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CRYSTALLIZATION AND ALTERATION HISTORY OF BRITHOLITE IN RARE-EARTH-ELEMENT-ENRICHED PEGMATITIC SEGREGATIONS ASSOCIATED WITH THE EDEN LAKE COMPLEX, MANITOBA, CANADA

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ABSTRACT

Pegmatitic segregations and quartzofeldspathic veins associated with the Eden Lake Complex, Manitoba, Canada, contain significant abundances of rare-earth elements (*REE*), U and Th, concentrated in minerals such as titanite, apatite, allanite and britholite. Titanite and apatite are typically found as discrete, zoned, and locally euhedral crystals. Allanite occurs both as discrete crystals as well as irregular segregations, whereas britholite occurs only as irregular masses. The allanite and britholite typically share sharp but irregular contacts with the host silicate minerals (aegirine-augite, K-feldspar and quartz). Allanite normally occurs between britholite and the silicate minerals, suggesting that it formed as the result of reaction between a *REE*-bearing fluid rich in P and F and the silicate minerals. Within the irregular masses of britholite, one sees an unusual polygonal mosaic-like texture with polygons ranging from 20 to 200 μm. Polygon boundaries are straight to slightly curved, intersect at triple junctions, and converge at angles from 60 to 180°. This texture is likely the product of reheating and annealing of the britholite. However, as a result of metamictization, the britholite retains little long-range order. Many of the polygons are altered preferentially along polygon boundaries. Chemical analyses indicate that U, Th, La, Ce, F and Cl were mobile during the alteration, whereas Y seems to have been immobile. Altered britholite has lower La and Ce contents than unaltered britholite, but the La/Ce value remains essentially unchanged. Altered britholite has lower F/Cl values than unaltered britholite, and U and Th contents show significant scatter that in turn is related to elevated Cl contents.

Keywords: britholite, titanite, allanite, annealed texture, rare-earth element, anorogenic, Eden Lake complex, Manitoba, Canada.

SOMMAIRE

Des ségrégations pegmatitiques et des veines quartzofeldspathiques associées au complexe du lac Eden, au Manitoba, Canada, contiennent des teneurs importantes en terres rares, uranium et thorium, concentrés dans des minéraux tels titanite, apatite, allanite et britholite. La titanite et l'apatite se présentent en général en cristaux individuels zonés et même idiomorphes dans certains cas. L'allanite se présente à la fois en cristaux bien formées et en ségrégations irrégulières, tandis que la britholite n'est présente qu'en masses irrégulières. L'allanite et la britholite partagent en général une interface irrégulière mais franche avec les silicates qui les englobent (augite aegyrinique, feldspath potassique et quartz). L'allanite est normalement interposée entre la britholite et le minéral silicaté, ce qui laisse supposer qu'elle s'est formée suite à une réaction entre une phase fluide porteuse de terres rares, P et F et le minéral silicaté. Parmi les masses irrégulières de britholite, on peut voir une texture polygonale en mosaïque assez inusitée, dans laquelle les polygones vont de 20 à 200 μm. Les bordures de ces polygones sont rectilignes ou légèrement courbes, définissent des points triples, et des angles de 60 à 180°. Cette texture serait le résultat d'un réchauffement et d'une recuisson de la britholite. Toutefois, suite à une métamictisation, la britholite possède très peu d'ordre cristallin à longue échelle. Dans plusieurs cas, les polygones ont été préférentiellement altéré le long de leur bordure. D'après les résultats d'analyses chimiques, les éléments U, Th, La, Ce, F et Cl étaient mobiles pendant l'altération, tandis que l'yttrium semble avoir été inerte. La britholite altérée possède des teneurs plus faibles en La et Ce que la britholite saine, mais la valeur du rapport La/Ce est restée quasiment inchangée. La britholite lessivée possède un rapport F/Cl plus faible que la britholite saine, et les teneurs en U et Th font preuve d'une dispersion importante des concentrations, qui serait fonction des teneurs élevées en Cl.

Mots-clés: britholite, titanite, allanite, texture de recuisson, terres rares, anorogénique, complexe du lac Eden, Manitoba, Canada.

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INTRODUCTION

Britholite, (Ca,*REE*,Y)$_5$(SiO$_4$,PO$_4$)$_3$(F,OH), is a member of an isomorphous series with apatite, Ca$_5$(PO$_4$)$_3$(F,Cl,OH); the series is defined by the substitution of the trivalent rare-earth elements (REE^{3+}) and Si^{4+} for Ca^{2+} and P^{5+} (Khudolozhkin *et al.* 1973, Mariano 1989). Abukumalite, the yttrian analogue of britholite, also forms a solid-solution series with apatite (Hughson & Sen Gupta 1964, Khudolozhkin *et al.* 1973). Britholite has been described as both hexagonal and orthorhombic (Winther & Böggild 1899), but later work has shown that it is hexagonal (Gay 1957).

Britholite was originally documented from the Julianehåb District in South Greenland (Winther & Böggild 1899); since then, occurrences have been described from several alkaline intrusions, including nepheline syenite complexes, in the Urals, Siberia, central-eastern Russia, South Africa, Argentina, and a carbonatite complex at Oka, Québec (Hughson & Sen Gupta 1964, Vlasov 1966, Mariano 1989, Lira & Ripley 1990). In most occurrences, britholite forms as a result of hydrothermal alteration, such as at the Rodeo de Los Molles deposit in Argentina (Lira & Ripley 1990) and in the Shonkin Sag laccolith (Nash 1972). However, at Naujakasik, Greenland, britholite occurs as "megacrysts" within a granitic pegmatite (Winther 1901).

A wide range of chemical compositions and physical properties have been reported for britholite. In hand samples, britholite appears brown with a resinous luster (Gay 1957, Hughson & Sen Gupta 1964); in thin section, britholite ranges from pale green with wavy extinction to colorless with straight extinction (Hughson & Sen Gupta 1964, Nash 1972). Britholite commonly occurs in a metamict or partly metamict state (Hughson & Sen Gupta 1964).

In this paper, we report on the compositional, textural and alteration characteristics of britholite from the Eden Lake Complex in northern Manitoba. The Eden Lake Complex (ELC) is part of a 15 km^2 intrusive suite located in north-central Manitoba within the Lynn Lake domain of the Churchill Province (Cameron 1988, McRitchie 1988, Halden & Fryer 1999). The complex is made up of a number of intrusive units, the most prominent of which is an aegirine-bearing monzonite. Reconnaissance petrological and geochemical analysis, as well as radiometric surveys, highlighted the unusual nature of the ELC (McRitchie 1988, 1989). Britholite is the principal mineral host for the rare-earth elements; it is found in association with allanite, fluorite, titanite and apatite in pegmatitic segregations in the intrusion. Whole-rock analysis of such segregations has shown that they are enriched in light rare-earth elements (*LREE*); in some cases they are up to 50,000× the levels in chondrites (McRitchie 1989). In addition, the britholite can contain up to 0.1% Th and 0.03% U, so the intrusive complex constitutes a significant radiometric anomaly. However, only a few relatively small britholite-bearing zones have been discovered to date, and consequently these *REE* deposits are currently not economically significant (McRitchie 1989). In this study, we describe the paragenesis of the britholite and the role of hydrothermal activity in the evolution of the Eden Lake Complex.

GEOLOGICAL SETTING

The Eden Lake complex (ELC) is emplaced in granitic rocks at the western end of the Leaf Rapids greenstone belt in the Reindeer Zone of the Trans-Hudson Orogenic terrane (Fig. 1). The ELC is a post-orogenic pluton with many characteristics of alkaline associations, including high *REE* and fluorine contents (Halden & Fryer 1999). The ELC comprises a number of intrusive phases, ranging in composition from monzonite to quartz monzonite; there are also several types of pegmatitic segregations associated with the complex, described in detail by Arden (1994). The complex has not yet been dated, but it is similar to other post-orogenic alkaline plutons dated at about 1710 Ma (Rb:Sr; Halden *et al.* 1990).

The mineralogy and textures of the phases of the intrusive complex are similar, tending to be both homogeneous and equigranular; the quartz monzonite is distinguished by having more quartz and K-feldspar (McRitchie 1988). However, monzonite is medium grained and slightly foliated; it contains schlieren of ferromagnesian minerals, dominantly aegirine-augite. The quartz monzonite, in contrast, is fine grained and non-foliated; it lacks ferromagnesian schlieren and contains angular blocky inclusions of the monzonite. Contacts between these two intrusive phases are irregular, and sharp to gradational over several meters; the contacts are well exposed on the outcrops, but cannot be traced from exposure to exposure owing to overburden.

The pegmatitic segregations associated with the ELC complex can be subdivided into four distinct types. Type-I mafic stringers are randomly distributed throughout the complex; they are coarse-grained segregations consisting of aegirine-augite, hornblende and magnetite, typically up to 20 cm long and 2 cm wide. Type-II segregations occur as patches and veins throughout the outcrop area; these range from a few cm wide to patches up to approximately 10 m^2, typically contain K-feldspar and quartz ± plagioclase (albite), and locally show a graphic intergrowth of K-feldspar and quartz. Type-III segregations occur as patches several cm^2 to 50 cm^2 on the prominent ridges of outcrop. They differ from Type II in that they contain aegirine-augite, fluorite, zircon, andradite, apatite and titanite, in addition to quartz and K-feldspar. Type-IV (radioactive) segregations are the least abundant, occurring only in the east of the outcrop area; they coincide with significant radiometric anomalies in regional scintillometer surveys (McRitchie 1989). They occur as discontinuous veins associated with shear zones, with the maximum width of the veins varying

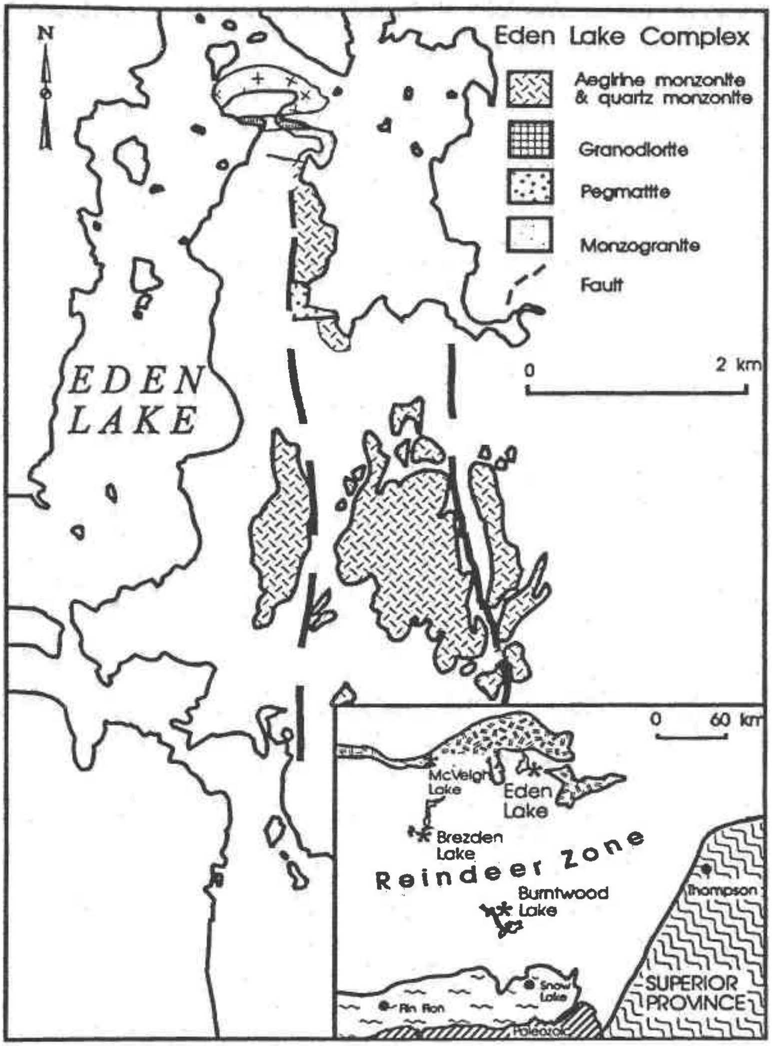

FIG. 1. Schematic map of the Eden Lake Complex showing the principal areas of outcrop (modified from McRitchie 1989). Inset map shows the location of Eden Lake within the Reindeer Zone of northern Manitoba.

from 30 to 50 cm. One vein can be traced in outcrop for 30 m, but most veins pinch out after 10 m. These veins cross-cut both the meso- and leucomonzonite with irregular but sharp contacts. The minerals found in the Type-IV segregations include aegirine-augite, quartz, K-feldspar, plagioclase (albite–oligoclase), titanite, britholite, allanite, apatite, fluorite, zircon, thorite and weloganite. The grain size attains 3 cm.

EXPERIMENTAL METHODS

Chemical analyses of the britholite samples were carried out on a Cameca SX–50 electron microprobe at the University of Manitoba. Proportions of major and minor elements (Si, Al, Fe, Ca, Ti, F, Cl, P) were determined using a specimen current of 20 nA, an excitation voltage of 15 kV, and a peak count-time of 20 seconds. Concentrations of trace elements (*REE*, Y, U and Th) were determined using a specimen current of 40 nA, an excitation voltage of 20 kV, and a peak count-time to 20 seconds. Rare-earth-element data were corrected for line overlaps following the method of Roeder (1985). Data reduction was done using the PAP method described by Pouchou & Pichoir (1985). The following standards were used: diopside (Si, Ca), almandine (Fe), pyrope (Al), titanite (Ti), monazite (P), riebeckite (F), tugtupite (Cl), the Drake & Weill (1972) glass standards *REE*-1, -2, -3, -4 (La, Ce, Nd, Sm, Eu, Gd, Dy), UO_2 (U), and ThO_2 (Th).

Bulk analyses of the britholite for H_2O content were done using a Mitsubishi Moisture Meter model CA–06; this instrument uses a coulometric titrimetry method that involves the quantitative reaction of water with iodine. Five separates of britholite were placed in an oven at 150°C for 72 hours to remove adsorbed water prior to analysis.

The degree of crystallinity of the britholite was determined qualitatively using a Buerger Precession Camera with beam conditions set to 40 kV and 20 nA. Britholite samples were exposed to unfiltered radiation and slowly rotated. Photographs were obtained after a ten-minute exposures.

Britholite: Optical and Textural Characteristics

Britholite is only found in the Type-IV pegmatitic segregations, typically occurring as anhedral irregular amorphous masses with no apparent cleavage. It can vary from 2 to 70 vol.% within the Type-IV veins, with individual grains or segregations ranging in size from 0.6 mm to 5 cm.

In plane-polarized light, the britholite is yellow to light orange, nonpleochroic, and isotropic; some grains have a darker orange color. The britholite forms anhedral and irregular grains with straight to sutured edges. Britholite is intimately associated with apatite, allanite and fluorite; crystals of apatite, titanite, aegirine-augite, allanite, fluorite and small grains of an unidentified U–Pb phase are found as inclusions. Britholite grains are commonly rimmed by allanite, and this assemblage usually has an irregular embayed contact with the silicate minerals (Figs. 2A, B). This embayed contact may be the product of a reaction between a F-, P-, *REE*-enriched fluid and the silicate minerals (Halden & Fryer 1999). Many grains of britholite contain an unusual polygonal texture (Fig. 3); the contacts between britholite and allanite crystals tend to be straight along the edges of polygons, and sutured where polygons are not easily seen. The britholite is commonly pervasively cracked (Figs. 2, 3); spatially associated minerals, including aegirine-augite, titanite, quartz, K-feldspar and apatite, are similarly fractured (Fig. 2B).

Examination of the segregations of anhedral britholite using back-scattered electrons (BSE) reveals that the segregations are made up of a number of smaller polygonal grains. These are distinguished by variations

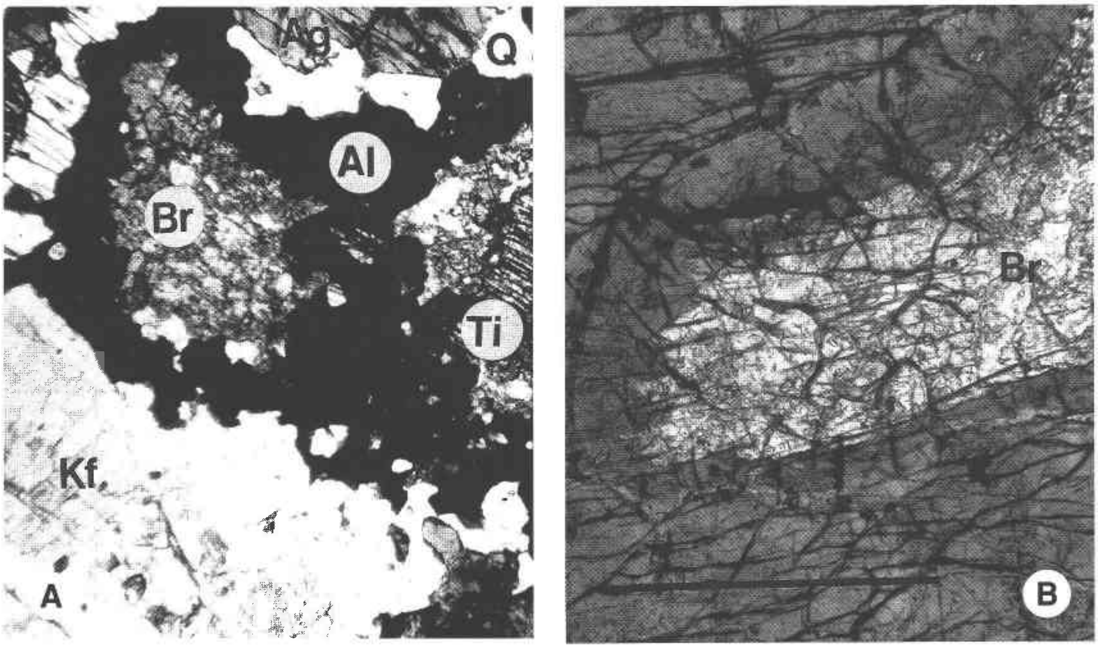

FIG. 2. A. Photomicrograph of an anhedral grain of britholite (Br). The britholite has irregular and sutured contacts with the other minerals. Associated minerals include allanite (Al), titanite (Ti), quartz (Q), aegirine-augite (Ag) and K-feldspar (Kf); apatite is visible as small bright inclusions in the britholite. Fractures are present within titanite, quartz and aegirine-augite. The width of the field of view is 1.5 mm. B. Photomicrograph of part of a grain of yellow britholite showing irregular contacts with an aegirine crystal; fractures run continuously through the grain contacts. The scale bar is 1 mm.

in grey level, which are related to chemical variations within the polygons (Fig. 4). The polygons range in size from 20 to 200 μm, averaging from 50 to 100 μm. Polygonal boundaries intersect at triple junctions, with interfacial angles ranging from 60 to 180°, although typical triple junctions intersect at angles of 120°. This texture suggests a stable arrangement, formed in conditions of equal free-energy of the grain surfaces (*cf.* Vernon 1976). In some britholite polygons, a faint oscillatory pattern (concentric about a central core) is apparent, whereas in others, a patchy discontinuous pattern is observed, possibly suggestive of remnants of crystalline domains. Anhedral to subhedral crystals of apatite, which lack well-defined crystal margins, occur ubiquitously in the margins between the britholite polygons (Fig. 4). These range in size from 10 to 100 μm. If the polygonal texture is interpreted as an annealed texture, this textural relationship between the apatite and britholite may indicate a form of zone refinement of the apatite phase.

Further examination of BSE images reveals that many of the britholite polygons are altered (Figs. 5A, B). The alteration has an overall vermicular to colloform character and is concentrated along the margins of the britholite polygons, decreasing in intensity from polygon boundaries to the center of the polygons. Polygons range from completely unaltered to completely altered; in the most altered samples, the polygonal texture is completely destroyed (Fig. 5B). The less altered polygons tend to be nearer the center of the segregations of anhedral britholite, whereas the more altered areas tend to be concentrated around the margins of the segregations, in contact with other rock-forming minerals. In some polygons, more than one alteration "front" is apparent (Fig. 6). These are seen as progressively darker regions in the BSE images, indicating that the average atomic number of the matrix in these regions is decreasing. Fractures are observed within the altered regions.

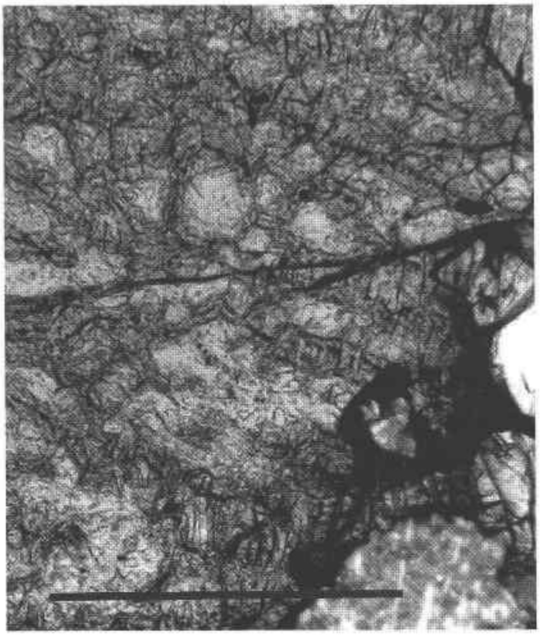

FIG. 3. Photomicrograph of part of a britholite grain in plane-polarized light. The irregular polygonal pattern is easily seen, the altered regions at the crystal edges being darker than the internal regions in the polygons. The scale bar is 1 mm.

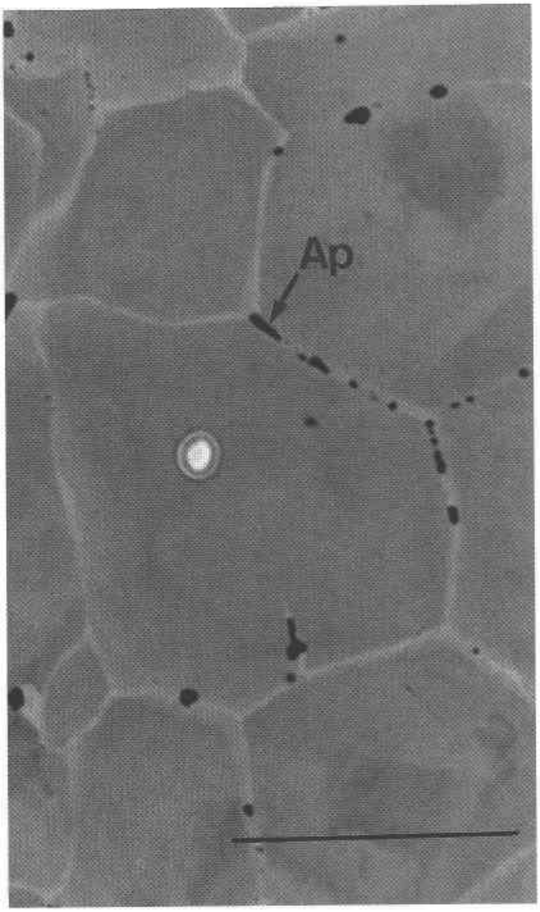

FIG. 4. Back-scattered electron (BSE) image of part of a britholite grain with polygonal texture. Individual polygons have straight margins (lighter owing to the topographic effect of scattering electrons) that intersect at triple junctions. Some polygons show a patchy zoning as variations in grey level. The anhedral dark grains at the margins of the polygons are apatite (Ap). The white spot visible in the center of the view is an ablation pit. The scale bar is 50 μm.

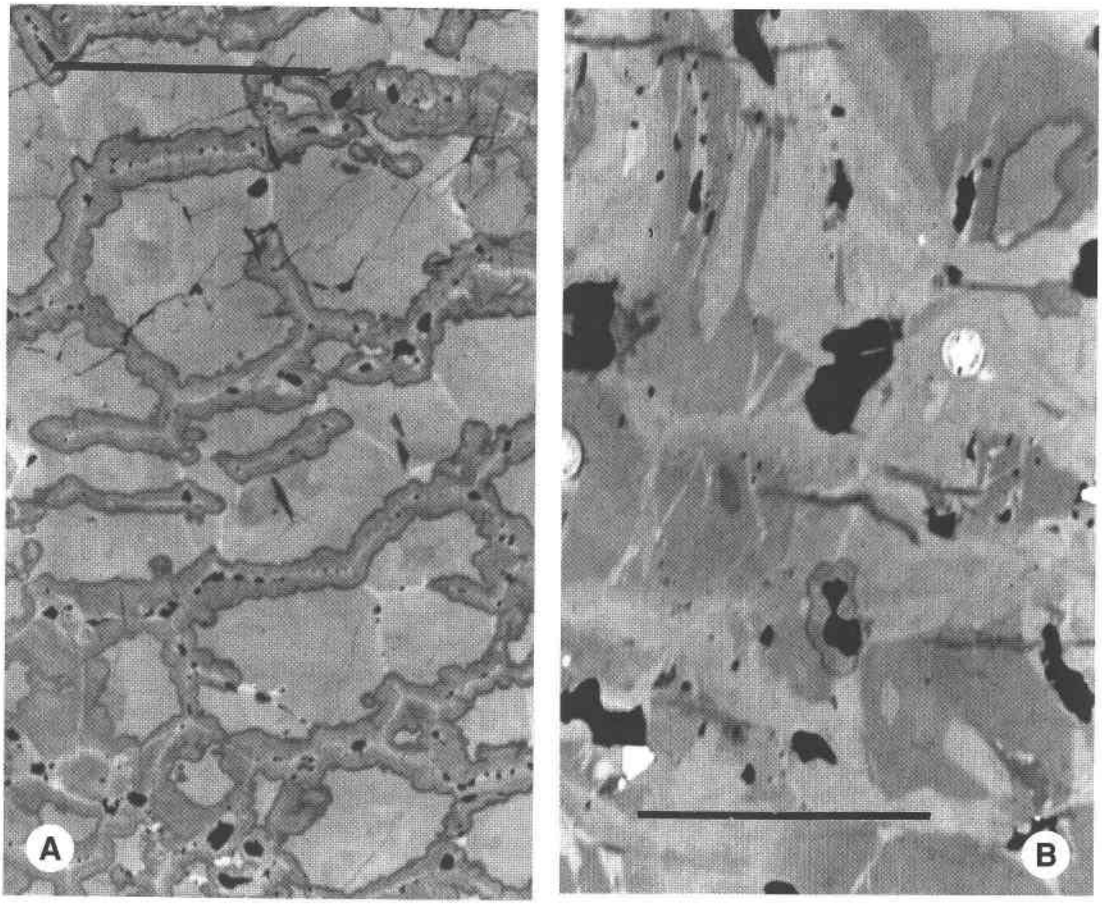

FIG. 5. BSE images of britholite grains. A. Britholite showing vermicular alteration concentrated along the margins of the polygons. B. Britholite showing extreme alteration to the point that polygon boundaries are almost completely obscured; the scale bar is 50 μm in each case.

These fractures are reminiscent of fractures seen in zoned zircon, where the decay of U and Th within certain zones results in a volume change within that zone (*cf.* Chakoumakos *et al.* 1987). The localization of the fractures within the altered zone suggests that this small-scale change in volume is restricted to the altered regions and that it occurred after the alteration. Moreover, the removal of decay products could be a contributing factor to the volume change, and this may also be related to the scatter observed in the U and Th contents (see below). The shapes of the interstitial grains of apatite do not seem to be affected by the alteration. In thin section, the altered britholite is darker tan and more intensely fractured.

Analysis of britholite grains using the precession camera showed only a few faint scattered reflections, indicating that the britholite has little or no crystallinity. This would require that the britholite either formed as an amorphous mass or the crystal structure was destroyed by post-crystallization metamictization and attendant amorphization.

BRITHOLITE: CHEMICAL CHARACTERISTICS

The altered and unaltered britholite have different levels of brightness in BSE images, suggesting that they have different compositions. In order to characterize these compositional differences, chemical analyses have been done (Table 1).

In terms of major elements, both the unaltered and altered britholite are similar to what is reported in the literature. The britholite contains both U and Th; no values are reported in the literature for UO_2, but the amount of ThO_2 determined is about five times lower

TABLE 1. COMPOSITION OF ALTERED AN UNALTERED BRITHOLITE COMPARED WITH COMPOSITIONS FROM OTHER STUDIES

	1	2	3	4	5	6	7	8	9
SiO_2 wt.%	18.70	19.28	18.68	20.04	20.22	19.91	16.77	12.28	16.20
ΣFe_2O_3	-	-	-	-	-	-	0.43	0.14	0.08
CaO	16.18	15.47	15.87	13.57	13.01	12.85	11.28	28.84	16.60
BaO	-	-	-	-	-	-	-	-	0.07
SrO	-	-	-	-	-	-	-	-	0.46
PbO	-	-	-	-	-	-	-	-	0.24
MgO	-	-	-	-	-	-	0.13	-	0.02
K_2O	-	-	-	-	-	-	-	-	0.07
Al_2O_3	-	-	-	-	-	-	-	0.47	0.09
TiO_2	0.02	0	0	0	0	0	-	-	-
P_2O_5	4.67	3.48	4.07	1.92	1.67	1.53	6.48	16.96	7.03
F	3.25	2.87	2.42	2.81	3.01	2.15	1.33	2.10	3.80
Cl	0.02	0.06	0.11	0.04	0.04	0.20	-	-	0.28
OH	-	-	-	-	-	-	1.27	0.54	-
S	-	-	-	-	-	-	-	-	0.07
UO_2	0.74	0.74	0.75	0.92	0.70	0.96	-	-	-
ThO_2	1.12	0.91	1.00	1.25	1.19	1.06	-	5.62	-
Y_2O_3	1.89	1.96	1.88	2.18	2.26	2.15	Σ60.54	Σ33.43	0.40
Ce_2O_3	24.75	24.90	24.30	26.06	26.19	25.37			22.50
La_2O_3	8.86	8.89	8.55	8.70	8.22	8.31			16.3
Pr_2O_3	-	-	-	-	-	-			2.79
Nd_2O_3	12.94	12.91	12.65	13.98	14.63	13.71			6.92
Sm_2O_3	1.74	1.92	1.83	2.09	2.34	1.98			1.66
Eu_2O_3	0.29	0.28	0.33	0.32	0.37	0.30			0.61
Gd_2O_3	1.35	1.06	1.11	1.34	1.32	1.31			2.85
Dy_2O_3	0.52	0.58	0.40	0.48	0.59	0.63			0.29
Ho_2O_3	-	-	-	-	-	-			0.98
Er_2O_3	-	-	-	-	-	-			0.26
Yb_2O_3	-	-	-	-	-	-			0.18
Nb_2O_5	-	-	-	-	-	-	-	-	0.13
Total	97.04	95.31	93.95	95.70	95.76	92.42	98.23	100.38	100.88
Si^{4+} *apfu*	2.442	2.588	2.532	2.753	2.782	2.843	3.52	1.625	2.064
Fe^{3+}	0	0	0	0	0	0	0.068	0.014	0.008
Ca^{2+}	2.264	2.225	2.305	1.997	1.918	1.966	2.537	4.09	2.266
Al^{3+}	0	0	0	0	0	0	0	0.073	0.014
Ti^{4+}	0.002	0	0	0	0	0	0	0	0
P^{5+}	0.516	0.395	0.467	0.223	0.195	0.185	1.152	1.9	0.758
F^-	1.342	1.218	1.038	1.221	1.31	0.971	0.883	0.879	1.531
Cl^-	0.004	0.014	0.025	0.009	0.009	0.048	0	0	0.06
U^{4+}	0.022	0.022	0.023	0.028	0.021	0.031	0	0	0
Th^{4+}	0.033	0.028	0.031	0.039	0.037	0.034	0	0.169	0
Y^{3+}	0.131	0.14	0.136	0.159	0.165	0.163	0	0	0.027
Ce^{3+}	1.183	1.224	1.206	1.311	1.319	1.326	0	0	1.05
La^{3+}	0.427	0.44	0.427	0.441	0.417	0.438	0	0	0.766
Pr^{3+}	0	0	0	0	0	0	0	0	0.13
Nd^{3+}	0.603	0.619	0.612	0.686	0.719	0.699	0	0	0.315
Sm^{3+}	0.078	0.089	0.085	0.099	0.111	0.097	0	0	0.073
Eu^{3+}	0.013	0.013	0.015	0.015	0.017	0.015	0	0	0.027
Gd^{3+}	0.058	0.047	0.05	0.061	0.06	0.062	0	0	0.12
Dy^{3+}	0.022	0.025	0.017	0.021	0.026	0.029	0	0	0.012
Ho^{3+}	0	0	0	0	0	0	0	0	0.04
Er^{3+}	0	0	0	0	0	0	0	0	0.01
Yb^{3+}	0	0	0	0	0	0	0	0	0.007
Nb^{5+}	0	0	0	0	0	0	0	0	0.007

Results of electron-microprobe data. Formulas are calculated on basis of 12 oxygen and 1 (F,Cl) atoms per formula unit (*apfu*). Columns: 1: A2 unaltered, 2: A2 unaltered, 3: A2 altered, 4: A4 unaltered, 5: A4 unaltered, 6: A4 altered, 7: Böggild (1905), 8: Hughson & Sen Gupta (1964), 9: Nash (1972).

than that reported by Hughson & Sen Gupta (1964; Table 1). Total *REE* contents in the britholite range from 52.8% to 54.56%; this is similar to total *REE* content reported by Nash (1972; Table 1). However, Nd abundances are significantly higher and La abundances are significantly lower than those of Nash (1972).

Comparison of the major-element contents of samples A2 and A4 in Table 1 illustrates the coupled substitution of Si^{4+} + REE^{3+} for Ca^{2+} + P^{5+}; a high concentration of SiO_2 correlates with high levels of the *REE*, whereas low Ca is coupled with low P, irrespective of the state of the britholite. Sample A4 also has higher Y contents, which might be anticipated, as Y^{3+} is likely to accompany the REE^{3+}; this covariation in the Y and *REE* contents is probably connected with the initial crystallization of the britholite. The oxide wt.% totals of the altered britholite found along polygon boundaries are consistently lower than the totals for the unaltered britholite (Table 1). This difference suggests a higher volatile content in the altered britholite. Analysis of bulk samples (containing both altered and unaltered britholite) for H_2O suggests the presence of about 1.5 wt.% H_2O (Table 1).

FIG. 6. Alteration fronts (seen as variations in grey level from dark to lighter grey) along polygon boundaries; younger alteration-fronts cross-cut older alteration-fronts (arrow). Apatite is still seen as anhedral (black) crystals concentrated along polygon boundaries. Fractures orthogonal to polygon boundaries are concentrated within altered margins. Scale bar is 20 µm.

Figure 7 shows a chondrite-normalized plot of rare-earth-element concentrations for selected samples; the britholite is significantly enriched in the light *REE*s. The most abundant *REE* is Ce, followed by La, then Nd. Both unaltered and altered britholite show a negative Eu anomaly, suggesting this is an original feature of the britholite rather than a product of alteration. Dy was the only heavy *REE* whose concentration was established with confidence; it was found to be typically on the order of 4000 to 5000 ppm. Figure 8 shows the concentration of La plotted against that of Ce for two selected samples of britholite; the altered britholite has systematically lower La and Ce contents than the unaltered britholite; within individual samples, however, the La/Ce value remains fairly constant. Furthermore, altered britholite has lower F and higher Cl contents than unaltered britholite (Fig. 9). The ratio of fluorine to chlorine is therefore lowered in altered regions of the polygons, suggesting a late exchange of Cl for F (Table 1).

Figure 10 shows a plot of Y *versus* (La + Ce) concentrations. Whereas the La/Ce value stays almost constant, the total (La + Ce) content of the britholite decreases during alteration, and the Y content also stays relatively constant, suggesting that Y is relatively immobile. There is a positive correlation between the Y and (La + Ce) in altered and unaltered britholite from sample A2; this correlation may reflect an original substitution-induced trend between Y and the *REE* in the britholite that has survived the alteration. The difference between alteration and the substitution trend becomes more apparent if Cl concentration is plotted against Y/[(La + Ce)/100] (Fig. 11). Here the alteration trending to higher Cl contents distinguishes the altered samples from the unaltered samples; the unaltered samples (A2 and A4) preserve the substitution trend of Y for the *REE*.

In contrast to Y, La and Ce, the U and Th content of both the altered and unaltered britholite show significant scatter (Fig. 12; the U:Th ratio ranges from about 0.65 to 0.9). The altered samples, characterized by higher Cl contents, show a wider range of U/Th values, from about 0.55 to 1 (Fig. 13). Both U and Th thus are probably mobile, but not in a particularly systematic way. Micro-PIXE (proton-induced X-ray emission) analysis across grain boundaries and fractures in minerals adjacent to the altered britholite show elevated abundances of U, Th, Pb, Y and Nd (Halden *et al.* 1995); the irregular distribution of these elements in such fractures is consistent with the scatter in the distribution of U and Th data points.

DISCUSSION

Origin of the britholite

Comparative studies of the minerals in the pegmatitic segregations indicate that those of Type III and IV have much in common: (i) the mineral assemblages (with the exception of britholite and allanite), (ii) zoning characteristics in titanite, zircon, and apatite, where crystallization is characterized by an early period of irregular growth followed by a later period of oscillatory growth, and (iii) compositional similarity in titanite,

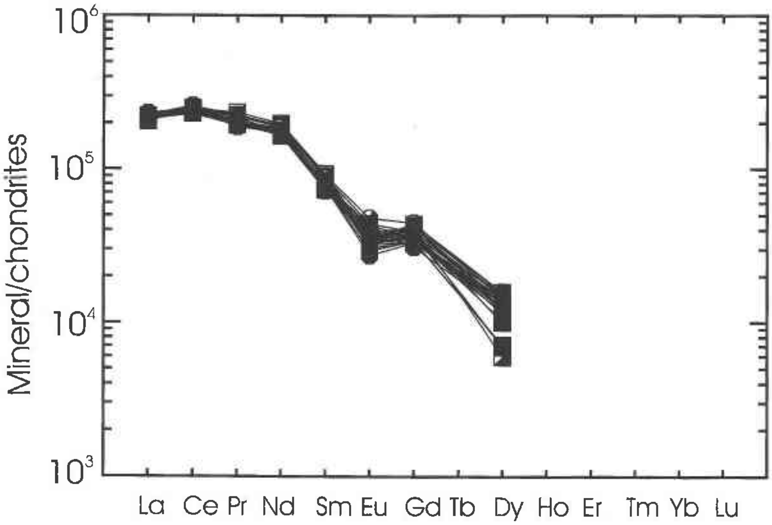

FIG. 7. Chondrite-normalized rare-earth-element plot of unaltered britholite and altered britholite (normalization values are from Sun 1982). At the scale of the plot, the differences in the *REE* content of the altered and unaltered britholite are not evident.

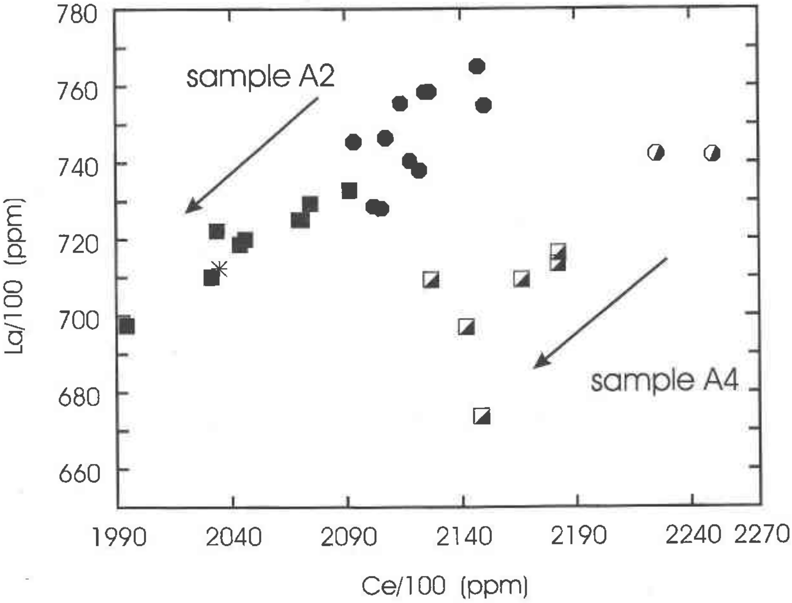

FIG. 8. Graph of La *versus* Ce concentrations for selected samples of britholite A2 (full symbols) and A4 (partially filled symbols). Circles are used for unaltered britholite, and squares for altered britholite. The analytical point shown with an asterisk was analyzed as unaltered material; the spot was close to a polygon margin, however, and the volume of excitation may have overlapped the altered region. The same symbols are used on subsequent plots. The altered samples have systematically lower La and Ce contents (in ppm); the arrows are used to indicate increasing alteration. The La/Ce value in altered and unaltered britholite stays the same within individual samples.

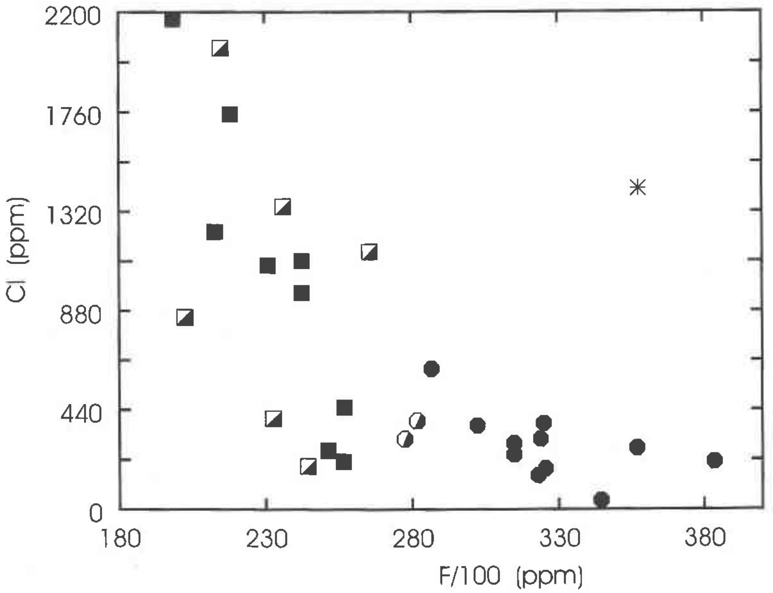

FIG. 9. Graph of Cl concentration *versus* F/100 for unaltered and altered britholite. Unaltered britholite tends to have higher F and lower Cl contents than altered britholite. The anomalous point shown with the asterisk has high F and Cl; the composition thus probably includes both altered and unaltered material.

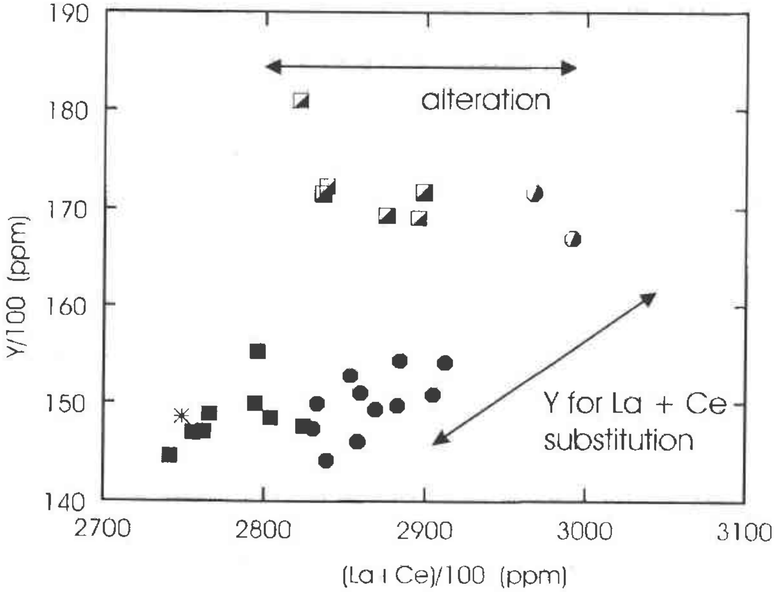

FIG. 10. Graph of Y/100 *versus* (La + Ce)/100 for unaltered and altered britholite. Samples A4 and A2 have distinctly different Y contents and La/Ce values, which are probably related to the original crystallization of the britholite and related to La–Ce–Y substitution. Alteration has reduced the total *REE* content of both samples.

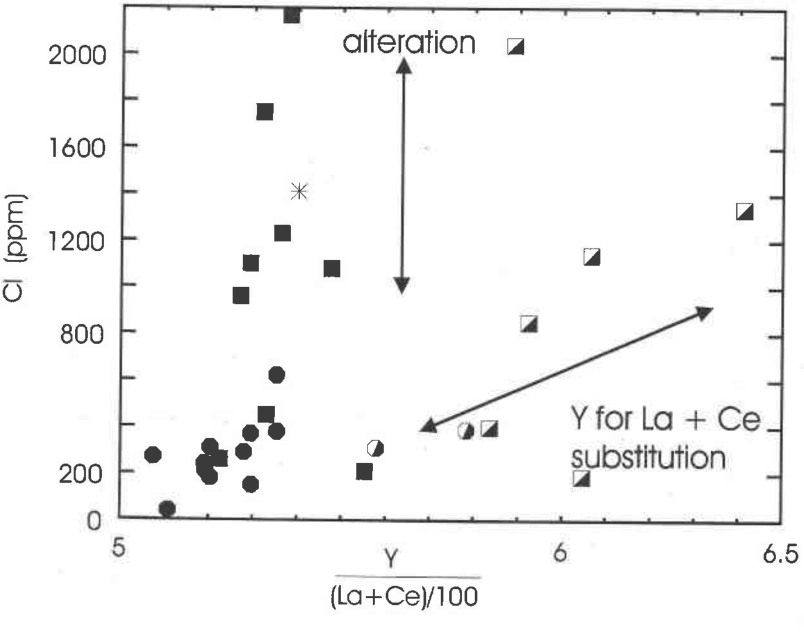

FIG. 11. Graph of Cl concentration *versus* Y/[(La + Ce)/100]. Samples A4 and A2 differ with respect to their La/Ce values and Y content, reflecting substitution (shown schematically by the diagonal arrow). However, the altered britholite becomes clearly distinguished as having distinctly different and higher Cl contents (shown schematically by the vertical arrow).

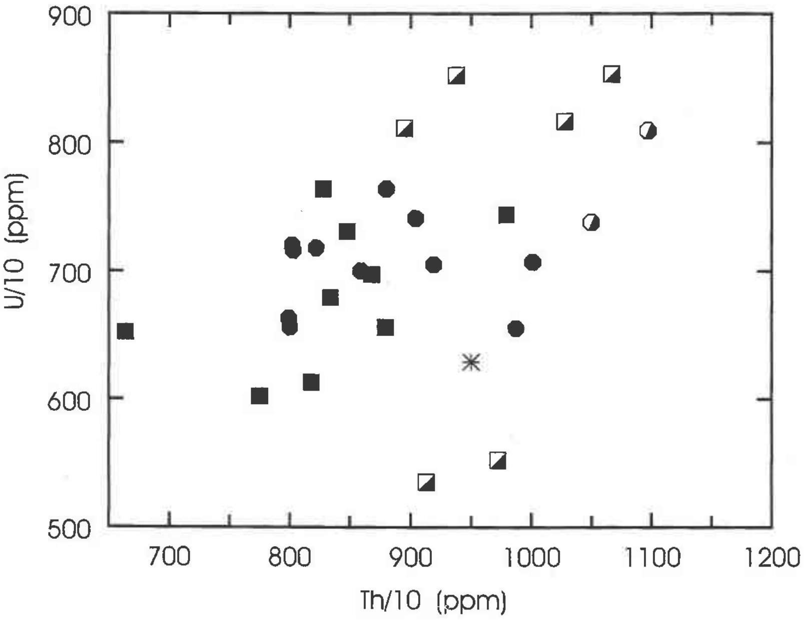

FIG. 12. Graph of U/10 *versus* Th/10. The U and Th values show much more scatter than what is seen for the Y, La and Ce values; the data points from A2 and A4 overlap.

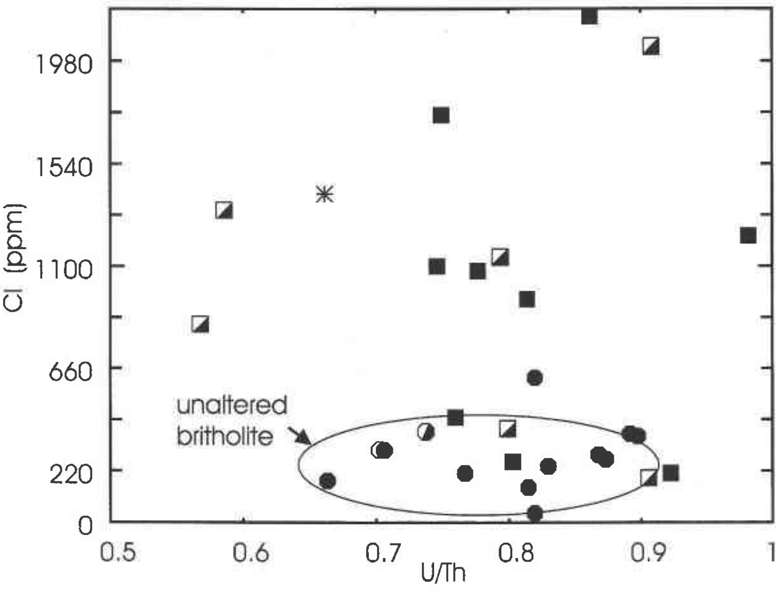

FIG. 13. Graph of Cl concentration *versus* U/Th. The unaltered britholite occupies a small region in the lower part of the diagram. Altered britholite occupies a much wider region and has higher Cl and more variable U/Th values.

zircon and apatite in terms of elevated *REE* contents. We contend that the pegmatitic segregations of Type IV probably formed from those of Type III through reaction with a *REE*-, F-, P-enriched fluid.

The crystal-fractionation history of the Eden Lake Complex points to an early stage of *REE* compatibility with an accessory assemblage that included titanite, zircon and apatite (accompanied by K-feldspar and aegirine; Halden & Fryer 1999). The more evolved, silica-rich rocks of the complex tend to be significantly depleted in *REE*. In terms of *REE* content, there is a distinct compositional gap between a more primitive monzonite and later quartz monzonites in the complex. This gap is not consistent with a smooth uninterrupted liquid line of descent dominated by crystal fractionation. Any *REE* not taken up by the accessory minerals during the early stages of crystallization will tend be concentrated in a liquid or vapor phase as the magma crystallizes. The association of the irregular pegmatitic segregations with the complex and their compositional similarities suggest a genetic association that could be maintained if a late-stage vapor-rich phase formed. This process would have involved segregation of the pegmatitic material from the more evolved magmas (Halden & Fryer 1999). Under these circumstances, such a *REE*-, F- and P-enriched fluid may have become immiscible with respect to the main magma, allowing it to migrate and undergo a separate evolution. This fluid could be introduced to some of the pre-existing pegmatitic material (Type III) along fractures and shears (Fig. 14). The fluid would then have reacted with the existing minerals, including apatite, aegirine, K-feldspar and quartz, to form britholite and allanite. This model of formation would account for the embayed and irregular boundaries between the britholite and the silicate minerals (consistent with the fluid being far from chemical equilibrium with the host minerals) and the association with allanite.

Origin of the polygonal texture

The absence of any well-defined crystalline domains in the polygons suggests metamictization of the britholite. If this is the case, however, preservation of the distinct, sharp polygon boundaries requires that this annealed texture formed after the crystallization and metamictization of the britholite. This requires also time for the

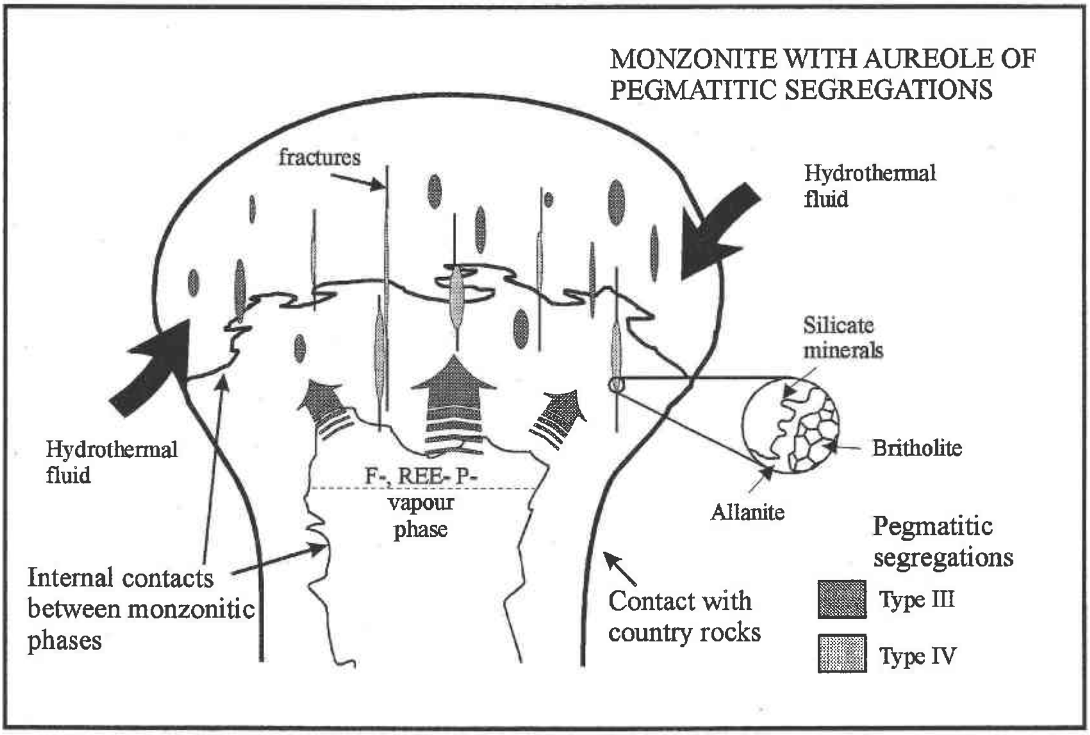

FIG. 14. Schematic diagram showing Type-III and Type-IV pegmatitic segregations and different stages of fluid ingress within and into the Eden Lake Complex (modified after Černý & Meintzer 1988). The first fluid modified the Type-III segregations to Type-IV, with the introduction of the F-, P-, *REE*-enriched fluid phase along fractures. Subsequent introduction of hydrothermal fluids modified the britholite polygons.

metamictization and annealing, and heat. Given the elevated abundances of *REE*, U and Th in the britholite, it is likely that self-amorphization or metamictization was caused by alpha-particle emission in the U and Th radionuclide series within the mineral itself (*cf.* Swanson *et al.* 1971, Eby *et al.* 1991, Weber 1992). Remnant heat from this process might also have contributed to some annealing. Evidence for radioactive-decay damage is seen in the fractures within associated silicate minerals (aegirine-augite, quartz, K-feldspar) and apatite.

Polygonal textures are common in annealed and sintered materials (*cf.* Vernon 1976). If the polygonal texture represents an annealed or sintered britholite, it would require a period of elevated temperatures that postdates the crystallization and metamictization of the britholite and predates the alteration of the britholite; as the other minerals within the pegmatitic segregations retain their igneous texture, the temperature required for the annealing process has to have been low enough not to affect any of the other minerals. Any remnant heat associated with amorphization of the britholite is an unlikely source to explain the annealed texture; studies on amorphized $Ca_2La_8(SiO_4)_6O_2$ crystals with the apatite structure indicate that annealing does not occur at temperatures below 500°C (Weber & Wang 1994). Heat derived from a regional thermal metamorphic event is difficult to constrain because of the lack of recrystallization in the host rocks. The complex has strong marginal foliation that McRitchie (1988) attributed to a metamorphic event; this foliation, however, is not pervasive throughout the intrusion. Heat connected with hydrothermal alteration of the pegmatitic segregations is an additional alternative; there is evidence that the polygon boundaries have been altered by some form of hydrothermal fluid.

Britholite alteration

The vermicular texture seen at the polygon boundaries indicates that the britholite has been altered. The hydrothermal fluids responsible moved along the polygon boundaries; alteration proceeded from the margins into the grains. The presence of more than one alteration front can be explained by (i) several stages of fluid ingress into the britholite, where the polygonal boundaries acted as the loci for fluid movement during each event, or (ii) local buffering of the fluid's composition resulting from alteration of the britholite.

The britholite probably underwent hydration and exchange reactions that removed F, Ce and La and at the same time replaced the F^- with $(OH)^-$ and Cl^-. The gains and losses of the *REE* during such alteration were a function of (1) initial abundances in the unaltered mineral and the stability of the minerals with respect to coexisting fluid, (2) the concentration of the *REE* in the fluid, (3) partitioning of the *REE* between the mineral and the fluid, (4) the ability of the fluid to transport the *REE*, and (5) the ability of secondary minerals to form during reactions (Humphris 1984, Mariano 1989). The transport of the rare-earth elements in hydrothermal fluids for any distance requires the formation of carbonate, fluoride or sulfate complexes. The removal of both F and *REE* from the britholite suggests that the *REE* were most likely transported out of the system as fluorinated complexes. The conversion of Ce to the oxidized state enables it to be mobilized more readily than the other rare-earth elements; La often shows similar behavioral trends, although it has only one valence state. Electron-microprobe results suggest that U and Th have not been similarly mobilized; however, U and Th show significant scatter, suggestive of local disturbances. Whereas this finding is consistent with previous work suggesting that U and Th are mobile under hydrothermal conditions (Pan *et al.* 1993), the pattern of alteration seems to be quite different from that shown by La and Ce. The chemical affinity among Y, La and Ce might suggest that yttrium too should be mobile; as Y is more comparable to the heavy *REE*, however, it is not likely to show significant effects attributed to alteration.

Late fluids

Fractional crystallization and the development of igneous layering have influenced the early history of the Eden Lake Complex (Halden & Fryer 1999). Later stages have been dominated by the segregation and movement of a vapor phase. This late, segregated fluid has altered the earlier-formed and consolidated rocks to make the type-IV pegmatites. The type-IV pegmatites record a longer history in the form of metamictized and subsequently annealed minerals. If the heat that annealed the minerals was introduced by another, later, hydrothermal fluid, the exact nature and source of this fluid cannot be constrained at present. The fluid may be related to late-magmatic fluids that postdated the formation of the britholite, or it may be a meteoric fluid mobilized by a later intrusion. Cameron (1988) indicated that there are two granitic bodies in the Eden Lake area that postdate the Eden Lake Complex; intrusion of these may have set up a hydrothermal cell causing circulation of fluids at elevated temperatures. In this case, heat preceding the intrusion of these bodies could have annealed metamictized britholite, and this would then have been followed by a period of fluid ingress to the Eden Lake Complex along fracture systems associated with deformation around the complex.

Insights into temperatures that might have been associated with the hydrothermal fluid can be gained from studies of other similar *REE* deposits. The peralkaline Strange Lake pluton, on the Quebec–Labrador border, was hydrothermally altered by a number of successive events and contains a Zr, Y and *REE* deposit (Currie 1985, Salvi & Williams-Jones 1990). The first event involved the introduction of an Na-enriched fluid; the second involved the introduction of an Ca-, Y- and *REE*-enriched fluid; the Y and *REE*s were transported as fluorinated complexes. Deposition of the mineralized zone occurred due to a reduction in ligand concentration accompanying fluorite deposition. Fluid-inclusion studies indicate that the formation of the deposit occurred at relatively low temperatures, less than 200°C, and that the hydrothermal fluid was meteoric in origin (Salvi & Williams-Jones 1990).

The Rodeo de Los Molles deposit, Las Chacras batholith, Argentina, has a mineral assemblage very similar to that of the Type-IV pegmatitic segregations, including aegirine, apatite, titanite, quartz, britholite and allanite (Lira & Ripley 1990, 1992). The *REE* deposit is hosted within a hydrothermally altered zone of alkali-feldspar granite and syenite that occurs within a biotite monzogranite. During hydrothermal alteration, the rocks gained Na and K, and lost Ca and Sr; continued alteration produced localized *REE* deposits. The fluids were of magmatic origin and were channeled from the base of the intrusive system to the top (Lira & Ripley 1992). The temperature of formation of the deposit is a point of controversy, with postulated values ranging from 500°C (Lira & Ripley 1992) to 200°C (Williams-Jones & Wood 1991). The Eden Lake Complex may have undergone a similar history of hydrothermal alteration after the formation of the Type IV segregations as is observed in the Rodeo de Los Molles deposit: hydrothermal alteration was superimposed on cross-cutting pegmatitic segregations (Fig. 14).

CONCLUSIONS

Britholite is one of the latest minerals to form in the Type-IV pegmatitic segregations of the Eden Lake Complex. These pegmatitic segregations are considered to have been derived from Type-III segregations by the introduction of *REE*-, P- and F-rich fluids along shear zones and fractures. This fluid reacted with the pegmatite-forming minerals, and led to the crystallization of the britholite. The fluid, incorporating the *REE*, was of late-magmatic origin and formed as the result of vapor-phase segregation during the late stages of crystallization of the complex.

The polygonal texture observed in the britholite is the result of annealing of metamictized britholite. The heat responsible for annealing was related to late hydrothermal alteration of the britholite; alteration post-dated the annealing process. The hydrothermal fluid responsible moved along the polygonal boundaries and may have been chemically buffered by the britholite; it introduced OH^- to the britholite and removed F^- and *REE*s. The latter were probably transported out of the system as fluorinated complexes.

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