Experimental formation of chlorites from montmorillonite.[1]

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One of the problems which occupy the mineralogist as well as the geologist or pedologist is the mechanism of the formation and evolution of minerals in nature. In this general connexion we have been trying to clarify the possibility of passing from montmorillonite to chloritic minerals. Already in a previous work[2] we showed that on precipitating magnesium with ammonia in the presence of montmorillonite, a substance is obtained which shows certain of the characteristics of vermiculite and chlorite. Having thus shown the possibility of passing from one type to the other, we wished to clarify the mechanism of the change. We wanted to know what are the conditions of the transformation, and then to follow the montmorillonite from the moment when it was in equilibrium with the solution of magnesium chloride to the end of the alteration. Finally, it had to be established to what extent the product obtained resembled or differed from the standard minerals. These different points will be considered in succession.

Mechanism of the transformation.

In the original technique, a very concentrated suspension of montmorillonite, of the order of 100 grams per litre, was mixed with a 20 % solution of magnesium chloride in the proportion of 300 c.c. of suspension to 200 c.c. of the solution. After three days the clear supernatant solution was decanted, then 20 drops of NH_4OH were slowly added, with vigorous shaking. We repeated this procedure, using $MgCl_2$ solutions of concentration varying from 5 to 40 %, adding 20 to 60 drops of pure ammonia for each concentration.

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[1] Read August 27, 1948, at the meeting of the Clay Minerals Group at the International Geological Congress, London, under the title: S. Caillère, Expérience sur la formation et l'évolution des chlorites et vermiculites. (Internat. Geol. Congr., Volume of Titles and Abstracts, 1948, p. 127.) Translated by Dr. D. M. C. MacEwan.

[2] S. Caillère and S. Hénin, Compt. Rend. Acad. Sci. Paris, 1947, vol. 224, p. 53. [M.A. 10–368.]

The results of this series of trials show that, up from the 10 % concentration, using 60 drops of ammonia, a constant result, according to X-ray examination, is obtained. On the other hand, previous trials in which the ammonia treatment was applied to a Mg-montmorillonite—that is to say, one in which the base-exchange capacity was saturated with Mg, without any excess of ions in the solution—did not show the transformation. In these circumstances, one is led to conclude that an excess of Mg ions can penetrate between the structural sheets, and be precipitated there. This conception makes us suppose that the variable space between the montmorillonite sheets, which we will call Δ (after MacEwan),[1] is accessible to an excess of cations and the corresponding anions. To justify this point of view, we first observed that this space remained open even when the mineral was immersed in a relatively concentrated solution; and secondly we sought to bring out the influence of time, since the question naturally arose whether the diffusion of ions in this relatively narrow space was slow or fast.

The determination of the principal spacing of the clay in concentrated salt solution was carried out in the following manner. After the clay had been in contact for three days with solutions of strengths varying from 5 to 40 %, a small quantity of substance, for X-ray examination, was taken from the flocculate which had come down to the bottom of the vessel. Despite the high scattering power of the solution, it was possible to find out that the principal spacing remained constant at 17·6 Å. Thus it may be concluded that there is no apparent effect which would allow one to suppose a notable concentration difference between the solution in the Δ space and the external solution. Consideration of the action of the ammonia leads one to suppose that the OH ions must penetrate between the structural sheets, to allow the precipitation of magnesium hydroxide there. This fact is rather surprising, for one might have thought that the anions would find it difficult to penetrate into this space in view of the presence of negative charges carried by the montmorillonite sheets.

However, this conception is supported by the results of F. Kayser and J. M. Moch,[2] who were able to precipitate silver chloride in the Δ space by treating a Ag-montmorillonite with sodium chloride. This experiment proves even more conclusively than the one just described the possibility of an anion penetrating between the structural sheets; for the existence of hydrolysis phenomena could be explained by the

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[1] D. M. C. MacEwan, Trans. Faraday Soc., 1948, vol. 44, p. 349.

[2] F. Kayser and J. M. Moch, Compt. Rend. Acad. Sci. Paris, 1948, vol. 226, p. 251.

presence of OH ions in the Δ space, without supposing that they come from the external medium. Such is clearly not the case in the formation of sodium chloride. We may thus conclude that substances can be precipitated in the Δ space.

To decide with what speed the magnesium chloride penetrates between the structural sheets, we precipitated the hydroxide after different times of contact of the clay with the solution. X-ray examination of the altered products did not allow any influence of time to be brought out, the product obtained after 5 minutes' contact, and after 3 days, giving essentially the same diagram. It follows that the penetration of the excess of salt must be very rapid if not almost instantaneous.

Let us consider now the mechanism of formation of the hydroxide layer. Initially, we have a Mg-montmorillonite and a solution of magnesium chloride. Adding ammonia, we get:

$$\text{Mg-montmorillonite} + MgCl_2 + 2NH_4OH = NH_4\text{-montmorillonite} + Mg(OH)_2 + 2NH_4Cl.$$

If an X-ray examination is made of the gel in equilibrium with the $MgCl_2$ solution before precipitation, the mineral shows a spacing of 17·6 Å. as already mentioned. A diagram taken immediately after the precipitation, without modification of the humidity of the medium, shows an almost identical spacing as far as one can judge, the diagram being diffuse.

Thus, a brucitic layer and a water layer must exist together in the Δ space. If, now, the product is allowed to dry in the air, we find that it has a principal spacing of 15·2 Å., and shows a (00*l*) series similar to that of the oven-dried product, but with more diffuse lines. Thus the water layer remaining in the product after precipitation of the magnesium is especially labile, and the stable form is the one we obtained. Furthermore, on damping the air-dried substance and making an X-ray diagram, one finds that already it is relatively stable, with only a slight tendency to swell. Finally, after drying to 105° a spacing of 14·1 Å. with a well-defined (00*l*) series is obtained, which is stable on moistening with water.

Treatment in the cold of the substance thus obtained, with a large excess of 5 % hydrochloric acid for one hour, leads to the complete disappearance of the (00*l*) series.

These trials show that it is relatively easy, by precipitating magnesium with ammonia from a concentrated solution, to obtain a stable 14 Å. micaceous product, whose X-ray diagram resembles that of a chlorite. We will now examine how far one can identify the two substances.

Comparative study of the artificial product and of the similar minerals montmorillonite, vermiculite, chlorite.

So far, the transformations have been followed only with X-rays. We will thus begin by comparing the diagrams of these different minerals.

Montmorillonite.	Treated montmorillonite.	Vermiculite.*	Chlorite.†
15·3 (vs)	—	—	—
—	14 (vs)	13·7 (9)	13·7 (7)
—	7·2 (m)	—	7·04 (8)
—	—	—	5·25 (2)
4·80 (vw)	4·76 (m)	—	4·68 (9)
4·42 (s)	4·42 (vs)	4·43 (1)	—
—	—	—	3·92 (2)
—	3·60 (w)	3·55 (3)	3·51 (10)
3·12 (m)	—	3·10 (1)	3·13 (1)
—	2·94 (w)	2·85 (3)	2·83 (7)
2·80 (vvw)	—	—	—
—	—	—	2·71 (0·5)
—	—	2·63 (1)	—
—	—	—	2·58 (7)
2·56 (vs)	—	—	2·54 (5)
—	2·43 (mw)	2·38 (3)	2·43 (6)
—	—	2·19 (1)	2·25 (4)
—	2·14 (vw)	2·07 (1)	2·02 (7)
—	—	—	2·00 (6)
1·72 (m)	1·86 (w)	1·73 (0·5)	—
—	—	1·67 (3)	—
1·60 (vvw)	1·57 (w)	—	1·56 (10)
1·51 (m)	1·52 (s)	1·53 (3)	1·53 (10)

* R. C. McMurchy, Zeits. Krist., 1934, vol. 88, p. 420. [M.A. **6**–45.]

† J. W. Gruner, Amer. Min., 1934, vol. 19, p. 557. [M.A. **6**-181.]

It may be seen that the diagram of the alteration product resembles that of chlorite. The first five lines of the (00*l*) series correspond to an approximately rational series of spacings, and are near to those of chlorites. These lines are absent from the vermiculite and montmorillonite diagrams. Further, we may recall that the diagrams of the alteration products of vermiculite and of chlorite are stable in water. Thus, a close analogy may be traced between the diagram of the treated montmorillonite and of chlorite.

However, if X-ray photographs are made, in air, of the treated product and of chlorite after heating them to 400° for 24 hours, a marked difference between the two is noted. The altered montmorillonite no longer gives the (00*l*) chlorite lines, showing that the brucitic layer formed was much less stable than that of chlorite itself. This result is in accord with the behaviour on hydrochloric acid treatment, which also pointed to the more labile nature of the magnesium hydroxide precipitated in the Δ space.

We thus cannot say that the product obtained is identical with chlorite. We have, further, already remarked in a previous work,[1] with reference to the water-loss and the result of acid attack of chlorite, that the brucitic layer must be attached by very strong chemical forces to the mica-type sheets, thus explaining in particular the fact that chlorite is decomposed only at 550° by heat, whereas gibbsite and brucite are completely dehydrated at 350° and 450° respectively. We may therefore suppose that, in the case of our product, the magnesium hydroxide is simply precipitated between the sheets.

The chemical analysis suggests an interpretation of this behaviour. The table below collects together the composition of the four dehydrated products.

	Initial montmorillonite.	Treated montmorillonite.	Vermiculite.*	Chlorite.†
SiO_2	55·4	49·8	46	35·80
Al_2O_3	36	29	23·2	23·40
CaO	2·5	2·3	—	—
MgO	6·1	18·9	30·8	41·00

* Mean composition according to J. W. Gruner, 1934. [M.A. 6–181.]

† Composition of clinochlore from Besafotra, Madagascar, after J. Orcel, 1927. [M.A. 3–372.]

We see that the altered product still differs quite notably in composition from clinochlore which, of all the chlorites, might come closest to our product. The magnesium deficit which emerges implies that the newly-formed brucitic layer is incomplete, and this would explain to a certain extent the behaviour of the product both on heat-treatment and on acid attack. The silica content is quite close to that of vermiculite, but there is still a magnesium deficit by comparison with this latter mineral which is rather difficult to explain. One may then conclude that from the chemical point of view the product tends to approximate to the chlorites and vermiculites without, however, being completely the same.

The comparison of the differential thermal curves obtained with the Saladin–Le Chatelier apparatus brings out the following special features. The curves of montmorillonite (M, fig. 1), of vermiculite (V), and of treated montmorillonite (Mt) all show an important endothermic feature

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[1] J. Orcel, S. Caillère, and S. Hénin, Compt. Rend. Congrès Soc. Savants, Strasbourg, 1947 (in the press).

due to the loss of hygroscopic water. However, the two latter substances do not show the feature so markedly as montmorillonite, corresponding to the fact that its Δ space is larger. In the altered product, a part of this space is filled with magnesium hydroxide. Furthermore, vermiculite shows a peak at 370°, and this feature is also found, very faintly, in the treated montmorillonite. Comparing now the high-temperature peaks, the four substances are seen to have a first endothermic feature, varying from large to small in the order: clinochlore (C) large peak at 670°; treated product, fairly large peak, spread out from 570° up; montmorillonite, medium, well-developed peak at 730°; vermiculite, small peak at 660°. Further, these substances have a second more or less marked endothermic peak between 800° and 820°. Finally, the chlorite, the altered montmorillonite, and the vermiculite show two little exothermic features, the one at 650°–700°, the other about 850°–870°. The curves have other less important features, whose interpretation is difficult, but which, together with the preceding data, further reinforce the analogy of the treated product with chlorite, and (more especially) with vermiculite. Thus thermal studies confirm the conclusion which emerges from an examination of the X-ray diagrams, that the treated montmorillonite resembles the chlorites and vermiculites.

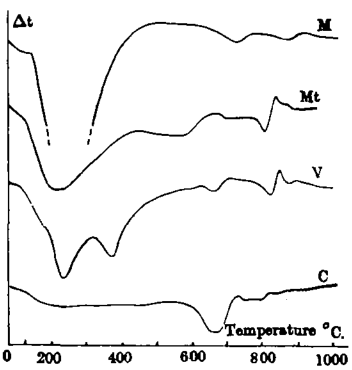

FIG. 1. Differential thermal curves.

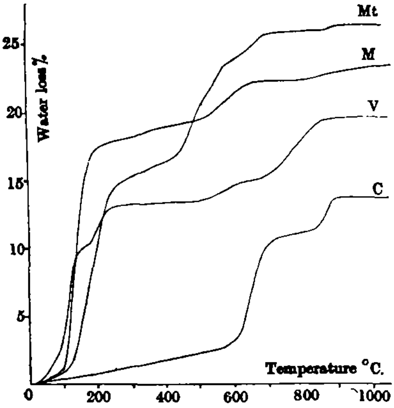

FIG. 2. Dehydration curves.

Montmorillonite (M), treated montmorillonite (Mt), vermiculite (V), chlorite (C).

The weight-loss curves (fig. 2), recorded with the Chevenard thermobalance, show first of all a loss of hygroscopic water taking place up to about 240°, about which the same remarks may be made as for the differential thermal analysis curves. Further, all four substances show two regions of water-loss whose relative and absolute magnitude vary from one to another. It may be noted that the curve of the treated product shows a markedly larger weight-loss than the initial montmorillonite, approaching the weight-loss of the vermiculite and the chlorite. However, this water goes off at a lower temperature from the artificial product than from the two minerals.

These results thus allow us to link up our magnesian product with chlorite and with vermiculite. Comparing the high-temperature water-loss of the initial montmorillonite and of the transformation product we see that, reckoning this water-loss from the base of the first inflexion, at 420° for the treated product and 430° for the initial montmorillonite, the first loses 9·5 % water and the second 4 %, an excess of 5·5 % water to be attributed to the water fixed as magnesium hydroxide. This amount would represent 12·2 % of MgO fixed between the structural sheets, or almost exactly the excess of magnesium shown by the chemical analysis. Without wanting to attach too much importance to this agreement, we can none the less say that the increase of water-loss at high temperatures confirms the fact that a part of the magnesium is precipitated between the sheets.

Use of different cations.

The composition of chlorites being very varied, the constituents of the brucitic layer ought also to differ considerably. Furthermore, several cations can give hydroxides with the gibbsite-brucite structure. For these two reasons, one might suppose that, applying the preceding treatment to montmorillonite in presence of solutions of cations having these characteristics, one could obtain the same sort of alteration.

Our experiments have been done with nickel, cobalt, ferrous and ferric iron, aluminium, and chromium ions. The results enable us to classify the cations into 2 groups:

(1) Those giving rise to the same modification as magnesium, such as nickel and cobalt;

(2) The others, whose behaviour is discussed below.

Treatment by cations of the first group.—Using the range of concentrations already used, the treatment leads to products whose X-ray diagrams can be classed between the following two extreme types.

With additions of ammonia of the order of 10 to 20 drops, the X-ray diagram shows a (00*l*) series with four successive orders, the first being by far the most intense. These substances are not very stable in water, because on taking an X-ray photograph of the moist substance, an increase of the (001) spacing is found.

With a larger quantity of ammonia (80 to 100 drops) the diagram remains quite stable even when the substance is moistened. It then shows the following characteristics: the first order has almost completely gone; the second order is extremely intense; the third order is weak; but the fourth order very clear. Thus the (00*l*) series of these products appears to be complementary to that of montmorillonite, since in the latter it is the even orders which disappear.

The result can be interpreted as follows: the presence of a layer of ions of high-scattering power in the Δ space leads to the formation of two 7 Å. layers of similar scattering power. One is formed by one of the tetrahedral layers, and the octahedral layer of the montmorillonite; the other by the second tetrahedral layer of the montmorillonite and the newly-formed octahedral layer. In these conditions, when the crystals make an angle with the incident beam having a Bragg angle corresponding to 14 Å. spacing, the reflecting planes 7 Å. apart give equal reflected intensities, but in opposite phase; the reflection corresponding to the 14 Å. spacing is thus extinguished, and all the odd-order reflections are weak or absent. The even-order reflections, on the other hand, are intensified.

It might obviously be wondered if the new diagram does not indicate the existence of free hydroxides. This objection does not seem tenable for the following reasons. The nickel hydroxide obtained by precipitation with ammonia gives no 7 Å. line. Further, though the diagram of the treated product does not have the large spacing line of montmorillonite, it none the less shows (*hk*0) lines of normal intensity. It is not very probable therefore that our result could be due to a mixture of nickel hydroxide and montmorillonite. Further, like the magnesian products, these substances are not heat-stable. After heating to 400° the 7 Å. line disappears and a halo appears situated around 10 Å. This behaviour seems readily attributable to the destruction of the hydroxide layer and the formation of a 10 Å. micaceous mineral.

It is further possible to get intermediate diagrams, in which the intensity of the (00*l*) series of lines varies, from which we may conclude that the behaviour of nickel and cobalt is quite analogous to that of magnesium. This analogy deserves to be stressed, for we had already noted it in our research on the synthesis of antigorite. In the course of this work we were able to obtain silicates of Mg, Ni, and Co at low temperatures and in similar conditions; while such preparations could not be obtained using the following group of ions.

Treatment by cations of the second group.—In contra-distinction to the facts observed in the preceding work we were never able, either with ferrous or ferric iron, chromium, or aluminium, to obtain a comparable alteration to those previously described, despite the existence of aluminous, ferriferous, and chromiferous chlorites.

After precipitation of the hydroxides by ammonia, the X-ray diagram is still very close to that of the initial montmorillonite; and furthermore the diagram of the moistened product shows an increase of the first-order spacing. The characteristics of the weight-loss curves are, however, greatly altered, which leads one to suppose that there is none the less a part of the hydroxides precipitated between the sheets. Only a more complete study of the treated montmorillonite after heating to different temperatures would enable a definite conclusion in this sense to be drawn. The special behaviour of this group of substances could be attributed to the fact that the second group cations on precipitation give rise to hydroxides with different structures from those of the first group hydrates.

Conclusion.

This work shows that, by precipitation of magnesium, nickel, and cobalt between the structural sheets of montmorillonite, substances are obtained which give X-ray diagrams similar to those of chlorite, or of certain vermiculites. The analogy between these two substances is also confirmed by thermal analysis, weight-loss diagrams, and chemical study.

Only a smaller stability on heating and on acid treatment distinguishes rather clearly this alteration product from the two minerals, chlorite and vermiculite. The analogy seems to us, however, to be good enough to warrant the consideration of this type of change as one of the possible mechanisms of alteration of montmorillonite in nature.

Finally, as a consequence of these results, it may be suggested that the vermiculites represent a type of mineral which comes close to the chlorites, but in which the brucitic layer is rudimentary.