

STUDIES OF RADIOACTIVE COMPOUNDS: VI— META-URANOCIRCITE¹

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ABSTRACT

Meta-uranocircite from Falkenstein, Saxony is tetragonal with a 6.96, c 16.90 Å; space group $P4/nmm$; cell contents near $2[\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}]$. A second, laboratory-prepared hydrate is tetragonal with a 6.96, c 17.57 Å; space group $P4_22$; cell contents probably $2[\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}]$ and not isostructural with autunite.

A specimen from Madagascar shows optical and structural properties which vary between those of meta-uranocircite and meta-autunite indicating that an isomorphous series exists between the two minerals.

The decrease in c with increase in ionic radius of the contained cation in the metaphosphates is thought to be due to the function of water within the hydrates. The increase in c with increase in ionic radius of the cation in the fully hydrated phosphates suggests that the cations occupy the (b) rather than the (a) positions in Beintema's structure. The stability of the fully hydrated structure increases with decrease in the ionic radius of the cation.

Meta-uranocircite is a hydrous Ba U phosphate. It is known to be one of a number of naturally occurring phosphates and arsenates with the general formula $A(\text{UO}_2)_2(\text{XO}_4)_2 \cdot n\text{H}_2\text{O}$ where A is Cu, Ca, Ba, Mg or HAl and X is As and/or P. These minerals form two structurally related groups known as the Torbernite and Meta-torbernite groups. In the Torbernites n varies zeolitically between 8 and 12 while in the Meta-torbernites n is 8 or less. For certain of the species the transition between the hydrates takes place near room temperatures and at low humidities and hence where the crystal development is poor, it is not known if the meta-types are of primary formation or are secondary dehydration products.

Beintema (1938) has pictured Ca-torbernite, that is autunite, as consisting of PO_4 tetrahedra and deformed UO_6 octahedra which are linked into two-dimensional sheets situated parallel to (001) (see Fig. 1a). The UO_6 octahedra deviate alternately upward and downward from the plane of the P atoms within the sheet and since adjacent sheets are related by a mirror plane, large cavities exist between the sheets. According to Beintema, water molecules and Ca atoms occupy the cavities. The lattice is body-centered. During the transformation to meta-autunite, the individually unchanged sheets are moved over a distance $[\frac{1}{2}\frac{1}{2}0]$ with respect to each other, permitting the sheets to lie more closely together

¹ Extracted from a thesis for the Ph.D. degree, University of Toronto 1951, entitled *A study of certain uranium-bearing minerals and compounds* by I. H. Milne.

and thus eliminating the large cavities (Fig. 1b). The lattice dimensions in the plane of the sheets remain unchanged but the distance between adjacent sheets is diminished from 10.35 to 8.47 Å. The large body-centered lattice is transformed into the two primitive lattices of meta-autunite and the *c* dimension normal to the sheets is reduced from 20.70 to 8.47 Å.

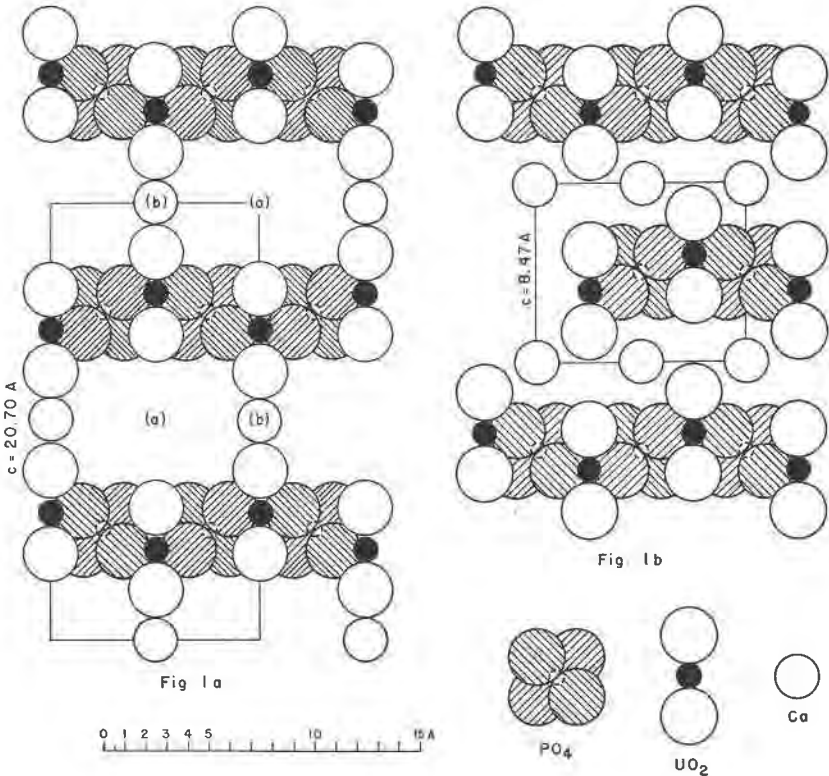


FIG. 1. The structure of autunite (1a) and meta-autunite (1b) projected on (110) (modified from Beintema, 1938). Half of the Ca positions are occupied in meta-autunite; all are occupied when the cation is monovalent.

A specimen labelled uranocircite from Falkenstein, Saxony in the form of an irregular intergrowth of yellow foliated crystals was available for this study. A spectrographic analysis kindly carried out by Mr. D. A. Moddle, Provincial Assayer for the Ontario Department of Mines, showed that the mineral consists essentially of Ba, U and P. Microchemical tests confirmed these results and indicated that the material is relatively free of calcium. The crystals although distorted, are obviously platy with a perfect cleavage parallel to the platy development. Two good cleavages at right angles to each other and normal to the platy

development are also evident. In the chosen orientation the three cleavages were later designated (001), and (100) tetragonal prismatic respectively. The mineral has a hardness of 2 and is brittle. The specific gravity was determined with the aid of Clerici's solution to be 4.08. These properties are generally in agreement with those recorded by previous writers with the exception of the specific gravity; Weissbach (1877, in Dana, 1951, p. 987) obtained a value of 3.53.

COMPOSITION

The original analysis of uranocircite by Winkler, quoted by Weissbach, indicated the formula $\text{BaO} \cdot 2\text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ or $\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$. Partial analyses by Church (1877) confirmed the water content. Fairchild (1929) produced an artificial uranocircite with 6.1 molecules of water.

Church discovered that the water content varies readily with the humidity and temperature. He found that 4 molecules are lost at low temperatures (9–16° C.) under the water vapour pressure of strong sulphuric acid, a further 2 molecules are lost at 100° C. in air and the remaining two are driven off at red heat. Beintema continued this course of investigation by preparing a dehydration curve for artificial uranocircite with water content plotted against water vapour pressure. He found three distinct hydrates stable under certain conditions of water vapour pressure. The stable conditions for these hydrates with water vapour pressure translated into per cent humidity at 20° C. are given below.

<i>Hydrate</i>	<i>Water vapour pressure</i>	<i>Humidity</i>
10H ₂ O	Above 11 mm. Hg	Above 63%
6H ₂ O	Between 1 and 5 mm. Hg	Between 6 and 20%
2H ₂ O	Below 0.5 mm. Hg	Below 3%

It is apparent that analyses of specimens will vary with the locality of the laboratory and the time of year. The usual range of 30 to 50% humidity in the average museum or laboratory would result in a hydrate with water content intermediate between 10H₂O and 6H₂O. It is therefore quite logical that Winkler's analysis and Church's partial analyses should show 8H₂O. The loss of 4H₂O as recorded by Church when the material is dehydrated over strong sulphuric acid is also compatible with Beintema's dehydration data. The vapour pressure of strong sulphuric acid (density 1.74) with respect to water at 20° C. is 0.6 mm. Hg (Hodgman 1945, p. 1878), a condition which falls in the transition range between the hydrate with 6H₂O and that with 2H₂O. Thus the product of dehydration over sulphuric acid could be expected to retain approximately 4 molecules of water after a loss of 4H₂O. A further two would be lost at 100° C. in air and the remaining two at red heat, exactly as recorded by Church.

X-RAY STUDIES

Material under atmospheric conditions

The material under atmospheric conditions may be presumed to contain approximately $8\text{H}_2\text{O}$ from a consideration of humidity and temperature conditions within the laboratory and from the chemical work of Winkler and Church.

Cleavage fragments are anisotropic as seen lying on the cleavage surface (001). Most of these plates show a "microcline type" of twinning in two directions at right angles, parallel to (100) and (010). The extinction position of individuals is not quite parallel to the twinning planes and was found to vary up to 6° to these directions. The twin lamellae all have the same index of refraction in a direction approximately 45° to the twinning planes. Small flakes showing no twinning or only a minor amount of twinning, give a good biaxial interference figure with $2E$ varying from 10 to 45° . The two indices of refraction in the plane of the plates were measured in Na light and are compared below with the optical data obtained by Larsen (1921) on material from the same locality.

	<i>Nuffield & Milne</i>	<i>Larsen</i>
$X=c$	—	1.610
Y	1.621	1.623
Z	1.622	1.623
Sign	neg.	neg.

Rotation and Weissenberg films were obtained by rotating twinned and untwinned fragments about the edge between the basal and the prismatic cleavage. Despite the biaxial optics, a geometrically tetragonal cell was obtained which showed that the fragments had been rotated about the a axis in the chosen orientation. A second set of films about the other a axis was identical with the first. It is probable that the twinning observed optically is an indication of an irregular arrangement of water molecules and does not represent a true twinning of the structure.

For comparison, single crystal x -ray films were obtained for the chemically and physically similar minerals, meta-torbernite I and meta-autunite I. Meta-torbernite from Cornwall, England has uniaxial positive optical properties. Two specimens of meta-autunite I, one from Sosa, Saxony and the other from Autun, France both show a faint birefringence in the plane of the plates although in each case the two indices in the plane of the plates are sensibly the same. Both are optically negative and show a very small $2V$. The extinction direction in the Sosa specimen corresponds to a diagonal in the tetragonal plates, while in the Autun specimen it is parallel to (100) or (010). Single crystal x -ray films of the two optical types are nevertheless identical and these films as well as

those of meta-torbernite lead to tetragonal cells. Evidently the optical properties are extremely sensitive to the water content and to the distribution of the water molecules within the structure.

The zero-layer Weissenberg films with $a[100]$ as the rotation axis of meta-torbernite I, meta-autunite I and the uranocircite specimen are remarkably similar except that there are extra, rather weak diffraction spots in the latter film which result in exactly doubling one of the dimensions of the cell:

	<i>Meta-torbernite I</i>	<i>Meta-autunite I</i>	<i>Meta-uranocircite</i>
<i>a</i>	6.96 Å	6.96 Å	6.96 Å
<i>c</i>	8.64	8.47	16.90 ¹

¹ Frondel (1951a, p. 674) states: "The [sabugalite $\text{HAl}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$] pattern cannot be completely indexed in terms of a cell with . . . c_0 halved to 9.65 Å. This point is of some importance since the 19.3 Å period is characteristic of the fully hydrated phases in the autunite group, while the meta-I hydrates have a cell . . . with c_0 halved." The new data for meta-uranocircite invalidates this criterion for distinguishing the hydrates.

The new cell constants for meta-torbernite and meta-autunite agree closely with those given in Dana (1951). Beitema did not detect the doubled c value for meta-uranocircite in his analysis of the powder pattern of artificial material.

The space group in each case is $P4/nmm$. It is certain therefore, that our specimen of uranocircite is actually meta-uranocircite. The doubled c length is most likely due to the larger ionic radius of Ba as compared to Cu and Ca (Ba^{2+} 1.43, Cu^+ 0.96, Ca^{2+} 1.06; Evans, 1948, p. 171).

The cell contents of meta-uranocircite were calculated using Winkler's analysis and the specific gravity 4.08, measured in this study. The calculated cell contents (Table 1) approach closely the ideal formula $2[\text{BaO}(\text{UO}_3)_2\text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}]$ or $2[\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}]$ which is the generally accepted formula for uranocircite (Dana, 1951, p. 987).

TABLE 1. META-URANOCIRCITE, ANALYSIS AND CELL CONTENTS

	I	II
BaO	15.08	2.0
UO ₃	56.86	4.0
P ₂ O ₅	15.06	2.1
H ₂ O	13.99	15.6
	100.99	

I. Falkenstein, Saxony; anal. Winkler (Weissbach, 1877 in Dana, 1892, p. 859). II. Unit cell contents.

As a check on the x -ray results obtained on natural meta-uranocircite, artificially prepared material was studied. A crystal of meta-autunite I from Autun, France which had been previously used for the determina-

tion of the cell constants of meta-autunite I was immersed in concentrated BaCl_2 solution at 100°C . for several hours and then used to obtain a zero-layer Weissenberg film about the a -axis. This film was identical with the one obtained from meta-uranocircite, Falkenstein, Saxony with the extra diffractions leading to a doubled c axis quite apparent. This crystal was found to be almost optically uniaxial with an index measured on the plates of 1.619 (as compared to 1.621, 1.622 measured on natural meta-uranocircite). Micro-chemical tests showed the presence of Ba, but no Ca.

A second specimen labelled uranocircite, this one from Madagascar (ROM M 15590) was found to show considerable variation in optical properties, ranging between those of meta-autunite and meta-uranocircite. At one end of the variation the plates have a low birefringence, very small $2V$ and faint twinning. The index in the plane of the plates is 1.607 and the extinction direction is approximately 45° to the twinning direction. These data agree closely with the data obtained from the Sosa meta-autunite used for the single crystal study and this identification was confirmed by a Weissenberg study which gave the lattice dimensions of meta-autunite: a 6.96, c 8.47 Å.

At the other end of this variation in optics, the plates have a higher birefringence and larger optic angle. The optical sign is negative. Indices of $Y=1.620$ and $Z=1.622$ measured in the plane of the plates are those of meta-uranocircite. The identification was again confirmed with single crystal x -ray films.

Single crystal films of a plate with refractive index intermediate to those of the two types described above showed only a faint indication of the doubled c length of meta-uranocircite. These observations suggest that an isomorphous series exists between meta-autunite and meta-uranocircite and that the Madagascar specimen contains several representatives of this series.

Material in moist atmosphere

It was decided to attempt the formation of a higher hydrate of Ba corresponding in structure to fully hydrated autunite. For comparison meta-autunite was first converted to autunite by immersion in cold water for several hours. It was observed that the newly-formed material had a minimum refractive index of 1.575 in the plane of the plates (Dana, 1951, p. 985 gives 1.575 and 1.578 for natural autunite) which increased rapidly during the oil immersion tests. Weissenberg films obtained from a cleavage flake indicated a tetragonal cell with dimensions which compare well with those determined by Beintema on natural autunite:

	<i>a</i>	<i>c</i>	Space Group
Nuffield & Milne	6.98 Å	20.70 Å	<i>I4/mmm</i>
Beintema	7.00	20.67	<i>I4/mmm</i>

Attempts to form torbernite by the same method were unsuccessful. This is the experience of other workers (Dana, 1951, p. 983).

Cleavage fragments of natural meta-uranocircite were immersed in cold water (between 0 and 5° C.) for 24 hours. When placed in immersion oils the optical properties of this hydrated material changed rapidly, approaching those of meta-uranocircite. This suggested that the compound is stable only in a moist atmosphere. A cleavage fragment of this hydrate was used to obtain Weissenberg films with *a*[100] as the rotation axis, a moist atmosphere being maintained in the camera to prevent loss

TABLE 2. X-RAY POWDER DATA FOR META-URANOCIRCITE
Tetragonal, *P4/mmm*; *a* 6.96, *c* 16.90 Å

<i>d</i>				<i>d</i>				<i>d</i>	
I	meas.	calc.	<i>hkl</i>	I	meas.	calc.	<i>hkl</i>	I	meas.
7	8.19	8.44	002	4	2.59	2.61	016	3	1.924
6	5.37	5.37	012	$\frac{1}{2}$	2.41	2.42	025	$\frac{1}{2}$	1.883
3	4.90	4.92	110	1	2.35	2.36	222	3	1.796
6	4.21	4.22	004	2	2.18	2.20	130	3	1.741
10	3.58	3.61	014			2.18	026	$\frac{1}{2}$	1.676
2	3.39	3.41	021			2.12	132	5	1.589
5	3.21	3.22	022	1	2.12	2.12	224	1	1.559
3	2.91	2.93	122	7	2.08	2.08	126	5	1.518
$\frac{1}{2}$	2.67	2.69	024	4	2.01	2.01	018		

Ni filtered Cu radiation; $\lambda = 1.54050$ Å.

of water and a return to the meta-uranocircite structure. The films are remarkably similar to those obtained from meta-uranocircite. They indicate that the lattice remains primitive (space group *P4₂2*) unlike the inversion from meta-autunite to autunite; the length of the *a* axis is unchanged at 6.97 Å while the *c* length is increased from 16.90 to 17.57 Å. It may be assumed that no shift of the U-P-O sheets occurred during the hydration; the sheets have merely been more widely separated by the addition of water. The compound is not isostructural with autunite. Beintema's dehydration experiments suggest that the new hydrate has ten molecules of H₂O. The cell contents are probably 2[Ba(UO₂)₂(PO₄)₂ · 10H₂O]. It is unlikely that it exists in nature.

X-ray powder data for this compound and for naturally-occurring meta-uranocircite are given in Tables 2 and 3.

TABLE 3. X-RAY POWDER DATA FOR LABORATORY-HYDRATED META-URANOCIRCITE
Tetragonal, $P4_22$; a 6.96, c 17.57 Å

d				d				d	
I	meas.	calc.	hkl	I	meas.	calc.	hkl	I	meas.
7	8.42	8.78	002	5	2.69	2.73	024	1	1.928
1	6.27	6.47	011	1	2.52	2.54	124	$\frac{1}{2}$	1.809
7	5.30	5.46	012	1	2.43	2.46	220	1	1.754
2	4.79	4.93	110	2	2.35	2.37	222	$\frac{1}{2}$	1.723
5	4.25	4.30	112	7	2.17	2.18	131	1	1.690
10	3.65	3.72	014	7	2.12	2.15	224	3	1.646
4	3.41	3.42	021	$\frac{1}{2}$	2.07	2.09	018	1	1.606
7	3.18	3.24	022	1	2.03	—	—	4	1.550
4	2.90	2.94	122	$\frac{1}{2}$	1.992	—	—	1	1.522

Ni filtered Cu radiation; $\lambda = 1.54050$ Å.

Further observations

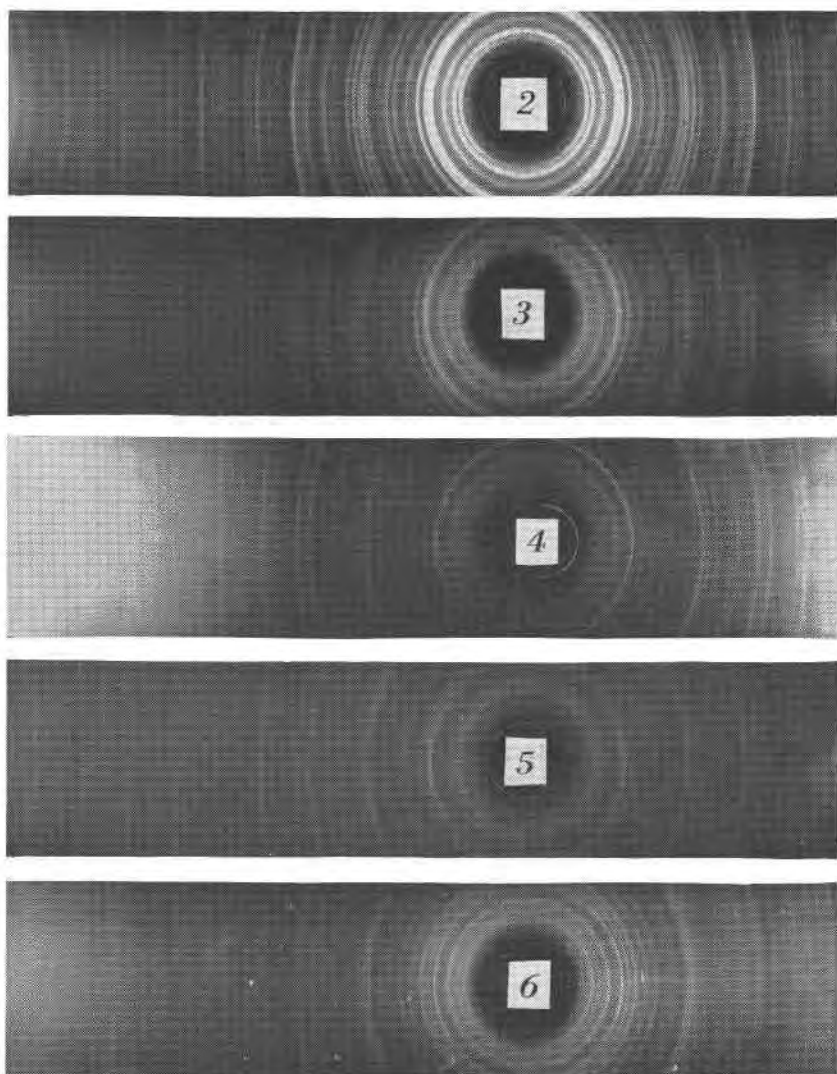
An interesting feature of the single crystal data which are available for the meta-phosphates is that the c dimension increases with decreasing ionic size of the cation:

Meta-uranocircite	Ba(UO ₂) ₂ (PO ₄) ₂ · nH ₂ O	$c = 8.45 \times 2$ Å
Meta-autunite	Ca(UO ₂) ₂ (PO ₄) ₂ · nH ₂ O	8.47
Meta-torbernite	Cu(UO ₂) ₂ (PO ₄) ₂ · nH ₂ O	8.64

Ionic radii for C. N. 6 (Evans, 1948): Ba²⁺ 1.43, Ca²⁺ 1.06, Cu⁺ 0.96 (the ionic radius of Cu²⁺ which applies here and elsewhere in this paper, was not available), O²⁻ 1.32.

Where a disparity in radius between cation and anion occurs in ionic structures, coordination between these ions may be effected by water molecules. According to Evans (1948): "In many hydrates the function of water is simply to coordinate the cations and thereby effectively surround them with a neutral shell which increases their radius and enables their charge to be distributed over a greater number of anions." Hence there is a possibility of a small, highly polarizing cation having a large effective radius when coordinated by water molecules. Evidently in such hydrates the coordinated water molecules play an essential part in determining the stability of the structure as a whole and when removed result in the breakdown of the structure. This is in contrast to structural or zeolitic water which adds little to the stability of a structure and which may be removed without change to the structure. Compounds containing both coordinated and structural water are known.

The c periods of the meta-phosphates and the ionic radii of the cations suggest that the amount of coordinated water increases from the Ba mem-



FIGS. 2 TO 6. X-ray powder patterns; Cu/Ni radiation; camera radius $90/\pi$ mm.; full size contact prints. 2—Meta-torbernite, Cornwall, England; 3—Meta-autunite, Sosa, Erzgebirge, Saxony; 4—Meta-uranocircite, Falkenstein, Saxony; 5—Autunite (artificial), prepared from meta-autunite, Autun, France; 6—hydrated meta-uranocircite, Falkenstein, Saxony; probable composition $\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$.

ber to a maximum in the Cu member. To test this, crystals of the three minerals were heated and their structures re-examined. A crystal of meta-torbernite from Cornwall, after heating at 110° C. for 24 hours gave single crystal films which indicated that the structure had collapsed forming a new cell, orthorhombic in symmetry and with dimensions a 6.57, b 6.95, c 6.75 Å (as compared to the original tetragonal cell with a 6.96, c 8.64 Å). A cleavage flake of meta-autunite from Autun, after heating for 24 hours at 130° C. gave single crystal films with rather diffuse diffraction spots. However it was readily deduced that the original tetragonal cell with a 6.96, c 8.47 Å had shrunk to a tetragonal cell with identical a dimensions but with c 8.14 Å.¹ A sample of meta-uranocircite heated to 105° C. for 40 hours and another heated to 500° C. confirmed the findings of Beintema that the meta-uranocircite structure is not destroyed under these conditions. It may therefore be assumed that the water in meta-uranocircite is largely zeolitic; that it is partly coordinated water in meta-autunite and largely coordinated in meta-torbernite. The optical data recorded above for the three compounds support this assumption. Our two meta-uranocircite specimens show pronounced birefringence in the plane of the plates and a measurable $2V$ angle. The meta-autunite specimens show faint birefringence but with the indices in the plane of the plates sensibly the same. The angle $2V$ is very small. The meta-torbernite specimen which was studied has uniaxial optical properties. However, the x -ray photographs show no departure from tetragonal symmetry in each of the three cases. Neither the presence of twinning in meta-uranocircite nor a variation in the extinction direction in meta-autunite can be detected by x -ray diffraction. It may be fairly assumed that these optical effects in meta-uranocircite and meta-autunite are anomalous which can be attributed only to water molecules which are relatively free to move within the structure, that is zeolitic rather than coordinated water. Because the anomalous effects are most evident in meta-uranocircite and absent in meta-torbernite, one is again led to the conclusion that the water in meta-uranocircite is largely zeolitic, decreasing in meta-autunite, and is largely coordinated in meta-torbernite. The above observations indicate further that the members of the meta-torbernite group are not strictly isostructural.

The fully hydrated phosphates in contrast to the meta-phosphates show an increase in the c period with increase in the size of the cation present:

¹ Beintema deduced an orthorhombic cell with dimensions a 6.46, b 6.98, c 8.67 Å from powder photographs of material heated to 70° C.

		c	Ionic Radii C.N. 6 Evans (1948)	
Sabugalite ^a	Al(UO ₂) ₂ (PO ₄) ₂ · nH ₂ O	19.3	Al ³⁺	0.57
Salceite ^b	Mg(UO ₂) ₂ (PO ₄) ₂ · nH ₂ O	19.84	Mg ²⁺	0.78
Torbernite ^c	Cu(UO ₂) ₂ (PO ₄) ₂ · nH ₂ O	20.54	Cu ⁺	0.96
Autunite	Ca(UO ₂) ₂ (PO ₄) ₂ · nH ₂ O	20.70	Ca ²⁺	1.06

^a Frondel 1951a, p. 674.

^b Frondel 1951b, p. 681.

^c Dana 1951, p. 982; converted to A units.

Beintema's analysis of the structure of autunite did not yield a unique position for the Ca atoms. Of the two possible positions between the sheets, he arbitrarily chose the large cavities (000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$) in preference to the (*b*) positions ($00\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$). The cavities provide ample space for even the largest of the cations. If the cations are not coordinated by water molecules, their size can in these positions have no effect upon the distance between adjoining sheets. On the other hand, if the cations are coordinated by water, highly charged, small cations such as Al might be expected to form the larger cells. However in sabugalite, the sheets are distinctly closer together than they are in autunite. In contrast, the (*b*) positions (see Fig. 1b) are sufficiently small to ensure that the distance between adjoining sheets will be sensitive to the ionic size of the cation occupying them. Since the single crystal data show a dependence of *c* period upon cation radius, it seems certain that the (*b*) rather than the (*a*) positions are occupied by the cations.¹

This view of the structure of autunite is supported by the data of Table 4 which shows the propensity of various ions to form compounds of the meta-phase or the fully hydrated-phase for both phosphates and arsenates. The data of the table indicate that under like conditions of temperature and humidity, the stability of the fully hydrated structure increases with decrease in the ionic radius of the cation. Uranospinite (Mrose, 1951) is not an anomaly; Beintema has pointed out that there are not enough identity positions in the fully hydrated structure to effect valence compensation by a monovalent ion. Uranocircite has the largest cation; it is found in nature with the meta-structure and cannot be transformed to the fully hydrated structure in the laboratory. Zeunerite (J. W. Frondel, 1951) occurs in nature as the meta-structure. Natural material cannot be converted to the fully hydrated structure although synthetic zeunerite may be precipitated from solution in the laboratory. Torber-

¹ It is interesting to note that for this arrangement of atoms, the U⁶⁺ ion may be calculated to have a maximum radius of 0.6 Å from the data given by Beintema for the structure of autunite.

nite and autunite are rarely found as fully hydrated structures, and then presumably in damp climates. Specimens of these two species collected and housed in North America are invariably of the meta-type. Autunite can be formed from meta-autunite; meta-torbernite cannot be prepared. Novacekite (Fron del, 1951b), saleeite and sabugalite exist in American collections as fully hydrated structures. The obvious explanation for these data is that as the radius of the cation which binds the sheets in

TABLE 4. RELATION BETWEEN COMPOSITION AND STRUCTURE

	A	X	Occurrence in Nature
Sabugalite	HA1	P	As fully hydrated structure only
Saleeite	Mg	P	
Novacekite	Mg	As	
Autunite	Ca	P	Rarely as fully hydrated structure; usually as meta-structure
Torbernite	Cu	P	
Zeunerite	Cu	As	As meta-structure only
Uranocircite	Ba	P	
Uranospinite	H	As	

the fully hydrated structure increases (see Fig. 1), the structure becomes more precarious. The radii of Cu^{2+} and Ca^{2+} apparently represent the transition zone when the structure becomes meta-stable and the tendency is for the sheets to slide over one another in order to form the more stable (for this ionic radius) meta-structure. The radius of Ba^{2+} may be of such a size as to make a stable, fully hydrated phase impossible.

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