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THE GEOCHEMISTRY AND CRYSTAL CHEMISTRY OF COLUMBITE-GROUP MINERALS FROM GRANITIC PEGMATITES, SOUTHWESTERN GRENVILLE PROVINCE, CANADIAN SHIELD

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ABSTRACT

Granitic pegmatites from the Grenville Province predominantly carry a NYF-type geochemical signature. Their accessory minerals includes a variety of (Nb,*Ln*,U)-oxide minerals, of which columbite-group minerals are infrequent members (nine occurrences to date). As compared to better-studied granitic pegmatites of LCT-type suites, the chemistry of these columbite-group minerals is anomalous: (1) there is a general shift toward (Fe,Nb)-rich compositions, (2) Ti is normally present in subordinate amounts, (3) levels of Zr, Mg, Sc, and W are significant, (4) U contents are several orders of magnitude higher than reported elsewhere, and (5) many lanthanons occur in concentrations detectable by electron microprobe. The structural state of the samples is variable, ranging from dominantly cation-disordered to dominantly ordered. For the Quadeville Beryl pegmatite, the structural state of columbite-group minerals shows a systematic variation with pegmatite zonation. Although the individual bodies of pegmatite have achieved low to moderate degrees of fractionation, the geochemical expressions of fractionation are detectable and can be used to evaluate the internal evolution of each body. Trace-element behavior is occasionally the reverse of expectations, and is not consistent from pegmatite to pegmatite; as a suite, NYF pegmatites have to be much better characterized before such discrepancies can be properly evaluated.

Keywords: columbite-group minerals, granitic pegmatites, trace elements, Grenville Province, Ontario.

SOMMAIRE

Les pegmatites granitiques de la province du Grenville font preuve d'une filiation géochimique de type NYF. Parmi leurs minéraux accessoires se trouve une suite d'oxydes à (Nb,*Ln*,U), dont les minéraux du groupe de la columbite sont relativement rares (neuf exemples connus à date). En comparaison des cas de pegmatites granitiques de type LCT, mieux connus, la composition chimique de ces minéraux est anomale: 1) il y a un net décalage vers les compositions riches en Fe et Nb, 2) le Ti est normalement présent en quantités secondaires, 3) les niveaux de Zr, Mg, Sc et W sont importants, 4) les quantités de U dépassent de plusieurs ordres de grandeur les concentrations documentées ailleurs, et 5) plusieurs des terres rares y sont présentes en quantités mesurables à la microsonde électronique. Le degré d'ordre cationique de ces échantillons est variable, de presque complètement désordonné à presque complètement ordonné. Dans le cas de la pegmatite dite de Quadeville Beryl, le degré d'ordre des minéraux du groupe de la columbite reflète de façon systématique la zonation interne. Quoique le degré de fractionnement atteint n'est que faible ou modéré dans les divers exemples, l'expression géochimique du fractionnement est décelable à la microsonde électronique, et peut servir à évaluer l'évolution interne de chaque massif. Le comportement des éléments traces est dans certains cas l'inverse de ce qui est attendu, et ne concorde pas nécessairement d'un cas à l'autre. Dans l'ensemble, les exemples de pegmatite granitique de type NYF devront être beaucoup mieux caractérisés avant d'évaluer convenablement ces aberrances.

(Traduit par la Rédaction)

Mots-clés: minéraux du groupe de la columbite, pegmatites granitiques, éléments traces, Province de Grenville, Ontario.

INTRODUCTION

Minerals of the columbite group have the general formula AB_2O_6, in which, most typically, A represents Fe^{2+}, Mn and Mg, and B, Nb and Ta. Columbite-group minerals also are known to host minor amounts of Fe^{3+}, Sc, Ti, Sn and W. They structurally range from cation-disordered ixiolite to cation-ordered columbite–tantalite. They are both an economically (Ta, Nb) and petrologically important group of minerals. Applied geological research in recent years has focused on the use of chemical and structural variations in columbite-group minerals as a means of characterizing regional and internal geochemical variations in granitic pegmatites and fertile granites. These studies are still in their infancy; to date, important questions remain, such as the complexing behavior of Nb and Ta, and the causes of structural variations in ixiolite and its derivatives.

The present study focuses on the geochemistry and crystal chemistry of columbite-group minerals from a class of granitic pegmatites that is not usually studied in detail, in part owing to its chemical complexity (*Ln*-, U-, Nb-bearing) and subeconomic status. The goals of the present study are: (1) to determine the crystal-chemical controls on the distribution of minor and trace elements in the columbite structure, (2) to delineate the chemical and structural properties of columbite-group minerals from the *NYF* (*N*b–*Y*–*F*) geochemical suite of granitic pegmatites, (3) to characterize the behavior of trace elements in columbite-group minerals during the internal evolution of these pegmatites, and (4) to apply the chemistry and structural properties of columbite-group minerals to the solution of petrological problems associated with individual pegmatites.

In this paper, the word "Grenville" is used as an adjective. In all cases, the adjective refers to the Grenville Province, not rocks of "Grenvillian" (*i.e.*, Neohelikian) age or of the classic Grenville Series. Furthermore, "Grenville columbite" necessarily refers to a "columbite-group mineral from a granitic pegmatite of the Grenville Province", as all known occurrences of columbite-group minerals in the Grenville Province are from such rocks.

GEOLOGY AND LOCATION

Granitic pegmatites have long been known from the southwestern Grenville Province. Largely barren, the pegmatites were principally mined in the past for their feldspar content; however, interest and economics permitted sporadic exploitation for uranium, beryllium, quartz and muscovite. Past exploration and investigation were largely dictated by the marginal economic status of the pegmatites; consequently, most pegmatite occurrences are located near historically important access routes in southeastern to central Ontario and southwestern Quebec. This places the majority of occurrences in the Central Metasedimentary Belt (CMB); although formally fewer in number, similar numbers most likely exist in the Central Gneiss Belt (CGB).

Granitic pegmatites of the Grenville Province are typically deep-seated and late tectonic, with ages averaging 1.0 Ga (Fowler & Doig 1983, van Breemen *et al.* 1986). They host accessory minerals of Nb, Y, *REE*, Ti, Zr, U and Th, and, particularly for the pegmatites of the CGB, they are poor in P and B, and thus belong to the NYF geochemical suite of granitic pegmatites of Černý (1991). The apparent lack of contemporaneous granitic plutons associated with the pegmatites and overall simple geochemistry led Goad (1990) to propose a (direct) anatectic origin for (most) pegmatites of the Bancroft area in Ontario. Alternatively, the occurrence of apparently cogenetic NYF pegmatites and A-type granites in the Mont Laurier and Baie-Johan-Beetz regions of Quebec led Černý (1990) to suggest that pegmatites of the CMB have a magmatic parentage; deceptive field-relationships may have hampered correct interpretation in the past. With these ambiguities, it is difficult to even classify most Grenville pegmatites, as the recent scheme of Černý (1991) requires some knowledge of genesis. Thus it is that Černý (1990) assigned Grenville pegmatites as transitional to the muscovite and rare-element classes (*i.e.*, showing or being inferred to have a relationship to a parental granite), whereas Goad (1990) would place them in the abyssal to muscovite classes (no relationship to granite).

Most exposures of worked pegmatites are poor; workings are commonly found to be completely flooded, with only dump materials available for examination. Consequently, much of the geology of the pegmatites has to be inferred from published descriptions. Unfortunately, the bulk of geological investigation is pre-Jahns (1955), so that the literature does not properly document internal zoning of the pegmatites (*e.g.*, the border zone is usually missed), nor spatial variations in mineralogy, and is plagued with misidentifications of accessory minerals. Consequently, past statements about pegmatite classification and about the degree and style of internal zoning have to be approached with caution.

The mineralogy of most Grenville granitic pegmatites is simple; they consist mainly of K-feldspar, plagioclase and quartz. Biotite and garnet are common accessory phases; much less common are muscovite and rare-element minerals: beryl, a variety of (Nb,*Ln*,U)-oxide minerals, allanite, thorite and zircon. The pegmatites typically show a Y + *HREE* enrichment, expressed in the mineralogy; thus there is not only allanite-(Ce), but also allanite-(Y), orthophosphates are more typically xenotime-(Y) than monazite-(Ce), and fergusonite-(Y) may be present. Pegmatite bodies bearing columbite-group minerals and beryl are rare and represent the products of ultimate fractionation for most regions (Fig. 1). In all, seven columbite-bearing granitic pegmatites have been reported for the Grenville Province of the Canadian Shield (*e.g.*, Hewitt 1967, Satterly 1977); six of these were sampled for the present study, and two more such pegmatites have been identified. The following sections describe these bodies of pegmatite.

Blue Star pegmatite

This pegmatite body is located 6 km northeast of the town of Magnetawan in lot 12, concession XIV of Chapman Township, Parry Sound District, Ontario. It is one of many (*Ln*,Nb)-oxide-bearing granitic pegmatites in the vicinity of the Kiosk Domain – Ahmic Subdomain boundary in the Central Gneiss Belt, which were worked for their feldspar contents at

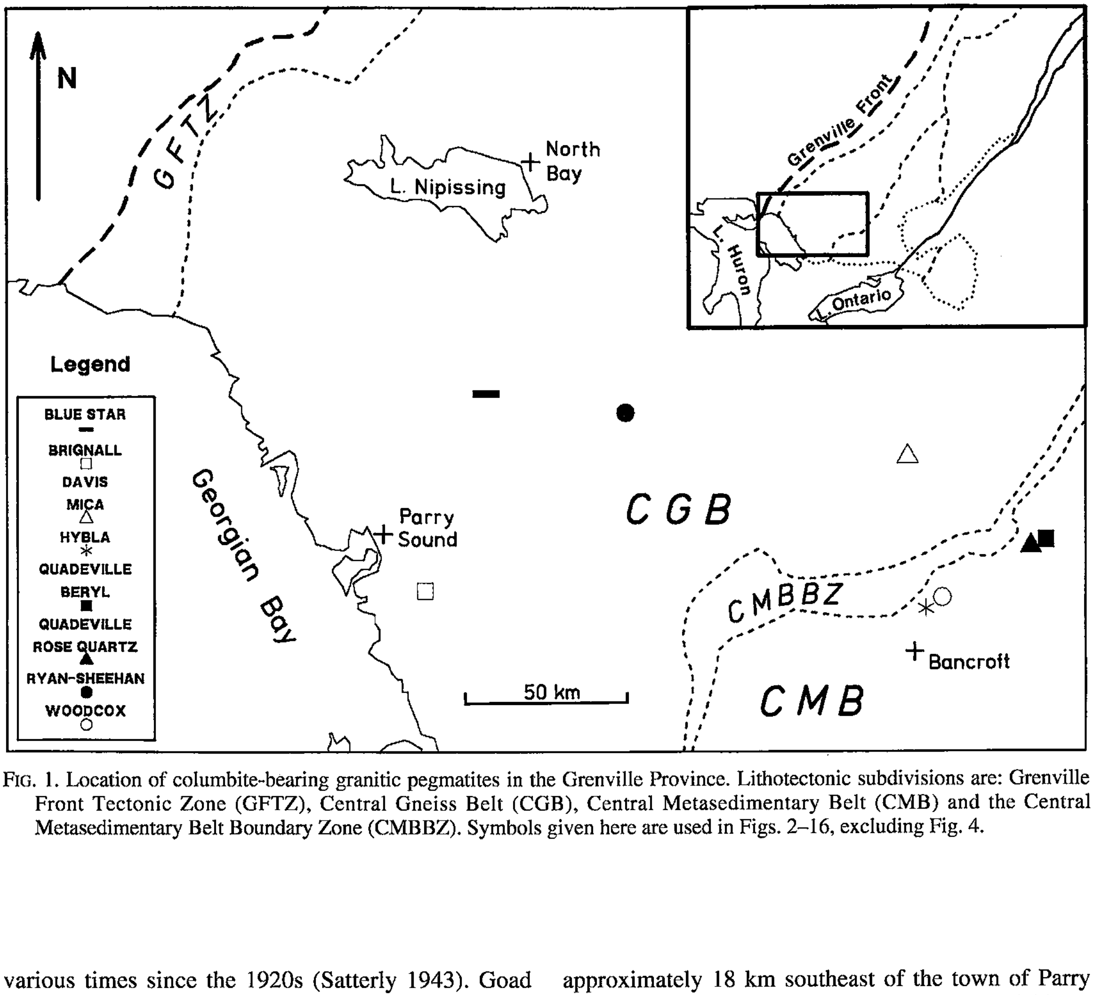

FIG. 1. Location of columbite-bearing granitic pegmatites in the Grenville Province. Lithotectonic subdivisions are: Grenville Front Tectonic Zone (GFTZ), Central Gneiss Belt (CGB), Central Metasedimentary Belt (CMB) and the Central Metasedimentary Belt Boundary Zone (CMBBZ). Symbols given here are used in Figs. 2–16, excluding Fig. 4.

various times since the 1920s (Satterly 1943). Goad (1990) has recently described the geology of the Blue Star pegmatite. It is poorly zoned, and its shape and contacts with metasandstone and biotite-bearing quartzofeldspathic gneiss are irregular. Most of the quartz and K-feldspar of the exposed pegmatite is relatively fine grained (to 4 cm); however, large K-feldspar crystals (to 0.5 m, and commonly of the variety "amazonite") are exposed in outcrop and in concentrations along the lower sections of the worked portion of the pegmatite. Given the limited present exposures, it is not possible to comment further on internal zoning of the pegmatite. Accessory minerals include garnet, biotite, samarskite-(Y), euxenite-(Y), manganocolumbite, ilmenite, pseudorutile, magnetite, rutile, anatase, cassiterite and fluorite.

Brignall pegmatite

The Brignall pegmatite is located in the Parry Sound Domain of the CGB, in lot 7, concession X of Conger Township, Parry Sound District, Ontario, approximately 18 km southeast of the town of Parry Sound. It is a large body; over 8,000 tonnes of feldspar were extracted during peak mining operations (Martin 1983). The geology of the pegmatite has not been well described, and present-day interpretations are limited to surface outcrop and above-water parts of the pit walls. The pegmatite is hosted by granitic and plagioclase–hornblende gneisses. It is syn- to late-tectonic; slickensided surfaces and schlieren-like (Goad 1990) muscovite-rich units indicate that the melt was tectonically disturbed during crystallization. Consequently, interpretation of internal zoning is difficult. The following units are recognizable: (1) a fine-grained wall zone of K-feldspar, quartz, biotite, muscovite and plagioclase, (2) a coarser K-feldspar – quartz – biotite intermediate zone, and (3) a narrow, contorted, yet somewhat lenticular muscovite-rich unit. The muscovite unit cannot be considered true schlieren, as revealed by its accessory mineralogy: it hosts abundant columbite and monazite-(Ce). Columbite is also found in the wall zone of the pegmatite, associated with samarskite-(Y).

Davis Mica pegmatite

The Davis Mica granitic pegmatite is located in lot 27, concession V of Dickens Township, Nipissing District, Ontario. It is part of a field of (*Ln*,Nb,U)-rich pegmatites near the town of Madawaska; these lie within the Opeongo Domain of the CGB. The pegmatite is narrow, sill-like and well zoned, and is hosted by a biotite–plagioclase gneiss. Storey & Vos (1981) have described the zoning: (1) a quartz–feldspar border zone, (2) a quartz – albite – muscovite – microcline – garnet wall zone, (3) a quartz–microcline intermediate zone, and (4) a quartz core. Present-day exposure is poor, and dumps are inextensive. Accessory minerals are mostly concentrated in the wall zone: garnet, euxenite-(Y), samarskite-(Y), monazite-(Ce), columbite, biotite and muscovite.

Hybla pegmatite

This pegmatite, also known as the Hybla showing (Goad 1990), is located in lot 25, concession VII of Monteagle Township, Hastings County, Ontario. It lies in the Bancroft Terrane of the Central Metasedimentary Belt, near the Central Metasedimentary Belt Boundary Zone. The pegmatite is small (70 m along strike; maximum width of 3.5 m), dyke-like in shape and is classified by Storey & Vos (1981) as a homogeneous granitic pegmatite. It would seem that the present exposure represents the base of a largely eroded pegmatite: the shallow workings have nearly completely removed the pegmatite (Storey & Vos 1981). As such, it is possible that the present exposure represents the wall zone of a zoned pegmatite, and not just an "unzoned" pegmatite.

The pegmatite consists dominantly of intergrown quartz and K-feldspar (crystals to 15 cm), with an albite-rich border zone. It is hosted by hornblende–biotite granitic gneiss and quartzofeldspathic paragneiss, which it cross-cuts. Accessory minerals include pervasive hornblende, and in lesser amounts, pyrite, columbite, allanite, thorite and pyrochlore.

Quadeville Beryl pegmatite

In addition to the above name, this granitic pegmatite is known as the T.B. Caldwell Occurrence (Satterly 1977), the Price Occurrence (Masson & Gordon 1981), the Wal–Gem Lapidary Company, East Quarry (Storey & Vos 1981), and the Wal–Gem East (Beryl Pit) pegmatite (Goad 1990). The pegmatite is located in lot 23, concession XV of Lyndoch Township, Renfrew County, Ontario, and is one of a small cluster of pegmatite bodies near the town of Quadeville, in the Bancroft Terrane of the CMB. It is hosted by interbanded hornblende-bearing and leucocratic granitic gneiss. It shares many features with the cogenetic Quadeville Rose Quartz pegmatite. Mineralogical and textural evidence indicates the Beryl pegmatite to be more fractionated than the Rose Quartz pegmatite: it shows a more diverse mineralogy, a more complex internal zonation, and hosts a replacement unit. Hewitt (1954) has delineated five internal units. The first four of these are designated as primary, the last as a replacement unit: (1) an albite – quartz – K-feldspar wall zone, (2) a microcline perthite intermediate zone, (3) a quartz core, (4) a K-feldspar – quartz – albite "micropegmatite", and (5) a "cleavelandite" – tourmaline – quartz unit. Earliest-formed units tend toward concentricity; however, the latest units show two styles of asymmetry. There is an along-strike asymmetry: in present and past exposures the innermost units of the east end of the pegmatite differ from those of the west end of the pegmatite. Then within the west end of the pegmatite, there is an asymmetry in the distribution of the innermost units, in part due to the disruptive effects of a replacement unit. The exact nature of the micropegmatite is uncertain: as one might expect for an intermediate unit, it concentrically occupies the central portions of the eastern end of the pegmatite; however, its cm-scale grain size makes it seem like a variety of the wall zone. In light of the limited present-day exposures of this unit and of extensive dump material, the micropegmatite seems to be a fine-grained intermediate unit: it hosts minor amounts of beryl, the albite of the unit appears to be either of a replacement origin or at least is a late fracture-filling phase in a K-feldspar – quartz matrix, and there is abundant equant columbite in the unit (misidentified in the past as smoky quartz). The accessory minerals present were described by Hewitt (1954). The list is too extensive to treat in detail here; among these minerals are euxenite-(Y) (wall zone), columbite (wall zone, micropegmatite zone), beryl (wall zone and micropegmatite zone, with greatest concentrations in inner portions of the wall zone), schorl (replacement unit), monazite-(Ce) and zircon.

Quadeville Rose Quartz pegmatite

This pegmatite is also known as the Canadian Beryllium Mines Occurrence (Masson & Gordon 1981), the Wal–Gem Lapidary Company, West Quarry (Storey & Vos 1981), the Wal–Gem West (Rose Quartz Pit) pegmatite (Goad 1990). The pegmatite is located west of the Quadeville Beryl pegmatite, in lots 30 and 31, concession XV, Lyndoch Township, Renfrew County, Ontario. The geology of the pegmatite was described by Hewitt (1954). Its exact size is not known, as it is incompletely exposed, but minimum estimates are 200 m along strike by 45 m wide. The host rocks consist of paragneiss and marble, which are cross-cut by granitic gneiss and undesignated mafic rocks (Hewitt 1954). The pegmatite is well zoned; Hewitt (1954) recognized three units: (1) a wall zone of K-feldspar, albite and quartz, (2) an intermediate zone of blocky K-feldspar and quartz, and (3) an extensive quartz core, which ranges from white to smoky to rose-colored. The exact relationship between these units and a fourth "micropegmatite" unit in the eastern workings of the body is uncertain; present-day exposures of the eastern workings are poor, and on the basis of the description of the unit in Hewitt (1954), the micropegmatite would seem to be a beryl-rich variety of the wall zone. Hewitt (1954) described the assemblage of accessory minerals, which includes abundant beryl in the eastern exposure of the wall zone, and euxenite-(Y) and columbite in both eastern and western exposures of the wall zone through to contacts with the intermediate zone.

Ryan–Sheehan pegmatite

The Ryan–Sheehan pegmatite (also known as the Ryan – Mann – Sheehan claims: Ellsworth 1922) is located in lots 1 to 3, concession VI, of Butt Township, Nipissing District, Ontario. It is one of a small swarm of muscovite-bearing granitic pegmatites in Butt Township, which is centrally located in the Kiosk Domain of the CGB. This is the only pegmatite occurrence of the present study that was not visited by the author. As the geology of the area is poorly characterized, and access difficult, the pegmatites of the region have received little attention since their only formal study by Ellsworth (1922), from which the following account of the geology of the Ryan–Sheehan pegmatite is derived. The pegmatite dyke extends in discontinuous outcrop for over 600 m, and has a maximal width of 5 m. It shows simple concentric zoning, with a finer-grained marginal K-feldspar – quartz – biotite – muscovite wall zone, a blocky K-feldspar and quartz intermediate zone, and a quartz core. Accessory minerals are concentrated in the wall zone. The widest sections of the pegmatite are the most enriched in accessory minerals, which include allanite, monazite-(Ce), uraninite, yttropyrochlore-(Y), euxenite-(Y), ferrocolumbite, chalcopyrite, pyrite and garnet.

Woodcox pegmatite

The Woodcox granitic pegmatite is located in lot 17, concession VII, Monteagle Township, Hastings County, Ontario, near the Hybla pegmatite. The host rocks are clastic metasedimentary units, carbonate units and syenitic gneiss (Storey & Vos 1981). The workings have been flooded since the early 1930s; consequently, all interpretations of the internal zoning are derived from early descriptions (Ellsworth 1932). The pegmatite is zoned, and zoning would seem to be simple: a graphic K-feldspar – quartz wall zone, a blocky K-feldspar and quartz intermediate zone (with sporadic "amazonite"), and a quartz core. Based on present-day exposures and published descriptions, it is not possible to tell whether most accessory minerals are concentrated strictly in the wall zone or continue into the intermediate zone. Accessory minerals include columbite, garnet, fluorite, schorl, allanite, pyrochlore, samarskite-(Y), fergusonite-(Y), zircon and titanite.

EXPERIMENTAL

A JEOL 733 electron microprobe with Tracor–Northern 5500 and 5600 automation was used for electron-microprobe analysis (wavelength dispersion). Operating conditions were 15 kV, 20 nA beam current, point focus to 10 μm beam diameter. All samples were examined for chemical heterogeneities by back-scattered electron imaging; the number of points analyzed per sample depended upon the degree and scale of chemical zoning. Data for standards were collected for 50 s or 0.25% precision (1σ level), whichever was attained first; data for samples were collected for 25 s or 0.5% precision. The exception to this was U, which was counted for 100 s to improve detectability. An element was considered as observed only if it was significant at the 4σ(meas.) level. Data reduction was done with a conventional ZAF routine in the Tracor–Northern TASK series of programs. Overlap of Y and Nb was corrected prior to data reduction; for W, the $M\beta$ line was used for analysis so as to avoid W–Ta overlap. The standards were: synthetic manganocolumbite (Mn$K\alpha$, Nb$L\alpha$), $NiTa_2O_6$ (Ta$M\alpha$), almandine (Fe$K\alpha$), cassiterite (Sn$L\alpha$), rutile (Ti$K\alpha$), zircon (Zr$L\alpha$), $CoWO_4$ (W$M\beta$), synthetic magnocolumbite (Mg$K\alpha$), synthetic fersmite (Ca$K\alpha$), a *REE*-bearing silicate glass (Sc$K\alpha$), various *Ln*PO_4 compounds (Ce$L\alpha$, Er$L\alpha$, Yb$L\alpha$), YIG (Y$K\alpha$), UO_2 (U$M\beta$).

Powder X-ray diffraction experiments were done with a Philips PW1965/40 powder diffractometer using Ni-filtered Cu$K\alpha$ radiation, a scan speed of ¼ °2θ/min, and annealed CaF_2 as an internal standard [a = 5.46379(4) Å]. Indexing and refinement of unit-cell parameters were done with a PC version of the CELREF program (Appleman & Evans 1973). Sharp peaks of normal width at half height were assigned unit weights; ragged or abnormally broad peaks were assigned weights of 0.1 to 0.6, depending upon the quality of the peak. Peaks that were obviously in an overlapping relationship were omitted from the refinement. Wherever possible, separate diffractograms were obtained from the core and rim of large crystals.

CRYSTAL CHEMISTRY

The composition of selected samples is given in Table 1; the total data-set is available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario

TABLE 1. REPRESENTATIVE COMPOSITIONS OF COLUMBITE-GROUP MINERALS, GRANITIC PEGMATITES, GRENVILLE PROVINCE

	1	2	3	4	5	6	7	8
MgO, *wt.%*	0.03	0.06	0.20	0.00	0.16	0.39	0.18	0.09
CaO	0.00	0.00	0.00	0.41	0.07	0.00	0.19	0.14
MnO	14.96	7.77	6.52	2.70	9.51	5.13	4.97	11.19
FeO	4.33	12.03	13.56	15.80	7.50	11.26	13.35	7.65
Sc_2O_3	1.17	0.00	0.39	0.28	0.80	0.87	0.40	0.64
Fe_2O_3	----	----	----	1.93	2.61	4.14	1.00	----
Y_2O_3	0.00	0.10	0.00	0.00	0.63	0.18	0.00	0.82
TiO_2	2.41	1.33	3.37	2.85	4.01	4.80	2.86	4.25
ZrO_2	0.00	0.15	0.13	0.00	0.00	0.00	0.18	0.40
SnO_2	0.00	0.00	0.00	0.00	0.20	0.16	0.00	0.54
UO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.31	0.00
Nb_2O_5	70.56	62.81	67.71	72.89	67.64	67.17	68.50	65.38
Ta_2O_5	6.36	14.81	7.85	2.69	4.72	5.13	5.89	7.52
WO_3	0.00	0.68	0.00	0.46	0.80	1.71	0.43	0.28
	99.82	99.74	99.73	100.01	98.65	100.94	98.26	98.90
				Cations per unit cell				
Mg	0.01	0.02	0.07	0.14	0.05	0.13	0.06	0.03
Ca	0.00	0.00	0.00	0.00	0.02	0.00	0.05	0.03
Mn	2.88	1.57	1.27	0.51	1.83	0.96	0.97	2.19
Fe^{2+}	0.82	2.40	2.60	2.95	1.42	2.09	2.58	1.47
Sc	0.23	0.00	0.08	0.05	0.16	0.17	0.08	0.13
Fe^{3+}	----	----	----	0.33	0.45	0.69	0.17	----
Y	0.00	0.01	0.00	0.00	0.08	0.02	0.00	0.10
Ti	0.41	0.24	0.58	0.48	0.69	0.80	0.50	0.74
Zr	0.00	0.02	0.01	0.00	0.00	0.00	0.02	0.05
Sn	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.05
U	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00
Nb	7.25	6.78	7.01	7.35	6.95	6.73	7.15	6.81
Ta	0.39	0.96	0.49	0.16	0.29	0.31	0.37	0.47
W	0.00	0.04	0.00	0.03	0.05	0.10	0.03	0.02
	11.99	12.04	12.11	12.00	12.00	12.00	12.00	12.09

Pegmatites (sample numbers in parentheses): 1. Blue Star (GP-3); 2. Brignall (38165); 3. Davis Mica (M31607); 4. Hybla (HS-1); 5. Quadeville Beryl (QB-91B); 6. Quadeville Rose Quartz (QR-1); 7. Ryan-Sheehan (E110-3); 8. Woodcox (M13384).

Formulae on a basis of 24 oxygens (and 12 cations for Fe^{3+}-bearing samples); "0.00": not detected; "----": not calculated.

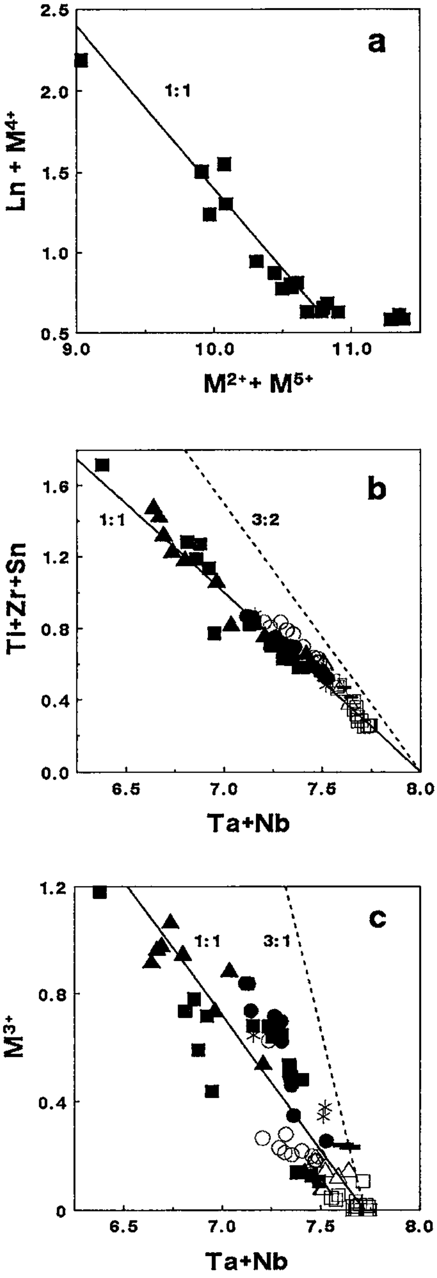

FIG. 2. Assessment of Y, Ti entry in the structure of columbite from Grenville granitic pegmatites. (a) Euxenite substitution: $M^{2+} + M^{5+} \rightarrow M^{3+} + M^{4+}$. (b) Plot of tetravalent *versus* pentavalent cations. Ti and other tetravalent cations follow a euxenite-type substitution, resulting in ordering of Ti at the *B* site (1:1 distribution), not a rutile-type substitution with disordered Ti (3:2 distribution). (c) Relative importance of euxenite (1:1) *versus* samarskite (3:1) mechanisms. In this and subsequent chemographic plots, units are atoms per unit cell, unless otherwise stated.

K1A 0S2. On the whole, samples are Nb-rich, and show moderate to low values of the ratio of Mn/(Mn+Fe). Impurity elements (*e.g.*, Sc, Ti) are commonly in minor to subordinate abundance. The cation sums of some analyses are excessively high, indicative of ferric iron; for unaltered samples that show strong evidence of ferric iron (cation sums more than 1% above ideal), the ratio Fe^{2+}:Fe^{3+} was calculated by normalizing on 12 cations and 24 anions per unit cell.

Substitution schemes

When mineral chemistry is used to evaluate the geochemistry of any system, crystal-chemical controls must be assessed before element–element variations can be interpreted from a geochemical viewpoint. This is important in (1) dealing with the absolute abundances of a trace element, or (2) trying to determine causal relationships from correlations. For example, in columbite-group minerals, if *all* Ti substitutes for Nb at the *B* site, then for charge balance a trivalent cation must substitute for Fe or Mn at the *A* site. It would be incorrect to assess Ti substitution at *B* independently of M^{3+} substitution at *A*, and similarly incorrect to assign significance to the occurrence of M^{3+} at *A* if its presence is largely due to Ti substitution at *B*.

It is difficult to assess crystal-chemical controls on concentrations of trace elements in columbite-group minerals from Grenville granitic pegmatites, as few data have been published on NYF-suite pegmatites from which to base comparisons; many of the elements reported here have not previously been reported to occur in columbite-group minerals. Consequently, the approach taken here is to infer crystal-chemical trends by comparison with structurally related phases.

(1) *Lanthanons and titanium.* Euxenite is related to columbite by the coupled substitution $A^{2+} + B^{5+} \rightarrow Ln^{3+} + Ti^{4+}$. This is a 1:1 substitution, yet the ratio of *A*:*B* cations in the columbite structure is 1:2; thus end-member euxenite necessarily has an intermediate ratio of Nb:Ti, hence the ideal formula $YNbTiO_6$. Figure 2a is a plot of $Ln^{3+} + M^{4+}$ *versus* $M^{2+} + M^{5+}$ for columbite-group minerals from the Quadeville Beryl pegmatite, the only pegmatite with consistently high concentrations of the lanthanons (*i.e.*, Y + *REE*). For high contents of $Ln^{3+} + M^{4+}$, the data have a –1 slope, which suggests that a "euxenite substitution" may be largely responsible for entry of trivalent and tetravalent cations into these samples. The validity of this operation is further supported by Figure 2b, a plot of tetravalent *versus* pentavalent cations. For a euxenite-type substitution to be valid, all Ti must (locally) order at the *B* site. In terms of Figure 2b, this scenario would result in a –1 slope; *i.e.*, all $M^{4+} + M^{5+}$ should sum to 8 cations per formula unit (pfu). The alternative, which most columbite-group minerals from pegmatites of *LCT* (*Li*–*Cs*–*Ta*) suites follow, is a rutile-type substitution. For this mechanism, Ti is disordered over the *A* and *B* sites: $A^{2+} + 2B^{5+} \rightarrow 3Ti^{4+}$. The importance of this mechanism is easily proved and detected by observing the sum of $M^{4+} + M^{5+}$. Where a rutile-type mechanism is the dominant one for entry of Ti, this sum will exceed 8 cations pfu, and where the data are plotted as in Figure 2b, they will scatter about a curve with a –3/2 slope, as the rutile-type substitution dictates. Although data for Grenville columbite tend to plot slightly above the ideal –1:1 curve, they nevertheless attest to the insignificance of a rutile-type substitution, and probable high significance of a euxenite-type substitution.

Samarskite (Warner & Ewing 1993) can generally be related to columbite by the coupled substitution $2A^{2+} + B^{5+} \rightarrow 3(Ln\text{+}Fe)^{3+}$. Thus a plot of M^{3+} *versus* M^{5+} (Fig. 2c) should serve as a measure of the relative significance of this mechanism *versus* a euxenite-type mechanism. A euxenite-type mechanism would result in a –1 slope for the data, whereas a samarskite-type mechanism should result in a –1/3 slope. The data have a –1 slope, hence the samarskite-type mechanism is relatively insignificant.

(2) *Tungsten.* As both the wolframite and columbite structures are derivatives of the ixiolite structure, it might be assumed that W enters the columbite structure by a wolframite-type substitution: $4B^{5+} \rightarrow Fe^{2+} + 3W^{6+}$. For the Grenville suite of columbite, Fe^{2+} concentrations are too high, and W concentrations too low, for this possibility to be assessed. However, inspection of W-rich columbite-group minerals from other localities (pers. comm., P. Černý) shows that entry of W is paralleled not by elevated M^{2+} contents, but rather by elevated M^{3+} contents. Figure 3, a plot of such data for columbite from the Grenville localities, shows a weak positive correlation between W and total M^{3+} cations. As entry of M^{3+} at the *A* site and W^{6+} at the *B* site would result in charge imbalance, the most likely mechanism for their entry in the columbite structure involves localization of both at the *B* site: $3B^{5+} \rightarrow M^{3+} + 2W^{6+}$. The low slope and high degree of scatter of the plot indicate that M^{3+} cations are introduced by more than this mechanism of substitution (see preceding section).

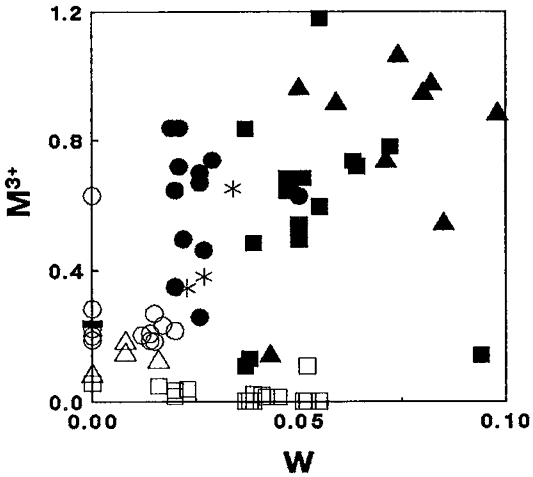

FIG. 3. Role of W in Grenville columbite. Tungsten is not introduced by a wolframite substitution involving excess Fe^{2+}, but rather by a mechanism that introduces Fe^{3+} to the *B* site. Note: an anomalous data-point with high W has been removed to emphasize variations at low W contents.

Subsolidus phenomena

The cooling histories of some of the samples of columbite-group minerals have resulted in complex textures. Samples from the Woodcox pegmatite show exsolution lamellae of samarskite in columbite (Fig. 4). Although energy-dispersion X-ray spectra unambiguously confirm their identity, the lamellae of samarskite are too fine for accurate quantitative analysis.

Most samples from the Quadeville Rose Quartz pegmatite and one sample from the Ryan–Sheehan

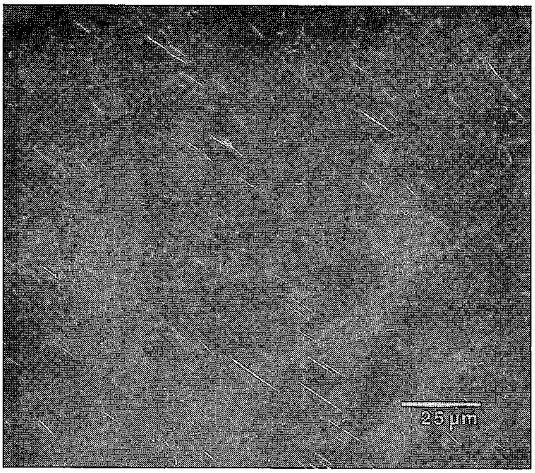

FIG. 4. Back-scattered-electron image of exsolution lamellae of samarskite in columbite.

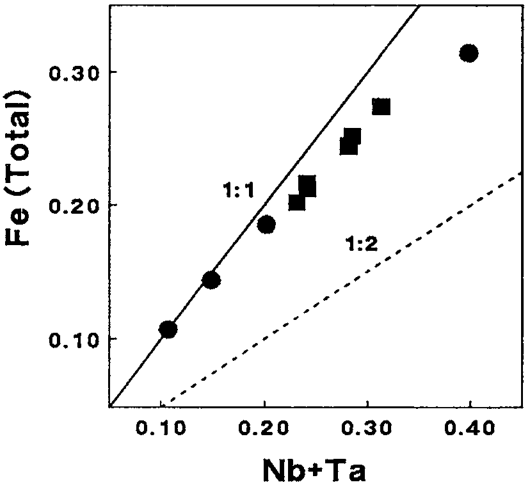

FIG. 6. Composition of rutile associated with columbite-group minerals. The data indicate a prevalence of Fe^{3+} (1:1 trend) over Fe^{2+} (1:2 trend) for charge balance against Nb and Ta.

pegmatite show what appears to be exsolution of a $FeNbO_4$ component (with or without rutile). Textures in these samples are relatively coarse, so that several electron-microprobe analyses were obtained. Some samples from the Quadeville Beryl pegmatite show evidence of exsolution of rutile. The combined data (Fig. 5) show evidence of a large three-phase region in the system $TiO_2 - FeNb_2O_6 - FeNbO_4$. This phenomenon and the phase $FeNbO_4$ have not previously been reported for columbite-group minerals and associates; comparison with synthesis studies is impossible, as this system has not been investigated. Phase relations along the AB_2O_6–MO_2 sideline (for M = Ti and with Nb >Ta at B), inferred from compositional and textural data for natural samples, indicate the presence of a large miscibility gap (Černý & Ercit 1985). The lack of natural occurrences of $FeNbO_4$ is worth consideration: do the textures shown by the present samples represent (1) exsolution indicative of extensive solubility of a $FeNbO_4$ component (and a TiO_2 component) in the ixiolite structure at high temperature, (2) subsolidus oxidation, such as is responsible for coexisting (hematite–ilmenite)$_{ss}$ and (magnetite–ülvospinel)$_{ss}$ pairs (Buddington & Lindsley 1964), or (3) some combination of both extremes? Whatever the case, the high proportion of Fe^{3+} (calc.) and identity of the unknown phase as $FeNbO_4$ are independently confirmed by preliminary X-ray-diffraction investigation, and by the chemistry of rutile in these intergrowths (Fig. 6). The ratio of Fe(total):(Ta+Nb) is very close to 1:1, indicating that a $FeNbO_4$-type substitution dominates over the usual ferrocolumbite-type ($FeNb_2O_6$) substitution (1:2 ratio) for entry of Fe, Nb and Ta in the rutile.

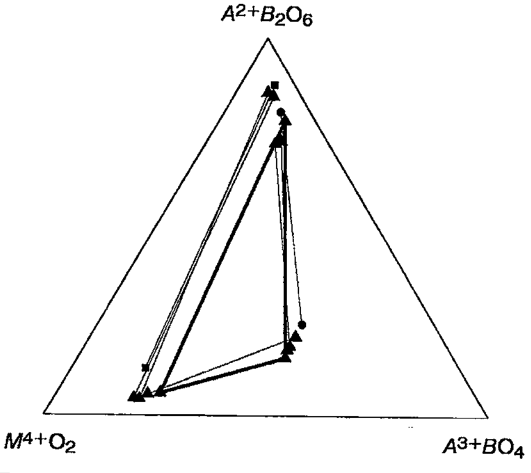

FIG. 5. Compositions of columbite-group minerals and associated rutile and $FeNbO_4$ solid-solution; coexisting pairs are in fine rule, and triplets (one set) are in heavy rule.

Unit-cell parameters

Both structural state and composition are variable for columbite-group minerals (Černý & Ercit 1989). In assessing the degree of order, and in making rudimentary estimates of the Fe:Mn ratio of columbite-group minerals, it is customary to examine the variation of the a and c cell edges of the minerals. Figure 7 is one such plot for columbite-group minerals from Grenville

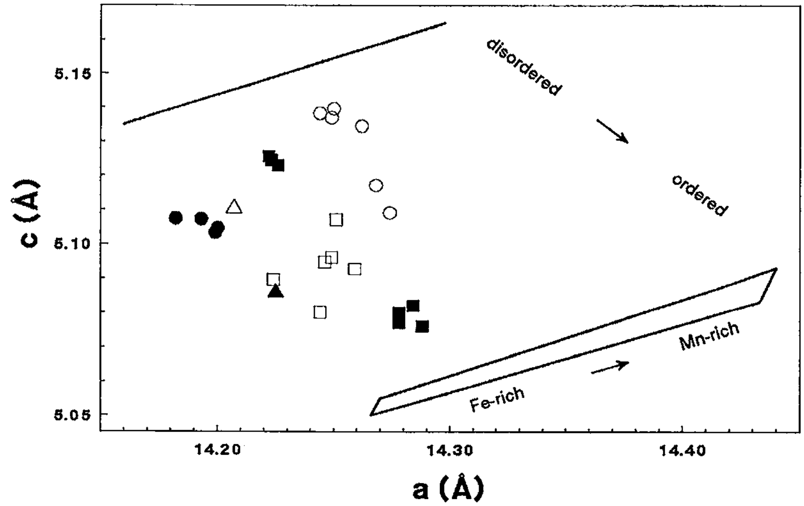

FIG. 7. An *a* – *c* diagram for columbite-group minerals from Grenville pegmatites. The line at the top of the diagram represents the anticipated upper bound for (fully) disordered samples; the box at the bottom of represents the range for ordered impurity-free samples (Wise *et al.* 1985). Iron-rich samples plot at low values of *a*, Mn-rich samples at higher values of *a*.

pegmatites, and the data are presented in Table 2. As a whole, the samples show a broad variation in chemistry and structural state, with little clustering about the field. Examination of samples from individual bodies of pegmatite shows that there is no norm. Samples from the Woodcox and Quadeville Beryl pegmatites show little variation in Fe:Mn ratio, but broad variations in structural state. Samples from the Brignall pegmatite show moderate variation in both chemistry and structural state. The samples from the other pegmatite bodies studied by X-ray diffraction are too few in number to assess their limited variations.

TABLE 2. UNIT-CELL PARAMETERS (Å) FOR COLUMBITE-GROUP MINERALS

Sample	*a*	*b*	*c*	Notes	Pegmatite
M13190	14.268(3)	5.731(1)	5.117(1)		Woodcox
M13384	14.274(4)	5.732(1)	5.109(1)		Woodcox
E299	14.262(4)	5.734(1)	5.135(1)	r	Woodcox
E299	14.249(3)	5.735(1)	5.137(1)	c	Woodcox
E87	14.244(2)	5.737(1)	5.138(1)	c	Woodcox
E87	14.250(3)	5.739(1)	5.140(1)	r	Woodcox
BM-20	14.251(3)	5.735(1)	5.107(1)	c	Brignall
BM-20	14.259(3)	5.734(1)	5.093(1)	r	Brignall
BM-2	14.249(6)	5.734(3)	5.096(2)		Brignall
GP-1-G	14.244(3)	5.731(1)	5.080(1)		Brignall
38122	14.246(2)	5.733(1)	5.095(1)		Brignall
31001	14.224(6)	5.729(2)	5.089(2)		Brignall
QB-8	14.278(2)	5.727(1)	5.077(1)	m	Quadeville Beryl
QB-20	14.278(3)	5.731(1)	5.080(1)	m	Quadeville Beryl
QB-91C	14.284(3)	5.732(1)	5.082(1)	m	Quadeville Beryl
QB-91D	14.288(3)	5.731(1)	5.076(1)	m	Quadeville Beryl
E126	14.223(6)	5.725(2)	5.124(2)	w,c	Quadeville Beryl
E126	14.226(5)	5.722(1)	5.123(1)	w,r	Quadeville Beryl
E126-2	14.222(4)	5.723(1)	5.126(1)	w	Quadeville Beryl
QR-3	14.225(2)	5.718(1)	5.086(1)		Quadeville Rose Qz
M31607	14.207(3)	5.727(1)	5.110(1)		Davis Mica
E110-1	14.199(3)	5.720(1)	5.103(1)		Ryan-Sheehan
E110-2	14.193(3)	5.721(1)	5.107(1)		Ryan-Sheehan
E110-3	14.182(4)	5.722(1)	5.107(1)		Ryan-Sheehan
E111	14.200(3)	5.722(1)	5.105(1)		Ryan-Sheehan

Notes. c: core, r: rim, m: micropegmatite, w: wall zone

Although much attention has been given to chemical variations in oxide minerals, considerably less has been directed toward study of variations in the structural state of oxide minerals during crystallization of a pegmatite body. By analogy with studies of mineral chemistry, three obvious directions for study exist: variation (1) across a pegmatite group, (2) across an individual body of pegmatite, and (3) within individual crystals. To date, only the first two courses have been followed, and results are seemingly diverse: Wise (1987) examined the structural state of columbite-group minerals from Yellowknife, and found regional variations to be nonsystematic. However, Černý *et al.* (1986), in a study of columbite-group minerals from the Greer Lake (Manitoba) pegmatitic granite and its derived pegmatites, found the degree of order of samples of columbite-group minerals to decrease with distance from the pegmatitic granite. Černý & Ercit (1985: Plex pegmatite, Baffin Island) and Černý *et al.* (1985: Peerless pegmatite, South Dakota) documented cases of nonsystematic variation of the degree of order of samples of columbite-group minerals within individual bodies of granitic pegmatite. However, Ercit (1986) showed that both columbite-group and wodginite-group minerals from the Tanco pegmatite attained higher degrees of cation order with the crystallization of successive units of the pegmatite.

As columbite-group minerals are not widely distributed across groups of granitic pegmatites in the Grenville Province, it is not possible to use the chemistry or structural properties of these minerals to study regional zoning of pegmatites. However, columbite-group minerals are occasionally found distributed across several units of individual pegmatites (*e.g.*, in the Brignall and Quadeville Beryl pegmatites), and are locally large enough for studies of internal zoning. Consequently, the latter two styles of distribution were studied.

Problems exist with the application of this type of study to structural variations across individual pegmatites and within single crystals. For instance, changes in structural state can occur rapidly in the crystallization history of a pegmatite. For the Tanco pegmatite (Ercit 1986), the bulk of variation in cation order for wodginite-group minerals occurs during the crystallization of one unit of the pegmatite. The same is true for columbite-group minerals; however, the variation occurs within a different internal unit of the pegmatite. The implication is that in order for structural variations to be detected, it is important to have a broad sampling. The converse is obvious, but requires statement: a null answer must not be interpreted as invariate unless it can be shown that the sampling adequately represents the population.

Of the two pegmatites that have columbite-group minerals distributed across more than one internal unit (Quadeville Beryl and Brignall), only the Quadeville Beryl shows a systematic variation in structural state with internal pegmatite zoning. In this particular case, samples from the wall zone are significantly less ordered than samples from the micropegmatite zone. This trend parallels (normal?) zoning shown by the Tanco pegmatite (Ercit 1986). The implication is that the micropegmatite zone crystallized later than the wall zone, which supports the interpretation presented earlier (see *Location and Geology*).

The study of intracrystalline zoning in structural state is limited by the scarcity of large crystals needed for accurate powder diffractometry. For the present study, only four crystals were found to be suitable. Although most of these show no significant internal variation in structural state, one crystal from the Brignall pegmatite shows a significant increase in the degree of cation order from core to rim (sample BM–20), which is consistent with anticipated normal zoning within pegmatites. This sample shows that the onset of significant degrees of cation ordering can occur during the growth of individual crystals. Detailed study of structural zoning within single crys-

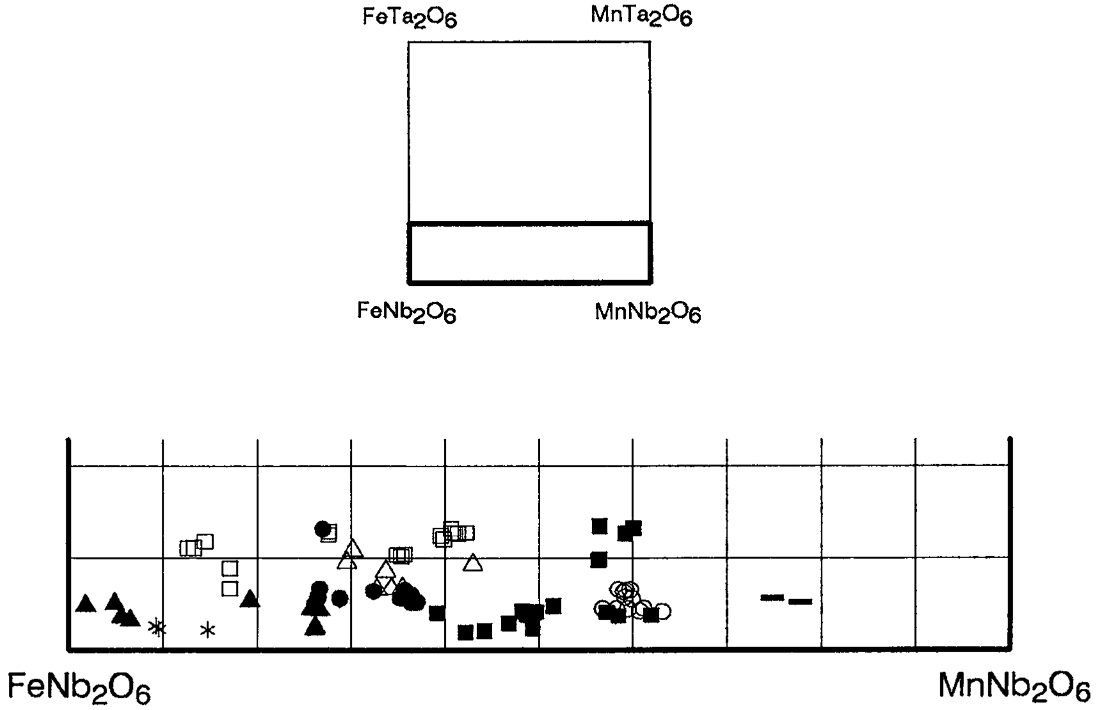

FIG. 8. Composition of Grenville columbite-group minerals in the columbite quadrilateral (mole %). Inset: bounds of the quadrilateral. Magnification: Grenville samples with grid lines at 10% intervals.

tals of columbite-group minerals would seem to have the potential of providing valuable information on how crystals of columbite-group minerals physically respond to local changes in melt conditions or late fluids.

GEOCHEMISTRY

The main constituents of columbite-group minerals are Fe, Mn, Nb and Ta. The element pairs Ta–Nb and Mn–Fe commonly are used to delineate fractionation trends in granitic pegmatites; fractionation tends to result in an increase in Mn at the expense of Fe and in Ta at the expense of Nb. For columbite-group minerals, variations in these elements are typically expressed graphically in the columbite quadrilateral (Černý & Ercit 1985, 1989). The representation for the Grenville suite is given in Figure 8. The samples show a broad range of Fe:Mn values, but a very limited variation in Ta:Nb, showing a low average Ta/(Ta+Nb). The data set as a whole would seem to imply that Grenville pegmatites show only Fe *versus* Mn fractionation and no Nb *versus* Ta fractionation; however, careful scrutiny of Figure 8 shows significant fractionation of Nb *versus* Ta within individual pegmatites, *e.g.* Quadeville Beryl pegmatite, where Nb/Ta (atomic) ranges from 53 to 7. Comparison of Figure 8 to broad compilations (Černý & Ercit 1985, 1989) shows the compositions of columbite in the Grenville suite to be anomalous: the Grenville data set extends from the $FeNb_2O_6$ corner toward the $MnNb_2O_6$ corner, which corresponds to a compositional void in these broad compilations. The lack of (published) compositions in this region may not have any geochemical significance; as columbite-group minerals from NYF pegmatites do not tend to be studied as closely or commonly as those from LCT pegmatites, the gap most likely represents a sampling bias.

On the whole, the timing of Fe *versus* Mn fractionation relative to Nb *versus* Ta fractionation shows some variation. The lack of correlation between Mn/(Mn+Fe) and Ta/(Ta+Nb) for most pegmatites shows that Fe *versus* Mn fractionation tends to take place at a different time (earlier) in the formation of these pegmatites than the bulk of Nb *versus* Ta fractionation. However, the good positive correlation between Mn/(Mn+Fe) and Ta/(Ta+Nb) for samples from the Quadeville Beryl pegmatite shows concomitant Fe *versus* Mn and Nb *versus* Ta fractionation for much of the crystallization history of this pegmatite.

Although the behavior of Fe, Mn, Nb and Ta during pegmatite crystallization is relatively well-characterized, the behavior of minor and trace elements in columbite-group minerals is poorly understood: data for the behavior of Sn, Ti and Sc in individual pegmatites and pegmatite groups have been published (*e.g.*, Černý *et al.* 1986), but data for the behavior of W, Mg, Y, U and Ca are largely lacking. Columbite-group minerals from the Grenville pegmatites host electron-microprobe-measurable concentrations of all of these elements; consequently, the present study affords an opportunity to examine the behavior of trace and minor elements with Nb *versus* Ta and Fe *versus* Mn fractionation.

Mg

Magnesium enters the columbite structure at the *A* site as a substituent for Fe and Mn. Magnesium-dominant columbite (≡ magnocolumbite) is rare, and seems to owe its origin to assimilation of dolomitic marble by granitic magma (Černý & Ercit 1985). Because it tends to occur in trace concentrations in the vast majority of columbite-group minerals, Mg is typically not reported in analyses. For most pegmatites of the present study, Mg does not show any systematic behavior during fractionation, as monitored by Ta/(Ta+Nb) or Mn/(Mn+Fe), perhaps owing to the influence of phases competing with the columbite-group minerals for Mg. However, samples from the Brignall and Quadeville Beryl pegmatites show a systematic decrease in Mg content with Fe *versus* Mn fractionation, to the extent that Mg is no longer detectable in the latest compositions to crystallize (Fig. 9c). That Mg behaves similarly with respect to Ta/(Ta+Nb) and Mn/(Mn+Fe) for samples from the Quadeville Beryl pegmatite further reinforces the earlier observation that much of the fractionation of Mn over Fe and of Ta over Nb was concomitant in this pegmatite body. Furthermore, the linear variation of Mg with respect to Mn/(Mn+Fe) *versus* the logarithmic variation of Mg with respect to Ta/(Ta+Nb) [initial sharp depletion of Mg followed by sharp increase in Ta/(Ta+Nb)] shows that the bulk of the Nb *versus* Ta fractionation tends to lag behind Fe *versus* Mn fractionation in this case. The Davis Mica pegmatite shows unusual behavior of Mg, which increases with fractionation of Ta over Nb (Fig. 9b). As data for this pegmatite represent zoning within a single sample, it would not seem prudent to overly emphasize the trend: reverse Mg zonation is observed; whether it is due to late assimilation, competition for Mg between coprecipitates, local disequilibrium, or other factors is not known.

Ca

Like Mg, calcium enters the columbite structure at the *A* site. Calcium-dominant columbite (≡ fersmite) is similarly rare; as a primary phase, it is typically found in poorly fractionated examples of the rare-element class of granitic pegmatites (Černý & Ercit 1985, Černý 1991, E.E. Foord, pers. comm.). Fersmite tends to be ordered, presumably owing to the greater discrepancy in ionic radius between Ca and Nb than between Fe^{2+} and Nb. Most columbite-group minerals *sensu stricto* have extremely low concentrations of Ca, to the extent that the element commonly is not detectable by electron microprobe. Most of the samples of the present study have no detectable Ca, and only samples from two pegmatite bodies show any systematic variation in Ca with respect to obvious indicators of fractionation. Surprisingly, that systematic variation is found with respect to Nb *versus* Ta fractionation, not Fe *versus* Mn fractionation (Fig. 9a). For one of these, the Woodcox pegmatite, this finding is understandable: no appreciable enrichment in Mn is recorded by columbite-group minerals. However, for the other, the Quadeville Rose Quartz pegmatite, Mn enrichment is appreciable. Nevertheless, the logarithmic variation of Ca relative to Ta/(Ta+Nb) indicates that in both pegmatites, Ca is rapidly extracted from the melt, before most of the enrichment in Ta takes place.

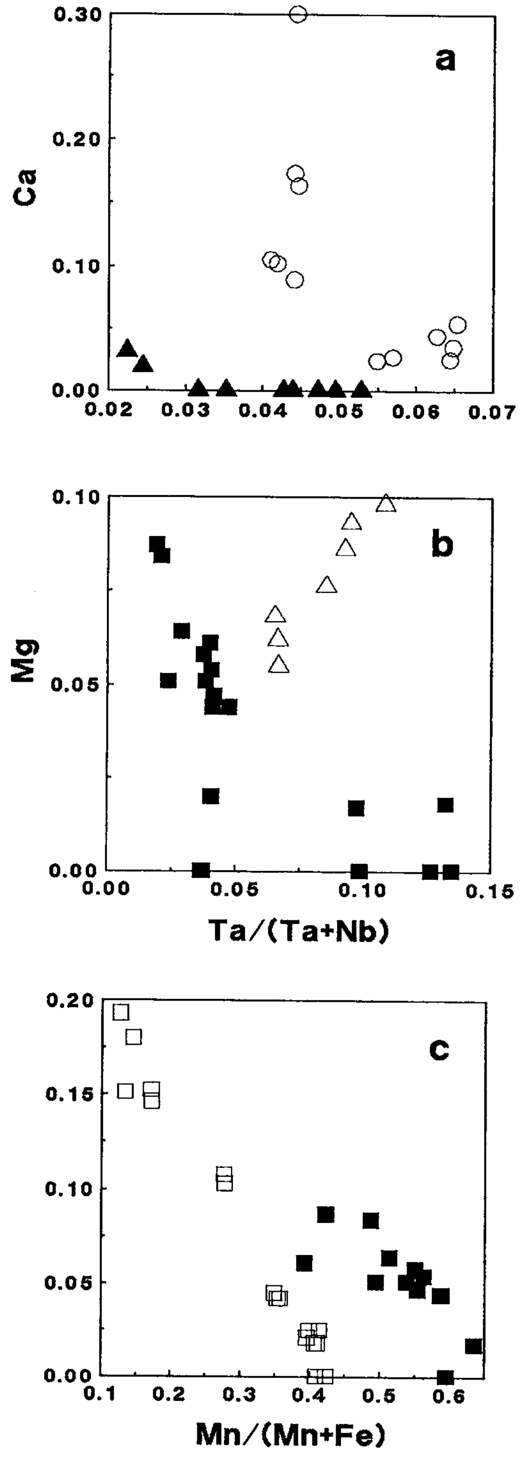

FIG. 9. Geochemical behavior of Ca and Mg in Grenville columbite. For this and following plots, pegmatites without significant correlations are not shown.

Sc

Columbite-group minerals are strong concentrators of Sc. Scandium is intermediate in charge and size to Fe and Nb; consequently, it is expected to disorder over the *A* and *B* sites of the columbite structure. As one would expect, high contents of Sc are favored by a disordered arrangement of cations (*i.e.*, the ixiolite structure). The behavior of scandium in granitic pegmatite systems is enigmatic. Foord *et al.* (1993) proposed that Sc behaves compatibly in most granitic melts, but that for systems rich in Sc, the element may be concentrated during late stages of melt evolution. Černý *et al.* (1986) described two possible mechanisms to account for Sc enrichment in pegmatites relative to their parental granites: (1) thermal stability of Sc complexes in parental granites, *versus* their relative instability in the (lower-temperature) derivative pegmatites; (2) acquisition of Sc *via* assimilation during migration of pegmatite-forming melts through metabasic country-rocks. For the amphibolite-hosted Tanco pegmatite, Manitoba (Ercit 1986), an assimilation origin is possible, and is supported by the behavior of scandium during the evolution of the pegmatite: the Sc contents of columbite-group minerals drop rapidly with the crystallization of successive units of the pegmatite. For the Greer Lake pegmatite group, Manitoba, with its host tonalitic and granitic gneisses, an assimilation origin for Sc is highly unlikely, and mechanism (1) seems most likely (Černý *et al.* 1986).

Figure 10 shows the behavior of Sc during crystallization of the Grenville pegmatites. Unlike the highly fractionated Tanco pegmatite, Sc in these poorly fractionated pegmatites tends most commonly to *increase* rather than decrease with Ta fractionation. The exception is the Brignall pegmatite, in which Sc shows no correlation with Ta/(Ta+Nb), but shows a negative correlation with Mn/(Mn+Fe) (Fig. 10b); *i.e.*, Sc

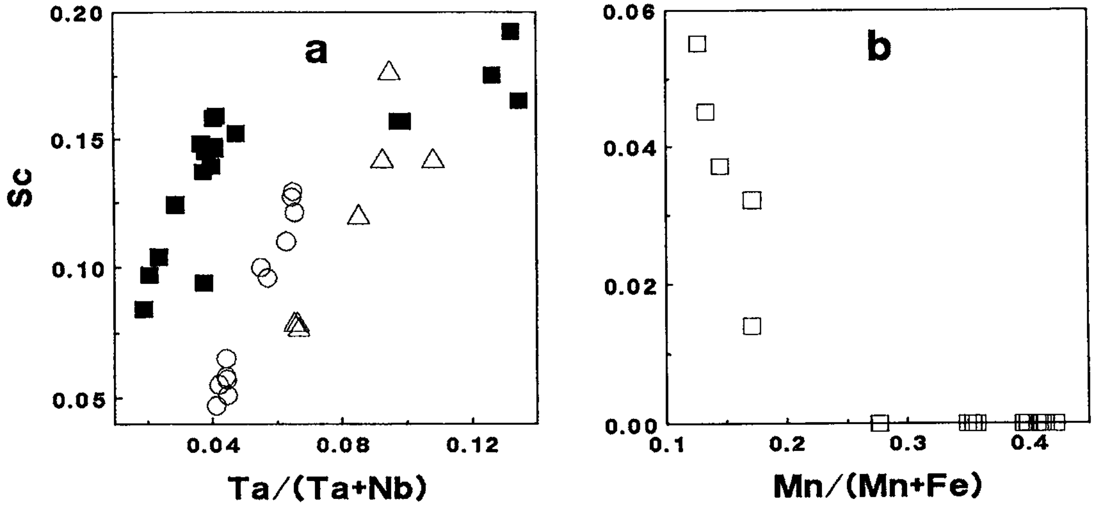

FIG. 10. Geochemical behavior of Sc in columbite, Grenville granitic pegmatites.

decreases with Mn enrichment. The most likely interpretation of the trends is that for most melt compositions that produced these pegmatites, Sc behaved incompatibly (*i.e.*, Sc complexes were stable and Sc persisted to later stages of crystallization); however, for a few compositions, of which the Brignall pegmatite is representative, the melt composition is such that Sc complexes were not stable, and Sc was incorporated into the earliest products of crystallization. The behavior of Sc described by Foord *et al.* (1993) does not seem to hold here. Scandium tends to behave incompatibly, although (1) the Grenville suite of pegmatites shows low to moderate enrichment in Sc [*cf.* von Knorring *et al.* (1969), Borisenko *et al.* (1969) for columbite-group minerals enriched in Sc; also: the pegmatites do not host Sc-excess phases like thortveitite or bazzite], and (2) the examples of Sc-concentrating columbite are early to intermediate products of crystallization of the pegmatite, not late. However, in agreement with Foord *et al.* (1993), the Brignall pegmatite, least enriched in Sc for the suite, is also the only body for which Sc behaves compatibly. Little more can be concluded until considerably more data are accumulated on the detailed behavior of Sc in granitic pegmatites.

Lanthanons

The behavior of the lanthanons in the columbite structure has not been previously documented. For the present data-set, Y is invariably the most abundant lanthanon, with the *REE* in trace to undetectable concentrations. The *HREE* tend to be more abundant than the *LREE*. Ytterbium is the most abundant *HREE*; the occasional high relative abundance of Ce might be due to secondary alteration, further supported by elevated Ca contents in these samples. Data for lanthanons in columbite of the Grenville suite are shown in Figure 11. Although it might be assumed that the lanthanons behave similarly to Sc, Figure 11 shows that this is rarely the case: for most pegmatites, there is no correlation between concentrations of Sc and *Ln*, for two of the pegmatites there is a negative logarithmic correlation between Sc and *Ln* (Fig. 11c), and for only one pegmatite (Quadeville Beryl) there is a positive logarithmic correlation between Sc and *Ln*. That the correlations are logarithmic and that $X_{\mathrm{Sc}}^{\mathrm{columbite}}$ increases mostly during the bulk of Ta enrichment indicates that most variation in *Ln* preceded variation in Sc. Correlations among concentrations of *Ln*, U and Ca are also shown in Figure 11. These correlations may in part be due to crystal-chemical entry of all three elements into the columbite structure as a euxenite component (see *Substitution Schemes*).

Tetravalent cations

Titanium is a common impurity element in columbite-group minerals. In many granitic pegmatites, Ti behaves compatibly, and is partitioned into the earliest-formed minerals, or is concentrated in the core of zoned crystals. Ti is expected to largely or wholly substitute at the *B* site; thus negative correlations with the total number of M^{5+} cations are observed (see Fig. 2b). Correlations between Ti and the fractionation indicators Ta/(Ta+Nb) and Mn/(Mn+Fe) are shown in Figure 12. Most columbite-group minerals from Grenville pegmatites show normal behavior of Ti; *i.e.*, $X_{\mathrm{Ti}}^{\mathrm{columbite}}$ decreases with fractionation (Brignall, Davis Mica, Quadeville

Rose Quartz pegmatites) or shows no significant change with fractionation (Woodcox, Ryan–Sheehan pegmatites). However, the Quadeville Beryl pegmatite shows Ti enrichment with both Nb *versus* Ta and Fe *versus* Mn fractionation. This is also reflected in the mineralogy of the pegmatite: rutile seems to be more abundant in the micropegmatite than the wall zone.

Figure 13 shows all significant correlations between Ti and other tetravalent cations (Sn, Zr, U). In all cases, the sign of the correlation is positive, indicating that Sn, Zr and U largely behave like Ti. The only exception exists for Sn: for columbite-group minerals from the Woodcox pegmatite (Fig. 14), Sn does not behave like Ti (Fig. 14c; no correlation) or U (Fig. 14b; negative correlation) and instead behaves like Ta (Fig. 14a).

The uranium contents of the columbite in this suite are very different from those of columbite-group minerals from most other pegmatite localities. Romer &

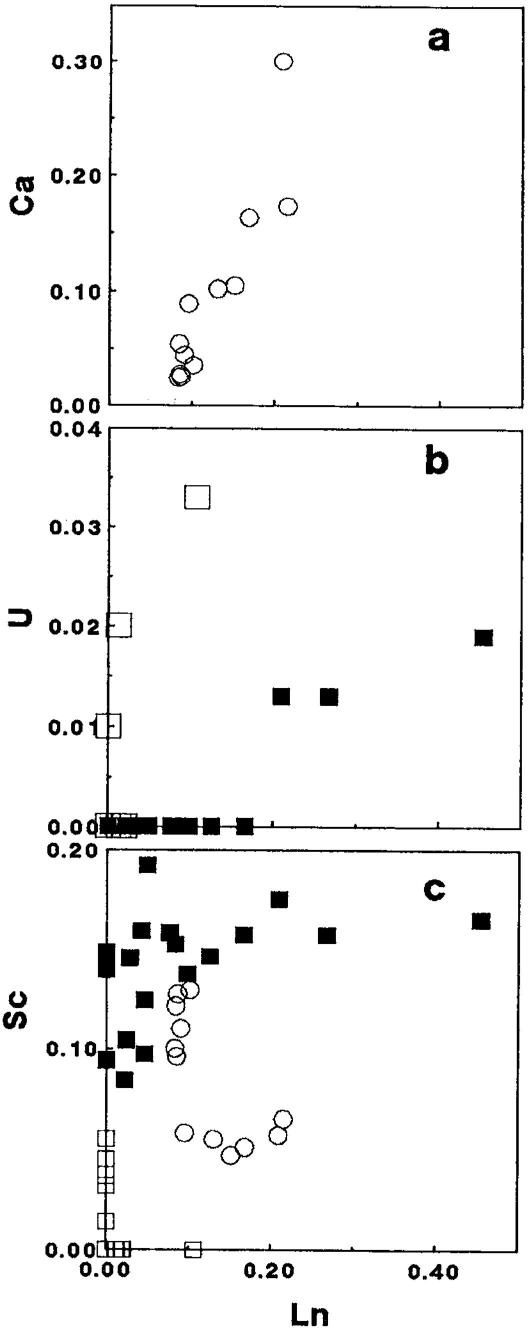

FIG. 11. Significant correlations involving lanthanide elements in columbite, Grenville granitic pegmatites.

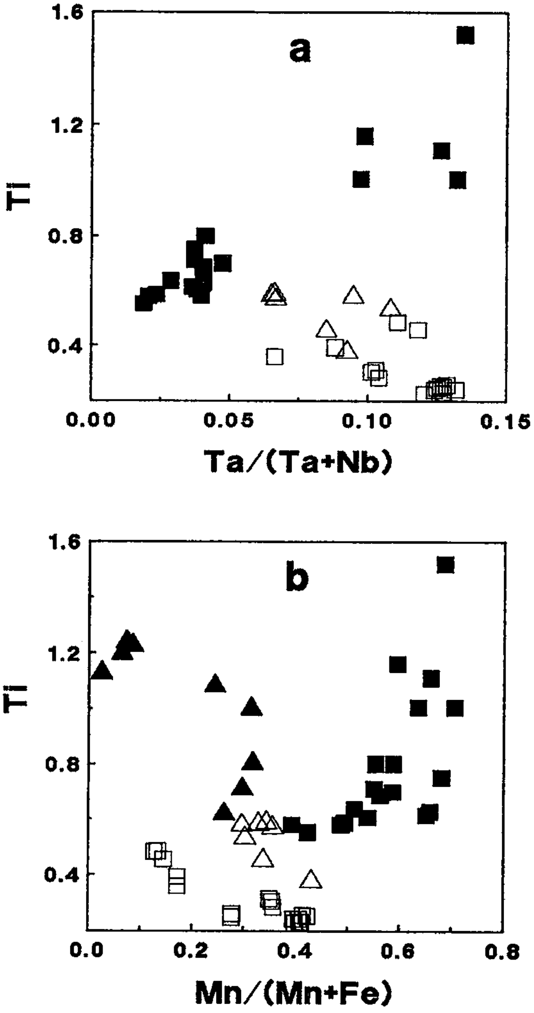

FIG. 12. Geochemical behavior of Ti in columbite, Grenville granitic pegmatites.

Wright (1992) reported that columbite-group minerals have (maximal) U concentrations in the range 500–1000 ppm; however, columbite-group minerals from the Grenville pegmatites examined have U concentrations commonly in excess of this range, with an upper limit of 9000 ppm. Samples with high Y and U contents commonly show evidence of exsolution of a samarskite component (Fig. 4); thus (*Ln*,U)-rich columbite-group minerals would seem to be stable only at relatively high temperatures. Figure 15 shows

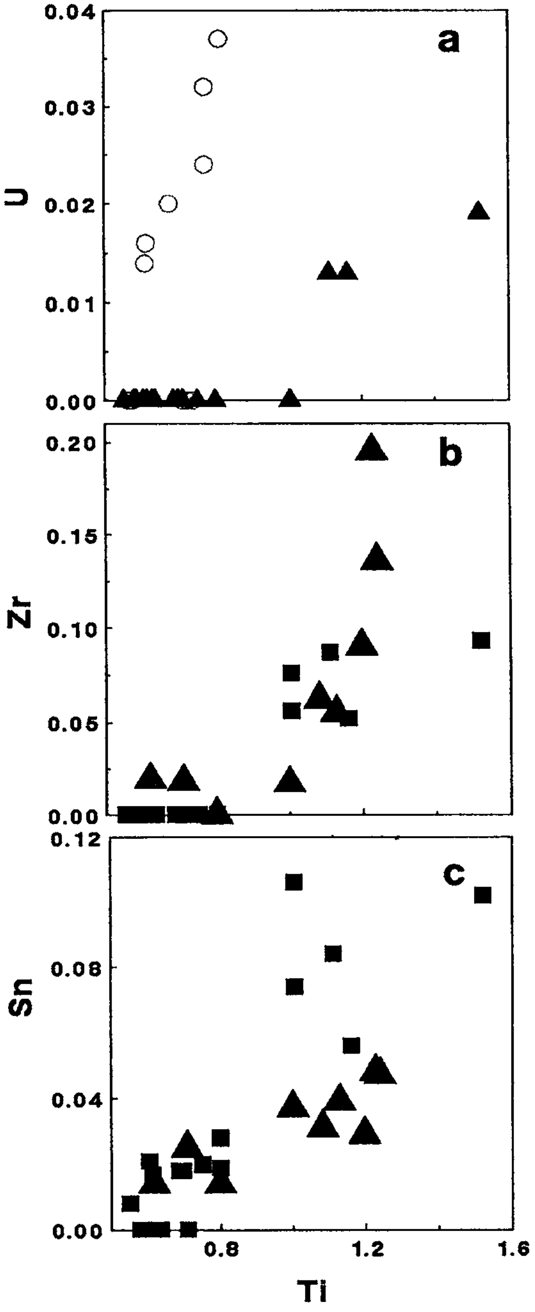

FIG. 13. Significant correlations involving Ti in columbite, Grenville granitic pegmatites.

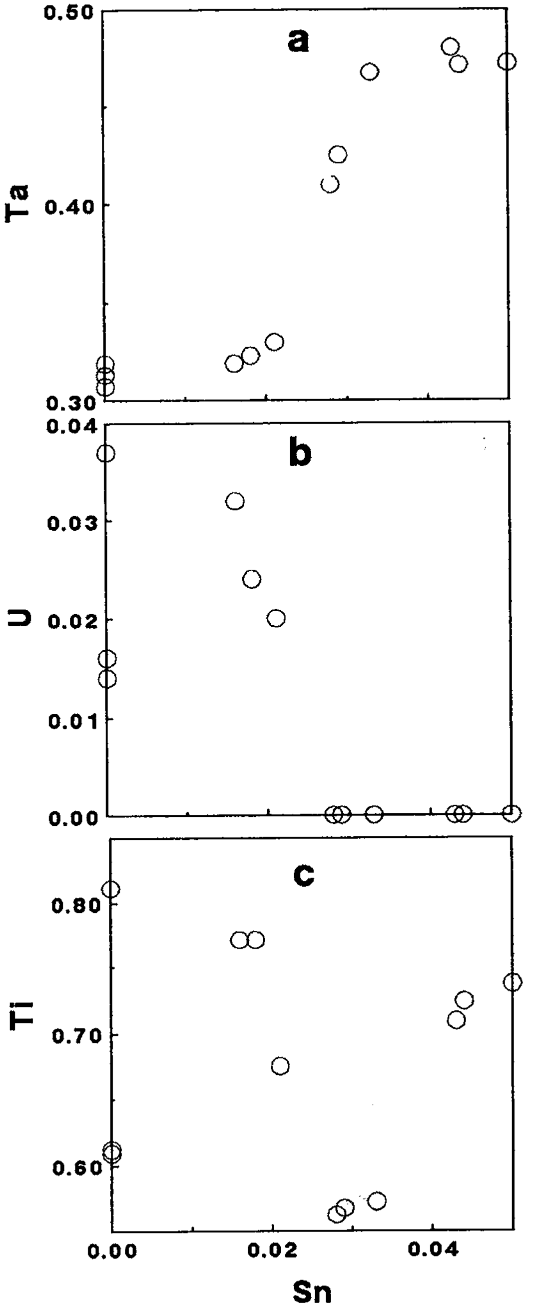

FIG. 14. Correlative data for Sn; all samples are from the Woodcox pegmatite.

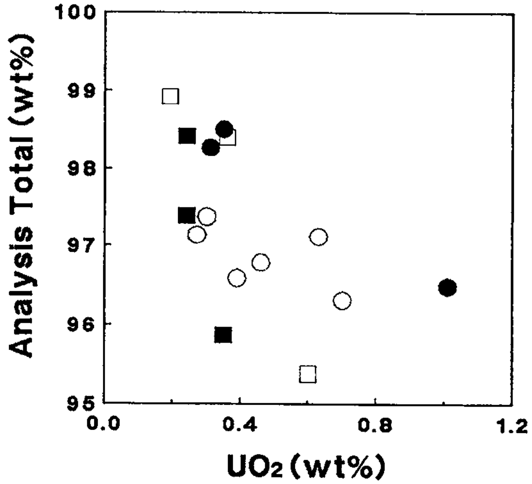

FIG. 15. Radiation damage in U-bearing columbite-group minerals from Grenville pegmatites, as monitored by analytical totals.

that as U contents increase, analytical sums drop; presumably high degrees of α-particle bombardment result either in an increase in adsorbed water or in the porosity of the samples, thus lower analytical sums. However, as none of the U-bearing samples is metamict, it is anticipated that much of the α-particle bombardment does not appear to affect the crystallinity of the samples as monitored by X-ray diffraction; *i.e.*, aperiodic regions are anticipated to be relatively minor in volume.

W

The occurrence and behavior of tungsten in oxide minerals from granitic pegmatites are poorly documented. This is in part due to the low concentrations of W that tend to occur in oxide minerals from granitic pegmatites, but may also in part be due to analytical oversight: W is difficult to detect in the energy-dispersion spectra of Ta- and Nb-bearing oxide minerals, and thus might not be sought in many cases.

Correlations involving W are shown in Figure 16. Variations in tungsten correlate in most cases with Ta/(Ta+Nb), where without exception the trend is toward higher W and Ta contents at the expense of Nb (Fig. 16a). Samples from the Brignall pegmatite show a well-defined increase in $X_W^{columbite}$ with enrichment of Mn relative to Fe (Fig. 16b). Samples from the Quadeville Beryl and Quadeville Rose Quartz pegmatites show a negative correlation between W and Ti (Fig. 16c), which indicates that W does not behave similarly to the tetravalent cations during crystallization of columbite. It is most likely that W behaved like Ta in these pegmatites; *i.e.*, for the geochemistry of this category of pegmatite, crystal–liquid fractionation was not effective in separating the two elements.

CONCLUSIONS

(1) Columbite-group minerals from granitic pegmatites of the Grenville Province have an unusual minor- to trace-element chemistry; samples tend to host Zr, U, Mg, W, and Y. Niobium:tantalum ratios are variable, but consistently high; Mn-for-Fe substitution is variable, ranging from extremely Fe^{2+}-dominant to moderately Mn-dominant. The lanthanons and titanium enter the structure by a euxenite-type mechanism of substitution. Tungsten enters not by a coupled wolframite-type substitution mechanism involving both the *A* and *B* sites, but rather together with Fe^{3+} at the *B* site.

(2) Samples with high Y and U contents show evi-

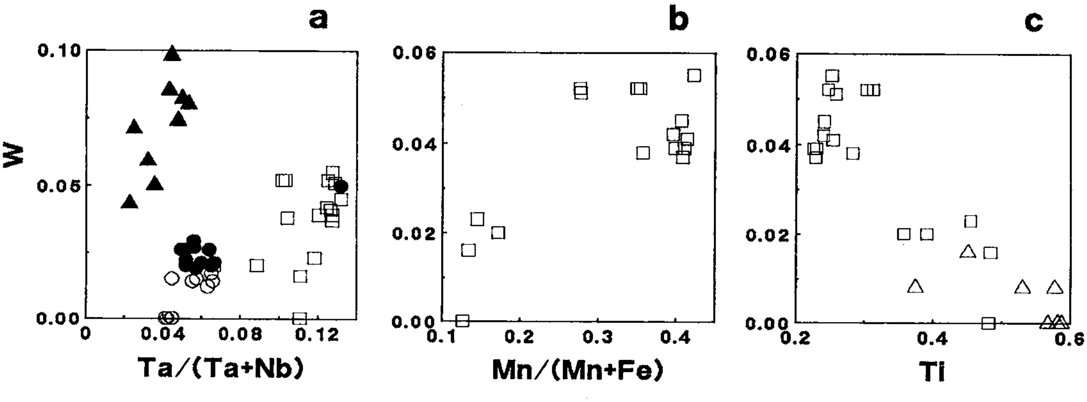

FIG. 16. Geochemical behavior of W in columbite, Grenville granitic pegmatites.

dence of exsolution of a samarskite component. Samples consisting of a rutile – columbite – $FeNbO_4$ intergrowth may represent exsolution or subsolidus oxidation.

(3) Columbite-group minerals from granitic pegmatites can show systematic variations in their structural state with respect to zoning at a variety of scales: regional among pegmatite bodies, internal within a single body, and intracrystalline zoning. This study of Grenville pegmatites outlines some structural variations in columbite-group minerals that correlate with zoning in a given body of pegmatite, and with intracrystalline zoning.

(4) Although granitic pegmatites from the Grenville Province generally achieve low to moderate degrees of fractionation, the geochemical expressions of fractionation are detectable and can be used to monitor and evaluate the internal evolution of these pegmatite bodies. The occurrence, chemistry and structural properties of columbite-group minerals in the Quadeville Beryl pegmatite show that the micropegmatite unit is not just an equigranular variety of the wall zone, but rather an evolved, intermediate unit of the pegmatite.

(5) The correlation of variations in trace-element chemistry with the fractionation indicators Nb *versus* Ta and Fe *versus* Mn indicates that Grenville pegmatites show measurable and significant geochemical changes during their evolution, and that trace elements behave systematically during the internal evolution of these pegmatites. Table 3 summarizes trace-element behavior for the six well-sampled pegmatites of the study. Comparison along rows of the table shows that trace elements do not tend to behave consistently from pegmatite to pegmatite, despite the fact that all pegmatites roughly represent one genetic type (columbite-bearing). Comparison with LCT pegmatites would lead one to expect that Mg, Ca, Sc and Ti should decrease with fractionation. Some reversals of these trends, for example the behavior of Mg in columbite-group minerals from the Davis Mica pegmatite, may simply be an artifact of sampling, and may represent local reversals in the normal behavior of these elements. However, for well-sampled sites like the Quadeville Beryl pegmatite, there can be no doubt that some elements (*e.g.*, Ti) show reverse behavior. Compared to LCT pegmatites, either different mechanisms of fractionation operate for some of these NYF-suite Grenville pegmatites, or the complexing behavior of certain minor elements in some pegmatites is different (given the potentially different composition of the volatile phase of NYF pegmatites as compared to LCT pegmatites). As the wealth of data available for the LCT pegmatites has only gradually furthered the state of knowledge on the mechanisms and causes of fractionation in these systems, clearly more data are needed for NYF pegmatites before inferences can be made about the mechanisms operating in these systems.

TABLE 3. SUMMARY OF TRACE-ELEMENT GEOCHEMICAL CORRELATIONS

Mg	↓	↓	↑			↓						
Ca							↓				↓	
Sc		↓	↑		↑						↑	
Ti	↓	↓	↓	↓	↑	↑		↓				
W	↑	↑					↑		↑		↑	
	Brignall		Davis Mica		Quade. Beryl		Quade. Rose Qz		Ryan-Sheehan		Woodcox	

For each box, left arrow: Ta/(Ta+Nb), right arrow: Mn/(Mn+Fe).

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