

CLAY MINERALS RESEARCH AT GHENT UNIVERSITY

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ABSTRACT

This contribution reviews the work done at Ghent University, together with some unpublished recent work. Next to the survey of clay minerals from soil samples for the soil mapping organization, the group has been concerned with the polytypism of micas, the alteration and transformation of clay minerals, and the role of migration of iron in mica-type structures under influence of temperature or chemical treatment. A study of growth spirals of biotite crystals threw some light on the origin and possibility of the existence of ordered sequences with great repeat distances, and also on the complexity of crystals of this type. The presence of dislocations in mica is also shown by examination of "bending figures" produced by indentation. A study of clay minerals in soil fractions from a limited area, reclaimed from the sea between the eleventh and nineteenth centuries, indicated great variation in mineral composition. If one accepts the logical working hypothesis that the mineral composition was homogeneously distributed at the start, one must accept a rapid transformation at particular spots. This evolution seems to proceed from muscovite (illite) toward montmorillonite. Neof ormation of a small quantity of kaolinite accompanies the transformation to montmorillonite.

Experiments carried out to achieve this process in the laboratory showed that micas submitted to a stream of CO₂ dissolve rather rapidly in presence of water. All attempts to obtain clay minerals from the obtained solutions failed, except one, when small quantities of montmorillonite and kaolinite were formed. The thermal evolution of glauconite and the location of iron ions were also studied. Some remarks on formulas of clay minerals are presented.

INTRODUCTION

Since 1948, the Institut belge pour l'encouragement de la recherche scientifique dans l'industrie et l'agriculture (I.R.S.I.A.) has supported a small group working on clay minerals in the crystallographic laboratory of Ghent University. This group operates in close collaboration with the Soil Mapping Organization, which is sponsored by the same institution. This paper reviews and discusses some of the results obtained so far; new evidence and hypotheses about defects are also presented.

EVOLUTION OF CLAY MINERALS

The study of samples from the region known as the "Polders" yielded interesting results concerning the evolution and transformation of clay minerals (Dekeyser, Hoebek, and Van Keymeulen, 1955). Such phenomena have been reported by other authors; the special interest here is that the time factor is known accurately. The region considered is a strip along the North Sea, between the Scheldt estuary and Dunkirk. It was flooded during the so-called Dunkirk transgressions I, II, and III which occurred in the fourth and eleventh centuries respectively. As it was reclaimed from the sea from the eleventh century until the

present, we are dealing in this area with a marine sediment, the date of deposition of which we know from records, and also the date of reconversion to dry land.

A detailed study revealed much variation in the nature of the clay minerals. Therefore rather closely spaced samples were taken. The various samples contained: (a) muscovite in all fractions ($\leq 2\mu$, $\leq 5\mu$, $\leq 10\mu$, $\leq 20\mu$); (b) illite in the finer fractions, muscovite in the coarser; (c) illite in all fractions; (d) montmorillonite associated with a small amount of kaolinite. A trace of kaolinite is found occasionally in the first groups. If the reasonable assumption is true that the sediment was homogeneous with respect to its mineralogical composition when it was deposited, then a rapid transformation must have taken place in some areas. The evidence suggests that, if this is so, the transformation took place following the scheme: muscovite—illite—montmorillonite, in one direction or the other.

Examination and comparison of soils reclaimed at well-known periods indicated no correlation with time. Aeration and drainage are important factors; they are invariably good in places where montmorillonite is found, and bad where muscovite is present. In order to check this indication and, if possible, to define more precisely the factors responsible for the transformation, an examination of offshore sediments is planned. Samples of the estuary mud, mainly brought in by tide, contained in the fine fraction ($\leq 2\mu$), montmorillonite, kaolinite and muscovite, and in the other fractions muscovite and kaolinite. Admixture with material from inland is a possibility, but the results support the ideas put forward.

A detailed study of these and other typical samples is now in progress in order to follow the different stages of the transformation as closely as possible and to determine whether mixed-layer materials are present; electronmicroscopic studies are also being made. So far, no definite results are available, but it seems certain that the transformation, or better, the establishment of new equilibrium forms of clay minerals, can be very rapid when the environment is changed.

These observations, together with data on the neoformation of kaolinite in some horizons in another locality, raise the question of whether dissolution and reprecipitation or reorganization of the lattices is involved.

In order to obtain information about this process, some simple experiments were performed in which muscovites and biotites are leached for rather long periods of time by water and CO_2 (Dekeyser, Van Keymeulen, Hoebeke, and Van Ryssen, 1955; Van Keymeulen and Dekeyser, 1952). Figure 1 shows the apparatus used. The minerals, deposited on a fine filter, are placed just above the CO_2 inlet and are at room temperature. Water distilled from the collector flask arrives in the inner tube. A filter is also present in the connection between the reaction flask and the collecting balloon. In this way ions are concentrated eventually in the collector, and long continuous runs are possible. It was found that biotite is extremely sensitive to CO_2 and decomposes rapidly. After some 100 hours, iron oxide flocculates as more or less spherical aggregates and these include very frequently a flake of biotite having dimensions much greater than those of the pores of the filter. No conclusions can be drawn concerning the origin of this biotite because it could be agglomerates of finer particles which can pass through the filter to the collecting flask. If, however, tartaric acid is added to the water in the latter flask no flakes are observed. Numerous analyses

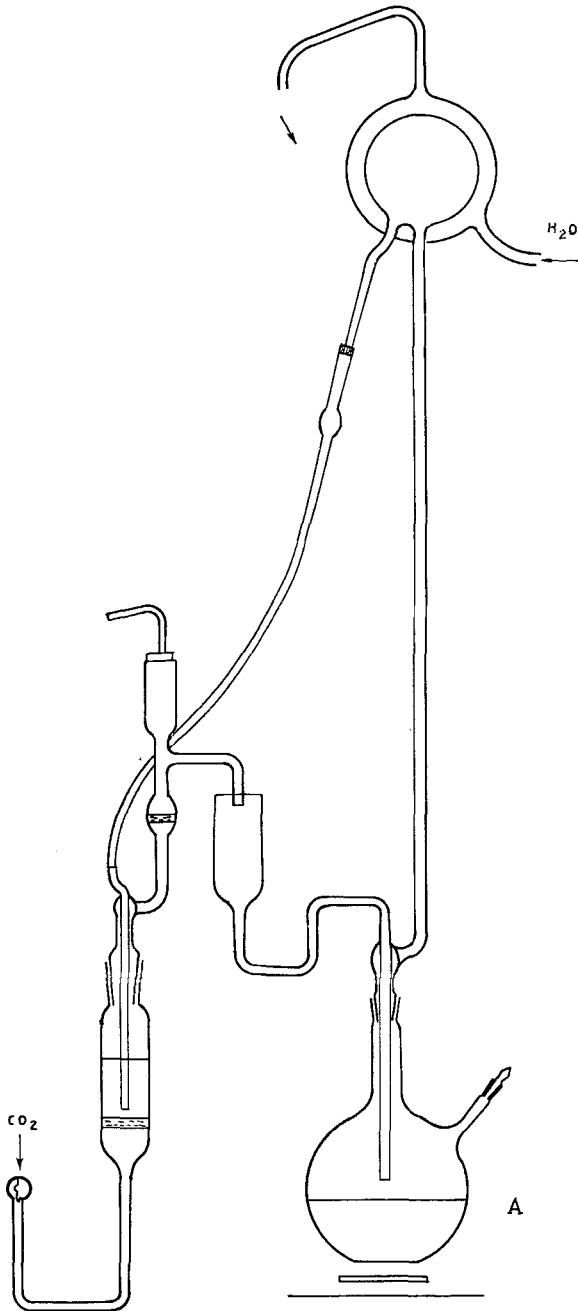


FIGURE 1. — Apparatus for leaching of biotites and muscovites by water and CO_2 .

(Van Keymeulen, in press) made after different periods and for several runs indicate that the minerals dissociate into ions. The curves indicating the increase of Si, Fe, and Al in the collector flask as a function of time are generally smooth at first, and very irregular for longer periods. This effect is due possibly to the rather poor control of the CO₂ stream. Evaporation of the contents of the collecting flask produced only once a powder that gave an x-ray diagram of a mixture of kaolinite and montmorillonite. The results for ten other runs were negative as far as formation of clay minerals is concerned. More severely controlled experiments will be necessary to settle these points. Muscovite behaves in the same way, although the dissolution rate is much smaller than that for biotite.

H₂S was also tried with a slightly different experimental arrangement. Its effect is at least as great as that of CO₂. Colloidal FeS is formed rapidly when iron is present in the minerals.

POLYTYPOISM OF CLAY MINERALS

The formation and growth of clay minerals, discussed in the previous paragraphs, led to research on more general aspects of these problems. The spiral growth of a number of substances was examined in detail. The elegant and logical explanation that the Frank (1949) theory provided for the occurrence of numerous polytypes of carborundum and other simple crystals brought us to consider the polymorphs, now the polytypes, of micas.

These so-called polymorphic forms of the micas, especially of the trioctahedral types, were discovered by Hendricks and Jefferson in 1939. They differ from the more usual types only in their *c*-repeat distances, which can attain very high values. Polymorphism in that restricted sense has been called polytypism by Baumhauer (1915), who studied the different forms of carborundum. Polytypism is in fact a rather common phenomenon in crystals whose structure can be described as the superposition of close-packed layers or of units terminated by close-packed layers (carborundum, zinc sulfide, long-chain alcohols, etc.). It results from the different manners of stacking of such layers. If geometry alone were involved, disordered stacking sequences should be the rule and order the exception. We can assume that binding forces assure the regularity of the stacking as far as short ranges are involved, but this becomes impracticable once the repeat distances become very great. This means that we must find an explanation for the formation of polytypes, or better, for the orderly perpetuation of complicated sequences.

To make this clear, we will consider the micas. They are formed by the stacking of units composed of planes of the following composition: K-O-Si(O, OH) Al(O, OH)-Si-O. This unit, which was begun for convenience with the K-layer, is monoclinic; we can represent the direction of the symmetry plane by an arrow. If a second unit is added, the O-layers that face each other have to be one above the other. This arrangement can be achieved in six different ways of which three are distinguishable. They correspond to relative rotations of 120° of the symmetry planes of both units. We can obtain in this representation $\uparrow\uparrow$ or $\uparrow\searrow$ or $\swarrow\uparrow$. The piling up of a great number of such units can give rise to an infinity of ordered or disordered stacking sequences. The most common structure can be represented by $\uparrow\uparrow\uparrow \dots \uparrow$ or simply \uparrow , some of the observed polytypes are strictly ordered repetitions of sequences

such as: $\downarrow \searrow$, $\uparrow \nwarrow$, $\downarrow \searrow \uparrow$ or more complicated ones. The available data are much too meager to allow any statement about possible and "forbidden" sequences, as can be done for carborundum. The problem, when complicated sequences are regularly repeated, can be stated as follows: in a polytype formed by m units, stacked according to a given code, how does the $(m + 1)$ unit know the relative position of the second unit with respect to the first? An explanation of long-range order is easy when one can prove that the crystals have grown at low supersaturation according to the mechanism proposed by Frank in 1949 in which screw dislocations play an important role. Frank showed that the step, or exposed edge, which is necessarily present on a face in which a screw dislocation emerges, is self-perpetuating and winds up as a spiral if growth takes place at low supersaturation. Growth under these conditions is then nothing other than the "lateral" extension of the exposed edge, and any sequence, however complicated it may be, is continued automatically as long as the dislocation exists (Amelinckx and Dekeyser, 1955).

As the steps involved are generally of the order of a unit cell or of small multiples of it, it was expected that growth spirals should not be accessible to observation, but this was disproved by experiment. Numerous examples proved the correctness of Frank's predictions, and step-heights of 5 Å are observed readily with ordinary, or better, with phase-contrast microscopy. Multiple beam interferometry and its numerous variants allow their precise measurement.

HELICOIDAL GROWTH OF MICAS

Now that we have a possible mechanism by which to explain how a complicated sequence can be repeated indefinitely without possible variation, we have to prove that it really happens in complicated lattices such as micas. To do so we must look for growth spirals on them, and unfortunately this needs crystals with nearly perfect faces. Among the numerous crystals that were examined, two from Monta Somma fulfilled the required conditions. On one of them, a complicated interlaced spiral with a step-height of 180 Å was found; the other showed a set of simple spirals with steps of 10 Å.

The complicated pattern, which was discovered first, could be analyzed by making some assumptions about the relative values of the velocities of growth fronts in different directions. These assumptions were proved to be correct by the examination of the spirals with unit step-heights; these allow direct deduction of these values. We refer to the original papers (Amelinckx and Dekeyser, 1952; Dekeyser and Amelinckx, 1955) for the full discussion of the observed growth figures and summarize here only the results. It was proved that the surface layer of the biotite crystal presenting the complicated pattern was a triclinic polytype with a c -repeat distance of 180 Å. In the notation described in the preceding section, we can represent this polytype as formed by p layers \uparrow , q layers \nwarrow , and r layers \nearrow , with ($p < q < r$, and $p + q + r = 18$).

The same crystals were examined by x-rays. Laue diagrams, one of which was taken with a rather large distance between crystal and film, indicated that the crystal was built up of three different polytypic forms: A part with random arrangement gave unresolved streaks; one showed the usual monoclinic structure; and on top was a thin layer of the 180 Å polytype giving a series of weak spots situated closely together and superimposed on the continuous streaks. Another possibility is that the spots corresponding to the usual type are a statistical

effect. If so there should be a part with random arrangement and superimposed on it a surface layer with $c = 180 \text{ \AA}$.

This gives an idea of the possible complications that can arise in such crystals, for another polytype could have been present on the other side, and other screw dislocations emerging near the first one could have originated parts having a different c value.

Now that we have proved the presence of screw dislocations in micas, and also that the exposed edges which are necessarily associated with them can give rise to complicated polytypes when growth continues at small supersaturation, we can with good probability generalize to those minerals which are similar but so small that direct observation is impracticable; e.g., kaolins and chlorites.

There has been much misunderstanding about helicoidal growth of crystals, and, in this respect it may be useful to stress the following points: (a) Growth by the Frank mechanism proceeds only when supersaturation is low; (b) ordered polytypes are generated only when the exposed edge corresponds to an imperfect dislocation or when the substrate is disordered.

GLAUCONITE

Study of samples from the central part of Belgium drew our attention to glauconite and this mineral was considered in some detail (Hoebeke and Dekeyser, 1954, 1955). In the D.T.A. diagram, a small peak at 375° C , neglected so far by other investigators, was attributed to oxidation of the divalent iron. This reaction is exothermic but, as a study with the thermobalance proved, it is accompanied by partial loss of hydroxyls, which is endothermic. These two effects, which work in opposite directions, diminish considerably the amplitude of the peak. The mechanism of this oxidation, which does not take place in a vacuum, is not clear at present. The peak at 550° C corresponds to loss of the hydroxyls as in the micas. At 975° C the lattice reorganizes and x-rays reveal only Fe_2O_3 or $\gamma\text{-Fe}_3\text{O}_4$ following the absence or presence of traces of organic material. As no loss of weight is observed, we must conclude that the other ions form a glass. This is confirmed by microscopic observation of the iron oxide grains; a glassy skin can occasionally be observed. At 375° C , glauconite grains gradually change from green to brown as the oxidation of the divalent iron becomes more complete; brown glauconite is sometimes mentioned in the French literature as "sable chamois" (brownish sand). As the ratio $\text{Fe}^{3+}/\text{Fe}^{2+}$ was nearly equal to 9 in the samples under investigation, the sensitivity of the color to the state of ionization of such a small fraction of the total iron content is surprising. We therefore tried to locate the position of the Fe^{2+} ions by the method used by Brindley and Youell in their acid-dissolution studies of the chlorites. When, by this method, all ions were extracted which should be in octahedral positions according to the ideal formula, the residue was still green and analysis proved that it contained all the Fe^{2+} ions. When the extraction was continued further in order to take out some of the tetrahedral ions, a white amorphous powder remained. These experiments led us to conclude that the Fe^{2+} ions are in tetrahedral positions insofar as sites are available for them.

This surprising result is logical when glauconite is considered as an unmixed mineral. As it now seems to be an interstratification of two mica-type minerals, it is well possible that the above conclusion will need revision.

COMMENT ON DEFECTS IN CLAYS

Clay minerals are known as poorly crystallized substances. By this, one means that they present a good deal of stacking disorder. Otherwise they are considered to be perfect, and a stoichiometric formula is assigned to them. Extensive study of the properties of nearly perfect crystals, such as the alkali and silver halides, pure and hyperpure metals, sulfides, spinels, and others, have revealed that they contain, in thermal equilibrium or under certain circumstances, a number of defects. These are: dislocations, vacant sites, interstitial sites, foreign ions or atoms, free electrons, positive holes, excitons. Thermal agitation and the surface can also be added. Nonstoichiometric composition, and its control in certain cases, are directly related to defects. It has furthermore been proved that they are, alone or combined, responsible for many of the basic properties of solids. Examples are plasticity, ionic conductivity, diffusion, luminescence, and, in general, the so-called structure-sensitive properties.

As far as clay minerals are concerned, their properties may be described as being more or less of the structure-sensitive type. Attempts to correlate them with an ideal structure have not been very successful. The discussions about the Hofmann and Edelman-Favejee models are a most striking example. The Hofmann structure, which is considered to be correct, cannot account for the physico-chemical behavior of the substance. Another model does, although strong evidence exists that it is incorrect. Both are handled, however, as if they were perfect. The way out of these difficulties may be, as has happened in other fields, to work with the correct structure containing lattice defects. That attempts in this sense have not been made is not surprising. Transposition of the vast and rather recent knowledge of lattice defects in simple crystals to more complicated lattices and extremely small crystallites, as we have in montmorillonite, is a difficult matter. Much experimental work will be needed before this can be achieved. We have started work in this direction, but have no definite results yet. This section is therefore intended to draw attention to these points and to present, tentatively, some possibilities. That they are still guesswork needs not be stressed.

As far as dislocations are concerned, they have been proved to exist in single crystals of muscovite (Votava, Amelinckx, and Dekeyser, 1955; Amelinckx and Dekeyser, 1955), with their Burgers vector both perpendicular and parallel to the (001) face; the latter are energetically favored. That they are still present as lines or as groups of lines in crystallites of the order of 1μ can safely be deduced from what is known from photographic emulsions. These crystallites have the same order of magnitude and, from direct evidence, one may safely conclude that the photographic process is directly related to the presence of dislocations. The situation is different, however, when the crystallites are much smaller, as in montmorillonite. In such crystals it seems unreasonable to hold to the concept of dislocations.

Point defects; e.g., vacant sites, interstitials, and foreign ions with charges equal to or different from the normal ions are easier to deal with.

Figure 2a represents the ion arrangement in a (100) plane of rock salt, in which are shown vacancies and some associations of vacancies for which experimental evidence exists. Figure 2b shows a simple lattice in which interstitial ions exist; the interstitial and the vacancy which was its normal place can diffuse separately. Crystals contain such defects in thermal equilibrium be-

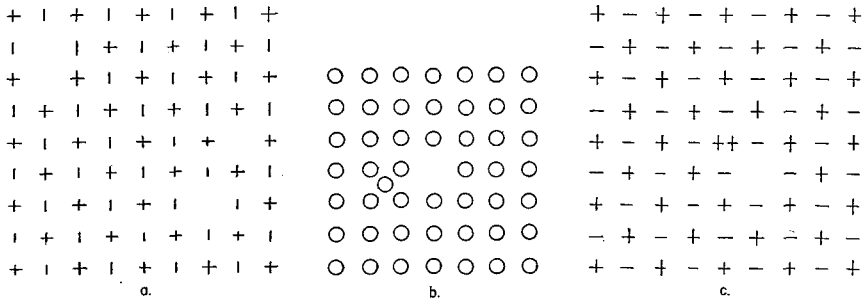


FIGURE 2.—(a) Ion arrangement in (100) plane of rock salt, showing vacancies for which experimental evidence exists. (b) Simple lattice showing vacancy and interstitial ion. (c) Lattice showing balance upset when ions having different charges are present.

cause these introduce some disorder in the lattice. This increases the entropy, S . For a given temperature T this gives a minimum of free energy $F_{\min} = U - TS$ in which U is not the minimum of potential (or mechanical) energy. The value of S corresponding to U_{\min} (ideal lattice) would give a value of F greater than that of the crystal containing a number of defects. Along these lines, one can calculate the number of vacancies and (or) interstitials in thermal equilibrium at a given temperature. The argument holds, if not quantitatively, certainly in a qualitative way for complicated lattices.

Some lattices contain preferentially vacancies, others contain interstitials related to the value of formation of each type, which depends largely on the geometry.

Simple considerations show that a positive ion vacancy behaves as a center of negative charge, and the inverse is true for a negative ion vacancy. This means that they exert long-range forces, that they attract each other, that a monovalent negative ion vacancy can trap an electron (if some are available), and that a monovalent positive ion vacancy can trap a positive hole.

So far, pure crystals alone were considered, which have an equal number of positive and negative ions. As Figure 2c indicates, this balance can be upset when ions of different charges are present. By this means a greater number of instances of a given defect than the equilibrium value can be introduced, and control is possible as far as the precipitation value is reached (e.g., BaCl_2 in NaCl). Summarizing, point defects in their various forms introduce local distortions and local fields. They can be considered as infractions to the rule of Pauling requiring electrical neutrality in the smallest possible volume.

In regard to clay minerals, it is obvious that isomorphous substitutions are to be considered as point defects and that they also introduce local departures from electrical neutrality, even if they are regularly distributed—a state of affairs which will be counteracted by thermal agitation.

But we can also consider vacancies, and some tentative possibilities are: a silicon ion or an aluminum ion in tetrahedral position can be missing and the charge deficiency be compensated by adsorbed ions or missing oxygens. A missing aluminum ion in a tetrahedral position can be compensated by an extra ion in octahedral position, the site for which is available, and it is then a kind

of interstitial on a possible site. Electrons or positive holes can eventually play a part in balancing charges, but there is no evidence that they exist in this type of crystal under normal conditions. In thin sheets, as in montmorillonite, it seems more probable that the balance is made up by externally adsorbed ions at spots where strong local charges exist owing to vacancies. We are trying to find out what numbers of vacancies should be present in order to have no discrepancy between observed and calculated values. The results will be published elsewhere.

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