Identity of “freyalite”, an alleged rare earth-rich variety of thorite, and its pre-metamict composition

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Abstract

This paper presents electron microprobe analyses of the type specimen of “freyalite”, a REE-Th mineral found in a nepheline syenite pegmatite of the Langesundfjord district (S.E. Norway). Freyalite was previously assumed to be related to thorite, but these data indicate that it is more accurately described as a thorian melanocerite (caryocerite) which has been altered with subsequent leaching of Na, Ca and F. The composition of the material may be expressed by the formula (REECa, etc.)(B, Si, etc.)(O, OH, F)r3. In an analysis of the least altered part of the specimen x = 4.017: (REE0.870Y0.167Th0.413Zr0.104Ca1.128Fe0.995Na0.239) (B1Si1.823P0.183S0.019) (O7.067OH3.174F2.757) (boron and hydroxyl contents estimates only). This evidence discredits the name “freyalite”. The crystalline precursor of the metamict melanocerite was probably a boron- and fluorine-rich member of the mosandrite-gotzenite or cerite groups.

The Subcommission on New Minerals and Mineral Names of the International Mineralogical Association has approved the discreditation of “freyalite”.

Introduction

In his classic monograph of the mineralogy of the nepheline syenite pegmatites of the Langesundfjord area, S.E. Norway, Brogger (1890) described a number of calcium and rare earth bearing minerals which he grouped together with thorite. These include calciothorite, eucrasite and freyalite. Of these, freyalite has the highest rare earth content and has gained a certain importance in mineralogical literature in regard to the proposed substitution of Cea+ for Tha+ in thorite. Frondel (1958) used Brogger’s (1890) results to postulate extensive solid solution between thorite and the hypothetical component CeSiO4, while Semenov (1963) extended the name “freyalite” to cover the CeSiO4 component. This approach is somewhat in conflict with the views of Brogger (1890), who expressed some doubt concerning the status of freyalite, and suggested that the mineral might be classified with tritomite or melanocerite rather than with thorite. Strunz (1977), on the other hand, classified freyalite as an alteration product of thorite; a view which is clearly not in agreement with Brogger’s (1890) descriptions.

Previous discussion of the chemical composition of freyalite has been based on an analysis by Damour (1878), which was cited by Brogger (1890). This analysis (Table 2) was recalculated by Neumann (1985) as: (Ce0.416REE0.016Th0.248Zr0.026Fe0.073Mn0.058Na0.174) (Si0.773Al0.227) (O2.716OH1.281), a formula which corresponds remarkably well with thorite stoichiometry, allowing substitution of hydroxyl for oxygen. However, as the material was analyzed by bulk, wet chemical techniques, determining groups of elements rather than single components and not taking into account any possible heterogeneities in the sample, it was felt that it was a poor foundation for some of the wider conclusions drawn from it. A reexamination of the freyalite type specimen was therefore undertaken.

The type specimen

The type specimen of freyalite was collected by M. Thr. Esmark who also named the mineral; it is in the possession of the Mineralogical-Geological Museum, University of Oslo. To the best of the present authors’ knowledge, no other samples of the assumed species exist. The locality where the sample was collected is not accurately known. The original labels of the specimen indicate the island Åra in the western part of the Langesundfjord (S.E. Norway); Brogger (1890) however suggested that the Barkevik skerries, which are islands a few kilometers further east in the Langesundfjord may be the true locality.

The material described as freyalite is closely similar to thorite from the Langesundfjord district in terms of its...
physical properties. It is yellowish brown, translucent in thin splinters, and has a vitreous luster. It forms the central part of a small nodule (diameter about 5 cm) and is enclosed by and partly intergrown with, the major minerals of the host pegmatite, which are alkali feldspar, nepheline and green pyroxene or amphibole. No external crystal faces or cleavages are present. Towards the edges, the material is darker, and has a duller luster; the material analyzed by Damour (1878) was taken from the central, vitreous part of the specimen, while no analyses of the outer zones of the nodule exist.

The material is completely metamict; on heating to 1000°C in air for 24 hours, it gives a tritomite-B X-ray diffraction pattern (see Neumann et al., 1957). This is a composite pattern, whose strongest lines originate from a cubic phase isostructural with uraninite.

Analytical methods

A polished, carbon-coated grain mount of the original freyalite specimen was analysed for major and minor elements with the electron microprobe. The instrument used was an ARL-EMX microprobe equipped with a LINK energy dispersive analyser unit. Data were reduced on-line with the program ZAF4/FLS, allowing a total of 14 elements in any single analysis. The acceleration voltage was 15 kV. The synthetic, three element standards of Amli and Griffin (1975) were used for calibration of the rare earths. Care had to be taken during calibration to choose energy intervals giving the least overlap of peaks. Accuracy and precision were checked against the synthetic REE-silicate glasses of Drake and Weill (1972). Standard chemical data are given in Table 1, together with approximate detection limits for the rare earth oxides estimated from counting statistics. Because of high ZAF-correction factors, the precision of these analyses is poor compared to those involving only the common major elements. It may be noted that for elements other than Yb, accuracy and precision are comparable to results obtained with the more comprehensive (ZAF4+FLS) program (for example Styles and Young, 1983). Thorium and the remaining constituents of the analyses present fewer peak overlap problems and were analysed with routine energy-dispersive microprobe techniques. Fluorine cannot be analyzed with sufficient accuracy and precision with an energy dispersive microprobe and was therefore analyzed separately using an automatic wavelength-dispersive Cameca Camebax instrument at the Central Institute for Industrial Research, Oslo. Electron backscatter photomicrographs of the sample were taken with a Jeol Superprobe scanning electron microscope at the Continental Shelf Institute (IKU), Trondheim, Norway. The bulk content of boron was determined semiquantitatively, using a Zeiss-Hilber emission spectograph at the Central Institute for Industrial Research, Oslo. A separate fragment of the central part of the specimen was used for this analysis. Another fragment of the specimen was used for combined thermogravimetry/DTA analysis, using a Mettler thermobalance at the Chemistry Department, University of Oslo. The sample was heated to 1000°C in a nitrogen atmosphere, with Al₂O₃ as a reference substance. The cold junction of the thermocouple was kept at 25°C.

Results

Heterogeneity

The grain mount made for microprobe analysis contains fragments of both dull (peripheral) and vitreous (central) parts of the freyalite specimen. Figure 1 shows a low magnification electron backscatter photomicrograph of the mount, illustrating differences in mean atomic number as shades of grey, the lightest shade representing the highest mean atomic number. At least five compositionally different phases may be recognized in Figure 1, forming domains with apparently sharp contacts. One of these, designated as phase 1, is found only as rounded relics. Along fractures and towards the rims of the specimen phase 1 is mantled by successive zones of phases 2 and 3, both of which have lower mean atomic numbers. The outermost part of the sample is a heterogeneous crust, consisting of intergrowths of phase 4 (black) and phase 5 (white). Phase 5 has the highest mean atomic number in the sample. From the relations illustrated in Figure 1, phase 1 is interpreted to be the best representative of the primary, nonmetamict mineral, while all other phases represent successive stages of replacement; these most probably evolved during or after metamictization.

Chemical composition

New microprobe analyses of phases 1, 2 and 3 found in the type specimen of freyalite are presented in Table 2. Wet chemical analyses of freyalite, melanocerite, tritomite and caryocerite (thorian melanocerite) from the Langesund fjord pegmatites (cited from Brøgger 1890), are included for comparison.

The microprobe analyses differ from the original bulk analysis of freyalite in several ways: Calcium and fluorine...
480°C is probably due to liberation of molecular (adsorbed) water. Loss of hydroxyl groups is probably the cause of the steep step on the curve at about 500°C; the smaller loss of weight at high temperatures is probably a result of liberation of fluorine or of volatile, fluorine-bearing components produced on heating (e.g., SiF₄). Only the low-temperature step of weight-loss corresponds to a well-defined endothermic peak on the DTA-curve (Fig. 3, lower curve). At higher temperatures the DTA-curve shows a broad endothermic continuum.

**Discussion of results**

**Identity of “freyalite”**

As can be seen from Table 2, the calcium content of phase 1 is much too high, and the silica too low, to justify the earlier assumption of its equivalence with thorite. The analyses cannot be constrained to conform with thorite stoichiometry, unless very extensive OH-substitution is

<table>
<thead>
<tr>
<th>Phase 1</th>
<th>Phase 2</th>
<th>Phase 3</th>
<th>FREY</th>
<th>MELAN</th>
<th>TRITOE</th>
<th>CARYO</th>
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<td>SiO₂</td>
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<td>16.57</td>
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<td>0.68</td>
<td>0.68</td>
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<tr>
<td>TiO₂</td>
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<td>4.70</td>
<td>4.70</td>
<td>4.70</td>
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<td>1.01</td>
<td>0.64</td>
<td>2.47</td>
<td>2.09</td>
<td>1.67</td>
</tr>
<tr>
<td>MgO</td>
<td>1.78</td>
<td>1.22</td>
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<td>0.67</td>
<td>0.67</td>
<td>0.67</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.96</td>
<td>0.48</td>
<td>0.11</td>
<td>2.33</td>
<td>1.45</td>
<td>1.40</td>
</tr>
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<td>CaO</td>
<td>8.23</td>
<td>6.94</td>
<td>2.70</td>
<td>8.62</td>
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<td>K₂O</td>
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<tr>
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<td>2.02</td>
<td>1.31</td>
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<tr>
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<td>2.31</td>
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<td>1.40</td>
</tr>
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</table>

Table 1. Rare earth compositions of the four standard glasses of Drake and Weill (1972).
valent rare earths and thorium), a ceric oxide and a glass 
(containing fluorine, boron, aluminum, ferric iron and 
excess rare earths). In the present case, the high propor-
tions of Th and Ce in the freyalite sample may be assumed 
to influence strongly the recrystallization process, stabiliz-
ing a cubic (Th, Ce)O₄ phase which is responsible for the 
tritomite-B pattern obtained. In the freyalite type specimen, 
both mean atomic numbers and the sums of the micro-
probe analyses decrease from phase 1 to phase 3. Simulta-
neously, the SiO₂-content increases. Although phase 1 is 
least affected by alteration processes, there is no reason to 
believe that its composition is identical to that of its crys-
talline precursor. Similar observations in other occurrences 
have led to suggestions that the crystalline precursors may 
have had compositions significantly different from that 
dicated by the idealized formula. Borneman-Starynkevich 
(1968) suggested that the melanocerite-group minerals 
could derive from minerals with datolite-type stoichiome-
try, while Hogarth et al. (1973) suggested hellandite as a 
precursor for the tritomite-(Y) phase from Bancroft, Onto-
tario (Canada). Although calculation of structural formulas 
for metamict and altered material may not be a valid pro-
postulated, both by the mechanism 4(OH) = SiO₄ and by 
substitution of OH for O bonded to Si. The material ana-
alyzed by Damour (1878) must have been strongly contami-
nated with the major phases of the pegmatite dyke, in 
order to account for the high aluminum, silica, potassium 
and manganese. On the other hand, the compositional 
similarity of the least altered part of the freyalite specimen 
with thorian melanocerite ("caryocerite") is striking. The 
composition of phase 1 differs from the old analysis of 
thorian melanocerite mainly in its higher SiO₂ content.

The melanocerite group is an imperfectly understood 
group of boron-bearing, metamict minerals, whose composi-
tion is commonly given as (Ce, Ca)₂(Si, B)₃O₁₂(OH, F) · 
H₂O (Fleischer, 1983). According to the usage of Clark 
(1984), only melanocerite (including the thorian variety 
"caryocerite") and tritomite may be recognized as valid 
species. Spencite, earlier assumed to be a distinct mineral 
(Jaffe and Molinski, 1962), should be classified as tritomite-
(Y). The members of the melanocerite group are distin-
guished from each other by minor chemical differences.

The nature of the crystalline precursor

No crystalline species with composition corresponding 
to the melanocerite formula are known. From the composi-
tional similarity with britholite, the minerals have com-
monly been assumed to belong structurally to the silicate 
apatites (Kupriyanova and Sidorenko, 1963; Ewing and 
Chakoumakos, 1982). The X-ray diffraction evidence used 
to support this assumption is ambiguous. Small differences 
in chemical composition of the metamict material and in 
the physical conditions during heating may stabilize differ-
ent crystalline phases (Neumann et al., 1957; Hogarth et 
al., 1973). Borneman-Starynkevich (1968) suggested that 
the melanocerite-group minerals give a mixture of three 
different phases on heating: A britholite (incorporating tri-
A general formula for a mineral giving rise to the present material on metamictization may be written as: $M_nZ_j(O, OH, F)_x$, where $Z$ represents tetrahedral cations ($Si^{4+}$ and those which may replace it, mainly $P^{5+}$, $S^{6+}$, $Al^{3+}$ and $B^{3+}$) and $M$ represents larger cations contained in non-tetrahedral position(s) (Frondel, 1958; Ito, 1968). Our data indicate that hydration and selective leaching of some components (sodium, calcium and fluorine) has taken place during or after the metamictization of the freyalite type specimen. The relative increase in silica on alteration indicates that the tetrahedral cations were the least mobile during alteration; therefore a fixed value for $x$ in the general formula is the best basis for calculation of cation distributions. Due to the lack of reliable boron data on the freyalite type specimen the formulas given in Table 3 for phases 1, 2 and 3 are based on fixed sums of $Si + P + S + Al$.

As can be seen from the formulas in Table 3, the old analysis of thorian melanocerite has a cation distribution in good agreement with the general formula for the melanocerite group, but with $F$ in excess of one atom per formula unit. The microprobe analyses cannot be recalculated to a similar formula on a boron-free basis. If a boron content corresponding to one atom per three tetrahedral sites is assumed (in agreement with Brogger’s (1890) data on thorian melanocerite, and roughly corresponding to the extent of $B^{3+}$ substitution which may be calculated from the maximum bulk boron content indicated by the spectrographic analysis); the analysis of phase 1 can be recalculated to a formula with $x = 4.017$: $(RE_{0.87} Y_{0.167} Th_{0.41} Zr_{0.10} Ca_{1.129} Fe_{0.095} Na_{0.239} K_{0.823} P_{0.159} S_{0.019})(O_{7.067} OH_{3.170} F_{2.757})$. Taking the selective leaching of some non-tetrahedral cations into account, there is no reason to believe that this formula represents the true composition of the crystalline precursor. It seems logical, however to postulate that the precursor probably had a formula of the type: $(RE, Y, Th, Zr, Ca, Fe, Na)_x( Si, B, P, Al, S)_{3}(O, OH, F)_{13}$, where $x > 4$, and to compare this with the formulas of known silicate minerals rich in rare earths and thorium in the search for the primary material (see compilations by Ewing and Chakumakos, 1982; Fleischer, 1983; Clark, 1984). Crystalline species with suitable cation distributions include boron-bearing analogs of britholite (Ce, Ca)_x(SiO_4, PO_4)_{3}(OH, F) and hypothetical boron-rich members of the cerite (Ce, Ca)_y(Mg, Fe)Si_4(O, OH, F)_x and mosandrite-gotzenite (Na, Ca, Ce)_z(Ti, Si)O_2(O, OH, F, 2 - (Ca, Na))_4(TI, Al)_5Si_2O_5(F, OH, H_2O) groups. Other suggested minerals such as hellandite and datolite are less probable as crystalline precursors for the material which was described as freyalite.

Nothing is known about the homogeneity of the melanocerite group minerals analyzed by Brogger (1890). The compositions indicated by the wet-chemical analyses are similar enough to the present phase 1 to suggest a similar mode of formation. This can only be checked by a restudy of the old materials with techniques like those used in the present study.

### Conclusions

From the new analytical data presented, it is concluded that the type material of freyalite is heterogeneous, consisting of thorian melanocerite (caryocerite) and alteration products. “Freyalite” should therefore be deleted from mineralogical terminology. It is not a variety of thorite (Brogger, 1890; Frondel, 1958), or a Ce^4SiO_4-component (Semenov, 1963), or an alteration product of thorite (Struntz, 1977). The Commission on New Minerals and Mineral Names of the International Mineralogical Association has approved the discreditation of “freyalite”.

It may further be concluded, that speculations in the literature about substitution mechanisms of rare earths in thorite, and the possible existence of a ThSiO_4–CeSiO_4 solid solution series, based on the old analysis (Frondel, 1958; Semenov, 1963) are not supported by the new data on the type material of “freyalite”. This should be reinvestigated, using other, preferably nonmetamict material.

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**Table 3. Structural formulas of phases 1, 2 and 3 found in the freyalite-type specimen, and of melanocerite-group minerals from the Langesundfjord district.**

<table>
<thead>
<tr>
<th>Phase 1</th>
<th>Phase 2</th>
<th>Phase 3</th>
<th>MELAN</th>
<th>TRITO</th>
<th>CARYO</th>
<th>TRITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>2.734</td>
<td>2.795</td>
<td>2.849</td>
<td>1.895</td>
<td>1.475</td>
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<tr>
<td>P</td>
<td>0.239</td>
<td>0.193</td>
<td>0.151</td>
<td>0.159</td>
<td>0.159</td>
<td>0.159</td>
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<tr>
<td>S</td>
<td>0.028</td>
<td>0.012</td>
<td></td>
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<tr>
<td>B</td>
<td></td>
<td></td>
<td>0.799</td>
<td>1.374</td>
<td>1.066</td>
<td>0.549</td>
</tr>
<tr>
<td>Al</td>
<td></td>
<td></td>
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<td>0.151</td>
<td>0.154</td>
<td>0.159</td>
</tr>
<tr>
<td>Ca</td>
<td>1.694</td>
<td>1.254</td>
<td>0.452</td>
<td>1.341</td>
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</tr>
<tr>
<td>Mg</td>
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<td>0.075</td>
<td>0.228</td>
<td>0.137</td>
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</tr>
<tr>
<td>Fe</td>
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<td></td>
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<td>0.033</td>
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</tr>
<tr>
<td>Mn</td>
<td></td>
<td></td>
<td>0.143</td>
<td>0.056</td>
<td>0.134</td>
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<tr>
<td>Na</td>
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<td>0.157</td>
<td>0.033</td>
<td>0.408</td>
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<tr>
<td>La</td>
<td>1.076</td>
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<td>0.860</td>
<td>0.645</td>
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<td>0.695</td>
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<tr>
<td>Ce</td>
<td>1.464</td>
<td>1.265</td>
<td>1.196</td>
<td>1.284</td>
<td>0.880</td>
<td>0.971</td>
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<tr>
<td>Y</td>
<td>0.250</td>
<td>0.167</td>
<td>0.170</td>
<td>0.709</td>
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<td>0.154</td>
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<td>Zr</td>
<td>0.156</td>
<td>0.093</td>
<td>0.100</td>
<td>0.032</td>
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<tr>
<td>Th</td>
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<td>0.318</td>
<td>0.517</td>
<td>0.055</td>
<td>0.236</td>
<td>0.409</td>
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<tr>
<td>Ta</td>
<td></td>
<td>0.140</td>
<td>0.035</td>
<td></td>
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<td>0.111</td>
</tr>
<tr>
<td>F</td>
<td>4.136</td>
<td>1.077</td>
<td>0.420</td>
<td>2.655</td>
<td>1.478</td>
<td>2.340</td>
</tr>
</tbody>
</table>

All structural formulas are calculated to a basis of 3,000 tetrahedral cations. The compositions of phases 1, 2 and 3 are recalculated on a boron-free basis from microprobe analyses given in Table 2. MELAN, TRITO and CARYO refers to minerals analyzed by Brogger (1969), the analyses are reproduced in Table 2. TRITY is a trinitite from an unknown locality in the Langesundfjord district analysed by Hogarth et al. (1971).

1: Includes Sm. 2: Includes Gd.
The crystalline precursor of the present material is not known with certainty, but may have been a boron-bearing member of the mosandrite-gotzenite or cerite groups. Boron-bearing britholite is less likely as a precursor. By inference, the other analyzed melanocerite-group minerals from the Langesundfjord district may have a similar origin.

The other, chemically distinct varieties of thorite described by Brogger (1890) (eucrasite and calciothorite), should be reinvestigated in order to determine their true status.

Acknowledgments

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Jaffe, H. W. and Molinski, V. J. (1962); Spencite, the yttrium analogue of tritomite from Sussex County, New Jersey. American Mineralogist, 47, 9–25.


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