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A STUDY OF UK27, A NEW THORIUM MINERAL,

WITH REMARKS ON THE MINERALOGY

AND IGNEOUS BEHAVIOUR OF THORIUM

by

VALERIE ELIZABETH ANSELL, B.Sc.

A thesis submitted to the Faculty of Graduate Studies
and Research in partial fulfillment of the requirements
for the degree of Master of Science.

Department of Geology

Carleton University
Ottawa, Ontario

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"A STUDY OF UK27, A NEW THORIUM MINERAL, WITH REMARKS ON THE MINERALOGY AND IGNEOUS BEHAVIOUR OF THORIUM"
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in partial fulfillment of the requirements for the degree of Master of Science

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ABSTRACT

UK27 ((Na,K,Ca)ThSi$_11$(O,H$_2$O,F,Cl)$_3$) is a new mineral from the altered pegmatite veins at Mont St-Hilaire, Quebec. It occurs as small, anhedral grains in patches of powdery, rhabdophane-like material associated with yofortierite and analcime. UK27 is rhombohedral, $R\bar{3}m$, $a=29.01(1)\AA$, $c=17.30(1)\AA$, $V=12608.7(6)\AA^3$, $Z=18$, $D_{\text{meas}}=2.62(2)g/cm^3$, and $D_{\text{calc}}=2.613g/cm^3$. The strongest lines of the x-ray powder diffraction pattern are $(d(\AA), I_{\text{obs}}, hkl)$: 7.27, 100, 220; 4.17, 70, 422; 8.17, 30, 012; 3.39, 30, 262; 2.890, 25, 811, 713; 14.54, 20, 110. The grains are brittle with pitted surfaces and a waxy lustre. Optical parameters are: uniaxial positive, $\omega=1.510$ and $\epsilon=1.512$.

Seventeen minerals are known to contain essential thorium. Th minerals are radioactive and often metamict. There are 2 oxides, thorianite (ThO$_2$) and thorutite (ThTi$_2$O$_6$). The only Th carbonate, thorbastnaesite (Th(Ca,RE)(CO$_3$)$_2$F$_2$.3H$_2$O), is secondary. Eyleettersite (Th,Pb)$_1$-xAl$_3$(PO$_4$.SiO$_4$)$_2$(OH)$_6$), kivuite (Th,Ca,Pb)$_2$H$_2$(UO$_2$)$_4$(PO$_4$)$_2$(OH)$_2$.3H$_2$O), brockite ((Ca,Th)(PO$_4$)$_2$.H$_2$O; hex.), and grayite ((Ca,Th)PO$_4$.H$_2$O; orth.) are secondary phosphates and cheralite ((Ca,Ce,Th)(P,Si)O$_4$) and brabantite (CaTh(PO$_4$)$_2$) are primary. The 8 Th silicates are: huttonite (ThSiO$_4$; mon.), thorite (ThSiO$_4$; tet.), thorogummite (Th(SiO$_4$)$_1$-x(OH)$_x$; secondary), ekanite (ThCa$_2$Si$_8$O$_{20}$), steacyite (Th(Na,Ca)$_2$(K$_{1-x}$)Si$_8$O$_{20}$), thorosteenstrupine ((Ca, Th, Mn)$_3$Si$_4$O$_{12}$F$_6$.6H$_2$O), umbozerite (Na$_3$Sr$_4$ThSi$_8$(O,OH)$_{24}$) and UK27.
$^{232}\text{Th}$ is the only Th isotope of major geochemical significance. It occurs in nature only as Th$^{4+}$, which is relatively immobile. Its solubility in natural waters is greatly increased by complex formation with fluoride, hydrogen phosphate and hydroxyl ions. In minerals, Th$^{4+}$ substitutes readily for U$^{4+}$ and Ce$^{4+}$ and often occurs in heterovalent substitution coupled with Ca$^{2+}$, Fe$^{3+}$ and Si$^{4+}$. Since Th is a large, highly-charged cation, it is concentrated in accessory minerals of the late-stage differentiates and associated veins and pegmatites.
ACKNOWLEDGEMENTS

The author wishes to express her appreciation of the help and encouragement extended by friends and members of the department. Much appreciation is due to Dr. G.Y. Chao, whose help, support and patience were invaluable in the completion of this study.

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Finally, I would like to thank my husband and family for their help and encouragement throughout the programme.
# TABLE OF CONTENTS

**ABSTRACT** .......................................................................................................................... iii

**ACKNOWLEDGEMENTS** ......................................................................................................... v

**TABLE OF CONTENTS** .......................................................................................................... vi

**LIST OF FIGURES** ............................................................................................................... vii

**LIST OF TABLES** ................................................................................................................ viii

**INTRODUCTION** .................................................................................................................... 1

1 **UK27: EXPERIMENTAL RESULTS** .................................................................................... 3
   Introduction......................................................................................................................... 3
   Occurrence and Associations............................................................................................. 3
   Physical and Optical Properties...................................................................................... 8
   Thermal Behaviour........................................................................................................... 9
   Crystallography................................................................................................................ 10
   Electron Microprobe Analysis.......................................................................................... 12
   Raman and Infrared Spectra............................................................................................. 12
   Thermogravimetric and Evolved Gas Analysis................................................................. 17
   Formula Calculation.......................................................................................................... 19
   Discussion......................................................................................................................... 21

2 **THORIUM MINERALS** ....................................................................................................... 23
   Introduction......................................................................................................................... 23
   The Metamict State........................................................................................................... 27
   Mineral Descriptions........................................................................................................ 30
   1) Oxides......................................................................................................................... 32
   2) Carbonates.................................................................................................................. 38
   3) Phosphates.................................................................................................................. 38
       Rhabdophane Group...................................................................................................... 43
       Monazite Group........................................................................................................... 50
   4) Silicates........................................................................................................................ 60
       Zircon Group............................................................................................................... 60
       Ekanite Group............................................................................................................. 68
       Thorosteenstrupine and Umbozerite............................................................................ 75

3 **CHEMISTRY AND IGNEOUS BEHAVIOUR OF THORIUM** .................................................. 78
   Introduction......................................................................................................................... 78
   General Chemistry............................................................................................................ 80
   1) Thorium Compounds.................................................................................................... 82
   2) Solution Chemistry...................................................................................................... 83
   Crystal Chemistry........................................................................................................... 85
   Igneous Geochemistry................................................................................................... 87

**SUMMARY AND CONCLUSIONS** ...................................................................................... 96

**REFERENCES** ....................................................................................................................... 103
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Sketch map of the Monceyregian Hills. From Chao et al., 1967.</td>
<td>4</td>
</tr>
<tr>
<td>2.</td>
<td>Geological map of Mont St-Hilaire. From Currie, 1983.</td>
<td>5</td>
</tr>
<tr>
<td>3.</td>
<td>Energy dispersive spectra of UK27.</td>
<td>15</td>
</tr>
<tr>
<td>4.</td>
<td>IR spectra of UK27.</td>
<td>16</td>
</tr>
<tr>
<td>5.</td>
<td>TGA, P&lt;sub&gt;total&lt;/sub&gt; and EGA curves for UK27.</td>
<td>18</td>
</tr>
<tr>
<td>7.</td>
<td>Structure of thorutite. From Ruh and Wadsley, 1966.</td>
<td>37</td>
</tr>
<tr>
<td>8.</td>
<td>Proposed structure of bastnaesite. From Donnay and Donnay, 1953.</td>
<td>40</td>
</tr>
<tr>
<td>10.</td>
<td>Composition diagram for monazite group minerals.</td>
<td>53</td>
</tr>
<tr>
<td>12.</td>
<td>Proposed revision of the nomenclature of the minerals of the monazite group.</td>
<td>56</td>
</tr>
<tr>
<td>13.</td>
<td>Co-ordination around A-site cation of a) huttonite and b) thorite. From Taylor and Ewing, 1978.</td>
<td>61</td>
</tr>
<tr>
<td>14.</td>
<td>Structure of a) steacyite and b) ekanite. From Szymanski et al., 1982.</td>
<td>70</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>-------</td>
<td>-------------</td>
<td>------</td>
</tr>
<tr>
<td>1a.</td>
<td>Minerals identified from Mont St-Hilaire.</td>
<td>6</td>
</tr>
<tr>
<td>1b.</td>
<td>Unconfirmed species from Mont St-Hilaire.</td>
<td>7</td>
</tr>
<tr>
<td>2.</td>
<td>X-ray powder diffraction data for UK27.</td>
<td>11</td>
</tr>
<tr>
<td>3.</td>
<td>Electron microprobe analysis of UK27.</td>
<td>15</td>
</tr>
<tr>
<td>4.</td>
<td>Formula calculation for UK27.</td>
<td>20</td>
</tr>
<tr>
<td>5.</td>
<td>Gladstone-Dale calculation for UK27.</td>
<td>22</td>
</tr>
<tr>
<td>6.</td>
<td>Thorium minerals.</td>
<td>24</td>
</tr>
<tr>
<td>7.</td>
<td>Minerals which contain minor thorium.</td>
<td>25</td>
</tr>
<tr>
<td>8.</td>
<td>Characteristics of metamict minerals.</td>
<td>29</td>
</tr>
<tr>
<td>9.</td>
<td>Abbreviations.</td>
<td>31</td>
</tr>
<tr>
<td>10.</td>
<td>Thorianite.</td>
<td>33</td>
</tr>
<tr>
<td>11.</td>
<td>Thorutite.</td>
<td>36</td>
</tr>
<tr>
<td>12.</td>
<td>Thorbastaesite.</td>
<td>39</td>
</tr>
<tr>
<td>13.</td>
<td>Kivuite.</td>
<td>41</td>
</tr>
<tr>
<td>14.</td>
<td>Eylettersite.</td>
<td>42</td>
</tr>
<tr>
<td>15.</td>
<td>Cell parameters of rhabdophane group minerals and related compounds.</td>
<td>44</td>
</tr>
<tr>
<td>16.</td>
<td>Comparison of x-ray powder diffraction data of CePO₄ and rhabdophane group minerals.</td>
<td>46</td>
</tr>
<tr>
<td>17.</td>
<td>Brockite.</td>
<td>47</td>
</tr>
<tr>
<td>18.</td>
<td>Grayite.</td>
<td>48</td>
</tr>
<tr>
<td>19.</td>
<td>Cell parameters of monazite-type structures.</td>
<td>51</td>
</tr>
<tr>
<td>20.</td>
<td>Cheralite.</td>
<td>57</td>
</tr>
<tr>
<td>21.</td>
<td>Brabantite.</td>
<td>58</td>
</tr>
<tr>
<td>22.</td>
<td>Huttonite.</td>
<td>59</td>
</tr>
<tr>
<td>23.</td>
<td>Thorite.</td>
<td>63</td>
</tr>
</tbody>
</table>
24. Thorogummite. 66
25. Comparison of ekanite group minerals. 69
26. Ekanite. 71
27. Iraquite. 73
28. Steacyite. 74
29. Thorostenstrupine. 76
30. Umbozerite. 77
31. Radioactive decay scheme of thorium. 79
32. Atomic structure data for thorium and related elements. 81
33. Averaged thorium abundances. 89
34. Selected partition coefficients of thorium. 90
INTRODUCTION

The purpose of this study is three-fold. The first is to describe UK27, \((Na,Ca,K)ThSi_{11}(O,H_{2}O,F,Cl)_{3}\), a new mineral from the alkaline intrusive rocks of Mont St-Hilaire, Quebec, the second is to provide a glossary of thorium minerals and the third is to explain the distribution of Th in the igneous environment.

Chapter 1 is the description of UK27, including its occurrence, physical and optical properties, thermal behaviour, crystallography and chemical composition. Raman and IR spectroscopy were performed in order to determine whether water was present and simultaneous thermogravimetric analysis (TGA) and evolved gas analysis (EGA) were used to determine water loss on heating. The empirical formula was calculated using the average of five microprobe analyses and the internal consistency of the chemical composition, calculated density and refractive indices were estimated using the Gladstone-Dale relationship.

Chapter 2 is a brief compilation of the information available for the other known thorium minerals, including descriptions of the species and a list of other minerals which contain minor thorium. Although Th is 3 to 4 times more abundant than uranium only 17 thorium minerals have been reported. A number of factors are considered in order to explain the limited number of thorium minerals. Since Th minerals are radioactive and many are metamict to varying degrees, the characteristics of metamict minerals are also listed.
The descriptions are listed according to composition: oxides, carbonates, phosphates and silicates and wherever possible they are grouped on the basis of structural affinities. Relationships and associated problems are briefly discussed at the beginning of each section. The individual descriptions are summaries of the properties of each species rather than a catalogue of all work done to date.

Chapter 3 is a brief summary of the radiochemistry, solution chemistry and igneous geochemistry of Th. The behaviour of Th during magmatic evolution is considered in order to explain the geochemical distribution of thorium in the igneous environment.
CHAPTER 1

UK27: EXPERIMENTAL RESULTS

INTRODUCTION

The mineral UK27, one of the unidentified minerals from the alkalic intrusive rocks of Mont St-Hilaire, Quebec, is a hydrous sodium thorium silicate of undetermined affiliation. A brief description of this mineral appears in Chao and Baker (1979).

Mont St-Hilaire, about 35 km east of Montreal, is one of the ten Montréal-Hills (Fig. 1). The geology of Mont St-Hilaire has been well documented by Pouliot (1969), Sørensen (1974), Currie (1976) and others. It is a crudely layered, funnel-shaped, elliptical pluton (Fig. 2) which was emplaced into the surrounding Ordovician sediments during the late Cretaceous (about 100 ma). The western half is layered gabbro-pyroxenite intruded by a ring dike of nepheline-olivine diorite (Currie, 1983). The eastern half is nepheline syenite. In the northeastern corner of the pluton, xenoliths, breccias, vugs and veins occur within the syenite. These patches are the major source of the many rare minerals, including UK27, which have been documented by Chao and other workers (Tables 1a and 1b).

OCCURRENCE AND ASSOCIATIONS

UK27 is closely associated with yofortierite (Perrault et al., 1975) in the hydrothermally altered pegmatite veins in the nepheline syenite at the De-Mix Quarry, Mont St-Hilaire. UK27 occurs in small quantities in patches (4-8 mm in diam.) of fine-grained, opaque, white, rhabdophane-like material, concentrated near the outer edges of the patches. The fibrous, pink yofortierite occurs in both spherulites and
FIGURE 1. Sketch map of the Montregean Hills, showing the location of Mont St-Hilaire, Quebec. From Chao et al., 1967.
### TABLE 1a. MINERALS IDENTIFIED FROM MONT ST-HILAIRE.

<table>
<thead>
<tr>
<th>Mineral</th>
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<td>Acmite</td>
<td>Eudidyrite</td>
<td>Monazite</td>
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<td>Actinolite</td>
<td>Ewaldite</td>
<td>Monteregianite</td>
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<td>Albite</td>
<td>Fluorite</td>
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<td>Franconite</td>
<td>Mosandrite</td>
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<tr>
<td>Almandine</td>
<td>*Galdonayite</td>
<td>Muscovite</td>
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<tr>
<td>Analcime</td>
<td>Galena</td>
<td>Narsarsukite</td>
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<td>Gibbsite</td>
<td>Natrophosphate</td>
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<td>Apatite</td>
<td>Goethite</td>
<td>Nordstrandite</td>
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<td>Apophyllite</td>
<td>Götzenite</td>
<td>Pygorskite</td>
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<td>Arfvedsonite</td>
<td>Grossular</td>
<td>*Paranatrolite</td>
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<td>Gypsum</td>
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<td>Hedenbergite</td>
<td>*Petasarite</td>
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<td>Phillipsite</td>
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<td>Polyliithionite</td>
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<td>Bastnaesite</td>
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<td>Labunstovite</td>
<td>Sabinite</td>
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<td>Lamprophylllite</td>
<td>Sandine</td>
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<td>Lavenite</td>
<td>Scheelite</td>
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<td>Leffite</td>
<td>Sepiolite</td>
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<td>*Lemoynite</td>
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<td>McKevelayite</td>
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<td>Marcasite</td>
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* Type locality: Mont St-Hilaire
TABLE 1a. CONTINUED.

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TABLE 1b. UNCONFIRMED SPECIES FROM MONT ST-HILAIRE.

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felted aggregates with massive to coarsely trapezohedral white analcime, light brown to black, prismatic acmite and massive to euhedral, medium to dark red-brown eudialyte. Irregular patches of serandite, in varying degrees of alteration from unaltered pink material to black, poorly crystallized birnessite pseudomorphs, crystalline aggregates of white polythionite and spherulites of white leifite are present in some samples. Small, individual crystals of natrolite, dog-toothed microcline, albite, mangan-neptunite, brown, prismatic steacyite, catapleiite, yellow, massive epididymite and minor calcite occur in vugs, interstices and veinlets in the specimens.

**PHYSICAL AND OPTICAL PROPERTIES**

UK27 occurs as anhedral, rarely subhedral, grains up to 0.7mm in diameter. The grains are transparent to translucent, colourless to very pale green with a vitreous to waxy lustre and a white streak. The surfaces of the grains often appear etched, commonly with an opaque, white, powdery coating of thorium-rich rhabdophane-like material. The coating be removed by means of an ultrasonic bath. There are often very fine-grained inclusions at or near the surface. The mineral is brittle with a conchoidal fracture. Attempts to determine microhardness were unsuccessful due to the mineral's brittle character. UK27 fluoresces bright apple-green under long and short wave ultra-violet light. The grains which fluoresce most intensely tend to give the poorest x-ray patterns. This may be the result of minor variations in the chemical composition, possibly in the Th/U ratio.

The density was determined by the floatation method using methylene
iodide (S.G. 3.3g/cm$^3$) and bromoform (S.G. 2.85g/cm$^3$). These liquids were diluted with acetone until the mineral grains were in suspension. The density was obtained by weighing the heavy liquid in a pycnometer of known weight and volume. The average density of three determinations is 2.62(2)g/cm$^3$. UK27 is only slightly attacked by 1:1 HCl at room temperature and is unaffected by either 1:1 HNO$_3$ or H$_2$SO$_4$.

The optical properties were determined on a spindle stage at room temperature using crystals previously oriented with a precession camera. The crystals gave very diffuse, uniaxial interference figures, perhaps due to the slightly metamic character of the mineral. The refractive indices were measured in sodium light ($\lambda$=5893nm) using Cargille immersion oils which were checked on a Bausch and Lomb Abbe 3L refractometer. The measured values are: $\omega$ = 1.510, $\epsilon$ = 1.512 and ($\epsilon - \omega$) = 0.002. The mineral is uniaxial positive.

**THERMAL BEHAVIOUR**

UK27 was heated in an attempt to improve its crystallinity. After heating to 110$^\circ$C for 17 hours in a Sybron Thermolyne 10500 furnace no change was observed in the x-ray powder pattern. After heating to 200$^\circ$C for 18 hours, UK27 was less translucent and more yellow, the birefringence was lower, the refractive index higher (1.516) and the extinction less distinct. The x-ray powder pattern had fewer lines. After heating to 300$^\circ$C for 18 hours, no further optical changes were noted but the mineral gave no x-ray powder pattern, suggesting the collapse of the structure at 300$^\circ$C after the partial loss of crystalline water.
CRYSTALLOGRAPHY

Suitable, untwinned grains of UK27 with relatively sharp extinction between crossed nicols were selected under the microscope. After checking the identity using a 114.6 mm Gandolfi camera with filtered CuKα radiation (λ=1.54055 Å), the grains were mounted for single crystal x-ray diffraction study. The poor quality of the powder pattern suggests that UK27 is slightly metamict.

A series of precession photographs were taken about the a-axis (0-level) and the c-axis (0-4 levels) using filtered MoKα radiation (λ=0.7107 Å). The spots are slightly diffuse and higher order reflections are absent, further suggesting a metamict character for UK27. The photographs indicate that UK27 is rhombohedral and the space group is R̃3m or R3m as evidenced by the systematic absences of hkl reflections with -h+k+l ≠ 3n. The mineral proved to be pyroelectric when cooled with liquid nitrogen. Therefore, UK27 lacks a centre of symmetry and the correct space group is R̃3m. Cell parameters were first determined from measurements of the precession photographs and then refined using a least-squares method (Hounslow and Chao, unpub.) and x-ray powder diffraction data obtained from photographs taken with a 114.6 mm diameter Gandolfi camera at room temperature with CuKα radiation and metallic silicon as an internal standard (Table 2). Intensities were estimated visually. The reflections were indexed by comparing the observed d-values with those calculated from the cell parameters measured on the precession photographs. The refined values are: a=29.01(1) Å and c=17.30(1) Å which give a cell volume of 12608.7(6) Å³.
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CuKα radiation (1.54018Å); 114.6mm Gandolfi camera; Si internal standard; visual intensities
ELECTRON MICROPROBE ANALYSIS

UK27 was first examined by energy dispersive and wavelength
 dispersive spectrometry using the Cambridge MK5 electron microprobe
 (Fig. 3) and found to contain the following elements: Th, Si, U, Al, Ca, K,
 Na and possibly Cl and F. Quantitative analyses were then carried out
 using the wavelength-dispersive method. The operating conditions were:
 accelerating voltage: 15kV; specimen current: 50na, as measured on pure
 Fe; counting time: 20 sec. for Th, Si, U, Ca, Al and K and 10 sec. for Na,
 Cl and F; diameter of beam: approx. 10 microns. Ka lines were used for
 all elements except Th and U, for which the Ms lines were used. The
 standards used were: Th: thorianite (GSC 19986, analysis unpublished);
 Si: Boettcher pyroxene PX-1 (Goldich et al., 1967); U: syn brannerite
 (CAMEB); Al, Ca, K, Na: Kakanui hornblende (Jarosewich et al., 1979);
 Cl: tugtupite; F: riebeckite (R2088, Rucklidge et al., 1971). Raw x-
 ray data were reduced using a modified version of the computer
 programme of Rucklidge and Gasparini (1969). The results of the
 microprobe analyses are given in Table 3. The sodium values decreased
 with time, reflecting the volatility of sodium under the electron beam.
 A defocussed beam was, therefore, used to reduce the damage. The
 presence of water was confirmed by infrared spectroscopy (Fig. 4) and
 the water content determined by thermogravimetric analysis.

RAMAN AND INFRARED SPECTRA

Continuous-wave micro-Raman spectroscopy was performed for UK27 to
 confirm the presence of water in the structure. However, the uranyl
 ion fluoresces very strongly in the same region as the much weaker
 Raman spectra of the different H-O bonds. The fluorescence completely
FIGURE 3. Energy dispersive spectra of UK27: Intensity/Energy(keV). NaKα (1.04keV), AlKα (1.48keV), SiKα (1.74keV), ThMα (2.99keV), Umα (3.17keV), KKα (3.31keV), CaKα (3.69keV).
TABLE 3. ELECTRON MICROPROBE ANALYSES OF UK27.

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<td>n.d.</td>
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<td>84.28</td>
<td>86.81</td>
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* water by TGA
masks the pertinent lines.

A mixture of 200mg of KBr and 0.76mg of UK27, was evacuated for 2 minutes then pressed under vacuum for 1 minute at 6T/in² to produce a 13x200mm pellet. Infrared spectra (Fig. 4) were obtained for UK27 with a Perkin Elmer model 683 Infrared Spectrophotometer with the beam balanced at 0.1 absorbance units.

The band in the 350-550cm⁻¹ region is characteristic of Si-O-Si bending and the strong band from 850 to 1250cm⁻¹ to Si-O stretching. The medium band centered at 1630cm⁻¹ is attributable to H-O-H bending, confirming the presence of structural water in UK27. The characteristic bands for BeO (700-800cm⁻¹), B₂O₃ (1200-1450cm⁻¹), (Farmer, 1974), CO₃ (1400-1550cm⁻¹), and H₂O⁺ (1575-1590cm⁻¹), (Healy, pers. com.) are absent. The poor resolution of the O-H stretching band in the region from 3000 to 3700cm⁻¹, and of the spectrum as a whole, indicates some disorder in the structure apparently resulting from the metamict character of UK27.

THERMOGRAVIMETRIC AND EVOLVED GAS ANALYSIS

Simultaneous thermogravimetric and evolved gas analysis (Fig. 5), carried out under high vacuum on 5.16mg of sample, show an initial loss of 0.445mg after 3.5hr of preliminary high-vacuum treatment. On heating at 10⁰C/min a steady loss of 0.26mg was observed up to 1135⁰C. Three peaks on the pressure curve correspond to water evolution at 105, 275 and 600⁰C (Fig. 5). At the higher temperature, a weak trace of CO₂ was also detected. Total weight loss after treatment was 0.71mg or 13.8(1.0)wt% which is interpreted as the water content of the mineral. The residue gives an x-ray powder diffraction pattern of thorianite.
FIGURE 5. TGA(A), P_{total}(B) and EGA(C) curves for UK27, 20-1135°C.
Plus huttonite. The water lost during the high-vacuum treatment is here designated as $H_2O^-$ which could be zeolitic water. The loss at 150°C and above is designated by $H_2O^+$ and may be either $H_2O$ or $OH$. The significance of the water loss at different temperatures cannot be adequately explained without a structural determination.

**FORMULA CALCULATION**

The empirical formula was calculated according to the method described in Deer et al. (1967) using the average of five microprobe analyses (Table 4). According to the relationship: cell content = atomic proportions x volume x density + 166.02 (Berry and Mason, 1959), the unit cell of UK27 contains 197.21 atoms of (Si+Al) and 17.66 atoms of (Th+U). Based on a cell content of 18 formula units ($Z=18$) and 11(Si+Al), the empirical formula is:

$$\text{(Na}_{0.56}\text{K}_{0.26}\text{Ca}_{0.03})_{E=0.84} \quad \text{(Th}_{0.94}\text{U}_{0.04})_{E=0.98} \quad \text{(Si}_{10.69}\text{Al}_{0.31})_{E=11.00}$$

$$\text{(O}_{24.37}\text{(H}_2\text{O})_{8.50}\text{F}_{0.23}\text{Cl}_{0.02})_{E=33.12}$$

This gives a formula weight of 1114.15 and a calculated density of 2.613g/cm³. Since the structural role of $H_2O$ is unknown, the ratio of $H_2O$ to OH is also unknown. Therefore, tentatively the formula is simplified to:

$$\text{(Na, K, Ca)}_{11}(0, H_2O, F, Cl)_{33}$$

The internal consistency of the chemical composition, calculated density and refractive indices may be estimated by the Gladstone-Dale relationship (Mandarino, 1976, 1979, 1981). The "chemical refractive energy", $\kappa_C$ (Table 5), is calculated from the chemical composition, using the constants given by Mandarino (1976, 1978) and the equation:
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scale factor = \( \frac{11}{0.9919} = 11.0898 \)

Number of anions: \( (2.1975 \times 11.0898) + 8.495 + 0.250 = 33.116 \)

Amount of water in formula.
$K_C = (E_k p_1)/100$

where $p_1$ is the weight percent and $k_1$ is the specific refractive energy constant of the constituent "1". The "physical refractive energy", $K_p$, is calculated according to:

$$K_p = (n-1)/D$$

where $n$ is the mean refractive index and $D$ is the calculated density.

For UK27 $K_p=0.195$ and $K_C=0.215$. This gives a compatibility index of 0.093 ($C=1-(K_p/K_C)$; (Table 5), indicating poor compatibility of physical and chemical data of UK27 (Mandarino, 1979). This may be due in part to the slightly metamict nature of UK27.

Several different values have been reported for the Gladstone-Dale constants of various oxides, including those of Th, U, Na, Ca, Al and Si (Mandarino, 1979). Therefore, the compatibility index will depend upon the value of the specific refractive energy constant which is chosen for each oxide. For example, a good compatibility index of 0.050 can be calculated for UK27 using a value of 0.124 for $\text{ThO}_2$.

**DISCUSSION**

The mineral, UK27 is a rhombohedral, hydrous sodium thorium silicate, $(\text{Na},\text{Ca},\text{K})\text{ThSi}_{11}(\text{O},\text{H}_2\text{O},\text{F},\text{Cl})_{33}$. No related thorium mineral or any other mineral of similar composition has been reported in the literature (see Chapter 2). The instability of sodium under the electron beam may indicate that the sodium is loosely bonded in the structure and may be surrounded by water molecules. Thorium (+4) must occur in octahedral or higher coordination with oxygen, because of the large ionic radius of Th.
<table>
<thead>
<tr>
<th></th>
<th>WEIGHT %</th>
<th>k1</th>
<th>k/100</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>57.93</td>
<td>0.208</td>
<td>0.1205</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>1.42</td>
<td>0.207</td>
<td>0.0029</td>
</tr>
<tr>
<td>ThO$_2$</td>
<td>22.45</td>
<td>0.167</td>
<td>0.0375</td>
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<tr>
<td>UO$_2$</td>
<td>0.88</td>
<td>0.100</td>
<td>0.0009</td>
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<tr>
<td>Na$_2$O</td>
<td>1.55</td>
<td>0.190</td>
<td>0.0029</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>1.10</td>
<td>0.196</td>
<td>0.0021</td>
</tr>
<tr>
<td>CaO</td>
<td>0.17</td>
<td>0.210</td>
<td>0.0004</td>
</tr>
<tr>
<td>F</td>
<td>0.40</td>
<td>0.047</td>
<td>0.0002</td>
</tr>
<tr>
<td>Cl</td>
<td>0.05</td>
<td>0.318</td>
<td>0.0002</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>13.76</td>
<td>0.340</td>
<td>0.0468</td>
</tr>
<tr>
<td>Total</td>
<td>99.52</td>
<td>0.340</td>
<td>0.2144</td>
</tr>
<tr>
<td>-O=F+Cl</td>
<td>0.18</td>
<td>0.203</td>
<td>0.0004</td>
</tr>
<tr>
<td>Recalc'd</td>
<td>100.00</td>
<td>0.203</td>
<td>0.2150</td>
</tr>
</tbody>
</table>
CHAPTER 2

THORIUM MINERALS

INTRODUCTION

The most comprehensive catalogues of thorium minerals (mineral species which contain essential thorium) describe only 5 species: one oxide (thorianite: ThO₂), one phosphate (cheralite: (Ca,Th)PO₄), and three silicates (huttonite: Th₅SiO₄(Mo), thorite: ThSiO₄(tet) and thorogummite: Th(SiO₄)₁₋ₓ(OH)ₓ) (Frondel, 1958; Heinrich, 1958). Since 1958 at least 11 more thorium minerals have been accredited. This chapter is a brief compilation of the information available for all known thorium minerals (Table 6) including descriptions of the species and a list of minerals which contain minor thorium (Table 7). All but 2 species are accessory minerals of carbonatites, Mg-skarns, granitic or alkalic rocks or their associated pegmatites and hydrothermal veins.

UK27 is a new species from Mont St-Hilaire, Quebec.

Thorium is capable of isomorphous substitution for U, RE and Zr and is 3 to 4 times more abundant than uranium (Wedepohl, 1978). Although at least 128 U minerals are known, only 17 thorium minerals have been reported to date. A number of factors must be considered in order to explain the limited number of thorium minerals.

In nature, Th occurs only as Th⁴⁺, the largest naturally occurring quadrivalent cation. In 8-fold coordination, the ionic radius of Th is 1.04Å compared with that of U⁴⁺=1.00Å and Zr⁴⁺=0.84Å (Shannon and Prewitt, 1969). Few mineral structures have cation sites capable of accommodating such a large, highly-charged cation. The 11 known primary thorium minerals (Table 6) occur in only eight structure types:
<table>
<thead>
<tr>
<th>NAME</th>
<th>GROUP</th>
<th>GENERAL FORMULA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxides</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thorianite</td>
<td>Fluorite</td>
<td>AX&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>Thorutite</td>
<td>Brannerite</td>
<td>AB&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;</td>
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<tr>
<td><strong>Carbonate</strong></td>
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<td></td>
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<tr>
<td>Thorbastaesite</td>
<td>Bastastaesite</td>
<td>-</td>
</tr>
<tr>
<td><strong>Phosphates</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eylettersite</td>
<td>Crandallite</td>
<td>-</td>
</tr>
<tr>
<td>Kivrite</td>
<td>Phosphuranylite</td>
<td>-</td>
</tr>
<tr>
<td>Brockite</td>
<td>Rhabdophane</td>
<td>ABO&lt;sub&gt;4&lt;/sub&gt;·2H&lt;sub&gt;2&lt;/sub&gt;O</td>
</tr>
<tr>
<td>Grayite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brabantite</td>
<td>Monazite</td>
<td>ABO&lt;sub&gt;4&lt;/sub&gt; (mon.)</td>
</tr>
<tr>
<td>Chernille</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Silicates</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Huttonite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thorite</td>
<td>Zircon</td>
<td>ABO&lt;sub&gt;4&lt;/sub&gt; (ret.)</td>
</tr>
<tr>
<td>Thorogummite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ekanite</td>
<td>Ekanite</td>
<td>AB&lt;sub&gt;2&lt;/sub&gt;CSi&lt;sub&gt;8&lt;/sub&gt;O&lt;sub&gt;20&lt;/sub&gt;</td>
</tr>
<tr>
<td>Steacylite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thorosteenstrupine</td>
<td>Steenstrupine</td>
<td>(Chapter 2)</td>
</tr>
<tr>
<td>Umbowerite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UK27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NAME</td>
<td>FORMULA</td>
<td>wt% ThO₂</td>
</tr>
<tr>
<td>---------------</td>
<td>-------------------------------------------------------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Aeschynite</td>
<td>(Ce, Ca, Fe, Th)(Ti, Nb)₂(0, OH)₆</td>
<td>up to 25.8</td>
</tr>
<tr>
<td>Aeschynite-(Y)</td>
<td>(Y, Ca, Fe, Th)(Ti, Nb)₂(0, OH)₆</td>
<td>20.3</td>
</tr>
<tr>
<td>Allanite</td>
<td>(Ce, Ca, Y)₂(Al, Fe)₃(SiO₄)(OH)</td>
<td>4.4</td>
</tr>
<tr>
<td>Bastnasite-s</td>
<td>RE(CO₃)F</td>
<td>2.8</td>
</tr>
<tr>
<td>Betaflite</td>
<td>(Ca, Na, U)₂(Ti, Nb, Ta)₂O₆(OH)</td>
<td>1.4</td>
</tr>
<tr>
<td>Brannerite</td>
<td>(U, Ca, Ce)(Ti, Fe)₂O₆</td>
<td>13.0</td>
</tr>
<tr>
<td>Britholite</td>
<td>(Ce, Ca)₃(SiO₄, PO₄)₃(OH, F)</td>
<td>19.6</td>
</tr>
<tr>
<td>Britholite-Y</td>
<td>(Y, Ca)₃(SiO₄, PO₄)₃(OH, F)</td>
<td>2.8</td>
</tr>
<tr>
<td>Cerianite</td>
<td>(Ce, Th)O₂</td>
<td>4.5</td>
</tr>
<tr>
<td>Chevkinite</td>
<td>(Ca, Ce, Th)₄(Fe, Mg)₂(Ti, Fe)₃Si₄O₂₂</td>
<td>18.4</td>
</tr>
<tr>
<td>Clarkeite (s)</td>
<td>(Na, Ca, Pb, Th, H₂O)₂U₂(0, H₂O)⁷</td>
<td>2.2</td>
</tr>
<tr>
<td>Crandallite (s)</td>
<td>(CaAl₃(PO₄)(OH)₅·H₂O</td>
<td>6.7</td>
</tr>
<tr>
<td>Datolite-Y</td>
<td>(Y, Ca)₂B(Si, Al)O₄</td>
<td>1.3</td>
</tr>
<tr>
<td>Euxenite</td>
<td>(Y, Ca, Ce, U, Th)(Nb, Ta, Ti)₂O₆</td>
<td>14.2</td>
</tr>
<tr>
<td>Fergusonite</td>
<td>YNbO₄</td>
<td>6.0</td>
</tr>
<tr>
<td>Fersmite</td>
<td>CaNb₂O₆</td>
<td>1.6</td>
</tr>
<tr>
<td>Formanite</td>
<td>RETaO₄</td>
<td>1.1</td>
</tr>
<tr>
<td>Gadolinite</td>
<td>Y₂FeBe₂Si₂O₁₀</td>
<td>2.0</td>
</tr>
<tr>
<td>Hellandite</td>
<td>(Ca, Y)₆(Al, Fe³⁺)Si₄B₄O₂₀(OH)₄</td>
<td>1.5</td>
</tr>
<tr>
<td>Kernasurtite</td>
<td>(Ce, La, Th)(Ti, Nb)(Al, Fe)(Si₁, P)₂O₇(OH)₄·3H₂O</td>
<td>6.2</td>
</tr>
<tr>
<td>Kobeite</td>
<td>(Y, Fe, U)(Ti, Nb, Ta)₂(0, OH)₆</td>
<td>1.0</td>
</tr>
<tr>
<td>Loparite</td>
<td>(Ce, Na, Ca)₂(Ti, Nb)₂O₆</td>
<td>13.0</td>
</tr>
<tr>
<td>Lueshite</td>
<td>(Na, Ca, Ce)(Nb, Ti)₃</td>
<td>2.9</td>
</tr>
<tr>
<td>Melanocerite</td>
<td>(Ce, Ca)₅(Si₁, B)₃O₁₂(OH, F)·nh₂O (?)</td>
<td>13.6</td>
</tr>
<tr>
<td>Monazite</td>
<td>(RE, Th)PO₄</td>
<td>31.0</td>
</tr>
<tr>
<td>Mosandrite</td>
<td>(Na, Ca, Ce)₃TiSiO₄)₂F</td>
<td>1.3</td>
</tr>
<tr>
<td>NAME</td>
<td>FORMULA</td>
<td>wt% THO$_2$</td>
</tr>
<tr>
<td>------------------</td>
<td>--------------------------------------------------------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>Niobo-aeschynite</td>
<td>(Ce, Ca, Th)(Nb, Ti)$_2$(O, OH)$_6$</td>
<td>up to 2.5</td>
</tr>
<tr>
<td>Orthobrannterite</td>
<td>$U^{4+}+^{6+}Tl_4O_{12}OH_2$</td>
<td>1.0</td>
</tr>
<tr>
<td>Parisite (s)</td>
<td>CaCe$_2$(CO$_3$)$_3$(F, OH)$_2$</td>
<td>5.4</td>
</tr>
<tr>
<td>Perrerite</td>
<td>(Ca, Ce, Th)$_4$(Mg, Fe$^{2+}$)$_2$(Ti, Fe$^{3+}$)$_3$Si$<em>4$O$</em>{22}$</td>
<td>3.6</td>
</tr>
<tr>
<td>Polycrase</td>
<td>$(Y, Ca, Ce, U, Th)(Tl, Nb, Ta)_2O_6$</td>
<td>7.7</td>
</tr>
<tr>
<td>Polymignite</td>
<td>$(Ca, Fe, Y, Th)(Nb, Tl, Ta, Zr)O_4$</td>
<td>3.9</td>
</tr>
<tr>
<td>Pyrochlore</td>
<td>$(Na, Ca)_2Nb_2O_6(OH, F)$</td>
<td>15.3</td>
</tr>
<tr>
<td>Rhabdophane</td>
<td>REPO$_4$·H$_2$O</td>
<td>4.4</td>
</tr>
<tr>
<td>Samarskite</td>
<td>(RE, U, Ca, Pb)(Nb, Ta, Ti, Sn)$_2$O$_6$</td>
<td>5.7</td>
</tr>
<tr>
<td>Saryarkite</td>
<td>Ca(Y, Th)Al$_3$(SiO$_4$)$_2$(PO$_4$, SO$_4$)$_2$(OH)$_2$·6H$_2$O</td>
<td>8.0</td>
</tr>
<tr>
<td>Steenstrupine</td>
<td>(RE, Th, Ca, Na)$_2$(Mn, Fe)(SiO$_3$)$_2$(OH)$_2$·2H$_2$O(?)</td>
<td>12.1</td>
</tr>
<tr>
<td>Tantalaeschynite-(Y)</td>
<td>(RE, Ca)(Ta, Ti, Nb)$_2$O$_6$</td>
<td>5.5</td>
</tr>
<tr>
<td>Tantaleuxenite</td>
<td>(RE, Ca)(Ta, Nb, Ti)$_2$(O, OH)$_6$</td>
<td>2.9</td>
</tr>
<tr>
<td>Thalinite</td>
<td>Y$_2$Si$_2$O$_7$</td>
<td>10.5</td>
</tr>
<tr>
<td>Tritomite (s)</td>
<td>(RE, Th)$_5$(Si, B)$_3$(O, OH, F)$_3$(?)</td>
<td>15.0</td>
</tr>
<tr>
<td>Uraninite</td>
<td>UO$_2$</td>
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</tr>
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<td>Wakefieldite (s)</td>
<td>YVO$_4$</td>
<td>1.1</td>
</tr>
<tr>
<td>Xenotime</td>
<td>YFPO$_4$</td>
<td>2.5</td>
</tr>
<tr>
<td>Yttrialite</td>
<td>$(Y, Th)_2$Si$_2$O$_7$</td>
<td>13.4</td>
</tr>
<tr>
<td>Yttrocrasite</td>
<td>$(Y, Th, Ca, U)_2$(O, OH)$_6$</td>
<td>8.8</td>
</tr>
<tr>
<td>Yttrotantalite</td>
<td>$(Fe, Y, U)(NbTa)O_4$</td>
<td>2.2</td>
</tr>
<tr>
<td>Zircon</td>
<td>ZrSiO$_4$</td>
<td>13.1</td>
</tr>
<tr>
<td>Zirkelite</td>
<td>(Ca, Th, Ce)Zr(Tl, Nb)$_2$O$_7$</td>
<td>20.4</td>
</tr>
</tbody>
</table>

(?) formula uncertain  (s) secondary

Note: Many of these analyses may have been made on impure material.
fluorite-, branerite-, monazite-, zircon-, ekanite- and steenstrupine-
type plus umbozerite and UK27.

Unlike $U^{6+}$, which is readily oxidized to the $U^{6+}$ state to form the
highly soluble uranyl ion, $UO_2^{2+}$, thorium is relatively immobile under
most geological conditions. It forms very few secondary minerals
(Table 6), including one carbonate, four phosphates and one silicate.
The carbonate, thorbasteatite, $(\text{Th(Ca,RE)}(\text{CO}_3)_2F_2\cdot3\text{H}_2\text{O})$, forms as a
result of the intense alteration of ferroan thorite by carbonate- and
fluorine-rich fluids (Pavlenko et al., 1965). Two phosphates,
eyletersite, $((\text{Th},\text{Pb})_{1-x}\text{Al}_3(\text{PO}_4,\text{SiO}_4)_2(\text{OH})_6)$, and kvivite,
$(\text{Th},\text{Ca,Pb})\cdot\text{H}_2(\text{UO}_2\cdot\text{PO}_4\cdot\text{OH})\cdot7\text{H}_2\text{O}$, are alteration products of Th-rich
uraninite (Van Wambke, 1972). The other two phosphates, brockite,
$((\text{Ca},\text{Th})\cdot\text{PO}_4\cdot\text{H}_2\text{O})$, hex.), and grayite, $((\text{Ca},\text{Th})\cdot\text{PO}_4\cdot\text{H}_2\text{O}$, orth.), are
rhabdophane-type minerals formed from the alteration of thorite.
Thorogummite, $(\text{Th(SiO}_4\cdot(\text{OH})\cdot4\text{H}_2\text{O})_x$, the only secondary thorium silicate,
is also an alteration product of thorite.

The susceptibility of thorium minerals to alteration is increased
by the radioactive decay of $^{90}\text{Th}$. Alpha-particle bombardment
damages the crystal structure and causes the mineral to become
partially or wholly metamict.

**THE METAMICT STATE**

Metamict minerals were once crystalline, but have become partly
or wholly amorphous while keeping their external morphology. This
transformation of a crystalline material to an amorphous pseudomorph is
the result of alpha-particle bombardment rather than chemical or
thermal alteration, although the disorder of atoms is commonly
accompanied by oxidation and hydration. The release of alpha-particles during the radioactive decay of Th and U damages the crystal structure both by the recoil of the emitting nucleus and by collision of the alpha-particles with the lattice atoms. High temperatures generated by recoil and collision may result in local fusion, producing glassy or amorphous regions in the crystal. Stable minerals may undergo self-annealing or local recrystallization and do not become metamict (Mitchell 1973). As metamictization progresses, the structure of the mineral becomes increasingly disordered and the properties of the mineral are systematically altered. Metamict minerals have a number of properties in common (Table 8; Pabst, 1952; Mitchell, 1973a,b)

The degree of metamictness of a mineral is dependant upon 1) number of alpha-particles produced through time, 2) age of the mineral and 3) stability of the structure. The degree of ionic bonding, the number and nature of shared structural elements and the degree of distortion caused by ions of different radii in isomorphous substitution all affect structural stability. Summaries of studies of the metamict state are given by Mitchell (1973) and Ewing (1975).

Thorium minerals are metamict to varying degrees. Those with high chemical stability because of closely packed or strongly bonded structures, such as thorianite and huttonite, are generally not metamict. The less stable minerals, such as thorite, \((\text{ThTi}_2\text{O}_6)\), and thorite, which have rather open structures with extensive isomorphous substitution in one or several structural positions, are usually metamict. The metamict character of each of the Th minerals is noted in the individual descriptions.
TABLE 3. SELECTED PROPERTIES OF METAMICT MINERALS.

- radioactive: contain Th or U
- partially or wholly optically isotropic, irrespective of external morphology, with lower refractive indices than nonmetamict equivalents
- partially to completely amorphous to x-rays, incipient metamictization is manifest by broadening of lines of x-ray powder diffraction pattern
- often dark brown to black
- vitreous to pitchy lustre
- brittle with a conchoidal fracture, often lacking cleavage
- decreased density, hardness, pleochroic effects, reflectivity with increasing metamictness
- often the site of radiating fractures which extend into the surrounding rock; fracture coronas common around zircons and allanites in pegmatites of the Grenville province
- often contain nonessential water
- Fe$^{2+}$ and U$^{4+}$ often oxidized to Fe$^{3+}$ and U$^{6+}$. Minerals become hydrated
- increasing susceptibility to chemical alteration particularly weathering and attack by acids
- may show thermoluminescence on heating (pyrognomic)
- many effects reversed after heating including increase in density, hardness, refractive indices and resistance to chemical attack, with a decrease in water content and lightening of colour
- structure may be restored by heating, but as a polycrystalline aggregate rather than the original discrete crystals
MINERAL DESCRIPTIONS

Any systematic classification of minerals should take into account both the composition and structure of the individual species. The following descriptions are listed according to composition: oxides, carbonates, phosphates and silicates. Wherever possible they are grouped on the basis of structural affinities. Huttonite, listed in the silicate section, is included in the discussion of the monazite group because of structural similarity to cheralite and monazite.

The structural analyses and cell parameters of huttonite, thorite, thorutite and thorianite have been derived primarily from synthetic material. This information has been included in the descriptions only when no data was available from natural material. Available references to synthetic work have been noted. Several species which have been poorly defined (grayite) or inadequately characterized (thorosteenstrupine, (Ca, Th, Mn)₃Si₄O₁₂F₆H₂O) have been included in the interests of completeness. Iraquite, while more correctly a RE mineral, has been included in this study because of its close structural affinity with the ekanite group.

The following descriptions are summaries of the properties of each species rather than a catalogue of all work done to date. For the more common minerals, such as thorite and thorianite, the most important and the most recent references are listed and for the rarer minerals, most or all references are included. A list of abbreviations used in the mineral descriptions can be found in Table 9.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>B, bal.</td>
<td>Berman balance</td>
</tr>
<tr>
<td>C.N.</td>
<td>coordination number</td>
</tr>
<tr>
<td>disc.</td>
<td>discredited</td>
</tr>
<tr>
<td>hex.</td>
<td>hexagonal</td>
</tr>
<tr>
<td>htd.</td>
<td>heated</td>
</tr>
<tr>
<td>'IR'</td>
<td>ionic radius</td>
</tr>
<tr>
<td>l.w.</td>
<td>long wave ultra-violet radiation</td>
</tr>
<tr>
<td>mon.</td>
<td>monoclinic</td>
</tr>
<tr>
<td>n.a.</td>
<td>not available</td>
</tr>
<tr>
<td>orth.</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>PDF</td>
<td>powder diffraction file</td>
</tr>
<tr>
<td>poly.</td>
<td>polymorph</td>
</tr>
<tr>
<td>p.s.</td>
<td>polished section</td>
</tr>
<tr>
<td>pyc.</td>
<td>pycnometer</td>
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<tr>
<td>RE</td>
<td>rare earth element(s)</td>
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<tr>
<td>s.w.</td>
<td>short wave ultra-violet radiation</td>
</tr>
<tr>
<td>:syn.</td>
<td>synthetic</td>
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<tr>
<td>:tet.</td>
<td>tetragonal</td>
</tr>
<tr>
<td>t.s.</td>
<td>thin section</td>
</tr>
<tr>
<td>unnec.</td>
<td>unnecessary</td>
</tr>
</tbody>
</table>
1) OXIDES

The two naturally-occurring oxides of Th are thorianite and thorutite. Thorianite is the Th analogue of uraninite, (UO$_2$), (Frondel, 1958) and thorutite the Th analogue of brannerite, (UTl$_2$O$_6$), (Gotman and Khapae, 1958).

A continuous solid solution series exists in the system ThO$_2$-UO$_2$ (Frondel, 1958). In natural materials, gaps have been reported between 17.6 and 27 wt% ThO$_2$ in uraninite (Robinson and Sabina, 1955) and between 15 and 25 wt% U$_3$O$_8$ in thorianite (Frondel, 1958). Analyses of material from the U.S.S.R. eliminate these gaps almost entirely (Makarov and Lipova, 1962). A number of unnecessary varietal names have been given to various members of the series, for example, uranothorianite for the intermediate composition and broggerite or thorian uraninite for uraninite with 10 to 40 wt% ThO$_2$ (Frondel, 1958 and Lang et al., 1962).

There is a complete series between synthetic ThTl$_2$O$_6$ and UTl$_2$O$_6$ (Ruh and Wadsley, 1966). However, natural brannerite has been reported to contain only up to 13 wt% ThO$_2$ and only one thorutite, with 1.6 wt% UO$_2$ has been analysed (Gotman and Khapae, 1958). Therefore, the existence of a natural series between brannerite and thorutite cannot be verified. The name absite was proposed for high-Th brannerite, but was deemed unnecessary by Fleischer, (1963).
### TABLE 10. THORIANITE

<table>
<thead>
<tr>
<th>Property</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isometric (Pm3n)</td>
<td>n = 2.2-2.35</td>
</tr>
<tr>
<td>Fluorite group</td>
<td>Occasional anomalous birefringence</td>
</tr>
<tr>
<td>Cell parameters:</td>
<td>Interpenetration twins, {111} common</td>
</tr>
<tr>
<td>a = 5.505-5.575Å</td>
<td>D\text{meas} = 9.7-9.8g/cm(^3)</td>
</tr>
<tr>
<td>a(syn) = 5.596(1)Å</td>
<td>D\text{calc} = 10.0g/cm(^3) (syn)</td>
</tr>
<tr>
<td>Volume = 167-173Å(^3)</td>
<td>H = 6.5-7</td>
</tr>
<tr>
<td>Z = 4</td>
<td>Lustre: submetallic to resinous</td>
</tr>
<tr>
<td>Forms: {100}, {111}, {113}</td>
<td>Colour: shades of dark grey, brown or black; white (syn) brown to opaque (t.s.)</td>
</tr>
<tr>
<td>Cleavage: 100 poor</td>
<td>Not fluorescent</td>
</tr>
<tr>
<td>Tenacity: brittle</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>Streak: buff to grey</td>
<td>Nonmagnetic</td>
</tr>
<tr>
<td>Habit: crystalline</td>
<td></td>
</tr>
</tbody>
</table>

Slightly soluble in HNO\(_3\) or H\(_2\)SO\(_4\).

Substitutions: ThO\(_2\)-UO\(_2\) solid-solution series; RE, Zr, Ca and Pb substitute for Th and U.

Analyses: Table 10a.

Thermal behaviour: unaffected to temperatures above 1000°C; melting point: 3300°C.

Structure: Fluorite structure (Fig. 6): 0 at 1/4,1/4,1/4 surrounded by 4 Th atoms and Th at 0,0,0 and 0,1/2,1/2 coordinated to 8 O atoms.

Three strongest x-ray lines (intensity) (indices) (syn): 3.234 (100) (111), 1.980 (58) (220), 1.689 (64) (311); PDF 4-566.

Occurrence: as euhedral cubes (up to 2.5cm) with octahedral faces in: - detrital deposits associated with thorite, zircon, ilmenite and other heavy minerals near Galle, Sri Lanka (Ceylon); Antanimora, Malagasy Republic (Madagascar); India; U.S.S.R. and U.S.A.; - pegmatites in Sri Lanka (Ceylon) and at Charlebois Lake, Saskatchewan; - calcite-fluorite-apatite veins, pegmatites and metasomatized marbles in the Grenville province, Ontario and Quebec; - magnesian, calc-silicate "skarns" in Siberia and southeast Malagasy Republic (Madagascar); - the alkaline rocks and associated carbonatites of the Kola peninsula, U.S.S.R. and the Palabora complex in southern Africa; - inclusions in the Allende meteorite (Chem. Abst. 91:42314q).

Type locality: gem gravels, Galle, Sri Lanka (Ceylon).

Name: for the Norse god, Thor.


Related species: cerianite, uraninite.

Best references: Robinson and Sabina (1955); Frondel (1958).
<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$</td>
<td>1.57</td>
<td>0.29</td>
<td>1.11</td>
<td>1.92</td>
<td>3.48</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CaO</td>
<td>0.97</td>
<td>-</td>
<td>0.59</td>
<td>-</td>
<td>0.17</td>
<td>0.42</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ThO$_2$</td>
<td>38.47</td>
<td>93.02</td>
<td>62.16</td>
<td>72.27</td>
<td>65.37</td>
<td>64.61</td>
<td>89.91</td>
<td>70.07</td>
<td>69.03</td>
</tr>
<tr>
<td>UO$_2$</td>
<td>4.44</td>
<td>4.73</td>
<td>40.32</td>
<td>11.19</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>U$_3$O$_8$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>23.47</td>
<td>12.94</td>
<td>6.86</td>
<td>16.84</td>
<td>27.88</td>
<td>-</td>
</tr>
<tr>
<td>UO$_3$</td>
<td>33.15</td>
<td>-</td>
<td>18.88</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RE$_2$O$_3$</td>
<td>2.49</td>
<td>-</td>
<td>1.84</td>
<td>6.90</td>
<td>0.29</td>
<td>-</td>
<td>0.42</td>
<td>0.31</td>
<td>0.53</td>
</tr>
<tr>
<td>PbO</td>
<td>5.21</td>
<td>1.80</td>
<td>2.29</td>
<td>2.25</td>
<td>2.87</td>
<td>3.99</td>
<td>2.40</td>
<td>12.73</td>
<td>1.56</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>4.39</td>
<td>-</td>
<td>1.05</td>
<td>-</td>
<td>0.61</td>
<td>0.14</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Rem.</td>
<td>8.70</td>
<td>-</td>
<td>0.77</td>
<td>5.43</td>
<td>3.42</td>
<td>2.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>99.39</td>
<td>99.84</td>
<td>99.01</td>
<td>99.93</td>
<td>99.68</td>
<td>99.28</td>
<td>99.59</td>
<td>99.95</td>
<td>99.27</td>
</tr>
</tbody>
</table>

1) Wells et al., 1933, in Frondel, 1958.
2) Lacroix, 1922, in Frondel, 1958.
3) Dunstan et al., 1906, in Frondel, 1958.
4) Dunstan et al., 1905, in Frondel, 1958.
5) Jakob et al., 1911, in Frondel, 1958.
TABLE 11.

THORUTITE

ThTi$_2$O$_6$

<table>
<thead>
<tr>
<th>Property</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoclinic *(C2/m)</td>
<td>n &gt; 2.1</td>
</tr>
<tr>
<td>Brannerite group</td>
<td>Isotropic</td>
</tr>
<tr>
<td>*Cell parameters:</td>
<td></td>
</tr>
<tr>
<td>a = 9.822(5)Å</td>
<td></td>
</tr>
<tr>
<td>b = 3.824(2)Å</td>
<td></td>
</tr>
<tr>
<td>c = 7.036(5)Å</td>
<td></td>
</tr>
<tr>
<td>$a\times c$ = 118.84(5)$^\circ$</td>
<td></td>
</tr>
<tr>
<td>Volume = 231.4Å$^3$</td>
<td></td>
</tr>
<tr>
<td>Z = 2</td>
<td></td>
</tr>
<tr>
<td>Fracture: conchoidal</td>
<td></td>
</tr>
<tr>
<td>Metamict</td>
<td></td>
</tr>
</tbody>
</table>

Substitutions: U, Ca for Th; Fe, Al, Nb, Ta, Si for Ti; OH for O.
Analysis: SiO$_2$ 0.44, TiO$_2$ 36.1, Al$_2$O$_3$ 1.50, Nb$_2$O$_5$ 1.12, Ta$_2$O$_5$ 0.08, Fe$_2$O$_3$ 1.10, CaO 1.07, ThO$_2$ 54.1, UO$_2$ 1.43, UO$_3$ 0.14, H$_2$O 0.94, loss on ignition 1.72, total 99.74 wt% (Gotman and Khapaev, 1958).

Thermal behaviour: turns golden brown and loses water when heated; natural material amorphous to x-rays, material heated to 1000°C for 1 hr. produces a unique powder pattern.

*Structure: distorted Ti-O octahedra in zig-zag sheets centred about (100), bound together by irregular Th-O octahedra (Fig. 7).

Three strongest x-ray lines (intensity): 3.17 (100), 1.728 (85), 1.695 (85); PDF 14-327 (htd.).

Occurrence: as short, prismatic crystals (up to 1x2cm) in microcline-nepheline veins in syenite, associated with thorite, zircon, calcite, minor barite and galena (location not reported).

Other names: smirnovite (disc.).
Related minerals: brannerite.
2) CARBONATES

The complex carbonate, thorbasnaesite, the thorium analogue of bastnaesite ((Ce,La)CO₃F), is the only reported thorium carbonate. It may be isostructural with bastnaesite (Fig. 8) with Th+Ca substituting for RE.

3) PHOSPHATES

Four secondary and two primary Th₄-phosphates have been reported. Kivuite is related to phosphuranylite (Ca(UO₂)₃(PO₄)₂(OH)₂·6H₂O), eylettersite to crandallite (CaAl₃(PO₄)₂(OH)₅·H₂O) and brockite and grayite to rhabdophane (REPO₄·H₂O). Cheralite and brabantite are primary minerals of the monazite group.

Eylettersite and kivuite were described from the same locality. Eylettersite occurs in intimate association with phosphuranylite-type phosphates - an association which may cast doubt on the existence of kivuite (Van Wambekke, 1972).
TABLE 12. THORBASTNAESITE

\[ \text{Th(} \text{Ca,RE)(CO}_3\text{)}_2\text{F}_2\cdot 3\text{H}_2\text{O} \]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value/Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexagonal ( \text{P}_{6}\text{2c} )</td>
<td></td>
</tr>
<tr>
<td>Cell parameters:</td>
<td></td>
</tr>
<tr>
<td>( a = 6.99(2) \text{Å} )</td>
<td></td>
</tr>
<tr>
<td>( c = 9.71(2) \text{Å} )</td>
<td></td>
</tr>
<tr>
<td>Volume = 411(3) \text{Å}^3</td>
<td></td>
</tr>
<tr>
<td>( Z = 3 )</td>
<td></td>
</tr>
<tr>
<td>Density ( \text{D}_{\text{calc}} )</td>
<td>5.70 g/cm(^3)</td>
</tr>
<tr>
<td>Colour: pale yellow to brown</td>
<td></td>
</tr>
<tr>
<td>Lustre: earthy</td>
<td></td>
</tr>
<tr>
<td>Habit: finely crystalline aggre-</td>
<td></td>
</tr>
</tbody>
</table>

Substitutions: U, Pb for Th; Al for Ca; OH for F. Fe treated as hematite impurity.

Analysis: SiO\(_2\) 2.01, Al\(_2\)O\(_3\) 1.75, Fe\(_2\)O\(_3\) 3.62, TiO\(_2\) 0.05, CaO 7.97, ThO\(_2\) 46.79, U\(_3\)O\(_8\) 0.11, RE\(_2\)O\(_3\) 7.46, PbO 0.33, CO\(_2\) 14.78, F 6.87, (O-F: 2.89), H\(_2\)O\(^+\) 9.04, H\(_2\)O\(^-\) 2.14, total 100.04 wt%.

DTA: diffuse break at 350°C, sharp break at 410°C.

IR: main bands at 750, 880, 1050, 1430, 1510 and 3700-3700 cm\(^{-1}\).

Three strongest x-ray lines (intensity) (indices): 3.54 (80) (110), 2.85 (100) (112), 2.03 (100b) (300,301); PDF 18-1362.

Structure: not determined; Figure 8 shows proposed structure of bastnaesite; in thorbastnaesite, Th + Ca may replace Ce.

Occurrence: finely crystalline aggregates in metasomatized alkaline intrusives of Eastern Siberia; also as crusty, pale-yellow, fine-grained material from the Beylikahir deposit, Eskisehir, Turkey.

Paragenesis: alteration of ferroan thorite by fluorine/carbonate-rich fluids.

Type locality: Siberia.

Name: for composition.

Related species: bastnaesite, parisite, vaterite.

Best reference: Pavlenko et al. (1965); Fleischer (1965).
FIGURE 8. The structure of bastnaesite as proposed by Donnay and Donnay (1953) a) projected onto the a-b plane, fluorine-cerium layer at 0 and 1/2, carbonate groups at 1/4 and 3/4; b) projected onto the a-c plane at y=1/3.
TABLE 13.  

**KIVUIE**  
\((\text{Th},\text{Ca},\text{Pb})\text{H}_2(\text{UO}_2)_4(\text{PO}_4)_2(\text{OH})_8\cdot 7\text{H}_2\text{O})\)

<table>
<thead>
<tr>
<th>Orthorhombic (Bmmb?)</th>
<th>(N\alpha = 1.618(2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphuranylite-dewindtite gp.</td>
<td>(N\beta = 1.654-1.655)</td>
</tr>
<tr>
<td><strong>Cell parameters:</strong></td>
<td><strong>N\gamma = 1.655(3)</strong></td>
</tr>
<tr>
<td>(a = 15.88\text{\AA})</td>
<td>(\gamma - \alpha = 0.037)</td>
</tr>
<tr>
<td>(b = 17.24\text{\AA})</td>
<td>(2V = 0-50^\circ)</td>
</tr>
<tr>
<td>(c = 13.76\text{\AA})</td>
<td>Uniaxial to biaxial (+)</td>
</tr>
<tr>
<td>Volume = 3630\text{\AA}^3</td>
<td>Dispersion: r&gt;v</td>
</tr>
<tr>
<td>(Z = 6)</td>
<td>Lustre: earthy</td>
</tr>
<tr>
<td>Nonmetamict</td>
<td>Colour: yellow</td>
</tr>
<tr>
<td>Habit: massive</td>
<td></td>
</tr>
</tbody>
</table>

**Analysis:**  
CaO 0.60, BaO 0.1, As2O5 0.1, BeO trace, ThO2 8.32, UO3 62.90, PbO 1.84, P2O5 6.04, H2O 6.24, H2O+ 8.09, total 94.23 wt%.

**Three strongest x-ray lines (intensity):**  
10.27 (vs), 7.96 (s-vs), 3.08 (s).

**Occurrence:**  
as earthy masses in the Koboko pegmatite at Kivu, Zaire, in association with uraninite, cyrtolite, colomboantalite and apatite.

**Paragenesis:** secondary.

**Type locality:** Kivu, Zaire.

**Name:** for locality.

**Other localities:** none

**Other names:** eyletersite (?)

**Related species:** phosphuranylite and dewindtite (?)

**References:** Fleischer (1959); Van Wambke (1972).
<table>
<thead>
<tr>
<th><strong>TABLE 14.</strong></th>
<th><strong>EYLETTERSITE</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>(Th,Pb)$_{1-x}$Al$_3$(PO$_4$,SiO$_4$)$_2$(OH)$_6$</td>
<td></td>
</tr>
</tbody>
</table>

| **Trigonal (R3m)** | **N$_{\omega}$** = 1.63 - 1.66 |
| **Crandallite group** | **N$_{c}$** = 1.61 - 1.64 |
| **Cell parameters:** | **$\epsilon$** - **$\omega$** = 0.01 - 0.05 |
| $a$ = 6.99(4)Å | Uniaxial (-) |
| $c$ = 16.7(1)Å | **D$_{meas}$** = 3.4(1)g/cm$^3$ (pyc.) |
| Volume = 706Å$^3$ | **D$_{calc}$** = 3.44 g/cm$^3$ |
| $Z$ = 1 | **Colour:** creamy white |
| **Lustre:** earthy | **Fluorescence:** creamy brown (l.w.) |
| **Streak:** white | colourless (t.s.) |
| **Nonmetallic** | yellow-green (s.w.) |
| **Habit:** massive | |

Inclusions: very fine limonite.
Substitutions: Ba, U, Ca, Sr, H for Th; CO$_3$, H$_2$O$_4$ for PO$_4$.
Analysis: SiO$_2$ 1.65, Al$_2$O$_3$ 35.7, Fe$_2$O$_3$ 0.09, CaO 0.72, BaO 1.45, SrO 0.1, ThO$_2$ 18.43, UO$_3$ 3.05, ZrO$_2$ 0.95, PbO 4.62, P$_2$O$_5$ 18.3, CO$_2$ 0.2, H$_2$O 15.0, total 100.26 wt%.

Alters partially to autunite.
Reacts slightly with warm H$_2$SO$_4$.
Thermal behaviour: Above 1000°C breaks down to form ThO$_2$, U$_3$O$_8$, Al$_2$O$_3$ and aluminum pyrophosphate (?).

DTA peaks: endothermic peak at 165-170°C; exothermic peaks at 730-740°C and 830°C.
Three strongest x-ray lines (intensity) (indices): 5.70 (55) (101), 3.51 (60) (110), 2.95 (100) (015, 113, 021); PDF 26-991.
Occurrence: as pulverulent nodules in the Kobokobo pegmatite at Kivu, Zaire in association with feldspar, apatite, columbite, crytoltite and phosphuranylite.
Paragenesis: formed by intense alteration of uraninite by hydrothermal and supergene phosphatic fluids.

Type specimen: C.C.R. EURATOM, Ispra, Italy.
Name: for Mrs. L. van Wambke.
Other names: Kivuite (?).
Related species: crandallite, plumbogummite.
Rhabdophane Group $\text{ABO}_4 \cdot n\text{H}_2\text{O}$

The poorly-defined rhabdophane group of minerals are hydrous phosphates with the general formula $\text{ABO}_4 \cdot n\text{H}_2\text{O}$ ($n=1-2$), where A=RE, Th or Ca (Th$>$Ca) and B=P or Si (P$>$Si) (Table 15). The minerals may be divided into two subgroups according to symmetry. The hexagonal subgroup includes rhabdophane (REPO$_4 \cdot \text{H}_2\text{O}$; Lettsom, 1878; Bertrand, 1880; Larsen, 1921; Palache et al., 1944; Hildebrand et al., 1957; Bowles and Morgan, 1984), brockite ($\text{(Ca, Th)}\text{PO}_4 \cdot \text{H}_2\text{O}$, Ca: Th$=1:1$; Bowie, 1956; Dooley and Hathaway, 1961; Fisher and Meyrowitz, 1962) and tristramite ($\text{(Ca, U)}\text{PO}_4 \cdot 1.5-2\text{H}_2\text{O}$; Atkin et al., 1984). The orthorhombic subgroup includes ningyoite ($\text{Ca}_1-x\text{U}_x\text{PO}_4 \cdot 1-2\text{H}_2\text{O}$; Muto et al., 1959; Belova et al., 1978; Boyle et al., 1981) and grayite ($\text{(Ca, Th)}\text{PO}_4 \cdot \text{H}_2\text{O}$; Bowie, 1956; Dooley and Hathaway, 1961; Fisher and Meyrowitz, 1962). Th is an essential element in brockite and grayite.

The members of the rhabdophane group are very fine-grained, secondary minerals which usually occur as radial, fibrous aggregates or as earthy patches, often coating grains of other minerals. The x-ray powder diffraction patterns of the hexagonal minerals are very similar to that of rhabdophane itself, and are distinguishable from the patterns of the orthorhombic ningyoite and grayite which have several extra lines (Table 16). On heating, all members of the group convert to a monazite structure.

The first member of the group to have been described was rhabdophane (Lettsom, 1878) which was determined to be uniaxial positive by Bertrand (1880) and Larsen (1921). The very fine-grained nature of the material prevented single crystal x-ray diffraction work.
<table>
<thead>
<tr>
<th>Mineral</th>
<th>Cation(s)</th>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>Volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CePO₄(hex)</td>
<td>Ce</td>
<td>7.06</td>
<td></td>
<td>6.44</td>
<td>278</td>
</tr>
<tr>
<td>BiPO₄(hex)</td>
<td>Bi</td>
<td>6.97</td>
<td></td>
<td>6.46</td>
<td>272</td>
</tr>
<tr>
<td>Rhabdophane</td>
<td>RE</td>
<td>6.98</td>
<td></td>
<td>6.39</td>
<td>270</td>
</tr>
<tr>
<td>Brockite</td>
<td>Th, Ca</td>
<td>6.98</td>
<td></td>
<td>6.40</td>
<td>270</td>
</tr>
<tr>
<td>Tristramite</td>
<td>U, Ca</td>
<td>6.91</td>
<td></td>
<td>6.42</td>
<td>266</td>
</tr>
<tr>
<td>Ningyoite</td>
<td>U, Ca</td>
<td>6.78</td>
<td>12.13</td>
<td>6.36</td>
<td>523</td>
</tr>
<tr>
<td>Grayite</td>
<td>Th, Ca</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>
The x-ray powder diffraction pattern of rhabdophane is similar to that of synthetic hexagonal hydrous cerium phosphate (CeP_4O_{12}; \text{P}_6\text{.}2\text{.}2\text{.}2\text{.}; Hildebrand et al., 1957) and can be indexed on a hexagonal cell with \(a=6.98\AA\), \(c=6.39\AA\).

Hexagonal symmetry is generally accepted for rhabdophane, brockite and tristramite. The x-ray powder diffraction patterns of ningyoite and grayite, while similar to those of the hexagonal members, have additional weak reflections (e.g., 120, 200 and 002 in both and 011, 202 and others in the ningyoite pattern) which cannot be indexed on the small hexagonal cell of rhabdophane. Orthorhombic symmetry was proposed for ningyoite (Muto et al., 1959) and grayite (Fisher and Meyrowitz, 1962) as their x-ray powder diffraction patterns can be indexed on an orthorhombic cell (Table 16) which is related to the hexagonal cell of tristramite and brockite by the transformation matrix 010/210/001. The orthorhombic symmetry of ningyoite has been confirmed by electron diffraction studies (Belova et al., 1978).

The hexagonal members tristramite and brockite are chemically similar to the orthorhombic ningyoite and grayite and are, therefore, dimorphous with the latter. Based on the similarities in the powder patterns, the rational relationship between the hexagonal and the orthorhombic cells and the presence of superlattice reflections in the powder patterns of the orthorhombic minerals, the dimorphism is most likely a result of order-disorder transformation, the orthorhombic forms being ordered. However, confirmation of this relationship requires further structural studies and more precise chemical analyses of ningyoite and grayite.
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1) Mooney, 1952.  
2) Muto et al., 1959.  
4) Atkin et al., 1984.  
5) Dooley and Hathaway, 1956.
| Table 17. BROCKITE  
(Ca, Th)(PO₄)·H₂O |
<table>
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<tr>
<td>Hexagonal (P6₃22)</td>
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<td>Cell parameters:</td>
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<tr>
<td>a = 6.98(3)Å</td>
</tr>
<tr>
<td>c = 6.40(3)Å</td>
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<td>Volume = 270Å³</td>
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<td>Fracture: conchoidal</td>
</tr>
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<td>Partially metamict</td>
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<tr>
<td>Habit: massive</td>
</tr>
<tr>
<td>Nₜ = 1.680(2)</td>
</tr>
<tr>
<td>Nₑ = 1.695(2)</td>
</tr>
<tr>
<td>ε - ω = 0.015</td>
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<tr>
<td>Uniaxial (+)</td>
</tr>
<tr>
<td>Extinction: undulatory, parallel</td>
</tr>
<tr>
<td>Elongation: (+)</td>
</tr>
<tr>
<td>Dmeas = 3.9(2)g/cm² (pyc.)</td>
</tr>
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<td>Dcalc = 4.0</td>
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Inclusions: hematite.
Substitutions: Sr,Ba for Ca; RE for Th; CO₃ for PO₄.
Analysis: Fe₂O₃ 4.6, BaO 0.1, SrO 1.3, CaO 9.7, UO₂ 0.07, RE₂O₃ 6.6, CO₃ 3.1, P₂O₅ 23.6, H₂O 7.5, insolubles 2.0, total 102.27 wt%.
Structure: isostructural with rhabdophane.
Three strongest x-ray lines (intensity) (indices): 4.37 (70) (101), 3.03 (100b) (200), 2.83 (70) (102); PDF 15-248.
Occurrence: as fine-grained, massive aggregates in nodules (up to 3.5cm in diameter) in vein-type carbonatites in deeply weathered granites of the Wet Mountains, Colorado, in association with hematite, pyrite, calcite, barite, apatite and quartz. It has also been reported from Sebungwe, Zimbabwe (S. Rhodesia) and Fremont Co., Wyoming.
Type locality: Wet Mountains, Colorado.
Paragenesis: formed at the expense of thorite, in veins localized along shear zones.
Named for: M. Brock (USGS).
Related species: ningyoite, rhabdophane; grayite (pol.)
TABLE 18. \textbf{GRAYITE} \hfill (Ca, Th)PO$_4$.H$_2$O

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<td>Rhabdophane group</td>
<td>$c - w$: moderate</td>
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<tr>
<td>Lustre: earthy to resinous</td>
<td>$D_{meas} = 3.7-4.3$ g/cm$^3$</td>
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<td>Fracture: conchoidal</td>
<td>$H = 3-4$</td>
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<tr>
<td>Polymorph: brockite (hex.)</td>
<td>Colour: yellow to red-brown</td>
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<tr>
<td>Partially metamict</td>
<td>Habit: fine-grained to earthy</td>
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Substitutions: RE, Fe$^3+$ for Th; Si for P.
Analysis: semiquantitative (Dooley and Hathaway, 1961).

Thermal behaviour: gives a rhabdophane powder pattern on unheated material and a monazite powder pattern after heating to 850°C.

Three strongest x-ray lines (intensity): 3.04 (100), 2.82 (80%), 2.14 (80%).

Occurrence: reported from thorium-bearing veins in Fremont Co., Wyoming and Gunnison, Colorado; as fine-grained surface coating and earthy yellow patches with massive zircon on columbite crystals from Mtoko, Zimbabwe (S. Rhodesia) and in monazite sands from Malawi (Nyasaland).

Type locality: Zimbabwe.

Related minerals: mingyoite, rhabdophane, tristramite; brockite.
A Th-bearing material which occurs at Mont St-Hilaire, in intimate association with UK27, gives a rhabdophane-like x-ray powder diffraction pattern. Variable P/Si ratios in preliminary electron microprobe analyses of this mineral indicate the presence of 2 different minerals. One has a composition similar to brockite, with P>Si and Th>Ca. The other is similar to thorogummite, with Si>P and Th>>Ca. Either the thorogummite-like phase is amorphous or both minerals produce very similar x-ray powder diffraction patterns. If the silicate is not amorphous, then it is a Th-silicate with the rhabdophane structure and is similar to the disputed species, silicosmirnovskite (Grigod’ev and Dolomonova, 1962). This mineral may be part of a solid solution series from (Ca,Th)PO₄·H₂O to ThSiO₄·H₂O, which would result from the coupled substitution Th+Si=1/2(Th+Ca)+P. There may be a continuous solid solution series in the system REPO₄·nH₂O→(Th,Ca)PO₄·nH₂O→ThSiO₄·nH₂O with the substitutions Ca+Th=2RE and Th+Si=RE+P.
Monazite Group: \( \text{ABO}_4 \) (\text{mon.})

The minerals of the monazite group are monoclinic, space group \( \text{P}2_1/\text{n}, \ z=4 \), with the general formula \( \text{ABO}_4 \), where A=RE, Ca or Th and B=P or Si (Table 19).

The Th minerals in this group are brazantite (\( \text{CaTh}(\text{PO}_4)_2 \)), cheralite ((\( \text{Ca,RE,Th} \))(\( \text{P,Si} \)O)\(_4 \)) and huttonite (\( \text{ThSiO}_4 \)). There is extensive solid solution in the system \( \text{CePO}_4-(\text{Ca,Th})\text{PO}_4-\text{ThSiO}_4 \), with coupled substitution of:

\[
2\text{RE}^{3+} = \text{Ca}^{2+} + \text{Th}^{4+}
\]

and

\[
\text{RE}^{3+} + \text{P}^{5+} = \text{Th}^{4+} + \text{Si}^{4+}.
\]

The monazite structure (Fig. 9) is a 3-dimensional network of edge-sharing \( \text{AO}_9 \) polyhedra interconnected by individual \( \text{BO}_4 \) tetrahedra. The A-site cation is coordinated by 9 O atoms and the B-site cation by four. Five of the O atoms around the A-site are equatorial and lie in a subplanar, pentagonal arrangement perpendicular to the c-axis. The other four are grouped as two pairs of O atoms on opposite sides of the \( \text{AO}_9 \) polyhedron, along the c-axis. The pairs represent edges which are shared with \( \text{BO}_4 \) tetrahedra. The \( \text{AO}_9 \) and \( \text{AO}_4 \) groups are linked by these shared edges to form chains parallel to the c-axis. The chains are cross-linked by the 5 equatorial bonds to form the 3-dimensional network.

In the system \( \text{RE-Ca-Th} \) (Fig. 10), there are no monazite-group minerals with \( \text{Ca}>\text{Th} \); however, there is a series between \( \text{Ce} \) and (\( \text{Th},\text{Ca} \)). Therefore, the ternary system, \( \text{CePO}_4-(\text{Th},\text{Ca})\text{PO}_4-\text{ThSiO}_4 \) best illustrates cation substitutions in the monazite group.

The current nomenclature of minerals in this system is essentially
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<td>Bi</td>
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<td>6.92</td>
<td>6.46</td>
<td>103.5°</td>
</tr>
<tr>
<td>1)</td>
<td>Brabantite</td>
<td>CaTh</td>
<td>6.73</td>
<td>6.93</td>
<td>6.45</td>
<td>103.9°</td>
</tr>
</tbody>
</table>

1) Rose, 1980.
2) Pabst and Hutton, 1951.
3) Bowie and Horne, 1953.
4) Mooney-Slater, 1962.
based on the scheme proposed by Bowie and Horne, (1953) and Rose (1980) (Fig. 11). Monazite, brabantite and huttonite are the minerals containing more than 75 wt% of the end-member molecules. Cheralite is intermediate in composition to monazite and brabantite, as illustrated in the diagram. According to this scheme, two names must be given to the minerals with compositions corresponding to analyses 6, 7, 28 and 29 (Fig. 10). It is unfortunate that six names must be used for this simple ternary system, particularly since monazite has no rock-forming significance. A simpler scheme is therefore proposed using only the names of the three end-member compositions (Fig. 12). Monazite and huttonite are retained for (Ce, Th, Ca)(P, Si)O₄ and (Th, Ce, Ca)(Si, P)O₄ (Si > 33.3 mole%) with end-member compositions of CePO₄ and ThSiO₄, respectively. Cheralite is adopted for the Ca-Th-rich minerals with an end-member composition of CaTh(PO₄)₂. The name cheralite is adopted because it has priority over brabantite and type-cheralite contains over 50 mole% CaTh(PO₄)₂. Brabantite, then, becomes unnecessary (Chao, 1981).

Examination of synthetic CePO₄(mon) and hydrous CePO₄(hex) indicate that these two forms are related (Mooney, 1950). The hydrous hexagonal form crystallizes from solution at moderate temperatures. It transforms to the more stable monoclinic form at high temperatures. Monazite is the natural analogue of monoclinic CePO₄ (Mooney, 1950) and rhabdophane group minerals, which convert to a monazite structure on heating, are probably the natural analogues of the low-temperature, hexagonal, hydrous CePO₄.
FIGURE 11. Current nomenclature of the minerals of the monazite group. Minerals corresponding to analyses 6, 7, 28 and 29 (see Fig. 10) are unnamed. After Bowie and Horne, 1953 and Rose, 1980.
FIGURE 12. Proposed revision of the nomenclature of the minerals of the monazite group.
TABLE 20.  

CHERALITE  
(Ca, Ce, Th)(P, Si)O₆

<table>
<thead>
<tr>
<th>Property</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoclinic (P2₁/n)</td>
<td>Nₐ = 1.779</td>
</tr>
<tr>
<td>Monazite group</td>
<td>N₈ = 1.780</td>
</tr>
<tr>
<td>Cell parameters:</td>
<td>N₉ = 1.816</td>
</tr>
<tr>
<td>a</td>
<td>= 6.74 Å</td>
</tr>
<tr>
<td>b</td>
<td>= 7.00 Å</td>
</tr>
<tr>
<td>c</td>
<td>= 6.43 Å</td>
</tr>
<tr>
<td>a/c</td>
<td>= 104.6°</td>
</tr>
<tr>
<td>Volume</td>
<td>= 294 Å³</td>
</tr>
<tr>
<td>Z</td>
<td>= 4</td>
</tr>
<tr>
<td>Fracture:</td>
<td>uneven</td>
</tr>
<tr>
<td>Cleavage:</td>
<td>{010} distinct</td>
</tr>
<tr>
<td></td>
<td>(100) difficult</td>
</tr>
<tr>
<td>Tenacity:</td>
<td>brittle</td>
</tr>
<tr>
<td>Streak:</td>
<td>white</td>
</tr>
<tr>
<td>Habit:</td>
<td>massive</td>
</tr>
<tr>
<td>Nonmetamict</td>
<td>Parting: {001} poor</td>
</tr>
</tbody>
</table>

Substitutions: RE for Th, Si for P.
Analysis: SiO₂ 2.10, Al₂O₃ tr., Fe₂O₃ tr., CaO 6.30, ThO₂ 31.51, U₃O₈ 4.05, RE₂O₃ 27.56, PbO 0.92, P₂O₅ 26.80, H₂O⁰ 0.06, total 99.29 wt% (Bowie and Horne, 1953).
IR: main bands at 540, 570 and 620 cm⁻¹ and between 850 and 1200 cm⁻¹.
Structure: isostructural with monazite with coupled substitution of Th⁴⁺+Ca³⁺ for 2RE (Fig. 9).
Three strongest x-ray lines (intensity) (indices): 3.26 (90) (200), 3.07 (100) (120), 2.86 (90) (112,012); ASTM 15-248.
Occurrence: as massive aggregates (to 5 cm across) in a kaolinitized pegmatite dyke in Travancore, India with tourmaline, chrysoberyl, zircon, smoky quartz and monazite; also reported near Verkhoyansk, U.S.S.R. and as green crystal fragments in sands from Semeling, Malaysia with zircon, pyrite, garnet and other heavy minerals.

Paragenesis: primary accessory mineral.
Type locality: Travancore, India.
Name: for Chera, ancient Dravidian kingdom.
Related species: monazite, brahantite and muttonite.
Best references: Bowie and Horne (1953); Finney and Rao (1965); Bowles and Morgan (1980).
TABLE 21.

*BRABANTITE
CaTh(PO₄)₂

Monoclinic (P2₁/n)
Monazite group
Cell parameters:
  a = 6.726(6)Å
  b = 6.933(6)Å
  c = 6.447(5)Å
  ß = 103.9(2)°
Volume = 292Å³
Z = 2

Cleavage: (001) distinct
(100) difficult
Partially metamict

Habit: crystalline aggregates

Inclusions: minute hematite plates
Substitutions: minor Mg, Mn, Al and Fe for Ca; U for Th and Si for P.
Analysis: SiO₂ 2.27, Al₂O₃ 0.74, Fe₂O₃ 0.05, MgO 0.56, MnO 0.32, CaO 11.94, ThO₂ 52.65, P₂O₅ 27.68, H₂O 3.07, total 99.28 wt%.
Thermal behaviour: x-ray powder pattern improved after heating above 900°C.
DTA: broad exothermic reaction between 100 and 460°C.
IR: main bands at 410, 450 and 610cm⁻¹ and between 850-1200cm⁻¹.
Structure: isostructural with monazite; equivalent amounts of Th⁴⁺ and Ca²⁺ substituting for trivalent rare earths (Fig. 9).
Three strongest x-ray lines (intensity) (indices): 3(26) (70) (200), 3.06 (100) (120), 2.85 (75) (112, 012); PDF 31-311.
Occurrence: as aggregates (to 1.5cm in diameter) of elongated crystals in Cretaceous microcrystalline mica pegmatite at Brabant, Namibia, in association with albite, quartz, muscovite and accessory thorite, uraninite, topaz, apatite and amblygonite.

Paragenesis: primary accessory mineral.
Type locality: Brabant, Namibia.
Type specimen: Institut fur Mineralogie und Kristallographie, Technische Universität, Berlin.
Name: for Brabant district.
Other localities: none
Other names: cathophorite (disc.)
Related species: monazite, cheralite and huttonite.
Reference: Rose (1980).

* see pg. 54
TABLE 22. HUTTONITE
ThSiO₄

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoclinic (P2₁/n)</td>
<td>N ₐ = 1.898(3)</td>
</tr>
<tr>
<td>Monazite group</td>
<td>N ₇ = 1.900</td>
</tr>
<tr>
<td>Cell parameters:</td>
<td>N ₇ = 1.922</td>
</tr>
<tr>
<td>a = 6.80(3)Å</td>
<td>y - a = 0.024</td>
</tr>
<tr>
<td>b = 6.96(3)Å</td>
<td>Z₁V = 25(1)°</td>
</tr>
<tr>
<td>c = 6.54(3)Å</td>
<td>Biaxial (+)</td>
</tr>
<tr>
<td>a/c = 104.9(2)°</td>
<td>γ near c</td>
</tr>
<tr>
<td>Volume = 299Å³</td>
<td>Dispersion: r&lt;υ (mod.)</td>
</tr>
<tr>
<td>Z = 4</td>
<td>D meas = 7.7(1)g/cm³</td>
</tr>
<tr>
<td>Fracture: conchoidal</td>
<td>D calc = 7.18g/cm³</td>
</tr>
<tr>
<td>Cleavage: {011} distinct</td>
<td>Lustre: adamantine</td>
</tr>
<tr>
<td>{100} indistinct</td>
<td>Colour: colourless to pale cream</td>
</tr>
<tr>
<td>Polymorph: thorite (tet.)</td>
<td>Fluorescence: dull white with pink tinge</td>
</tr>
<tr>
<td>Nonmetamict</td>
<td></td>
</tr>
<tr>
<td>Habit: anhedral grains</td>
<td></td>
</tr>
</tbody>
</table>

Not affected by acid.

Analysis: SiO₂ 19.7, Fe₂O₃ 1.2, ThO₂ 76.6, RE₂O₃ 2.6, total 100.1 wt% (Prondel, 1958).

Structure: isostructural with monazite: Th is coordinated to 9 oxygens forming polyhedra which share opposite edges with SiO₄ tetrahedra, forming chains parallel to "c" (see thorite), and 5 corners with SiO₄ groups to form a three dimensional network (Fig. 9, 13).

Three strongest x-ray lines (intensity) (indices): 4.23 (75) (111), 3.09 (100) (120), 2.89 (90) (112, 012); PDF 4-613.

Occurrence: as minute (0.2mm) grains in placer gravels (derived from granitic pegmatites and alaskit granite) near South Westland, New Zealand with scheelite, cassiterite, zircon, uranothorite, ilmenite and gold.

Type locality: South Westland, New Zealand.

Name: for C.O. Hutton.

Varietal names: cerphosphorhuttonite.

Related species: cheralite, monazite and brabantite; thorite (poly.).

4) SILICATES

The eight natural Th silicates include members of the zircon, and ekanite groups as well as thorosteenstrupine, umbozerite and UK27. Huttonite, which has already been described under the monazite group, is the polymorph of thorite.

Zircon Group: $\text{ABO}_4$ (tet.)

Thorite ($\text{ThSiO}_4$) and thorogummite ($\text{Th(SiO}_4)_{1-x}\text{(OH)}_x$) are isostructural with zircon ($\text{ZrSiO}_4$) and coffinite ($\text{U(SiO}_4)_{1-x}\text{(OH)}_x$) (Frodel, 1953). In thorite, Th occurs in 8-fold coordination, surrounded by 4 "equatorial" and 4 "axial" oxygen atoms (Figure 13; Taylor and Ewing, 1978). The 4 axial atoms represent opposite sides of the $\text{SiO}_4$ tetrahedra which are shared with sides of $\text{ThO}_8$ polyhedra to form chains of alternating $\text{SiO}_4$ and $\text{ThO}_8$ groups parallel to the c-axis. The chains are cross-linked via the 4 equatorial O atoms which represent corners shared by adjacent $\text{ThO}_8$ and $\text{SiO}_4$ polyhedra (Robinson et al., 1971). This arrangement produces an open structure which has a network of interconnected voids, making thorite susceptible to damage by alpha-particle bombardment and water diffusion and probably increasing its tendency to become metamict (Taylor and Ewing, 1978).

In huttonite, the chains are comprised of $\text{ThO}_8$-$\text{SiO}_4$ groups which are cross-linked by 5 equatorial oxygen atoms. The higher coordination results in a more closely packed and denser structure, which is less susceptible to damage than that of thorite.

The composition of thorite and thorogummite is variable, with $\text{U, RE, Zr, Ca, Fe,}$ and $\text{Pb}$ substituting for Th in the A-site and P for Si in the B-site. Many of the compositional variants have been given
FIGURE 13. Coordination around A-site cation of a) huttonite and b) thorite. ● - Th, ○ - Si, O - O. From Taylor and Ewing (1978).
unnecessary varietal names, for example, uranothorite for high-U thorite (Tables 23 and 24; Frondel, 1958; Frondel et al., 1967). The extent of substitution of U in thorite is limited. Robinson et al. (1957) reported 20 wt% U₂O₈ in thorite, but some uraninite may have been present in the sample. Frondel (1958) reported about 16.5 wt% UO₂ in thorite from Hybla, Ontario. No significant amount of Th has been found in coffinite.

Studies of the synthetic, anhydrous system ThSiO₄-USiO₄ have produced conflicting results. Fuchs and Gebert, (1958) suggested that there is a complete solid solution series, but gave no experimental data. Mumpton and Roy (1961) were unable to synthesize thorite containing more than about 20 wt% USiO₄, nor could they produce a Th-bearing USiO₄.

Thorogummite, the hydrous equivalent of thorite, has a maximum of 15 wt% H₂O (Frondel, 1953). The water may be present as molecular water (Mumpton and Roy, 1961) or as hydroxyl (Frondel, 1953). The relationship between thorogummite and coffinite is unclear.
### TABLE 23. THORITE

<table>
<thead>
<tr>
<th>Property</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetragonal (14/amd)</td>
<td></td>
</tr>
<tr>
<td>Zircon group</td>
<td></td>
</tr>
<tr>
<td>Cell parameters:</td>
<td></td>
</tr>
<tr>
<td>a = 7.12(3)Å</td>
<td></td>
</tr>
<tr>
<td>c = 6.32(3)Å</td>
<td></td>
</tr>
<tr>
<td>Volume = 320(5)Å³</td>
<td></td>
</tr>
<tr>
<td>Z = 4</td>
<td></td>
</tr>
<tr>
<td>Fracture</td>
<td>conchooidal to splintery</td>
</tr>
<tr>
<td>Cleavage</td>
<td>{100} indistinct</td>
</tr>
<tr>
<td>Tenacity</td>
<td>brittle</td>
</tr>
<tr>
<td>Streak</td>
<td>yellow to brown</td>
</tr>
<tr>
<td>Lustre</td>
<td>vitreous to greasy</td>
</tr>
<tr>
<td>Nonmetamict to metamict</td>
<td></td>
</tr>
<tr>
<td>Paramagnetic</td>
<td></td>
</tr>
<tr>
<td>Habit: massive to crystalline</td>
<td></td>
</tr>
</tbody>
</table>

**Unaffected by acids.**

**Alter to thorogummite.**

**Inclusions:** magnetite, oriented zircon.

**Substitutions:** Zr, U, RE for Th; P for Si; OH for O.

**Analyses:** Table 23a.

**IR:** Broad band at 460 and 1020 cm⁻¹.

**Thermal behaviour:** recrystallizes to fine-grained material when heated above 800°C producing variable x-ray powder patterns which indicate the presence of thorite, huttonite and/or thorlanite plus amorphous SiO₂.

**DTA:** continuous water loss below 250°C, sharp exothermic peak at 880°C.

**Raman spectra:** Syne et al. (1977).

**Structure:** zircon structure: Th is coordinated to 8 oxygens to form triangular dodecahedra (Robinson et al., 1971) which share opposite edges with SiO₄ tetrahedra, forming chains parallel to "c", and 4 edges with other ThO₆ dodecahedra forming lateral links between chains, interconnected octahedral voids form channels parallel to "c" (Fig. 14).

**Three strongest x-ray lines (intensity) (indices):** 4.69 (90) (011), 3.56 (100) (200), 1.84 (100) (312); PDF 11-419.

**Occurrence:** as massive aggregates or translucent to opaque, stubby dipyramids (up to 4 cm), occasionally with prism faces developed, in a variety of environments:
- in pegmatites from Langesund Fiord, Norway; as irregular blebs (up to 1 cm) of waxy, yellow material associated with calcite, spinel and thorlanite from Abatomika, Malagasy Republic (Madagascar); with RE minerals from Baringer Hill, Texas and in pegmatites from many other locations.
TABLE 23. CONTINUED.

- in thorium-bearing veins at Lemhi Pass, Idaho/Montana and associated with alkaline intrusives in both the Wet Mountains, and the Powderhorn district, Colorado;
- in alkaline intrusives including Ilitmaussaq, Greenland and Lovozero and Khibina massifs on the Kola peninsula, U.S.S.R.
- in gem gravels and detrital deposits in Nigeria; near La Grange, California; Cache Creek, Alaska; and near South Westland, New Zealand; Pekoerogan River, Central Sulawesi (Celebes); in Sri Lanka (Ceylon) and Sicily;

Some Canadian occurrences: as dark brown, subhedral, vitreous grains (up to 2cm) in granitic pegmatites at the Macdonald mine, Nybba, Ontario; as yellow to brown, acicular grains in calcite-fluorite-apatite veins in Huddersfield, Twp., Quebec; and as orange to brown, vitreous, anhedral grains (up to 2mm) with calcite and hornblende in metasomatized marbles near Bancroft, Ontario, and throughout the Grenville province; in radioactive granites at Surprise Lake, British Columbia (Ballantyne et al., 1982) and at Fury and Hecla Straits, Baffin Island (Maurice, 1982). Fine-grained, colloform thorite has been identified as an alteration product of allanite from Sharbot Lake, Ontario (Littlejohn, 1981).

Type locality: Langesund Fjord, Norway.
Name: for Thor, the Norse god of war.
Varietal names: aeurilite - phosphatic thorite: P_04:S_102 = 0.8:1.0
calciothorite: calcian thorite
enalite: uranoan thorite
eucrasite: RE thorite: RE:Th up to 1:1
ferrithorite: high iron thorite
fre yalite: RE thorite
jiningite: thorite with Fe_2O_3, P_2O_5 and V_2O_5
mozambikite
orangite: orange thorite
parathorite: poorly characterized
shentulite: with P_2O_5 and As_2O_5
silicosmirnovskite: smirnovskite with Si>P
smirnovskite: (Th, Ca, Ce)(P, Si, Al)(OH)(O, OH, F)_4
uranotherite: uranoan thorite (up to 10%)
wasikasonite: metamict uranoan thorite
yanshallahyntite: phosphatic thorite

Related species: xenotime, zircon; huttonite (poly.).

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>19.20</td>
<td>17.96</td>
<td>19.56</td>
<td>19.81</td>
<td>9.40</td>
<td>17.47</td>
<td>19.38</td>
<td>15.4</td>
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<td>TiO$_2$</td>
<td>-</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>-</td>
<td>0.32</td>
<td>0.13</td>
<td>-</td>
<td>0.50</td>
<td>0.12</td>
<td>0.33</td>
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<tr>
<td>Fe$_2$O$_3$</td>
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<td>-</td>
<td>0.75</td>
<td>0.20</td>
<td>0.30</td>
<td>6.59</td>
<td>4.01</td>
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<tr>
<td>FeO</td>
<td>1.75</td>
<td>0.58</td>
<td>0.43</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.40</td>
<td>11.1</td>
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<td>MgO</td>
<td>-</td>
<td>0.07</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
<td>0.04</td>
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<tr>
<td>CaO</td>
<td>0.40</td>
<td>0.42</td>
<td>4.38</td>
<td>5.17</td>
<td>-</td>
<td>1.39</td>
<td>2.34</td>
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<td>ThO$_2$</td>
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<td>72.93</td>
<td>46.33</td>
<td>40.37</td>
<td>52.8</td>
<td>48.66</td>
<td>52.07</td>
<td>50.4</td>
</tr>
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<td>UO$_2$</td>
<td>4.20</td>
<td>6.95</td>
<td>7.67</td>
<td>-</td>
<td>-</td>
<td>9.00</td>
<td>-</td>
<td>-</td>
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<tr>
<td>UO$_3$</td>
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<td>9.46</td>
<td>20.73*</td>
<td>7.00</td>
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<td>10.87</td>
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<tr>
<td>RE$_2$O$_3$</td>
<td>1.15</td>
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<td>&gt;0.2</td>
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<td>3.12</td>
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<tr>
<td>PbO</td>
<td>0.55</td>
<td>0.10</td>
<td>1.32</td>
<td>1.72</td>
<td>0.21</td>
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<td>-</td>
<td>4.3</td>
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<td>P$_2$O$_5$</td>
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<td>-</td>
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<td>0.70</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10.0</td>
<td>-</td>
</tr>
<tr>
<td>H$_2$O$^+$</td>
<td>-</td>
<td>-</td>
<td>5.67</td>
<td>-</td>
<td>-</td>
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<td>10.88</td>
<td>11.31</td>
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<tr>
<td>H$_2$O$^-$</td>
<td>-</td>
<td>0.22</td>
<td>3.57</td>
<td>9.88</td>
<td>5.6</td>
<td>3.5</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Rem.</td>
<td>0.07</td>
<td>0.12</td>
<td>0.22</td>
<td>-</td>
<td>-</td>
<td>0.73</td>
<td>0.11</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>99.89</td>
<td>99.95</td>
<td>99.94</td>
<td>98.08</td>
<td>100.1</td>
<td>100.20</td>
<td>100.86</td>
<td>92.3</td>
</tr>
</tbody>
</table>

1) Rozina, 1967.
5) Staatz et al., 1976.
8) partial analyses from Rimsaitė, 1983.
TABLE 24.

<table>
<thead>
<tr>
<th>THOROGUMMITE</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Th(SiO}<em>4\text{)}</em>{1-x}(\text{OH})_x )</td>
</tr>
</tbody>
</table>

Tetragonal
Zircon group
Cell parameters:
- \( a = 7.07-7.08\text{Å} \)
- \( c = 6.26-6.28\text{Å} \)
Volume = 313 - 315\( \text{Å}^3 \)
- \( Z = 4 \)
Nonmetamict
Habit: massive

- \( n = 1.54-1.64 \)
- Isotropic to weakly anisotropic
- Parallel extinction
- \( D_{\text{meas}} = 3.2-5.4\text{g/cm}^3 \)
- \( H = 5.5 \)
- Lustre: dull to subvitreous
- Colour: yellow or grey to black
- (uraniferous)
- Fluorescence: yellow-white

Substitutions: RE, U, Zr, Pb for Th; P for Si.
Analyses: Table 24a.

Thermal behaviour: samples, both unheated and heated to 610\( \text{°C} \), give a thorite powder pattern; after heating to 1000\( \text{°C} \) powder pattern shows a mixture of: \( \text{ThO}_2 \) and \( \text{ThSiO}_4 \).

DTA: loss of water at 150\( \text{°C} \); exothermic peak at 750\( \text{°C} \) (loss of OH).

Three strongest x-ray lines (intensity) (indices): 4.69 (90) (011), 3.537 (100) (200), 2.653 (60) (112); PDF 8-440.

Structure: Maybe similar to thorite (Fig. 13) with OH replacing some 0.

Paragenesis: secondary mineral formed by the alteration of thorite.
Occurrence: as fine-grained, massive aggregates, pseudomorph after thorite, in pegmatites at Baringer Hill, Texas and Langesund Fiord, Norway; in waxy, yellow, irregular masses from Fort Dauphin, Malagasy Republic (Madagascar); as opaline crusts on thorite from Hybla, Ontario and associated with kosalite at Wodgina, Western Australia.

Type locality: Baringer Hill, Texas.
Name: for thorium plus "gummite" (bright-coloured fine-grained alteration product).
Other names: chloroorthorite, hyblite, hydrothorite, hydroxyl-thorite, mackintoshite, maiorlandite, nicolayite, pilbarite, (thorogummite plus kosalite).

Related species: coffinite, thorite.
### TABLE 24a. THOROGUMMITE ANALYSES.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>13.09</td>
<td>15.30</td>
<td>21.10</td>
<td>15.77</td>
<td>13.90</td>
<td>14.43</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.97</td>
<td>-</td>
<td>2.22</td>
<td>0.88</td>
<td>-</td>
<td>8.84</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.85</td>
<td>-</td>
<td>8.67</td>
<td>-</td>
<td>-</td>
<td>2.84</td>
</tr>
<tr>
<td>MgO</td>
<td>-</td>
<td>0.16</td>
<td>-</td>
<td>0.60</td>
<td>0.10</td>
<td>-</td>
</tr>
<tr>
<td>CaO</td>
<td>0.41</td>
<td>1.62</td>
<td>0.95</td>
<td>1.65</td>
<td>0.59</td>
<td>-</td>
</tr>
<tr>
<td>ThO₂</td>
<td>41.44</td>
<td>24.46</td>
<td>25.05</td>
<td>57.79</td>
<td>45.30</td>
<td>21.20</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>-</td>
<td>-</td>
<td>4.78</td>
<td>-</td>
<td>0.88</td>
<td>0.05</td>
</tr>
<tr>
<td>UO₃</td>
<td>22.43</td>
<td>37.33</td>
<td>7.91</td>
<td>2.98</td>
<td>23.73*</td>
<td>18.53</td>
</tr>
<tr>
<td>RE₂O₃</td>
<td>6.69</td>
<td>0.44</td>
<td>12.76</td>
<td>0.97</td>
<td>1.86</td>
<td>18.55</td>
</tr>
<tr>
<td>PbO</td>
<td>2.16</td>
<td>7.78</td>
<td>tr.</td>
<td>1.25</td>
<td>3.74</td>
<td>0.17</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>1.19</td>
<td>-</td>
<td>1.77</td>
<td>1.33</td>
<td>0.67</td>
<td>2.63</td>
</tr>
<tr>
<td>H₂O⁺</td>
<td>7.88</td>
<td>8.37</td>
<td>10.80</td>
<td>6.06</td>
<td>4.31</td>
<td>7.82</td>
</tr>
<tr>
<td>H₂O⁻</td>
<td>1.23</td>
<td>4.19</td>
<td>9.12</td>
<td>0.50</td>
<td>5.61</td>
<td>-</td>
</tr>
<tr>
<td>Rem.</td>
<td>-</td>
<td>0.40</td>
<td>4.48</td>
<td>1.50</td>
<td>2.25</td>
<td>8.28</td>
</tr>
<tr>
<td>Total</td>
<td>98.33</td>
<td>100.05</td>
<td>100.49</td>
<td>99.90</td>
<td>96.50</td>
<td>100.05</td>
</tr>
</tbody>
</table>

1) Hidden et al., 1889, in Frondel, 1953.
2) Simpson, 1930, in Frondel, 1953.
3) Imori et al., 1938, in Frondel, 1953.
4) Simpson, 1927, in Frondel, 1953.
5) Hidden et al., 1893, in Frondel, 1953.
6) Henmi, 1951, in Frondel, 1953.

* reported as UO₂.
Ekanite Group: $AB_2CSi_8O_{20}$

The minerals of the tetragonal ekanite group are ekanite, iraquite, steacyite and one unnamed species from central Asia (Table 25). The general formula is $AB_2CSi_8O_{20}$, where $A=Th$ or RE; $B=Na$, Ca or RE and $C=K$ or vacancies.

Ekanite was originally described as a metamict Th-Ca silicate from Ceylon (Anderson et al., 1961). A similar, nonmetamict Th-Na-Ca-K ekanite-like mineral (UK4; Chao and Baker, 1967), from Mont St-Hilaire was first described as a nonmetamict equivalent of ekanite, even though it contained Na and K and less than half the Ca of ekanite (Richard and Perrault, 1972). Later, Szymanski et al. (1982) described a nonmetamict Th-Ca ekanite from the Yukon, which is very similar chemically to the original material. Since both the composition and structure of the Yukon material differed significantly from those of UK4, the name ekanite has been redefined as the Th-Ca member and the name steacyite has been given to the Th-Na-Ca-K ekanite-like material (UK4) from Mont St-Hilaire (Perrault and Szymanski, 1982).

The primary structural difference between ekanite and steacyite (Figure 14) is the arrangement of the $Si_8O_{20}$ groups. In ekanite, the C-site is completely vacant, allowing bridging between adjacent $Si_8O_{20}$ groups, forming infinite, puckered, silicate sheets of open silicate "baskets". The presence of K in more than 50% of the C-sites of steacyite prevents the bridging between adjacent $Si_8O_{20}$ groups and closes the "baskets", producing discrete double-ring $Si_8O_{20}$ units which resemble cubes (Perrault and Szymanski, 1982). The structure of iraquite is probably similar to steacyite, with RE and Th in the A-
<table>
<thead>
<tr>
<th>Mineral</th>
<th>Cations</th>
<th>a(Å)</th>
<th>c(Å)</th>
<th>Space Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ekanite</td>
<td>ThCa₂⁺</td>
<td>7.48</td>
<td>14.89</td>
<td>I422</td>
</tr>
<tr>
<td>Iraquite</td>
<td>1/2[(RE,Th)₂₋ₓ(Ca,RE)₄(K₂₋ₚ)]</td>
<td>7.61</td>
<td>14.72</td>
<td>P4/mcc</td>
</tr>
<tr>
<td>Steacyite</td>
<td>Th(Na,Ca)₂(K₁₋ₓ[Cl]ₓ)</td>
<td>7.58</td>
<td>14.77</td>
<td>P4/mcc</td>
</tr>
<tr>
<td>Unnamed</td>
<td>Th(Ca,Na)₂(K₁₋ₓ[Cl]ₓ)</td>
<td>7.58</td>
<td>14.82</td>
<td>P4/mcc</td>
</tr>
</tbody>
</table>
FIGURE 14. The structure of a) ekanite and b) steacyite projected on the y-z plane. Fractional coordinates (x100) in the "x" direction are given for each atom. Note the K in the C-site of the steacyite structure. From Szymanski et al., 1982.
### Table 26. Ekanite

<table>
<thead>
<tr>
<th>Property</th>
<th>Value/Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetragonal (1422)</td>
<td></td>
</tr>
<tr>
<td>Ekanite group</td>
<td></td>
</tr>
<tr>
<td>Cell parameters:</td>
<td></td>
</tr>
<tr>
<td>(a = 7.483(3) \text{\AA} )</td>
<td></td>
</tr>
<tr>
<td>(c = 14.893(6) \text{\AA} )</td>
<td></td>
</tr>
<tr>
<td>Volume = 831(1) \text{\AA}^3</td>
<td></td>
</tr>
<tr>
<td>(Z = 2)</td>
<td></td>
</tr>
<tr>
<td>Forms: {010}, {110}, {001} and {100}</td>
<td></td>
</tr>
<tr>
<td>Fracture: irregular</td>
<td></td>
</tr>
<tr>
<td>Cleavage: {101} distinct</td>
<td></td>
</tr>
<tr>
<td>{001} indistinct</td>
<td></td>
</tr>
<tr>
<td>Tenacity: brittle</td>
<td></td>
</tr>
<tr>
<td>Streak: white</td>
<td></td>
</tr>
<tr>
<td>Nonmetamict to metamict</td>
<td></td>
</tr>
</tbody>
</table>

Inclusions: hematite and thorogummite; most numerous in red grains. Substitutions: U for Th; Fe, Mn for Ca and Al for Si. Analyses: Table 26a. Alters, characteristically, to fine-grained, red to red-brown material. Thermal behaviour: weight loss of 9%, but no structural change when heated to 900°C. Structure: metal layers stacked at \(z = 0, 1/2\) separated by a puckered silicate sheet of open double rings which form zeolitic channels in the \(x\) and \(y\) directions (Fig. 14). Three strongest x-ray lines (intensity) (indices): 4.137 (100) (103), 3.343 (96) (202), 3.265 (65) (211). Occurrence: Nonmetamict ekanite occurs as discrete anhedral, to euhedral grains (2-3 mm x 1 mm) or clusters in a glacial syenite boulder from the Tombstone Mountains, Yukon Territory. It is associated with fluorite, garnet, quartz, perthitic microcline, clinopyroxene, apatite, sodic plagioclase, hematite, thorogummite, zircon and titanite. Green, subhedral grains (up to 1 cm) of ekanite occur in syenite from Turkestans, U.S.S.R. A metamict variety comes from the gem pits at Raknapura, Sri Lanka. Type locality: Sri Lanka. Name: for F.L.D. Ekanayake. Related species: steacyite and iraquite. Best references: Anderson et al. (1961), Perrault and Szymanski (1982).
<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2*</th>
<th>3*</th>
<th>4*</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>55.6</td>
<td>45.1</td>
<td>41.7</td>
<td>47.6</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>tr.</td>
<td>0.5</td>
<td>1.3</td>
<td>0.8</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FeO</td>
<td>-</td>
<td>0.3</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>MgO</td>
<td>tr.</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MnO</td>
<td>tr.</td>
<td>0.2</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>CaO</td>
<td>13.7</td>
<td>9.0</td>
<td>8.1</td>
<td>9.6</td>
</tr>
<tr>
<td>ThO₂</td>
<td>27.6</td>
<td>36.0</td>
<td>37.1</td>
<td>37.8</td>
</tr>
<tr>
<td>UO₂</td>
<td>2.1</td>
<td>1.9</td>
<td>0.5</td>
<td>1.1</td>
</tr>
<tr>
<td>PbO</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>100.3</td>
<td>92.9</td>
<td>89.3</td>
<td>97.5</td>
</tr>
</tbody>
</table>

1) Anderson et al., 1961.
2) unheated specimen
3) Szymanski et al., 1982.
4) heated specimen

Bulk chemical analysis of hand-picked grains gave 7.8 wt% H₂O and 3.4 wt% F.
TABLE 27. IRAQUIE
(RE, Th)₂₋ₓ(Ca, RE)ₓ₂₋ₓS₁₋ₓ₁₆₀₄₀

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetragonal (P4/mnc)</td>
<td></td>
</tr>
<tr>
<td>Ekanite group</td>
<td></td>
</tr>
<tr>
<td>Cell parameters:</td>
<td></td>
</tr>
<tr>
<td>a = 7.61(1)Å</td>
<td></td>
</tr>
<tr>
<td>c = 14.72(1)Å</td>
<td></td>
</tr>
<tr>
<td>Volume = 853(4)Å³</td>
<td></td>
</tr>
<tr>
<td>Z = 1</td>
<td></td>
</tr>
<tr>
<td>Fracture:</td>
<td>uneven</td>
</tr>
<tr>
<td>Cleavage:</td>
<td>2 good, 1 poor</td>
</tr>
<tr>
<td>Nonmetallic</td>
<td>colourless (t.a.)</td>
</tr>
<tr>
<td>Habit:</td>
<td>crystalline</td>
</tr>
</tbody>
</table>

Inclusions: minor calcite and pyrite
Substitutions: U, Zr and Pb for RE; Na for Ca and Al for Si.
Analysis: SiO₂ 51.7, Al₂O₃ 0.77, Fe₂O₃ 0.10, MgO 0.02, CaO 10.73, Na₂O 0.27, K₂O 2.76, ThO₂ 9.54, UO₂ 0.65, ZrO₂ 0.17, PbO 0.35, RE₂O₃ 15.06, CuO 0.07, Pb₂O₅ 0.01. F 0.07, H₂O⁺ 3.51, H₂O⁻ 0.90, total 96.65 wt% (Livingstone et al., 1976).

Thermal behaviour: x-ray powder pattern unchanged to 1000°C, apatite-type pattern produced on heating to 1250°C.
D TA: ill-defined endotherm attributable to moisture loss then a shallow endotherm between 200 and 900°C.
TGA: weight loss of 5.2% after heating to 1000°C.
Three strongest x-ray lines (intensity (indices): 5.28 (100) (102), 3.31 (100) (211,104), 2.64 (100) (204); PDF-29-955.
Occurrence: in coarsely crystalline granite in contact with dolomitic marble at Shakh-Rash Mountain, Iraq.
Type locality: Iraq.
Name: for country.
Related species: steeleyte, ekanite.
Best references: Livingstone et al. (1976), Perrault and Szymanski (1982).
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetragonal (P4/mmc)</td>
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</tr>
<tr>
<td>Ekanite group</td>
<td></td>
</tr>
<tr>
<td>Cell parameters:</td>
<td></td>
</tr>
<tr>
<td>a = 7.58(1)Å</td>
<td></td>
</tr>
<tr>
<td>b = 14.77(2)Å</td>
<td></td>
</tr>
<tr>
<td>Volume = 849(3)Å³</td>
<td></td>
</tr>
<tr>
<td>Z = 2</td>
<td></td>
</tr>
<tr>
<td>Forms: {100}, {001}</td>
<td></td>
</tr>
<tr>
<td>Fracture: irregular</td>
<td></td>
</tr>
<tr>
<td>Tenacity: brittle</td>
<td></td>
</tr>
<tr>
<td>Nonmetamict</td>
<td></td>
</tr>
<tr>
<td>Habit: prismatic crystals</td>
<td></td>
</tr>
<tr>
<td>Substitutions:</td>
<td></td>
</tr>
<tr>
<td>Analysis: Sio₂ 50.0, MgO 0.15, MnO 142, CaO 4.25, Na₂O 2.90, K₂O 2.95, ThO₂ 2.42, CeO₂ 0.4, PbO 0.06, H₂O⁻ 11.6, total 97.94 wt% (Perrault and Richard, 1973).</td>
<td></td>
</tr>
<tr>
<td>IR: main bands at 490-500, 585-610, 900-1300, 1660 and 3200-3700cm⁻¹.</td>
<td></td>
</tr>
<tr>
<td>Thermal behaviour: loss of weight, but no change in x-ray powder pattern after heating to 800°C.</td>
<td></td>
</tr>
<tr>
<td>Structure: metal layers at z=1/4,3/4 separated by a silicate sheet of closed double rings (compare with ekanite) (Fig. 14).</td>
<td></td>
</tr>
<tr>
<td>Three strongest x-ray lines (intensity) (indices): 5.30 (45) (102), 3.38 (100) (210,202), 3.32 (55) (104,211); PDF 25-678.</td>
<td></td>
</tr>
<tr>
<td>Occurrence: as short euhedral crystals (up to 2mm long) and clusters in vugs and veins in pegmatite dykes within the nepheline syenite at Mont St-Hilaire, Quebec; associated with analcime, natrolite, microcline, euchalyte, acmite, nenadkevichite, catapleite and epididymite.</td>
<td></td>
</tr>
<tr>
<td>Type locality: Mont St-Hilaire.</td>
<td></td>
</tr>
<tr>
<td>Name: for H.R. Steacy, (GSC).</td>
<td></td>
</tr>
<tr>
<td>Other names: ekanite, kanaekanite (disc.).</td>
<td></td>
</tr>
<tr>
<td>Related species: ekanite, fraprite.</td>
<td></td>
</tr>
</tbody>
</table>
sites, Ca and RE in B and K in C (53% occupied).

In stoichiometric ekanite, the charge balance is altered when Na or RE substitute for Ca in the B-site. Electronic neutrality is maintained by partial occupancy of the C-site by K.

Thorosteestarupine and Umbrozerite

Thorosteestarupine \((\text{Ca}, \text{Th}, \text{Mn})_3 \text{Si}_4 \text{O}_{11} \text{F}^+6\text{H}_2\text{O}; \text{Kuprianova et al., 1962}\) was so named because it was thought to be the Th analogue of the hexagonal RE silicate, steenstrupine \((\text{Ce}, \text{La}, \text{Na}, \text{Mn})_6 \text{Si}_6 \text{O}_{18} \text{OH}\)).

The composition of steenstrupine is complex and variable, with \((\text{Na}_2\text{O}+\text{CaO})\) varying from 5.62 to 11.1 wt% and \((\text{P}_2\text{O}_5+\text{SiO}_2)\) from 30.4 to 38.71 wt% (Machatschki, 1931; Makovicky and Karup-Moller, 1981). The general formula: \(\text{Na}_{1-12} \text{H}_7\text{O} \text{CaRE}_6 \text{M}_5((\text{Si}_6 \text{O}_{18})_2((\text{P}, \text{Si})_4 \text{O}_6)\text{nH}_2\text{O (n<15)}\) (Makovicky et al., 1981) takes into account this wide range of composition. According to crystal structure analysis, a possible end-member formula is: \(\text{Na}_{14}\text{Ce}^{3+}\text{Mn}^{2+}\text{Mn}^{3+}\text{Fe}^{3+}\text{Zr}^{4+}((\text{OH})_2\text{P}_4\text{O}_{18})\text{Si}_6\text{O}_{18}\text{H}_2\text{O}\) (Moore and Shen, 1983).

Although thorosteestarupine has no \(\text{Na}_2\text{O}\) or \(\text{P}_2\text{O}_5\) and has a high water content, the \text{CaO} and \text{SiO}_2 content of thorosteestarupine are similar to the \((\text{Na}_2\text{O}+\text{CaO})\) and \((\text{P}_2\text{O}_5+\text{SiO}_2)\) values of steenstrupine. Since thorosteestarupine (Kuprianova et al., 1961) is metamict, the x-ray powder diffraction pattern is for the heated material. All but 3 reflections can be indexed on the hexagonal cell of steenstrupine. The relationship of thorosteestarupine to steenstrupine cannot be confirmed without detailed structural studies.

The only other Th silicates are umbozerite from the U.S.S.R. and UK27 from Mont St-Hilaire.
TABLE 29.  
THOROSTEENSTRUPINE 
(Ca, Th, Mn)$_3$Si$_4$O$_{12}$F$_2$.6H$_2$O

<table>
<thead>
<tr>
<th>Property</th>
<th>Value/Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous</td>
<td>n = 1.63-1.66</td>
</tr>
<tr>
<td>Fracture:</td>
<td>conchoidal</td>
</tr>
<tr>
<td>Tenacity:</td>
<td>brittle</td>
</tr>
<tr>
<td>Streak:</td>
<td>dark Brown</td>
</tr>
<tr>
<td>Lustre:</td>
<td>greasy to vitreous</td>
</tr>
<tr>
<td>Metamict</td>
<td>Colour: dark brown to black, red-brown on thin edges.</td>
</tr>
<tr>
<td>Weakly magnetic</td>
<td>brown (t.s.)</td>
</tr>
<tr>
<td>Habit:</td>
<td>fine, platy crystals</td>
</tr>
</tbody>
</table>

Substitutions: RE, Fe for Th; Al for Si.
Analysis: SiO$_2$ 31.87, Al$_2$O$_3$ 0.31, Fe$_2$O$_3$ 0.65, MnO 7.75, CaO 8.38, ThO$_2$ 35.70, RE$_2$O$_3$ 1.12, P 2.43, H$_2$O$_2$ 13.77, total 100.16 wt%.
IR: main bands at 1000, 1620 and 3000-3700cm$^{-1}$.
Thermal behaviour: natural material amorphous, gives a powder pattern of 57 lines after heating to 900°C for 30 min., may be a mixture of ekanite and monazite.
DTA: diffuse endothermic event around 200°C; sharp exothermic peak at 890°C.
Three strongest x-ray lines (intensity): 4.08 (100), 3.25 (100), 2.61 (100); PDF 16-608 (htd).
Occurrence: as fine, platy crystals (2-10 mm in length) in metamorphic veins of eastern Siberia, with microcline, albite, aegirine, quartz, fluorite and miserite.
Name: for composition.
Related species: steenstrupine.
Best references: Kupriyanov et al. (1962, 1963).
<table>
<thead>
<tr>
<th>Property</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetragonal</td>
<td>n = 1.640</td>
</tr>
<tr>
<td>Fracture</td>
<td>Conchoidal</td>
</tr>
<tr>
<td>Tenacity</td>
<td>Brittle</td>
</tr>
<tr>
<td>Lustre</td>
<td>Vitreous</td>
</tr>
<tr>
<td>Metamict</td>
<td>Translucent to clear</td>
</tr>
<tr>
<td>Habit</td>
<td>Massive to crystalline</td>
</tr>
<tr>
<td>Substitutions</td>
<td>K for Na, Ba, Ca, Mn for Sr; U, Fe, Ce, Ti for Th.</td>
</tr>
<tr>
<td>Analysis</td>
<td>SiO₂ 37.1, TiO₂ 0.3, Fe₂O₃ 1.8, MnO 2.2, BaO 2.0, SrO 27.7, CaO 0.2, Na₂O 6.13, K₂O 0.74, ThO₂ 17.6, U₃O₈ 0.4, Ce₂O₃ 0.3, loss on ignition 0.43, total 96.8 wt%</td>
</tr>
<tr>
<td>Thermal behaviour</td>
<td>Recrystallizes when heated to 900°C for 1 hr to give an x-ray powder pattern of thorium plus many other lines.</td>
</tr>
<tr>
<td>Three strongest x-ray lines (intensity):</td>
<td>3.38 (60), 3.29 (100), 1.701 (80); PDF 26-1384.</td>
</tr>
<tr>
<td>Occurrence</td>
<td>As irregular masses and poorly formed, mottled, tetragonal crystals (up to 1x3mm) in veins, with ussingite, belovite, sphalerite and pectolite in alkaline rocks near Umbozera, Kola Peninsula, U.S.S.R.</td>
</tr>
<tr>
<td>Name</td>
<td>For locality.</td>
</tr>
<tr>
<td>Best reference</td>
<td>Es'kova et al. (1975).</td>
</tr>
</tbody>
</table>
CHAPTER 3
CHEMISTRY AND IGNEOUS BEHAVIOR OF THORIUM

INTRODUCTION

Thorium was discovered in 1828 by Berzelius in the mineral thorite. Both the element and the mineral were named for Thor, the Norse god of war. The element was discovered to be radioactive by both Mme. M. Curie and G. C. Schmidt in 1898. Thorium is most useful today as a radioelement in breeder reactors as a source of fissile $^{233}$U. Irradiation of $^{232}$Th with slow neutrons forms $^{233}$Th which decays according to the scheme:

$$^{233}\text{Th} \xrightarrow{23.3 \text{ min.}} ^{233}\text{Pa} \xrightarrow{27.4 \text{ da.}} ^{233}\text{U}$$

to produce $^{233}$U which is fissionable by slow neutrons (Katz and Seaborg, 1957).

Thirteen isotopes of thorium have been discovered, but only $^{232}$Th, with a half-life of $1.4 \times 10^{10}$ years (Lederer and Shirley, 1978), is of major geochemical importance. The other isotopes are daughter products of radioactive thorium, uranium or actinium. $^{230}$Th (protactinium), half-life $8.0 \times 10^{4}$ y, is the only other isotope found in nature in significant amounts (Katz and Seaborg, 1957).

$^{232}$Th undergoes radioactive decay (Table 31) to form the stable isotope $^{208}$Pb, which accounts for the accumulation of lead in thorium minerals. Some authors show an additional, but incorrect, pathway from $^{216}$Po to $^{212}$Bi. This error arose in the literature in the 1950's (Wiles, pers. com.) and still persists (Boyle, 1983) even though Lederer et al. (1978) clearly indicate that $^{216}$Po is beta stable.

Excellent reviews of the chemistry of thorium are available
<table>
<thead>
<tr>
<th>Particle Energy in MeV (Intensity)</th>
<th>Gamma Energy in MeV</th>
<th>$t_{1/2}$</th>
<th>Particle Energy in MeV (Intensity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>232_{Th}</td>
<td></td>
<td></td>
<td>4.016(77%)</td>
</tr>
<tr>
<td>0.059 → 228_{Ra}</td>
<td>1.41x10^{10}y</td>
<td>3.957(23%)</td>
<td>3.834(0.2%)</td>
</tr>
<tr>
<td>0.0067 → 228_{Ac}</td>
<td>5.77y</td>
<td>0.039(60%)</td>
<td>0.015(40%)</td>
</tr>
<tr>
<td>0.9111 → 228_{Th}</td>
<td>6.13b</td>
<td>2.18(10.1%)</td>
<td>1.85(9.6%)</td>
</tr>
<tr>
<td>0.0844 → 224_{Ra}</td>
<td>1.913y</td>
<td>1.70(6.7%)</td>
<td>0.64(7.6%)</td>
</tr>
<tr>
<td>0.2410 → 220_{Rn}</td>
<td>3.665d</td>
<td>0.45(13%)</td>
<td>others</td>
</tr>
<tr>
<td>0.5497 → 216_{Po}</td>
<td>55.61s</td>
<td>5.432(72.7%)</td>
<td>5.341(26.7%)</td>
</tr>
<tr>
<td>0.8049 → 212_{Pb}</td>
<td>0.145m</td>
<td>others</td>
<td>5.685(94.9%)</td>
</tr>
<tr>
<td>0.2386 → 212_{Bi}</td>
<td>10.64h</td>
<td>6.288(99%)</td>
<td>5.747(0.07%)</td>
</tr>
<tr>
<td>2.2505</td>
<td>64%</td>
<td>6.779(99%)</td>
<td>5.569(12%)</td>
</tr>
<tr>
<td>8.784 others</td>
<td>0.296 s 2.615</td>
<td>0.3307</td>
<td>0.3307</td>
</tr>
<tr>
<td>212_{Po}</td>
<td>60.60m</td>
<td>3.053m</td>
<td>others</td>
</tr>
<tr>
<td>84</td>
<td>0.0399</td>
<td>60.60m</td>
<td>2.38(0.03%)</td>
</tr>
<tr>
<td>84</td>
<td>0.727</td>
<td>6.051(69.9%)</td>
<td>1.80(48.8%)</td>
</tr>
<tr>
<td>81</td>
<td>36%</td>
<td>5.769(1.7%)</td>
<td>1.52(22.7%)</td>
</tr>
<tr>
<td>82</td>
<td>others</td>
<td>2.38(0.03%)</td>
<td>1.29(23.9%)</td>
</tr>
<tr>
<td>82</td>
<td>2.615</td>
<td>others</td>
<td>1.04(4.6%)</td>
</tr>
<tr>
<td>82</td>
<td>(stable)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From Lipari and Shirley, 1978.
including those by Katz and Seaborg, (1958), Wedepohl (1978) and Gmelin (1979) as well as one by Hyde (1960) on the radiochemistry of thorium. Little attempt will be made here to discuss either the chemistry or synthetic compounds of thorium, except where they have specific geochemical significance. The purpose of this chapter is to account for the small number of thorium minerals and to explain the geochemical distribution of thorium in the igneous environment.

GENERAL CHEMISTRY

Thorium is the last element of the tetravalent titanium transition series, Group IVB (Ti, Zr, Hf, Th), and the second member of the actinide or 5f transition series. Since the outer electronic configuration of thorium is similar to that of Ti, Zr and Hf (Table 32) the chemical properties and bond characteristics should be similar. However, Ti has a much smaller ionic radius and Hf has a filled 4f-shell. Zr is the only Group IVB element which is geochemically similar to Th. The tetravalent elements of Group IVA, with completely filled d-orbitals, have different electronic configurations and are chemically dissimilar to Th. The inner electronic configurations and ionic radii of U and the rare earth elements (REE), particularly the light rare earth elements (LREE), are similar to those of Th. Therefore, the geochemical behaviour of Th is similar to that of U and LREE.

Thorium occurs in nature only as the tetravalent ion Th\(^{4+}\). This valence state is accomplished by shedding the 6d\(^2\) and 7s\(^2\) electrons together to achieve the very stable configuration of the noble gas radon. Therefore, unlike U\(^{4+}\) ((Rn)5f\(^2\)6d\(^0\)7s\(^0\)) which readily loses the two 5f electrons to form the uranyl ion (UO\(_2^{2+}\)), Th\(^{4+}\) cannot easily be
<table>
<thead>
<tr>
<th>ELEMENT SYMBOL</th>
<th>ATOMIC NUMBER</th>
<th>VALENCE STATE</th>
<th>COORDINATION NUMBER</th>
<th>IONIC RADIUS</th>
<th>ELECTRON CONFIGURATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>20</td>
<td>2</td>
<td>VIII</td>
<td>1.12Å</td>
<td>(Ar)4s²</td>
</tr>
<tr>
<td>Ti</td>
<td>22</td>
<td>4</td>
<td>VI</td>
<td>0.61Å</td>
<td>(Ar)3d² 4s²</td>
</tr>
<tr>
<td>Zr</td>
<td>40</td>
<td>4</td>
<td>VIII</td>
<td>0.84Å</td>
<td>(Kr)4d² 5s²</td>
</tr>
<tr>
<td>La</td>
<td>57</td>
<td>3</td>
<td>VIII</td>
<td>1.18Å</td>
<td>(Xe)4f⁶ 5d¹ 6s²</td>
</tr>
<tr>
<td>Ce</td>
<td>58</td>
<td>3</td>
<td>VIII</td>
<td>1.14Å</td>
<td>(Xe)4f² 5d⁰ 6s²</td>
</tr>
<tr>
<td>Gd</td>
<td>64</td>
<td>3</td>
<td>VIII</td>
<td>1.06Å</td>
<td>(Xe)4f⁷ 5d¹ 6s²</td>
</tr>
<tr>
<td>Hf</td>
<td>72</td>
<td>3</td>
<td>VIII</td>
<td>0.83Å</td>
<td>(Xe)4f¹⁴ 5d² 6s²</td>
</tr>
<tr>
<td>Th</td>
<td>90</td>
<td>4</td>
<td>VIII</td>
<td>1.04Å</td>
<td>(Rn)5f⁰ 6d² 7s²</td>
</tr>
<tr>
<td>U</td>
<td>92</td>
<td>4</td>
<td>VIII</td>
<td>1.00Å</td>
<td>(Rn)5f³ 6d¹ 7s²</td>
</tr>
</tbody>
</table>
further oxidized. The uranyl ion is a highly soluble complex which accounts for a large number of secondary uranium minerals. Since thorium cannot form a similar complex, many of the secondary uranium minerals have no thorium analogue. Therefore, the behaviour of Th$^{4+}$ is similar to that of uranium only in the $4^+$ state and can substitute for uranium only in primary minerals or in secondary minerals formed under conditions of restricted oxidation.

I. Thorium Compounds

Thorium alloys with Be, Mg and metals of Groups IB and IIB, but is completely immiscible in the alkali metals (Bailar et al., 1973). No naturally occurring Th-alloys have been reported.

The only thorium oxide to occur as a mineral is ThO$_2$ (thorianite), a highly stable phase which retains its FCC structure up to its melting point of 3390°C (the highest melting point for an oxide) (Bailar et al., 1973). This extremely high melting point makes ThO$_2$ useful for incandescent gas mantles, welding electrodes and crucibles for high temperature research (Lang et al., 1963). The unstable monoxide, ThO, has been produced synthetically. Oesling (1978) gives an excellent outline of the properties of thorium oxides. Since thorium forms no simple oxides there are no naturally occurring thorates (Boyle, 1982).

Thorium is readily hydrolyzed to form Th hydroxide monomers and polymers, for example:

\[
\text{Th}^{4+} + 4\text{H}_2\text{O} \rightarrow \text{Th(OH)}_2^{2+} + 2\text{H}_3\text{O}^+ \\
\text{or:} \quad 2\text{Th}^{4+} + 4\text{H}_2\text{O} \rightarrow \text{Th}_2(\text{OH})_4^{6+} + 2\text{H}_3\text{O}^+.
\]

Higher polymers may exist as chain-like structures with cross-linkages at the hydroxyl groups. Colloidal monomers and polymers of thorium
hydroxide have been reported, and are similar to complexes of Si, Ti, Zr and Hf (Gmelin, 1978; Boyle, 1982). The form taken by hydrolyzed thorium has been a matter of contention for some years. Katz and Seaborg (1957), Langmuir and Herman (1980) and Boyle (1983) report the existence of thorium hydroxide. Bailar et al. (1973) argued that the hydroxide was more likely ThO₂aq since the x-ray powder diffraction pattern showed diffuse lines of ThO₂ and Gmelin (1978) agrees with this interpretation. No attempt will be made here to verify either claim. In accordance with common usage, hydrolysed thorium shall be referred to as thorium hydroxide. Th(OH)₄ is highly insoluble but can be dissolved in strong acids or in solutions containing complexing agents such as carbonates (Katz and Seaborg, 1957). Th⁴⁺ tends to remain dissociated in solutions more acid than pH 3 (Katz and Seaborg, 1957).

II. Solution Chemistry

Since Th³⁺ is unstable in water, thorium occurs in aqueous solution only as the highly-charged, positive cation Th⁴⁺ which has a strong tendency to complex with HF, H₃PO₄, Cl⁻ and NO₃⁻ as well as SO₄²⁻ and CO₃⁻ (in the presence of alkali metal ions) (Katz and Seaborg, 1957). The phosphates and tetrafluoride are insoluble and the chloride, nitrate and sulphate are only slightly soluble. Th carbonates are much more soluble than similar RE carbonates, and less soluble than similar uranium carbonates.

Thorium minerals, including an oxide, a carbonate, several phosphates and silicates are almost all very insoluble and resistant to weathering. For example, the solubility of thorianite as Th(OH)₄ in
pure water is $10^{-5}$ ppb above pH 5. Solubility diagrams for thorium complexes and ThO$_2$ in various solutions indicate that "the concentration of Th in natural waters .... is greatly increased by thorium complex formation" (Langmuir and Herman, 1980; p. 1754). Therefore, complexers in solution greatly increase the mobility of thorium. Complexing of Th with Cl$^-$ and NO$_3^-$ is weak and unimportant. Sulphate, fluoride, various forms of phosphate, hydroxyl, oxalate ($C_2O_4^{2-}$), citrate ($C_6H_5O_7^{3-}$) and EDTA ($C_{10}H_{12}O_8N_2^{4-}$) all form strong thorium complexes which greatly increase the solubility and the mobility of Th$^{4+}$. Sulphate complexes are important only in very acid solutions (below pH 3), particularly in fluids associated with mine tailings. In organic-free waters, the order of importance of inorganic Th-complexes with increasing pH is: Th(SO$_4$)$_2$, ThF$_2^{2-}$, Th(HPO$_4$)$_2$, Th(HPO$_4$)$_3^{2-}$ and Th(OH)$_4$. For example, at pH 3, fluoride concentration of 0.2 ppm increases ThO$_2$ solubility from $10^{-2}$ ppb to 10 ppb. At pH 5, phosphate concentration of 0.1 ppm increases ThO$_2$ solubility a thousand-fold. Organic ligands also form complexes with Th. Studies of Th complex formation found that EDTA (a multi-dentate chelating compound) complexes with Th from pH 2 to pH 8 and, over pH 8, OH$^-$ is the principal complexer of Th. (Langmuir and Herman, 1980).

According to Langmuir and Herman (1980), in alkaline waters Th(OH)$_4$ is the dominant thorium complex. This complex "will have little tendency to associate with the carbonate ion" (p. 1755). Katz and Seaborg (1957) report that, in the presence of CO$_2$, thorium hydroxide forms an insoluble oxycarbonate, ThO(CO$_3$)$_2$. Various Russian authors, including Shcherbina and Abakirov (1967), found that thorium
carbonate complexing is important in alkaline waters. More work is necessary before the role of the carbonate ion in thorium complexing is fully understood.

In summary, chlorine and nitrate ions are unimportant in the solubility of thorium in natural waters. Sulphate is important only in solutions more acid than pH 3. With increasing pH, the most important complexers are: fluoride (pH 3-4), hydrogen phosphate (pH 4-7) and hydroxyl (above pH 7). The literature disagrees about the effect of the carbonate ion on the complexing of Th. Organic complexers, including oxalate, citrate and chelating compounds play an important part in the solubility of thorium.

**CRYSTAL CHEMISTRY**

Th is the largest naturally-occurring quadrivalent cation. The large ionic radius (1.04 Å; Shannon and Prewitt, 1970) is a major factor influencing the distribution of Th in minerals. Because of the large ionic radius, Th$^{4+}$ usually occupies 8- or 9-fold coordination sites with oxygen. Jensen (1973) reports that the major cation in a structure rarely differs from optimum ionic radius by more than 0.1 Å. Therefore, Th$^{4+}$ can only be accommodated readily in 8- or 9-fold sites having a site-radius of 0.94 to 1.14 Å (i.e., sites capable of holding cations of radius 0.84 to 1.24 Å). The only other quadrivalent cations with radii in this range are U(1.00 Å), Ce(0.97 Å), Pb(0.94 Å) and Zr(0.84 Å). The bonding characteristics and chemical behaviour of Pb, which result from filled 4f and 5d shells, are sufficiently different from those of thorium, that only limited amounts of Th-Pb substitution occur. Most Pb in Th minerals is radiogenic. As a result of its smaller radius
ratio, Zr usually occupies 6-fold coordination sites which are too small for Th. Therefore, Th does not normally substitute for Zr. However, Zr in zircon occupies an 8-fold coordination site, allowing limited substitution of Th for Zr in zircon. Humpton and Roy (1961) found that a miscibility gap exists between 6 mol% thorite in zircon and 4 mol% zircon in thorite. The larger Th$^{4+}$ in a Zr$^{4+}$ site can locally expand and deform the structure. This may result in local concentrations of Th and eventual separation of a thorite phase within the zircon (Navrotsky, 1978). Zircon with high ThO$_2$ analyses may contain exsolved patches of thorite. The substitution of the smaller Zr$^{4+}$ in a Th$^{4+}$ site in thorite may distort the structure sufficiently to result in the separation of a zircon phase within the thorite. The difference in ionic radii between Th$^{4+}$ and Zr$^{4+}$ limits the degree of Th-Zr substitution. U and Ce are the only quadrivalent cations for which Th substitutes readily, as a result of the similarity in size and behaviour of Th$^{4+}$, U$^{4+}$ and Ce$^{4+}$, complete solid solution exists in the uraninite-thorianite-cerianite series (Frondel, 1958).

Many trivalent cations have ionic radii within the permitted range of 0.84 to 1.24Å, particularly the light rare earth elements (LREE: La, 1.18Å to Eu, 1.07Å). When quadrivalent Th substitutes for trivalent cations, it is necessary to have coupled substitution of the type:

$$M^{4+} + M^{2+} = 2M^{3+},$$

$$2M^{4+} = M^{3+} + M^{5+}$$

or:

$$M^{4+} + \square = 2M^{2+}$$

(in some pyrochlores) to maintain the charge balance. For example, in cheralite the substitutions...
\[ \text{Th}^{4+} + \text{Ca}^{2+} = 2\text{RE}^{3+} \]

and/or:

\[ \text{Th}^{4+} + \text{Si}^{4+} = \text{RE}^{3+} + \text{P}^{5+} \]

help maintain electronic neutrality. It is also important to minimize structural distortion by balancing cation size. For example, substitution of the appropriate ionic radii above gives:

\[ 1.09\text{"} + 1.18\text{"} = 2.27\text{"} \]

and

\[ 2 \times 1.15\text{"} = 2.30\text{"}. \]

Here, the substitution Th+Ca=2Ce maintains both overall site-volume and charge balance. In the vast majority of minerals (Table 7) Ca is the only divalent cation to occur in coupled substitution with Th.

The coupled substitution \( \text{Th}^{4+} + \text{Si}^{4+} = \text{Ce}^{3+} + \text{P}^{5+} \) (in the cheralite-buttonite series) not only maintains charge balance, but also reduces structural instability by minimizing distortion. Comparing the sums of the corresponding radii gives:

\[ 1.09\text{"} + 0.26\text{"} = 1.35\text{"} \]

and

\[ 1.15\text{"} + 0.17\text{"} = 1.32\text{"}. \]

In summary, Th occurs in extensive isomorphous substitution only with U and Ce and in partial solid solution series with Zr. When cations of different valence are involved in substitution with Th, coupled substitution is necessary to 1) maintain overall site-volume, 2) minimize structural defects and 3) maintain charge balance. The size and charge restrictions imposed by these requirements severely limits the substitution behaviour of Th. Few minerals have sites capable of accommodating such a large, high valence cation. Therefore, Th, in more than trace amounts (>1000 ppm), occurs in only a limited number of accessory and secondary minerals (Chapter 2).
Thorium, RE and U are dispersed lithophile elements which occur in all rock types. Th is the 35th most abundant crustal element and is 3-4 times more common than U (Bailar et al., 1973). The extreme enrichment of crustal Th over bulk earth abundance (Table 33) emphasizes the intensely lithophile character of Th. The crustal enrichment results from the increased concentration of Th throughout the magmatic cycle (e.g. dunite: 4 ppb, granite: 17 ppm). The distribution of Th in the late stage differentiates is a result of the low affinity of Th for the rock-forming minerals. The mineral/melt partition coefficient measures the proportion of an element which is incorporated into a mineral relative to the amount remaining in the melt (Irving, 1978; Henderson, 1982). Element partitioning is primarily controlled by the ionic radius relative to the size of the available cation sites (Onuma et al., 1968). Other factors including valence state coordination polyhedra, bond type and bond strength also influence partitioning (Navrotsky, 1978). At present, few partition coefficients have been determined for Th. The high coefficients for accessory minerals and the low coefficients for the rock forming minerals (Table 34) illustrates the extreme preference of Th for accessory minerals. The preferential partitioning of Th into minerals with suitable sites suggests that the behaviour of Th in a silicate melt is largely controlled by the availability of suitable cation sites, and only accessory minerals have appropriate cation sites. Clearly, the rock forming minerals are not capable of accommodating much Th and do not remove much Th from the melt. However,
<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Terrestrial</strong></td>
<td>65.0 ppb</td>
<td>Henderson 1982</td>
</tr>
<tr>
<td><strong>Crustal</strong></td>
<td>9.6 ppm</td>
<td></td>
</tr>
<tr>
<td><strong>Dunite</strong></td>
<td>4.0 ppb</td>
<td>Turekian and Wedepohl 1961</td>
</tr>
<tr>
<td><strong>Basalt</strong></td>
<td>4.0 ppm</td>
<td></td>
</tr>
<tr>
<td><strong>Diorite</strong></td>
<td>5.0 ppm</td>
<td>Davidson 1982</td>
</tr>
<tr>
<td><strong>Granodiorite</strong></td>
<td>9.3 ppm</td>
<td>Turekian and Wedepohl 1961</td>
</tr>
<tr>
<td><strong>Rhyolite</strong></td>
<td>14.2 ppm</td>
<td>Dostal and Dupuy 1983</td>
</tr>
<tr>
<td><strong>Low-Ca Granite</strong></td>
<td>17.0 ppm</td>
<td>Turekian and Wedepohl 1961</td>
</tr>
<tr>
<td><strong>Alkali Granite</strong></td>
<td>20.0 ppm</td>
<td>Clark et al. 1966</td>
</tr>
<tr>
<td><strong>Syenite</strong></td>
<td>38.0 ppm</td>
<td>Gerasimovsky 1974</td>
</tr>
<tr>
<td><strong>Shale</strong></td>
<td>12.0 ppm</td>
<td>Turekian and Wedepohl 1961</td>
</tr>
<tr>
<td><strong>Graywacke</strong></td>
<td>6.7 ppm</td>
<td>Rogers and Richardson 1964</td>
</tr>
<tr>
<td><strong>Arkose</strong></td>
<td>5.0 ppm</td>
<td></td>
</tr>
<tr>
<td><strong>Orthoquartzite</strong></td>
<td>4.3 ppm</td>
<td></td>
</tr>
<tr>
<td><strong>Limestone</strong></td>
<td>1.7 ppm</td>
<td>Turekian and Wedepohl 1961</td>
</tr>
<tr>
<td></td>
<td>Basalts/andesites</td>
<td>Dacites/rhyolites</td>
</tr>
<tr>
<td>----------------</td>
<td>------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>opx</td>
<td>-</td>
<td>0.13</td>
</tr>
<tr>
<td>cpx</td>
<td>0.04</td>
<td>0.13</td>
</tr>
<tr>
<td>amph</td>
<td>-</td>
<td>0.22</td>
</tr>
<tr>
<td>bio</td>
<td>-</td>
<td>0.31</td>
</tr>
<tr>
<td>plag</td>
<td>-</td>
<td>0.04</td>
</tr>
<tr>
<td>ksp</td>
<td>-</td>
<td>0.02(^3)</td>
</tr>
<tr>
<td>qtz</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>zirc</td>
<td>-</td>
<td>91.20(^3)</td>
</tr>
<tr>
<td>all</td>
<td>-</td>
<td>548.00(^3)</td>
</tr>
</tbody>
</table>

orthopyroxene (opx), clinopyroxene (cpx), amphibole (amph), biotite (bio), plagioclase (plag), potassium feldspar (ksp), quartz (qtz), zircon (zirc), allanite (all).

---

2) Mittelfehldt and Miller, 1983.
the more open structures of amphibole and biotite can accommodate more Th than either pyroxene, quartz or feldspars. The increase in Th from ultrabasic to intermediate rocks results mainly from the incorporation of Th into the larger, more flexible cation sites in amphibole and biotite. From intermediate to felsic rocks, Th concentration may be controlled by the accessory minerals.

The changing structure of a silicate melt during crystallization controls both the structures of the major crystallizing mineral phases and the behaviour of the large ion lithophile elements (e.g. Th) in the melt. High temperature, high metal/silicon (M/Si) and low silicon:oxygen (Si/O) ratios are the primary characteristics of the early stages of magmatic evolution. Metal ions in the melt can interfere with Si-O-polymerization and this produces a melt structure largely comprised of free SiO₄ tetrahedra and interspersed metal cations (Henderson, 1982). The early melt structure is open and has sites capable of accommodating incompatible elements such as RE (Flynn et al., 1978) and Th. The earliest crystallizing phases tend to have low Si/O and high M/Si ratios and are either single tetrahedral or single chain silicates, (olivine: Si:O=1:4, M/Si=2:1; pyroxene: Si:O=1:3, M/Si=1:1; Deer et al., 1968) These minerals have sites capable of accommodating only a limited range of monovalent or divalent cations (ideally Fe or Mg in olivine, Ca, Mg or Fe in pyroxene). The crystallization of these minerals removes metal cations and oxygen, resulting in lower M/Si ratios and higher Si/O ratios in the melt.

These changes produce a more polymerised melt of intermediate composition with fewer sites available for the larger, high valence
cations. Minerals with higher Si/O ratios form, particularly double
chain and sheet silicates (amphibole: \( \text{Si}:0 = 4:11 \); mica: \( \text{Si}:0 = 2:5 \); Deer
et al., 1967) (Jensen, 1973). The more open structures of these
minerals have more flexible cation sites which can accommodate more
incompatible ions than either olivine or pyroxene. As these phases
crystallize, the depletion of the metal cations and enrichment of the
silica continues. The melt structure is highly polymerized and
tectosilicates (e.g. quartz and alkali feldspars) are the major
crystallizing phases. There are fewer sites in the melt for the
incompatible elements, therefore, they must either be incorporated into
the rock-forming minerals or form accessory phases. Th cannot be
readily accommodated by quartz or feldspar structures without producing
severe distortions. Therefore, at low concentrations, Th will be
accommodated either in extended defects or at grain boundary deposits
(Navrotsky, 1978). At higher concentrations, Th and other large, high-
valence cations will form accessory minerals such as zircon, allanite
or monazite.

When an accessory mineral capable of accommodating Th is on the
liquidus during crystallization, Th behaves as a compatible element and
becomes depleted. Accessory minerals are important as concentrators of
trace elements, including Th, during magmatic crystallization. 80 to
95% of RE can be concentrated in accessory minerals such as titanite
and allanite (Gromet and Silver, 1983). Monazite on the liquidus
during crystallization of the Sweet Water Wash pluton concentrated Th
during the entire crystallization history (Mittelfehldt and Miller,
1983). Fourcade and Allegre (1981) emphasize the importance of
considering the role of allanite and sphene when modelling trace element behaviour.

At the end of crystallization, the presence of a volatile phase will have a marked effect on the behaviour of Th. If the volatiles are retained in hydrous minerals and no suitable accessory minerals are formed, the most incompatible trace elements will not be expelled, but will precipitate along grain boundaries, be trapped in defects or be frozen in volcanic glass. These loosely bound components will then be susceptible to leaching by post-magmatic fluids. The unusual mobility of Th in the Cambrian silicic volcanic rocks of Nova Scotia has been linked to the failure of accessory minerals to concentrate the radioactive elements and the resultant concentration of Th in unstable volcanic glass (Dostal et al., 1983). If the trace-element rich, late stage volatile phase is expelled, either a vein system or a metasomatic zone enriched in trace elements will form around the intrusion. The vein systems described by Stas (1974) were probably generated by the expulsion of an enriched fluid phase from associated plutons.

Another factor to consider when examining the behaviour of Th during the late stages of the magmatic cycle is the role of fluid phases, such as OH, Cl, F and P₂O₅, and the effects of complexers on the fluid/melt partitioning of trace elements. Although very little information is available on Th complexes at magmatic conditions, some information is available at lower temperatures and pressures. Combining the known behaviour of Th with complexers at surface conditions with the available data on the behaviour of trace elements
during the late stages, some extrapolations are possible.

In an aqueous magma, H$_2$O depolymerizes the melt structure by utilizing bridging oxygens to form two hydroxyl groups (Flynn and Burnham, 1978). This produces a more open melt structure and increases the abundance of favourable sites for the larger, high valence cations. Th remains in a hydrous melt complexed with the hydroxyl groups (Constable and Hubbard, 1981). Smithson and Decker (1973) demonstrated a positive correlation between Th concentration and hydrous mineralogy in the wet facies of a syenite associated with the Laramie anorthosite. The concentration of Th in the hydrous minerals (e.g. hornblende and biotite) indicate that Th must have been carried in a fluid phase or associated with the large cation sites produced by OH in the melt.

Other volatiles such as fluorine and chlorine also depolymerize a silicate melt and can hold the larger cations in the melt (Mahood and Hildreth, 1983). However, if a fluid phase is present, fluorine remains in the melt and chlorine, while sodalite is stable, partitions strongly into the fluid phase (Fuge, 1977). The effect of chlorine on the solubility of Th is negligible. In acidic solutions, fluorine increases the solubility of Th at surface conditions (Langmuir and Herman, 1980). Th preferentially remains in the melt with fluorine rather than follow chlorine into a fluid phase. However, the behaviour of Th does not always parallel that of fluorine and the effect of varying pH and water content should be evaluated before the role of fluorine in the distribution of Th can be fully understood.

P$_2$O$_5$ occurs in a silicate melt as monomers which have a greater affinity for metal cations than does SiO$_4$. P$_2$O$_5$ increases Si-O
polymerization by complexing with the metal cations and removing them from the silicate network (Ryerson and Hess, 1980). Th may remain in the melt associated with the phosphate sites. In the absence of information on the partitioning of P₂O₅ between melt and vapour phase, the effect of P₂O₅ on Th partitioning between melt and fluid cannot be evaluated.

To summarize, during crystallization, Th behaves as a compatible element when suitable accessory minerals are on the liquidus. Th bound in stable accessory phases will remain immobile during post-magmatic events. If Th behaves incompatibly, its final distribution depends on 1) the availability of a final stage accessory phase, 2) the presence of suitable defect or intergranular sites and 3) the behaviour and composition of a fluid phase. If volatiles are retained, residual trace elements, including Th, will be loosely bound and susceptible to post-magmatic leaching. If volatiles are expelled, residual trace elements will be carried into vein deposits if suitable complexers are present in the volatile phase.
SUMMARY AND CONCLUSIONS

UK27 (Na, Ca, K)ThSi$_{11}$(O, H$_2$O, F, Cl)$_3$ is a new hydrous sodium thorium silicate, which is unrelated to any other reported mineral. It occurs in association with yofortierite from the hydrothermally altered veins at Mont St-Hilaire, Quebec. UK27 is rhombohedral, R3m, a=29.01(1)Å, c=17.30(1)Å, V=12608.7(6)Å$^3$, Z=18, $D_{\text{meas}}$=2.62(2)g/cm$^3$, and $D_{\text{calc}}$=2.613g/cm$^3$. Optical parameters are: uniaxial positive, $\omega$=1.510 and $\epsilon$=1.512. Without further structural information, the Gladstone-Dale relationship is of limited use for assessing the compatibility of the data for UK27.

Several factors are responsible for the occurrence of only 17 minerals with essential Th. Few primary mineral structures have cation sites capable of accommodating Th, which is the largest naturally-occurring quadrivalent cation. Unlike $U^{4+}$, which is readily oxidized to the $U^{6+}$ state to form the highly soluble uranyl ion, $UO_2^{2+}$, Th occurs only as $Th^{4+}$ which is relatively immobile under most geological conditions. Therefore, there are very few secondary Th minerals.

$^{232}$Th undergoes radioactive decay, producing alpha-particles which bombard the crystal structure and damage it, causing minerals to become partially or wholly metamict. The degree of metamictness of a mineral is dependant upon 1) number of alpha-particles produced through time, 2) age of the mineral and 3) stability of the structure. The degree of ionic bonding, the number and nature of shared structural elements and the degree of distortion caused by ions of different radii in isomorphous substitution all affect structural stability (Mitchell, 1973).
The 17 known Th minerals include: two oxides, thorianite and thorutite; one complex carbonate, thorbastnaesite; four secondary and two primary phosphates kivuite, eylettersite, brockite, grayite, cheralite and brabantite; and eight silicates huttonite, thorite, thorogummite (secondary), ekanite, steacyite, thorosteenstrupine, umbsoerite and UK27.

Thorianite and thorutite are the Th-analogues of uraninite and brannerite, respectively (Frondel, 1958; Gotman and Khapaev, 1958). Thorbastnaesite may be the analogue of bastnaesite.

Kivuite, reportedly related to phosphuranylite and renardite, may be an impure sample of eylettersite, which is a crandallite-type mineral (Van Wambeke, 1972). Brockite and grayite are members of the poorly-defined rhabdophane group. The minerals of this group are too fine-grained for single-crystal x-ray diffraction work. However, x-ray powder diffraction data (Dooley and Hathaway, 1961) indicates that grayite is the orthorhombic polymorph of hexagonal brockite. Based on the similarities between the x-ray powder diffraction patterns, the rational relationship between the hexagonal and the orthorhombic cells and the presence of superlattice reflections in the powder pattern of orthorhombic grayite, the dimorphism is most likely a result of order-disorder transformation, the orthorhombic form being ordered. However, confirmation of this relationship requires further structural studies and more precise chemical analyses of grayite. Cheralite and brabantite are members of the monoclinic monazite group. Extensive solid solution occurs among the minerals of this group. In the current nomenclature, monazite, brabantite and huttonite are the names of the
and cheralite is intermediate in composition between monazite and brabantite (Rose, 1980). A simpler nomenclature scheme is proposed using monazite (CePO$_4$), huttonite (ThSiO$_4$) and cheralite (CaTh(PO$_4$)$_2$) as end-members. This scheme eliminates the need for intermediate members. The name cheralite is adopted because it has priority over brabantite and type-cheralite contains over 50 mole% CaTh(PO$_4$)$_2$.

Huttonite (mon.) is a dimorph of thorite (tet.; Pabst, 1951). Thorogummite is the hydrous equivalent of thorite (Frondel, 1953). Steacyite appears to be the Th-Na-Ca-K equivalent of ekanite, a Th-Ca silicate. However, the structure of steacyite differs significantly from that of ekanite. The primary structural difference between ekanite and steacyite is the arrangement of the Si$_8$O$_{20}$ groups (Szymanski et al., 1982).

Thorosteensrupine is thought to be the Th analogue of steensrupine (Kuprianova et al., 1962). The other Th silicates umbazelite and UK27 are unrelated to any other mineral or mineral group.

$^{232}$Th (Lederer and Shirley, 1978) is the only Th isotope of major geochemical importance. Although thorium is a member of both Group IVB and the 5f transition series, the geochemical behaviour of Th is most similar to that of U and LREE. The behaviour of Th$^{4+}$ is similar to that of uranium only in the 4$^+$ state and it can substitute for uranium only in primary minerals or in secondary minerals formed under conditions of restricted oxidation.

Thorium is readily hydrolyzed to form Th hydroxide monomers and
polymers and occurs in aqueous solution only as the highly-charged, positive cation Th\(^{4+}\) which has a strong tendency to complex with HF, H\(_3\)PO\(_4\), Cl\(^-\) and NO\(_3\)^- as well as SO\(_4\)^{2-} and CO\(_3\)^-{\text{Katze and Seaborg, 1957}}. The phosphates and tetrafluoride are insoluble and the chloride, nitrate and sulphate are only slightly soluble. Th carbonates are much more soluble than similar RE carbonates, and less soluble than similar uranium carbonates.

Thorium minerals are almost all very insoluble and resistant to weathering (Langmuir, and Herman, 1980). However, complexers in solution greatly increase the mobility of thorium. With increasing pH, the most important complexers are: fluoride (pH 3-4), hydrogen phosphate (pH 4-7) and hydroxyl (above pH 7). Chlorine and nitrate ions are unimportant in the solubility of thorium in natural waters. Sulphate is important only in solutions more acid than pH 3.

The large ionic radius (1.04\(\text{Å}\); Shannon and Prewitt, 1970) limits Th\(^{4+}\) to 8- or 9-fold coordination sites with oxygen, usually to sites capable of holding cations of radius 0.84 to 1.24\(\text{Å}\). The only quadrivalent cations with radii in this range are U(1.00\(\text{Å}\)), Ce(0.97\(\text{Å}\)), Pb(0.94\(\text{Å}\)) and Zr(0.84\(\text{Å}\)). However, U and Ce are the only quadrivalent cations for which Th substitutes readily.

Many trivalent cations have ionic radii within the permitted range of 0.84 to 1.24\(\text{Å}\), particularly the light rare earth elements. When cations of different valence are involved in substitution with Th, coupled substitution is necessary to 1) maintain overall site-volume, 2) minimize structural defects and 3) maintain charge balance. The size and charge restrictions imposed by these requirements severely
limits the substitution behaviour of Th. Few minerals have sites capable of accommodating such a large, high valence cation. Therefore, Th occurs as an essential element only in a small number of minerals.

The extreme enrichment of crustal Th over bulk earth abundance, results from the increased concentration of Th throughout the magmatic cycle, illustrating the intensely lithophile character of Th. The distribution of Th in the late stage differentiates is a result of the low affinity of Th for the rock-forming minerals and its high affinity for accessory minerals. The preferential partitioning of Th into minerals with suitable sites suggests that the behaviour of Th in a silicate melt is largely controlled by the availability of suitable cation sites, and only accessory minerals have appropriate cation sites.

The structures of the major crystallizing mineral phases and the behaviour of the large ion lithophile elements (LIL) in the melt are controlled by the changing structure of a silicate melt during crystallization. During the early and intermediate stages, few accessory minerals are formed; therefore, Th remains in the melt. In the final stage of crystallization, LIL, including Th, may be concentrated by accessory minerals. For example, 80 to 95% of RE can be concentrated in accessory minerals such as titanite, allanite (Gromet and Silver, 1983), monazite (Mittelfeldt and Miller, 1983) and sphene (Fourcade and Allegre, 1981). When Th is bound in suitable, stable, accessory minerals it is immobile during post-magmatic events.

The presence of a volatile phase, at the end of crystallization will have a marked effect on the behaviour of Th. If the volatiles are
retained in hydrous minerals and no suitable accessory minerals are formed, there will be little or no residual fluid phase. The incompatible trace elements will not be expelled, but will precipitate along grain boundaries, be trapped in defects or be frozen in volcanic glass. These loosely bound components will then be susceptible to leaching by post-magmatic fluids. When a trace-element rich, late-stage volatile phase is present, either a vein system or a metasomatic zone will form around the intrusion if the fluid phase is expelled.

In an aqueous magma, H₂O depolymerizes the melt structure by utilizing bridging oxygens to form two hydroxyl groups (Flynn and Burnham, 1978). This produces a more open melt structure and increases the abundance of favourable sites for the larger, high valence cations. Th remains in a hydrous melt complexed with the hydroxyl groups (Constable and Hubbard, 1981).

Other volatiles such as fluorine and chlorine also depolymerize a silicate melt and can hold the larger cations in the melt (Mahood and Hildreth, 1983). If a fluid phase is present, fluorine remains in the melt and chlorine, unless sodalite is stable, partitions strongly into the fluid phase (Fuge, 1977). The effect of chlorine on the solubility of Th is negligible. In acidic solutions, fluorine increases the solubility of Th at surface conditions (Langmuir and Herman, 1980). However, the behaviour of Th does not always parallel that of fluorine and the effect of varying pH and water content should be evaluated before the role of fluorine in the distribution of Th can be fully understood.

The final distribution of Th in an igneous environment depends on
1) the availability of a suitable accessory phase, 2) the presence of suitable defect or intergranular sites and 3) the behaviour and composition of a fluid phase. If Th-rich volatiles are retained, Th will be loosely bound and susceptible to post-magmatic leaching. If volatiles are expelled, Th will be carried into vein deposits if suitable complexers are present in the volatile phase.

During the crystallization of the syenite at Mont St-Hilaire, the nepheline and feldspar structures would have been unable to accommodate any significant amount of Th. Therefore, Th would be expected to occur in the accessory minerals of the pegmatites and hydrothermal veins. The occurrence of staceyite in pegmatite veins and UK27 in hydrothermally altered veins supports this hypothesis.
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