

X-RAY EXAMINATION OF URANOTHORITE

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ABSTRACT

Earlier x -ray studies of thorite have indicated that it is metamict (Vegard, 1916) or have led to cell dimensions (Boldyrev, 1938) that seem out of line with those of related materials.

Single crystal x -ray diffraction patterns have been obtained from unaltered uranothorite from Gillespie's Beach, South Westland, New Zealand. Rotation patterns on the a and c axes are very similar to zircon patterns but show a certain amount of streaking along "powder arcs." A cell of dimensions a_0 7.12 Å, c_0 6.32 Å contains 4ThSiO_4 . Th is substituted by U in the ratio of about 1/7. Observed and calculated densities agree at 6.7 ± 0.05 . The space group is $D_{4h}^{19} - I4/amd$. The similarity of the rotation patterns to those of zircon leaves no doubt that the structure of this uranothorite is of the $H3$ (zircon) type.

MATERIAL

Through the courtesy of Professor C. O. Hutton of Stanford University the writer received some single crystals of uranothorite for x -ray study. This uranothorite consists of minute detrital grains concentrated from sand of Gillespie's Beach, South Westland, New Zealand. It has recently been described and pictured by Hutton (1950). The material available for study comprised about a score of small rough prismatic crystals, closely resembling Hutton's Fig. 47, Plate 3. The largest of these was about 0.18 by 0.10 millimeter. The total weight of the sample was less than half a milligram.

X-RAY EXAMINATION

Rotation patterns were made from three crystals. These included c axis patterns from two crystals and an a axis pattern from another. Calibration of the films was obtained by photographing the c axis zero layer line of quartz on the same film between the zero and first layer lines of the specimen being examined.¹ All patterns were made with Cu radiation, filtered by Ni, in a camera of 57.3 mm. diameter.

As may be seen from Fig. 1 (top) the patterns are closely similar to those obtained from zircon. The differences are of two sorts. All spots on the uranothorite patterns are closer to the center due to the greater cell dimensions. Spots on all uranothorite patterns are streaked along "powder arcs." They are not broadened or frayed. High intensities are observed even at large angles. This suggests a disorientation of mosaic

¹ This is easily accomplished in a Weissenberg camera by replacing the beam catcher with the layer line screen set for the zero level, displacing the camera parallel to the rotation axis about half the distance between the zero and first layer lines of the material under study and recording a quartz c axis pattern with this screening.

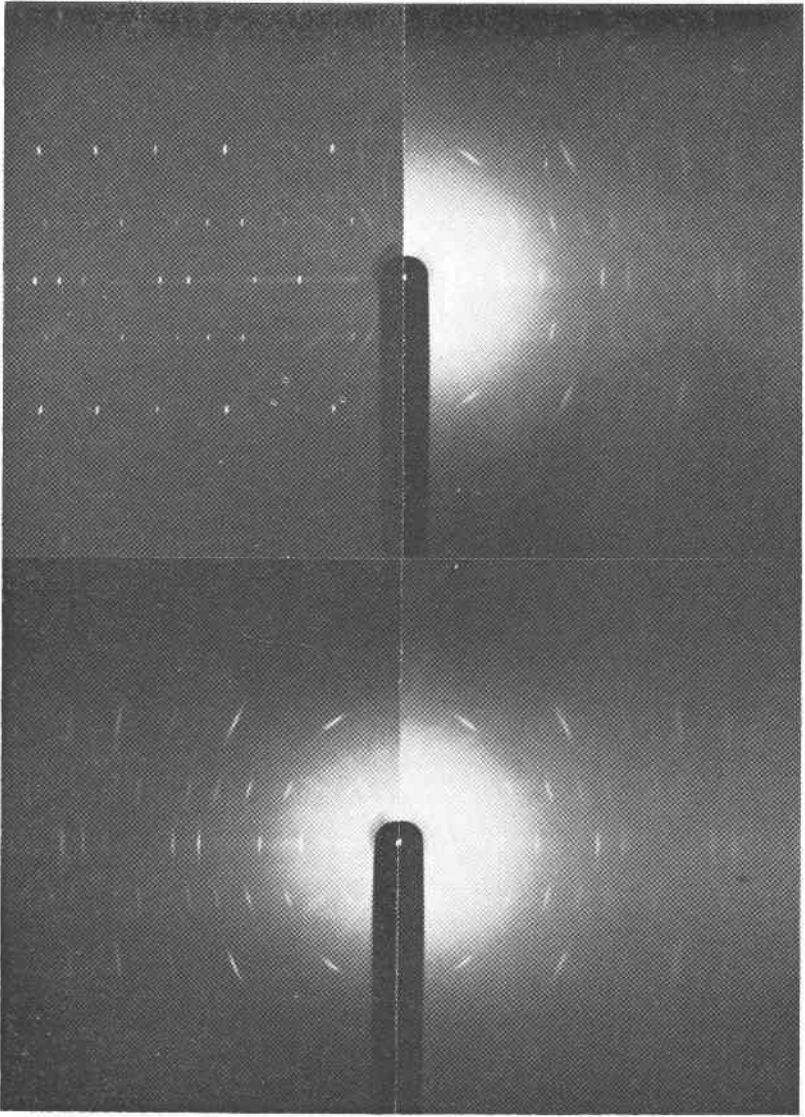


FIG. 1. *c* axis rotation patterns

Top left

Zircon, near Lincoln, California

Exposure 2 hours

Bottom left

Same crystal as used for top right after heating to 850° for 75 minutes.

Exposure 20 hours

Top right

Uranothorite, Gillespie's Beach, S. Westland, N. Z.

Exposure 25 hours

Bottom right

Same as above.

blocks more or less uniformly distributed over a small angular range.

The cell dimensions, taking $\text{CuK}\alpha$ as 1.542 Å, derived from these patterns are:

$$a_0 7.12 \pm 0.03 \text{ \AA}$$

$$c_0 6.32 \pm 0.03 \text{ \AA}$$

The space group, indicated by systematic extinctions, is $D_{4h}^{19} - I4/amd$, the same as for zircon. The close correspondence in the intensities of all observed diffraction spots to those of zircon leaves no doubt that the structure is of the same type, $H3$.

Table 1 shows the results of a calculation of the cell content. The analysis there quoted was "recalculated to 100% after eliminating

TABLE 1. CELL CONTENT OF URANOTHORITE

	A		B		C	
	Wt%	Cell Content	Wt%	Cell Content	Wt%	Cell Content
Pb	0.47	0.03				
UO ₂	11.5	0.55	12.3	0.59		
ThO ₂	62.6	3.06	67.9	3.32	81.5	4.00
CeO ₂	1.1	0.08	1.2	0.09		
Fe ₂ O ₃	2.3	0.18				
CaO	0.3	0.07				
MgO	0.3	0.10				
SiO ₂	19.5	4.20	18.6	4.00	18.5	4.00
H ₂ O -	0.25	1.38				
H ₂ O +	1.68					
	100.00					
	G _{obs.} 6.7 ± 0.05 Uranothorite, Gillespie's Beach, South Westland, N.Z. Analyst F. T. Seelye, Hutton (1950)		G _{calc.} 6.70 4(Th, U, Ce)SiO ₄		G _{calc.} 6.72 4ThSiO ₄	

zircon, scheelite, ilmenite and 1.83% of undetermined material." The density given with the analysis and used in the cell content calculation is not that previously published with the analysis (Hutton 1950, Table 11, column A). It is a value determined by micropycnometer "using approximately 8 mgm. portions of pure uranothorite" (Hutton 1950, p. 678) and stated by Hutton (private communication, August 12, 1950) to be preferable to the lower figure previously published with this analy-

sis which was determined on the analyzed material including the impurities mentioned above.

The cell content obtained from the analysis suggests that this uranothorite, aside from being contaminated, has an excess of SiO_2 or a deficiency of ThO_2 and substituents. A similar departure from the ideal proportions has been found in many other thorites, which, however, are metamict and contain much more water. The observed density agrees within the limits of error with the density calculated for an ideal uranothorite of the observed cell dimensions with the proportions of Th/U/Ce indicated by the analysis (Table 1, column *B*) or with the ideal composition ThSiO_4 (Table 1, column *C*).

COMPARISON WITH PREVIOUS WORK

The isomorphism of thorite with zircon has long been recognized but crystals of thorite suitable for precise goniometric measurement have not been found. The axial ratio usually quoted for thorite, $a:c=1:0.6402$, nearly the same as for zircon, $a:c=1:0.6404$, is based on "measurement of two crystals of orangeite" "made with a common goniometer" by E. Zschau, and reported by him in a letter to G. J. Brush.² Measurements were given to $\frac{1}{4}^\circ$. The axial ratio corresponding to the cell dimensions here reported is $a_0:c_0=1:0.888=1:0.628\sqrt{2}$, the structural cell being turned 45° from the usual morphological setting. This corresponds to a difference from the angles measured by Zschau of about $\frac{1}{2}^\circ$. One of the crystals examined gave measurable reflections from prism and pyramid faces but due to the small size and roughness of the crystal an uncertainty of at least $\frac{1}{2}^\circ$ attached to the measurement.

X-ray observations on thorite have previously been reported by Vegard (1916) and by Boldyrev (1938). Vegard obtained only very weak and diffuse diffraction effects as was to be expected from the metamict material he examined. He reported no cell dimensions.

Boldyrev published a powder pattern of thorite from "Lövö, Lange-sundfjord in Norway" with the comment "This pattern has only the lines with rather weak intensity as consequence of transformation of nearly whole mass of mineral to metamict state i.e. isotropic state of secondary origin." Nevertheless he indexed the pattern and derived the cell dimensions a_0 6.315, c_0 5.667. The writer has previously pointed out (Pabst and Hutton, 1950) that these dimensions "are to be regarded with some reserve" because such a cell would have a much smaller volume than might be expected from a knowledge of the cell volumes of zircon and of the newly recognized monoclinic thorium silicate, huttonite (Pabst and Hutton, 1950). No powder pattern was prepared from the

² Sixth supplement to Dana's Mineralogy, *Am. J. Sci.*, **26**, 359 (1858).

TABLE 2. POWDER PATTERNS OF NATURAL THORIUM SILICATES

Uranothorite, New Zealand (calculated)			Thorite, Norway (quoted from Boldyrev, 1938)			Huttonite, New Zealand (amplified from Pabst and Hutton, 1950)		
<i>I</i>	<i>d</i> _{calc.}	<i>hkl</i>	<i>I</i>	<i>d</i>	<i>hkl</i>	<i>I</i>	<i>d</i> _{obs.}	<i>hkl</i>
st.	4.73	011				3	5.29	$\bar{1}01$
						5	4.71	011
						6	4.23	$\bar{1}11$
v.st.	3.56	200				4	4.08	101
						4	3.53	111
						6	3.29	200
			1	3.141	200	8	3.09	120
m.-st.	2.84	121	3	2.855	120, 002	3	2.98	210
st.	2.68	112				7	2.89	$\bar{1}12, 012$
			4	2.583	102	3	2.65	$\bar{2}02$
m.-st.	2.52	$\bar{2}20$				3	2.48	$\bar{2}12$
			1	2.233	220	1	2.44	112
st.	2.22	031				4	2.19	031
						2	2.156	$\bar{1}03, \bar{3}11$
						3	2.110	221
w.	2.020	013	1	1.984	301, 130	4	1.953	212
m.	1.874	321	2	1.882	003, 311	3	b 1.893	
						2	{ 1.857	
v.st.	1.834	312				2	1.810	
st.	1.780	040				2	1.784	
m.	1.757	123				4	b 1.749	
						2	1.692	
m.	1.667	411	3	1.665	321	2	1.646	
						3	1.603	
m.-st.	1.592	420						
w.	1.580	004	2	1.579	400			
w.	1.576	033						
w.-m.	1.482	332				3	b 1.550	
						1	1.486	
w.-m.	1.444	024				2	b 1.454	
w.	1.440	323						
			1	1.418	420			

uranthorite examined but one can calculate what it would be like with great assurance. This has been done. Table 2 shows the results of this calculation for spacings down to 1.40. It will be noted that there is little correspondence with Boldyrev's pattern. Likewise, his pattern shows no agreement with the observed pattern of huttonite. It may further be noted that the indices 120, 102, 130, 003 and 311 given by Boldyrev would be incompatible with the zircon-thorite space group. No reconciliation of these discrepancies has been found.

TABLE 3. PHYSICAL CONSTANTS OF NATURAL THORIUM SILICATES

	<i>Uranthorite</i>		<i>Huttonite</i>	
Space Group	<i>I4/amd</i>		<i>P2₁n</i>	
Cell dimensions	a_0	7.12 Å	a_0	6.80 Å
	c_0	6.32	b_0	6.96
			c_0	5.54
Cell volume	320 Å ³		299 Å ³	
Density (Obs.)*	6.7		7.1	
Refractive Indices*	α	1.818-1.825	α	1.898
	γ	1.839-1.840	β	1.900
			γ	1.922

* As determined by C. O. Hutton.

In view of the possibility that heat treatment might effect a transformation between the two natural thorium silicates whose constants are contrasted in Table 3, a crystal of uranthorite which had been used for a c -axis rotation pattern was dismantled and subjected to a temperature of 850° C. in a platinum crucible in a furnace for 75 minutes. The crystal suffered no visible change. As may be seen from Fig. 1 (bottom) no substantial changes are indicated by comparison of the patterns. If anything, the pattern of the heated material is slightly sharper. Though it is evident from this that brief heating to 850° produced no transformation it is not suggested that any firm conclusions regarding stability relations are to be drawn from this result.

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