Uranospathite and arsenuranospathite

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SUMMARY. A reinvestigation of uranospathite from the type locality, Redruth, Cornwall, shows that it is an aluminium uranyl phosphate belonging to the torbernite series but more highly hydrated than other members thereof. The composition $(HAl)_{0.5}(UO_2)_2(PO_4)_2 . 20H_2O$ was derived by indirect methods and by making use of analysis by the electron microprobe, which showed an Al_2O_3 content 2·6 % in the partially dehydrated state. Unit-cell dimensions: a 7·00, c 30·02 Å, $Z = 2$. Probable space group $P4_2/n$. Strongest lines of the powder pattern: 15·22 (10) 002, 7·60 (10) 004, 4·93 (10) 110, 111, 3·50 (8) 116, 200, 201.

The mineral is unstable and unless preserved at low temperature or in a humid atmosphere converts into a new phase with a loss of 10–12H_2O. This phase $(HAl)_{0.5}$ $(UO_2)_2(PO_4)_2 . 8$–$10H_2O$ is identical with the mineral sabugalite. Experimental work led to the synthesis of a hydrate with the composition $(HAl)_{0.5}(UO_2)_2(PO_4)_2$. $16H_2O$, but not to fully hydrated uranospathite. This synthetic compound also dehydrates rapidly under normal conditions, converting into the same phase as does natural uranospathite. Arsenian uranospathite occurs at Menzenschwand in the Southern Black Forest.

Arsenuranospathite proper is a new mineral found at Menzenschwand and also at Wittichen in the Central Black Forest. It forms lathlike or wedge-shaped crystals of orthorhombic symmetry. Forms: {100}, {010}, {110}, {001}. Cleavage {001} perfect, {100} and {010} good. Hardness probably about 2, ρ_{calc} 2·54 g cm^{-3}. White to pale yellow. Streak white. Fluoresces greenish in ultra-violet light with variable intensity.

Optical properties: $\beta \approx 1·538$, γ 1·542 ± 0·003, 2V_α about 52°, $r > v$, straight extinction, length positive. Unit-cell dimensions: a 7·16, c 30·37 Å, $Z = 2$, probable space group $P4_2/n$. Strongest lines of the powder pattern: 14·62 (10) 002; 7·62 (10) 004; 5·03 (8) 110, 006, 111; 3·49 (9) 202.

Analytical work showed arsenuranospathite to be an aluminium-bearing uranyl arsenate. According to analyses by the electron microprobe the content of Al_2O_3 amounts to $\approx 2·8$ % for the partially dehydrated mineral, which is compatible with the formula $(HAl)_{0.5}(UO_2)_2$ $(AsO_4)_2 . 20H_2O$ derived for the fully hydrated mineral.

Arsenuranospathite, like uranospathite, is unstable under normal conditions and converts to a lower hydrate containing about 10 H_2O per formula unit. Optical properties of the lower hydrate: α 1·564, colourless, β 1·594, γ 1·596, yellowish, all ± 0·002, 2V_α about 28°, $r > v$. Unit-cell dimensions: a 7·15, c 20·52 Å, $Z = 2$, ρ_{calc} 3·20 g cm^{-3}.

Strongest lines of the powder pattern: 10·54 (10) 002;

5·13 (6) 004, 110; 3·54 (10) 105, 201. The experiments aimed at synthesizing fully hydrated arsenuranospathite were not successful and only yielded a hydrate with the composition $(HAl)_{0.5}(UO_2)_2(AsO_4)_2 . 16H_2O$. This compound changes to a phase with 10 H_2O identical with the dehydration phase of natural arsenuranospathite.

URANOSPATHITE was described by Hallimond (1915) as a new species from Redruth, Cornwall. The mineral was previously catalogued as autunite, but its low refractive indices and specific gravity distinguish it from autunite and the other members of the torbernite group and though its chemical composition remained unknown, it seemed justifiable to consider it a distinct species.

A new investigation of uranospathite was carried out by Frondel (1954). He cites a semiquantitative spectrographic analysis of a type specimen by Annell and Valentine, which shows that U, As, and P with As > P are the main constituents, whereas Cu and Fe are present in smaller amounts. An analysis by Gonyer of a non-type sample supposed to be identical with the original material gave a composition close to that of zeunerite: $Cu(UO_2)_2$ $(AsO_4, PO_4)_2 . 11H_2O$. Frondel therefore concluded that uranospathite is a copper uranyl arsenate-phosphate related to the torbernite group, but more highly hydrated than other members of this group.

Hallimond (1954), however, raised objections to this assumption. He pointed out that the yellow colour of the mineral speaks against a high copper content. His objections were supported by the discovery of a uranospathite-like mineral in France (La Crouzille and Sagnes, Haute-Vienne), which has the same low indices of refraction as Hallimond's original material (Chervet and Branche, 1955). It contains U and P, but no Cu and As; the exact composition, however, could not be determined for lack of material. In addition Guillemin (cited by Frondel, 1954, and by Chervet and Branche, 1955) tested a type specimen of uranospathite furnished by Hallimond and found no copper.

The new investigation of uranospathite from Cornwall and Menzenschwand as well as of the

arsenate analogue from the latter locality confirms the findings of Chervet and Branche and of Guillemin and hence the view of Hallimond that uranospathite is not a cupriferous uranium mineral. It contains aluminium as additional cation and hence is closely related to sabugalite. There can be no doubt that Frondel investigated an impure sample.

In particular the non-type specimen analysed by Gonyer must have contained a high proportion of zeunerite or mixed crystals of the torbernite–zeunerite series.

Preliminary results of the new investigations have already been published (Walenta, 1965, 1967, 1972). They mainly referred to the arsenate analogue arsenuranospathite.

The author is indebted to Mr. E. A. Jobbins, Geological Survey and Museum, London, for furnishing a type sample of uranospathite from Redruth, Cornwall (part of specimen No. L. 1941 belonging to the Ludlam Collection) as well as to Dr. G. Jung, Albbruck, for a specimen of uranospathite from Menzenschwand.

Uranospathite from Redruth, Cornwall

The type sample from Cornwall is composed of loose tabular crystals of yellow colour. Closer inspection reveals that only part of the crystals have the same properties as those given by Hallimond for uranospathite in his description. The other part is composed of bassetite. Hallimond (1915) also mentions the association of bassetite and uranospathite and describes a parallel growth of the two minerals. The crystals of bassetite and uranospathite (fig. 1) look very much alike, though they differ slightly in colour and transparency.
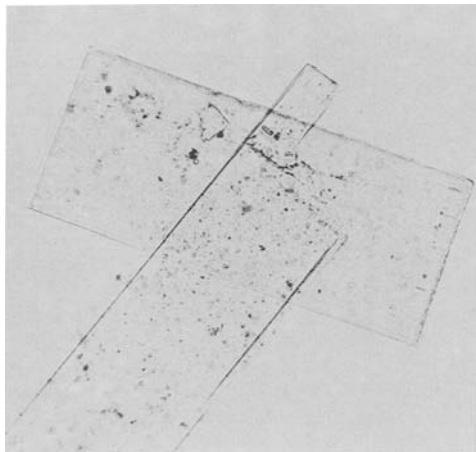

FIG. 1. Rectangular crystals of uranospathite. Redruth, Cornwall. Magnification about 60 ×.

Both form rectangular plates flattened on {001} and bounded laterally by faces of {100} and {010}.

Physical and optical properties. The cleavage {001} is perfect, {100} and {010} good. The specific gravity is 2·50 according to Hallimond (1915). Hardness 2 to $2\frac{1}{2}$ (Chervet and Branche, 1955, p. 67). Colour yellow, translucent, distinct yellowish-green fluorescence in ultra-violet light. The optical properties of fully hydrated uranospathite given by different authors are listed in Table I. The indices of refraction determined by the author agree well with those cited by Hallimond for the original material and by Chervet and Branche for uranospathite from Sagnes, but differ somewhat from Frondel's values, which vary and are higher except those for α. As shown by the spectrochemical analysis Frondel's material contained P and As and so the indices of refraction in all probability are influenced by the partial substitution of P by As. The optical behaviour conforms to orthorhombic symmetry: $\alpha \perp$ (001), the other two optical directions coincide with the horizontal axes.

Chemical composition. Microchemical and spectrochemical investigations as well as an analysis by the electron microprobe show that uranospathite is a uranyl phosphate with Al as additional cation. Microchemical and electron-probe tests found only Al and U, but spectroscopy (H. Wilk, Chemisches Untersuchungsamt der Stadt Stuttgart) revealed minor Cu, Fe, and Co, and traces of Co and Si. The Cu and Fe content must be well below 1 % because the rather sensitive microchemical tests gave no indication of the presence of these elements in pure samples.[1] Arsenic could not be detected by any method so it can be concluded that uranospathite is a pure phosphate. Definite proof that uranospathite is an aluminium-bearing mineral was furnished by an electron-probe analysis, which showed that the content of Al_2O_3 of the partially dehydrated phase is 2·6 % (analyst H. Lauckner, Standard Elektrik Lorenz AG, Stuttgart). It is not difficult now to establish the complete formula of uranospathite even if no complete quantitative analysis is available for lack of material, by making use of the well-known basic formula of the members of the torbernite group: $(X_2^+, X^{2+}, (HX^{3+})_{0.5})(UO_2)_2(P, AsO_4)_2 . nH_2O$, where X is the additional cation, in our case Al,

[1] First microchemical analyses showed the presence of small amounts of Fe (see Walenta, 1965, p. 275). Later tests of very pure material, however, did not conform this and it must be concluded that the material first investigated was contaminated by bassetite. This result also ruled out the possibility that the missing cation might be Fe^{3+}, which was taken into consideration before Al was discovered among the constituents.

TABLE I. *Optical properties of fully hydrated uranospathite*

Cornwall present study	Cornwall (Hallimond, 1915, p. 230)	Cornwall (Frondel, 1954, pp. 351-2)	Sagnes, Haute-Vienne (Chervet and Branche, 1955, p. 67)
α 1·492±0·002		1·485-1·459	1·492
β 1·511±0·002	1·510	1·522-1·527	1·510
γ 1·521±0·002	1·521	1·527-1·532	1·522
$2V_\alpha$ 76°, $r > v$	69°	55-60°	72°
pleochroism: α colourless β, γ yellow	pleochroism: α pale yellow β, γ deep yellow	distinct pleochroism: α colourless to pale yellow β, γ deep yellow to greenish-yellow	pleochroism: $\alpha < \beta$, γ

so the only unknown is the number of water molecules.

For determining the water content it is possible to apply an indirect method using the unit-cell dimension of uranospathite as reference. The size of the unit cell of members of the torbernite group varies with the water content, the higher the water content, the larger the unit cell. As the water molecules are arranged in layers parallel to (001) in the lattice, an increase or decrease in the water content mainly affects the c axis, whereas the a axis more or less remains unchanged. Therefore, the value of c gives a clue to the water content (see Walenta, 1965). In case of uranospathite c is about 30 Å, which makes it probable that the water content amounts to 20 molecules (loc. cit., p. 275) and that the formula of uranospathite consequently is $(HAl)_{0.5}(UO_2)_2(PO_4)_2.20H_2O$; this leads to a calculated density of 2·49 g cm^{-3}, a value very close to the observed value of 2·50 (Hallimond, 1915).

The formula of Gladstone and Dale can also be applied for testing the composition. Calculation of the mean index of refraction gives a value of 1·506 when using the derived composition and the ρ value of 2·50. This result is in excellent agreement with the experimental mean index of refraction of 1·508. It is therefore justified to ascribe the formula $(HAl)_{0.5}(UO_2)_2(PO_4)_2.20H_2O$ to uranospathite, which differs from that of sabugalite only in its water content. That this is indeed so is further proven by the fact that dehydration of uranospathite leads to a phase identical with sabugalite. This raises some problems of nomenclature (see below). The theoretical composition of $(HAl)_{0.5}(UO_2)_2(PO_4)_2.20H_2O$ is Al_2O_3 2·31, UO_3 51·80, P_2O_5 12·85, H_2O 33·04, total 100·00%.

X-ray data. The powder diffraction pattern for fully hydrated uranospathite from Cornwall is given in Table II together with the data for the mineral from La Crouzille, France, obtained by Branche and Morignat (Chervet, 1960). The two patterns agree very well. Two lines in the pattern of uranospathite from Cornwall, which do not belong to the fully hydrated but to the partially dehydrated phase, were eliminated from the table.

The powder pattern was used for calculating the unit-cell dimensions: a 7·00 Å, c 30·02 Å, Z = 2. Probable space group $P4_2/n$. The agreement between measured and calculated d values is satisfactory. There is no indication that the symmetry is lower than tetragonal as might be expected from the biaxial optical behaviour. This discrepancy is probably due to the arrangement of the water molecules. It may be concluded that the position of the latter in the uranospathite structure is such that lower symmetry results as in case of other members of the torbernite group (see Walenta, 1965). Therefore, the derived tetragonal unit cell may be only a pseudo cell. Good single-crystal photographs of uranospathite probably would facilitate the solution of this problem. However, in view of the easy dehydration of the fully hydrated mineral, it is difficult to obtain such photographs.

Dehydration behaviour. As stated above, fully hydrated uranospathite is apt to dehydrate at normal room temperature, particularly if the humidity is low. It is, however, more stable than some other fully hydrated members of the torbernite group, as for instance uranocircite I and II and novacekite I. Nevertheless, all the fully hydrated material at the disposal of the author did dehydrate in the course of several years though it was kept in a well-sealed vial. New original material supplied by the British Museum in 1973 turned out to be dehydrated. So in all probability fully hydrated uranospathite from the type locality no longer exists in collections. Attempts to rehydrate the dehydrated crystals were fruitless.

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TABLE II. *X-ray powder data for fully hydrated uranospathite*

Cornwall		La Crouzille/Haute-Vienne (Branche and Morignat, cited by Chervet, 1960, p. 200)			
d (Å)	I	d (Å)	I	d_{calc} (Å)	hkl
15·22	10	15·46	10	15·01	002
7·60	10	7·52	8	7·51	004
—	—	6·36	2	6·34	102
5·72	2	5·85	3	5·74	103
4·93	10	4·92	10	4·95; 4·88	110; 111
4·48	6*	4·48	8	4·44	113
4·08	4	4·07	5	4·07	106
3·84	1/2	3·85	5	3·82	115
3·65	1	3·66	5	3·66	107
3·50	8	3·51	8	3·52; 3·50; 3·48	116; 200; 201
3·43	4	3·42	8	3·41	202
3·30	3	3·31	6	3·31; 3·30	108; 203
3·17	2	3·18	6	3·17	204
3·00	1	2·995	2	3·02; 3·01; 3·00; 2·99	205; 109; 0.0.10; 118; 213
2·86	1/2	2·892	2	2·89; 2·87	214; 206
2·76	1/2	2·774	2	2·78; 2·77; 2·76	215; 119; 1.0.10
2·47	2	2·483	2	2·47	220; 221
2·35	1	2·348	2	2·36; 2·35	1.0.12; 224
2·28	1/2	2·651†	2	2·29; 2·28; 2·27	225; 219; 2.0.10; 303
2·21	6	2·218	7	2·23; 2·22; 2·21	1.1.12; 226; 304; 310; 311
2·16	1	2·167	5	2·17; 2·16; 2·15	305, 2.1.10; 313; 2.0.11
—	—	1·987	2	1·988; 1·982	229; 308
—	—	1·956	2	1·954	2.1.12
—	—	1·918	2	1·924; 1·912	1.0.15; 309
—	—	1·882	2	1·880	324
1·849	1	1·852	3	1·855; 1·847; 1·844	1.1.15; 319; 325
—	—	1·779	1	1·782	3.1.10
—	—	1·751	1	1·754; 1·750; 1·747	1.1.16; 400; 401
1·656	2	1·655	1		
—	—	1·633	1		
—	—	1·599	1		
1·560	1/2	1·564	1		
1·498	1/2	1·500	1		
—	—	1·486	1		
1·380	1	1·381	1		
—	—	1·339	1		
—	—	1·285	1		
1·203	1	1·204	1		
—	—	1·142	1		
—	—	1·109	1		
1·081	1/2	1·085	1	* diffuse.	
—	—	0·9923	1	† misprint in the original table.	

The dehydrated phase differs from fully hydrated uranospathite in its optics and powder pattern and so can be easily recognized. As to the optical properties the crystals no longer behave uniformly. They show mottled extinction on the (001) face and variable birefringence. Isotropic parts are uniaxial, the birefringent ones biaxial (with $\alpha \parallel [001]$ as in fully hydrated uranospathite), $2V_\alpha$ up to 26°. γ is variable, 1·580 to 1·590; Frondel (1951) found γ 1·584 for sabugalite.

In Table III the X-ray powder data for partially dehydrated uranospathite, sabugalite, and synthetic sabugalite are given. The agreement between the five powder patterns is not always satisfactory, probably because of variations in the water content and concomitant small structural changes. As to the unit cell determined by Frondel, it can be regarded only as a pseudo-cell, because it is not possible to index all the reflections on the basis of it, as has already been stated by Magin et al. (1959, p. 420). Single-crystal studies are required for solving the problem of the true cell and of the structural variations evidenced by the powder patterns. Unfortunately good crystals for carrying out such studies are not available for the time being.

Synthesis. Aluminium uranyl phosphate has already been synthesized by Magin et al. (1959) using uranyl acetate, aluminium chloride, and phosphoric acid. They obtained a hydrate with $8H_2O$, evidently identical with the natural mineral sabugalite described by Frondel (1951). The author synthesized the compound by means of uranyl acetate, phosphoric acid, and either aluminium chloride or aluminium nitrate. In most cases very dilute solutions served for the experiments.

Attempts to obtain the fully hydrated uranyl phosphate identical in composition to uranospathite were not successful. This is not astonishing as it is difficult to synthesize the fully hydrated phases of other members of the torbernite series (Walenta, 1965). So, for instance, uranocircite I with $12H_2O$ found in nature could not be synthesized despite the use of dilute solutions under variable conditions of precipitation. Further it should be mentioned that the small crystals that usually form under artificial conditions dehydrate more rapidly than the larger natural ones. Dehydration of such small crystals may take place within seconds at normal room temperature and air humidity. So even if water-rich hydrates form in the hydrous solution, it may be difficult to prove their existence if normal procedures are applied. The best means to avoid such difficulties is to check the artificial product by means of X-ray investigations using samples immersed in water in a sealed capillary tube.

In case of the aluminium uranyl phosphate syn-thesis led to a hydrate with the formula $(HAl)_{0.5}(UO_2)_2(PO_4)_2 \cdot 16H_2O$, intermediate in composition between uranospathite with 20 and sabugalite with 10 or less H_2O (see Walenta, 1965, p. 274). This compound has a tetragonal unit cell with a 6·97, c 26·43 Å, $Z = 2$, ρ_{calc} 2·67 g cm^{-3}. The powder pattern is given in Table IV. The optical properties could not be determined with accuracy because of the small particle size and rapid dehydration. However, it was found that γ is 1·524 $\pm$0·003. This is close to the γ-value of uranospathite, but the X-ray data prove that it is a distinct hydrate. Calculation of the mean index of refraction by means of the rule of Gladstone and Dale yields a value of 1·514 and so shows that the value of γ of 1·524 determined experimentally is compatible with the derived formula of the hydrate in question and the density calculated from it and the unit-cell dimensions.

Mention should be made that in one case a hydrate was obtained from very dilute solutions of aluminium chloride, uranyl acetate, and phosphoric acid that according to the preliminary X-ray investigation was more hydrated than the phase with $16H_2O$. Its basal spacing is close to 28·9 Å and so approaches c of uranospathite. Further investigation of this product was impeded by its very fine-grained and poorly crystalline nature and attempts to obtain a better crystallized product of similar properties failed. This, however, gives as a clue as to how fully hydrated uranospathite might form, i.e. by using still more dilute solutions and taking care that precipitation proceeds slowly under conditions permitting the formation of a well-crystallized product. Unless preserved in water, the synthetic hydrate with $16H_2O$ is unstable at room temperature and rapidly converts to sabugalite, with γ 1·584$\pm$0·002.

The Al and water content of the dehydrated synthetic material were checked: Al_2O_3 2·59%, H_2O 17·5%. This is close to the theoretical composition of sabugalite $(HAl)_{0.5}(UO_2)_2(PO_4)_2 \cdot 8H_2O$: Al_2O_3 2·87, UO_3 64·41, P_2O_5 15·99, H_2O 16·73%.

As to the water content of sabugalite Frondel (1951, p. 677) states that when the mineral is heated in air to 44 or 68 °C part of the water is lost and the indices of refraction increase, whereas there is no accompanying change in the powder pattern.[2] He attributes this to variations in the contents of zeolitic water (probable range 6 to $8H_2O$ per formula unit). The present investigation leads to the conclusion that the water content of subugalite and the respective synthetic phase varies between 8 and

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[2] Such a behaviour is not compatible with the rule of Gladstone and Dale. If water is lost without any change of the unit cell, the refractive indices must decrease and not increase.

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TABLE III. *X-ray powder data for partially dehydrated uranospathite and for sabugalite*

Uranospathite, Cornwall, partially dehydrated at room temperature		Sabugalite, La Crouzille/ Haute-Vienne (Branche and Morignat, cited by Chervet, 1960, p. 193)		Sabugalite, Mina de Quarta Seira (Frondel, 1951, p. 673)		Sabugalite, Mina de Quarta Seira (Magin et al., 1959, pp. 421-2)		Sabugalite, synthetic (Magin et al., 1959, pp. 421-2)		
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	hkl
9·88	10	9·86	10	9·69	10	9·61	100	9·61	100	002
—	—	—	—	—	—	8·93*	9	9·03*	9	—
—	—	—	—	—	—	—	—	8·43	1	—
—	—	—	—	6·56	1	6·76	3	6·71	3	—
—	—	—	—	—	—	6·37	4	6·37	3	—
5·71	3	—	—	5·59	1	—	—	—	—	—
—	—	—	—	—	—	—	—	5·31	4	—
4·93	8	4·86	9	4·86	9	4·93	35	4·93	19	110
—	—	—	—	—	—	4·80	35	4·80	18	004
—	—	—	—	—	—	4·58	13	4·55	25	—
4·41	6	4·41	4	4·39	4	4·40	9	4·40	9	112
—	—	—	—	—	—	4·19	2 b.	4·17	2 vb.	—
4·03	4	—	—	—	—	—	—	3·97	2	—
3·48	8	3·47	8	3·47	8	3·48	50	3·48	35	200
3·30	6 d.	3·33	2	3·36	1	3·36	13	3·36	9	105
—	—	3·20	2	3·22	1/2	3·22	9 b.	3·22	9 b.	006
—	—	—	—	3·06	1/2	3·08	2	3·05	2 b.	211
2·97	4	—	—	—	—	2·93	6	2·94	3	—
—	—	—	—	—	—	—	—	2·88	3	—
—	—	—	—	2·818	1	—	—	—	—	204
2·65	1/2 d.	—	—	—	—	2·62	4	2·63	6	—
2·47	2	—	—	2·452	2	2·47	4 b.	2·46	4 b.	220
2·40	1	2·400	1	2·389	2	2·40	9	2·40	6	008
—	—	—	—	—	—	2·30	2	2·29	2	301
2·25	1/2	—	—	—	—	2·25	1	2·24	2	—
2·20	4	2·179	4	2·188	6	2·20	13 b.	2·19	9	310, 224
2·15	1/2	—	—	—	—	—	—	—	—	312
2·09	1/2	2·109	2	—	—	2·10	4 vb.	2·08	3 vb.	—
—	—	2·066	1	—	—	—	—	—	—	217
—	—	—	—	—	—	1·998	1	1·989	2	—
—	—	—	—	—	—	1·926	6	1·918	4	—
1·889	1/2 d.	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	1·863	3	1·859	3	—
—	—	—	—	1·792	1	1·794	4 vb.	1·791	3 b.	—
1·736	1/2 d.	1·7374	—	1·726	1	1·743	9	1·740	4	—
—	—	—	—	—	—	1·684	1	1·670	2	—
—	—	—	—	1·641	1/2	—	—	—	—	—
—	—	—	—	—	—	1·605	2	1·603	1	—
—	—	—	—	—	—	1·583	3	1·578	2	—
1·546	1/2 d.	1·543	1	1·552	1	1·556	2	1·551	2	—
—	—	—	—	—	—	1·528	3	1·523	2	—
—	—	—	—	—	—	1·423	2 b.	1·421	1 b.	—
—	—	—	—	1·364	1	1·370	4 vb.	1·366	3 b.	—

b. = broad.   vb. = very broad.   d. = diffuse.
* Possibly a lower hydration state of sabugalite according to Magin et al., 1959.

TABLE IV. *X-ray powder data for synthetic* $(HAl)_{0.5}(UO_2)_2(PO_4)_2.16H_2O$

d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
13·15	10	2·40	1/2	1·638	2 vd.	1·238	1 d.
6·61	8	2·30	1	1·559	6 d.	1·202	1/2 d.
4·94	3	2·20	8	1·494	1/2 d.	1·108	3 vd.
3·48	7	2·15	1/2	1·471	1 d.	1·060	2 d.
3·25	5	2·09	1/2	1·430	1/2 d.	1·042	1/2 vd.
3·05	1	2·04	1	1·399	1	1·023	2 d.
2·94	1	1·895	3	1·377	2	1·013	1 d.
2·83	2	1·774	1	1·332	1	1·006	1 d.
2·47	3	1·745	2	1·280	1/2	0·989	3 vd.

d. = diffuse.   vd. = very diffuse.

$10H_2O$ at room temperature and decreases further at higher temperatures. The powder patterns change somewhat with the water content and are not fully identical; in particular the basal spacing decreases somewhat with the loss of water whereas the indices of refraction increase. So the hydrates with a water content ranging between 10 and $6H_2O$ do not have the same unit cell though the differences are not very conspicuous.

In Table V the powder patterns of two synthetic phases are listed that show such differences. Both also differ somewhat from the patterns for natural and synthetic sabugalite given in Table III. Judging from the basal spacing it can be assumed that the water content of the compound whose powder pattern is given first is higher than that of the other synthetic phase. In the first case it is probably near $10H_2O$, in the second near $8H_2O$ per formula unit. It is difficult to correlate the powder patterns with a certain water content even if direct water determinations of the compounds in question have been carried out, because uncontrolled loss of water may occur during the X-ray investigation.

TABLE V. *X-ray powder data for two samples of synthetic* $(HAl)_{0.5}(UO_2)_2(PO_4)_2.8-10H_2O$ *(sabugalite) showing differences in structure*

d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
9·75	10	9·46	10	2·95	2 d.	2·46	1
6·44	1/2 d.	5·55	4 d.	2·47	4	2·39	1
5·52	1 d.	4·91	7	2·39	2	2·18	4 d.
4·93	8	4·38	5 d.	2·19	6	2·08	1/2 d.
4·57	1	3·89	4 d.	2·09	1 vd.	1·909	1/2 d.
4·40	5	3·48	7	1·896	1/2 vd.	1·738	1 d.
3·88	2 d.	3·28	4 d.	1·735	4	1·643	1/2 d.
3·48	8	2·95	2 d.	1·642	1/2 d.	1·548	1 d.
3·36	2	2·81	1/2 d.	1·558	2 d.		
3·18	1	2·61	1/2 d.	1·366	1 vd.		
				1·194	1/2 vd.		
d. = diffuse.				1·162	1/2 vd.		
vd. = very diffuse.				1·101	1/2 vd.		

The studies of Frondel (1951) on the thermal behaviour at higher temperatures were not repeated. Frondel found that between 68 and 110 °C a new phase isostructural with meta-autunite II is formed.

Arseniferous uranospathite

Uranospathite from Menzenschwand occurs in clusters of euhedral crystals in a vug in barite. The wedge-shaped tabular crystals (fig. 2), which reach about 1 mm in length, have the same habit as those from Sagnes, Haute-Vienne (France) depicted by Chervet (1960, p. 201). The combination consists of {001}, {100}, and {110}. The yellow crystals are transparent to translucent and show a somewhat variable moderate greenish fluorescence in ultra-violet light. The indices of refraction, α 1·494±0·002, β 1·515±0·002, γ 1·524±0·002, ($2V_\alpha$ 65°), are somewhat higher than those of uranospathite from Cornwall and La Crouzille. This is due to the replacement of part of the P by As as shown by a microchemical analysis, which also proved the presence of Al in substantial amounts.
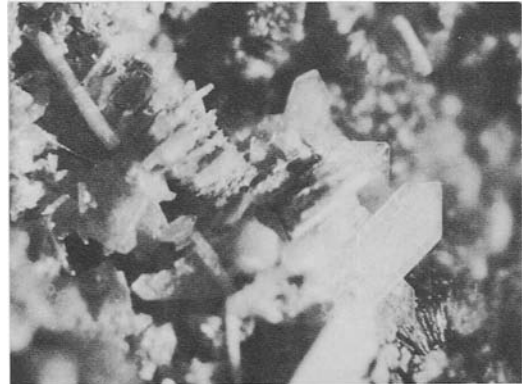

FIG. 2. Crystals of arseniferous uranospathite on quartz. Menzenschwand, Black Forest. Magnification about 25 ×.

P, however, predominates, so the mineral from Menzenschwand is in fact an arsenian uranospathite. The X-ray powder data are given in Table VI. The d-values and the unit-cell dimensions derived from it (a 7·06, c 30·09 Å) are intermediate between those of pure uranospathite and those of arsenuranospathite, but nearer those of the former, thus confirming the interpretation of the mineral as a mix-crystal with P predominant. Dehydration of the arseniferous uranospathite at room temperature yields a lower hydrate as in case of pure uranospathite and arsenuranospathite. The refractive index γ is near 1·590. As is to be expected this value is somewhat higher than that for dehydrated

uranospathite from Cornwall. The unit-cell of the lower hydrate calculated from the powder pattern (Table VI) is: a 7·01, c 19·83 Å.

TABLE VI. *X-ray powder data for arseniferous uranospathite from Menzenschwand*

Arseniferous uranospathite, fully hydrated		Arseniferous uranospathite, partially dehydrated		Ditto heated to 45 °C	
d (Å)	I	d (Å)	I	d (Å)	I
7·62	7	9·84	10	9·75	10
6·48	1	4·92	7	8·79	3
5·82	2	4·41	3 d.	5·73	5 d.
4·97	10	3·50	8	5·51	2 d.
4·50	6	3·28	4 d.	4·97	8
4·09	3 d.	2·96	1/2 vd.	4·41	4 d.
3·54	6	2·47	1 d.	3·91	2 vd.
3·45	10	2·20	2 d.	3·68	2
3·21	5			3·51	8
2·91	4			3·29	6 d.
2·47	3			2·96	2 d.
2·37	1			2·48	2
2·23	5			2·40	2
2·18	2			2·22	4
2·14	2			2·16	1
2·06	1 d.			1·896	1/2 d.
1·840	1 d.			1·747	1/2 d.
1·764	1/2 vd.			1·559	1/2 vd.
1·656	4				
1·572	1/2 vd.				
1·505	2 d.				
1·380	1 vd.				
1·280	1 vd.				
1·206	1 vd.				
1·141	2 vd.				
1·085	1/2 vd.			d. = diffuse.	
1·021	1/2 vd.			vd. = very diffuse.	

Arsenuranospathite

This new mineral, which is the arsenate analogue of uranospathite, was found by the author among the secondary minerals of the uranium deposit of Menzenschwand. Only two specimens exist, which were collected at the deposit during an excursion in 1959. The same mineral also occurs at Wittichen in the Black Forest, but only in extremely minute amounts (Walenta, 1972, p. 301). The name arsenuranospathite ('Arsen-Uranospathit') for the mineral from Menzenschwand was first used by the author (1963, p. 116). Later a preliminary description was published (Walenta, 1965, p. 275; 1967, p. 159). The following detailed description is restricted to the mineral from Menzenschwand; for particulars of the occurrence at Wittichen see Walenta, 1972, p. 301.

Mode of occurrence. Arsenuranospathite occurs in crusts on baryte. It is associated with limonite and secondary uranium minerals, such as zeunerite, mixed crystals of the series uranocircite-heinrichite, uranophane, and studtite.
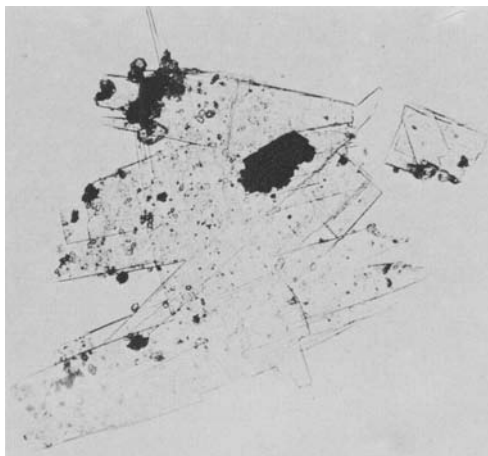

FIG. 3. Aggregate of arsenuranospathite crystals embedded in Canada balsam. Menzenschwand, Black Forest. Magnification about 100 ×.

The arsenuranospathite crusts are composed of minute tabular crystals, which are elongated along a horizontal axis (figs. 3 and 4). Their maximum length is about 0·3 mm. Almost a needle-like habit results if the elongation is pronounced. The lateral edges of the crystals are sometimes slightly curved. Form and optical orientation of the crystals conform to orthorhombic symmetry.
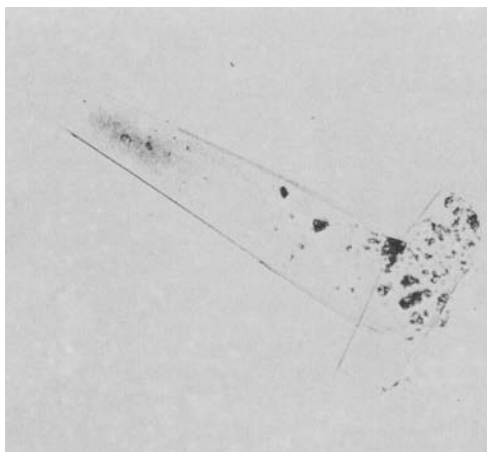

FIG. 4. Elongated crystal of arsenuranospathite embedded in Canada balsam. Menzenschwand, Black Forest. Magnification about 260 ×.

The observed forms are: $\{100\}$, $\{010\}$, and $\{001\}$. Rarely the edges are truncated by small $\{110\}$ faces.

Physical and optical properties. Like other members of the torbernite series arsenuranospathite has a perfect cleavage $\{001\}$ and two other less-pronounced cleavage planes parallel to $\{100\}$ and $\{010\}$. The colour of the transparent to translucent crystals is pale yellow or almost white. The hardness could not be determined with accuracy, it is probably about 2, ρ_{calc} 2.54 g cm^{-3}. The crystals are weakly fluorescent in ultra-violet light. The smallness of the crystals renders observation of the greenish fluorescence difficult. If low-powered ultra-violet lamps are used, hardly any fluorescence is visible (see Walenta, 1967, p. 159). The optical properties are: $\alpha \ll 1.538$, $\beta \approx 1.538$, γ 1.542 ± 0.003, $2V_\alpha$ $52°$, $r > v$, straight extinction, $\alpha \parallel$ [001], $\gamma \parallel$ elongation. The rapid dehydration of the mineral made the determination of all three indices of refraction impossible. The determined indices are higher than those of uranospathite, as is to be expected if AsO$_4$ substitutes for PO$_4$.

Chemical composition. Investigation by microchemical and spectrochemical methods showed the presence of U, As, and Al. In addition very small amounts of Fe could be detected. Impurities such as limonite might be responsible for the presence of Fe. Several small crystals of arsenuranospathite were analysed by the electron microprobe (analyst: H. Lauckner, Standard Elektrik Lorenz AG, Stuttgart). According to these investigations the content of Al$_2$O$_3$ is $\approx 2.8\%$. This refers to the mineral in the partially dehydrated state. Synthetic $(HAl)_{0.5}(UO_2)_2(AsO_4)_2 . 10H_2O$ was used as standard.

The formula of arsenuranospathite therefore undoubtfully corresponds to that of uranospathite with As replacing P: $(HAl)_{0.5}(UO_2)_2(AsO_4)_2 . 20H_2O$. The theoretical composition is: Al$_2$O$_3$ 2.14, UO$_3$ 47.98, As$_2$O$_5$ 19.28, H$_2$O 30.60, total 100%. If the value of 2.8% cited above is recalculated for the fully hydrated phase, an Al$_2$O$_3$ content of 2.4% results, in better agreement with the theoretical composition.

X-ray data. The powder pattern, which is given in Table VII, resembles that of uranospathite. The d-values, however, are greater than in the case of uranospathite, which is due to the replacement of P^{5+} by the larger As^{5+} ion in the lattice. Consequently the unit-cell dimensions derived from the powder diagram also are larger than those of uranospathite: a 7.16, c 30.37 Å, $Z = 2$. Probable space group $P4_2/n$. As in the case of uranospathite the optical behaviour and to some degree also the form of the crystals, which conform to orthorhombic symmetry, lead to the conclusion that the true unit cell also is orthorhombic and that

TABLE VII. *X-ray data for fully hydrated arsenuranospathite from Menzenschwand*

d (Å)	I	d_{calc} (Å)	hkl
14.62	10	15.19	002
7.62	10	7.59	004
5.03	8	5.06; 4.99	110, 006; 111
4.56	1	4.53	113
4.16	1	4.13	106
3.59	6	3.58	200, 116
3.49	9	3.48	202
3.36	1/2	$\begin{Bmatrix}3.38; 3.37;\\3.35\end{Bmatrix}$	203; 009; 108
3.24	4	3.24	204
3.11	1/2	3.13	212
2.94	1/2	2.95; 2.92	214; 206
2.53	1	2.53; 2.52	$\begin{cases}220, 0.0.12;\\221\end{cases}$
2.48	2	2.50; 2.46	222; 223, 209
2.40	1	2.40; 2.39	224; 300, 1.0.12
2.25	3	2.26; 2.24	$\begin{cases}310, 226, 1.1.12,\\311; 312\end{cases}$
2.21	1/2	$\begin{cases}2.22; 2.21;\\2.20\end{cases}$	305, 1.0.13;\ 313; 2.1.10
2.12	2 d.	2.12; 2.11	315, 1.1.13; 228
1.911	1/2 d.	1.921; 1.898	324; 0.0.16
1.854	2	1.856; 1.849	2.0.14; 326
1.789	2	$\begin{cases}1.790; 1.787;\\1.786\end{cases}$	400, 2.2.12;\ 401; 0.0.17
1.774	2	1.778; 1.777	402; 1.1.16
1.740	1	$\begin{cases}1.742; 1.737;\\1.736\end{cases}$	404; 410;\ 3.0.12
1.654	2		
1.602	2 d.		
1.566	1/2		
1.499	1 d.		
1.390	1 d.		
1.292	1/2 d.		
1.148	1/2 d.	d. = diffuse.	
1.130	1/2 d.	vd. = very diffuse.	

the above data refer only to a tetragonal pseudo-cell.

Dehydration. As already stated fully hydrated arsenuranospathite is unstable at room temperature and normal air humidity. It is converted into a dehydration phase the properties of which correspond to those of synthetic $(HAl)_{0.5}(UO_2)_2$ $(AsO_4)_2 . 10H_2O$. A definite intermediate hydrate with a water content between 20 and 10 molecules does not seem to exist. The conversion of arsenuranospathite into the lower hydrate is reversible to a certain degree. Dehydrated arsenuranospathite exposed to a cold humid atmosphere only a short time after dehydration could be converted again into the fully hydrated phase. If, however, more time elapsed between dehydra-

tion and the attempts of rehydration, they were not successful. It seems that small changes in the lattice take place in the dehydrated state which make rehydration impossible.

The optical properties of dehydrated arsen-uranospathite are: α 1.564 ± 0.002, colourless, β 1.594 ± 0.002, γ 1.596 ± 0.002, yellowish, $2V_\alpha$ about $28°$, $r > v$, straight extinction, length positive, $\alpha \parallel [001]$. The unit-cell dimensions derived from the powder pattern (Table VIII) are: a 7.15, c 20.52 Å, $Z = 2$, ρ_{calc} 3.20 g cm^{-3}. However, as in case of partially dehydrated uranospathite (sabugalite) not all the reflections can be indexed on the basis of this cell, so it can only be regarded as a tetragonal pseudo-cell.

TABLE VIII. *X-ray data for partially dehydrated arsenuranospathite from Menzenschwand*

d (Å)	I	d_{calc} (Å)	hkl
10·54	10	10·26	002
5·13	6 d.	5·13; 5·06	004; 110
4·55	3 d.	4·54	112
4·13	1	4·17; 4·10	104; 005
3·73	1 d.		
3·54	10	3·56; 3·52	105; 201
3·34	1/2		
3·17	5	{3·19; 3·17; 3·16	115; 203; 211
2·53	4	{2·54; 2·53; 2·52; 2·51	117; 220; 215; 221
2·45	4	2·45	222
2·25	5	2·26; 2·25	{310; 303; 311
2·11	1	2·08	104
2·05	1	2·06; 2·05	305; 0.0.10
1·909	1 vd.	{1·914; 1·905; 1·901	227; 323; 1.1.10
1·788	3 d.	{1·790; 1·788; 1·786	317; 400; 325
1·760	3 d.	1·761	402
1·597	4		
1·406	1/2		
1·320	1/2		
1·291	1/2		
1·262	1/2		
1·192	1/2 vd.	d. = diffuse.	
1·132	1 vd.	vd. = very diffuse.	

The hydrate with $10H_2O$ is more or less stable at room temperature. X-ray investigations show that there is no marked change in the powder pattern after heating arsenuranospathite to 40 °C. If, however, the mineral is heated to 60° for two hours, a phase change occurs and γ rises to 1.608 ± 0.002.

The powder pattern upon heating is more or less identical with that of the synthetic product

given in Table X*b*, but of much poorer quality as only a minute quantity of the mineral could be used for these investigations, and therefore is not cited here. Stronger heating causes further dehydration, which is accompanied by an additional increase in the indices of refraction. Detailed studies of the thermal behaviour could not be carried out for lack of material (see also synthetic $(HAl)_{0.5}(UO_2)_2(AsO_4)_2 \cdot 10H_2O$, below).

Synthesis. All attempts to synthesize an aluminium uranyl arsenate with the same degree of hydration as the natural mineral arsenuranospathite were fruitless. The substances used for this work were aluminium chloride or nitrate, uranyl acetate, and arsenic acid.

As in the case of aluminium uranyl phosphate a hydrate with $16H_2O$ was obtained. The water content was determined by an indirect method (Walenta, 1965, p. 273). The aluminium content was checked upon conversion to the lower hydrate (see below). The instability of the hydrate, which can be preserved only if immersed in water, excluded direct determinations of its constituents.

The synthesized material has a refractive index γ of 1.540 ± 0.003. As in case of the phosphate analogue, this is close to the respective index of refraction of the fully hydrated natural mineral. The X-ray investigation proved again that despite the similar γ-value of the synthetic and the natural phase, their degree of hydration is not identical. The lattice constants of synthetic $(HAl)_{0.5}(UO_2)_2(AsO_4)_2 \cdot 16H_2O$ are: a 7.15, c 26.54 Å, $Z = 2$, ρ_{calc} 2.74 g cm^{-3}. The powder pattern is listed in Table IX.

TABLE IX. *X-ray powder data for synthetic* $(HAl)_{0.5}(UO_2)_2(AsO_4)_2 \cdot 16H_2O$

d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
13·23	10	2·33	2	1·754	1	1·351	1 d.
6·69	8	2·26	2	1·709	1	1·297	1 d.
4·45	3	2·21	5	1·665	2	1·262	2 d.
3·57	7 d.	2·14	1	1·642	2	1·231	1/2 d.
3·44	1	2·07	2 d.	1·598	4 d.	1·187	1/2 d.
3·33	5	1·993	1/2	1·558	1/2 d.	1·132	4 d.
3·23	1/2	1·940	1/2	1·520	2 d.	1·114	1/2 d.
2·87	1	1·902	4	1·477	1/2 d.	1·091	1/2 d.
2·52	2	1·863	1/2	1·431	1/2 d.	1·025	1 d.
2·46	1/2	1·809	2	1·393	2 d.	1·014	2 vd.
		1·792	1				

d. = diffuse. vd. = very diffuse.

As already mentioned, the hydrate with $16H_2O$ is very unstable, like the analogous phosphate compound. It, too, converts to a lower hydrate that contains about $10H_2O$ per formula unit, according to two water determinations, which yielded 18·73

and 19.15%. The content of Al_2O_3 amounts to 2.81% according to a determination by the Institut Fresenius, Taunusstein. These values are in satisfactory agreement with the theoretical composition for $(HAl)_{0.5}(UO_2)_2(AsO_4)_2 . 10H_2O$: UO_3 56.52, Al_2O_3 2.52, As_2O_5 22.71, H_2O 18.25, total 100.00%.

The optical properties of this hydrate as well as the powder pattern and the unit-cell dimensions derived from it are within limits of error identical to those of the dehydration product of arsenuranospathite and so furnish important evidence for the identity of the two substances. The refractive index γ is 1.598 ± 0.002. The unit-cell dimensions are: a 7.14, c 20.53 Å. The powder pattern is given in Table X, col. (a).

TABLE X. *X-ray powder data for synthetic* $(HAl)_{0.5}(UO_2)_2(AsO_4)_2 . 8$–$10H_2O$

(a) composition close to $10H_2O$		(b) water content less than in sample (a)		(a) composition close to $10H_2O$		(b) water content less than in sample (a)	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
10·29	10	9·71	10	2·05	1/2	2·45	4
5·08	6	5·73	4	1·900	2 d.	2·32	1
4·59	5 d.	5·08	6	1·786	4	2·25	4 d.
3·81	1 vd.	4·63	4	1·762	2	2·13	1 d.
3·56	9	4·47	4	1·689	1/2 d.	1·939	1 vd.
3·35	2	3·94	4	1·598	5	1·782	3 d.
3·19	5 d.	3·57	8	1·493	1 vd.	1·597	3 d.
2·84	1/2 d.	3·36	5	1·401	1/2 d.	1·430	1/2 vd.
2·53	5	3·17	1/2	1·378	1/2 d.	1·380	1/2 vd.
2·45	4	3·02	3	1·317	1/2 d.	1·258	1/2 vd.
2·32	1/2 d.	2·85	2	1·290	1 d.	1·194	1 vd.
2·25	5	2·64	1/2	1·189	2 d.	1·131	2 vd.
2·17	1/2	2·53	5	1·130	3 vd.		

d. = diffuse.   vd. = very diffuse.

The powder pattern of the dehydration product obtained at a time when the air humidity was very low differs somewhat from the normal one (see Table X, col. b). The c lattice constant is reduced to less than 20 Å. This is accompanied by an increase in the value of γ to more than 1.606. It may be assumed that under such conditions more water is lost so that the content approaches $8H_2O$. This hydrate is identical to the phase obtained by heating the natural mineral to 60 °C.

Conclusions

The present investigations show that uranospathite and its arsenate analogue, arsenuranospathite, are aluminium-bearing members of the torbernite group that contain more water per unit cell in the fully hydrated state than other members. This difference in behaviour may be explained by the small ionic radius of Al^{3+} (see Walenta, 1965). There is a general tendency towards an increase of the water content in the fully hydrated state with decreasing ionic radius and increasing valence of the additional cation.

Some important data for the investigated minerals are listed in Table XI. As in the case of other members of the mineral group in question characteristic differences between the properties of the phosphate and the analogous arsenate become evident (Walenta, 1965).

Problems of nomenclature

Though it is not unusual to give hydrated minerals having the same basic composition and differing only in the number of water molecules different mineral names (as, for instance, kieserite $MgSO_4.H_2O$, sanderite $MgSO_4.2H_2O$, leonhardtite $MgSO_4.4H_2O$, etc.), fortunately this has not been the custom in case of members of the torbernite group until now. The prefix meta is used for the lower hydrate and if more than two hydrates exist in nature, roman numbers may be applied in addition. In the case of the barium uranyl phosphate uranocircite four hydrates exist which have been termed uranocircite I, uranocircite II, metauranocircite I, and metauranocircite II (Walenta, 1963, 1965).

This kind of nomenclature could also be used in the case of the aluminium-bearing members. However, it must be decided first whether the name uranospathite or sabugalite should have priority. Uranospathite was described first, sabugalite later, but the data for uranospathite were insufficient so the question of priority is not easy to decide. Therefore, it might perhaps be warranted to make an exception in this special case and to retain the name uranospathite for the fully hydrated mineral and the name sabugalite for the stable lower hydrate.

In the case of the arsenate analogue the problem is less difficult. Though the presumed arsenate analogue of sabugalite has been named paulite in 1960 by Bültemann, no data for the new mineral were supplied and the name therefore was rejected by the Commission on New Minerals and Mineral Names. Consequently the name arsenuranospathite could be used as a basic term for all hydrates.

As there does not seem to exist a stable hydrate that corresponds in its structure to the hydrates usually designated with the prefix meta, it might be advisable to use only roman numbers for

TABLE XI. *Comparison of some properties of uranospathite and arsenuranospathite*

	Uranospathite $(HAl)_{0.5}(UO_2)_2(PO_4)_2.20H_2O$	Arsenuranospathite $(HAl)_{0.5}(UO_2)_2(AsO_4)_2.20H_2O$
Unit-cell dimensions		
a	7·00 Å	7·16 Å
c	30·02 Å	30·37 Å
$a:c$	1:4·2886	1:4·2416
Z	2	2
Probable space group	$P4_2/n$	$P4_2/n$
ρ	2·49 g cm^{-3}	2·54 g cm^{-3}
Optical cata		
α	1·492 ± 0·002	
β	1·511 ± 0·002	1·538
γ	1·521 ± 0·002	1·542 ± 0·003
$2V_\alpha$	76°	52°

differentiating between the hydrates. The highest hydrate would then be arsenuranospathite I, that stable at room temperature arsenuranospathite III, and not II because the name arsenuranospathite II should be reserved for the hydrate with $16H_2O$ known only as a synthetic compound until now, but possibly also occurring in nature.

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