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RARE-ELEMENT MINERALOGY AND INTERNAL EVOLUTION OF THE RUTHERFORD #2 PEGMATITE, AMELIA COUNTY, VIRGINIA: A CLASSIC LOCALITY REVISITED

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ABSTRACT

The Rutherford #2 granitic pegmatite is a steeply dipping, symmetrically zoned body emplaced within Late Precambrian to early Paleozoic gneisses in the Amelia District of central Virginia. An important suite of rare-element accessory minerals is present and provides evidence relating to internal fractionation of the melt – fluid during crystallization. *Allanite* crystallized primarily in the wall zone and outer intermediate zone (perthite hood), and contains up to 5.0 wt.% ThO_2. *Fergusonite* also crystallized in the wall zone and in the second intermediate zone. With increasing fractionation, the Ta/(Ta + Nb) ratio increases from 0.08 to 0.22, accompanied by an increase in Th and a decrease in the amounts of Ti, U and Ca. *Monazite* mainly occurs in the second intermediate zone and contains up to 29 wt.% ThO_2, 6.0 wt.% SiO_2, and 1.4 wt.% CaO. *Columbite – tantalite* compositions vary systematically from ferrocolumbite with a Mn/(Mn + Fe) value of 0.22 and a Ta/(Ta + Nb) value of 0.17 in the second intermediate zone to manganotantalite with Mn/(Mn + Fe) = 0.86 and Ta/(Ta + Nb) = 0.53 toward the quartz core, accompanied by a general decrease in minor element contents. X-ray-diffraction data indicate that columbite is well ordered (f in the range 0.73–1.00, Q in the range 0.79–0.98). *Microlite* exhibits significant changes in composition from the second intermediate zone toward the quartz core, characterized by an increase in Ta/(Ta + Nb) value from 0.72 to 0.89, decreasing amounts of Ti and U, and increasing amounts of Ca, Na, and F. Additional minor accessory phases present in the second to inner intermediate zones are *cassiterite, fersmite, thorite*, *wodginite, xenotime*, and *zircon*. The data indicate that extensive fractionation of Mn, Fe, and rare elements occurred during crystallization of the Rutherford #2 pegmatite. From wall zone to quartz core, the melt – fluid evolved from a system enriched in *REE*, Fe, Nb, Ti, Th, and U to one enriched in Mn, Ta, Sn, Zr, and Hf. These observations are discussed in relation to the major mineral assemblages and the behavior of H_2O, Li, B, F, and P in the pegmatite system.

Keywords: granitic pegmatite, fractionation, allanite, fergusonite, zircon, monazite, columbite – tantalite, microlite, fersmite, wodginite, cassiterite, Amelia, Virginia.

SOMMAIRE

La pegmatite granitique de Rutherford #2, formant une lentille à pendage aigu zonée symétriquement, a été mise en place dans une séquence de gneiss d'âge tardi-précambrien ou bien paléozoïque précoce dans le district d'Amelia, en Virginie centrale. Elle contient une importante association de minéraux accessoires enrichis en éléments rares; ceux-ci servent de moniteurs du degré de fractionnement interne du système magma + fluide au cours de sa cristallisation. L'*allanite* a cristallisé surtout dans la zone de la paroi externe et dans la zone intermédiaire externe (chapeau de perthite); elle contient jusqu'à 5.0% de ThO_2 (en poids). La *fergusonite* a aussi cristallisé dans les mêmes zones; avec le fractionnement du système, le rapport Ta/(Ta + Nb) augmente de 0.08 à 0.22, la teneur en Th augmente, et les teneurs en Ti, U et Ca diminuent. On trouve la *monazite* surtout dans la deuxième zone intermédiaire; elle contient jusqu'à 29% de ThO_2, 6.0% de SiO_2, et 1.4% de CaO (proportions pondérales). Les compositions de *columbite – tantalite* varient de façon systématique de ferrocolumbite ayant une valeur de Mn/(Mn + Fe) de 0.22 et de Ta/(Ta + Nb) de 0.17 dans la deuxième zone intermédiaire à manganotantalite avec Mn/(Mn + Fe) = 0.86 et Ta/(Ta + Nb) = 0.53 vers le noyau de quartz; cette zonation est accompagnée d'une diminution générale en teneur des éléments mineurs. Une caractérisation par diffraction X montre que la columbite est bien ordonnée (f compris entre 0.73 et 1.00, Q entre 0.79 et 0.98). Le *microlite* fait preuve de changements importants de composition dans la transition de deuxième zone intermédiaire vers le noyau de quartz, dont une augmentation en Ta/(Ta + Nb) de 0.72 à 0.89, une diminution du niveau de Ti et de U, et une augmentation dans la teneur de Ca, Na, et F. Parmi les autres accessoires dans les zones intermédiaires figurent *cassitérite, fersmite, thorite*, *wodginite, xénotime*, et *zircon*. Les données témoignent d'un fractionnement marqué de Mn, Fe, et des éléments rares au cours de la cristallisation de la pegmatite de Rutherford #2. De la paroi vers le noyau

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de quartz, le système magma + fluide a évolué; d'abord enrichi en terres rares, Fe, Nb, Ti, Th, et U, il est devenu enrichi en Mn, Ta, Sn, Zr, et Hf. Ces comportements découlent des assemblages de minéraux dominants dans le système et aussi de la distribution de H_2O, Li, B, F, et P.

(Traduit par la Rédaction)

Mots-clés: pegmatite granitique, fractionnement, allanite, fergusonite, zircon, monazite, columbite – tantalite, microlite, fersmite, wodginite, cassitérite, Amelia, Virginie.

INTRODUCTION

The Rutherford #1 and #2, Champion, and Morefield pegmatites are the major zoned, rare-element granitic pegmatites of the Amelia District, Virginia. The history of the Rutherford pegmatites dates back over 100 years, during which time the deposits have been mined for commercial book mica and small quantities of gem and mineral specimens. However, owing to poor exposures typical of the Piedmont of central Virginia, scientific investigations at the locality have been limited mainly to field observations during several brief periods when mining operations were in progress. Apart from the chemical composition of late "sericitic" muscovite discussed by Glass (1935), and the electron-microprobe data on spessartine reported by Sinkankas & Reid (1966), and on selected samples of microlite reported by Lumpkin (1989) and Lumpkin & Ewing (1992), there have been no systematic studies of the mineral chemistry of the Rutherford pegmatites.

The purpose of this investigation is to present an updated description of the rare-element mineralogy and internal evolution of the Rutherford #2 pegmatite based primarily on new information obtained from a suite of specimens collected during the 1960s, supplemented by the previous field observations of Lemke *et al.* (1952) and Sinkankas (1968). The results of this study provide important new information on the mineralogy and internal evolution of an unusual type of granitic pegmatite and hopefully will contribute to the development of models of pegmatite crystallization (*e.g.*, London 1987, 1992, 1996).

Following a brief account of previous work, a description of the rare-element minerals, including allanite, cassiterite, columbite – tantalite, fergusonite, microlite, monazite, and zircon, will be given. In addition to these well-known species, the minerals fersmite, thorite, wodginite, and xenotime are reported from the Rutherford #2 pegmatite for the first time. Preliminary analytical data are summarized, and followed by a synthesis of the overall mineral paragenesis. The results of this study are briefly discussed in relation to recent work on the internal evolution and geochemistry of rare-element granitic pegmatites, especially the effects of H_2O, Li, B, F, and P on the temporal development of mineral assemblages (*e.g.*, Černý 1989a, Černý *et al.* 1985, London 1987, London *et al.* 1988, 1989, Rockhold *et al.* 1987).

PREVIOUS WORK

The earliest summary of the mineralogy of the Rutherford and Morefield pegmatites was given by Fontaine (1883), who described fifteen mineral species from the Rutherford locality, including the rare-element minerals allanite, columbite, fergusonite, microlite, and monazite. An excellent description of the mineralogy of the Rutherford and Morefield pegmatites, by Glass (1935), includes a valuable summary of previous investigations. Glass (1935) documented the presence of 27 minerals from the Rutherford pegmatites, several of which were described in detail. A partial chemical analysis of platy albite indicated a composition close to end-member albite (the Rutherford #2 is the likely source of the microprobe standard "Amelia albite"). Partial chemical analyses of green and white microcline revealed alkali contents of 14.3–15.5 wt.% K_2O, 0.9–1.6 wt.% $(Na, Li)_2O$, 0.4–1.1 wt.% Rb_2O, and up to 0.1 wt.% Cs_2O. An important contribution was made in determining the composition of fine-grained muscovite that occurs with topaz as an alteration product of feldspars. Five different colored varieties of muscovite were analyzed and found to contain 0.5–2.3 wt.% MgO, 0.2–1.5 wt.% FeO, 4.7–5.7 wt.% H_2O^+, up to 0.7 wt.% Na_2O, and minor amounts of Ca and Mn. Two of the samples were analyzed for Li and F, but neither was detected.

During the course of strategic mineral investigations during the period 1943–1945, Lemke *et al.* (1952) identified 83 mica-bearing pegmatites or prospects in the Amelia District. In addition to a description of the local geology, this investigation provided a detailed description of many of the granitic pegmatites of the area, giving for the first time a clear indication of the internal zonation and crystallization sequence. Lemke *et al.* (1952) demonstrated that the pegmatites crystallized from the walls inward and generally consist of a plagioclase-rich wall zone, perthite-rich intermediate zones, and a quartz-rich core. The Rutherford #1 and #2 pegmatites were examined during this time, and most of the rare-element minerals (*e.g.*, columbite – tantalite, microlite, cassiterite) were observed in association with platy albite that formed late in the crystallization sequence and partly at the expense of earlier quartz and feldspars (Lemke *et al.* 1952).

What is perhaps the classic description of the Rutherford pegmatites was given by Sinkankas (1968),

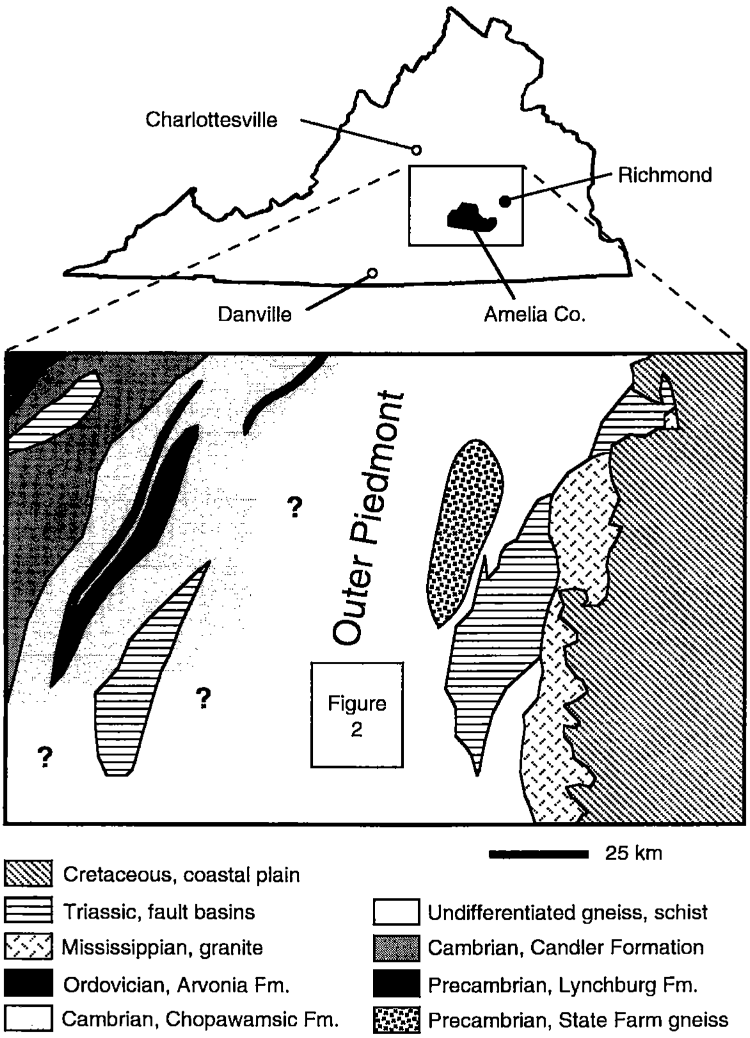

FIG. 1. Location map and general geology of an area of central Virginia including Amelia County. Most of the granitic pegmatites of the Amelia District occur within the area of Figure 2. Outlying pegmatites are located within the Outer Piedmont belt to the north.

who made careful observations of the internal structure and mineralogy when exposures into the #1 and #2 pegmatites were opened to depths of approximately 21 m and 35 m, respectively. His work provided the crucial link between internal zonation and temporal development of rare-element minerals, and forms a basis for the genetic understanding of the pegmatites. A revised series of lithologic units was proposed for the Rutherford #2 pegmatite, with the intermediate zone subdivided into four separate units. The outer intermediate zone was recognized as a perthite hood, followed by three albite-rich units. Sinkankas (1968) also recognized a central system of vugs lined by euhedral albite in the Rutherford #2 pegmatite, and gave a very detailed account of the crystallization, brecciation, and hydrothermal alteration of the vug system and quartz core. His paper concluded with a substantial description of the major minerals and accessory phases, including five minerals new to the locality.

LOCATION AND GENERAL GEOLOGY

The Rutherford pegmatites are located approximately 2 km due north of the town of Amelia in the Outer Piedmont province of Virginia (Figs. 1, 2). Granitic pegmatites of the Amelia District are concentrated

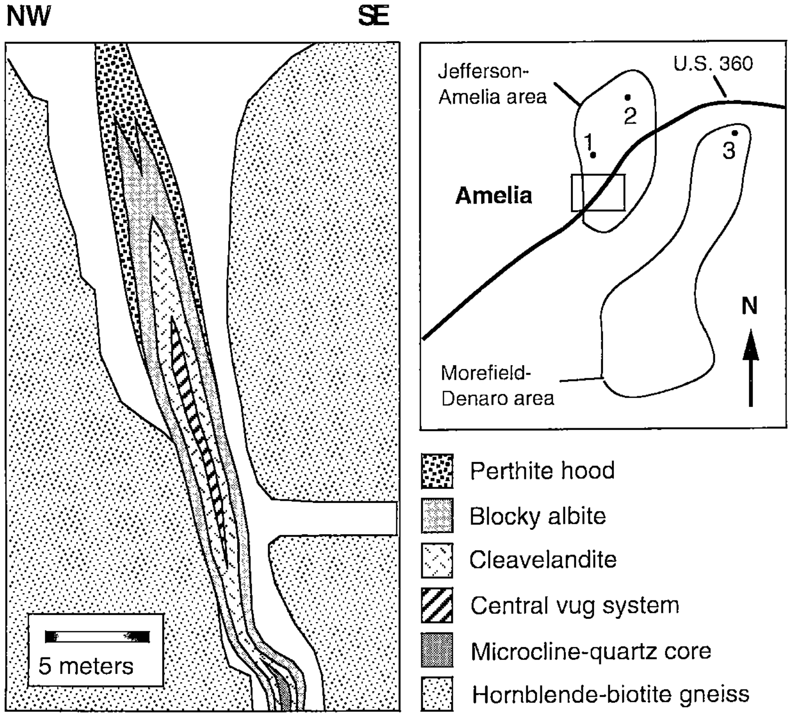

FIG. 2. Location map of the main area of the Amelia District showing the positions of the Rutherford (1), Champion (2), and Morefield (3) pegmatites and including a cross-section of the Rutherford #2 pegmatite, modified from Sinkankas (1968).

in two areas: the Jefferson – Amelia and Morefield – Denaro areas (Lemke *et al.* 1952). Pegmatites of the Jefferson – Amelia area, including the mineralogically complex Champion and Rutherford pegmatites, are relatively small, steeply dipping, discordant bodies that generally strike to the east and pinch out at depths of less than 40–45 m. In comparison, pegmatites of the Morefield – Denaro area tend to be larger, sharply discordant dikes that strike to the northeast and persist to depths of 65–70 m or more. The mineralogically complex Morefield dike is the major rare-element pegmatite in this area. All of the pegmatites are clearly post-metamorphic, and Deuser & Hertzog (1962) have determined a Rb–Sr muscovite age of 279 ± 14 Ma for the Rutherford #2 pegmatite. This age indicates that the Rutherford #2 pegmatite was emplaced near the end of the 270–330 Ma period of granitic magmatism in the Outer Piedmont and after the peak of metamorphism at approximately 380–420 Ma (Fullagar 1971, Wright *et al.* 1975).

Owing to the deeply weathered nature of the region, the age and origin of the metamorphic and igneous rocks of the Outer Piedmont belt of Virginia are poorly understood (Conley 1978). Metamorphic rocks of the Amelia District have been referred to as the Wissahickon gneiss (Lemke *et al.* 1952). The major rock-types include a variety of metasedimentary and metavolcanic lithologies, transformed to quartz – biotite schist, biotite augen gneiss, garnet – mica schist and gneiss, and hornblende schist and gneiss. Graphite is present locally in the biotite augen gneiss and also occurs with sillimanite in garnet – mica gneiss. The predominant foliation generally strikes to the northeast and dips moderately to steeply to the northwest. Age relationships in the area are poorly constrained; however, the available field relations and radiometric dates indicate that rocks in the Amelia area may be temporally correlative with or older than the Chopawamsic Formation and associated rocks (530–595 Ma, Conley 1978), indicating a late Precambrian to early Cambrian age.

In central Virginia, metamorphic grade increases toward the east and southeast from greenschist facies on the southeast flank of the Blue Ridge anticlinorium to upper amphibolite facies in the Outer Piedmont (*e.g.*, Espenshade & Potter 1960, Nelson 1962, Smith *et al.* 1964, Conley 1978, Good 1978). Prograde metamorphism in this area is characteristic of a Barrovian

TABLE 1. LITHOLOGIC UNITS AND ACCESSORY MINERALOGY OF THE RUTHERFORD #2 PEGMATITE, AMELIA COUNTY, VIRGINIA

Border Zone

Discontinuous unit of aplitic plagioclase + quartz + muscovite ± almandine. Present mainly as patches along the footwall.

Wall Zone

Discontinuous unit of blocky plagioclase + quartz + muscovite. Accessory allanite, apatite, microcline, and fergusonite. Minor amounts of tourmaline also present.

Outer Intermediate Zone

Perthite + quartz + muscovite hood unit present in upper part of pegmatite. Allanite and purple fluorite are the major accessory minerals.

Second Intermediate Zone

Generally continuous unit of blocky albite + muscovite. Variable accessory mineralogy includes columbite-tantalite, apatite, microlite, spessartine, monazite, zircon, and fergusonite. Also contains minor fersmite and rare grains of xenotime and thorite.

Middle Intermediate Zone

Generally continuous unit of massive bladed albite + muscovite + quartz. Minor accessory microlite, spessartine, and columbite-tantalite. Crystals of zircon, cassiterite and wodginite are rare.

Inner Intermediate Zone

Generally continuous unit of euhedral bladed albite + muscovite. Contemporaneous accessory minerals are microlite, columbite-tantalite, spessartine, green fluorite, and cassiterite. Central vug system contains hydrothermal minerals deposited on albite blades, including apatite, bavenite, calcite, chlorite, galena, helvite, herderite, pyrite, quartz, sphene, and fibrous tourmaline.

Core Zone

Coarse microcline + quartz present in lower part of pegmatite. Muscovite, apatite, and spessartine are the principle accessory minerals. Minor tourmaline and galena also present.

Alteration

Minor replacement of albite ± microline in the outer, second, and middle intermediate zones by sericitic muscovite ± topaz.

sequence; for instance, with increasing grade, pelitic rocks develop biotite, garnet, staurolite or kyanite or both, and finally sillimanite. A pressure range of 4–8 kbar is generally consistent with the occurrence of staurolite together with kyanite and sillimanite during prograde metamorphism northwest of the Amelia District (Holdaway 1971, Winkler 1979). The metamorphic grade within the Amelia District is not well constrained, but appears to be within the stability field of sillimanite (Lemke *et al.* 1952).

PEGMATITE STRUCTURE AND LITHOLOGIC UNITS

The Rutherford #2 pegmatite is a lens-shaped body (Fig. 2) that has a strike of approximately N56°E and a length of at least 60 m; it plunges to a depth of approximately 40 m with an average dip of 65–70° SE (Lemke *et al.* 1952, Sinkankas 1968). A maximum thickness of 4–5 m was observed in the upper part of the body at a depth of 10–15 m during the course of mining operations. Based on the terminology of Cameron *et al.* (1949), the following lithologic units are characteristic of the Rutherford #2 pegmatite: a fine-grained, discontinuous *border zone*, a *wall zone* mainly consisting of blocky plagioclase, quartz, and muscovite, an *intermediate zone* subdivided into four separate units, and a *core* primarily composed of quartz and green to white microcline. A description of these units is given in Table 1, together with a brief list of the typical accessory minerals. The lithologic units are arranged symmetrically about the core and central vug system. As shown in Figure 2, the core is primarily developed below the 35 m level, whereas the central system of vugs occurs at a depth of 15–30 m. Metasomatic effects in the adjacent wallrocks are primarily restricted to a zone along the hanging wall at a depth of 13–35 m where plagioclase is the principal feldspar of the outermost units. The maximum thickness of the alteration zone is 15–30 cm and is defined by enrichment in biotite and muscovite (Sinkankas 1968).

RARE-ELEMENT MINERALOGY AND CHEMISTRY

On the basis of the new observations and analytical data accumulated to date, the rare-element mineral paragenesis of the Rutherford #2 pegmatite is developed below, incorporating to a certain extent the previous work of Glass (1935), Lemke *et al.* (1952), and especially Sinkankas (1968). Each rare-element mineral is described separately in the approximate order in which the mineral first appears in the crystallization sequence of the pegmatite. Relevant details of the mineral compositions are given in summary form with representative analyses given in tables.

Allanite

Allanite crystals up to 35 cm in length were previously reported from the blocky plagioclase of the wall zone and coarse-grained perthite of the outer intermediate zone. Associated minerals in these lithologic units include quartz, brown muscovite, and apatite. The bladed morphology, reddish brown surface color, and black interior color with conchoidal fracture are diagnostic features of allanite from the Rutherford #2 pegmatite. Crystals up to 5 cm were observed in this study, although most are less than 2 cm in length. Rare grains of allanite also were observed in the blocky albite of the second intermediate zone in association with microlite, columbite, and fersmite. These grains appear to be overgrown and partially replaced by the Nb–Ta oxides. At the time of writing, only a limited number of analyses have been completed. The available data indicate that the early allanite contains 0.3–5.0 wt.% ThO_2, 0.1–1.2 wt.% Y_2O_3, 16–24 wt.% Ln_2O_3 (La or Ce dominant, Ln: lanthanides), 0.7–1.6 wt.% MnO, up to 0.3 wt.% MgO, and up to 0.9 wt.% Na_2O. The late allanite from the second intermediate zone is depleted in Al, Ca, and Th, and has higher levels of the *REE* (rare-earth elements, *i.e.*, Y + Ln) and Fe relative to samples from the wall zone.

Fergusonite

Fergusonite was originally reported from the Rutherford pegmatites by Fontaine (1883), but was later dismissed by Sinkankas (1968) as possibly being

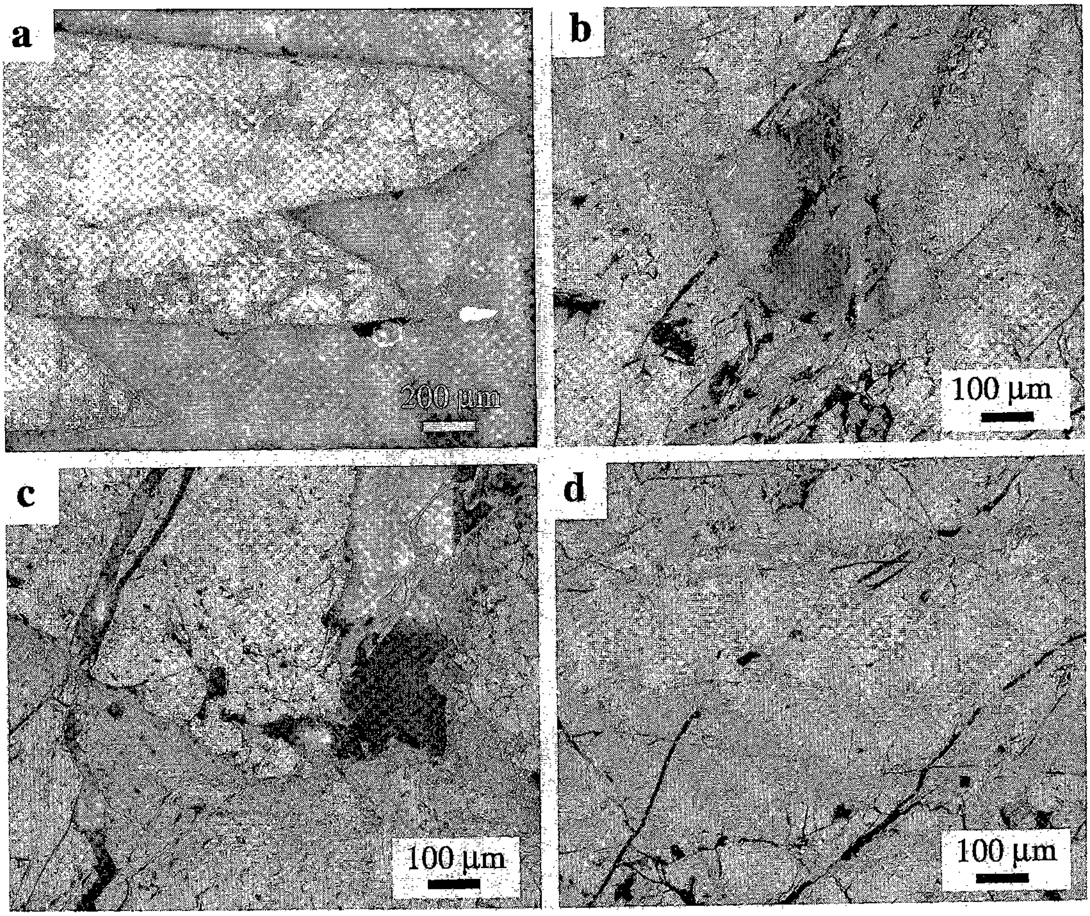

FIG. 3. Representative back-scattered electron images of rare-element minerals from the Rutherford #2 pegmatite. a) Fergusonite from the wall zone; note alteration along grain boundaries and fractures. b) Zircon inclusions (dark gray) in altered monazite from the second intermediate zone. c) Microlite (light gray), monazite (gray, at bottom), and fergusonite (gray, at right) from the second intermediate zone. Note alteration of monazite and fergusonite along grain boundaries. d) Altered thorite (middle of photo) associated with monazite from the second intermediate zone.

misidentified as zircon. In this study, the presence of fergusonite in the Rutherford #2 pegmatite has been confirmed. The mineral occurs as dark brown crystals up to 1 cm in length and is an important rare-element accessory phase in the wall zone and second intermediate zone. Fergusonite in the wall zone occurs as sharp, well-terminated prismatic individual crystals or groups enclosed within plagioclase (~An_{15}) and commonly associated with tourmaline, quartz, and microcline (~Or_{90}). Specimens examined by SEM exhibit minor alteration, mainly concentrated along fractures (Fig. 3a). Crystals from the second intermediate zone tend to be smaller and are more rounded in shape. These samples are enclosed within blocky albite (~$An_{0.5}$) and are commonly associated with monazite, microlite, and columbite – tantalite. The crystals are moderately to heavily altered along grain boundaries and fractures (Figs. 3b, c).

Analytical data indicate that fergusonite from the wall zone and second intermediate zone contains as much as 2.0 wt.% WO_3, 6.5–17 wt.% Ta_2O_5, 0.2–0.6 wt.% TiO_2, 2.2–4.7 wt.% ThO_2, 1.5–7.4 wt.% UO_2, 5.5–8.7 wt.% Ln_2O_3, and 0.6–1.4 wt.% CaO. With progressive crystallization from the wall zone to the second intermediate zone, the Ta/(Ta + Nb) value increases from 0.08 to 0.22 and is accompanied by an increase in the Th content and a decrease in the amounts of Ti, U, and Ca. Fergusonite from the wall zone is typically Yb-dominant, whereas samples from the second intermediate zone are generally Nd-, Sm-, Dy- or Yb-dominant, indicating a relatively flat *REE* distribution beyond Nd. Most of the fergusonite

TABLE 2. REPRESENTATIVE COMPOSITIONS OF FERGUSONITE, RUTHERFORD #2 GRANITIC PEGMATITE, AMELIA DISTRICT, VIRGINIA

	wall zone		second intermediate zone			
	core	rim	core	rim	core	rim
WO_3	0.9	0.6	0.7	0.9	0.9	0.8
Nb_2O_5	42.9	41.3	38.8	38.0	41.1	39.8
Ta_2O_5	5.0	8.3	13.5	14.5	10.7	13.0
TiO_2	0.5	0.4	0.3	0.2	0.3	0.2
SnO_2	0.3	< 0.1	< 0.1	0.1	< 0.1	< 0.1
ThO_2	2.9	3.2	4.1	3.7	3.6	3.3
UO_2	7.8	5.9	1.6	1.7	3.0	1.6
Y_2O_3	29.0	29.9	30.2	31.3	31.3	31.8
Ce_2O_3	0.2	< 0.1	0.6	0.3	0.2	0.3
Nd_2O_3	0.6	0.6	1.7	1.4	1.1	1.2
Sm_2O_3	0.8	0.9	1.4	1.3	1.0	1.0
Gd_2O_3	1.2	1.3	1.3	1.4	1.3	1.2
Dy_2O_3	1.7	1.5	1.4	1.7	1.6	1.5
Er_2O_3	0.6	1.0	0.5	0.7	0.7	0.8
Yb_2O_3	2.1	1.9	1.4	1.5	1.7	1.7
CaO	1.4	1.3	0.9	0.7	1.0	0.8
MnO	< 0.1	< 0.1	0.1	< 0.1	0.1	0.1
PbO	0.5	0.5	0.5	0.4	0.4	0.3
Total	98.4	98.6	99.0	99.8	100.0	99.4

*Al_2O_3, Sc_2O_3, La_2O_3, Pr_2O_3, MgO, and FeO were below 0.1 wt.%.

crystals are relatively homogeneous; however, a few grains exhibit weak progressive zoning from core to rim characterized by increasing amounts of Ta and light to middle lanthanides, together with decreasing amounts of Ti, U, and Ca. The Th contents do not appear to change systematically in the zoned crystals. Representative compositions of fergusonite are given in Table 2.

Columbite – tantalite

Minerals of the columbite – tantalite group were previously reported from the second and inner intermediate zones of the pegmatite. Black, tabular crystals up to 4 cm in size were reported from the blocky albite of the second intermediate zone in association with muscovite, spessartine, microlite, apatite, monazite, and zircon. Black to reddish brown crystals and masses up to 13 cm in size were also found in the euhedral albite of the inner intermediate zone associated with spessartine, microlite, and cassiterite. Smaller (less than 2 cm) examples from both lithologic units were found in this study together with a few small (less than 1 cm) angular, black grains wedged between albite plates in the middle intermediate zone. Samples from the middle intermediate zone are in some cases found in association with microlite, wodginite, and cassiterite.

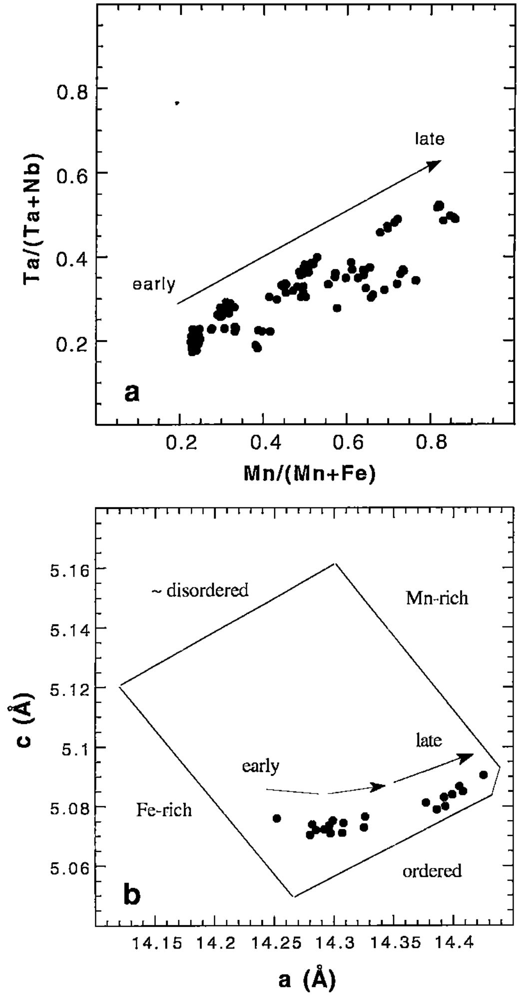

FIG. 4. Composition and structural state of columbite – tantalite. a) Columbite quadrilateral showing evolution of compositions from second intermediate zone to core. b) XRD results shown in the *a–c* plot exhibit relatively ordered distributions of cations. The samples become more ordered with progressive crystallization of the pegmatite.

In terms of the columbite quadrilateral shown in Figure 4a, the available samples define a compositional trend ranging from ferrocolumbite with a Mn/(Mn + Fe) of 0.22 and a Ta/(Ta + Nb) of 0.17, through the compositional field of manganocolumbite, to manganotantalite having a Mn/(Mn + Fe) of 0.86 and a Ta/(Ta + Nb) of 0.53. Analytical results also indicate that the minor-element contents vary considerably. In general, the columbite – tantalite samples contain Ti as the principal minor element (0.3–2.9 wt.% TiO_2), with maximum concentrations of 1.7 wt.% WO_3, 1.3 wt.% SnO_2, 0.5 wt.% UO_2, 1.9 wt.% Y_2O_3, 0.7 wt.% Ln_2O_3, and 0.2 wt.% CaO. Although there appears to be an overall decrease in the minor-element concentrations

TABLE 3. SUMMARY OF AVERAGE COMPOSITIONS OF COLUMBITE-TANTALITE FROM THE RUTHERFORD #2 PEGMATITE

	$\frac{\text{Ta}}{\text{Ta+Nb}}$	$\frac{\text{Mn}}{\text{Mn+Fe}}$	W pfu	Ti pfu	Sn pfu	REEs pfu
CT3	0.535	0.829	0.004	0.022	0.006	0.004
CT3a	0.524	0.823	0.006	0.027	0.006	0.004
CT4	0.350	0.466	0.007	0.045	0.003	0.006
CT5	0.188	0.259	0.011	0.060	0.002	0.009
CT5a	0.175	0.254	0.010	0.065	0.000	0.009
CT6	0.512	0.809	0.004	0.033	0.006	0.004
CT6a	0.490	0.794	0.006	0.038	0.006	0.011
CT7	0.191	0.246	0.011	0.056	0.002	0.009
CT8	0.217	0.263	0.008	0.056	0.002	0.005
CT8a	0.185	0.248	0.014	0.060	0.002	0.009
CT9	0.496	0.844	0.005	0.021	0.006	0.007
CT9a	0.490	0.833	0.004	0.026	0.003	0.004
CT12	0.316	0.441	0.007	0.049	0.003	0.003
CT19	0.351	0.480	0.005	0.040	0.003	0.007
CT20	0.213	0.259	0.010	0.051	0.002	0.012
CT49	0.521	0.820	0.007	0.032	0.007	0.008
CT49a	0.525	0.807	0.005	0.030	0.007	0.005
CT53	0.193	0.230	0.019	0.070	0.003	0.012
CT53a	0.192	0.238	0.010	0.075	0.003	0.008

with increasing fractionation, the results are complicated by unusually high contents of W, Sn, and *REE* in samples associated with microlite, monazite, and fergusonite in the second intermediate zone. These samples plot near the middle of the trend shown in Figure 4a and have somewhat lower Ta/(Ta + Nb) values compared to the main group of analyses.

The structural state of columbite – tantalite from the Rutherford #2 pegmatite is shown in Figure 4b. Most of the samples plot near the lower right side of the *a–c* diagram, indicating a relatively ordered arrangement of Mn + Fe and Ta + Nb over the octahedral sites of the columbite structure. Furthermore, the samples appear to become more ordered with increasing Mn content, a feature noted in columbite – tantalite samples from other localities (Černý & Ercit 1985). Using the compositional data and unit-cell parameters given in Tables 3 and 4, the fractional degree of cation order (*f*) and the "corrected" cation distribution (*Q*) were calculated using equations given by Ercit *et al.* (1995). Results of the calculations show that *f* ranges from 0.73 to 1.00. The bimodal distribution shown in Figure 4b may be in part due to a sampling bias in favor of the larger crystals of ferrocolumbite and manganotantalite. However, the presence of minor elements contributes to this effect, *e.g.*, some data points in the Fe-rich group have been shifted to a more Fe-rich and disordered position in *a–c* space owing relatively high Ti contents. This effect is confirmed by the calculated values of *Q*, which range from 0.79 to 0.98. Unfortunately, the equations presented by Ercit *et al.* (1995) do not take into account the presence of *REE* and U. The ionic radii of these elements are considerably larger than Fe and Mn and could have a significant effect on the positions of the points in *a–c* space.

Zircon

Zircon was described by Sinkankas (1968) as a relatively common mineral in the second intermediate zone, where it was found as prismatic crystals or radiating groups up to 1.5 mm in length, each crystal with a dark brown core and a thin yellow rim. Larger dark brown to black metamict crystals were also observed, and identified as Fe-rich zircon. In this study, several submillimeter-size crystals of zircon were observed during SEM work on samples from the second intermediate zone (Fig. 3b). Zircon also was found in the middle and inner intermediate zones, where it occurs as light brown to straw yellow, radiating sprays of crystals up to 1 cm in length. Electron-microprobe analyses indicate that zircon from the Rutherford #2 pegmatite has considerable chemical variability characterized by the presence of 0.3–2.6 wt.% P_2O_5, 8.2–35 wt.% HfO_2, 0.2–2.9 wt.% Y_2O_3, and 0.5–4.7 wt.% Ln_2O_3 (mainly Yb). The zircon grains also contain up to 0.7 wt.% ThO_2, 1.3 wt.% UO_2, and 0.2 wt.% CaO. In general, the compositions become enriched in Hf and depleted in Th and U with increasing fractionation of the pegmatite-forming magma. Representative compositions are given in Table 5.

TABLE 4. UNIT-CELL DIMENSIONS AND ESTIMATES OF CATION ORDER IN COLUMBITE-TANTALITE FROM THE RUTHERFORD #2 PEGMATITE

	a (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)	*f*	*Q*
CT3	14.408(3)	5.765(1)	5.085(1)	422.4(1)	0.99	0.89
CT3a	14.393(2)	5.751(1)	5.080(1)	420.47(9)	1.00	0.98
CT4	14.308(2)	5.7501(8)	5.0745(9)	419.59(8)	0.87	0.86
CT5	14.296(2)	5.7482(8)	5.0736(9)	416.93(8)	0.85	0.86
CT5a	14.280(3)	5.7353(9)	5.0705(9)	415.27(8)	0.84	0.92
CT6	14.392(1)	5.7643(4)	5.0831(6)	421.69(5)	0.97	0.92
CT6a	14.377(2)	5.7514(6)	5.0812(6)	420.15(6)	0.95	0.96
CT7	14.425(3)	5.7718(9)	5.0906(9)	423.83(9)	0.85	0.88
CT8	14.299(2)	5.7492(9)	5.0752(9)	417.22(8)	0.84	0.85
CT8a	14.285(3)	5.7364(9)	5.072(1)	415.62(9)	0.84	0.92
CT9	14.425(3)	5.7718(9)	5.0906(9)	423.83(8)	0.97	0.80
CT9a	14.405(2)	5.7566(6)	5.0868(6)	421.82(6)	0.96	0.92
CT12	14.307(2)	5.7520(8)	5.0711(9)	417.32(8)	0.90	0.88
CT19	14.325(3)	5.753(1)	5.073(1)	418.1(1)	0.92	0.92
CT20	14.297(3)	5.741(1)	5.071(1)	416.2(1)	0.87	0.91
CT49	14.399(3)	5.752(1)	5.084(2)	421.1(1)	0.98	0.94
CT49a	14.386(3)	5.748(1)	5.079(1)	420.0(1)	0.99	0.97
CT53	14.252(3)	5.723(1)	5.076(2)	414.0(2)	0.73	0.79
CT53a	14.282(3)	5.734(1)	5.074(1)	415.5(1)	0.81	0.90

Monazite

Previous investigations indicate that monazite occurs predominantly in the blocky albite of the second intermediate zone in association with microlite,

TABLE 5. REPRESENTATIVE COMPOSITIONS OF ZIRCON, THORITE AND MONAZITE, RUTHERFORD #2 GRANITIC PEGMATITE, AMELIA DISTRICT, VIRGINIA

	zircon		thorite		monazite	
	second inter.	inner inter.	second inter.		second inter.	
P_2O_5	1.4	0.9	0.9	12.3	24.8	23.1
SiO_2	29.7	28.2	18.0	10.0	3.0	4.3
ZrO_2	54.6	45.8	0.1	< 0.1	—	—
HfO_2	9.3	21.3	< 0.1	< 0.1	—	—
ThO_2	0.5	< 0.1	64.4	44.8	18.4	21.4
UO_2	1.2	0.2	6.7	0.4	< 0.1	< 0.1
Y_2O_3	1.6	0.4	4.0	0.7	2.1	1.2
La_2O_3	< 0.1	< 0.1	0.1	6.1	10.1	10.3
Ce_2O_3	< 0.1	0.1	0.2	14.6	21.0	25.1
Pr_2O_3	< 0.1	< 0.1	< 0.1	1.9	3.0	2.7
Nd_2O_3	0.1	< 0.1	0.4	5.7	11.2	9.1
Sm_2O_3	< 0.1	< 0.1	0.4	0.9	1.9	1.2
Gd_2O_3	< 0.1	0.1	0.3	0.3	0.5	0.4
Dy_2O_3	< 0.1	0.2	0.2	< 0.1	0.2	< 0.1
Er_2O_3	0.1	0.4	0.2	< 0.1	0.1	< 0.1
Yb_2O_3	0.4	1.5	0.1	< 0.1	< 0.1	< 0.1
CaO	< 0.1	< 0.1	0.7	0.2	1.0	0.5
PbO	< 0.1	< 0.1	0.5	0.4	0.2	0.2
Total	98.9	99.1	97.2	98.3	97.5	99.5

*Al_2O_3, MnO, and FeO were below 0.1 wt.%.

columbite – tantalite, and zircon, and possibly with manganotantalite in the inner intermediate zone. Most of the crystals from the #2 body were described as tabular, dull brown, and less than 1 cm in diameter (Sinkankas 1968), and similar crystals up to 5 mm in size were observed in this study. In addition to the smaller crystals of the brown variety of monazite, larger brownish green crystals up to 2 cm in diameter also were found in this unit in association with zircon, microlite, fergusonite, columbite – tantalite, and thorite (Figs. 3b–d). Compositions of monazite are characterized by 2.1–6.0 wt.% SiO_2, 13–29 wt.% ThO_2, up to 0.7 wt.% UO_2, 1.2–2.3 wt.% Y_2O_3, 41–56 wt.% Ln_2O_3 (La or Ce dominant), and 0.2–1.1 wt.% CaO (see Table 5).

Microlite

The Rutherford #2 pegmatite is famous for the large, olive green to black, euhedral crystals of microlite from blocky albite of the second intermediate zone. Historically, some of these crystals have been reported to reach up to 5 cm across. Large masses were also reported, some weighing up to 3.6 kg. Additional, smaller crystals ranging from reddish brown to brownish yellow also were found in the massive bladed albite of the middle intermediate zone and in the euhedral albite of the inner intermediate zone. In this study, maximum crystal sizes of 1–2 cm were observed for samples taken from blocky albite of the second intermediate zone (Fig. 3c). These crystals all exhibit the classic olive green or mottled green-black coloration. Additional samples were obtained from the middle and inner intermediate zones. Flattened, dark green to brownish black octahedra less than 1 cm in diameter were found between albite plates in samples from the middle intermediate zone. Samples from the inner intermediate zone are represented by rare, brownish yellow to golden yellow grains less than 5 mm in diameter.

Microlite samples from the intermediate zones contain up to 1.2 wt.% WO_3, 5.5–13 wt.% Nb_2O_5, 0.2–1.6 wt.% TiO_2, 1.7–3.1 wt.% SnO_2, 0.1–3.5 wt.% UO_2, 10–15 wt.% CaO, 1.6–5.5 wt.% Na_2O, and 1.8–3.6 wt.% F. Minor amounts of the *REE*, Sb, Bi, Mn, Fe, and Pb also are present, but Ba, K, and Cs are generally below detection limits. Analytical totals are in the range of 95–100 wt.%, suggesting that a significant amount of H_2O is present. This has been confirmed by infrared spectroscopy and thermogravimetric analysis of selected samples, indicating total H_2O contents of 0.5–3.8 wt.%, mainly as H_2O as opposed to OH (Lumpkin 1989). The Ta/(Ta + Nb) value of microlite increases from a mimimum of ~0.72 in the second intermediate zone to a maximum of ~0.89 in the inner intermediate zone. This trend is accompanied by a general decrease in Ti, U, and Ca, coupled with an increase in the amounts of Na and F, *i.e.*, with progressive crystallization the composition approaches the end-member $NaCaTa_2O_6F$. Pronounced zoning has not been observed in any of the crystals examined so far; however, some crystals exhibit moderate to weak progressive core–rim zoning. Zoned crystals have a core relatively enriched in Nb, Ti, U, and Ca, whereas the rim is relatively enriched in Ta, Na, and F. Minor secondary alteration is localized along microfractures in some crystals from the second intermediate zone and involved leaching of Na and F, an increase in the number of *A*- and *Y*-site vacancies, and increased hydration (Lumpkin & Ewing 1992). Representative compositions of microlite are listed in Table 6.

Fersmite

Fersmite was discovered at the Rutherford #2 pegmatite in association with microlite, monazite, columbite – tantalite, and fergusonite in the second intermediate zone. The fersmite is closely associated with the alteration products of fergusonite and may not be a primary phase in this particular assemblage. Analyses of these samples indicate that the fersmite contains up to 1.2 wt.% WO_3, 0.8–2.9 wt.% TiO_2, 0.1–1.0 wt.% SnO_2, up to 0.5 wt.% UO_2, 1.0–2.9 wt.% Y_2O_3, 0.1–0.8 wt.% Ln_2O_3 (mainly Nd–Yb), and small amounts of Mn and Fe (see Table 7). The high Y content and heavy lanthanide signature are consistent with crystallization of this fersmite during alteration of

TABLE 6. REPRESENTATIVE COMPOSITIONS OF MICROLITE, RUTHERFORD #2 GRANITIC PEGMATITE, AMELIA DISTRICT, VIRGINIA

	second inter.		middle inter.		inner inter.	
	core	rim	core	rim	core	rim
WO_3	0.5	0.2	0.2	0.4	0.4	0.3
Nb_2O_5	12.4	12.5	9.8	9.6	5.9	6.0
Ta_2O_5	58.8	58.9	63.8	63.7	72.7	71.8
TiO_2	1.6	1.5	0.9	0.9	0.3	0.3
SnO_2	2.2	2.2	2.7	2.6	2.1	2.1
ThO_2	0.2	0.2	< 0.1	< 0.1	< 0.1	< 0.1
UO_2	2.9	2.7	1.3	1.4	0.3	0.3
Y_2O_3	0.2	0.2	0.2	0.1	0.1	0.1
Ln_2O_3	0.4	0.3	0.3	0.3	0.4	0.2
Sb_2O_3	0.1	0.1	0.1	0.1	0.1	0.1
Bi_2O_3	0.2	0.0	0.2	0.2	0.3	0.3
CaO	13.0	12.8	12.3	12.0	10.7	10.7
MnO	0.1	0.1	< 0.1	< 0.1	0.2	0.2
FeO	< 0.1	< 0.1	< 0.1	< 0.1	0.1	< 0.1
PbO	0.1	0.1	0.1	< 0.1	< 0.1	< 0.1
Na_2O	3.5	3.5	4.5	4.4	5.4	5.3
F	2.4	2.3	3.1	3.1	3.2	3.4
Subtotal	98.6	97.6	99.5	98.8	102.2	101.1
$O \equiv F$	-1.0	-1.0	-1.3	-1.3	-1.3	-1.4
Total	97.6	96.6	98.2	97.5	100.9	99.7

*Al_2O_3, Sc_2O_3, MgO, BaO. and Cs_2O were below 0.1 wt.%.

TABLE 7. REPRESENTATIVE COMPOSITIONS OF FERSMITE, WODGINITE AND CASSITERITE, RUTHERFORD #2 GRANITIC PEGMATITE, AMELIA DISTRICT, VIRGINIA

	fersmite		wodginite		cassiterite	
	second inter.		middle inter.	inner inter.	middle inter.	
WO_3	0.3	0.5	0.3	0.4	< 0.1	< 0.1
Nb_2O_5	42.0	52.8	9.8	10.2	0.2	0.1
Ta_2O_5	36.4	28.4	62.0	61.5	7.3	3.0
TiO_2	2.9	1.8	3.7	3.7	0.5	0.3
SnO_2	0.3	0.4	11.2	11.6	90.4	95.7
UO_2	0.4	< 0.1	0.2	< 0.1	< 0.1	< 0.1
Y_2O_3	2.2	1.7	< 0.1	< 0.1	< 0.1	< 0.1
Ln_2O_3	0.3	0.6	0.1	< 0.1	< 0.1	< 0.1
CaO	12.9	13.4	< 0.1	< 0.1	< 0.1	< 0.1
MnO	< 0.1	0.2	6.5	8.6	0.1	< 0.1
FeO	< 0.1	0.3	6.1	4.0	1.3	0.9
Total	97.7	100.1	99.9	100.0	99.8	100.0

*Al_2O_3, Sc_2O_3, MgO. and PbO were below 0.1 wt.%.

fergusonite. During an examination of some of the columbite – tantalite samples by analytical electron microscopy (AEM), a Ca-rich phase was occasionally encountered as a fine-grained product of alteration along fractures and grain boundaries of ferrocolumbite, with Ta/(Ta + Nb) in the range 0.15–0.24. This phase was positively identified by electron diffraction and AEM work as fersmite. AEM analyses of the replacement fersmite indicate that it has a Ta/(Ta + Nb) value in the range 0.14–0.20 and contains ~0.1–0.8 wt.% WO_3, 0.8–1.8 wt.% TiO_2, 0.2–0.7 wt.% SnO_2, 0.1–0.4 wt.% Y_2O_3, and 0.2–1.7 wt.% FeO, closely reflecting the composition of the host ferrocolumbite and retaining a small amount of Fe.

Wodginite

Wodginite was discovered as small (<5 mm) black crystals in association with columbite – tantalite and cassiterite crystals from the second and middle intermediate zones. Analyses completed to date indicate a rather restricted range of compositions, including up to 1.4 wt.% WO_3, 9.7–11 wt.% Nb_2O_5, 60–63 wt.% Ta_2O_5, 3.2–4.0 wt.% TiO_2, 9.8–12 wt.% SnO_2, 6.1–8.8 wt.% MnO, and 3.5–6.2 wt.% FeO. In parallel with columbite – tantalite, the wodginite appears to become more enriched in Mn with increasing fractionation. The composition determined in this study is similar to that of wodginite from the intermediate zones of the Herbb #2 pegmatite (Wise & Černý 1984), located approximately 25 km to the north in Powhatan County. In particular, there is a striking similarity in the amounts of Ti and Sn in wodginite from the two localities. For comparison, Wise & Černý (1984) reported 3.5–4.0 wt.% TiO_2 and 11–13 wt.% SnO_2 in four samples from the Herbb #2 pegmatite. Representative compositions of wodginite are given in Table 7.

Cassiterite

Cassiterite is a relatively rare mineral at the Rutherford #2 pegmatite, but was found in the middle intermediate zone as massive, black to brownish black grains up to 2 cm in diameter, and in the inner intermediate zone as smaller, dark brown, twinned crystals. In the middle intermediate zone, cassiterite is associated with muscovite, quartz, spessartine, microlite, and wodginite. Mineral associations in the inner intermediate zone include spessartine, microlite, and manganotantalite. Specimens observed in this study consist of grayish black crystals up to 1 cm in maximum dimension. On the basis of a limited number of analyses, the cassiterite contains up to 0.8 wt.% Nb_2O_5, 2.9–7.9 wt.% Ta_2O_5, 0.2–0.7 wt.% TiO_2, and 0.9–1.6 wt.% FeO. Only one sample was large enough for XRD work. The unit-cell parameters of this specimen are a 4.7309(4), c 3.1765(4) Å, and V 71.09(1) $Å^3$.

Additional uncommon or poorly characterized phases

Rare grains of *xenotime* were found at the Rutherford #2 pegmatite as inclusions within columbite – tantalite from the second intermediate zone. The grains are associated with muscovite, quartz, fluorite, and monazite, all of which are found in the inclusions in varying proportions. The xenotime grains contain 4–6 wt.% Ln_2O_3 (Yb dominant), 0.6–0.9 wt.% CaO, and minor amounts of SiO_2, Mn, and Fe. *Thorite* was found as an uncommon phase in the second intermediate zone in association with allanite, where both phases are partially replaced by monazite, microlite, and columbite – tantalite. Thorite grains in this association contain 6–7 wt.% UO_2 and minor amounts of *REE*, P, and Ca. Altered thorite also occurs as inclusions in monazite. This material appears to have a composition intermediate between $ThSiO_4$ and *REE*PO_4 (Table 5). Very rare grains of a Pb-rich phase also were found by AEM during the course of this investigation. The grains are associated with fersmite and appear to be an alteration product of ferrocolumbite. The mineral is tentatively identified as *plumbopyrochlore*, has a Ta/(Ta + Nb) value in the range 0.31–0.45, and contains ~25–30 wt.% PbO, 5–6 wt.% UO_2, 4–7 wt.% FeO, and minor amounts of Ti, Sn, Th, *REE*, Ca, Mn, and Na. The alteration product of fergusonite remains to be identified, but preliminary SEM–EDS results indicate that it has a variable Ta/(Ta + Nb) value, in the range 0.45–0.70, contains 5–17 wt.% ThO_2, 2–6 wt.% FeO, and has variable amounts of the minor elements Ti, U, Al, *REE*, Ca, Mn, Ba, Pb, Na, and K. This mineral is most likely a defect pyrochlore – microlite or a phase related to the natrotantite – calciotantite family (Černý & Ercit 1985).

DISCUSSION

Rare-element mineral paragenesis

The rare-element mineral paragenesis of the Rutherford #2 pegmatite is summarized in Figure 5, where it is immediately apparent that the rare-element minerals crystallized in essentially a continuous sequence from the wall zone to the inner intermediate zone. Allanite and fergusonite were the earliest phases to form in the wall zone with plagioclase; allanite also crystallized in the outer intermediate zone (perthite hood), and both phases continued to crystallize in the second intermediate zone with blocky albite. In the second intermediate zone, the early accessory phases are superseded by columbite – tantalite, monazite, microlite, and minor amounts of zircon. Columbite – tantalite and microlite were the major accessory phases to form during the latter stages of pegmatite crystallization, in the middle and inner intermediate zones. Some monazite and zircon also formed during this latter stage, and wodginite and cassiterite appear as minor accessory phases. The position of fersmite and xenotime in the paragenetic sequence requires further investigation. The entire suite of rare-element minerals of the Rutherford #2 pegmatite is remarkable, exhibiting characteristics of the rare-earth, beryl, and complex pegmatite types (Černý 1989a, 1994).

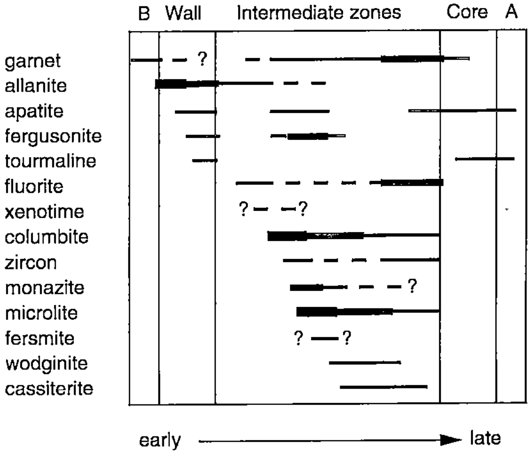

FIG. 5. Schematic diagram showing the paragenesis of rare-element minerals together with garnet, apatite, tourmaline, and fluorite. B: border zone; A: alteration of the microcline – quartz core and precipitation of hydrothermal minerals in the central vug system.

In addition to the rare-element minerals discussed above, apatite, fluorite, garnet, and tourmaline are included in Figure 5 for comparison. Garnet is a major accessory mineral in the Rutherford #2 pegmatite, ranging from dark red almandine in the border zone to pale orange spessartine in the inner intermediate zone and amazonitic microcline – quartz core (Sinkankas & Reid 1966, Sinkankas 1968). Minor amounts of apatite and tourmaline crystallized during formation of the wall zone, amazonitic microcline – quartz core, and finally in vugs in "cleavelandite" and quartz during the latest, hydrothermal stage of pegmatite consolidation (Lemke *et al.* 1952, Mitchell 1964, Sinkankas 1968). Apatite is uncommon in the second intermediate zone, where monazite is a major accessory phase, and tourmaline is largely absent from the intermediate zones. Fluorite first appeared in the outer intermediate zone and continued to form sporadically through the formation of the intermediate zones to the quartz core. The early fluorite is purple to brownish purple in color, and the later examples are colorless, pale green to yellowish green, or deep green. Evidence from this group of accessory minerals indicates that the Rutherford #2 pegmatite-forming magma was strongly enriched in F and P, and moderately enriched in B.

Based on recent studies of feldspars in granitic pegmatites (*e.g.*, Černý *et al.* 1985, Černý 1989, 1994), the K, Rb, and Cs contents of the microcline samples studied by Glass (1935) generally indicate that a moderate level of Rb and Cs enrichment was reached during the final stages of magmatic crystallization. However, the Li abundance appears to be quite low; *e.g.*, there are no primary Li minerals, the overall abundance of tourmaline is quite low, and the early-formed tourmaline is the Li-poor variety schorl.

Internal evolution of the pegmatite

The mineral paragenesis outlined above demonstrates that, from wall zone to quartz core, the melt – fluid evolved from a system enriched in *REE*, Fe, Nb, Ti, Th, and U to one enriched in Mn, Ta, Sn, Zr, and Hf. This change in character is borne out by the presence of early allanite + fergusonite followed by assemblages consisting of fergusonite + columbite – tantalite + monazite + microlite, and finally giving way to columbite – tantalite + microlite + wodginite + cassiterite. Although extreme Ta enrichment is not observed in columbite – tantalite *per se*, the trend of Mn and Ta enrichment (see Fig. 4) is very similar to those shown by samples from the Li-rich Bob Ingersoll and Tin Mountain pegmatites in the Black Hills, South Dakota (Spilde & Shearer 1992). The comparative evidence suggests that effective Fe–Mn fractionation can also occur in F-rich and Li-poor systems, which is strongly supported by the behavior of garnet in the Rutherford #2 pegmatite. There, the available data indicate that X_{Sps} varies from ~0.5 to 0.9 (Sinkankas & Reid 1966, unpublished SEM–EDS analyses of the author).

There is little evidence to indicate that the magma was saturated with H_2O at the time of emplacement. The first indication of the presence of an aqueous fluid phase is the alteration of fergusonite in the wall zone, but this fluid may have exsolved at a later time during formation of the interior units and migrated toward the wall zone of the pegmatite. The occurrence of the perthite hood unit is consistent with the model of Jahns & Burnham (1969), and suggests early separation of an aqueous fluid phase that migrated upward, carrying K, Si, and perhaps B. However, this process clearly requires extensive fractionation of K from Na, and is inconsistent with more recent results (Burnham & Nekvasil 1986).

The role of aqueous fluid has been questioned on several grounds by London and coworkers; London (1996) provided a recent review. Experiments conducted by London *et al.* (1989) clearly demonstrate that many of the textural features of granitic pegmatites are reproduced by the non-equilibrium crystallization of undercooled, H_2O-undersaturated melts. In the Rutherford #2 pegmatite, the best textural evidence of a free fluid phase is provided by the second, middle, and inner intermediate zones, where the morphology of albite changes from blocky, to massive bladed, to euhedral bladed with an increase in the volume of open space between albite blades toward the microcline – quartz core. Textural evidence cited here provides only a rough bracket for saturation in an aqueous fluid at some time between the formation of the wall zone and inner intermediate zones, but is in general agreement with the results of London *et al.* (1989).

Additional evidence for the presence of a fluid phase during formation of the intermediate zones includes fine-grained muscovite ± topaz alteration (Glass 1935, Lemke *et al.* 1952, Sinkankas 1968), together with continued alteration of fergusonite along grain boundaries and fractures. In the final stages of pegmatite consolidation, residual aqueous fluid present after crystallization of the inner intermediate zone and microcline – quartz core reacted with and dissolved portions of the core zone and also deposited a significant suite of late-stage minerals in the central system of vugs (Table 1).

In summary, the lithologic units of the Rutherford #2 pegmatite crystallized more or less sequentially from wall zone to core under non-equilibrium, initially H_2O-undersaturated conditions. From the mineral assemblages, the melt is inferred to have been peraluminous and enriched in F, P, and Ca, and to have contained moderate amounts of B, Rb, and Cs, but the Li content was low. Owing to the presence of B, F, and possibly P, the solubility of H_2O in the melt was enhanced relative to the haplogranite – H_2O system (Pichavant 1987, London *et al.* 1988, Holtz *et al.* 1993, Keppler 1993). The activity of H_2O gradually increased through crystallization of the border, wall, and outer intermediate zones. Crystallization of apatite, fluorite, and tourmaline near the end of this stage may have contributed to the increase in H_2O activity, caused a decrease in the activity of SiO_2, and ultimately promoted the development of albite-rich intermediate zones and of saturation in an aqueous fluid (London 1987, 1992, 1996). The presence of F and P (but not B) in the melt allowed for enhanced solubilities of high-field-strength cations (Keppler 1993, London 1996), resulting in a continuous sequence of crystallization of rare-element accessory minerals from wall zone to core.

Mineral alteration: relevance to nuclear waste disposal

Results of this study demonstrate that potential actinide host phases such as fergusonite, microlite, monazite, and zircon structure-types behaved differently when exposed to the hydrothermal fluid generated by crystallization of the Rutherford #2 pegmatite. From the observations made to date, it is clear that fergusonite, monazite, and thorite are all susceptible to alteration. Of these phases, thorite and fergusonite have experienced the most severe alteration, primarily along grain boundaries and fractures. Alteration of fergusonite involved exchange of Nb for Ta, loss of *REE*, and minor increases in Th and other minor elements. In the case of monazite, back-scattered image contrast in SEM images combined with the available analyses suggest that exchange of the $ThSiO_4$ component for the *REE*PO_4 component occurred during alteration. Microlite and zircon, on the other hand, appear to have been relatively resistant to hydrothermal alteration. Minor late "secondary" alteration localized along microfractures has been reported in microlite from the Rutherford #2 pegmatite (Lumpkin & Ewing 1992).

Although the composition of the hydrothermal fluid is not well constrained, the suite of hydrothermal minerals (Table 1) qualitatively indicates that the fluid contained Be, B, F, Si, P, S, Ca, Mn, Fe, and CO_2. Furthermore, a relatively acidic composition is suggested by dissolution of the microcline – quartz core and the alteration of feldspars to muscovite ± topaz (Burt & London 1982). The temperature at the time of alteration is uncertain, but the available experimental data provide a temperature range of approximately 450–700°C, *i.e.*, somewhere between the vapor-saturated liquidus and solidus temperature (*e.g.*, Jahns & Burnham 1969, Burnham & Nekvasil 1986, Fenn 1986, London 1987, Webster *et al.* 1987). If saturation in an aqueous fluid occurred during development of the intermediate zones, as suggested above, then maximum temperatures on the order of 500–600°C would be expected.

The results of this study demonstrate that alteration of potential actinide host phases is strongly dependent on the composition of the fluid phase. Microlite and thorite from the Harding pegmatite were chemically altered by a relatively basic, Ca-rich and Na-poor aqueous fluid phase at P and T in the range 2–4 kbar and 350–550°C (Lumpkin & Chakoumakos 1988, Lumpkin & Ewing 1992). This fluid also contained significant amounts of CO_2, F, P, Mn, and Fe. In fact, thorite from granitic pegmatites and other rocks is commonly microfractured, hydrated, and chemically altered (Frondel 1958). In contrast, zircon is generally known to be highly resistant to alteration by an aqueous fluid, but some corrosion of zircon has been observed in F-rich fluids at ~600°C during metamorphism of granitic gneiss and at >250°C during hydrothermal alteration of rhyolite [Wayne *et al.* (1992), Rubin *et al.* (1993); see Ewing *et al.* (1995) for a brief summary].

Monazite is also known to be a highly durable phase in aqueous fluids, but there is some evidence that it is unstable in pelitic rocks below ~450–500°C, where allanite, apatite, florencite, titanite, and *REE*- and Th-oxides appear to be stable instead [Akers *et al.* (1993), Kingsbury *et al.* (1993); see Boatner & Sales (1988) for a review]. Under these conditions, the fluid phase is typically dominated by H_2O, CO_2, and CH_4, together with variable concentrations of Na, K, Ca, Fe, and Cl, but it is relatively F-poor (Ferry & Burt 1982). The composition of the metamorphic fluid is quite different from that of a fluid derived from the igneous assemblage described above, indicating that monazite may react with a broad range of hydrothermal fluids. Clearly, detailed experimental studies using aqueous fluids of different composition are required in order to fully understand the behavior of actinide host phases in nuclear waste forms.

Implications of cation order in columbite – tantalite

The relatively high degree of cation order in columbite – tantalite from the Rutherford #2 pegmatite is unusual, considering the small size of the pegmatite and the presence of significant amounts of minor elements in the samples. Previous work indicates that the development of cation order is a function of several parameters, including cooling rate and the presence of minor elements (*e.g.*, Černý *et al.* 1986, Wenger & Armbruster 1991, Spilde & Shearer 1992, Ercit *et al.* 1995). The qualitative aspects of these studies indicate that relatively ordered samples tend to form in large granitic intrusions and pegmatites, whereas highly disordered samples crystallize in the smaller granitic pegmatites. In many of these examples, the columbite – tantalite samples exhibit lower concentrations of minor elements in the ordered samples, prompting speculation that elements like Ti, Sn, and Sc may influence the overall distribution of cations.

In a detailed study of columbite – tantalite from the Harding pegmatite, Lumpkin (1998) demonstrated a range of cation order as a function of position in the pegmatite. Early samples from the wall zones are partially to highly disordered, whereas samples from the interior lithologic units tend to be highly ordered. Owing to the low concentrations of minor elements in the columbite – tantalite crystals, it was suggested that the range of cation order is primarily related to the cooling rate, estimated to have decreased by as much as two to three orders of magnitude during emplacement of the pegmatite (see the cooling model of Chakoumakos & Lumpkin 1990). The cooling rate is ultimately related to the size of the igneous body and the difference in temperature between the intrusion and the surrounding rocks. Although the thermal history of the Rutherford #2 pegmatite is currently poorly constrained, the relatively ordered distribution of cations in columbite – tantalite suggests that the cooling rate was relatively slow during crystallization of the second intermediate zone and subsequent lithologic units.

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