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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

January, 1985.

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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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Thesis Supervisor

Chairman, Department of Geology

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ABSTRACT

UK27 $((\text{Na}, \text{K}, \text{Ca})\text{ThSi}_{11}\text{P}(\text{O}, \text{H}_2\text{O}, \text{F}, \text{Cl})_{33})$ 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, $R\bar{3}m$, $a=29.01(1)\text{\AA}$, $c=17.30(1)\text{\AA}$, $V=12608.7(6)\text{\AA}^3$, $Z=18$, $D_{\text{meas}}=2.62(2)\text{g/cm}^3$, and $D_{\text{calc}}=2.613\text{g/cm}^3$. The strongest lines of the x-ray powder diffraction pattern are ($d(\text{\AA})$, I_{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_2O_6). The only Th carbonate, thorbastnaesite ($\text{Th}(\text{Ca}, \text{RE})(\text{CO}_3)_2\text{F}_2 \cdot 3\text{H}_2\text{O}$), is secondary. Eylettersite $((\text{Th}, \text{Pb})_{1-x}\text{Al}_3(\text{PO}_4, \text{SiO}_4)_2(\text{OH})_6)$, kivuïte $((\text{Th}, \text{Ca}, \text{Pb})\text{H}_2(\text{UO}_2)_4(\text{PO}_4)_2(\text{OH})_8 \cdot 7\text{H}_2\text{O})$, brockite $((\text{Ca}, \text{Th})(\text{PO}_4) \cdot \text{H}_2\text{O}; \text{hex.})$ and grayite $((\text{Ca}, \text{Th})\text{PO}_4 \cdot \text{H}_2\text{O}; \text{orth.})$ are secondary phosphates and cheralite $((\text{Ca}, \text{Ce}, \text{Th})(\text{P}, \text{Si})\text{O}_4)$ and brabantite $(\text{CaTh}(\text{PO}_4)_2)$ are primary. The 8 Th silicates are: huttonite (ThSiO_4 ; mon.), thorite (ThSiO_4 ; tet.), thorogummite $(\text{Th}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}; \text{secondary})$, ekanite $(\text{ThCa}_2\text{Si}_8\text{O}_{20})$, steacyite $(\text{Th}(\text{Na}, \text{Ca})_2(\text{K}_{1-x}[\text{I}]_x)\text{Si}_8\text{O}_{20})$, thorosteenstrupine $((\text{Ca}, \text{Th}, \text{Mn})_3\text{Si}_4\text{O}_{12}\text{F}_6 \cdot 6\text{H}_2\text{O})$, umbozerite $(\text{Na}_3\text{Sr}_4\text{ThSi}_8(\text{O}, \text{OH})_{24})$ and UK27.

^{232}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+} , P^{5+} 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.

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INTRODUCTION

The purpose of this study is three-fold. The first is to describe UK27, $(\text{Na,Ca,K})\text{ThSi}_{11}(\text{O,H}_2\text{O,F,Cl})_{33}$, a new mineral from the alkalic 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 Monteregian 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 (4-8mm 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 Monteregian Hills, showing the location of Mont St-Hilaire, Quebec. From Chao et al., 1967.

FIGURE 2. Geological map of Mont St-Hilaire. From Currie, 1983.

TABLE 1a. MINERALS IDENTIFIED FROM MONT ST-HILAIRE.

Acmite	Eudidymite	Monazite
Actinolite	Ewaldite	*Monteregianite
Albite	Fluorite	Montmorillonite 15Å
Allanite	Franconite	Mosandrite
Almandine	*Gaidonnayite	Muscovite
Analcime	Galena	Narsarsukite
Anatase	Genthelvite	Natrolite
Ancylite	Gibbsite	Natrophosphate
Andradite	Gismondine	Nenadkevichite
Anglesite	Gmelinite	Nepheline
Apatite	Goethite	Nordstrandite
Apophyllite	Götschite	Palygorskite
Arfvedsonite	Grossular	*Paranatrolite
Arsenopyrite	Gypsum	Parisite
Ashcroftite	Harmotome	Pectolite
Astrophyllite	Hedenbergite	*Petarosite
Augite	Helvite	Phillipsite
Barite	Hematite	Phlogopite
Barylite	Hemimorphite	Polyolithionite
Bastnaesite	*Hilairite	Pyrite
Behoite	Hiortdahlite	Pyrochlore
Berthierine	Hornblende	Pyrophanite
Biotite	Hydrogrossular	Pyrrhotite
Birnessite	Hydrotalcite	Quartz
Britholite	Ilmenite	Raite
Brookite	Joaquinite	Rhabdophane
Burbankite	Kaersutite	Rhodochrosite
Calcioancylite	Kainosite	Richterite
Calcite	Kaolinite	Riebeckite
Cancrinite	Kupletskite	Rutile
Carbonate-apatite	Labuntsovite	Sabinaite
*Carletonite	Lamprophyllite	Sanidine
Catapleite	Lavenite	Scheelite
Cerussite	Leifite	Sepiolite
Chabazite	*Lemoynite	Serandite
Chalcopyrite	Leucophanite	Serpentine
Chlorite gp.	Leucosphenite	Siderite
Cordylite	Loellingite	Sodalite
Datolite	Lorenzenite	Sphalerite
Dawsonite	McKelveyite	*Steacyite
Delhayelite	Magnetite	Stillwellite
Diopside	Mangan-ankerite	Strontianite
Dolomite	Mangan-neptunite	Synchysite
*Donnayite	Manasseite	Talc
Dorfmanite	Marcasite	Tetranatrolite
Elpidite	Microcline	Thaumasite
Epididymite	Molybdenite 2H	Thermonatrite
Eudialyte	Molybdenite 3R	Thomsonite

* Type locality: Mont St-Hilaire

TABLE 1a. CONTINUED.

Thorite	Willemite
Titanite	Woehlerite
Tundrite	Wollastonite
Vesuvianite	Wulfenite
Villiaumite	Wurtzite
Vinogradovite	*Yofortierite
Vuonnemite	Zircon

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

Ankerite	Neptunite
Aragonite	Orthoclase
Brockite	Pyrolusite
Grunerite	Steenstrupine
Malachite	Taeniolite
Minnesotaite	Tobermorite
Murmanite	Weloganite

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 polyolithionite and spherulites of white leifite are present in some samples. Small, individual crystals of natrolite, dog-toothed microcline, albite, mangan-neptunite, brown, prismatic steacyite, catapleite, 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 $2.62(2)\text{g/cm}^3$. UK27 is only slightly attacked by 1:1 HCl at room temperature and is unaffected by either 1:1 HNO_3 or H_2SO_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 metamict character of the mineral. The refractive indices were measured in sodium light ($\lambda=5893\text{nm}$) 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°C for 17 hours in a Sybron Thermolyne 10500 furnace no change was observed in the x-ray powder pattern. After heating to 200°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°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°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 114.6mm Gandolfi camera with filtered CuK_α radiation ($\lambda=1.54018\text{\AA}$), 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 MoK_α radiation ($\lambda=0.7107\text{\AA}$). 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 $R\bar{3}m$ or $R3m$ as evidenced by the systematic absences of hkl reflections with $-h+k+l \neq 3n$. The mineral proved to be pyroelectric when cooled with liquid nitrogen. Therefore, UK27 lacks a centre of symmetry and the correct space group is $R3m$. 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 114.6mm diameter Gandolfi camera at room temperature with CuK_α 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: $a=29.01(1)\text{\AA}$ and $c=17.30(1)\text{\AA}$ which give a cell volume of $12608.7(6)\text{\AA}^3$.

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR UK27.

h	k	l	d _{calc} Å	d _{obs} Å	I/I ₀	h	k	l	d _{calc} Å	d _{obs} Å	I/I ₀
1	1	0	14.543	14.54	20	2	10	4	2.094	1.987	<1
3	0	0	8.396	8.41	10	1	12	1	1.997		
0	1	2	8.171	8.17	30	3	11	1	1.960	1.968	1
2	2	0	7.271	7.27	100	5	10	1	1.893	1.892	<1
1	3	1	6.477	6.47	10	1	10	6	1.840	1.840	<1
1	1	3	5.355	5.37	<1	2	6	8	1.839		
0	4	2	5.089	5.09	20	8	8	0	1.818	1.818	2
2	3	2	4.803	4.81	15	7	9	1	1.803	1.801	2
2	4	1	4.590	4.57	<1	8	0	8	1.781		
5	1	1	4.377	4.37	5	5	11	0	1.777	1.780	4
4	2	2	4.169	4.17	70	3	8	7	1.776		
1	5	2	4.008	4.01	10	1	13	3	1.772		
1	6	1	3.750	3.745	<1	6	10	2	1.762	1.762	7
3	2	4	3.460	3.457	15	14	0	2	1.762		
5	2	3	3.304	3.303	5	14	1	1	1.725	1.726	1
2	6	2	3.238	3.239	30	13	3	1	1.702	1.698	7
2	4	4	3.199	3.196	<1	5	11	3	1.698		
3	1	5	3.097	3.099	<1	7	9	4	1.672		
8	0	2	2.958	2.959	20	14	2	0	1.668	1.666	3
8	1	1	2.906	2.890	25	10	6	4	1.661		
7	1	3	2.887			0	14	4	1.661		
9	0	0	2.799			9	7	5	1.606	1.606	1
1	8	2	2.790	2.788	15	3	14	1	1.596	1.596	<1
6	3	3	2.779			11	7	1	1.596		
2	8	0	2.748	2.748	7	13	1	6	1.564	1.566	<1
6	4	2	2.740			10	2	8	1.563		
6	2	4	2.717	2.716	<1	0	16	2	1.549	1.549	2
3	7	2	2.693	2.687	5	6	12	3	1.530	1.530	1
5	5	3	2.596	2.598	5	1	15	4	1.519	1.513	1
5	4	4	2.584			1	5	11	1.485	1.485	<1
0	8	4	2.544	2.546	7	4	6	10	1.484		
0	10	2	2.418	2.419	3	16	1	3	1.474	1.474	1
4	6	4	2.402	2.399	<1	15	3	3	1.459	1.458	2
4	7	3	2.379	2.377	4	16	2	2	1.453		
6	0	6	2.375							1.444	<1
4	8	2	2.295	2.288	<1					1.410	<1
4	4	6	2.257	2.258	4					1.391	<1
10	1	3	2.208	2.205	<1					1.341	1
10	2	2	2.188	2.187	7					1.327	<1
10	0	4	2.176							1.292	<1
3	9	3	2.159	2.159	7					1.275	<1
12	0	0	2.099	2.092	2					1.232	<1
8	4	4	2.085							1.188	1
7	7	0	2.078	2.076	2					1.174	<1
8	5	3	2.070							1.148	<1
4	10	0	2.017	2.017	7					1.136	<1
8	6	2	2.014								

CuK α radiation (1.54018 Å);
Si internal standard;

114.6 mm Gandolfi camera;
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. K α lines were used for all elements except Th and U, for which the M α 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 (CANMET); 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).
NaK α (1.04keV), AlK α (1.48keV), SiK α (1.74keV), ThMa
(2.99keV), UMa (3.17keV), KK α (3.31keV), CaK α (3.69keV).

TABLE 3. ELECTRON MICROPROBE ANALYSES OF UK27.

Sample number:	UNK-1	UNK-2	UNK-3	UNK-4	UNK-5	AVG
SiO ₂	56.99	58.30	57.22	58.02	59.12	57.93
Al ₂ O ₃	1.20	1.16	1.20	1.77	1.79	1.42
ThO ₂	22.30	21.90	22.38	22.20	23.49	22.45
UO ₂	0.56	0.58	0.69	1.22	1.37	0.88
Na ₂ O	2.06	1.67	1.66	1.17	1.17	1.55
K ₂ O	0.92	0.83	0.97	1.40	1.40	1.10
CaO	n.d.	n.d.	n.d.	0.17	0.17	0.17
F	0.20	0.20	0.14	0.75	0.73	0.40
Cl	0.03	0.01	0.02	0.11	0.10	0.05
H ₂ O ⁻ *	-	-	-	-	-	8.62
H ₂ O ⁺ *	-	-	-	-	-	5.14
-F=O	-	-	-	-	-	0.17
-Cl=O	-	-	-	-	-	<u>0.01</u>
Total	84.26	84.66	84.28	86.81	89.34	99.52

* water by TGA

FIGURE 4. IR spectra of UK27, from 300-4000 cm^{-1} .

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), BO₃ (1200-1450cm⁻¹), (Farmer, 1974), CO₃ (1400-1550cm⁻¹, and H₃O⁺ (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 10°C/min a steady loss of 0.26mg was observed up to 1135°C. Three peaks on the pressure curve correspond to water evolution at 105, 275 and 600°C (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 $150^\circ C$ 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 $\times$ volume $\times$ density $\div$ 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:

This gives a formula weight of 1114.15 and a calculated density of $2.613 g/cm^3$. 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:

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", K_C (Table 5), is calculated from the chemical composition, using the constants given by Mandarino (1976, 1978) and the equation:

TABLE 4. FORMULA CALCULATION FOR UK27.

	WEIGHT %	"MOLECULAR" PROPORTIONS	OXYGEN PROPORTIONS	CATION PROPORTIONS	NO. OF IONS IN FORMULA BASED ON 11 (Si+Al)
SiO ₂	57.93	0.9641	1.9282	0.9641	0.9919 10.692
Al ₂ O ₃	1.42	0.0139	0.0417	0.0278	
ThO ₂	22.45	0.0850	0.1700	0.0850	0.943
UO ₂	0.88	0.0033	0.0066	0.0033	
Na ₂ O	1.55	0.0250	0.0250	0.0500	0.555
K ₂ O	1.10	0.0117	0.0117	0.0234	
CaO	0.17	0.0030	0.0030	0.0030	0.033
F	0.40	0.0211	0.0211	—	
Cl	0.05	0.0014	0.0014	—	0.015
Total	85.95		2.2087		
-F=O	0.17		- 0.0105 (=0.5x0.0211)		
-Cl=O	0.01		- 0.0007 (=0.5x0.0014)		
Total	85.77		2.1975		
H ₂ O _{tot}	13.76	0.7660			*8.495 8.50
Total	99.52				

$$\text{scale factor} = \frac{11}{0.9919} = 11.0898$$

Number of anions: $(2.1975 \times 11.0898) + 8.495 + 0.250 = 33.116$
 *Amount of water in formula.

$$K_C = (E \sum k_i p_i) / 100$$

where p_i is the weight percent and k_i is the specific refractive energy constant of the constituent "i". 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 ($C_I=1-(K_p/K_C)$); (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 ThO_2 .

DISCUSSION

The mineral, UK27 is a rhombohedral, hydrous sodium thorium silicate, $(\text{Na,Ca,K})\text{ThSi}_{11}(\text{O,H}_2\text{O,F,Cl})_{33}$. 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 5. GLADSTONE-DALE CALCULATION FOR UK27.

	WEIGHT %	k ₁	k/100
SiO ₂	57.93	0.208	0.1205
Al ₂ O ₃	1.42	0.207	0.0029
ThO ₂	22.45	0.167	0.0375
UO ₂	0.88	0.100	0.0009
Na ₂ O	1.55	0.190	0.0029
K ₂ O	1.10	0.196	0.0021
CaO	0.17	0.210	0.0004
F	0.40	0.047	0.0002
Cl	0.05	0.318	0.0002
H ₂ O	<u>13.76</u>	0.340	<u>0.0468</u>
Total	99.52		0.2144
-O=F+Cl	0.18	0.203	0.0004
Recalc'd	100.00		0.2150

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: ThO_2), one phosphate (cheralite: $(\text{Ca,Th})\text{PO}_4$), and three silicates (huttonite: $\text{ThSiO}_4(\text{mon})$, thorite: $\text{ThSiO}_4(\text{tet})$ and thorogummite: $\text{Th}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$) (Fron del, 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 Th^{4+} , the largest naturally occurring quadrivalent cation. In 8-fold coordination, the ionic radius of Th is $1.04\text{\AA}$ compared with that of $\text{U}^{4+}=1.00\text{\AA}$ and $\text{Zr}^{4+}=0.84\text{\AA}$ (Shannon and Prewitt, 1969). Few mineral structures have cation sites capable of accomodating such a large, highly-charged cation. The 11 known primary thorium minerals (Table 6) occur in only eight structure types:

TABLE 6. THORIUM MINERALS.

NAME	GROUP	GENERAL FORMULA
<u>Oxides</u>		
Thorianite	Fluorite	AX_2
Thorutite	Brannerite	AB_2O_6
<u>Carbonate</u>		
Thorbastnaesite	Bastnaesite	- -
<u>Phosphates</u>		
Eylettersite	Crandallite	- -
Kivuite	Phosphuranylite	- -
Brockite	Rhabdophane	$ABO_4 \cdot 2H_2O$
Grayite	"	"
Brabantite	Monazite	ABO_4 (mon.)
Cheralite	"	"
<u>Silicates</u>		
Huttonite	"	"
Thorite	Zircon	ABO_4 (tet.)
Thorogummite	"	"
Ekanite	Ekanite	$AB_2CSi_8O_{20}$
Steacyite	"	"
Thorostenstrupine	Steenstrupine	(Chapter 2)
Umbozerite	- -	- -
UK27	- -	- -

TABLE 7. MINERALS WHICH CONTAIN APPRECIABLE THORIUM.

NAME	FORMULA	wt% ThO ₂
Aeschynite	(Ce,Ca,Fe,Th)(Ti,Nb) ₂ (O,OH) ₆	up to 25.8
Aeschynite-(Y)	(Y,Ca,Fe,Th)(Ti,Nb) ₂ (O,OH) ₆	20.3
Allanite	(Ce,Ca,Y) ₂ (Al,Fe) ₃ (SiO ₄)(OH)	4.4
Bastnaesite (s)	RE(CO ₃)F	2.8
Betafite	(Ca,Na,U) ₂ (Ti,Nb,Ta) ₂ O ₆ (OH)	1.4
Brannerite	(U,Ca,Ce)(Ti,Fe) ₂ O ₆	13.0
Britholite	(Ce,Ca) ₅ (SiO ₄ ,PO ₄) ₃ (OH,F)	19.6
Britholite-Y	(Y,Ca) ₅ (SiO ₄ ,PO ₄) ₃ (OH,F)	2.8
Cerianite	(Ce,Th)O ₂	4.5
Chevkinite	(Ca,Ce,Th) ₄ (Fe,Mg) ₂ (Ti,Fe) ₃ Si ₄ O ₂₂	18.4
Clarkeite (s)	(Na,Ca,Pb,Th,H ₂ O) ₂ U ₂ (O,H ₂ O) ₇	2.2
Grandallite (s)	(CaAl ₃ (PO ₄)(OH) ₅ ·H ₂ O	6.7
Datolite-Y	(Y,Ca)B(Si,Al)O ₄	1.3
Euxenite	(Y,Ca,Ce,U,Th)(Nb,Ta,Ti) ₂ O ₆	14.2
Fergusonite	YNbO ₄	6.0
Fersmite	CaNb ₂ O ₆	1.6
Formanite	RETaO ₄	1.1
Gadolinite	Y ₂ FeBe ₂ Si ₂ O ₁₀	2.0
Hellandite	(Ca,Y) ₆ (Al,Fe ³⁺)Si ₄ B ₄ O ₂₀ (OH) ₄	1.5
Karnasurtite	(Ce,La,Th)(Ti,Nb)(Al,Fe)(Si,P) ₂ O ₇ (OH) ₄ ·3H ₂ O	6.2
Kobeite	(Y,Fe,U)(Ti,Nb,Ta) ₂ (O,OH) ₆	1.0
Loparite	(Ce,Na,Ca) ₂ (Ti,Nb) ₂ O ₆	13.0
Lueshite	(Na,Ca,Ce)(Nb,Ti)O ₃	2.9
Melanocerite	(Ce,Ca) ₅ (Si,B) ₃ O ₁₂ (OH,F)·nH ₂ O (?)	13.6
Monazite	(RE,Th)PO ₄	31.0
Mosandrite	(Na,Ca,Ce) ₃ TiSiO ₄) ₂ F	1.3

TABLE 7. CONTINUED.

NAME	FORMULA	wt% ThO_2
Niobo-aeschnite	$(\text{Ce}, \text{Ca}, \text{Th})(\text{Nb}, \text{Ti})_2(\text{O}, \text{OH})_6$	up to 2.5
Orthobrannerite	$\text{U}^{4+}\text{U}^{6+}\text{Ti}_4\text{O}_{12}(\text{OH})_2$	1.0
Parisite (s)	$\text{CaCe}_2(\text{CO}_3)_3(\text{F}, \text{OH})_2$	5.4
Perrierite	$(\text{Ca}, \text{Ce}, \text{Th})_4(\text{Mg}, \text{Fe}^{2+})_2(\text{Ti}, \text{Fe}^{3+})_3\text{Si}_4\text{O}_{22}$	3.6
Polycrase	$(\text{Y}, \text{Ca}, \text{Ce}, \text{U}, \text{Th})(\text{Ti}, \text{Nb}, \text{Ta})_2\text{O}_6$	7.7
Polymignite	$(\text{Ca}, \text{Fe}, \text{Y}, \text{Th})(\text{Nb}, \text{Ti}, \text{Ta}, \text{Zr})\text{O}_4$	3.9
Pyrochlore	$(\text{Na}, \text{Ca})_2\text{Nb}_2\text{O}_6(\text{OH}, \text{F})$	15.3
Rhabdophane	$\text{REPO}_4 \cdot \text{H}_2\text{O}$	4.4
Samarskite	$(\text{RE}, \text{U}, \text{Ca}, \text{Pb})(\text{Nb}, \text{Ta}, \text{Ti}, \text{Sn})_2\text{O}_6$	5.7
Saryarkite	$\text{Ca}(\text{Y}, \text{Th})\text{Al}_5(\text{SiO}_4)_2(\text{PO}_4, \text{SO}_4)_2(\text{OH})_7 \cdot 6\text{H}_2\text{O}$	8.0
Steenstrupine	$(\text{RE}, \text{Th}, \text{Ca}, \text{Na})_2(\text{Mn}, \text{Fe})(\text{SiO}_3)_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}(?)$	12.1
Tantalaeschnite-(Y)	$(\text{RE}, \text{Ca})(\text{Ta}, \text{Ti}, \text{Nb})_2\text{O}_6$	6.5
Tanteuxenite	$(\text{RE}, \text{Ca})(\text{Ta}, \text{Nb}, \text{Ti})_2(\text{O}, \text{OH})_6$	2.9
Thalenite	$\text{Y}_2\text{Si}_2\text{O}_7$	10.5
Tritomite (s)	$(\text{RE}, \text{Th})_5(\text{Si}, \text{B})_3(\text{O}, \text{OH}, \text{F})_{13}(?)$	15.0
Uraninite	UO_2	36.9
Wakefieldite (s)	YVO_4	1.1
Xenotime	YPO_4	2.5
Yttrialite	$(\text{Y}, \text{Th})_2\text{Si}_2\text{O}_7$	13.4
Yttrocrasite	$(\text{Y}, \text{Th}, \text{Ca}, \text{U})_2(\text{O}, \text{OH})_6$	8.8
Yttrotantalite	$(\text{Fe}, \text{Y}, \text{U})(\text{NbTa})\text{O}_4$	2.2
Zircon	ZrSiO_4	13.1
Zirkelite	$(\text{Ca}, \text{Th}, \text{Ce})\text{Zr}(\text{Ti}, \text{Nb})_2\text{O}_7$	20.4

(?) formula uncertain

(s) secondary

Note: Many of these analyses may have been made on impure material.

fluorite-, brannerite-, monazite-, zircon-, ekanite- and steenstrupine-type plus umbozerite and UK27.

Unlike U^{4+} , 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, thorbastnaesite, $(Th(Ca, RE)(CO_3)_2F_2 \cdot 3H_2O)$, forms as a result of the intense alteration of ferroan thorite by carbonate- and fluorine-rich fluids (Pavlenko et al., 1965). Two phosphates, eylettersite, $((Th, Pb)_{1-x}Al_3(PO_4, SiO_4)_2(OH)_6)$, and kivuïte, $(Th, Ca, Pb)H_2(UO_2)_4(PO_4)_2(OH)_8 \cdot 7H_2O$, are alteration products of Th-rich uraninite (Van Wambeke, 1972). The other two phosphates, brockite, $((Ca, Th)PO_4 \cdot H_2O, \text{hex.})$, and grayite, $((Ca, Th)PO_4 \cdot H_2O, \text{orth.})$, are rhabdophane-type minerals formed from the alteration of thorite. Thorogummite, $(Th(SiO_4)_{1-x}(OH)_{4x})$, 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 $^{90}Th^{232}$. 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 thorutite, (ThTi_2O_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 8. 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 (pyrogonomic)
 - 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, $(\text{Ca,Th,Mn})_3\text{Si}_4\text{O}_{12}\text{F}\cdot 6\text{H}_2\text{O}$) 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 9. ABBREVIATIONS.

B. bal.	Berman balance
C.N.	coordination number
disc.	discredited
hex.	hexagonal
htd.	heated
'IR'	ionic radius
l.w.	long wave ultra-violet radiation
mon.	monoclinic
n.a.	not available
orth.	orthorhombic
PDF	powder diffraction file
poly.	polymorph
p.s.	polished section
pyc.	pycnometer
RE	rare earth element(s)
s.w.	short wave ultra-violet radiation
syn.	synthetic
tet.	tetragonal
t.s.	thin section
unnec.	unnecessary

1) OXIDES

The two naturally-occurring oxides of Th are thorianite and thorutite. Thorianite is the Th analogue of uraninite, $(\text{UO}_2)_2$, (Fron del, 1958) and thorutite the Th analogue of brannerite, (UTi_2O_6) , (Gotman and Khapaev, 1958).

A continuous solid solution series exists in the system $\text{ThO}_2\text{-UO}_2$ (Fron del, 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_3O_8 in thorianite (Fron del, 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 (Fron del, 1958 and Lang et al., 1962).

There is a complete series between synthetic ThTi_2O_6 and UTi_2O_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 Khapaev, 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

Isometric (Fm3m)	n = 2.2-2.35
Fluorite group	Occasional anomalous birefringence
Cell parameters:	Interpenetration twins, {111} common
a = 5.505-5.575Å	D _{meas} = 9.7-9.8g/cm ³
a(syn) = 5.596(1)Å	D _{calc} = 10.0g/cm ³ (syn)
Volume = 167-173Å ³	H = 6.5-7
Z = 4	Lustre: submetallic to resinous
Forms: {100}, {111}, {113}	Colour: shades of dark grey, brown
Cleavage: 100 poor	or black; white (syn)
Tenacity: brittle	brown to opaque (t.s.)
Streak: buff to grey	Not fluorescent
Nonmetamict	Diamagnetic
Habit: crystalline	

Slightly soluble in HNO₃ or H₂SO₄.

Substitutions: ThO₂-UO₂ 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): O 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.

Varietal names: aldanite: U- and Pb-bearing thorianite.

Related species: cerianite, uraninite.

Best references: Robinson and Sabina (1955); Frondel (1958).

TABLE 10a. THORIANITE ANALYSES.

	1	2	3	4	5	6	7	8	9
Fe ₂ O ₃	1.57	0.29	1.11	1.92	3.48	-	-	-	-
CaO	0.97	-	0.59	-	0.17	0.42	-	-	-
ThO ₂	38.47	93.02	62.16	72.27	65.37	64.61	89.91	70.07	69.03
UO ₂	4.44	4.73	40.32	11.19	-	-	-	-	-
U ₃ O ₈	-	-	-	-	23.47	12.94	6.86	16.84	27.88
UO ₃	33.15	-	18.88	-	-	-	-	-	-
RE ₂ O ₃	2.49	-	1.84	6.90	0.29	-	0.42	0.31	0.53
PbO	5.21	1.80	2.29	2.25	2.87	3.99	2.40	12.73	1.56
H ₂ O	4.39	-	1.05	-	0.61	0.14	-	-	-
Rem.	8.70	-	0.77	5.43	3.42	2.01	-	-	-
Total	99.39	99.84	99.01	99.93	99.68	99.28	99.59	99.95	99.27

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.

6) Hecht, 1906, in Frondel, 1958.

7-9) Makarov and Lipova, 1962.

FIGURE 6. Structure of thorianite (fluorite-type). After Bragg and Claringbull, 1965.

TABLE 11.

THORUTITE
ThTi₂O₆

Monoclinic *(C2/m)	n > 2.1
Brannerite group	Isotropic
*Cell parameters:	*D _{meas} = 6.0(5)g/cm ³
a = 9.822(5)Å	*D _{calc} = 6.08g/cm ³
b = 3.824(2)Å	Lustre: resinous
c = 7.036(5)Å	Colour: black
a/c = 118.84(5) ^o	Streak: pale brown
Volume = 231.4Å ³	Habit: short prismatic crystals
Z = 2	
Fracture: conchoidal	
Metamict	
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.	
Best references: Gotman and Khapaev (1958), Ruh and Wadsley (1966)	
*syn.

FIGURE 7. Structure of thorutite: small circles=Ti, large circles=O, hatched circles=Th. From Ruh and Wadsley (1966).

2) CARBONATES

The complex carbonate, thorbastnaesite, the thorium analogue of bastnaesite $((\text{Ce}, \text{La})\text{CO}_3\text{F})$, 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 Th phosphates have been reported. Kivuite is related to phosphuranylite $(\text{Ca}(\text{UO}_2)_3(\text{PO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O})$, eylettersite to crandallite $(\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O})$ and brockite and grayite to rhabdophane $(\text{REPO}_4 \cdot \text{H}_2\text{O})$. 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 Wambeke, 1972).

TABLE 12.

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

Hexagonal $\bar{6}2c$	$n = 1.670-1.678$
Bastnaesite group	$D_{\text{meas}} = 4.04\text{g/cm}^3$ (pyc.)
Cell parameters:	$D_{\text{calc}} = 5.70\text{g/cm}^3$
$a = 6.99(2)\text{\AA}$	Colour: pale yellow to brown
$c = 9.71(2)\text{\AA}$	Lustre: earthy
Volume = $411(3)\text{\AA}^3$	Habit: finely crystalline aggregates
$Z = 3$	

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

Analysis: SiO_2 2.01, Al_2O_3 1.76, Fe_2O_3 3.62, TiO_2 0.05, CaO 7.97, ThO_2 46.79, U_3O_8 0.11, RE_2O_3 7.46, PbO 0.33, CO_2 14.78, F 6.87 (O=F: 2.89), H_2O^+ 9.04, H_2O^- 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 $3000-3700\text{cm}^{-1}$.

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 2Ce. Pavlenko et al. (1965) prefer a separate site for Th.

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.

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

Orthorhombic (Bmmb?)	$N_\alpha = 1.618(2)$
Phosphuranylite-dewindtite gp.	$N_\beta = 1.654-1.655$
Cell parameters:	$N_\gamma = 1.655(3)$
a = 15.88Å	$\gamma - \alpha = 0.037$
b = 17.24Å	$2V = 0-5^\circ$
c = 13.76Å	Uniaxial to biaxial (+)
Volume = 3630Å ³	Dispersion: $r > v$
Z = 6	Lustre: earthy
Nonmetamict	Colour: yellow
Habit: massive	
Analysis: CaO 0.60, BaO 0.1, As ₂ O ₅ 0.1, BeO trace, ThO ₂ 8.32, UO ₃ 62.90, PbO 1.84, P ₂ O ₅ 6.04, H ₂ O ⁻ 6.24, H ₂ O ⁺ 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 Kobokobo 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: eylettersite (?)	
Related species: phosphuranylite and dewindtite (?)	
References: Fleischer (1959); Van Wambeke (1972).	

TABLE 14.

EYLETTERSITE
 $(\text{Th}, \text{Pb})_{1-x}\text{Al}_3(\text{PO}_4, \text{SiO}_4)_2(\text{OH})_6$

Trigonal ($\bar{R}3m$)	$N_\omega = 1.63 - 1.66$
Crandallite group	$N_\epsilon = 1.61 - 1.64$
Cell parameters:	$\epsilon - \omega = 0.01 - 0.03$
$a = 6.99(4)\text{\AA}$	Uniaxial (-)
$c = 16.7(1)\text{\AA}$	$D_{\text{meas}} = 3.4(1)\text{g/cm}^3$ (pyc.)
Volume = $706\text{\AA}^3$	$D_{\text{calc}} = 3.44\text{ g/cm}^3$
$Z = 1$	Colour: creamy white
Lustre: earthy	colourless (t.s.)
Streak: white	Fluorescence: creamy brown (l.w.)
Nonmetamict	yellow-green (s.w.)
Habit: massive	

Inclusions: very fine limonite.

Substitutions: Ba, U, Ca, Sr, H for Th; $\text{CO}_3, \text{H}_4\text{O}_4$ for PO_4 .

Analysis: SiO_2 1.65, Al_2O_3 35.7, Fe_2O_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_2O_5 18.3, CO_2 0.2, H_2O 15.0, total 100.26 wt%.

Alters partially to autunite.

Reacts slightly with warm H_2SO_4 .

Thermal behaviour: Above 1000°C breaks down to form $\text{ThO}_2, \text{U}_3\text{O}_8, \text{Al}_2\text{O}_3$ and aluminum pyrophosphate (?).

DTA peaks: endothermic peak at $165\text{--}170^\circ\text{C}$;
 exothermic peaks at $730\text{--}740^\circ\text{C}$ 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, cyrtolite 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 Wambeke.

Other names: Kivuite (?).

Related species: crandallite, plumbogummite.

Best reference: Van Wambeke (1972).

Rhabdophane Group $ABO_4 \cdot nH_2O$

The poorly-defined rhabdophane group of minerals are hydrous phosphates with the general formula $ABO_4 \cdot nH_2O$ ($n=1-2$), 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 ($REPO_4 \cdot H_2O$; Lettsom, 1878; Bertrand, 1880; Larsen, 1921; Palache et al., 1944; Hildebrand et al., 1957; Bowles and Morgan, 1984), brockite ($((Ca, Th)PO_4 \cdot H_2O, Ca:Th=1:1$; Bowie, 1956; Dooley and Hathaway, 1961; Fisher and Meyrowitz, 1962) and tristramite ($((Ca, U)PO_4 \cdot 1.5-2H_2O)$; Atkin et al., 1984). The orthorhombic subgroup includes ningyoite ($Ca_{1-x}U_x(PO_4) \cdot 1-2H_2O$; Muto et al., 1959; Belova et al., 1978; Boyle et al., 1981) and grayite ($((Ca, Th)PO_4 \cdot H_2O$; 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 15. CELL PARAMETERS OF RHABDOPHANE GROUP MINERALS AND RELATED COMPOUNDS.

	A-site cations	a(Å)	b(Å)	c(Å)	Volume (Å ³)
CePO ₄ (hex)	Ce	7.06	-	6.44	278
BiPO ₄ (hex)	Bi	6.97	-	6.46	272
Rhabdophane	RE	6.98	-	6.39	270
Brockite	Th,Ca	6.98	-	6.40	270
Tristramite	U,Ca	6.91	-	6.42	266
Ningyoite	U,Ca	6.78	12.13	6.36	523
Grayite	Th,Ca	n.a.	n.a.	n.a.	n.a.

The x-ray powder diffraction pattern of rhabdophane is similar to that of synthetic hexagonal hydrous cerium phosphate (CePO_4 ; $P6_222$; Hildebrand et al., 1957) and can be indexed on a hexagonal cell with $a=6.98\text{\AA}$, $c=6.39\text{\AA}$.

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.

TABLE 17.

BROCKITE
(Ca,Th)(PO₄)·H₂O

Hexagonal (P6 ₂ 22)	N _w = 1.680(2)
Rhabdophane group	N _E = 1.695(2)
Cell parameters:	ε - ω = 0.015
a = 6.98(3)Å	Uniaxial (+)
c = 6.40(3)Å	Extinction: undulatory, parallel
Volume = 270Å ³	Elongation: (+)
Z = 3	D _{meas} = 3.9(2)g/cm ³ (pyc.)
Forms: {100}	D _{calc} = 4.0
Lustre: earthy to vitreous	Colour: red-brown to yellow
Fracture: conchoidal	yellow to red (t.s.)
Partially metamict	Polymorph: grayite (orth.)?
Habit: massive	

Inclusions: hematite.

Substitutions: Sr, Ba for Ca; RE for Th; CO₃ for PO₄.

Analysis: Fe₂O₃ 4.6, BaO 1.1, SrO 1.3, CaO 9.7, UO₂ 0.07, RE₂O₃ 6.6, CO₂ 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 (poly.)

Reference: Fisher and Meyrowitz (1962).

TABLE 18.

GRAYITE
(Ca,Th)PO₄.H₂O

Orthorhombic (psuedohexagonal)	$\bar{n} = 1.66-1.69$
Rhabdophane group	$\epsilon - \omega$: moderate
Lustre: earthy to resinous	$D_{\text{meas}} = 3.7-4.3\text{g/cm}^3$
Fracture: conchoidal	$H = 3-4$
Polymorph: brockite (hex.)	Colour: yellow to red-brown
Partially metamict	Habit: fine-grained to earthy

Substitutions: RE, Fe³⁺ 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: ningyoite, rhabdophane, tristramite; brockite.

Best references: Bowie (1956), Dooley and Hathaway (1961).

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 $Th \gg Ca$. 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 $(Ca,Th)PO_4 \cdot H_2O$ to $ThSiO_4 \cdot H_2O$, 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 $REPO_4 \cdot nH_2O - (Th,Ca)PO_4 \cdot nH_2O - ThSiO_4 \cdot nH_2O$ with the substitutions $Ca + Th = 2RE$ and $Th + Si = RE + P$.

Monazite Group: ABO_4 (mon.)

The minerals of the monazite group are monoclinic, space group $P2_1/n$, $Z=4$, with the general formula ABO_4 , where $A=RE$, Ca or Th and $B=P$ or Si (Table 19).

The Th minerals in this group are brabantite ($CaTh(PO_4)_2$), cheralite ($(Ca,RE,Th)(P,Si)_2O_7$) and huttonite ($ThSiO_4$). There is extensive solid solution in the system $CePO_4-(Ca,Th)PO_4-ThSiO_4$, with coupled substitution of:

The monazite structure (Fig. 9) is a 3-dimensional network of edge-sharing AO_9 polyhedra interconnected by individual 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 AO_9 polyhedron, along the c-axis. The pairs represent edges which are shared with BO_4 tetrahedra. The AO_9 and BO_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 $RE-Ca-Th$ (Fig. 10), there are no monazite-group minerals with $Ca > Th$; however, there is a series between Ce and (Th,Ca) . Therefore, the ternary system, $CePO_4-(Th,Ca)PO_4-ThSiO_4$ best illustrates cation substitutions in the monazite group.

The current nomenclature of minerals in this system is essentially

TABLE 19. CELL PARAMETERS OF MONAZITE-TYPE STRUCTURES.

	A	B	a(Å)	b(Å)	c(Å)	a ² c	Volume (Å ³)
1) Monazite	Ce	P	6.80	7.01	6.47	103.9 ⁰	299
2) Huttonite	Th	Si	6.80	6.96	6.54	104.9 ⁰	299
3) Cheralite	Ca, Th	P	6.74	7.00	6.43	104.6 ⁰	294
4) BiPO ₄	Bi	P	6.74	6.92	6.46	103.5 ⁰	293
1) Brabantite	CaTh	P	6.73	6.93	6.45	103.9 ⁰	292

- 1) Rose, 1980.
- 2) Pabst and Hutton, 1951.
- 3) Bowie and Horne, 1953.
- 4) Mooney-Slater, 1962.

FIGURE 9. Structure of monazite group minerals projected on the a-c plane. Circles represent A-site cations. Tetrahedra represent BO_4 groups. Dashed lines show position of axial bonds, fine lines show position of equatorial bonds around one cation. After Finney and Rao, 1967.

FIGURE 10. Composition diagram for monazite group minerals in the system RE-Ca-Th. 1) Gramaccioli and Segalstad, 1978. 2) Finney and Rao, 1967. 3-6) Bowie and Horne, 1953. 7) Pabst and Hutton, 1951. 8-13) Charbonneau, 1980. 14-23) Palache et al., 1944. 24) Bowles et al., 1980. 25) Rose, 1980. 26-27) Mohr, 1984. 28-33) Kucha, 1980.

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 $(\text{Ce,Th,Ca})(\text{P,Si})\text{O}_4$ and $(\text{Th,Ce,Ca})(\text{Si,P})\text{O}_4$ ($\text{Si} > 33.3$ mole%) with end-member compositions of CePO_4 and ThSiO_4 , respectively. Cheralite is adopted for the CaTh-rich minerals with an end-member composition of $\text{CaTh}(\text{PO}_4)_2$. The name cheralite is adopted because it has priority over brabantite and type-cheralite contains over 50 mole% $\text{CaTh}(\text{PO}_4)_2$. Brabantite, then, becomes unnecessary (Chao, 1981).

Examination of synthetic $\text{CePO}_4(\text{mon})$ and hydrous $\text{CePO}_4(\text{hex})$ 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 CePO_4 (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 CePO_4 .

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)O₄

Monoclinic (P2 ₁ /n)	N _α = 1.779
Monazite group	N _β = 1.780
Cell parameters:	N _γ = 1.816
a = 6.74Å	• γ - α = 0.037
b = 7.00Å	2V = 18.1°
c = 6.43Å	zΛc = 7°
aΛc = 104.6°	Biaxial (+)
Volume: 294Å ³	D _{meas} = 5.30(1)g/cm ³ (pyc)
Z = 4	D _{calc} = 5.41 g/cm ³
Fracture: uneven	H: 5
Cleavage: {010} distinct	Lustre: resinous to vitreous
{100} difficult	Colour: pale to dark green
Tenacity: brittle	pale green (t.s.)
Streak: white	pleochroic: x & y = green
Habit: massive	z = yellow-green
Nonmetamict	Parting: {001} poor

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, H₂O⁺ 0.06, total 99.29 wt% (Bowie and Horne, 1953).

IR: main bands at 540, 570 and 620cm⁻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 5cm 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, brabantite and huttonite.

Best references: Bowie and Horne (1953); Finney and Rao (1965); Bowles and Morgan (1980).

TABLE 21.

*BRABANTITE

Monoclinic ($\text{P2}_1/\text{n}$)	$\text{N}\alpha$ --
Monazite group	$\text{N}\beta = 1.73$
Cell parameters:	$\text{N}\gamma$ --
a = 6.726(6) Å	$\text{D}_{\text{meas}}: 4.72 \text{ g/cm}^3$
b = 6.933(6) Å	$\text{D}_{\text{calc}}: 5.26 \text{ g/cm}^3$
c = 6.447(5) Å	H: 5.5
$a/c = 103.9(2)^\circ$	Lustre: dull
Volume = 292 Å ³	Colour: grey-brown
Z = 2	brown-grey (t.s.)
Cleavage: {001} distinct	grey (p.s.)
{100} difficult	reflectance: 7%
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: SiO_2 2.27, Al_2O_3 0.74, Fe_2O_3 0.05, MgO 0.56, MnO 0.32, CaO 11.94, ThO_2 52.65, P_2O_5 27.68, H_2O 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 400°C.

IR: main bands at 410, 450 and 610 cm^{-1} and between 850-1200 cm^{-1} .

Structure: isostructural with monazite; equivalent amounts of Th^{4+} and Ca^{2+} 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 1.5 cm 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 für 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

Monoclinic (P2 ₁ /n)	N _α = 1.898(3)
Monazite group	N _β = 1.900
Cell parameters:	N _γ = 1.922
a = 6.80(3)Å	γ - α = 0.024
b = 6.96(3)Å	2V = 25(1)°
c = 6.54(3)Å	Biaxial (+)
a c = 104.9(2)°	γ near c
Volume = 299Å ³	Dispersion: r<v (mod.)
Z = 4	D _{meas} = 7.1(1)g/cm ³
Fracture: conchoidal	D _{calc} = 7.18g/cm ³
Cleavage: {001} distinct	Lustre: adamantine
{100} indistinct	Colour: colourless to pale cream
Polymorph: thorite (tet.)	Fluorescence: dull white with pink tinge
Nonmetamict	
Habit: anhedral grains	

Not affected by acid.

Analysis: SiO₂ 19.7, Fe₂O₃ 1.2, ThO₂ 76.6, RE₂O₃ 2.6, total 100.1 wt% (Fron del, 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 alaskitic granites) 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.).

Best references: Pabst and Hutton (1951), Taylor and Ewing (1979), Kucha (1980).

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: ABO_4 (tet.)

Thorite ($ThSiO_4$) and thorogummite ($Th(SiO_4)_{1-x}(OH)_x$) are isostructural with zircon ($ZrSiO_4$) and coffinite ($U(SiO_4)_{1-x}(OH)_x$) (Fron del, 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 SiO_4 tetrahedra which are shared with sides of ThO_8 polyhedra to form chains of alternating SiO_4 and 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 ThO_8 and 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 ThO_9-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 U, RE, Zr, Ca, Fe, and 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. 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% U_3O_8 in thorite, but some uraninite may have been present in the sample. Frondel (1958) reported about 16.5 wt% UO_2 in thorite from Hybla, Ontario. No significant amount of Th has been found in coffinite.

Studies of the synthetic, anhydrous system $ThSiO_4$ - $USiO_4$ 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% $USiO_4$, nor could they produce a Th-bearing $USiO_4$.

Thorogummite, the hydrous equivalent of thorite, has a maximum of 15 wt% H_2O (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
 ThSiO_4

Tetragonal (I4/amd)	$N_{\omega} = 1.818-1.825$
Zircon group	$N_{\epsilon} = 1.839-1.840$
Cell parameters:	$\epsilon - \omega = 0.01-0.02$
$a = 7.12(3)\text{\AA}$	Uniaxial (+), metamict varieties
$c = 6.32(3)\text{\AA}$	isotropic
Volume = $320(5)\text{\AA}^3$	Zoning in some crystals
$Z = 4$	$D_{\text{meas}} = 6.7-4.1\text{g/cm}^3$ (decreases
Forms: {110}, {111}	with increase in H_2O)
Fracture: conchoidal to	$H = 4.5-5$
splintery	Colour: shades of yellow, brown or
Cleavage: {100} indistinct	green, may be dichroic in
Tenacity: brittle	thin section ($\omega < \epsilon$)
Streak: yellow to brown	Elongation: (+)
Lustre: vitreous to greasy	May have striations parallel to c
Nonmetamict to metamict	Polymorph: huttonite (monoclinic)
Paramagnetic	Nonfluorescent
Habit: massive to crystalline	
Unaffected by acids.	
Alters 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 1020cm^{-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	
thorianite plus amorphous SiO_2 .	
DTA: continuous water loss below 250°C , sharp exothermic peak at	
880°C .	
Raman spectra: Syme 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 SiO_4 tetrahedra, forming chains	
parallel to "c", and 4 edges with other ThO_8 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 4cm), occasionally with prism faces	
developed, in a variety of environments:	
- in pegmatites from Langesund Fiord, Norway; as	
irregular blebs (up to 1cm) of waxy, yellow material	
associated with calcite, spinel and thorianite 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 alkalic intrusives in both the Wet Mountains, and the Powderhorn district, Colorado;
- in alkaline intrusives including Ilimaussaq, 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; Pekoeringan 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, Hybla, 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: Langésund Fiord, Norway.

Name: for Thor, the Norse god of war.

Varietal names: auerlite - phosphatic thorite: $\text{PO}_4:\text{SiO}_2 = 0.8:1.0$

calciorthorite: calcian thorite

enalite: uranoan thorite

eucrasite: RE thorite: RE:Th up to 1:1

ferrithorite: high iron thorite

freyalite: 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 $\text{Si} > \text{P}$

smirnovskite: $(\text{Th}, \text{Ca}, \text{Ce})(\text{P}, \text{Si}, \text{Al})(\text{OH})(\text{O}, \text{OH}, \text{F})_4$

uranothorite: uranoan thorite (up to 10%)

wiskasonite: metamict uranoan thorite

yanshainshynite: phosphatic thorite

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

Best references: Frondel (1958), Frondel et al. (1967), Heinrich (1958), Syme et al. (1977), Taylor and Ewing (1977).

TABLE 23a. THORITE ANALYSES.

	1	2	3	4	5	6	7	8
SiO ₂	19.20	17.96	19.56	19.81	9.40	17.47	19.38	15.4
TiO ₂	-	0.04	-	-	-	-	-	-
Al ₂ O ₃	-	0.32	0.13	-	0.50	0.12	0.33	1.1
Fe ₂ O ₃	0.20	-	0.75	0.20	0.30	6.59	4.01	-
FeO	1.75	0.58	0.43	-	-	-	0.40	11.1
MgO	-	0.07	0.01	-	-	0.05	0.04	-
CaO	0.40	0.42	4.38	5.17	-	1.39	2.34	-
ThO ₂	72.00	72.93	46.33	40.37	52.8	48.66	52.07	50.4
UO ₂	4.20	6.95	7.67	-	-	9.00	-	-
UO ₃	0.37	-	9.46	20.73*	7.00	-	10.87	-
RE ₂ O ₃	1.15	0.24	0.44	>0.2	20.04	3.12	-	-
PbO	0.55	0.10	1.32	1.72	0.21	1.26	-	4.3
P ₂ O ₅	-	tr.	-	-	0.70	0.93	-	-
SO ₃	-	-	-	-	-	-	-	10.0
H ₂ O ⁺	-	-	5.67	9.88	{ 5.6 3.5	10.88	11.31	-
H ₂ O ⁻	-	0.22	3.57			-	-	-
Rem.	0.07	0.12	0.22	-	-	0.73	0.11	-
Total	99.89	99.95	99.94	98.08	100.1	100.20	100.86	92.3

- 1) Rozina, 1967.
- 2) Hutton, 1952, in Frondel, 1958.
- 3) Ellsworth, 1927, in Frondel, 1958.
- 4) Robinson and Abbey, 1957. * as U₃O₈.
- 5) Staatz et al., 1976.
- 6) Lindstrom, 1881, in Frondel, 1958.
- 7) Collier, 1880, in Frondel, 1958.
- 8) partial analyses from Rimsaite, 1983.

TABLE 24.

THOROGUMMITE
 $\text{Th}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$

Tetragonal	$n = 1.54-1.64$
Zircon group	Isotropic to weakly anisotropic
Cell parameters:	Parallel extinction
$a = 7.07-7.08\text{\AA}$	$D_{\text{meas}} = 3.2-5.4\text{g/cm}^3$
$c = 6.26-6.28\text{\AA}$	$H = 5.5$
Volume = $313 - 315\text{\AA}^3$	Lustre: dull to subvitreous
$Z = 4$	Colour: yellow or grey to black
Nonmetamict	(uraniferous)
Habit: massive	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°C , give a thorite powder pattern; after heating to 1000°C powder pattern shows a mixture of: ThO_2 and ThSiO_4 .

DTA: loss of water at 150°C ; exothermic peak at 750°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 O.

Paragenesis: secondary mineral formed by the alteration of thorite.

Occurrence: as fine-grained, massive aggregates, pseudomorphic 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 kasolite at Wodgina, Western Australia.

Type locality: Baringer Hill, Texas.

Name: for thorium plus "gummite" (bright-coloured fine-grained alteration product).

Other names: chlorothorite, hyblite, hydrothorite, hydroxyl-thorite, mackintoshite, maitlandite, nicolayite, pilbarite, (thorogummite plus kasolite).

Related species: coffinite, thorite.

Best references: Frondel (1958), Fuchs and Gebert (1958).

TABLE 24a. THOROGUMMITE ANALYSES.

	1	2	3	4	5	6
SiO ₂	13.09	15.30	21.10	15.77	13.90	14.43
Al ₂ O ₃	0.97	-	2.22	0.88	-	8.84
Fe ₂ O ₃	0.85	-	8.67	-	-	2.84
MgO	-	0.16	-	0.60	0.10	-
CaO	0.41	1.62	0.95	1.65	0.59	-
ThO ₂	41.44	24.46	25.05	57.79	45.30	21.20
ZrO ₂	-	-	4.78	-	0.88	0.05
UO ₃	22.43	37.33	7.91	2.98	23.73*	18.53
RE ₂ O ₃	6.69	0.44	12.76	0.97	1.86	18.55
PbO	2.16	7.78	tr.	1.25	3.74	0.17
P ₂ O ₅	1.19	-	1.77	1.33	0.67	2.63
H ₂ O ⁺	7.88	8.37	10.80	6.06	4.31	7.82
H ₂ O ⁻	1.23	4.19	-	9.12	0.50	5.61
Rem.	-	0.40	4.48	1.50	2.25	8.28
Total	98.33	100.05	100.49	99.90	96.50	100.05

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, iraqite, 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 iraqite is probably similar to steacyite, with RE and Th in the A-

TABLE 25. COMPARISON OF EKANITE GROUP MINERALS.

	Cations/Si ₈ O ₂₀	a(Å)	c(Å)	Space Group
Ekanite	ThCa ₂ []	7.48	14.89	I422
Iraquite	1/2[(RE,Th) _{2-x} (Ca,RE) ₄ (K _{2-y})]	7.61	14.72	P4/mcc
Steacyite	Th(Na,Ca) ₂ (K _{1-x} [] _x)	7.58	14.77	P4/mcc
Unnamed	Th(Ca,Na) ₂ (K _{1-x} [] _x)	7.58	14.82	P4/mcc

a)

b)

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
 $\text{ThCa}_2\text{Si}_8\text{O}_{20}$

Tetragonal (1422)	$N_\omega = 1.580(3)$
Ekanite group	$N_\epsilon = 1.568(3)$
Cell parameters:	$\epsilon - \omega = 0.012$
$a = 7.483(3)\text{\AA}$	Uniaxial (-), some biaxial
$c = 14.893(6)\text{\AA}$	$2V = 0 - 15^\circ$
Volume = $831(1)\text{\AA}^3$	Zoning in some crystals
$Z = 2$	$D_{\text{meas}} = 3.08(5)\text{g/cm}^3$
Forms: {010}, {110}, {001}	$D_{\text{calc}} = 3.36\text{g/cm}^3$
and {100}.	$H = 4.5$
Fracture: irregular	Lustre: vitreous
Cleavage: {101} distinct	Colour: straw-yellow to dark red
{001} indistinct	straw-yellow to red (t.s.)
Tenacity: brittle	Striations parallel to x.
Streak: white	Habit: crystalline
Nonmetamict to metamict	

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 (2-3mm x 1mm) 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 1cm) of ekanite occur in syenite from Turkestan, 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 26a. EKANITE ANALYSES.

	1	2*	3*	4*
SiO ₂	55.6	45.1	41.7	47.6
Al ₂ O ₃	tr.	0.5	1.3	0.8
Fe ₂ O ₃	0.5	-	-	-
FeO	-	0.3	0.3	0.4
MgO	tr.	-	-	-
MnO	tr.	0.2	0.3	0.2
CaO	13.7	9.0	8.1	9.6
ThO ₂	27.6	36.0	37.1	37.8
UO ₂	2.1	1.9	0.5	1.1
PbO	0.8	-	-	-
Total	100.3	92.9	89.3	97.5

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.

IRAQUITE

Tetragonal (P4/mcc)	$N_\omega = 1.590$
Ekanite group	$N_\epsilon = 1.585$
Cell parameters:	$c - \omega = 0.005$
$a = 7.61(1)\text{\AA}$	Uniaxial (-), some biaxial
$c = 14.72(1)\text{\AA}$	Extinction: $0-7^\circ$
Volume = $853(4)\text{\AA}^3$	$H = 4.5$
$Z = 1$	Streak: whitish
Fracture: uneven	Lustre: dull to pearly
Cleavage: 2 good, 1 poor	Colour: pale green-yellow
Nonmetamict	colourless (t.s.)
Habit: crystalline	

Inclusions: minor calcite and pyrite

Substitutions: U, Zr and Pb for RE; Na for Ca and Al for Si.

Analysis: SiO_2 51.7, Al_2O_3 0.77, Fe_2O_3 0.10, MgO 0.02, CaO 10.73, Na_2O 0.27, K_2O 2.76, ThO_2 9.54, UO_2 0.65, ZrO_2 0.17, PbO 0.35, RE_2O_3 15.06, CuO 0.07, P_2O_5 0.01, F 0.07, H_2O^+ 3.51, H_2O^- 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 .

DTA: 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 29-995.

Occurrence: in coarsely crystalline granite in contact with dolomitic marble at Shakhi-Rash Mountain, Iraq.

Type locality: Iraq.

Name: for country.

Related species: steacyite, ekanite.

Best references: Livingstone et al. (1976), Perrault and Szymanski (1982).

TABLE 28.

STEACYITE
 $\text{Th}(\text{Na}, \text{Ca})_2(\text{K}_{1-x}\text{Li}_x)\text{Si}_8\text{O}_{20}$

Tetragonal (P4/mcc)	$N_w = 1.573(1)$
Ekanite group	$N_e = 1.572(1)$
Cell parameters:	$\epsilon - \omega = 0.001$
$a = 7.58(1)\text{\AA}$	Uniaxial (-)
$b = 14.77(2)\text{\AA}$	$D_{\text{meas}} = 2.95(2)\text{g/cm}^3$ (B. bal.)
Volume = $849(3)\text{\AA}^3$	$D_{\text{calc}} = 3.32\text{g/cm}^3$
$Z = 2$	$H = 4.9(5)$
Forms: {100}, {001}	Twinning: 3-dimensional cruciform
Fracture: irregular	Streak: white
Tenacity: brittle	Colour: dark brown to dark grey
Nonmetamict	dark brown (t.s.)
Habit: prismatic crystals	

Substitutions: Ce, Pb for Th; Mn, Mg for Ca.
 Analysis: SiO_2 50.0, MgO 0.15, MnO 142, CaO 4.25, Na_2O 2.90, K_2O 2.95, ThO_2 24.20, CeO_2 0.41, PbO 0.06, H_2O^- 11.6, total 97.94 wt% (Perrault and Richard, 1973).
 IR: main bands at 490-500, 585-610, 900-1300, 1660 and 3200-3700 cm^{-1} .
 Thermal behaviour: loss of weight, but no change in x-ray powder pattern after heating to 800°C.
 Structure: metal layers at $z=1/4, 3/4$ separated by a silicate sheet of closed double rings (compare with ekanite) (Fig. 14).
 Three strongest x-ray lines (intensity) (indices): 5.30 (45) (102), 3.38 (100) (210,202), 3.32 (55) (104,211); PDF 25-678.
 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, eudialyte, acmite, nenadkevichite, catapleite and epididymite.
 Type locality: Mont St-Hilaire.
 Name: for H.R. Steacy, (GSC).
 Other names: ekanite, kanaekanite (disc.).
 Related species: ekanite, iraquite.
 Best references: Perrault and Richard (1973), Perrault and Szymanski (1982).

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.

Thorosteenstrupine and Umbozerite

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

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: $\text{Na}_{1-12}\text{H}_{7-0}\text{CaRE}_6\text{M}_5((\text{Si}_6\text{O}_{18})_2((\text{P,Si})\text{O}_4)_6\cdot n\text{H}_2\text{O})$ ($n < 15$) (Makovicky et al., 1981) takes into account this wide range of composition. According to crystal structure analysis, a possible end-member formula is: $\text{Na}_{14}\text{Ce}^{3+}\text{Mn}^{2+}\text{Mn}^{3+}\text{Fe}^{3+}\text{Zr}^{4+}(\text{OH})_2(\text{PO}_4)_7(\text{Si}_6\text{O}_{18})_2 \cdot 3\text{H}_2\text{O}$ (Moore and Shen, 1983).

Although thorosteenstrupine has no Na_2O or P_2O_5 and has a high water content, the CaO and SiO_2 content of thorosteenstrupine 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 thorosteenstrupine (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 thorosteenstrupine 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)₃Si₄O₁₂F₆H₂O

Amorphous	n = 1.63-1.66
Fracture: conchoidal	Isotropic
Tenacity: brittle	D _{meas} = 3.02(2)g/cm ³
Streak: dark brown	H = 4
Lustre: greasy to vitreous	Colour: dark brown to black, red-
Metamict	brown on thin edges.
Weakly magnetic	brown (t.s.)
Habit: fine, platy crystals	

Substitutions: RE, Fe for Th; Al for Si.
 Analysis: SiO₂ 31.87, Al₂O₃ 0.31, Fe₂O₃ 0.65, MnO 7.75, CaO 8.38, ThO₂ 35.70, RE₂O₃ 1.12, F 2.43, H₂O⁺ 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 (2-10mm in length) in metasomatic veins of eastern Siberia, with microcline, albite, acmite, quartz, fluorite and miserite.
 Name: for composition.
 Related species: steenstrupine.
 Best references: Kupriyanov et al. (1962, 1963).

TABLE 30.

UMBOZERITE
 $\text{Na}_3\text{Sr}_4\text{ThSi}_8(\text{O},\text{OH})_{24}$

Tetragonal	$n = 1.640$
Fracture: conchoidal	Isotropic
Tenacity: brittle	$H = 5$
Lustre: vitreous	Colour: shades of green
Metamict	Translucent to clear
Habit: massive to crystalline	

Substitutions: K for Na; Ba, Ca, Mn for Sr; U, Fe, Ce, Ti for Th.
 Analysis: SiO_2 37.1, TiO_2 0.3, Fe_2O_3 1.8, MnO 2.2, BaO 2.0, SrO 27.7, CaO 0.2, Na_2O 6.13, K_2O 0.74, ThO_2 17.6, U_3O_8 0.4, Ce_2O_3 0.3, loss on ignition 0.43, total 96.8 wt%.

Thermal behaviour: recrystallizes when heated to 900°C for 1 hr to give an x-ray powder pattern of thorianite plus many other lines.

Three strongest x-ray lines (intensity): 3.38 (60), 3.29 (100), 1.701 (80); PDF 26-1384.

Occurrence: 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.

Name: for locality.

Best reference: Es'kova et al. (1975).

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:

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 1.41×10^{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 (ionium), half-life 8.0×10^4 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 31. RADIOACTIVE DECAY SCHEME OF THORIUM.

Particle Energy in MeV (Intensity)	Gamma Energy in MeV	$t_{1/2}$	Particle Energy in MeV (Intensity)
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From Lederer 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 (RE), 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+} ($(\text{Rn})5f^2 6d^0 7s^0$) which readily loses the two 5f electrons to form the uranyl ion (UO_2^{2+}), Th^{4+} cannot easily be

TABLE 32. ATOMIC STRUCTURE DATA FOR THORIUM AND RELATED ELEMENTS (AFTER SHANNON AND PREWITT, 1969, 1970).

ELEMENT SYMBOL	ATOMIC NUMBER	VALENCE STATE	COORDINATION NUMBER	IONIC RADII	ELECTRON CONFIGURATION
Ca	20	2	VIII	1.12Å	(Ar)4s ²
Ti	22	4	VI	0.61Å	(Ar)3d ² 4s ²
Zr	40	4	VIII	0.84Å	(Kr)4d ² 5s ²
La	57	3	VIII	1.18Å	(Xe)4f ⁰ 5d ¹ 6s ²
Ce	58	3	VIII	1.14Å	(Xe)4f ² 5d ⁰ 6s ²
Gd	64	3	VIII	1.06Å	(Xe)4f ⁷ 5d ¹ 6s ²
Hf	72	3	VIII	0.83Å	(Xe)4f ¹⁴ 5d ² 6s ²
Th	90	4	VIII	1.04Å	(Rn)5f ⁰ 6d ² 7s ²
U	92	4	VIII	1.00Å	(Rn)5f ³ 6d ¹ 7s ²

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. Omelin (1978) gives an excellent outline of the properties of thorium oxides. Since thorium forms no simple oxyions there are no naturally occurring thorates (Boyle, 1982).

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

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. Bailer et al. (1973) argued that the hydroxide was more likely $\text{ThO}_2\cdot\text{aq}$ since the x-ray powder diffraction pattern showed diffuse lines of ThO_2 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. $\text{Th}(\text{OH})_4$ is highly insoluble but can be dissolved in strong acids or in solutions containing complexing agents such as carbonates (Katz and Seaborg, 1957). Th^{4+} tends to remain dissociated in solutions more acid than pH 3 (Katz and Seaborg, 1957).

II. Solution Chemistry

Since Th^{3+} is unstable in water, thorium occurs in aqueous solution only as the highly-charged, positive cation Th^{4+} which has a strong tendency to complex with HF , H_3PO_4 , Cl^- and NO_3^- as well as SO_4^{2-} and CO_3^{2-} (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 $\text{Th}(\text{OH})_4$ 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 ($\text{C}_2\text{O}_4^{2-}$), citrate ($\text{C}_6\text{H}_5\text{O}_7^{3-}$) and EDTA ($\text{C}_{10}\text{H}_{12}\text{O}_8\text{N}_2^{4-}$) 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: $\text{Th}(\text{SO}_4)$, ThF_2^{2-} , $\text{Th}(\text{HPO}_4)_2$, $\text{Th}(\text{HPO}_4)_3^{2-}$ and $\text{Th}(\text{OH})_4$. For example, at pH 3, fluoride concentration of 0.2ppm increases ThO_2 solubility from 10^{-2} ppb to 10ppb. At pH5, phosphate concentration of 0.1ppm 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 $\text{Th}(\text{OH})_4$ 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, ThOCO_3 . 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 (1.04Å; 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 0.1Å. Therefore, Th^{4+} can only be accommodated readily in 8- or 9-fold sites having a site-radius of 0.94 to 1.14Å (i.e. sites capable of holding cations of radius 0.84 to 1.24Å). The only other quadrivalent cations with radii in this range are U(1.00Å), Ce(0.97Å), Pb(0.94Å) and Zr(0.84Å). 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. Mumpton 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 (Fronzel, 1958).

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

or:

to maintain the charge balance. For example, in cheralite the substitutions

2 2
OF / DE

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:

$$1.09\text{\AA} + 1.18\text{\AA} = 2.27\text{\AA}$$

and
$$2 \times 1.15\text{\AA} = 2.30\text{\AA}.$$

Here, the substitution $\text{Th}+\text{Ca}=2\text{Ce}$ 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-huttonite series) not only maintains charge balance, but also reduces structural instability by minimizing distortion. Comparing the sums of the corresponding radii gives:

$$1.09\text{\AA} + 0.26\text{\AA} = 1.35\text{\AA}$$

and
$$1.15\text{\AA} + 0.17\text{\AA} = 1.32\text{\AA}.$$

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 (>1000ppm), occurs in only a limited number of accessory and secondary minerals (Chapter 2).

IGNEOUS BEHAVIOUR

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 (Bailliar 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 accomodating much Th and do not remove much Th from the melt. However,

TABLE 33. AVERAGE THORIUM ABUNDANCES.

Terrestrial	65.0 ppb	Henderson 1982
Crustal	9.6 ppm	"
Dunite	4.0 ppb	Turekian and Wedepohl 1961
Basalt	4.0 ppm	"
Diorite	5.0 ppm	Davidson 1982
Granodiorite	9.3 ppm	Turekian and Wedepohl 1961
Rhyolite	14.2 ppm	Dostal and Dupuy 1983
Low-Ca Granite	17.0 ppm	Turekian and Wedepohl 1961
Alkali Granite	20.0 ppm	Clark et al. 1966
Syenite	38.0 ppm	Gerasimovsky 1974
Shale	12.0 ppm	Turekian and Wedepohl 1961
Graywacke	6.7 ppm	Rogers and Richardson 1964
Arkose	5.0 ppm	"
Orthoquartzite	4.3 ppm	"
Limestone	1.7 ppm	Turekian and Wedepohl 1961

TABLE 34. SELECTED PARTITION COEFFICIENTS OF THORIUM.

	Basalts/ andesites ¹⁾	Dacites/ rhyolites ¹⁾	Felsic intrusives ²⁾
opx	-	0.13	-
cpx	0.04	0.13	-
amph	-	0.22	-
bio	-	0.31	0.310 ¹⁾
plag	-	0.04	0.013 ¹⁾
ksp	-	0.02 ³⁾	0.007
qtz	-	-	0.001
zirc	-	91.20 ³⁾	-
all	-	548.00 ³⁾	-

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

1) Henderson, 1982.

2) Mittelfehldt and Miller, 1983.

3) Mahood and Hildreth, 1983.

the more open structures of amphibole and biotite can accommodate more Th than either pyroxene, quartz or feldspar. 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 SiO_4 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 polymerized 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: Si:O=4:11; mica: Si:O=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 as 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 Staar (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 P_2O_5 , 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_2O 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, 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). 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_2O_5 occurs in a silicate melt as monomers which have a greater affinity for metal cations than does SiO_4 . P_2O_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 P_2O_5 between melt and vapour phase, the effect of P_2O_5 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 $(\text{Na,Ca,K})\text{ThSi}_{11}(\text{O,H}_2\text{O,F,Cl})_{33}$ 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, $R\bar{3}m$, $a=29.01(1)\text{\AA}$, $c=17.30(1)\text{\AA}$, $V=12608.7(6)\text{\AA}^3$, $Z=18$, $D_{\text{meas}}=2.62(2)\text{g/cm}^3$, and $D_{\text{calc}}=2.613\text{g/cm}^3$. 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 accomodating 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, umbozerite and UK27.

Thorianite and thorutite are the Th-analogues of uraninite and brannerite, respectively (Fronzel, 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

end-members 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 ($\text{CaTh}(\text{PO}_4)_2$) 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% $\text{CaTh}(\text{PO}_4)_2$.

Huttonite (mon.) is a dimorph of thorite (tet.; Pabst, 1951). Thorogummite is the hydrous equivalent of thorite (Fron del, 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_8O_{20} groups (Szymanski et al., 1982).

Thorosteenstrupine is thought to be the Th analogue of steenstrupine (Kuprianova et al., 1962). The other Th silicates umbozerite 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_3PO_4 , Cl^- and NO_3^- as well as SO_4^{2-} and CO_3^{2-} (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 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 (1.04Å; 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 1.24Å. The only quadrivalent cations with radii in this range are U (1.00Å), Ce (0.97Å), Pb (0.94Å) and Zr (0.84Å). 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 1.24Å, 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 accomodating 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 (Mittelfehldt 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, H_2O 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 accomodate 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 steacyite in pegmatite veins and UK27 in hydrothermally altered veins supports this hypothesis.

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