

THE FORMATION OF CHLORITE-LIKE STRUCTURES FROM MONTMORILLONITE¹

by

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ABSTRACT

Chlorite-like complexes of montmorillonite with magnesium hydroxide or aluminum hydroxide have been prepared under a variety of physical and chemical conditions. Requirements for the preparation of these complexes have been simplified considerably by the use of rapid mixing techniques. A complex may be formed either by precipitating the hydroxide in a clay suspension or by preparing the precipitate separately and mixing it immediately with the clay suspension. It is suggested that the process involves the adsorption of a layer of the precipitate over the entire surface of the montmorillonite unit layer rather than the direct formation of a structure in the interlayer space. It is considered that there is no appreciable permanent association of unit 10 Å layers of montmorillonite in a well stirred suspension, even in the presence of strong salt solution, but that instead most clay surfaces are exposed continually. The chlorite-like structure develops only upon association of the unit layers through aging or dehydration.

The aluminum hydroxide complex with montmorillonite differs somewhat from the magnesium type, but it has the approximate chlorite basal spacing. The complex shows a second-order basal diffraction spacing of low intensity, and forms regular expanded structures with water or ethylene glycol. A gibbsite structure for the interlayer material is most compatible with the x-ray data.

The occurrence of this process in sediments and soils is considered to be very probable, although it is premature to consider precise environments until more experimental data are available.

INTRODUCTION

The widespread occurrence of varieties of chlorite in soils and sedimentary rocks has been explained frequently as the result of precipitation of hydroxides of magnesium, iron or aluminum between the unit sheets of expanding clay minerals. This explanation has been supported by reports of the laboratory preparation of chlorite-like materials as a result of the precipitation of hydroxides in montmorillonite suspensions. The original description of this process was given by Caillère and Hénin (1949). Subsequent papers by Caillère and Hénin (1950), Longuet-Escard (1950) and Youell (1951) have indicated that the hydroxides or hydrous oxides of magnesium, aluminum, nickel, cobalt, zinc and ferrous iron can form montmorillonite-hydroxide complexes.

A wide variation exists in the conditions under which these chlorite-like structures have been prepared. Caillère and Hénin (1949) used fairly con-

¹ Publication authorized by Executive Vice-President, Gulf Research & Development Company.

centrated suspension-solution mixtures containing 6 percent clay and 1 N to 4 N concentrations of magnesium chloride. The precipitation of magnesium hydroxide was carried out by dropwise addition of ammonium hydroxide solution accompanied by vigorous shaking. Longuet-Escard (1950) on the other hand reported the formation of aluminum hydroxide and nickel hydroxide complexes with montmorillonite in systems containing 0.5 to 1 percent clay and less than 0.1 N concentrations of the metal nitrates. Youell (1951) reported, without details, a successful electrolytic method of precipitating magnesium and zinc hydroxides within the interlayer space of montmorillonite.

The present studies were undertaken to assess the possible geological significance of this method of formation of chlorite, by defining more clearly the range of conditions under which montmorillonite-hydroxide complexes may be produced in the laboratory.

EXPERIMENTAL PROCEDURE AND RESULTS

Magnesium Hydroxide-Montmorillonite Complexes

The present study has been confined almost entirely to the magnesium hydroxide-montmorillonite and the aluminum hydroxide-montmorillonite systems. These systems provide considerable contrast in chemical conditions of precipitation and in the properties of the hydroxide precipitate. Most of the experiments have been carried out with crude montmorillonite from Clay Spur, Wyoming. A few experiments carried out with fractionated samples, saturated with sodium, magnesium or aluminum indicated that such treatment was unimportant in preparing chlorite-like structures. Samples were washed by centrifugation and prepared as oriented aggregates for x-ray diffraction analysis.

The precipitate obtained by adding an alkali hydroxide solution to a solution of a soluble magnesium salt has the well defined chemical formula and structure of brucite $[\text{Mg}(\text{OH})_2]$. A calculation of the quantity of this material that can be introduced between unit sheets of montmorillonite in a chlorite-like structure indicates approximately 16 meq/g of pure clay. The same calculation is applicable to the aluminum hydroxide precipitate if the gibbsite structure is assumed.

Initial experiments in the preparation of magnesium hydroxide complexes were carried out under conditions similar to those reported by Caillère and Hénin. Thick suspensions of montmorillonite (2 to 10 percent) in concentrated solutions (1-2 N) of magnesium chloride were employed. Precipitation of the hydroxide was effected by additions of lithium, sodium or ammonium hydroxide solutions. The thick clay suspensions necessitated mechanical stirring and the principal variable appeared to be the rate of addition of the hydroxyl ion. More-or-less brucite, as a separate phase, was obtained in most of these experiments. Chlorite-like structures of varying quality were produced by these procedures. The best products as evidenced by x-ray diffraction properties were obtained with lithium hydroxide as precipitant,

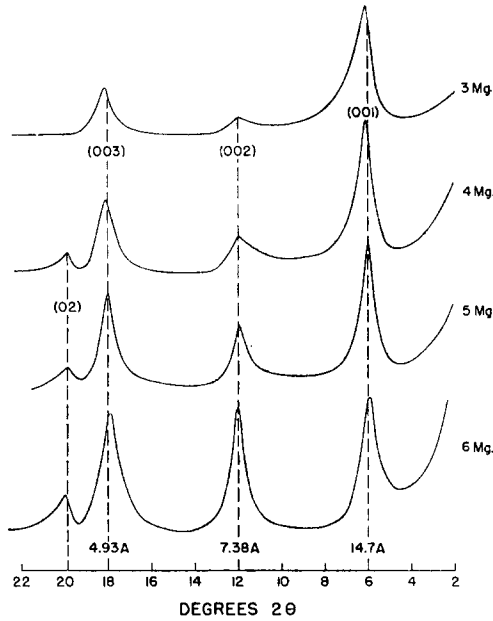


FIGURE 1.—Magnesium hydroxide-montmorillonite complex: diffraction patterns of samples dried at 100°C showing effect of increasing magnesium atoms per structural unit.

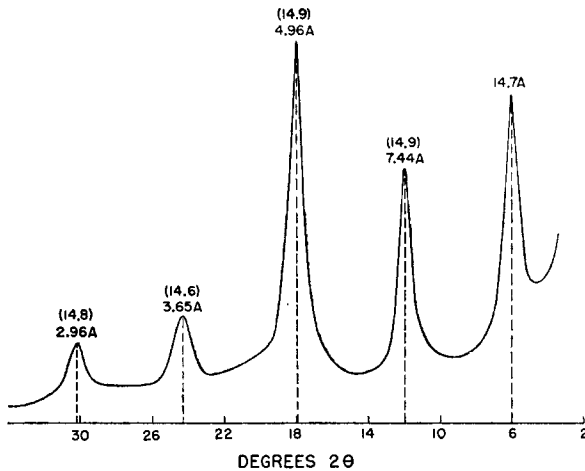


FIGURE 2.—Magnesium hydroxide-montmorillonite complex: x-ray diffraction pattern of material dried at 100°C.

added at a rate such that the treatment of 3-4 g of clay required approximately 8 hr. Precipitation was carried normally beyond the point calculated as necessary for the complete development of a brucite layer. The diffraction diagrams of Fig. 1 show the gradual development of the brucite interlayer

as magnesium hydroxide is precipitated in the clay suspension up to the calculated maximum of 6 [Mg(OH)₂] per structural unit of clay.

The diffraction pattern (Fig. 2) is considered to represent the most complete development of a brucite interlayer. The relative intensities for the first five basal reflections from this material have been compared in Table 1 with calculated values. The calculated intensities were prepared for the Clay Spur montmorillonite used in these experiments, of composition

$\frac{M_{0.82}^{n+}}{n} (Al_{3.04}Fe_{0.44}^{3+}Mg_{0.54}) (Si_{7.68}Al_{0.32}) O_{20}(OH)_4$ and interlayer brucite of 6[Mg(OH)₂]. Good agreement has been obtained between observed and calculated intensities except for the third-order peak. The relatively high intensity observed for this peak may be caused by a poorly crystallized separate brucite phase which gives a diffraction maximum in this vicinity.

The completeness of the brucite layer in these preparations appears to decrease upon aging of the product in the final solution for several hours. This decrease coincides with an increase in intensity of a separate brucite phase.

TABLE 1.—RELATIVE CALCULATED AND OBSERVED X-RAY DIFFRACTION INTENSITIES MAGNESIUM HYDROXIDE-MONTMORILLONITE COMPLEX

(00l)	<i>I</i> _{obs}	<i>I</i> ¹ _{calc.}
001	71	71
002	70	70
003	120	100
004	29	34
005	17	22

¹ 6[Mg(OH)₂] per unit cell.

It has been found possible to modify this method of preparation of the magnesium hydroxide-montmorillonite complex drastically by employing a Waring Blendor to mix the fluid system during the reaction process. Clay concentrations have been varied from 1 to 0.2 percent without any apparent effect. The calculated quantity of magnesium chloride has been added to the clay suspension and the alkali hydroxide solution added within hours or seconds to produce in either case a complex of good quality. Simultaneous addition of the required amounts of normal magnesium chloride and sodium hydroxide solutions into the clay suspension within a few minutes also produces a fully developed complex. The diffraction results from three of these procedures are illustrated in Fig. 3. Fig. 3(a) shows the diffraction characteristics of the product obtained when sodium hydroxide solution is added within 15 sec to a mixture of 1 g of clay and magnesium chloride in 500 ml of water. Fig. 3(b) shows the diffraction pattern of the product obtained when the magnesium chloride and sodium hydroxide solutions are reacted outside the clay suspension and added to the suspension immediately. The complex formed in this case appears to be more than 50 percent complete.

Formation of the material characterized by the diffraction pattern in Fig. 3(c) was accomplished by including the sodium hydroxide with the clay suspension and adding the magnesium chloride solution rapidly. The product again shows a brucite interlayer which is more than 50 percent complete. These results suggest that the essential requirement for complex formation lies in the complete dispersal of the freshly precipitated magnesium hydroxide throughout the clay suspension. The apparent ability of the clay particles to adsorb freshly precipitated magnesium hydroxide, perhaps of molecular dimensions, does not preclude the possibility that precipitation can take place directly in the interlayer space under appropriate conditions.

Additional observations that may be important in understanding the process of interlayer brucite formation were made during the preparation of slide-mounted samples for diffraction analysis. Continuous diffraction obser-

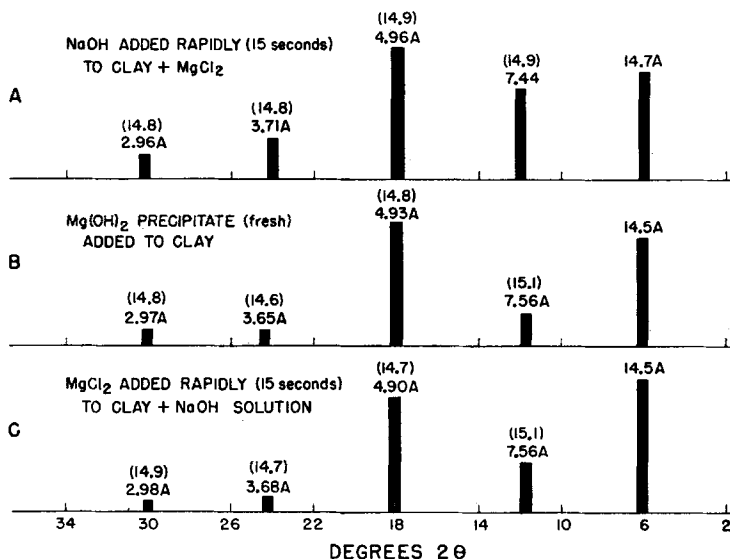


FIGURE 3.—Magnesium hydroxide—montmorillonite complexes (rapid procedures):¹ diagrammatic representation of x-ray diffraction patterns.

vation of samples during the drying process failed to reveal basal diffraction lines until samples were almost dry. At this point regular orders of the 14.8 Å basal spacing appeared. This has been interpreted as indicating that a large part of the Mg(OH)₂ is present as an adsorbed layer on individual clay surfaces and that the brucite structure is formed only when the surfaces are brought close together by removal of water. It was found, however, that aging of samples in water did result in the appearance of a 14.8 Å spacing even when samples were wet.

Samples with fully developed brucite interlayers have not given definite evidence of the development of a regular expanded structure with water or ethylene glycol. However, with incomplete brucite interlayers, regularly

expanded structures of 18.8 Å with water and 17 Å with ethylene glycol may be obtained. These expanded structures apparently are connected with the clay surface which is not covered with magnesium hydroxide.

Aluminum Hydroxide-Montmorillonite Complexes

The properties of the precipitate that is formed upon addition of an alkali hydroxide solution to a solution of an aluminum salt have been the subject of much discussion (Weiser, 1926, 1949). Recent evidence (Mackenzie, 1957) has indicated that the freshly formed gelatinous precipitate from chloride or nitrate solutions shows the structure of boehmite [$\alpha\text{AlO}(\text{OH})$]. Upon aging the boehmite structure changes into bayerite [$\alpha\text{Al}(\text{OH})_3$] and finally into gibbsite [$\gamma\text{Al}(\text{OH})_3$]. Longuet-Escard (1950) described a procedure for preparing a montmorillonite-aluminum hydroxide complex and apparently assumed or found that the interlayer material had the gibbsite structure.

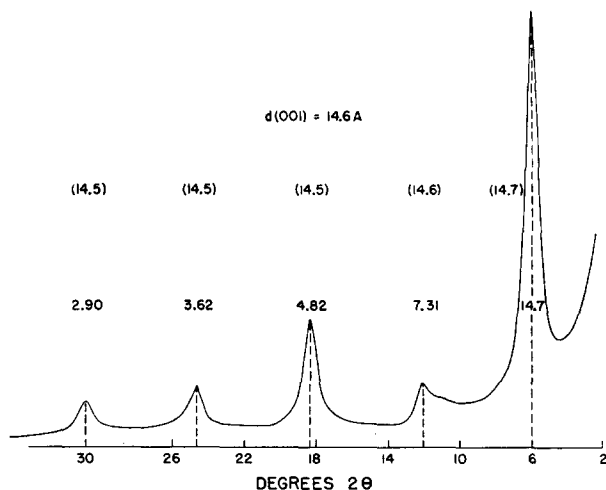


FIGURE 4.—Aluminum hydroxide-montmorillonite complex: x-ray diffraction pattern of material dried at <1 percent relative humidity.

In this study the preparation of the montmorillonite-aluminum hydroxide complex has been carried out with the Waring Blender technique. A stable complex may be formed over a wide range of conditions as in the precipitation of magnesium. The best and simplest procedure was found to be a simultaneous dropwise addition of aluminum nitrate and sodium hydroxide solutions to a dilute suspension (0.2 percent) agitated in the Waring Blender. The diffraction pattern of a typical product is illustrated in Fig. 4. If the preparation is dried at <1 percent relative humidity, a well developed 14.6 Å basal spacing is apparent, but the intensity of 002 relative to that of 001 is slightly less than might be expected from a fully developed gibbsite layer. The structure reaches maximum development stability when 16 meq of

aluminum have been precipitated as would be expected if a gibbsite layer were being formed. However, the material shows, in the process of drying, two regular hydration stages which are illustrated in Fig. 5. Regular orders of a basal spacing of 20.0 Å appear at a very wet stage while a 17.2 Å basal spacing is obtained at 80 percent relative humidity. These structures suggest two and one layers of water added to the collapsed spacing of 14.6 Å.

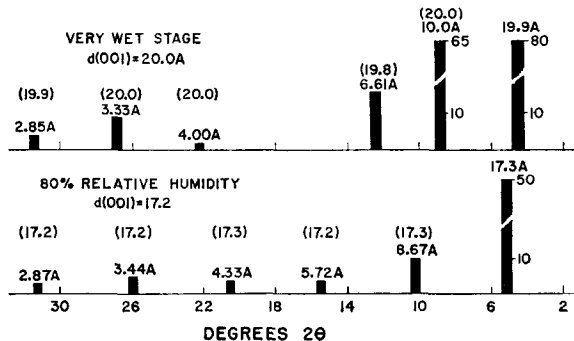


FIGURE 5.—Aluminum hydroxide-montmorillonite complex: x-ray diffraction properties of hydration stages.

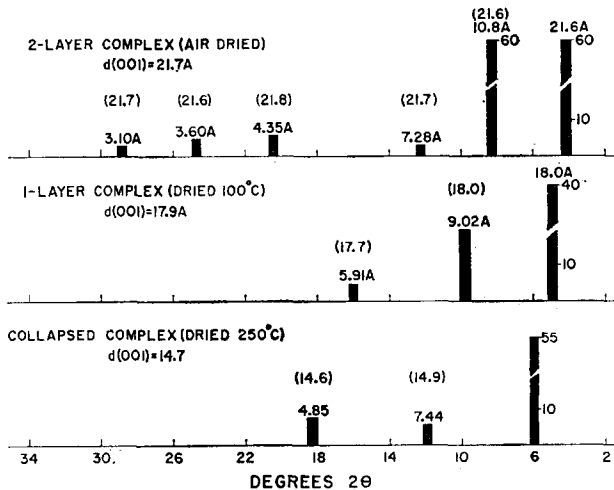


FIGURE 6.—Aluminum hydroxide-montmorillonite complex: x-ray diffraction properties of ethylene glycol complexes.

Ethylene glycol as illustrated in Fig. 6 forms stable two- and one-layer complexes at 21.7 and 17.9 Å, apparently additive to the collapsed 14.6 Å structure. For comparison the hydration stages and ethylene glycol complexes of an aluminum-saturated montmorillonite are illustrated in Figs. 7 and 8. The expansion properties of the aluminum hydroxide-montmorillonite complex and its collapsed basal spacing of 14.6 Å again suggest that the precipitate is present initially as an adsorbed layer on the montmorillonite

surfaces and that a layer of water or ethylene glycol is associated structurally with it. The complex cannot be re-expanded once it has been collapsed.

A comparison of the measured basal diffraction intensities given by the aluminum hydroxide-montmorillonite complex after drying at 100°C with

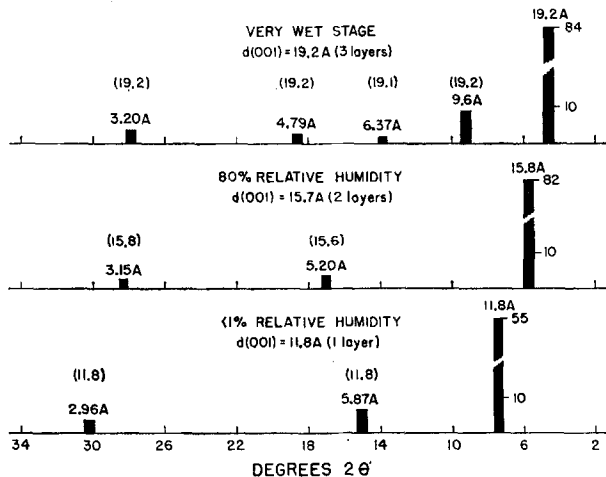


FIGURE 7.—Aluminum saturated montmorillonite: x-ray diffraction properties in hydration stages.

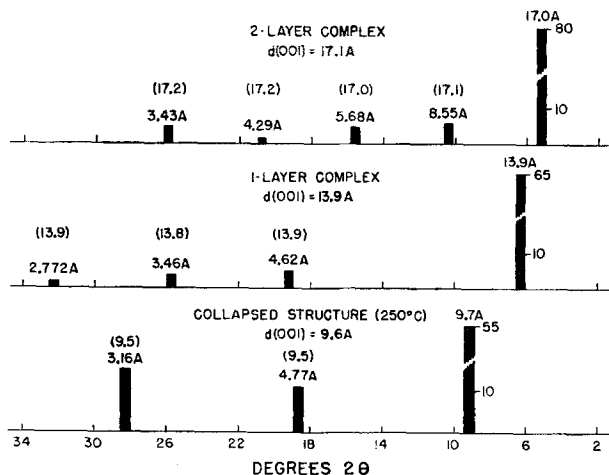


FIGURE 8.—Aluminum saturated montmorillonite: x-ray diffraction properties of ethylene glycol complexes.

values calculated assuming a gibbsite-like interlayer structure is given in Table 2. It is evident that good agreement is obtained with a slightly deficient gibbsite-like interlayer [3.75 Al(OH)₃ per unit cell]. It is considered, therefore, that the precipitate adsorbed by the clay surfaces becomes organized into a gibbsite-like interlayer structure upon dehydration.

TABLE 2.—RELATIVE CALCULATED AND OBSERVED X-RAY BASAL DIFFRACTION INTENSITIES ALUMINUM HYDROXIDE-MONTMORILLONITE COMPLEX

(00 <i>l</i>)	<i>I</i> _{obs}	<i>I</i> ¹ _{calc.}	<i>I</i> ² _{calc.}
001	100	100	100
002	13	24	13
003	35	43	30
004	12	17	12
005	9	18	13

¹ 4[Al(OH)₃] per unit cell.

² 3.75[Al(OH)₃] per unit cell.

The thermal properties of the two chlorite-like structures which have been studied in detail are illustrated in Fig. 9. The magnesium hydroxide

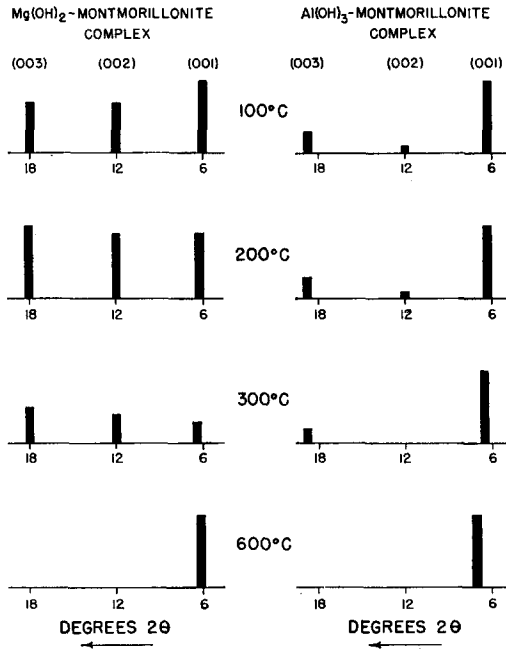


FIGURE 9.—X-Ray diffraction properties of heated complexed structures.

complex is fairly stable at 200°C but at 300° the diffraction peaks have become broad and weak. At 600°C the 001 peak is increased in intensity while the other orders have disappeared, as would be expected with a chlorite structure. The aluminum hydroxide complex is stable also to 200°C; the 002 diffraction peak disappears at 300°C and at 600°C only the 001 peak remains.

Nickel Hydroxide and Ferric Hydroxide Complexes

A nickel hydroxide complex has been produced by the simple procedure, again, of adding sodium hydroxide and nickel nitrate solutions simultaneously to a 0.2 percent clay suspension agitated in a Waring Blender. The diffraction properties of the product are illustrated in Fig. 10. The nickel hydroxide interlayer almost completely suppresses the 001 diffraction peak.

Attempts to prepare a ferric hydroxide complex have not been successful; the difficulty may be related to the fact that a ferric hydroxide structure has not been identified.

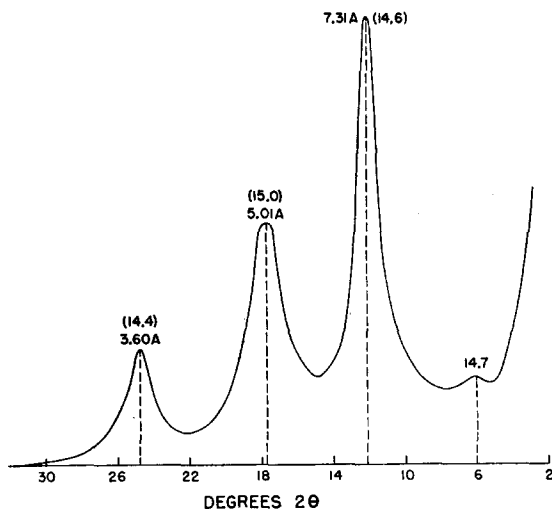


FIGURE 10.—Nickel hydroxide-montmorillonite complex: x-ray diffraction pattern of material dried at 100°C.

SUMMARY AND DISCUSSION

Chlorite-like structures from montmorillonite and the hydroxide precipitates of magnesium and aluminum are formed so readily under laboratory conditions that the process is almost certain to be operative in nature. The laboratory process seems to require simply that the freshly precipitated hydroxide be dispersed immediately and intimately throughout a clay suspension. The presence or absence of significant concentrations of a soluble salt of the precipitating hydroxide does not seem important. It is considered that the process involves the adsorption of a layer of the precipitated hydroxide through hydrogen bonding over the entire surface of the montmorillonite rather than the direct formation of a brucite or gibbsite-like layer in the interlayer space. In fact it appears likely that there is no permanent association of the fundamental 10 Å layers of montmorillonite in a well stirred suspension even in the presence of strong salt concentrations, but that instead, each clay surface is exposed continually. The chlorite-like structure develops only upon association of the unit layers through aging or dehydration.

The exact structure of the hydrated interlayer material developed in the aluminum hydroxide-montmorillonite complex appears to warrant further study. It is fairly evident that the gibbsite structure is the most probable one after the product has been dehydrated at 100°C.

The basal spacings of the complexes that have been produced, ranging from 14.6 to 14.8 Å, are larger than the normal 14.2 Å of natural chlorites. This may result from the necessity of accommodating the original exchange cations of the montmorillonite.

It is obvious that extrapolation of this mechanism of chlorite formation to specific natural environments is premature. Many additional variables must be considered and the work at this stage must be considered only a basis for additional work in understanding the formation of chlorite in soils and sediments.

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