American Mineralogist, Volume 58, pages 471–479, 1973

Hydroxyl Orientation in Kaolinite, Dickite, and Nacrite

R. F. GIESE, JR. AND P. DATTA

Department of Geological Sciences, State University of New York at Buffalo,
P. O. Box U, Station B, Buffalo, New York

Abstract

The orientations of the hydoxyl groups in the minerals kaolinite, dickite and nacrite have been determined by an iterative process based on the minimization of the total electrostatic energy of the respective crystal structures. The hydroxyl shared by the tetrahedral and octahedral sheets is directed toward the empty octahedral sites in all three structures. The remaining three hydroxyls which form the surface of the octahedral sheet are nearly normal to the layer in dickite, two are nearly normal, and one is inclined at an angle of 38° to the kaolin layer in nacrite, and in kaolinite two are nearly normal and the third is inclined at an angle of 14° to the layer. In each mineral, the hydroxyls forming the surface of the octahedral sheet are directed away from the kaolin layer.

Introduction

The general principles of the crystal structures of the kaolin minerals ($Al_2Si_2O_5(OH)_4$) kaolinite, dickite, and nacrite have been known for some time (Brindley and Robinson, 1946; Newnham and Brindley, 1956; Hendricks, 1938). Recent refinements of the structures of kaolinite (Zvyagin, 1967; Drits and Kashaev, 1960), dickite (Newnham, 1961), and nacrite (Blount *et al*, 1969) show substantial differences in detail from the original descriptions. None of these studies provided direct information about the positions of the hydrogen atoms in the structures.

The kaolin layer consists of a tetrahedral sheet with silicon filling the tetrahedral sites and an octahedral sheet with aluminum filling two thirds of the octahedral sites. These two sheets share a common plane of oxygen/hydroxyl atoms. Of the four hydroxyls in the formula, one is in this shared plane of atoms and will be designated in this paper as the *inner hydroxyl.* The remaining three form the outer surface of the octahedral sheet and are designated *inner surface hydroxyls* as distinct from hydroxyls on the surface of the clay crystal. All the kaolin minerals contain this layer, but the manner in which the layers are stacked differs for each. Hendricks (1938) noted the importance of the juxtaposition of the basal oxygen atoms of the silica tetrahedra in one layer and the hydroxyl oxygen atoms of the aluminum octahedra in the next layer. The distances for the three O—OH contacts between layers in the kaolin minerals (Table 1) reveal two distinct types of oxygen-hydroxyl distances: one group less than 3.0 Å and the other group greater than 3.0 Å. The observation of the close proximity between OH and O of neighboring layers had led to the proposal that there is a long hydrogen bond between each interlayer hydroxyl and the corresponding basal oxygen in the next layer (Newnham, 1961; Grim, 1968; Farmer, 1964; Farmer and Russell, 1964). The alternate view that some of the interlayer hydroxyls are involved in long hydrogen bonds and some are not has also been proposed (Wada, 1967; Ledoux and White, 1964a; Serratosa *et al,* 1962, 1963; Wolff, 1963). The location of the inner hydroxyl hydrogen is also uncertain. On the basis of infrared absorption data, Serratosa *et al* (1962, 1963) and Wolff (1963) conclude that the inner OH is perpendicular to the kaolin layer in kaolinite and is directed toward the opening in the tetrahedral sheet which is formed by a ring of six tetrahedra. Ledoux and White (1964a) propose an orientation toward the empty octahedral site.

The disagreement regarding the orientation of hydroxyls in the kaolin minerals indicates the difficulty involved in interpreting infrared absorption spectra and suggests that a different approach might be more fruitful. It has been shown that the orientation of the hydrogen atoms of water molecules is such that the electrostatic energy of the crystal is minimized (Baur, 1965; Ladd, 1968). This has been extended to the orientation of hydroxyls in simple compounds

TABLE 1. Oxygen—(Hydroxyl) Oxygen Distances between Kaolin Layers

mineral	O - O(H)	distance	reference
kaolinite	O(1)* - O(8)	2.90A	Zvyagin (1967)
	O(2) - O(9)	2.89	
	O(3) - O(7)	3.02	
dickite	O(2) - O(1)	2.95	Newnham (1961)
	O(3) - O(3)	3.10	
	O(4) - O(2)	2.97	
nacrite	O(2) - O(1)	3.06	Blount et al (1969)
	O(3) - O(2)	2.97	
	O(4) - O(3)	2.98	

*hydroxyl oxygen atoms

such as diaspore, AlOOH, and goethite, FeOOH (Giese *et al,* 1971) and complex silicates such as muscovite (Giese, 1971). This technique of locating hydroxyl hydrogens by minimization of the electrostatic energy has been applied to the kaolin minerals and the results are reported here.

Method

If the atomic positional parameters of an ionic compound are known, then the electrostatic energy is obtained from the relation (Sherman, 1932)

$$\phi = -\frac{e^2}{2}\sum_{i=1}^{N}\sum_{j=1}^{\infty}\frac{Z_iZ_j}{r_{ij}} \qquad (1)$$

where e is the charge on the electron, Z is the ionic charge, N is the number of atoms in the unit cell, and r is the interatomic distance. A more rapidly converging algorithm has been described by Bertaut (1952) and programmed for digital computer by Baur (1965). We have used a modification of this program.

In using equation (1) we assume that 1) the non hydrogen ion positional parameters are correct; 2) the ions have full charge; 3) the hydroxyl oxygens have been correctly identified; and 4) the O-H distances are known. There is no question about which oxygens are the hydroxyl oxygens and, for the purposes of this study, the O-H distance is held fixed at 0.97A. The positional parameters for nacrite are from Blount *et al.* (1969), those for dickite are from Newnham (1961) with reference to the new unit cell of Bailey (1963), and those for kaolinite are from Zvyagin (1967).

In a situation where the positional parameters of the non-hydrogen atoms but not the hydrogen atoms are known, the electrostatic energy (Eq. 1) consists of three types of terms. These terms result from 1) pairs of ions where both have known positional parameters, 2) pairs where both have unknown positional parameters, and 3) pairs where one ion is known and the other is not.

The location of the hydrogen ions involves location of the minimum of ϕ as a function of the hydrogen ion positional parameters. Since the O-H distance is fixed, as is the position of the oxygen, the variation of the positional parameters is best done in terms of spherical coordinates. For each hydroxyl oxygen ion, a reference axis is established which goes through the oxygen ion and is approximately perpendicular to the clay layers. This direction (Fig. 1) is then used as an axis for the generation of a cone of half angle α. The program computes hydrogen atom positions which lie on the specified cone at 0.97 Å distance from the oxygen ion. The number and spacing between points on the cone as well as the cone angle may be varied and the energy for each point can be calculated. The "correct" orientation for the OH is the minimum and is obtained by interpolation. If the crystal structure has only one hydroxyl hydrogen in the asymmetric part of the unit cell, such as in $2M_1$ muscovite, the electrostatic energy ϕ consists predominantly of type 1 terms with a smaller contribution from type 3 and smaller still from type 2. As ϕ approaches the minimum (by varying the hydroxyl hydrogen ion position), the terms of types 2 and 3 also approach the correct values and the procedure is complete once the minimum is found.

For the kaolin minerals where there are four hydrogen ions in the asymmetric part of the unit cell, the initial set of seventeen atoms consists of positions for thirteen non hydrogen atoms and four "guesses" for the hydrogen atoms. For each hydrogen the previously described procedure will yield a "minimum" which is a better approximation than the original guess but is not correct since ϕ contains terms of the second and third types which are still inaccurate because they involve hydrogens not yet refined. But if the procedure is repeated, the values for the positional parameters of the four hydrogen atoms will converge to the correct ones. This iterative approach, in practice, is terminated when shifts in the positional parameters of the hydrogen atoms are less than the standard deviations of the known heavier atoms. In the case of the kaolin minerals described here, four cycles were sufficient to locate the hydrogen atoms. The exact number depends to some extent on how correct the initial guesses are.

Results

The positional parameters for all the hydrogen atoms are listed in Table 2 along with the angles made by the OH bonds relative to the plane of the kaolin layer as well as the angle between the *b*-axis and the projection of the OH bond onto the kaolin layer. The interatomic distances and angles involving the hydrogen atoms are listed in Table 3.

Random errors in the heavy atoms positions produce approximate errors in the hydroxyl orientation determined by the electrostatic energy minimization process for dickite, nacrite, and kaolinite. To assess these approximate errors, one can look at change in OH orientation as a function of change in the fractional positional parameters of nearby atoms. Since the standard deviations in the fractional coordinates are similar for all three structures, only dickite has been examined in detail; the results should be directly applicable to nacrite and kaolinite. The computational procedure was to redetermine the OH orientation after changing one of the atomic positional parameters by one standard deviation as determined from the structure refinement process. Since, in dickite, all the inner surface hydroxyls have the same environment, the calculations were done for only one surface hydroxyl, O(4)—H(4), and the inner hydroxyl, O(1)—H(1). The influence of an atom on the electrostatic energy decreases with increasing interatomic distance, so that the calculation has to be done only for nearest neighbor ions of each type and the hydroxyl group itself. The results are shown in Table 4. The angular changes

TABLE 2. Fractional Positional Parameters for the Hydrogen Atoms in the Kaolin Minerals

Mineral	x	y	z	designation	b*	c**
Kaolinite	.273	.669	-.262	H(1)***	77	-83
	.727	.512	-.271	H(2)	77	132
	.853	.914	-.159	H(3)	14	-152
	.633	.594	.120	H(6)	14	30
Dickite	.678	.565	.174	H(1)	12	30
	.066	.496	.361	H(2)	76	-35
	.598	.315	.361	H(3)	69	174
	.079	.172	.359	H(4)	66	81
Nacrite	.707	.454	.172	H(1)	19	111
	.511	.710	.329	H(2)	38	-62
	.235	.662	.351	H(3)	79	3
	.408	.131	.349	H(4)	73	-162

* the angle between the kaolin layer and the O-H bond

** the angle between the projection of the O-H bond on the kaolin layer and the b axis. A negative sign indicates a counter-clock-wise rotation.

*** the number of hydrogen atoms corresponds to the number of the hydroxyl oxygen atom in the original structure description (see Table 1).

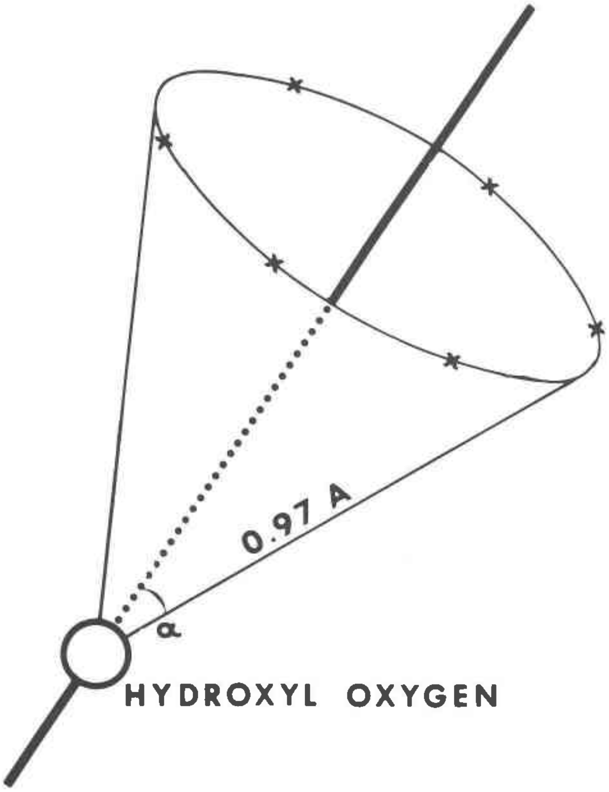

FIG. 1. The coordinate system used to find the electrostatic energy minimum for a hydroxyl group. The reference axis is arbitrarily chosen to be approximately normal to the kaolin layer and passes through the hydroxyl oxygen. By choosing various values for the angle α, the electrostatic energy may be computed for a number of possible hydrogen positions, designated by *x*'s, and the minimum is obtained by interpolation.

TABLE 3. Distances and Angles for the Interlayer Hydrogens in the Kaolin Minerals

kaolinite	O(1) - H(1) --- O(8)	173°
	H(1) - O(8)	1.93 A
	O(2) - H(2) --- O(9)	162
	H(2) - O(9)	1.95
	O(3) - H(3) --- O(7)	96°
	H(3) - O(7)	2.76
dickite	O(2) - H(2) --- O(1)	165°
	H(2) - O(1)	2.00 A
	O(3) - H(3) --- O(3)	170
	H(3) - O(3)	2.14
	O(4) - H(4) --- O(2)	163
	H(4) - O(2)	2.02
nacrite	O(2) - H(2) --- O(1)	109°
	H(2) - O(1)	2.60 A
	O(3) - H(3) --- O(2)	166
	H(3) - O(2)	2.02
	O(4) - H(4) --- O(3)	173°
	H(4) - O(3)	2.02

TABLE 4. Angular Changes in the OH Orientation in Dickite due to a Shift in the Fractional Positional Parameters (by one standard deviation) of Neighboring Ions.

Hydroxyl	$(Z_1Z_2)/r_{12}$ *	Atom	Shifted Parameter	Change Angular	Distance **
O(4) - H(4)	1.17 Å^{-1}	Al(1)	x	2.0°	0.003 Å
			y	2.5	0.005
			z	2.9	0.005
	1.32	Si(2)	x	2.0	0.002
			y	3.0	0.003
			z	2.0	0.006
	0.99	O(2)	x	3.0	0.003
			y	2.0	0.003
			z	2.9	0.014
	0.69	OH(2) - H(2)	x	2.0	0.001
			y	2.0	0.013
			z	2.0	0.005
	-	O(4) - H(4)	x	2.0	
			y	2.0	-
			z	2.0	
O(1) - H(1)	1.32	Al(2)	x	0.5	0.002
			y	0.6	0.008
			z	0.5	0.003
	1.26	Si(2)	x	0.5	0.005
			y	0.5	0.002
			z	0.5	0.006
	0.55	O(2)	x	0.5	0.007
			y	0.5	0.007
			z	0.6	0.009

* The contribution to eq. 1 of the hydroxyl hydrogen and the ion which is shifted.

** The change in the distance from the hydroxyl hydrogen to the ion which is shifted. In the case of O(2) - H(2), the distance is to O(2).

due to shifts in Al, Si and O are similar even though the charges on these ions are very different. To assess the relative influence of shifts in these ions on the orientation change of the hydroxyl, one can look at the contribution to equation (1) due to the interaction of each of these ions with the hydroxyl hydrogen. These values are listed in the first column of Table 4 and suggest that the relative influences of the standard deviation shifts of the nearest neighbor ions are approximately the same. The higher charged ions are at greater distances from the hydroxyl hydrogen than are the lower charged ions. The change in interionic distance between the hydroxyl hydrogen and the shifted ion is also a factor since this changes the denominator in equation (1) for the ion pair involved. The change in the interionic distance due to the shifts in the fractional coordinates of the nearest neighbors about the two hydroxyl hydrogens are listed in the last column of Table 4 and are approximately the same with a few exceptions. The large distance change due to the shift along the *c*-axis of O(2) has relatively less effect on the O(4)—H(4) orientation because the hydroxyl is oriented approximately along the *c*-axis in the same direction as the shift in O(2). Since the O-H distance is not varied during the computations, the orientation change is not as large as might be expected. Other apparent anomalies are not as readily explained, as for example the *x* and *y* shifts for O(2)—H(2). A change in the positional parameters of one ion changes not only the terms in equation (1) due to the shifted ion and the hydroxyl hydrogen pair but all terms which involve the shifted ion and these also contribute to moving the electrostatic energy minimum.

It is clear from Table 4 that the inner surface hydroxyls are more sensitive than the inner hydroxyl to small shifts in the neighboring atoms. The average angular change for the surface hydroxyls is 2.4°, which is sufficiently accurate to assure that the orientations are meaningful. The average change in the inner hydroxyl is 0.5° and is the same order of magnitude as the standard deviations for other bond angles in the structure.

Hydroxyl Orientation

Figure 2 is a projection of the dickite structure onto (001) showing the aluminum atoms, their coordinating inner surface hydroxyls, the silicon atoms in the next layer and their coordinating basal oxygen atoms. Al(1), its three hydroxyl oxygens, and the hydroxyl hydrogens H(2), H(3), and H(4) are centered in the large almost hexagonal opening in the base of the silica tetrahedra and the immediate environment of each of the hydroxyls is very similar; hence one would expect them to behave similarly, which they do. All three O-H bonds tilt slightly toward the empty octahedral site and, in fact, the small deviations from perpendicularity in view of the asymmetry of the dioctahedral layer cations are surprising.

A similar projection of kaolinite (Fig. 3) shows a less symmetrical arrangement. All three OH bonds still tilt in toward the empty octahedral site, two only slightly, H(2) and H(1), but the third H(3) is almost horizontal. A possible explanation for the different behavior of H(3) is that the stacking of kaolin layers is such that Si(1) in the next layer interferes with and repulses H(3). If the OH bond were to rotate toward O(7) in the plane bisecting Al(1) and Al(2) and containing O(3)—H(3), its distance to Si(1) and Si(2) in the next layer would decrease, which is not energetically desirable. If it were to rotate in the other direction, the distances to the aluminums would be shorter and this also is a

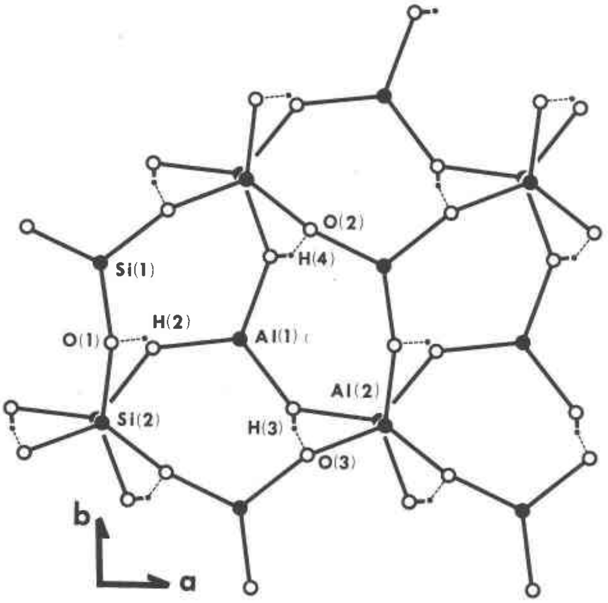

FIG. 2. The projection onto (001) of the aluminum ions, their coordinating hydroxyls, and the silicon ions in the next layer with their coordinating basal oxygen ions in the dickite structure. The open circles are oxygen ions, the larger solid circles are cations and the smaller solid circles are hydrogen ions. The dashed line represents the possible hydrogen bonds as explained in the text.

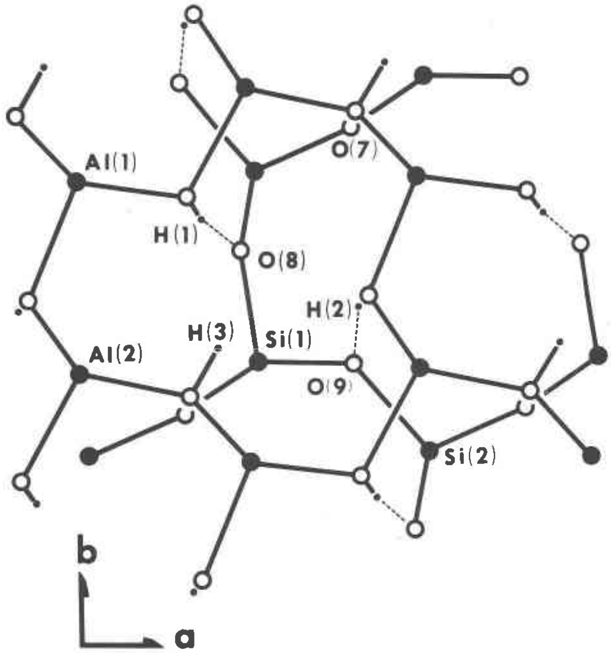

FIG. 3. A view of the kaolinite structure as in Figure 2.

less stable situation. It is also interesting to note that the O(3)—O(7) distance is the longest of the three interlayer distances.

A less clear cut case is that of nacrite (Fig. 4) where H(3) and H(4) are nearly vertical but tilted slightly toward the vacant octahedral site whereas H(2) is inclined to the kaolin layer by 38°. The environment of O(2) is very similar to O(3) in terms of placement of cations and anions with the exception that the O(3)—O(2) distance is 2.97Å while the O(2)—O(1) distance is 3.06Å. There is, therefore, a stronger attractive interaction between H(3) and O(2) than between H(2) and O(1). The origin of this longer distance for O(3)—O(1) lies in the buckling of the bases of the tetrahedral layer which raises O(1) above O(2) and O(3).

The inner hydroxyl in each structure is effectively isolated from influences due to stacking differences and, since the OH is directed toward a large opening in the structure, the distortions in the kaolin layers in the different structures will have relatively little effect on the OH orientation. If the OH vectors of

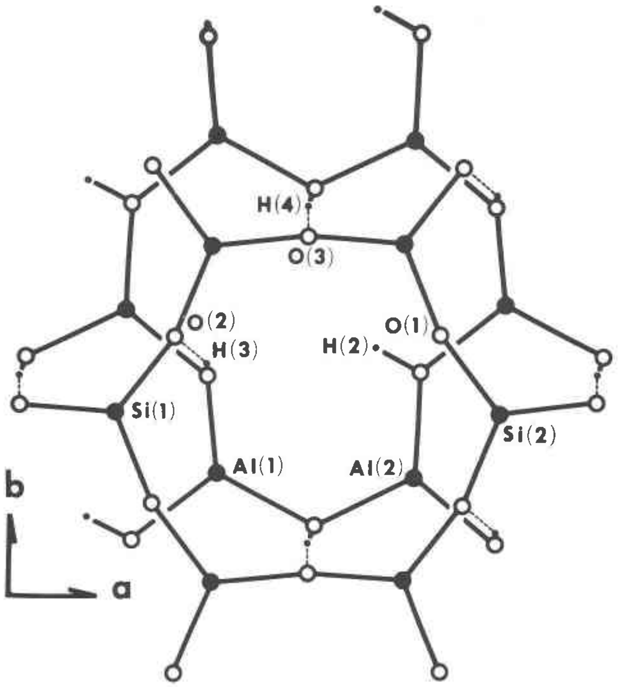

FIG. 4. A view of the nacrite structure as in Figure 2.

the three structures are plotted on a stereographic projection such that the inner hydroxyls point in the same sense and the octahedral layers are oriented similarly, an interesting pattern is evident. In Figure 5, a portion of the hydroxyl sheet of dickite is shown with the inner surface hydroxyls at the top of the octahedra (1, 2 and 4) and the oxygen-hydroxyl sheet below (3 is the inner hydroxyl at the bottom of the octahedra). The OH vectors for the hydroxyls in the three structures are shown in stereographic projection (Fig. 5, right) with the projected point being indicated by the lower case letter appropriate to the mineral and a number identifying the particular hydrogen. Hydroxyls 2, 3 and 4 plot closely together for the three structures. One would expect group 3 hydroxyls to be closely aligned because, as mentioned earlier, these are the inner hydroxyls and are relatively unperturbed by the structural differences between minerals. The closeness of groups 2 and 4 must indicate that these hydroxyls have approximately the same environment in all three structures and the differences in orientation in group 1 may be due to the differences in stacking and variations in hydroxyl-oxygen distances as indicated above.

There are differences in the distortions in the kaolin layer in the three minerals and in the stacking of the layers which perturb the orientations of the hydroxyls. These perturbations can be seen if one looks at the angles Al-O-H of which there are two for each hydroxyl. Hypothetically, one would expect that if there are no outside influences (hydrogen bonding would be one such influence), these two angles should be equal. The formation of a long hydrogen bond or the close approach of another cation would tend to make the angles unequal except in the rare circumstance when the perturbing ion is also symmetrically oriented. A plot of the two Al-O-H angles, one along the *x*-axis (arbitrarily the A1(1) angle) against the other, along the *y*-axis (arbitrarily the Al(2) angle) would show, if this simple picture is correct, the points due to the inner hydroxyls along a 45° line of equal angles. The points for oxygens which are involved in hydrogen bonds would tend to lie off this 45° line. Figure 6 shows this general picture is correct. The data points for inner hydroxyls all lie on or near the line, the inner surface hydroxyls of kaolinite and nacrite which are inclined to the layer surface are very close to the line, and the other inner surface hydroxyls which satisfy most closely the requirements for hydrogen bond formation tend to lie off the line with two of the dickite hydroxyls closest. This is not surprising in view of the symmetrical stacking arrangement in that structure (Fig. 2).

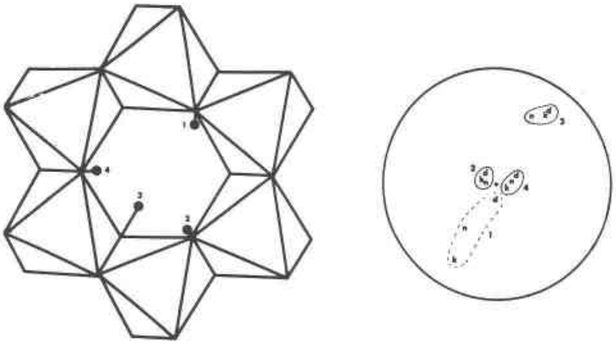

FIG. 5. A portion of the octahedral sheet in dickite is shown on the left with the inner surface hydroxyls on top. The hydroxyls are arbitrarily numbered. On the right is a stereographic projection of the OH bonds in all three kaolin minerals—each indicated by the first letter of the mineral name. Three of the hydroxyls form closely aligned groups (2, 3 and 4) and in the other group are the hydroxyls which have a different orientation in each of the minerals.

In summary, then, the hydroxyls of all three minerals tend to orient themselves in a similar sense, being influenced largely by the atoms in the same layer. The major differences among the structures is in one of the inner surface hydroxyls, the one which with the inner hydroxyl forms a shared edge in the octahedral sheet. The differences here appear to be due to 1) the stacking of the next layer which may or may not present interfering cations, and 2) distortions of the oxygen sheets which make some OH—O distances larger than others. It should be pointed out that the contributions to the electrostatic energy from next nearest neighbors and ions farther away are substantial. Thus it may be an over simplification to draw cause and effect relationships just from inspection as is done here. These observations should be regarded as tentative until tested directly.

Discussion

The question of hydrogen bonding involving the inner surface hydroxyls and the basal tetrahedral oxygens in the next layer is of great interest. It brings up, however, the question of what evidence is required to demonstrate the existence of a long hydrogen bond. A general rule which is often cited is that OH—O contacts of less than about 3.0Å which are not the edges of coordination polyhedra are indicative of a hydrogen bond (Hamilton and Ibers, 1968). In the case of the kaolin minerals, all contacts of this nature are close to or greater than 3.0Å (Table 1) so this is of little aid in deciding on hydrogen bonding. Another characteristic of hydrogen bonding is a tendency for the O—H. . . O angle to be in the region of 150° – 180° although there is a small number of observed cases for angles down to 110° (Hamilton and Ibers, 1968, p. 214). In addition, the distance between the hydroxyl hydrogen and the acceptor oxygen should be less than the sum of the van der Waals radii; in this case the observed value of the sum is 1.7Å and the calculated value is 2.6Å, both ± 0.1Å (Hamilton and Ibers, 1968). If one applies these criteria to the data in Table 3, one can conclude that for kaolinite, H(3) is not involved in hydrogen bonding while H(1) and H(2) meet the requirements as stated above except for the observed H. . . . O distances both of which are greater than 1.7Å. In fact, all the hydroxyl hydrogens in the kaolin minerals have H. . . . O distances greater than this. Ignoring this requirement for the moment, in dickite, all three inner surface hydrogens are involved in hydrogen bonding, and in nacrite H(3) and H(4) are involved in hydrogen bonding while H(2) is not.

If one requires H. . . . O distances to be 1.7Å or less, then there is no hydrogen bonding between layers, and the question is what holds the layers together. Theoretical treatments of hydrogen bonding (Coulsen and Danielsson, 1954) indicate it to have a large electrostatic component. Accepting this, one could rephrase the hydrogen bond question as—is there a net electrostatic attraction between kaolin layers and, if the hydrogens are removed (for example by substituting F^- for OH^-), is there still a net attraction or a repulsion? If the answer to the first question is yes and to the second is no, then this would demonstrate that the presence of the inner surface hydrogens is a necessary feature of the kaolin structures. We are presently investigating this aspect of the problem.

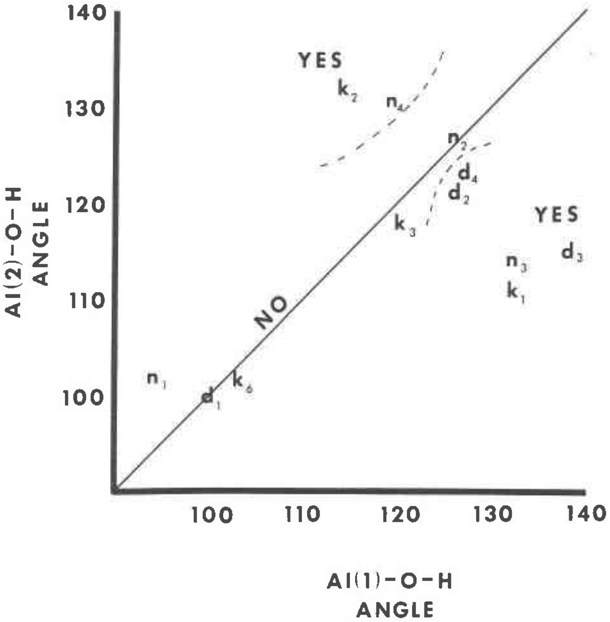

FIG. 6. A plot of one Al-O-H angle against the other for all hydroxyls in kaolinite (k), dickite (d) and nacrite (n). The subscript is the number used to identify the hydrogen as described in the text. The fields marked YES contain hydroxyl hydrogens which participate in hydrogen bonding and the area along the solid line and between the two dashed lines marked NO contains nonhydrogen bonded hydroxyl hydrogens.

As indicated earlier, there is little agreement on the interpretation of the IR studies in terms of hydroxyl orientation. The intercalation and deuteration experiments of Wada (1967) and Ledoux and White (1964a, b) on kaolinite indicated that of the three unique inner surface hydroxyls, two were nearly perpendicular to the kaolin layers and were pointing toward the basal oxygens of the next layer and the third was directed either toward the empty octahedral site (Ledoux and White 1964a) or else perpendicular to and down toward the kaolin layer so as to participate in a long hydrogen bond with the oxygens in the plane shared by the tetrahedral and octahedral sheets (Wada, 1967). The kaolinite model described here is in general agreement in that two of the three inner surface hydroxyls are normal to the layer and available for deuteration while the third is nearly in the hydroxyl sheet, making a small angle away from the kaolin layer. It is unlikely that this latter hydroxyl is directed down toward the empty octahedral site at any great angle because (Fig. 6) the inner hydroxyl is also directed in toward the empty site and the two hydrogen ions will repel each other. Several other investigators have suggested a similar orientation based on IR studies of untreated kaolinite (Serratosa *et al*, 1962, 1963; Farmer, 1964) but with less convincing evidence. Kukovsky (1968, 1969) in a quantitative study of hydrogen bonding in kaolinite based on the relative intensities of the high and low frequency hydroxyl stretching bands concluded that of the four hydroxyls, 2.1 are not involved in hydrogen bonding. The model presented in this work has 2.0 hydroxyls, H(3) and H(6), which definitely do not participate in hydrogen bonding and this close agreement is strong support for the correctness of the model.

There is much less experimental data on dickite and nacrite to use as a check on the electrostatic energy models. The dickite model presented here agrees with the one proposed by Newnham (1961) but this may just be fortuitous since his assignment of IR bands has been questioned (Farmer, 1964). Wada (1967) studied the deuteration of a "dickite-nacrite" rather than pure samples and suggested that only two of three inner surface hydroxyls are available for deuteration. Our models suggest that, in dickite, all inner surface hydroxyls should be available for deuteration while in nacrite, since one of the hydroxyls makes an angle of 38° with the kaolin layer, it may not deuterate as readily as the other two which are nearly normal to the kaolin layer. The apparent discrepancy with Wada's work may be a result of the impure nature of his samples. Of more interest is the result of Kukovsky's study of dickite (as described above) in which he finds that only 1.2 hydrogens are not hydrogen bonded. The present model has only H(1), the inner hydroxyl hydrogen, definitely not hydrogen bonded. It is unfortunate that Kukovsky did not also look at nacrite.

The most recent IR work on kaolinite is by Jacobs (1971). He concludes that the transition moments for the 3620, 3652 and 3670 cm^{-1} bands show no pleochroism whereas the 3700 cm^{-1} does. Hence the first three have transition moments nearly parallel to the kaolinite layer and the last is 65° to the layer. In addition, partially deuterated samples show that there is coupling between the inner surface hydroxyls and therefore there is not a one-to-one correspondence between absorption band and hydroxyl group, so that the orientation of the transition moment need not coincide with the orientation of any OH group. If this is true, it means that the determination of OH orientations from IR data is extremely difficult if not impossible for complex cases like the kaolin minerals.

A refinement of the kaolinite structure by powder neutron diffraction is being done (personal communication, Dr. S. Spooner) but the results at present are only qualitative and as yet do not provide a test of the OH orientations described here.

Conclusions

Under the assumptions of full ionic charges, O-H distance of 0.97Å, and the correctness of the crystal structures of kaolinite, dickite and nacrite, it is possible to arrive at models for the hydroxyl orientations in these minerals by an iterative method of minimizing the electrostatic energy. In dickite, all three inner surface hydroxyls are nearly normal to the kaolin layer and point toward the basal oxygens in the next layer; in kaolinite two of the three inner surface hydroxyls are similarly oriented while the third is nearly parallel to the kaolin layer pointing away from the octahedral sheet; in nacrite two of the inner surface hydroxyls are normal and the third is inclined at 52° to the kaolin layer. In all three, the inner hydroxyl is directed toward the empty octahedral site and makes a small angle with the O, OH sheet to which it belongs.

Acknowledgments

We are grateful to Dr. V. C. Farmer for his comments on recent IR experimental work and their interpretation, and to Drs. J. L. White, G. W. Brindley, and V. C. Farmer for reviewing the manuscript. The research was supported in part by the National Aeronautics and Space Administration.

References

Bailey, S. W. (1963) Polymorphism of the kaolin minerals. *Amer. Mineral.* **48,** 1196–1209.

Baur, W. H. (1965) On hydrogen bonds in crystalline hydrates. *Acta Crystallogr.* **19,** 909–916.

Bertaut, F. (1952) L'energie electrostatique de reseaux ioniques. *J. Phys. Radium,* **13,** 499–505.

Blount, A. M., I. M. Threadgold, and S. W. Bailey (1969) Refinement of the crystal structure of nacrite. *Clays Clay Minerals,* **17,** 185–194.

Brindley, G. W., and K. Robinson (1946) The structure of kaolinite. *Mineral Mag.* **27,** 242–253.

Coulson, C. A., and U. Danielsson (1954) Ionic and covalent contributions to the hydrogen bond. *Arkiv for Fysik,* **Bd. 8,** 239–244.

Drits, V. A., and A. A. Kashaev (1960) An X-ray study of a kaolinite single crystal. *Kristallografiya,* **5,** 224–227.

Farmer, V. C. (1964) Infrared absorption of hydroxyl groups in kaolinite. *Science,* **145,** 1189–1190.

———, and J. D. Russell (1964) The infrared spectra of layer silicates. *Spectrochim. Acta,* **20,** 1149–1173.

Giese, R. F. (1971) Hydroxyl orientation in muscovite as indicated by electrostatic energy calculations. *Science,* **172,** 263–264.

———, S. Weller, and P. Datta (1971) Electrostatic energy calculations of diaspore (alpha AlOOH), geothite (alpha FeOOH) and groutite (alpha MnOOH). *Z. Kristallogr.* **134,** 275–284.

GRIM, R. E. (1968) *Clay mineralogy.* McGraw-Hill Book Co., New York.

HAMILTON, W. C., AND J. IBERS (1968) *Hydrogen bonding in solids.* W. A. Benjamin, Inc.

HENDRICKS, S. B. (1938) The crystal structure of nacrite $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ and the polymorphism of the kaolin minerals. *Z. Kristallogr.* **100,** 509–518.

JACOBS, H. (1971) *Etude des hydroxyle de la kaolinite par Spectroscopie la Infrarouge.* Thesis, University of Louvain.

KUKOVSKY, E. G. (1968) *Ukranian chemical magazine special copy.* Naukova Dumka, Kiev.

——— (1969) Alteration processes in clay minerals. *Clay Minerals,* **8,** 234–237.

LADD, M. F. C. (1968) The location of hydrogen atoms in crystalline ionic hydrates. *Z. Kristallogr.* **126,** 147–152.

LEDOUX, R. L., AND J. L. WHITE (1964a) Infrared study of the OH groups in expanded kaolinite. *Science,* **143,** 244–246.

———, AND ——— (1964b) Infrared study of selective deuteration of kaolinite and halloysite at room temperature. *Science,* **145,** 47–49.

NEWNHAM, R. E. (1961) A refinement of the dickite structure and some remarks on polymorphism in kaolin minerals. *Mineral Mag.* **32,** 683–704.

———, AND G. W. BRINDLEY (1956) Structure of dickite. *Acta Crystallogr.* **9,** 759–764.

SERRATOSA, J. M., A. HIDALGO, AND J. M. VINAS (1962) Orientation of OH bonds in kaolinite. *Nature,* **195,** 486–487.

———, ———, AND ——— (1963) Infrared study of the OH groups in kaolin minerals. *Proc. Int. Clay Conf.* **1,** 17–26.

SHERMAN, J. (1932) Crystal energies of ionic compounds and thermochemical applications. *Chem. Rev.* **11,** 93–170.

WADA, K. (1967) A study of hyroxyl groups in kaoline minerals utilizing selective deuteration and infrared spectroscopy. *Clay Minerals,* **7,** 51–61.

WOLFF, R. G. (1963) Structural aspects of kaolinite using infrared absorption. *Amer. Mineral.* **48,** 390–399.

ZVYAGIN, B. B. (1967) *Electron-diffraction analysis of clay mineral structures.* Plenum Press, New York. 364 pp.

Manuscript received, November 12, 1971; accepted for publication, January 18, 1973.