Polylithionite from the rare-metal deposits of the Blachford Lake alkaline complex, N.W.T., Canada

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Abstract

Extensive deposits of rare lithophile elements are located within albitized and greisenized peralkaline granite and syenite at Thor Lake, in the Blachford Lake complex east of Yellowknife, Northwest Territories in Canada. Five structural zones, affected by metasomatic alteration and locally also brecciation, host zoned assemblages with Be, Nb-Ta, REE, Y, Zr and Ga mineralization. Polylithionite is a major phase in several units of the mineralized zones; its abundance amounts to tens of thousands of tons. The chemistry, physical properties and structural characteristics of two polylithionite samples from widely separated locations are almost identical, and are close to the typical properties of the end-member 1M polylithionite. Ti, Nb, Mg, Rb/Cs and Fe³⁺/Fe²⁺ are much higher whereas Rb and Cs are remarkably lower than their ranges in lepidolites from orogenic to post-orogenic peraluminous granitic pegmatites. However, the compositional field of 1M polylithionites is apparently transitional into that of 1M lepidolites which partly overlaps with 2M₁ and 2M₂ polytype ranges.

Introduction

In contrast to the widespread occurrence of lithian muscovite and lepidolite sensu lato in granitic pegmatites of orogenic affiliation, polylithionite K(Li₂Al)Si₄O₁₀(F,OH)₂ is restricted to alkalic and peralkaline paragenesis of anorogenic igneous suites. There are only a few documented localities of polylithionite, as reviewed by Raade and Larsen (1980): the Ilimaussaq massif in Greenland; Lille Arey, Låven and Vara in Norway; Mount St. Hilaire in Canada; the Lovozero massif in Kola peninsula, and the Transangara massif in Siberia. In most of these occurrences, polylithionite is present in subordinate quantities or as a rarity among later minerals lining walls of miarolitic cavities. The Thor Lake, N.W.T. polylithionite reported here is all the more interesting because the abundance of this mica, as currently estimated at this locality, may amount to tens of thousands of tons. However, this exceptional accumulation of polylithionite is not the only facet of the Thor Lake deposits that deserves attention. The broad array of Be, Nb, Y, REE, Zr and Ga-bearing minerals identified in them, their paragenetic relationships within different mineralization zones, and the economic potential of the district will undoubtedly attract much attention in the future.

Regional setting

The Thor Lake occurrence of polylithionite is located at the southern margin of the Archean Slave Province of the Canadian Shield, approximately 100 km southeast of Yellowknife and about 5 km north of the north shore of Great Slave Lake (Fig. 1). The locality is centered within the Blachford Lake complex of alkaline to peralkaline affinity. This intrusive complex penetrates Archean metasediments and calc-alkaline granitoid intrusions of the Slave Province to the north, but on its southern side it is closely adjacent to the Aphebian metasediments, metavolcanics and intrusions of the so-called East Arm or Athapuscow aulacogen of Great Slave Lake (Hoffman et al., 1977).

The Blachford Lake complex was first described by Stockwell (1932) and it was thought to be of Archean age, as are the surrounding host rocks. Later work by Davidson (1972, 1978) and Hoffman et al. (1977), and more recently by Bowring et al. (1984) have confirmed Aphebian ages within the complex; U-Pb zircon study from two components, the Hearne Channel granite and the Thor Lake syenite gave 2175 ± 10 and 2094 ± 10 m.y. respectively.

The Blachford Lake complex

The Blachford Lake complex is a relatively large (16 × 33 km in outcrop), subcircular, high-level plutonic complex (Fig. 1). It has been described by Davidson (1972, 1978, 1982) as consisting of an earlier, western suite of gabbr o, quartz syenite and granite, and a later intrusion of volumetrically dominant Grace Lake granite, with a core of Thor Lake syenite (Fig. 1). The early suite is relatively aluminous, whereas the two members of the late suite are
distinctly peralkaline, with acmite in their norms. They show a marked enrichment in Fe, Mn and Na relative to the granitoid members of the early suite, and they also are prominently rich in Nb, REE's, F and partly in Be and Li (Davidson 1982). In general, however, both suites are considered consanguineous.

The Grace Lake granite is described by Davidson (1978) as a remarkably uniform, massive, coarse-grained, equigranular rock. Its color is variable from reddish pink through buff to pale gray. Mesoperthitic alkali feldspar, quartz and riebeckite mark this rock as a hypersolvus riebeckite granite. Accessory minerals include fluorite, magnetite, zircon, carbonates and probable monazite and phenacite.

The Thor Lake syenite is more variable in its texture and composition but similar to the Grace Lake granite in many respects, except the quartz content. It is medium- to coarse-grained, greenish gray, buff to rusty brown weathering, and massive to locally schistose. Rock-forming minerals of this hypersolvus hornblende syenite include perthitic alkali feldspar (locally phenocrystic) and riebeckite, with subordinate magnetite and minor quartz. Accessory minerals include ubiquitous zircon and a ferromagnesian mica. A more mafic, pyroxene + olivine bearing syenite forms a thin rim along the margins of the syenite body.

Subhorizontal pods and sheets of syenite pegmatite are found within the Thor Lake syenite. They consist of giant euhedra of hornblende and/or pyroxene and perthitic alkali feldspar, imbedded in a matrix of fine-grained aplitic to coarse albite.

Contact relations between the granite and syenite are obscure. In the west the granite is transitional into the syenite, with an abrupt disappearance of quartz in the former. In the north and east, the granite seems to dip under the border unit of syenite, and the contact of the two rocks is knife-sharp.

**The Thor Lake mineral deposits**

Mineralized zones occur for the most part within the western part of the Thor Lake syenite, except one that crosses its northwest margin into the Grace Lake granite (Fig. 1). Five zones of mineralization are noted at Thor Lake: the Lake, Fluorite, R, S and T zones (Fig. 2). It is the T zone that crosscuts the granite-syenite boundary, and by virtue of its paragenetic and geochemical similarities to the other zones, it implies an age postdating that of both rocks for all mineralized zones in the area. The investigation of the mineralized zones is only in its initial stages (Trueman et al., 1984, 1985; de St. Jorre and Smith, 1984); consequently, the following account is incomplete. Nevertheless, the deposits seem to fall close to the albitite and greisen types of Be, Nb, Y, REE, U and Th mineralization of Smirnov (1977).

The Lake zone is approximately central to the array of mineralized zones. It has largely been defined by diamond drilling and seems to consist of three units, two of which concentrically envelop a central brecciated core (Fig. 2). The outer unit consists essentially of fine-grained albite and quartz, with local aggregates of platy albite and scattered micas. The intermediate unit is marked by extensive albite-
Fig. 2. Disposition of the mineralized metasomatic zones in the western part of the Thor Lake syenite and in the adjacent Grace Lake granite (cf. Fig. 1), and location of the polylithionite samples S and T.

zation, with rounded inclusions of magnetite and hornblende, coarse fragments of perthitic alkali feldspar, fluorite and inclusions of ultramylonite. The core of the Lake zone is occupied by breccias, the fragments of which consist of syenite pegmatite (feldspar + hornblende + magnetite). The fragments are cemented by fine- to coarse-grained matrix of albite and ferromagnesian mica. Accessory minerals include zircon, uranothorite, allanite, magnetite, hematite, columbite, pyrochlore, rhombohedral carbonates, bastnaesite and lanthanite.

The Fluorite zone, the least investigated one in the district, is located on the southeast side of the Lake zone and along the southeastern projection of the T-zone trend (Fig. 2). Fluorite is the dominant mineral in this zone; the altered rock is enriched in Nb and REE's.

The R zone lies north of the Lake zone and follows a vertical fault in strongly foliated Thor Lake syenite. This east-north-east trending fault truncates the T zone near its south end. For the most part, the R zone consists of foliated syenite, with local patches of syenite aplite and syenite pegmatite. Although albitization is evident along some 1000 meters along strike, alteration is not clearly noticeable in the field. The albitized segments, however, are enriched in Th, REE's, Be and F.

The S zone strikes northeasterly away from the northern margin of the Lake zone; at its southeastern terminus it seems to point towards a focus common with the southern termination of the T zone and the western extrapolation of the R zone (Fig. 2). For the most part, the S zone is similar to the R zone. The S zone consists of a linear but slightly branching system, locally offset by east-north-easterly faulting and broadened by diffuse patches of albitization. In one location such albitization swells to approximately 20 meters, and is characterized by a core of mica-rich assemblages subhorizontally disposed in the albite. The mineralogy of this alteration zone has not been examined in detail, but the polylithionite sample S examined in this study comes from this zone (Fig. 2). Assays of the altered rock from this zone indicate considerable enrichment in Th, Ce and particularly Nb which locally reaches 20 wt.%.

The T zone is currently the subject of extensive diamond drilling, geological documentation and geochemical analysis, as a part of feasibility studies for beryllium, yttrium, niobium, REE's and gallium. It is described in more detail below.

The T zone

This zone is north-north-westerly trending for approximately 1,000 meters. It pinches and swells along strike, reaching a maximum horizontal east-west thickness of nearly 300 meters. The down-dip extent has been verified to a 150 meters minimum, and in most parts of the zone it remains open.

For descriptive purposes the T zone can be subdivided into two parts: an upper member at the northern extremity, and a lower member which underlies the northern extremity, shoals upward and extends south towards the Lake zone. The northern portion of the T zone, hosted by the Grace Lake granite, is shown in a longitudinal section in Figure 3; it is essentially representative of both members and all their mineral assemblages (Trueman et al., ms. in prep.; Jambor, 1985).

In Figure 3, mineral assemblages of the T zone are subdivided into four units: (1) a border unit consisting predominantly of albite; (2) a lower intermediate unit consisting of feldspars, quartz, riebeckite and micas, with magnetite and fluorite; (3) an upper intermediate unit of quartz, albite, micas, acmite and fluorite; and (4) a core unit essentially of quartz with lenticular streaks of the lower and upper intermediate units.

The border unit is a massive, fine- to coarse-grained (locally pegmatitic) feldspathic rock developed around the overlying, more severely altered rocks. The unit is characteristically light pink to brownish-red on weathered surfaces, and it consists largely of fine-grained albite and platy radial cleavelandite. The quartz and K-feldspar contents of the rock are variable, with much of the quartz as blebs or veinlets of late origin. Fluorite is common, whereas fine-grained sulphides, magnetite, zircon, chlorite, Ca,Fe,Mg-carbonates, columbite, ilmenite, phenacite, parsite, synchisite and roentgenite are accessory to rare.

In a number of outcrops in the north end of the T zone, brecciation of the border unit is common; large angular
blocks of albite are seen imbedded in a matrix of massive quartz.

The term lower intermediate unit is applied to a massive rock which is coarse-grained and black to dark brownish-gray on weathered surface, due to extensive staining by manganese oxides. Textural similarities and preserved relics of granite in the north end, and syenite in the south end of the T zone, are particularly abundant in the lower intermediate unit. The assemblage consists principally of albite, quartz, riebeckite, various micas, magnetite, chlorite and Ca, Fe, Mg, Mn-carbonates. Mica types are diversified; preliminary identification indicates the presence of biotite, phlogopite, muscovite and lepidolite. Accessory minerals include fluorite, yttriofluorite, topaz, zircon, pyrrhotite, chalcopyrite, gersdorfftite, sphalerite, hematite, pyrochlore, rutile, anatase, columbite, phenacite, bertrandite, gadolinite, helvite-danalite, xenotime, monazite, apatite and REE-bearing fluorocarbonates of the bastnaesite group.

Rock types of the upper intermediate unit are located above, or intercalated with the assemblages of the lower intermediate unit, or they are in contact with the overlying quartz unit. In outcrop these rocks are massive, coarse-grained, and rather unweathered in appearance. They consist of quartz, polylithionite, lepidolite, muscovite, zinnwaldite, biotite, albite of variable morphology and grain size, acmite, and phenacite. Magnetite, pyrochlore, ilmenite, columbite, hematite, rutile, anatase, chloride, bertrandite, gadolinite, zircon, yttriofluorite, fluorite, Ca, Fe, Mg, Mn-carbonates, xenotime, monazite, apatite, sphalerite, chalcopyrite, galena, molybdenite, pyrite and the REE-bearing species of the bastnaesite group are present in accessory amounts. The second sample of polylithionite examined in this study comes from this unit (Figs. 2, 3).

The quartz unit lies in contact with the assemblages of all the other units—border, lower intermediate, and upper intermediate. In the foremost case, brecciation is noted, and in the latter case contacts are usually intercalated but sharp. In sections other than that shown in Figure 3, rocks assigned to the quartz unit are also found discontinuously disposed in the lower intermediate unit (cf. Fig. 2).

The quartz unit is composed predominantly of quartz, with local assemblages carrying albite, muscovite, polylithionite, Ca, Fe, Mn-carbonates, hematite, fluorite, yttriofluorite, zircon, phenacite, sphalerite, pyrite, chalcopyrite, parisite, synchisite and roentgenite. Fluorite is a common accessory forming zoned crystals of a dodecahedral habit, ranging from colorless to green or purple and up to 8 cm in size.

Vugs and crystal-lined cavities are common, with quartz crystals coated with carbonates, sulfides and several as yet unidentified minerals.

Polylithionite Two samples of polylithionite were examined in the present study, one from each of the zones S and T (see Figures 2 and 3 for sampling localities). The polylithionite sample from the S zone is medium- to coarse-grained (1-12 mm across the mica flakes). The polylithionite is associated with subordinate fluorite, pyrite, sphalerite, columbite and rutile, in part Nb-bearing. The color of the mica is medium to dark gray. In contrast, the sample from zone T is pale yellowish gray; the mica is accompanied by subordinate milky quartz, pyrite and magnetite. Individual flakes range from 2 to 8 mm in size.

In both samples, polylithionite flakes and crystals usually consist of a “euhedral” six-sided core, with flat and smooth basal cleavage surfaces. The core is rimmed by a subhedral to euhedral outer zone which is finely striated to corrugated in a sectorial pattern, the direction of the strain being normal to the adjacent {110} or {010} faces. The
Table 1. Physical properties of the Thor Lake polylithionite

<table>
<thead>
<tr>
<th>Sample</th>
<th>S</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1.544(1)</td>
<td>1.544(1)</td>
</tr>
<tr>
<td>e</td>
<td>1.545(1)</td>
<td>1.555(1)</td>
</tr>
<tr>
<td>γ</td>
<td>1.560(1)</td>
<td>1.559(1)</td>
</tr>
<tr>
<td>z</td>
<td>30-40°</td>
<td>30-40°</td>
</tr>
<tr>
<td>n(α+ω+γ)/3</td>
<td>1.553</td>
<td>1.553</td>
</tr>
<tr>
<td>P(α+ω+γ)/3 calc.</td>
<td>1.562</td>
<td>1.563</td>
</tr>
<tr>
<td>D, g/cm³ (meas.)</td>
<td>2.83(2)</td>
<td>2.82(2)</td>
</tr>
<tr>
<td>D, g/cm³ (calc.)</td>
<td>2.847</td>
<td>2.841</td>
</tr>
<tr>
<td>ρ</td>
<td>5.192(4)</td>
<td>5.191(5)</td>
</tr>
<tr>
<td>ρ calc.</td>
<td>8.961(4)</td>
<td>8.960(5)</td>
</tr>
<tr>
<td>c</td>
<td>10.047(2)</td>
<td>10.044(3)</td>
</tr>
<tr>
<td>w</td>
<td>100.40(3)</td>
<td>100.40(6)</td>
</tr>
<tr>
<td>V, Å³</td>
<td>459.8(3)</td>
<td>459.4(4)</td>
</tr>
</tbody>
</table>

Structural characteristics

X-ray powder diffraction diagrams of the polylithionites were obtained from glass-slide smear mounts of filed powders on the Philips PW1710 automated apparatus, using Cu Kα radiation. The local fix and LazyCell procedures of T. S. Erzet were applied to adjust the instrumental peak readings for the desired wavelength, and to enter the data into the CELREF program. Both polylithionite samples proved to belong to the IM polytype characteristic of the species. Unit cell dimensions of the two examined samples listed in Table 1 are identical within stated error, and they fall within the extremely narrow ranges reported for the mineral (Takeda and Donnay, 1965; Munoz, 1968; Takeda and Burnham, 1969; Raade and Larsen, 1980).

Chemical composition

Chemical analyses were performed at the Laboratoire de Géochimie Analytique, Ecole Polytechnique in Montreal (Dr. G. Perrault and Mr. V. Kubat): SiO₂, Al₂O₃, Fe by X-ray fluorescence spectrometry, TiO₂, MnO, MgO, CaO, Li₂O, Na₂O, K₂O, Rb₂O, Cs₂O and BeO by atomic absorption spectrophotometry. TiO₂ was determined using a
modified method of Fratta (1974), and $Ga_2O_3$ was analyzed by X-ray fluorescence spectrometry of cupferron precipitates (cf. Černý and London 1983 for details). The above results were complemented by additional data obtained at the Geochemical Laboratory, Department of Earth Sciences, University of Manitoba (K. Ramlal): $H_2O$ by combustion, FeO by titration, $F_2$ by pyrolysis, and BaO and SrO by atomic absorption spectrophotometry.

Electron microprobe checks for Nb and Ta proved these elements below the detection limit (~0.1 wt. %). However, Zn was found variable from undetectable to about 0.5 wt.% in sample T and undetectable in sample S.

Results of the analyses and the unit cell contents based on 22 oxygen equivalents per unit cell are shown in Table 2. Crystal chemistry of these micas conforms to the characteristic features of polylithionite. The micas are near-ideally tetrasilicic, nearly trioctahedral, and the occupancy of the interlayer sites is close to theoretical. The deviations of the octahedral populations from ideally trioctahedral is evidently due to the relatively high Ti content, and some Ca in the interlayer sites. The (F,OH) contents are close to theoretical. Oxygen complementary to (F,OH) is calculated in Table 2 to increase the total of anions to the ideal charge of -44. However, this calculation does not necessarily correspond to the actual population of the (F,OH) sites, as the determinations of $F_2$ and particularly $H_2O$ are notorious for relatively low accuracy.

Discussion

Composition and polytypism of polylithionite

In Figure 4, polylithionite compositions are shown in the muscovite-trilithionite-polylithionite triangle. Besides the compositions of samples S and T, and that of the Vøra mica (Raade and Larsen 1980), four polylithionites quoted by Foster (1960) are plotted: #37 and 55 (Shilin 1953, no localities), #57 (Stevens 1938, no. 16, Antsongombato, Madagascar) and #58 (Stevens 1938, no. 17, Kangerdluarsuk, Greenland). For comparison, compositional fields characterizing different polytypes of (Li,Al)-micas from orogenic-related granitic pegmatites are shown in Figure 4, based on plots of individual data from Černý and Burt (1984).

Polylithionite data from Soviet localities quoted by Vlasov, ed. (1966, p. 26) are not used here. One of these analyses gives the formula $K_{1.44}Na_{0.46}Ca_{0.10}Fe_{2.02}Al_{2.28}Mg_{0.43}Ti_{0.04}Fe_{3.02}Nb_{0.01}Si_{7.84}Al_{0.16}O_{2.02}O_2(OH,F)_4$ which is stoichiometric but substantially deviates from polylithionite composition. The remaining analyses show $\Sigma(K,Na,Ca)$ from 2.18 to 2.82 because of unusually high NaO, which varies from 1.70 to 2.60 wt.%. Octahedral Na$^+$ has been proven to exist in alkaline igneous environments (Hazen et al., 1981), and the formulas of Vlasov's polylithionites could accommodate excess Na$^+$ in octahedral sites. However, in the absence of...
X-ray diffraction data (and Rb determination) for Vlasov's micas is it preferable not to attempt an interpretation of their crystal chemistry.

The method of calculating and plotting the mica composition (M. Rieder, pers. comm. 1969) is self-evident from the diagram; data points fall outside the triangle because of appreciable contents of either $R^+ + Li^+$ or $R^+$ independent of the $Al^{3+} + Li^{+} \approx 2R^{2+}$ substitution, or both.

All the mica compositions considered here fall into the vicinity of the polylithionite corner of Figure 4. With the exception of Shilin's (1953) samples no. 37 and 55, for which no X-ray diffraction data are available, all the other polylithionites belong to the 1M polytype. The 1M population of the polylithionite of anorogenic peralkaline igneous suites evidently adjoins the field of 1M micas of orogenic magmatic sequences with intermediate trilithionite-polylithionite chemistry. From a purely crystallochemical viewpoint, disregarding genetic affiliation, the total compositional field of the 1M polytype is very extensive and close to the degree of compositional variability found in the $2M_1$ structures.

**Geochemical signature of polylithionite**

The differences between the mineral parageneses and geochemical characteristics of anorogenic peralkaline associations and those of late-tectonic orogenic descent are well known in general, and it is noteworthy to point out this contrast as it is reflected in the compositions of (Li,Al)-micas.

In terms of major components, the Si-rich, Al-poor and alkali-rich composition of polylithionite with (K,Na, Rb) $\geq \Sigma Al$ is to be expected in a peralkaline environment. Lepidolites from peraluminous calc-alkaline pegmatites invariably have (K,Na,Rb,Cs) $< \Sigma Al$.

Among the subordinate elements, the range of Mg contents of polylithionite (0.04-0.58 per 22 oxygen equivalents) is distinctly higher than that of the lepidolites (generally less than 0.12). This feature is accentuated by the peralkaline provenance of the (Mg$_4$Li$_2$)-mica taeniolite, with which polylithionite may form intermediate compositions via the octahedral substitution $Al^{3+} + Li^+ \approx 2Mg^{2+}$. Elevated contents of Ti and Nb, and very high Fe$_{3+}$/Fe$_{2+}$ ratio are characteristic of polylithionite (Table 2; Raade and Larsen 1980) but rarely encountered in lepidolite.

Trace elements have not been sufficiently investigated in polylithionite. If the data of Table 2 are taken as representative, the low Ba and Sr contents are in accord with the expected high fractionation levels of polylithionite-bearing parageneses, and they are comparable with those of lepidolites (Černý and Burt, 1984). However, the Rb and particularly Cs contents are much lower than lepidolite averages; the Rb/Cs ratio is extremely high but the Rb/Ti values are within the usual limits of terrestrial igneous compositions (cf. Černý et al., 1985). The two Ga determinations quoted in Table 2 show widely different results and no conclusions can be drawn from them. However, the Al/Ga ratio 402 of the T mica is among the lowest ever recorded in silicates, and rather low even among the notoriously Ga-enriched micas (Černý et al., 1985).

**Concluding remarks**

The above description of polylithionite represents only the first of many contributions to the mineralogy of mineralized peralkaline granitoid rocks that can be expected from the Blachford Lake complex. With progress of exploration and eventual mining, the Thor Lake deposits will undoubtedly provide excellent material for crystallochemical, paragenetic and geochemical studies. Among the variety of rock-forming and rare-element minerals, the micas should attract particular attention. Several mica types encountered in diverse assemblages suggest compositional variability that ought to be indicative of changes in the composition, redox potential and pH of parent fluids, and in their reaction with igneous protoliths. Thus the mica mineralogy will provide a powerful tool for deciphering the conditions of crystallization of their parent assemblages.

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