amblygonite–montebrasite, muscovite, lepidolite and microlite was obtained by use of an ion-selective electrode technique (Bodkin 1977). A modified Penfield method (Shapiro & Brannock 1955) was used to estimate the total water content of two samples of microlite from Tin Mountain pegmatite. Because of insufficient quantities of microlite from the Bob Ingersoll pegmatite, neither H_2O^+ nor F could be determined. Ferrous iron was determined following the method of Goldich (1984).

Cell parameters were determined for 16 of the analyzed oxide minerals by X-ray powder diffraction. Hand-picked samples were finely ground and dispersed onto glass-fiber filters using a method of aerosol suspension that eliminates preferred orientation of particles (Davis 1986). Analysis of the mounted filters was performed with Cu$K\alpha$ radiation in a Norelco diffractometer equipped with a θ-compensator, graphite monochromator and sample spinner. The patterns were calibrated using fluorite (a = 5.4630 Å, ASTM) as an internal standard, except for the microlite patterns, in which corundum (a = 4.7589, c = 12.991 Å, ASTM) was used to avoid peak overlap. Cell parameters were refined from a minimum of eight reflections.

Columbite–tantalite

Within the Bob Ingersoll pegmatite, columbite is the most abundant in the albite – quartz – muscovite wall zone. The mineral typically occurs as blade-like subhedral to euhedral crystals flattened on the (010) plane. Thin tabular crystals up
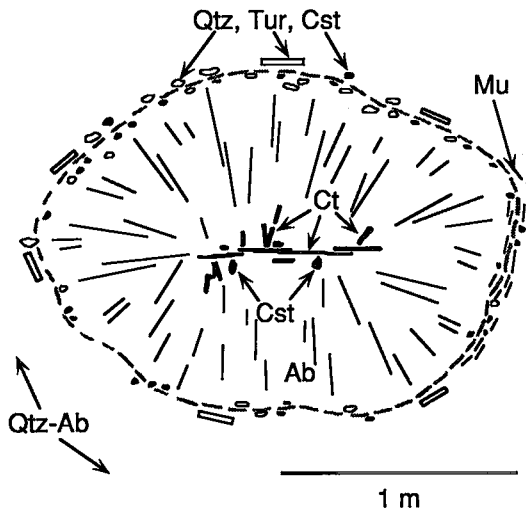

FIG. 3. Sketch of columbite in radial albite from the wall zone at Bob Ingersoll (sample no. B12). Columbite-tantalite (Ct), cassiterite (Cst), albite (Ab), tourmaline (Tur), quartz (Qtz) and muscovite (Mu).

to 76 cm in length and 61 cm in width have been found in this zone (Page *et al.* 1953). The tabular crystals commonly occur at the center of large radial aggregates of albite (cleavelandite habit). One large central blade of columbite may have several smaller tabular crystals of columbite extending from it, either perpendicular or radiating (Fig. 3). Anhedral blebs of cassiterite usually occur adjacent to or intermixed with the columbite.

The columbite from the albite – quartz – muscovite zone displays the highest overall Nb of any Ta–Nb oxide in the entire pegmatite, with a Ta/(Ta+Nb) of 0.12 (Table 2a). This ratio increases slightly in the upper portions of the zone, to around 0.35. The Mn/(Mn+Fe) ratio increases within the zone, from a low of 0.35 to 0.89. The major-element ratios can be highly variable. In a sample containing two crystals of columbite–tantalite separated by 2 mm of albite, one crystal has a Ta/(Ta+Nb) of 0.15 and a Mn/(Mn+Fe) of 0.44, whereas the neighboring crystal displays values of 0.19 and 0.76, respectively (Table 2a, analyses F1). High variability on such a small scale has also been noted in *REE* patterns and abundances in apatite from the Bob Ingersoll pegmatite (Jolliff *et al.* 1989). Radical chemical variations may be attributed to disequilibrium crystallization, as proposed by London (1990, 1991) and London *et al.* (1988, 1990). Individual crystals may show varying degrees of zoning involving Ta, Nb, Mn, and Fe. Small-scale increases in Ta/(Ta+Nb) and Mn/(Mn+Fe) ratios were commonly noted from

TABLE 2a. REPRESENTATIVE COMPOSITIONS OF COLUMBITE-TANTALITE (CT) AND TAPIOLITE (TPL) FROM THE BOB INGERSOLL PEGMATITE

	Wall Zone				Intermediate Zones			Core	
Sample	B5C	F1	F1	B12R	G4	G	C7A	S2	CD
Locations	Tpl	Ct	Ct	Ct	Ct	Ct	Ct	Ct	Ct
MnO	0.48	8.20	13.76	11.40	13.43	16.16	6.93	12.02	14.51
FeO	14.29	10.63	4.47	6.74	3.21	2.63	12.55	3.39	0.69
Ta$_2$O$_5$	69.55	17.66	22.43	16.81	34.79	25.47	43.29	66.34	62.38
Nb$_2$O$_5$	12.59	62.14	57.32	63.08	45.54	55.26	36.77	16.95	18.84
SnO$_2$	1.16	0.06	0.11	0.18	0.02	0.20	0.06	0.46	0.36
TiO$_2$	0.40	0.15	0.13	0.15	0.16	0.12	0.22	0.21	0.15
WO$_3$	0	-	-	0	1.47	0	0	0	0
Total	98.47	98.84	98.22	98.36	98.62	99.83	99.91	99.37	96.93
A site									
Mn	0.032	0.424	0.732	0.590	0.753	0.855	0.402	0.785	0.985
Fe	0.956	0.543	0.235	0.345	0.178	0.137	0.718	0.219	0.045
Total	0.988	0.976	0.967	.935	0.935	0.992	1.120	1.004	1.003
B site									
Ta	1.513	0.293	0.383	0.277	0.626	0.434	0.806	1.387	1.323
Nb	0.455	1.717	1.627	1.738	1.362	1.559	1.138	0.590	0.664
Sn	0.037	.001	0.003	0.004	0	0	0.002	0.016	0.011
Ti	0.008	0.002	0.002	0.008	0.003	0.004	0.004	0.012	0.003
W	0	-	-	0	0.028	0	0	0	0
Total	2.013	2.013	2.015	2.027	2.019	2.001	1.950	2.005	2.001
Mn/(Mn+Fe)	0.03	0.44	0.76	0.63	0.81	0.86	0.36	0.78	0.96
Ta/(Ta+Nb)	0.77	0.15	0.19	0.14	0.31	0.22	0.41	0.70	0.67

- Not analyzed. Cation formula based on 6 atoms of oxygen. Oxides in wt.%.

core to rim for individual crystals in normal progressive zoning (*cf.* Lahti 1987). However, decreases in these ratios also were encountered (reverse zoning: Lahti 1987), particularly involving Mn/(Mn + Fe). Oscillatory or rhythmic zoning was encountered as well in individual grains from this zone. Both oscillatory and progressive zoning of columbite–tantalite has been reported from several localities (Foord 1976, von Knorring & Condliffe 1984, Lahti 1987).

Discrete crystals of columbite–tantalite larger than a few millimeters are rarely found in the interior of the pegmatite. In the perthite – quartz – albite zone, small crystals are associated with cassiterite and apatite in the albite and quartz matrix that surrounds the large crystals of perthite. The columbite from this assemblage shows slight enrichment of both Ta and Mn (Table 2a), with minor variation in Mn/(Mn + Fe) between adjacent crystals. Within the quartz-rich intermediate zones and the core, columbite–tantalite occurs primarily as microscopic inclusions in, overgrowths on, or as fracture-fillings in cassiterite. The inclusions are commonly disseminated throughout individual crystals of cassiterite, dispersed along fractures and grain boundaries as small irregular blebs, or they occur as subhedral to euhedral inclusions scattered along the margins of the cassiterite (Figs. 4a, c). The scale of the inclusions is on the order of 0.001 to 0.1 mm. The small irregular inclusions occur as swarms of dispersed blebs within individual crystals

of cassiterite but without any particular crystallographic orientation. Subhedral inclusions of columbite–tantalite are commonly subparallel to the margin of the cassiterite crystals (Fig. 4a), and elongate inclusions have an orientation that is more or less perpendicular to the margin.

Whereas discrete crystals of columbite–tantalite from a given zone tend to plot in closely grouped patterns on the FeTa$_2$O$_6$–MnTa$_2$O$_6$–FeNb$_2$O$_6$–MnNb$_2$O$_6$ quadrilateral (Fig. 5a), the compositions of the inclusions do not seem to follow any readily distinguishable trend. The largest inclusions and, to some extent, those nearest the margin of the host cassiterite, tend to have Ta/(Ta + Nb) and Mn/(Mn + Fe) values similar to the discrete crystals in that zone. Inclusions in wall-zone cassiterite have Ta/(Ta + Nb) values from 0.28 to 0.62, with intermediate Mn/(Mn + Fe) values of 0.50 to 0.65. In the quartz–albite assemblage, the columbite–tantalite inclusions tend to have slightly narrower Ta/(Ta + Nb) ratios (0.4 – 0.61), but a wider spread in Mn/(Mn + Fe) (0.1 – 0.85). However, most of the inclusions are in the lower Mn range. In comparison, the majority of inclusions in cassiterite from the lepidolite-rich core fall within a narrow range of Ta/(Ta + Nb) (0.5 – 0.6) and Mn/(Mn + Fe) (0.2 – 0.4). As a result, a crude trend toward the FeTa$_2$O$_6$ corner of Figure 5a is defined by increasing Ta and Fe in columbite–tantalite inclusions in cassiterite from the wall zone inward toward the core.

Inclusions of columbite–tantalite and tapiolite in cassiterite are noted in several descriptions and apparently are common (*cf.* Černý & Turnock 1971, Černý *et al.* 1985). Ramdohr (1980) described oriented exsolution-related "needles" of tapiolite and anhedral "grains" of (Fe,Mn)(Ta,Nb)$_2$O$_6$ that exsolve from cassiterite. The presence of columbite as an exsolution phase is limited to high-temperature deposits, *i.e.*, granites. Maximyuk & Lebedeva (1968) concluded that for Ta and Nb in excess of 0.1 wt.%, (Ta,Nb)$_2$O$_5$ will not substitute into the cassiterite structure but will be incorporated as microinclusions. Povarennykh (1972), on the other hand, stated that up to 5% Ta$_2$O$_5$ and 2.5% Nb$_2$O$_5$ may be present in the cassiterite structure. Much of the cassiterite at the Bob Ingersoll contains up to 5.7 wt.% Ta$_2$O$_5$ and coexists with inclusions of columbite–tantalite. This is consistent with compositions of coexisting columbite–tantalite and cassiterite from other localities (Černý & Ercit 1985, Černý *et al.* 1986a,b). This suggests that the swarms of small irregular inclusions are the result of exsolution. The subhedral and larger irregular inclusions close to the margin of cassiterite grains may be the result of epitaxic overgrowths of columbite–tantalite (*cf.* Ginsburg 1956) that have been overtaken and surrounded by the cassiterite.
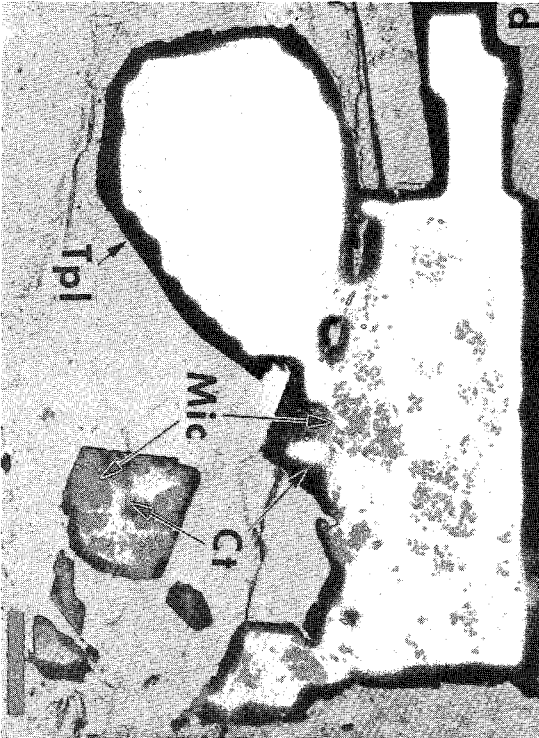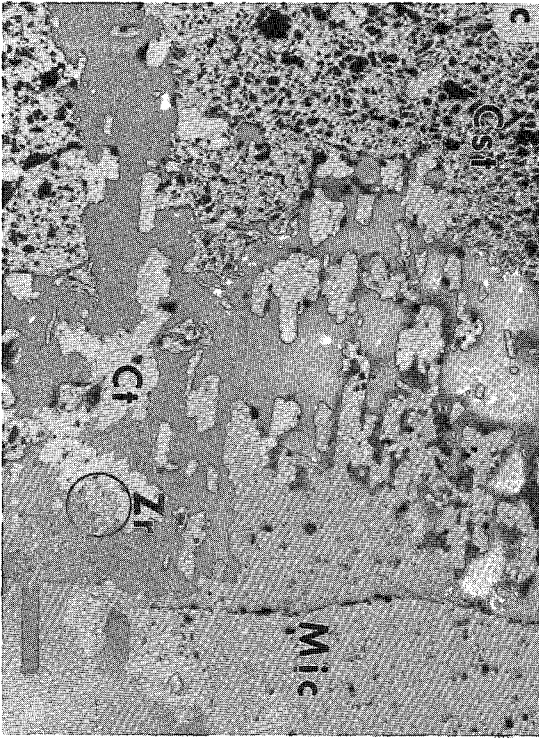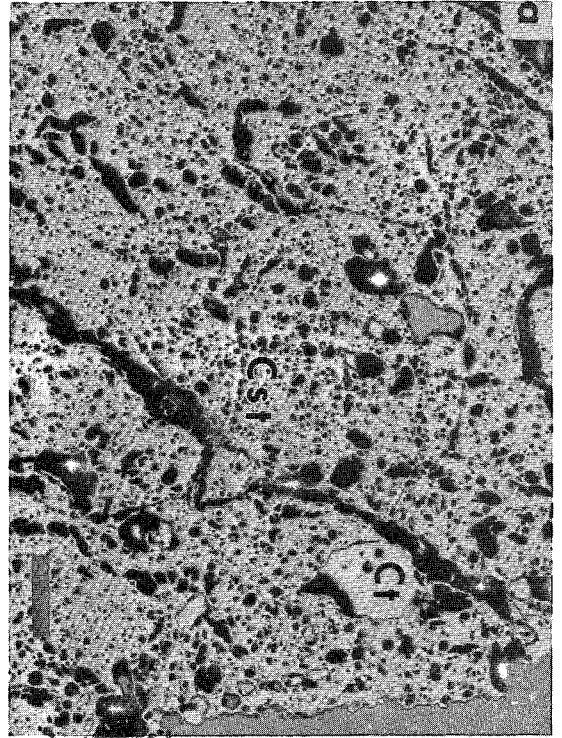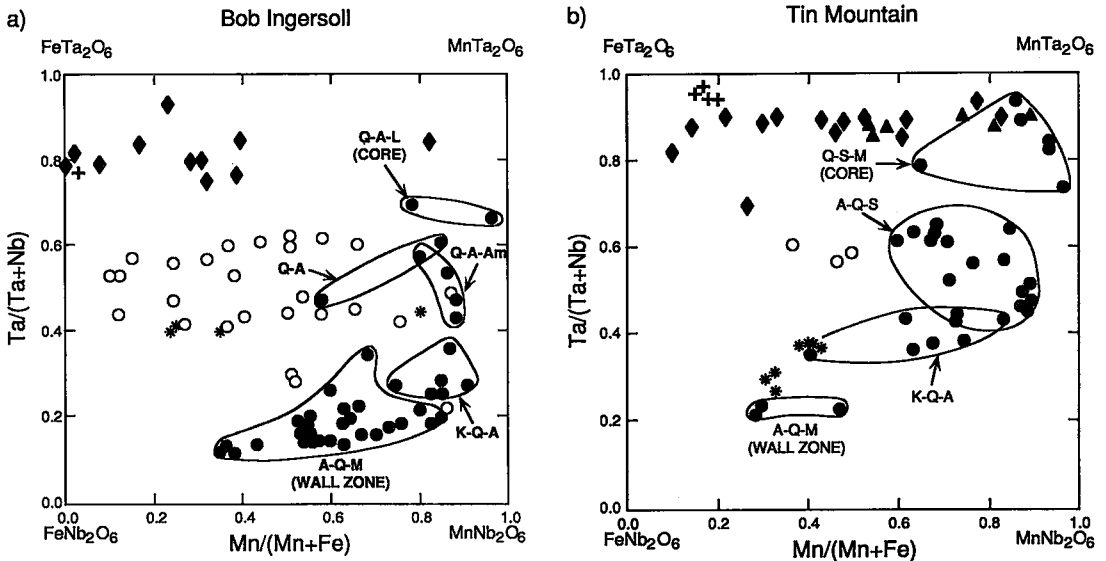
FIG. 5. Nb–Ta oxides from the Bob Ingersoll (a) and the Tin Mountain pegmatites (b) plotted in the $FeTa_2O_6$–$MnTa_2O_6$–$FeNb_2O_6$–$MnNb_2O_6$ quadrilateral. $Ta/(Ta+Nb)$ and $Mn/(Mn+Fe)$ values express ratios of atoms per formula unit. Columbite–tantalite(●), inclusions of columbite–tantalite in cassiterite (○), wodginite (▲), microlite (♦) and tapiolite (+). Columbite–tantalite fracture filling (*).

TABLE 2b. REPRESENTATIVE COMPOSITIONS OF COLUMBITE-TANTALITE (CT) AND TAPIOLITE (TPL) FROM THE TIN MOUNTAIN PEGMATITE

Sample Locations	Wall Zone E5 Ct	Intermediate Zones TM Ct	C9 Ct	TM2 Ct	C8 Ct	Core C10B Ct	C10C Ct	C10C Tpl	Fracture Filling G10 Ct
MnO	5.23	7.30	12.04	10.55	12.15	15.38	12.29	2.72	6.64
FeO	12.92	10.07	5.71	5.17	4.71	0.38	2.09	11.03	10.61
Ta₂O₅	24.91	38.85	40.40	60.69	53.87	67.67	78.06	80.77	40.27
Nb₂O₅	54.28	40.87	39.76	21.44	28.16	14.25	5.07	2.78	41.62
SnO₂	0.51	0.44	0.13	0.25	0.10	0.08	0.20	0.71	0.42
TiO₂	0.74	0.47	1.23	0.40	0.33	-	0.11	0.14	0.52
WO₃	-	0	-	-	-	-	0	0	-
Total	98.59	98.01	99.27	98.50	99.32	97.76	97.82	98.15	100.14
				A site					
Mn	0.281	0.422	0.684	0.676	0.742	1.038	0.875	0.195	0.375
Fe	0.684	0.574	0.320	0.324	0.285	0.026	0.148	0.785	0.590
Total	0.965	.996	1.004	1.000	1.027	1.064	1.023	0.980	0.965
				B site					
Ta	0.426	0.719	0.738	1.246	1.055	1.461	1.785	1.871	0.730
Nb	1.547	1.254	1.207	0.730	0.918	0.512	0.191	0.105	1.254
Sn	0.012	0.012	0.004	0.008	0.004	0.004	0.008	0.023	0.012
Ti	0.035	0.023	0.063	0.023	0.020	-	0.008	0.008	0.027
W	-	0	-	-	-	-	0	0	-
Total	2.020	2.008	2.012	2.007	1.997	1.977	1.992	2.007	2.023
Mn/(Mn+Fe)	0.29	0.42	0.68	0.68	0.72	0.97	0.86	0.20	0.39
Ta/(Ta+Nb)	0.22	0.36	0.38	0.63	0.53	0.74	0.90	0.95	0.38

Cation formula based on 6 atoms of oxygen. Oxides in wt.%.

At the Tin Mountain pegmatite, discrete crystals of columbite–tantalite can be found in all zones. In the albite – quartz – muscovite wall zone, columbite occurs in trace amounts, commonly with cassiterite. The columbite in this albite-rich assemblage is very similar to that in the Bob Ingersoll pegmatite, with moderate $Mn/(Mn+Fe)$ (0.3 – 0.5), but slightly higher $Ta/(Ta+Nb)$ (0.23) (Fig. 5b, Table 2b). The Ta content is still within range of columbite from the albite-rich wall zone at the Bob Ingersoll.

Columbite in the perthite – quartz – albite zone occurs with cassiterite in the quartz and albite matrix, particularly near the contact with other zones. Crystals are blocky, several centimeters in largest dimension, and contain microscopic inclusions of silicate minerals. Staatz *et al.* (1963) reported minor amounts of columbite–tantalite in the perthite zone. We were unable to confirm this observation.

FIG. 4. Photomicrographs of Sn, Ta and Nb minerals from the Bob Ingersoll pegmatite (a,c) and the Tin Mountain pegmatite (b,d). Scale bars = 0.5 mm. (a) Columbite inclusions (Ct) and overgrowths on cassiterite (Cst) (C7A S). (b) Intergrowth of columbite–tantalite and cassiterite (TM2). $Ta/(Ta+Nb)$ increases in the direction of the arrow. (c) Columbite–tantalite, microlite (Mic) and zircon (Zr, in circle) assemblage in quartz-filled fracture from the quartz–albite zone (C3). (d) Microlite replacing columbite. Note euhedral tapiolite (Tpl) (C10–C1).
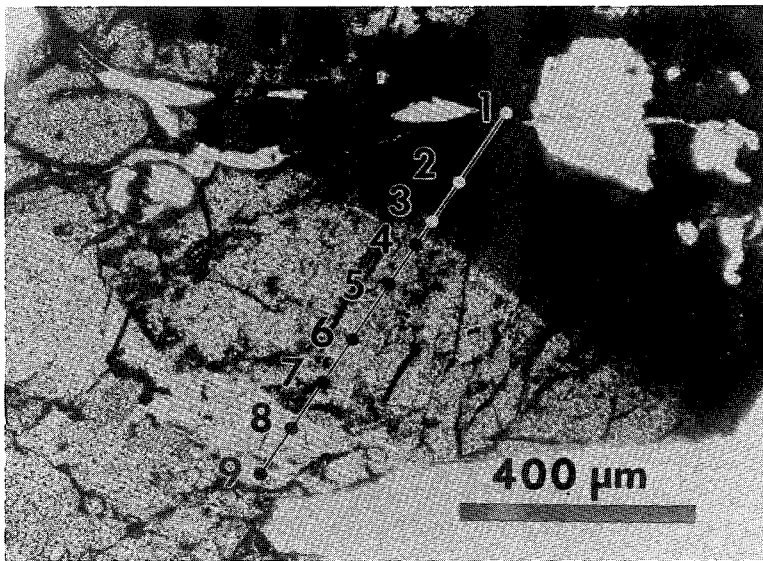
FIG. 6. Photomicrograph of wodginite and manganotantalite. Numbers correspond to analytical results listed in Table 3.

Large subhedral crystals of columbite–tantalite in the albite – quartz – spodumene zone are commonly associated with long radiating blades of albite (cleavelandite habit) and curved "ball peen"

TABLE 3. COMPOSITION OF WODGINITE AND TANTALITE (C10-C) FROM AN ALBITE-MICA REPLACEMENT RIM SURROUNDING SPODUMENE IN THE CORE OF THE TIN MOUNTAIN PEGMATITE

	Wodginite							Tantalite	
	1	2	3	4	5	6	7	8	9
MnO	6.18	6.35	6.54	6.99	8.71	9.83	10.36	14.4	14.06
FeO*	4.34	4.14	4.09	3.52	1.64	0.50	0.00	0.82	0.94
Fe2O3	1.35	1.55	1.68	1.56	1.36	1.27	1.29	-	-
Ta2O5	63.74	64.50	63.82	65.70	66.27	67.25	66.52	74.00	75.10
Nb2O5	5.76	5.48	5.40	4.64	4.06	4.25	4.04	8.08	7.89
SnO2	15.65	14.92	14.96	15.23	15.51	15.55	15.46	0.23	0.26
TiO2	0.38	0.35	0.40	0.23	0.25	0.25	0.30	0.19	0.16
Total	97.40	97.29	96.98	97.87	97.79	98.90	97.97	97.37	98.41

A site

Mn	2.286	2.356	2.432	2.594	3.249	3.626	3.857	0.984	0.977
Fe2+	1.584	1.516	1.500	1.289	0.604	0.181	0.000	0.059	0.066
□ A	0.130	0.128	0.067	0.117	0.147	0.193	0.143	-	-
Total	4.000	4.000	4.000	4.000	4.000	4.000	4.000	1.043	1.043

B site

Ta	6.863	6.915	6.928	7.081	7.192	7.163	7.197	1.664	1.676
Nb	1.137	1.085	1.072	0.919	0.808	0.837	0.803	0.301	0.293
Sn	-	-	-	-	-	-	-	0.008	0.008
Ti	-	-	-	-	-	-	-	0.012	0.012
Total	8.000	8.000	8.000	8.000	8.000	8.000	8.000	1.985	1.989

C site

Sn	2.725	2.606	2.619	2.660	2.724	2.700	2.710		
Ti	0.125	0.115	0.132	0.076	0.079	0.082	0.099		
Fe3+	0.444	0.511	0.557	0.515	0.451	0.416	0.427		
Ta	0.706	0.768	0.692	0.748	0.746	0.802	0.754		
□ C	0.000	0.000	0.000	0.000	0.000	0.000	0.010		
Total	4.000	4.000	4.000	4.000	4.000	4.000	4.000		

Structural formula of wodginite based on 32 atoms of oxygen; for tantalite, 6 atoms of oxygen.
* Total Fe reported as FeO. For Fe2O3 calculation, see text. Oxides in wt.%. Each analysis point is shown in Fig. 6.

muscovite or with amblygonite. The columbite–tantalite is locally intergrown with cassiterite (Fig. 4b). The mutual interpenetration of the two minerals suggests simultaneous crystallization (Craig & Vaughan 1981). Where one end of a euhedral crystal of tantalite is embedded in cassiterite, the crystal displays a progressive increase in Ta/(Ta + Nb) and a decrease in Mn/(Mn + Fe) away from the cassiterite. In all probability, this is the result of continued growth along the c axis, away from the cassiterite.

Columbite–tantalite tends to be particularly abundant in associations with amblygonite in the core of the Tin Mountain pegmatite. Stout tabular crystals 15 X 2.5 cm have been reported in amblygonite (Roberts & Rapp 1965). Tantalite also occurs sparingly with microlite, tapiolite, and wodginite in albite – lithian muscovite rims surrounding spodumene. In this occurrence, nearly pure manganotantalite coexists with and is rimmed by wodginite (Fig. 6, Table 3). The tantalite from the core of the Tin Mountain achieves the highest Ta/(Ta + Nb) value of either pegmatite, 0.94.

Individual columbite–tantalite crystals from the Tin Mountain pegmatite display several types of zoning. Crystals from the wall zone and perthite – quartz – albite zone typically show progressive enrichment of Mn from core to rim at nearly constant Ta values. Specimens from the albite – quartz – spodumene zone exhibit enrichment in Ta

TABLE 4. ELECTRON-MICROPROBE DATA ON PROGRESSIVELY ZONED COLUMBITE-TANTALITE FROM THE TIN MOUNTAIN ALBITE-QUARTZ-SPODUMENE ZONE

	rim					core
	1	2	3	4	5	6
MnO	14.75	15.18	15.00	14.76	15.03	15.52
FeO	1.83	2.09	1.85	1.99	2.09	1.99
Ta$_2$O$_5$	52.30	53.12	50.85	49.16	48.16	48.89
Nb$_2$O$_5$	30.09	31.03	33.12	33.23	32.85	34.64
SnO$_2$	0.23	0.33	0.26	0.20	0.19	0.20
TiO$_2$	0.29	0.22	0.21	0.23	0.17	0.22
Total	99.50	101.96	101.29	99.57	98.95	101.46
			A site			
Mn	0.891	0.895	0.879	0.875	0.898	0.902
Fe	0.109	0.121	0.105	0.117	0.125	0.114
Total	1.000	1.016	0.984	0.992	1.023	1.016
			B site			
Ta	1.012	1.004	0.957	0.938	0.934	0.912
Nb	0.969	0.973	1.035	1.051	1.047	1.074
Sn	0.008	0.008	0.008	0.004	0.004	0.005
Ti	0.016	0.012	0.012	0.012	0.008	0.004
Total	2.005	1.997	2.012	2.005	1.993	1.995
Mn/(Mn+Fe)	0.89	0.88	0.89	0.88	0.88	0.89
Ta/(Ta+Nb)	0.51	0.51	0.48	0.47	0.47	0.46

Sample TM1 step traverse. Cation formula based on 6 atoms of oxygen. Oxides in wt.%.

TABLE 5. REPRESENTATIVE CELL PARAMETERS FOR COLUMBITE-TANTALITE FROM THE BOB INGERSOLL (BI) AND TIN MOUNTAIN (TM) PEGMATITES

		a,Å	b,Å	c,Å	V,Å^3
BI	B3	5.750(2)	14.346(5)	5.099(1)	420.7(2)
	B12C	5.747(1)	14.336(4)	5.087(1)	419.1(1)
	B12R	5.745(1)	14.321(4)	5.090(1)	418.8(1)
	B21	5.736(2)	14.320(8)	5.080(3)	417.3(2)
	F1	5.775(4)	14.400(8)	5.092(4)	423.5(4)
TM	TM1	5.756(1)	14.323(7)	5.133(3)	422.4(2)
	TM3	5.739(2)	14.289(6)	5.104(2)	418.5(2)
	C7	5.733(1)	14.267(5)	5.116(2)	418.4(2)
	C9'	5.733(1)	14.267(5)	5.116(2)	418.4(2)

Individual sample numbers follow BI and TM designations.
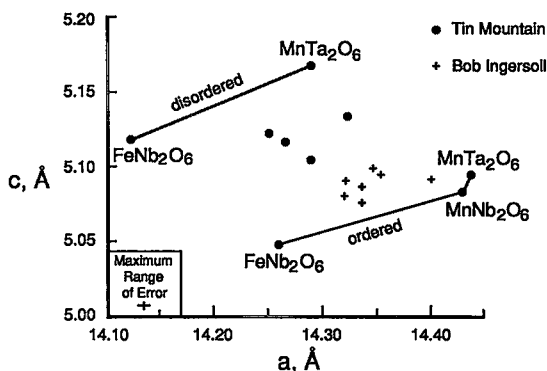

FIG. 7. Cell parameters for columbite-tantalite plotted on an a versus c diagram. End-member values from Černý & Ercit (1985). Length of error bar is equal to 1σ.

from core to rim with both increasing and decreasing Mn content (Table 4).

The cell parameters a and c presented in Table 5 are plotted in Figure 7. The columbite-tantalite from each pegmatite plot within distinct groups.

That from the Tin Mountain pegmatite exhibits an intermediate structural state, but those samples from the Bob Ingersoll pegmatite apparently have a considerably more ordered structure. These differences may reflect the influence of substitution of minor elements on the unit-cell dimensions (Černý & Ercit 1985).

Cassiterite

In the wall zone of the Bob Ingersoll pegmatite, cassiterite occurs as irregular masses up to several centimeters in diameter associated with columbite-tantalite at the core of radial albite aggregates (Fig. 3). The masses consist of irregular individual "grains" or crystals of cassiterite at a scale of 1 to 0.1 mm and commonly host columbite-tantalite inclusions. At the perimeter of the radial aggregates of albite, fine-grained euhedral crystals of cassiterite are scattered between albite laths and the quartz, tourmaline, and muscovite that surround the aggregates.

Cassiterite is most common in the albite-rich intermediate zones and core. In the quartz – albite – amblygonite unit, cassiterite occurs as irregular granular masses intergrown with albite and amblygonite–montebrasite. Masses of up to 45 kg have been reported (Roberts & Rapp 1965). In the quartz–albite zone, cassiterite is intergrown with albite and also occurs as thin veins (<1 cm in width) in quartz-rich fracture fillings. Stringers of quartz rimmed by several centimeters of radiating albite comprise the fracture fillings. The cassiterite veins occur in the quartz stringers, whereas cassiterite appears as small, irregular masses in the albite rim. Fractures within massive cassiterite are filled with quartz and an assemblage of anhedral to subhedral columbite-tantalite, tapiolite, microlite, apatite and zircon (Fig. 4c). The quartz – albite – lepidolite core contains irregular masses and granular aggregates of very fine (0.1 – 0.4 mm) euhedral cassiterite, intergrown with albite laths and lepidolite. Cassiterite from the albite-rich intermediate zones hosts microscopic inclusions and overgrowths of columbite-tantalite. Inclusions in cassiterite from the core are rare and are predominantly ferrotantalite.

Cassiterite shows significant variation in its composition, from 0.78 to 9.67 wt.% combined Ta, Nb, Mn, and Fe oxides (Table 6). Minor-element substitution involves less than 0.50 wt.% each of Mn and W. The compositions plot close to the trend defined by the ideal substitution $(Fe,Mn)^{2+}$ + $2(Nb,Ta)^{5+} = 3(Sn, Ti)^{4+}$ (Černý et al. 1985, Černý & Ercit 1985) or close to the pure $(Sn,Ti)O_2$ corner of the $(Sn,Ti) - (Ta,Nb) - (Fe,Mn)$ diagram (Fig. 8). In addition, considerable variation occurs among individual grains making up the massive

TABLE 6. SELECTED ELECTRON-MICROPROBE DATA ON CASSITERITE

			Bob Ingersoll				Tin Mt
	B5C*	GX-19	GX-20	GX-21	CD-4	CD-5	G10
FeO	1.22	0.13	0.20	0.66	0.04	0.72	0.16
Ta2O5	5.60	0.45	0.96	2.05	0.64	5.74	0.75
Nb2O5	1.68	0	0.44	1.33	0.05	1.32	0
SnO2	90.76	99.86	98.43	95.66	98.45	91.73	98.16
MnO	0.35	0.32	0.32	0.32	0.46	0.43	0
WO3	0.42	0	0	0	0	0	1.05
Total	100.33	100.77	100.35	100.02	99.64	99.94	100.12
Fe	0.025	0.004	0.004	0.016	00.015	0.004	
Ta	0.038	0.004	0.008	0.016	0.004	0.039	0.005
Nb	0.019	0	0.004	0.016	00.015	0	
Sn	0.899	0.988	0.977	0.949	0.984	0.916	0.979
Mn	0.013	0.012	0.012	0.012	0.016	0.017	0
W	0.003	0	0	0	00	0.007	
Total	0.997	1.008	1.005	1.009	1.004	1.002	0.995

Cation formula based on 2 atoms of oxygen. * Average of 5 analyses. Oxides in wt.%.
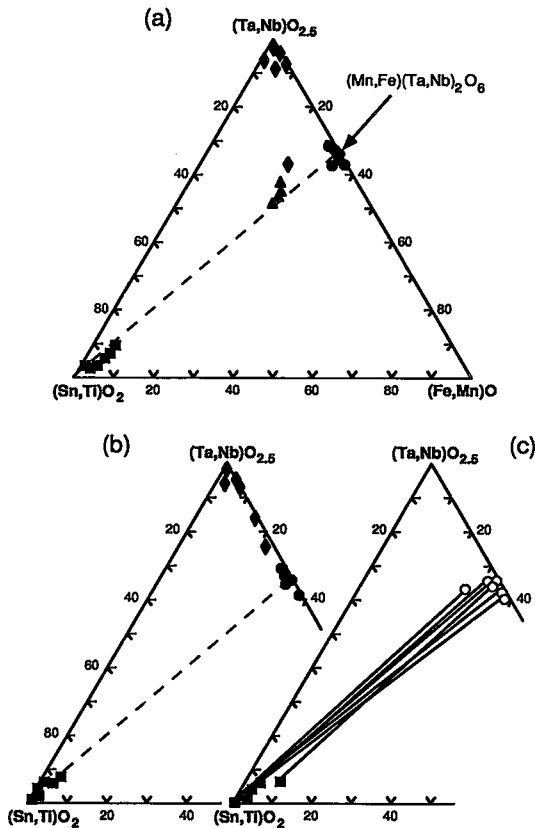

FIG. 8. $(Sn,Ti)O_2$-$(Ta,Nb)O_{2.5}$-$(Fe,Mn)O$ plots for (a) Ta, Nb, Sn oxide minerals from the Tin Mountain, (b) Ta, Nb, Sn minerals from the Bob Ingersoll, and (c) coexisting cassiterite and columbite–tantalite inclusions from the Bob Ingersoll. Symbols: columbite–tantalite (●), cassiterite (■), columbite–tantalite inclusions (○), microlite (◆), wodginite (▲).

cassiterite. Nearly pure SnO_2 (Table 6, analysis CD–4) may occur adjacent to cassiterite containing over 5 wt.% Ta (analysis CD–5). In thin section, the pure cassiterite appears translucent white to tan, but becomes deep red and eventually opaque with increasing Fe and Ta content. Typically, swarms of columbite–tantalite inclusions appear in cassiterite that is rich in Ta (around 3 wt.% or more), whereas crystals low in Ta, Nb, Mn, and Fe have only a few isolated inclusions or none at all. Within Ta-rich cassiterite, compositional gradients have been found. Immediately adjacent to an inclusion, the Ta content of the cassiterite is low and increases with distance from the inclusion (Table 6, analyses GX–19 to GX–21).

Cassiterite in the Tin Mountain pegmatite is much finer grained and much less abundant than in the Bob Ingersoll pegmatite. Anhedral to euhedral crystals 3–6 mm in diameter are found in the albite – quartz – muscovite wall zone. Cassiterite occurs as small masses with amblygonite in both the albite – quartz – spodumene zone and the quartz – spodumene – mica core. Inclusions of columbite in cassiterite tend to be large and isolated, unlike the swarms of small inclusions found in the Bob Ingersoll cassiterite. The chemistry of the Tin Mountain cassiterite is somewhat different from that in the Bob Ingersoll pegmatite: Nb is much lower, never exceeding 1.0 wt.%, the Fe content is less, and the maximum W content is higher (1.05 wt.%). Ta, Nb, Mn and Fe ranges from 0.91 to 6.44 wt.% in the Tin Mountain cassiterite.

Microlite

In the core of the Bob Ingersoll pegmatite, microlite is found as anhedral grains averaging 0.6 mm in diameter. These microlite grains appear to be primary. Other irregular grains display relict inclusions of tantalite. This latter type of texture has been interpreted by Černý & Turnock (1971) and Černý & Ercit (1985) as a replacement of columbite–tantalite by microlite. The Ta content of the Bob Ingersoll microlite ranges from 62.90 to 75.90 wt.% Ta_2O_5, whereas CaO and Na_2O are as high as 10.56 and 4.96 oxide wt.%, respectively. Uranium ranges from 1.62 to 10.13 wt.% UO_3; the mineral may be classified as uranmicrolite (Hogarth 1977). The microlite is zoned from core to rim: concentrations of Ca, Na, U, and Pb generally decrease; that of Mn shows an increase, and Ta/Nb may increase or decrease (Table 7, analyses S3–C and S3–R).

Within the quartz–albite zone, microlite is associated with small-scale albitic replacement-units surrounding quartz-filled fractures. Microlite in that assemblage occurs with cassiterite, euhedral columbite–tantalite and zircon (Fig. 4c). The

TABLE 7. ELECTRON-MICROPROBE DATA ON SELECTED MICROLITE

	Bob Ingersoll			Tin Mountain				
	M1 (3)	S3 C	S3 R	C10B RS	C10B C	C10B R	B4 (6)	C10B (11)
CaO	10.56	7.25	2.95	3.63	7.52	8.38	4.88	5.96
Na2O	4.96	3.79	0.79	0.39	2.66	3.51	0.30	1.24
Cs2O	0.12	0.01	0.08	0.07	0.06	0.11	0.06	0.06
UO3	0.25	10.13	9.37	11.34	9.81	7.14	9.10	8.94
PbO	-	4.73	4.79	2.65	1.77	0.73	2.13	1.64
Y2O3	-	0	0	0.11	0.19	0.18	0.07	0.10
MgO	-	0.05	0.16	0.20	0.03	0.04	0	0.11
MnO	-	0.09	0.50	0.75	0.22	0.09	0.70	0.42
FeO	-	1.01	0.78	0.48	0.26	0.58	*1.06	*0.76
SnO2	-	0	0	0	0	0	10.00	0
Ta2O5	77.98	62.90	65.30	65.14	70.98	71.99	69.07	70.18
Nb2O5	3.24	9.77	11.66	6.39	6.01	5.64	6.11	5.30
TiO2	-	-	-	-	-	-	0.11	0.00
F	-	-	-	-	-	-	1.24	1.18
H2O(+)	-	-	-	-	-	-	3.26	3.52
H2O(-)	-	-	-	-	-	-	0.84	1.46
O = F	-	-	-	-	-	-	-0.52	-0.50
Total	97.11	99.73	96.38	91.15	99.51	98.39	98.41	100.37
				A site				
Ca	0.998	0.722	0.740	0.378	0.732	0.812	0.483	0.595
Na	0.848	0.683	0.133	0.073	0.468	0.615	0.054	0.224
Cs	0.004	0.000	0.003	0.003	0.002	0.004	0.002	0.002
U	0.005	0.198	0.171	0.231	0.187	0.136	0.177	0.175
Pb	-	0.118	0.112	0.069	0.043	0.018	0.053	0.041
Y	0	0	0	0.006	0.009	0.009	0.003	0.005
Mg	-	0.007	0.021	0.029	0.004	0.005	0	0.015
Mn	-	0.007	0.037	0.062	0.017	0.007	0.055	0.033
Fe	-	0.078	0.057	0.039	0.020	0.044	0.082	0.059
□A	0.145	0.187	0.726	1.110	0.518	0.350	1.091	0.851
Total	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
				B site				
Ta	1.499	1.590	1.542	1.720	1.753	1.770	1.737	1.777
Nb	0.129	0.410	0.458	0.280	0.247	0.230	0.255	0.223
Ti	-	-	-	-	-	-	0.008	0.000
Sn	-	0	0	0	0	0	0	0
Total	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
				Y site				
O	0.438+	0.867+	0.081+	0.317+	0.627+	0.615+	0.876	1.655
F	-	-	-	-	-	-	0.145	0.139
OH	-	-	-	-	-	-	0.404	0.437
Total	0.438	0.867	0.081	0.317	0.627	0.615	1.423	2.231

Notes: R = rim; C = core; RS = rim adjacent to spodumene. Number in parentheses is the number of electron-microprobe analyses that were averaged for the tabulated value. Cation formula normalized to Σ B = 2.000. Sum of A-site + □ = 2.000.
- = Not determined
+ oxygen equivalents of Σ(O, OH, F)
* Fe determined as FeO on microprobe. Mineral separates yield:
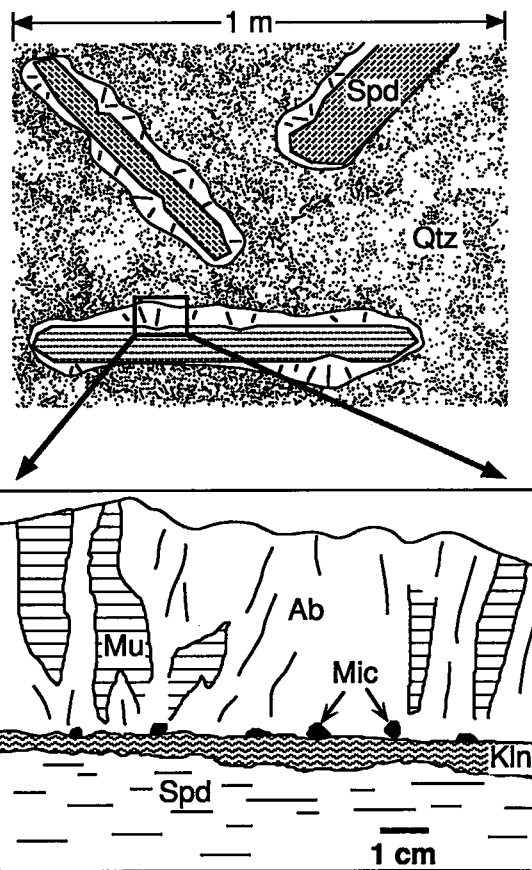B4, FeO = 0.30, Fe2O3 = 0.84; C10B, FeO = 0.30, Fe2O3 = 0.65.

FIG. 9. Sketch of microlite in albite–mica replacement rim surrounding spodumene from the core of the Tin Mountain pegmatite. Albite (Ab) is approximately perpendicular to (110) cleavage of spodumene (Spd), and the basal cleavage of the lithian mica (001) is perpendicular to albite laths. Kaolinite (Kln) coats spodumene; quartz (Qtz) is a dark smokey color throughout.

microlite is high in Ta and Ca and low in U, relative to microlite from the core (Table 7, analysis BI M1-3).

Uranmicrolite is common in the quartz – spodumene – mica core at the Tin Mountain, as both large anhedral grains and octahedra over 1 cm across. The X-ray-diffraction patterns of several specimens indicate that the mineral ranges from crystalline to nearly metamict. Uranmicrolite occurs within thick rims (>2 cm) of albite and lavender lithian muscovite surrounding large laths of spodumene that have been altered to green cookeite and white kaolinite (Fig. 9).

Uranmicrolite from the core and microlite from the albite – quartz – spodumene zone replace tantalite along grain boundaries and fractures (Fig. 4d); in other cases, incipient alteration of columbite–tantalite appears as an atoll-type replacement texture. Stannomicrolite in at least one specimen

appears to replace wodginite with a corroded texture.

Like the Bob Ingersoll specimens, uranmicrolite from Tin Mountain displays compositional variation across the crystals. In general, U and Pb increase from core to rim. In samples adjacent to altered spodumene, the composition varies from one rim to the other. From the side closest to the relict spodumene to the opposite rim, Ca, Na, and Ta show consistent increases, and Mn decreases. Concentrations of Pb, U, Fe, and Nb are variable (Table 7, analyses C10B-RS, -C, and -R). Analytical totals decrease and A-site vacancies increase toward the spodumene rim. We thus infer

that H_2O increases in that direction (*cf.* Lumpkin *et al.* 1986). The proportion of ferric iron in two specimens of microlite is 0.84 and 0.65 (Table 7, analyses B4 and C10B, respectively).

Wodginite

Wodginite occurs with microlite and pale bluish gray apatite in the albite – lithian muscovite rims surrounding spodumene within the core of the Tin Mountain pegmatite. In Figure 6, manganotantalite (Table 3) occurs in the interior of the specimen, which suggests precipitation of wodginite over tantalite. Textural evidence for replacement is ambiguous. In most cases, the two minerals appear to coexist. The rim of the wodginite grains contains inclusions of anhedral microlite and apatite that display serrated intergrowths with adjacent lithian muscovite.

Wodginite from the Tin Mountain is Fe-rich (Table 3, Fig. 5b) compared to specimens from the only reported occurrence of wodginite in the Black Hills, at the Peerless pegmatite in Keystone (Černý *et al.* 1985). The proportion of ferric iron in the Tin Mountain wodginite was determined on the basis of *C*-site vacancies, with site assignments made according to the method of Černý *et al.* (1985). The darker margin in Figure 6 coincides with increasing Fe, up to 1.55 wt.% Fe_2O_3 and 4.14 wt.% FeO near the rim. The maximum amount of ferric iron calculated in wodginite from the Tin Mountain is 1.79 wt.% Fe_2O_3.

Tapiolite

Microscopic crystals of tapiolite occur in fracture-filling assemblages with microlite at the Bob Ingersoll pegmatite. The tapiolite (Table 2a, analysis B5C) is distinguished by its low Mn content and its position within the tapiolite field on the $FeTa_2O_6$–$MnTa_2O_6$–$FeNb_2O_6$–$MnNb_2O_6$ quadrilateral (Fig. 5). Tapiolite was observed in thin section from the core unit of the Tin Mountain pegmatite as microscopic euhedral twinned crystals (Fig. 4d, Table 2b, C10C). The composition is slightly Mn-rich compared to that from other localities in the Black Hills (*cf.* Černý *et al.* 1985).

DISCUSSION

Paragenesis

Although a distinct succession of Ta–Nb minerals can be recognized within each pegmatite, the general sequence ferrocolumbite → manganocolumbite → manganotantalite → microlite is present at both. This represents a trend of primary crystallization that has been documented from

many Li-rich pegmatites (Černý & Ercit 1985). At the Tin Mountain pegmatite, the sequence is modified in the albite-rich portions of the core to maganotantalite → wodginite + tapiolite + microlite. Manganotantalite + tapiolite + microlite occur in fracture-filling assemblages in the quartz–albite unit at the Bob Ingersoll pegmatite. Microlite in both of these pegmatites represents both a product of primary crystallization and a secondary replacement after tantalite and wodginite. The obvious replacement textures are limited to the core zone of each pegmatite.

Cassiterite appears in small amounts in the albite-rich wall zone in both pegmatites. Cassiterite occurs abundantly in the inner zones of the Bob Ingersoll pegmatite, but sparingly throughout the Tin Mountain body. In contrast, columbite–tantalite becomes the dominant oxide in the inner zones of the Tin Mountain pegmatite, but is subordinate to cassiterite at the Bob Ingersoll pegmatite.

Fractionation of Ta and Mn

Figures 5 and 10 show that Ta enrichment proceeds from the wall zone to the core in both pegmatites. Samples of discrete columbite–tantalite from a particular zone tend to plot within distinct groups, albeit with some overlap. Each zone defines a progressive increase in Ta/(Ta + Nb). Likewise, Mn enrichment occurs toward the core, although there is considerably more overlap among zones.

The albite – quartz – muscovite wall zone in the Bob Ingersoll pegmatite shows a wide spread in both Ta/(Ta + Nb) and Mn/(Mn + Fe) values. Columbite from the upper wall-zone tends to show an enrichment of Ta with respect to the lower portions of the zone (Fig. 5a). Enrichment of Ta occurs from the lower wall-zone to the perthite – quartz – albite zone. Tantalum enrichment occurs from the wall zone to the perthite zones. The quartz-rich intermediate zones overlap in Ta/(Ta + Nb). Finally, Ta fractionation reaches the highest levels in the lepidolite core [Ta/(Ta + Nb) = 0.70].

Manganese enrichment precedes Ta fractionation in the Bob Ingersoll system (Figs. 5, 10). The Mn/(Mn + Fe) ratio displays a wide spread in the wall zone, and reaches levels of over 0.90 in the perthite zone at relatively low values of Ta/(Ta + Nb). Tantalum enrichment then proceeds in the quartz-rich intermediate zones and core at the high levels of Mn/(Mn + Fe) established in the wall zone and the perthite – quartz – albite zone.

The Ta/(Ta + Nb) ratio in the albite – quartz – muscovite wall zone at the Tin Mountain pegmatite is comparable to that at the Bob Ingersoll pegmatite. Both Ta/(Ta + Nb) and Mn/(Mn + Fe)
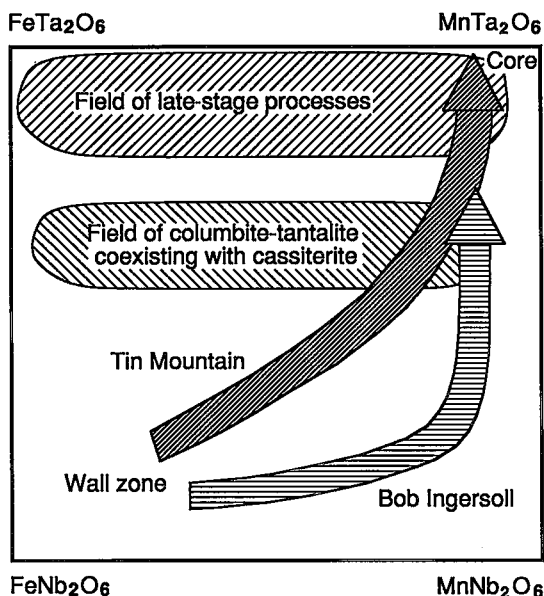
FIG. 10. Fractionation trends for the Bob Ingersoll (BI) and the Tin Mountain (TM). BI and TM indicate magmatic trends of columbite–tantalite only. Subsolidus trends are represented by columbite–tantalite inclusions in cassiterite. Late-stage processes include the fractionation of microlite, wodginite, and tapiolite.

ratios increase in the perthite – quartz – albite zone. Fractionation of Ta and Mn continues to increase in the quartz – spodumene – mica core (Fig. 10).

The fractionation of Ta from Nb during the course of pegmatite crystallization has been well documented (e.g., Ginsburg 1956, Grice et al. 1972, Foord 1976, Černý et al. 1986a,b, Ercit 1986). The fractionation trend proceeds toward Ta enrichment in both primitive barren pegmatites and in the highly evolved Li- and F-enriched pegmatites, e.g., Greer Lake pegmatites, Manitoba (Černý et al. 1986a,b), the Himalaya pegmatite district (Foord 1976) and the Peerless pegmatite at Keystone (Černý et al. 1985).

The pattern of fractionation of Ta from Nb with pegmatite evolution compares favorably with the sequence of crystallization proposed for the Bob Ingersoll system by Jolliff et al. (1986). The wall zone was the first to crystallize, and it contains Nb–Ta oxides with the lowest $Ta/(Ta+Nb)$ values. The crystallization of the inner wall zone overlapped with the perthite – quartz – albite zone, which is reflected in the overlap of $Ta/(Ta+Nb)$ for the oxides of these two zones. Crystallization of the inner wall-zone also occurred simultaneously with the crystallization of the quartz-rich inter-

mediate units. This simultaneous consolidation is reflected in the nearly equal $Ta/(Ta+Nb)$ values of the quartz – albite – amblygonite unit and the quartz–albite unit. Finally, the quartz – albite – lepidolite core was the last unit to crystallize, as indicated by the high $Ta/(Ta+Nb)$ values in this zone. In addition, saturation of fluorine in the residual melt is reflected by the presence of lepidolite and F-bearing microlite.

The fractionation of Ta from Nb at the Tin Mountain comparably reflects a sequence of enrichment in Ta relative to Nb with progressive crystallization (Walker et al. 1986b). Again, the albite – quartz – muscovite wall zone was the first to consolidate; the lowest values of both the $Ta/(Ta+Nb)$ and $Mn/(Mn+Fe)$ ratios occur in the columbite of this unit. The perthite – quartz – albite zone, the next unit to crystallize, displays increased Ta-enrichment relative to the wall zone. Feldspar geothermometry and REE data indicate that crystallization of this upper portion of the perthite hood was, to some degree at least, simultaneous with the other intermediate zones and that consolidation of the core was delayed, like in the crystallization sequence at the Bob Ingersoll pegmatite.

A quartz–spodumene fracture-filling in the upper wall-zone of the Tin Mountain reflects the mineralogy of the quartz – spodumene – mica core. However, Figure 5b shows that $Ta/(Ta+Nb)$ and $Mn/(Mn+Fe)$ ratios of columbite from the fracture-filling plot closer to the wall-zone values than to those of the core. Likewise, fracture-fillings in cassiterite from the quartz–albite zone of the Bob Ingersoll pegmatite host columbite that exhibits low $Ta/(Ta+Nb)$ values (Fig. 5a). Furthermore, the fracture-filling assemblage commonly includes a high-Ta and low-U microlite. At the Harding pegmatite, a zoned Li-enriched pegmatite in New Mexico, Lumpkin et al. (1986) found that early-formed microlite tends to be higher in Ta and lower in U than that which formed later in the crystallization of the pegmatite. The fracture-filling assemblage of columbite and microlite at the Bob Ingersoll pegmatite is not consistent with late fracture-fillings. These data suggest that at both pegmatites, internal fracturing and healing of the pegmatite occurred prior to crystallization of the innermost units.

Subtle differences can be observed in the trends of Mn- and Ta-enrichment between the two pegmatites. First, columbite from the Bob Ingersoll pegmatite contains the lowest Ta values (15 wt.%) of the two pegmatites, whereas the Tin Mountain pegmatite displays the highest values (75 wt.%). Second, the perthite zone, the quartz-rich intermediate zone, and the quartz – lithium silicate core in the Tin Mountain pegmatite have slightly higher

overall Ta/(Ta + Nb) ratios than the respective zones in the Bob Ingersoll pegmatite. In addition, the tantalite from the core of the Tin Mountain pegmatite (Fig. 10) reaches a much higher Ta/(Ta + Nb) value (0.94) than at the Bob Ingersoll pegmatite (0.70). Finally, early enrichment of Mn is not as prevalent at the Tin Mountain pegmatite. Mn/(Mn + Fe) ranges from less than 0.4 to 0.9 with low values of Ta/(Ta + Nb) (<0.3) at the Bob Ingersoll pegmatite. At the Tin Mountain pegmatite, these high values of Mn/(Mn + Fe) are not achieved until Ta/(Ta + Nb) is greater than 0.5.

Effects of F-enrichment

For rare-element granitic pegmatites, a strong increase in Mn/(Mn + Fe) in the columbite–tantalite commonly parallels increases in the activity of F (Černý *et al.* 1986b). For example, at the Himalaya (California) pegmatites, which contain F-rich lepidolite (up to 8 wt.% F: Foord 1976), early Mn-enrichment precedes fractionation of Ta from Nb. However, beryl–columbite pegmatites that are not Li- and F-enriched generally do not exhibit high Mn/(Mn + Fe) ratios (Černý & Ercit 1985). This suggests that the fractionation of Mn from Fe is enhanced by increased activity of fluorine (Černý *et al.* 1986b). There is indirect evidence for F–Mn complexing in pegmatite-forming melts (Černý & Ercit 1985, Černý *et al.* 1986a, b).

The Bob Ingersoll pegmatite is F-rich, with up to 5.09 wt.% F in amblygonite, and 7.23 wt.% F in lepidolite (Jolliff *et al.* 1987). In addition, the fluid dispersion-halo surrounding the pegmatite suggests a high F content of the parental melt (Shearer *et al.* 1986). From the fractionation trends in Figure 10, it is evident that early Mn-enrichment of the columbite at the Bob Ingersoll pegmatite coincides with an early enrichment in F proposed by Jolliff *et al.* (1986, 1987). The lower F content of the Tin Mountain pegmatite relative to the Bob Ingersoll pegmatite, as indicated by the stability of spodumene rather than lepidolite, the F content of the minerals and the lack of a F-bearing exomorphic halo (Shearer *et al.* 1986, Walker 1984) may explain the delayed fractionation of Mn over Fe.

The higher F content in the Bob Ingersoll pegmatite corresponds to the more extensive Sn mineralization associated with that pegmatite. The typical association of Sn mineralization with fluorite implies that F is an important complexing ligand in such systems (Barnes 1979). Therefore, in the Bob Ingersoll pegmatite, the higher content of F (and probably B and P) was instrumental in concentrating Sn in the pegmatite.

Late-stage processes

Late-stage re-equilibration is best displayed at the Tin Mountain pegmatite, where manganotantalite, microlite, wodginite, and tapiolite all coexist in the albite–mica intergrowths in the core. The Fe increases significantly toward the margin of the wodginite (Fig. 6, Table 3). The presence of Fe^{3+} in wodginite and microlite may indicate an increase in $f(O_2)$ (Foord 1982). This is consistent with the conclusion of Walker *et al.* (1986b) that $f(O_2)$ increased after the formation of the first intermediate zone.

The albite – lithian muscovite intergrowths that host Ta–Nb mineralization at the Tin Mountain pegmatite appear to be the result of metasomatic alteration of spodumene (London & Burt 1982a). The subsolidus replacement of spodumene reflects a two-stage process: 1) Li-for-Na exchange in the presence of an alkaline fluid, with which spodumene in contact with primary quartz reacts to form albite, and 2) increasing acidity of the fluids, which results in formation of lepidolite and lithian muscovite (London & Burt 1982b). Increasing activities of P and F would produce an acidic environment that promotes stability of lithium aluminum phosphate (London & Burt 1982b). Likewise, microlite and tantalite are stable in acidic environments (3 < pH < 8), whereas tapiolite is stable at lower pH (between 2 and 4) (Foord 1982).

CONCLUSIONS

Complex variations in the composition of columbite–tantalite and in Nb–Ta–Sn mineral assemblage have been documented in the Li-rich Bob Ingersoll and Tin Mountain pegmatites. Fractionation of Ta from Nb during pegmatite crystallization results in an overall, progressive increase in Ta/(Ta + Nb) ratio in the columbite–tantalite inward from the pegmatite contract. Complex zoning and compositional diversity of adjacent crystals suggest a dynamic, disequilibrium process involving fractional crystallization. This is also suggested by *REE* studies of apatite by Jolliff *et al.* (1989). The highest level of Ta fractionation over Nb is reached in the core. Likewise, Mn/(Mn + Fe) exhibits an increase toward the core. However, the Mn fractionation over Fe does not increase in a smooth progression. The changing Ta/(Ta + Nb) and Mn/(Mn + Fe) values result in a wall-to-core succession of ferrocolumbite → manganocolumbite → manganotantalite → microlite + tapiolite. Wodginite is present in the final sequence at the Tin Mountain pegmatite. In each pegmatite, microlite occurs as both a primary mineral and as a secondary replacement of tantalite. Two types of "inclusions" of columbite–tantalite are common in

cassiterite from the Bob Ingersoll. Subhedral inclusions are probably epitaxic overgrowths on cassiterite protocrystals, whereas swarms of small irregular inclusions are almost certainly the result of exsolution of $(Fe,Mn)(Ta,Nb)_2O_6$ from the cassiterite structure.

The compositional variations in columbite–tantalite and microlite mirror the crystallization sequences proposed for the Bob Ingersoll and Tin Mountain pegmatites as deduced from granitic textures and mineral chemistries (tourmaline, feldspar, mica) (Jolliff 1985, Walker et al. 1986b). Early crystallization of the wall zone is reflected by a low $Ta/(Ta+Nb)$ value in columbite. The simultaneous crystallization of the inner wall-zone, the perthite-rich and the quartz-rich intermediate zones is indicated by overlapping $Ta/(Ta+Nb)$ values for these zones. Late consolidation of the core zones is coincident with the highest $Ta/(Ta+Nb)$ and $Mn/Mn+Fe)$ values.

Tantalum–niobium oxides show slight but important variations in composition between the two pegmatites. The main differences are an early Mn-enrichment and the development of late-stage assemblages. An early fractionation of Mn from Fe at the Bob Ingersoll pegmatite parallels an early F-enrichment in the melt. The higher concentration of F in the Bob Ingersoll magma also influenced the differences in Sn mineralization between the two pegmatites. Evidence of saturation of the residual melt in F is seen in the dominance of microlite over tantalite in the core of the pegmatite. At the Tin Mountain pegmatite, the lower activity of F may have delayed Mn-enrichment in columbite–tantalite, relative to the Bob Ingersoll pegmatite. Wodginite, microlite and tapiolite, associated with spodumene alteration in the core of the Tin Mountain, may be evidence for an increase in the activity of Fe in the residual pegmatite fluids, and increasing $f(O_2)$ during crystallization. Pseudomorphic replacements of spodumene by cookeite and kaolinite in Tin Mountain are certainly indicators of low-pH fluids. The hydrothermal alteration of microlite may have resulted from these same fluids.

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