STRUCTURES OF KAOLIN AND TALC-PYROPHYLLITE HYDRATES AND THEIR BEARING ON WATER SORPTION OF THE CLAYS

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Clays as constituents of soils are of great interest in their influence on texture, water retention, and distribution of soil solutions. These properties are probably determined by the peculiar sorption of water by clays which is but little understood, although it must depend upon the structures of the constituent minerals. Increased knowledge of the crystal structures of minerals related to the micas now permits a first study of the problem.

Interest in montmorillonite as a constituent of many clays has focused attention upon its imbibition of water. Both it and the vermiculites are hydrates of pyrophyllite- or talc-like minerals in which water molecules are present between alumino-silicate layers. Hydrated halloysite seems to have a similar relationship to the kaolin structure. In the following work hypotheses are advanced to account for the structures of these hydrates and their bearing on the water sorption of the clay minerals.

STRUCTURE OF WATER LAYERS

Pauling[1] showed that a number of silicate minerals having micaceous cleavage possess the common structural element of tetrahedral SiO_4 groups joined by the sharing of oxygen ions at tetrahedron corners, into an extended hexagonal net having the composition $(Si_2O_5)_n$. These layers are combined with octahedral groupings of oxygen ions, common to SiO_4 groups, and hydroxyl ions about Mg^{+2}, Al^{+3}, and Fe^{+3} to form multiple layers, such as are found in pyrophyllites, talc, micas, and kaolin minerals. In chlorites[2] the multiple $((OH)_2Mg_3Si_4O_{10})_n$ layers of the talc structure are interleaved with neutral brucite layers, $Mg(OH)_2$, formed by octahedral coordination of hydroxyl ions about Mg^{+2}.[3]

It is here proposed that the hydrates of the silicate layer minerals related to the micas contain layers of water molecules joined into hexagonal groups of an extended hexagonal net. A layer of this type is shown

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[1] Pauling, L., *Proc. Nat. Acad. Sci.*, vol. **16**, pp. 578–582, 123–129, 1930.

[2] McMurchy, R. C., *Zeits. Krist.*, vol. **88**, pp. 420–432, 1934.

[3] For a general discussion of the compositions and structures as well as drawings representing the structures of these minerals see W. L. Bragg, Atomic Structure of Minerals, pp. 203–229, *New York*, **1937.**

in projection in Fig. 1. Its stability arises from the attraction between hydrogen atoms of water molecules and neighboring oxygen ions of the silicate layers, or oxygen atoms of other water molecules in the net.[4] The arrangement is partially a result of a tetrahedral distribution of charge about a water molecule; two corners of the tetrahedron being occupied by hydrogen atoms and the other two corners by an excess of electrons.[5] In the language of Bernal and Megaw, each side of the hexagon of Fig. 1 must correspond to a hydroxyl bond, the hydrogen-oxygen bond of one water molecule being directed toward the negative charge of a neighboring molecule. Since there are $3n/2$ sides for a net of n water molecules having $2n$ hydrogen atoms, one fourth the hydrogen atoms or hydrogen atoms of half the water molecules are not involved in binding within the net. These hydrogen atoms indicated at K, M, and O of Fig. 1 join the net to oxygen ions in the top of the neighboring silicate layer.

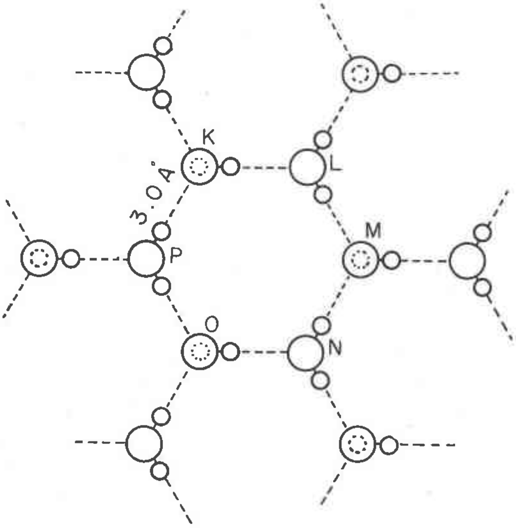

FIG. 1. Hexagonal net of water molecules. In this and the following figures large spheres represent oxygen atoms and small spheres hydrogen atoms; dotted lines indicate bonding through hydrogen.

The distribution of hydrogen atoms along the sides of hexagons shown

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[4] The general discussion of the role of hydrogen in crystal structure as presented by Bernal, J. D., and Megaw, H. D., *Proc. Roy. Soc. (London)*, vol. **A 151**, pp. 384–420, 1935, is applicable to this work.

[5] The tetrahedral character of the water molecule has been discussed by Bernal, J. D., and Fowler, A. H., *Jour. Chem. Phys.*, vol. **1**, pp. 515–548, 1933.

in Fig. 1 is but one of many possible arrangements. In it the hydrogen atoms can be in positions required by space group *Cm* or *Cc* without increasing the size of the unit of structure required by the silicate framework. If the separation of the oxygen atoms of the water molecules is about 3.0Å in projection, then the net has just the *a* and *b* dimensions of the silicate layer minerals. This distance is somewhat greater than 2.74Å, the separation of oxygen atoms in ice.

A similar hexagonal arrangement of water molecules is present in acetaldehyde-ammonia,[6] $CH_3COH \cdot NH_3$, which is a hydrate, $(CH_3 \cdot CHN)_3 \cdot 3H_2O$. In this compound the separation of the water molecules is 3.0Å. Six water molecules forming a hexagon in projection do not lie in one plane but so alternate with the symmetry of the point group $\bar{3}$ as to preserve a regular tetrahedral distribution of bonds to oxygen atoms. Boric acid[7] also contains similar hexagonal rings formed by six (OH) groups, the separation of the oxygen atoms being 2.71Å. In boric acid, however, the proton might be equidistant from two oxygen ions.

In the remainder of the work it will be assumed that the oxygen atoms are in one plane, there being considerable evidence in favor of such an assumption. Displacement from a plane similar to that of $(CH_3 \cdot CHN)_3 \cdot 3H_2O$, would increase the separation of the oxygen atoms, which already are rather far apart, for binding through hydrogen. Even though the oxygen atoms are coplanar the hydrogen atoms of the hexagonal net need not be in the plane of the oxygen atoms but rather are displaced from it.

ARRANGEMENT OF WATER MOLECULES IN VERMICULITES AND WATER SORPTION ON THE SURFACES OF CLAY MINERALS

The atomic arrangement parallel to the micaceous cleavage, (00*l*), of vermiculite as derived in the preceding paper is shown in Fig. 2. In agreement with Gruner[8] it was found that the structure is formed of talc-like multiple layers with water molecules between the layers. Analyses, as listed by Gruner, indicate that eight water molecules at the maximum must be fitted into the space in the unit of structure between the silicate layers. This corresponds to two layers of four molecules each, which is the number required by the arrangement shown in Fig. 1. Moreover, the Fourier analysis of the (00*l*) reflections indicates that the oxygen atoms of the water molecules are probably coplanar.

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[6] Moerman, N. F., *Zeits. Krist.*, vol. **98**, pp. 447–455, 1938.

[7] Zachariasen, W. H., *Zeits. Krist.*, vol. **88**, pp. 150–161, 1934.

[8] Gruner, J. W., *Am. Mineral.*, vol. **19**, pp. 557–575, 1934.

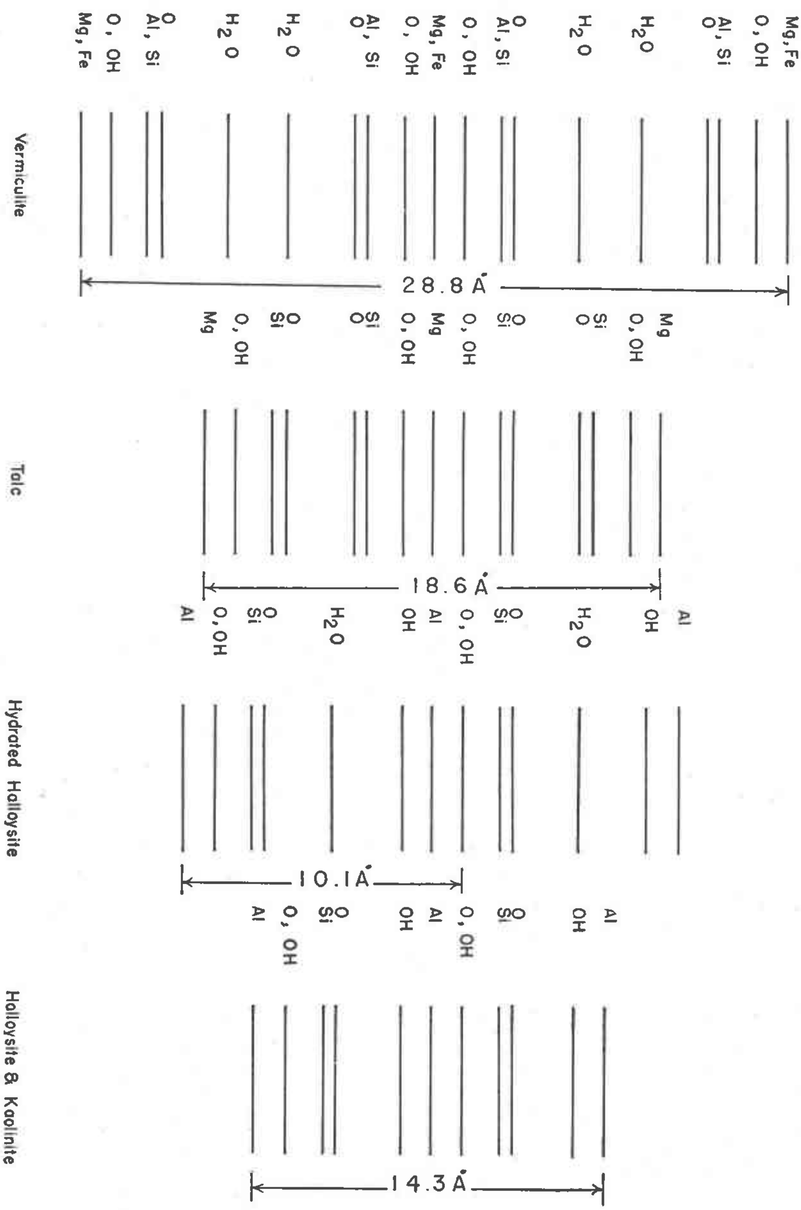

FIG. 2. Atomic arrangement parallel to (001) in some of the minerals related to the clays.

A possible manner of superimposing the net of water molecules upon the talc-like alumino-silicate layers of vermiculite is shown in Fig. 3. The exact manner of doing this was not found in the preceding work since it was possible to explain approximately the intensities of reflections without considering water molecules. However, absence of (*hkl*) reflections with *l* odd and *k* a multiple of three lends further support to the hexagonal framework structure in that it too would require them to be absent. A third of the oxygen ions in the top of a talc layer, or one crystallographically equivalent set, have neighboring water molecules. Superposition of the water molecules upon oxygen ions at *B* or *C* gives equivalent structures as far as the oxygen ions are concerned, and the actual structure might be one in which these three methods of superposition are randomly mixed.

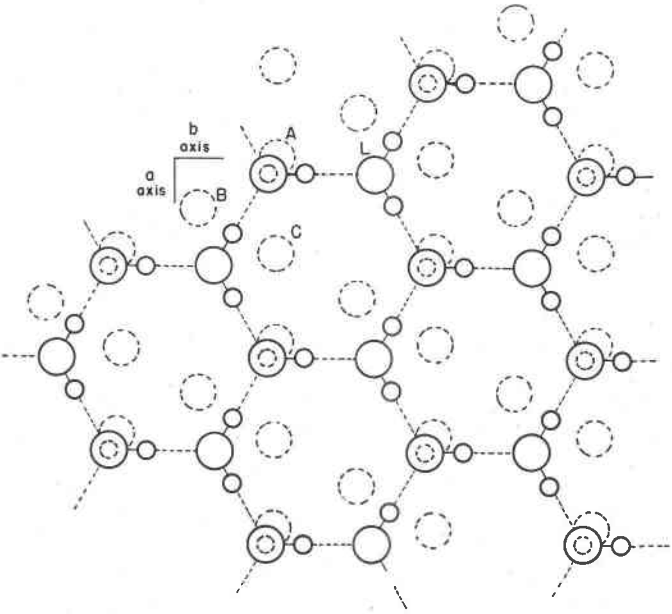

FIG. 3. Combination of water and vermiculite layers by binding through hydrogen. The oxygen atoms represented by large dotted circles are 2.73Å below the plane of the water molecules.

Water molecules would be expected to form similar layers on the surfaces of clay minerals, and could be held in other layers after the manner of Fig. 4. It is for this structural reason that water is unique in many sorptive properties of the clays, such as swelling of montmorillonite. Other hydroxylic compounds would, by the same binding, be expected to show preferential adsorption on surfaces containing oxygen ions. However, the adsorbed layer, in general, would not be expected to have a regular transverse structure.

In general, the same forces causing condensation of a vapor to a liquid are responsible for multimolecular adsorption[9] on the surface of a solid, and thus such layers appear to a considerable extent only near the saturation pressure. Expressed in another manner, a second layer of adsorbed nitrogen on the surface of mica is held by approximately the same forces as the surface layer of liquid nitrogen.

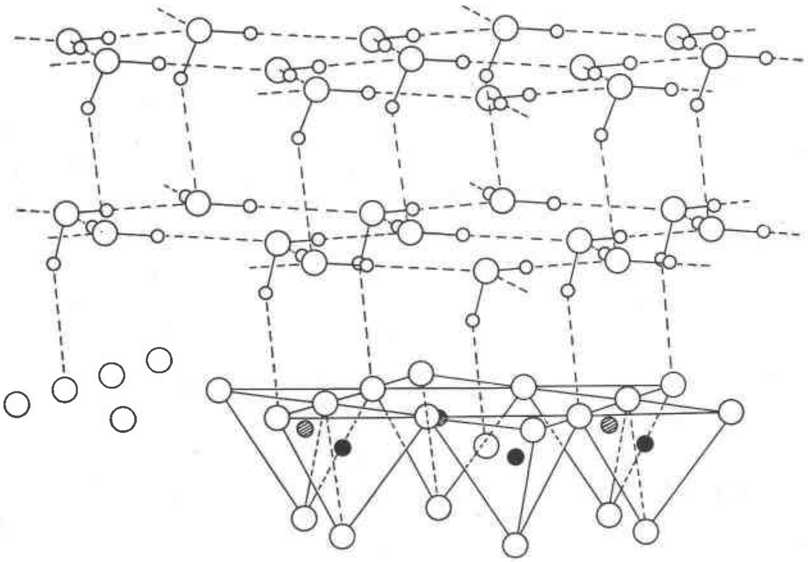

FIG. 4. Probable structure of multiple water layers on the surfaces of clays. Small black or shaded circles represent silicon atoms.

A network of water molecules like that of Fig. 1 would not be the stable configuration in liquid water where tetrahedral coordination is satisfied in other ways. However, if some force establishes such a structure, it in turn would be expected to cause surrounding molecules to take up the same structure. Formation of this type of layer at less than saturation pressures on the surfaces of silicate layer minerals shows that it is the more stable surface configuration. Stability of the layer arises from its geometrical relationship to oxygen ions of the silicate framework, after the manner of Fig. 3. Presence of the first layer still favors

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[9] Brunauer, S., Emmett, P. H., and Teller, E., *Jour. Am. Chem. Soc.*, vol. **60**, pp. 309–319, 1938.

formation of a second, and the structure is thus propagated away from the surface. The dissociation pressure of successive layers considered as hydrates would finally approach the vapor pressure of water at the temperature of observation.

Both layers of water molecules between two talc-like layers of vermiculite would be expected to have similar relationships to oxygen ions of neighboring silicate layers. However, sufficient doubt exists about the details of the arrangement to leave considerable freedom in the choice of relative positions of water molecules in the two layers. For this reason the remainder of the drawings are merely schematic, indicating the type of bonding expected.

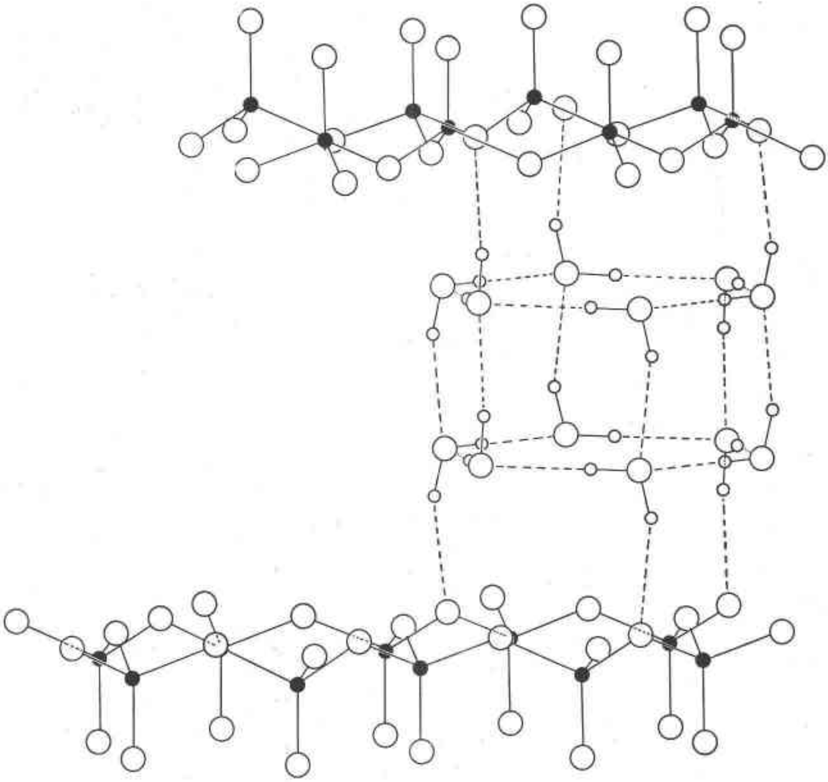

FIG. 5. Combined water layers in partially dehydrated vermiculite.

Gruner showed that as much as one half of the water can be driven off without changing the structure of vermiculite and that the water content is seldom as high as sixteen molecules for the unit of structure. The hexagonal nets of water molecules thus are not complete and as a consequence hydrogen atoms are free for binding between the water layers. Even for complete layers there is probably some interlayer binding by hydrogen atoms of water molecules such as *L* of Figs. 1 and 3. Water molecules of separate layers, therefore, might be expected to pack together, preserving tetrahderal coordination.

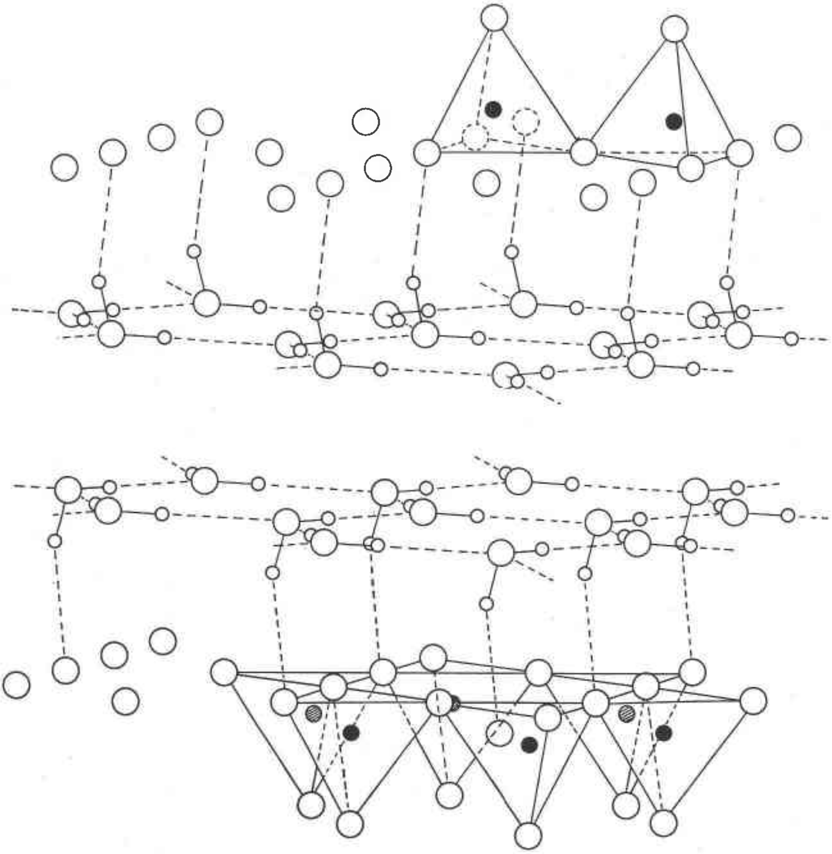

FIG. 6. A portion of the vermiculite structure showing layers of water molecules.

A vermiculite containing only 8 water molecules in the unit of structure according to these concepts would have the schematic structure shown in Fig. 5. The energy of binding between the talc layers would be expected to be greater than that of completely hydrated vermiculite shown in Fig. 6, since there is the same number of bonds to each water molecule but more bonds between the water layers.

ARRANGEMENT OF WATER MOLECULES IN HYDRATED HALLOYSITE

Hydrated halloysite has been shown to have the composition $Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$[10] and to be formed by superposition of neutral $((OH)_4Si_2Al_2O_5)_n$ layers, as present in the kaolin minerals, and layers of water molecules.[11] Its relationship to kaolin is somewhat analogous to that between vermiculite and talc. However, it differs in that there is only one layer of water molecules between the alumino-silicate layers corresponding to four water molecules in the unit of structure. Water molecules present in the layers can be expelled by drying at 50° and the mineral has not yet been rehydrated in the laboratory.[10,12]

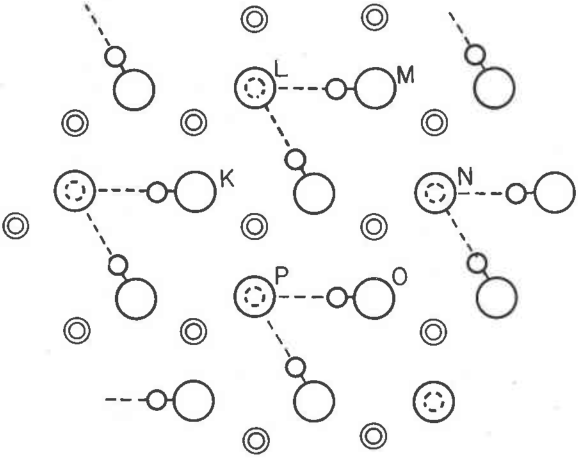

FIG. 7. The probable type of binding between hydroxyl groups in the $((OH)_4Al_2Si_2O_5)n$ layers of the kaolin minerals. Aluminum atoms, shown by double circles, are about 1.1Å above the plane of the hydroxyl groups.

The arrangement of oxygen ions in one side of a kaolin layer is the same as in the top of a talc layer; thus the structures shown in Figs. 1, 3, and 4 hold equally well for halloysite. The other side of a kaolin layer, however, contains only hydroxyl groups, and these in part are free for binding through hydrogen to oxygen atoms in the water layer. Part of the hydroxyl groups are involved in binding within the alumino-silicate layer, probably in a manner similar to that described for hydrargillite by Bernal and Megaw (*loc. cit.*). The principle of the arrangement is that hydrogen atoms should be as far as possible from aluminum ions consistent with the requirements of binding to other hydroxyl

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[10] Hofmann, U., Endell, K., and Wilm, D., *Angew. Chem.*, vol. **47**, p. 539, 1934.

[11] Hendricks, S. B., *Am. Mineral.*, vol. **23**, pp. 295–301, 1938.

[12] Note Mehmel, M., *Fort. d. Mineral., Krist., u. Petro.*, vol. **21**, p. 80, 1937; *Chemie d. Erde*, vol. **11**, p. 1, 1937.

groups. This is accomplished for a kaolin layer after the manner shown in Fig. 7.

Hydrogen atoms of hydroxyl groups at *L*, *N*, and *P* of Fig. 7 are free for binding to oxygen atoms *L*, *N*, and *P* of water molecules in a layer of the type shown in Fig. 1. Each water molecule of the layer would be bound through hydrogen to four other oxygen atoms. The complete structure is schematically shown in Fig. 8.

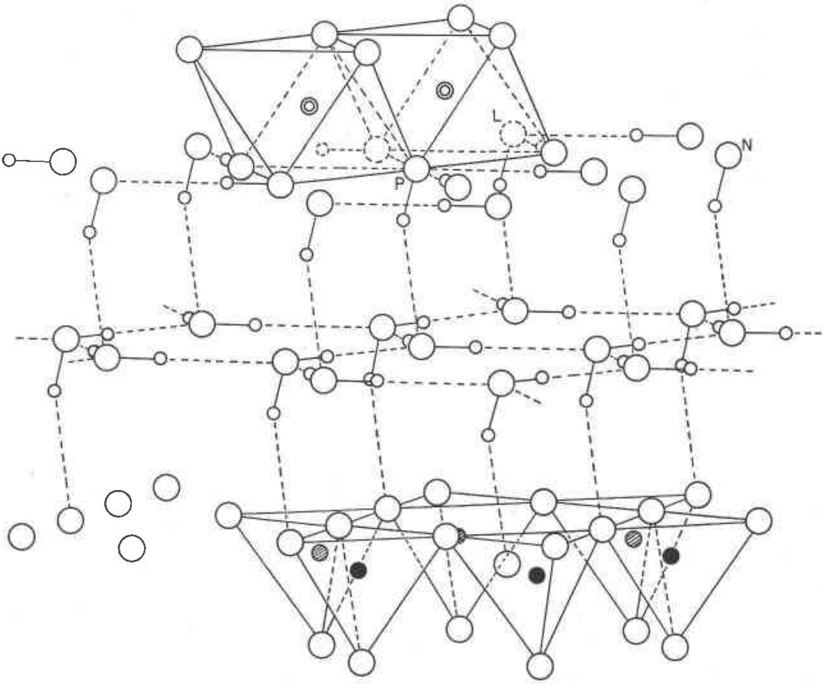

FIG. 8. A portion of the hydrated halloysite structure showing a single layer of water molecules.

Possibility of binding through the hydroxyl ions is apparently the factor that limits the water molecules to a single layer. If these are expelled by heating, the structure collapses to the ordinary type found for the kaolin minerals in which the hydroxyl groups give binding directly to oxygen ions of the adjacent alumino-silicate layer. This structure would probably be more stable than that of the hydrate since the heat of formation of each hydroxyl bond would be expected to exceed that of a bond formed by hydrogen atoms of a water molecule, being more ionic in character. Ease of dehydration and failure of reversible hydration thus are quite reasonable.

HYDRATION OF MONTMORILLONITE

Much attention has been devoted to the swelling of montmorillonite. Hofmann, Endell, and Wilm[13] were the first to show that the imbibition of water is accompanied by an increase in the (001) spacing. They studied the change of spacing with water content and advanced the explanation that molecules are introduced between the talc-pyrophyllite layers. Maegdefrau and Hofmann[14] have studied the structure of montmorillonite in more detail and have concluded that the spacing varies continuously as a function of water content. A similar conclusion was reached by Nagelschmidt.[15] Bradley, Grim, and Clark[16] on the other hand found evidence for definite hydrates corresponding to certain (001) spacings. All of these workers agree that the water content approaches the amount required for close packing, which is six molecules for each layer in the unit of structure.

There are many difficulties in accepting these interpretations. Montmorillonite cyrstals are very thin and have a great amount of surface for water sorption. The analyses thus cannot give the amount of water between the layers. This is particularly true for the more hydrous specimens that can only be prepared by drying wet samples. Moreover, no hydrate structure has yet been found in which water molecules have close packed arrangements.

Even though some of the x-ray measurements seem to indicate that the separation of talc-pyrophyllite layers varies continuously with water content, closer analysis shows that this is neither required, nor in fact probable. Consider the diffraction of a parallel beam of radiation from a random stacking of plates.[17] The wave motion at P, Fig. 9, is given by

$$E_p=\frac{E_0Fe^2}{m_0\rho c^2}\left[\sum_m \exp.\,[2\pi i/\lambda][m\bar{d}+\bar{w}_m]\cdot[\bar{S}-\bar{S}_0]\right]\exp\,[2\pi i/\lambda]\,[ct-\rho]$$

where F is the structure for the plane and $[m\bar{d}+\bar{w}_m]\cdot[\bar{S}-\bar{S}_0]$ gives the path difference for rays scattered from various planes. The amplitude of the scattered wave will be:

$$E\sim\sum_m \exp\,[2\pi i/\lambda]\,[m\bar{d}+\bar{w}_m]\cdot[\bar{S}-\bar{S}_0]$$

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[13] *Zeits. Krist.*, vol. **86,** pp. 340–348, 1933.

[14] *Zeits. Krist.*, vol. **98,** pp. 299–324, 1937.

[15] *Zeits. Krist.*, vol. **93,** pp. 481–487, 1936.

[16] *Zeits. Krist.*, vol. **97,** pp. 216–222, 1937.

[17] The treatment given here is based upon that of Compton, A. H., and Allison, S. K., X-Rays in Theory and Experiment, p. 406 ff., *New York,* **1935.**

and the intensity:

$$I \sim \left[\sum_m \cos\frac{2\pi}{\lambda}[m\bar{d}+\bar{w}_m]\cdot[\bar{S}-\bar{S}_0]\right]^2 + \left[\sum_m \sin\frac{2\pi}{\lambda}[m\bar{d}+\bar{w}_m]\cdot[\bar{S}-\bar{S}_0]\right]^2$$

If the crystal is thick and the separations of the planes have a random variation, then the observed spacing would be near the average value, $d+w_m/m$. A second case is a restricted lattice, say of the order of ten layers thick, but with random distribution within a number of lattices.

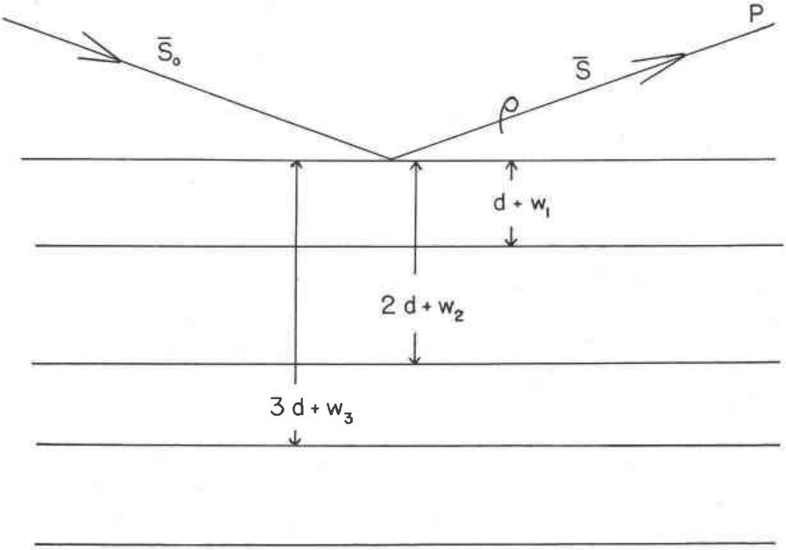

FIG. 9. *X*-ray diffraction from a random stacking of planes.

Again the average value will be observed but the reflections will be broader since they will be formed by summation of intensities from separate lattices.

That reflection will be sharp for which $w_m/\lambda\cdot[\bar{S}-\bar{S}_0]$ is any integer. Thus with montmorillonite there is always one high order of reflection present, (003) to (007), depending upon the hydration, with a spacing of about 3.0Å, which is usually sharp and intense. This is just the expected additional spacing required for a layer of water molecules. The reflection would appear sharp even though the number of layers of water molecules varied within a crystal giving some intermediate apparent spacing.

High order interference maxima would not be obtained for a lattice of this type and this is observed to be the case for montmorillonite. The situation is quite analogous to a solid solution between two hydrocarbons such as $C_{29}H_{60}$ and $C_{31}H_{64}$[18] which give an average spacing, but very few orders of reflection from (001) as compared with the pure hydrocarbons.

It thus is not inconsistent with any of the experimental data so far obtained for water molecules in montmorillonite to be present in layers of the type shown in Fig. 1. The structure is similar to that of vermiculite, Fig. 6, except that additional water layers can be reversibly added between the talc-pyrophyllite layers. This difference in behavior is partially a result of the very small particle size of montmorillonite which makes the total cohesive force per layer sufficiently small as to be overcome by molecular forces. A prosaic analogy would be the comparative ease of splitting a shingle as compared with a log. However, it also probably depends upon the presence of ions external to the talc-pyrophyllite layers that account for the base exchange of the mineral.

SUMMARY

Vermiculites, montmorillonite, and hydrated halloysite contain layers of water molecules joined into extended hexagonal nets of the type shown in Fig. 1. The peculiar water sorptive properties of clays are considered to arise from the formation of successive layers of this type over the surfaces.

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[18] Piper, S. H., Chibnall, A. C., Hopkins, S. J., Pollard, H., Smith, J. A. B., and Williams, E. F., *Biochemical Journal*, vol. **25**, p. 2084, 1931.