

CLAY MINERAL STUDIES

J. SHEARER

Department of Physics, University of Western Australia, Nedlands, W.A.

GENERAL

CLAY is the term applied to material naturally occurring in a finely divided state in sediments and in soils, and exhibiting under suitable hydration the property of plasticity. The degree of hydration required for the material to be plastic occurs when the added water is in excess of the amount that can be adsorbed on the surface of the clay mineral particles with some definite configuration. Clay commonly comprises a mixture of one or more aluminium silicate minerals characterised, in general, by their layer structure, and a limited amount of foreign material comprising non-clay minerals and organic matter.

It is the occurrence in soils that is perhaps of special interest. Clay minerals commonly constitute the bulk of the colloid fraction of a soil and so they are of special importance to the soil scientist. They occur as products of the weathering process. The type of clay or clay mixture occurring in a soil depends on many factors, such as nature of the parent rock, climate and topography. Distribution in depth is an interesting study in relation to the weathering process for under ideal conditions of uniform climate over a sufficient period of time and favourable topography and drainage one may expect to find the weathering sequence extend from parent rock beneath to the most highly weathered product near the surface.

Of special interest in agriculture is the study of the occurrence and properties of clay minerals in relation to plant nutrition and soil fertilisation and to soil classification. These relationships are obscure with the result that the full significance of a mineralogical analysis in the case of a particular soil has still to be determined.

Clay minerals are important in many fields of technological interest. In the oil industry certain clays have important catalytic activity. They are also used as drilling muds. The stability of engineering structures depends on the physical properties of the supporting soil and these properties will depend on the prevalence and kind of clay present. In the foundry industry clays are used for molding purposes in association with molding sands. The import-

ance of clay mineralogy to the ceramic industry is obvious.

STRUCTURE

Although the number of recognized clay minerals is large, the number of groups is relatively small. The structures characterising common groups will be described in this brief review.

The majority of clay minerals are layer structures and of these the majority belong to the ideal type of aluminium silicates, the remainder to the ideal type of magnesium silicates. Isomorphous replacement alters considerably the chemical nature of these two types. The two types may be described as follows:

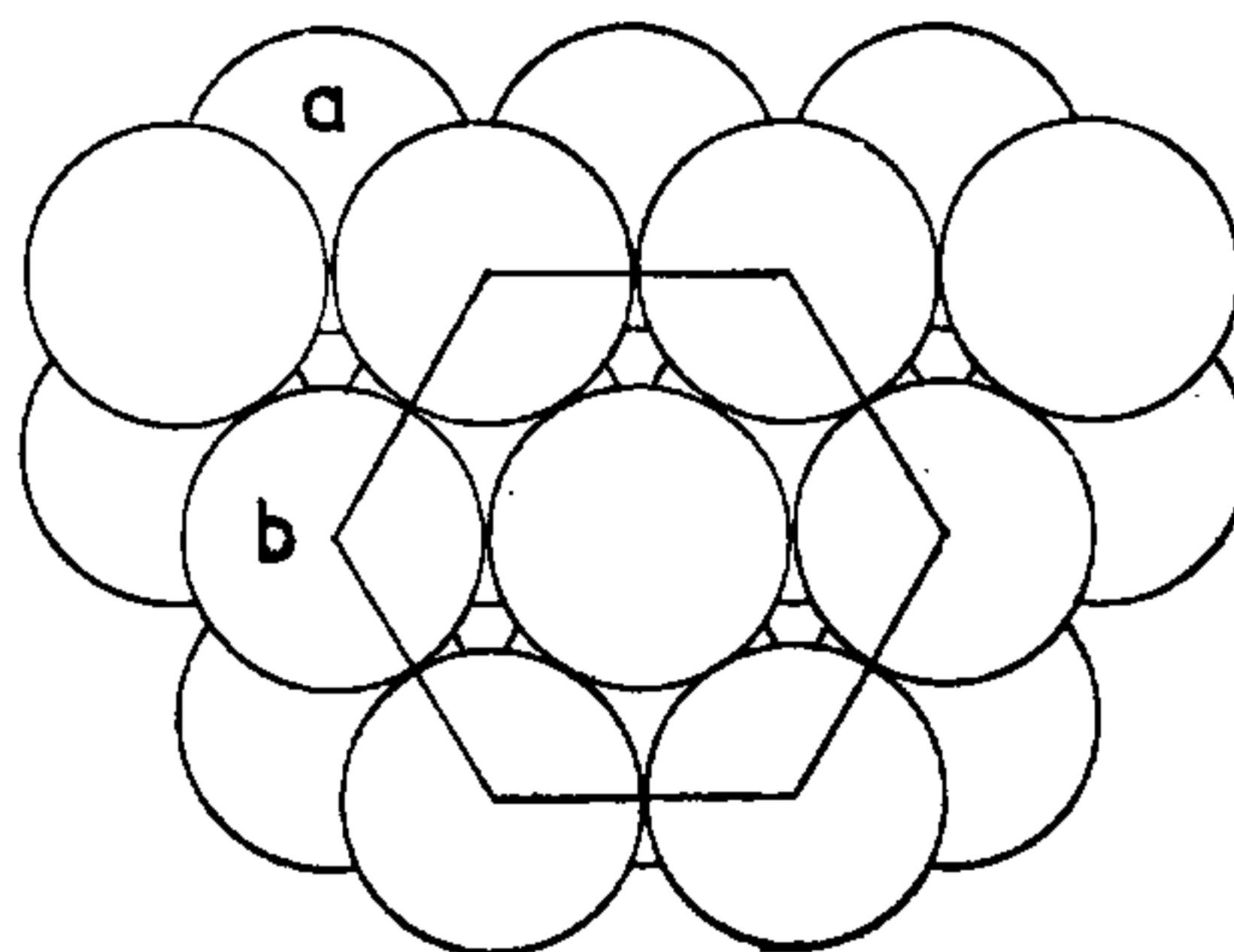


FIG. 1

Fig. 1 represents in plan two indefinitely extended sheets, parallel to the plane of the paper and one on top of the other, of close-packed OH ions. Ions like *b* are in the upper sheet. Ions like *a* are in the lower sheet. Midway between these two sheets, where gaps in the upper sheet overlie gaps in the lower sheet, are centres of octahedral co-ordination. For example ion *b* is one apex of an octahedron of which ion *a* is the other apex.

Just as there are the same number of OH ions in each of the two OH sheets so there are as many octahedral centres as there are ions in each of the two sheets.

In the ideal type of magnesium silicate clays the octahedral centres are occupied by Mg ions, giving $\text{Mg}(\text{OH})_2$. In the other ideal type— $\text{Al}(\text{OH})_3$ —two-thirds of the octahedral centres

are occupied by Al ions. Since the ratio of occupied octahedral sites in the two ideal type is 3 : 2 they have been termed trioctahedral and dioctahedral respectively. In clay minerals, in spite of extensive replacement and variation from the ideal 3 : 2 ratio, the distinction between the two types tends to be preserved.

The silicate contribution to the two types is a tetrahedral layer made up as follows:

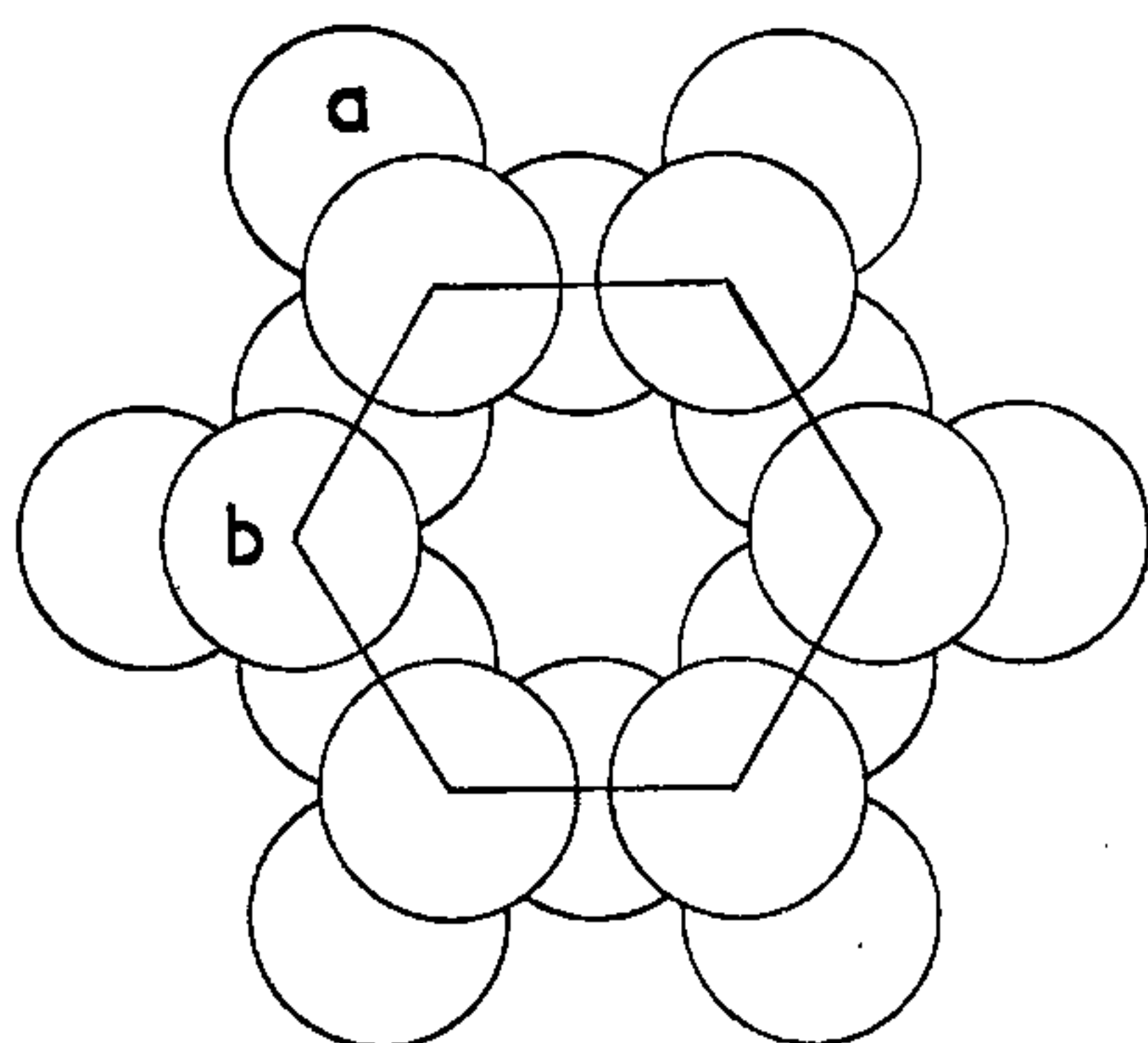
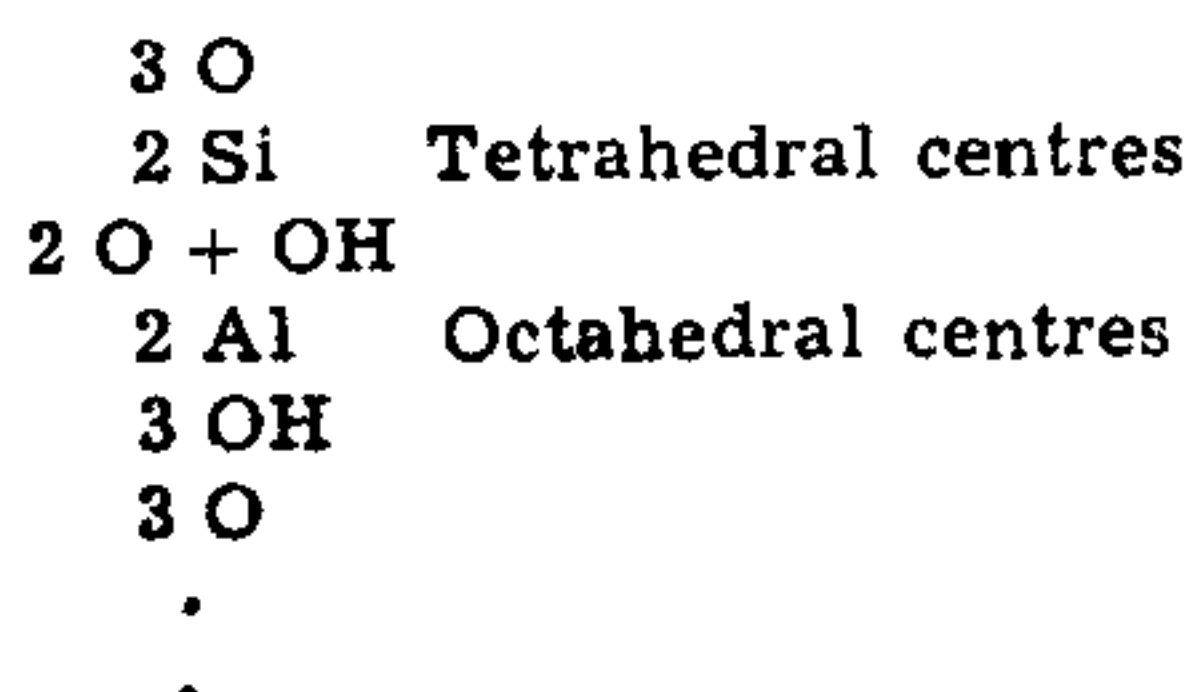


FIG. 2

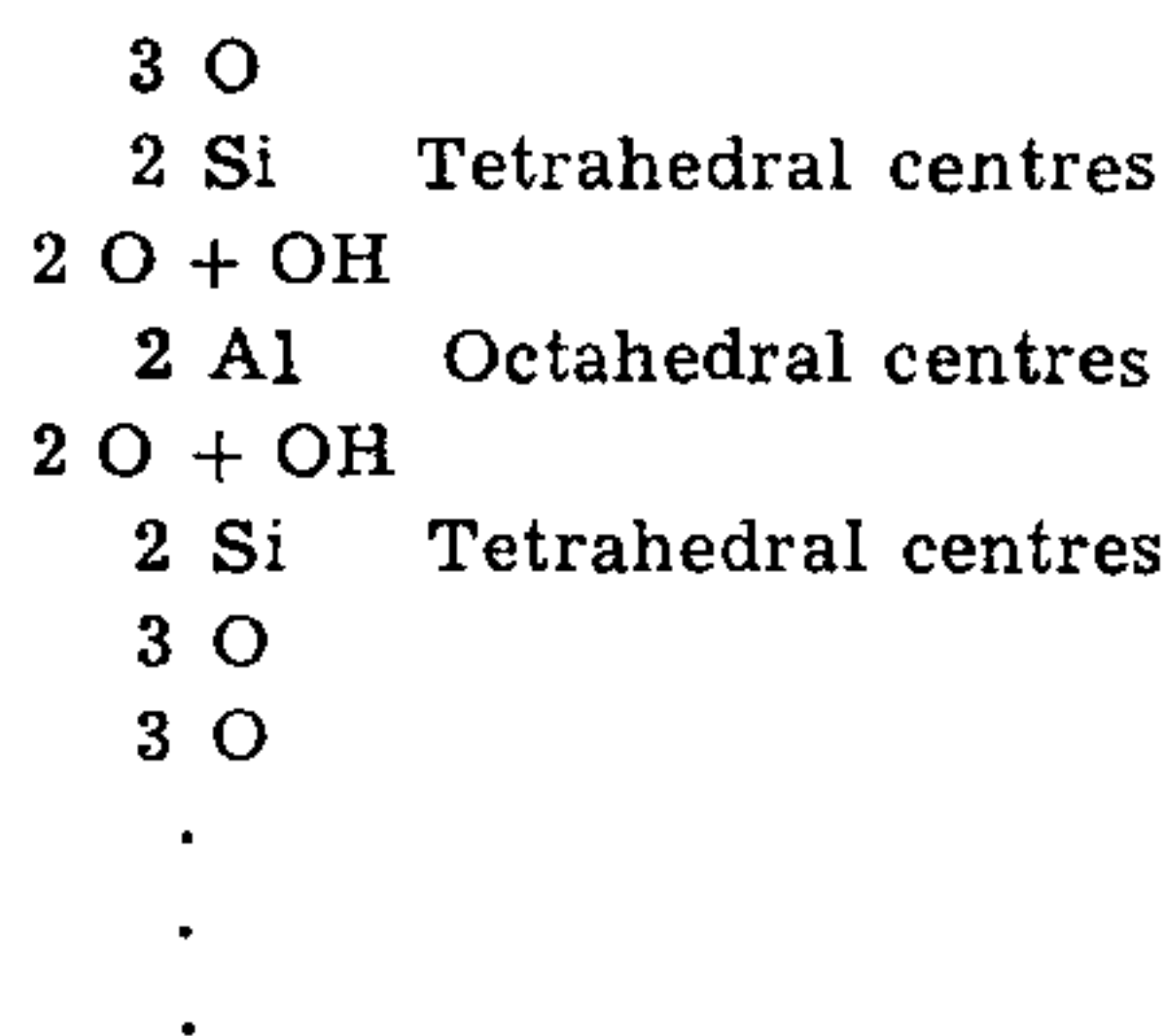
Fig. 2 represents linked $(\text{SiO}_4)^{4-}$ tetrahedra (Si not shown) indefinitely extended in all directions in the plane of the paper. The formula is $(\text{Si}_2\text{O}_5)^{2-}$. All O ions like b lie in a plane above that containing O ions like a. Each ion like b is the apex of a tetrahedron and directly beneath each such ion is a tetrahedral centre (not shown) occupied by a Si ion.

The first group of clay minerals belongs to the dioctahedral type. The octahedral and tetrahedral layers are combined as follows. In Fig. 1 the six OH ions in layer b occurring at the six vertices of the hexagon shown are replaced by the six O ions in layer b in Fig. 2. In the resulting composite structure indefinitely extended in 2 dimensions valency is satisfied and the formula is $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. This is the Kandite (or Kaolin) group, and the successive sheets of ions and the relative number of ions in each sheet may be represented thus:



There is a strong bond between the sheet of O ions and the adjacent sheet of OH ions. The different ways in which these two sheets are disposed in relation to one another differentiate the minerals within the kandite group. In halloysite a molecular sheet of water about 2.9 Å thick intrudes between sheets giving a basal spacing (perpendicular to the sheets) of 10.1 Å. The basal spacing of other members of the group and of the dehydrated form of halloysite (namely, metahalloysite) is about 7.1 Å. A very small cation exchange capacity observed for this group of clay minerals is attributed to broken bonds at surfaces.

Layer clay mineral structures other than the kandite group arise from a slightly more complicated way of combining octahedral and tetrahedral layers. Each of the two OH sheets of an octahedral layer may be modified to take a tetrahedral layer. The dioctahedral composite type may then be represented



The bond O to O is a van der Waals bond. The trioctahedral type will have 3 Mg replacing 2 Al in octahedral centres. The two formulæ are $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ and $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ respectively. Two non-clay minerals, pyrophyllite and talc, occur in nature with these ideal formulæ. By reference to these two minerals the structures of two more groups of clay minerals—clay micas and smectites (or montmorillonoids)—may be illustrated. Both arise from substitutional replacement accompanied by interlayer cations interrupting the van der Waal's bond.

In clay micas some of the Si is replaced by Al in tetrahedral centres, and the charge deficiency is balanced by interlayer K. Some randomness of stacking of adjacent layers occurs. On an external surface the K is exchangeable. Clay micas are usually dioctahedral like muscovite. In fact muscovite may be regarded as a highly crystalline form of clay mica with more Al in tetrahedral centres, more bound interlayer K and less H_2O ; hence arises the

term "hydrous micas" for all forms of clay micas. The basal spacing of clay micas is about 10 Å. Hydration accompanied by reversible expansion to 12 Å (perhaps $10 + 2 \cdot 9$) is sometimes observed. Clay micas with "fixed" basal spacing are termed illites.

In smectites the charge deficiency arising from substitutional replacement is balanced by interlayer cations that are exchangeable. The exchange capacity of these clays is therefore high. Water and other polar molecules also enter between layers. This process is reversible and so this clay group is characterised by high expansibility. When saturated with water, the basal spacing is about 15 Å. When dehydrated and collapsed by heating, it is about 10 Å as in mica. When treated with glycerol the basal spacing is 18 Å.

Two dioctahedral members of this clay group are montmorillonite and nontronite. In the former about 1 in 6 Al ions are replaced by Mg. Nontronite is characterised by a balanced substitution of Fe for Al in octahedral centres and a charge deficiency in tetrahedral centres arising from substitution of Al for Si. Saponite is a trioctahedral member with tetrahedral substitutions similar to those in nontronite.

Clay micas and collapsed smectites may both be regarded as being of mica type. One other clay group which is also a mica type is vermiculite. This is another expansible mineral with a basal spacing, when collapsed, of approximately 10 Å. When fully hydrated or treated with glycerol the basal spacing expands to 14 Å. It is basically a trioctahedral mica like biotite with charge deficiency arising from tetrahedral substitution of Al for Si. Inter-layer cations (predominantly Mg) and inter-layer water complete the structure. The cation exchange capacity is again high as in the case of smectites.

A fifth group of clay minerals which comprise a distinct type from the kaolinite group and the mica group is the chlorite group. This group is characterised by a fixed basal spacing, unaffected by heating, of 14 Å and a cation exchange capacity about the same as that for clay micas. Structurally it is trioctahedral like biotite with charge deficiency arising from tetrahedral substitution of Al for Si. But in this case the charge deficiency is balanced not by cations but by another trioctahedral layer with equivalent excess charge arising from replacement of Mg by Al in octahedral centres. Chlorite occurs in clays as well as in highly crystalline form, and is similar to vermiculite in this respect. The distinction may be similar to

that between clay micas and highly crystalline micas.

Apart from the five groups of layer structures above described, there is X-ray evidence for the occurrence of mixed layer structures with random interstratification of, for example, mica and montmorillonite. Finally there is a group of clay minerals showing chain or fibre structure instead of layer structure.

IDENTIFICATION AND ANALYSIS

We shall consider only the five groups of layer structures, and neglect mixed layer structures, chain structures, and mineral species within a group. The simplest technique is the X-ray powder diffraction technique with a camera capable of recording reflection from spacings up to at least 18 Å, supplemented by suitable hydration or solvation and heat treatment of the sample. Photographic recording is convenient. Advantage is taken of the plate-like character of all clay particles (except halloysite), and a powder sample is prepared with highly preferred orientation and mounted to give enhanced intensity of basal reflections. This preparation may be done in a number of simple ways.

Approximately pure samples may be identified as follows. Assume the sample has been treated with glycerol.

	1st order Basal Spacing	Basal Spacing after heat treatment at 600° C.
Kandite	7 Å	Destroyed
Mica	10 Å	10 Å
Smectite	18 Å	10 Å
Vermiculite	14 Å	10 Å
Chlorite	14 Å	14 Å

So that ideally the first order basal spacing of glycerol-treated "oriented" specimen is sufficient, except to distinguish vermiculite and chlorite. Then the heat treatment is essential, unless chemical methods (and they have been suggested) are adopted. The heat treatment is always desirable, particularly to avoid confusion between first order Kandite and second order vermiculite or chlorite.

When dealing with mixtures of clays heat treatment is essential. Quantitative analysis of such mixtures is difficult. Further evidence is sometimes then invoked provided by differen-

tial thermal analysis or chemical analysis. The accuracy is low so that the method of standard mixtures may be used even though it is impossible to rely on the identity of the standard mineral and the mineral in the unknown mixture. Kandites are much less susceptible to isomorphous replacement and can reasonably be assumed identical from standard to sample. The effect of composition on intensity may be considerable. For example, the intensities of 10 Å reflections of collapsed montmorillonite and collapsed nontronite, each with interlayer K, are theoretically in the ratio of 1:9.

One of the minerals present in a mixture may be used as an internal standard. This overcomes the difficulty of using an external standard, but other assumptions are inevitably involved that reduce the accuracy.

Finally a quantitative mineralogical analysis may be made from a qualitative X-ray mineralogical analysis in combination with a chemical

analysis for SiO_2 , Al_2O_3 , MgO , K_2O , lattice Fe_2O_3 (i.e., total Fe_2O_3 less free Fe_2O_3) and ignition loss at 900°C . If a mica is present the amount may be assessed from the amount of K_2O . If a smectite is present it may be assumed to be of composition intermediate between a pure Mg species (montmorillonite) and a pure Fe species (nontronite). The amount (and composition) of the smectite may be estimated from the amounts of MgO (giving the amount of montmorillonite component) and of lattice Fe_2O_3 (giving the amount of nontronite component). This procedure for a smectite neglects the possibility of the existence of a pure aluminium silicate smectite analogous to muscovite mica.

Each unknown clay mixture to be mineralogically analysed, must be treated as a separate problem, particularly because non-clay minerals involving Si, Al and Fe may also be present.

THE TWISTOR

A NEW concept in memory devices has emerged from exploratory work by A. H. Bobeck at Bell Telephone Laboratories. This concept, which has been named the "Twistor", is expected to make possible, memory systems which are simpler to fabricate and more economical to manufacture than existing systems.

The "Twistor" concept opens the way for the construction of magnetic memory arrays by merely interweaving horizontal copper wires and vertical magnetic wires, in much the same way as a window screen is woven. Such a device would be similar in appearance to a ferrite core array, but without the cores, and would operate in much the same manner as a core array.

This new concept gets its name "Twistor" from a characteristic of wire made of magnetic material. Torsion, applied to such a wire shifts the preferred direction of magnetization from a longitudinal to a helical path. The coincidence of a circular and a longitudinal magnetic field can then be used to insert information into this wire in the form of a

polarized helical magnetization, and the magnetic wire itself can be used as a sensing means.

In practice, the circular magnetic field is provided by a current pulse through the magnetic wire, and the longitudinal field by a current pulse through the copper wire which is perpendicular to the magnetic wire. Thus, storing a bit requires two coincident current pulses. One pulse by itself is insufficient to store a bit. Readout is accomplished by overdriving the longitudinal field in the reverse direction. The readout signal is sensed across the magnetic wire. Because the lines of magnetic flux along the helical path wrap the magnetic conductor many times, a favourable increase in the output signal is obtained.

Present indications are that the drive circuits for a "Twistor" array can be readily transistorized. Thus, a memory system using the "Twistor" concept will retain all of the advantages of ferrite core or sheet systems, and will be much simpler and more economical to fabricate. (Frank, *Inst. Jour.*, Feb. 1958.)