

THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 50

JANUARY-FEBRUARY, 1965

Nos. 1 and 2

STUDIES OF THE TORBERNITE MINERALS (III): ROLE OF THE INTERLAYER OXONIUM, POTASSIUM, AND AMMONIUM IONS, AND WATER MOLECULES¹

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ABSTRACT

Structural and chemical evidence is given to show that solid-solution series probably exist in the torbernite mineral group between the following pairs of end members: $K(UO_2AsO_4) \cdot 3H_2O$ (abernathyite) and $H_3O(UO_2AsO_4) \cdot 3H_2O$ (troegerite), $K(UO_2PO_4) \cdot 3H_2O$ (meta-ankoleite) and $H_3O(UO_2PO_4) \cdot 3H_2O$, $NH_4(UO_2AsO_4) \cdot 3H_2O$ and troegerite, and $NH_4(UO_2PO_4) \cdot 3H_2O$ (uramphite) and $H_3O(UO_2PO_4) \cdot 3H_2O$. These series are expressed by the formula



where $A = K^+$ or NH_4^+ , and $X = As$ or P . Other possible solid-solution series are also given. The structures of $K(UO_2AsO_4) \cdot 3H_2O$ (abernathyite), $NH_4(UO_2AsO_4) \cdot 3H_2O$, $K(H_3O)(UO_2AsO_4)_2 \cdot 6H_2O$, and $Cu(UO_2PO_4)_2 \cdot 8H_2O$ (meta-torbernite) are related to other torbernite minerals and possible structural similarities are suggested. The role of the interlayer cations and water molecules in the torbernite minerals is related to other mineral groups including the zeolites, the feldspars and micas, the clay minerals, the jarosites and alunites, and the clathrate compounds. It is predicted that the distribution of the cations H_3O^+ , K^+ , and NH_4^+ over the water molecules sites observed in the abernathyite-like compounds may be a common feature of the interlayer structure of the hydrous layer silicates and of the intercage structure of the zeolites and clathrate compounds. The special nature of the oxonium ion in hydrous structures is discussed.

INTRODUCTION

In the previous papers of this series, Ross and Evans (1964), and Ross *et al.* (1964), hereafter referred to as Part I and Part II, respectively, the detailed descriptions of the crystal structures of $K(UO_2AsO_4) \cdot 3H_2O$ (abernathyite), $NH_4(UO_2AsO_4) \cdot 3H_2O$, $K(H_3O)(UO_2AsO_4)_2 \cdot 6H_2O$, and $Cu(UO_2PO_4)_2 \cdot 8H_2O$ (meta-torbernite) have been given. The present paper relates the crystal structures and the chemical compositions of these compounds to those of other torbernite minerals and also suggests possible similarities of the interlayer structure of the torbernite minerals to other hydrous minerals and compounds. The interrelationship between

¹ Publication authorized by the Director, U. S. Geological Survey.

cations and water molecules is emphasized. We also summarize our evidence for the presence of oxonium² ions in certain of the torbernite minerals and compounds and propose general substitution mechanisms involving this ion.

CRYSTAL CHEMISTRY OF THE TORBERNITE MINERALS

From the evidence given in Part I it is now clear that the cations H_3O^+ , NH_4^+ , and K^+ , and the water molecules play essentially the same structural role in the crystal structures of abernathyite, $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$, and $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Part I). In $\text{K}(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ and $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$, one potassium or one ammonium ion plus three H_2O molecules are found to be distributed randomly over four water molecule sites of the interlaminar region. In the compound $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$, one-half a potassium ion, one-half an oxonium ion, and three water molecules are distributed randomly over four H_2O sites. Although the chemical formulas of these compounds suggest a stoichiometric relationship between the number of cations and water molecules, there is good chemical evidence that this is not so. On the contrary, it appears that there is probably a complete solid-solution series between the oxonium, potassium, and ammonium end members.

Solid-solution series. González García (1959) has chemically analyzed a large number of synthetic uranyl phosphates and arsenates. He reports that a solid-solution series exists between the compounds $\text{H}(\text{UO}_2\text{PO}_4) \cdot y\text{H}_2\text{O}$ and $\text{K}(\text{UO}_2\text{PO}_4) \cdot y\text{H}_2\text{O}$, and he suggests the formula $\text{K}_x\text{H}_{1-x}(\text{UO}_2\text{PO}_4) \cdot y\text{H}_2\text{O}$ to represent this series. The amount of potassium and hydrogen in these compounds is found to depend upon the experimental conditions of pH and potassium ion activity. The degree of hydration is variable and higher in the potassium-deficient phases. González García also shows that a solid solution exists between various phosphate and arsenate end members, thus substantiating the mineralogical evidence for such a series (Fron del, 1958). In view of the interrelationship of oxonium and potassium ions and H_2O molecules, discussed in Part I, a better representation of the series described by González García is:



or



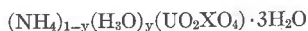
for the arsenate analogues. Also, we now know that a better formula for $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Part I) is $\text{K}_{0.45}(\text{H}_3\text{O})_{0.55}(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$,

² For a definition of the oxonium ion, see Part I, p. 1591.

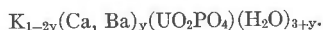
indicating that the compound is probably a member of an isomorphous series.

We predict that a naturally occurring isomorphous series exists between abernathyite and troegerite. We also predict that representatives of the series, $K_{1-y}(H_3O)_y(UO_2PO_4) \cdot 3H_2O$, of which meta-ankoleite is the potassium end member, probably occur naturally. The occurrence of any particular member of the isomorphous series of uranyl phosphates and arsenates will depend upon the pH and activity of potassium ion in the aqueous solutions from which they precipitate. Extensive solid-solution series may also occur between the phosphate and arsenate end members.

The discovery of the mineral uramphite, $NH_4(UO_2PO_4) \cdot 3H_2O$ (Nekrasova, 1957), indicates that solid-solution series similar to those containing potassium and oxonium ions probably exist involving ammonium and oxonium ions. For these series we propose the formula



where $X = P$ and (or) As . There is some indication that calcium and barium may partially substitute for potassium in meta-ankoleite (Gallagher and Atkin, 1964), which suggests that a limited isomorphous series exists between $K(UO_2PO_4) \cdot 3H_2O$, $Ca(UO_2PO_4)_2 \cdot nH_2O$ and (or) $Ba(UO_2PO_4)_2 \cdot nH_2O$. If such is true, the solid solution is expressed by the formula



As will be mentioned later, Wadsley (1953) found Ba^{2+} ions distributed over certain water molecule sites in psilomelane.

The barium, magnesium, lead and calcium uranyl salts appear to have more complex interlayer structures. Ross (1963) has discussed the complex nature of the meta-autunite (I) structure. Some of these compounds, such as autunite, also form higher hydrates which have the $(UO_2XO_4)_n^{n-}$ layers positioned with respect to one another as shown in Fig. 1A of Part I. In structures of this type two sets of cavities lie between the uranyl ions of adjacent layers. One set consists of very large cavities or cages that can contain a cation coordinated by a number of water molecules. The other set consists of cavities similar in size and shape to those found in abernathyite. There are an equal number of large cavities and divalent interlayer cations. We can postulate two different arrangements of water molecules within these more fully hydrated structures: one in which possibly six or eight H_2O molecules surround the interlayer cations, and one in which the water molecules are arranged in a manner similar to that found in abernathyite. A statistical distribution of interlayer cations over the water molecule sites may also occur.

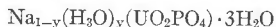
The crystal structure of meta-torbernite, $Cu(UO_2PO_4)_2 \cdot 8H_2O$, has

been described in Part II. Meta-zeunerite, $\text{Cu}(\text{UO}_2\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$, is probably isostructural with meta-torbernite. The nickel, cobalt, iron, and manganese uranyl phosphates and arsenates may also be structurally related to this mineral.

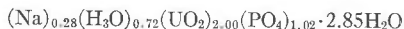
Although the random distribution of cations such as K^+ , NH_4^+ and H_3O^+ over the water molecule sites of a crystal structure has not been generally reported before, it does not seem surprising, for H_2O , H_3O^+ , NH_4^+ and K^+ have very similar radii, all approximately 1.4 Å. Also, it appears that these chemical species show similar properties in aqueous solution, especially in regard to their coordination. The presence of these ions and molecules in tetrahedral coordination within the crystal structure tends to preserve the aqueous environment, which is rather open. For example, Buslaeva and Samoilov (1961) found by thermochemical techniques that the coordination number of K^+ and NH_4^+ ions in dilute solutions at 25° C. is 4.0 and 4.3, respectively. Brady and Krause (1957) found by *x*-ray diffraction techniques that the hydration number of the potassium ion is 4.0 in concentrated KOH and KCl solutions. This is in agreement with the theoretically calculated value of Bernal and Fowler (1933). Brady and Krause (1957, p. 304) state, "K⁺ which is close in size to the H₂O molecule enters substitutionally into the pseudo structure of H₂O without disturbing the structure to any marked extent." The model of an aqueous solution containing monovalent cations such as K^+ , NH_4^+ and H_3O^+ , conforming to a tetrahedral ice-like structure with the cations (and anions?) randomly distributed over the H₂O positions, fits nicely with the structural scheme found for the interlayer material of the abernathyite-like compounds. Buslaeva and Samoilov (1961) show that Li^+ , Na^+ , Rb^+ and Cs^+ ions also have a coordination number of approximately 4 in dilute aqueous solutions, which is in agreement with the prediction of Bernal and Fowler (1933, p. 534). This suggests that these monovalent cations may also form compounds isostructural with abernathyite. If so, solid solutions may form between the various end members, *i.e.*,



where $\text{A}^+ = \text{Li}^+$, Na^+ , K^+ , Rb^+ , Cs^+ , NH_4^+ and (or) H_3O^+ ; and $\text{X} = \text{As}^{5+}$ and (or) P^{5+} . Fairchild (1929) gives chemical evidence that the solid-solution series



exists. Recalculation of the chemical analysis of his "anomalous sodium-autunite," assuming that oxonium ions make up the deficiency of sodium, gives the formula



in good agreement with the above theoretical formula.

A distribution of cations and anions over the water molecule sites in ice was found in the system $\text{NH}_4\text{F}-\text{H}_2\text{O}$ by Zaromb and Brill (1956). The ice crystals dissolved as much as 10 weight per cent NH_4F , with one NH_4^+ and one F^- ion each replacing an H_2O molecule. Because NH_4^+ , F^- , and H_2O have similar radii, 1.43, 1.36 and 1.41 Å, respectively, and because the total number of hydrogen bonds is the same in pure ice and in ice- NH_4F solid solution, it is plausible that a stable isomorphous series forms.

Hydrogen bonding. As is described in Part I, there is a complex system of hydrogen bonding in the abernathyite-like compounds. A maximum of 40 hydrogen bonds can exist within the unit cell of these compounds ($a=b \cong 7$ Å, $c \cong 18$ Å). Distribution of four potassium ions and twelve water molecules over sixteen water molecule sites eliminates four hydrogen bonds per potassium atom. In the proposed solid-solution series, $\text{K}_{1-y}(\text{H}_3\text{O})_y(\text{UO}_2\text{XO}_4) \cdot 3\text{H}_2\text{O}$, the ratio of the number of protons to the number of possible hydrogen bonds per unit cell is given by the relation

$$(1) \quad \frac{\text{No. protons}}{\text{No. possible H-bonds}} = \frac{24 + 12y}{24 + 16y}$$

For the potassium end members, abernathyite and meta-ankoleite, there are an equal number of protons and possible H-bonds. Thus no statistical distribution of protons over proton sites is required. For the oxonium end members, troegerite and $\text{H}_3\text{O}(\text{UO}_2\text{PO}_4) \cdot 3\text{H}_2\text{O}$, 36 protons must be distributed over 40 proton sites.

In the proposed series, $(\text{NH}_4)_{1-y}(\text{H}_3\text{O})_y(\text{UO}_2\text{XO}_4) \cdot 3\text{H}_2\text{O}$, the ratio of the number of protons to the number of possible H-bonds is given by the relation

$$(2) \quad \frac{\text{No. protons}}{\text{No. possible H-bonds}} = \frac{40 - 4y}{40}$$

Relations (1) and (2) give the "proton occupancy factor," which is 1.0 for the potassium and ammonium end-members, and 0.9 for the oxonium end members. The deficiency of protons in the oxonium-rich uranyl arsenates and phosphates may make them less stable than the potassium and ammonium end members.

The oxonium ion. As emphasized in Part I, we do not infer any particular geometry for the so-called oxonium ion once it is present within a crystal structure. In some compounds it may be that three protons are closely bound to one oxygen atom. If so, the H_3O^+ group will have a true identity in the crystal structure. On the other hand, it may be that there is a statistical distribution of protons about certain oxygen atoms such that only "part of the time" does a true oxonium group exist. For the present,

however, it seems best to assume that the protons of the H_3O^+ ion distribute themselves within the crystal structure such that the charges on all oxygen atoms are as nearly neutralized as possible. The exact geometrical nature of the oxonium ion is left to be described from precise neutron diffraction experiments on each particular compound in question.

NOMENCLATURE OF THE TORBERNITE MINERALS

Unfortunately, in the past the names of the various torbernite minerals were given without respect to the hydration state. As new hydration states were discovered, the prefix "meta" was usually attached to the name of the lower hydrate. Roman numerals were also used to distinguish between three or more hydrates, for example, autunite, meta-autunite (I), and meta-autunite (II). Mineralogists also attempted to infer a structural relationship between the members of various subgroups of the torbernite minerals having the same or similar hydration state. For example, it was inferred that meta-autunite (I) was isostructural with meta-uranocircite (I) (Part I). Single-crystal precession photographs taken by the present authors, however, show that these two minerals definitely are not isostructural. Meta-autunite (I) and meta-uranocircite (I) must have quite different arrangements of interlayer cations and water molecules, for the two minerals have different unit-cell sizes and symmetry. Meta-autunite (I) is tetragonal with $a = 19.78 \text{ \AA}$ and $c = 16.92 \text{ \AA}$ (Ross, 1963), and meta-uranocircite (I) is orthorhombic with $a = 9.81 \text{ \AA}$, $b = 9.91 \text{ \AA}$, and $c = 16.87 \text{ \AA}$ (unpublished data).

It is suggested that in the naming of these minerals in the future the following rules or conventions be used:

- (1) If only one hydrate is known, no prefix or Roman numeral will be used in the mineral name.
- (2) If two hydrates are known, the lower hydrate will have the prefix "meta" attached to the mineral name.
- (3) If three or more hydrates are known, the highest hydrate will have no prefix or Roman numeral, all other hydrates will have the prefix "meta" attached to the name, and the Roman numerals will in increasing order designate progressively lower hydration states.

ROLE OF OXONIUM, POTASSIUM AND AMMONIUM IONS IN OTHER MINERAL GROUPS

The jarosite group and related compounds. There are several compounds and minerals reported that bear an interesting relationship to abernathyite, $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$, and $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$ with regard to the structural role of NH_4^+ , K^+ and H_3O^+ . Shishkin (1951) has found that the compounds $\text{NH}_4\text{Al}(\text{SO}_4)_2$ and $\text{H}_3\text{OAl}(\text{SO}_4)_2$ form solid solutions, as do also the compounds $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ and $\text{H}_3\text{OFe}(\text{SO}_4)_2$,

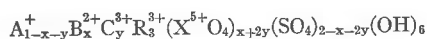
indicating that the isomorphous replacement of H_3O^+ for NH_4^+ occurs. Shishkin, in the same paper, also reported the synthesis of oxonium and ammonium jarosite with the formulas $\text{H}_3\text{OFe}_3(\text{SO}_4)_2(\text{OH})_6$ and $\text{NH}_4\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$, respectively. Krogius (1959) confirmed Shishkin's work on $\text{NH}_4\text{Al}(\text{SO}_4)_2$ and $\text{H}_3\text{OAl}(\text{SO}_4)_2$ and also showed that the oxonium and ammonium alunites, $\text{H}_3\text{OAl}_3(\text{SO}_4)_2(\text{OH})_6$ and $\text{NH}_4\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$, form solid solutions with one another. Kubisz and Michalek (1959) found potassium-deficient jarosites in the menilite beds of the Carpathian Mountains and showed that H_3O^+ replaced some of the alkali. Recently, Johansson (1963) completely described the structure of $\text{H}_3\text{OGa}_3(\text{SO}_4)_2(\text{OH})_6$, the gallium analogue of oxonium jarosite. He found the H_3O^+ ion to be coordinated by six (OH) groups at 2.82 Å and by six sulfate oxygen atoms at 2.92 Å.

The discovery of the interchangeability of potassium, oxonium and ammonium ions in the jarosites and alunites was 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 $\text{H}_3\text{OFe}_3(\text{SO}_4)_2(\text{OH})_6$, and assumed that the structural formula was $\text{H}_2\text{OFe}_3(\text{SO}_4)_2(\text{OH})_5\text{H}_2\text{O}$ with a water molecule substituting for both one K^+ ion and one OH^- group of jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$. In the light of the present work it is 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 $\text{H}_3\text{OBF}_3(\text{OH})$ has been reported (Wamser, 1951).

In summary, the following solid-solution series appears to exist in the jarosite-alunite mineral group:



where $\text{A}^+ = \text{H}_3\text{O}^+$, NH_4^+ , K^+ , Na^+ , and (or) Ag^+ ; and $\text{R}^{3+} = \text{Fe}^{3+}$ and (or) Al^{3+} . Small amounts of Ca^{2+} or Mg^{2+} may substitute for A^+ concomitantly with P^{5+} or As^{5+} for S^{6+} . The beudantite mineral group, which structurally is closely related to the jarosite group, may form solid-solution series such as



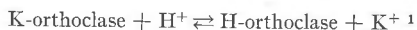
where $\text{A}^+ = \text{H}_3\text{O}^+$, NH_4^+ , K^+ , Na^+ , and (or) Ag^+ ; $\text{B}^{2+} = \text{Ca}^{2+}$, Mg^{2+} , Pb^{2+} , and (or) Ba^{2+} ; $\text{C}^{3+} = \text{Ce}^{3+}$ and other trivalent elements having similar radii; $\text{R}^{3+} = \text{Al}^{3+}$ and (or) Fe^{3+} ; and $\text{X}^{5+} = \text{P}^{5+}$ and (or) As^{5+} . The plumbogummite group, also structurally related to the jarosites, appears to form

even more complicated isomorphous series. A careful chemical study and crystal structure analyses are needed to clearly describe this group.

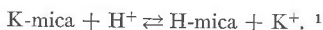
Psilomelane. Wadsley (1953) has described the substitution of barium ions for water molecules in the structure of psilomelane, $(\text{Ba}, \text{H}_2\text{O})_2 \text{Mn}_5\text{O}_{10}$. Tunnels within the structure were found to be occupied by a double row of barium ions and water molecules which are crystallographically indistinguishable. It is considered probable that each tunnel contains an ordered sequence of barium ions and water molecules. The ratio of $\text{Ba}:\text{H}_2\text{O}$ is nearly 1:2.

The feldspars and micas. The substitution of NH_4^+ for K^+ certainly must occur in many other mineral systems. There is particularly good evidence that this happens in some micas and feldspars. The mineral buddingtonite, $\text{NH}_4\text{AlSi}_3\text{O}_8 \cdot 1/2\text{H}_2\text{O}$, recently discovered by Erd and others (1964), appears to be closely related, structurally, to sanidine. Barker (1964) has prepared synthetic ammonium feldspars at various pressures and temperatures, and they appear to be quite similar to buddingtonite. Ammonium micas have been known for many years (see Gruner, 1939).

The isomorphous replacement of H_3O^+ for K^+ may also occur in the feldspars and micas. Garrels and Howard (1959) show that, at least below pH 10, the following reactions occur when finely ground orthoclase or mica is placed in water:



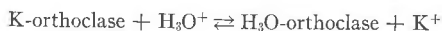
and



Their experiments indicate that H-orthoclase and H-mica are favored over the potassium analogs at 25° C. except in solutions in which the ratio of $a_{\text{K}^+}/a_{\text{H}^+}$ is exceedingly high. It would be extremely interesting if a true oxonium feldspar, $\text{H}_3\text{OAlSi}_3\text{O}_8$, could be prepared for chemical and crystallographic analysis. There have been a number of reports of oxonium micas in the literature, for example, see Brown and Norrish (1952) and White and Burns (1963).

The clay and zeolite mineral groups. The system of cation distribution over

¹ In view of our present knowledge of the oxonium ion it would be better to write these reactions as



and



water molecule sites described in this paper and in Part I may also exist in the intercage structure of many of the zeolites and in the interlayer structure of the expanding clay minerals such as montmorillonite and vermiculite. Indeed the unusual role of K^+ , H_3O^+ , and NH_4^+ in the abernathyite-like structures may account for the unusual properties of the montmorillonites and vermiculites. Potassium, oxonium, and ammonium ions, instead of entering in between the layers with a hydration sphere of water molecules about them, may be randomly distributed over some of the water molecule positions of the interlayer framework. The layer-lattice minerals may be thought of as "trapping" a portion of the solution from which they crystallized, preserving the tetrahedral environment of the water molecules and the oxonium, ammonium, and potassium ions. On further dehydration, these clay minerals become isostructural with the micas; the potassium, ammonium, and oxonium ions moving from the interlayer water structure to the cavities within the $(Si_2O_5)_n^{2n-}$ sheets. Bokii and Arkhipenko (1962) give evidence of oxonium ions occurring in vermiculite.

The arrangement of the water molecules between the sheets of the clay minerals may be based on a number of structural schemes. Hendricks and Jefferson (1938) proposed that water molecules may be jointed into hexagonal groups that form a single extended hexagonal net. Specifically, the OH_4 tetrahedra share three out of four corners with other OH_4 tetrahedra with the tetrahedra arranging themselves as do the SiO_4 groups in a single layer of the tridymite structure. Possible multi-layer models may be based on the ice-I and ice-Ic structures, in which the OH_4 tetrahedra link into a framework isostructural with tridymite and cristobalite respectively; or on the ice-III structure (Kamb and Datta, 1960) in which the tetrahedra link into a keatite-like (SiO_2) structure. An infinite number of other arrangements may be proposed, but because the clay mineral sheets possess pseudo-hexagonal symmetry the disposition of the water molecules is probably based on six or threefold symmetry. The idealized arrangement of the OH_4 tetrahedra within the abernathyite structure (Fig. 1) is based on fourfold symmetry in which the OH_4 tetrahedra link into eight- and four-membered rings such as are found in feldspar, harmotome, and paracelsian. Smith and Rinaldi (1962) have given 28 simple ways of linking the eight- and four-membered rings of this type. The interlayer structure of abernathyite (Fig. 1) corresponds to the model labeled "Na-Pl" of their Fig. 4. The apophyllite structure is based on a sheet of SiO_4 tetrahedra linked in exactly the same way as the OH_4 tetrahedra in abernathyite.

The clathrate compounds. Even more complicated arrangements of water

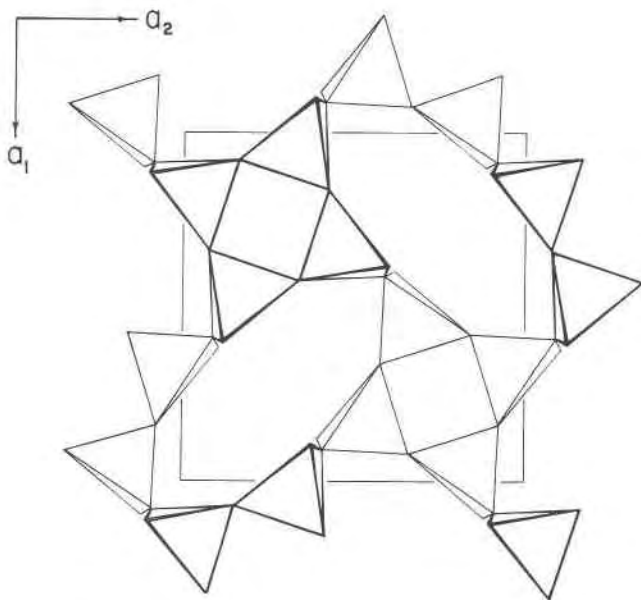


FIG. 1. Representation of the interlayer structure of abernathyite as linked OH_4 tetrahedra. The tetrahedra link into infinite sheets parallel to (001). At the apices of each tetrahedron lie protons; at the center, an oxygen atom. The tetrahedra are idealized for the exact positions of the protons are unknown.

molecules are found in the clathrate hydrates which have large cages of linked H_2O molecules. In the case of tetra *iso*-amyl ammonium fluoride, $(i\text{-C}_5\text{H}_{11})_4\text{N}^+ \cdot \text{F}^- \cdot 38\text{H}_2\text{O}$, (Feil and Jeffrey, 1961) the structural unit is a hydrogen bonded clathrate cage in the form of an $\text{H}_{40}\text{O}_{20}$ pentagonal dodecahedron. This cage is linked to two other types of cages; one a tetrakaidecahedron and the other a pentakaidecahedron. Four out of the 80 water molecules in the framework of the clathrate structure are replaced by two N^+ and two F^- ions; a situation somewhat analogous to that found in abernathyite.

In clathrate compounds which have crystallized from concentrated salt solutions a random distribution of cations such as K^+ , H_3O^+ and NH_4^+ into the water molecule sites of the H_2O framework may occur. The charge balance could be accomplished in two ways—either by substitution of anions such as F^- , Cl^- or Br^- into the framework proper, or by inclusion of the anions within the large cages or voids.

REFERENCES

- BARKER, D. S. (1964) Ammonium in alkali feldspars. *Am. Mineral* 49, 851-858.
 BERNAL, J. D. AND R. H. FOWLER (1933) A theory of water and ionic solution, with particular reference to hydrogen and hydroxyl ions. *Jour. Chem. Phys.*, 1, 515-548.

- BOKII, G. B. AND D. K. ARKHIPENKO (1962) Oxonium groups in vermiculite. *J. Structural Chem.*, **3**, 670-674 (Engl. transl. of *Zh. strukt. khimii*, **3**, 697-702, Consultants Bureau).
- BRADY, G. W. AND J. T. KRAUSE (1957) Structure of solutions. I. *Jour. Chem. Phys.* **27**, 304-308.
- BROWN, G. AND K. NORRISH (1952) Hydrous micas. *Mineral Mag.*, **29**, 929-932.
- BUSLAEVA, M. N. AND O. YA. SAMOILOV (1961) Coordination numbers of certain ions in aqueous solutions, and effect of temperature on them. *Jour. Struct. Chem.* **2**, 510-515 (Engl. transl. of *Zh. strukt. khimii*, **2**, 551, Consultants Bureau).
- ERD, R. C., D. E. WHITE, J. J. FAHEY AND D. E. LEE (1964) Buddingtonite, an ammonium feldspar with zeolitic water. *Am. Mineral.* **49**, 831-850.
- FAIRCHILD, J. G. (1929) Base exchange in artificial autunites. *Am. Mineral.* **14**, 265-275.
- FEIL, D. AND G. A. JEFFREY (1961) The polyhedral clathrate hydrates, Part 2. Structure of the hydrate of tetra *iso*-amyl ammonium fluoride. *Jour. Chem. Phys.*, **35**, 1863-1873.
- FRONDEL, C. (1958) Systematic mineralogy of uranium and thorium. *U. S. Geol. Survey Bull.* **1064**.
- GALLAGHER, M. J. AND D. ATKIN (1964) Meta-ankoleite, hydrated potassium uranyl phosphate. *Great Britain Geol. Survey Bull.* (in press).
- GARRELS, R. M. AND P. HOWARD (1959) Reactions of feldspar and mica with water at low temperature and pressure. *Nat. Conf. Clays Clay Minerals*, **6th Proc.**, 68-88.
- GONZÁLEZ GARCÍA, F. (1959) Constitución y propiedades de algunos fosfatos dobles de uranilo y sustancias analogas, I, II, III, IV. *Estos Anales*, **55B**, 383-428.
- GRUNER, J. W. (1939) Ammonium mica synthesized from vermiculite. *Am. Mineral.* **24**, 428-433.
- HENDRICKS, S. B. (1937) The crystal structure of alunite and the jarosites. *Am. Mineral.* **22**, 773-784.
- and M. E. JEFFERSON (1938) Structures of kaolin and talc-pyrophyllite hydrates and their bearing on water sorption of the clays. *Am. Mineral.* **23**, 863-875.
- JOHANSSON, GEORG (1963) On the crystal structure of a basic gallium sulfate related to alunite. *Arkiv Kemi*, **20**, 343-352.
- KAMB, W. B. AND S. K. DATTA (1960) Crystal structures of the high-pressure forms of ice: Ice III. *Nature* **187** (4732), 140-141.
- KROGINS, E. A. (1959) Oxonium compounds in the alumina-sulfur trioxide-water system. *Zhur. Neorg. Khim.* **4**, 2146-2150.
- KUBISZ, J. AND Z. MICHALEK (1959) Minerals of the oxidized zone of the menilite beds in the Carpathians. *Bull. Acad. Polon. Sci., Sér. sci., chim., géol. géogr.* **7**, 765-771.
- NEKRASOVA, Z. A. (1957) Hydrous uranyl phosphate (uramphite)— $\text{NH}_4(\text{UO}_2\text{PO}_4) \cdot 3\text{H}_2\text{O}$. *Atomnaya Energiya, Voprosy Geol. Urana, Suppl.* **6**, 78-82.
- ROSS, MALCOLM (1963) The crystallography of meta-autunite (I). *Am. Mineral.*, **48**, 1389-1393.
- and H. T. EVANS, JR. (1964) Studies of the torbernite minerals (I). The crystal structure of abernathyite and the structurally related compounds $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ and $\text{K}(\text{H}_2\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$. *Am. Mineral.* **49**, 1578-1602.
- H. T. EVANS, JR. AND D. E. APPLEMAN (1964) Studies of the torbernite minerals (II). The crystal structure of metatorbernite. *Am. Mineral.* **49**, 1603-1621.
- SHISHKIN, N. V. (1951) The oxonium ion in the crystal lattices of inorganic compounds. *Zhur. Obshchei Khim.* **21**, 456-467.
- SMITH, J. V. AND F. RINALDI (1962) Framework structures formed from parallel four- and eight-membered rings. *Mineral. Mag.* **33**, 202-212.
- WADSLAY, A. D. (1953) The crystal structure of psilomelane, $(\text{Ba}, \text{H}_2\text{O})_2\text{Mn}_5\text{O}_{10}$. *Acta Cryst.* **6**, 433-438

- WAMSER, C. A. (1951) Equilibrium in the system boron trifluoride-water at 25°. *Jour. Am. Chem. Soc.* **73**, 409-416.
- WHITE, J. L. AND A. F. BURNS (1963) Infrared spectra of hydronium ion in micaceous minerals. *Science*, **141**, 800-801.
- ZAROMB, S. AND R. BRILL (1956) Solid solutions of ice and NH_4F and their dielectric properties. *Jour. Chem. Phys.* **24**, 895-902.

Manuscript received, June 15, 1964; accepted for publication, August 14, 1964.