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. I 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+M) 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+M) ratios. The intermediate zones crystallized simultaneously and show an overlap in Ta/(Ta+M) 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/(Ta+M) 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(O2) during crystallization may be indicated by Fe3+ in the wodginite and microlite.

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

Nous comparons les assemblages de minéraux de Ta–Nb de deux pegmatites granitiques enrichies en éléments rares et en lithium mais à caractéristiques minéralogiques distinctes, situées dans les Black Hills, Dakota du Sud. La pegmatite Bob Ingersoll No. I 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 → manganocolumbite → manganotantalite → microlite + tapiolite (+ wodginite). Dans les deux cas, le rapport Ta/(Ta+M) de la columbite-tantalite (CT) augmente systématiquement à partir de la bordure vers le sein du complexe. 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+M). 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 cœur 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. L'augmentation 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 cœur 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 l'évidence d'une altération hydrothermale suite à la cristallisation. La présence de Fe3+ dans la wodginite et la microlite pourrait indiquer une augmentation en f(O2) au cours de la cristallisation.

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 H2O/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).

GEORGY OF THE HANNE 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 Walter et al. 1986, Fig. 2).
(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 H₂O-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), LiTaO3 (TaMa), uranium (U) and LiNbO3 (NbZcv). 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 H2O+ 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 CuKα radiation in a Norelco diffractometer equipped with a β-compensator, graphite monochromator and sample spinner. The patterns were calibrated using fluorite (α = 5.4630 Å, ASTM) as an internal standard, except for the microlite patterns, in which corundum (α = 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 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
than a few millimeters are rarely found in the localities (Foord 1976, von Knorring & Condliffe zone. Both oscillatory and progressive zoning of encountered as well in individual grains from this Mn/(Mn + Fe). Oscillatory or rhythmic zoning was core to rim for individual crystals in normal minor variation in Mn/(Mn+Fe) between adjacent matrix that surrounds the large crystals of perthite. - albite zone, small crystals are associated with interior of the pegmatite. In the perthite - qtafiz columbite-tantalite has been reported from several (reverse zoning: Lahti 1987), particularly involving decreases in these ratios also were encountered.

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 FeTa2O5-MnTa2O5-FeNb2O6-MnNb2O6 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 FeTa2O5 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)2O6 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)2O5 will not substitute into the cassiterite structure but will be incorporated as microinclusions. Povarennykh (1972), on the other hand, stated that up to 5% Ta2O5 and 2.5% Nb2O5 may be present in the cassiterite structure. Much of the cassiterite at the Bob Ingersoll contains up to 5.7 wt.% Ta2O5 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 epitaxial overgrowths of columbite–tantalite (cf. Ginsburg 1956) that have been overtaken and surrounded by the cassiterite.

<table>
<thead>
<tr>
<th>Sample Location</th>
<th>Wall Zone</th>
<th>Intermediate Zones</th>
<th>Core</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>A site</td>
<td>B site</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.034</td>
<td>0.034</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.034</td>
<td>0.034</td>
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<tr>
<td>Total</td>
<td>0.068</td>
<td>0.068</td>
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</table>

- Not analyzed. Cation formula based on 6 atoms of oxygen. Oxides in wt.%.
FIG. 5. Nb–Ta oxides from the Bob Ingersoll (a) and the Tin Mountain pegmatites (b) plotted in the FeTa$_2$O$_5$–MnTa$_2$O$_6$–FeNb$_2$O$_6$–MnNb$_2$O$_6$ 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 (*).

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 (Cs) (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).
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" 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...
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-montebasite. 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, tapiroite, 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 $(\text{Fe,Mn})^2+ + 2(\text{Nb,Ta})^{2+} = 3(\text{Sn,Ti})^{4+}$ (Černý et al. 1985, Černý & Ercit 1985) or close to the pure $(\text{Sn,Ti})_2O_5$ corner of the $(\text{Sn,Ti}) - (\text{Ta,Nb}) - (\text{Fe,Mn})$ diagram (Fig. 8). In addition, considerable variation occurs among individual grains making up the massive...
Cassiterite. Nearly pure SnO₂ (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 cX-19 to GX-21).

Cassiterite in the Tin Mountarn 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.% Ta₂O₅, whereas CaO and Na₂O are as high as 10.56 and 4.96 oxide wt.%, respectively. Uranium ranges from 1.62 to 10.13 wt.% UO₃; 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 albite replacement-units surrounding quartz-filled fractures. Microlite in that assemblage occurs with cassiterite, euhedral columbite–tantalite and zircon (Fig. 4c).
TABLE 7. ELECTRON-MICROPROBE DATA ON SELECTED MICROLITES

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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 Z'E = 2.000. Sum of A-site + Li = 2.000.

- Not determined
* Fe determined as FeO on electron probe. Mineral separates yield:
  10M4, FeO = 0.30, Fe2O3 = 0.84; 10C10B, FeO = 0.30, Fe2O3 = 0.65.

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

Uranomicrolite 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. Uranomicrolite 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).

Uranomicrolite 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, uranomicrolite 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

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.
that \( \text{H}_2\text{O} \) 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.% \( \text{Fe}_2\text{O}_3 \) and 4.14 wt.% \( \text{FeO} \) near the rim. The maximum amount of ferric iron calculated in wodginite from the Tin Mountain is 1.79 wt.% \( \text{Fe}_2\text{O}_3 \).

**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 \( \text{FeTa}_2\text{O}_6-\text{MnTa}_2\text{O}_6-\text{FeNb}_2\text{O}_6-\text{MnNb}_2\text{O}_6 \) 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 manganotantalite → 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 \( \text{Ta}/(\text{Ta}+\text{Nb}) \). 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 \( \text{Ta}/(\text{Ta}+\text{Nb}) \) and \( \text{Mn}/(\text{Mn}+\text{Fe}) \) 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 \( \text{Ta}/(\text{Ta}+\text{Nb}) \). Finally, Ta fractionation reaches the highest levels in the lepidolite core \( \text{[Ta}/(\text{Ta}+\text{Nb}) = 0.70] \).

Manganese enrichment precedes Ta fractionation in the Bob Ingersoll system (Figs. 5, 10). The \( \text{Mn}/(\text{Mn}+\text{Fe}) \) 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 \( \text{Ta}/(\text{Ta}+\text{Nb}) \). Tantalum enrichment then proceeds in the quartz-rich intermediate zones and core at the high levels of \( \text{Mn}/(\text{Mn}+\text{Fe}) \) established in the wall zone and the perthite – quartz – albite zone.

The \( \text{Ta}/(\text{Ta}+\text{Nb}) \) ratio in the albite – quartz – muscovite wall zone at the Tin Mountain pegmatite is comparable to that at the Bob Ingersoll pegmatite. Both \( \text{Ta}/(\text{Ta}+\text{Nb}) \) and \( \text{Mn}/(\text{Mn}+\text{Fe}) \)...
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.

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 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 intermediate 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 \(\text{Ta}/(\text{Ta} + \text{Nb})\) 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 \(\text{Ta}/(\text{Ta} + \text{Nb})\) 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 \(\text{Ta}/(\text{Ta} + \text{Nb})\) (<0.3) at the Bob Ingersoll pegmatite. At the Tin Mountain pegmatite, these high values of Mn/(Mn + Fe) are not achieved until \(\text{Ta}/(\text{Ta} + \text{Nb})\) 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 \(\text{[Cerný et al. 1986b]}\). For example, at the Himalaya (California) pegmatites, which contain F-rich lepidolite (up to 8 wt.% F: \[\text{Foord 1976}\]), 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 \(\text{[Cerný & Ercit 1985]}\). This suggests that the fractionation of Mn from Fe is enhanced by increased activity of fluorine \(\text{[Cerný et al. 1986b]}\). There is indirect evidence for F–Mn complexing in pegmatite-forming melts \(\text{[Cerný & Ercit 1985, Cerný et al. 1986a, b]}\).

The Bob Ingersoll pegmatite is F-rich, with up to 5.09 wt.% F in amblygonite, and 7.23 wt.% F in lepidolite \(\text{[Jolliff et al. 1987]}\). In addition, the fluid dispersion-halo surrounding the pegmatite suggests a high F content of the parental melt \(\text{[Shearer et al. 1986]}\). 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. \(\text{[1986, 1987]}\). 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 \(\text{[Shearer et al. 1986, Walker 1984]}\) 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 \(\text{[Barnes 1979]}\). 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 \(\text{[Fig. 6, Table 3]}\). The presence of Fe\(^{3+}\) in wodginite and microlite may indicate an increase in \(f(\text{O}_2)\) \(\text{[Foord 1982]}\). This is consistent with the conclusion of Walker et al. \(\text{[1986b]}\) that \(f(\text{O}_2)\) increased after the formation of the first intermediate zone.

The albite – lithium muscovite intergrowths that host Ta–Nb mineralization at the Tin Mountain pegmatite appear to be the result of metasomatic alteration of spodumene \(\text{[London & Burt 1982a]}\). 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 lithium muscovite \(\text{[London & Burt 1982b]}\). Increasing activities of P and F would produce an acidic environment that promotes stability of lithium aluminum phosphate \(\text{[London & Burt 1982b]}\). Likewise, microlite and tantalite are stable in acidic environments \((3 < \text{pH} < 8)\), whereas tapiolite is stable at lower pH \((\text{between 2 and 4})\) \(\text{[Foord 1982]}\).

**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 \(\text{Ta}/(\text{Ta} + \text{Nb})\) ratio in the columbite-tantalite inward from the pegmatite contact. 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. \(\text{[1989]}\). 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 \(\text{Ta}/(\text{Ta} + \text{Nb})\) 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 \((\text{Fe, Mn})(\text{Ta, Nb})_2\text{O}_6\) 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 (toumaline, feldspar, mica) (Jolliff 1985, Walker et al. 1986b). Early crystallization of the wall zone is reflected by a low \(\text{Ta}/(\text{Ta} + \text{Nb})\) value in columbite. The simultaneous crystallization of the inner wall-zone, the perthite-rich and the quartz-rich intermediate zones is indicated by overlapping \(\text{Ta}/(\text{Ta} + \text{Nb})\) values for these zones. Late consolidation of the core zones is coincident with the highest \(\text{Ta}/(\text{Ta} + \text{Nb})\) and \(\text{Mn}/(\text{Mn} + \text{Fe})\) 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 \(f(\text{O}_3)\) during crystallization. Pseudomorphic replacements of spodumene by cookeite and kaolin 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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