THE TORBERNITE MINERALS AS MODEL COMPOUNDS FOR THE HYDROUS LAYER SILICATES*

by

Malcolm Ross

U.S. Geological Survey, Washington, D.C.

ABSTRACT

A number of minerals and compounds of the torbernite group are represented by the formula $A(UO_2)(As,P)O_4 \cdot 3H_2O$ where $A = K^+$, NH_4^+, and/or H_3O^+. Crystal-structure analyses of $K(UO_2AsO_4) \cdot 3H_2O$, $NH_4(UO_2AsO_4) \cdot 3H_2O$, and $K_{0.45}(H_3O)_{0.55}(UO_2AsO_4) \cdot 3H_2O$ recently completed by Ross and Evans (1964) reveal the exact nature of their atomic arrangements. All three compounds have interlayer structures formed by hydrogen bonding of water molecules into infinite sheets composed of four- and eight-membered rings, isostructural with the $[Si_8O_{20}]_n^{8n-}$ layers of apophyllite. The interlayer K^+, NH_4^+, and H_3O^+ ions, instead of entering in between the $[UO_2AsO_4]_n^{n-}$ layers co-ordinated by a hydration sphere of water molecules, are randomly distributed over the water molecule sites. The formula of the interlayer structure is written $[(H_2O)_3A]_n^{n+}$.

A similar structural scheme may apply to the expanding layer silicates, such as the montmorillonites and vermiculites. For these minerals, particularly those with low to moderate cation-exchange capacity, the potassium and ammonium analogs usually do not fully contract to the 10 Å basal spacing on immersion in K^+ or NH_4^+ solutions, but rather obtain a spacing of 11–14 Å. In these structures it is proposed that a single or double layer of water molecules, arranged in a manner related to one of the silica or ice polymorphs, enters between the 2 : 1 layers, the charge being balanced by random distribution of K^+, NH_4^+, and perhaps H_3O^+ ions over the H_2O sites. The formula of the interlayer structure is written $[(H_2O)_{b-y}Ay]_n^{ny+}$ where $A = K^+$, NH_4^+, and/or H_3O^+ and ny^+ is the charge required to balance that on the 2 : 1 layer. Other Group IA or Group IIA cations may also be randomly distributed over water-molecule sites.

INTRODUCTION

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 about the crystal chemistry of these phases, detailed crystal-structure studies of $K(UO_2AsO_4) \cdot 3H_2O$ (abernathyite), $NH_4(UO_2AsO_4) \cdot 3H_2O$, $K_{0.45}(H_3O)_{0.55} \cdot (UO_2AsO_4) \cdot 3H_2O$, and $Cu(UO_2PO_4)_2 \cdot 8H_2O$ (metatorbernite) have been made. An unusual relationship between the interlayer cations and water molecules has been discovered in

---

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

65

these compounds, and this may have an important bearing on the interlayer structure of the hydrous layer silicates, such as the montmorillonites and vermiculites. In the following, the structures of the torbernite minerals thus far examined will be briefly described and possible relations to the layer silicates will be discussed.

Beintema (1938), in his now classic paper, first described the basic structure of the $(UO_2PO_4)_n{}^{n-}$ sheets of autunite, $Ca(UO_2PO_4)_2 \cdot nH_2O$. He was able to locate the positions of the uranium atoms within the sheet experimentally and by astute crystal-chemical reasoning predicted the positions of the other atoms of the sheets with fair accuracy. The techniques of the time would not permit the location of the light atoms, such as oxygen, in the presence of the heavy uranium atoms. These sheets consist of dumbbell-shaped uranyl ions, with the uranium further co-ordinated by four oxygen atoms of four different $PO_4{}^{3-}$ tetrahedra. The tetrahedra and uranyl ions link into two-dimensional sheets (comparable with those of Fig. 1) lying parallel to (001). These sheets are puckered, with the uranyl ion displaced upward and downward from the plane of the phosphorus atoms.

CRYSTAL STRUCTURE OF THE TORBERNITE MINERALS

Ross and Evans (1964) have recently completed a determination of the crystal structures of $K(UO_2AsO_4) \cdot 3H_2O$ (abernathyite), $NH_4(UO_2AsO_4) \cdot 3H_2O$, and $K_{0.45}(H_3O)_{0.55}(UO_2AsO_4) \cdot 3H_2O$. The structure of $K(UO_2AsO_4) \cdot 3H_2O$ is depicted in Fig. 1, which shows the structural scheme projected on (100). The $(UO_2AsO_4)_n{}^{n-}$ sheets are isostructural with the $(UO_2PO_4)_n{}^{n-}$ sheets found in autunite by Beintema. As can be seen in this figure, four " apparent " water molecules are situated between the uranyl ions of adjacent sheets. The water molecules are also symmetrically arranged about the fourfold axes to form square groups. In $K(UO_2AsO_4) \cdot 3H_2O$, as well as in $NH_4(UO_2AsO_4) \cdot 3H_2O$ and $K_{0.45}(H_3O)_{0.55}(UO_2AsO_4) \cdot 3H_2O$, 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 the square groups mentioned above. Each water molecule of a square group is also hydrogen-bonded to a water molecule of an adjacent $(H_2O)_4$ square and to an arsenate oxygen atom. The interlayer water molecules thus attain a distorted tetrahedral co-ordination with tetrahedral bond angles of 115°, 121°, 90°, 109°, 100°, and 115°. The hydrogen bond lengths between water molecules within the square, between water molecules of adjacent squares and between the water molecules and the arsenate oxygen atoms are 2.80, 2.83, and 2.75 Å respectively.

This " ideal " arrangement of H_2O molecules is modified by the random distribution of cations over the water-molecule sites. In $K(UO_2AsO_4) \cdot 3H_2O$, one potassium ion and three H_2O molecules are distributed randomly over four water-molecule sites; in $NH_4(UO_2AsO_4) \cdot 3H_2O$, one $NH_4{}^+$ ion and three H_2O molecules are distributed over four sites; and in $K_{0.45}(H_3O)_{0.55}(UO_2AsO_4) \cdot 3H_2O$, 0.45 K^+ ions, 0.55 H_3O^+ ions and three water molecules are randomly

distributed over four H_2O sites. To express this distribution of cations and H_2O molecules over water-molecule sites, the structural formula of these phases are written as $(K \cdot 3H_2O)(UO_2AsO_4)$, $(NH_4 \cdot 3H_2O)(UO_2AsO_4)$, and $[K_{0 \cdot 45}(H_3O)_{0 \cdot 55} \cdot 3H_2O](UO_2AsO_4)$. A more detailed discussion of the structures, including tabulations of atomic co-ordinates and interatomic distances, is given by Ross and Evans (1964).

Ross and Evans (1965) have presented the evidence for the existence in the torbernite minerals of extensive solid-solution series involving the oxonium ion and various other monovalent cations. These series are expressed by the formulae $A_{1-y}(H_3O)_y(UO_2AsO_4) \cdot 3H_2O$ and $A_{1-y}(H_3O)_y (UO_2PO_4) \cdot 3H_2O$ for the phosphate analogues, where A = NH^+ or K^+. There is also evidence that other monovalent cations such as Li^+, Na^+, Rb^+ and Cs^+ may also substitute into the interlayer-water framework. Indirect mineralogical evidence exists for limited solid-solution series involving divalent cations, e.g. $K_{1-2y}(Ca,Ba)_y (UO_2PO_4)(H_3O)_{3+y}$.

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, this 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 co-ordination. The presence of these ions and molecules in tetrahedral co-ordination 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 co-ordination 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 H_2O molecule enters substitutionally into the pseudo-structure of H_2O 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 icelike structure with the cations (and anions?) randomly distributed over the H_2O positions, fits nicely with the structural scheme found for the interlayer material of the abernathyitelike compounds. Buslaeva and Samoilov (1961) show that Li^+, Na^+, Rb^+ and Cs^+ ions also have a co-ordination number of approximately 4 in dilute aqueous solutions, which is in agreement with the prediction of Bernal and Fowler (1933, p. 534).

THE EXPANDABLE CLAY MINERALS

The following discussion will be concerned with those clay minerals that have a variable layer separation depending upon the number of water molecules and the number and kind of cations lying within the interlaminar

region. When such clays are immersed in aqueous solutions containing various Group IA and Group IIA cations, the separation of the layers characteristically changes, the magnitude of the separation being dependent upon the following factors: (1) the magnitude of the charge on each layer, (2) the distribution of the charge within the layer, (3) variation of charge magnitude and charge distribution between the layers, (4) particle size, (5) size of the exchangeable cations, (6) charge on the exchangeable cations, (7) pressure and temperature and (8) activities of H_2O and the various dissolved ionic species in equilibrium with the clay. The clay minerals that characteristically exhibit the property of variable interlayer spacing are: the montmorillonites, the vermiculites and certain of the so-called mixed-layer 2 : 1 clays. Included among the mixed-layer types are probably some of the clay minerals referred to as " illites ", " hydrous micas ", and " glauconites ".

The Interlayer Structure

Numerous models for the structural arrangement of the water molecules lying between the layers of various clay minerals have been proposed. Many of them are based, at least in part, on the original postulate of Hendricks and Jefferson (1938). They proposed that the water molecules are joined into hexagonal rings through hydrogen bonds that, in turn, link into a single extended hexagonal net. Three-fourths of the protons are involved in hydrogen bonds within the hexagonal net, and one-fourth are free to hydrogen bond to oxygen atoms (or water molecules) in layers above or below the extended $(H_2O)_n$ sheet. Macey (1942) made a similar proposal for the structure of the layer of water molecules adsorbed onto the exposed sheet surface of the layer clay minerals. He related this layer of adsorbed H_2O molecules to the structure of ice and showed the geometric relationship between a single layer of the ice structure and the surface oxygens of the $(Si_2O_5)_n{}^{2n-}$ sheet.

The proposals of Hendricks and Jefferson and of Macey may be formulated as follows: Hexagonal ice-I (Barnes, 1929) possesses the wurtzite structure in which the oxygen atoms occupy the positions of the Zn and S atoms. Alternatively, ice-I may be considered to be isostructural with β-tridymite, with the oxygen and hydrogen atoms of the H_2O molecules occupying respectively the silicon and oxygen positions of the tridymite structure. Ice-I may be thought of as being composed of linked OH_4 tetrahedra; each corner of the tetrahedra is occupied by a proton and each proton is shared between two OH_4 tetrahedra to form a three-dimensional four-connected structure. A single layer of the ice-I structure taken parallel to (001) is shown in idealized form in Fig. 2. This layer is drawn showing the apical protons that link to like layers above and below. Thus, the sheet, as depicted in Fig. 2, has the composition $(O_2H_5)_n{}^{n+}$. We see that three of five protons of the $(O_2H_5)_n{}^{n+}$ layer are involved in bonding the water molecules together within the sheet. The remainder of the protons project alternately up and down, to be able to hydrogen-bond to oxygen atoms above and below the sheet. It should
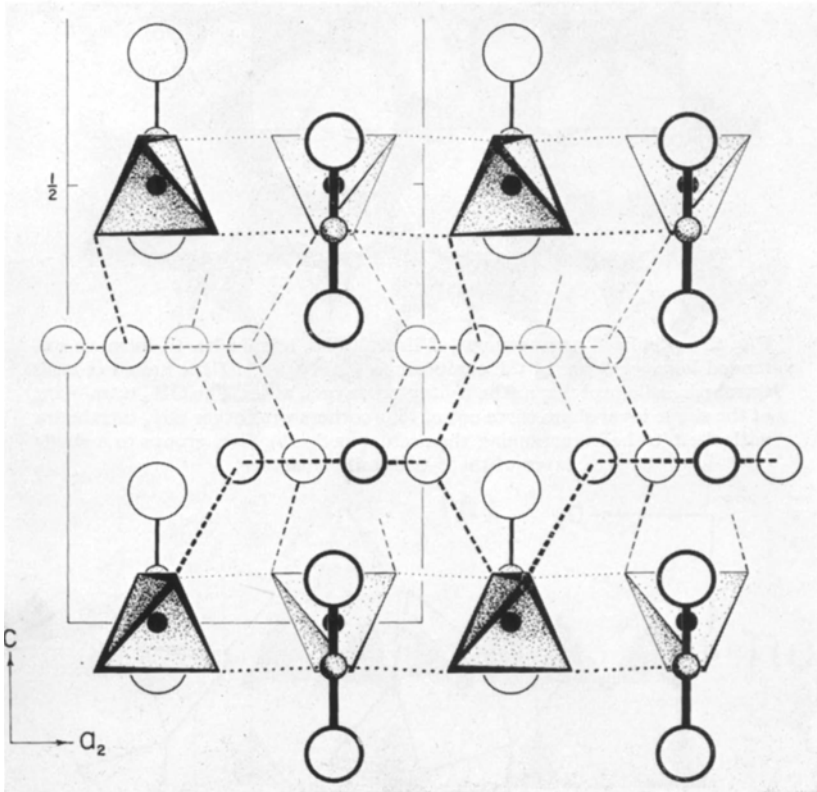
FIG. 1.—Projection of the $K(UO_2AsO_4) \cdot 3H_2O$ structure on (100) The dotted lines indicate $U—O_c$ bonds; the dashed lines indicate hydrogen bonds. Large open circles, uranyl oxygens, smaller open circles, water molecules and potassium atoms; small stippled circles, uranium atoms; small solid circles, arsenic atoms (after Ross and Evans, 1964)
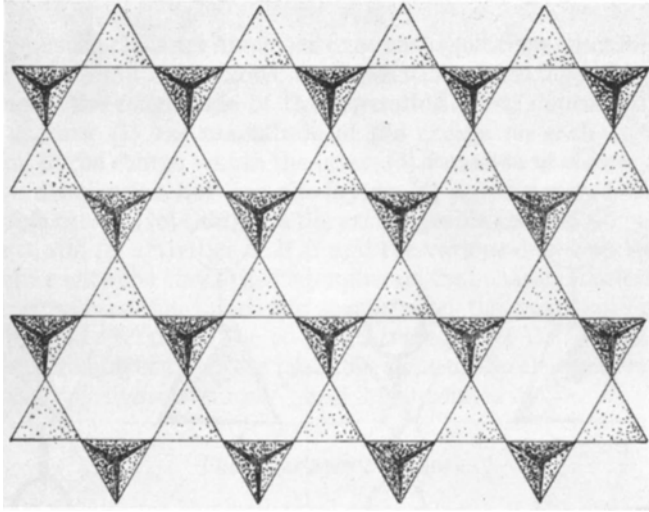
FIG. 2.—Idealized arrangement of linked OH_4 tetrahedra to form an extended hexagonal net of the composition $(O_2H_5)_n{}^{n+}$. At the apices of each tetrahedron lie protons; at the center, an oxygen atom The OH_4 tetrahedra of the single layer share three out of four corners with other OH_4 tetrahedra with the tetrahedra arranging themselves as do the SiO_4 groups in a single layer of the β-tridymite structure
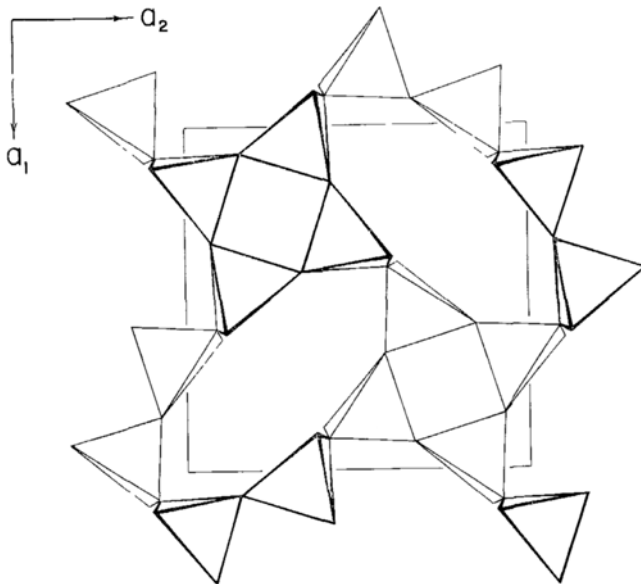

FIG. 3.—Representation of the interlayer structure of abernathyite as linked OH_4 tetrahedra. The tetrahedra link into infinite sheets parallel to (001). At the apices of each tetrahedron lie protons; at the center, an oxygen atom. The tetrahedra are idealized for the exact positions of the protons are unknown (after Ross and Evans, 1965).
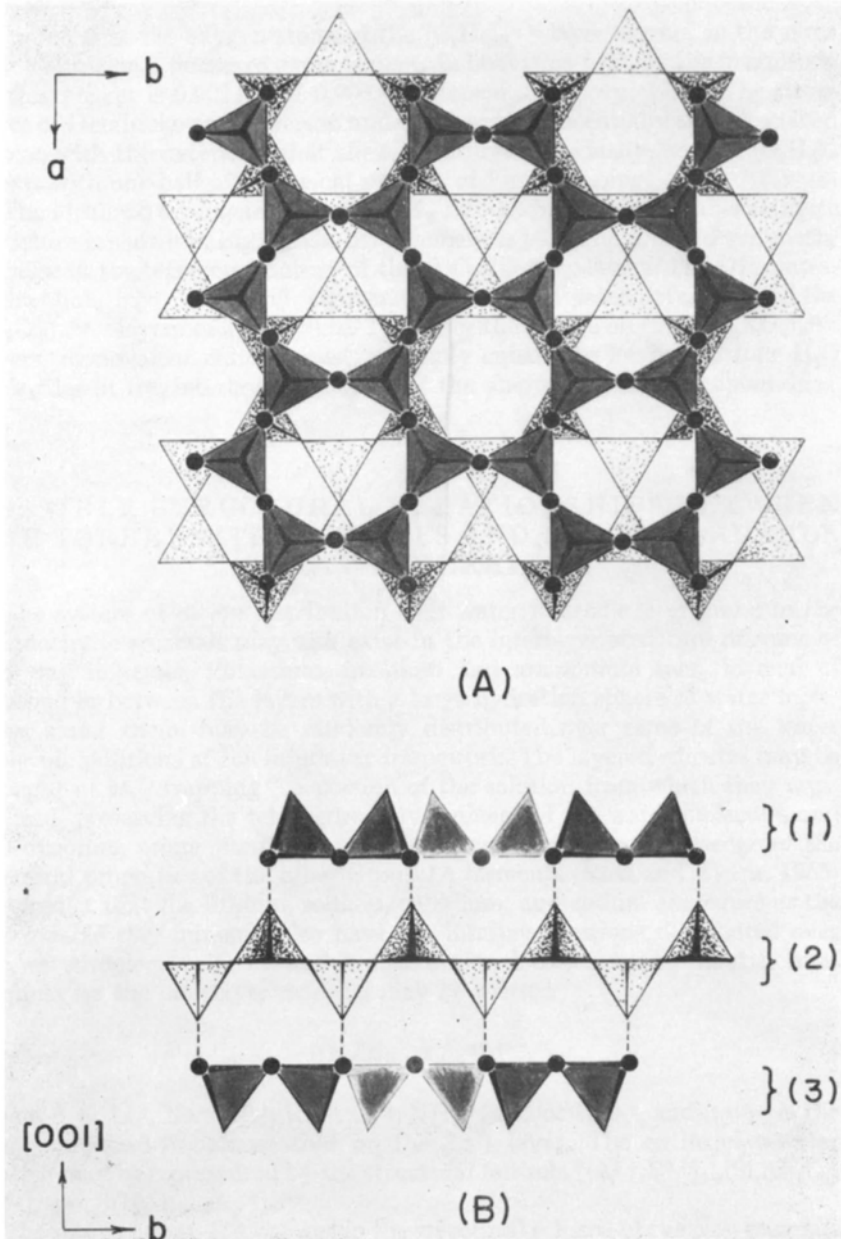
FIG. 4 Plan (A) and side (B) view showing the relationship between an extended hexagonal layer of water molecules (2) and the $(Si_2O_5)_n^{2n-}$ tetrahedral layers (1, 3) of a clay mineral such as montmorillonite. The layer of H_2O molecules is represented as linked OH_4 tetrahedra (stippled). The SiO_4 tetrahedra of the $(Si_2O_5)_n^{2n-}$ layers are shaded with the surface oxygen atoms of these layers shown as solid circles. Hydrogen bonds between the apical protons of the OH_4 tetrahedra and the surface oxygen atoms are shown as dashed lines. In order to satisfy the charge on the 2:1 layers of the clay, some of the water molecules are randomly replaced by cations.

be noted that the oxygen atoms of the $(O_2H_5)_n{}^{n+}$ layer are not in the same plane but form a puckered arrangement. In heavy ice-I (D_2O), the magnitude of this pucker is 0.901Å and 0.903Å (Peterson and Levy, 1957). The structures of Hendricks and Jefferson and of Macey are essentially that described above, with the exception that their structures are, ideally, neutral $(O_2H_4)_n$ sheets with one-half of the apical protons of Fig. 2 missing.

The idealized arrangement of the OH_4 tetrahedra within the abernathyite structure is shown in Fig. 3. The arrangement is based on fourfold symmetry because of the tetragonal nature of the $(UO_2XO_4)_n{}^{n-}$ layers. The OH_4 tetrahedra link into four- and eight-membered rings isostructural with the $(Si_8O_{20})_n{}^{8n-}$ layers of apophyllite. To satisfy the charge on the $(UO_2XO_4)_n{}^{n-}$ layers, monovalent cations must randomly substitute for one of four H_2O molecules in the interlayer structure of the abernathyitelike compounds.

POSSIBLE STRUCTURAL RELATIONSHIPS BETWEEN THE TORBERNITE MINERALS AND THE EXPANDABLE CLAY MINERALS

The system of cation distribution over water molecule sites found in the abernathyite minerals may also exist in the interlayer structure of some of the clay minerals. Potassium, oxonium and ammonium ions, instead of entering in between the layers with a large hydration sphere of water molecules about them, may be randomly distributed over some of the water molecule positions of the interlayer framework. The layered silicates 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. From our knowledge of the chemical properties of the other Group IA elements (Ross and Evans, 1965) we predict that the lithium, sodium, rubidium, and cesium analogues of the expandable clay minerals also have the interlayer cations distributed over the water-molecule sites. If such a distribution does occur then the structural formula for the interlayer material may be written

$$[(H_2O)_{b-y}A_y]_n{}^{ny+}$$

where $A = Li^+$, Na^+, K^+, Rb^+, Cs^+, $NH_4{}^+$, and/or H_3O^+, and $(ny+)$ is the charge required to balance that on the $2:1$ layer. The entire clay-water system may be represented by the structural formula $[(A^{2+},B^{3+})_{2-3}(Si,Al)_4O_{10} (OH)_2]_n{}^{ny-}[(H_2O)_{b-y}A_y{}^+]_n{}^{ny+}$.

The role of Group IIA cations in the structural scheme of the clay minerals is probably much more complicated, particularly in the moderate to high exchange capacity clays, than that of the monovalent ions. Some clay minerals, however, appear to exchange monovalent with divalent cations readily

without affecting the interlayer spacing appreciably. Thus it may be inferred that Group IIA cations under some circumstances can also be randomly distributed over water-molecule sites.

A possible single-layer interlaminar structure for the clay minerals, based on a distortion of the ice-I model, is shown in Fig. 4. The good fit of the $(Si_2O_5)_n{}^{2n-}$ sheet of a layer silicate upon the water layer, represented as linked OH_4 tetrahedra, is apparent. The projected H_2O—H_2O bond distances of heavy ice-I are 2.60 and 2.61 Å (Peterson and Levy, 1957) which are close in value to the average O—O bond distances found in the SiO_4 tetrahedra of the micas. The hexagonal layer of water molecules is idealized in Fig. 4 as having the composition $(O_2H_5)_n{}^{n+}$ (Fig. 2). The predicted composition of such a layer is $[(H_2O)_{b-y}A_y{}^{z+}]_n{}^{nyz+}$, A being the Group IA or IIA interlayer cations. Some of the apical protons of Fig. 4 must thus be randomly missing and certain of the H_2O molecules randomly replaced by monovalent or divalent cations.

The proposed random distribution of cations over water-molecule sites gives us an extremely flexible structural scheme capable of accommodating a variable number and different kinds of interlayer cations without affecting to any appreciable extent the interlayer framework. It is thus possible for clay minerals with widely varying cation exchange capacities to have nearly identical interlayer structures—only the number of cations replacing water molecules differing.

Although a model related to the ice-I structure appears to be a plausible one for the interlaminar structure of the clay minerals, particularly because the layer silicates possess pseudohexagonal symmetry to which an extended hexagonal net of H_2O molecules could readily adapt, there are certainly many other possible arrangements. In the clay minerals that absorb more than one layer of water molecules the interlayer framework may be structurally related to one of the other silica polymorphs, such as cristobalite, keatite, quartz or coesite; or to one of the other forms of ice such as ice-III (Kamb and Datta, 1960) or ice-II (Crute and Calvert, 1964). These other possible interlayer structures are all based on three-dimensional four-connected nets as described by Wells (1954) for various hydrogen bonded structures.

REFERENCES

BARNES, W. H. (1929) The crystal structure of ice between 0°C and −183°C, *Proc. Roy. Soc. (London)* A **125**, 670–93.

BEINTEMA, J. (1938) On the composition and the crystallography of autunite and the meta-autunites, *Rec. trav. chim.* **57**, 155–75.

BERNAL, J. D., and FOWLER, R. H. (1933) A theory of water and ionic solution, with particular reference to hydrogen and hydroxyl ions, *J. Chem. Phys.* **1**, 515–48.

BRADY, G. W., and KRAUSE, J. T. (1957) Structure of solutions, I, *J. Chem. Phys.* **27**, 304–8.

BUSLAEVA, M. N., and SAMOILOV, O. YA. (1961) Coordination numbers of certain ions in aqueous solutions, and effect of temperature on them, *J. Structural Chem.* **2**, 510–15.

CRUTE, M. B., and CALVERT, L. D. (1964) The crystal structure of ice-II, *American Crystallographic Association, Program and Abstracts*, Ann. Meet., p. 65.

HENDRICKS, S. B., and JEFFERSON, M. E. (1938) Structures of kaolin and talc-pyrophyllite hydrates and their bearing on water sorption of the clays, *Am. Mineralogist* **23**, 863–75.

KAMB, W. B., and DATTA, S. K. (1960) Crystal structures of the high-pressure forms of ice, Ice III, *Nature* **187**, 140–1.

MACEY, H. H. (1942) Clay-water relationships and the internal mechanism of drying, *Trans. Brit. Ceram. Soc.* **41**, 73–121.

PETERSON, S. W., and LEVY, H. A. (1957) A single-crystal neutron diffraction study of heavy ice, *Acta Cryst.* **10**, 70–6.

ROSS, M., and EVANS, H. T., JR. (1964) Studies of the torbernite minerals (I). The crystal structure of abernathyite and the structurally related compounds $NH_4(UO_2AsO_4) \cdot 3H_2O$ and $K(H_3O)(UO_2AsO_4)_2 \cdot 6H_2O$, *Am. Mineralogist.* **49**, 1578–1602.

ROSS, M., and EVANS, H. T., JR. (1965) Studies of the torbernite minerals, (III), Role of the interlayer oxonium, potassium, and ammonium ions, and water molecules, *Am. Mineralogist.* **50**, 1–12.

WELLS, A. F. (1954) The geometrical basis of crystal chemistry, Parts 1, 2, 3, 4, *Acta Cryst.* **7**, 536–44, 545–54, 842–8, 849–53.

6