Compositional variation and structural state of columbite-tantalite in rare-element granitic pegmatites of the Preissac-Lacorne batholith, Quebec, Canada

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ABSTRACT

Rare-element-enriched granitic pegmatites in and near the Lamotte and Lacorne plutons of the Archean Preissac-Lacorne batholith (Quebec) are zoned from a least fractionated beryl type in the parental pluton through a transitional spodumene + beryl type at the edge of the plutons to a most fractionated spodumene type in the country rocks. Columbite-tantalite is the only primary niobium tantalum oxide mineral; its composition is dominated by Nb, Ta, Fe, and Mn. Ti is present in minor quantities (≤ 0.1 atoms per formula unit). In both plutons, the Ta/(Ta + Nb) and Mn/(Mn + Fe) of columbite-tantalite correlate positively with the degree of pegmatite evolution. These correlations are interpreted to reflect the greater solubility of Mn relative to Fe and of Ta relative to Nb in the melt. In the Lacorne suite, there is a much greater increase in Mn/(Mn + Fe) over Ta/(Ta + Nb) of columbite-tantalite with pegmatite evolution. In pegmatite bodies in the Lacorne suite, where columbite-tantalite crystallization was accompanied by garnet, the Ta/(Ta + Nb) of columbite-tantalite increases at constant Mn/(Mn + Fe) values. We interpret this to indicate that garnet saturation buffered the activities of Fe and Mn in the liquid. The degree of order of columbite-tantalite decreases with the evolution of the pegmatite suites and reflects increased cooling rates of the more evolved, and more distal, bodies of pegmatite.

INTRODUCTION

Minerals of the columbite-tantalite group [(Fe,Mn)(Nb,Ta)$_2$O$_6$] are potentially important in deciphering the internal evolution of rare-element-enriched granitic pegmatites (Lahti 1987; Ercit 1994) and hence in understanding their petrogenesis (Ercit 1996). Trueman and Černý (1982) proposed a model in which batches of rare-element-enriched felsic magma, with increasing distance from the parental pluton, become saturated first in beryl, then spodumene; as the magma crystallizes, Nb and Fe are predicted to become depleted first, and Ta and Mn to become progressively enriched in the residual liquid. Černý et al. (1986) anticipated that with more rapid crystallization of the successive melt fractions at an increasingly greater distance from the source, the columbite-tantalite would tend to be stranded in a more disordered state. However, these propositions have not been adequately tested because most published studies of columbite-tantalite have been restricted to single bodies of granitic pegmatite (Černý and Turnock 1971; Grice et al. 1972; Wenger and Armbruster 1991; Spilde and Shearer 1992), to suites of granitic pegmatite in which the magmas underwent limited fractionation (Černý et al. 1986; Lahti 1987; Ercit 1994, 1996), or to groups of pegmatite bodies in which petrogenetic links have not been established (Wise 1987).

In this contribution, we report the results of a detailed study of the paragenesis, composition, and structural state of columbite-tantalite in two suites of comagmatic rare-element-enriched granitic pegmatite from the Preissac-Lacorne batholith, northwestern Quebec (Fig. 1). The pegmatite bodies are not deformed or metamorphosed, are well described in terms of their geology and petrochemistry (Dawson 1966; Mulja et al. 1995a, 1995b), and are zoned regionally from a least evolved beryl type emplaced in the parental pluton to a most evolved spodumene type emplaced in the country rocks 2–3 km away from the respective pluton. Such a regional zonation, although an essential feature of the evolutionary model proposed for rare-element granitic pegmatites, is seldom encountered. The pegmatite suites of the Preissac-Lacorne batholith thus offer a rare opportunity to elucidate the factors that control the relationship between the crystal-chemical properties of columbite-tantalite and the evolution of fractionated felsic liquids in a model rare-element pegmatite system.
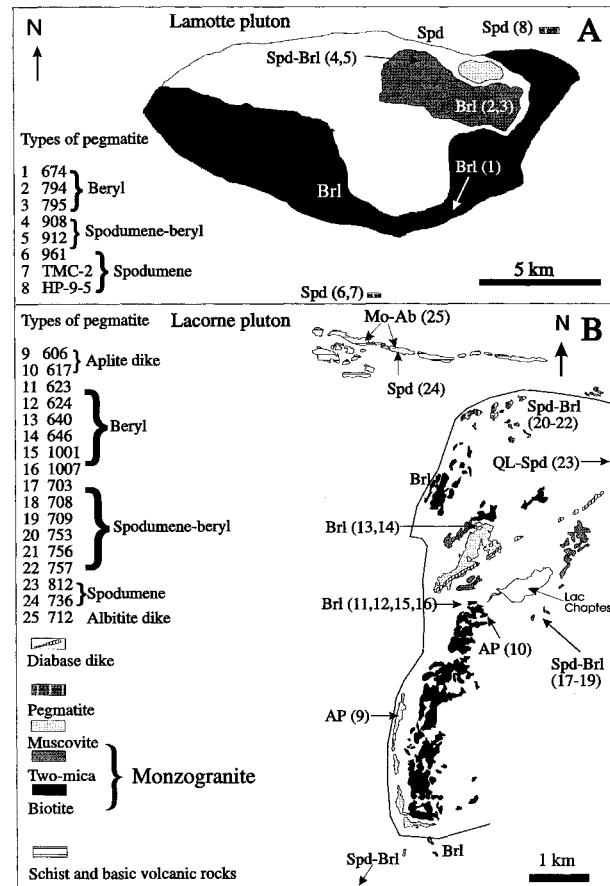
GEOLOGY AND PETROGRAPHY OF THE PEGMATITES

The columbite-tantalite–bearing granitic pegmatites are part of the Archean Preissac-Lacorne batholith (~2.64–2.7 Ga: Gariépy and Allègre 1985; Feng and Kerrich 1991), which hosts the largest swarm of spodumene-bear-
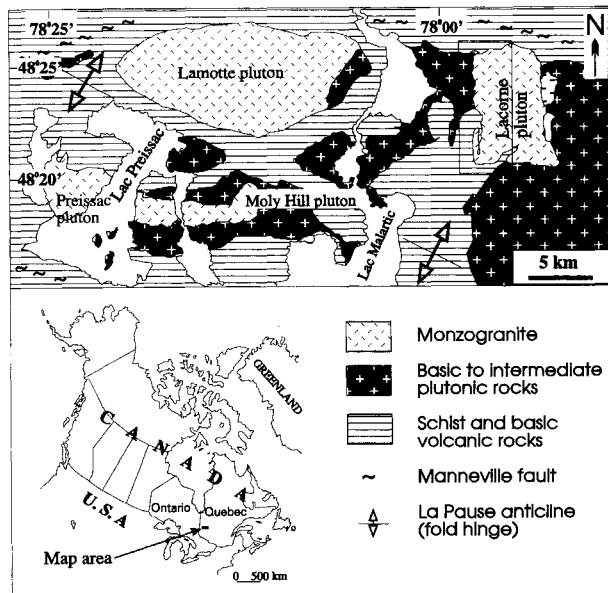
FIGURE 1. A simplified geological map of the Preissac-Lacorne batholith showing the distribution of intercalated schists and volcanic rocks, basic plutonic rocks, and four monzogranitic plutons and structures. The boundaries of the plutons are based on the farthest granitic pegmatite or monzogranite outcrops (Dawson 1966). Recent mapping by Mulja et al. (1995a) showed that the Lacorne pluton (Fig. 2B) is most likely smaller than previously outlined. Only the boxed area in the Lacorne pluton, where most outcrops exist, is enlarged in Figure 2B.

FIGURE 2. Geological maps of the Lamotte (A) and Lacorne (B) plutons depicting the field relationships among the various subtypes of monzogranite as well as the zonal distribution of the three main types of pegmatite [beryl (Brl), spodumene + beryl (Spd-Brl), and spodumene (Spd)] and the number and location of samples used in this study. In the Lacorne pluton, spodumene pegmatite from the former Quebec Lithium mine (QL) is about 3 km east of the margin of the map, on the eastern side of the pluton. Columbite-tantalite- and molybdenite-bearing albitite dikes (Mo-Ab) occur only in the northernmost part of the Lacorne pluton.

ing pegmatites in eastern Canada (formerly exploited by the Quebec Lithium mine; Fig. 2B) and many other beryl- and spodumene-bearing types of pegmatite of subeconomic grade. The batholith, which intruded mafic lavas and biotite schists of the Kinojevis and Malartic groups in the Abitibi greenstone belt of the Superior province, is made up of an older suite of gabbro, monzodiorite, and granodiorite, and four younger plutons of peraluminous monzogranite. Each pluton (Preissac, Moly Hill, Lamotte, and Lacorne) is zoned compositionally from biotite through two-mica to muscovite monzogranite (Mulja et al. 1995a). The mineralized (Be, Li, Nb, Ta, and Mo) pegmatites, which are the focus of this study, are associated with the Lamotte and Lacorne plutons.

The pegmatites occur as tabular dikes ranging from tens of centimeters to 8 m in width and up to hundreds of meters in length, as lenticular bodies up to 5 × 24 m in plan, and as dike swarms, particularly along the margin of the plutons. They filled zones of dilation (pinch and swell) in the monzogranite and existing fractures in the country rocks, which were possibly reactivated during the emplacement of the batholith. Most pegmatite bodies in the Lacorne pluton strike east and southeast, whereas those in the Lamotte pluton show no preferred orientation. In both plutons, the pegmatite bodies dip vertically to subhorizontally. Their intrusive contact with the monzogranite varies from gradational to sharp (planar to con-

voluted) and shows no evidence of metasomatism. Contacts between spodumene pegmatites and amphibolite are marked by a narrow halo in the amphibolite in which holmquistite replaced hornblende.

On the basis of the predominant rare-element-bearing minerals, the mineralized pegmatites are subdivided into beryl-, spodumene + beryl-, and spodumene-bearing types. In the text that follows, these types of pegmatite are referred to as beryl, spodumene + beryl, and spodumene pegmatite. The pegmatite bodies are zonally distributed from beryl type in and at the margin of the parental plutons, to spodumene + beryl type at the margins of the plutons, and to spodumene type in the country rocks (Figs. 2A and 2B). Mineral and whole-rock geochemical data indicate that they are comagmatic; beryl

pegmatite represents the geochemically least evolved type, and spodumene pegmatite is the most evolved type (Mulja et al. 1995a, 1995b). Adjacent to the spodumene pegmatite in the northern part of the Lacorne pluton (Fig. 2B), dikes of molybdenite- and columbite-tantalite–bearing albitite occur in the intercalated biotite schist and basalt.

Beryl pegmatite

Small bodies of beryl pegmatite (<1 m wide) are generally vertical to subvertical, symmetrically zoned from (1) a narrow border zone of sodic aplite through (2) an assemblage of coarse-grained quartz, potassium feldspar, albite, and muscovite to (3) a central zone of beryl, potassium feldspar, and quartz megacrysts. Small pockets consisting of quartz and muscovite occur sporadically in the border-zone aplite. The transition between zones 1 and 2 is sharp and is marked locally by books of muscovite; whereas, the transition between zones 2 and 3 is gradational. Columbite-tantalite is concentrated in fine layers of spessartine garnet, which occur mostly in the aplite. Larger, subvertical bodies of beryl pegmatite (up to 8 m wide) typically display an asymmetrical zonation as follows: (1) a sodic aplite border zone that is texturally and mineralogically similar to the aplite in the small dikes, (2) muscovite + albite + quartz ± perthite, (3) beryl + albite + perthite + quartz ± muscovite, (4) quartz + perthite ± beryl, (5) large irregular lenses of quartz intergrown with perthite megacrysts (up to 1 m long) or monotonous masses of quartz (up to 3 m wide), and (6) a marginal facies consisting of muscovite, albite, quartz, and, locally, perthite. The muscovite occurs mostly as books along the contact with the host monzogranite. Columbite-tantalite occurs in zones 1, 2, 3, and 6.

Spodumene + beryl pegmatite

Spodumene + beryl pegmatite is found in the northern part of the Lamotte pluton (nos. 4 and 5, Fig. 2A). There, the bodies are subvertical and asymmetrically zoned, with sodic aplite at the footwall and an assemblage of coarse crystals (up to 5 cm across) of albite + potassium feldspar + muscovite at the hanging wall. Like that in beryl pegmatite, the aplite contains fine layers of spessartine. The intermediate zone is simple, comprising albite, potassium feldspar, and quartz, and the central zone consists of quartz, potassium feldspar, and spodumene (up to 4 × 10 cm in size). Disseminated columbite-tantalite occurs mainly in the border-zone aplite and has not been found in any other zone. From these observations, it is clear that, in the Lamotte suite, the spodumene + beryl pegmatite differs subtly from the beryl-bearing pegmatite by the presence of spodumene in the core.

In the Lacorne suite, there are three subtypes of spodumene + beryl pegmatite. One is represented by the spodumene + beryl pegmatite at the Valor prospect (nos. 17–19, Fig. 2B), which is hosted by the two-mica monzogranite. This pegmatite is vertical and exhibits a crude

symmetrical zonation from a border zone of aplite, which has corrugated banding, is extremely rich in spessartine (concentrations are an order of magnitude higher than in the aplite zone of the Lamotte spodumene + beryl pegmatite), and contains appreciable amounts (~1%) of columbite-tantalite and traces of schorl and pyrophanite. This zone grades inward into an intermediate zone through a thin transitional zone marked by books of muscovite and prisms of beryl. Beryl also occurs as euhedral crystals, >3 cm across, at the contact between the pegmatite and the host monzogranite, where aplite is locally absent. Spodumene (up to 20 cm × 2 m in section) occurs in the inner part of the intermediate zone and along the aplite-free contact with the monzogranite. Albite is present in rosettes of blades, up to 3–4 cm across. In this intermediate zone, small flakes of lepidolite partially replace spodumene. The core of the pegmatite consists mainly of quartz, spodumene, and lepidolite. Here, lepidolite occurs as large crystals (~2–3 cm across), is intergrown with quartz and albite, and is interpreted to be primary.

The second subtype of the spodumene + beryl pegmatite, exemplified by an inclined dike near the northern edge of the Lacorne pluton (no. 21, Fig. 2B), also is zoned. The border-zone aplite contains accessory garnet. This zone has a sharp contact with the next spodumene-bearing zone, which contains small amounts of beryl along the contact. The crystals of spodumene are relatively equigranular (up to 5 cm long) and are intergrown with quartz, albite, and minor muscovite. The next zone is dominated by massive lepidolite, albite, and quartz and contains no spodumene. Columbite-tantalite is disseminated throughout the spodumene and lepidolite zones. Although additional zones are not exposed, we believe, on the basis of the internal zonation of the other bodies of spodumene + beryl pegmatite, that there is a core that consists mainly of quartz and that the pegmatite body is asymmetrically zoned.

The third subtype of spodumene + beryl pegmatite is a lepidolite-free variety that occurs subhorizontally in contact with biotite schist and basalt of the country rocks (nos. 19 and 22, Fig. 2B). It has a narrow zone of sodic aplite, which hosts thin layers of garnet and scattered crystals of columbite-tantalite. Beryl crystals are small and occur sporadically along the contact between the aplite and an intermediate zone of spodumene + albite + quartz + muscovite. The interior part of this pegmatite is massive, comprising megacrysts of quartz and potassium feldspar.

From the above description, it is clear that in the transition from the main Lacorne pluton toward the country rocks, the variants of spodumene + beryl pegmatite show a systematic decrease in beryl and garnet content, develop separate zones of spodumene and lepidolite, and eventually become lepidolite-free. These observations indicate that the spodumene-beryl pegmatite at the Valor prospect is the least evolved subtype, the one near the northern margin of the pluton (no. 21, Fig. 2B) is an

intermediate subtype, and those at the contact are the most evolved.

Spodumene pegmatite

The group of spodumene pegmatites also can be subdivided. Less fractionated examples are located south of the Lamotte pluton (nos. 6 and 7, Fig. 2A) and east of the Lacorne pluton (no. 23, Fig. 2B). The former make up subhorizontal layered bodies, which are characterized by alternating zones, from 20 to 60 cm thick, of massive aplite and pegmatite. The contacts between the two zones are sharp, marked by vertical, acicular crystals of spodumene (up to 1 × 20 cm in size) in the pegmatite. In the upper level of the intrusion, spodumene forms short, columnar crystals (2 cm across) interlocking with quartz, muscovite, potassium feldspar, and albite. The less evolved spodumene pegmatite at Lacorne is massive, consisting of spodumene laths, quartz, albite, and potassium feldspar, as well as traces of fluorite. Muscovite, of variable grain size, is less abundant than in other types of pegmatite. In these bodies of spodumene pegmatite, the minor minerals are, in order of decreasing abundance, columbite-tantalite (up to 0.5 cm across), molybdenite, beryl, and cerianite. Unlike the beryl and spodumene + beryl pegmatites, the aplite in the spodumene pegmatites lacks garnet.

The more evolved type of spodumene pegmatite is represented by bodies in the country rocks north of the Lamotte (no. 8, Fig. 2A) and Lacorne (no. 24, Fig. 2B) plutons. The texture and major mineralogy of the Lamotte pegmatites are similar to those of the less evolved Lacorne spodumene pegmatite. The more evolved bodies of spodumene pegmatite associated with the Lacorne pluton dip at a high angle toward the pluton. In contrast to their equivalents at Lamotte, these pegmatites are zoned from a marginal aplite to a core of coarse-grained perthite + spodumene + quartz. In this subtype of pegmatite from both suites, columbite-tantalite crystals (up to 1 cm across) occur throughout, but garnet is present only in the Lacorne suite. Beryl and molybdenite (both of which also are present in the less evolved subtype) are absent in this more evolved subtype.

Albitite dikes

Albitite dikes occur along joints in the metavolcanic rocks and schist (no. 25, Fig. 2B). The dikes, which consist almost entirely of euhedral albite, locally host spectacular molybdenite-rich layers. Columbite-tantalite and Ta-bearing ilmenite are minor interstitial phases, whereas garnet, secondary muscovite, and zircon are accessory phases.

SAMPLES AND ANALYTICAL METHODS

Locations of representative examples of the three types of pegmatite from the Lamotte and Lacorne plutons are shown in Figures 2A and 2B. Although both plutons host a series of rare-element pegmatites, there are more bodies of pegmatite in and around the Lacorne pluton than in

and adjacent to the Lamotte pluton. This difference is reflected in the larger number of samples examined from the Lacorne pluton. We also analyzed columbite-tantalite from discrete dikes of aplite from the Lacorne and Moly Hill plutons, and from a dike of muscovite + garnet monzogranite in the Preissac pluton.

The major-element compositions of columbite-tantalite and related Nb-Ta minerals were determined with an automated CAMECA electron microprobe at McGill University; the operating conditions were as follows: 20 kV acceleration voltage, 20 nA beam current (measured on MgO), 2 μm spot size, and 25 s counting time. Synthetic $MnNb_2O_6$ and Ta_2O_5 were used as standards for Mn and Nb, and Ta, respectively, pure metal for U, albite for Na, rutile for Ti, diopside for Ca and Mg, and magnetite for Fe. Data reduction was accomplished with the full PAP correction procedures of Pouchou and Pichoir (1985).

Unit-cell dimensions of columbite-tantalite were determined using X-ray diffraction (powder method). In two cases, two sets of diffraction maxima were observed, indicating two distinct columbite-tantalite phases in the crystals ground for analysis. The pulverized material was mixed with synthetic $MgAl_2O_4$ spinel (a = 8.0833 Å at room temperature). Powder patterns of columbite-tantalite, obtained with a Guinier-Hägg focusing camera ($CuK\alpha_1$ radiation), were corrected and then indexed by referring to PDF 16-337 and to the indexed pattern of Wise et al. (1985). Cell parameters were calculated with the program of Appleman and Evans (1973), as modified by Garvey (1986).

COLUMBITE-TANTALITE

Nomenclature

Minerals of the columbite-tantalite group have the general formula of AB_2O_6, in which the A position is occupied mostly by Fe^{2+} and Mn^{2+} and, to a lesser extent, by Mg^{2+} and trivalent cations; the B position is occupied mainly by Nb^{5+} and Ta^{5+} and, subordinately, by Ti^{4+} and Sn^{4+}. These orthorhombic minerals include the endmembers ferrocolumbite ($FeNb_2O_6$), manganocolumbite ($MnNb_2O_6$), manganotantalite ($MnTa_2O_6$), and magnocolumbite ($MgNb_2O_6$). Although ferrotantalite [(Fe > Mn)(Ta > Nb)$_2$O$_6$] is a member of the columbite-tantalite group in the classification of niobium tantalum oxides, the end-member $FeTa_2O_6$ is tetragonal and belongs to the tapiolite series (Černý and Ercit 1989). Magnocolumbite and ferrotantalite were not observed in this suite.

To describe the compositional variation of columbite-tantalite within and between bodies of pegmatite, the names ferrocolumbite, manganocolumbite, and manganotantalite are restricted to the compositions Ta/(Ta + Nb) and Mn/(Mn + Fe) < 0.5, Ta/(Ta + Nb) < 0.5 and Mn/(Mn + Fe) > 0.5, and Ta/(Ta + Nb) and Mn/(Mn + Fe) > 0.5, respectively. The presence of manganotantalite, which has a bulk chemistry similar to that of ixiolite ($Mn,Fe,Ti,Ta,Nb)_4O_8$, was confirmed by retention of
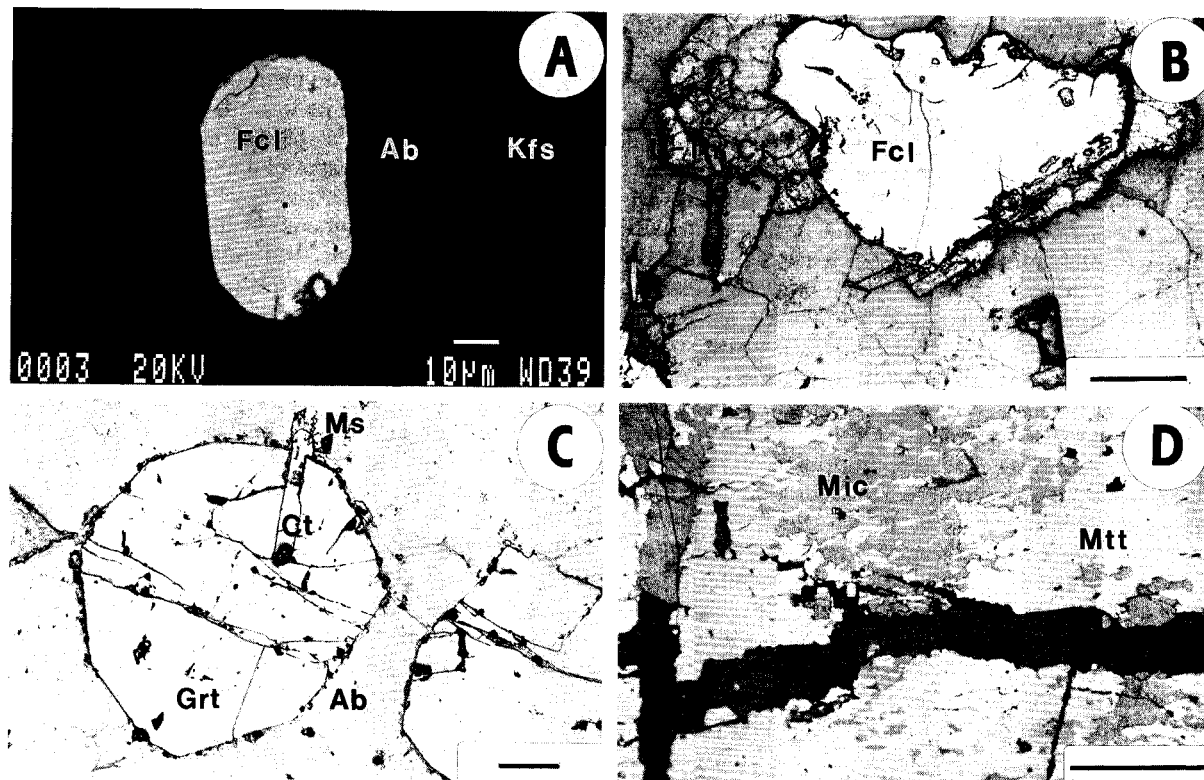
FIGURE 3. Photomicrographs exemplifying various modes of occurrence of columbite-tantalite (Ct) and related Nb-Ta minerals from the Preissac-Lacorne pegmatites and albitite. Figures **B–D** were taken with a reflected light microscope; **A** is a backscattered electron image. (**A**) Euhedral inclusion of ferrocolumbite (Fcl) in albite (Ab) from a discrete aplite dike. Kfs = potassium feldspar. (**B**) Anhedral grain of interstitial ferrocolumbite in a beryl pegmatite, intergrown partially with metamict columbite-tantalite (U-Th Ct). (**C**) Ferrocolumbite prism enclosed mostly in euhedral garnet (Grt) and partly in albite in a beryl pegmatite. Secondary muscovite (Ms) rims the garnet and ferrocolumbite. (**D**) Manganotantalite (Mtt) replaced by patchy microlite (Mic) and cut by albite veinlets in a spodumene pegmatite. All scale bars are 100 μm.

the orthorhombic structure after heat treatment at 1000 °C for 16 h. Ixiolite would convert to a monoclinic structure (wodginite) upon such heat treatment (Černý and Ercit 1985). Columbite-tantalite occurs in a wide range of structural states in granitic pegmatites, as seen in the continuum of data points in a plot of cell parameters a vs. c (Černý and Ercit 1985, their Fig. 1A).

Petrography of columbite-tantalite

Columbite-tantalite (CT) forms finely disseminated crystals, particularly in the garnet-rich aplite, irrespective of whether the aplite is a discrete dike (nos. 9 and 10, Fig. 2B) or part of a composite aplite-pegmatite dike. In the aplite zone of beryl and spodumene + beryl pegmatites from both suites, CT crystals are generally small and euhedral (up to 2×3 mm) and occur as inclusions, mostly in garnet and albite and rarely in perthite, muscovite, and quartz (Fig. 3A). In almost all cases, coarser grains of this oxide are interstitial (Fig. 3B). Some euhedral crystals of CT occur between garnet and albite (Fig. 3C). In the intermediate zone of the beryl and spodumene + beryl pegmatites, CT crystals are generally interstitial to the

silicate minerals mentioned above and to spodumene in the spodumene + beryl pegmatite. They were not observed in the core of beryl pegmatite, where large crystals of quartz and potassium feldspar occur, or in the core of spodumene + beryl pegmatite, where large crystals of quartz, spodumene, and lepidolite occur. These textural relationships indicate that most crystals of CT precede the silicate phases in the aplite zone, and almost all in the intermediate zone are late. This interpretation suggests that the columbite-tantalite in the aplite zone generally precedes beryl and spodumene. In contrast, columbite-tantalite in spodumene pegmatite is mostly either intergrown with, or interstitial to, spodumene, quartz, and albite, pointing to crystallization contemporaneous with and later than these silicate minerals.

The extent of alteration in columbite-tantalite is minimal. Some paragenetically late CT grains in beryl pegmatite are rimmed by masses of U-Th–bearing niobium tantalum oxide (Fig. 3B). In spodumene pegmatites, veinlets and patches of microlite occur in manganotantalite (Fig. 3D), suggesting that the microlite was precipitated at a subsolidus stage and filled fractures in, and partially

TABLE 1. Representative compositions of columbite-tantalite from the Preissac (PR), Moly Hill (MH), and Lamotte (LM) plutons

Pluton Lithology* Sample	PR MGG 471	MH AP 30	LM Brl 764	LM Brl 795	LM Spd + Brl 912	 912	LM Spd C-2	LM Spd C-2	LM Spd 9-5	LM Spd 9-5
Nb_2O_5 (wt%)	71.51	68.31	72.48	71.28	71.22	67.77	52.73	34.04	23.72	8.33
Ta_2O_5	5.34	9.70	6.81	7.14	5.63	11.62	29.00	48.42	61.42	77.40
TiO_2	1.08	1.02	0.58	0.45	0.60	0.40	0.09	0.18	0.15	0.20
MgO	0.02	0.11	0.09	0.17	0.06	0.06	0.00	0.02	0.02	0.00
CaO	0.01	0.01	0.00	0.00	0.02	0.05	0.02	0.02	0.00	0.02
FeO	10.69	13.90	13.15	15.42	13.28	12.79	5.39	5.66	3.77	0.45
MnO	9.98	6.00	6.73	4.22	7.68	6.42	12.47	10.71	11.62	14.12
Total	98.69	99.05	99.84	98.68	98.49	99.11	99.70	99.05	100.7	100.5
Structural formula on the basis of six O atoms										
Nb	1.873	1.813	1.886	1.881	1.874	1.813	1.513	1.078	0.786	0.303
Ta	0.084	0.155	0.107	0.113	0.089	0.187	0.501	0.922	1.225	1.691
Ti	0.047	0.045	0.025	0.019	0.026	0.018	0.004	0.009	0.008	0.012
Mg	0.002	0.010	0.007	0.014	0.005	0.005	0.000	0.010	0.002	0.000
Ca	0.001	0.001	0.000	0.000	0.001	0.003	0.001	0.001	0.000	0.002
Fe	0.517	0.682	0.633	0.753	0.644	0.633	0.286	0.332	0.231	0.030
Mn	0.489	0.298	0.328	0.209	0.375	0.322	0.670	0.635	0.722	0.961
A site	1.009	0.991	0.994	0.996	1.024	0.963	0.957	0.978	0.955	0.993
B site	2.005	2.012	2.018	2.013	1.990	2.018	2.018	2.010	2.019	2.005
Ta/(Ta + Nb)	0.043	0.079	0.054	0.057	0.045	0.094	0.249	0.461	0.609	0.848
Mn/(Mn + Fe)	0.486	0.304	0.341	0.217	0.368	0.337	0.701	0.657	0.757	0.970

Note: A site = Fe, Mn, Mg, and Ca; B site = Nb, Ta, and Ti.
* MGG = muscovite + garnet monzogranite, AP = aplite dike, Brl = beryl pegmatite, Spd + Brl = spodumene + beryl pegmatite, Spd = spodumene pegmatite.

replaced, the manganotantalite. A less common type of alteration involved the partial replacement of opaque ferrocolumbite by translucent manganocolumbite in an evolved spodumene + beryl pegmatite in the Lamotte pluton. Some CT crystals in dikes of aplite and albitite are intergrown with fersmite. The nature of this intergrowth cannot be ascertained owing to the rarity of the occurrence and the small size of the crystals.

Compositional variations

The composition of columbite-tantalite from the Lamotte and Lacorne pegmatites is dominated by Fe (total as Fe^{2+}), Mn, Nb, and Ta (Tables 1 and 2). There is a minor amount of Ti (up to 0.1 atoms per formula unit, apfu) and, in some cases, trace amounts of Mg and Ca. The fersmite noted in the albitite has a composition as follows: $(Ca_{0.82}Mn_{0.19}Fe^{2+}_{0.08})_{\Sigma1.09}(Nb_{1.06}Ta_{0.88}Ti_{0.03})_{\Sigma1.97}O_6$.

TABLE 2. Representative compositions of columbite-tantalite in various rock types from the Lacorne pluton

Lithology* Sample	AP 606	Brl 1001E	Brl 1001L	Spd + Brl 708	 756.S	 756.Lp	Spd 812	Spd 736	Ab 721
Nb_2O_5 (wt%)	69.12	69.63	43.42	62.29	62.65	36.43	62.16	1.73	35.85
Ta_2O_5	9.23	8.79	36.86	17.74	17.14	46.70	18.13	82.39	47.93
TiO_2	0.52	0.67	1.23	0.80	0.45	0.44	1.07	0.63	0.41
MgO	0.08	0.07	0.06	0.05	0.02	0.00	0.09	0.00	0.52
CaO	0.01	0.02	0.03	0.02	0.01	0.04	0.19	0.05	0.06
FeO	11.05	12.78	11.25	10.45	4.96	0.31	2.44	2.87	9.15
MnO	9.11	7.50	6.29	8.84	14.57	16.57	16.29	10.65	6.78
Total	99.12	99.46	99.14	100.2	99.80	100.5	100.4	98.32	100.7
Structural formula on the basis of six O atoms									
Nb	1.833	1.830	1.296	1.690	1.705	1.124	1.680	0.067	1.105
Ta	0.147	0.139	0.662	0.289	0.281	0.867	0.295	1.908	0.889
Ti	0.023	0.029	0.061	0.036	0.021	0.022	0.048	0.041	0.021
Mg	0.007	0.006	0.006	0.005	0.002	0.000	0.008	0.000	0.053
Ca	0.001	0.001	0.002	0.001	0.001	0.003	0.012	0.005	0.004
Fe	0.542	0.621	0.622	0.524	0.250	0.018	0.122	0.205	0.522
Mn	0.453	0.369	0.352	0.449	0.743	0.958	0.825	0.768	0.392
A site	1.003	0.998	0.981	0.980	0.995	0.979	0.967	0.978	0.971
B site	2.004	1.998	2.019	2.015	2.006	2.013	2.023	2.016	2.015
Ta/(Ta + Nb)	0.074	0.071	0.338	0.146	0.141	0.435	0.149	0.966	0.446
Mn/(Mn + Fe)	0.455	0.737	0.361	0.461	0.749	0.982	0.871	0.790	0.429

Note: E = early, L = late, S and Lp = from spodumene and lepidolite zones, respectively.
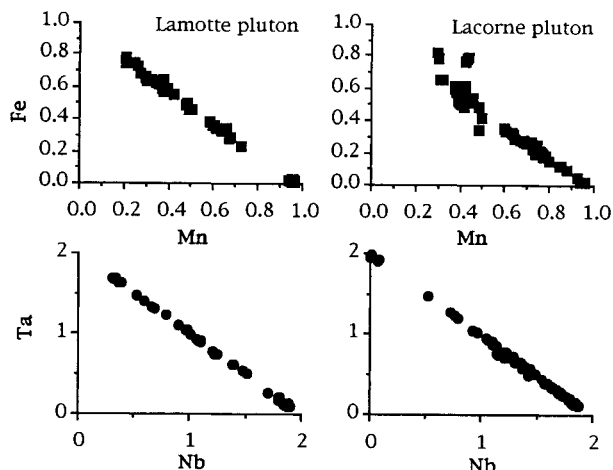* Same as those in Table 1. Ab = albitite dike.

FIGURE 4. Plots showing a linear correlation between Fe and Mn, and between Nb and Ta (in atoms per formula unit) in columbite-tantalite from the various types of pegmatite discussed in the text and from albitite. These trends indicate homovalent exchanges, mainly Fe ↔ Mn and Nb ↔ Ta.

For all crystals of CT, the sum of cations ranges from 2.96 to 3.02 apfu; only four out of 176 analyses gave a cation sum between 3.03 and 3.05 apfu. High totals, i.e., >1% above the ideal value of 3, indicate the presence of trivalent cations (Ercit 1994). The closeness of the majority of compositions to the ideal stoichiometry and the small number having slightly higher total cations suggest that the columbite-tantalite in both suites of pegmatite contains a negligible proportion of trivalent cations. This inference is supported by the linear relationship between Nb and Ta and between Fe and Mn in crystals of CT (Fig. 4). The TiO_2 content of columbite-tantalite varies from <10.1 to 1.3 wt%, with most crystals containing between 0.1 and 0.4 wt% (Lamotte suite) and between 0.4 and 0.8 wt% (Lacorne suite). The presence of minor Ti in the structure is made possible by a coupled substitution involving $3Ti^{4+}$ ↔ $2(Nb,Ta)^{5+}$ + $(Fe,Mn)^{2+}$. This exchange mechanism is confirmed by the sum Nb + Ta + Ti slightly above 2.0 apfu in almost all analyzed crystals. The wide range of compositions of columbite-tantalite, therefore, mainly reflects the homovalent exchanges Ta ↔ Nb and Mn ↔ Fe (Fig. 4).

Back-scattered electron images of all crystals of columbite-tantalite do not show evidence of compositional zoning. These images are consistent with compositional homogeneity in the small, included crystals, and with subtle chemical variations across the large, mostly interstitial crystals. In the case of the latter, the composition varies subtly; in one example, the core is $(Fe_{0.49}Mn_{0.48}Ti_{0.02})_{\Sigma 0.99}$-$(Nb_{1.49}Ta_{0.5})_{\Sigma 1.99}O_6$, and the rim is $(Fe_{0.51}Mn_{0.45}Ti_{0.03})_{\Sigma 0.99}$-$(Nb_{1.37}Ta_{0.6})_{\Sigma 1.97}O_6$.

Columbite-tantalite in both suites shows compositional variations in Mn/(Mn + Fe) and Ta/(Ta + Nb) from one type of pegmatite to another (Fig. 5) but is invariant
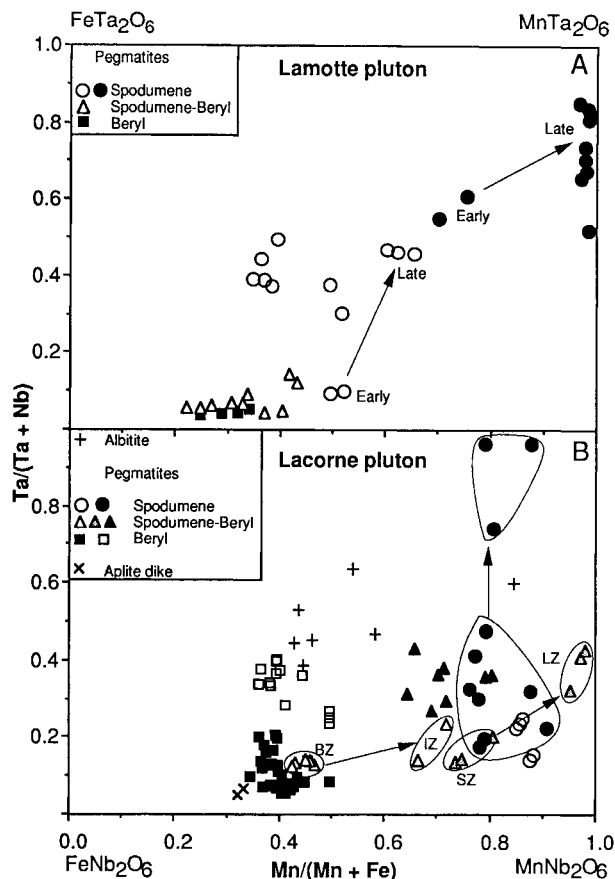

FIGURE 5. Compositions of columbite-tantalite from the Lamotte (**A**) and Lacorne (**B**) pegmatite suites plotted in the quadrilateral diagram ferrocolumbite ($FeNb_2O_6$)–manganocolumbite ($MnNb_2O_6$)–manganotantalite ($MnTa_2O_6$)–ferrotapiolite ($FeTa_2O_6$). The symbols for the Ct are as follows: solid and open squares = early and late ferrocolumbite, respectively; open triangles = least evolved spodumene + beryl pegmatite; shaded triangles = transitional spodumene + beryl pegmatite; solid triangles = most evolved spodumene + beryl pegmatite; open circles = less evolved spodumene pegmatite; solid circles = more evolved spodumene pegmatite. Compositional trends in different internal zones of pegmatite are indicated by arrows (see text for discussion): the terms BZ and IZ in the least evolved spodumene + beryl pegmatite (open triangles) refer to columbite-tantalite from the aplite border zone and the intermediate zone, respectively. Similarly, the terms SZ and LZ in the more evolved spodumene + beryl pegmatite refer to the spodumene zone and lepidolite zone, respectively.

in terms of Ti vs. either Ta/(Ta + Nb) or Mn/(Mn + Ta) (not shown). In the Lamotte pluton, the columbite-tantalite shows a broad linear trend from ferrocolumbite in beryl and spodumene + beryl pegmatites to an intermediate composition in the less evolved spodumene pegmatite to manganotantalite in the more evolved spodumene pegmatite (Fig. 5). This trend is similar to that shown by columbite-tantalite within single bodies of peg-
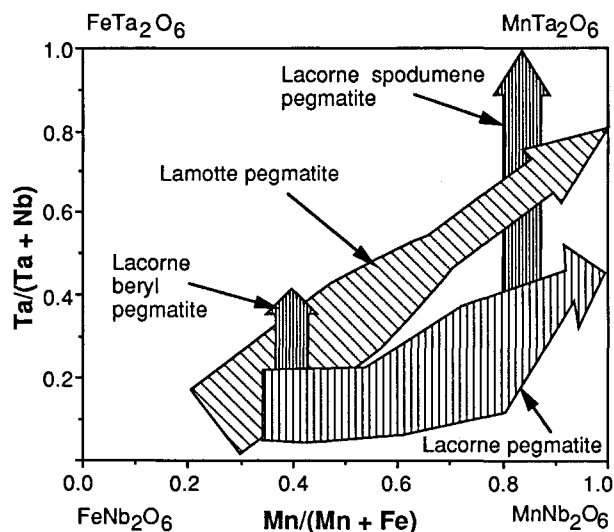
FeTa$_2$O$_6$ MnTa$_2$O$_6$

FIGURE 6. Compositional trends of columbite-tantalite from the various Lamotte and Lacorne pegmatites. Data are from Figure 5.

matite (indicated by arrows), in which the paragenetically early crystals are richer in Fe and Nb than the later ones. There is a large overlap in composition between columbite-tantalite in beryl pegmatite and that in spodumene + beryl pegmatite (aplite zone in both cases).

In contrast to the Lamotte suite, the overall compositional variation of columbite-tantalite in the Lacorne suite is from ferrocolumbite in beryl pegmatite to manganocolumbite in spodumene pegmatite, i.e., there is greater enrichment in Mn than Ta. Examples of manganotantalite are scarce here, as it is present only in the pegmatite portion of the most evolved spodumene pegmatite. Interstitial (late) ferrocolumbite in the beryl pegmatites invariably has higher Ta values but similar Mn values relative to the included (early) grains (Fig. 5). Columbite-tantalite in the least evolved spodumene + beryl pegmatite ranges from ferrocolumbite in the aplite zone to manganocolumbite in the intermediate zone, with a very small corresponding increase in Ta. The most extreme Mn enrichment in manganocolumbite occurs in the intermediate spodumene + beryl pegmatite, where Mn/(Mn + Fe) ranges from a value of 0.75 in the spodumene zone to a high of 0.98 in the lepidolite zone. Unlike columbite-tantalite compositions in the least evolved spodumene + beryl pegmatite, these have a substantially higher Ta/(Ta + Nb) value.

In summary, the composition of columbite-tantalite in the Lamotte suite ranges from ferrocolumbite in beryl pegmatite to manganotantalite in spodumene pegmatite and reveals a concomitant increase in Mn/(Mn + Fe) and Ta/(Ta + Nb) with pegmatite evolution (Fig. 6). In contrast, the columbite-tantalite in the Lacorne suite varies from ferrocolumbite to manganocolumbite. Within single bodies of beryl pegmatite and the most evolved spodumene pegmatite at Lacorne, the Ta/(Ta + Nb) value of

TABLE 3. Unit-cell parameters of columbite-tantalite, Lamotte, and Lacorne pegmatite swarms

Sample	a (Å)	b (Å)	c (Å)	V (Å^3)	Ψ
Beryl pegmatite					
794*	14.2610(19)	5.7360(7)	5.1010(5)	417.27(6)	51
795*	14.2579(27)	5.7347(9)	5.1013(7)	417.11(8)	50
623.1	14.3357(32)	5.7456(11)	5.0960(9)	419.74(10)	72
623.2	14.2800(50)	5.7410(16)	5.0975(15)	417.90(15)	59
623.p	14.2272(62)	5.7362(17)	5.1213(21)	417.95(16)	25
624	14.2180(44)	5.7326(11)	5.1163(10)	417.01(11)	27
1001	14.2508(41)	5.7403(14)	5.111(11)	418.11(12)	40
Spodumene + beryl pegmatite					
908*	14.2746(27)	5.7389(9)	5.0922(8)	417.16(8)	63
912*	14.2759(62)	5.7397(19)	5.0953(18)	417.51(19)	60
912-2*	14.2390	5.7340(26)	5.1235(22)	418.27(22)	25
703	14.2914(27)	5.7579(9)	5.1606(8)	424.66(8)	2
708	14.2365(24)	5.7376(10)	5.1332(8)	419.30(9)	16
709	14.2918(56)	5.7556(18)	5.1553(17)	424.07(17)	7
753.1	14.2622(37)	5.7512(13)	5.1502(11)	422.45(11)	5
753.2	14.2663(33)	5.7534(12)	5.1468(10)	422.45(10)	90
756.S (D)	14.2711(38)	5.7491(13)	5.1434(10)	421.99(11)	14
756.S (S)	14.2847(55)	5.7497(19)	5.1298(14)	421.33(16)	29
756.S (♦)	14.3857(32)	5.7458(11)	5.0805(9)	419.94(10)	98
Spodumene pegmatite					
9-5* (D)	14.2883(28)	5.7530(14)	5.1669(9)	424.72(11)	0
9-5* (S)	14.2433(37)	5.7440(14)	5.1460(11)	421.01(12)	5
9-5*	14.3060(77)	5.7534(24)	5.1413(28)	423.17(24)	23
9-5-2*	14.2696(35)	5.7477(12)	5.1491(11)	422.31(11)	8
9-5* (♦)	14.4205(30)	5.7603(11)	5.0935(8)	423.10(9)	93
812	14.3059(55)	5.7447(19)	5.1345(16)	421.97(16)	30
812.2	14.2867(48)	5.7519(17)	5.1455(13)	422.83(15)	15
736	14.2315(174)	5.7760(56)	5.1534(59)	423.62(49)	0

Note: The degree of cation order, Ψ, was calculated from coordinates in the a-c quadrilateral using the equation proposed by Ercit et al. (1995). Two samples give evidence of two sets of diffraction maxima, each of which was refined. The dominant phase is labeled (D) and the subsidiary phase, (S). Two samples (♦) were heated at 1000 °C for 16 h, a treatment that caused the structure to become highly ordered. Samples 1001, 753, 756.S, and 812 are from the intermediate zone of the pegmatite portion of composite pegmatite-aplite bodies. All others are from the border-zone aplite or pegmatite.
* Samples from the Lamotte pegmatite swarm. All other samples come from the Lacorne pegmatite swarm.

columbite-tantalite increases at a constant Mn/(Mn + Fe) value.

Crystals of ferrocolumbite in discrete dikes of aplite in the Lacorne and Moly Hill plutons are similar compositionally and have lower values of Mn/(Mn + Fe) (i.e., are less evolved) than their equivalents in the Lacorne beryl pegmatites. Columbite-tantalite from the Preissac muscovite + garnet monzogranite has a very low value of Ta/(Ta + Nb), <0.04, and the Mn/(Mn + Fe) values range from 0.47 to 0.52. In the albitite dikes, the columbite-tantalite compositions vary widely, from a Ta/(Ta + Nb) of 0.4 and a Mn/(Mn + Fe) of 0.45 to a Ta/(Ta + Nb) of 0.6 and a Mn/(Mn + Fe) of 0.85. Most of the columbite-tantalite in these dikes thus has a composition between ferrocolumbite and manganotantalite.

Structural states

Unit-cell dimensions were refined on columbite-tantalite from representative types of pegmatite; the nature of the host rocks sampled is indicated in the footnotes to Table 3. At Lamotte (Fig. 7), most of the columbite-tan-
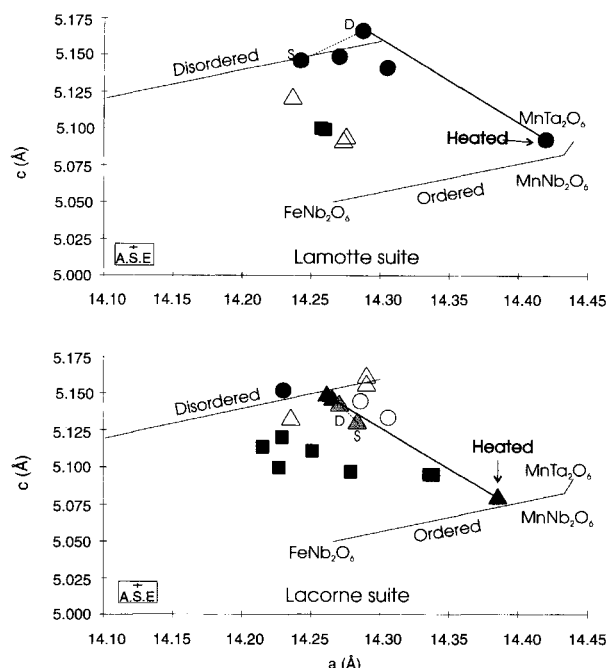
Figure 7. Plots of unit-cell parameters a vs. c showing an increasingly disordered structure of columbite-tantalite from beryl to spodumene pegmatite. In each plot, a heavy solid line links unheated and heated (1000 °C, 16 h) manganotantalite. The unit-cell values of the ordered end-members are from Wise et al. (1985). Symbols are the same as those in Figure 5. D and S = dominant and subsidiary domains (see text for details). A.S.E. = average standard error, i.e., less than the size of the symbols.

talite in the aplite zone of both beryl and spodumene + beryl pegmatites has an intermediate degree of order (50–63%; Table 3) and Mn/(Mn + Fe) value; only one sample is relatively disordered (25%). The CT in the spodumene pegmatite is more disordered (in the range 0–23% order) and relatively Mn enriched. Note that in one sample of

manganotantalite, there are two sets of diffraction maxima, with the dominant domains being more disordered (0 vs. 5%) and richer in Mn (higher value of a).

At Lacorne (Fig. 7), the ferrocolumbite from the aplite border zone of beryl pegmatite is more ordered (59–72% order; Table 3) than that from the intermediate zone (25–41% order). All other samples plotted, from spodumene + beryl pegmatite and from spodumene pegmatite, are significantly more disordered (0–30% order) and more Mn enriched. The most strongly disordered crystals are from the geochemically most evolved bodies of each grouping. The trend of increasing Mn/(Mn + Fe) inferred from the cell dimensions is consistent with the measured value (Fig. 5). As in the Lamotte suite, only one sample displays two sets of diffraction maxima. In this case, the two lattices belong to domains with similar degree of inferred Mn enrichment but differing slightly in degree of cation order; the dominant set is more strongly disordered (14 vs. 29% order).

To confirm that the disordered members of the suite do indeed have the columbite-tantalite structure and not the ixiolite structure, one sample from each locality was placed in a platinum crucible, heated in an oven to 1000 °C for 16 h, and then analyzed by X-ray diffraction. In both cases, the highly disordered starting material became highly ordered manganotantalite as a result of the heat treatment (Fig. 7, Table 3), as would be expected in light of the findings of Černý and Ercit (1985). The rapid increase in degree of cation order at 1000 °C indicates that the ordered structure is strongly favored over one showing a disordered distribution of divalent and pentavalent cations and the resultant local departure from ideal bond-valence sums that are anticipated.

Microlite

As described earlier, microlite $[A_{2-m}B_2O_6(O,OH,F)_{1-n} \cdot pH_2O$ $(m,n = 0-1; p = 0-?)]$ occurs as a secondary phase

Table 4. Representative compositions of microlite

| Sample | 756.S | 756.S | 756.S | 721 | 9-5 | 9-5 | 812 | 812 |
Analyses	1	2	3	4	5	6	7	8
Nb_2O_5 (wt%)	9.44	11.24	17.66	16.21	2.30	1.76	9.58	11.60
Ta_2O_5	55.55	51.55	48.33	54.75	78.48	79.98	54.42	50.90
TiO_2	5.31	8.33	4.90	1.50	0.58	0.51	5.16	5.98
UO_2	6.95	7.88	3.97	0.00	0.00	0.50	8.60	6.72
MgO	0.00	0.00	0.00	0.07	0.00	0.00	0.00	0.00
CaO	14.19	14.48	15.19	13.48	10.70	10.74	13.81	15.15
FeO	0.02	0.00	0.16	6.80	0.04	0.00	0.02	0.09
MnO	0.46	0.63	1.05	3.68	0.09	0.39	0.69	0.71
Na_2O	0.00	0.00	0.00	0.00	4.82	3.59	1.23	1.00
Total	91.92	94.11	91.26	96.49	97.00	97.47	93.51	92.15
Structural formula on the basis of full B-site occupancy (Nb + Ta + Ti = 4)								
Nb	0.730	0.852	1.287	1.256	0.182	0.139	0.752	0.889
Ta	2.586	2.350	2.119	2.551	3.741	3.794	2.573	2.348
Ti	0.684	0.798	0.594	0.193	0.077	0.067	0.675	0.763
U	0.265	0.286	0.142	0.000	0.000	0.019	0.333	0.254
Mg	0.000	0.000	0.000	0.018	0.000	0.000	0.000	0.000
Ca	2.603	2.597	2.624	2.475	2.010	2.007	2.572	2.753
Fe	0.003	0.000	0.022	0.974	0.059	0.000	0.003	0.013
Mn	1.092	0.895	0.143	1.620	0.013	0.058	1.143	1.151
Na	0.000	0.000	0.000	0.000	1.638	1.214	0.415	0.329

replacing columbite-tantalite, mostly in spodumene pegmatites and, very rarely, in beryl pegmatites (Fig. 3D). Electron microprobe data show that the sum of oxides ranges from 91 to 97.5 wt% (Table 4). Low totals are common in microlite (e.g., Spilde and Shearer 1992; Wise and Černý 1990) and have been attributed by Wise and Černý to the presence of H_2O, F, or both. Energy-dispersive analysis of microlite did not indicate the presence of F; H_2O, therefore, is probably the dominant volatile species in this case.

The composition of microlite is highly variable, ranging from uranian microlite (Table 4, analyses 1–3 and 7) to Na-rich microlite (analyses 5 and 6) and U- and Na-free microlite (analysis 4). Na-rich microlite is restricted to spodumene pegmatites, whereas uranian microlite occurs in both spodumene (812) and spodumene-beryl (756.S) pegmatites. The dominant major-element oxides are Ta_2O_5 (54–80 wt%), Nb_2O_5 (2.3–17.6 wt%), and CaO (10.7–15.2 wt%). The Ti content ranges from 0.5 to 6.3 wt% TiO_2. Fe and Mn are minor constituents. The composition of microlite in this study lies within the compositional field of microlite compiled by Wise and Černý (1990) (Fig. 8) and compares well with that of microlite from the Yellowknife pegmatites, Northwest Territories (Wise and Černý 1990) and the lepidolite pegmatites from South Africa and Namibia (Baldwin 1989).
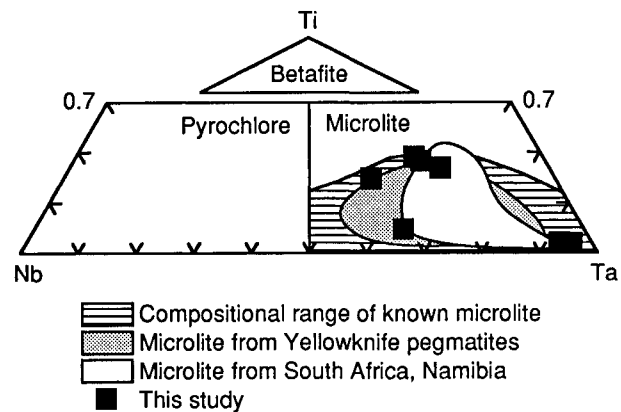

FIGURE 8. Nb-Ti-Ta triangular diagram (atomic proportions) showing the B-site occupancy in microlite. The field boundaries of the three pyrochlore-group minerals are after Hogarth (1977). The compositional fields of known microlite are after Černý and Ercit (1989), Baldwin (1989), and Wise and Černý (1990).

DISCUSSION

Compositional trends and pegmatite evolution

Textural evidence presented earlier indicates that columbite-tantalite in the Lamotte and Lacorne pegmatites is magmatic; the crystals are relatively homogeneous and free of subsolidus alteration except where noted. The composition of columbite-tantalite, like that of any other magmatic mineral, was therefore controlled by the abundances of Nb, Ta, Fe, and Mn in the evolving magma, the relative solubilities of the end-members, the nature of the coexisting minerals on the liquidus, and the corresponding mineral-liquid partition coefficients for the above elements.

In the Lamotte suite as a whole, columbite-tantalite displays a trend of simultanouelsy increasing Mn/(Mn + Fe) and Ta/(Ta + Nb) values from beryl to spodumene pegmatite, indicating that the residual liquid was progressively depleted in Fe and Nb and enriched in Mn and Ta (Figs. 5 and 7). The same trend is shown by columbite-tantalite within individual bodies of spodumene pegmatite, i.e., from early to late stages of crystallization. These trends can be explained by the relative solubility of the two end-members in the liquid. Ferrocolumbite is less soluble and crystallized first, thereby enriching the residual liquid in Mn and Ta and causing later crystallization of manganotantalite. This simple explanation is partially supported by experiments of Keppler (1993), who showed that $MnTa_2O_6$ is approximately nine times more soluble than $MnNb_2O_6$ in F-free haplogranite. Although there are no experimental data for ferrocolumbite, it can

be argued on theoretical grounds that because the field strengths (Z/r) of Nb and Fe are higher than those of Ta and Mn, respectively, ferrocolumbite is less soluble than either manganocolumbite or manganotantalite.

In the Lacorne suite, columbite-tantalite also displays an overall trend of increasing Mn/(Mn + Fe) and Ta/(Ta + Nb) from beryl to spodumene pegmatite. However, in contrast to the Lamotte suite, the increase in Ta/(Ta + Nb) is relatively subordinate, and the dominant trend is one of Mn enrichment. Similar trends of dominant Mn enrichment in columbite-tantalite composition were reported by Černý et al. (1985, 1986) from several granitic pegmatite fields and by Spilde and Shearer (1992) for the Black Hills granitic pegmatites (South Dakota). Černý et al. (1985, 1986) attributed such a trend to the presence of F in the melt and the resultant formation of Mn- and Ta-fluoride complexes, which would increase the partitioning of Mn and Ta (presumably mostly the latter) in favor of the liquid and delay crystallization of manganotantalite until the latest stages of pegmatite evolution. However, this hypothesis could account for a trend toward manganocolumbite in Figure 6 only if the partitioning of Ta relative to Nb into the liquid were stronger than that of Mn relative to Fe.

Although Keppler (1993) showed that the solubility of manganotantalite in haplogranitie melts does increase sharply with increasing F content, his data provide no evidence of a corresponding preferential increase in the solubility of manganotantalite over that of manganocolumbite. Indeed, the value of $K_{MnTa_2O_6}/K_{MnNb_2O_6}$ (K is the solubility product) is highest in the F-free system, decreases until the F content of the melt is 2 wt%, and then is essentially constant for higher F contents. These data would appear to rule out fluoride complexing as a viable explanation of the relative suppression of Ta in the crystal. There are no experimental data to test the hypothesis

of preferential complexing of Mn relative to Fe by fluoride. However, theoretical considerations do not support this hypothesis. Both Fe and Mn are divalent cations, are intermediate in terms of the hard-soft classification of metals, and are therefore unlikely to form strong complexes with a hard ligand like F^- (Pearson 1963). Moreover, Al, Na, and Li, which are major components of the magma, all complex strongly with fluoride in the melt (e.g., Manning et al. 1980), and thus it seems unlikely that Fe- and Mn-bearing complexes with F would be important.

An alternative explanation, which we prefer for the small increase in Ta/(Ta + Nb) in the Lacorne suite, is that the Ta/(Ta + Nb) values of the primitive felsic liquid were lower than those of the corresponding liquid for the Lamotte suite. Thus, assuming that the melt-partitioning coefficients for Nb and Ta were the same for the two batches of magma, the Ta/(Ta + Nb) would have been much lower for columbite-tantalite in the Lacorne suite. This explanation is supported by bulk geochemical data, which show that the above ratio for muscovite monzogranite is higher in the Lacorne pluton than in the Lamotte pluton. Mulja et al. (1995a) concluded that the pegmatite crystallized from the residual monzogranitic liquid.

In the Lacorne suite, with the exception of the beryl pegmatite and the most evolved spodumene pegmatite, the trend of columbite-tantalite composition with crystallization of individual bodies of pegmatite (Figs. 5 and 6) parallels the overall trend of columbite-tantalite composition from beryl to spodumene pegmatite, i.e., enrichment in Mn. In contrast, the evolution of columbite-tantalite composition in beryl and most evolved spodumene pegmatites from this suite follows a distinct vector off the main trend in Figure 6, along which Ta/(Ta + Nb) increases at a constant Mn/(Mn + Fe) value. We believe that this latter trend reflects the fact that garnet crystallized contemporaneously with columbite-tantalite during all stages of evolution of these bodies, whereas in other pegmatites, garnet crystallization terminated early. Crystallization of garnet (the principal Fe- and Mn-bearing mineral in these rocks) would have buffered Fe and Mn activities and thus caused local decoupling of Fe and Mn from Nb and Ta.

Relationship between degree of cation order in columbite-tantalite and degree of geochemical evolution of the system

The striking increase in the extent of disorder with increasing Mn enrichment, i.e., with evolution of the pegmatite from beryl to spodumene pegmatite, and the complete absence in these suites of ordered columbite-tantalite (Fig. 7) require explanation. One hypothesis generally mentioned in evaluations of such observations involves the incorporation of other cations, such as Ti, leading to a redistribution of the essential cations over the A and B sites and promoting disorder. Although Ti can reach important levels in minerals of this group, these CT contain

only low concentrations of Ti, not surpassing 0.1 apfu. A plot of degree of order vs. Ti content (not shown) does not suggest any dependence on this variable. We tentatively conclude in light of these facts and the close approach of the compositions to stoichiometry (Tables 1 and 2; Fig. 4) that coupled substitution involving Ti or other extraneous cations cannot explain the observed disorder.

We believe, therefore, that the degree of order of the columbite-tantalite in this suite is a function of environmental factors. Černý et al. (1986) found, in the case of the Greer pegmatite field, that disorder in columbite-tantalite increases from large, proximal bodies of less evolved pegmatite to small bodies of relatively evolved pegmatite in the country rocks and concluded that the degree of order is related to cooling rate. They proposed that columbite-tantalite crystallized as a disordered phase and that the small bodies of pegmatite in the country rocks, by cooling much more rapidly than larger, proximal bodies, preserved the degree of cation order imposed at the time of crystal growth. The same interpretation is proposed for the Lamotte and Lacorne pegmatites, where less evolved beryl pegmatite occurs in the pluton (46 ± 16% ordered columbite-tantalite) and more evolved spodumene pegmatite occurs in the country rocks (relatively disordered columbite-tantalite). Unfortunately, there is no information in the literature concerning the kinetics of ordering of columbite-tantalite solid solutions as a function of temperature and time of annealing.

An enigmatic aspect of the problem concerns the improbability that a divalent and a pentavalent cation could adopt a disordered distribution in an oxide phase of stoichiometry AB_2O_6. One would predict such serious departures from local charge balance that, "on paper," one would not expect disorder to be possible. Yet, the consensus of structural crystallographers is that such crystals really are disordered. The fact that such disorder is strongly metastable is proved by the efficient conversion of disordered manganotantalite to the ordered equivalent at a temperature far above the inferred temperature of crystallization of the evolved felsic liquids (~550 °C). We conclude that crystallization of these batches of melt was very rapid and that the oxide phase crystallized with a pattern of cation distribution resembling that in the melt.

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