

STUDIES OF THE TORBERNITE MINERALS (I): THE
CRYSTAL STRUCTURE OF ABERNATHYITE AND
THE STRUCTURALLY RELATED COMPOUNDS
 $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ and $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}^1$

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ABSTRACT

A large number of minerals and synthetic compounds belonging to the torbernite mineral group can be represented by the formula $\text{A}^{z+}(\text{UO}_2\text{XO}_4)_z \cdot n\text{H}_2\text{O}$, where A may be almost any monovalent or divalent cation and X=P or As. In order to learn more of the crystal chemistry of these phases, detailed crystal-structure studies of (I) $\text{K}(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ (abernathyite); (II), $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$; and (III), $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$ have been carried out. The structures were refined by least-squares analysis. The well-known waffle-like $(\text{UO}_2\text{XO}_4)_n^{n-}$ sheet structure proposed by Beintema is confirmed and details of the interlayer structure are revealed through a complete resolution of all atoms except hydrogen in the electron density maps. In all three structures studied, the positions of the interlayer water molecules are based on an "ideal" arrangement in which four water molecules are hydrogen-bonded together to form squares which lie between the uranyl ions of successive layers. Each water molecule of a square group is also hydrogen-bonded to a water molecule in an adjacent square and to an arsenate oxygen atom, thus attaining a distorted tetrahedral coordination. In phase (I), one potassium ion and three water molecules are distributed randomly over four water molecule sites; in phase (II) an ammonium ion and three water molecules are distributed over four H_2O sites; and in phase (III) one-half a potassium ion, one-half an oxonium ion, and three water molecules are distributed randomly over four H_2O sites. To express this distribution of cations over water molecule sites the structural formulas of phases (I), (II), and (III) are written $(\text{K} \cdot 3\text{H}_2\text{O})(\text{UO}_2\text{AsO}_4)$, $[(\text{NH}_4) \cdot 3\text{H}_2\text{O}](\text{UO}_2\text{AsO}_4)$, and $[\text{K}_{\frac{1}{2}}(\text{H}_3\text{O})_{\frac{1}{2}} \cdot 3\text{H}_2\text{O}](\text{UO}_2\text{AsO}_4)$ respectively. X-ray powder data for (I), (II), and (III) are given.

INTRODUCTION

The purpose of this paper is to give a detailed discussion of the crystallography and crystal structure of three compounds belonging to the torbernite mineral group. Of particular interest is the crystal chemical role of the water molecules and interlayer cations which lie between the sheets of these layer-lattice compounds.

Most torbernite-like minerals are characterized by the formula $\text{A}^{z+}(\text{UO}_2\text{XO}_4)_z \cdot n\text{H}_2\text{O}$, where X=P and/or As, and A, a large variety of cations. The designation, torbernite group, is used here to include all uranyl phosphates and uranyl arsenates which possess infinite sheets of the type $(\text{UO}_2\text{PO}_4)_n^{n-}$ or $(\text{UO}_2\text{AsO}_4)_n^{n-}$, isostructural with the sheets pro-

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² Based on a dissertation submitted by M. Ross to the Department of Geological Sciences, Harvard University (1962) in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

posed for autunite and meta-autunite (I) by Beintema (1938). These sheets consist of dumbbell-shaped uranyl ions, with the uranium further coordinated by four oxygen atoms of four different PO_4^{3-} tetrahedra. The tetrahedra and uranyl ions link into two-dimensional sheets (Fig. 1) lying parallel to (001). These sheets are puckered with the uranyl ion displaced upward and downward from the plane of the phosphorus atoms. In the fully hydrated autunite, adjacent sheets are related to each other by a mirror plane lying half-way between the uranyl ions and perpendicular to the c -axis. As can be seen in Fig. 1A, large cavities appear between alternate uranyl ions in which a large cation and/or hydration sphere can lie. If the sheets are translated with respect to one another by the vector $[\frac{1}{2}, -\frac{1}{2}, 0]$ the structure proposed by Beintema (1938) for meta-autunite (I) is obtained (Fig. 1B). In this structure the large cavities between the sheets are eliminated. The translation of the sheets accounts for the loss of water and permits the sheets to move closer together.

Beintema (1938), in his now classic paper, first described the basic structure of the sheets. He was able to locate the positions of the uranium atoms within the sheet experimentally and by astute crystal-chemical reasoning predicted the positions of the other atoms of the sheets with fair accuracy. The techniques of the time would not permit the location of the light atoms such as oxygen in the presence of the heavy uranium atoms. The structure of the layers is essentially confirmed by the present work, and the light atoms (except hydrogen) have been clearly resolved from our diffraction data.

MINERALS OF THE TORBERNITE GROUP

The naturally occurring minerals belonging to the torbernite group are listed in Table 1. The number of water molecules in the chemical formulas of most of these minerals is not accurately known. There may be several hydration states for each of the minerals listed, though many are probably unstable at room temperature and low humidity. Frondel (1958) has summarized in detail the mineralogy of these phases.

A large number of synthetic compounds belonging to the torbernite group have been prepared. The uranyl phosphates of Cu^{2+} , Ca^{2+} , (HAl^{4+}) , Ba^{2+} , Sr^{2+} , Pb^{2+} , Mg^{2+} , Mn^{2+} , Ni^{2+} , Co^{2+} , Na^+ , $(\text{NaH})^{2+}$, K^+ , NH_4^+ , H^+ , and Li^+ , and uranyl arsenates of Cu^{2+} , Mg^{2+} , Ca^{2+} , Na^+ , K^+ , NH_4^+ , H^+ , and Li^+ , have been synthesized. All of these uranyl phosphates and arsenates crystallize with water of hydration but in most cases the exact amount of water present has not been determined.

The torbernite minerals and compounds exhibit the property of cation exchange. There probably exists an extensive solid solution between the

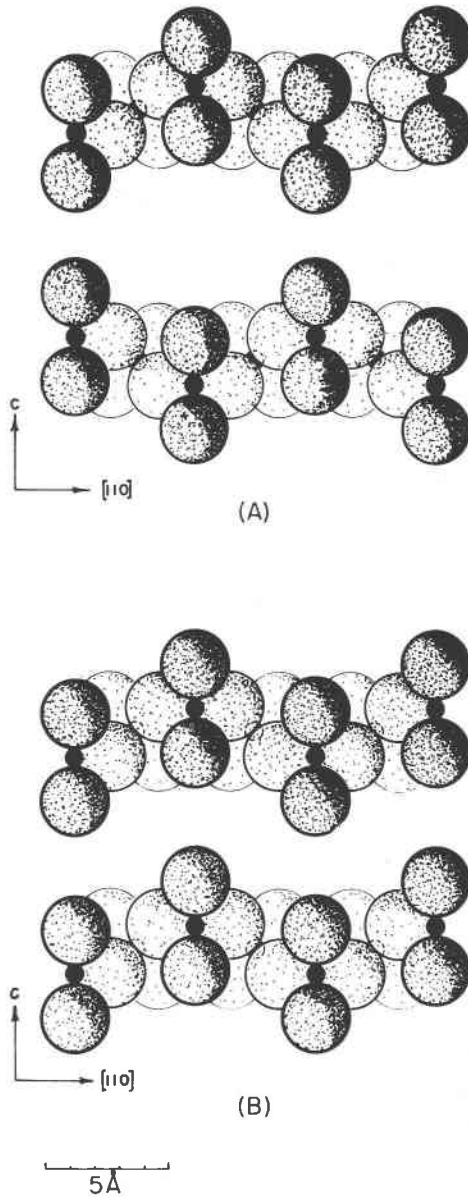


FIG. 1. (A) The structure of autunite projected on $(\bar{1}10)$ (after Beintema, 1938).
 (B) The structure of meta-autunite (I) projected on $(\bar{1}10)$ (after Beintema, 1938).

TABLE 1. MINERALS OF THE TORBERNITE GROUP¹

Phosphates	Arsenate analogues
autunite, $\text{Ca}(\text{UO}_2\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$	uranospinite, $\text{Ca}(\text{UO}_2\text{AsO}_4)_2 \cdot n\text{H}_2\text{O}$
meta-autunite(I), $\text{Ca}(\text{UO}_2\text{PO}_4)_2 \cdot y\text{H}_2\text{O}$	
meta-autunite(II), $\text{Ca}(\text{UO}_2\text{PO}_4)_2 \cdot z\text{H}_2\text{O}$	zeunerite, $\text{Cu}(\text{UO}_2\text{AsO}_4)_2 \cdot n\text{H}_2\text{O}$
torbernite, $\text{Cu}(\text{UO}_2\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$	meta-zeunerite, $\text{Cu}(\text{UO}_2\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$
meta-torbernite, $\text{Cu}(\text{UO}_2\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	heinrichite, $\text{Ba}(\text{UO}_2\text{AsO}_4)_2 \cdot 10\text{-}12\text{H}_2\text{O}$
uranocircite, $\text{Ba}(\text{UO}_2\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$	meta-heinrichite, $\text{Ba}(\text{UO}_2\text{AsO}_4)_2 \cdot n\text{H}_2\text{O}$
meta-uranocircite(I), $\text{Ba}(\text{UO}_2\text{PO}_4)_2 \cdot y\text{H}_2\text{O}$	
meta-uranocircite(II), $\text{Ba}(\text{UO}_2\text{PO}_4)_2 \cdot z\text{H}_2\text{O}$	novacekite, $\text{Mg}(\text{UO}_2\text{AsO}_4)_2 \cdot n\text{H}_2\text{O}$
saléeite, $\text{Mg}(\text{UO}_2\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$	troegerite, $\text{H}(\text{UO}_2\text{AsO}_4) \cdot 4\text{H}_2\text{O}$
sabugalite, $\text{AlH}(\text{UO}_2\text{PO}_4)_4 \cdot n\text{H}_2\text{O}$	kahlerite, $\text{Fe}(\text{UO}_2\text{AsO}_4)_2 \cdot n\text{H}_2\text{O}$
bassetite, $\text{Fe}(\text{UO}_2\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$	abernathyite, $\text{K}(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$
meta-ankoleite, $\text{K}(\text{UO}_2\text{PO}_4) \cdot 3\text{H}_2\text{O}$	sodium uranospinite, $\text{Na}(\text{UO}_2\text{AsO}_4) \cdot n\text{H}_2\text{O}$
sodium autunite, $\text{Na}(\text{UO}_2\text{PO}_4) \cdot n\text{H}_2\text{O}$	
uramphite, $\text{NH}_4(\text{UO}_2\text{PO}_4) \cdot 3\text{H}_2\text{O}$	

¹ The exact number of water molecules per formula unit is not known for most of these minerals.

arsenate and phosphate analogues of these compounds as well as between end-members having different interlayer cations.

CRYSTALLOGRAPHY AND CHEMICAL COMPOSITION OF $\text{K}(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ (ABERNATHYITE), $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$, AND $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$

Abernathyite was described by Thompson *et al.* (1956) as a hydrous potassium uranyl arsenate with the chemical formula $\text{K}(\text{UO}_2\text{AsO}_4) \cdot 4\text{H}_2\text{O}$. It occurs as small, thick, tabular transparent yellow crystals. The mineral possesses perfect (001) cleavage, has a hardness of 2 to 3 and shows the forms {001} and {110}. Abernathyite is very rare and is definitely reported from only one locality; the Fuemrol No. 2 mine at Temple Mountain, Emery County, Utah, where it occurs as a coating lining a fracture in the sandstone. As we shall see later the true chemical composition of abernathyite is $\text{K}(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$.

The specimen used in the present study was obtained from Miss Thompson and is from the type material. Type material at the U. S. National Museum (U.S.N.M. 112650) was also examined. Only a few milligrams of this mineral are known to exist so that the present study was restricted to the examination of a few individual crystals of a size less than $0.5 \times 0.5 \times 0.10$ millimeters. The crystals examined were bright and transparent but some others in the sample were slightly darker in color because of a thin coating of another mineral, probably scorodite, (Fe,

Al)AsO₄·2H₂O. The optical properties obtained for the present study by C. S. Ross, U. S. Geological Survey, are: uniaxial negative, $\epsilon = 1.570 \pm 0.003$ and $\omega = 1.608 \pm 0.003$.

X-ray single-crystal studies of abernathyite, NH₄(UO₂AsO₄)·3H₂O, and K(H₃O)(UO₂AsO₄)₂·6H₂O were made with the Buerger precession camera using molybdenum radiation. Photographs of the *0kl*, *1kl*, *2kl*, *3kl*, *hk0*, *hk1*, *hk2*, and *hhl* nets of abernathyite show this mineral to be tetragonal with *4/mmm* Laue symmetry. All reflections are sharp showing no evidence of atomic disorder or mechanical distortion. The special extinctions observed among the recorded *x*-ray reflections conform uniquely to the space group *P4/ncc*. The *hkl* reflections in which *l* is odd are extremely weak, only eighteen of this type appearing in the *hk1*, *1kl*, *2kl*, and *3kl* photographs. Donnay and Donnay (1955, also G. Donnay in Thompson *et al.*, 1956) did not observe these weak reflections and thus reported the *c*-dimension of abernathyite to be 9.07 Å instead of 18.126 Å as found in the present study. The *x*-ray and optical data of abernathyite obtained in the present study are compared in Table 2 to those given in the original descriptions.

TABLE 2. X-RAY AND OPTICAL DATA FOR K(UO₂AsO₄)·3H₂O (ABERNATHYITE), NH₄(UO₂AsO₄)·3H₂O, AND K(H₃O)(UO₂AsO₄)₂·6H₂O

System	Abernathyite		NH ₄ (UO ₂ AsO ₄)·3H ₂ O	K(H ₃ O)(UO ₂ AsO ₄) ₂ ·6H ₂ O
	Present study	Donnay & Donnay, 1955	Present study	Present study
	Tetragonal	Tetragonal	Tetragonal	Tetragonal
<i>a</i> (Å)	7.176 ± 0.008	7.17 ± 0.01	7.189 ± 0.005	7.171 ± 0.005
<i>c</i> (Å)	18.126 ± 0.010	9.07 ± 0.01	18.191 ± 0.014	18.048 ± 0.010
Laue Group	<i>4/mmm</i>	<i>4/mmm</i>	<i>4/mmm</i>	<i>4/mmm</i>
Space Group	<i>P4/ncc</i>	<i>P4/nmm</i>	<i>P4/ncc</i>	<i>P4/ncc</i>
V (Å ³)	933.4	466.3	940.2	928.1
Z	4	2	4	2
Density (calc.) g/cm ³ .	3.572	3.575	3.429	3.521
Pseudo-cell				
<i>a'</i>	7.176	—	7.189	7.171
<i>c'</i>	9.063	—	9.095	9.024
Pseudo-space group	<i>P4/nmm</i>	—	<i>P4/nmm</i>	<i>P4/nmm</i>
Optical Properties				
ϵ	1.570 ± 0.003	1.570 ± 0.003 ¹	1.601 ± 0.003 ²	1.572 ± 0.003
ω	1.608 ± 0.003	1.597 ± 0.003 ¹	1.611 ± 0.003 ²	1.611 ± 0.003
(2 ω + ϵ)/3(calc.)	1.606	—	1.636	1.607
(2 ω + ϵ)/3(obs.)	1.595	—	1.608	1.598
Forms	{001}, {110}	{001}, {110}	{001}, {100}	{001}, {100}

¹ Thompson, *et al.*, 1956.

² Mrose, 1953.

The $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ crystals are bright yellow in color and are optically uniaxial negative with $\epsilon = 1.601$ and $\omega = 1.611$ (Mrose, 1953). The crystals exist as very small tablets, flattened on $\{001\}$ with $\{100\}$ also present. The chemical analysis as made by Robert Meyrowitz (U. S. Geological Survey) is shown in Table 3 and is compared to the original analysis of this material by Gonyer (Mrose, 1953).

The $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$ crystals are bright yellow, and are nearly identical in appearance to the $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ crystals. They are tabular, flattened on $\{001\}$ and with $\{100\}$ also present. The

TABLE 3. CHEMICAL ANALYSES OF $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ AND $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$

	$\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$				$\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}^1$	
	Present Study ¹		Mrose, 1953 ²		Present Study	
	Wt. %	Ratios ³	Wt. %	Ratios ⁴	Wt. %	Ratios ⁵
$(\text{NH}_4)_2\text{O}$	5.5	0.507	5.11	0.470	—	—
K_2O	—	—	—	—	4.4	0.451
UO_3	59.6	1.000	59.70	1.000	59.2	2.000
As_2O_5	23.1	0.482	23.14	0.482	22.5	0.946
H_2O	11.7	3.127	12.13	3.226	13.3	7.135
	99.9		100.08		99.4	

¹ Analyst, R. Meyrowitz.

² Analyst, F. A. Gonyer.

³ $(\text{NH}_4)_{1.00}(\text{UO}_2)_{1.00}(\text{AsO}_4)_{0.96}(\text{H}_2\text{O})_{3.13}$, number of ions on the basis of $\text{UO}_3 = 1.000$.

⁴ $(\text{NH}_4)_{0.94}(\text{UO}_2)_{1.00}(\text{AsO}_4)_{0.96}(\text{H}_2\text{O})_{3.23}$, number of ions on the basis of $\text{UO}_3 = 1.000$.

⁵ $\text{K}_{0.90}(\text{H}_3\text{O})_{1.10}(\text{UO}_2)_2.00(\text{AsO}_4)_{1.99}(\text{H}_2\text{O})_{5.49}$, number of ions on the basis of $\text{UO}_3 = 2.000$.

optical properties as determined by C. S. Ross are: uniaxial negative, $\epsilon = 1.572$, $\omega = 1.611$. The chemical analysis of this compound is given in Table 3. The analysis indicates that this compound has the approximate formula $\text{KH}(\text{UO}_2\text{AsO}_4)_2 \cdot 7\text{H}_2\text{O}$, although as we shall see the formula is better written $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$ to indicate a relationship between K^+ and (H_3O^+) .

The space group of $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ and $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$ was determined from $hk0$, $hk1$, $0kl$, and $1kl$ Buerger precession photographs. These photographs appear identical to those of abernathyite. The $hk1$ photographs are particularly revealing in this respect for they show the same distribution and intensity of the very weak spots as do the $hk1$ photographs of abernathyite. The x-ray and optical data of these two compounds are compared to those of abernathyite in Table 2.

The indexed x -ray powder data for abernathyite, $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$, and $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$ are given in Table 4.

PRELIMINARY STRUCTURE DETERMINATION OF ABERNATHYITE

Two small crystals ($0.06 \times 0.17 \times 0.19$ mm and $0.07 \times 0.11 \times 0.13$ mm) were used to collect the abernathyite intensity data. The data were gathered by photographing the $hk0$, $0kl$, $1kl$, $2kl$, and $3kl$ reciprocal lattice nets with the Buerger precession camera. Molybdenum zirconium-filtered radiation was used for all photographs. The intensities of the spots were estimated visually with a calibrated intensity strip prepared with the Buerger precession camera. Lorentz and polarization corrections ($1/L_p$) were made to the observed intensities by means of a computer program based on the formulas of Waser (1951).

There are four uranium atoms per unit cell, and in the space group $P4/ncc$ we will expect to find these atoms in positions $4a$, $4b$, or $4c$. Since reflections of the type hkl are weak or missing only when $l = 2n + 1$, uranium is probably in position $4c$. If the uranium atoms were in positions $4b$ or $4a$, reflections of the type hkl where $h + k = 2n + 1$ would also be weak or missing. Reference to Beintema's work now permits us to place the arsenic atoms in positions $4b$.

To locate the four uranium atoms precisely and also to confirm the positions of the arsenic atoms, a Patterson projection was made on (100). This projection gave the following coordinates for the heavy atoms:

$$4\text{U in } 4c \text{ at } x = \frac{1}{4}, y = \frac{1}{4}, z = 0.0516$$

$$4\text{As in } 4b \text{ at } x = \frac{3}{4}, y = \frac{1}{4}, z = 0$$

No uranium-potassium interactions could be observed in the Patterson map.

Phases were calculated for 82 of the 84 observed $0kl$ structure factors on the basis of these heavy atom coordinates. Fourier projections of the electron density on (100) confirmed the uranium and arsenic positions and also resolved the uranyl and arsenate oxygen atoms and gave some indication of the positions of the interlayer water molecules. An electron density map was also computed using all observed $hk0$ structure factors. This map resolved only the uranium and arsenic atoms.

A tentative model was proposed in which infinite sheets of the type $(\text{UO}_2\text{AsO}_4)_n^{n-}$ are arranged in a manner similar to that of the $(\text{UO}_2\text{PO}_4)_n^{n-}$ sheets of meta-autunite (I) according to Beintema. On the basis of the approximate positions of the uranium, arsenic, uranyl oxygen, and arsenate oxygen atoms as obtained from the preliminary electron density maps, $0kl$ structure factors were calculated. The temperature and scaling factors were refined together by the method of least-squares

TABLE 4. X-RAY POWDER DATA FOR $K(UO_2AsO_4) \cdot 3H_2O$ (ABERNATHYTE),
 $NH_4(UO_2AsO_4) \cdot 3H_2O$, AND $K(H_3O)(UO_2AsO_4)_2 \cdot 6H_2O$ ¹

$K(UO_2AsO_4) \cdot 3H_2O$ (abernathyite)				$NH_4(UO_2AsO_4) \cdot 3H_2O$				$K(H_3O)(UO_2AsO_4)_2 \cdot 6H_2O$			
I ²	d _(meas)	d _(calc) ²	hkl	I ²	d _(meas)	d _(calc) ³	hkl	I ²	d _(meas) ⁴	d _(calc) ³	hkl
22	9.1	9.063	002	22	9.1	9.096	002	22	8.9	9.024	002
15	5.64	5.626	102	16	5.64	5.640	102	17	5.59	5.614	102
13	5.08	5.074	110	13	5.10	5.083	110	14	5.07	5.071	110
13	4.53	4.532	004	14	4.55	4.548	004	15	4.42	4.512	004
12	4.42	4.428	112	10	4.43	4.437	112	12	4.42	4.421	112
19	3.83	3.832	104	18	3.84	3.843	104	18	3.77	3.819	104
16	3.59	3.588	200	15	3.59	3.595	200	16	3.58	3.586	200
		3.380	114			3.389	114			3.371	114
17	3.34	3.336	202	16	3.34	3.343	202	17	3.33	3.332	202
6	3.15	3.160	211	4	3.16	3.166	211	4	3.15	3.158	211
13	3.02	3.025	212			3.032	006			3.022	212
		3.021	006	13	3.03	3.031	212	14	3.02	3.008	006
		2.834	213			2.840	213			2.830	213
14b	2.788	2.813	204	14b	2.797	2.820	204	11	2.788	2.807	204
		2.784	106			2.794	106	14	2.734	2.774	106
11	2.617	2.619	214	12b	2.616	2.625	214	12	2.600	2.614	214
8	2.596	2.596	116			2.604	116	13	2.543	2.587	116
11	2.536	2.537	220	11	2.543	2.542	220	13	2.543	2.535	220
13	2.442	2.443	222	12	2.449	2.448	222	13	2.436	2.441	222
		2.403	215			2.409	215			2.397	215
10	2.309	2.313	302	10	2.321	2.318	206	11	2.304	2.311	302
		2.311	206			2.317	302			2.304	206
13	2.267	2.269	310	13	2.276	2.274	008	12	2.265	2.268	310
		2.266	008			2.273	310	11	2.222	2.256	008
		2.252	311			2.256	311			2.250	311
		2.214	224			2.219	224			2.210	224
13	2.201	2.201	312	13	2.206	2.206	216	9	2.196	2.199	312
		2.200	216			2.206	312	11	2.171	2.194	216
9	2.163	2.161	108	9	2.171	2.168	108	12	2.108	2.152	108
		2.124	313			2.129	313			2.122	313
11	2.115	2.115	304	11	2.122	2.120	304	13	2.032	2.112	304
12	2.069	2.069	118	12	2.077	2.076	118			2.061	118
		2.029	314			2.033	314			2.026	314
		2.015	217			2.021	217			2.009	217
		1.978	321			1.982	321			1.977	321
9	1.943	1.944	322	9	1.949	1.948	226	11	1.937	1.942	322
		1.943	226			1.948	322			1.939	226
7	1.916	1.923	315	6	1.926	1.928	315	9	1.884	1.920	315
		1.916	208			1.922	208			1.909	208
		1.890	323			1.894	323			1.888	323
9	1.875	1.875	306	9	1.883	1.880	306	11	1.855	1.871	306
7	1.850	1.851	218	7	1.859	1.856	218			1.845	218
		1.822	324			1.826	324			1.820	324
12b	1.817	1.814	316	12b	1.823	1.819	00, 10	11	1.814	1.811	316
		1.813	00, 10			1.819	316			1.805	00, 10
10	1.791	1.794	400	9	1.797	1.797	400	11	1.791	1.793	400
10	1.759	1.760	402	10	1.765	1.764	10, 10	11	1.755	1.758	402
		1.757	10, 10			1.763	402			1.750	10, 10
12	1.707			12	1.713			7	1.704		
5	1.689							12	1.675		
10	1.660			9	1.667			9	1.647		
2	1.645							9	1.618		
10	1.621			9	1.626			9	1.600		
13	1.603			12	1.608			12b	1.583		
9	1.581			10	1.584			9b	1.499		
9	1.508			9	1.514			10	1.447		
9	1.478			10	1.484			9	1.415		
9	1.448			10	1.455			11	1.397		
12	1.416			11	1.421			10	1.365		
2	1.392							10	1.342		
9	1.368			8	1.372						
7	1.355			6	1.361						
7	1.296			6	1.299						
9	1.277			10	1.280						
9	1.258			9	1.261						
7	1.237			6	1.241						
6	1.218			6	1.221						
8	1.206			8	1.206						
6	1.197										

¹ Cu K α radiation, Ni filter ($\lambda=1.5418 \text{ \AA}$). Camera diameter: 114.59 mm. Lower limit 2θ measurable: approximately 8° (11.0 \AA).

² Intensities were measured with a calibrated intensity strip, b=broad line.

³ d-spacings were calculated from the unit-cell data given in Table 2. All calculated spacings $\geq 1.750 \text{ \AA}$ permitted by the space group are listed.

⁴ Careful measurement of this x-ray powder pattern shows that it was taken of material that has a somewhat smaller c-dimension (17.8 \AA) than that given in Table 2 (18.048 \AA). This is probably due to a sampling problem wherein the powder pattern was made on more potassium-deficient material.

to obtain the best fit to the observed data. The contributions of the uranium and arsenic atoms to the structure factors were then calculated and subtracted from the scaled observed structure factors. An electron density subtraction synthesis using the remainders for amplitudes was calculated. The subtraction map projected on (100) revealed clearly the interlayer water molecules as well as the arsenate and uranyl oxygen atoms. No evidence for potassium was noted. From this map new atomic positions for all atoms except potassium and hydrogen were assigned. The observed $0kl$ structure factors were again fitted to a set of calculated structure factors by least-squares analysis. This time the atomic parameters as well as the temperature and scaling factors were allowed to vary. After three cycles of refinement, individual temperature factors were assigned to each atom except potassium and refinement was continued for four more cycles. Again, the calculated uranium and arsenic contributions to the $0kl$ structure factors were subtracted from the observed structure factors and the remainders used to calculate another subtraction map (Fig. 2A). The same type of least-

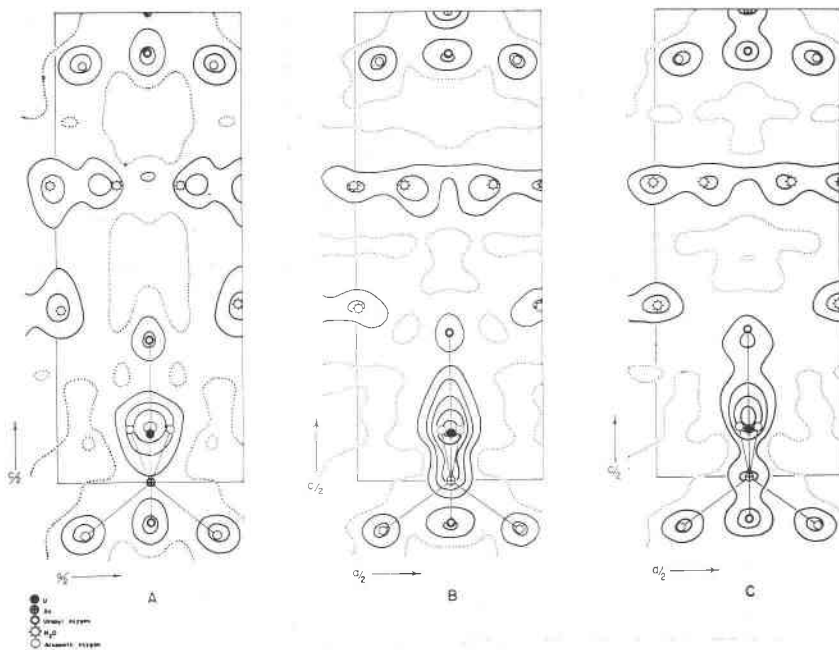


FIG. 2. Electron-density subtraction maps projected on (100) of (A) abernathyite, (B) $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$, and (C) $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$. Contours are drawn at intervals of $5e\text{\AA}^{-2}$ starting at zero (dotted contour). The uranium and arsenic contributions to the electron density have been removed. The final positions of the atoms as given in Tables 6 and 8 are shown.

squares analysis was also carried out with the $hk0$ data in order to obtain a subtraction map projected on (001) (Fig. 3). The subtraction map prepared with $0kl$ data resolved clearly all the oxygen atoms including the water molecules. The subtraction map prepared with $hk0$ data shows the arsenate oxygen atoms and the water molecules not completely resolved because of the overlap of these atoms in this projection. The final $0kl$ and $hk0$ subtraction maps obtained after two-dimensional least-squares analysis (shown in Fig. 2A and 3 respectively) show no evidence for the presence of potassium in the structure, which should appear as peaks of roughly twice the density of the oxygen peaks.

The four peaks appearing in the interlayer region of the $0kl$ subtraction map are assumed to represent a square of four water molecules. As a first consideration, the potassium atom might be expected to lie at the center of this square. However, no peak is present at this position on the subtraction map. Furthermore, calculation reveals that there is no room for potassium in this position, for it would yield K-O bond distances of about 2.0 \AA , an impossibly low value. Also, no room could be found elsewhere in

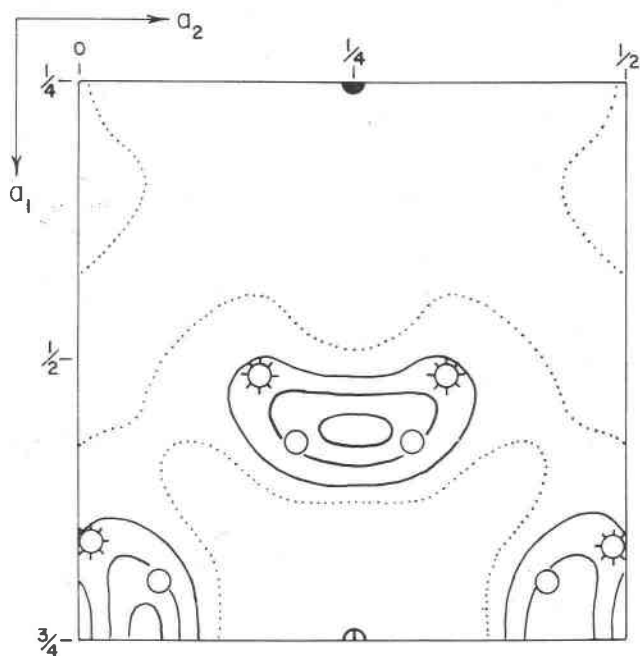


FIG. 3. Electron-density subtraction map projected on (001) of the abernathyite structure. The uranium, uranyl oxygen, and arsenic contributions to the electron density have been removed. Contours are drawn at intervals of $5e\text{\AA}^{-2}$ starting at zero (dotted contour). The designation of the atoms is the same as that given in Fig. 2.

the structure for potassium unless the water molecules were arranged in a most unsymmetrical way.

If it were not for the chemical evidence, the nonexistence of the potassium peak would lead one to believe that abernathyite is in fact troegerite, $\text{H}(\text{UO}_2\text{AsO}_4) \cdot 4\text{H}_2\text{O}$, with the structural formula $(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$. Discussion of the potassium problem with Frank S. Grimaldi and Blanche Ingram of the U. S. Geological Survey, who were associated with the original chemical analysis of abernathyite, showed that there was no reason to doubt the chemical evidence and that the presence of potassium must somehow be reconciled with the diffraction data. This led to the tentative proposal that the actual formula for abernathyite is $\text{K}(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ with one potassium ion and three water molecules distributed randomly over four water molecule sites. The proof for this hypothesis is difficult to establish, but it is felt that the evidence presented in the following sections has indeed shown that this substitution occurs.

First, the rule of Gladstone and Dale (Larsen and Berman, 1934) was applied to the various possible chemical compositions for abernathyite. The mean index of refraction for each formula was found to be as follows:

1) $\text{K}(\text{UO}_2\text{AsO}_4) \cdot 4\text{H}_2\text{O}$:	$(2\omega + \epsilon)/3 = 1.654$
2) $\text{H}(\text{UO}_2\text{AsO}_4) \cdot 4\text{H}_2\text{O}$:	$(2\omega + \epsilon)/3 = 1.619$
3) $\text{K}(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$:	$(2\omega + \epsilon)/3 = 1.606$
4) $\text{H}(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$:	$(2\omega + \epsilon)/3 = 1.564$

The third formula gives the best agreement with the observed value, 1.595 (see Table 2).

Jaffe (1956) has shown that the measured mean index of refraction should not be expected to deviate from the calculated mean index by more than ± 0.020 . Of the 121 minerals representing a wide variety of structure types examined by Jaffe only six showed deviations greater than 0.020 from the mean calculated index. The results of applying the Gladstone-Dale rule suggest that the formula $\text{K}(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ is the correct one.

Additional support for assuming the formula $\text{K}(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ to be the correct one for abernathyite comes from the work of Lienau (1898) who synthesized the compounds $\text{H}(\text{UO}_2\text{PO}_4) \cdot 4\text{H}_2\text{O}$, $\text{K}(\text{UO}_2\text{PO}_4) \cdot 3\text{H}_2\text{O}$, $\text{K}(\text{UO}_2\text{AsO}_4) \cdot 2 \cdot 5\text{H}_2\text{O}$ and $\text{NH}_4(\text{UO}_2\text{PO}_4) \cdot 3\text{H}_2\text{O}$; from Rimbach (1904) who prepared the compound $\text{K}(\text{UO}_2\text{AsO}_4) \cdot 3 \cdot 5\text{H}_2\text{O}$; from Werther (1948) who prepared $\text{H}(\text{UO}_2\text{AsO}_4) \cdot 4\text{H}_2\text{O}$; from Mrose (1953) who synthesized $\text{H}(\text{UO}_2\text{AsO}_4) \cdot 4\text{H}_2\text{O}$ (troegerite) and $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$; from González García (1959) who prepared $\text{K}(\text{UO}_2\text{PO}_4) \cdot 3\text{H}_2\text{O}$ and $\text{K}(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$; from the discovery of uramphite $\text{NH}_4(\text{UO}_2\text{PO}_4) \cdot 3\text{H}_2\text{O}$ (Nekrasova, 1957); and from R. Meyrowitz (personal communi-

cation) who synthesized the compound $K(UO_2PO_4) \cdot 3H_2O$. The latter compound gave an x -ray powder pattern very similar to that of abernathyite (Daphne R. Ross, pers. comm.). The chemical analysis of Meyrowitz's compound is given in Table 5. Recently the mineral meta-ankoleite, $K(UO_2PO_4) \cdot 3H_2O$, was discovered by Gallagher and Atkin (1964) occurring in a beryl-bearing pegmatite in the Ankole district of Uganda. The chemical analysis of meta-ankoleite is given in Table 5. The

TABLE 5. CHEMICAL ANALYSIS OF SYNTHETIC $K(UO_2PO_4) \cdot 3H_2O$ AND META-ANKOLEITE

	Synthetic $K(UO_2PO_4) \cdot 3H_2O$ ¹		Meta-ankoleite ²	
	Wt. %	Ratios ³	Wt. %	Ratios ⁴
K ₂ O	10.3	0.501	8.7	0.434
BaO	—	—	3.2	0.098
UO ₂	62.4	1.000	60.8	1.000
P ₂ O ₅	15.1	0.488	15.5	0.514
H ₂ O	11.9	3.028	11.8	3.082
	99.7		100.0	

¹ Synthesized and analyzed by R. Meyrowitz.

² Recalculated to 100%; analysts, G. A. Sergeant and K. L. H. Murray (Gallagher and Atkin, 1964).

³ $K_{1.00}(UO_2)_{1.00}(PO_4)_{0.98}(H_2O)_{3.03}$, number of ions on the basis of $UO_3=1.000$.

⁴ $(K,Ba)_{0.97}(UO_2)_{1.00}(PO_4)_{1.03}(H_2O)_{3.08}$, number of ions on the basis of $UO_3=1.000$.

chemical analysis and x -ray powder data indicate that meta-ankoleite is identical to Meyrowitz's compound.

Although the formulas of the above-listed compounds may be in error, particularly as to water content, cumulative evidence suggests that the potassium and ammonium uranyl arsenates and phosphates contain fewer than four molecules of water per formula unit. Lienau, Rimbach, and González García prepared $K(UO_2AsO_4) \cdot 2 \cdot 5H_2O$, $K(UO_2AsO_4) \cdot 3 \cdot 5H_2O$, and $K(UO_2AsO_4) \cdot 3H_2O$ respectively. It is likely that the three compounds are identical and are in fact synthetic abernathyites. The fact that $H(UO_2AsO_4) \cdot 4H_2O$ and the phosphate analogue $H(UO_2PO_4) \cdot 4H_2O$ possess four H_2O molecules suggests strongly that there is a relationship between H^+ , K^+ , and NH_4^+ and the number of water molecules. Since the AsO_4 and PO_4 groups play the same role in most crystal structures, one should expect $K(UO_2PO_4) \cdot 3H_2O$ to be isostructural with $K(UO_2AsO_4) \cdot 3H_2O$. Thus, meta-ankoleite is probably the phosphate analogue of abernathyite.

In order to obtain further evidence for the special role of cations in these structures, we decided to try to solve the crystal structures of some

other compounds that might bear a structural resemblance to abernathyite. Of the compounds available only two formed crystals large enough for single crystal x -ray work. These were the ammonium uranyl arsenate prepared by Mrose (1953) and a potassium-hydrogen uranyl arsenate synthesized by Frank S. Grimaldi; the chemical composition and crystallography of which have been presented in the previous section.

Because of the nearly identical appearance of the $hk0$, $hk1$, $0kl$, and $1kl$ photographs and near identical unit-cell size to abernathyite it was assumed tentatively that $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ and $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$ are isostructural with abernathyite. Intensity data from the $0kl$ zones of both compounds were collected with the Buerger precession camera and were measured and processed in the same manner as the abernathyite data. Due to the small size of the crystals photographed ($0.01 \times 0.05 \times 0.06$ mm for $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ and $0.03 \times 0.15 \times 0.08$ mm for $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$) extremely long exposure times (100–200 hours) using unfiltered molybdenum radiation were required.

The structures of $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ and $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$ were solved by assuming that the uranium and arsenic positions in these structures are identical to those in the abernathyite structure. An electron-density subtraction map projected on (100) was made with coefficients obtained by subtracting the calculated uranium and arsenic contributions to the $0kl$ structure factors of abernathyite (F_H) from the observed $0kl$ structure factors of the ammonium and the potassium-oxonium uranyl arsenates (KF_{obs}). The scaling constant K was obtained by the relation

$$K = \frac{\sum F_A}{\sum F_{\text{obs}}}$$

where F_A refers to the observed structure factors of abernathyite based on an absolute scale. The subtraction syntheses are of the form

$$\rho(y, z) = \frac{1}{A} \sum_k \sum_l (\text{KF}_{\text{obs}} - F_H) \cos 2\pi(ky + lz).$$

The resulting subtraction maps of these two phases are compared to that of abernathyite in Fig. 2. The maps show that both $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ and $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$ are isostructural with abernathyite. Four "apparent" water molecules can be seen in the interlaminar region of all three subtraction maps. Since no additional potassium, ammonium, or oxonium peaks can be seen in the electron density maps we must propose that K^+ , NH_4^+ , and H_3O^+ are distributed randomly among the water molecule sites. In the $\text{K}(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ and $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ structures K^+ and NH_4^+ respectively plus three H_2O molecules are distributed randomly over four sites. In $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$,

one-half a potassium ion, one-half an oxonium¹ ion and three water molecules are distributed randomly over four water molecule sites.

REFINEMENT AND DESCRIPTION OF THE ABERNATHYITE STRUCTURE

To obtain more accurate bond distances three-dimensional data were collected for abernathyite. The three-dimensional data were also needed to choose between four possible structure models indicated by the two-dimensional electron density maps. Furthermore, in the (100) electron density map the uranium atom overlaps the arsenate oxygen atom making it impossible to obtain a good atomic position for the latter.

In addition to the $0kl$ data already processed, $1kl$, $2kl$, and $3kl$ data were measured and processed in the usual manner. No absorption corrections were made. Of the 602 reflections measured, 330 were observed to be greater than zero. The large number of zero terms is due to the fact that only the water molecules and arsenate oxygen atoms contribute to the reflections for which l is odd.

The three-dimensional least-squares refinement using a program written by J. Marsheck and D. E. Appleman, U. S. Geological Survey, was carried out on a digital computer (B220) using all of the hkl data mentioned above. The program uses the full matrix of the normal equations. The atomic positions obtained from the two-dimensional refinement were used as a starting point. Three cycles of refinement were made using a general isotropic temperature factor. Five more cycles of refinement were made using separate isotropic temperature factors for each atom. In this refinement the observed F values were all assigned unit weight, and the nonobserved values were excluded. Table 6 gives the final atomic positions, temperature factors, and the standard errors of the parameters. The final reliability factor $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$, for the non-zero structure factors is 8.4%. Table 7 gives the bond distances and their standard errors obtained from the data given in Table 6.

In the least-squares refinement the following atomic scattering-factor curves were used: U° from Thomas and Umeda (1957), reduced uniformly by 5.6 electrons to correct for anomalous dispersion (James, 1948 and Zachariasen, 1954), and As° , and O° from Berghuis *et al.* (1955). No correction in the O_d oxygen scattering curve was made to account for the assumed replacement of K^+ for one out of four water molecules.

Many tetragonal structures give ambiguous solutions to the x or y parameters of certain equivalent positions if only two-dimensional data

¹ Following the rules for chemical nomenclature accepted by the International Union for Pure and Applied Chemistry (IUPAC) the monohydrated proton, H_3O^+ , is to be called the *oxonium* ion. The name *hydronium* ion is reserved for the case where the degree of hydration is unspecified, i.e. $H(H_2O)_n^+$.

are used. This problem was encountered in abernathyite. In the abernathyite structure Fourier projections on either (100) or (001) cannot distinguish between the positions x and $(\frac{3}{2})-x$ for O_c and the position x and $(\frac{1}{2})-x$ for O_d . A shift of either O_c to $(\frac{3}{2})-x$ or O_d to $(\frac{1}{2})-x$ would cause the water-arsenate oxygen bond to lengthen from 2.75 Å to 3.18 Å, thus indicating the absence of a hydrogen bond. Such a situation is chemically unlikely but nevertheless the four possible models were tested with the hkl , $1kl$, $2kl$, and $3kl$ structure factors. Only the model with $x(O_c)=0.6963$ and $x(O_d)=0.1650$ cycles gave agreement with the observed hkl structure factors for which l is odd.

TABLE 6. FINAL ATOMIC PARAMETERS AND STANDARD ERRORS FOR
ABERNATHYITE, $K(UO_2AsO_4) \cdot 3H_2O^1$

Atom	Position	Parameters ²	Standard Error ⁴
O_a	$4c$	$x=\frac{1}{4}$	—
		$y=\frac{1}{4}$	—
		$z=0.1515$	0.0029
		$B=2.99$	0.87
O_b	$4c$	$x=\frac{1}{4}$	—
		$y=\frac{1}{4}$	—
		$z=0.9575$	0.0026
		$B=2.48$	0.77
O_c	$16f$	$x=0.6963$	0.0061
		$y=0.0729$	0.0044
		$z=0.4433$	0.0014
		$B=2.75$	0.50
O_d^3	$16g$	$x=0.1650$	0.0051
		$y=0.9876$	0.0053
		$z=0.3154$	0.0016
		$B=3.71$	0.72
As	$4b$	$x=\frac{3}{4}$	—
		$y=\frac{1}{4}$	—
		$z=0$	—
		$B=1.84$	0.10
U	$4c$	$x=\frac{1}{4}$	—
		$y=\frac{1}{4}$	—
		$z=0.0514$	0.00013
		$B=1.90$	0.05

¹ Space group $P4/ncc$ (No. 130b), origin at $\bar{1}$. A complete list of the observed and calculated structure factors for abernathyite, $NH_4(UO_2AsO_4) \cdot 3H_2O$, and $K(H_2O)(UO_2AsO_4)_2 \cdot 6H_2O$ can be found in Ross (1962) or may be obtained by writing the authors.

² Atomic coordinates in cycles, temperature factors B in Å².

³ O_d atoms are the interlayer water molecules, one out of four of which is randomly replaced by potassium.

⁴ The standard errors of the atomic parameters which are refined by the method of least-squares are evaluated with the relationships given by Clark et al. (1962, p. 213).

TABLE 7. BOND DISTANCES AND BOND ANGLES IN ABERNATHYITE

Bond ¹	Multiplicity	Length (angle) ²	Standard Error ³
I. Uranyl ion			
U ₁ -O _{a-1}	4	1.81 Å	0.05 Å
U ₁ -O _{b-1}	4	1.70	0.05
O _{a-1} -O _{b-1}	4	3.52	0.10
O _{a-1} -U ₁ -O _{b-1}	4	180°	0
II. AsO₄ ion			
As ₃ -O _{c-1}	16	1.68 Å	0.03 Å
O _{c-1} -O _{c-13}	8	2.66	0.05
O _{c-1} -O _{c-8}	16	2.78	0.04
O _{c-1} -As ₃ -O _{c-13}	8	104° 36' 111° 58' } 108° 32' (average)	
O _{c-1} -As ₃ -O _{c-8}	16		
III. UO₂-AsO₄ environment			
U ₃ -O _{c-8}	16	2.35 Å	0.05 Å
O _{a-1} -O _{c-4}	16	2.91	0.04
O _{b-1} -O _{c-4}	16	2.96	0.04
O _{c-1} -O _{c-7}	16	3.32	0.05
O _{b-3} -O _{c-1}	16	3.46	0.04
O _{c-8} -O _{c-7}	16	3.64	0.05
O _{a-1} -U ₁ -O _{c-4}	16	85° 56'	
O _{b-1} -U ₁ -O _{c-4}	16	94° 04'	
IV. H₂O environment (including potassium)			
O _{d-7} -O _{d-13}	16	2.80 Å ⁴	0.05 Å
O _{d-13} -O _{d-16}	16	2.83 ⁴	0.05
O _{c-1} -O _{d-7}	16	2.75 ⁴	0.04
O _{a-1} -O _{d-7}	16	3.57	0.05
O _{b-3} -O _{d-7}	16	3.25	0.05
O _{a-1} -O _{d-16}	16	3.48	0.05
O _{d-1} -O _{d-13}	16	3.62	0.05
O _{c-13} -O _{d-7}	16	3.64	0.05
O _{d-11} -O _{d-13} -O _{c-7}	16	115° 35'	} 108° 26' (average)
O _{d-11} -O _{d-13} -O _{d-16}	16	121° 21'	
O _{d-11} -O _{d-13} -O _{d-7}	16	90°	
O _{d-7} -O _{d-13} -O _{c-7}	16	108° 33'	
O _{d-7} -O _{d-13} -O _{d-16}	16	99° 46'	
O _{c-7} -O _{d-13} -O _{d-16}	16	115° 20'	

¹ Atomic Positions as assigned from *International Tables* (1952), space group 130b, p. 226, are listed as follows:

Atom	Position	Atom	Position	Atom	Position
U ₁	$\frac{1}{4}, \frac{1}{4}, z$	O _{b-3}	$\frac{1}{4}, \frac{1}{4}, z - \frac{1}{2}$	O _{c-13}	$\frac{3}{2} - x, \frac{1}{2} - y, z$
U ₃	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z$	O _{c-1}	x, y, z	O _{d-7}	$\frac{3}{2} - y, x, z$
As ₃	$\frac{3}{4}, \frac{1}{4}, \frac{1}{2}$	O _{c-4}	$y, 1 - x, \frac{1}{2} - z$	O _{d-11}	$y - 1, \frac{1}{2} - x, z$
O _{a-1}	$\frac{1}{4}, \frac{1}{4}, z$	O _{c-7}	$\frac{1}{2} - y, x - 1, z$	O _{d-13}	$\frac{1}{2} - x, \frac{3}{2} - y, z$
O _{b-1}	$\frac{1}{4}, \frac{1}{4}, z - 1$	O _{c-8}	$\frac{1}{2} + y, 1 - x, 1 - z$	O _{d-16}	$y - \frac{1}{2}, \frac{1}{2} + x, \frac{1}{2} - z$

² All interatomic distances less than 3.70 Å are listed.

³ Standard errors of the interatomic distances were calculated by the method given by Clark, Christ, and Appleman (1962, p. 213).

⁴ Hydrogen bonds.

The structural scheme of abernathyite projected on (100) and (001) is shown in Figs. 4 and 5, respectively. As can be seen in these figures the AsO_4 tetrahedra are rotated about a line parallel to c so that their horizontal edges do not lie parallel to the a -axis. The twisting of these tetrahedra about their $\bar{4}$ axes, as we shall see later, results from hydrogen-bonding between the arsenate oxygen atoms (O_e) and the water molecules (O_a). Four arsenate oxygen atoms of four different AsO_4 tetrahedra coordinate the uranium atom, giving a $\text{U}-\text{O}_e$ bond distance of 2.35 \AA (see also Fig. 7). The light dotted lines in Figs. 4 and 5 represent the uranium-arsenate oxygen bonds. The uranium atom is displaced 0.09 \AA above the plane of the four arsenate oxygens. The $(\text{UO}_2\text{AsO}_4)_n^{n-}$ sheets of abernathyite are positioned relative to one another in the same manner as those of meta-autunite (I) (Figure 1B).

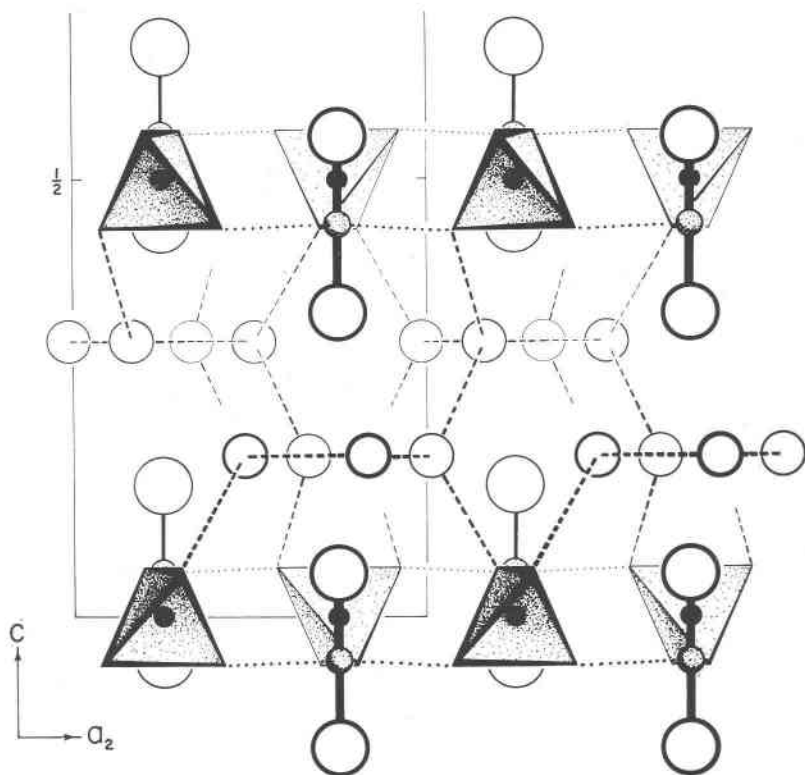


FIG. 4. Projection of the abernathyite structure on (100). The dotted lines indicate $\text{U}-\text{O}_e$ bonds; the dashed lines indicate hydrogen bonds. Large open circles—uranyl oxygens, smaller open circles—water molecules and potassium atoms, small stippled circles—uranium atoms, small solid circles—arsenic atoms.

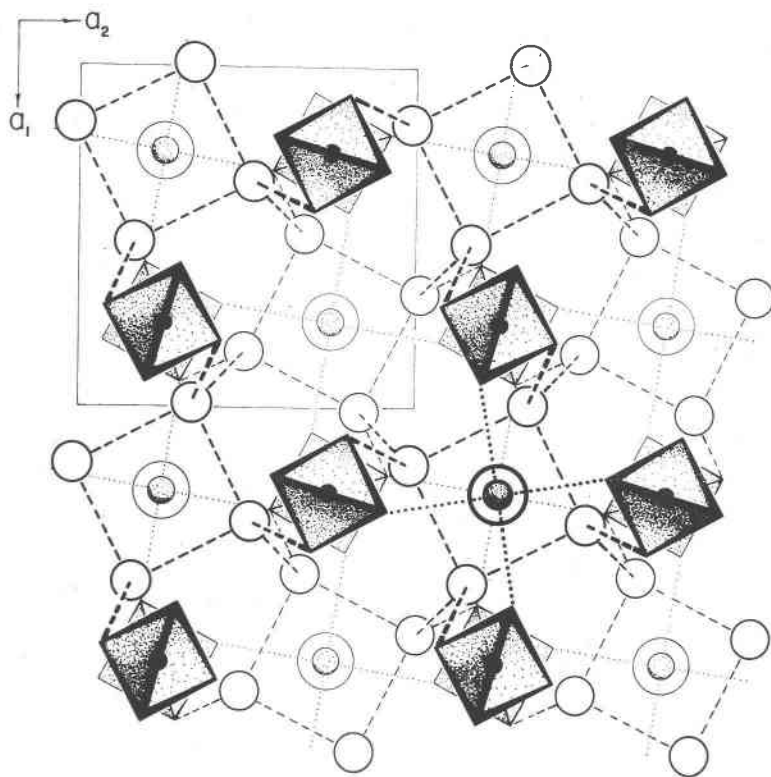


Fig. 5. Projection of the abernathyite structure on (001). The designation of the various bonds and atoms is the same as that given in Fig. 4.

The As-O_c bond distance is 1.68 Å and is in exact agreement with the As-O bond distance found in the structure of cahnite, Ca₂BAsO₄(OH)₄, accurately refined by Prewitt and Buerger (1961). In abernathyite the two horizontal edges of the AsO₄ tetrahedra are somewhat shortened (2.65 Å) with respect to the other four edges (2.78 Å). A similar distortion of this group was found in the cahnite structure. Giuseppetti (1963) found the average As-O bond length to be 1.668 Å in the accurately determined eucroite, Cu₂(AsO₄)(OH)·3H₂O, structure. Qurashi and Barnes (1963) found the average As-O distance in conichalcite, CaCu(AsO₄)(OH), to be 1.685 Å.

The axis of the uranyl ion lies on a four-fold axis and is thus exactly linear. The U-O_a and U-O_b bond distances are found to be 1.81 and 1.70 Å, respectively; both with a standard error of 0.05 Å. As can be seen in Figure 4, the uranyl ion is situated in a highly asymmetrical environment. One uranyl oxygen (O_a) is adjacent to only four arsenate oxygen atoms at

2.91 Å while the other uranyl oxygen (O_b) has 8 arsenate oxygen atom neighbors, four at 2.96 Å and four at 3.46 Å. Atom O_a is adjacent to eight water molecules (including potassium) four at 3.48 Å and four at 3.57 Å whereas O_b approaches only four water molecules at 3.25 Å. This asymmetrical environment of the uranyl ion is probably the cause of the displacement of the uranyl ion out of the plane of the four arsenate oxygens and also may cause polarization of the uranyl ion. The $U-O_a$ and $U-O_b$ bond lengths deviate from the average of 1.76 Å by an amount which is equal to the standard error so that we cannot claim conclusively that the difference in these bond lengths signifies polarization. The displacement of the uranium atom from the plane of the four arsenate oxygens is approximately three times the standard error and thus is probably real.

Between the uranyl ions and symmetrically arranged about the four-fold axes lie square groups of four water molecules one out of four of which is statistically replaced by potassium. We shall now for convenience of explanation assume that all atoms in the squares are water molecules and consider only later the effect of potassium on the structural scheme about to be presented. Figure 6 shows an electron density section, $\rho(x, y, z_1)$, taken in the plane of the $(K \cdot 3H_2O)$ squares. The detailed environment of

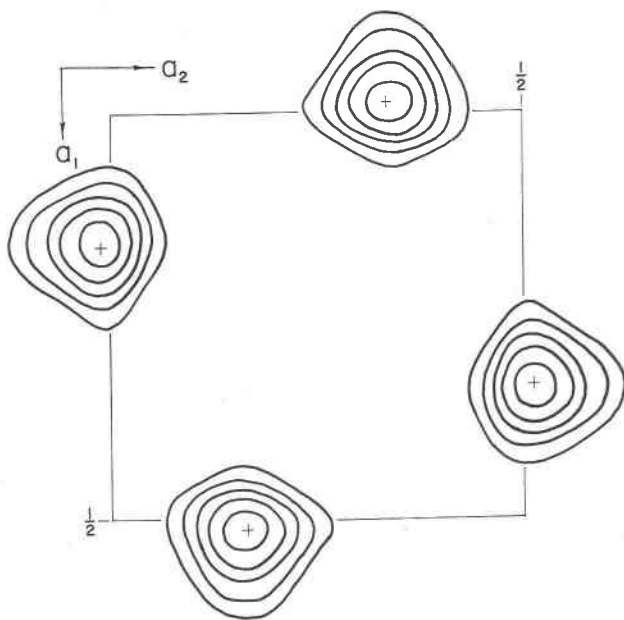


FIG. 6. Section of electron density, $\rho(x, y, z_1=0.3154)$, through the center of the potassium ions and water molecules of the $(K \cdot 3H_2O)$ squares in abernathyite. Contours are at intervals of $1e \text{ \AA}^{-3}$ starting at $3e \text{ \AA}^{-3}$.

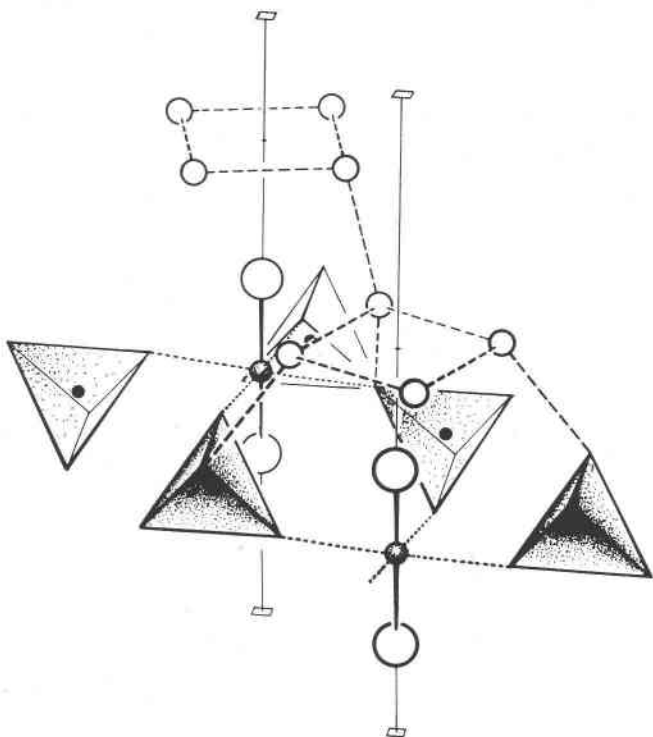


FIG. 7. Pictorial diagram of abernathyite showing the detailed environment of the UO_2^{2+} ion and the $(\text{K} \cdot 3\text{H}_2\text{O})$ squares. Hydrogen bonds are shown as dashed lines; the uranium-arsenate oxygen bonds as dotted lines.

the UO_2^{2+} ion and the $(\text{K} \cdot 3\text{H}_2\text{O})$ squares is shown pictorially in Figure 7.

The groups of water molecules are hydrogen-bonded to form squares as is indicated by the $\text{O}_{d-7}-\text{O}_{d-13}$ bond distance of 2.80 Å. Each water molecule of the square is also hydrogen-bonded to one water molecule of an adjacent square and to an arsenate oxygen atom. These bond distances are respectively 2.83 and 2.75 Å. The oxygen atoms of the H_2O molecules are thus coordinated in a nearly tetrahedral manner by four protons. The hydrogen bonding between the water molecules and the arsenate oxygen atoms causes a clockwise 18° rotation of the arsenate tetrahedra at $z = \frac{1}{2}$ and a counter-clockwise 18° rotation of the tetrahedra at $z = 0$ as viewed down the c -axis. The hydrogen bonding between the water molecules and the arsenate oxygen atoms causes a clockwise 18° rotation of the arsenate tetrahedra at $z = \frac{1}{2}$ and a counter-clockwise 18° rotation of the tetrahedra at $z = 0$ as viewed down the c -axis. The hydrogen-bonds are shown as dashed lines in Figures 4 and 5. The evidence of the O_a-O_e hydrogen bond is strengthened by the fact that there seems to be no other way to account for the twisting of the arsenate tetrahedra. In fact, it is this rotation and the resulting alternate left and right orientation of the squares of water molecules in adjacent layers which doubles the cell in the c -direction and

changes the space group from $P4/nmm$ to $P4/ncc$. The sheets are held together only by the complex system of hydrogen-bonding which explains the perfect (001) cleavage found in the crystals.

The presence of potassium within the squares must modify this system of hydrogen-bonding to the extent that certain hydrogen bonds are randomly missing. Within the unit cell of abernathyite there are 24 protons and 40 possible hydrogen bonds; 16 between water molecules within the squares, 16 between the water molecules and the arsenate oxygens, and 8 between the water molecules of adjacent squares. If four potassium atoms are randomly distributed over the 16 water molecule positions, 16 of the possible hydrogen bonds are eliminated giving an equal number of hydrogen bonds and protons. The positive charge on the potassium ions is distributed to the negatively charged $(\text{UO}_2\text{AsO}_4)_n^{n-}$ sheets in part by direct coordination of K^+ to an arsenate oxygen atom and in part (and indirectly) by hydrogen bonding between the H_2O molecules and the AsO_4 oxygen atoms. The three types of hydrogen bonds present in the structure are the only interatomic vectors involving a water molecule which are less than 3.25 Å. To express the random distribution of one potassium ion and three water molecules over four water molecule sites the structural formula of abernathyite can be written $(\text{K} \cdot 3\text{H}_2\text{O})(\text{UO}_2\text{AsO}_4)$. The structure of abernathyite will be compared to those of $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ and $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$ in the following section.

REFINEMENT OF THE STRUCTURE OF $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ AND $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$

Nine cycles of least-squares refinement were carried out on $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ using the original $0kl$ intensity data consisting of 97 terms of which 82 were greater than zero. Seven cycles of refinement were carried out on $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$ using $0kl$ data consisting of 96 terms of which 84 were greater than zero. A general isotropic temperature factor was used for the first few cycles and then individual isotropic temperature factors for each atom in the last cycles of refinement. Because of the overlap of the uranium and arsenate oxygen atoms it was necessary to fix the x parameter of O_c during the refinement. Due to the rather poor intensity data, the least-squares refinement and subtraction maps did not give more than an estimate of the z parameter of the uranyl oxygen O_a of $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$. Also, the refinements did not give, it was judged, as reliable y and z coordinates for O_c as could be obtained from the subtraction maps. The final structure factors were thus calculated using the coordinates as obtained from the last cycle of least-squares refinement for atoms U, As, O_b , and O_d . The x coordinate of O_c and, in the case of $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$, the z coordinate of O_a were assumed to

be the same as those found in abernathyite. The y and z coordinates for O_c were taken from the subtraction maps.

Table 8 gives the atomic coordinates, temperature factors, and standard errors obtained from the last cycle of refinement and from the sub-

TABLE 8. ATOMIC PARAMETERS AND STANDARD ERRORS FOR
 $NH_4(UO_2AsO_4) \cdot 3H_2O$ AND $K(H_3O)(UO_2AsO_4)_2 \cdot 6H_2O^1$

Atom	Position	Parameters ²	
		$NH_4(UO_2AsO_4) \cdot 3H_2O$	$K(H_3O)(UO_2AsO_4)_2 \cdot 6H_2O$
O_a	4c	$x = \frac{1}{4}$ $y = \frac{1}{4}$ $z = 0.151^3$	$x = \frac{1}{4}$ $y = \frac{1}{4}$ $z = 0.150 (0.005)$ $B = 3.6 (1.8)$
O_b	4c	$x = \frac{1}{4}$ $y = \frac{1}{4}$ $z = 0.956 (0.005)$ $B = 3.0 (1.9)$	$x = \frac{1}{4}$ $y = \frac{1}{4}$ $z = 0.958 (0.004)$ $B = 2.9 (1.7)$
O_c^4	16g	$x = (0.696)$ $y = 0.076$ $z = 0.447$	$x = (0.696)$ $y = 0.071$ $z = 0.448$
O_d^5	16g	$x = 0.158 (0.008)$ $y = 0.993 (0.008)$ $z = 0.317 (0.002)$ $B = 3.3 (1.0)$	$x = 0.150 (0.008)$ $y = 0.993 (0.009)$ $z = 0.315 (0.002)$ $B = 4.1 (1.0)$
As	4b	$x = \frac{3}{4}$ $y = \frac{1}{4}$ $z = 0$ $B = 1.68 (0.22)$	$x = \frac{3}{4}$ $y = \frac{1}{4}$ $z = 0$ $B = 1.59 (0.21)$
U	4c	$x = \frac{1}{4}$ $y = \frac{1}{4}$ $z = 0.0512 (0.0003)$ $B = 2.54 (0.11)$	$x = \frac{1}{4}$ $y = \frac{1}{4}$ $z = 0.0520 (0.0003)$ $B = 2.27 (0.10)$

¹ Space Group $P4/ncc$ (No. 130b), origin at $\bar{1}$.

² Atomic coordinates in cycles, and temperature factors B in \AA^2 . Standard errors are given in parentheses.

³ Assumed by analogy to abernathyite.

⁴ The y and z coordinates were obtained from the subtraction maps; the value of the x coordinate is assumed by analogy to abernathyite to be 0.696 cycles and was fixed during refinement.

⁵ O_d atoms are the interlayer water molecules of which one out of four are replaced randomly by NH_4^+ in $NH_4(UO_2AsO_4) \cdot 3H_2O$ and of which two out of eight are replaced randomly by potassium and oxonium ions in $K(H_3O)(UO_2AsO_4)_2 \cdot 6H_2O$.

TABLE 9. BOND DISTANCES AND BOND ANGLES IN $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$
AND $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$

Bond ¹	Multi- plicity	Length (angle) ²	
		$\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$	$\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$
I. Uranyl ion			
$\text{U}_1\text{-O}_{a-1}$	4	1.81 Å ³	1.77 Å (0.09)
$\text{U}_1\text{-O}_{b-1}$	4	1.73 (0.09)	1.70 (0.07)
$\text{O}_{a-1}\text{-U}_1\text{-O}_{b-1}$	4	180°	180°
II. AsO_4 ion			
$\text{As}_3\text{-O}_{c-1}$	16	1.63 Å	1.64 Å
$\text{O}_{c-1}\text{-O}_{c-13}$	8	2.62	2.68
$\text{O}_{c-1}\text{-O}_{c-8}$	16	2.67	2.67
$\text{O}_{c-1}\text{-As}_3\text{-O}_{c-13}$	8	107° 18'	110° 0'
$\text{O}_{c-1}\text{-As}_3\text{-O}_{c-8}$	16	110° 14' } 108° 46' (ave.)	109° 12' } 109° 36' (ave.)
III. $\text{UO}_2\text{-AsO}_4$ environment			
$\text{U}_3\text{-O}_{c-8}$	16	2.37 Å	2.33 Å
IV. H_2O environment (hydrogen bonds only)			
$\text{O}_{d-7}\text{-O}_{d-13}$	16	2.78 Å (0.09)	2.80 Å (0.08)
$\text{O}_{d-13}\text{-O}_{d-16}$	16	2.88 (0.09)	2.76 (0.09)
$\text{O}_{c-1}\text{-O}_{d-7}$	16	2.79	2.81

¹ Atomic positions are the same as those assigned in Table 7.

² Approximate standard errors are given in parentheses.

³ Bond distance assumed equal to that in abernathyite.

traction maps. The final reliability factor (R) of the observed non-zero $0kl$ data is 9.2 per cent for $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ and 9.4 per cent for $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$. Table 9 gives the bond lengths and angles as obtained from the coordinates given in Table 8. The standard errors of the bond lengths are estimated where possible.

Although the positions of the atoms could not be determined as accurately as in the case of abernathyite, there is no doubt that the compounds are isostructural. The presence of NH_4^+ instead of K^+ within the $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ structure gives enough protons to allow forty hydrogen bonds per unit cell, the maximum number possible in these structures. The structural formula of $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ can be written $[(\text{NH}_4) \cdot 3\text{H}_2\text{O}](\text{UO}_2\text{AsO}_4)$ to indicate the random distribution of one ammonium and three water molecules over four H_2O sites.

In $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$ one-half a potassium ion, one-half an oxonium ion (H_3O^+), and three water molecules are randomly distributed over four water molecule sites. The structural formula can be written

$[\text{K}_{\frac{1}{2}}(\text{H}_3\text{O})_{\frac{1}{2}} \cdot 3\text{H}_2\text{O}](\text{UO}_2\text{AsO}_4)$ to indicate this distribution. The two potassium atoms per unit cell eliminate eight of the forty possible hydrogen bonds. There are only thirty protons to satisfy the thirty-two remaining hydrogen bonds; thus we must invoke a further statistical distribution of thirty protons over thirty-two positions.

In the structures described here it must be emphasized that the (H_3O^+) ions may not exist as discrete groups. The protons may be expected to be distributed within the crystal structure in such a way as to make the positive charge about each oxygen atom nearly equal to 2.0. In structures reported to contain true oxonium ions (*e.g.*, $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$, $\text{HClO}_4 \cdot \text{H}_2\text{O}$, and $\text{HCl} \cdot \text{H}_2\text{O}$) some of the oxygen atoms are closely associated with three protons; thus the positive charge about them may be considerably in excess of 2.0.

In Part II of this series (Ross *et al.* 1964) the crystal structure of metatorbernite, $\text{Cu}(\text{UO}_2\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, will be given. In Part III (Ross and Evans, 1965) a detailed discussion of the crystal chemistry of the torbernite minerals in light of the present structure studies will be presented.

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