SYNTHESIS OF CLAY MINERALS AT LOW TEMPERATURES

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ABSTRACT

Numerous attempts have shown that it seems to be impossible to crystallize co-precipitates of silica and hydroxides; we therefore attempted to prepare clay minerals starting from solutions of their constituents. By allowing these dilute solutions (tenths of milligrams per liter) to pass slowly into a flask containing distilled water, it has been possible to prepare substances similar to clay minerals. These have been identified by x-rays, chemical analysis, dehydration curves, and electron micrographs.

Using as cations Mg, Fe^{2+}, Fe^{3+}, and Ni, minerals of the montmorillonite type have been prepared for various pH values (generally greater than 7). Below this value, depending on the cations; oxides, hydroxides, or amorphous materials are obtained.

Under certain conditions in the absence of silica the glass vessel was attacked, and antigorites of Mg and Ni were then obtained. Always when the supply of silica was small, and with the cation introduced in the form of a very dilute solution, the process gave rise to montmorillonite. In the presence of K, illites were sometimes formed.

The method seems to be of very general application. Only the purely aluminum minerals offer difficulties of preparation. The significance of these results is discussed.

INTRODUCTION

Various authors have tried to prepare clay minerals at low temperatures. Sedletsky (1937) succeeded in synthesizing a montmorillonite. Karsulin and Stubican (1951) may have obtained halloysite but the result seems somewhat doubtful in view of the conditions of preparation. The methods employed were probably laborious, as these researches have not been developed extensively. We have therefore sought a method as general as possible for the preparation of clay minerals, limiting the temperature to a maximum of 100° C. These investigations have been carried out partly at the Laboratoire des Sols, Versailles, but also extensively at the Mineralogical Laboratory of the Muséum d'Histoire Naturel, Paris V, in collaboration with Mlle. Caillère.

EXPERIMENTAL

In a preliminary series of experiments, we tried to make co-precipitates of silica and alumina or iron. During a period of one year, the initial precipitates were subjected to 250 alternations of wetting and drying without producing any significant development of clay minerals apart from the crystallization, in some samples, of a small quantity of hydroxides. During a like period, other co-precipitates of silica, alumina, and iron were kept at 90° C in distilled water without any indication of crystallization. This method, therefore, seems to be ineffective (Caillère and Hénin, 1950).

As it seemed probable that the amorphous character of the products obtained by co-precipitation may have been due to a tendency for the molecules of silica

54

to be absorbed in a disordered manner, we have tried to facilitate the orientation of the constituents by using a method of electrolytic attack. In a vessel containing a silicate solution of several grams per liter is placed a platinum electrode which acts as the negative pole, together with a positive electrode of the metal that will furnish the constituents of the octahedral layer. Under certain experimental conditions (temperature about 40° to 50° C) substances are obtained giving x-ray diagrams that show large spacings and that resemble the x-ray diagrams of antigorites. In particular, the first and second orders of a $00l$ reflection can be obtained. However, chemical analysis shows a considerable deficit of silica and, in addition, the substances are destroyed at about 350° C. It seems, then that we may have obtained a substance formed of hydroxide layers which at a number of points have fixed a small quantity of silica (Fig. 1, a). This result has been observed only with Mg, Ni, and Co, whereas Al and Fe gave colloidal products. Similar results have been obtained on replacing the silicate by aluminates and chromates; that is to say the products have a very considerable deficit of anions (Caillère, Hénin and Esquevin, 1953).
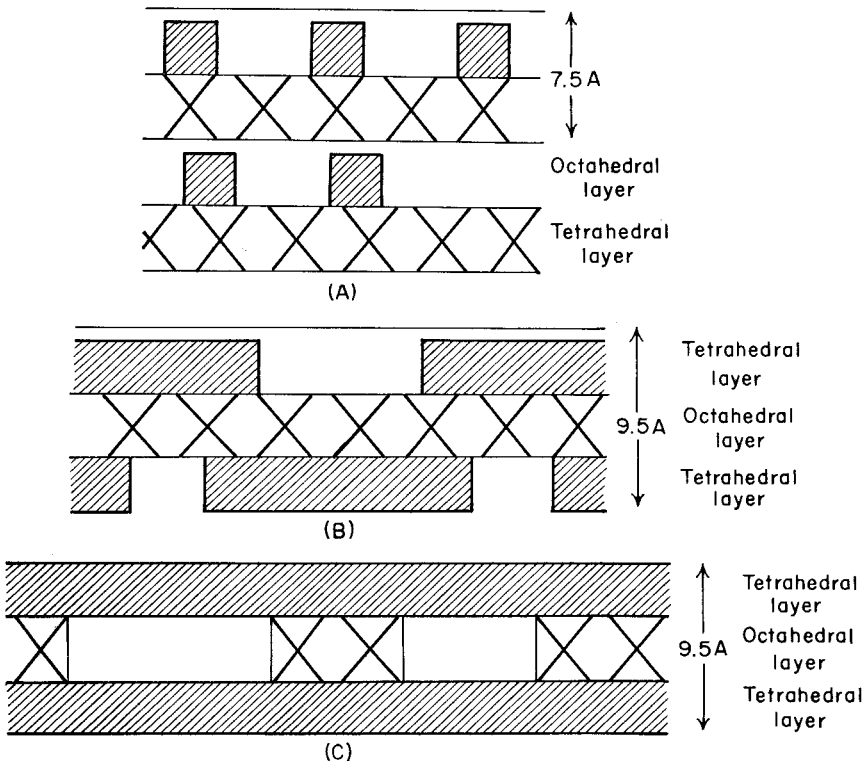

FIGURE 1. — (a) Product obtained from electrolytic attack. (b) Structural scheme of products of montmorillonite type with deficit of SiO_2 obtained from dilute solutions. (c) Supposed structure of montmorillonite-type product with excess of silica.
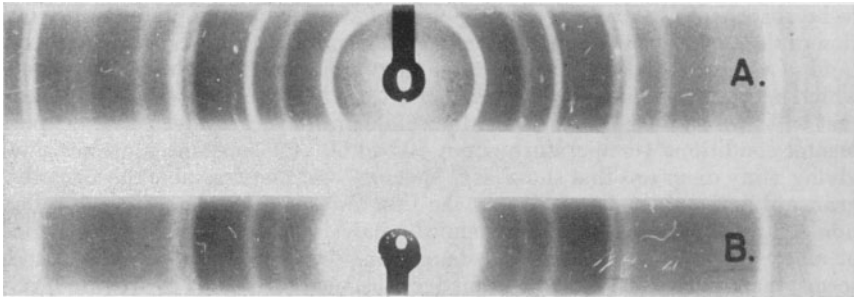
FIGURE 2. — X-ray diagrams. A. Nickel antigorite (natural). B. Nickel antigorite (synthetic, at 80° C).

Being unable to improve this method, we considered the possibility of a third approach which was suggested by the fact that, in nature, solutions are very dilute. We have, therefore, worked with concentrations of several tenths of a milligram per liter. The following experimental arrangement was used: Stable alkaline solutions of silicates or aluminates are placed in one flask and stable acid solutions in another flask. These two solutions are allowed to flow at a rate of several cc per day into a large glass vessel of 5 liters capacity containing 2 liters of distilled water. A cooling system allowed the evaporation to be controlled (Hénin and Robichet, 1953). Under these conditions it has been possible to obtain the following products: Montmorillonites of Mg (stevensite, saponite), of Fe^{2+} (bowlingite), of Fe^{3+} (nontronite) (Caillère, Hénin, and Esquevin, 1953), of Zn (sauconite), and of Ni.

If in place of distilled water, a solution of Mg or Ni cations of a concentration of several grams per liter is added in addition to electrolytes (NaCl, $CaSO_4$, etc. . .) in the large flask, antigorites are formed (Fig. 2). This result has been obtained with Mg (Hénin and Robichet, 1954) and with Ni (Caillère, Hénin, and Esquevin, 1954).

STUDY OF SYNTHETIC CLAY MINERALS

All the substances prepared have been examined with x-rays. When they seemed to be like montmorillonite, two additional x-ray diagrams were obtained: (1) after heating at 450° C; (2) after glycerol treatment. Only those substances that show the normal behavior of montmorillonite in these tests have been regarded as synthetic montmorillonite. X-ray diagrams of natural and synthetic montmorillonites are shown in Figure 3.

Several substances have shown an intrastructural swelling in water, but they have not contracted when heated and these have been regarded provisionally as swelling chlorites. Products showing a 10 A spacing are first placed in a solution of magnesium chloride; the x-ray diagram is then taken with the substance placed in a solution of glycerol. Products have been labelled "micas" only when they do not swell, or swell only partially by this treatment.

We have considered as antigorites only those substances which show a stable 7 A spacing when heated at 400° C.
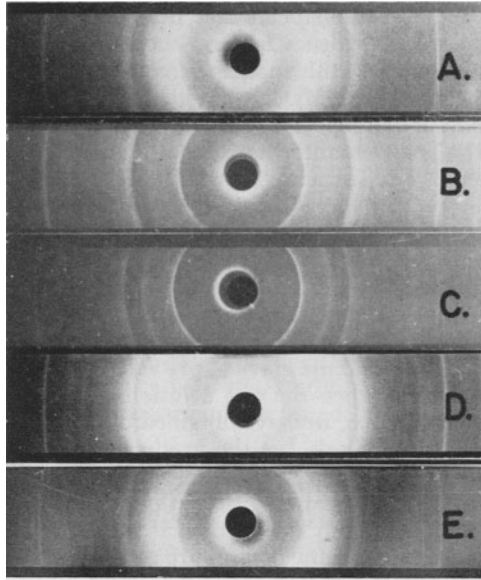
FIGURE 3. — X-ray diagrams. A. Al-montmorillonite, heated at 500° C. B. Al-montmoril-
lonite. C. Mg-montmorillonite (natural specimen). D. Synthetic Mg-montmorillonite
(stevensite type). E. Synthetic Mg-montmorillonite, heated at 500° C.

The dehydration curve as a function of temperature has been obtained for
the best products, and their chemical compositions have been determined.
Finally, in several cases the base-exchange capacity has been measured.

Effect of Conditions of Synthesis on the Nature of the Product Obtained

The crystallinity of the synthetic products, as determined from the definition
of the 00l reflections after heating or after placing the products in glycerol
solution, depends to a large extent on the electrolytes that do not enter into
the composition of the mineral but are present in the solution from which the
synthesis occurs. Thus, for example, NaCl having a concentration of 100 to 200
g/liter, or saturated $CaSO_4$ solution, have improved the crystallinity and the
rate of formation of the synthetic minerals.

The nature of the substances obtained depends little on the ratio of silicate
to cation in the large flask, provided this ratio does not exceed too greatly that
of the constituents in the mineral. On the other hand, this ratio may be too
small; but if so the glass of the large pyrex flask furnishes the silica necessary
for the synthesis. Table 1 shows the effect of pH on the results of the synthesis.

Although we have not carried out extensive work in the range of high pH
values, there seem to be no clearly defined limits in this direction. On the other
hand, there seems to exist a minimum pH below which synthesis is no longer
possible; this result is quite clear in clays containing ferric iron, nickel, and
zinc, which have been studied particularly from this standpoint. The results
with other cations seem to be similar.

If aluminate is added to the silicate and if the water in the flask contains KCl in solution, there is a tendency to form clays of a mica type. If the products show a clear 10 A spacing, this spacing is more or less stable when the product is brought into contact with $MgCl_2$ or is immersed in a solution of glycerol. We have been able to obtain a perfectly stable mica of the phlogopite type, and several products similar to biotite that are of rather variable stability. The presence of potassium ions seems to impede the formation of well-crystallized products.

The method employing flowing solutions has not allowed us to obtain minerals with a spacing of 7 A; antigorites are formed only when there is an excess of cations in the large glass vessels. If a small quantity of silicate is allowed to flow into the glass vessel, either a mixture of montmorillonite and antigorite or a pure montmorillonite clay is obtained. Under these conditions, it has been possible to obtain montmorillonite clays at pH values that are lower than those which seem to set a limit when the two solutions flow into the flask. With nickel cations at about pH 6.5, we have obtained talc-like substances that were attached to the walls of the flask, but the products deposited within the flask were montmorillonite.

Study of the products obtained at different pH values shows that the silica content is smaller if the medium is acid than if it is neutral or alkaline. This result is particularly clear when the cations are placed in the large flask. When the two solutions of silicate and of the cation both flow into the receiving vessel, one obtains at low pH mixtures of oxides or hydroxides and of montmorillonites; it is impossible to determine the composition of the latter. When the cation is Fe, the amount of silica in the mixture prepared at pH 5 is always less than 10 percent, but it increases towards 30 percent at pH 7 and exceeds 50 percent at pH 8. Similarly, the magnesium content of the product for the same two mother solutions is smaller at low pH than at high pH values.

The study of synthetic products obtained at different pH values shows that their composition depends on the conditions of the medium. At low pH values, the tetrahedral layers are largely complete and the hydroxide layer is continuous. At higher pH values, the reverse situation seems to occur and the silica layers are continuous and the hydroxide layer discontinuous; the products then contain an excess of silica.

CONCLUSIONS

An attempt will now be made to develop a mechanism for the formation of clay minerals, based on the experimental results.

First of all, it seems to be much easier to prepare clay minerals using cations yielding hydroxides that crystallize with the brucite structure. This is not in every case a general rule, as one obtains similar results with ferric iron, but well-crystallized products have not been obtained with aluminum. A possible reason is that this cation tends to yield boehmite under the conditions of the experiments, and the structure of boehmite is rather far from that of the octahedral layer in clays. The results lead us to consider first the formation of hydroxyl layers on which silica is subsequently fixed. There are two objections to this conception. In the first place, clay minerals are formed under concentrations of cations and at pH values where the hydroxides could not be expected

to crystallize (Table 1) ; and secondly, at high pH values an excess of silica is found.

In answer to the first objection, it may be noted that before hydroxides are precipitated, basic salts are formed. In these experiments, the substances formed always contain hydroxide associated with some impurity, and the clays themselves can be considered as basic salts. As regards the second objection, a somewhat similar reply may be given; the experiments show that a very weak concentration of cations is sufficient to bring about the precipitation of silica. The excess of silica at relatively high pH values could result from an extension of the tetrahedral layers normally formed at the surface of the continuous hydroxide layers, the layers of excess silica being stabilized by small quantities of hydroxides (Fig. 1, c).

The effects of the solubility of the cations and of the activity of the silica defined by the ratio SiO_3H^-/SiO_3Na_2 are nevertheless apparent in the course of the experiments. In conformity with these properties the content of silica, or of a soluble cation such as magnesium, is found to diminish at the same time as the pH.

The role of the electrolytes that do not take part in the composition of the synthetic mineral, such as chlorides and sulfates, is difficult to interpret. It seems impossible to invoke either their influence on the fixation of silica, or the precipitation of cations before forming the octahedral layer. Only investigations of the kinetics of these reactions, such as are now being undertaken in our laboratory, will yield information on these points.

The method that has been employed is certainly very general as it has yielded clays from a great variety of initial components. There are two general possibilities: the formation of the mineral in the solution or (what is equally possible) in contact with the wall of the glass container. It is very difficult to distinguish experimentally between these two. The necessity for a complete rearrangement of the elements of a mineral in order to form a clay has induced us always to select a process in which the silica first passes into solution. We have now obtained proof that certain lavas allow the formation of montmorillonites (namely, by contact of a basalt with a magnesian solution).

The fact that this may be true only under conditions that have led to the formation of antigorites leads us to think that the appearance of minerals of the 1:1 and 2:1 types is determined by the rate of arrival of silica in relation to the rate of formation of hydroxides. Furthermore, orientation effects may operate.

TABLE 1. — pH LIMITS WITHIN WHICH THE CLAY MINERALS ARE FORMED

Cations	Beginning of precipitation of hydroxide, M 10^{-2}	Montmorillonites	Antigorites	Oxides or hydroxides
Al	3.8	9 - 8.5		
Mg	10	11 - 6.5	6.5 - 6	
Ni	7.4	8 - 6	6.5 - 5.5	
Fe²⁺	5.8	9 - 7		7 - 6
Fe³⁺	2.2	9 - 7		7 - 6
Zn	6.8	12 - 5		

These experiments show that synthesis of hydrated silicates is possible at low temperatures, and the conditions used in the experiments seem to be applicable to natural conditions.

Although we have generally operated at 100° C in order to produce enough material, we have obtained crystalline products at temperatures as low as 20° C. The rate of production is then considerably reduced.

Extrapolation from the results shows that the rate of formation varies in the ratio 1:560 between 0° and 100° C. Furthermore, we have succeeded in preparing clays by very slowly concentrating the drainage water, originally deprived of its calcium bicarbonate by boiling for a short time in pyrex beakers. There again the silica must have been furnished by the glass.

The results obtained do not always agree with observations of natural processes. In these experiments, we can control the composition of the mother solutions, which are prepared artificially. This is not so in nature, where the pH and composition depend on circulating water. This may explain the fact that the range of pH for the formation of certain clay minerals in the laboratory seems to be greater than in soils. Conversely, if we take as a basis for interpretation the results of these attempted syntheses, the detailed study of clays (especially their chemical composition) ought to allow us to reconstruct the conditions holding at the time of formation. It is especially in this direction that the experiments are useful in permitting an analysis of complex phenomena which are not amenable to classical physical chemistry.

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