

CHAPTER I

INTRODUCTION



General Introduction

Clay minerals are mostly hydrous aluminosilicates. Bentonite and kaolinite have been extensively studied in their chemical properties and in biological systems as a specific antidote for the herbicide paraquat by many investigators (13,14).

Properties such as cation and anion exchange capacities (3,5,9), crystal structure (25,29), and complex formation (3-7,10,22) of kaolinite and bentonite from various localities have been extensively studied. In these studies several techniques have been applied, viz, x-ray diffraction (6,7,10) and spectrophotometric techniques (10, 22,34). Cation exchange capacities of bentonite, kaolinite and marl can be determined by atomic absorption spectrophotometry and flame photometry. Hydroxyl groups in kaolinite can be detected by infrared spectroscopy (8,22,34) and information provided by these spectra in the hydroxyl absorption region can be used to study hydrogen bonding in kaolinite. The analysis of infrared spectrum of kaolinite can be done on a computer (35). X-ray diffraction patterns and infrared spectra are more or less essential in studying complex formation in kaolinite and, needless to say, the detailed crystal structure of kaolinite has been elucidated by means of x-ray diffraction techniques (29).

Clay Minerals

Geologists have used the word "Clay" in two senses: as a size term, to refer to material of any composition whose average grain size is less than approximately 0.004 mm, and as a mineralogic term, referring to a group of minerals with a specific range of composition and a particular kind of crystallographic structure. The two meanings often overlap or coincide, because the fine grained part of a soil or sediment commonly consists largely of clay minerals (26).

In general the term clay implies a natural, earthy, fine-grained material which develops plasticity when mixed with a limited amount of water. By plasticity, it means that the property of the moistened material is deformed under the application of pressure, with the deformed shape being retained when the deforming pressure is removed. Chemical analysis of clays shows them to be composed of silica, alumina, and water, frequently with appreciable quantities of iron, alkali and alkaline earth metals (1).

1) Classification of Clay Minerals

Clay minerals have been classified in various ways (1,27) but a usual classification, based on their crystal chemistry, is shown in Table 1.1 (40).

As shown in Table 1.1, Clay minerals can be subdivided into three groups on the basis of the number of sheets making up their basis structure (unit cell). These three groups are further subdivided on the basis of the population of the octahedral sheet. A final subdivision is based on the swelling properties of the

Table 1.1 Classification of Principal Clay Minerals (40)

Sheets	Population of octahedral sheet	Expansion	Species	Ideal formula
Two *	Diocahedral [#]	Nonswelling	Kaolinite	$Al_4Si_4O_{10}(OH)_8$
		Swelling	Halloysite	$Al_4Si_4O_{10}(OH)_8 \cdot 4H_2O$
Three **	Triocahedral ^{##}	Nonswelling	Septechlorite	$Mg_6Si_4O_{10}(OH)_8$
		Swelling	Montmorillonite	$Al_4Si_8O_{20}(OH)_4 \cdot nH_2O$
		Nonswelling	Illite	$K_{0-2}Al_4(Al,Si)_8O_{20}(OH)_4$
Three+one [@]	Triocahedral	Swelling	Vermiculite	$Mg_6Si_8O_{20}(OH)_4 \cdot nH_2O$
	Triocahedral	Nonswelling	Chlorite	$Mg_3Si_4O_{10}(OH)_2 \cdot Mg_3(OH)_6$

* Two : An octahedral layer is linked on one side with a tetrahedral layer.

** Three : An octahedral layer is linked on both sides with a tetrahedral layer.

@ Three+one : A structure consists of alternation between three-layer structure and an octahedral layer.

Diocahedral : Only two-thirds of possible positions for aluminum in an octahedral sheet are filled.

Triocahedral : Three octahedral positions are filled by three divalent magnesium atoms.

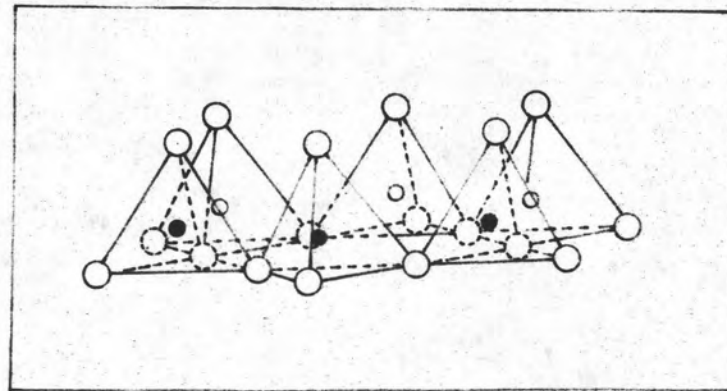
minerals. The major mineral of the two-sheet group is kaolinite. Kaolinite is non-swelling and very little substitution occurs for the aluminum and silicon ions of the sheets (28). Bentonite is in the three-sheet group under the name of montmorillonite.

2) Structure of the Clay Minerals (1)

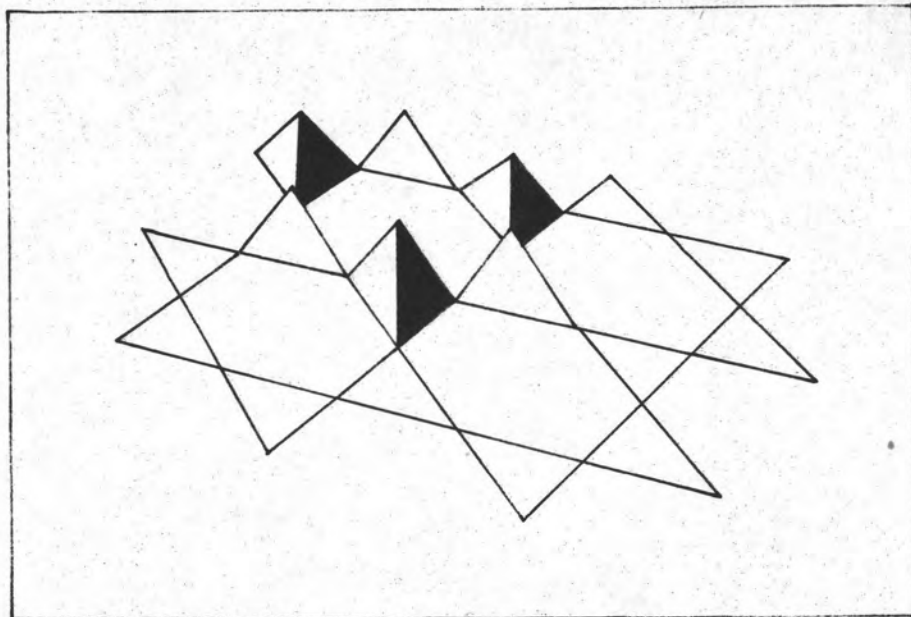
The atomic structure of the common clay minerals have been determined in considerable detail by numerous investigators. Two structural units are involved in the atomic lattices of most of the clay minerals. One unit consists of two sheets of closely packed oxygens or hydroxyls in which aluminium, iron, or magnesium atoms are embedded in octahedral coordination, so that they are equidistant from six oxygens or hydroxyls (Fig. 1.1). The second unit is built of silicate tetrahedra which can be described as follows, assuming no distortions. In each tetrahedron a silica atom is equidistant from four oxygens, or hydroxyls if needed to balance the structure, arranged in the form of a tetrahedron with a silicon atom at the center (Fig. 1.2). The silica tetrahedral groups are arranged to form a sheet of composition $\text{Si}_4\text{O}_6(\text{OH})_4$.

(2.1) Kaolinite Minerals

The structure of kaolinite was first suggested in general outlines by Pauling and later in detail by numerous investigators (29-32). The structure (1) is composed of a single silica tetrahedral sheet and a single alumina octahedral sheet combined in a unit so that the tips of the silica tetrahedra and one of the hydroxyl layers of the octahedral sheet form a common layer (Fig. 1.3). All the tips of the silica tetrahedra point

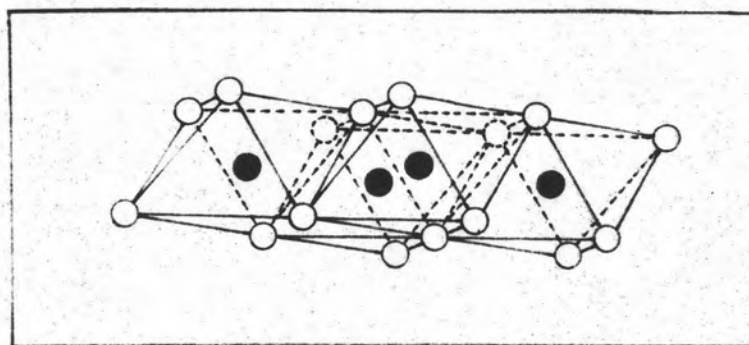


(a) ○ and ○ = oxygens
○ and ● = silicons

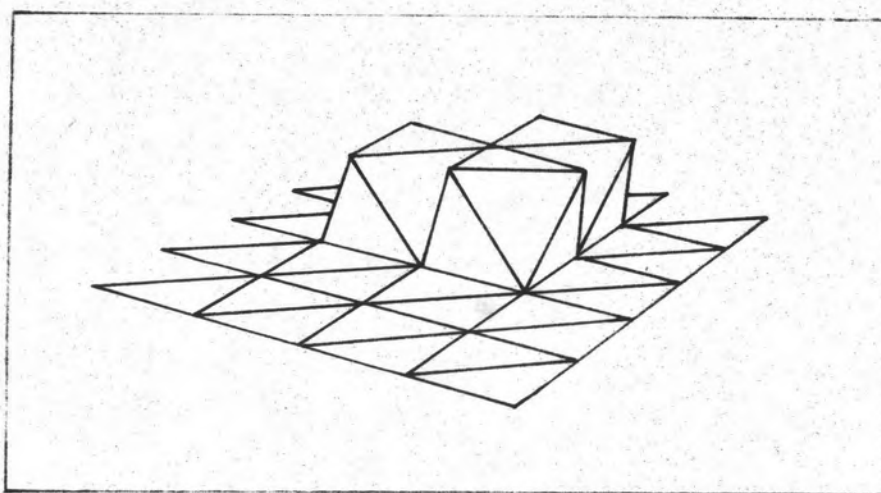


(b)

Figure 1.1 Diagrammatic sketch showing a) the sheet structure of silica tetrahedra arranged in a hexagonal network
b) the sheet structure of silica tetrahedra arranged in many hexagonal networks



(a) ○ and ○ = Hydroxyls
● = Aluminums

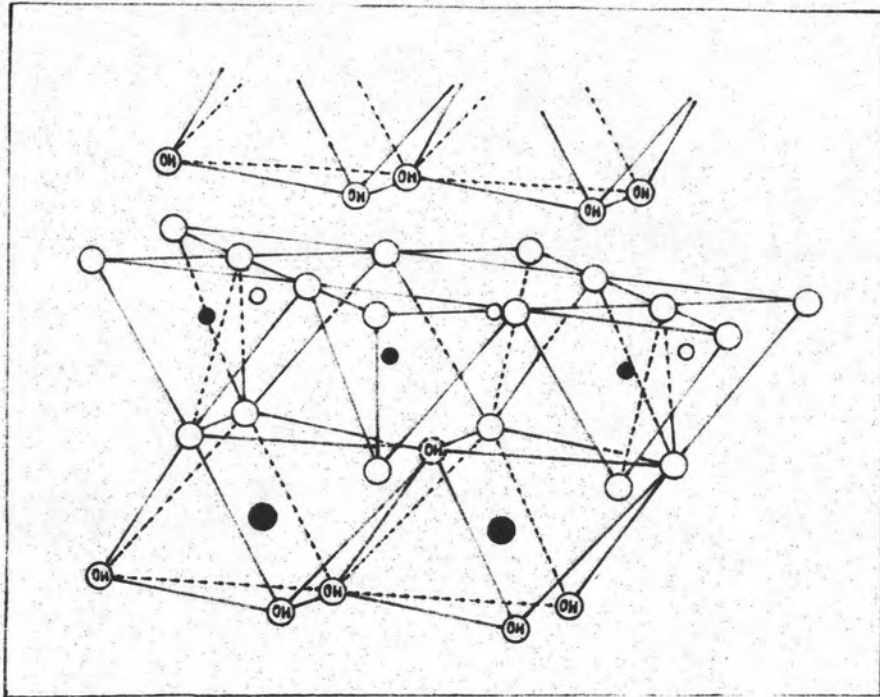


(b)

Figure 1.2 Diagrammatic sketch showing a) the sheet structure of the octahedral units
b) the sheet structure of the octahedral units which leaves triangular openings

in the same direction and towards the center of the unit made by the silica and octahedral sheets. The structural formula is $(\text{OH})_8\text{Si}_4\text{Al}_4\text{O}_{10}$, and the theoretical composition expressed in oxides is 46.54 % SiO_2 , 39.50 % Al_2O_3 , 13.96 % H_2O . The analyses of many samples of kaolinite minerals have shown that there is very little substitution within the lattice. The mineral is triclinic, with the lattice parameter given in Table 1.2.

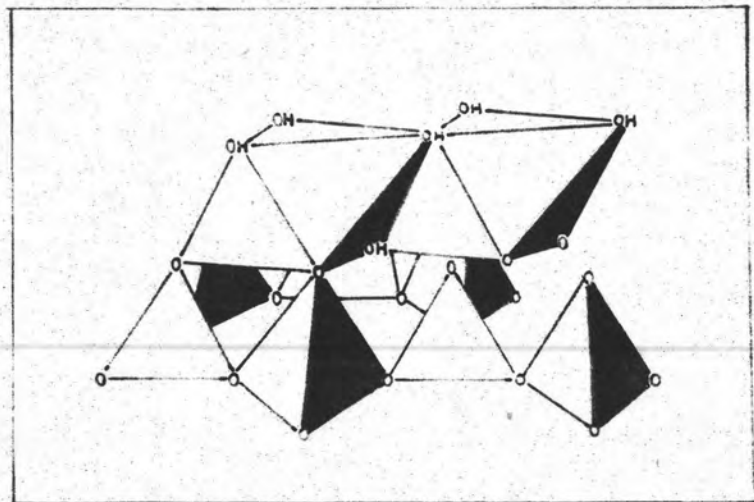
Evidently, successive layers of the kaolinite structure are held together by hydrogen bonds formed between oxygen atoms of the tetrahedral sheet in each layer and hydroxyl groups of the adjacent layer. These bonds give rise to many interesting properties, especially the ability of kaolinite to form intercalation complexes with several hydrogen-bond forming species.



(a)

Alumina sheet

Silica sheet



(b)

Figure 1.3 a) and b) are diagrammatic sketches of the structure of the kaolinite layer.

Table 1.2 Lattice Parameters of Kaolinite

	Newnham (42)	Brindley and Robinson (41)
a	$5.139 \pm 0.014 \text{ \AA}$	5.15 \AA
b	$8.392 \pm 0.016 \text{ \AA}$	8.95 \AA
c	$7.371 \pm 0.019 \text{ \AA}$	7.39 \AA
α	$91.6^\circ \pm 0.2^\circ$	91.8°
β	$104.8^\circ \pm 0.2^\circ$	$104.5\text{--}105^\circ$
γ	$89.9^\circ \pm 0.1^\circ$	90°

(2.2) Bentonite

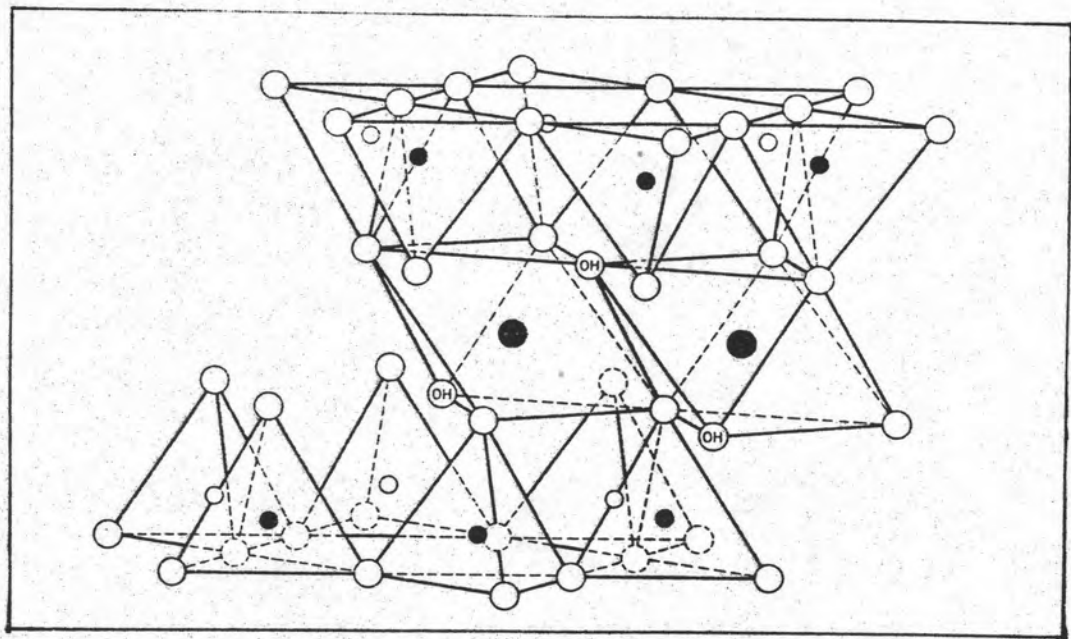
The term bentonite was first applied by Knight (1898) to a particular, highly colloidal, plastic clay found near Fort Benton in the cretaceous beds of Wyoming. It has the unique characteristic of swelling to several times its original volume when placed in water (15,16). Later Ross and Shannon (33) pointed out that such clays are largely composed of smectite clay minerals and that they are generally highly colloidal and plastic. Gillson (15) and Grim (16) also defined bentonites as "fine-grained" clays containing not less than 85 percent montmorillonite (montmorillonite is one of the members of the smectite group).

Today the term bentonite to most people, other than some mineralogists and geologists, carries with it the connotation of a highly plastic, colloidal, swelling clay. Also, the term is used frequently for clays with these properties without reference to a particular mode of origin. Bentonite varies in color from white to gray, yellow, green, blue and black but is most often found to be yellow or yellowish green.

With regard to exchangeable cations, most bentonites carry Ca^{2+} as the most abundant ion. Only a few are known to carry Na^+ or K^+ as the dominant ions.

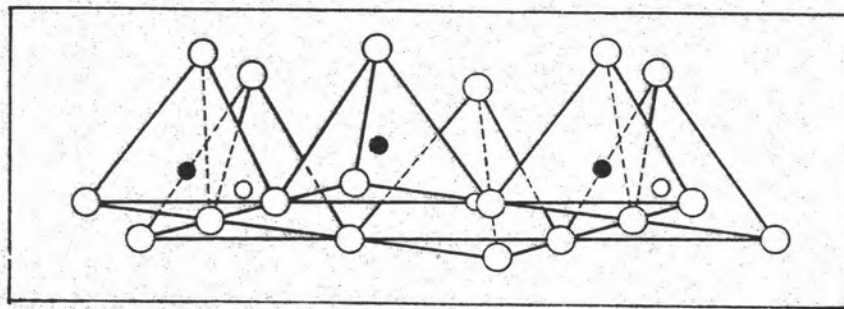
(2.3) Smectite

Smectite is composed of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet. All the tips of the tetrahedra point in the same direction and towards



Exchangeable cations

nH_2O



- Oxygens ⊙ Hydroxyls ● Aluminum, iron, magnesium
 ○ and ● Silicon, occasionally aluminum

Figure 1.4 Diagrammatic sketch of the structure of smectite.



the center of the unit. The tetrahedral and octahedral sheets are combined so that the tips of the tetrahedra of each silica sheet and one of the hydroxyl layers of the octahedral sheet form a common layer. The atoms common to both the tetrahedral and octahedral layer become oxygen atom instead of hydroxyl group. The layers are continuous in a and b directions and stacked one above the other in c direction. In the stacking of the silica-alumina-silica units, oxygen layers of each units are adjacent to oxygen layers of the neighboring units, with the consequence that there is a very weak bond and an excellent cleavage between them. Figure 1.4 is a diagrammatic sketch of this structure of smectite.

Exchangeable cations occur between the silicate layers, and the c-axis spacing of completely dehydrated smectite depends somewhat on the size of the interlayer cation, being larger the larger the cation. In the case of adsorption of polar organic molecules between the silicate layers, the c-axis dimension also varies with size and geometry of the organic molecule.

(2.4) Marl

Marl is a natural mixture of calcium carbonate and clay in varying proportions, often found with fragments of shells. If calcium carbonate predominates, it is a calcareous marl, if clay predominates it is an argillaceous marl (17-18). Both marine and fresh-water marls are most commonly earthy and of a white, gray or brownish color. However red and black marls are also found.

Many clay minerals are found in marl. For example illite (36,39), chlorite (38), sepiolite (37) etc. However many

investigators have found that most clay minerals found in marl as a dominant clay mineral was illite.

(2.5) Illite Minerals

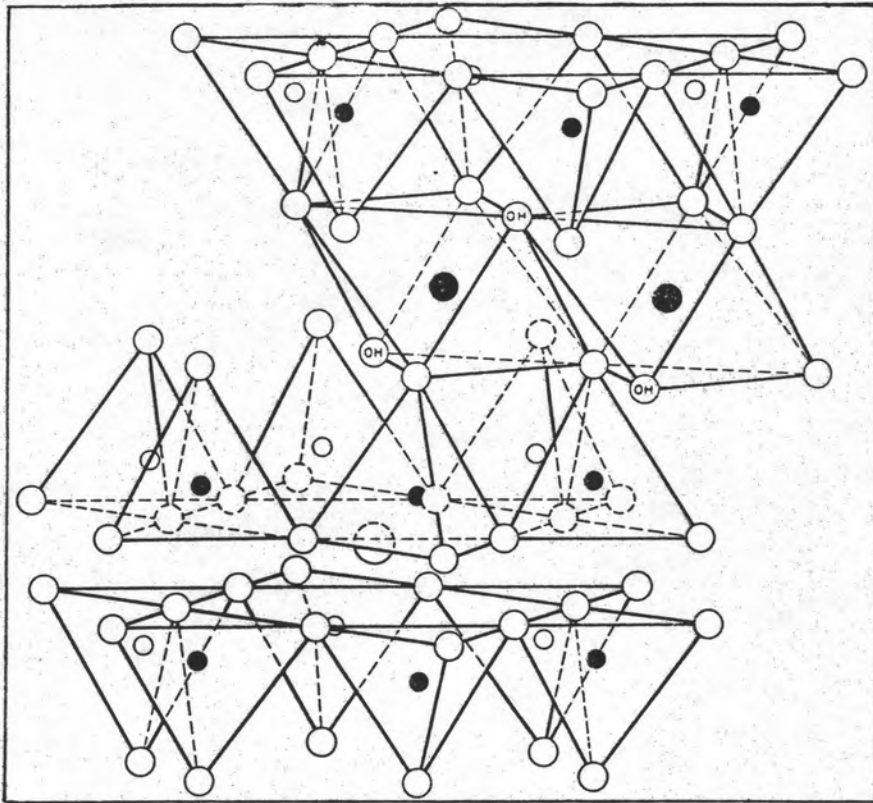
The basic structure unit is a layer composed of two silica tetrahedral sheets with a central octahedral sheet. The tips of the tetrahedra in each silica sheet point towards the center of the unit and are combined with the octahedral sheet in a single layer with suitable replacement of hydroxyl group by oxygen.

The unit is the same as that for montmorillonite except that some of the silicons are always replaced by aluminums and the resultant charge deficiency is balanced by potassium ions. The unit layers extend indefinitely in a and b directions and are stacked in c direction. The potassium ions occur between unit layers (Fig. 1.5).

Grim, Allaway, and Cuthbert (1) showed that illite reacted with organic ions up to its exchange capacity. The ions were thought to be limited to the exterior surface of the illite particles; i.e., they did not replace the potassium ions between the silicate layers. The cation exchange capacity of illite was 10-40 milliequivalent/100 g clay.

Cation-Exchange Capacity (CEC)

The CEC of clay minerals is believed to be largely due to broken bonds around the edges of the silica-alumina units, isomorphous substitution in the clay structure and, in some cases, replacement of the hydrogen of exposed hydroxyls (1). CEC's are influenced, therefore, by factors such as chemical pretreatment, type of saturating cation,



○ Oxygen , ⊙ OH Hydroxyl , ● Aluminum, ○ Potassium
 ○ and ● Silicon (one fourth replaced by aluminum)

Figure 1.5 Diagrammatic sketch of the structure of illite

particle size, temperature and pH of the saturating solution.

Since the CEC may vary with many factors, wide ranges of values have been reported. For example, for kaolinite 2.6-8.7 (11), 3-15 (1), 5.1 (5,6) milliequivalents/100 g clay, for montmorillonite (one of the members of the smectite group which is the dominant clay-mineral component of bentonite) 80-150 (1), 84.7 (5,6), 6.0 (3) milliequivalent/100 g clay.

To determine the CEC of clay minerals, a considerable variety of methods have been used. One of the commonly used methods involves saturation of the clay mineral with calcium by leaching with calcium chloride solution, after which the adsorbed calcium is displaced by leaching with ammonium acetate solution and then determination of calcium ions after precipitation as oxalate, by titration with permanganate (3,19). Other methods based on the same principle but involving saturation with manganese (9), ammonium (3,9), sodium (5,9), potassium (11) and other bases are in use.

Intercalation Complexes

The term intercalation literally refers to the insertion of guest species into lamellar host structure with substantial maintenance of the structural features of the host (2).

Many investigators have shown that organic ions and organic compounds with polar active groups could be adsorbed by the clay minerals (3,7,13,14). In recent studies particular attention has been given to the orientation of the organic molecules when they are intercalated in the silicate structure and to the nature of the bond tying them to the structure.

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In kaolin minerals, some compounds can intercalate directly into kaolinite, some can be introduced by displacement of a previously intercalated (7,22). Some compounds cannot intercalate into the basal spacing of kaolinite but are adsorbed on the edges or faces of the clay particles (5,6). Little systematic work appears to have been done to explain why kaolin minerals spontaneously expand in some polar organic compounds, but not in others.

Considering previous work (20,21), it would seem that to achieve direct intercalation into kaolinite, the organic compound should have small size and possess a large dipole moment (or basicity).

In montmorillonite, organic compounds are adsorbed in the interlayer space of the clay (3,5,6,10). Desorption investigations indicated that the cations adsorbed on the edge of the kaolinite clay particles are not held as strong as those bound within the clay lattice of the montmorillonite (5). The mechanism of organic adsorption on clay minerals (5,6) is depicted according to the following exchange reaction.



On the basis of one-dimensional Fourier syntheses of diffraction data, Bradley (22) concluded that polar organic molecules are held to the clay surface through hydrogen bonds of the type C-H---O-(clay surface). The oriented organic molecules between the basal surface of clay may be perpendicular or inclined at any angle or parallel to the plane of the clay surface (5-7,23).

Certain inorganic salts were observed to be intercalated in kaolinite (24) and bentonite (12). These include potassium acetate,

ammonium acetate and some other acetates. It was found (24) that the reaction is strongly dependent upon pH. It has also been noted that inorganic salt-kaolinite and inorganic salt-bentonite complexes (25) could be formed either by soaking clays in concentrated solutions of the appropriate salts or by grinding the clay with the solid salts. In all cases kaolinite was regenerated by washing the complexed clay with water.

The study of cation exchange capacity and intercalation on marl are not found.

Hydrogen Bonding

Hydrogen bonding is an interaction between a covalently bound H atom (A-H), with some tendency to be donated, and a region of high electron density on an electronegative atom or group of atoms, which can accept the proton (B) (47).

1) Criteria for Hydrogen Bonding (47)

Some convenient operational criteria for the existence of hydrogen bonding are listed below.

1.1 Hydrogen bonding occurs between a proton donor group A-H and a proton acceptor group B, where A is an electronegative atom: O, N, S, X (F, Cl, Br, I) or C, and the acceptor group is a lone electron pair of an electronegative atom or a π -electron orbital of a multiple bond (unsaturated) system. Generally, a hydrogen bond can be characterized as a proton shared by two lone electron pairs.

1.2 Hydrogen bonding is a distinctly directional and specific interaction. It is more localized than any other type of weak intermolecular interaction. Hydrogen bonds are linear, but appreciable



variation in the angle $\angle A-H-B$ can occur.

1.3 The total hydrogen bond length $R (A \dots B)$ is equal to or less than the sum of the van der Waals radii of atoms A and B, that is, the total bond length contraction caused by hydrogen bond formation is equal to or is greater than twice the van der Waals radius of the hydrogen atom.

1.4 The enthalpy of hydrogen bonds generally fall in the range of 1 to 10 Kcal/mole (4.184 to 41.84 kJ/mol). Intermolecular interactions other than hydrogen bonding also fall within this range.

1.5 Hydrogen bonding is an association phenomenon. It causes a decrease in the total number of free molecules and an increase in the average molecular weight (except in the case of intramolecular hydrogen bonding).

1.6 In hydrogen bonding a specific covalent A-H group interacts with a specific acceptor site. The A-H bond is thereby weakened but not broken, and the properties of the acceptor group are also affected.

2) Hydrogen Bonding in Kaolinite

At the 1972 Clay Conference in Madrid was generally believed that the layers in kaolinite are bound together by hydrogen bonds (48). I.R. absorption bands at about 3700 cm^{-1} , 3670 cm^{-1} , 3650 cm^{-1} were attributed by several authors to OH-O stretching vibrations (8, 48-52).

It is well known from structural data that oxygens and hydroxyls of adjacent layers are nearly superimposed in the c direction, and that X-ray and electron diffraction-measured distances between the three pairs of OH-O are within the limits typical for long (weak) hydrogen bonds.

The forces of cohesion between the kaolinite layers should obey the general rules of hydrogen bonds applicable to other chemical compounds in which hydrogen bonds are the major cohesion forces. It should be possible to use spectroscopic criteria to prove the existence of such bonds.

In order to study hydrogen bonds by the I.R. method, one must know the frequency of vibrations of free hydroxyls which form the external OH plane in the octahedral sheet, and which are not involved in H-O bonds with adjacent kaolinite layers. In the literature, the 3750 cm^{-1} band is the generally accepted frequency for the free OH, it comes from vibration of OH^- associated with silica (53). Using the I.R. reflection method, Tadeusz Wieckowski (48) recorded the absorption band at 3742 cm^{-1} related to oscillations of free OH in a superficial plane of the octahedral sheet of kaolinite.

3) Bond length Calculations

The most precise semi-empirical relation describing the decrease of stretching frequency vibrations in comparison to vibration of free OH was proposed by Bellamy and Owen (54). According to these authors the decrease of frequency in cm^{-1} can be calculated from the Lemard-Jones 12-6 potential function:

$$\Delta = 50 \left[\left(\frac{d}{R} \right)^{12} - \left(\frac{d}{R} \right)^6 \right] \quad (1)$$

where :

- Δ = frequency shift free OH-OH in hydrogen bond
- d = a value close to the sum of collision radii of atoms X and Y in the X-H...Y bonding
- R = total hydrogen bond length.

4) Semiempirical Potential Function for Hydrogen Bonding

Energy of hydrogen bond can be calculated by using a potential function

$$V = D_0 \left[1 - \exp(-n\Delta r^2/2r) \right] \quad (1)$$

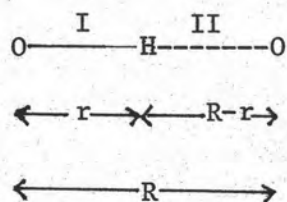
where $D =$ bond dissociation energy

$$\Delta r = r - r_0$$

$$n = k_0 r_0 / D$$

In the above form the function is applicable to bond in diatomic and polyatomic molecules and should form a basis for a model of hydrogen bonding provided that it can be modified suitably.

To make the problem tractable we make the following assumptions, which are illustrated as follows for OH...O bonding.



$$\Delta r_{\text{I}} = r - r_0$$

$$\Delta r_{\text{II}} = R - r - r_0^*$$

The asterisk will be used to identify the properties of bond II, if it were an unperturbed OH bond.

(a) The hydrogen atom is located along the line of centers between the two electronegative atoms making up the bond.

(b) Bond I is equivalent to a slightly stretched typical covalent bond, the amount of stretching being $r - r_0$.

(c) Bond II is a weak bond which is equivalent to a highly stretched bond, the amount of stretching being $R-r-r_o^*$.

(d) There is a Van der Waals repulsion between the two oxygen atoms which may be described by an exponential potential.

(e) There is an electrostatic potential between the two oxygens atom which may be represented as $-B/R^m$.

(f) The potential energy of stretching in both bonds may be obtained through application of the simple potential function (1).

Because of these assumptions our model will better approximate a hydrogen bond in the crystalline state than one in the liquid or vapor state; therefore any composition with experimental data will be based on studies of the hydrogen bond in crystals. This model should be more applicable to hydrogen bond dimers than polymers.

The potential energy for this model consists of the sum of four terms

$$V = V_1 + V_2 + V_3 \text{ (repulsion)} + V_4 \text{ (electrostatic)}. \quad (2)$$

It is convenient to choose $V = 0$ when the molecules are completely separated. From the above assumptions.

$$V_1 = D \left[1 - \exp(-n r^2/2r) \right] \quad (3)$$

$$\begin{aligned} V_2 &= D^* \left\{ 1 - \exp \left[-n^* (R-r-r_o^*)^2/2(R-r) \right] \right\} - D^* \\ &= -D^* \left\{ \exp \left[-n^* (R-r-r_o^*)^2/2(R-r) \right] \right\} \end{aligned} \quad (4)$$

$$V_3 = A e^{-bR} \quad (5)$$

$$V_4 = -B/R^m \quad (6)$$

Before this potential function may be applied, it is necessary to have some knowledge of the properties of bonds I and II in their unperturbed or unstretched configurations. As the potential function (1) is assumed applicable to both bonds in their unstretched configurations the following relations hold, $nD = k_o r_o$ and $n^* D^* = k_o^* r_o^*$. Since bond I is essentially a slightly stretched OH bond, the values for n , D , k_o , and r_o may be taken from the corresponding values for the H_2O molecule. For bond II a knowledge of the quantities n^* , D^* , k_o^* , and r_o^* is not readily available. This bond is more properly considered as a highly stretched HO^+R_2 bond rather than as a highly stretched HOR bond. Because the parameter, n , is related to atomic ionization potentials of the atoms making up the bond we would expect $n^* \neq n$. Furthermore, although the bond lengths associated with H-OR and $H-O^+R_2$ are not quite the same, we will assume that $r_o = r_o^*$ for lack of information. Likewise, although k_o^* is not necessarily the same as k_o we will assume $k_o^* = k_o$ for lack of further information. These assumptions imply that $n^* D^* = nD$. Since all properties of bonds I and II in their unperturbed positions may now be evaluated except n^* , we write

$$n^* = gn \quad (7)$$

where g is chosen such that the best results are obtained. A suitable value of g is 1.45. The evaluation of g in principle requires the use of one frequency shift or one OH bond length.

Other schemes may be chosen to evaluate the properties of bond II in the unperturbed position. For example one might put n^* equal to some function of $R-r$. The scheme used here has the advantage of simplicity and makes use of only one empirically evaluated parameter. Any other

method would of necessity involve at least one or more such parameters.

For motion of the nuclei along the axis of the hydrogen bond the following conditions characteristic of a stable equilibrium are applicable.

$$\left(\frac{\partial V}{\partial r}\right)_{eq} = 0 \quad (8)$$

$$\left(\frac{\partial^2 V}{\partial r^2}\right)_{eq} = k_H \quad (9)$$

$$\left(\frac{\partial V}{\partial R}\right)_{eq} = 0 \quad (10)$$

$$\left(\frac{\partial^2 V}{\partial R^2}\right)_{eq} = k_{O\text{---}O} \quad (11)$$

where k_H is the force constant associated with the motion of the hydrogen atom and $k_{O\text{---}O}$ is the force constant associated with the motion of the oxygen atoms.

Before we use these conditions it will be convenient to modify the repulsion and electrostatic terms, so that they contain two constants and not three. To do this we write

$$V_3 + V_4 = V_o \left\{ 2 \exp[-b(R-R_o)] - \left(\frac{R}{R_o}\right)^m \right\} \quad (12)$$

where V_o is equal to $V_3 + V_4$ when $R = R_o$. On Comparing (12) with (5) and (6) one has

$$A = 2V_o e^{+bR_o} \quad (13)$$

$$B = V_o R_o^m \quad (14)$$

By dividing (14) by (13) one obtains B in terms of A and Eq. (5), (6) becomes on substitution:

$$V_3 + V_4 = A \left[e^{-bR} - \left(\frac{1}{2}\right) (R_o/R)^m e^{-bR_o} \right] \quad (15)$$

The constant A may be evaluated by using the condition $(\partial V/\partial R) = 0$, while b can be evaluated through the use of a known hydrogen bond energy.

It is necessary to choose a value for the exponent m in the electrostatic term. For hydrogen bond dimers, involving nonequivalent oxygen atoms, such as one has with the carboxylic acids, m may be given a value of 1 since the oxygen atoms carry fractional charges. For bonds involving equivalent oxygen atoms such as in ice, a more suitable value of m can be chosen between 3 and 6. Since the electrostatic term does not appear in the equations used to determine the O-H distance or O-H frequency shifts and gives only a minor contribution to the energy $k_{O\text{---}O}$ force constant, we will uniformly choose $m = 1$. Although for particular cases of O-H---O hydrogen bonding a more suitable electrostatic potential may be chosen, the one used here has the advantage of simplicity. We have used a value of $m = 6$ and the results are as good as those with $m = 1$.

This elementary model is capable of predicting a relation between the OH bond distance and the O---O distance for hydrogen bonds. From (2) and the condition that $(\partial V/\partial r) = 0$, we have on solving for Δr

$$\Delta r = \left(\left\{ \exp \left[-n^* (R-r-r_o^*)^2 / 2(R-r) \right] \right\} / \exp(-n\Delta r^2/2r) \right) \times \left[r^2 (R-r-r_o^*) (R-r+r_o^*) / (R-r)^2 (r+r_o) \right] \quad (16)$$

Since R_o , r_o and n are known from experimental data and $r_o^* = r_o$ and $n^* = gn$, Eq. (5) is suitable for calculating Δr as a function of R_o by the method of successive approximations. The following values were obtained by Lippincott and Schroeder (49) and are used in

the present calculations:

$$\begin{aligned} r_o &= 0.97 \times 10^{-8} \text{ cm} \\ n &= k_o r_o / D = 9.18 \times 10^8 \text{ cm}^{-1} \\ n^* &= (1.45 \times n) = 13.32 \times 10^8 \text{ cm}^{-1} \end{aligned}$$

The graph of r versus R_o is shown in Fig. 1.6. from which r was found to be 1.107 Å, 1.091 Å. and 1.058 Å when R was 2.51 Å, 2.53 Å, and 2.58 Å, respectively.

The constant A can be evaluated by using the condition $(\partial V / \partial R) = 0$, and is found to be

$$A = \frac{(D_o^* n^* / 2) [1 - (r_o^* / r^*)^2] [\exp(-\beta)]}{[\exp(-bR_o)] [b - (\frac{1}{2}R_o)]} \quad (17)$$

Finally, the formula used for the entire energy calculation can be written:

$$\begin{aligned} V &= D_o [1 - \exp(-\alpha)] - D_o^* [\exp(-\beta)] + A [\exp(-bR) - \\ &\quad (R_o / 2R)^m \exp(-bR_o)] \quad (18) \\ \alpha &= n(r - r_o)^2 / 2r \text{ and } \beta = n^* (r - r_o^*)^2 / 2r^* \end{aligned}$$

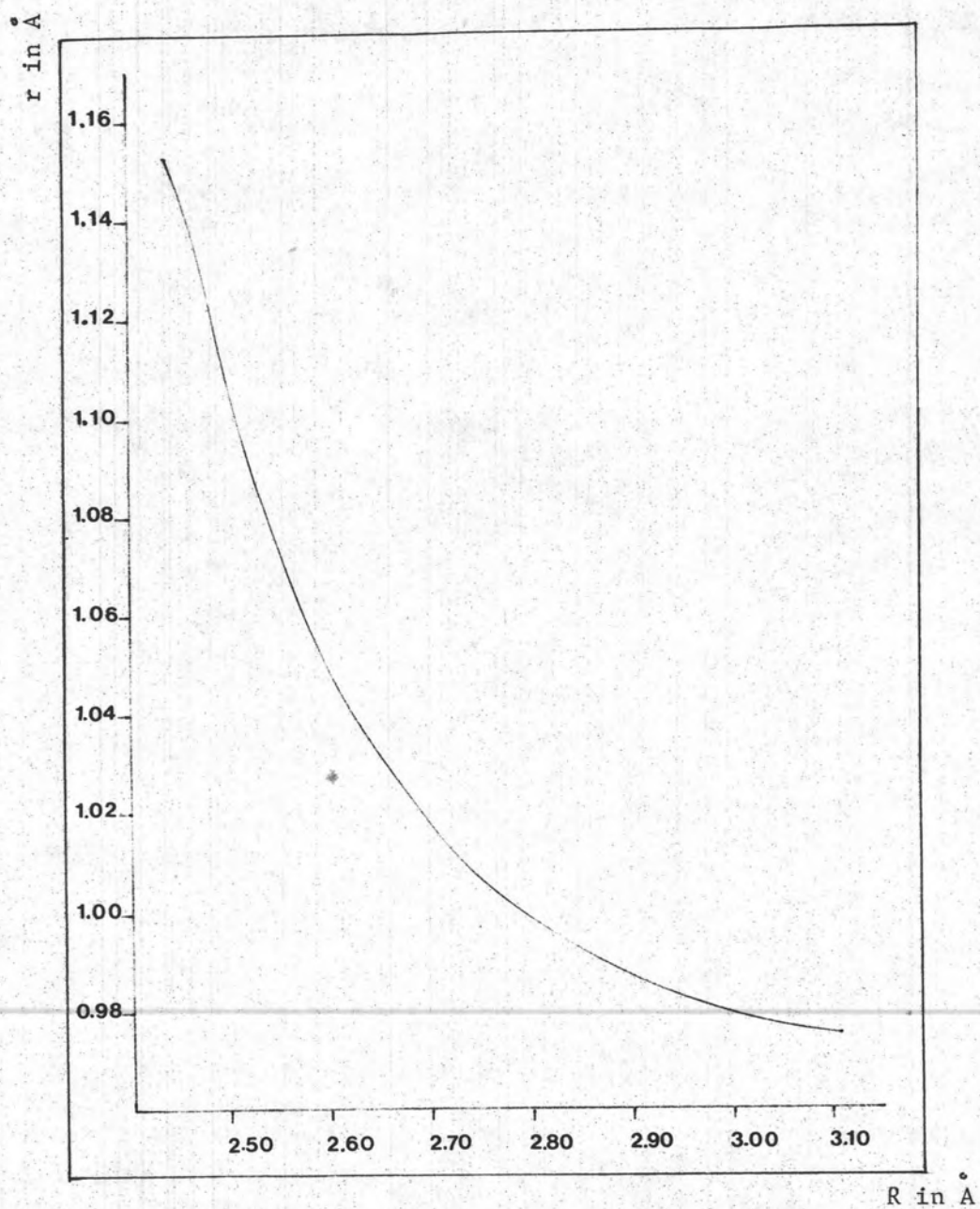


Fig 1.6 O-H distance as a function of O...O distance for hydrogen bonds.