

# HYDROXYL SUBSTITUTION IN THORITE AND ZIRCON\*

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## ABSTRACT

The ill-defined thorite-like minerals thorogummite, nicolayite, hydrothorite, maitlandite, mackintoshite and hyblite are found to be minor chemical variants of a single phase, for which the name thorogummite has priority. Thorogummite is isostructural with thorite and has virtually the same unit-cell dimensions. It differs from thorite in being secondary in origin, in being formed by the alteration of primary thorium minerals including thorite itself, in occurring as fine-grained aggregates that are not metamict but crystalline, and in containing essential water. Chemically, thorogummite seems to be a hydroxyl-containing variant of thorite,  $\text{ThSiO}_4$ , in which there is a serial substitution of  $(\text{OH})_4$  for  $(\text{SiO}_4)$  with the formula  $\text{Th}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$ .

Cytolite apparently stands in an analogous relation to zircon.

## INTRODUCTION

Thorite, like zircon, is surrounded by a diffuse nomenclatural halo of ill-defined minerals. These minerals approximate in composition hydrous thorite, and like thorite often contain uranium, lead, rare earths or other elements in variable and sometimes large amounts in substitution for thorium. Because of their composition and the occasional evidence of tetragonal crystal form, they are commonly listed in textbooks as synonyms or varieties of thorite. Table 1 lists these minerals, and notes are made therein of authentic specimens that were available for the present study.

There are features of occurrence and composition that make the identification of these minerals as thorite seem doubtful or unusual. Thorite hitherto has been known only as a primary mineral. It occurs chiefly in pegmatites, but also in small amounts in hydrothermal deposits formed probably at moderate temperature. Hence it is of interest to find that many of the thorite-like substances listed in Table 1 clearly are of secondary origin. The thorogummite from Japan is a yellow earthy alteration product of yttrialite. Both the thorogummite (nicolayite) and hydrothorite from Wodgina, Western Australia, occur as yellow earthy nodules in the weathered outcrops of pegmatites and have been derived by the alteration of primary thorium silicates—sometimes observed as black residuals within the nodules. The thorogummite from Easton, Pennsylvania, is a secondary product formed by the alteration of thorianite, apparently during serpentinization of the matrix. Hyblite, from Hybla, Ontario, is an alteration of thorite itself. It occurs as white crusts in cracks

\* Publication authorized by the Director, U. S. Geological Survey.

TABLE 1. THORITE-LIKE MINERALS

- Auerlite *Hidden and Mackintosh* (Am. Jour. Sci. 36, 461, 1888). Henderson County, North Carolina.
- Calciorthorite *Brögger* (Geol. fören. Förh. 9, 258, 1887). Langesund Fiord, Norway.
- Chlorothorite *Hidden* (New York Acad. Sci. Trans. 8, 185, 1889). Baringer Hill, Texas. [Name intended as a synonym of thorogummite.]
- Enalite *Kimura and Miyako* (Chem. Soc. Japan Jour. 53, 93, 1932). Naegi, Japan.
- Eucrasite *Paijkull* (Geol. fören. Förh. 3, 350, 1877). Langesund Fiord, Norway.
- Ferrothorite *Lacroix* (Min. de Madagascar 3, 309, 1923). Befarita, Madagascar. [Name given to a supposed ferroan variety of thorite.]
- Freyalite *Esmark* cited in *Damour* (Soc. Franç. Miner. Bull. 1, 33, 1878). Langesund Fiord, Norway.
- \*Hyblite *Ellsworth* (Am. Mineralogist 12, 368, 1927). Two types were distinguished, called alpha- and beta-hyblite. Harvard specimen verified personally by Ellsworth in 1952.
- \*Hydrothorite *Simpson* (Royal Soc. Western Australia Jour. 13, 27, 1927). Wodgina, Western Australia. Harvard specimen labelled as a gift from Simpson.
- \*Mackintoshite *Hidden and Mackintosh* (Am. Jour. Sci. 46, 98, 1893). Baringer Hill, Texas. A supposed later occurrence described by Simpson, Geol. Surv. Western Australia Bull. 48, 1912, and Nat. History Soc. Western Australia Jour. 4, 1912, from Wodgina, Western Australia [see also maitlandite]. A U. S. National Museum specimen answering description, but without direct evidence of authenticity.
- \*Maitlandite *Simpson* (Royal Soc. Western Australia Jour. 16, 33, 1930). Wodgina, Western Australia. [Name applied to material earlier described under the name mackintoshite.] U. S. National Museum specimen originally obtained from Simpson.
- \*Nicolayite *Simpson* (Royal Soc. Western Australia Jour. 16, 25, 1930). Wodgina, Western Australia. [Name applied to material earlier described under the name thorogummite.]
- \*Pilbarite *Simpson* (Chem. News 102, 283, 1910). Wodgina, Western Australia. U. S. National Museum specimen originally from Simpson; and a specimen from the O. I. Lee collection originally from the Government Museum, Western Australia. These specimens gave unlike x-ray patterns, and neither mineral was found to be related to thorite.
- \*Thorium gummite *Wells, Fairchild and Ross* (Am. Jour. Sci. 26, 45, 1933). Easton, Pennsylvania. Commonly called thorogummite. Thorogummite, uranophane and two unidentified minerals, all alterations of thorianite, were found in a suite of 60 specimens from the locality. None of these minerals could be identified with certainty with the analyzed material of Wells, Fairchild and Ross, as the several substances very closely resemble each other; none of analysis material is extant (C. S. Ross, personal communication, 1952).
- \*Thorogummite *Hidden and Mackintosh* (Am. Jour. Sci. 38, 480, 1889); also mentioned by *Hidden and Hillebrand*, Am. Jour. Sci. 46, 98, 1893, and *Hidden*, Am. Jour. Sci. 19, 425, 1905. Baringer Hill, Texas. Three later occurrences were described by *Iimori and Hata*, Tokyo Inst. Phys. Chem. Res., Sci. papers 34, 447, 1938, from *Iisaka*, Japan; by *Simpson*, Geol. Surv. Western Australia Bull. 48, 1912 and Nat. History Soc. Western Australia Jour. 4, 1912, from *Wodgina*, Western Australia [see also nicolayite]; and by *Henmi*, Geol. Soc. Japan Jour. 57, 345, 1951, from *South Manchuria*. The material available here included a Harvard specimen from *Iisaka* labelled as a gift from *Iimori*; a Harvard specimen and a U. S. National Museum specimen from *Wodgina*, the latter a gift from *Simpson*; and four specimens from the *Harvard* and *O. I. Lee* collections from *Baringer Hill*, Texas, all of which answered the description but none of which is known to be type material.

\* Material examined in the present study.

between uranoan thorite and the weathered feldspathic matrix, and locally grades into the glassy black thorite from which it has been derived. The thorogummite from Baringer Hill, Texas, is found as dull gray-green pseudomorphs after thorite and locally encloses glassy residuals of metamict black thorite. The thorogummite from Manchuria also seems to be a pseudomorph after thorite. Metamict thorite from Jamestown, Colorado, has altered to a weakly birefringent, hydrated substance that was tentatively identified by Phair and Shimamoto (1952) as hydrothorite, and a similar alteration has been observed in metamict thorite from California (George, 1951) and other places.

## X-RAY AND OPTICAL DATA

All of the thorite-like substances listed in Table 1 for which specimens were available, except pilbarite, were found to give an identical x-ray pattern for unheated material. This pattern is virtually identical with that of tetragonal  $\text{ThSiO}_4$ , thorite. The  $\text{ThSiO}_4$  samples used for comparison were prepared by sintering coprecipitated  $\text{ThO}_2$  and  $\text{SiO}_2$  with  $\text{NaCl}$  in air at  $1000^\circ\text{C}$ ., and by heating coprecipitated  $\text{ThO}_2$  and  $\text{SiO}_2$

TABLE 2. X-RAY POWDER SPACING DATA FOR THOROGUMMITE, BARINGER HILL, TEXAS. INDEXING FOR TETRAGONAL CELL WITH  $a_0=7.068\text{ \AA}$ ,  $c_0=6.260\text{ \AA}$ ,  $c_0/a_0=0.8857$ . COPPER RADIATION, NICKEL FILTER. CORRECTED FOR FILM SHRINKAGE

I	d(meas.)	d(calc.)	hkl	I	d(meas.)	d(calc.)	hkl
9	4.695	4.686	011	2	1.379	1.379	431
10	3.537	3.534	200	3	1.326	1.326	224
4	2.821	2.821	121	2	1.267	1.267	152
6	2.653	2.653	112	4a	1.172	1.171	044
3	2.499	2.499	220	1a	1.130	1.130	532
$\frac{1}{2}$	2.336	2.343	022	2	1.112	1.112	244
4	2.203	2.205	031	$\frac{1}{2}$ a	1.088	1.087	541
4	2.000	2.001	013	$\frac{1}{2}$ a	1.055	1.052	622
3	1.869	1.871	321	$\frac{1}{2}$ a	1.039	1.039	631
6	1.818	1.819	312	1b	1.021 to 1.013	1.011	415
1	1.767	1.767	400	3a	0.976	0.976	444
1	1.740	1.741	123	2b	0.953 to 0.951	0.952	552
1	1.653	1.653	411	3a	0.908	0.909	624
1	1.582	1.580	420	a	0.888	0.884	800
1	1.565	1.565	004	c	0.833	0.831	644
2	1.469	1.470	332	c	0.807	0.805	662
3	1.431	1.431	024	c	0.791	0.790	840

a = diffuse line; b = diffuse line, possibly a doublet; c = broad bands centering as given, relative intensity uncertain.

with  $\text{ThF}_4$  and water in a steel bomb at  $240^\circ \text{C}$ . The pattern of the natural thorite-like minerals was completely indexed in terms of a tetragonal cell identical with that of  $\text{ThSiO}_4$ , and with almost the same cell dimensions. The  $x$ -ray powder data are given in Table 2. Similar cell dimensions have been obtained by others on natural, nonmetamict thorite, as shown in Table 3.

Four specimens of ordinary, coarsely crystallized isotropic thorite from pegmatites also were examined by  $x$ -rays. Unheated samples of the Hybla material described by Ellsworth (1927) gave a few very faint and diffuse thorite lines, and two different specimens from Arendal, Norway, gave no pattern at all. Glassy yellow crystals from Ambatofotsikely, Madagascar, gave no pattern; but yellow, opaque material veining the crystals gave a

TABLE 3. TETRAGONAL UNIT CELL DIMENSIONS OF THORITE AND THOROGUMMITE

$a_0$ (Å)	$c_0$ (Å)	Material	Locality	Reference
7.03	6.25	Thorite	Nettuno, Sicily	Bonatti and Gallitelli (1951)
7.08	6.28	Thorogummite	Manchuria	Henmi (1951)
7.12	6.32	Uranothorite	New Zealand	Pabst (1951)
7.068	6.260	Thorogummite	Texas	Present study
7.117	6.295	$\text{ThSiO}_4$	Synthetic	Present study

sharp thorite pattern for unheated material. Pabst (1952) also has noted that an unheated thorite from Madagascar gave an  $x$ -ray pattern. The behavior of these metamict thorites on heating is described below. The very faint diffraction patterns given by some isotropic, glassy, pegmatitic thorite (and zircon) crystals are conventionally attributed to residual order.

None of the substances listed in Table 1 had to be heated in order to give a good  $x$ -ray pattern. The thorogummite from Baringer Hill, Easton, and Wodgina was seen under oil immersion to be microcrystalline. Most of the material is barely resolved as formless birefringent specks, but some minute rods that have parallel extinction can be distinguished. Hyblite, hydrothorite, and the Japanese thorogummite were sensibly isotropic, although some grains of hyblite showed weak birefringence presumably due to strain or to parallel aggregation of submicroscopic crystallites. The thorogummite from Manchuria is described by Henmi (1951) as birefringent in part. The mean index of refraction of all samples was low and variable but increased when the samples were heated, presumably due to loss of water. Similar observations have been made by

others (Pabst, 1952; Larsen, 1921) both on supposed thorite proper and on alteration products.

## CHEMISTRY

The pertinent chemical analyses are listed in Table 4. The empirical formulas derived by the original authors are given in Table 5. The ratio of

TABLE 4. CHEMICAL ANALYSES OF THOROGUMMITE AND RELATED SUBSTANCES

	1	2	3	4	5	6	7	8
ThO <sub>2</sub>	41.44	24.46	25.05	57.79	45.30	24.72	21.20	
ZrO <sub>2</sub>			4.78		0.88		0.05	47.82
UO <sub>3</sub>	22.43	37.33	7.91	2.98			18.63	
UO <sub>2</sub>					22.40	35.60		
(Ce, La) <sub>2</sub> O <sub>3</sub>	6.69	0.12	0.57	0.24	tr.	0.10	0.08	1.42
(Y, Er) <sub>2</sub> O <sub>3</sub>		0.32	12.19	0.73	1.86	0.25	9.47	
CaO	0.41	1.62	0.95	1.65	0.59	1.28		4.72
MgO		0.16		0.60	0.10	0.15		0.17
PbO	2.16	7.78	tr.	1.25	3.74	7.90	0.17	
Al <sub>2</sub> O <sub>3</sub>	0.965		2.22	0.88			8.84	0.71
Fe <sub>2</sub> O <sub>3</sub>	0.845		8.67				2.84	1.56
SiO <sub>2</sub>	13.085	15.30	21.10	15.77	13.90	16.19	14.43	28.84
P <sub>2</sub> O <sub>5</sub>	1.19		1.77	1.33	0.67		2.63	
H <sub>2</sub> O+	7.88	8.37	10.80	6.06	4.31	12.04	7.82	1.56
H <sub>2</sub> O-	1.23	4.19		9.12	0.50	0.88	5.61	8.52
Rem.		0.40	4.48	1.50	2.25	0.94	8.28	4.69
Total	98.325	100.05	100.49	99.90	96.50	100.05	100.05	100.01
Sp. gr.	4.43- 4.54	4.13	3.26- 3.31		5.361- 5.438	4.31- 4.45		3.76

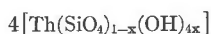
1. Thorogummite, Baringer Hill, Texas. Hidden and Mackintosh (1889). Atomic weight of rare earths given as 135.
2. Thorogummite (nicolayite). Wodgina, Western Australia. Simpson (1930). Remainder is (Nb, Ta)<sub>2</sub>O<sub>5</sub> 0.40.
3. Thorogummite, Iisaka, Japan. Iimori and Hata (1938). Remainder is (Nb, Ta)<sub>2</sub>O<sub>5</sub> 0.40, MnO 0.35, (As, Sb)<sub>2</sub>O<sub>3</sub> 0.32, CO<sub>2</sub> 3.01.
4. Hydrothorite, Wodgina, Western Australia. Simpson (1927). Remainder is CO<sub>2</sub> 1.50.
5. Mackintoshite, Baringer Hill, Texas. Hidden and Hillebrand (1893). Remainder is K<sub>2</sub>O 0.42, (Na, Li)<sub>2</sub>O 0.68, FeO 1.15.
6. Maitlandite, Wodgina, Western Australia. Simpson (1930). Remainder is (Nb, Ta)<sub>2</sub>O<sub>5</sub> 0.67, MnO 0.07, FeO 0.20. Another partial analysis is cited by Simpson.
7. Thorogummite, Haicheng Prefecture, South Manchuria. Yosimura and Yamada analysis in Henmi (1951). Remainder is BeO 0.16, SnO<sub>2</sub> 0.31, Nb<sub>2</sub>O<sub>5</sub> 7.81.
8. Zircon (cyrtolite), Karelia, U.S.S.R. Kostyleva (1946). Remainder is TiO<sub>2</sub> 0.02, HfO<sub>2</sub> 1.70, U<sub>3</sub>O<sub>8</sub> 1.27, MnO 0.11, Na<sub>2</sub>O 0.59, K<sub>2</sub>O 0.28, SO<sub>3</sub> 0.72.

TABLE 5. FORMULAS OF THORITE-LIKE MINERALS

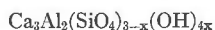
Analysis no.	Oxide ratios of original authors	Atomic ratios referred to thorite-type formula
1	3ThO <sub>2</sub> · UO <sub>3</sub> · 3SiO <sub>2</sub> · 3H <sub>2</sub> O	[Th <sub>1.34</sub> U <sub>0.66</sub> Ce <sub>0.32</sub> Al <sub>0.22</sub> Fe <sub>0.13</sub> Ca <sub>0.09</sub> Pb <sub>0.12</sub> ](SiO <sub>4</sub> ) <sub>2.60</sub> (PO <sub>4</sub> ) <sub>0.31</sub> ((OH) <sub>1</sub> ) <sub>0.14</sub> ]. <sub>4.21</sub>
2	3ThO <sub>2</sub> · 4UO <sub>3</sub> · 2(Pb, Ca)O · 8SiO <sub>2</sub> · 21H <sub>2</sub> O	[Th <sub>1.25</sub> U <sub>1.75</sub> Ce <sub>0.01</sub> Y <sub>0.04</sub> Ca <sub>0.30</sub> Mg <sub>0.02</sub> Pb <sub>0.47</sub> Nb <sub>0.04</sub> ](SiO <sub>4</sub> ) <sub>2.43</sub> ((OH) <sub>1</sub> ) <sub>0.50</sub> ]. <sub>4.43</sub>
3	(ThO <sub>2</sub> , UO <sub>3</sub> , Y <sub>2</sub> O <sub>3</sub> , etc.) · SiO <sub>2</sub> · 2H <sub>2</sub> O	
4	ThO <sub>2</sub> · SiO <sub>2</sub> · 4H <sub>2</sub> O	[Th <sub>2.79</sub> U <sub>0.21</sub> Ce <sub>0.02</sub> Y <sub>0.08</sub> Ca <sub>0.37</sub> Mg <sub>0.32</sub> Pb <sub>0.07</sub> Al <sub>0.22</sub> ](SiO <sub>4</sub> ) <sub>3.34</sub> (PO <sub>4</sub> ) <sub>0.24</sub> ((OH) <sub>1</sub> ) <sub>0.09</sub> ]. <sub>3.67</sub>
5	3ThO <sub>2</sub> · UO <sub>3</sub> · 3SiO <sub>2</sub> · 3H <sub>2</sub> O	[Th <sub>1.96</sub> U <sub>0.96</sub> Zr <sub>0.08</sub> Y <sub>0.19</sub> Ca <sub>0.12</sub> Mg <sub>0.03</sub> Fe <sub>0.18</sub> Pb <sub>0.19</sub> K <sub>0.10</sub> Na <sub>0.25</sub> ](SiO <sub>4</sub> ) <sub>2.44</sub> (PO <sub>4</sub> ) <sub>0.31</sub> ((OH) <sub>1</sub> ) <sub>0.71</sub> ]. <sub>3.46</sub>
6	3ThO <sub>2</sub> · 4UO <sub>3</sub> · 2(Pb, Ca)O · 8SiO <sub>2</sub> · 23H <sub>2</sub> O	[Th <sub>1.28</sub> U <sub>1.71</sub> Ce <sub>0.01</sub> Y <sub>0.03</sub> Ca <sub>0.21</sub> Mg <sub>0.08</sub> Fe <sub>0.04</sub> Pb <sub>0.49</sub> Mn <sub>0.01</sub> Nb <sub>0.07</sub> ](SiO <sub>4</sub> ) <sub>2.43</sub> (OH) <sub>1</sub> ]. <sub>3.70</sub>
7		[Th <sub>0.48</sub> U <sub>0.52</sub> Zr <sub>0.002</sub> Sn <sub>0.02</sub> Nb <sub>0.46</sub> Y <sub>0.66</sub> Ce <sub>0.002</sub> Al <sub>1.37</sub> Fe <sub>0.25</sub> Pb <sub>0.01</sub> Be <sub>0.08</sub> ](SiO <sub>4</sub> ) <sub>1.90</sub> (PO <sub>4</sub> ) <sub>0.29</sub> ((OH) <sub>1</sub> ) <sub>0.27</sub> ]. <sub>4.26</sub>

SiO<sub>2</sub> to the sum of RO<sub>2</sub>, R<sub>2</sub>O<sub>3</sub>, etc., ranges from virtually 1:1 to about 3:4, with water regarded as essential in all instances. As the x-ray work shows that all of the substances are isostructural with anhydrous ThSiO<sub>4</sub>, with SiO<sub>2</sub>:RO<sub>2</sub>=1:1, the departure from the ideal thorite formula must be explained on crystallochemical grounds. The principal problem is to account for the presence of water and for the diminished ratio of SiO<sub>2</sub>. It may be assumed that the apparent deficiency of Si is due to a substitution of (OH)<sub>4</sub> for (SiO<sub>4</sub>). To test this, the cations were calculated to a total of 4, the ideal unit cell contents of thorite being Th<sub>4</sub>(SiO<sub>4</sub>)<sub>4</sub>. Enough O was then assigned to Si to make SiO<sub>4</sub> and to P or S (when present) to make PO<sub>4</sub> or SO<sub>4</sub>, and (OH)<sub>4</sub> was then calculated in the amount needed to balance the remaining charge of the cations. The test of agreement with the thorite type of formula is that the sum of SiO<sub>4</sub>, PO<sub>4</sub>, SO<sub>4</sub>, and (OH)<sub>4</sub> is 4, or that (OH)+O=16. This is a stringent test because all of the analytical error is thrown into the (OH). The atomic ratios derived in this way are given in Table 5.

Analyses 1 and 2 are the best of those available. The calculated cation to anion ratios are 1:1.05 and 1:1.12, respectively, indicating that these substances conform to a thorite-type formula in which an omission of (SiO<sub>4</sub>)<sup>-4</sup> is balanced by a substitution of (OH)<sub>4</sub><sup>-4</sup>. The mechanism of compositional variation may be formulated in terms of the ideal unit cell contents as



with  $x=1.31$  in the Baringer Hill material of analysis 1 and  $x=0.99$  in the Wodgina material of analysis 2. This general mechanism has already been identified in the so-called hydrogarnets by Flint and others (1941), Pabst (1942), and Hutton (1943), in which an isostructural series conforming to the formula



extends from grossularite, Ca<sub>3</sub>Al<sub>2</sub>(SiO<sub>4</sub>)<sub>3</sub>, through hibschite to calcium aluminate, Ca<sub>3</sub>Al<sub>2</sub>(OH)<sub>12</sub>. Griphite is a phosphate that shows the same mechanism (McConnell, 1942).

In both analyses 1 and 2 only part of the available H<sub>2</sub>O+(110°) is required for valence compensation. The water content of the derived formulas (Table 5) is 4.11 and 2.95 per cent, respectively. The point +110° is a wholly arbitrary limit for essential water. The thermal data described below indicate that a considerable amount of water is lost at not much higher temperatures and this may well be nonessential. The large and variable content of nonessential water and the fine-grained to earthy nature of some of the substances make the measured specific gravities uncertain; the calculated values are higher.

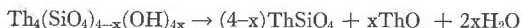
The remaining analyses conform to a thorite-type formula, but less closely. Analysis 3 has been disregarded because the large content of  $\text{CO}_2$  and other evidence indicates that the sample contains much impurity. The material of analysis 4 was stated to contain about 10 per cent impurities; here only the  $\text{CO}_2$  was disregarded. Analysis 7 probably contained admixed fergusonite,  $\text{YNbO}_4$ , according to Henmi (1951). Analysis 5 has a very low summation. Both analyses 5 and 6 show an anion deficiency after valence compensation of the cations is effected, and in analysis 6 not only is no  $(\text{OH})_4$  required but a small amount of  $(\text{OH})$  must be calculated as  $\text{Si}(\text{O}, \text{OH})_4$ . The anion deficiency of these analyses would be remedied if a small amount of the U reported as  $\text{U}^4$  were present as  $\text{U}^6$ . It also may be noted that the requirement of  $(\text{OH}) + \text{O} = 16$  is satisfied if  $(\text{H}_2\text{O})_4$  is assigned to the vacant anion positions.

The substitution of  $(\text{PO}_4)$  for  $(\text{SiO}_4)$  in the thorite structure type is well known, with  $\text{Si}:\text{P} = 1:0.8$  in the auerlite variety of thorite and  $\text{Si}:\text{P} = 1:0.2$  in the yamaguchilite variety of zircon. Xenotime,  $\text{YPO}_4$ , an isotype of thorite, has been reported to contain  $(\text{SO}_4)$ ; and the unanalyzed hyblite of the present study was found qualitatively by Ellsworth (1927) to contain  $(\text{SO}_4)$ .

Roughly four dozen analyses of thorite have been reported in the literature. It is frequently impossible to tell from the description whether the material was the original (metamict) thorite or a crystalline alteration product like that discussed here. Most analyses show a deficiency of Si together with more than enough water to effect the mechanism  $(\text{SiO}_4) = (\text{OH})_4$ . The question whether primary thorite may contain essential  $(\text{OH})$  remains open.

#### THERMAL DATA

Thermal study indicates that the  $\text{H}_2\text{O} + (110^\circ)$  reported in these thorite-like minerals is, at least in part, essential and is retained presumably as  $(\text{OH})$  until it reaches high temperatures. Simpson (1927) found that the hydrothorite of analysis 4 lost 9.12 per cent  $\text{H}_2\text{O}$  at  $100^\circ$ , about 5 per cent  $\text{H}_2\text{O}$  at  $600^\circ$ , and the remaining 1.06 per cent  $\text{H}_2\text{O}$  at about  $800^\circ$ . Differential thermal analysis of the Baringer Hill thorogummite showed a gradual loss of water at about  $150^\circ$  and an exothermic peak at  $750^\circ$ , with no further change to  $1050^\circ$ . Separate samples heated in air for 60 minutes at  $110^\circ$ ,  $470^\circ$ , and  $610^\circ$  gave a thorite x-ray pattern, as did unheated material, and the  $1050^\circ$  DTA sample gave a thorite pattern plus distinct lines of  $\text{ThO}_2$ . The thermal break at  $750^\circ$  is interpreted as loss of  $(\text{OH})$  with accompanying recrystallization to a mixture of  $\text{ThSiO}_4$  and  $\text{ThO}_2$ , as follows





Another sample of Baringer Hill thorogummite that differed from typical material in its wholly isotropic nature and yellow color gave a DTA curve with a low broad exothermic peak at about  $575^{\circ}$  instead of  $750^{\circ}$ . Samples of hydrothorite and thorogummite from both Wodgina and Baringer Hill showed a mixture of tetragonal  $\text{ThSiO}_4$  and  $\text{ThO}_2$  when heated for 30 minutes in air at  $1000^{\circ}$ . The hydrothorite that has the lower content of  $(\text{OH})_4$  showed the less amount of  $\text{ThO}_2$ .

Differential thermal analyses also were made of two metamict thorite crystals from Arendal and of one from Hybla. These all showed a gradual loss of water at  $100^{\circ}$  to  $225^{\circ}$  and a sharp single exothermic break at  $875^{\circ}$  to  $880^{\circ}$  due to crystallization. Separate samples of these proved to be still metamict when heated in air at  $470^{\circ}$  and  $610^{\circ}$ , but at  $920^{\circ}$  a faint  $\text{ThO}_2$  pattern appeared. The  $1050^{\circ}$  DTA samples gave patterns with lines of both  $\text{ThO}_2$  and the monoclinic polymorph of  $\text{ThSiO}_4$ , huttonite. Normal crystalline  $\text{ThSiO}_4$  and  $\text{ZrSiO}_4$  gave DTA graphs without breaks. Microcrystalline thorogummite and metamict thorite react differently when heated to  $1000^{\circ}$ ; the former develops the tetragonal, the latter the monoclinic polymorph of  $\text{ThSiO}_4$ .  $\text{ThO}_2$  also is formed in both cases. It is formed in relatively larger amounts when metamict thorite is heated, and here too it may be ascribed to crystallization from a  $(\text{SiO}_4)$ -deficient matrix. The Hybla material, for which a superior analysis is available (Ellsworth, 1927), has a cation to Si ratio of 1:0.945. The conventional explanation for the appearance of  $\text{ThO}_2$  or  $\text{ZrO}_2$  on heating metamict thorite or zircon is that an equivalent amount of  $\text{SiO}_2$  remains unreacted and amorphous and does not give an x-ray pattern.

#### ZIRCON

Zircon is isostructural with thorite and, at least in synthetic material made at a high temperature by sintering the mixed oxides with  $\text{SiO}_2$ , forms a complete series with that substance. Zircon often alters chemically, especially when it contains U, Th, Pb, and cations of valence lower than four. It is then characterized by the presence of 10 to 12 per cent of water and by a deficiency of silica. These features provide grounds for suspecting the existence of an  $(\text{OH})_4 = (\text{SiO}_4)$  substitution such as that indicated for thorite. It also is found that many altered zircons, especially the reddish-brown crystals with curved faces commonly termed cyrtolite, are microcrystalline, pseudomorphous, recrystallization products of metamict zircon. George (1949) has noted the microcrystalline granular to fibrous structure of cyrtolite. A cauliflower-like aggregate of cyrtolite crystals from a pegmatite at Hybla, Ontario, was examined here in some detail. The outer parts of the crystals are dull and are composed of an aggregate of microscopic crystalline grains with a variable amount of an

isotropic groundmass. This material grades inwardly into veins between residual areas of clear metamict zircon on both a macroscopic and a microscopic scale. It locally follows lineage boundaries or cracks, as shown in Figure 1, and sometimes particular growth zones are strongly affected. Unheated samples of the recrystallized portions gave a strong  $x$ -ray pattern of zircon. A DTA curve of material containing about 15 per cent of metamict material showed a gradual loss of water at  $100^{\circ}$  to  $225^{\circ}$ , a broad exothermic peak at  $460^{\circ}$  to  $550^{\circ}$ , and a single sharp peak at  $880^{\circ}$  due to crystallization of the metamict material. Kulp, Volchok, and Holland (1952) obtained a similar curve on metamict zircon from Hybla and Bedford, N. Y., except that, as in other metamict zircons examined by them, they obtained a distinct double peak at  $890^{\circ}$  to  $910^{\circ}$ .

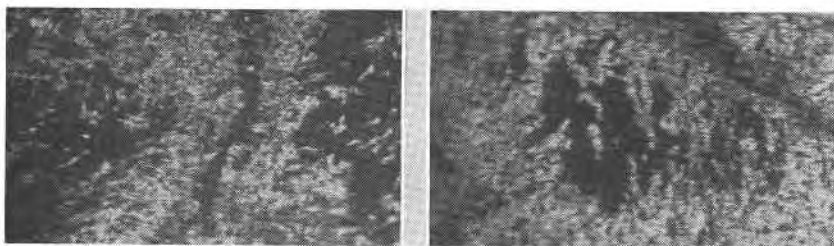
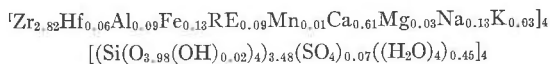


FIG. 1. Thin sections of Hybla cyrtolite crystals showing secondary zircon developed along an open crack and embaying a residual area of metamict zircon. Crossed nicols,  $\times 60$ . The dark isotropic areas are metamict. The recrystallized areas are a mosaic of isolated grains of irregular and sometimes elongate or vermicular shape. These areas extinguish uniformly, but  $x$ -ray Laue photographs taken through them show disorientation effects.

The only metamict zircon for which an analysis and  $x$ -ray, dehydration, and thermal data are available is a cyrtolite from northern Karelia described by Kostyleva (1946) (analysis 8, Table 4). This material had  $a_0 = 6.455 \text{ \AA}$ ,  $c_0 = 5.938$ , and sp. gr. 4.14 after ignition (3.76 unheated). The dehydration curve showed a gradual loss of 5.22 per cent  $\text{H}_2\text{O}$  up to  $200^{\circ}$ , where there was a slight inflection, a gradual loss of 4.78 per cent  $\text{H}_2\text{O}$  from  $200^{\circ}$  to  $600^{\circ}$  where there was a slight inflection, and a gradual loss of the remaining 1 to 1.5 per cent  $\text{H}_2\text{O}$  from  $600^{\circ}$  to  $1000^{\circ}$ . The DTA curve showed a single recrystallization break at  $860^{\circ}$ . Above  $600^{\circ}$  the water is regarded by Kostyleva as essential and required for valence compensation in the structure. If the 1.27 per cent  $\text{U}_3\text{O}_8$  is disregarded as due to admixture, and if Al, Fe, and S are reckoned in four-coordination with Si, then (Zr, Hf, RE, Ca, Mg, Mn, Na, K):(Si, Al, Fe, S) = 1:1 and a substitution of (OH) for O in the  $(\text{XO}_4)$  tetrahedra is required. Each (OH) would nullify a Si-O-cation bond and, as Kostyleva recognizes, make the

crystal prone to metamictization. If the Al and Fe are reckoned with the cations then there is a deficiency of  $(\text{XO}_4)$ ; a small substitution of  $(\text{OH})$  as  $\text{Si}(\text{O}, \text{OH})_4$  is still required but no  $(\text{OH})_4$ , and the summation of  $(\text{XO}_4)$  is only 3.55. Possibly  $(\text{H}_2\text{O})_4$  is present in the 0.45 anion vacancies, and the formula then becomes:



This formula gives a total water content of 5.27 per cent, 0.18 from  $\text{Si}(\text{O}, \text{OH})_4$  and 5.09 from  $(\text{H}_2\text{O})_4$ . If the U is regarded as essential then  $(\text{OH})_4$  is required.

The water characteristically present in metamict substances is generally disregarded as nonessential and due to alteration, but it now seems that its role might be fundamental. This matter and that of the natural recrystallization of metamict material, as in thorogummite and cyrtolite, with its implication of the readjustment of the original composition, also bear on the use of thorite and zircon in geologic age studies by thermal, x-ray and chemical methods.

#### ACKNOWLEDGMENTS

The writer wishes to express his appreciation to Dr. Arthur Montgomery of Lafayette College, Dr. S. E. Clabaugh of the University of Texas, and the late Mr. O. I. Lee of Jersey City, N. J., for the loan of specimens. This work was done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

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