MINERALOGY OF RARE-EARTH-BEARING "THUCHOLITE", PARRY SOUND, ONTARIO

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ABSTRACT

Examination of a rare-earth-bearing "thucholite" from Parry Sound, using combined back-scattered electron imagery and electron-microprobe techniques, shows that the "thucholite" consists of pyrobuitumen with inclusions of several minerals. The rare earths are concentrated in three phosphate phases: 1) irregular masses of lanthanum-rich phosphate that may predate the pyrobuitumen, 2) stringers and dense networks of cerium-rich phosphate crystals, and 3) subhedral ellipsoidal crystals of thorium-rich phosphate. The stringers and ellipsoids contain authigenic phases precipitated following local remobilization of elements from the pegmatite.

Keywords: hydrocarbon, pegmatite, pyrobuitumen, rare earths, "thucholite", Parry Sound, Ontario.

INTRODUCTION

Metal-rich solid pyrobuitumen described as "thucholite" occur at numerous localities in southern Ontario. The term "thucholite" was introduced by Ellsworth (1928a) to describe a substance from Conger Township, Parry Sound, Ontario, which consists predominantly of thorium, uranium, carbon, hydrogen and oxygen (Th, U, C, H, O – lite). The Conger occurrence, like many elsewhere, is in a pegmatite dyke that cuts Precambrian gneisses. Shortly after the discovery in Conger Township, thucholite was recorded at Besner mine, Henvey Township, Parry Sound district (Spence 1930).

Thucholite was subsequently recorded from Quebec (Ellsworth 1928b, Spence 1940) and from several districts of Ontario, including Algoma (Joubin 1954), Eldorado (Boyle & Steacy 1973), South March (Charbonneau et al. 1975, Jonasson et al. 1977) and Elliot Lake (Ruzicka & Steacy 1976, Stevenson et al. 1990).

The occurrence of thucholite in several pegmatite dykes has suggested to some workers a magmatic origin for the carbon (Ellsworth 1928a, 1932, Barthauer et al. 1953, Mueller 1969). However, at the Besner mine, the pegmatite also contains oil and asphalt-like bitumen in cross-cutting fractures, and thucholite tends to occur in the vicinity of the oil-bearing zones (Spence 1930). Given that there are numerous oil shows, and some oil production, in the Lower Paleozoic of Ontario (e.g., Becker & Patton 1968), it is very likely that petroleum fluids percolated downward from the Lower Paleozoic rocks into underlying Precambrian basement, and were polymerized (solidified) by radiation from nearby radiogenic minerals in the pegmatite. It is known that some petroleum samples from Ontario leave a solid residue that is permanently active (Burton 1904).

Thucholite from the Parry Sound district has been subject to several geochemical studies because of its abnormal content of heavy metals. Determination of metals in thucholite ash (Ellsworth 1928a, Barthauer et al. 1953, Hoekstra & Fuchs 1960), X-ray spectroscopy (Faessler 1931) and infrared absorption spectrophotometry (Hoekstra & Fuchs 1960), and X-ray diffraction (Kelley & Kerr 1958) have contributed to our knowledge of thucholite chemistry. The high uranium content of the Parry Sound thucholite made it a subject of early studies in radiometric age dating (Faessler 1931, Muench 1937, Nier et al. 1941). The detailed chemical study by Hoekstra & Fuchs (1960) has since shown that thucholite samples can be divided into three populations, each particularly rich in uranium, thorium, or the cerium group of rare earths. Uranium thucholite is known to contain uraninite inclusions or to have a core of solid uraninite (Spence 1930, Ellsworth 1932; see examples from elsewhere in Parnell & Eakin 1987). Thorium-rich thucholite typically contains thorite or thorianite (e.g., Parnell 1988). The distribution of heavy metals in a rare-earth thucholite has not been previously described. The present paper reports an investigation of rare-earth-enriched thucholite from the Besner mine, using combined back-scattered electron
imagery (BSE) and electron-microprobe techniques. The study reports the distribution of the major rare-earth components (present at above the 0.05 wt. % level, the limit of the analytical facility). The elements detected at this level are those recorded by Faessler (1931) and Hoekstra & Fuchs (1960) to be relatively abundant; Ce, Nd and La. Qualitative analysis indicated that other elements also are present. The study forms part of a wider investigation of ore-mineral inclusions in metalliferous bitumens and pyrobitumens.

**Occurrence**

Ellsworth (1928a) described nodules of thucholite in a pegmatite dyke in Conger Township. The nodules were found to be embedded in feldspar, mica and quartz, and intergrown with mica and cyrtolite, a variety of zircon enriched in Be, U and REE. Subsequently, Spence (1930) recorded thucholite in a variety of nodular morphologies and as veinlets in feldspar from the wall zone of a pegmatite dyke in biotite gneiss at the Beneser mine, Henvey Township. Samples from the Beneser mine show surface striations, apparently due to extrusion in a semisolid state. The samples are commonly associated with megascopic crystals of cyrtolite and allanite, and occur in a portion of pegmatite containing relatively large amounts of uraninite (Spence 1930). The Beneser mine sample used in the present study is black, solid, apparently homogeneous, and with no visible crystallinity, no inclusions, and no associated minerals.

**Chemistry and Petrography**

**Previous chemical data**

The first analysis of thucholite ash, from Conger Township, yielded 5.80 U2O8, 48.48 ThO2, 10.95 (Yb,Er)2O3, 5.45 (Ce,La,Dy)2O3, 2.25 V2O3, 0.80 ZrO2, and 3.21 P2O5, totalling 76.94 wt.% (Ellsworth 1928a). By contrast, an ashed sample from the Beneser mine yielded 53.30 U2O8, 0.54 ThO2 + Ce2O3 and 18.96 wt.% REE2O3 (Barthauer et al. 1953). The respective U/Th oxide ratios of 0.12 and 98.7+ demonstrate the wide range in thucholite composition. Hoekstra & Fuchs (1960) confirmed that thucholite has a variable metal content, and divided the Beneser samples into uranium-rich, thorium-rich and light-rare-earth-rich types (Table 1).

In addition to the REE data in Table 1, REE data for Beneser thucholite were obtained by Faessler (1931) and Barthauer et al. (1953). Faessler detected the presence of U, Th, Pb, Yb, Er, Ho, Dy, Tb, Gd, Sm, Nd, Pr, Ce, La, Ru(?), Zr, Y, Sr, As, Zn, Fe, W and Ca. Of the rare earths, Ce and Nd accounted for about 10%, and La for about 5% of the total.

**New data**

A portion of the thucholite from the Beneser mine was submitted to neutron activation analysis at the Imperial College Reactor Centre, Silwood Park, Berkshire. The sample was irradiated for 22.5 hours in the core-tube of the reactor under a flux of 10^{12} n cm^{-2} s^{-1}, then counted for 90 minutes after 4 days decay. Specific determinations yielded 2.5 U, 26.5 Th and 0.1 wt.% Au. A qualitative assessment of the data showed that significant quantities of V, Yb, Sm, La, Dy, Nd, Eu and Tb also were present.

**Electron microscopy**

Examination of the thucholite using BSE imagery showed that it is distinctly heterogeneous. The several types of inclusion present (Figs. 1, 2) are distinguishable by shape and by intensity of the image. Inclusions of metallic minerals show a marked contrast with the host pyrobitumens. Three main types of inclusion are distinguishable by bright-image intensity: (a) Masses of irregular shape; the largest are up to 100 μm (Fig. 1) and may be coalesced smaller masses. The larger masses are intergrown with a second mineral with a darker image. (b) Crystals up to 5 μm in size that form isolated stringers that cross-cut the pyrobitumens, and also dense networks (Fig. 2). (c) Isolated ellipsoids of constant size 5 to 10 μm across (Fig. 2). The ellipsoids are randomly distributed and appear to postdate the other inclusions.

**Electron-microprobe analysis**

The inclusions were analyzed using a JEOL-733 microprobe, with a beam 1 μm in diameter and the standards CeAl2, LaB6, NdF3, UO2, GaP, pure metallic Th, Y and V and natural wollastonite. Oxygen contents were determined by wavelength-dispersion analysis using the UO2 standard, and the
other elements were determined by energy-dispersion analysis.

The three types of inclusion have different compositions (Table 2). All are rich in P and can be assumed to be phosphates. They consistently contain Ca, Ce, La, Nd and Th. The Ce, La and Th contents distinguish the three types of inclusion (Fig. 3). The irregular masses are particularly La-rich, the stringers are Ce-rich, and the ellipsoids have the highest Th contents. The ellipsoids also contain between 2 and 4 wt. % U (Table 2). The dark-image mineral intergrown with the La-rich monazite is quartz. In addition, the pyrobitumen contains sheaf-like aggregates of a second low-intensity mineral, which proved to be chlorite.

**DISCUSSION**

As noted above, the spatial relationship of the thucholite to "oil shows" strongly suggests that the thucholite is a pyrobitumen derived from petroleum fluids. The thucholite therefore postdates the pegmatite. The common association with cyrtolite and allanite, the restriction of thucholite to uraninite-bearing portions of the pegmatite, and the occurrence of thucholite coatings around uraninite cores, strongly suggest that the pyrobitumen was localized by radiation from radioactive minerals. This is a common phenomenon and is responsible for the occurrence of thucholite in pegmatites worldwide (Davidson & Bowe 1951, Boyle 1982). Radiation causes polymerization and condensation reactions in fluid hydrocarbons, which result in the precipitation of solid pyrobitumens (for a detailed discussion of this process, see Schidlowkski 1975, Curiale et al. 1983).

A characteristic feature of thucholite is its property of replacing other minerals, including silicates (e.g., Abdel-Gawad & Kerr 1961, Parnell & Eakin 1987). Uraninite and zircon crystals that have acted as a nucleus for thucholite precipitation generally exhibit irregular outlines owing to marginal replacement (e.g., Welin 1964, McKirdy & Kantsler 1980). The replacement process causes mobility of elements in the replaced minerals. In the Besner thucholite the ellipsoidal crystals and the cross-cutting veinlets are clearly authigenic precipitates rather than relics of a partial replacement process. These two phases probably represent the mobilization and reprecipitation of elements from the host pegmatite. The irregular masses do not appear to be authigenic and may be a primary mineral of the pegmatite or an alteration product of a mineral in situ. The occurrence of thucholite within feldspar, mica and quartz, and crystals embedded in thucholite (see above), suggests that the thucholite replaced inorganic minerals.

The major elements recorded in the inclusions of the thucholite would be expected to occur enriched in the minerals of the pegmatite, including monazite. The allanite with which the thucholite is closely associated would be a ready source for the Ca, Th, Ce and La in the thucholite. The large amount of P in the inclusions necessitates mobilization from
TABLE 2. COMPOSITIONS OF INCLUSIONS PLOTTED IN FIGURE 3*

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**Atomic ratios**

N/P+V+Si: 1.08 1.07 1.06 1.02 1.03 1.03 1.08 1.00 1.10 0.99 1.08 1.11 0.99 0.91 0.94 0.92 0.95 0.90


* expressed in weight %. M is the sum of Nd, Ce, Ca, La, Th, U and Y.

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Fig. 3. Relative compositions of Ce, La and Th in three phosphate phases. Filled circles represent irregular masses, triangles represent stringers and networks, and crosses represent ellipsoids.

phosphatic minerals in addition to silicates. Indeed, as all the REE-bearing inclusions recorded in this study are phosphates, phosphates must have been dissolved to facilitate their recrystallization. However, phosphate minerals have not been reported from the pegmatite.

Low Si and V contents are recorded in each type of inclusion, and probably substitute for P. Similarly, Th, U and Ca substitute for the REE. The substitution of Th or U for REE creates a problem of charge balance, which would be accommodated by concomitant substitution of Ca for REE or substitution of Si for P (or both). Total metal/P + V + Si ratios are in the range 0.90 to 1.11 (Table 2). The stoichiometric balance between metals and anionic elements indicates that the ideal formula $MPO_4$ is
generally upheld. However, the direct measurement of oxygen contents shows that oxygen is present in excess of the levels expected according to stoichiometry. Assuming that no (OH) ions are present, the excess oxygen is probably present as water molecules. An abnormal degree of damage sustained by the inclusions under the electron beam could be explained by the dehydration of a hydrated phase. The most likely hydrated phosphate phase would be rhabdophane, whose formula includes a single water molecule, consistent with oxygen/metal atomic ratios between 4 and 5 found in two of the three phases (Table 2). These two phases are distinguished by high enrichments in either La or Ce, and rhabdophane is recorded elsewhere as both La-rich and Ce-rich varieties (Hildebrand et al. 1957, Van Wambeke 1977). Variations in Ce content have been explained as due to the partial fractionalization of REE following oxidation of Ce$^{3+}$ to Ce$^{4+}$ ions at some stage preceding rhabdophane precipitation (Adams 1968). Rhabdophane described by Hildebrand et al. (1957) contains Pr, Sm, Eu, Gd, Dy, Er and Yb at oxide concentrations over 0.5%, but none of these elements was detected in the phases analyzed in this study and, if present, must occur at concentrations less than 0.05%. The high Th content in the third phase suggests affinities with brockite. However, the brockite described by Fisher & Meyrowitz (1962) contains an excess of Nd over Ce, La and Y, opposite to the trend recorded in this phase. The phase contains a greater excess of oxygen than the other two and may be more hydrated. Several Y and REE phosphates are known with multiple hydration, including churchite (Y,REE)PO$_4$.2H$_2$O, lermontovite (Ca,U,RED$^2$(P0$_4$)$_4$.6H$_2$O, ningyoite (Ca,U,Ce)PO$_4$.nH$_2$O, and an unnamed phase (Y,U,Ca)PO$_4$.6H$_2$O (Parnell 1989). The oxygen/metal atomic ratios close to 6 suggest a formula with two water molecules, similar to churchite.

Of the two authigenic phases, the low-(Ce/La) ellipsoids appear to postdate the high-(Ce/La) veinslets. Few data are available elsewhere for the paragenesis of rare-earth phosphate phases. Van Wambeke (1977) reported the precipitation of Ce-rich rhabdophane before La-rich rhabdophane, and an account by Read et al. (1987) of zoned authigenic monazite shows that Ce-rich monazite precipitated before La-rich monazite. In both cases, the sequence is the same as that in the thucholite. A possible explanation suggested by Read et al. (1987) is the slightly greater solubility of LaPO$_4$ than CePO$_4$ (see data in Kolthoff et al. 1969), which would cause an earlier precipitated phase to be relatively Ce-rich. Similarly, Murata et al. (1953) predicted from solubility trends (at that time theoretical) that if two generations of monazite were found in a single deposit, the later phase would be richer in La.

It is likely that the mobilization–reprecipitation process occurred on a very localized scale. This would explain the fact that at the same locality, different varieties of thucholite can be distinguished, which are rich in U, Th, or the Ce group of rare earths. The varieties represent alteration of different primary minerals. In the case of the RE-rich thucholite, the alteration of allanite to chlorite would have released the metals that formed the monazite inclusions.

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lite and related hydrocarbon—uraninite complexes. 


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