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9056 - 62

THE CRYSTALLOGRAPHY, CRYSTAL STRUCTURE, AND CRYSTAL CHEMISTRY OF VARIOUS MINERALS AND COMPOUNDS BELONGING TO THE TORBERNITE MINERAL GROUP

by

Malcolm Ross, 1929-

U. S. Geological Survey. [Reports - Open file series, no. 645]
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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 $A^{z+}(UO_2XO_4)_z \cdot nH_2O$, where A may be one of a large variety of monovalent and divalent cations, and where X = As and/or P. In order to learn more about these minerals and compounds, detailed crystal structure analyses of $K(UO_2AsO_4) \cdot 3H_2O$ (abernathyite), $KH_3O(UO_2AsO_4)_2 \cdot 6H_2O$, $NH_4(UO_2AsO_4) \cdot 3H_2O$, and $Cu(UO_2PO_4)_2 \cdot 8H_2O$ (meta-torbernite) were made. New crystallographic and chemical data are also given for these compounds. In addition, new crystallographic data were obtained for meta-autunite (I), $Ca(UO_2PO_4)_2 \cdot nH_2O$; uranocircite, $Ba(UO_2PO_4)_2 \cdot nH_2O$; and meta-uranocircite (I), $Ba(UO_2PO_4)_2 \cdot nH_2O$.

The structures were refined by two and three-dimensional least-squares analysis of intensity data measured on Buerger precession photographs made with molybdenum radiation. The well-known waffle-like $(UO_2XO_4)_n^{n-}$ sheet structure proposed by J. Beintema for meta-autunite (I) is confirmed in all four crystal structures examined. The sheets are arranged relative to one another in the same manner as those of meta-autunite (I).

In these compounds, the positions of the interlayer water molecules are based on an ideal arrangement in which four H_2O molecules are hydrogen-bonded together to form squares about the four-fold rotation axes, lying between the uranyl ions of successive sheets. In abernathyite,

$K(UO_2AsO_4)\cdot 3H_2O$, K^+ substitutes randomly for one out of four water molecules. In the $KH_3O(UO_2AsO_4)_2\cdot 6H_2O$ structure potassium and oxonium (H_3O^+) ions substitute randomly for two out of eight H_2O molecules. In $NH_4(UO_2AsO_4)\cdot 3H_2O$ ammonium ions substitute for one out of four H_2O molecules. In the meta-torbernite structure cation substitution of water does not occur, but rather Cu^{2+} occupies special positions at the center of half of the square groups of water molecules.

In all four structures each water molecule of a square group is also hydrogen-bonded in a nearly tetrahedral manner to a water molecule of an adjacent square, and to an arsenate or phosphate oxygen atom. The latter bond causes a slight distortion of the $(UO_2XO_4)_n^{n-}$ sheet from the ideal symmetry.

The presence of K^+, H_3O^+, and NH_4^+ within the squares must modify this system of hydrogen-bonding to the extent that certain H-bonds may be randomly missing. Within the unit cell of abernathyite there are 40 possible hydrogen bonds and 24 protons. When four potassium atoms are randomly distributed over the 16 water molecule positions, 16 of the possible H-bonds are destroyed giving an equal number of real hydrogen bonds and protons. The presence of NH_4^+ instead of K^+ within the $NH_4(UO_2AsO_4)\cdot 3H_2O$ structure gives enough protons to form 40 hydrogen bonds per unit-cell, the maximum number possible in these structures. In $KH_3O(UO_2AsO_4)_2\cdot 6H_2O$ one K^+ and one H_3O^+ ion replace randomly two out of eight H_2O molecules. The two potassium atoms per unit-cell eliminate eight of the 40 possible H-bonds. There are only 30 protons to satisfy the 32 remaining hydrogen bonds; thus a further statistical distribution of 30 protons over 32 positions in invoked.

An isomorphous series probably exists between the end-members $K(UO_2AsO_4)\cdot 3H_2O$ (abernathyite) and $H_3O(UO_2AsO_4)\cdot 3H_2O$ (troegerite) and also between $NH_4(UO_2AsO_4)\cdot 3H_2O$ and troegerite. These solid-solution series may be expressed as

(1) $$K_{1-y}(H_3O)_y(UO_2XO_4)\cdot 3H_2O$$

and

(2) $$(NH_4)_{1-y}(H_3O)_y(UO_2XO_4)\cdot 3H_2O$$

where X = As and/or P.

The abernathyite structure was refined by three-dimensional least-squares analyses using 330 non-zero structure factors. The final reliability factor (R) is 8.4%. The uranyl oxygen-uranium bond lengths are 1.70 and 1.81 $\pm$ 0.05 Å. The arsenic-arsenate oxygen bond lengths are 1.68 $\pm$ 0.03 Å. The uranium-arsenate oxygen bond distances are 2.35 $\pm$ 0.05 Å. and the hydrogen bond lengths are 2.80, 2.83, and 2.75 $\pm$ 0.05 Å.

The $NH_4(UO_2AsO_4)\cdot 3H_2O$ and $KH_3O(UO_2AsO_4)_2\cdot 6H_2O$ structures were refined by two-dimensional least-squares analysis using 82 and 84 non-zero structure factors respectively. The final reliability factor for $NH_4(UO_2AsO_4)\cdot 3H_2O$ is 9.2%, and for $KH_3O(UO_2AsO_4)_2\cdot 6H_2O$, 9.4%. The bond lengths found in these structures are close to the values obtained for the abernathyite bond distances.

The meta-torbernite structure was refined by three-dimensional least-squares techniques using 672 non-zero terms. The final reliability factor is 9.7%. In this structure two Cu atoms lie at the center of two $(H_2O)_4$ squares, one at 1/4, 1/4, 0.810, and one at 3/4, 3/4, 0.190 cycles. The distance between the copper atom and water molecules is 1.91 $\pm$ 0.03 Å.

The next nearest atoms to the copper atom are the uranyl oxygens in the $(UO_2PO_4)_n^{n-}$ sheets above and below the $Cu(H_2O)_4$ squares. These Cu-O distances are 2.40 and 2.66 ± 0.07 Å. The coordination polyhedron about the copper atom is thus in the form of a distorted octahedron. There are no H-bonds between the water molecules of the $Cu(H_2O)_4$ squares. Eight additional H_2O molecules form two squares at 1/4, 1/4, 0.311 and 3/4, 3/4, 0.689 cycles. The water molecules of these squares are hydrogen-bonded together (2.81 ± 0.04 Å) and are also H-bonded to a water molecule of an adjacent $Cu(H_2O)_4$ square (2.67 ± 0.05 Å) and to a phosphate oxygen atom (2.77 ± 0.05 Å). The hydrogen bond length between the water molecules of the $Cu(H_2O)_4$ squares and the phosphate oxygen atoms is 2.89 ± 0.05 Å.

The mineral uranocircite, $Ba(UO_2PO_4)_2 \cdot nH_2O$, not previously found occurring naturally, is described. This mineral is found in specimens from Freiberg, Saxony and Wölsendorf, Bavaria. The uranocircite crystals, possessing a "gridiron" structure resembling that of microcline, are composed of two sets of lamellae. One set of lamellae, uniaxial in character, is uranocircite. The other set of lamellae, showing marked birefringence, is meta-uranocircite (I). Uranocircite is found to be tetragonal with a = 6.97 Å and c = 17.65 Å. The space group is $P\bar{4}2$ or $P4_2/m$.

TABLE OF CONTENTS

TABLE OF CONTENTS - contd.

TABLE OF CONTENTS - contd.

LIST OF TABLES

LIST OF TABLES - contd.

LIST OF TABLES - contd.

LIST OF FIGURES

LIST OF FIGURES - contd.

INTRODUCTION

The minerals autunite, torbernite, and related species have long interested mineralogists and chemists because of their unusual physical and chemical properties and also because of their uranium content. Torbernite was first found at the famous mines at Joachimsthal, Saxony in 1772 but it was not until 1797 that its uranium content was discovered. A whole series of closely related minerals has since been described. Frondel (1958) has presented the systematic mineralogy of these minerals.

The torbernite-like minerals are characterized by the formula $A^{z+}(UO_2XO_4)_2 \cdot nH_2O$, where X = P and/or As, and A, a large variety of cations. Also a large number of synthetic compounds isostructural with these minerals is known. The role of hexavalent uranium in these compounds and minerals has been the most important impetus for the early studies of this group. More recently, however, the role of water and the interlayer cations has received more attention and it is to this subject that the present study is particularly directed.

It is the purpose of this investigation to study in detail by X-ray diffraction techniques the crystallography, crystal structure, and crystal chemistry of a number of minerals and compounds belonging to the torbernite group. Of particular interest is the crystal chemical role of the water molecules and interlayer cations which lie between the sheets of these mica-like compounds. The variety of formulas which appear for these compounds and minerals indicate the complexity that exists in the interlaminar region. It is hoped that the solution of a number of crystal structures of these interesting hydrates will help

establish their crystal chemistry, contribute further to their mineralogy and crystallography, and also give more exact bond distances for structures containing the uranyl ion. The X-ray crystallography of meta-autunite (I), $Ca(UO_2PO_4)_2 \cdot nH_2O$; meta-torbernite, $Cu(UO_2PO_4)_2 \cdot 8H_2O$; abernathyite, $K(UO_2AsO_4) \cdot 3H_2O$; uranocircite, $Ba(UO_2PO_4)_2 \cdot nH_2O$; meta-uranocircite (I), $Ba(UO_2PO_4)_2 \cdot n'H_2O$; $NH_4(UO_2AsO_4) \cdot 3H_2O$; and $KH(UO_2AsO_4)_2 \cdot 7H_2O$ will be given. The detailed crystal structures and the crystal chemistry of abernathyite, $NH_4(UO_2AsO_4) \cdot 3H_2O$, $KH(UO_2AsO_4)_2 \cdot 7H_2O$ and meta-torbernite will be presented.

THE CHEMICAL AND GEOLOGIC BEHAVIOR OF HEXAVALENT URANIUM

General

Aqueous solutions containing hexavalent uranium are characterized by the presence of the uranyl ion (UO_2^{2+}), and by the tendency of this ion to form soluble complexes with a number of common anions such as SO_4^{2-}, NO_3^-, and CO_3^{2-}. Ahrland in 1949 showed that the ionic species U^{6+} does not exist in aqueous solution. Hexavalent uranium exists in the form of the uranyl ion over a pH range from the most acid solutions up to about a pH of 2.5. As the pH is further increased, hydrolysis occurs with the formation of complexes that were first thought to be $(UO_2)_2O^{2+}$ or $(UO_2)_2(OH)_2^{2+}$. In a more recent study (Ahrland, Hietanen, and Sillén, 1954) it is shown that the most probable complexes have the formula $UO_2\left[(OH)_2UO_2\right]_n^{2+}$ or $UO_2(OUO_2)_n^{2+}$. The former agrees more closely with structural data, which indicates that in crystals the complexes are probably sheet-like, with double (OH) bridges. Garrels (1955) has given the fields of stability of uranium (VI) and uranium (IV) hydroxides and oxides in aqueous solution at 25° C.

The theoretical model of the uranyl ion proposed by Connick and Hugus (1952) consists of a dumbbell-shaped linear O-U-O group. In a zone perpendicular to the length of the uranyl group and bisecting the uranium atom, the uranyl ion appears as a highly charged cation. When viewed from the end of the dumbbell, the uranyl group appears as a weakly charged cation.

Crystal-chemical studies of compounds of hexavalent uranium, summarized by Zachariasen (1954b), have shown that the uranyl ion is invariably present; and in all structures in which the shape of the uranyl ion has been directly determined, it is symmetrical and collinear. Fankuchen (1935) was the first to demonstrate that the uranyl ion is collinear in the crystal structure of sodium uranyl acetate.

In addition to the two uranyl oxygen atoms of the uranyl ion the uranium atom in crystal structures is coordinated by four, five, or six additional atoms lying in a plane perpendicular to the O-U-O axis of the uranyl ion. The uranium atom is thus found in 6, 7, or 8-fold coordination. The coordination polyhedron around the 6-coordinated uranium atom is a distorted octahedron; about the 7-coordinated uranium atom, a pentagonal bipyramid; and about the 8-coordinated uranium atom, a hexagonal bipyramid. In the succeeding pages only the coordination of the uranyl ion will be given.

Uranyl Sulfate Complexes

The reaction of uranyl ions with sulfate ions in acid solution where hydrolysis is negligible, has been investigated by Ahrland (1951). He found by electrometric and extinctiometric methods that monomuclear complexes with the following association constants were formed:

$$UO_2^{2+} + SO_4^{2-} \rightarrow UO_2SO_4 \qquad K_1 = 50 \pm 10$$

$$UO_2^{2+} + 2SO_4^{2-} \rightarrow UO_2(SO_4)_2^{2-} \qquad K_2 = 350 \pm 150$$

$$UO_2^{2+} + 3SO_4^{2-} \rightarrow UO_2(SO_4)_3^{4-} \qquad K_3 = 2500 \pm 1000 .$$

Appleman (1957) in the crystal structure determination of johannite, $Cu(UO_2)_2(SO_4)_2(OH)_2 \cdot 6H_2O$, shows that discrete uranyl sulfate ions are not present. The structure instead contains sheets of the type $\left[(UO_2)_2(SO_4)_2(OH)_2\right]_n^{2n-}$. Ross and Evans (1960) found in the compound $Cs_2(UO_2)_2(SO_4)_3$ sheets of the type $\left[(UO_2)_2(SO_4)_3\right]_n^{2n-}$. In both johannite and $Cs_2(UO_2)_2(SO_4)_3$, the UO_2^{2+} ion is coordinated by five sulfate oxygens. This five-fold coordination of the uranyl ion also has been found in $K_3UO_2F_5$ (Zachariasen, 1954a); uranophane, $Ca(HO)_2(UO_2)_2(SiO_4)_2 \cdot 3H_2O$ (Smith, Gruner, and Lipscomb, 1957); and in the potassium analogue of carnotite, $K_2(UO_2)_2V_2O_8$ (Appleman and Evans, 1957).

Uranyl Carbonate Complexes

Bullwinkel (1954) has found that in solutions containing a high concentration of carbonate ions a very stable anion complex is present which has the formula $UO_2(CO_3)_3^{4-}$. This complex is unstable at lower CO_3^{2-} concentrations and alters to $UO_2(CO_3)_2(H_2O)_2^{2-}$. In the reaction

$$UO_2(CO_3)_3^{4-} + 2H_2O \longrightarrow UO_2(CO_3)_2(H_2O)_2^{2-} + CO_3^{2-}$$

the equilibrium lies far to the left. The equilibrium constant is 1.7×10^{-4}. The $UO_2(CO_3)_3^{4-}$ complex is one of the most stable ones involving the uranyl ion.

Appleman (1956) has found the $UO_2(CO_3)_3^{4-}$ complex in the structure of liebigite, $Ca_2UO_2(CO_3)_3 \cdot 10H_2O$. In this structure the linear uranyl ion is surrounded by three carbonate ions which lie in a plane perpendicular to the O-U-O axis. Two oxygen atoms from each of the three CO_3^{2-} groups coordinate the uranyl ion.

The uranyl ion is also found in six-fold coordination in rutherfordine, UO_2CO_3 (Christ, Clark, and Evans, 1955). In this structure instead of discrete $UO_2(CO_3)_3^{4-}$ groups appearing, each CO_3^{2-} group coordinates three different uranyl ions to form an infinite sheet of the composition UO_2CO_3. Probably most of the uranyl carbonate minerals have structures related to either rutherfordine or liebigite.

Other Uranyl Complexes

The uranyl ion also complexes with acetate, chloroacetate, thiocyanate, chloride, bromide, nitrate, phosphate, and arsenate ions. Appleman (1956, p. 32) has summarized the equilibrium constants of some of these complexes. In both the nitrate and the acetate complexes the uranyl ion has six-fold coordination. This coordination is also found in the compounds UO_3, UO_2F_2 and $CaUO_4$. The phosphate and arsenate complexes which are of particular interest to us will be discussed in greater detail in later chapters.

Geologic Implications

Garrels and Christ (1959) have described the crystal chemistry of the uranium minerals of the Colorado Plateau in some detail. The following discussion is based partly on their work.

The predominant U(IV) minerals on the Colorado plateau are uraninite (ideally UO_2) and coffinite [probably $U_2(SiO_4)_{2-x}(OH)_{4x}$]. It is believed that uraninite and coffinite slowly oxidize by solid state reaction to U(VI), perhaps as amorphous UO_3. UO_3 is relatively unstable in pure water and will hydrolize to give various soluble complexes such as $(UO_2)_2(OH)^{3+}$, $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_4^{2+}$ described by Hietanen and Sillén (1959) and Peterson (1961). If the pH is sufficiently high various uranyl hydroxide hydrates [e.g. $UO_2(OH)_2 \cdot H_2O$, and $UO_2(OH)_2$] will precipitate. Structurally these hydrates are members of a more general class of compounds represented by UO_2F_2 and $Ca(UO_2)O_2$ which contain layers of the type $(UO_2O_2)_n^{2n-}$ with the cations lying between the sheets. Christ and Clark (1960) discuss these uranyl

oxide hydrates in detail. Examples of these minerals are: schoepite I, $UO_2(OH)_2 \cdot H_2O$; becquerelite, $Ca(OH)_2 \cdot 6UO_2(OH)_2 \cdot 4H_2O$; billietite, $Ba(OH)_2 \cdot 6UO_2(OH)_2 \cdot 4H_2O$; and fourmarierite, $Pb(OH)_2 \cdot 4UO_2(OH)_2 \cdot 2H_2O$. The general formula of these compounds may be written as $xMe(OH)_2 \cdot yUO_2(OH)_2 \cdot (z-x-y)H_2O$ (Christ and Clark, 1955).

If the ground water precipitating the uranyl salts is sufficiently high in CO_3^{2-} the U (VI) may complex as $UO_2(CO_3)_2(H_2O)_2^{2-}$ or $UO_2(CO_3)_3^{4-}$. Rutherfordine, UO_2CO_3 or other carbonates such as liebigite, bayleyite, sharpite, and andersonite may then crystallize.

The uranyl ion may combine with sulfate ions to form various complexes such as UO_2SO_4, $UO_2(SO_4)_2^{2-}$, and $UO_2(SO_4)_3^{4-}$ (Ahrland, 1951). In more alkaline solutions the sulfate ion may combine with uranyl hydroxide complexes such as $(UO_2)_2(OH)_2^{2+}$ to form $(UO_2)_2(OH)_2SO_4$ or with $(UO_2)_6(OH)_{10}^{2+}$ to form $(UO_2)_6(OH)_{10}SO_4$. The minerals zippeite, $(UO_2)_2(OH)_2SO_4 \cdot 4H_2O$?; johannite, $Cu(UO_2)_2(OH)_2(SO_4)_2 \cdot 6H_2O$; and uranopilite, $(UO_2)_6(OH)_{10}(SO_4) \cdot 12H_2O$ may precipitate from solutions such as these (Peterson, 1961).

With small amounts of vanadate, phosphate, or arsenate ions in the ground water containing hexavalent uranium, the very insoluble minerals such as carnotite, $K_2(UO_2)_2V_2O_8 \cdot 3H_2O$; autunite, $Ca(UO_2PO_4)_2 \cdot nH_2O$; and meta-zeunerite, $Cu(UO_2AsO_4)_2 \cdot 8H_2O$ may precipitate. These minerals have structures which consist of sheets made up of a combination of uranyl ions and vanadate, phosphate, or arsenate ions. Between the sheets lie the various cations and water molecules. In carnotite the

coordination of the uranyl ion is five-fold whereas in autunite and meta-torbernite it is four-fold.

THE TORBERNITE GROUP

Crystal Chemical Considerations

The designation, torbernite group, is used here to include all uranyl phosphates and uranyl arsenates which possess infinite sheets of the type $(UO_2PO_4)_n^{n-}$ or $(UO_2AsO_4)_n^{n-}$, that are isostructural with the sheets proposed for autunite and meta-autunite(I) by Beintema (1938). These sheets consist of dumbbell-shaped uranyl ions coordinated by four oxygen atoms of four different PO_4^{3-} tetrahedra. The tetrahedra and uranyl ions link into two-dimensional sheets lying parallel to (001), (Fig. 1). The sheets are puckered with the uranyl ion deviating 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. This structure (excluding the symmetry of the interlayer material) is body-centered. If the sheets are translated with respect to one another by the vector $[1/2, -1/2, 0]$ the structure proposed by Beintema (1938) for meta-autunite(I) is obtained (Fig. 1B). This structure has a primitive lattice and 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.

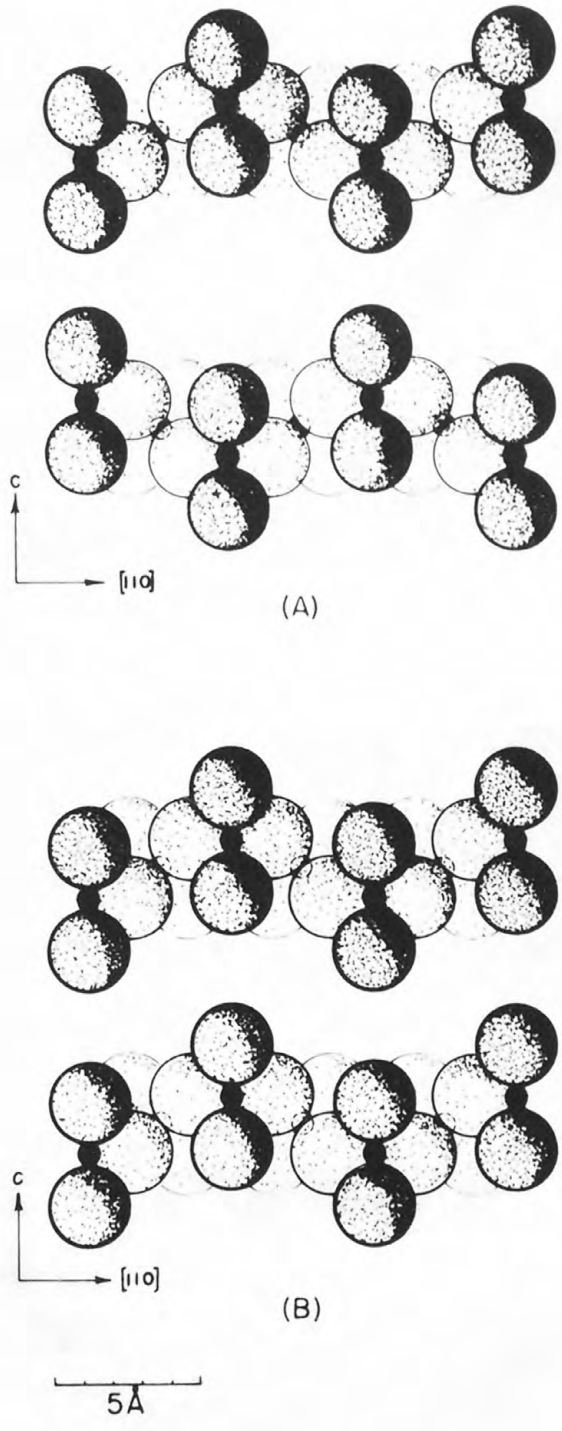


Figure 1. (A) The structure of autunite projected on ($\bar{1}10$) (after Beintema, 1938).

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

Beintema (1938), in what is now a classic paper, first solved the basic structure of the sheets with data obtained from X-ray rotation photographs. He was able to locate the positions of the uranium atoms within the sheet experimentally and by astute crystal-chemical reasoning positioned 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 heavy atoms such as uranium. The structure of the layers is essentially confirmed by the present work, and will be discussed in more detail in later chapters.

The Minerals of the Torbernite Group

There appear to be at least three hydration states for autunite, $Ca(UO_2PO_4)_2 \cdot nH_2O$. Autunite is the fully-hydrated phase, meta-autunite(I) is in the next lower hydration state, and meta-autunite(II) is in the lowest hydration state. The exact number and positions of the water molecules in the autunites are not known.

In the following discussion the term "meta" will be used for all but the fully hydrated species. Since the names of these minerals have been given without regard to their structure the various hydration states may not be structurally identical to the similarly designated autunites. Some of the compounds probably have only one hydration state whereas others may have as many as three or four.

Probably the best known minerals, whence the name of group is derived are torbernite $Cu(UO_2PO_4)_2 \cdot nH_2O$ and meta-torbernite, $Cu(UO_2PO_4)_2 \cdot 8H_2O$. The arsenate analogues are zeunerite, $Cu(UO_2AsO_4)_2 \cdot nH_2O$,

and meta-zeunerite, $Cu(UO_2AsO_4)_2 \cdot 8H_2O$. The exact hydration state of the fully-hydrated phases is not known.

Synthetic uranocircite, $Ba(UO_2PO_4)_2 \cdot 10H_2O$; meta-uranocircite(I), $Ba(UO_2PO_4)_2 \cdot 8H_2O$; and meta-uranocircite(II), $Ba(UO_2PO_4)_2 \cdot 2H_2O$ have been studied by Nuffield and Milne (1953). Heinrichite, $Ba(UO_2AsO_4)_2 \cdot 10\text{-}12H_2O$ and meta-heinrichite, $Ba(UO_2AsO_4)_2 \cdot 8H_2O$ are the arsenate analogues of uranocircite and have only recently been described by Gross, Corey, Mitchell, and Walenta (1958). The number of water molecules given in the above formulas of these barium compounds is only approximate.

Saléeite, $Mg(UO_2PO_4)_2 \cdot nH_2O$ and the arsenate analogue, novacekite, $Mg(UO_2AsO_4)_2 \cdot nH_2O$ are known to form a solid-solution series between the end-members (Frondel, 1958, p. 178). This series is probably the best evidence that phosphorus and arsenic substitute mutually, forming perhaps a complete series between these end-members.

Uranospinite, $Ca(UO_2AsO_4)_2 \cdot 8H_2O$ is the arsenate analogue of meta-autunite(I). The exact number of water molecules per formula unit is also not known.

Other minerals of the torbernite group are: troegerite, $H(UO_2AsO_4) \cdot 4H_2O$; sabugalite, $AlH(UO_2PO_4)_4 \cdot nH_2O$; bassetite, $Fe(UO_2PO_4)_2 \cdot nH_2O$; kahlerite, $Fe(UO_2AsO_4)_2 \cdot nH_2O$; abernathyite, $K(UO_2AsO_4) \cdot 3H_2O$; sodium-autunite, $Na(UO_2PO_4) \cdot nH_2O$; uramphite, $NH_4(UO_2PO_4) \cdot 3H_2O$; and sodium uranospinite, $Na(UO_2AsO_4) \cdot 5H_2O$. The minerals uranospathite and fritzscheite once attributed to the torbernite group are considereddby Frondel (1958) to be ill-defined species. Frondel (1958)

gives the detailed mineralogy of the torbernite minerals. The physical and chemical properties of the minerals described since Frondel's study are presented in Tables 1, 2, and 3.

A large number of synthetic compounds belonging to the torbernite group have been prepared. Frondel (1958, p. 167) gives a list of these compounds. The uranyl phosphates of Cu^{2+}, Ca^{2+}, $(HAl)^{4+}$, Ba^{2+}, Sr^{2+}, Na^{+}, Pb^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, $(NaH)^{2+}$, K^{+}, NH_4^{+}, H^{+}, and Li^{+} have been synthesized. The uranyl arsenates of Cu^{2+}, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}, H^{+}, and Li^{+} have been described. 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.

Physical and Chemical Properties

The torbernite minerals are sometimes referred to as "uranium micas" in allusion to the perfect (001) cleavage. Often indistinct (100) and (110) cleavages are also noted. The hardness is about 2 to 2-1/2 and specific gravities vary from about 3.0 to 4.1. Luster is often vitreous in fresh material but dull in dehydrated specimens. The color is usually yellow, yellow-green, or green. The most common forms are {001}, {100}, and {110}.

The optical properties of these minerals are very confusing. Ideally the minerals are uniaxial but in many specimens an anomalous biaxial character is observed. Apparently the optical properties can vary from specimen to specimen of the same mineral. Leo (1960) and Volborth (1959) have studied the unusual optical properties of autunite which will be discussed in greater detail later.

Table 1. Crystal Data for Various Torbernite Minerals

Mineral and Formula	Ref.	System	a (Å)	c (Å)	Space Group	Specific Gravity (Obs.)	Z	ϵ	ω
heinrichite $Ba(UO_2AsO_4)_2 \cdot 10\text{-}12H_2O$	1	tetragonal	-	-	-	-	-	1.573	1.605
meta-heinrichite $Ba(UO_2AsO_4)_2 \cdot 8H_2O$	1	tetragonal	7.07	17.74	$P4_2$, $P4_2/m$ or $P4_222$	4.04	2	1.609 1.609	1.637 1.641
arsenuranocircite $Ba(UO_2AsO_4)_2 \cdot 8H_2O$	2	tetragonal	-	-	-	-	-	1.623	1.632
uramphite $NH_4(UO_2PO_4) \cdot 3H_2O$	3	tetragonal	-	-	-	3.7	-	1.564	1.585
synthetic $NH_4(UO_2PO_4) \cdot 3H_2O$	3	tetragonal	-	-	-	-	-	1.564	1.585
sodium-autunite $Na(UO_2PO_4) \cdot 4H_2O$	4	tetragonal	-	-	-	3.584	2	1.559 1.564	1.578 1.585
sodium-autunite $Na(UO_2PO_4) \cdot nH_2O$	5	(biaxial)	-	-	-	-	-		1.617 1.618 1.641
sodium-uranospinite $Na_2(UO_2AsO_4)_2 \cdot 5H_2O$	6	tetragonal	7.12	8.61	-	3.846	-	1.585	1.612

1. Gross, Corey, Mitchell, and Walenta (1958)
2. Polikarpova and Ambartsumian (1958)
3. Nekrasova (1957)
4. Chernikov, Krutetskaia, and Organova (1957)
5. White (1958)
6. Kopchenova and Skvortsova (1957)

Table 2. Chemical Analyses of Various Torbernite Minerals

	1.	2.	4a.	4b.	6.
BaO	13.3%	12.99	-	-	-
UO_3	52.5	50.03	61.9	62.53	58.29
As_2O_5	15.8	23.46	-	-	20.84
P_2O_5	2.4	-	15.56	14.69	1.65
PbO	0.9	-	-	-	-
CaO	0.1	-	1.2	0.14	1.87
CO_2	0.6	-	0.24	-	-
SiO_2	-	-	1.6	-	2.39
MgO	-	-	0.43	-	-
Al_2O_3	-	-	0.32	-	0.91
Fe_2O_3	-	-	0.97	-	0.57
K_2O	-	-	-	-	-
Na_2O	-	-	5.62	-	3.91
H_2O^+	0.8	12.00	4.05	6.88	3.49
H_2O^-	10.6		9.02	14.84	6.00
Insol.	2.4	-	-	-	-
Total	100.2	98.48	100.91	99.08	99.92

1. Meta-heinrichite (Gross, Corey, Mitchell, and Walenta, 1958)
2. Arsenuranocircite (Polikarpova and Ambartsumian, 1958)

4a, b. Sodium-autunite (Chernikov, Krutetskaia, and Organova, 1957)

6. Sodium-uranospinite (Kopchenova and Skvortsova, 1957)

Table 3. Chemical Analyses of Uramphite and Synthetic $NH_4(UO_2PO_4)\cdot 3H_2O$ (Nekrasova, 1957)

	Uramphite		$NH_4(UO_2PO_4)\cdot 3H_2O$	
	Wt. %	Ratios	Wt. %	Ratios
NH_4	4.6	1.07	5.09	1.23
U	57.0	1.00	54.45	1.00
P	6.92	0.94	6.56	0.93
H_2O	11.0	2.56	12.35	3.00

The thermal behavior of these minerals has been the subject of a large number of studies most of which have led to inconclusive results because of the inability to determine the exact hydration state. Additional work is needed to establish the transition temperatures and water content of these hydrous compounds. Also, it is necessary to ascertain whether the water content varies continuously between certain limits and if hydration and dehydration is always a reversible process. Frondel (1958, p. 164-166) has given a good summary of this subject.

The minerals of the torbernite group are tetragonal or pseudo-tetragonal with a $\tilde{=}$ 7 Å and c $\tilde{=}$ 8-10 Å or 16-20 Å. The phosphate end-members have an a-dimension of 6.94 $\pm$ 0.06 Å and the arsenate end-members an a-dimension of 7.14 $\pm$ 0.06 Å. The measurement of the a-parameter is a useful way of distinguishing between the two types. Some of these minerals although pseudo-tetragonal show lower symmetry in the X-ray photographs (e.g., meta-uranocircite (I) and bassetite). Bassetite (Frondel, 1954) exhibits a monoclinic habit albeit with marked tetragonal pseudosymmetry.

One of the most remarkable properties shown by these minerals is that of base exchange. Fairchild (1929) was apparently the first to observe the phenomenon in this group of minerals. He showed that on treating synthetic autunite crystals with a concentrated solution of sodium chloride sodium-autunite could be produced. On treatment of the product with a calcium chloride solution autunite could be reproduced.

Mrose (1953) prepared sodium and ammonium-uranospinite by base-exchange with hydrogen-uranospinite.

Problems Concerning the Study of Torbernite Compounds

The large variety of cations which lie between the layers of these minerals and compounds presents a unique opportunity to study their hydration properties in the essentially identical environment formed by the infinite $(UO_2PO_4)_n^{n-}$ or $(UO_2AsO_4)_n^{n-}$ sheets.

The primary difficulties in studying these minerals are: (1) unavailability of adequate amounts of pure material for chemical analysis, (2) difficulty in determining the exact amount of water present, and (3) the tendency of the minerals to hydrate or dehydrate during analysis. The latter problem can be made apparent by the following observation. During the present study "single crystals" of so-called meta-uranocircite showing a "gridiron" structure were photographed by Buerger precession techniques at a relative humidity of about 70 to 90% and at temperatures of about 25°C. The precession photographs of the 0kl net showed the presence of two phases: meta-uranocircite(I) and the hydrated phase uranocircite. During the study, lasting for several weeks, the crystals were subjected to hydration and dehydration experiments while undergoing X-ray photography. The "meta" phase disappeared when air saturated with water vapor was passed over the crystal. Two phases would reappear upon discontinuing the current of wet air. When dry air (by use of a column of anhydrous calcium sulfate) was passed over the crystal the more fully hydrated phase would disappear. The changes described above were completely reversible and the diffraction patterns were always sharp indicating no

progressive mechanical disorder. A chemical analysis of this material would obviously give erroneous results if conducted at the temperatures and humidities given above.

Another problem encountered in describing these capricious minerals is in obtaining X-ray data that truly reflects the symmetry of all the atoms within the unit-cell. The difficulty here is due partly to the fact that the large contributions of the heavy uranium atoms to the observed intensities tend to obscure the contributions of the light oxygen atoms. Also, compounds which contain heavy elements such as uranium absorb X-rays to a much greater extent than compounds composed of only light atoms. Since absorption varies with path-length of the incident and diffracted X-ray beam the absorption errors will vary with each particular $hk\ell$ reflection. These errors will generally be rather large and will tend to further obscure the contributions of the light atoms.

To overcome these difficulties one must make every attempt to secure very small well-crystalized samples. The Buerger precession method should be employed. Weissenberg or rotation methods often will not give evidence for the large super-cells found in some of these uranium minerals. Lastly, molybdenum Kα radiation should be used to minimize the absorption errors. For example, the linear absorption coefficient for the compound, $Ba(UO_2PO_4)_2 \cdot 8H_2O$, is 1226 cm^{-1} for copper Kα radiation and 342 cm^{-1} for molybdenum Kα radiation.

The scattering contributions of the interlayer water molecules and cations to the observed intensities are usually very small because of the reasons given above. Often the symmetry of these atoms is lower

than the symmetry of the heavy atoms within the sheets and they thus produce weak super-lattice reflections which are particularly diagnostic. It is then extremely important, if we are to describe the interlaminar structure, to record these often very weak super-lattice reflections.

X-RAY CRYSTALLOGRAPHY

Experimental Procedures

Single-crystal X-ray diffraction studies were made using quartz-calibrated Buerger precession cameras with molybdenum radiation. Film measurements were corrected for the horizontal and vertical film shrinkage. A large number of small crystals of each specimen were photographed before one was chosen which appeared to give exceptionally good photographs. Usually photographs were made of the hhℓ , hk0, hk1, hk2, 0kℓ , and 1kℓ , reciprocal lattice nets. Exceptionally long exposures were made to insure that any possible super-cells would be observed. No particular reliance was placed on the 0kℓ , 1kℓ , and hhℓ photographs to indicate the conditions limiting the possible reflections. The best results in finding the correct extinction criteria were obtained from the hk0, hk1, and hk2 photographs. Because of the use of tabular crystals which are very thin in the c-direction, absorption errors are minimized in those reciprocal lattice nets which lie perpendicular to the c-axis. Donnay and Donnay (1955) explain the reasons for this minimization of absorption errors.

In the photographs of some of the minerals studied the doubling of the c-dimension was indicated only by long exposures of the hk1 reciprocal lattice net. Often the 0kℓ, 1kℓ, and hhℓ , nets did not show evidence for this.

The minerals studied were also examined by optical techniques. Often the optical properties of these minerals indicate a lower symmetry than

do the X-ray photographs. We shall try to explain some of the reasons for these findings from the experience gained in examining uranocircite and meta-uranocircite (I). It must be emphasized, however, that light is much more sensitive to small deviations of crystal symmetry than are X-rays. The technique of X-ray diffraction is not capable in all cases of giving the true symmetry of the crystal and it must remain for more sensitive techniques such as neutron-diffraction to give more precise information.

Meta-autunite (I)

Meta-autunite(I) crystals from the Daybreak mine, Mt. Spokane, Washington were studied. This material has been previously examined by Leo (1960) and Volborth (1959). The Mt. Spokane material appears both as light green and very dark green or black tablets. Leo (1960) found the U^{4+} content of the darker crystals to be higher than in the lighter crystals. The darker phase also had higher indices of refraction and a higher density than the lighter phase. Leo gives the formula

$$(Ca,Sr,U^{4+})_{0.99}(UO_2)_{1.96}(PO_4)_{2.00}\cdot 10.64H_2O$$

for the lighter phase and the formula

$$(Ca,Sr,U^{4+})_{0.97}(UO_2)_{1.86\text{-}1.98}(PO_4)_{2.00}\cdot 9.77H_2O$$

for the darker phase.

In the present study both light and dark crystals were examined and were found to be identical with respect to unit-cell size and space-group. The unit-cell data found in the present study are compared in Table 4 to those given by Donnay and Donnay (1955) for meta-autunite(I) from Lauter, Saxony. A strong pseudo-cell appears with a = 6.99 Å and

Table 4. Unit-cell Data for Meta-autunite (I), $Ca(UO_2PO_4)_2 \cdot 6H_2O$[1]

	Present Study[2]	Donnay and Donnay (1955)
a (Å)	19.78 ± 0.17	19.82
c (Å)	16.917 ± 0.034	8.49
a′ (Å)	6.99 ± 0.006	7.01
c′ (Å)	8.458 ± 0.017	-
Laue Group	4/mmm	4/mmm
Space Group	$P4_22$ (Probable)	P^{***}
Pseudo-Space Group	$P4/nnm$	$P4/nnm$
Specific Gravity (calc.)	3.53	3.50
Specific Gravity (obs.)	3.45 - 3.55[3]	3.48
V (Å^3)	6616	3335
Z	16	8
$\beta = \gamma$	1.579 - 1.586[3]	-
Forms	{110}, {001}	-
Locality	Spokane, Washington	Lauter, Saxony

1. Hydration state is not definitely known.
2. Size and color of crystals examined were:
   a) black, 0.05x0.20x0.35 mm
   b) dark green, 0.04x0.20x0.24 mm
   c) green, 0.03x0.20x0.42 mm
3. Leo, 1960

c = 8.46 Å and belongs to space group $P\bar{4}/nmm$- the space group found by Beintema (1938). The pseudo-cell is rotated 45° about the c-axis with respect to the true cell. The data obtained in the present study are in agreement with those of Donnay and Donnay except for the doubling of the c-parameter. This doubling is indicated only by hkl photographs which show a few extremely weak spots.

All X-ray photographs show 4/mmm Laue symmetry. The following conditions limiting the possible reflections were observed:

$$00l : l = 2n.$$

The pseudo-cell shows the following conditions:

$$hk0 : h+k = 2n.$$

The probable space group is $P4_22$ (No. 93). Because of the great difficulty in interpreting the hkl photographs this space group designation must be considered tentative. Fig. 2A shows the hk0 net and Fig. 2B shows the hk2 net. The weak super-lattice reflections can be seen in the center of the photographs.

Takano (1961) has suggested that the large super-cell found by Donnay and Donnay (1955) is incorrect and that the pseudo-cell with a = 6.99 Å and c = 8.46 Å is the correct one. Takano obtained his data with a diffractometer using a powdered specimen. Such a technique cannot be expected to pick up the very weak reflections that indicate a larger unit-cell.

Makarov and Ivanov (1960) have attempted to solve the structure of meta-autunite(I). Their unit-cell data are given in Table 5.

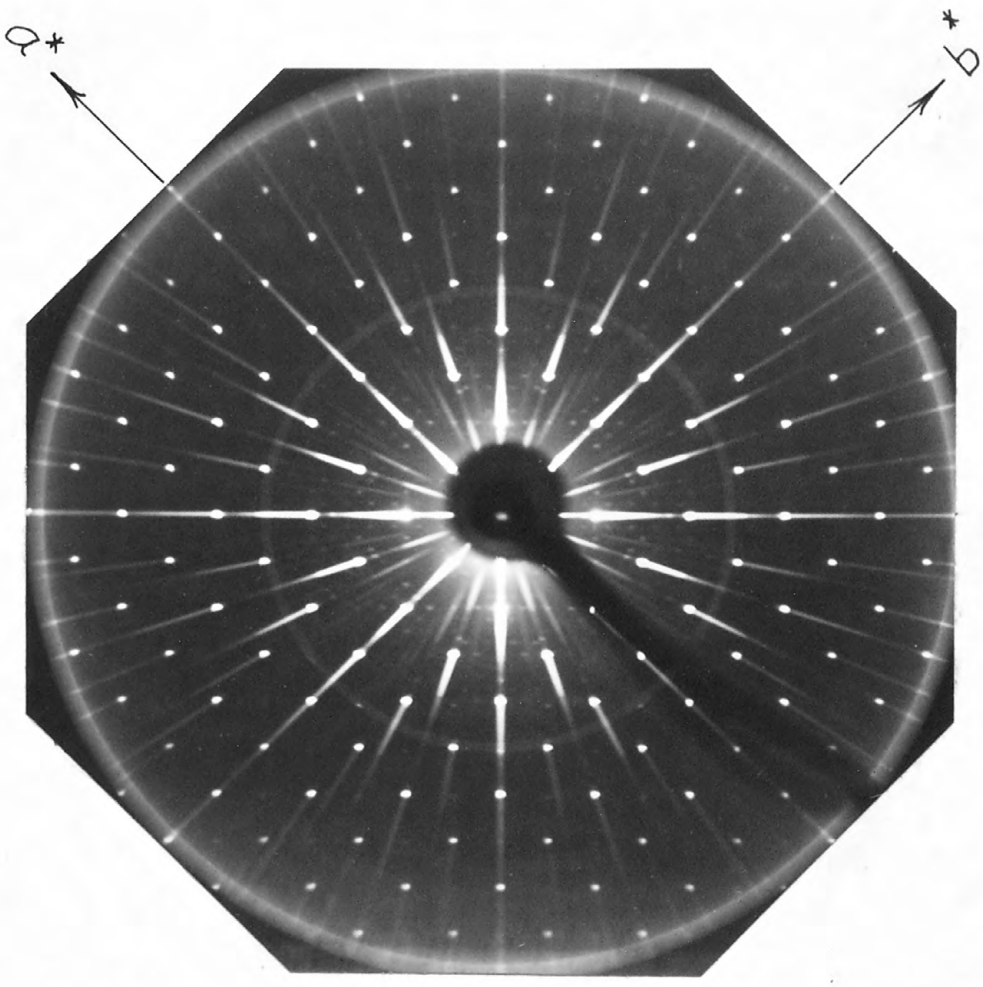


Figure 2 (A). hk0 Buerger precession photograph for meta-autunite (I) showing weak super-lattice reflections (Mo/Zr radiation).

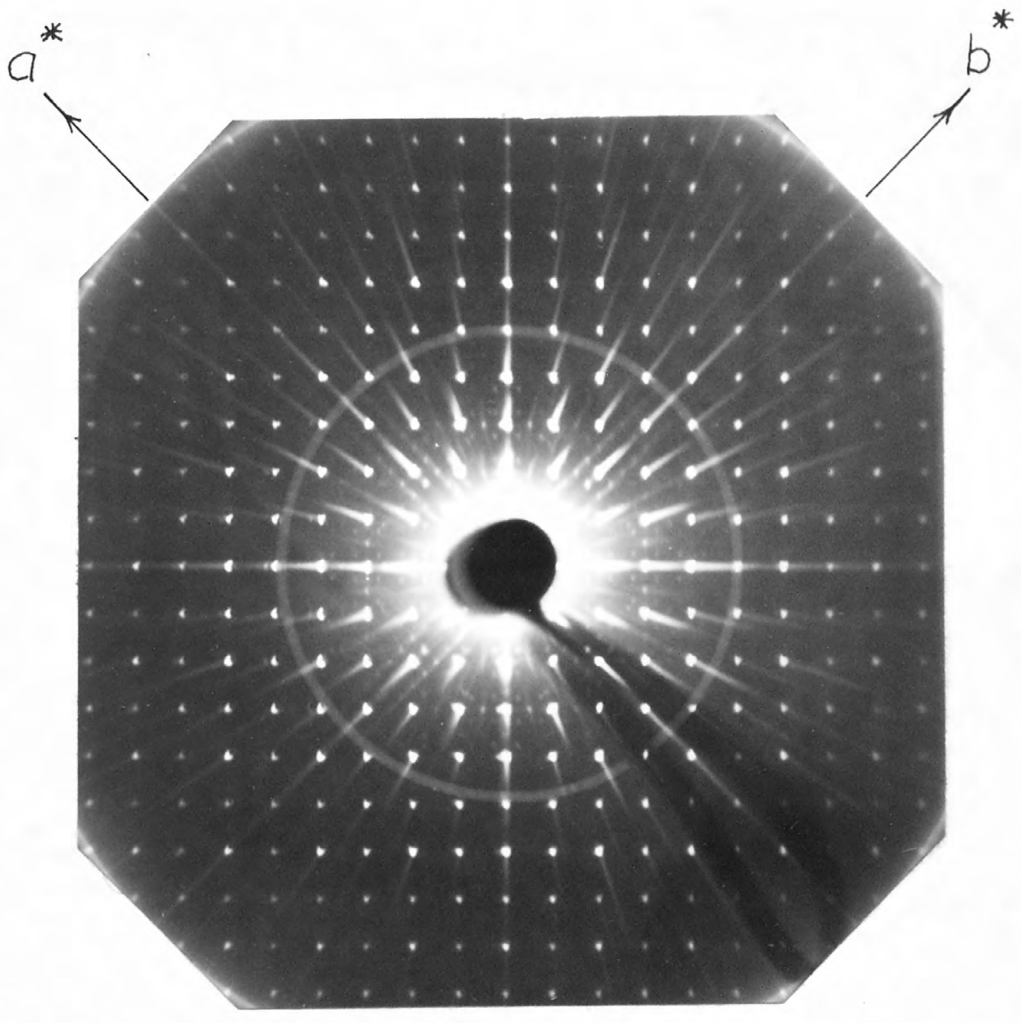


Figure 2(B). hk2 Buerger precession photograph of meta-autunite (I) showing weak super-lattice reflections (Mo/Zr radiation).

Table 5. Unit-cell Data for Meta-autunite (I), $Ca(UO_2PO_4)_2 \cdot 6H_2O$*

a	= 6.96 ± 0.01 Å
c	= 8.40 ± 0.02
Space Group	P4/nmm
Specific Gravity	3.44 (calc.)

* Makarov and Ivanov (1960)

As can be seen the unit-cell found by these workers corresponds to the pseudo-cell found in the present study and by Donnay and Donnay, (1955).

Makarov and Ivanov collected $0k\ell$ and $hk0$ intensity data with rotation techniques using copper radiation. The choice of an incorrect space group by these workers forced them to propose a structural model in which one calcium atom must be distributed over two positions (2c) and six water molecules over eight positions (8j). Their structure, based on electron density maps projected on (100) confirms Beintema's proposed structure of the $(UO_2PO_4)_n^{n-}$ sheets. Their proposal for the position of the interlayer calcium and water molecules cannot be considered correct. By calculating Fourier projections in the incorrect space group they have forced a false statistical distribution of these atoms.

The optical properties of meta-autunite (I) are sometimes anomalous. Slight birefringence is present and lamellae similar to those seen in uranocircite but on a much finer scale were observed. Birefringence is especially strong along the edges and cracks of the crystals. This is probably the result of local hydration or dehydration.

The relation of these unusual optical properties to the X-ray data is not apparent. There is perhaps true twinning on a fine scale. The discussion of uranocircite and meta-uranocircite (I) will treat this problem in greater detail.

Meta-uranocircite (I) and Uranocircite

Two samples of "meta-uranocircite" were examined; one from Bavaria (U.S.N.M. R-9432) and one from Saxony (U.S.N.M. C-4395). Spectrographic analyses (K. V. Hazel, analyst) of these two specimens show:

	USNM C-4395	USNM R-9432
U	10%	10%
P	5-10%	5-10%
Ba	1-5%	1-5%
Si	0.5-1%	-
Ca	0.1-0.5%	-
Na	0.1-0.5%	-

Examination by Buerger precession techniques shows that apparent single crystals from both samples are composed of two phases. This can be readily seen in the "Okl" photograph shown in Fig. 3. The a-dimensions of the two phases appear identical in the photograph but the c-dimensions are quite different (16.87 vs 17.65 Å). The apparent a and c-axes of the two phases are in parallel orientation. The 16.87 Å phase appears to give spots much weaker than those of the 17.65 Å phase indicating that the latter phase accounts for perhaps 75% of the crystal volume. The relative intensities of the spots of the two phases are almost the same in the diffraction patterns of both samples.

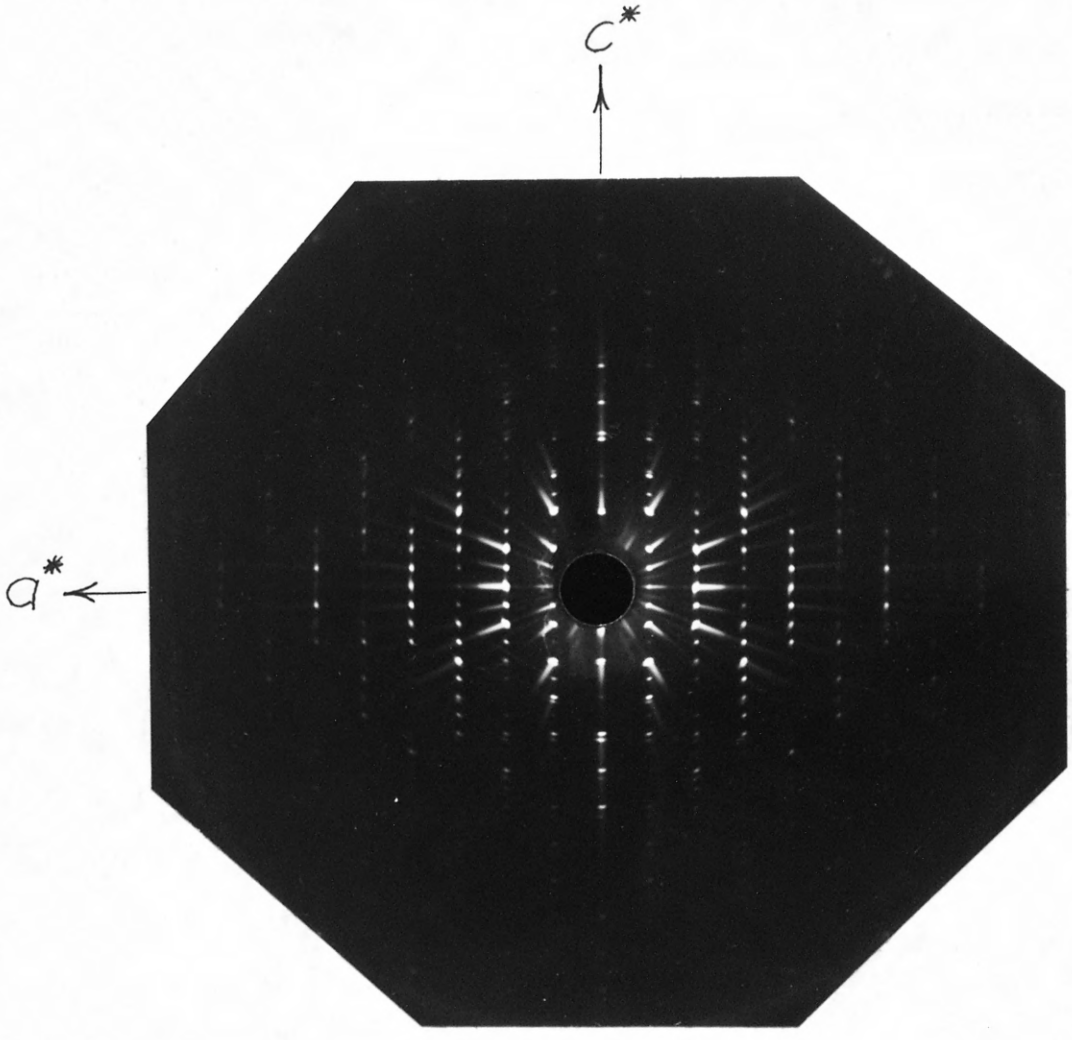


Figure 3. "0kℓ" photograph of "meta-uranocircite" showing the diffraction pattern of two phases; uranocircite, and meta-uranocircite (I), Mo/Zr radiation.

As mentioned before, the crystals may be converted completely to either phase simply by blowing air saturated with water vapor over the crystal or by using air from which most of the water vapor had been removed. The conversion is reversible. After converting the crystal entirely to either one of the two phases and then allowing the crystal to come into equilibrium with the normal room atmosphere, X-ray photographs were obtained that were identical to the original ones.

The 16.87 Å phase has a cell almost identical in size to that given by Donnay and Donnay (1955) for meta-uranocircite (I). Nuffield and Milne (1953) found the same pseudo-cell for meta-uranocircite (I)as that found in the present study for the 16.87 Å phase. We can be thus justified in designating the 16.87 Å phase meta-uranocircite (I), reserving the name uranocircite for the 17.65 Å phase. Table 6 compares the X-ray data obtained in the present study for meta-uranocircite (I) to the data of Donnay and Donnay (1955), Nuffield and Milne (1953), and Alver and Sellevoll (1957). The latter workers, although observing orthorhombic symmetry chose a *C*-centered cell with a=b=2x6.95 Å. Such a cell could have been chosen in the present study with a=13.94 Å but the axes would not have been compatible with the observed orthorhombic symmetry. The symmetry requires a primitive cell with a=9.805 Å and b=9.913 Å. It appears that Alver and Sellevoll did not examine the distribution of the intensities carefully enough and thus chose the wrong orientation.

Table 6. Unit-cell Data for Meta-uranocircite (I), $Ba(UO_2PO_4)_2 \cdot 8H_2O$*

	Present Study	Donnay and Donnay (1955)	Nuffield and Milne (1953)	Alver and Sellevoll (1957)
a (Å)	9.805 ± 0.011	9.87	6.96	13.9
b (Å)	9.913 ± 0.011	9.87	6.96	13.9
c (Å)	16.872 ± 0.011	16.85	16.90	16.9
a′ (Å)	6.97	6.98	-	6.95
Crystal System	orthorhombic	tetragonal	tetragonal	orthorhombic
Laue Group	mmm	4/mmm	4/mmm	mmm
Pseudo-Space Group	$P\bar{4}/nmm$	-	-	-
Space Group	$P222_1$ (probable)	$P\bar{4}/nmm$	$P\bar{4}/nmm$	Cmmm
Specific Gravity (calc.)	4.10	4.10	4.11	4.12
Specific Gravity (obs.)	-	4.08	4.08	
V ($Å^3$)	1640	1641	818.7	3265
Z	4	4	2	8
Forms	{110}, {001}	-	-	-
Locality	Wölsendorf, Bavaria	Madagascar	Falkenstein Saxony	Wölsendorf, Bavaria

* Hydration state not definitely known

Meta-uranocircite (I) possesses a marked tetragonal pseudo-cell with a=6.97 Å and c=16.87 Å. This cell is rotated about the c-axis 45° with respect to the true cell. It is this pseudo-cell that Nuffield and Milne discovered. Donnay and Donnay discovered the super-cell but did not observe the orthorhombic symmetry. The only extinctions observed in the present study were: 00ℓ where $\ell=2n+1$; thus the probable space group is $P222_1$, (No. 17).

The 17.65 Å phase has not been previously found occurring naturally but Nuffield and Milne (1953) have described a 17.6 Å phase which they obtained by immersing meta-uranocircite (I) in cold water for 24 hours. Frondel (1958, p. 177) suggests that the name uranocircite be reserved for natural occurrences of the fully-hydrated phase. Following this recommendation the name uranocircite will be used.

Table 7 compares the unit-cell data for uranocircite from Freiberg, Saxony with those given for synthetic uranocircite by Nuffield and Milne (1953). The agreement with Nuffield and Milne is good. The extinction criteria are 00ℓ : $\ell=2n+1$. Thus the tetragonal space groups $P4_22$, $P4_2$, or $P4_2/m$ are possible. The hk0 and hkl films, however, show very slight evidence for 4/m Laue symmetry so that space group $P4_2$ (No. ~~77~~) ~~or~~ $P4_2/m$ (No. 84) is probably the correct one for this mineral. The evidence for 4/m symmetry should be slight since probably the arrangement of the uranium, phosphorus, and barium atoms possesses 4/mmm Laue symmetry. We encounter this situation with meta-torbernite. The sample of uranocircite from Wölsendorf, Bavaria gave a unit-cell with a=6.96 Å, c=17.66 Å.

Table 7. Unit-cell Data for Uranocircite, $Ba(UO_2PO_4)_2 \cdot 10H_2O$*

	Present Study	Nuffield and Milne, 1953
a	6.970 ± 0.007 Å	6.96 Å
c	17.652 ± 0.036	17.57
Laue Group	4/m	4/mmm
Space Group	$P\bar{4}2_1$ or $P\bar{4}2_1/m$	$P4_122$
Specific Gravity (calc.)	4.06	4.09
V	857.6 $Å^3$	851.1
Z	2	2
Forms	{100} , {001}	-
Locality	Freiberg, Saxony	Falkenstein, Saxony**

* Hydration state not definitely known.

** Material was hydrated by immersing meta-uranocircite (I) in cold water for 24 hours.

Both of the samples of "meta-uranocircite" show a lamellar or "gridiron" structure, resembling that of microcline. The lamellae are oriented parallel to (100) and (010) of the uranocircite phase or parallel to (110) and ($\bar{1}$10) of the meta-uranocircite phase. The crystals are canary yellow in transmitted light. Emerson and Wright (1957) give a photomicrograph of "twinned" uranocircite crystals (Fig. 2, p. 227).

The lamellae of both samples as viewed looking down the c-axis appear to be of two types. One set of lamellae show marked birefringence and an extinction angle of 7°. The second set of lamellae appear to be uniaxial with little or no birefringence. Examination of some of the lamellar crystals on a heating stage showed that at about 100° C the lamellae disappeared leaving what appeared to be homogeneous crystals showing marked biaxial character. On lowering the temperature to below 100° C the lamellae reappeared. This experiment suggests that the two sets of lamellae correspond to the two phases that appeared in the X-ray photographs. The set of lamellae that shows biaxial character is the 16.87 Å phase, meta-uranocircite (I). The set of lamellae showing uniaxial character is the 17.65 Å phase, uranocircite. Other optical properties observed in these crystals were: (1) an acute bisectrix figure and (2) a β and γ index of refraction of 1.622 $\pm$ 0.002.

The mechanism by which the above described phenomenon takes place may be the result of an original twin pattern set up in the crystal at the time of precipitation. As the crystal was isolated

from the original environment one set of lamellae dehydrated with respect to the other. Since the two sets of lamellae probably present different surfaces to the external environment, one of the sets may be relatively more stable than the other. Compositional variation between the two sets may also stabilize one relative to the other.

The original twinning then may have permitted the growth of two sets of lamellae, one of which is relatively more stable than the other at atmospheric conditions. One set then hydrated (or dehydrated) with respect to the other giving the two phases which appear in the X-ray photographs. The inclined extinction of the biaxial set of lamellae must indicate that the 16.87 Å phase has lower symmetry than that which appears in the X-ray photographs. Dr. C. S. Ross (U. S. Geological Survey, personal communication) has observed in a weathered albite from Corundum Hill, North Carolina showing albite twinning, that one set of lamellae appears highly altered whereas the other set appears fresh.

The crystallography of the minerals abernathyite and meta-torbernite, and the compounds $NH_4(UO_2AsO_4)\cdot 3H_2O$ and $KH(UO_2AsO_4)_2\cdot 7H_2O$ will be presented in later chapters.

THE CRYSTAL STRUCTURE OF ABERNATHYITE AND RELATED COMPOUNDS

The Crystallography of Abernathyite

Abernathyite was described by Thompson, Ingram and Gross (1956) as a hydrous potassium uranyl arsenate with the chemical formula $K(UO_2AsO_4)\cdot 4H_2O$. It occurred as 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. It occurs as a coating lining a fracture in the sandstone and is associated with yellow-brown, earthy scorodite, $FeAsO_4\cdot 2H_2O$. Jarosite, $KFe_3(SO_4)_2(OH)_6$; pitticite, $Fe(AsO_4)(SO_4)(OH)\cdot nH_2O$?; meta-zeunerite, $Cu(UO_2AsO_4)_2\cdot 8H_2O$; native arsenic; orpiment, As_2S_3; and realger, AsS, have also been found in specimens containing abernathyite.

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 0.5x0.5x0.10 millimeters. The crystals examined were bright, transparent, straw-yellow in color and appeared as thick tablets with the forms {001} , and {110} . Some of the crystals were slightly darker in color because of a thin coating of another mineral (probably scorodite). The optical properties obtained in the present

study by C. S. Ross are: uniaxial negative, $\epsilon = 1.570 \pm 0.003$ and $\omega = 1.608 \pm .003$. Thompson, Ingram, and Gross (1956) found ϵ to be equal to 1.570 ± 0.003 and ω to be equal to 1.597 ± 0.003. The low ω index determination found in the original study was perhaps caused by interference from the thin coating of a foreign material on the mineral grains.

X-ray single crystal studies were made with the Buerger precession camera using molybdenum radiation. Table 8 gives the reciprocal lattice nets, exposure times, and radiation used for the determination of the unit-cell and space group of abernathyite. The sizes of the crystals photographed are 0.06x0.17x0.19 mm and

Table 8. X-ray Photography of Abernathyite

Net	Exposure	Radiation
0kℓ	64 hours	Mo-unfiltered
1kℓ	120	Mo-unfiltered
2kℓ	117	Mo-unfiltered
3kℓ	156	Mo-Zr filtered
hk0	65	Mo-unfiltered
hk1	72	Mo-unfiltered
hk2	23	Mo-Zr filtered
hhℓ	75	Mo-unfiltered

0.07x0.11x0.13 mm. The mineral is tetragonal and shows 4/mmm Laue symmetry. The conditions limiting the possible reflections are:

$hk\ell$: no conditions

$hk0$: $h+k=2n$

$0k\ell$: $\ell=2n$

$hh\ell$: $\ell=2n$

These conditions unequivocally fix the space group as $P4/ncc$ (No. 130).

The $hk\ell$ reflections in which ℓ is odd are extremely weak, only eighteen of this type appearing in the hkl, $1k\ell$, $2k\ell$ and $3k\ell$ photographs. Figure 4 shows the hkl reciprocal lattice net. The 4/mmm Laue symmetry is apparent. Donnay and Donnay (1955, see also G. Donnay in Thompson, Ingram, and Gross, 1956) did not observe these weak reflections and thus found the c-dimension to be 9.07 Å instead of 18.126 Å as found in the present study. Table 9 compares the X-ray and optical data obtained in the present study to those obtained in the original descriptions.

The observation and measurement of the weak $hk\ell$ spots for which ℓ is odd is critical for, as will be shown later, only these reflections reflect completely the symmetry of the interlayer matter. All other reflections are so dominated by the uranium and arsenic contributions that the higher symmetry of only these heavy atoms is apparent.

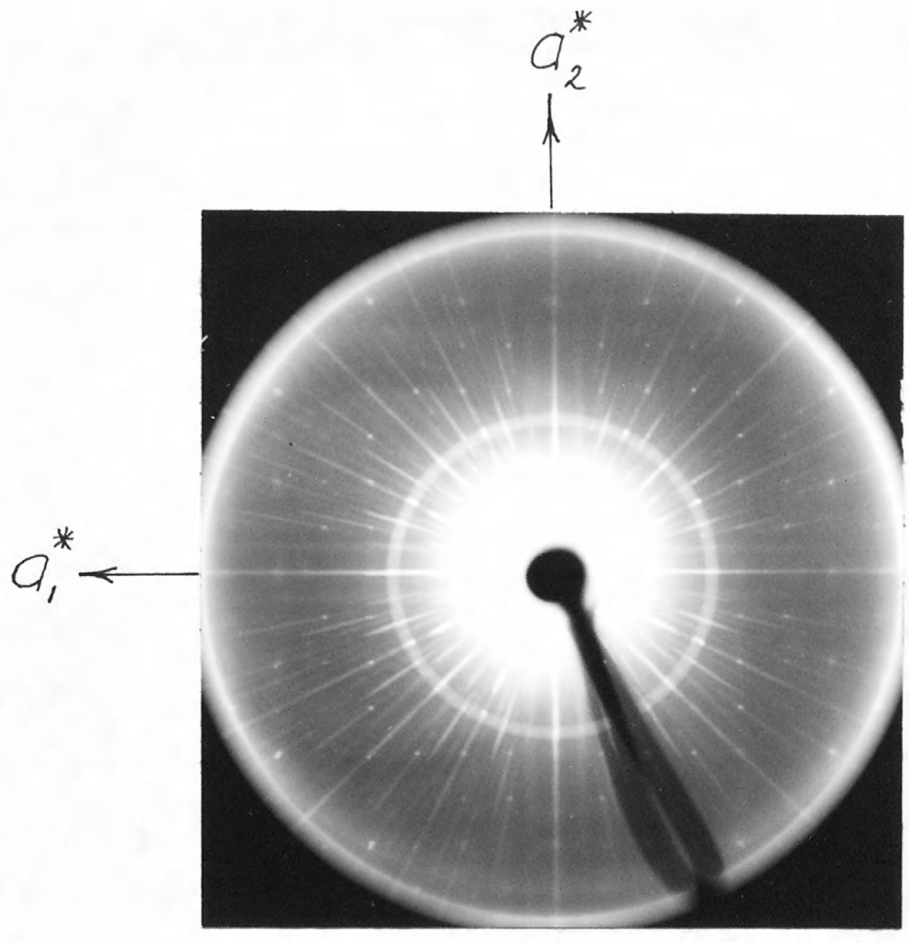


Figure 4. hkl Buerger precession photograph of abernathyite (Mo/unfiltered radiation).

Table 9. X-ray and Optical Data for Abernathyite, $K(UO_2AsO_4)\cdot 3H_2O$

Unit cell	Present study	Donnay and Donnay, 1955
a (Å)	7.176 ± 0.008	7.17 ± 0.01
c (Å)	18.126 ± 0.010	9.07 ± 0.01
Laue Group	4/mmm	4/mmm
Space Group	$P\bar{4}2_1c$ (No. 130)	$P\bar{4}2_1m$
V ($Å^3$)	933.4	466.3
Z	4	2
Specific Gravity (Obs.)	-	-
Specific Gravity (Calc.)	3.572	3.575
Pseudo-cell		
a′	7.176	-
c′	9.063	-
Pseudo-space group	$P\bar{4}2_1m$	-

Optical Properties	Present Study	(Thompson, Ingram, and Gross, 1956)
ϵ	1.570 ± 0.003	1.570 ± 0.003
ω	1.608 ± 0.003	1.597 ± 0.003
Forms	{001}, {110}	{001} , {110}

The Preliminary Structure Determination of Abernathyite

Two small crystals (0.06x0.17x0.19 mm, 0.07x0.11x0.13 mm) were used to collect the 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 exposure times are as follows:

hk0 66, 22, 10, 5, 2.5, and 1 hour

0kℓ 69, 29, 16, 5 and 2 hours

1kℓ 48, 17, and 7 hours

2kℓ 112, 70, 32, 15, and 5 hours

3kℓ 156, 88, 25, and 6 hours .

The intensities of the spots were estimated visually with a calibrated intensity strip prepared with the Buerger precession camera. The controlled exposures on the intensity strip were made so that the intensity of the nth spot is given by

$$I_n = I_a \, (2)^{n/2}$$

where I_a corresponds to a barely perceptible blackening of the film. The films of a particular reciprocal lattice net were scaled together by finding the average exposure difference for each spot. The intensities of each spot of each scaled film were then averaged to give the final observed intensity (relative exposure time, $I_{obs.}$). Lorentz and polarization corrections ($1/Lp$) were made to the observed intensities by means of a computer program based on the method of

Waser (1951) and the resulting $F^2_{obs.}$ values were then converted to the observed structure factors ($F_{obs.}$).

The space group of abernathyite is as already mentioned $P4/ncc$ (No. 130). The coordinates of the equivalent positions of this space group are tabulated in Figure 5. There are four uranium atoms per unit-cell and we will expect to find these atoms in positions 4a, 4b, or 4c. Since reflections of the type $hk\ell$ 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 $hk\ell$ where h+k=2n+1 would also be weak or missing. Knowledge of 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 is shown in Figure 6. The uranium-uranium interactions for atoms in position 4c correspond to peak No. 1 in Figure 6. The uranium-arsenic interactions correspond to peaks No. 2 and confirm the special position 4b for arsenic. No uranium-potassium interactions could be observed in the Patterson map. The peak assignments give the following coordinates for the heavy atoms:

4U in 4c at x=1/4, y=1/4, z=0.0516

4As in 4b at x=3/4, y=1/4, z=0 .

$P4/ncc$ D_{4h}^{8} No. 130 $P\,4/n\,2_1/c\,2/c$ $4/m\,m\,m$ Tetragonal

Origin at $\bar{1}$, at $\frac{1}{4},\frac{1}{4},0$ from $\bar{4}$ (compare previous page for alternative origin)

Number of positions, Wyckoff notation, and point symmetry			Co-ordinates of equivalent positions	Conditions limiting possible reflections
				General:
16	g	1	x,y,z; $\frac{1}{2}-x,y,\frac{1}{2}+z$; $x,\frac{1}{2}-y,\frac{1}{2}+z$; $\frac{1}{2}-x,\frac{1}{2}-y,z$; $\bar{x},\bar{y},\bar{z}$; $\frac{1}{2}+x,\bar{y},\frac{1}{2}-z$; $\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$; $\frac{1}{2}+x,\frac{1}{2}+y,\bar{z}$; $y,x,\frac{1}{2}+z$; $\frac{1}{2}-y,x,z$; $y,\frac{1}{2}-x,z$; $\frac{1}{2}-y,\frac{1}{2}-x,\frac{1}{2}+z$; $\bar{y},\bar{x},\frac{1}{2}-z$; $\frac{1}{2}+y,\bar{x},\bar{z}$; $\bar{y},\frac{1}{2}+x,\bar{z}$; $\frac{1}{2}+y,\frac{1}{2}+x,\frac{1}{2}-z$.	hkl: No conditions $hk0$: $h+k=2n$ $0kl$: $l=2n$ hhl: $l=2n$
				Special: as above, plus
8	f	2	$\bar{x},x,\frac{1}{4}$; $\frac{1}{2}-x,\bar{x},\frac{1}{4}$; $x,\frac{1}{2}+x,\frac{1}{4}$; $\frac{1}{2}+x,\frac{1}{2}-x,\frac{1}{4}$; $x,\bar{x},\frac{3}{4}$; $\frac{1}{2}+x,x,\frac{3}{4}$; $\bar{x},\frac{1}{2}-x,\frac{3}{4}$; $\frac{1}{2}-x,\frac{1}{2}+x,\frac{3}{4}$.	hkl: $h+k+l=2n$
8	e	2	$\frac{3}{4},\frac{1}{4},z$; $\frac{3}{4},\frac{3}{4},\frac{1}{2}+z$; $\frac{1}{4},\frac{3}{4},z$; $\frac{1}{4},\frac{1}{4},\frac{1}{2}+z$; $\frac{3}{4},\frac{3}{4},\bar{z}$; $\frac{3}{4},\frac{1}{4},\frac{1}{2}-z$; $\frac{1}{4},\frac{1}{4},\bar{z}$; $\frac{1}{4},\frac{3}{4},\frac{1}{2}-z$.	hkl: $h+k=2n$; $l=2n$
8	d	$\bar{1}$	$0,0,0$; $0,0,\frac{1}{2}$; $\frac{1}{2},0,0$; $\frac{1}{2},0,\frac{1}{2}$; $0,\frac{1}{2},0$; $0,\frac{1}{2},\frac{1}{2}$; $\frac{1}{2},\frac{1}{2},0$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$.	hkl: $h,k,l=2n$
4	c	4	$\frac{1}{4},\frac{1}{4},z$; $\frac{3}{4},\frac{3}{4},\bar{z}$; $\frac{1}{4},\frac{1}{4},\frac{1}{2}+z$; $\frac{3}{4},\frac{3}{4},\frac{1}{2}-z$.	hkl: $l=2n$
4	b	$\bar{4}$	$\frac{3}{4},\frac{1}{4},0$; $\frac{1}{4},\frac{3}{4},0$; $\frac{3}{4},\frac{1}{4},\frac{1}{2}$; $\frac{1}{4},\frac{3}{4},\frac{1}{2}$.	hkl: $h+k=2n$; $l=2n$
4	a	222	$\frac{3}{4},\frac{1}{4},\frac{1}{4}$; $\frac{1}{4},\frac{3}{4},\frac{1}{4}$; $\frac{3}{4},\frac{1}{4},\frac{3}{4}$; $\frac{1}{4},\frac{3}{4},\frac{3}{4}$.	

Figure 5. Equivalent positions and conditions limiting possible reflections of space group P4/ncc (No. 130b), (from International Tables, p. 226).

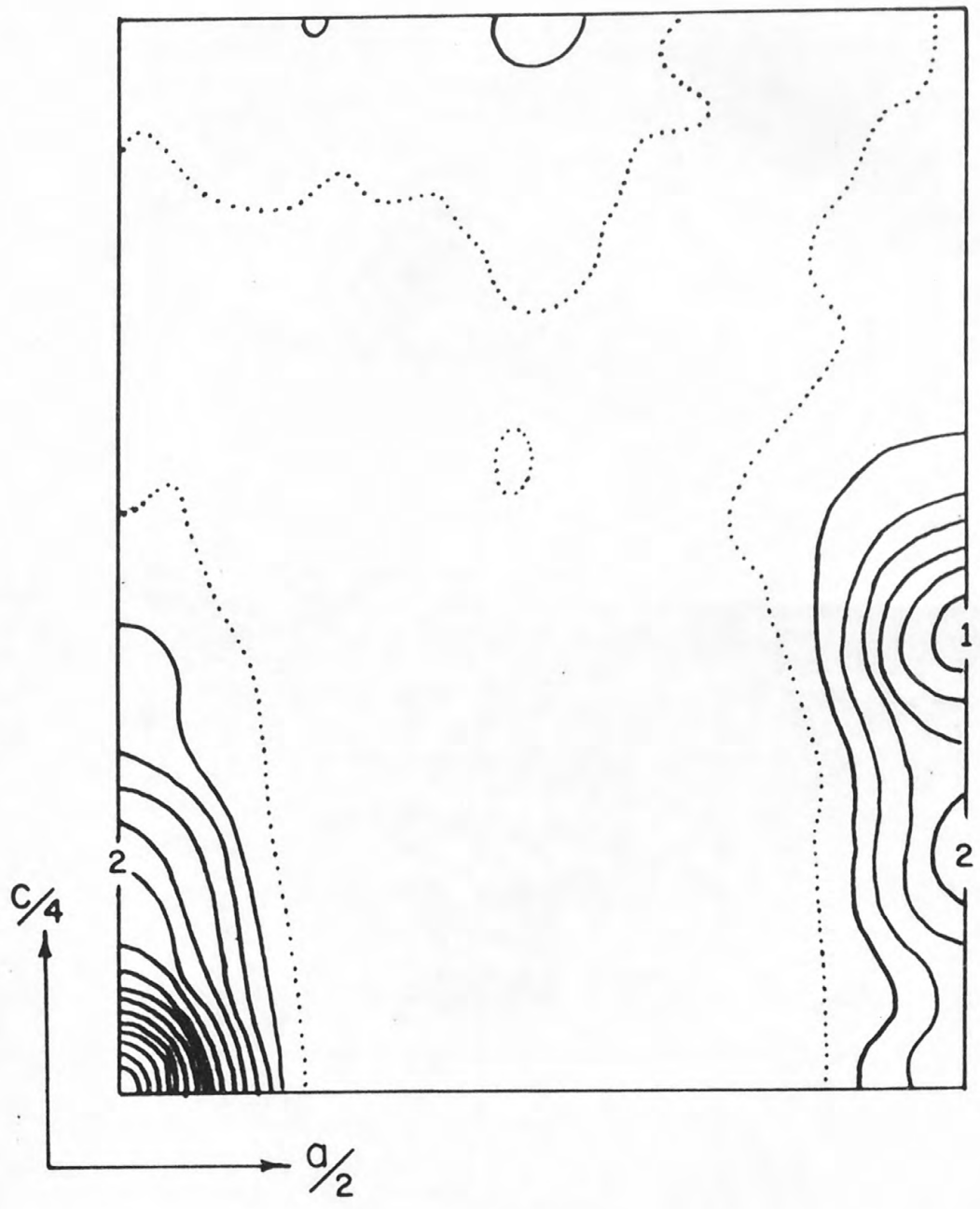


Figure 6. Patterson projection of the abernathyite structure on (100).

Peak No. 1, uranium-uranium interactions.

Peaks No. 2, uranium-arsenic interactions.

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.

On the basis of the approximate positions of the uranium, arsenic, uranyl oxygen, and arsenate oxygen atoms a tentative model was proposed in which infinite sheets of the type $(UO_2AsO_4)_n^{n-}$ are arranged in a manner similar to that of the $(UO_2PO_4)_n^{n-}$ sheets of meta autunite(I). On the basis of the positions of these atoms as obtained from the preliminary Fourier maps, 0kℓ structure factors were calculated. The temperature and scaling factors were determined together by the method of least-squares to obtain the best fit to the observed data. The contributions of the uranium and arsenic atoms (F_H) to the structure factors were then calculated and subtracted from the scaled observed structure factors ($KF_{obs.}$). A Fourier subtraction synthesis using the remainders for amplitudes was calculated. The synthesis is of the form

$$\rho(y,z) = \frac{C}{A} \sum_k \sum_\ell (KF_{obs.} - F_H) \exp\{-2\pi i(ky+\ell z)\}$$

where ρ is the electron density for a particular value of y and z, C/A is a constant, and K is the scaling factor. 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 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 structure factors were subtracted from the observed structure factors and the remainders used to calculate another 0kℓ subtraction map. The same type of least-squares analysis was also carried out with the hk0 data in order obtain a subtraction map projected on (001). The 0kℓ subtraction map resolved clearly all the oxygen atoms including the water molecules. The hk0 subtraction map shows the arsenate oxygens and the water molecules not completely resolved because of the slight overlap of these atoms in this projection. Figure 7 shows the final 0kℓ subtraction map and Figure 8 shows the final hk0 subtraction map obtained after two-dimensional least-squares analysis. As can be seen, in neither map is there any evidence for the presence of potassium in the structure, which should appear as peaks of roughly twice the density of the oxygen peaks.

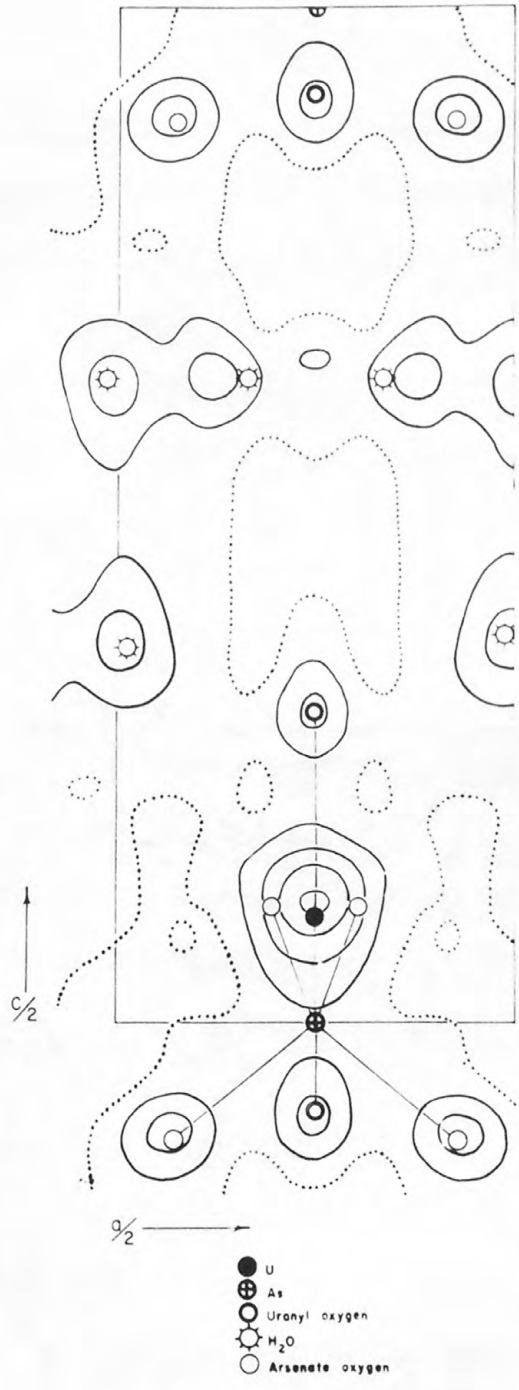


Figure 7. Final 0kℓ subtraction map of the abernathyite structure. Uranium, and arsenic contributions subtracted.

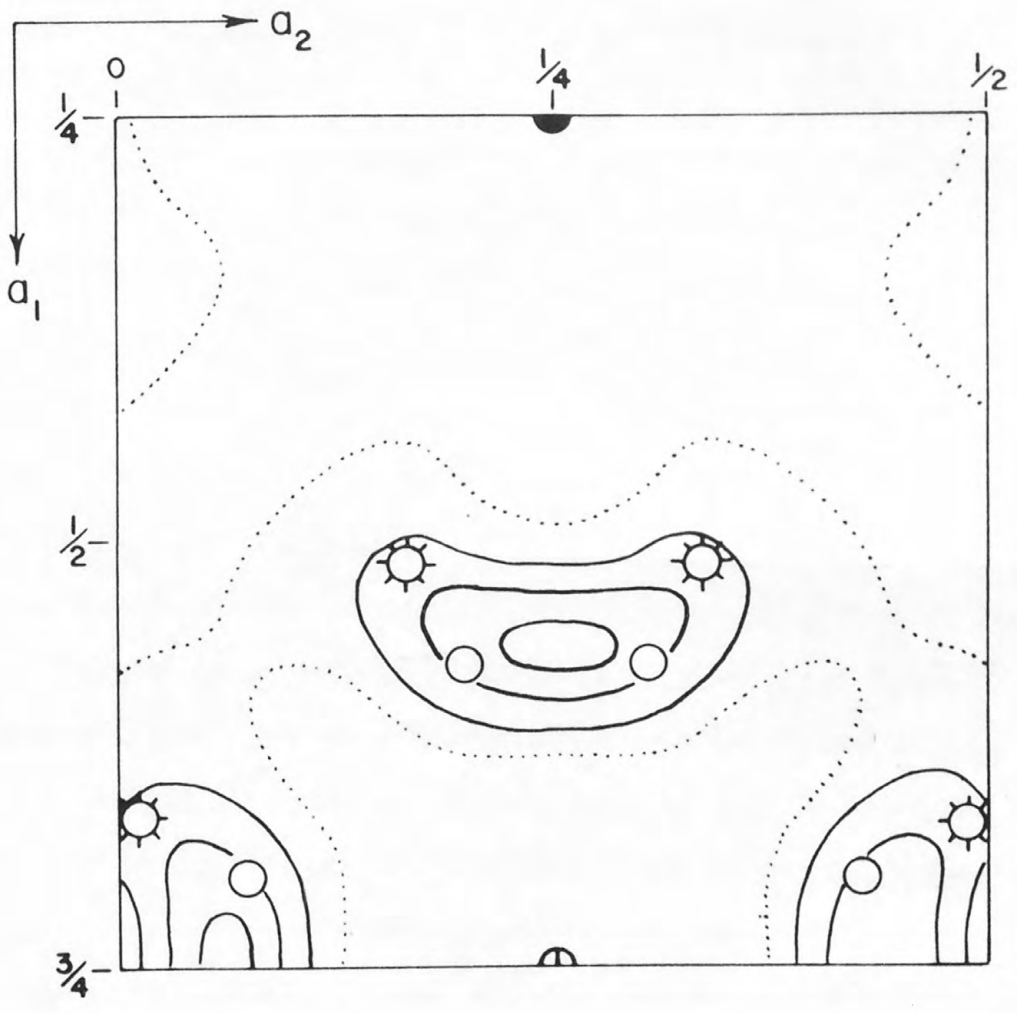


Figure 8. Final hk0 subtraction map of the abernathyite structure. Uranium, uranyl oxygen, and arsenic contributions subtracted.

From the coordinates of the atoms given by the final two-dimensional least-squares analysis interatomic distances were calculated and are listed as follows:

Atoms		Distance	Group
$U\text{-}O_a$	(4)	1.77 Å	UO_2^{2+}
$U\text{-}O_b$	(4)	1.71	UO_2^{2+}
$U\text{-}O_c$	(16)	2.26	
$As\text{-}O_c$	(16)	1.66	AsO_4^{3-}
$H_2O\text{-}H_2O$	(16)	3.02, 2.59	
$H_2O\text{-}O_c$	(16)	2.79 .	

These interatomic distances appeared plausible. At first inspection, the potassium atom would be thought to be positioned at the center of the square of four water molecules which were assumed to be represented by the four peaks appearing in the interlaminar region of the Okℓ subtraction map. No peak is present in this region of the subtraction maps. Furthermore, calculation reveals that there is no room for potassium in this position for it would require K-O bond distances of about 2.0 Å, an impossible value. Also, no room in the structure could be found for potassium unless the water molecules were arranged in a most unsymmetrical way.

The nonexistence of the potassium peak would lead one to believe if it were not for the chemical evidence that abernathyite is in fact troegerite, $H(UO_2AsO_4)\cdot 4H_2O$ with the following structure. The dumbbell-shaped uranyl ions, UO_2^{2+}, lie perpendicular to the sheets. The uranium

atom is further coordinated by four oxygens (O_c) of four different AsO_4 tetrahedra. The sheets are isostructural with the $(UO_2PO_4)_n^{n-}$ sheets proposed for meta-autunite (I) by Beintema (1938). The sheets are also arranged relative to one another in the same manner as those of meta-autunite (I). Between the uranyl ions of successive sheets lie groups of four water molecules, hydrogen-bonded to form squares. Each water molecule of the square is also hydrogen-bonded to one water molecule of an adjacent square and to an arsenate oxygen. The extra proton is assumed to be distributed randomly over the water molecules thus making one out of four molecules an oxonium ion (H_3O^+).

Discussion of the potassium problem with Frank Grimaldi and Blanche Ingram of the U. S. Geological Survey, who were associated with the original chemical analysis of abernathyite, led to the conclusion that potassium is definitely in the structure since the quantitative analysis for potassium was unequivocally correct. This led to the tentative conclusion that the actual formula for abernathyite is $K(UO_2AsO_4)\cdot 3H_2O$ with potassium substituting randomly for one out of four water molecules. The proof for such a hypothesis is difficult to establish, but it is felt that the approach given in the following 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 results are shown in Table 10.

Table 10. Optical Properties of Abernathyite

measured: $\epsilon = 1.570$	$(2\omega+\epsilon)/3=1.595$
$\omega = 1.608$	
calculated:	
$K(UO_2AsO_4)\cdot 4H_2O$	$(2\omega+\epsilon)/3=1.654$
$H(UO_2AsO_4)\cdot 4H_2O$	$(2\omega+\epsilon)/3=1.619$
$K(UO_2AsO_4)\cdot 3H_2O$	$(2\omega+\epsilon)/3=1.606$

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 shown in Table 10 suggest that the formula $K(UO_2AsO_4)\cdot 3H_2O$ is the correct one. The formula $K(UO_2AsO_4)\cdot 4H_2O$ seems to be out of the question.

Additional support for assuming the formula $K(UO_2AsO_4)\cdot 3H_2O$ to be the correct one for abernathyite comes from the work of Lienau (1898) who synthesized the compounds $H(UO_2PO_4)\cdot 4H_2O$, $K(UO_2PO_4)\cdot 3H_2O$, $K(UO_2AsO_4)\cdot 2\text{-}1/2H_2O$ and $NH_4(UO_2PO_4)\cdot 3H_2O$; from Rimbach (1904) who prepared the compound $K(UO_2AsO_4)\cdot 3\text{-}1/2H_2O$; from Werther (1948) who prepared $H(UO_2AsO_4)\cdot 4H_2O$; from Mrose (1953) who synthesized $H(UO_2AsO_4)\cdot 4H_2O$ (troegerite) and $NH_4(UO_2AsO_4)\cdot 3H_2O$; from González García who prepared $K(UO_2PO_4)\cdot 3H_2O$ and $K(UO_2AsO_4)\cdot 3H_2O$; from the

discovery of uramphite $NH_4(UO_2PO_4)\cdot 3H_2O$ (Nekrasova, 1957); and from R. Meyrowitz of the U. S. Geological Survey (personal communication) 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 (D. R. Ross, personal communication). The chemical analysis of Meyrowitz's compound is given in Table 11.

Table 11. Chemical Analysis of $K(UO_2PO_4)\cdot 3H_2O$*

	Wt. %	Ratios
K_2O	10.3	0.50
UO_2	62.4	1.00
P_2O_5	15.1	0.49
H_2O	11.9	3.03
	99.7	

* Analyst, R. Meyrowitz

Although the formulas of the above listed compounds may be in error, particularly as to water content, there is a definite indication that the potassium and ammonium uranyl arsenates and phosphates contain less than four molecules of water per formula unit. Lienau and Rimbach prepared $K(UO_2AsO_4)\cdot 2\text{-}1/2H_2O$ and $K(UO_2AsO_4)\cdot 3\text{-}1/2H_2O$ respectively. It is suspected that the two compounds are identical and are in fact synthetic abernathyites. The fact that $H(UO_2AsO_4)\cdot 4H_2O$ and the phosphate

analogue $K(UO_2PO_4)\cdot 4H_2O$ 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 $K(UO_2AsO_4)\cdot 3H_2O$.

It was then decided to try to solve the crystal structures of some other compounds that might bear a structural resemblance to abernathyite. Of the compounds then available only one crystallized in large enough crystals for single crystal X-ray work. This was the ammonium arsenate prepared by Mrose (1953).

The Preliminary Structure Determination of $NH_4(UO_2AsO_4)\cdot 3H_2O$

The compound $NH_4(UO_2AsO_4)\cdot 3H_2O$ was prepared by Mary Mrose a number of years ago at Harvard University. The crystals are bright yellow in color and are optically uniaxial negative with ω=1.611 and ϵ=1.601 (Mrose, 1953). The crystals exist as very small tablets, flattened on {001} with {100} also present. The chemical analysis as found by Meyrowitz is shown in Table 12 and is compared to the original analysis of this material by Gonyer (Mrose, 1953).

Table 12. Chemical Analyses of $NH_4(UO_2AsO_4)\cdot 3H_2O$

	Present Study*		Mrose, 1953**	
	Wt. %	Ratios	Wt. %	Ratios
$(NH_4)_2O$	5.5	0.50	5.11	0.47
UO_3	59.6	1.00	59.70	1.00
As_2O_5	23.1	0.48	23.14	0.49
H_2O	11.7	3.12	12.13	3.22
	99.9		100.08	

* Analyst, R. Meyrowitz

** Analyst F. A. Gonyer

Only minute tablets of $NH_4(UO_2AsO_4)\cdot 3H_2O$ were available for X-ray analysis. The size of the crystal used for the structure determination is 0.01x0.05x0.06 mm. The space group was determined from hk0, hk1, hk2, 0kℓ , and 1kℓ precession photographs. The photographs appear identical to those of abernathyite. The hk1 photograph is particularly revealing in this respect for it shows the same distribution and intensity of spots as do the hk1 photographs of abernathyite. Table 13 compares the X-ray and optical data to those of abernathyite.

Because of the extremely small size of the crystal used to gather intensity data long exposures were necessary. Intensity data from the 0kℓ zone were collected with the Buerger precession camera using unfiltered molybdenum radiation for the 199, 136, 72, and 46 hour exposures and zirconium-filtered radiation for the 48, 23, and 7 hour exposures. The intensity data were measured and converted into observed structure factors by the same methods as were used with abernathyite.

Because of the nearly identical appearance of the hk0, hk1, hk2, 0kℓ , and 1kℓ photographs and near identical cell-size to abernathyite it was assumed tentatively that $NH_4(UO_2AsO_4)\cdot 3H_2O$ was isostructural with abernathyite with ammonium ions substituting for one out of four water molecules instead of potassium ions. The structure of this compound was solved by assuming that the uranium and arsenic positions in the structure are identical to those in the abernathyite structure. An electron density subtraction map projected on (100) was made from data obtained by subtracting the calculated uranium and arsenic contributions to the 0kℓ structure factors of abernathyite ($F_{N,aber.}$)

Table 13. X-ray and Optical Properties of $NH_4(UO_2AsO_4)\cdot 3H_2O$ and Abernathyite

	$NH_4(UO_2AsO_4)\cdot 3H_2O$	Abernathyite
a (Å)	7.189 ± 0.005	7.176 ± 0.008
c (Å)	18.191 ± 0.014	18.126 ± 0.010
V (Å^3)	940.2 Å^3	933.4 Å^3
Z	4	4
Specific Gravity (obs.)	-	> 3.32
Specific Gravity (calc.)	3.429	3.572
Laue Group	4/mmm	4/mmm
Space Group	P4/ncc	P4/ncc
ϵ	1.601 ± 0.003*	1.570 ± 0.003
ω	1.611 ± 0.003*	1.608 ± 0.003
$(2\omega+\epsilon)/3$(calc.)	1.636	1.606
$(2\omega+\epsilon)/3$(obs.)	1.608	1.595
Forms	{001}, {100}	{001}, {110}

* Mrose, 1953

from the observed 0kℓ structure factors of $NH_4(UO_2AsO_4)\cdot 3H_2O$ ($K'F_{obs.,NH_4}$). The scaling constant K' was obtained by the relation

$$K' = \frac{KF_{obs.,aber.}}{F_{obs.,NH_4}} .$$

The subtraction synthesis is of the form

$$\rho(y,z) = \frac{C}{A} \sum_k \sum_\ell (K F_{obs.,NH_4} - F_{H,aber.}) \exp\{-2\pi i(ky+\ell z)\}.$$

The resulting subtraction map is shown in Figure 9. The map shows that the compound is isostructural with abernathyite. No NH_4 peak can be seen in the structure. The "squares" of four water molecules can be seen in the interlaminar region. Knowing that the formula of this compound contains only 12 water molecules per unit-cell and observing that 16 peaks appear in the interlaminar region it seems fairly certain that one ammonium ion is substituting randomly for one out of four water molecules. Before discussing the final refinement of this structure we shall first consider a second compound believed to be isostructural with abernathyite.

The Preliminary Structure Determination of $KH(UO_2AsO_4)_2\cdot 7H_2O$

A second compound was obtained through the efforts of Frank Grimaldi who synthesized a number of potassium and hydrogen uranyl arsenates for this study. The particular compound examined was the only one obtained in which the crystals were large enough for single crystal X-ray study. This compound, interestingly, was the one in the series which gave powder patterns closest in appearance to

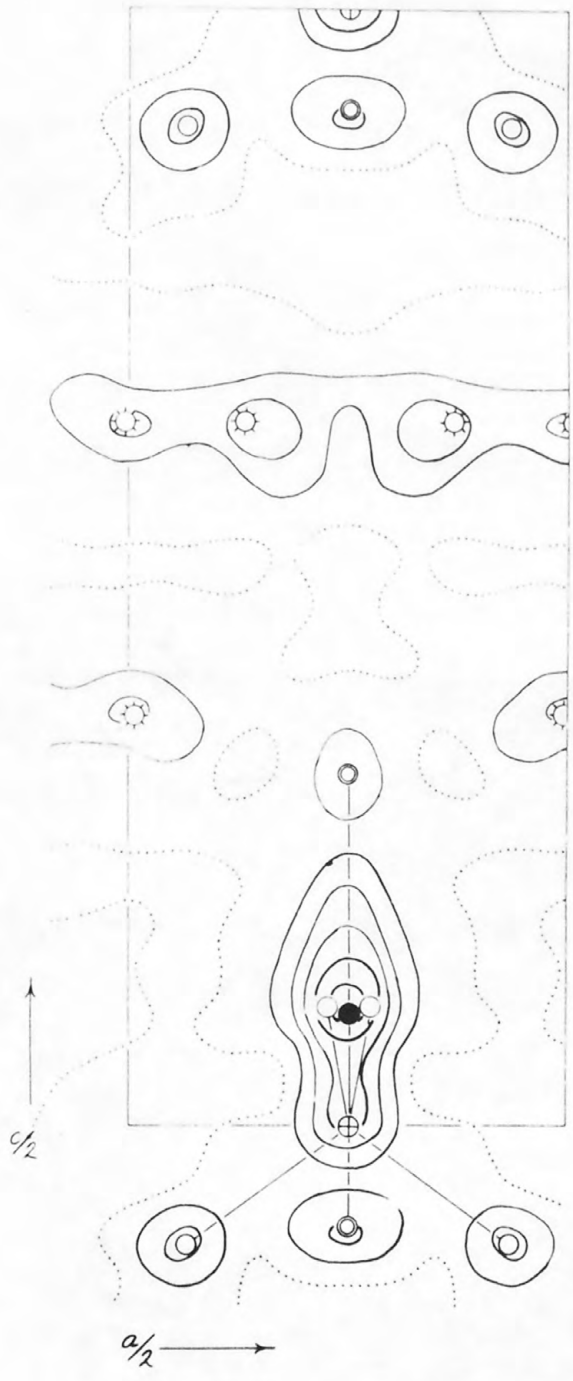


Figure 9. 0kℓ subtraction map of the $NH_4(UO_2AsO_4)\cdot 3H_2O$ structure.

those of abernathyite (D. R. Ross, personal communication).

The crystals are bright yellow, and are nearly identical in appearance to the $NH_4(UO_2AsO_4)\cdot 3H_2O$ crystals. The crystals are tabular, flattened on {001} and with {100} also present. The 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 14.

Table 14. Chemical Analysis of $KH(UO_2AsO_4)_2\cdot 7H_2O$*

	Wt. %	Ratios
K_2O	4.4	0.45
UO_3	59.2	2.00
As_2O_5	22.5	0.95
H_2O	13.3	7.15
	99.4	

* Analyst, R. Meyrowitz

The space group, using Buerger precession techniques, was determined from hk0, hkl, hhℓ, 0kℓ and 1kℓ photographs. The photographs appear identical to those obtained from abernathyite and $NH_4(UO_2AsO_4)\cdot 3H_2O$. Table 15 compares the X-ray and optical data to those of abernathyite.

Intensity data from the 0kℓ zone were collected with the Buerger precession camera using unfiltered molybdenum radiation. The dimensions of the crystal photographed are 0.03x0.15x0.08 mm. Exposure times were 88, 44, 17, 7, and 3 hours. The intensity data were measured

Table 15. X-ray and Optical Properties of $KH(UO_2AsO_4)_2 \cdot 7H_2O$ and Abernathyite

	$KH(UO_2AsO_4)_2 \cdot 7H_2O$	Abernathyite
a (Å)	7.171 ± 0.005	7.176 ± 0.008
c (Å)	18.048 ± 0.010	18.126 ± 0.010
V ($Å^3$)	928.1	933.4
Z	2	4
Specific Gravity (obs.)	-	> 3.32
Specific Gravity (calc.)	3.521	3.572
Laue Group	4/mmm	4/mmm
Space Group	$P\bar{4}2_1c$	$P\bar{4}2_1c$
ϵ	1.572	1.570 ± 0.003
ω	1.611	1.608 ± 0.003
$(2\omega + \epsilon)/3$, calc.	1.607	1.606
$(2\omega + \epsilon)/3$ obs.	1.598	1.595
Forms	{001}, {100}	{001}, {110}

and converted to observed structure factors by the same methods as mentioned previously.

The structure of $KH(UO_2AsO_4)_2 \cdot 7H_2O$ was assumed tentatively to be the same as that of abernathyite and $NH_4(UO_2AsO_4) \cdot 3H_2O$. The formula of $KH(UO_2AsO_4)_2 \cdot 7H_2O$ is perhaps better recast as $K(H_3O)(UO_2AsO_4)_2 \cdot 6H_2O$ to express the assumed substitution of one potassium ion and one oxonium ion, H_3O^+, for two out of eight water molecules.

As with $NH_4(UO_2AsO_4) \cdot 3H_2O$ the uranium and arsenic positions in the $KH(UO_2AsO_4)_2 \cdot 7H_2O$ structure were assumed to be identical to those in the abernathyite structure. An electron density subtraction map projected on (100) was made from data obtained by subtracting the calculated uranium and arsenic contributions to the $0k\ell$ structure factors of abernathyite ($F_{H,aber.}$) from the observed $0k\ell$ structure factors of $KH(UO_2AsO_4)_2 \cdot 7H_2O$ ($K'' F_{obs.,KH}$). The scaling constant K'' was obtained by the relation

$$K'' = \frac{K F_{obs.,\ aber}}{F_{obs.,\ KH}} .$$

The subtraction synthesis is of the form

$$\rho(y,z) = \frac{c}{A} \sum_k \sum_\ell (K'' F_{obs.,KH} - F_{H,aber.}) \exp\{-2\pi i(ky + \ell z)\}.$$

The resulting subtraction map is shown in Figure 10. The map shows that the compound is isostructural with abernathyite and $NH_4(UO_2AsO_4) \cdot 3H_2O$. As in the subtraction maps shown previously the "squares" of four water molecules can be seen in the interlaminar region.

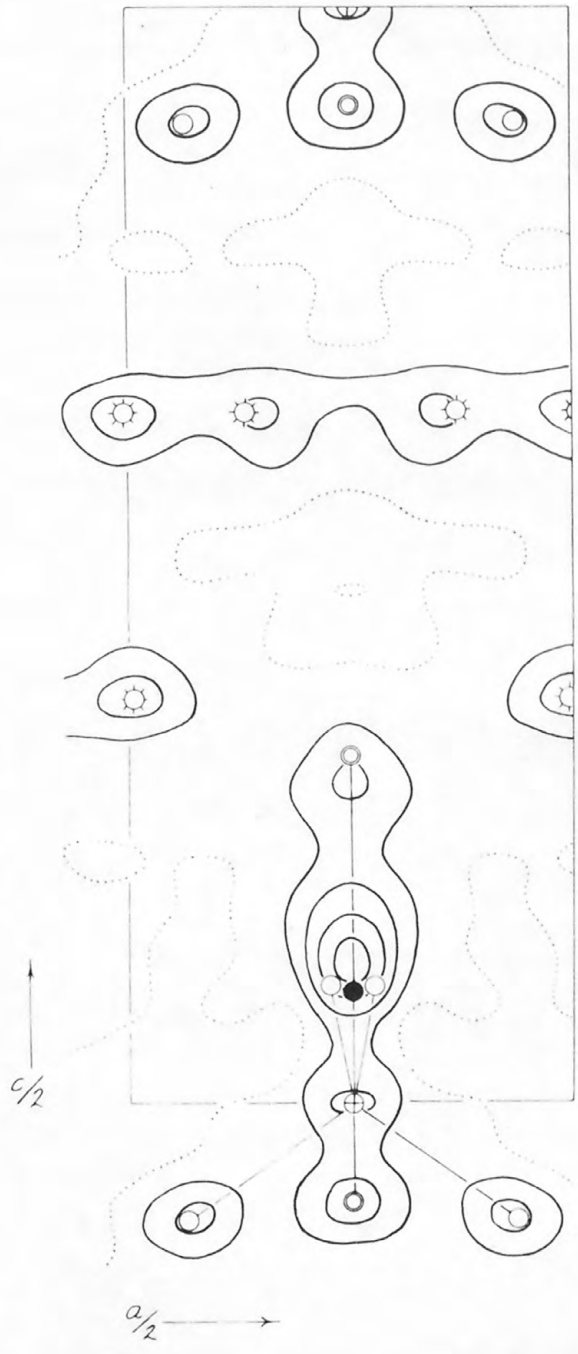
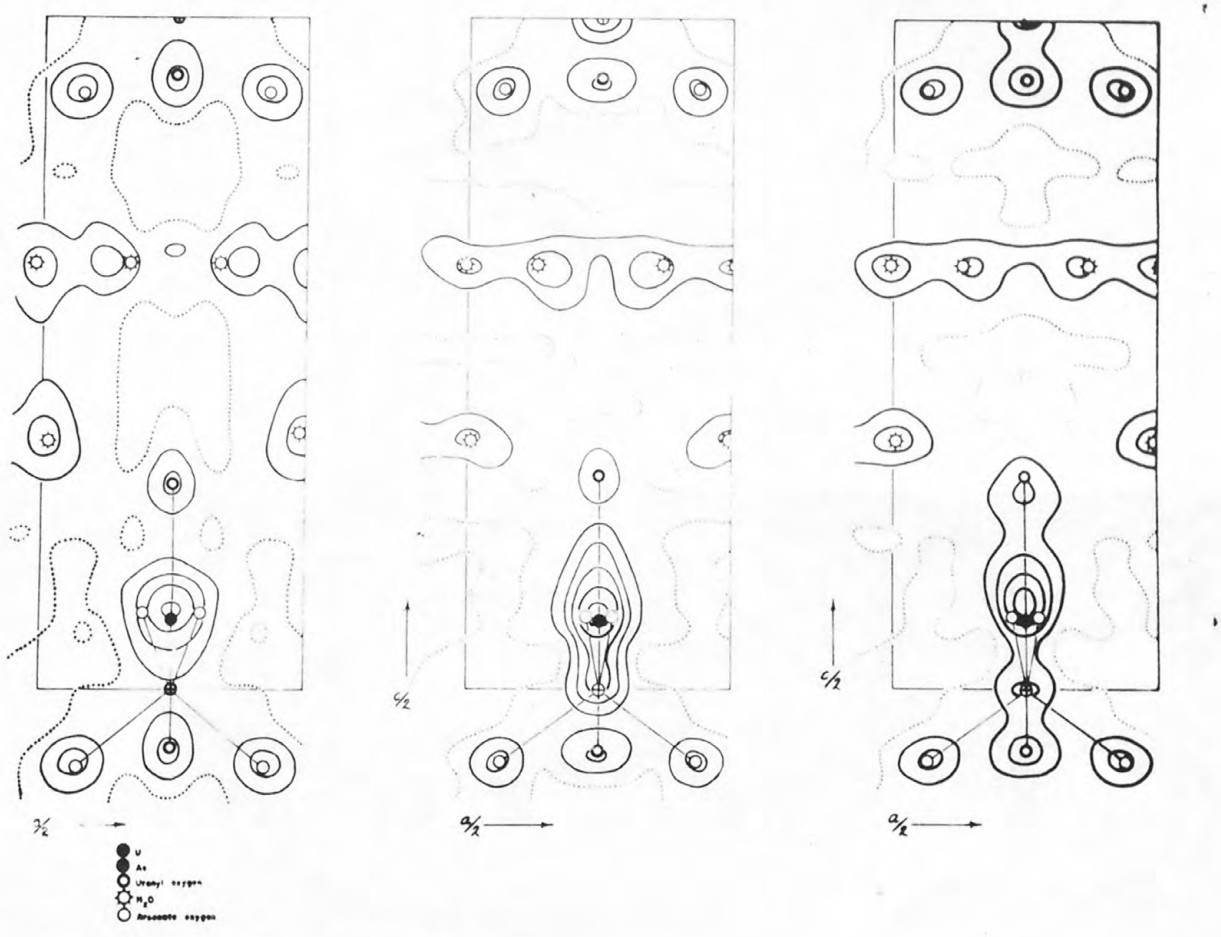


Figure 10. 0kℓ subtraction map of the $KH(UO_2AsO_4)_2 \cdot 7H_2O$ structure.

No potassium peak can be identified in the electron density maps so again it appears certain that the potassium atoms are substituting randomly for one out of eight water molecules. To maintain charge balance oxonium ions (H_3O^+) must be assumed to also substitute randomly for one out of eight water molecules.

Figure 11 compares the 0kℓ subtraction map of abernathyite to that of $NH_4(UO_2AsO_4)\cdot 3H_2O$ and $KH(UO_2AsO_4)_2\cdot 7H_2O$.



$K(UO_2AsO_4)\cdot 3H_2O$
Abernathyite

$NH_4(UO_2AsO_4)\cdot 3H_2O$

$KH(UO_2AsO_4)_2\cdot 7H_2O$

Figure 11. Okℓ subtraction maps of abernathyite, $NH_4(UO_2AsO_4)\cdot 3H_2O$, and $KH(UO_2AsO_4)_2\cdot 7H_2O$.

The 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 two possible structure models indicated by the two-dimensional electron density maps. Also, in the (100) electron density maps the uranium atom overlaps the arsenate oxygens making it difficult to obtain good atomic positions for the latter atoms.

In addition to the $0k\ell$ data already collected, $1k\ell$, $2k\ell$, and $3k\ell$ data were collected and processed in the usual manner. A list of the data is given in Table 16.

Table 16. Intensity Data Used for the Abernathyite Three-Dimensional Least-Squares Refinement

Net	$F_{obs.} > 0$	$F_{obs.} = 0$
$0k\ell$	84	12
$1k\ell$	91	91
$2k\ell$	82	90
$3k\ell$	73	79
Total	330	272

The large number of zero terms are due to the fact that only the water molecules and arsenate oxygen atoms contribute to the reflections in which ℓ is odd. The $F_{obs.\ (minimum)}$ is equal to 19.5.

The three-dimensional least-squares refinement was carried out on a Burroughs 220 computer using all the hkℓ data listed 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 isotropic temperature factors for each atom. No weighting factors were used in the refinement. Table 17 gives the final atomic positions, temperature factors, and the standard errors of these parameters. The final reliability factor (R) where

$$R = \frac{\sum \| F_{obs} | - | F_{calc.} \|}{\sum | F_{obs.} |}$$

is 8.4 percent. The reliability factor for the nine reflections for which ℓ is odd is 14.3 percent.

Table 18 gives the bond distances obtained from the data given in Table 17. The standard errors of bond distances are also given. The method of calculation of these standard errors is given in Appendix I. Appendix II gives the observed and calculated structure factors.

Figures 12 and 13 show the structural scheme of abernathyite projected on (100) and (001), respectively. As can be seen in these figures the AsO_4 tetrahedra are rotated so that their horizontal edges do not lie parallel to the a-axes. This rotation of these tetrahedra about four-fold rotatory-inversion axes as we shall see later is the result of hydrogen-bonding between the arsenate oxygen atoms (O_c) and

Table 17. Final Atomic Parameters and Standard Errors for

Abernathyite, $K(UO_2AsO_4)\cdot 3H_2O$*

Atom	Position	Parameters**	Standard Error
O_a	4c	x = 1/4	--
		y = 1/4	--
		z = 0.1515	0.0029
		B = 2.99	0.87
O_b	4c	x = 1/4	--
		y = 1/4	--
		z = 0.9575	0.0026
		B = 2.48	0.77
O_c	16g	x = 0.6963	0.0061
		y = 0.0729	0.0044
		z = 0.4433	0.0014
		B = 2.75	0.50
O_d***	16g	x = 0.1650	0.0051
		y = 0.9876	0.0053
		z = 0.3154	0.0016
		B = 3.71	0.72
As	4b	x = 3/4	--
		y = 1/4	--
		z = 0	--
		B = 1.84	0.100
U	4c	x = 1/4	--
		y = 1/4	--
		z = 0.0514	0.00013
		B = 1.90	0.048

* Space Group $P\bar{4}/ncc$ (No. 130b), origin at $\bar{1}$.

** Atomic coordinates in cycles, the temperature factor B in $Å^2$.

*** O_d atoms are the interlayer water molecules one out of four of which is substituted randomly by potassium.

Table 18. Bond Distances and Bond Angles in Abernathyite

Bond*	Equivalence	Length (angle)	Standard Error
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
$O_{a-1} - U_1 - O'_{b-1}$	4	180°	
II. AsO_4 ion			
$As_3 - O_{c-1}$	16	1.68 Å	0.03 Å
$O_{c-1} - O_{c-13}$	8	2.65	0.05
$O_{c-1} - O_{c-8}$	16	2.78	0.04
$O_{c-1} - As_3 - O_{c-13}$	8	104° 36′	
$O_{c-1} - As_3 - O_{c-8}$	16	111° 58′	
		108° 32′ (average)	
III. $UO_2 - AsO_4$ environment			
$U_3 - O_{c-8}$	16	2.35 Å	0.05 Å
$O_{a-3} - O_{c-8}$	16	2.91	0.04
$O_{b-3} - O_{c-8}$	16	2.96	0.04
$O_{c-8} - O_{c-14}$	16	3.32	0.05
$O_{b-3} - O_{c-13}$	16	3.45	0.04
$O_{b-3} - O_{c-1}$	16	4.18	0.05
$O_{c-8} - O_{c-7}$	16	3.64	0.05
$O_{a-1} - U_1 - O_{c-4}$	16	85° 56′	
$O'_{b-1} - U_1 - O_{c-14}$	16	94° 04′	

Table 18 - Contd.

Bond*	Equivalence	Length (angle)	Standard error
IV. H_2O environment			
$O_{d-7} - O_{d-13}$	16	2.80 Å	0.05 Å
$O_{d-13} - O_{d-16}$	16	2.83	0.05
$O_{c-1} - O_{d-7}$	16	2.75	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
$O_{c-8} - O_{d-7}$	16	4.51	0.05
$O_{c-13} - O_{d-7}$	16	3.65	0.05
$O'_{d-11} - O_{d-13} - O_{c-7}$	16	115° 35'	
$O'_{d-11} - O_{d-13} - O_{d-16}$	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'	
		108° 26' (Average)	

Table 18 cont'd.

*Atomic positions as assigned from International Tables, space group 130 b, p. 226, are listed as follows:

Atom	Position	Atom	Position	Atom	Position
U_1	1/4,1/4, z	O'_{b-1}	1/4,1/4,z-1	O_{c-13}	1/2-x,1/2-y, z
U_3	1/4,1/4,1/2+z	O_{b-3}	1/4,1/4,1/2+z	O_{c-14}	1/2+x,1/2+y,$\bar{z}$
As_3	3/4,1/4,1/2	O_{c-1}	x, y, z	O_{d-7}	1/2-y, x, z
O_{a-1}	1/4,1/4, z	O_{c-4}	$\bar{y}$, $\bar{x}$, 1/2-z	O'_{d-11}	y-1,1/2-x, z
O_{a-3}	1/4,1/4,1/2+z	O_{c-7}	1/2-y,x,z	O_{d-13}	1/2-x,1/2-y,z
O_{b-1}	1/4,1/4, z	O_{c-8}	1/2+y,$\bar{x}$,$\bar{z}$	O_{d-16}	1/2+y,1/2+x,1/2-z

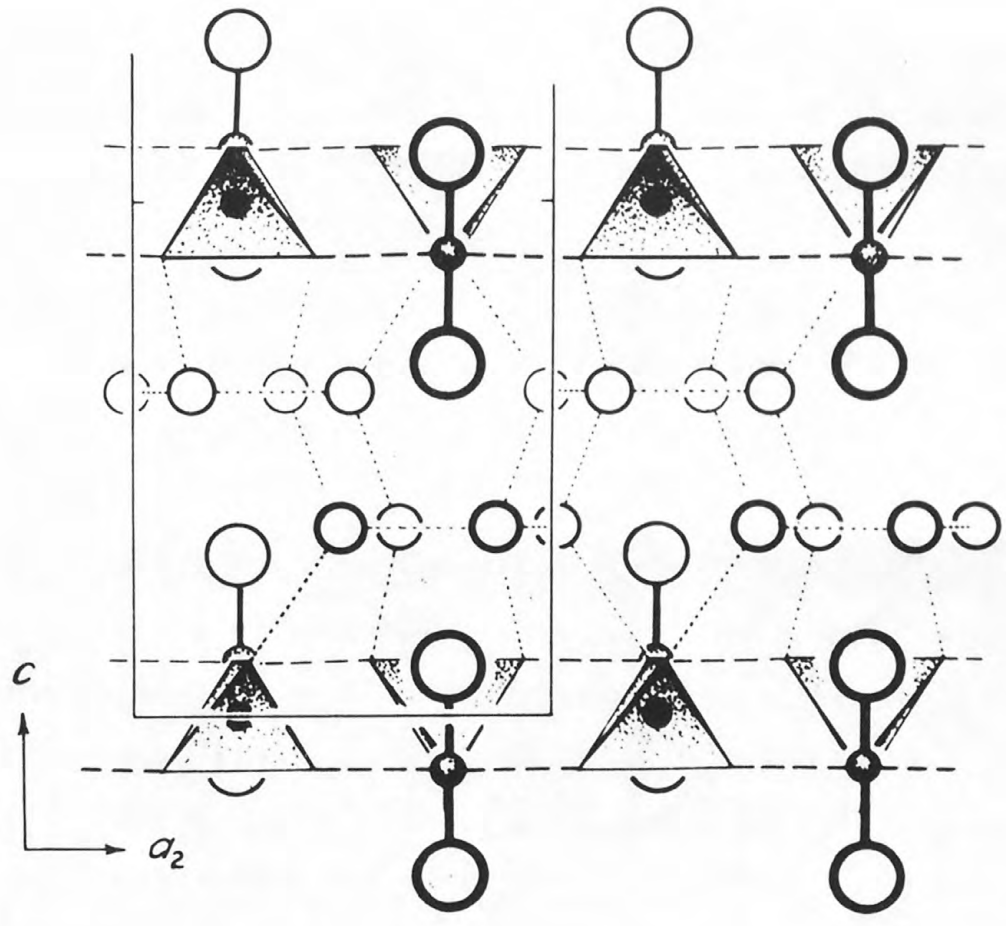


Figure 12. Projection of the abernathyite structure on (100). Heavy dashed lines indicate U-O_c bonds; light dotted lines indicate hydrogen bonds. Large open circles-uranyl oxygens, small open circles-water molecules, small stippled circles-uranium atoms, small solid circles-arsenic atoms.

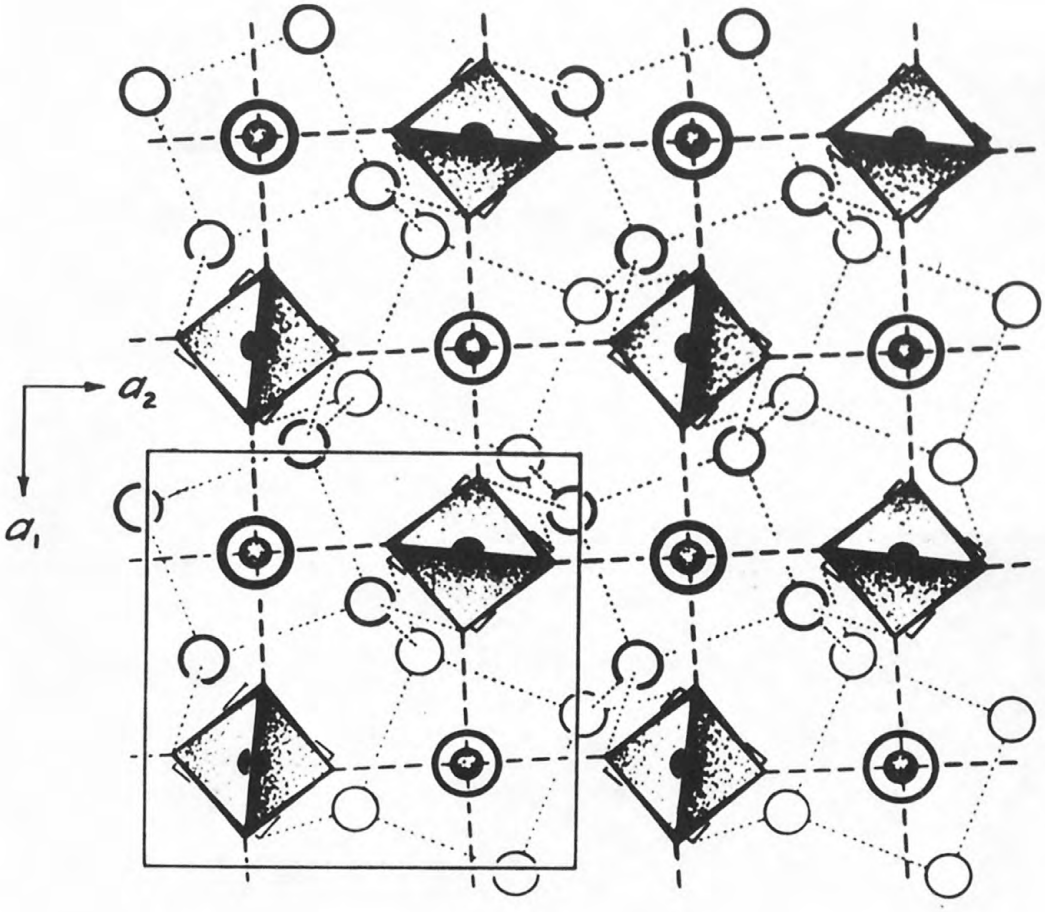


Figure 13. Projection of the abernathyite structure on (001).

the water molecules (O_d). Four arsenate oxygen atoms of four different AsO_4 tetrahedra coordinate the uranyl ion giving a U-O_c distance of 2.35 Å. Figures 12 and 13 show this arrangement of the AsO_4 tetrahedra about the uranyl ion. The heavy dashed lines in these figures represent the uranium-arsenate oxygen bonds. The uranium atom is displaced 0.09 Å above the plane of the four arsenate oxygens. The $(UO_2AsO_4)_n^{n-}$ sheets of abernathyite are positioned relative to one another in the same manner as those of meta-autunite (I).

The As-O_c bond distance is 1.68 Å and is in exact agreement with the As-O bond distance found in cahnite, $Ca_2BAsO_4(OH)_4$, by Prewitt and Buerger, 1961. In abernathyite the two horizontal edges of the AsO_4 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.

The axis of the uranyl ion lies on the four-fold axis and is thus exactly linear. The U-O_a and U-O_b bond distances are 1.81 and 1.70 Å. As can be seen in Figures 12 and 13, the uranyl ion is situated in a highly asymmetrical environment. One uranyl oxygen (O_a) is adjacent to only four arsenate oxygens at 2.91 Å while the other uranyl oxygen (O_b) is adjacent to 12 arsenate oxygens, four at 2.96 Å, four at 3.45 Å, and four at 4.18 Å. O_a is adjacent to eight water molecules (including potassium) four at 3.48 Å and four at 3.57 Å whereas O_b is adjacent to 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 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 appears real.

Between the uranyl ions symmetrically arranged about the four-fold axes lie groups of four water molecules one out of four of which are 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 14 is a pictorial diagram showing the detailed environment of the UO_2^{2+} ion and the $(H_2O)_4$ squares.

The groups of water molecules are hydrogen-bonded to form squares as is indicated by the $O_{d-7} - O_{d-13}$ 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. These bond distances are respectively 2.83 and 2.75 Å. The hydrogen-bonds are shown as light dashed lines in Figures 12, 13, and 14. The evidence of the $O_d - O_c$ hydrogen bond is quite clear for if no bonding were present between these two atoms the arsenate tetrahedra would not be rotated. In fact, it is this rotation and the placement of the water molecules off of the x,x,z position which doubles the cell in the c-direction and changes the space group from $P\bar{4}/nmm$ to $P\bar{4}/ncc$. The sheets are held together by this complex system of hydrogen-bonding and give a structure which shows perfect (001) cleavage.

The presence of potassium within the squares must modify this

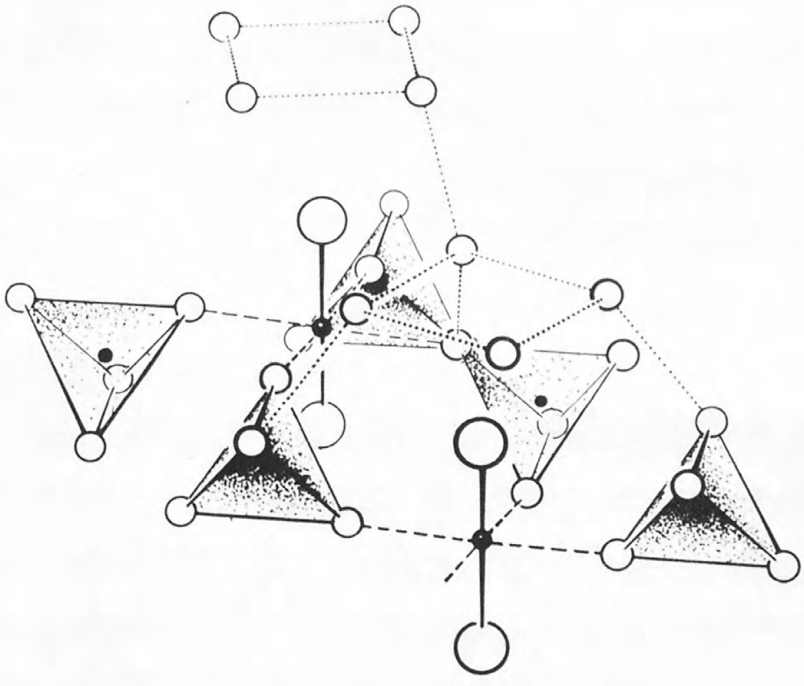


Figure 14. Pictorial diagram showing the detailed environment of the UO_2^{2+} ion and the $(H_2O)_4$ squares.

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 destroyed giving an equal number of real hydrogen bonds and protons. The three hydrogen bonds present in the structure are the only interatomic vectors involving a water molecule which are less than 3.25 Å. The structure of abernathyite will be compared to that of $NH_4(UO_2AsO_4)\cdot 3H_2O$ and $KH(UO_2AsO_4)_2\cdot 7H_2O$ in the following sections of this chapter.

The Refinement and Description of the Structure of $NH_4(UO_2AsO_4)\cdot 3H_2O$

Nine cycles of two-dimensional least-squares refinement were carried out on $NH_4(UO_2AsO_4)\cdot 3H_2O$ using the original 0kℓ intensity data consisting of 97 terms of which 82 were greater than zero. A general isotropic temperature factor was used for the first four cycles and then individual isotropic temperature factors for each atom in the last five cycles. 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. Because of the rather poor intensity data obtained for this compound the least-squares refinement and subtraction maps did not give more than an estimate of the z parameter of the uranyl oxygen O_a. Also, the refinement did not give, it was thought, 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 ninth cycle of least-squares refinement for atoms U, As, O_b and O_d. The z coordinate of O_a and the x coordinate of O_c were assumed to be the same as those found in abernathyite. The y and z coordinates for O_c were taken from the subtraction map.

Table 19 gives the atomic coordinates, temperature factors, and standard errors obtained from the last cycle of refinement and from the subtraction map. Appendix III gives the observed structure factors and the calculated structure factors as obtained from the parameters given in table 19. The final reliability factor (R) of the observed data is 9.2 percent.

Table 19. Atomic Parameters and Standard Errors for $NH_4(UO_2AsO_4)\cdot 3H_2O$[1]

Atom	Position	Parameters[2]	Standard Error
O_a	4c	x = 1/4	
		y = 1/4	
		z = 0.151[3]	
O_b	4c	x = 1/4	
		y = 1/4	
		z = 0.956	0.005
		B = 3.0	1.9
O_c[4]	16g	x = (0.696)	
		y = 0.076	
		z = 0.447	
O_d[5]	16g	x = 0.158	0.008
		y = 0.993	0.008
		z = 0.317	0.002
		B = 3.3	1.0
As	4b	x = 3/4	
		y = 1/4	
		z = 0	
		B = 1.68	0.22
U	4c	x = 1/4	
		y = 1/4	
		z = 0.0512	0.0003
		B = 2.54	0.11

Table 19 cont'd.

(1) Space Group $P\bar{4}/ncc$ (No. 130b), origin at $\bar{1}$.

(2) Atomic coordinates in cycles, the temperature factor B in $Å^2$.

(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^+.

Although the positions of the atoms could not be determined as accurately as in the case of abernathyite, there is no doubt that the two compounds are isostructural. The bond distances as given in Table 20 agree fairly well with those found in abernathyite. The standard errors of the bond lengths are estimated where possible.

The presence of NH_4^+ instead of K^+ within the structure gives enough protons to form forty hydrogen bonds per unit-cell, the maximum number possible in these structures.

Table 20. Bond Distances and Bond Angles in $NH_4(UO_2AsO_4)\cdot 3H_2O$

	Bond*	Equivalence	Length(Angle)	Standard Error
I.	Uranyl ion			
	$U_1 - O_{a-1}$**	4	1.81 Å	
	$U_1 - O'_{b-1}$	4	1.73	0.09 Å
	$O_{a-1} - U_1 - O'_{b-1}$	4	180°	
II.	AsO_4 ion			
	$As - O_{c-1}$	16	1.63 Å	
	$O_{c-1} - O_{c-13}$	8	2.62	
	$O_{c-1} - O_{c-8}$	16	2.67	
	$O_{c-1} - As_3 - O_{c-13}$	8	107° 18'	
	$O_{c-1} - As_3 - O_{c-8}$	16	110° 14'	
			108° 46' (average)	
III.	UO_2-AsO_4 environment			
	$U_3 - O_{c-8}$	16	2.37 Å	
IV.	H_2O environment			
	$O_{d-7} - O_{d-13}$	16	2.78 Å	0.09 Å
	$O_{d-13} - O_{d-18}$	16	2.88	0.09
	$O_{c-1} - O_{d-7}$	16	2.79	

* Atomic positions are the same as those assigned in Table 18.

** Bond distance assumed equal to that in abernathyite.

The Refinement and Description of the Structure of $KH(UO_2AsO_4)_2 \cdot 7H_2O$

As with $NH_4(UO_2AsO_4) \cdot 3H_2O$ the two-dimensional refinement was carried out using the original $0k\ell$ intensity data consisting of 96 terms of which 84 were greater than zero. Seven cycles of two-dimensional least-squares refinement using at first a general isotropic temperature factor and then individual isotropic temperature factors were made. The refinement did not give, it was thought, as reliable y and z parameters for the arsenate oxygen atoms as could be obtained from the subtraction maps. Because of the overlap of the uranium atoms and arsenate oxygen atoms the x parameter of the arsenate oxygen was fixed at 0.696 cycles during refinement. Table 21 gives the atomic coordinates, temperature factors, and standard errors obtained from the last cycle of refinement and from the subtraction maps. Appendix IV gives the observed and calculated structure factors and Table 22 gives the bond lengths and bond angles as obtained from the coordinates given in Table 21. The final reliability factor is 9.4%

$KH(UO_2AsO_4)_2 \cdot 7H_2O$ is isostructural with abernathyite and $NH_4(UO_2AsO_4) \cdot 3H_2O$. In this compound one potassium and one oxonium ion (H_3O^+) replace randomly two out of eight water molecules. 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.

Table 21. Atomic Parameters and Standard Errors for $KH(UO_2AsO_4)_2 \cdot 7H_2O$[1]

Atom	Position	Parameters[2]	Standard Error
O_a	4c	x = 1/4	
		y = 1/4	
		z = 0.150	0.005
		B = 3.6	1.8
O_b	4c	x = 1/4	
		y = 1/4	
		z = 0.958	0.004
		B = 2.9	1.7
O_c[3]	16g	x = (0.696)	
		y = 0.071	
		z = 0.448	
O_d[4]	16g	x = 0.150	0.008
		y = 0.993	0.009
		z = 0.315	0.002
		B = 4.1	1.0
As	4b	x = 3/4	
		y = 1/4	
		z = 0	
		B = 1.59	0.21
U	4c	x = 1/4	
		y = 1/4	
		z = 0.0520	0.0003
		B = 2.27	0.10

Table 21 contd.

(1) Space Group $P\bar{4}/ncc$ (No. 130b), origin at $\bar{1}$.

(2) Atomic coordinates in cycles, the temperature factor B in $\mathring{A}^2$.

(3) The y and z coordinates were obtained from subtraction maps; the x coordinate was fixed during refinement and was assumed by analogy to abernathyite to be equal to 0.696 cycles.

(4) O_d atoms are the interlayer water molecules of which two out of eight are replaced randomly by potassium and oxonium ions.

Table 22. Bond Distances and Bond Angles in

$KH(UO_2AsO_4)_2 \cdot 7H_2O$

	Bond*	Equivalence	Length(angle)	Standard Error
I.	Uranyl ion			
	$U_1 - O_{a-1}$	4	1.77 Å	0.09 Å
	$U_1 - O'_{b-1}$	4	1.70	0.07
	$O_{a-1} - U_1 - O'_{b-1}$	4	180°	
II.	AsO_4 ion			
	$As_3 - O_{c-1}$	16	1.64 Å	
	$O_{c-1} - O_{c-13}$	8	2.68	
	$O_{c-1} - O_{c-8}$	16	2.67	
	$O_{c-1} - As_3 - O_{c-13}$	8	110° 0′	
	$O_{c-1} - As_3 - O_{c-8}$	16	109° 12′	
			109° 36′ (average)	
III.	UO_2-AsO_4 environment			
	$U_3 - O_{c-8}$	16	2.33 Å	
IV.	H_2O environment			
	$O_{d-7} - O_{d-13}$	16	2.80 Å	0.08 Å
	$O_{d-13} - O_{d-16}$	16	2.76	0.09
	$O_{c-1} - O_{d-7}$	16	2.81	

* Atomic positions are the same as those assigned in Table 18.

The Crystal Chemistry of Abernathyite and the Related Compounds $NH_4(UO_2AsO_4)\cdot 3H_2O$ and $KH(UO_2AsO_4)_2\cdot 7H_2O$

It now seems clear that the cations H_3O^+, NH_4^+, and K^+ are substituting at random for water molecules in various proportions in these compounds. Although a substitution of this type has not been reported before it does not seem surprising for H_2O, H_3O^+, NH_4^+, and K^+ have very similar radii; all approximately 1.4 Å. Also, it appears that these chemical species show similar properties in aqueous solution, especially in regard to their coordination. The appearance of these groups in tetrahedral coordination tends to preserve the watery environment which is rather open.

González García (1959) in a very extensive study of a large number of synthetic uranyl phosphates and arsenates has found that an isomorphous series exists between the compounds $H(UO_2PO_4)\cdot yH_2O$ and $K(UO_2PO_4)\cdot yH_2O$ and he suggests the formula $K_xH_{1-x}(UO_2PO_4)\cdot yH_2O$ to represent this series. He states that the amount of potassium and hydrogen ion in these compounds depends upon the experimental conditions of pH and potassium ion activity. The degree of hydration is found to be variable and higher in the potassium-deficient phases. He also shows that a solid solution exists between various phosphate and arsenate end-members, thus substantiating the mineralogical evidence for such a series (Frondel, 1958, p. 177-183).

In view of the X-ray structure determinations given in the present study, a better representation of the series proposed by González García would be:

$$K_{1-y}(H_3O)_y(UO_2PO_4)\cdot 3H_2O,$$

or $K_{1-y}(H_3O)_y(UO_2AsO_4)\cdot 3H_2O$ for the arsenate analogues. In light of his work a better formula for $KH(UO_2AsO_4)_2\cdot 7H_2O$ is $K_{0.45}(H_3O)_{.55}(UO_2AsO_4)\cdot 3H_2O$ indicating that the compound is probably not stoichiometric.

In summary, we predict that an isomorphous series exists between abernathyite $K(UO_2AsO_4)\cdot 3H_2O$ and troegerite, $H(UO_2AsO_4)\cdot 4H_2O$ with probably some substitution of phosphorus for arsenic depending on the local availability. Although the phosphate analogues of abernathyite and troegerite have not been shown to occur, the same series has been shown to exist in synthetic compounds by González García, and we can predict that representatives of this series probably occur naturally. The occurrence of any particular member of these isomorphous series of uranyl phosphates and arsenates will depend upon the pH and activity of potassium in the aqueous solutions from which they precipitate.

The occurrence of the new mineral uramphite, $NH_4(UO_2PO_4)\cdot 3H_2O$ (Nekrasova, 1957) indicates that a possible solid-solution series similar to those containing potassium may exist involving the ammonium ion. For this series we may propose the formula

$$(NH_4)_{1-y}(H_3O)_y(UO_2XO_4)\cdot 3H_2O$$

where $X = P$ and/or As.

There are several compounds and minerals reported that bear an interesting relationship to abernathyite and the related compounds. Shishkin (1951) has found that the compounds $NH_4Al(SO_4)_2$ and $H_3OAl(SO_4)_2$ form solid-solutions as do also the compounds $NH_4Fe(SO_4)_2$ and $H_3OFe(SO_4)_2$, indicating that the isomorphous replacement of H_3O^+ for NH_4^+ occurs. Shishkin, in the same paper, also reports the synthesis of oxonium and ammonium jarosite with the formulas $H_3OFe_3(SO_4)_2(OH)_6$ and $NH_4Fe_3(SO_4)_2(OH)_6$. Krogius (1959) has confirmed Shishkin's work on $NH_4Al(SO_4)_2$ and $H_3OAl(SO_4)_2$ and also has shown that the oxonium and ammonium alunites, $H_3OAl_3(SO_4)_2(OH)_6$ and $NH_4Al_3(SO_4)_2(OH)_6$, form solid-solutions with one another. Kubisz and Michalek (1959) found alkali deficient jarosites in the menilite beds of the Carpathian Mountains and predict that H_3O^+ replaces some of the alkali.

The discovery of the interchangeability of oxonium and ammonium ions in the jarosites and alunites has been foreshadowed by the work of Hendricks (1937) who showed that a number of alunites and jarosites are isostructural and are simple replacement compounds in which a number of cations may replace the 12-coordinated potassium atom. Hendricks recognized the existence of the compound $H_3OFe_3(SO_4)_2(OH)_6$ but assumed that the structural formula was $H_2OFe_3(SO_4)_2(OH)_5H_2O$ with an H_2O molecule substituting for both K^+ and one OH^- group of jarosite, $KFe_3(SO_4)_2(OH)_6$.

In light of the present work it seems quite reasonable to assume that K^+, H_3O^+, and NH_4^+ substitute for one another in the jarosites and alunites although the presence of both OH^- and H_3O^+ groups in a crystal may be somewhat surprising. In this connection the compound $H_3OBF_3(OH)$ has been reported (Wamser, 1951).

THE CRYSTAL STRUCTURE OF META-TORBERNITE

The Crystallography of Meta-torbernite

A sample of meta-torbernite from Schneeberg, Germany (U.S.N.M. 84318) was obtained for single crystal studies. The sample showed two types of crystals, both bright green and tabular in habit. One type, however, is quite clear and transparent while the other is cloudy and somewhat opaque. Only the clear crystals were used for X-ray, optical, and spectrographic work.

Spectrographic analysis (K. V. Hazel, analyst) showed

> 10%	U
1-5%	P, Cu
0.1-0.5%	Mn .

X-ray powder patterns (D. R. Ross, analyst) confirmed that the material is meta-torbernite.

X-ray single crystal studies were made with the Buerger precession camera using molybdenum radiation. The space group was determined from the inspection of the hk0, hkl, hk3, hk5, 0kℓ , and 1kℓ photographs. The condition limiting the possible reflections is:

$$hk0 : h + k = 2n .$$

The hkl, hk3, and hk5 photographs show distinct 4/m Laue symmetry. Thus the space group is $P4/n$ (No. 85). The 4/m Laue symmetry is not apparent in the hk0, 0kℓ , and 1kℓ photographs and if only these were used for the space group determination it would appear that meta-torbernite possesses 4/mmm Laue symmetry and belongs in space group $P4/nmm$ (No. 130). As will be shown later, the strong pseudo-symmetry

is due to the fact that the uranium, phosphorus, copper, and uranyl oxygen atoms occupy special positions compatible with the higher 4/mmm symmetry. Figure 15 shows the hkl net which clearly reveals the 4/m Laue symmetry. Table 23 gives the unit-cell and optical data found for metatorbernite in the present study and compares them to the unit-cell data found for this mineral by Donnay and Donnay (1955) and by Makarov and Tobelko (1960). Donnay and Donnay did not observe the weak 003 and 005 reflections and thus assumed that meta-torbernite possessed a screw axis parallel to c. As a result they assigned the space group $P4_{2/n}$ (No. 86). With the exception of this finding the present study is in agreement. Makarov and Tobelko did not observe the 4/m symmetry and thus assigned the space group P4/nmm to this mineral. If in the present study, we had used Weissenberg and rotation techniques as did Makarov and Tobelko instead of the precession method we would probably have also assigned the space group P4/nmm. The erroneous assignment of the space group led Makorov and Tobelko to propose a structure somewhat different from the one given in this study. More on this subject will be written later.

The optical properties of meta-torbernite are: uniaxial negative, $\omega = 1.626 \pm 0.002$. No birefringence was noted.

The Solution of the Crystal Structure of Meta-torbernite

A small crystal measuring 0.02x0.30x0.42 mm, mounted with the thin direction parallel to the precession axis, was used to collect the hk0, hk1, hk2, hk3, hk4, and hk5 intensity data. The thinness of

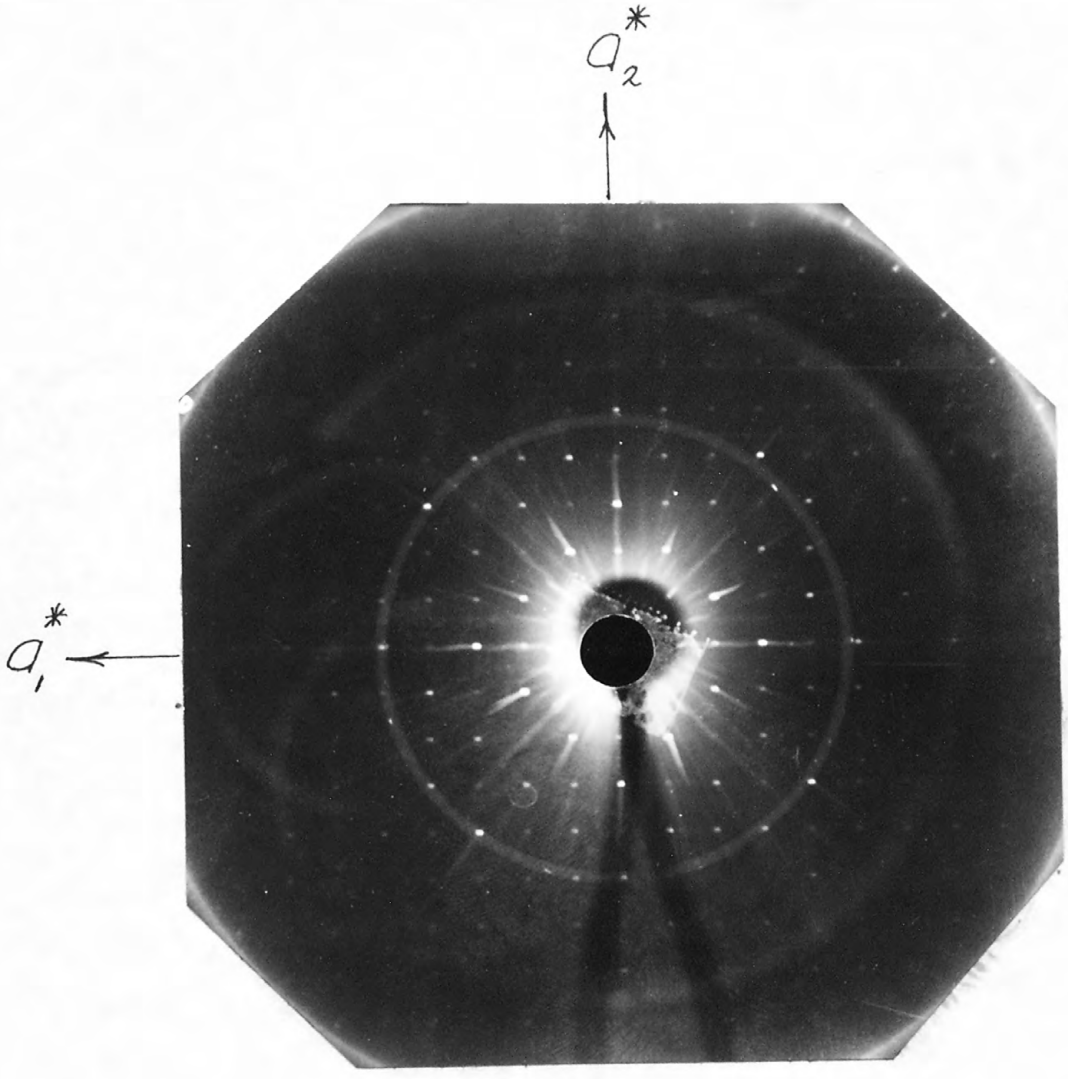


Figure 15. hk1 Buerger precession photograph of meta-torbernite showing 4/m Laue symmetry (Mo/Zr radiation).

Table 23. X-ray and Optical Properties of Meta-torbernite, $Cu(UO_2PO_4)_2 \cdot 8H_2O$

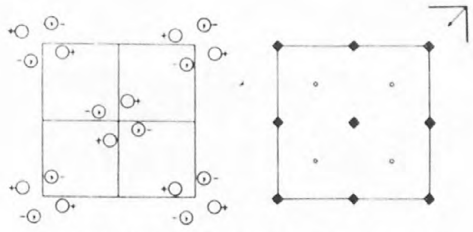
	Present Study	Donnay and Donnay, 1955	Makarov and Tobelko, 1960
a (Å)	6.963 ± 0.007	6.98	6.95
c (Å)	17.297 ± 0.018	17.41	17.26
V ($Å^3$)	838.6	848.2	833.7
Z	2	2	2
Specific Gravity(obs.)	-	3.70	3.79
Specific Gravity(calc.)	3.71	3.67	3.73
Laue Group	4/m	4/m	4/mmm
Space Group	P4/n	$P4_2/n$	P4/nmm
ϵ	-	-	-
ω	1.626	-	-
Forms	{100}, {001}	-	-
Locality	Schneeberg, Germany	Cornwall, England	-

the crystal in the c-direction minimizes the absorption (Donnay and Donnay, 1955). To collect the 0kℓ , 1kℓ, and 2kℓ data, a pyramidal-shaped crystal was used, measuring 0.05x0.06x0.10 mm. This crystal was mounted with the long direction parallel to the dial axis. The hk1, hk3, and hk5 photographs were made with unfiltered molybdenum radiation, the others with Zr-filtered molybdenum radiation. The intensity data were processed in the same manner as was done for abernathyite.

The assumption was made at first that the structure of the $(UO_2PO_4)_n^{n-}$ sheet of meta-torbernite is identical to the $(UO_2AsO_4)_n^{n-}$ sheet of abernathyite. The four uranium atoms were placed tentatively in position 2c, 2 at z=0.051, and 2 at z=0.551 of space group $P4/n$, No. 85b (Figure 16). The four phosphorus atoms were placed in positions 2b and 2a. The 16 water molecules and also the 16 phosphate oxygen atoms were placed in two eight-fold positions (8g) at coordinates equivalent to those given the water molecules and arsenate oxygens in abernathyite. The two copper atoms were placed in position 2c at z=0.815. This positioning permits each copper atom to be coordinated by four water molecules so as to form square planar $Cu(H_2O)_4$ groups. With the exception of copper, the tentative structure was given atomic coordinates identical to those of abernathyite.

Instead of first preparing Fourier projections as was done with the previous compounds it was decided to subject the proposed structure directly to least-squares analysis. The 0kℓ data, consisting of 126 non-zero terms, was subjected to four cycles of refinement using

Tetragonal $4/m$ $P\,4/n$ No. 85 $P4/n$ C_{4h}^{3}



Origin at $\bar{4}$ at $\frac{1}{4},\frac{1}{4},0$ from $\bar{1}$ (compare below for alternative origin)

Number of positions, Wyckoff notation, and point symmetry			Co-ordinates of equivalent positions	Conditions limiting possible reflections
				General:
8	g	1	x,y,z; $\bar{x},\bar{y},z$; $\frac{1}{2}+x,\frac{1}{2}+y,\bar{z}$; $\frac{1}{2}-x,\frac{1}{2}-y,\bar{z}$; $y,\bar{x},\bar{z}$; $\bar{y},x,\bar{z}$; $\frac{1}{2}-y,\frac{1}{2}+x,z$; $\frac{1}{2}+y,\frac{1}{2}-x,z$.	hkl: No conditions $hk0$: $h+k=2n$ $00l$: No conditions
				Special: as above, plus
4	f	2	$0,0,z$; $0,0,\bar{z}$; $\frac{1}{2},\frac{1}{2},z$; $\frac{1}{2},\frac{1}{2},\bar{z}$.	hkl: $h+k=2n$
4	e	$\bar{1}$	$\frac{1}{4},\frac{3}{4},\frac{1}{4}$; $\frac{3}{4},\frac{1}{4},\frac{1}{4}$; $\frac{1}{4},\frac{3}{4},\frac{3}{4}$; $\frac{3}{4},\frac{1}{4},\frac{3}{4}$.	hkl: $h,k=2n$
4	d	$\bar{1}$	$\frac{1}{4},\frac{1}{4},0$; $\frac{3}{4},\frac{3}{4},0$; $\frac{1}{4},\frac{3}{4},0$; $\frac{3}{4},\frac{1}{4},0$.	
2	c	4	$0,\frac{1}{2},z$; $\frac{1}{2},0,\bar{z}$.	no extra conditions
2	b	$\bar{4}$	$0,0,\frac{1}{2}$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$.	2 a $\bar{4}$ $0,0,0$; $\frac{1}{2},\frac{1}{2},0$. hkl: $h+k=2n$ (a and b)

Origin at $\bar{1}$ at $\frac{1}{4},\frac{1}{4},0$ from $\bar{4}$ (compare above for alternative origin)

8	g	1	x,y,z; $\frac{1}{2}-x,\frac{1}{2}-y,z$; $\frac{1}{2}-y,x,z$; $y,\frac{1}{2}-x,z$; $\bar{x},\bar{y},\bar{z}$; $\frac{1}{2}+x,\frac{1}{2}+y,\bar{z}$; $\frac{1}{2}+y,\bar{x},\bar{z}$; $\bar{y},\frac{1}{2}+x,\bar{z}$.	General and special conditions as above
4	f	2	$\frac{1}{4},\frac{3}{4},z$; $\frac{1}{4},\frac{1}{4},\bar{z}$; $\frac{3}{4},\frac{3}{4},\bar{z}$; $\frac{3}{4},\frac{1}{4},z$.	
4	e	$\bar{1}$	$0,0,\frac{1}{2}$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$; $0,\frac{1}{2},\frac{1}{2}$; $\frac{1}{2},0,\frac{1}{2}$.	
4	d	$\bar{1}$	$0,0,0$; $\frac{1}{2},\frac{1}{2},0$; $0,\frac{1}{2},0$; $\frac{1}{2},0,0$.	
2	c	4	$\frac{1}{4},\frac{1}{4},z$; $\frac{3}{4},\frac{3}{4},\bar{z}$.	
2	b	$\bar{4}$	$\frac{1}{4},\frac{3}{4},\frac{1}{4}$; $\frac{3}{4},\frac{1}{4},\frac{1}{4}$.	2 a $\bar{4}$ $\frac{1}{4},\frac{3}{4},0$; $\frac{3}{4},\frac{1}{4},0$.

175

Figure 16. Equivalent positions and conditions limiting possible reflections of space group P4/n (No. 85b), from p. 175 of International Tables.

an overall temperature factor. The reliability factor dropped from 30.0 to 8.3% during this refinement. There were some large shifts in the positions of the oxygen atoms and some small shifts in the heavy atom positions. From these new atomic positions, the following bond distances were calculated:

U – O 1.74, 1.80, 1.71, 1.75, 2.28, 2.24 Å

Cu – H_2O 2.02 Å

H_2O – H_2O 2.85, 2.58, 2.76 Å

P – O 1.55, 1.52 Å .

The above bond distances are plausible and with the low R-factor it appears that most of the atoms have been correctly positioned.

A heavy atom subtraction map, projected on (100), was then prepared by subtracting the calculated contributions of the copper, uranium, and phosphorus atoms to the structure factors from the observed structure factors. This subtraction map showed clearly all the oxygen atoms in the structure.

It appeared at this point that meta-torbernite has essentially the same structure as abernathyite with the following exceptions: (1) the center of two of the four squares of water molecules are occupied by copper; (2) no atoms substitute for H_2O; (3) the 16 water molecules and 16 phosphate oxygens lie in two eight-fold positions. This permits a different configuration of water molecules in the $Cu(H_2O)_4$ squares than is found in the $(H_2O)_4$ squares.

Next, the least-squares refinement was continued using three-dimensional data. The classes of data used are given in Table 24.

Table 24. Intensity Data Used for Final Least-Squares Analysis of Meta-torbernite

hk	F>0	F=0
hk0	35	1
hk1	57	9
hk2	79	3
hk3	35	11
hk4	59	27
hk5	29	9
0kℓ	100	63
1kℓ	158	179
2kℓ	120	193
	672	495

After four cycles of three-dimensional least-squares refinement were completed using an overall temperature factor it was found that the hkℓ data with ℓ odd would not refine below an R factor of 43%. Since only the copper and phosphate-oxygen atoms and the water molecules contribute appreciably to these structure factors it was apparent that there was a significant error in the positioning of one or more of these atoms. It was observed that the water molecule O_7 was

positioned with an x coordinate of 0.160. With this parameter hydrogen-bonding of the O_7 water molecules to other atoms is not possible. Since in tetragonal structures there is often an ambiguous solution to the x or y parameters if two-dimensional data are used, it was thought that the x parameter of O_7 should be 0.340, not 0.160. To test this new model, three-dimensional least-squares analysis was carried out using only the hk1, hk3, and hk5 data. With this new parameter the refinement of this data proceeded smoothly, the R-factor dropping from 43% to 19% in nine cycles.

Least-squares analysis was then continued with the full three-dimensional data for seven more cycles starting with the coordinates and individual temperature factors given by the 9th cycle of the previous refinement. The refinement then proceeded satisfactorily to completion. The final reliability factor is 9.7% for the complete set of three-dimensional data consisting of 1167 terms. The final R-factor for the hk1, hk3, and hk5 data is 16.0%. The higher R-factor for this data is to be expected due to the fact that the structure factors of these reflections are very small. The $F_{obs.}$(minimum) is 9.8. Table 25 gives the final atomic parameters for the meta-torbernite structure as given by the last cycle of refinement. The standard errors of the parameters were evaluated as shown in Appendix I.

Table 26 gives the bond distances and bond angles and the standard errors of these measurements. The method of calculating the standard errors of these bond distances and bond angles is given in Appendix I.

Table 25. Final Atomic Parameters and Standard Errors for Meta-torbernite, $Cu(UO_2PO_4)_2 \cdot 8H_2O$ *

Atom	Position	Parameters**	Standard Error
O_1	2c	x = 1/4	-
		y = 1/4	-
		z = 0.1564	0.0045
		B = 1.58	0.95
O_2	2c	x = 1/4	-
		y = 1/4	-
		z = 0.6563	0.0044
		B = 1.22	0.83
O_3	2c	x = 1/4	-
		y = 1/4	-
		z = 0.9488	0.0037
		B = 0.67	0.75
O_4	2c	x = 1/4	-
		y = 1/4	-
		z = 0.4403	0.0041
		B = 1.54	1.07
O_5	8g	x = 0.7834	0.0036
		y = 0.0802	0.0035
		z = 0.4466	0.0019
		B = 1.59	0.42

Table 25 - contd.

Atom	Position	Parameters**	Standard Error
O_6	8g	x = 0.7038	0.0029
		y = 0.0818	0.0026
		z = 0.9486	0.0014
		B = 0.40	0.28
$O_7(H_2O)$	8g	x = 0.3476	0.0039
		y = 0.9814	0.0039
		z = 0.3105	0.0024
		B = 2.74	0.52
$O_8(H_2O)$	8g	x = 0.2225	0.0038
		y = 0.9768	0.0039
		z = 0.8095	0.0024
		B = 2.62	0.52
P_1	2a	x = 1/4	-
		y = 3/4	-
		z = 0	-
		B = 0.136	0.196
P_2	2b	x = 1/4	-
		y = 3/4	-
		z = 1/2	-
		B = 0.133	0.195

Table 25 - contd.

Atom	Position	Parameters**	Standard Error
Cu	2c	x = 1/4	-
		y = 1/4	-
		z = 0.8099	0.0007
		B = 1.058	0.151
U_1	2c	x = 1/4	-
		y = 1/4	-
		z = 0.0510	0.0002
		B = 0.7571	0.0476
U_2	2c	x = 1/4	-
		y = 1/4	-
		z = 0.5524	0.0002
		B = 0.6269	0.0443

* Space Group $P4/n$ (No. 85b), origin at $\bar{1}$.

** Atomic coordinates in cycles, the temperature factor B in $\mathring{A}^2$.

Table 26. Bond Distances and Bond Angles in Meta-torbernite

Bond*	Equivalence	Length (angle)	Standard Error
I. Uranyl ions			
$U_{1-1} - O_{1-1}$	2	1.82 Å	0.08 Å
$U_{1-1} - O_{3-1}$	2	1.77	0.07
$O_{3-1} - U_{1-1} - O_{1-1}$	2	180°	0
$U_{2-1} - O_{2-1}$	2	1.80	0.07
$U_{2-1} - O_{4-1}$	2	1.94	0.07
$O_{4-1} - U_{2-1} - O_{2-1}$	2	180°	0
II. PO_4 ions			
$P_{1-2} - O_{6-1}$	8	1.51 Å	0.02 Å
$O_{6-1} - P_{1-2} - O_{6-3}$	4	107.6°	1.7°
$O_{6-1} - P_{1-2} - O_{6-6}$	8	110.4°	0.9°
$O_{6-1} - O_{6-6}$	8	2.47	0.04
$O_{6-1} - O_{6-3}$	4	2.43	0.04
$P_{2-2} - O_{5-1}$	8	1.52	0.03
$O_{5-1} - P_{2-2} - O_{5-3}$	4	105.1°	2.2°
$O_{5-1} - P_{2-2} - O_{5-6}$	8	111.7°	1.2°
$O_{5-1} - O_{5-6}$	8	2.51	0.06
$O_{5-1} - O_{5-3}$	4	2.41	0.04

Table 26 - contd.

Bond*	Equivalence	Length (angle)	Standard Error
III. UO_2-PO_4 environment			
$U_{1-1} - O_{6-6}$	2	2.33 Å	0.02 Å
$O_{6-6} - U_{1-1} - O_{1-1}$	2	89.8°	0.6°
$U_{2-1} - O_{5-6}$	2	2.31	0.03
$O_{5-6} - U_{2-1} - O_{2-1}$	2	89.6°	0.8°
$O_{6-6} - O_{1-1}$	8	2.96	0.05
$O_{6-6} - O_{3-1}$	8	2.93	0.05
$O_{6-1} - O_{3-1}$	8	3.37	0.02
$O_{6-3} - O_{3-1}$	8	3.98	0.02
$O_{6-6} - O_{6-4}$	4	3.30	0.03
$O_{6-6} - O_{6-5}$	4	3.54	0.04
$O_{5-6} - O_{2-1}$	8	2.92	0.05
$O_{5-6} - O_{4-1}$	8	3.03	0.05
$O_{5-1} - O_{4-1}$	8	3.90	0.03
$O_{5-3} - O_{4-1}$	8	3.46	0.03
$O_{5-6} - O_{5-4}$	4	3.27	0.03
$O_{5-3} - O_{5-4}$	4	3.71	0.05

Table 26 - contd.

Bond*	Equivalence	Length (angle)	Standard Error
IV. Cu environment			
$Cu_1 - O_{8-3}$	8	1.91 Å	0.03 Å
$O_{8-3} - Cu_1 - O_{8-1}$	4	179.6°	2.6°
$O_{8-3} - Cu_1 - O_{8-5}$	8	90.0°	0.0°
$Cu_1 - O_{3-1}$	2	2.40	0.07
$Cu_1 - O_{2-1}$	2	2.66	0.07
$Cu_2 - O_{7-5}$	2	3.84	0.03
V. H_2O environment			
$O_{7-6} - O_{7-4}$	8	2.81 Å	0.04 Å
$O_{7-6} - O_{8-3}$	8	2.67	0.05
$O_{7-6} - O_{5-4}$	8	2.77	0.05
$O_{7-4} - O_{7-6} - O_{7-2}$	8	90°	0
$O_{7-4} - O_{7-6} - O_{8-3}$	8	109.8°	1.1°
$O_{7-2} - O_{7-6} - O_{8-3}$	8	122.0°	1.1°
$O_{7-4} - O_{7-6} - O_{5-4}$	8	112.0°	1.0°
$O_{7-2} - O_{7-6} - O_{5-4}$	8	112.0°	1.0°
$O_{8-3} - O_{7-6} - O_{5-4}$	8	109.5°	1.3°
$O_{8-3} - O_{8-5}$	8	2.70	0.04
$O_{8-3} - O_{6-5}$	8	2.89	0.05
$O_{8-5} - O_{8-3} - O_{8-7}$	8	90°	0

Table 26 - contd.

Bond*	Equivalence	Length (angle)	Standard Error
V. H_2O environment			
$O_{8-5} - O_{8-3} - O_{7-6}$	8	85.7°	1.1°
$O_{8-7} - O_{8-3} - O_{7-6}$	8	128.7°	0.9°
$O_{8-5} - O_{8-3} - O_{6-5}$	8	97.1°	1.0°
$O_{8-7} - O_{8-3} - O_{6-5}$	8	122.6°	0.8°
$O_{7-6} - O_{8-3} - O_{6-5}$	8	108.7°	1.2°
$O_{7-3} - O_{1-1}$	8	3.33	0.07
$O_{7-3} - O_{4-1}$	8	3.00	0.06
$O_{7-3} - O_{2-2}$	8	4.50	0.03
$O_{7-6} - O_{5-2}$	8	3.52	0.04
$O_{8-3} - O_{3-1}$	8	3.08	0.06
$O_{8-3} - O_{2-1}$	8	3.27	0.07
$O_{8-3} - O_{1-2}$	8	3.70	0.03
$O_{8-3} - O_{6-7}$	8	3.56	0.04

* Atomic positions are given in Table 27.

Table 27. Atomic Positions* for Atoms Listed in Table 26

Atom	Position	Atom	Position
U_{1-1}	x, y, z	O_{5-6}	1/2 + y, 1 − x, 1 − z
U_{2-1}	x, y, z	O_{6-1}	x, y, z
P_{1-2}	1/2 + x, y − 1/2, z	O_{6-3}	3/2 − x, 1/2 − y, z
P_{2-2}	1/2 + x, y − 1/2, z	O_{6-4}	x − 1/2, 1/2 + y, 1 − z
Cu_1	x, y, z	O_{6-5}	1/2 − y, x, z − 1
Cu_2	x, 1/2 + y, 1 − z	O_{6-6}	1/2 + y, 1 − x, 1 − z
O_{1-1}	x, y, z	O_{6-7}	y, 3/2 − x, z
O_{2-1}	x, y, z	O_{7-2}	1 − x, 2 − y, 1 − z
O_{3-1}	x, y, z − 1	O_{7-3}	1/2 − x, 3/2 − y, z
O_{4-1}	x, y, z	O_{7-4}	1/2 + x, y − 1/2, 1 − z
O_{1-2}	1/2+x, 1/2+y, 1 − z	O_{7-5}	3/2 − y, x, z
O_{2-2}	1/2+x, 1/2+y, 1 − z	O_{7-6}	y − 1/2, 1 − x, 1 − z
O_{5-1}	x, y, z	O_{8-1}	x, y − 1, z
O_{5-2}	1 − x, 1 − y, 1 − z	O_{8-3}	1/2 − x, 3/2 − y, z
O_{5-3}	3/2 − x, 1/2 − y, z	O_{8-5}	3/2 − y, x, z
O_{5-4}	x − 1/2, 1/2 + y, 1 − z	O_{8-7}	y − 1, 1/2 − x, z

* The equivalent positions are taken from International Tables, p. 175, Space Group P4/n (No. 85b).

The final observed and calculated structure factors are given in Appendix V.

As stated previously many tetragonal structures give ambiguous solutions to the x or y parameters of certain equivalent positions. This problem was encountered in abernathyite. In the abernathyite structure Fourier projections on either (100) or (001) cannot distinguish between the positions x and (3/2)-x for O_c and the positions x and (1/2)-x for O_d. A shift of either O_c to (3/2)-x or O_d to (1/2)-x would break all the hydrogen bonds between the water molecules and the arsenate oxygens. Such a situation is chemically untenable but nevertheless the four possible models (H-bonded, H-bonded enantiomorph, unbonded, unbonded enantiomorph) were tested with the hkl structure factors. Only the H-bonded model gave good agreement with the observed structure factors.

The meta-torbernite structure offers a similar problem. Here, however, we have 16 possible models due to the fact that there are twice as many sets of equivalent positions to be treated. The low R-factor of 16.0% for the hkl, hk3, and hk5 data seemed to indicate that the final model, with hydrogen bonds between O_8 and O_7, O_8 and O_6, O_7 and O_7, and O_7 and O_5, is the correct one. Although least-squares analysis is to be expected to give the correct model it was thought that an independent test of all the possible models should be made. These models were tested by taking the parameters given by the 11th cycle of three-dimensional refinement and calculating the R-factor of the hkl, hk3, and hk5 structure factors. The various

models were formed by taking the various combinations of

O_5 at x = 0.7834 or 0.7166 (aA)

O_6 at x = 0.7047 or 0.7953 (bB)

O_7 at x = 0.3474 or 0.1526 (cC)

O_8 at x = 0.2229 or 0.2771 cycles (dD) .

Table 28 gives the various models, the R-factor obtained, and the H-bonds broken by the particular model. As can be seen the model (abcd) gives the lowest reliability factor. A shift of x of O_8 0.055 cycles raises the R-factor to 23% - quite a significant increase for such a small displacement of one atom. The other models give even higher R-factors. This test clearly shows that the model which permits hydrogen bonds between O_8 and O_7, O_8 and O_6, and O_7 and O_5 is the correct one.

Description of the Meta-torbernite Structure

As stated previously, the meta-torbernite structure is quite similar to that of abernathyite. The most interesting feature of this structure is the copper coordination and the associated hydrogen-bonding. The two copper atoms in the unit-cell lie at the center of squares of four water molecules, one at 1/4, 1/4, 0.810, and one at 3/4, 3/4, 0.190. The distance between the copper atom and each water molecule of the square is 1.91 Å. This unusually short distance indicates a rather strong covalent copper-oxygen bond. The water molecules here must be highly polarized with a rather large positive charge directed away from the copper atom. Short

Table 28. Test of the possible models for Meta-torbernite using hk1, hk3, and hk5 Data

Model	R-factor	H-bonds Broken
abcd	16.4%	none
aBcd	34.0	$O_8 - O_6$
Abcd	29.9	$O_7 - O_5$
ABcd	37.2	$O_8 - O_6$, $O_7 - O_5$
abcD	23.1	$O_8 - O_7$, $O_8 - O_6$
abCd	29.3	$O_7 - O_8$, $O_7 - O_5$
abCD	37.4	$O_8 - O_6$, $O_7 - O_5$
aBcD	37.0	$O_8 - O_7$
aBCd	36.2	$O_8 - O_7$, $O_7 - O_5$, $O_8 - O_6$
aBCD	44.5	$O_7 - O_5$
AbcD	33.8	$O_8 - O_7$, $O_8 - O_6$, $O_7 - O_5$
AbCd	35.2	$O_8 - O_7$
AbCD	43.3	$O_8 - O_6$
ABcD	44.5	$O_8 - O_7$, $O_7 - O_5$
ABCd	42.3	$O_8 - O_7$, $O_8 - O_6$
ABCD	50.9	none

copper-water bonds have been discovered in the compounds $CuF_2 \cdot 2H_2O$ (Geller and Bond, 1958), $CuCl_2 \cdot 2H_2O$ (Peterson and Levy, 1957) and $CuSeO_3 \cdot 2H_2O$ (Gattow, 1958). In the very precisely determined $CuF_2 \cdot 2H_2O$ and $CuCl_2 \cdot 2H_2O$ structures copper-water bonds were found to be 1.93 and 1.925 Å respectively. A Cu-H_2O bond of 1.94 Å was found in $CuSeO_3 \cdot 2H_2O$.

The copper atom in meta-torbernite is also bonded to two uranyl oxygens O_2 and O_3 at 2.66 and 2.40 Å respectively. The next nearest atom to Cu is O_7 at 3.84 Å. The copper atom is within 0.007 Å of being exactly in the plane of the four O_8 water molecules. The O_8-Cu-O_8 angles are 179.6° and 90.0°.

The planar coordination of copper with four bonds of 1.9 to 2.0 Å and two additional bonds of greater length to form a distorted tetragonal dipyramid has been found in a number of crystal structures; $CuCl_2 \cdot 2H_2O$, $CuF_2 \cdot 2H_2O$ and $CuSeO_3 \cdot 2H_2O$ are examples.

Eight additional water molecules form squares at 1/4, 1/4, 0.311 and 3/4, 3/4, 0.689. The H_2O molecules of these squares do not coordinate a cation. They are, however, hydrogen-bonded together as in abernathyite. The O_7 - O_7 bond distance within these squares is 2.81 Å. The O_7 water molecules are also hydrogen-bonded to the phosphate oxygen O_5 (2.77 Å) and to an adjacent O_8 water molecule (2.67 Å). The O_8 water molecules of the $Cu(H_2O)_4$ squares are each bonded to O_7 and to the O_6 phosphate oxygen (2.89 Å). Within the $Cu(H_2O)_4$ square the O_8 - O_8 distance is 2.70 Å. This short distance is not caused by hydrogen bonding. It is the result of the close attraction of the H_2O molecules to the copper atom. The

hydrogen bonds between O_7 and O_7, O_7 and O_8, O_7 and O_5 and O_8 and O_6 account for all of the 32 protons found in the unit-cell. The next nearest atom to the O_7 water molecule is O_4 at 3.00 Å. The next nearest atom to the O_8 water molecule is O_3 at 3.08 Å. About the O_7 water molecules lie two O_7 water molecules, one O_8 water molecule and one O_5 oxygen in a distorted tetrahedral arrangement. The tetrahedral angles are: 90°, 109.8°, 122.0°, 112.0°, 112.0°, and 109.5°. The average angle is 109.2°. About the O_8 water molecules lie two O_8 water molecules, an O_7 water molecule, an O_6 oxygen, and a copper atom. The water molecules and oxygen atoms are grouped about O_8 in a highly distorted tetrahedron. This distortion is due to the fact that O_8 is bonded only to the copper atom, the O_7 water molecule, and the O_6 oxygen. The O_6-O_8-O_7, Cu-O_8-O_7, and the Cu-O_8-O_6 angles are 108.7°, 113.0°, and 117.7° respectively.

The distribution of the positive charge on the copper atoms to the negatively charged $(UO_2PO_4)_n^{n-}$ sheets is accomplished through the copper-uranyl oxygen bonds (Cu-O_2, Cu-O_3) and through the various hydrogen bonds. The $(UO_2PO_4)_n^{n-}$ sheets at z=o and z=1/2 contain the uranyl oxygens O_3 and O_2 respectively. Since the Cu-O_3 bond is shorter (2.40 Å) than the Cu-O_2 bond (2.66 Å) it is to be expected that a greater charge will be distributed through the uranyl oxygens to the sheet which lies at z=o. The sheet at z=1/2 should then receive a greater positive charge through the hydrogen bonds than does the sheet at z=o. This appears to be so. The remaining positive charge on the copper is distributed through the H_2O molecules to the phosphate oxygens

O_6 and O_5 lying in the sheets at z=o, and z=1/2 respectively. The long O_8 - O_6 hydrogen bond of 2.89 Å indicates that a smaller amount of this charge goes to the sheet at z=o.

Figure 17 shows the structural scheme of meta-torbernite projected on (100). The $(UO_2PO_4)_n^{n-}$ sheets of meta-torbernite are positioned relative to one another in the same manner as those of meta-autunite (I).

The phosphate tetrahedra are rotated about the 4-fold rotary-inverson axis as are the AsO_4^{3-} tetrahedra in abernathyite. Consequently their horizontal edges do not lie parallel to the a-axes. The two types of tetrahedra in meta-torbernite are rotated through slightly different angles because of the requirements of hydrogen-bonding to the two different types of water molecules, O_7 and O_8. The P_1 - O_6 and the P_2 - O_5 bond lengths of 1.51 and 1.52 Å respectively compare favorably with other determinations of this interatomic distance.

The PO_4 tetrahedra are distorted with the horizontal edges somewhat shortened (2.41, 2.43 Å) and the other edges somewhat lengthened (2.51, 2.47 Å). The average O_5-P_2-O_5 angle is 108.4°. The average O_6-P_1-O_6 angle is 109.0°.

The phosphate oxygen-uranium interatomic distances are 2.33 and 2.31 Å. The value of the arsenate oxygen-uranium bond in abernathyite is 2.35 Å. The uranium-uranyl oxygen bond lengths have large standard errors associated with them (0.07-0.08 Å); thus the

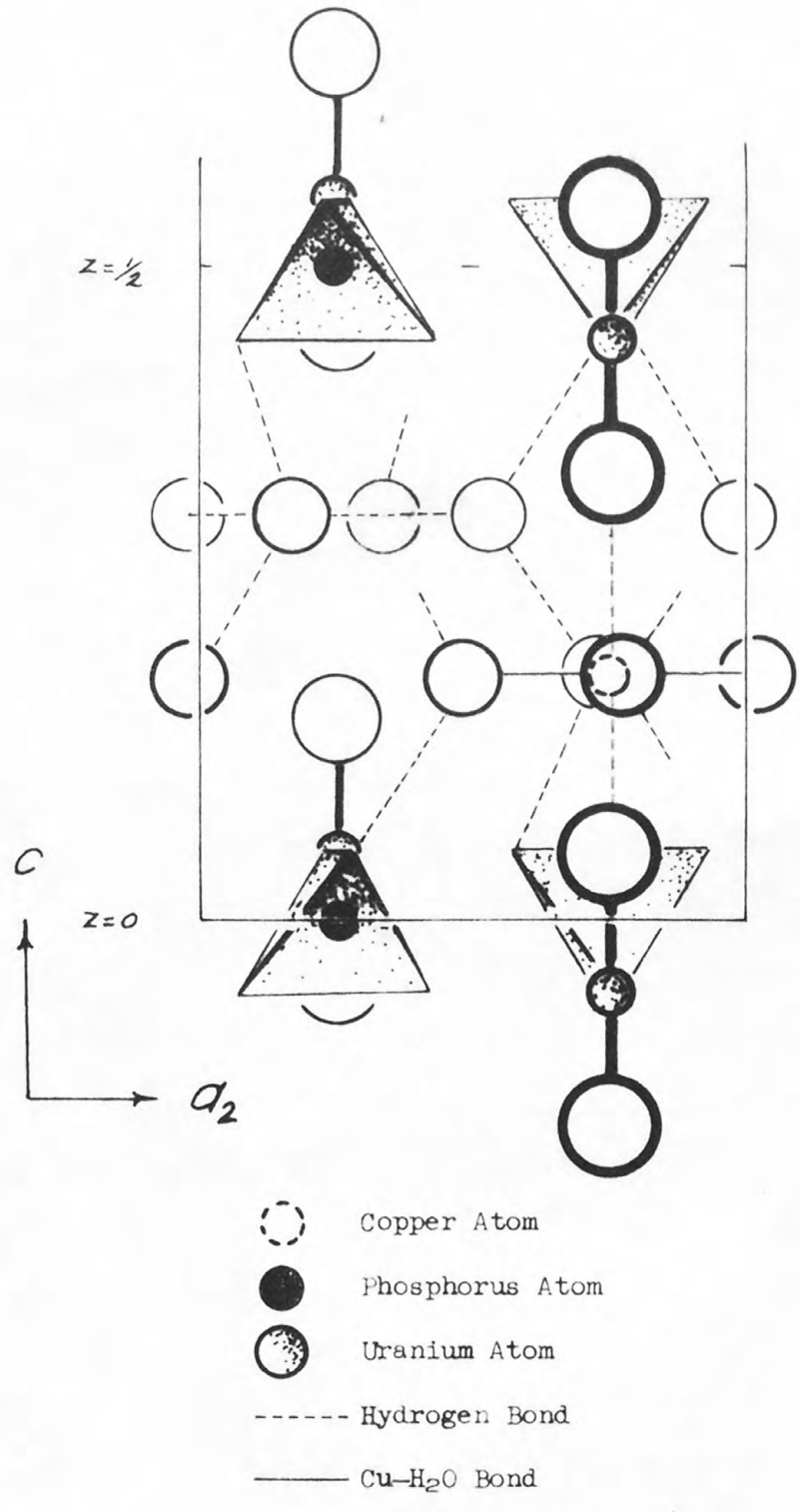


Figure 17. Projection of the meta-torbernite structure on (100). $Cu–O_2$, $Cu–O_3$ bonds in red.

values can only be considered approximate. The average uranium-uranyl oxygen interatomic distance is 1.83 Å. The value of 1.94 Å obtained for U_2-O_4 is anomalously large. The asymmetrical environment of the UO_2^{2+} ions is retained in meta-torbernite. O_1 is adjacent to four O_6 atoms at 2.96 Å and eight water molecules (four at 3.33 Å, and four at 3.70 Å). O_2 is associated with four phosphate oxygens at 2.92 Å, and eight H_2O molecules (four at 3.27 and four at 4.50 Å). O_3 is associated with the copper atom at 2.40 Å, with four water molecules at 3.08 Å, and with twelve phosphate oxygen atoms (four at 2.93 Å, four at 3.37 Å, and four at 3.98 Å). The O_4 atoms are adjacent to the copper atom (2.66 Å), to four water molecules (3.00 Å), and to twelve phosphate oxygens (four at 3.03 Å, four at 3.46 Å and four at 3.90 Å).

The U_1 and U_2 atoms deviate from the plane of the four phosphate oxygen atoms by 0.007 Å and 0.02 Å respectively. This value is smaller than the standard error and is thus probably not significant.

The structure proposed for meta-torbernite by Makarov and Tobelko (1959) is correct in that they confirm the sheet structure proposed by Beintema and find that copper is coordinated in a square-planar arrangement by four water molecules. Their placement of the heavy atoms is essentially the same as that found in the present study. The position of the light atoms is not correct and is due partly to the fact that the wrong space group was chosen and partly to the poor quality of their data. They propose hydrogen-bonds between the water molecules

and the uranyl oxygens which is not correct.

Meta-zeunerite

Meta-zeunerite, $Cu(UO_2AsO_4)_2 \cdot 8H_2O$ is probably isostructural with meta-torbernite. Hanic (1960), however, has proposed a structure for meta-zeunerite which differs from that of meta-torbernite. He gives the following unit-cell data for meta-zeunerite:

$$a = 7.10_5$$

$$c = 17.70_4$$

Space Group - $P4_2/nmc$ (No. 137).

This choice of space group forces Hanic to distribute two copper atoms over four positions (4d), and two sets of eight water molecules over two 16-fold positions (16h). He confirms Beintema's proposed structure for the $(UO_2XO_4)_n^{n-}$ layer and also finds the copper atoms coordinated by four water molecules in a square-planar arrangement. Hanic also states that hydrogen-bonds are formed between the water molecules and the uranyl oxygens. He gives values of 1.94 and 1.78 Å for the uranium-uranyl oxygen bonds; 2.55 and 2.50 Å for the copper-uranyl oxygen bonds; 2.18 Å for the uranium-arsenate oxygen distance; 2.14 Å for the copper-water bond; and 1.77 Å for the arsenic-arsenate oxygen bond.

A large number of specimens of so-called meta-zeunerite were examined for the present study. Only one specimen contained significant amounts of arsenic but it gave such poor X-ray patterns that no useful crystallographic information could be obtained.

SUMMARY

A large number of minerals and synthetic compounds belonging to the torbernite mineral group can be represented by the formula $A^{z+}(UO_2XO_4)_z \cdot nH_2O$, 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), $K(UO_2AsO_4)\cdot 3H_2O$ (abernathyite); (II), $NH_4(UO_2AsO_4)\cdot 3H_2O$; (III), $KH(UO_2AsO_4)_2\cdot 7H_2O$; and (IV), $Cu(UO_2PO_4)_2\cdot 8H_2O$ (meta-torbernite) have been carried out. The structures were refined by two and three-dimensional least-squares analysis of intensity data measured on Buerger precession photographs made with MoKα radiation. The well-known waffle-like $(UO_2XO_4)_n^{n-}$ sheet structure proposed by Beintema (1938) is confirmed, and details of the interlayer structure are also revealed through a complete resolution of all except the hydrogen atoms in the electron density maps. In all four structures studied, the positions of the interlayer water molecules are based on an ideal arrangement in which four molecules are hydrogen-bonded together to form squares about the four-fold rotation axes, lying between the uranyl ions of successive layers. In Phases I and II, K^+ and NH_4^+ substitute randomly for one out of four water molecules and in Phase III, K^+ and H_3O^+ substitute randomly for two out of eight water molecules. An isomorphous series probably exists between the end-members $K(UO_2AsO_4)\cdot 3H_2O$ (abernathyite) and $H_3O(UO_2AsO_4)\cdot 3H_2O$ (troegerite) and also between $NH_4(UO_2AsO_4)\cdot 3H_2O$ and troegerite. The ratio of cation (including oxonium) to water of 1:3 required by the cation replacement of water found in these structures has been confirmed by careful chemical analysis.

In meta-torbernite (IV) cation substitution of water does not occur but rather Cu^{2+} occupies special positions at the center of half of the square groups of water molecules, thus giving a cation-water ratio of 1:8.

In all four structures each water molecule of a square group is also hydrogen-bonded in a nearly tetrahedral manner to a water molecule in an adjacent square, and to an arsenate or phosphate oxygen atom. The latter bond causes a slight distortion of the $(UO_2XO_4)_n^{n-}$ sheet from ideal symmetry and accounts for the doubling of the ideal one-layer c axis.

At some future time it would be useful to examine the sodium uranyl arsenate (sodium-uranospinite) and the sodium uranyl phosphate (sodium-autunite). It is of interest to see if sodium substitutes randomly for H_3O^+ as do K^+ and NH_4^+. This is particularly important for it may relate to the unusual expanding properties of the sodium montmorillonite clay minerals. It would also be useful to examine compounds such as meta-autunite and uranocircite which contain the larger divalent cations Ca^{2+} and Ba^{2+}. Both compounds are much more complex than has been suspected and it appears that the hydration sphere about these cations is not a simple one. Finally, it will be of interest to examine the fully hydrated compounds such as torbernite, $Cu(UO_2PO_4)_2 \cdot 12H_2O$. The arrangement of the copper atoms and water molecules in the very large cavities of this compound may be similar to the arrangement of the material in the cavities of the zeolites.

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Appendix I

The standard errors E_p in the atomic parameters p which are refined by least-squares methods, are given by

$$E_p = \sqrt{d_{ii}\left[\sum (w^{1/2}\Delta F)^2 - \sum \Delta p_i v_i\right]/(n-p)}$$

where d_{ii} are the diagonal elements of the inverse matrix of the normal equations, w is the least-squares weight of an observation, $\Delta F = F_{obs.} - F_{calc.}$, Δp_i are the parameter changes, v_i are the elements of the vector v of the normal equations, n is the total number of observations for which $(F_{obs.}) > 0$; and p is the number of parameters refined (Clark, Christ, and Appleman, 1962).

The standard errors E_r of the interatomic distances in meta-torbernite were calculated with a computer program written by D. S. Handwerker and is based on relationships given in the following.

The standard error of the bond distance R is given by

(1) $$E_r = (E_1^2 + E_2^2)^{1/2}$$

where

(2) $$E_1^2 = \sum_{j=i}^{n}\sum_{i=1}^{n}(2-\delta_{ij})\left(\frac{\partial f}{\partial p_i}\right)\left(\frac{\partial f}{\partial p_j}\right)V_{ij},$$

(3) $$E_2^2 = \sum_{j=i}^{6}\sum_{i=1}^{6}(2-\delta_{ij})\left(\frac{\partial f}{\partial a_i}\right)\left(\frac{\partial f}{\partial a_j}\right)U_{ij},$$

and where

δ_{ij} = Kronecker delta = 0 for $i \neq j$, = 1 for $i = j$,

p_i = atomic parameters x, y, z associated with atom i,

V_{ij} = element of the variance-covariance matrix that describes the errors of the atomic parameters,

a_{ij} = unit-cell parameters a, b, c, and angles,

U_{ij} = element of the variance-covariance matrix that describes the errors of the unit-cell parameters (estimated in the present study).

The standard error E_r of the interatomic distances R of abernathyite, $NH_4(UO_2AsO_4)\cdot 3H_2O$ and $KH(UO_2AsO_4)_2\cdot 7H_2O$ were calculated by hand with the relation

$$(1) \quad E_R^2 = \left(\frac{\partial R}{\partial x_1}\right)^2 \epsilon_{x_1}^2 + \left(\frac{\partial R}{\partial x_2}\right)^2 \epsilon_{x_2}^2 + \left(\frac{\partial R}{\partial y_1}\right)^2 \epsilon_{y_1}^2 + \cdots + \left(\frac{\partial R}{\partial z_2}\right)^2 \epsilon_{z_2}^2$$

where ϵ_i is the standard error associated with atom i and where

$$(2) \quad \left(\frac{\partial R}{\partial p_j}\right)^2 = a_j^4 (p_i - p_j)^2 / R^4.$$

With this relation we assume that the off-diagonal terms are very small and may be neglected. Also, we assume that the errors in R due to the errors in the cell edges (E_2) are small compared with E_1 (D. E. Appleman, personal communication).

NOTES ON APPENDICES II - V

The non-observed structure factors are denoted by a blank in the F(obs.) column of these appendices. These non-observed structure factors are of two types: (1) those which are too weak to be observed, and (2) those which are not observed due to the geometry of the Buerger precession camera.

The standard error of fit of the observed and calculated structure factors has the following values for the compounds studied:

Compound	Standard Error
Abernathyite	11.7
$NH_4(UO_2AsO_4)\cdot 3H_2O$	14.6
$KH(UO_2AsO_4)_2\cdot 7H_2O$	15.7
Meta-torbernite	12.7

This standard error (E) is given by the relation

$$E = \frac{\left[\sum (\Delta F)^2\right]^{1/2}}{\left[n-p\right]^{1/2}}$$

where

$$\Delta F = \left||F(obs.)| - |F(calc.)|\right| ,$$

p is the number of parameters refined, and n equals the number of non-zero observations.

APPENDIX II

Observed and Calculated Values of the Abernathyite Structure Factors

ABERNATHYITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
00	00	02		416.4
00	00	04	194.6	201.2
00	00	06	55.8	41.1
00	00	08	268.7	267.0-
00	00	10	182.8	190.5-
00	00	12	89.3	92.7-
00	00	14		9.2
00	00	16	134.8	144.4
00	00	18	144.0	162.0
00	00	20	136.4	147.4
00	00	22	90.9	95.9
00	01	02	207.9	189.5-
00	01	04	328.8	313.3-
00	01	06	206.9	219.0-
00	01	08	125.3	132.9-
00	01	10		15.9
00	01	12	149.8	159.0
00	01	14	138.4	152.9
00	01	16	102.6	119.3
00	01	18	54.8	58.4
00	01	20		28.0-
00	01	22	51.2	66.8-
00	01	24	49.4	68.3-
00	02	00	517.9	437.2-
00	02	02	436.3	373.0-
00	02	04	183.5	171.6-
00	02	06		2.4
00	02	08	103.1	108.3
00	02	10	149.3	164.1
00	02	12	66.4	79.7
00	02	14	21.0	28.8-
00	02	16	84.6	94.8-
00	02	18	129.1	144.2-
00	02	20	112.6	135.0-
00	02	22	71.1	82.0-
00	02	24	19.3	30.9-
00	03	02	220.8	192.0
00	03	04	269.1	264.9
00	03	06	235.1	222.2
00	03	08	123.4	120.4
00	03	10	33.0	31.3-
00	03	12	119.2	141.2-
00	03	14	134.5	150.9-
00	03	16	102.6	113.3-

ABERNATHYITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
00	03	18	46.7	47.6-
00	03	20		26.6
00	03	22	62.8	65.4
00	04	00	347.4	334.8
00	04	02	251.1	248.9
00	04	04	127.4	126.4
00	04	06		14.5
00	04	08	110.7	98.9-
00	04	10	116.5	117.9-
00	04	12	61.4	61.8-
00	04	14		15.2
00	04	16	79.0	84.4
00	04	18	109.3	117.6
00	04	20	103.2	111.9
00	04	22	67.8	72.2
00	05	02	117.8	118.3-
00	05	04	118.7	119.0-
00	05	06	140.7	142.0-
00	05	08	82.1	81.0-
00	05	10		22.3
00	05	12	63.8	71.4
00	05	14	95.2	103.3
00	05	16	76.7	82.8
00	05	18	32.5	34.4
00	06	00	196.7	203.6-
00	06	02	190.2	196.7-
00	06	04	81.7	91.4-
00	06	06		15.6
00	06	08	63.9	57.3
00	06	10	89.7	100.3
00	06	12	46.0	51.2
00	06	14		22.0-
00	06	16	53.7	57.5-
00	06	18	92.1	95.2-
00	07	02	66.0	73.1
00	07	04	103.7	99.3
00	07	06	92.0	96.3
00	07	08	54.7	55.7
00	07	10		9.9-
00	07	12	53.9	57.5-
00	07	14	73.9	73.2-
00	07	16	57.1	59.6-
00	08	00	129.4	131.4
00	08	02	78.2	104.8

ABERNATHYITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
00	08	04	49.7	56.8
00	08	06		7.3
00	08	08	44.5	37.9-
00	08	10	43.3	49.7-
00	08	12	24.4	28.5-
00	09	02	46.1	49.3-
00	09	04	64.0	68.0-
00	09	06	62.0	65.9-
00	09	08	31.7	36.9-
01	01	04	51.1	40.4
01	01	06	162.7	161.8
01	01	08	258.8	264.1
01	01	10	266.5	293.6
01	01	12	190.5	203.0
01	01	14	67.3	89.7
01	01	16		3.5
01	01	18	55.0	58.7-
01	01	20	58.3	67.1-
01	01	22	30.3	30.1-
01	02	01	68.5	53.9
01	02	02	203.9	181.1
01	02	03		18.2
01	02	04	137.6	152.8
01	02	05		14.9
01	02	06	189.8	195.3
01	02	07	37.2	44.7
01	02	08	101.2	116.0
01	02	09	20.3	21.0-
01	02	10	30.2	31.0-
01	02	11		8.5-
01	02	12	77.3	96.4-
01	02	13		5.6-
01	02	14	128.2	135.2-
01	02	15		18.2-
01	02	16	88.8	108.6-
01	02	17		3.7
01	02	18	39.8	46.7-
01	02	19		2.5
01	02	20		11.9
01	02	21		1.7
01	02	22	51.4	58.6
01	02	23		6.3
01	02	24	43.9	62.5
01	03	00	273.0	231.3

ABERNATHYITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
01	03	01		7.5
01	03	02	151.2	133.3
01	03	03	70.6	59.9
01	03	04	33.1	21.1-
01	03	05	48.0	43.6-
01	03	06	152.4	153.4-
01	03	07		7.6-
01	03	08	247.9	266.9-
01	03	09		2.7-
01	03	10	248.7	274.6-
01	03	11	31.1	32.9-
01	03	12	180.6	185.6-
01	03	13		13.3
01	03	14	73.4	76.3-
01	03	15		3.6
01	03	16		13.4
01	03	17		.6
01	03	18	62.8	63.7
01	03	19		12.3
01	03	20	71.2	65.7
01	04	01		20.9-
01	04	02	127.4	112.2-
01	04	03		7.1-
01	04	04	200.1	189.5-
01	04	05		6.0-
01	04	06	145.3	146.1-
01	04	07		18.8-
01	04	08	81.9	91.1-
01	04	09		9.3
01	04	10		7.0
01	04	11		4.1
01	04	12	88.4	107.3
01	04	13		2.6
01	04	14	109.6	112.4
01	04	15		9.1
01	04	16	80.5	91.5
01	04	17		1.9-
01	04	18	49.7	47.0
01	04	19		1.3-
01	04	20		18.7-
01	04	21		.9-
01	04	22	43.6	50.4-
01	04	23		3.5-
01	04	24	42.4	53.6-

ABERNATHYITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
01	05	00	120.3	120.5-
01	05	01		20.3-
01	05	02	85.4	79.6-
01	05	03		9.7-
01	05	04		16.3
01	05	05		3.7
01	05	06	113.5	106.9
01	05	07		13.5
01	05	08	163.8	173.2
01	05	09		14.7
01	05	10	183.0	193.4
01	05	11		8.7
01	05	12	132.9	137.8
01	05	13		1.0
01	05	14	52.6	60.0
01	05	15		4.9-
01	05	16		1.1-
01	05	17		6.7-
01	05	18	35.9	44.3-
01	05	19		4.8-
01	05	20	43.4	49.0-
01	06	01		6.2
01	06	02	110.8	107.7
01	06	03		10.2
01	06	04	144.4	136.1
01	06	05		10.5
01	06	06	145.7	134.7
01	06	07		7.8
01	06	08	80.3	72.8
01	06	09		1.7-
01	06	10		21.1-
01	06	11		5.3-
01	06	12	82.9	79.0-
01	06	13		6.2-
01	06	14	100.3	98.9-
01	06	15		5.3-
01	06	16	78.3	76.1-
01	06	17		.7-
01	06	18	30.3	30.3-
01	06	19		1.7
01	06	20		14.3
01	06	21		2.6
01	06	22	48.0	44.0
01	07	00	98.9	98.5

ABERNATHYITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
01	07	01		3.1
01	07	02	76.2	58.8
01	07	03		.5
01	07	04		8.3-
01	07	05		.2
01	07	06	99.7	74.7-
01	07	07		2.2-
01	07	08	154.6	132.8-
01	07	09		2.6-
01	07	10	142.8	138.4-
01	07	11		.8-
01	07	12	93.2	99.2-
01	07	13		.6-
01	07	14	43.1	43.9-
01	07	15		.9
01	07	16		7.2
01	07	17		1.4
01	07	18	42.3	34.9
01	07	19		.6
01	07	20	47.6	36.9
01	08	01		4.3
01	08	02	61.0	56.2-
01	08	03		5.3-
01	08	04	102.6	88.7-
01	08	05		6.1-
01	08	06	86.3	77.1-
01	08	07		2.9
01	08	08	51.3	44.9-
01	08	09		3.7-
01	08	10		5.6
01	08	11		2.7
01	08	12	51.0	51.5
01	08	13		4.2
01	08	14	59.9	59.8
01	08	15		1.1-
01	08	16	49.0	48.8
01	08	17		2.1
01	08	18	32.4	23.8
01	09	00	72.9	62.2-
01	09	01		3.2-
01	09	02	43.5	44.2-
01	09	03		3.6
01	09	04		3.7
01	09	05		3.5-

ABERNATHYITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
01	09	06	72.3	53.4
01	09	07		2.0
01	09	08	101.4	86.0
01	09	09		2.9
01	09	10	99.9	94.0
01	09	11		2.3-
01	09	12	75.1	66.5
01	09	13		2.2
01	09	14	32.8	26.3
01	10	01		1.5-
01	10	02	41.4	39.5
01	10	03		1.3-
01	10	04	68.8	55.1
01	10	05		1.3-
01	10	06	67.6	53.1
02	02	06	16.5	5.9
02	02	08	61.6	61.6-
02	02	10	117.1	134.5-
02	02	12	58.9	68.1-
02	02	14	26.9	26.8
02	02	16	75.0	77.2
02	02	18	123.8	129.2
02	02	20	120.6	124.3
02	02	22	75.6	76.8
02	02	24	36.1	33.1
02	03	01		13.1-
02	03	02	150.4	152.5-
02	03	03		21.3
02	03	04	194.1	209.4-
02	03	05		22.9
02	03	06	153.5	182.7-
02	03	07		6.5-
02	03	08	92.1	104.9-
02	03	09		9.7
02	03	10		21.6
02	03	11		8.3-
02	03	12	107.1	117.0
02	03	13		11.4-
02	03	14	124.5	131.1
02	03	15		1.1
02	03	16	102.0	102.3
02	03	17		4.4-
02	03	18	45.3	45.9
02	03	19		1.8

ABERNATHYITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
02	03	20		20.5-
02	03	21		4.2
02	03	22	54.3	57.6-
02	03	23		.3
02	03	24	56.0	59.3-
02	04	00	305.7	313.0-
02	04	01	22.8	27.6
02	04	02	219.1	217.2-
02	04	03	23.4	23.1
02	04	04	113.5	116.0-
02	04	05		12.6-
02	04	06	29.9	22.9-
02	04	07		18.5-
02	04	08	81.2	97.0
02	04	09		18.8-
02	04	10	85.4	103.2
02	04	11		17.2-
02	04	12	48.8	56.0
02	04	13		1.5
02	04	14		9.9-
02	04	15		6.6
02	04	16	75.9	81.6-
02	04	17		8.0
02	04	18	103.0	109.1-
02	04	19		8.4
02	04	20	107.2	105.1-
02	04	21		1.4
02	04	22	71.8	70.3-
02	05	01		14.7-
02	05	02	92.3	92.7
02	05	03		1.3-
02	05	04	144.9	148.3
02	05	05		.3-
02	05	06	124.6	123.2
02	05	07		13.2-
02	05	08	76.3	74.9
02	05	09		7.7
02	05	10		7.5-
02	05	11		1.3
02	05	12	74.6	85.8-
02	05	13		.2-
02	05	14	84.1	95.1-
02	05	15		6.8
02	05	16	73.1	77.7-

ABERNATHYITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
02	05	17		2.3-
02	05	18	38.0	39.1-
02	05	19		.6-
02	05	20		14.7
02	05	21		.1
02	05	22	39.8	42.7
02	05	23		2.6-
02	05	24	47.0	45.9
02	06	00	225.6	224.9
02	06	01		7.3-
02	06	02	190.9	172.2
02	06	03		1.0
02	06	04	88.1	85.5
02	06	05		2.2-
02	06	06		.4-
02	06	07		4.8
02	06	08	76.3	78.2-
02	06	09		5.9
02	06	10	84.9	89.4-
02	06	11		.3
02	06	12	47.3	47.4-
02	06	13		1.9
02	06	14		12.1
02	06	15		1.8-
02	06	16	64.3	65.7
02	06	17		3.0-
02	06	18	92.7	89.9
02	06	19		.7-
02	06	20	86.1	84.1
02	06	21		1.1-
02	06	22	61.0	53.4
02	07	01		1.7-
02	07	02	79.8	69.3-
02	07	03		11.1
02	07	04	123.7	114.2-
02	07	05		12.2
02	07	06	104.9	94.5-
02	07	07		.9
02	07	08	57.7	54.6-
02	07	09		3.1
02	07	10		7.1
02	07	11		5.9-
02	07	12	64.7	66.3
02	07	13		8.1-

ABERNATHYITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
02	07	14	71.3	73.2
02	07	15		1.9-
02	07	16	60.6	58.7
02	07	17		2.6-
02	07	18		28.3
02	07	19		1.8
02	07	20		12.9-
02	07	21		3.7
02	07	22	42.1	33.4-
02	07	23		1.4
02	07	24	38.7	35.5-
02	08	00	155.1	138.0-
02	08	01		.5-
02	08	02	109.8	106.7-
02	08	03		1.7
02	08	04	60.0	55.5-
02	08	05		1.5-
02	08	06		2.8-
02	08	07		.3
02	08	08	50.9	46.7
02	08	09		.6
02	08	10	55.7	54.1
02	08	11		1.2-
02	08	12	39.8	30.0
02	08	13		.8
02	08	14		6.7-
02	08	15		.1-
02	08	16	43.3	42.6-
02	08	17		.3-
02	08	18	71.8	59.1-
02	08	19		.6
02	08	20	69.5	57.0-
02	08	21		.3-
02	08	22	45.1	37.8-
02	09	01		1.1-
02	09	02	61.8	51.0
02	09	03		1.6
02	09	04	80.2	71.9
02	09	05		1.8
02	09	06	80.1	67.9
02	09	07		.7-
02	09	08	40.2	36.8
02	09	09		1.0
02	09	10		9.1-

ABERNATHYITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
02	09	11		.8-
02	09	12	47.1	42.0-
02	09	13		1.3-
02	09	14	55.5	52.0-
02	09	15		.2
02	09	16	45.5	40.8-
02	10	00	104.2	82.9
02	10	01		2.0-
02	10	02	95.4	70.8
02	10	03		.7
02	10	04	40.2	35.1
03	03	06	127.4	137.5
03	03	08	237.3	229.7
03	03	10	225.9	241.8
03	03	12	160.8	164.1
03	03	14	61.4	64.7
03	03	16	19.4	13.1-
03	03	18	58.8	59.4-
03	03	20	62.2	60.0-
03	03	22	27.6	24.8-
03	04	01	20.9	25.4-
03	04	02	101.7	116.5
03	04	03		10.5-
03	04	04	130.3	154.5
03	04	05		9.4-
03	04	06	130.2	145.4
03	04	07		24.1-
03	04	08	84.1	83.3
03	04	09		11.7
03	04	10	24.7	17.7-
03	04	11		5.9
03	04	12	91.5	89.4-
03	04	13		4.6
03	04	14	105.7	107.5-
03	04	15		12.8
03	04	16	83.0	85.1-
03	04	17		2.4-
03	04	18	36.7	37.8-
03	04	19		2.1-
03	04	20		15.1
03	04	21		1.7-
03	04	22	52.0	47.6
03	04	23		5.2-
03	04	24	53.7	49.9

ABERNATHYITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
03	05	00	93.8	108.5
03	05	01		12.1
03	05	02	67.0	71.4
03	05	03		13.1-
03	05	04	20.5	12.9-
03	05	05		12.6
03	05	06	101.1	94.4-
03	05	07		7.1-
03	05	08	149.2	154.6-
03	05	09		10.0-
03	05	10	169.8	171.3-
03	05	11		7.1
03	05	12	125.6	122.5-
03	05	13		6.7-
03	05	14	50.4	53.3-
03	05	15		2.2
03	05	16		2.5
03	05	17		5.0
03	05	18	50.0	40.4
03	05	19		2.4-
03	05	20	47.3	44.2
03	05	21		2.6
03	05	22	24.3	19.6
03	06	01		4.7-
03	06	02	85.7	83.1-
03	06	03		.1
03	06	04	123.0	114.4-
03	06	05		.4
03	06	06	114.9	108.2-
03	06	07		4.3-
03	06	08	70.0	61.2-
03	06	09		2.8
03	06	10		12.7
03	06	11		.2
03	06	12	73.9	66.4
03	06	13		.4-
03	06	14	90.5	81.7
03	06	15		2.4
03	06	16	71.7	65.1
03	06	17		1.0-
03	06	18	33.9	28.8
03	06	19		.2-
03	06	20		11.4-
03	06	21		.2

ABERNATHYITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
03	06	22	41.7	36.7-
03	06	23		1.0-
03	06	24	41.8	38.9-
03	07	00	73.5	74.0-
03	07	01		10.9
03	07	02	52.1	49.4-
03	07	03		4.1-
03	07	04		7.9
03	07	05		5.4
03	07	06	68.8	65.8
03	07	07		7.2-
03	07	08	128.1	108.5
03	07	09		9.3-
03	07	10	130.2	119.6
03	07	11		1.3
03	07	12	93.8	86.9
03	07	13		4.1-
03	07	14	40.1	38.6
03	07	15		2.8
03	07	16		1.7-
03	07	17		5.2
03	07	18	37.9	28.9-
03	07	19		.2
03	07	20	41.8	31.8-
03	08	01		1.8
03	08	02	51.7	49.4
03	08	03		1.3
03	08	04	73.3	70.7
03	08	05		1.3
03	08	06	73.7	67.2
03	08	07		2.1
03	08	08	48.2	39.3
03	08	09		.9-
03	08	10		5.6-
03	08	11		.8-
03	08	12	41.3	40.6-
03	08	13		.9-
03	08	14	49.5	51.8-
03	08	15		1.4-
03	08	16	41.9	42.9-
03	08	17		.1
03	08	18	24.8	20.6-
03	08	19		.3
03	08	20		5.9

ABERNATHYITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
03	08	21		.4
03	08	22	28.7	23.5
03	08	23		.7
03	08	24	32.0	26.3
03	09	00	49.8	49.6
03	09	01		1.6
03	09	02	35.4	32.5
03	09	03		1.4
03	09	04		4.5-
03	09	05		.8-
03	09	06	54.6	42.9-
03	09	07		1.2-
03	09	08	84.3	72.1-
03	09	09		1.3-
03	09	10	84.5	78.2-
03	09	11		1.4-
03	09	12	59.8	57.2-
03	09	13		.2
03	09	14	25.0	25.7-
03	09	15		.6
03	09	16		2.2
03	09	17		.8
03	09	18	29.1	19.7
03	09	19		.9
03	09	20	33.6	21.5
03	10	01		1.7-
03	10	02	36.2	31.4-
03	10	03		3.0
03	10	04	55.7	46.8-
03	10	05		3.5
03	10	06	50.8	43.3-

APPENDIX III

Observed and Calculated Values of the $NH_4(UO_2AsO_4)\cdot 3H_2O$ Structure Factors

NH4(UO2ASO4).3H2O STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
00	02	00	441.0	431.3-
00	04	00	316.9	319.5
00	06	00	195.7	184.9-
00	08	00	129.0	118.8
00	00	02		423.2
00	01	02	193.0	185.0-
00	02	02	377.9	376.2-
00	03	02	201.4	189.7
00	04	02	254.2	242.9
00	05	02	117.2	110.5-
00	06	02	189.3	187.7-
00	07	02	76.9	61.6
00	08	02	110.2	92.0
00	09	02	49.3	36.5-
00	00	04	190.1	207.4
00	01	04	327.0	310.9-
00	02	04	182.7	175.0-
00	03	04	267.6	249.4
00	04	04	118.5	126.0
00	05	04	116.1	109.7-
00	06	04	84.2	92.1-
00	07	04	110.7	83.7
00	08	04	53.1	54.0
00	09	04	69.8	55.1-
00	00	06	61.6	58.9
00	01	06	182.2	218.0-
00	02	06		3.1
00	03	06	214.4	221.7
00	04	06		18.6
00	05	06	135.1	130.6-
00	06	06		10.7
00	07	06	101.6	81.2
00	08	06		14.8
00	09	06	58.9	50.4-
00	00	08	244.9	255.8-
00	01	08	99.5	130.7-
00	02	08	87.7	96.8
00	03	08	112.5	122.0
00	04	08	91.0	83.9-
00	05	08	74.9	73.1-
00	06	08	55.5	38.6
00	07	08	49.0	45.4
00	08	08	31.4	26.1-
00	09	08	27.7	27.6-

NH4(UO2ASO4).3H2O STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
00	00	10	152.9	184.3-
00	01	10		5.2
00	02	10	113.0	151.0
00	03	10	24.1	23.1-
00	04	10	99.2	99.6-
00	05	10		21.9
00	06	10	84.8	79.1
00	07	10		8.1-
00	08	10	25.8	29.3-
00	00	12	85.8	87.6-
00	01	12	127.4	144.5
00	02	12	57.5	73.1
00	03	12	91.4	119.5-
00	04	12	39.7	48.9-
00	05	12	44.9	59.1
00	06	12	34.7	40.1
00	07	12	39.3	44.0-
00	00	14		3.9-
00	01	14	124.0	140.1
00	02	14	25.9	32.1-
00	03	14	116.3	136.5-
00	04	14		18.5
00	05	14	77.0	87.3
00	06	14		26.8-
00	07	14	67.7	56.9-
00	00	16	127.1	133.3
00	01	16	103.8	106.4
00	02	16	74.5	88.7-
00	03	16	85.8	103.3-
00	04	16	71.0	78.7
00	05	16	66.5	69.5
00	06	16	48.2	50.6-
00	07	16	49.9	45.3-
00	00	18	131.6	148.2
00	01	18	45.9	54.8
00	02	18	126.2	130.4-
00	03	18	31.2	43.7-
00	04	18	110.8	103.9
00	05	18	30.6	24.7
00	06	18	86.0	80.9-
00	00	20	122.3	130.3
00	01	20		20.4-
00	02	20	116.3	120.2-
00	03	20		15.8

NH4(UO2ASO4).3H2O STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
00	04	20	101.3	95.5
00	00	22		96.2
00	01	22	44.4	50.9-
00	02	22	52.0	73.5-
00	03	22	54.8	48.5
00	04	22	62.6	65.4
00	00	24		27.3
00	01	24	53.3	51.4-
00	02	24	50.0	33.3-

APPENDIX IV

Observed and Calculated Values of the $KH(UO_2AsO_4)_2 \cdot 7H_2O$ Structure Factors

KH(UO2ASO4)2.7H2O STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
00	02	00	427.4	426.6-
00	04	00	329.2	324.6
00	06	00	206.7	196.5-
00	08	00	138.4	130.0
00	00	02		420.3
00	01	02	194.0	191.5-
00	02	02	399.6	376.9-
00	03	02	209.3	196.1
00	04	02	259.5	250.2
00	05	02	128.2	114.8-
00	06	02	199.9	187.8-
00	07	02	79.7	67.5
00	08	02	104.8	98.5
00	09	02	51.8	40.8-
00	00	04	150.7	209.4
00	01	04	296.9	312.6-
00	02	04	168.2	168.6-
00	03	04	259.6	245.3
00	04	04	120.6	124.2
00	05	04	131.5	116.9-
00	06	04	92.1	89.3-
00	07	04	105.4	95.5
00	08	04	60.9	54.9
00	09	04	74.4	61.7-
00	00	06	46.4	50.0
00	01	06	168.4	214.9-
00	02	06		8.7
00	03	06	211.7	220.8
00	04	06		9.9
00	05	06	133.2	132.5-
00	06	06		9.2
00	07	06	100.0	86.4
00	08	06		11.0
00	09	06	63.7	54.2-
00	00	08	235.0	246.4-
00	01	08	98.7	126.7-
00	02	08	89.9	97.8
00	03	08	103.7	117.4
00	04	08	98.0	85.2-
00	05	08	71.5	69.5-
00	06	08	55.7	47.5
00	07	08	51.7	46.7
00	08	08	42.1	32.4-
00	09	08	29.9	29.0-

KH(UO2ASO4)2.7H2O STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
00	00	10	144.4	178.2-
00	01	10		19.2
00	02	10	126.1	153.7
00	03	10	34.2	32.4-
00	04	10	101.5	106.7-
00	05	10		27.5
00	06	10	86.6	82.8
00	07	10		12.3-
00	08	10	44.6	36.2-
00	00	12	76.9	88.3-
00	01	12	137.7	154.3
00	02	12	53.2	69.6
00	03	12	109.5	126.3-
00	04	12	41.3	48.7-
00	05	12	60.6	72.0
00	06	12	43.6	38.3
00	07	12	60.5	55.7-
00	00	14	46.2	10.8
00	01	14	125.3	144.5
00	02	14	40.2	40.7-
00	03	14	119.3	140.1-
00	04	14		27.8
00	05	14	85.7	95.1
00	06	14		28.5-
00	07	14	69.5	64.5-
00	00	16	139.9	135.4
00	01	16	97.7	106.3
00	02	16	86.3	96.9-
00	03	16	91.0	101.0-
00	04	16	84.8	86.0
00	05	16	62.1	69.3
00	06	16	50.6	59.1-
00	07	16	53.1	48.2-
00	00	18	135.0	148.3
00	01	18	47.8	46.7
00	02	18	129.3	136.7-
00	03	18	37.5	38.3-
00	04	18	103.5	111.2
00	05	18	25.5	23.3
00	06	18	91.9	86.7-
00	00	20	118.7	133.8
00	01	20	31.8	28.6-
00	02	20	110.4	121.6-
00	03	20	31.4	22.5

KH(UO2ASO4)2•7H2O STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
00	04	20	100.4	100.2
00	00	22		86.8
00	01	22	62.3	59.4-
00	02	22	61.1	71.2-
00	03	22	58.3	55.5
00	04	22	61.3	61.8
00	00	24		22.8
00	01	24	52.8	56.7-

APPENDIX V

Observed and Calculated Values of the Meta-torbernite Structure Factors

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
00	00	01		21.7
00	00	02		298.0
00	00	03	30.7	40.6-
00	00	04	124.4	154.8
00	00	05	47.3	58.6
00	00	06	23.8	6.1-
00	00	07		10.8-
00	00	08	339.4	378.2-
00	00	09		6.7-
00	00	10	207.9	219.3-
00	00	11		16.6
00	00	12	178.4	170.4-
00	00	13		46.4-
00	00	14	44.4	32.5-
00	00	15		.4-
00	00	16	183.7	168.4
00	00	17		7.1-
00	00	18	165.0	168.5
00	00	19		12.5-
00	00	20	235.1	200.5
00	00	21		28.1
00	00	22	126.0	122.9
00	01	01	63.2	55.4
00	01	02	156.4	153.0-
00	01	03	24.1	21.7-
00	01	04	319.1	359.9-
00	01	05	19.9	13.5-
00	01	06	163.8	195.0-
00	01	07	41.6	36.5
00	01	08	139.6	161.8-
00	01	09	49.0	43.5-
00	01	10		3.6-
00	01	11		10.5
00	01	12	197.2	196.5
00	01	13		1.6-
00	01	14	150.6	148.9
00	01	15	23.0	22.0-
00	01	16	161.4	162.8
00	01	17		26.4
00	01	18	99.2	85.8
00	01	19		2.8-
00	01	20	60.0	53.4-
00	01	21		10.6
00	01	22	95.4	80.1-

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
00	01	23		17.6
00	01	24	109.5	114.7-
00	02	02	284.8	279.4-
00	02	04	126.0	109.9-
00	02	05	65.5	60.8-
00	02	06	34.0	39.8
00	02	07	25.1	14.3
00	02	08	208.0	226.4
00	02	09		7.2
00	02	10	179.8	203.4
00	02	11	34.8	25.4-
00	02	12	119.6	129.5
00	02	13	37.3	43.8
00	02	14	22.8	9.0
00	02	15		1.9-
00	02	16	132.2	123.6-
00	02	17		7.4
00	02	18	169.3	157.0-
00	02	19		18.0
00	02	20	196.8	170.9-
00	02	21		23.6-
00	02	22	120.7	103.8-
00	03	03	36.3	23.5
00	03	04	363.9	341.2
00	03	06	225.4	212.7
00	03	07	55.6	41.5-
00	03	08	156.3	155.9
00	03	09	60.3	51.4
00	03	10		3.8-
00	03	11		12.7-
00	03	12	202.2	192.4-
00	03	13		1.1
00	03	14	158.4	160.3-
00	03	15	28.6	23.1
00	03	16	166.0	165.9-
00	03	17	35.2	31.1-
00	03	18	97.4	84.3-
00	03	19		3.3
00	03	20	63.5	52.7
00	03	21		9.8-
00	03	22	100.6	84.8
00	04	06		13.3-
00	04	07	21.4	12.8-
00	04	08	209.4	199.1-

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
00	04	09		3.2-
00	04	10	141.0	149.3-
00	04	11	38.7	27.9
00	04	12	111.4	108.7-
00	04	13	33.8	39.6-
00	04	14	24.1	13.2-
00	04	15		3.6
00	04	16	123.0	118.1
00	04	17		8.3-
00	04	18	139.2	134.0
00	04	19		19.6-
00	04	20	182.2	154.1
00	04	21		20.9
00	04	22	96.2	95.4
00	05	03		11.2-
00	05	05		6.0-
00	05	06	157.9	153.0-
00	05	07	46.1	35.4
00	05	08	110.6	101.0-
00	05	09	39.5	35.6-
00	05	10		10.9
00	05	11		7.4
00	05	12	115.2	122.2
00	05	13		4.1-
00	05	14	127.3	124.0
00	05	15		24.6-
00	05	16	116.7	120.1
00	05	17	24.1	20.3
00	05	18	66.5	60.8
00	05	19		3.9-
00	05	20	32.6	34.5-
00	06	01		9.6-
00	06	05	47.8	36.4-
00	06	06	40.4	33.0
00	06	07		7.5
00	06	08	150.9	150.8
00	06	09		2.4
00	06	10	150.6	148.1
00	06	11	24.3	19.6-
00	06	12	89.6	97.9
00	06	13	24.3	30.9
00	06	14		5.1
00	06	15		.9-
00	06	16	94.7	95.0-

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
00	06	17		6.5
00	06	18	133.6	128.3-
00	07	03		2.2
00	07	05		1.5-
00	07	06	116.2	107.7
00	07	07	29.0	24.2-
00	07	08	81.9	79.0
00	07	09	24.2	22.6
00	07	10		1.6-
00	07	11		2.2-
00	07	12	112.2	105.8-
00	07	13		8.1
00	07	14	105.8	92.3-
00	07	15		20.7
00	07	16	103.1	97.7-
00	08	01		1.1-
00	08	03		17.0-
00	08	05		18.7
00	08	06		9.5-
00	08	07		.5
00	08	08	106.1	103.0-
00	08	09		5.2
00	08	10	92.4	87.2-
00	08	11		15.3
00	08	12	68.2	62.1-
00	09	01		14.1
00	09	03		.5
00	09	05		1.8
00	09	06	102.2	99.1-
00	09	07		12.9
00	09	08	63.1	63.7-
00	01	01		55.5
00	02	01	24.6	22.6-
00	03	01	66.1	63.4-
00	04	01	17.0	15.4
00	05	01	38.4	43.5
00	06	01	13.1	9.7-
00	07	01	25.2	27.3-
01	09	01		1.2-
01	01	01		18.1-
01	02	01	78.8	79.5-
01	03	01	13.9	8.4
01	04	01	45.1	47.4
01	05	01	15.0	12.0

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
01	06	01	30.4	33.1-
01	07	01		.1-
01	08	01	14.6	19.0
02	01	01	33.1	3.7
02	02	01	9.9	8.7
02	03	01	35.3	30.1
02	04	01	31.1	33.6-
02	05	01	12.1	1.8
02	06	01	15.5	21.3
02	07	01	15.3	17.1
03	01	01	23.9	24.6
03	02	01	24.9	10.9
03	03	01	14.4	14.2-
03	04	01	34.0	21.8-
03	05	01	11.6	9.7-
03	06	01	24.7	26.1
03	07	01	14.3	11.9-
03	08	01	14.6	17.8-
04	01	01	25.1	15.4
04	02	01	19.8	17.7
04	03	01	63.2	65.7-
04	04	01	16.5	17.0
04	05	01	26.6	30.8
04	06	01		3.8
04	07	01	22.2	26.3-
04	08	01	11.0	9.0-
05	01	01	30.2	31.4-
05	02	01	21.7	23.6-
05	03	01	18.6	20.2
05	04	01	20.8	19.4
05	05	01		4.9-
05	06	01	10.9	12.5-
05	07	01	20.3	23.3
06	01	01	19.3	12.3-
06	02	01	13.8	7.5-
06	03	01	19.6	19.0
06	04	01	16.7	17.0-
06	05	01		12.4-
06	06	01		2.8-
06	07	01	13.9	13.6
07	01	01	14.3	14.2
07	02	01	21.9	22.6
07	03	01		6.8
07	04	01	22.0	20.3-

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
07	05	01	13.0	10.3-
07	06	01	16.3	20.2
08	01	01	14.4	15.4
08	02	01	11.0	3.6-
08	03	01	18.3	20.7-
08	04	01	19.6	20.1
08	05	01	14.5	16.7
09	01	01	10.5	12.6-
09	02	01	13.5	17.0-
00	02	03	55.3	49.9
00	03	03		23.5
00	04	03	50.2	46.8-
00	05	03		11.2-
00	06	03		29.9
01	02	03	13.1	4.5
01	03	03	79.5	74.9-
01	04	03	11.9	4.0-
01	05	03	31.9	33.6
01	06	03		.9-
01	07	03	21.2	24.4-
02	01	03	29.1	25.6
02	02	03	19.5	13.7-
02	03	03	26.9	29.4-
02	04	03	21.4	10.9-
02	05	03		5.4
02	06	03	10.8	5.6-
02	07	03	19.8	20.6-
03	01	03	44.5	15.2
03	02	03	16.8	11.1
03	03	03		37.6
03	04	03	16.5	18.4
03	05	03	17.8	15.2-
03	06	03		3.7-
03	07	03	20.4	20.7
04	01	03	19.0	18.8-
04	02	03	42.7	41.8
04	03	03		8.6
04	04	03	36.1	38.1-
04	05	03	16.0	13.3
04	06	03	28.3	28.6
05	01	03	15.3	4.4
05	02	03		.4
05	03	03	29.1	27.8-
05	04	03	30.0	31.1-

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
06	01	03	16.7	19.7
06	02	03	11.8	12.5-
06	03	03		1.1-
06	04	03	14.6	4.9
07	01	03	17.8	11.0-
07	02	03	12.5	9.8
07	03	03	21.3	24.2
07	04	03		6.5
07	05	03	19.9	22.9-
08	01	03	14.3	13.8-
08	02	03	15.5	19.0
00	03	05	17.4	15.7
00	04	05	44.7	53.9
01	03	05	62.3	74.7
01	04	05		3.3
01	05	05	20.4	30.7-
01	06	05		5.1-
01	07	05	25.2	26.5
02	03	05	27.4	27.3-
02	04	05	16.1	13.6-
02	05	05		7.2
02	06	05	16.7	20.8
02	07	05	21.8	20.6-
03	01	05	34.5	10.7
03	02	05	18.3	13.1
03	03	05	45.4	47.3-
03	04	05	17.8	17.2
03	05	05	16.3	16.3
03	06	05		1.1-
03	07	05	24.5	27.7-
04	01	05	23.3	17.7-
04	02	05	37.8	36.0-
04	03	05		.8-
04	04	05	42.9	45.4
04	05	05	16.2	18.7
04	06	05	26.4	28.7-
05	01	05	19.6	23.9-
05	02	05		2.5-
05	03	05	38.0	38.5
05	04	05	27.9	31.6-
06	01	05	22.0	21.1
06	02	05	18.7	15.1
06	03	05		.8
06	04	05	19.5	17.4-

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
07	01	05	23.9	21.0
07	02	05		13.7
07	03	05	24.3	23.1-
07	04	05		4.6
07	05	05	21.0	19.8
02	00	00	443.1	446.0-
04	00	00	371.7	363.0
06	00	00	267.0	263.6-
08	00	00	191.5	185.5
01	01	00		308.6-
03	01	00	353.9	359.5
05	01	00	201.1	195.9-
07	01	00	184.6	166.2
09	01	00	141.3	130.0-
02	02	00	293.5	310.1
04	02	00	321.5	302.4-
06	02	00	269.1	258.6
08	02	00	189.0	185.9-
01	03	00	352.3	322.5
03	03	00	321.6	310.1-
05	03	00	204.1	203.0
07	03	00	180.9	159.0-
09	03	00	121.0	120.1
02	04	00	321.9	317.3-
04	04	00	262.9	257.7
06	04	00	222.6	220.6-
08	04	00	166.3	169.3
01	05	00	196.0	207.9-
03	05	00	200.1	194.1
05	05	00	174.1	166.8-
07	05	00	131.6	126.5
02	06	00	254.9	254.3
04	06	00	223.6	224.8-
06	06	00	180.5	183.0
01	07	00	173.2	180.1
03	07	00	140.0	147.1-
05	07	00	144.7	144.2
02	08	00	176.5	182.7-
04	08	00	150.8	167.4
01	09	00	124.5	139.8-
03	09	00	112.5	115.1
01	00	02		152.9-
01	01	02		142.0-
01	02	02	162.8	160.3

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
01	03	02	166.6	167.7
01	04	02	80.9	92.6-
01	05	02	91.2	101.6-
01	06	02	92.6	104.7
01	07	02	65.5	77.0
01	08	02	53.8	64.6-
01	09	02	72.1	79.2-
02	00	02		279.2-
02	01	02	173.5	145.0
02	02	02	277.8	235.9
02	03	02	155.9	146.6-
02	04	02	188.8	170.9-
02	05	02	87.3	96.7
02	06	02	146.9	171.9
02	07	02	66.6	81.4-
02	08	02	91.3	117.8-
02	09	02	60.4	73.3
03	00	02	182.8	162.0
03	01	02	156.8	152.9
03	02	02	138.5	131.5-
03	03	02	147.6	157.8-
03	04	02	94.0	108.7
03	05	02	92.4	105.5
03	06	02	90.7	101.9-
03	07	02	74.2	85.0-
03	08	02	54.8	65.1
03	09	02	59.8	67.5
04	00	02	198.1	187.0
04	01	02	100.2	97.8-
04	02	02	187.8	164.0-
04	03	02	106.6	107.4
04	04	02	144.0	159.7
04	05	02	82.4	84.4-
04	06	02	133.5	140.0-
04	07	02	63.9	72.4
04	08	02	92.4	105.6
04	09	02	58.1	60.4-
05	00	02	111.3	115.3-
05	01	02	102.3	122.1-
05	02	02	103.7	99.4
05	03	02	111.6	108.2
05	04	02	91.7	94.7-
05	05	02	79.6	86.5-
05	06	02	69.1	74.9

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
05	07	02	70.7	74.1
05	08	02	59.2	60.9-
05	09	02	58.7	60.5-
06	00	02	220.8	183.0-
06	01	02	116.6	117.0
06	02	02	157.8	162.3
06	03	02	91.8	91.6-
06	04	02	148.9	149.0-
06	05	02	82.6	80.3
06	06	02	112.5	116.2
06	07	02	61.2	64.4-
06	08	02	79.4	94.1-
07	00	02	75.6	74.8
07	01	02	90.0	87.7
07	02	02	72.1	72.2-
07	03	02	76.3	69.7-
07	04	02	76.7	74.7
07	05	02	76.9	74.3
07	06	02	64.1	60.2-
07	07	02	56.2	62.7-
07	08	02	48.7	54.2
08	00	02	119.7	112.3
08	01	02	72.4	75.9-
08	02	02	119.5	118.9-
08	03	02	77.2	62.0
08	04	02	118.1	113.9
08	05	02	68.8	65.2-
08	06	02	92.2	91.3-
08	07	02	45.5	52.4
09	00	02	83.5	69.6-
09	01	02	99.0	85.3-
09	02	02	82.5	73.6
09	03	02	81.0	64.3
09	04	02	65.8	62.9-
09	05	02	66.1	63.0-
01	01	01		18.1-
01	01	02		142.0-
01	01	03	42.4	37.6
01	01	04	20.4	12.6-
01	01	05	39.9	47.7-
01	01	06	88.5	95.1
01	01	07		10.0
01	01	08	266.6	268.5
01	01	09		4.5

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
01	01	10	211.9	237.9
01	01	11		22.0-
01	01	12	151.6	173.0
01	01	13		36.6
01	01	14	58.5	64.4
01	01	15		.8-
01	01	16	53.1	63.1-
01	01	17		8.6
01	01	18	95.6	94.5-
01	01	19		18.8
01	01	20	110.0	115.2-
01	01	21		19.2-
01	01	22	52.2	57.6-
01	01	23		.4-
01	01	24		24.3
01	02	04	183.3	176.6
01	02	05	20.5	6.5-
01	02	06	173.0	185.0
01	02	07	49.6	65.4-
01	02	08	113.4	117.0
01	02	09	35.2	46.8
01	02	10		19.6-
01	02	11		8.0-
01	02	12	112.6	126.2-
01	02	13		12.5
01	02	14	144.1	138.3-
01	02	15		39.4
01	02	16	129.5	130.1-
01	02	17		20.4-
01	02	18	62.9	66.0-
01	02	19		6.4
01	02	20	30.3	35.5
01	02	21		13.5-
01	02	22	67.8	73.8
01	02	23		26.9-
01	02	24	95.0	94.2
01	03	01		8.4
01	03	06	84.9	102.2-
01	03	07		10.5-
01	03	08	302.3	273.8-
01	03	09		3.4
01	03	10	247.2	244.8-
01	03	11	34.7	43.1
01	03	12	156.0	176.5-

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
01	03	13	31.0	45.7-
01	03	14	58.2	62.7-
01	03	15		4.3
01	03	16	61.4	70.5
01	03	17		11.6-
01	03	18	91.2	104.6
01	03	19		26.2-
01	03	20	133.5	121.9
01	03	21		21.8
01	03	22	62.1	61.6
01	03	23		1.0-
01	03	24		23.9-
01	04	03		4.0-
01	04	05		3.3
01	04	06	149.0	129.3-
01	04	07	34.6	41.7
01	04	08	118.5	108.6-
01	04	09	30.3	34.4-
01	04	10		3.0-
01	04	11		5.4
01	04	12	140.0	144.2
01	04	13		9.7-
01	04	14	102.9	111.9
01	04	15		29.4-
01	04	16	116.8	125.4
01	04	17		17.5
01	04	18	65.8	67.2
01	04	19		4.7-
01	04	20	33.8	42.9-
01	04	21		12.5
01	04	22	61.4	62.1-
01	04	23		22.4
01	04	24		90.9-
01	05	01		12.0
01	05	04	21.9	14.9-
01	05	06	75.2	73.9
01	05	07		6.5-
01	05	08	244.2	204.6
01	05	09		14.5-
01	05	10	187.0	180.7
01	05	11		28.7-
01	05	12	124.5	139.2
01	05	13		20.8
01	05	14	38.0	52.9

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
01	05	15		2.6
01	05	16	39.0	52.7-
01	05	17		15.3
01	05	18	86.7	76.3-
01	05	19		24.2
01	05	20	94.7	93.7-
01	05	21		8.1-
01	05	22	49.5	46.6-
01	05	23		1.6
01	05	24		21.7
01	06	01		33.0-
01	06	03		.9-
01	06	05		5.1-
01	06	06	177.0	145.3
01	06	07		29.6-
01	06	08	97.5	97.9
01	06	09		26.1
01	06	10		7.7-
01	06	11		.7-
01	06	12	119.4	125.6-
01	06	13		10.3
01	06	14	111.1	120.0-
01	06	15		23.3
01	06	16	103.0	118.6-
01	06	17		14.6-
01	06	18	51.4	59.7-
01	06	19		1.6
01	06	20		36.6
01	06	21		11.4-
01	06	22	62.2	65.8
01	06	23		18.3-
01	06	24		88.7
01	07	01		.1-
01	07	03		24.4-
01	07	04		15.4
01	07	05		26.4
01	07	06	55.3	56.9-
01	07	07		1.0-
01	07	08	187.2	178.2-
01	07	09		5.3
01	07	10	144.8	145.2-
01	07	11		19.9
01	07	12	102.9	118.2-
01	07	13		21.0-

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
01	07	14	43.3	48.5-
01	07	15		.3-
01	07	16	42.8	51.1
01	07	17		10.0-
01	07	18	69.4	64.8
01	07	19		17.3-
01	07	20	87.8	83.6
01	08	01		19.0
01	08	03		5.7
01	08	05		8.7
01	08	06	103.8	94.7-
01	08	07		20.3
01	08	08	73.2	69.6-
01	08	09		13.8-
01	08	10		.7
01	08	11		2.9-
01	08	12	85.8	96.1
01	08	13		11.4-
01	08	14	70.5	81.7
01	08	15		19.4-
01	08	16	79.7	87.2
01	08	17		5.7
01	08	18	41.1	46.1
01	09	01		1.2-
01	09	03		12.9
01	09	04		14.8-
01	09	05		16.4-
01	09	06	60.7	57.1
01	09	07		.5
01	09	08	130.6	142.9
01	09	09		2.0-
01	09	10	127.7	133.0
01	09	11		10.0-
01	09	12	94.5	102.7
01	09	13		15.8
01	09	14		37.1
01	10	01		16.5-
01	10	02		57.2
01	10	03		1.5
01	10	04		108.8
01	02-	04	218.0	212.6
01	02-	05	26.5	27.4
01	02-	06	173.0	176.7
01	02-	07	32.1	7.8

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
01	02-	08	113.4	123.8
01	02-	09	27.1	18.5
01	02-	10		9.4-
01	02-	11		6.7-
01	02-	12	112.6	140.8-
01	02-	13		5.9-
01	02-	14	144.1	137.3-
01	02-	15		4.8
01	02-	16	118.8	136.7-
01	02-	17		19.4-
01	02-	18	57.8	72.4-
01	02-	19		.9-
01	02-	20	36.1	39.1
01	02-	21		6.7-
01	02-	22	67.8	74.5
01	02-	23		11.4-
01	02-	24	95.0	99.4
01	03-	06	101.0	88.2
01	03-	07		8.8
01	03-	08	329.6	300.5
01	03-	09		15.2
01	03-	10	226.5	239.1
01	03-	11	29.3	10.0
01	03-	12	156.0	185.9
01	03-	13	31.0	28.0
01	03-	14	63.5	70.6
01	03-	15		4.5
01	03-	16	51.8	78.8-
01	03-	17		2.1
01	03-	18	76.6	101.8-
01	03-	19		2.2
01	03-	20	133.5	127.0-
01	03-	21		21.6-
01	03-	22	62.1	66.5-
01	03-	23		7.3-
01	03-	24		25.1
01	04-	03		18.9-
01	04-	04	315.3	225.2-
01	04-	05		17.6-
01	04-	06	136.3	136.3-
01	04-	07	29.2	8.1
01	04-	08	118.5	110.5-
01	04-	09	30.3	24.1-
01	04-	10		2.4-

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
01	04-	11		7.1
01	04-	12	140.0	143.8
01	04-	13		3.1
01	04-	14	102.9	116.9
01	04-	15		9.4-
01	04-	16	116.8	128.2
01	04-	17		19.3
01	04-	18	55.5	69.2
01	04-	19		.8-
01	04-	20	36.8	41.9-
01	04-	21		7.4
01	04-	22	61.4	64.9-
01	04-	23		12.2
01	04-	24		93.8-
01	05-	04	26.2	16.8
01	05-	05	28.9	23.8
01	05-	06	89.5	85.8-
01	05-	07		18.2-
01	05-	08	258.1	193.2-
01	05-	09		20.0-
01	05-	10	187.0	197.7-
01	05-	11		1.7-
01	05-	12	124.5	140.4-
01	05-	13		30.9-
01	05-	14	35.0	51.4-
01	05-	15		1.0
01	05-	16	42.6	48.0
01	05-	17		1.7
01	05-	18	86.7	88.2
01	05-	19		3.6-
01	05-	20	94.7	99.2
01	05-	21		21.8
01	05-	22	41.7	51.3
01	05-	23		4.9
01	05-	24		17.4-
01	06-	03		19.7
01	06-	05		21.0
01	06-	06	192.5	159.5
01	06-	07		1.5-
01	06-	08	115.9	99.2
01	06-	09	34.8	22.8
01	06-	10		12.7-
01	06-	11		6.9-
01	06-	12	130.2	119.2-

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
01	06-	13		8.3-
01	06-	14	111.1	130.3-
01	06-	15		1.3
01	06-	16	112.3	121.4-
01	06-	17		21.5-
01	06-	18	56.1	60.7-
01	06-	19		1.9-
01	06-	20	35.3	32.6
01	06-	21		3.7-
01	06-	22	62.2	72.9
01	06-	23		5.1-
01	06-	24		92.3
01	07-	01		14.2-
01	07-	03		11.0
01	07-	04	30.0	14.9-
01	07-	05		20.9-
01	07-	06	60.2	64.6
01	07-	07		8.9
01	07-	08	171.2	169.7
01	07-	09		8.0
01	07-	10	158.2	154.4
01	07-	11		5.7-
01	07-	12	112.2	120.4
01	07-	13		23.4
01	07-	14	43.3	45.8
01	07-	15		.3-
01	07-	16	50.9	45.2-
01	07-	17		2.3
01	07-	18	69.4	70.6-
01	07-	19		7.1
01	07-	20	87.8	84.3-
01	08-	01		15.3
01	08-	03		13.8-
01	08-	05		13.5-
01	08-	06	123.4	107.4-
01	08-	07		8.1
01	08-	08	87.1	70.3-
01	08-	09		20.1-
01	08-	10		6.4
01	08-	11		6.2
01	08-	12	93.6	88.5
01	08-	13		4.4
01	08-	14	83.9	91.7
01	08-	15		5.8-

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
01	08-	16	94.8	89.3
01	08-	17		16.6
01	08-	18	44.9	45.9
01	09-	01		12.6
01	09-	03		6.1-
01	09-	04		14.5
01	09-	05		15.2
01	09-	06	60.7	61.8-
01	09-	07		7.7-
01	09-	08	142.4	133.2-
01	09-	09		8.7-
01	09-	10	139.2	138.5-
01	09-	11		1.0
01	09-	12	103.0	100.1-
01	09-	13		19.6-
01	09-	14	33.3	35.1-
01	10-	01		10.8-
01	10-	02	67.8	56.6
01	10-	03		1.6
01	10-	04	133.8	102.6
02	02	01		8.7
02	02	02		235.8
02	02	03		13.7-
02	02	04		87.4
02	02	05	24.7	25.0
02	02	06	28.8	36.8-
02	02	07		2.7-
02	02	08	127.5	153.1-
02	02	09	18.4	2.5-
02	02	10	185.9	174.2-
02	02	11		11.9
02	02	12	111.4	98.3-
02	02	13		26.8-
02	02	14		.8-
02	02	15		3.0-
02	02	16	100.5	101.6
02	02	17		8.0-
02	02	18	139.4	144.9
02	02	19		15.0-
02	02	20	148.1	150.4
02	02	21		15.5
02	02	22	100.9	92.7
02	02	23		2.7
02	02	24		14.7

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
02	03	06	145.0	189.6-
02	03	07	18.9	15.4
02	03	08	112.7	129.3-
02	03	09	32.0	36.5-
02	03	10		9.5
02	03	11		11.7
02	03	12	155.8	154.4
02	03	13		7.3
02	03	14	166.2	147.0
02	03	15		10.5-
02	03	16	148.5	145.2
02	03	17		27.1
02	03	18	72.0	74.2
02	03	19		1.1-
02	03	20	41.5	42.4-
02	03	21		6.4
02	03	22	85.9	78.6-
02	03	23		11.2
02	03	24		105.5-
02	04	06		10.3
02	04	07		16.7
02	04	08	152.7	176.7
02	04	09		21.8
02	04	10	123.9	137.5
02	04	11		10.8
02	04	12	100.4	102.1
02	04	13		28.0
02	04	14		12.5
02	04	15		1.0
02	04	16	110.4	108.4-
02	04	17		1.8-
02	04	18	125.7	125.8-
02	04	19		.1-
02	04	20	142.4	145.9-
02	04	21		21.5-
02	04	22	94.9	91.7-
02	04	23		5.9-
02	04	24		10.0-
02	05	01		1.8
02	05	03		5.4
02	05	05		7.2
02	05	06	165.4	134.0
02	05	07		3.8
02	05	08	101.3	94.7

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
02	05	09		8.9
02	05	10		4.2-
02	05	11		1.0
02	05	12	128.5	120.3-
02	05	13		1.1
02	05	14	121.9	112.6-
02	05	15		3.9
02	05	16	115.7	114.3-
02	05	17		10.6-
02	05	18	59.6	60.6-
02	05	19		2.8-
02	05	20	30.4	34.8
02	05	21		7.4-
02	05	22	61.7	62.1
02	05	23		9.7-
02	05	24		85.3
02	06	01		21.3
02	06	03		5.6-
02	06	05		20.7
02	06	06	27.0	28.5-
02	06	07		12.2-
02	06	08	170.2	143.9-
02	06	09		14.2-
02	06	10	159.2	140.3-
02	06	11		.9-
02	06	12	105.5	92.3-
02	06	13		27.3-
02	06	14		7.0-
02	06	15		.5-
02	06	16	92.6	92.9
02	06	17		.9
02	06	18	122.3	125.6
02	06	19		2.2-
02	06	20	123.2	134.5
02	06	22	85.8	84.4
02	06	23		6.1
02	06	24		11.6
02	07	01		17.1
02	07	03		20.6-
02	07	05		20.5-
02	07	06	151.2	116.3-
02	07	07		6.8
02	07	08	90.8	80.1-
02	07	09		24.5-

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
02	07	10		4.3
02	07	11		9.5
02	07	12	120.5	103.1
02	07	13		8.3
02	07	14	93.9	99.4
02	07	15		3.7-
02	07	16	94.7	100.7
02	07	17		21.2
02	07	18	61.4	52.4
02	07	19		1.0-
02	07	20	30.6	30.1-
02	07	21		3.1
02	07	22	67.8	56.1-
02	07	23		5.9
02	07	24		77.9-
02	08	01		7.6-
02	08	03		8.8
02	08	05		15.5-
02	08	06	28.2	14.0
02	08	07		4.5
02	08	08	122.8	104.0
02	08	09		3.4
02	08	10	123.3	93.6
02	08	11		5.8-
02	08	12	87.3	66.6
02	08	13		17.4
02	08	14		4.6
02	08	15		.9
02	08	16	86.4	71.6-
02	08	17		3.7
02	08	18	109.4	90.8-
02	08	19		7.4
02	08	20	121.9	101.8-
02	08	21		11.4-
02	08	22		64.7-
02	09	01		10.9-
02	09	03		8.2
02	09	05		8.4
02	09	06	124.9	104.4
02	09	07		5.2-
02	09	08	74.0	65.6
02	09	09		15.0
02	09	10		7.6-
02	09	11		2.9-

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
02	09	12	86.5	83.1-
02	09	13		1.8-
02	09	14	100.9	90.1-
02	09	15		3.9
02	09	16	97.0	85.5-
02	09	17		13.5-
02	09	18	44.4	42.8-
02	09	19		1.2-
02	10	01		10.4
02	10	02		95.6
02	10	03		9.2-
02	10	04		43.7
02	03-	04	218.0	257.9
02	03-	06	145.0	173.4
02	03-	07		20.7-
02	03-	08	112.7	126.0
02	03-	09	24.7	17.0
02	03-	10		4.7-
02	03-	11		4.5
02	03-	12	142.8	157.8-
02	03-	13		12.8
02	03-	14	139.8	137.7-
02	03-	15		20.2
02	03-	16	136.2	141.0-
02	03-	17		11.8-
02	03-	18	66.1	73.1-
02	03-	19		1.0-
02	03-	20	49.1	44.8
02	03-	21		12.8-
02	03-	22	72.3	74.2
02	03-	23		18.3-
02	03-	24	104.4	101.6
02	04-	06		9.9
02	04-	07		8.8-
02	04-	08	152.7	166.6
02	04-	09		19.0-
02	04-	10	113.6	129.0
02	04-	11		34.4-
02	04-	12	100.4	94.1
02	04-	13		22.3
02	04-	14		8.0
02	04-	15		2.4
02	04-	16	92.8	105.1-
02	04-	17		17.5

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
02	04-	18	125.7	119.4-
02	04-	19		27.3
02	04-	20	142.4	137.5-
02	04-	21		8.1-
02	04-	22	86.9	84.7-
02	04-	23		2.5
02	04-	24		8.2-
02	05-	03		.4-
02	05-	05		2.4
02	05-	06	139.1	135.4-
02	05-	07		22.1
02	05-	08	92.9	93.4-
02	05-	09		20.5-
02	05-	10		6.7
02	05-	11		.3
02	05-	12	99.2	117.3
02	05-	13		7.6-
02	05-	14	94.0	112.6
02	05-	15		19.6-
02	05-	16	97.2	112.4
02	05-	17		12.0
02	05-	18	59.6	58.3
02	05-	19		1.2-
02	05-	20	30.4	34.0-
02	05-	21		10.7
02	05-	22	61.7	61.5-
02	05-	23		17.8
02	05-	24		83.3-
02	06-	01		7.4-
02	06-	03		12.5-
02	06-	05		15.0
02	06-	06	25.0	22.9-
02	06-	07		7.0
02	06-	08	170.2	147.2-
02	06-	09		8.9
02	06-	10	133.9	131.4-
02	06-	11		12.4
02	06-	12	81.3	89.1-
02	06-	13		15.0-
02	06-	14		7.4-
02	06-	15		5.8-
02	06-	16	77.8	95.1
02	06-	17		11.0-
02	06-	18	122.3	119.7

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
02	06-	19		13.7-
02	06-	20	146.4	130.4
02	06-	21		8.7
02	06-	22	85.8	81.5
02	06-	23		3.4
02	06-	24		9.0
02	07-	01		22.5-
02	07-	03		9.8-
02	07-	05		13.7-
02	07-	06	127.1	104.6
02	07-	07		24.7-
02	07-	08	83.2	76.6
02	07-	09		14.7
02	07-	10		1.3-
02	07-	11		4.4
02	07-	12	101.3	104.7-
02	07-	13		14.9
02	07-	14	93.9	89.6-
02	07-	15		23.8
02	07-	16	94.7	94.9-
02	07-	17		5.0-
02	07-	18	51.7	49.7-
02	07-	19		1.3
02	07-	20	35.9	32.5
02	07-	21		13.0-
02	07-	22	57.0	51.4
02	07-	23		20.2-
02	07-	24		71.6
02	08-	01		3.6-
02	08-	03		19.0
02	08-	05		22.4-
02	08-	06		14.6
02	08-	07		3.1
02	08-	08	122.8	106.6
02	08-	09		1.2-
02	08-	10	103.6	94.5
02	08-	11		14.9-
02	08-	12	67.4	67.7
02	08-	13		19.5
02	08-	14		4.4
02	08-	15		.2-
02	08-	16	66.8	72.9-
02	08-	17		6.8
02	08-	18	100.3	92.5-

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
02	08-	19		13.3
02	08-	20	111.9	102.5-
02	08-	21		10.7-
02	08-	22		64.6-
02	09-	01		16.9
02	09-	03		1.3-
02	09-	05		.2
02	09-	06	124.9	104.4-
02	09-	07		14.7
02	09-	08	62.2	65.4-
02	09-	09		15.8-
02	09-	10		8.0
02	09-	11		.2
02	09-	12	86.5	83.6
02	09-	13		4.3-
02	09-	14	92.5	89.7
02	09-	15		12.2-
02	09-	16	97.0	84.9
02	09-	17		10.6
02	09-	18	44.4	42.0
02	09-	19		.2
02	10-	01		3.9-
02	10-	02	113.7	92.6
02	10-	03		14.2-
02	10-	04	43.8	43.2
00	02	04		110.1-
00	03	04		341.8
00	01	04		360.5-
00	04	04	97.8	91.1
00	05	04	206.1	186.4-
00	06	04	75.1	77.2-
00	07	04	160.4	161.4
00	08	04	53.7	55.4
00	09	04	110.6	124.9-
01	01	04		12.6-
01	02	04		177.1
01	03	04	29.7	29.9
01	04	04	219.5	226.5-
01	05	04		14.9-
01	06	04	197.8	196.2
01	07	04		15.4
01	08	04	128.4	146.0-
01	09	04		14.9-
02	01	04		213.1

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
02	02	04	88.8	87.7
02	03	04	245.7	251.4-
02	04	04	76.5	83.3-
02	05	04	170.4	183.8
02	06	04	60.8	74.8
02	07	04	144.1	157.7-
02	08	04	46.2	55.5-
02	09	04	97.0	127.0
03	01	04	31.7	33.4
03	02	04		258.6-
03	03	04	32.5	32.9-
03	04	04	218.2	219.1
03	05	04		16.5
03	06	04	159.6	170.9-
03	07	04		13.2-
03	08	04	102.4	118.1
03	09	04		10.7
04	01	04		225.9-
04	02	04	80.4	79.3-
04	03	04	227.1	212.0
04	04	04	46.3	74.0
04	05	04	151.0	164.0-
04	06	04	51.8	65.3-
04	07	04	125.3	144.7
04	08	04	48.1	50.6
04	09	04	97.9	119.1-
05	01	04		16.6-
05	02	04	216.9	178.1
05	03	04		18.9
05	04	04	169.2	169.2-
05	05	04		14.5-
05	06	04	140.9	159.1
05	07	04		14.4
05	08	04	100.7	116.5-
05	09	04		10.9-
06	01	04	204.9	185.6
06	02	04	79.8	73.5
06	03	04	183.5	185.4-
06	04	04	64.0	66.2-
06	05	04	135.8	143.5
06	06	04	56.5	54.9
06	07	04	105.6	118.9-
06	08	04	40.8	42.5-
06	09	04	84.8	87.1

META-TORBERNITE STRUCTURE FACTORS

H	K	L	F(OBS)	F(CALC)
07	01	04		15.0
07	02	04	180.0	160.0-
07	03	04		12.7-
07	04	04	146.6	137.1
07	05	04		11.0
07	06	04	115.4	117.6-
07	07	04		10.7-
07	08	04	90.3	93.9
07	09	04		7.6
08	01	04	157.6	134.5-
08	02	04	63.0	56.0-
08	03	04	133.1	130.8
08	04	04	49.0	52.6
08	05	04	106.2	116.4-
08	06	04	37.3	44.5-
08	07	04	92.6	106.5
08	08	04	34.4	38.3
09	01	04		14.4-
09	02	04	134.4	127.8
09	03	04		11.1
09	04	04	111.2	115.1-
09	05	04		10.5-
09	06	04	86.8	91.4

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