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THE LATTICE STRUCTURE OF CLAY MINERALS

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ABSTRACT. A review of the work done so far on the crystal structure of 8 clay minerals has been given.

INTRODUCTION

Clay, or, the clay fraction of soil and natural deposits such as bentonite and kaolin comprises all inorganic ingredients included in the mechanically separated fraction of these systems having particle-size smaller than 2 microns in diameter (Atterberg, 1912). It is mainly colloidal in nature. Most of the physical and chemical properties of soils and other clayey deposits which are of importance in practical agriculture, in ceramics and in constructional engineering are now known to be determined to a large extent by the nature and amount of their colloidal constituents, and the importance of detailed investigations of these constituents by physical and chemical methods is now increasingly felt for purposes of soil systematics, soil classification, and standardisation of clay material for use in the industries.

CRYSTALLINE CHARACTER OF CLAYS
THE PRINCIPAL GROUPS OF CLAY MINERALS

Following Van Bemmelen (1888), the finest fraction of soil has often been regarded as a loose 'absorption compound' or a mixed gel of silica, alumina, iron oxide and water (Wiegner, 1924) present in indefinite proportions so as to constitute some sort of an 'absorption complex'. From studies of synthetic precipitates formed under different conditions from solutions comparable to those which might be expected to give rise to the 'absorption complex' of soil, (Mattson, 1930) postulated that this complex arises from a mutual precipitation of electropositive and electronegative sols. such as colloidal alumina, ferric oxide and silica under isoelectric conditions.

The 'mixed gel' hypothesis for a long time kept in the background the crystalline character of soil colloids now fully established through x-ray studies (Hendricks *et al.*, 1930 ; Kelley *et al.*, 1931 ; Hofmann *et al.*, 1934 ; Nagelchmidt, 1934) and optical (Ross *et al.*, 1930, 1934 ; Marshall, 1930, 1935 ; Correns and Mehmel, 1936). These investigations have shown that the clay fraction is made up of a number of secondary silicate minerals with occasional admixtures of small quantities of rock-forming minerals , silica and oxides as well as hydroxides of iron and aluminium ; and in some cases, of certain amorphous inorganic substances.

Secondary silicate minerals which occur only in the clay fraction are usually known as *clay minerals*. Four groups of these clay minerals have been distingtished. These are—

(*a*) the *kaolin group* (Ross, *loc.cit*), comprising (*i*) the four polymorphic forms kaolinite, dickite, nacrite and halloysite, having the same chemical composition $Al_2O_3. 2SiO_2.2H_2O$, (*ii*) anauxite often considered as a variety of kaolinite but having a $SiO_2 : Al_2O_3$ ratio greater than 2.0, and (*iii*) hydrated halloysite (Hofmann, *loc. cit*) which has the chemical composition $Al_2O_3.2SiO_2.4H_2O$ and which on drying in air loses two molecules of water giving halloysite.,

(*b*) the *montmorillonite group* consisting of the minerals montmorillonite, beideliite, saponite, nontronite, etc., having the general formula $(R_{2-n}^{+++} \underset{\underset{R_n^{+}}{\downarrow}}{R_n^{++}})(\underset{\underset{R_m^{+}}{\downarrow}}{Al_m^{+++}} Si_{4-m}^{++++})O_{10}(OH)_2, xH_2O$ (Ross and Hendricks, 1941; Hendricks, 1942) derived from the ideal formula $(Al_2)(Si_4)O_{10}(OH)_2$ of pyrophyllite ;

(*c*) the *illite group* or the hydrous micas having the general formula (Grim *et al.*, 1937) $2K_2O.3R^{++}O.8R_2^{+++}O_3.24SiO_2, 12H_2O$ and distinguished from muscovite mica, $K(Al_2)(AlSi_3)O_{10}(OH)_2$,by their relatively small content of potassium and large percentage of water ; and

(*d*) the *attapulgite group*, whose only known member is the fibrous clay mineral, attapulgite, having the composition $(OH_2)_4(OH)_2Mg_5Si_8O_{20}.4H_2O$ (Bradley, 1940).

THE ATOMIC STRUCTURE OF CLAY MINERALS

As the clay minerals are the dominant constituents of most clays, the physical and chemical properties of the latter will be largely determined by their nature and relative proportions in the clay. Characteristic differences between the properties of the individual clay minerals have been observed. These have often been traced to differences in their crystalline structure.

The elucidation of the general scheme of structure of the clay minerals and certain other minerals, *e.g.*, micas, chlorites, talc and pyrophyllite, related to them, is due to Pauling, (1930). From dimensional considerations of the unit in the basal plane of the two forms of silica, β-tridymite and β-cristoballite, as well as of the pseudo-hexagonal (monoclinic) crystals of hydrargillite and muscovite, Pauling was led to postulate two structural units for clay and other related minerals. One is the octahedral hydrargillite or gibbsite unit composed of two sheets of closely packed hydroxyl groups built around Al^{+++} ions occupying the interstices of the hydroxyl groups In accordance with the electrostatic valence rule of Pauling (1929), each octahedron shares three edges and only two-thirds of the possible aluminium positions are occupied. In the octahedral brucite unit, having a similar structure, all the available positions are filled up by magnesium ions. The second unit of structure consists of hexagonal layers of linked SiO_4-tetrahedra, each tetrahedron containing a Si^{+++}ion at the centre and four oxygen ions at the corners. Unlike β-tridymite and β--cristobalite where alternate vertices of the tetrahedra point in opposite directions, these hexagonal layers of linked tetrahedra have all their vertices pointing in the same direction. Oxygen ions forming the bases of the

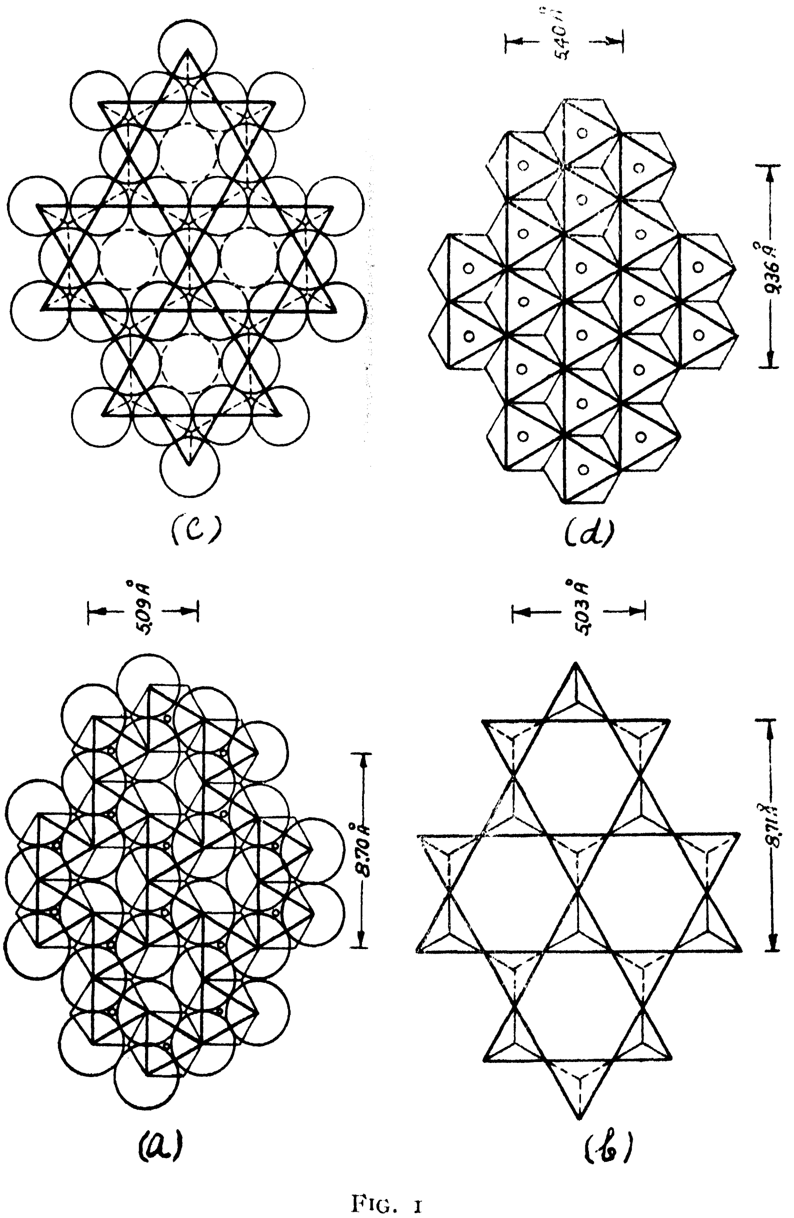

FIG. 1

(After Pauling)

(*a* A hydrargillite layer of octahedra

(*b*) A tetrahedral layer from β-cristobalite or β-tridymite. A silicon ion is located at centre of each tetrahedron and an oxygen ion at each corner.

(*c*) A tetrahedral layer in which all the tetrahedra point in the same direction.

(*d*) A complete layer of octahedra (Brucite layer).

tetrahedra have their valencies satisfied, each $O^=$ ion being common to two SiO_4 tetrahedra. But the oxygen ions at the unshared tetrahedral corners have only half of their valencies satisfied and it is necessary that they be held by further bonds. This is achieved by the superposition of the silica layer on the hydrargillite layer such that the tetrahedral vertices coincide with two thirds of the shared octahedral corners. This superposition is really a fusion of the two layers such that the vertical oxygens replace the OH groups at the shared octahedral corners and act as connecting links between the two layers. The unsymmetrical packet thus formed is found in clay minerals of the kaolin group. Symmetrical packets also occur as in montmorillonites and micas, and are formed by attaching a second tetrahedral layer to the other side of the hydrargillite layer. The various clay mineral and minerals related to them are distinguished by the manner of stacking of these packets (further discussed on pp. 5-6). Minerals like chlorite (Pauling, *loc. cit*) and vermiculite (Gruner, 1934; Hendricks 1938) are formed by the superposition of such packets interleaved respectively with units of brucite and neutral water molecules.

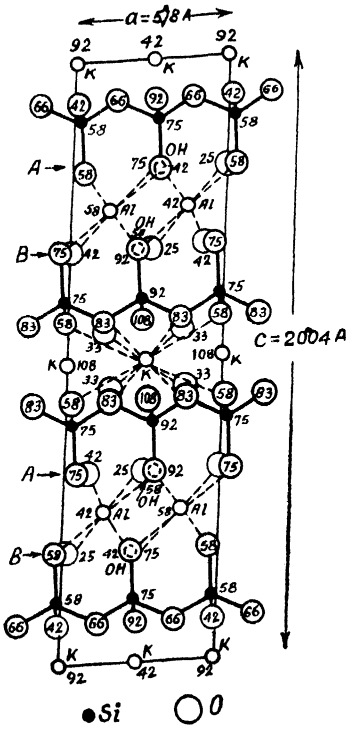

FIG. 2

The structure of Mascovite projected on (010)

(After Jackson and West)

The heights of the atoms above the face of the unit cells, as measured along the axis of projection, are indicated by the numbers. An atom on the lower face of the unit cell is indicated by 0, on the top face by 100, and intermediate heights are given accordingly

A crystal consisting of symmetrical packets of fused silica and hydrargillite layers has the composition $Si_4Al_2O_{10}(OH)_2$ and represents the mineral pyrophyllite. When octahedral layers of brucite replace those of hydrargillite we get talc having the composition $Si_4Mg_3O_{10}(OH)_2$. Gruner (*loc. cit.*) and Hendricks (1938) have verified these structures for talc and pyrophyllite. From single crystal measurements Hendricks concluded that the structures are fixed in the *a*- and *c*-directions but the individual $(OH)_2Al_2Si_4O_{10}$ or $(OH)_2Mg_3Si_4O_{10}$ packets are randomly shifted along the *b*-axis. He preferred the space group C_s^4 to the space group C_{2h}^6 proposed by Gruner.

When silicon ions in pyrophyllite are replaced by aluminium ions of coordination number 4, negatively charged layers are developed. Electroneutrality is maintained by the incorporation of further positive ions into the structure. There is room for these ions between the layers in pockets formed by two opposite hexagonal rings of the basal oxygen ions belonging to contiguous tetrahedral silica layers. In muscovite mica having the composition $K(Si_3Al)Al_2O_{10}(OH)_2$ every fourth Si^{++++} ion is replaced by an Al^{+++} ion and the pockets are filled up by K^+ ions (Fig. 2)

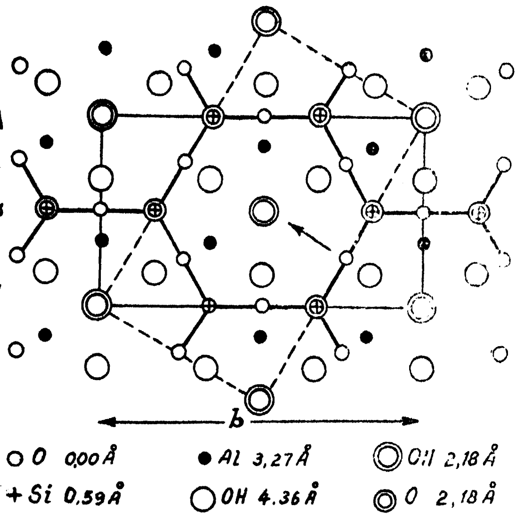

Fig. 3

(After Gruner)

Sheet of $2[(OH)_4Al_2Si_2O_5]$ proposed by Pauling. Height of atomic positions may vary slightly.

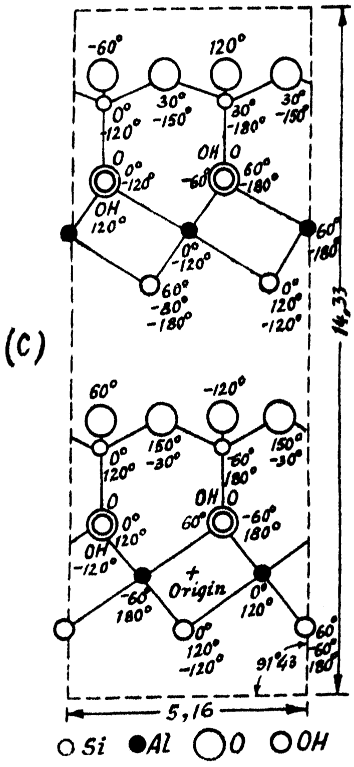

Fig. 4

(After Gruner)

One half of the unit cell of nacrite. The plane of the paper is the principal glide plane containing the origin.

A similar replacement in talc gives rise to biotite having the formula $K(Si_3Al)Mg_3O_{10}(OH)_2$.

In chlorites the negative charge of the substituted pyrophyllite layers is balanced by brucite layers which have acquired a positive charge through the replacement of a part of Mg^{++}ions by Al^{+++}ions.

(*i*) *Minerals of the kaolin group.*—Ross and Kerr (1931) made an extensive study of the mineralogy and chemical composition of the kaolin group of minerals including the amorphous substance allophane. Almost a complete lack of isomorphous replacement is one of the distinctive features of these minerals. This has been traced to the unsymmetrical structure of kaolins which cannot bear the strain arising from the incorporation of cations other than Si^{++++} and Al^{+++} or of layers (*e.g.*, brucite) having lattice dimensions different from those of gibbsite or silica (Pauling, *loc. cit.*). Gruner (1932, *a*, *b*; 1933) worked out the detailed crystal structures of the three polymorphic varieties, kaolinite, dickite and nacrite. All the three give monoclinic crystals and are formed by the stacking of unsymmetrical packets of fused silica and hydrargillite layers; the packet of kaolinite is shown in Fig. 3, but each shows a characteristic manner of stacking which is different from that of the others and gives rise to different monoclinic angles (β) as will appear from Fig. 4(*a*-*c*). Gruner's crystallographic data are given below :—

Kaolinite	Dickite	Nacrite
a=5.138Å	a=5.14Å	a=5.16Å
b=8.900Å	b=8.94Å	b=8.93Å
c=14.506Å	c=14.42Å	c=18.66Å
β=100°.12′	β=96°.50′	β=91°.43′
Z=4	Z=4	Z=8
$C_s^4=Cc$.	$C_s^4=Cc$	$C_s^5=Cc$.

Z—denotes the number of molecules of the formula $Al_2Si_2O_5(OH)_4$; $C_s^4=Cc$ represents the notation of the space group.

A displacement of the packets relative to one another is possible along both the a and b-axes. The monoclinic angle β is determined by the shift of one packet over the other in the direction of the a-axis. The shifts are respectively $\pi/2$, $\pi/3$ and $\pi/12$ for kaolinite, dickite and nacrite ($a=2\pi$). As the (010) plane constitutes a glide plane of symmetry any amount of shift parallel to the b-axis is theoretically possible consistent with a fixed monoclinic angle. Certain observed reflections in the case of kaolinite limit the shifts to intervals of $\pi/3$, $2\pi/3$, and $4\pi/3$ ($b=2\pi$). But Gruner found that only the two positions A and B (Fig. 5a) in which the shifts along the b-axis are respectively 0 and $4\pi/3$ are in equally good agreement with the calculated intensities and a choice between the two is difficult. For a particular sample of Brooklyn kaolinite he preferred the B-position. For dickite, the A-position (Fig. 5b) in which the shift along the b-axis is $\pi/3$ is accepted. In nacrite the shift is $2\pi/3$ (Fig. 5d).

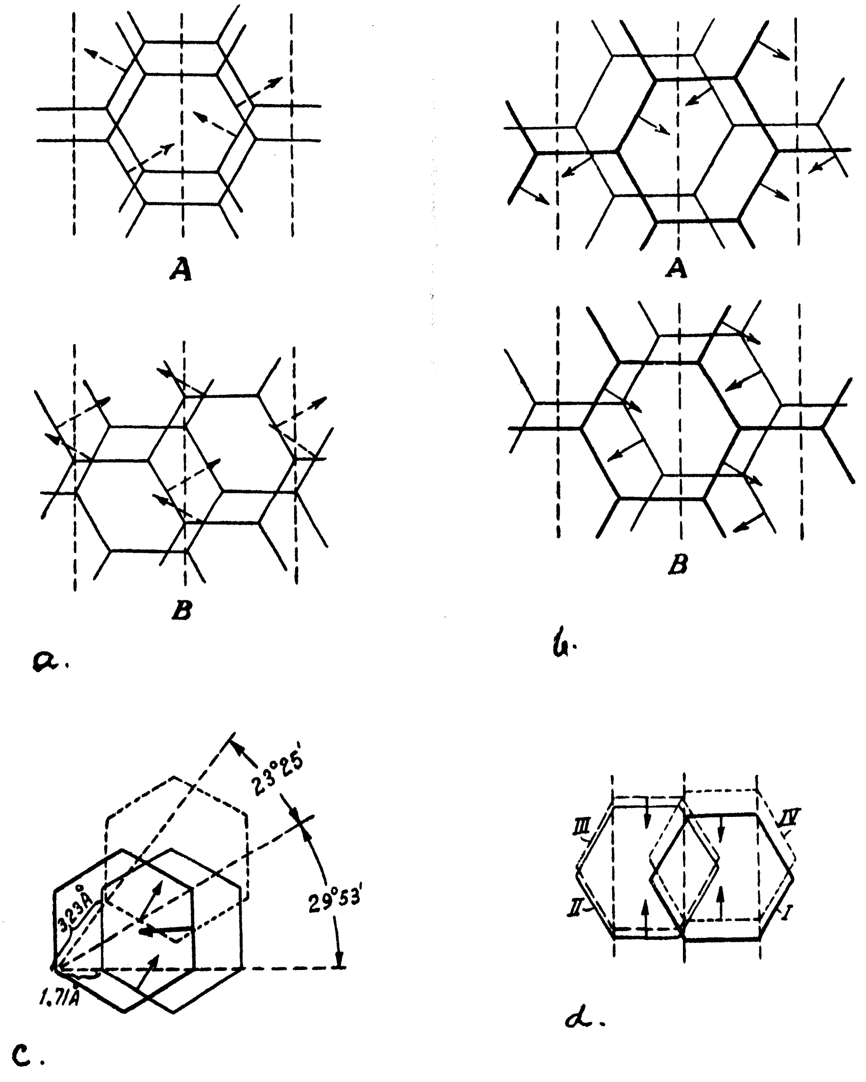

FIG. 5
(After Gruner)

(*a*) The two possible shifts of sheets in the kaolin structure. Dotted lines are glide plane of C's. Arrows indicate planes of synemery in individual sheets.

(*b*) The two possible shifts of sheets in the dickite structure. Dotted lines are glide planes of C's. Arrows indicate planes of symmetry in individual sheets. Heavy lines represent lower layers.

(*c*) The shift in dickite as compared with that of kaolinite. Heavy-lined hexagon represents stationary SiO_4 sheet for both dickite and kaolinite, Light-lined hexagon represents upper adjoinjng sheet of kaolinite.

(*d*) The shifts of the four layers in nacrite when seen in a direction normal to the base (001). The dotted lins are glide planes of symmetry of C's.

The space group which is identical for the three minerals contains only a glide plane of symmetry which lies in the plane of the a- and c-axes. All packets face in the same direction giving rise to the polar hemihedral space group C_s^4.*

The unit cell of kaolinite and dickite consists of two unsymmetrical packets while that of nacrite is made up of four such packets (Fig. 5, a-d). The ordinary planes of symmetry of contiguous sheets make angles of 120° in kaolinite and dickite ; but in nacrite each sheet is rotated through 180° in its own plane with respect to its nearest neighbour and the sheets 2 and 3 are each shifted through $2\pi/3 \times b$ relative to packets 1 and 4 respectively.

From measurements on single crystals Hendricks (1938) later on gave the following crystallographic data for nacrite.

$$a=8.94\text{Å}$$
$$b=5.14\text{Å}$$
$$c=43.00\text{Å}$$
$$\beta=90^\circ.20'$$
$$Z=6[(OH)_8Al_4Si_4O_{10}]$$
$$C_s^4=Cc.$$

This structure is different from the one due to Gruner in that the former postulates 6 kaolinitic layers in the unit cell instead of 4 and the directions of the a and b axes have been reversed.

In order to explain the high silica-alumina ratio of anauxite Gruner assumed a replacement of octahenral Al^{+++} by Si^{++++}. Bragg (1937) and Hendricks (1936), doubted this hypothesis. The latter suggested a defect of $Al(OH)_3$ giving rise to holes in the structure. Gruner (1937), showed that this structure does not agree with the observed densities. Gruner's alternative suggestion that whole units of tetrahedral SiO_4 occupy positions of octahedral units of $AlO_2(OH)_4$ is not structurally convincing according to Hendricks. The latter finally suggested a structure of anauxite formed by the incorporation of excess of silica in the kaolinite lattice as neutral silica layers following the kaolinite layers in irregular sequence.

There is some confusion regarding the nomenclature of halloysite, $Al_2O_3 2SiO_2 2H_2O$, and the hydrated mineral, $Al_2O_3 2SiO_2 4H_2O$. Hofmann, Endell and Wilm (1934) described the latter as halloysite. On heating at 50°C it gave a product which they identified as kaolinite. Mehmel (1935) showed that this product is not kaolinite but a new mineral which he designated as metahalloysite. The following nomenclature due to Hendricks (1939) will be adhered to in the sequel.†

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* The space group C^6_{2h} suggested by Ksanda and Barth (1936) has been eliminated (Hendricks, 1938) as single crystals show strong pyroelectric effect by the Martin method.

† Recently Hendricks (1943) suggested the name 'endellite' for the more hydrated mineral.

Halloysite, $Al_2O_3 2SiO_2 2H_2O$ (metahalloysite of Mehmel).

Hydrated halloysite. $Al_2O_3 2SiO_2 4H_2O$ (halloysite of Hofmann, *et al*, Mehmel and others).

According to Mehmel, hydrated halloysite (Mehmel's halloysite) is built up in the direction of the c-axis from alternating layers of $H_2Si_2O_5$ and $Al(OH)_3$. They are not linked up by principal valencies and do not form a fused packet. In halloysite (Mehmel's metahalloysite), on the other hand, the two layers are condensed with the elimination of $2H_2O$ giving rise to a fused packet having the composition $(OH)_4.Si_2Al_2O_5$ of kaolinite. Mehmel gave the following crystallographic data for the two minerals :—

Hydrated halloysite.	Halloysite.
$a = 5.20 Å$	$a = 5.15 Å$
$b = 8.92 Å$	$b = 8.00 Å$
$c = 10.25 Å$	$c = 7.57 Å$
$\beta \sim 100°$	$\beta \sim 100°$
$Z = 2$	$Z = 1$
$C_s^3 = Cm.$	$C_s^3 = Cm.$

The structures indicated in Fig. 6(b,c) differ from that of kaolinite Fig. (6a). The space group C_s^3 contains an ordinary plane of symmetry parallel to (010) while the space group C_s^4 to which kaolinite belongs has a glide plane of symmetry parallel to (010). This difference in the space groups is reflected in the dimensions of the unit cells. That of hailoysite consists of only one packet while two packets go to form the unit cell of kaolinite.

Hendricks objected to the above structures on the ground that the interaction of the hydroxyl groups of the layers of $Si_2O_3(OH)_2$ and $Al(OH)_3$ as a result of which water is considered to be eliminated (see above) would require a large activation energy and consequently would not be expected to take place readily at such low temperatures as 50°C. He further pointed out that the intensity data do not agree with the proposed structures. He suggested an alternative structure for hydrated halloysite in which neutral kaolinitic layers $[(OH)_4Si_2Al_2O_5]_n$, are interleaved with single layers of water molecules. According to Hendricks there is no reason for considering halloysite to possess a structure different from kaolinite, dickite and nacrite. In his opinion, the slight difference between the powder diagrams of halloysite and other kaolinitic minerals may be considered to arise from differences in the degree of organisation of the crystallities, (*cf.* also Nagelschmidt, 1939).

Edelman and Favejee (1940) suggested a structure of hydrated halloysite in which every alternate SiO_4-tetrahedron is inverted and the vertical oxygens are replaced by hydroxyl groups to balance the charges. This layer together with one of $Al_2(OH)_6$ would give the composition $[Al_2(OH)_5OSi_2O_3(OH)]_n$ or $[Al_2O_3 2SiO_2 3H_2O.]_n$ Additional water molecules required for the formula, $Al_2O_3 2SiO_2 4H_2O$, of hydrated halloysite are supposed to exist in

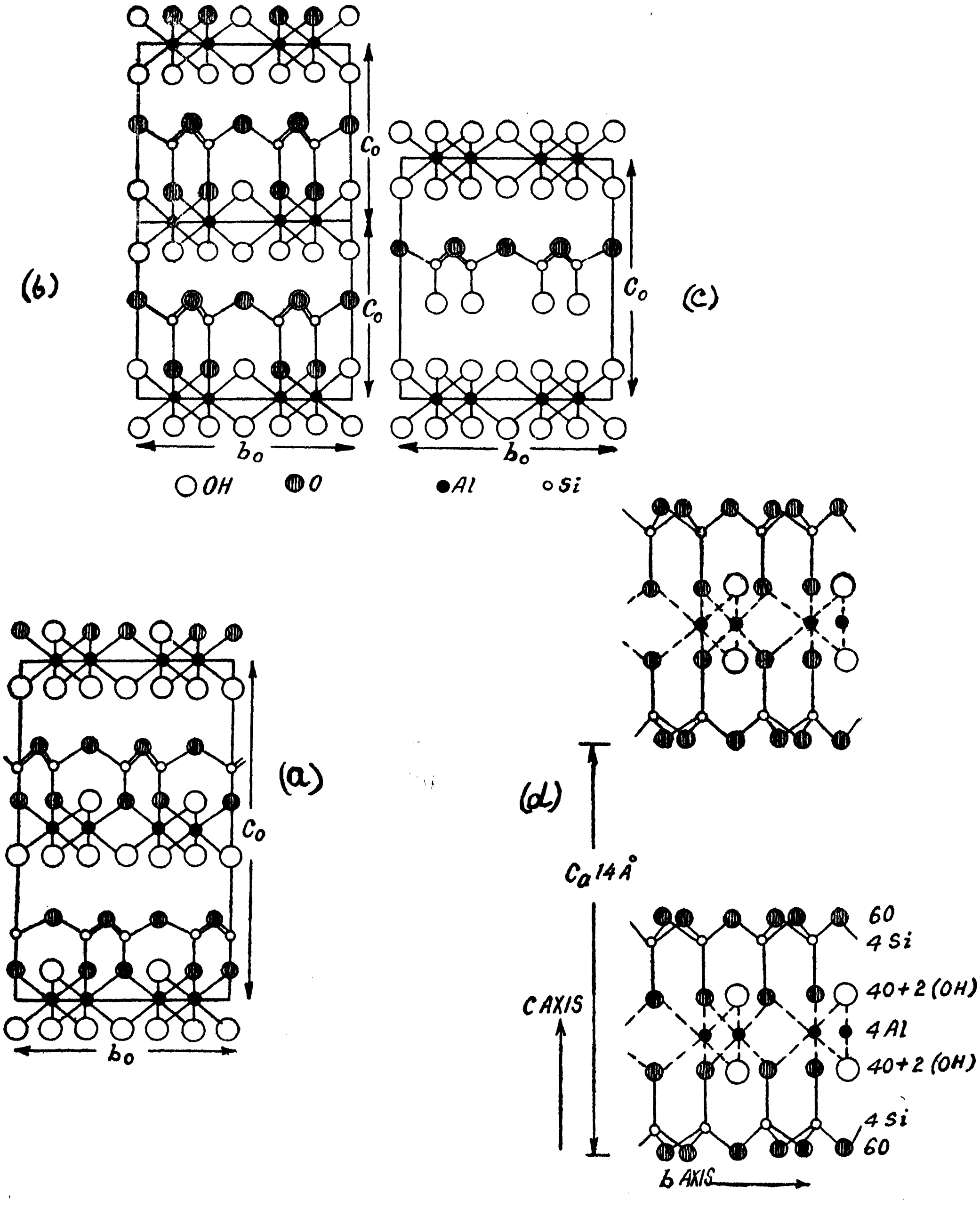

Fig. 6

(*a*—*c* after Mehmel)

(*a*) Schematic diagram of the projection on the plane (100) of (*a*) kaolinite.

(*b*) Schematic diagram of the projection on the plane (100) of (*b*) halloysite.

(*c*) Hydrated halloysite.

(*d*) Schematic diagram of the crystal structure montmorillonite. (After Hofmann).

between the sheets. The change to halloysite takes place by the loss of one such water molecule, the other molecule being obtained from the interaction of an (OH) group of the hydrated silica sheet with an (OH) group af the adjacent sheet of $Al_2(OH)_6$. The two sheets are thus linked through the residual oxygen atom (see Fig. 7). This structure is also open to Hendricks' criticism stated above.

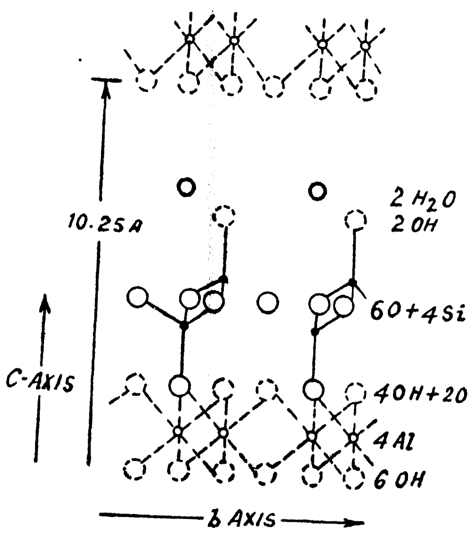

FIG. 7
(After Edelman and Favejee)
Schematic presentation of the crystal structure of hadrated halloysite

A monoclinic holohedral structure (C_{2h}) of halloysite has been suggested by Stout (1939) from a study of the x-ray diagrams of halloysite before and after fixation phosphates by this mineral. The unit cell in this structure would consist of two kaolinitic packets having their OH-layers facing each other.

(*ii*) *Minerals of the montmorillonite group*.—Hofmann, Endell and Wilm (1933), proposed a symmetrical pyrophyllite-like structure of montmorillonitic minerals (Fig. 6d). These minerals, however, seldom have the ideal composition $Al_2O_3 4SiO_2 H_2O$, of pyrophyllite. Wide variations in composition are encountered. Isomorphous replacements within the lattice are responsible for them. In the mineral montmorillonite, $[Al_{1.67}Mg_{.33}(Si_4)O_{10}(OH)_2]Na_{.33}$, having a SiO_2/Al_2O_3 ratio of about 4·0, isomorphous replacements, *e.g.*, of octahedral Al^{+++} by Mg^{++} or Fe^{+++} and of Si^{++++} by tetrahedral Al^{+++} are limited. Extensive replacements give rise to a number of end members.

Beidellite having the SiO_2/Al_2O_3 ratio 3:1, is the end member obtained by the replacement of a part of the Si by tetrahedral Al*. The negative charge developed in the silica layer as a result of this replacement is balanced by the

* Grim (1942) believes beidellite to be a mixture of montmorillonite and limonite.

incorporation of mono-, or, bi-valent cations as in micas and/or by the replacement of octahedral Al^{+++} by Mg^{++}. A small quantity of the octahedral Al^{+++} may also be replaced by Fe^{+++} and Fe^{++}. Complete replacement of octahedral Al^{+++} by Mg^{++} would give rise to saponite. Nontronite is the end member obtained by the replacement of the octahedral Al^{+++} by Fe^{+++} and Fe^{++}. A differentiation of these end members on the basis of the powder diagrams alone is not possible excepting perhaps nontronite whose Fe has a much higher scattering power than Al or Mg.

Hofmann, Endell, and Wilm assume an orthorhombic cell for montmorillonite with dimensions a=5.095 Å, b=8.83 Å and c=15.2 Å. Gruner (1935) however, believes that minerals of the montmorillonite group belong to the monoclinic system. According to Hofmann and Maegdefrau (1937), the individual packets lie parallel to and equidistant from one another but are not similarly oriented in the a- and b-directions. Because of this random orientation there is, strictly speaking, no space lattice but each packet forms some sort of a surface lattice. This 'cross-grating effect' follows from the complete absence of (hkl) interferences. Only (hko) and (001) interferences referred to the space lattice are observed.

Some orientation of the packets in the a-and b-directions has been suggested by Hendricks and Ross (1939).

A characteristic feature of the montmorillonite lattice, one which differentiates it from pyrophyllite having a similar structure, is the variable *c*-axis of the former depending on the content of water. This unique property of unidimensional inner-crystalline swelling is shown by only two other known substances, graphitic acid (Hofmann and Frenzel, 1932) and violet basic cobalt sulphate (Feitknechet and Fischer, 1935), The water molecules are loosely held between the packets and are readily given up on heating. Hofmann observed a reversible dehydration up to a temperature of 550°C. The lattice is preserved even at 800°C but breaks down at about 1000°C. Maegdefrau and Hofmann found a continuous variation of the swelling with the humidity. Nagelschmidt (1936), however, observed a stepwise variation; the (001) spacing increased from 10.5 Å to 15.2 Å and from 15.2 Å to 15.6 Å as the number of water molecules per 'ignited' unit cell, *i.e.*, per $Al_4\ Si_8O_{22}$, increased respectively from 2 to 10 and from 10 to 21. For a number of water molecules varying from 10 to 21 no significant variation in the spacing was observed but in the range 20-40 H_2O the spacing increased rapidly to 18.4 Å. From studies of x-ray diagrams of oriented samples of montmorillonite Bradley, Grim and Clark (1937) showed that the stepwise increase in swelling is to be attributed to the formation of definite hydrates containing 2, 8, 14, 20 and 26 molecules of water corresponding to (001) spacings respectively equal to 9.6 Å, 12.4 Å, 15.4 Å, 18.4 Å, and 21.4 Å.

No entirely satisfactory and generally accepted explanation has been offered regarding the manner in which the water molecules are held between the packets. Hofmann (1937), Nagelschmidt and others believe that the water molecules form closely packed sheets between the basal planes. According to Hendricks and Jefferson (1938), however, the water molecules are not densely packed but form a hexagonal net by secondary bonds between O and H atoms of adjacent water molecules in a given net as shown in Fig. 8(*a-b*). One-fourth of the hydrogen atoms in the net, or in other words, one hydrogen atom in every two water molecules remains 'free', *i.e.*, not bonded in this manner. The net itself is tied up to the neighbouring silica layer or other hexagonal layers by the attraction between such 'free' H atoms and oxygen atoms of the adjacent layers*. The

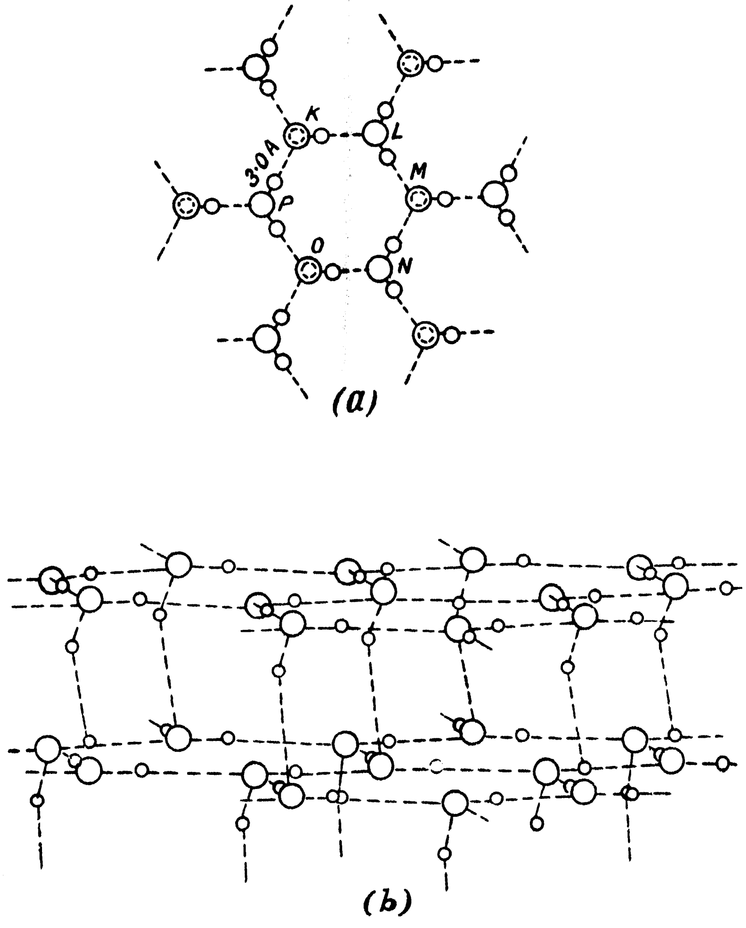

FIG. 8

(After Hendricks and Jefferson)

(*a*) Hexagonal net of water molecules. Large spheres represent oxygen atoms and small spheres hydrogen atoms, dotted lines indicate bonding through hydrogen.

(*b*) Probable structure of multiple water layers.

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* When the surface of the clay mineral contains hydroxyl groups (*e.g.*, kaolinite) some of these hydroxyl groups are free so as to bind their hydrogen atoms to oxygen atoms of the water layer.

oxygen atoms in a given water layer lie in one plane. In this configuration each layer contributes 4 molecules of water to the structural unit as against 6 molecules in the close packed arrangement. The observed variation in the (001) spacing arises from a variation in the spacing between the cleavage planes. Cleavages along (001) planes give rise to crystallites containing different numbers of water layers corresponding to the different hydrates $2H_2O$, $6H_2O$, $10H_2O$, etc. The observed (001) spacing at a fixed humidity is only an average of the spacings of the various hydrates. It is this average spacing which varies continuously with the humidity. The stepwise variation observed by Nagelschmidt is difficult to explain in the light of this hypothesis. It is also difficult to understand why other clay minerals and even pyrophyllite which has the same structure as montmorillonite do not swell.

Hofmann and Bilke (1937) showed that at a fixed humidity the swelling of montmorillonite depends on the nature of the exchangeable cations as well as on the p_H. No satisfactory explanation of this 'cation effect' has also been forthcoming. A mere hydration of the cations (Wiegner, 1931; Bär and Tenderloo, 1936) would explain neither the magnitude of the swelling nor the differences in the relative effects of the various cations. From a study of the low temperature endothermic effect shown by 'thermal curves', Hendricks, Alexander and Nelson (1940) concluded that only a very small fraction of the water can be attributed to a hydration of the cations in the case of Mg-, Ca- and Ba-montmorillonites, the greater part of the water beings tacked between the packets as hexagonal nets. No water of hydration could be detected in the case of Na-, K-, and Cs-montmorillonites.

The characteristic swelling of montmorillonite is probably to be attributed to the polarising properties of the cations (W. Russel, 1934) lying on the surface of the packets. Montmorillonite contains a much larger quantity of such cations than any other clay mineral. In view of extensive and different types of isomorphous replacements in montmorillonite considerable strains are brought to bear on the lattice which hamper the growth of the crystals to large dimensions and only minute crystallites are formed (*cf.* Hendricks, 1942). This gives rise to an extensive outer surface and a large number of exposed cations. The latter have their coordination valencies only partially satisfied and this further reinforces the tendeney of the cations to polarise water molecules and draw them to the surface. A layer of water molecules thus condensed on the surface may be covered by other layers in accordance with the mechanism suggested by Hendricks and Jefferson.

Clay minerals other than montmorillonite and also pyrophyllite do not contain any appreciable quantity of cations on the surface and consequently do not swell. The micas which also do not swell no doubt contain some cations in between the packets. However, unlike montmorillonite, a comparatively small percentage of these cations is exposed. This is due to the formation of larger crystals favoured by absence of strains arising from different types of isomorphous replacements.

There is yet another reason for the nonexpanding lattice of the micas (Grim *loc. cit*). Unlike montmorillonite where isomorphous replacements mainly take place in the octahedral layer, they are almost entirely restricted to the silicate layer in the micas. The centre of the negative charge within the packets lies nearer to their surfaces in micas than in montmorillonite and consequently the cations in the former are strongly bonded to the surface and, through them, the packets themselves are firmly held and do not admit of any expansion in the c-direction. On account of a greater separation of the charges in montmorillonite, the packets are tied together comparatively loosely through the cations interposed between them and thus help the water molecules to force the packets apart.

Several investigators (Holzner, 1936 ; Bragg, 1938 ; De Lapparent, 1938) have taken exception to the pyrophlyllite structure of montmorillonite on the ground that it does not satisfactorily explain the characteristic swelling (and high base exchange capacity) of this mineral. Edelman and Favejee (1940) proposed an alternative structure (Fig. 9) in which the silica layer on either side of the hydrargillite layer has the configuration of β-cristobalite (Fig. 1, b) hydrated as in halloysite and has the formula $O_2Si_4O_6(OH)_2$. The mineral

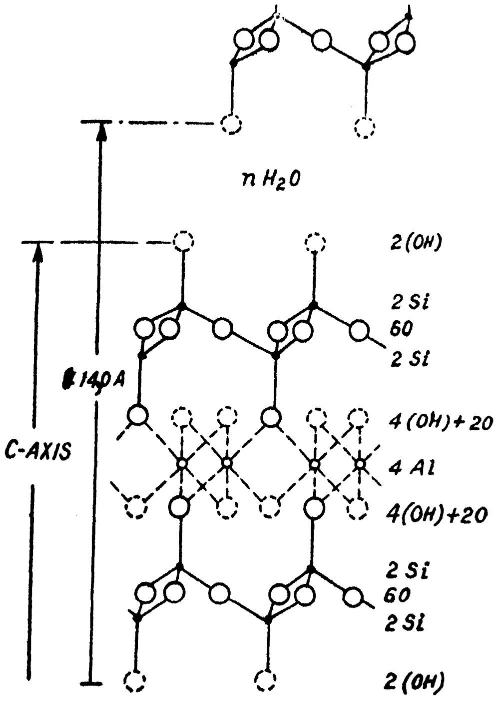

FIG. 9
(After Edelman and Favejee)
Schematic presentation of the structure of Montmorillonite.

itself has the composition $(OH)_{12}Al_4Si_8O_{16}.nH_2O$. Grim prefers this structure as in his opinion it offers a better explanation of the swelling. He considers that the projecting OH ions in this structure favour the formation of water layers as suggested by Hendricks and Jefferson.

Other structures have been suggested but have not met with general approval as they have no particularly strong points in their favour. The pyrophyllite structure suggested by Hofmann is usually accepted as it provides the best all round explanation of the behaviour of montmorillonites if isomorphous replacements as well as individual properties of cations are also taken into consideration.

Minerals of the illite group or hydrous micas.—Until recently there has been some confusion regarding the existence of micas as a distinct group of clay minerals. Hendricks and Fry (1930) recognised certain minerals in soil colloids which they designated as ordovician bentonite', a term used by Ross and Shannon (1926). Ross and Kerr (1931) described similar minerals as potassium bearing clay minerals. Hofmann and his coworkers (1937) first definitely distinguished mica-like minerals as essentlal constitutents of clays and named them 'glimmerton'. Almost simultaneously, Grim, Bray and Bradley detected mica-like clay minerals in a variety of soils, clays and shales from Illinois and placed them in a distinct group under the name "illite". The group-name "hydrous micas" proposed by Hendricks for all such micaceous clay minerals is more suggestive as it brings out their chemical and structural relationships to muscovite mica ; the hydrous micas, though structurally similar to muscovite, contain more water and less K than the latter.

The general formula, $2K_2O, 3R^{++}O. 8R_2^{+++}O_3.24SiO_2.2H_2O$ of hydrous micas is derived from the ideal formula $K(Al_2)\ (AlSi_3)\ O_{10}(OH)_2$ of muscovite mica by the replacement of some K by H_2O. Balancing of the charges is effected by the replacement of Si^{++++} by tetrahedral Al^{+++} or of O^{--} by OH^- (Hendricks, 1937). Only 15%of the Si, and not 25% as in muscovite mica, is replaced by Al giving a relatively smaller amount of K. Possible replacements of Mg^{++} for octahedral Al^{+++} balanced by the substitution of $(OH)^-$ for O^{--} may partly account for a higher percentage of water in the hydrous micas than in muscovite (Hofmann and Maegdefrau 1937). Both ferrous and ferric iron may also replace some octahedral Al. Isomorphous replacements, however, are not so extensive in the hydrous micas as in montmorillonites.

Gruner (1935) and others have postulated a monoclinic cell for hydrous micas similar to that of muscovite ; the cell dimensions, however, have not been recorded*. Hofmann and Maegdefrau, on the other hand, believe that their diffraction data can be explained by assuming an orthorhombic cell having the dimensions $a = 5.18$ Å, $b = 8.97$ Å, $c = 19.84$Å.

(*iv*) *Minerals of the attapulgite group.*—J. Delapparent (1935) gave the name attapulgite to a clay mineral found in fuller's earth from Attapulgus,

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* Presumably they have accepted the cell dimensions of muscovite ;

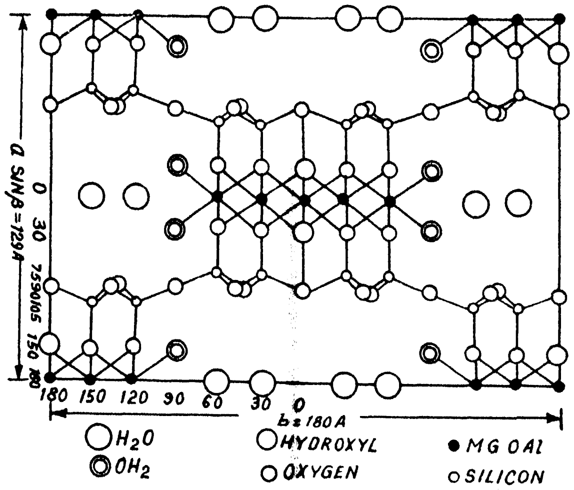

FIG. 10

(After Bradley)

Idealized proposed structure for attapulgite projected on to (001).

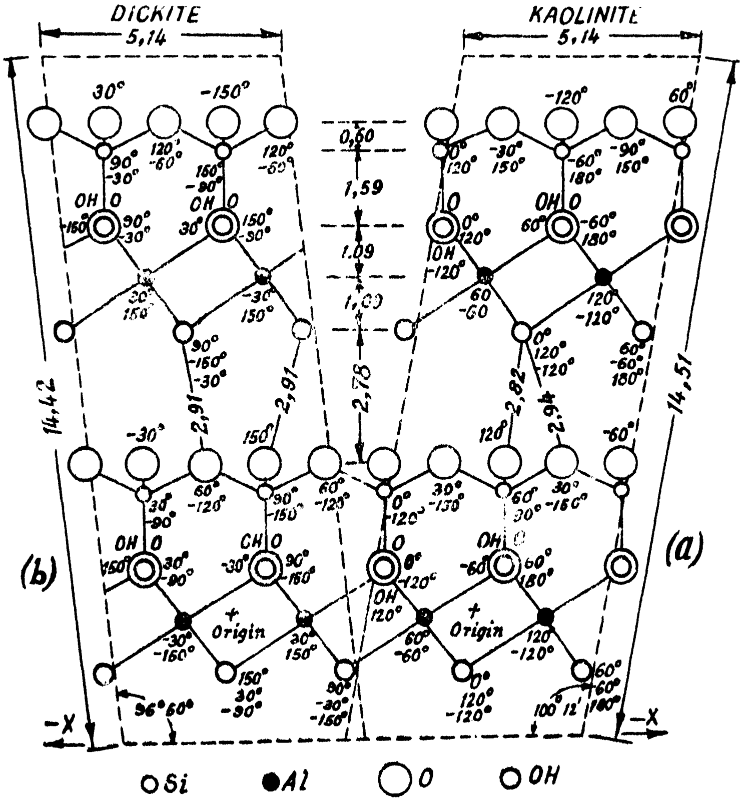

FIG. 11

Comparison of the dickite and kaolinite unit cells. The plane of the paper is the principal glide plane of symmetry containing the origin. Y-co-ordinates are given in degrees.

Georgia and Mormoiron in France. Formerly (Kerr, 1937) it was considered to belong to the montmorillonitic group of minerals. X-ray studies by Bradley (1940) however, showed "fibre diagrams".

The structure proposed by Bradley (Fig. 10) consists of a brucite layer fused between two silica layers. The brucite layer is, however, not continuous and the structure extends only in one direction instead of two as in the case of other clay minerals. Consequently, instead of sheets, fibres or rods with the c-axis parallel to the length of the fibres are obtained. The silicon-oxygen chains running parallel to the c-axis along (ooZ) and ($\frac{1}{2}\frac{1}{2}$Z) are similar to amphibole chains (Warren, 1929) so that the silicate layer as viewed from above is continuous. Chains of water molecules wich also run parallel to the c-axis fill the interstices between the ribbons and this water is lost below 100°C without materially altering the diffraction patterns. An equal amount of water is co-ordinated about Mg. It is less easily removed. Finally, the water which is expelled above 500-600°C comes from the OH groups of the lattice, the unit cell containing four of them.

The periodicity along the c-axis is 5.29 Å. Bradley gives the following dimensions of the cell:

$$a \sin\beta = 12.9\ \text{Å},\quad b = 18{,}0\ \text{Å},\ c = 5.20\ \text{Å}$$

The cell has the ideal composition $(OH_2)_4(OH)_2\ Mg_5\ Si_8\ O_{20}\ 4H_2O$. There are two such molecules in the unit cell and the space group is probably $C^3_{2h} - C^{2/m}$.

(*v*) *Mixed Structures.*—Mixed structures formed by the interstratification of more than one mineral have been encountered in minerals like vermiculites (22,23), cronstedite and faratsihite (Hendricks, 1939). The possibility of occurrence of such mixed structures in clays was pointed out by Hendricks. He Hendricks, and Teller, 1942) has given a theoretical treatment of diffraction of x-rays by such mixed structures. Another type of mixed structures has been visualised by Nagelschmidt (1944). It might result, say, "from weathering of illite particles in which the centre would have illite, the outer layers montmorillonite, composition. If the weathering had not gone very far such particles would give mica bulk effects (for instance, x-ray diffraction, chemical analysis) but montmorillonite surface effects (for instance, mixed base equilibria)" Definite evidence for such mixed structures in clays is however still lacking.

IDENTIFICATION OF CLAY MINERALS IN SOIL COLLOIDS

The importance of identification of clay minerals and assessment of their relative proportions in clay fractions for purposes of soil systematics and from the point of view of theoretical as well as applied soil science is now generally recognised. Both physical and chemical methods have been requisitioned for this purpose. In view of isomorphous replacements and the possibility of occurrence of more than one clay mineral in the same clay fraction and owing, further to the association of silica, sesquioxides and other necessary materials, identification of the mineral constituents of the clay fraction on the basis of total analysis alone is not possible though a fairly satisfactory correlation has often been obtained between the mass chemical composition of the clay fraction expressed as its SiO_2/R_2O_3 ratio and various physical and chemical properties of clays, *e.g.*, swelling, viscosity, dispersibility, heat of wetting and base exchange capacity. While this ratio as a 'single value' soil constant is apparently of some importance, it is of little value for the identification of the mineral constituents of the clay fraction. Marshall (1935) tried to identify clay minerals in some clays by properly fitting their analytical data in the known lattice structures of the clay minerals. For this purpose, he assumed the following major replacements within the lattice (*a*) tetrahedral Al^{+++} for Si^{++++}, the resultant negative charge being balanced by one equivalent of cation per atom of Al; (*b*) Fe^{+++} for Al^{+++} in the octahedral layer; (*c*) either one Mg^{++} for one octahedral Al^{+++} with incorporation of cations to balance the negative charge, or, 3 Mg^{++} for 2 Al,$^{+++}$ which gives a neutral layer. The following minor replacements were also considered: (*a*) octahedral Al^{+++} by Ti^{++++}, the positive charge developed when the latter is tetravalent being balanced within the lattice by the replacement of Al^{+++} by Mg^{++} (*b*) Si^{++++} by P^{+++++}, the resulting positive charge being balanced by the simultaneous replacement of Si^{++++} by tetrahedral Al^{+++}. However, even when such replacements are taken into account, a correct fitting of the analytical data in the lattice structures will hardly be possible when more than one clay mineral are present in the clay fraction and their relative proportions are not known.

Methods using adsorption of dyes (Hardy, 1931; Huttig, 1931) and preferential adsorption of certain cations (Schatchtschabel, 1940; Hendricks and Alexander, 1940) are not sufficiently developed for purposes of unequivocal identification or differentiation of the various clay minerals. Physical methods have been found to be more suitable for this purpose. These are based on a comparative study of clays and standard specimens of clay minerals by x-ray, thermal and optical methods. On being heated, these clay minerals lose water (present both as H_2O molecules and as OH groups of the lattice) each in a characteristic manner and methods have been proposed for identifying them based on this effect of heat. One of them, the so-called 'differential thermal' method which is originally due to Le Chatelier (1887), consists in following the temperature of the specimen relative to an inert material, *e.g.*, calcined alumina, when the two are heated continuously at the same rate. An endothermic change is indicated by a lag in the temperature of the specimen and an exothermic change by a sudden elevation of the temperature relative to the inert material. The number and character of such breaks, and the temperatures at which they occur serve as the criteria for identifying the clay minerals. Nagelschmidt considers that endothermic effects in clay minerals are to be attributed to the release of adsorbed water and to a breakdown of the lattice, exothermic effects probably arising from oxidation of divalent Fe^{++} ion, or the formation of new silicates at higher temperatures. The 'thermal method' was first applied to clays by Orcel (1926) and to soils by Agafonoff (1935). Norton (1939) and more recently, Grim and Rowland (1942) have introduced improvements in the technique for differential thermal analysis.

In the so-called vapour pressure method used by Puri (1925) Orcel (1927), Thomas (1928) and Alexander (1936), the temperature of the material kept in vacuum is gradually raised and changes in the vapour pressure measured. The curve obtained by plotting the vapour pressure against temperature is considered characteristic of the mineral.

In the 'dehydration methods,' the loss in weight of the sample when heated to constant weights at various temperatures is measured and identification carried out from an analysis of such features of the temperature-dehydration curves as relative propertions of 'adsorbed' and crystal lattice' water and the critical temperature at which the lattice water is expelled, it being assumed that the loss of weight is due entirely to loss of water and no volatile matter or substance which gives up volatile matter on heating is present. Three different techniques are followed in regard to the manner of heating the specimen giving what are called methods, of (*a*) continuous heating, (*b*) single heating, and (*c*) intermittent heating. In (*a*) heating is done at a constant rate over the range 20°C to 1000°C andthe specimen weighed in *situ* (Longchambon, 1936). In (*b*) several lots of the same specimen are heated each to a different temperature, cooled, and then weighed (Dunstall, 1938). In (*c*), which is the most common in use, the same sample is heated and weighed at suitable intervals of temperature (Kelley and others, 1939)

In the so-called 'rehydration-dehydration' method suggested by Berkelhamer (1943), the amount of water taken up by clay minerals previously heated to 300°C and that lost between 300°C and 600°C is used as criterion for their differentiation and identification.

Examination under the microscope and determinations of refractive indices are the optical methods usually employed for the identification of minerals. Owing to the fine grain-size of clay minerals a direct microscopic examination of individual crystals is not possible.* However, in view of the platy nature of the crystallites they may be deposited from a suspension as fairly oriented optical units of microcrystalline aggregates which are more suitable for optical studies. These units show double refaction but in the majority of cases, the extinction is neither perfect nor sharp. Sometimes, when the particles are not deeply coloured, they show pleochroism. On account of the imperfectly crystallised state of the aggregates and in view of the presence of materials other than clay minerals in the clay fractions, Hendricks (1930) measured only the mean refractive index (r.i.) of the aggre-

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* Ross and Kerr (1930), found a few comparatively large single crystals of kaolinite, dickite and nacrite.

gates. Kelley (1939) and others (Grimetal, 1937) however, determined the refractive indices in three directions. All of them used the immersion method.

Several limitations of the optical method for purposes of identifying clay minerals in clays, however, exist. The r.i. of any clay mineral varies within wide limits owing to isomorphous replacements with a consequent overlapping of the refractive index of different clay minerals. The r.i. of some clay mineral also varies with their water content and the immersion liquid (Correns and Mehmel 1936, Barner 1936). In the case of soil colloids further difficulties arise from coatings of oxides and hydroxides of iron on the aggregates. On account of these complications identification of clay minerals is seldom possible by the optical method alone.

X-ray analysis offers the most powerful method for identifying the mineral constituents of clays. It is also the only method with the help of which in addition to the dominant clay minerals in the clay fraction, accessory minerals as also clay minerals occurring in much smaller quantities can be detected. It was first used by Hendricks and Fry (1930) and subsequently by Kelley (1931), Hofmann (1934), Negelschmidt (1934), Edelman (1939), Grim (1935), Clark (1937) and others (Mehmel) 1938). The identification is carried out in a strictly empirical manner by comparing the powder diagram of the clay fraction with those of known minerals. Since all the clay minerals have essentially the same general scheme of structure, their diffraction patterns are extremely similar. The most characteristic differences are provided by their basal spacings (001) which permit an unequivocal identification and differentiation of the clay minerals even in mixtures; other lines are practically of no value for this purpose.

In addition to the peculiar and specific difficulties confronting each of the above physical methods of identification, they are all subject to the common limitation that they normally do not go beyond indicating the general group to which a clay mineral found in a given clay fraction belongs. Distinction between closely related individual members of the same group, *e.g.*, kaolinite and halloysite, or, montmorillonite and beidellite, is often not possible. The occurrence of mixed structure would further enhance the difficulties. However, a judicious combination of these physical methods supplemented by exhaustive chemical analysis is likely to give an insight into the detailed mineralogical make-up of the clay fraction.

A powerful tool for the differentiation of clay minerals has been recently provided by the electron microscope. The various clay minerals give characteristic and sufficiently distinctive electron micrographs (Ardenne 1940, Eitel 1939-40, Shaw 1941, Humbert 1941, Shaw 1942). The montmorillonites (except nontronite) and illite "show structures ranging from a fluffy, amorphous-appearing material to well defined, extremely thin plates. Nontronite is characterised by flat, frayed fibres. Kaolinite and dickite both have hexagonal plate-shaped crystals. Dickite crystals are much thicker than most kaolinite crystals. Halloysite is characterised by long split rods."*

BASE EXCHANGE AND CRYSTAL STRUCTURE

Differences in the lattice structures of clay minerals are strongly reflected in their base exchange properties. Since Way (1860), a part of the mono and bi-valent cations of clay has been known to be readily exchanged for the cations of added salts. These are the so-called exchangeable cations or bases of the clay. The work of Kelley (1936), Marshall (1930-1935) and Nagleschmidt (1938) has definitely shown that the exchangeable cations are integral constituents of the lattice. The relation between base exchange and crystal structure has been discussed by Hofmann (1934-1937), Van der Meulen (1935), Edelman (1935) Schofield (1934) and others. Two factors mainly determine cation exchange, *viz.*, the physical accessibility of the cation and the nature and strength of the force with which it is held within the lattice. Grinding facilitates physical accessibility, as by this process the cations in the interior of the lattice are brought to the surface. Kelley and his co-workers have shown that grinding increases the base exchange capacity (b.e.c.) of a wide variety of minerals. The b.e.c. of the felspars which are considered to give some of the clay minerals on weathering increases markedly on grinding, *e.g.*, from 5.0 to 91.5 milliequivalents per 100 gms. in the case of orthoclase. Felspars are composed of linked Si- and Al-tetrahedra, one equivalent of cations, *e.g.*, K, Na, or Ca being required for each Al atom to balance the charge. These balancing cations are exposed on grinding and are readily exchanged.

Zeolites have a high base exchange capacity. They are also built up by linked Si and Al tetrahedra but unlike the felspars they have a honeycombed structure and the bases required to balance the negative charges of the Al-tetrahedra are accessible being located inside intercommunicating channels which permit the free passage of added cations through the interior of the crystals. Hence, as also pointed out by Kelley and Jenny, the size of the crystals need not be reduced by grinding in order to replace the balancing cations.† The b.e.c. of permutite is not affected by grinding which is consistent with the amorphous nature of this substance.

Grinding tends to reduce the sheets of mica to extreme thinness, thus exposing a large number of K^+ ions originally lying inaccessible in between the packets. The b.e.c. of muscovite increases from 10.5 to 76.0 m.e./100 gm. Both K and Mg are 'extracted' from biotite by a neutral solution of NH_4Ac and the quantity of each especially that of Mg, increases on grinding. The solid

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* Electronmicroscopy appears to be the only method for differentiating raolintie from halloysite.

† The data recorded in their paper, however, indicate an increase in the b.e.c. of the zeolite, natrolite, from 74.5 to 108.5 m.e. per 100 gm. on grinding. No reference to this increase has been made by the authors nor have they tried to explain it.

always adsorbs a quantity of NH_4 equivalent only to that of K found in the extract. Apparently the exposed Mg^{++} ions of the broken octahedra are replaced by NH_4^+ but NH_4 silicate being unstable the solid readily parts with this NH_4.

Talc shows no base exchange capacity even after extensive grinding as indicated by the fact that particularly no NH_4 is adsorbed by the solid. As in the case of biotite, however, Mg is extracted by the NH_4Ac solution and its amount considerably increases on grinding ; "at the same time, the substance appears to undergo decomposition".

Pyrophyllite and kaolinite which usually do not contain any appreciable quantity of mono-and bi-valent cations and have a small base exchange capacity show increases in b.e.c. ranging from 4 to 158.5 m.e./100 gm. and 8 to 100.5 gm. respectively on being ground to extreme fineness.* Kelley and his co-workers believe that the cation exchange power of these minerals is traceable to the H^+ ions of the OH groups of the crystal lattice. Kaolinite possesses two types of OH planes, one immediately on the exposed surface of a lattice package and the other, a subsurface OH plane covered by a network of O ions. The latter OH groups are also accessible through the hexagonal gaps in the superimposed O-network Only the subsurface OH planes are present in pyrophyllite. Grinding in a ball mill may split the crystals parallel to the basal planes or perpendicular to them. In the first case, new planes containing H^+ions would be exposed. In the second, the octahedral and tetrahedral layers would be broken. Hofmann, Endell and Wilm (1934) suggested that the cations are held by the free valency of the broken tetrahedra on the edges of the Si-O planes. Kelley and Jenny criticised this hypothesis as it, according to their opinion, violates the law of electroneutrality. They, however, lose sight of the fact that when a crystal is broken, simultaneously with the negative part of the bond there exists the corresponding positive part which would remove from the solution equivalent amount of the anion. The large increase in b.e.c. of kaolinite and pyrophyllite as a result of extensive grinding is, according to Kelley and Jenny, "due in large part, octahedral layers". The broken bonds may also polarise and adsorb water molecules which dissociate on the clay surface into OH and H^+ ions.

Hofmann, Endell and Wilm (1934) suggest that the high b.e.c. of extremely fine-grained kaolinite is due to lattice distortion. They have, however, not discussed the nature of such distortion and the part it is expected to play in fixing cations. Lattice distortion may produce an electrical field in the neighbourhood but it is not likely to explain the high b.e.c. of finely ground kaolinite.

Shaw (1942) studied the effect of 'dry' as well as 'wet' grindings on the b.e.c. and 'electronmicrography' of kaolinite. The b.e.c. increased to a greater extent on dry grinding. Wet grinding gave thinner flakes by cleavages along (001) planes having the hexagonal shape characteristic of unground kaolinite. The increase

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* Schachtschabel (1940) could not find any increase in the b.e.c. of kaolinite on grinding.

in b.e.c. on wet grinding should be attributed in the light of Kelley's hypothesis to the greater number of planar OH groups thus exposed. Here again, some doubt as to the acid character of these OH groups and their possible contribution to the b.e.c. is cast by the fact that talc which also contains similar OH groups, shows practically no b.e.c. even on extensive grinding. It is, however, possible that the acidic properties of the OH groups is not shown up in view of the stronger basic character of Mg compared with Al.

The electronmicrographs reveal thicker but smaller particles as a result of dry grinding but their hexagonal character has almost disappeared. The smaller particle-size indicates a large number of broken bonds to which the high b.e.c observed on dry grinding is attributed.

Shaw and also Grim consider that a large portion of the b.e.c. of the hydrous micas is also due to broken bonds.

Montmorillonite is differentiated from other clay minerals by its high b.e.c. The b.e.c. is attributable in a large measure to the mono-- and bi-valent cations which are incorporated into the lattice for balancing the negative charges developed as a result of isomorphous replacements. A quantitative agreement between the observed b.e.c. and that calculated on the basis of isomorphous replacement has been claimed by Nagelschmidt (1940) (see also Marshall 1935). Gieseking (1939) as also Hendricks and co-workers 1943) showed that these balancing cations can be exchanged for large organic cations. Different organic cations give different values of the basal spacing (001) which definitely show that the exchangeable cations are held in between the packets. Hendricks, Nelson and Alexander (1940) consider that about 80 of the exchange positions of montmorillonite are located on the basal planes and the remainder on the edges of the flakes. Kelley and Jenny (1936) report a considerable increase in the b.e.c. of bentonite on grinding. One palausible explanation of this increase is that the grinding exposes fresh layers of the blancing cations and also subsurface OH planes of the lattice. Electronmicrographs show that while very fine fractions of montmorillonite consist of particles having the thickness of a unit cell, coarser fraction contain thicker particles which on "wet washing" give particles unit cell thick. From studies of adsorption of gases Hendricks and Nelson (1943) concluded that air-dried montmorillonite usually gives aggregates having the thickness of about 50 unit cells. Hence it is probable that montmorillonite also contains aggregates having thickness of several cells and grinding like 'wet washing' reduces their thickness.

The increase in b.e.c. on grinding may also be brought about by the appreance of a large number of broken bonds.

Grinding obviously reduces the average particle-size of the clay crystals. However, no quantitative information regarding the variation of the average particle-size on grinding as also the effect of such variations on the b.e.c. is available. The clay fraction, even in the unground state, is a heterodisperse system. Subfractions having particle-sizes [more correctly, equivalent spherical diameters, (e.s.d.)] ranging between specified limits have been isolated by the controlled centrifugalisation of the entire clay fraction and their b.e.c.'s determined. In the case of kaolinite and kaolinitic clays the b.e.c. increases with diminishing particle size (Harman 1940, Spiel, 1940, Mukherjee, *et al.*, 1942). An inspection of the electronmicrograph (Shaw 1942) shows that a decrease in the average e.s.d. is accompanied by a decrease in both the cross-sectional area and the thickness of the particles. Consequently, the broken bonds as well as the exposed basal OH groups of the lattice increase in number thus giving rise to a larger b.e.c. There is some confusion regarding the part played by the e.s.d. on the b.e.c. of montmorillonite. Hauser and co.workers (Hauser, 1941; Hauser *et al.*, 1937) claim to have shown that the b.e.c. does not depend on the e.s.d. According to them, this is due to the peculiar lattice structure of montmorillonite which admits of ionic exchange in between the packets. A definite increase in the b.e.c. with diminishing e.s.d. has, however, been observed in the case of bentonites as well as montmorillonitic hydrogen clays by Marshall (1935) and also Mitra *et al* (1942, 1943). Electronmicrographs (Shaw 1942) show that coarser particles of bentonites are not only thicker than the finer ones but have definitely larger cross-sectional areas. The smaller this area the greater will be the number of broken bonds, which would account for the higher b.e.c. of the finer fractions even if a complete exchange of the cations in between the packets took place. The finer fractions, amongst themselves, do not appear to show any great difference in regard to the cross-sectional area and the thickness. It is just possible that the very fine fractions studied by Hauser and coworkers consisted of particles having practically the same cross-sectional area but slightly different thickness. In that case, the number of broken bonds remaining practically constant no alteration in the b.e.c. of such fractions would be expected if all the interplanar cations were exchangeable.

Of the two factors, physical accessibility and the nature and strength of the force with which the cations are held by the lattice, the latter mainly determines the differences in the relative effects of various cations in regard to their capacity to replace the cations of the clay lattice. The lyotrope series Ba$>$Ca$>$Sr$>$Mg$>$Cs$>$K$>$Na$>$Li has often been observed in these exchange reactions. Considerations of ionic size, valency, mobility and hydration have been brought forward to account for this series. The H^+ ion often occupies an anomalous position in the series, and usually has a much greater exchanging power than the monovalent cations (Wiegner, 1925; Jenny, 1932, 1936).

Most of the earlier work on cation exchange in clays was done on systems whose mineralogical compositions were not unequivocally known. The pure clay minerals have been used only recently for these investigations. Page (1939), Bär and Tenderloo (1934) and Schachtschabel (1940) have observed certain specificities in the exchange behaviour of the various clay minerals which have been traced to their characteristic lattice configurations. Page brought forward evidence to show that ions of a size permiting them to fit closely into the cavities formed by the hexagonal net of oxygens are least replaceable. Schachtschabel (1940) found that for NH_4-montmorillonite, H^+ and K^+ have nearly the same exchanging power; all the divalent cations have nearly the same effect which is definitely smaller than that of the univalent cations. NH$_4$-kaolinite gives the same sequence of the relative effects of cations as NH$_4$-montmorillonite. H$^+$, K$^+$ and in particular NH$^+_4$, are more tightly held by muscovite than the divalent cations. The relative ease of replacement of NH$_4^+$ from the three minerals follows the order montmorillonite $>$ kaolinite $>$ muscovite. When a mixture of montmorillonit and muscovite is treated with a solution containing Ca-and NH$_4$-acetates, the mica takes up more of the NH$_4$ and the montmorillonite more of the Ca^{++}. Hendricks and Alexander (1940) found a preferential adsorption of H$^+$ by mica and of Ce^{+++} by montmorillonite from a solution containing the two cations.

The work of Schachtschabel and Hendricks illustrates the modern trend of base exchange studies in clays which points to an increasingly wider acceptance of the clay mineral concept for a clearer understanding of base exchange phenomena. Further, base exchange criteria such as those suggested by Schachtschabel and Hendricks are sufficiently promising to warrant more systematic studies for their acceptance as a method for an unequivocal differentiation of the clay minerals and their identification in soil colloids.

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