STUDIES OF URANIUM MINERALS (VII): ZEUNERITE*

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ABSTRACT

X-ray study by the Weissenberg method on zeunerite from Tintic, Utah, gave a space group $P_4/nmm-D_{4h}{}^7$ and cell dimensions $a_0=7.13$ Å, $c_0=8.83$ Å, with $a_0:c_0=1:1.238$. The unit cell contents are $Cu(UO_2)_2(AsO_4)_2 \cdot 8H_2O$. The calculated specific gravity is 3.79; the measured specific gravity of Schneeberg material is 3.64.

Study of synthetic zeunerite indicated the existence of two and possibly three hydrates, one with 16 to $10H_2O$, one with 8 to $5H_2O$, and possibly a still lower hydrate. In this respect the synthetic material is similar to autunite and torbernite, both of which have been found in the fully hydrated form and as lower hydrates, meta I and meta II. Natural zeunerite corresponds in water content and *x*-ray structure to meta-autunite I and to synthetic zeunerite with $8H_2O$.

Variation in water content affects both the optical and the fluorescent properties of the material.

Zeunerite, from the Weisser Hirsch mine near Schneeberg, Saxony, was named and first described by Weisbach (1872, 1873, 1877). Since then the mineral has been reported (Hintze, 1931) from at least seven other localities. The only available analysis of the Schneeberg material, made by Winkler (1873), established the composition as $Cu(UO_2)_2(AsO_4)_2 \cdot 8H_2O$.

The mineral occurs as pale-green to emerald-green tetragonal crystals which usually are rectangular tablets flattened on {001}. The crystal habit closely resembles that of the isostructural mineral torbernite, $Cu(UO_2)_2(PO_4)_2 \cdot 8\text{–}12H_2O$. The poor quality of the available crystals of zeunerite from Schneeberg probably was responsible for the deviation in the later morphological measurements of Schrauf (1872) from those of Weisbach. Schrauf's elements, which correspond in unit and orientation to the *x*-ray cell found by the present author, are $a:c=1:1.250$. An angle table based on his elements is given in Table 1. Crystals from Schneeberg, described by Ježek (1922) as zeunerite, were probably torbernite; the figures he reported for indices of refraction (Table 2) and specific gravity (3.28) are lower than those found by others for zeunerite.

An *x*-ray study by the Weissenberg method (copper radiation) was made of zeunerite crystals from the Centennial Eureka mine, Tintic, Utah. The mineral occurs as tiny tablets associated with secondary copper arsenates in oxidized limonitic vein material. The forms *c*{001}, *m*{110}, *p*{021}, *s*{023}, and *v*{111} were identified on the crystals by goniometric measurements; the poor quality of the reflections did not

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warrant the derivation of new morphological elements. Rotation, zero-layer, and second-layer photographs were taken about the c axis, and rotation and zero-layer photographs were taken about the two possible choices of horizontal axes. The space group was determined as $P4/nmm = D_{4h}^7$, it being assumed that the point symmetry is tetragonal holohedral. No x-ray evidence was found for less than tetragonal symmetry. The unit cell dimensions are $a_0 = 7.13$ Å, $c_0 = 8.83$ Å, with $a_0 : c_0 = 1 : 1.238$. The unit cell contents are $Cu(UO_2)_2(AsO_4)_2 \cdot 8H_2O$. Beintema (1938) in his work on the structure of meta-autunite I, suggests that only half of the holes in the structure into which the Ca atoms can be fitted are actually occupied by Ca atoms. This explanation may also serve here and account for the fact that the chemical formula gives only one Cu atom per unit cell although the space group demands that there are two equivalent positions for the Cu atom in each unit cell. The calculated specific gravity for the composition is 3.79. The specific gravity of Schneeberg material was redetermined as 3.64. This is probably low, as the crystals contained minute air holes and some inclusions of limonite and the available sample was too small to give an accurate result. The true specific gravity is probably nearer to the calculated value than to that obtained by this measurement.

TABLE 1. ANGLE TABLE FOR NATURAL ZEUNERITE

$a:c = 1:1.250;\ p_0:r_0 = 1.250:1$

Forms	ϕ	ρ	A	$\overline{M}$
o 001	—	0°00′	90°00′	90°00′
a 010	0°00′	90 00	90 00	45 00
n 013	0 00	22 37	90 00	74 13
f 043	0 00	59 02	90 00	52 40½
p 021	0 00	68 12	90 00	48 58
i 041	0 00	78 41½	90 00	46 06

Doubtful: *m* 110, *g* 012, *s* 023, *y* 011, *v* 111.

The x-ray powder pattern data of the Tintic material is given in Table 3. Zeunerite from Schneeberg yielded identical patterns. The presence of arsenic in all the specimens examined was verified by qualitative tests. The indices of refraction, newly measured on this material together with the previously reported measurements, are summarized in Table 2. The observed variation in the indices of refraction suggests that the composition of zeunerite varies in some respects. Possibly there is isomorphous substitution of (PO_4) for (AsO_4) causing a reduction in the indices of refraction toward those of torbernite; no analytical work has been done to determine whether this is so.

Hallimond (1916, 1920) has shown that torbernite forms three different hydrates: torbernite, meta-torbernite I, and meta-torbernite II. Beintema's work (1938) gave similar information for the isostructural mineral autunite. The water content of each hydrate is in part zeolitic and variable between limits depending on the humidity and temperature. The present study of synthetic zeunerite has shown the existence of at least two, and possibly three, hydrates of the copper uranium arsenate. The synthetic material was prepared according to Winkler's (1873) method: freshly precipitated copper carbonate was dissolved in excess arsenic acid, and to this solution uranium nitrate was added, which precipitated the hydrous copper uranium arsenate in distinct but small crystals, less than 0.01 mm. in diameter. Two Penfield water determinations on the fully hydrated material gave 16 molecules of water. After standing in air overnight, the material had dehydrated to $10H_2O$ and apparently had reached equilibrium. Heating in an oven caused no further loss of water until 65° C was reached. At this temperature the material dehydrated to $8H_2O$ and stayed in equilibrium up to 85° C.

Table 2. Optical Data for Natural and Synthetic Zeunerite

All uniaxial negative (−)

	*n*O	*n*E
Natural zeunerite		
From Schneeberg*	1.647	—
From Schneeberg*	1.647	—
From Schneeberg*	1.642	—
From Schneeberg*	1.640	—
From Eureka mine, Tintic, Utah*	1.647	1.630
From Eureka mine, Tintic, Utah*	1.643	—
Majuba Hill, Nevada*	1.645	—
Hintze (1931)	1.651	1.635
Millosevich (1912)	1.629	—
Ježek (1922)	1.585	1.576 probably torbernite
Larsen and Berman (1934)	1.643	1.623
Synthetic zeunerite		
With $16H_2O$	1.602	
With $10H_2O$	1.610	
With $8H_2O$	1.645–1.648	
With $5H_2O$	1.654	

* In the Mineralogical Museum, Harvard University.

TABLE 3. INTERPLANAR SPACINGS FROM *X*-RAY POWDER PATTERNS (Å)
Cu/Ni radiation = 1.5418 Å.

Synthetic zeunerite				Natural zeunerite	
Fully hydrated (16H_2O)		Dehydrated to 8H_2O		8H_2O	
d	*I**	*d*	*I**	*d*	*I**
10.65	10	8.76	10	8.93	10
6.86	5	—	—	6.56	1
5.04	8	—	—	5.95	1
4.55	2	5.47	5	5.54	6
3.59	9	5.04	4	5.04	5
3.39	7	4.35	3	4.35	3
3.18	2	—	—	4.15	1
3.07	1	3.71	9	3.72	9
2.93	4	3.55	7	3.56	7
2.86	4	3.28	8	3.30	8
2.73	3	—	—	3.12	1
2.54	4	2.99	3	3.01	3
2.47	4	2.75	2	2.77	2
2.42	1	2.67	2	2.71	2
2.38	1	2.57	4	2.59	3
2.31	2	2.51	4	2.52	4
2.27	3	2.42	3	2.42	3
2.19	4	2.29	1	2.30	1
2.08	5	2.24	2	2.26	2
1.985	1	2.18	2	2.19	2
1.926	6	2.15	2	2.15	2
1.873	2	2.08	3	2.09	4
1.797	5	1.994	3	2.01	4
1.768	1	1.922	1	1.937	1
1.734	1	1.841	1	1.855	2
1.704	2	1.784	3	1.797	3
1.658	1	1.746	1	1.749	2
1.642	4	1.689	1	1.695	2
1.610	3	1.637	2	1.656	4
1.590	1	1.600	2	1.605	3
1.563	2	1.566	6	1.570	5
1.533	4	1.486	1	—	—
1.512	1	1.451	1	—	—
1.429	3	1.423	1	1.429	2
1.382	3	1.400	1	1.406	2
1.365	3	1.375	2	1.382	3
1.332	1	1.354	1	1.358	2
1.313	2	1.324	1	1.329	2
1.298	1	1.281	1	1.290	1
1.275	3	1.262	1	1.265	1
1.248	2	1.242	1	1.247	1
1.222	1	1.224	1	1.225	1
1.211	2	1.208	1	1.209	1
1.202	2	1.175	2	1.176	2
1.191	1	1.160	1	1.161	1
1.181	1	1.127	2	1.130	1
1.168	2	1.118	1	—	—
1.143	2	1.088	1	1.092	1
1.118	1	1.077	1	—	—
1.094	2	1.065	1	1.055	1
1.086	2				
1.060	1				

* Intensities estimated visually.

From this temperature up to 105° C the material lost water slowly but continuously and finally reached equilibrium with $5H_2O$. This hydrate, however, is not stable under atmospheric conditions; after standing in air for one day it had rehydrated to $8H_2O$. The entire dehydration process, from 16 to 5 molecules of water, took about two weeks.

Bergman (1925) dehydrated zeunerite over sulfuric acid and changed the vapor pressure by changing the concentration of the acid. He indicated the existence of at least two hydrates. From Fig. 1, which graphically represents the course of dehydration with increase in temperature, it would appear that there are four hydrates of the synthetic material. *X*-ray powder patterns for the material with 16 molecules of water and 10 molecules of water are the same. Also, the *x*-ray powder patterns (Fig. 2) for the hydrates with 8 and 5 molecules of water are

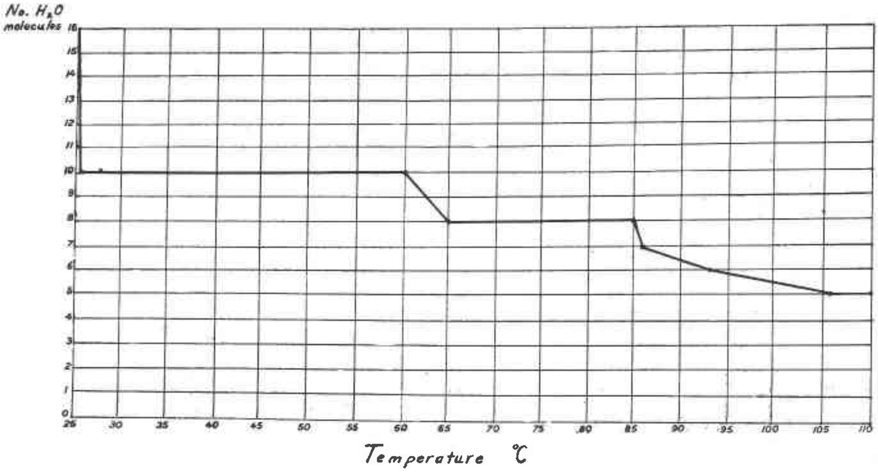

FIG. 1. Dehydration Curve for Synthetic Zeunerite.

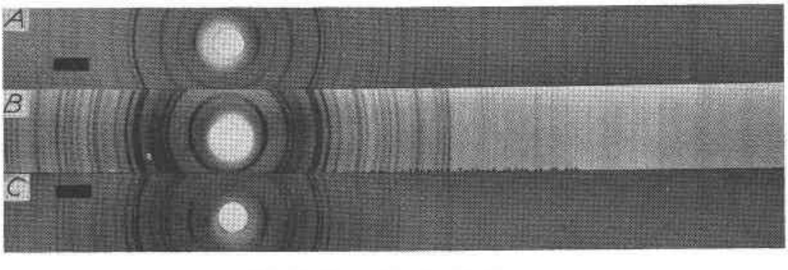

FIG. 2. *X*-ray Powder Patterns.

A. Synthetic zeunerite, fully hydrated, $16H_2O$.
B. Synthetic zeunerite, dehydrated to $8H_2O$.
C. Natural zeunerite, with $8H_2O$.

identical and are similar to the patterns of natural zeunerite, meta-autunite I, and meta-torbernite I. One sample of dehydrated material with $5H_2O$ was allowed to remain in the oven for 24 hours at 110° C. This material gave an *x*-ray powder pattern different from the others but like those of meta-autunite II and meta-torbernite II. The pattern was faint, and, although attempts were made to obtain a better one, the results could not be duplicated. All other samples with $5H_2O$ gave patterns like those of the material with $8H_2O$. It is possible that above 110° C the material will dehydrate still further, perhaps down to $2\frac{1}{2}$ molecules of water, like meta-autunite II. The copper uranium arsenate thus may occur as three hydrates, each with a water content that varies within certain limits according to temperature and humidity. Beintema found that the change from autunite to meta-autunite I was reversible under suitable atmospheric conditions. The behavior of zeunerite is somewhat different. The synthetic material with $8H_2O$ (corresponding to meta-autunite I) apparently is stable, even in a humid atmosphere (Cambridge, Massachusetts, in the summer), and natural zeunerite with $8H_2O$ failed to hydrate further after soaking in cold water for seven days.

Variation in water content of zeunerite causes a variation in the indices of refraction. The index of refraction (O) of natural zeunerite varies from 1.629 to 1.651 (see Table 2). The fully hydrated synthetic material has $n\mathrm{O} = 1.602$. With a decrease in water content to $10H_2O$, $n\mathrm{O}$ increases to 1.610. The considerable increase in $n\mathrm{O}$ to 1.645–1.648 with the loss of only two more molecules of water is consistent with the *x*-ray data which show a change in crystal structure at this point in the dehydration process (Table 3). Further dehydration to $5H_2O$ caused an increase of $n\mathrm{O}$ to 1.654. Upon standing in air the synthetic material with $5H_2O$ rehydrated to $8H_2O$ and $n\mathrm{O}$ lowered to 1.645.

Fluorescence also varies with water content. All of the natural zeunerite specimens fluoresced weakly under both long- and short-wave ultraviolet light. The fully hydrated synthetic zeunerite did not fluoresce; the air-dried material ($10H_2O$) showed faint yellow-green fluorescence under long-wave ultraviolet light; and the heated material dehydrated to $8H_2O$ fluoresced faintly yellow-green under the short-wave ultraviolet light and somewhat more strongly under the long-wave ultraviolet light. The property of fluorescence in these minerals, then, is not dependent solely upon the nature of the divalent cations, as suggested by Meixner (1940), but also upon the number of water molecules in the structure. A similar relationship of fluorescence to degree of hydration has been noted by Axelrod et al. (1951) for the minerals bayleyite and andersonite.

To be consistent with the nomenclature used in the torbernite and autunite studies, the natural mineral zeunerite might be called metazeunerite, and the possibility that a higher hydrate (true zeunerite) exists in nature as it does in the synthetic material must be considered. One hesitates, however, to set aside an established name and to assign a new name in anticipation of finding another mineral species, no matter how well grounded the reasoning behind this assignment may be.

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