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HYDROXY INTERLAYERS IN EXPANSIBLE LAYER SILICATES*

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Abstract—Vermiculites and smectites in soils and sediments are frequently partially interlayered or "chloritized". Dioctahedral expansible layer silicates are those most frequently interlayered, and hydroxy-Al appears to be the principal component of the non-exchangeable interlayer material.

The most favorable soil conditions for interlayer formation appear to be: moderate pH (4·6–5·8), frequent wetting and drying cycles, and low organic matter content.

In marine sediments, hydroxy-Mg interlayering may be significant. Soil-derived clays containing partially filled hydroxy-Al "brucite" sheets may be filled out with hydroxy-Mg. Under reducing conditions, hydroxy-Fe interlayers may be important.

Depending on the OH/Al ratio and Al content of hydroxy-Al interlayers, expansible layer silicate may either promote or retard the formation of gibbsite. Interlayered expansible layer silicates also may be precursors to kaolinite.

INTRODUCTION

IN THIS paper the discussion of "interlayering" is restricted to the occurrence, formation, and properties of hydroxy-cation systems between the unit layers of phyllosilicates. Furthermore, the discussion is restricted to interlayering of smectites and vermiculites.

In 1950 MacEwan noted that the sharp 14 Å reflection of a soil clay, on heating of the clay to 540°C, became diffuse and shifted toward the 10 Å region. Heating also increased the central scattering, whereas with 14 Å minerals containing only cations and water in the interlayer space central scattering was decreased. He concluded that there was some material irregularly distributed between the mica layers which prevented them from coming completely in contact when the water was expelled. Furthermore, he suggested that the interlayer material was a form of iron or aluminum oxide rather than amorphous silica because of the abundance of free iron and aluminum oxides in the soil. MacEwan suggested that "partial chloritization" might be a suitable name for the phenomenon.

Pearson and Ensminger (1949) found in Alabama soils a 14 Å mineral which had properties that did not fit those of montmorillonite, vermiculite, or chlorite. In (1960) Dixon and Jackson identified the mineral as "intergradient chlorite-expansible layer silicate."

Although earlier Caillère and Hénin (1949, 1950) had prepared chlorite-like material by precipitating $Mg(OH)_2$ in the presence of montmorillonite, interest in the natural process of interlayering stems largely from the observation of MacEwan (1950) noted above and particularly from the papers of Brown. In 1953, Brown described an English soil clay as a "dioctahedral analogue of vermiculite." The clay showed evidence of "blocking material" in the interlayer space, and extraction of the material with KOH-HCl indicated that aluminum was the principal component of this blocking material. The usual Al^{3+} saturation of the "cleaned" vermiculite, however, did not produce blocking. In 1954, Brown proposed that the blocking material was organic matter or $[Al_m(OH)_n]^{3m-n}$ ions.

At about the same time, Grim and Johns (1954) found similar minerals in recent sediments in the vicinity of Rockport, Texas. The weak higher order reflections relative to first order indicated "an interlayer population considerably deficient in brucite as compared to material that definitely can be called chlorite." The authors suggested that "islands" of brucite occur with sufficient frequency to keep the layers apart on heating but too few in number to prevent expansion with glycol.

Subsequently, partially interlayered expansible layer silicates have been reported in many soils and sediments (Table 1).

Because of the marked effects of interlayers on the cation exchange capacity, fixation of cations, and on swelling and shrinking of clays, many attempts have been made to determine the nature

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Table 1. Occurrence of interlayers in expansible-layer silicates in soils and sediments

Location	Reference
	Soils
Australia	Jones *et al.*, 1964
	Loughnan *et al.*, 1962
	Turton *et al.*, 1962
Canada	Brydon *et al.*, 1961
	Pawluk, 1963
England	Brown, 1953, 1954
	MacEwan, 1950
Germany	Kuron *et al.*, 1961; Schwertman, 1961
	Reuter and Menning, 1964, 1965
	Scheffer *et al.*, 1961
Japan	Matsui and Tontani, 1963
	Sudo, 1963
South Africa	Le Roux and de Villiers (1965)
Scotland	Wilson, 1966
Turkey	Jackson, 1963*a*
U.S.S.R.	Zverev, 1954
U.S.A.	
Alabama	Bryant and Dixon, 1964
	Dixon and Jackson, 1960
California	Whittig, 1959
Connecticut	Tamura, 1956; Tamura *et al.*, 1959;
	Sawhney, 1960*b*, 1960*c*; Frink, 1965
Indiana	Klages and White, 1957; Post and White, 1967
Massachusets	Quigley and Martin, 1963
Mississippi	Glenn, 1960; Glenn and Nash, 1964; Nash, 1963
New Jersey	Krebs and Tedrow, 1957; Douglas, 1965
North Carolina	Leith and Craig, 1965; McCracken and Weed, 1963;
	Weed and Nelson, 1960
Oregon	Singleton, 1965
Pennsylvania	Johnson and Jeffries, 1957
	Kunze and Jeffries, 1953
Virginia	Hathaway, 1955
	Rich, 1954; Rich and Obenshain, 1955
Wisconsin	Glenn *et al.*, 1960
	Jackson *et al.*, 1954
General Occurrence	Jackson, 1959, 1965
	Van der Marel, 1964
	Sediments
Eastern U.S.A.	
Neuse River estuary	Brown and Ingram, 1954
	Griffin and Ingram, 1955
James River estuary	Nelson, 1960, 1963
Chesapeake Bay	Powers, 1954
Gulf of Mexico	Grim and Johns, 1954
California	
San Pablo Bay	Lynn and Whittig, 1966

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of interlayers and the processes by which they form. These studies have involved studies of soil profiles and sediments, laboratory syntheses of interlayers in smectites and vermiculites, and removal of natural and synthesized interlayers.

IDENTIFICATION OF EXPANSIBLE LAYER SILICATES WITH INTERLAYERING

X-ray diffraction

Vermiculite with interlayers does not collapse readily when K-saturated. The basal spacings of smectites on K-saturation depend on their charge density and on humidity conditions (Sayegh *et al.*, 1965) as well as on the presence of interlayer material. Thus, in a moist atmosphere low-charge smectites do not easily collapse on K-saturation even if interlayers are absent. Interlayered expansible layer silicates may not expand with glycerol solvation (Tamura, 1957, 1958), but montmorillonite does when interlayers are removed and the clay is then Mg-saturated and glycerol-solvated.

The principal problem is to distinguish a partially interlayered vermiculite or smectite from a randomly interstratified vermiculite (or smectite)-chlorite. Partial collapse should reveal non-integral higher orders in X-ray diffraction of the interstratified minerals, but higher orders may not be distinct. For the intergradient mineral there is an increase in central scattering (MacEwan, 1950) and a broadening of the 10 Å peak on K-saturation and 550°C. heating (Jackson, 1963*a*).

The relative intensities of the first and second order reflections is also indicative of interlayering. Generally, as the degree of interlayering increases, the $I_{(002)}/I_{(001)}$ (7 Å/14 Å) intensity ratio increases (Bradley, 1963, and Table 2). Kaolinite is frequently present and its 7 Å peak confounds this relationship. Furthermore, chloritization may not be uniform in all interlayers and a type of interstratification may develop (Cotton, 1965). The $I_{(002)}/I_{(001)}$ ratio, however, is useful where the problems mentioned can be avoided or are not important. Where kaolinite is present the $I_{(003)}/I_{(001)}$ ratio may be more useful.

Thermal analysis

Interlayers contribute OH groups which give endothermic reactions at temperatures somewhat higher than for $Al(OH)_3$ but, by keeping the interlayer space open, may lower the dehydroxylation temperature for octahedral OH in the mica layer. Rich and Obenshain (1955) found a 490°C endotherm for a Virginia soil clay which was attributed to interlayer OH groups. Glenn and Nash (1964) also observed 450°C endotherms for Mississippi soil clays containing interlayers. Similar observations were made for certain German soils by Reuter and Menning (1965).

Synthetically interlayered montmorillonite also has been analyzed by D.T.A. (Shen and Rich, 1962; Barnhisel and Rich, 1963; Brydon and Kodama, 1966). These patterns are somewhat varied because of different methods of perparation and different forms of hydroxy-Al in the systems. A decrease in the mica layer OH endotherm area and a new endotherm at 400°C were noted.

Infrared analysis

Brydon and Kodama (1966) found that the Alberni clay, containing a dioctahedral chlorite, showed a peak at 3700 cm^{-1} which was also observed for hydroxy-Al interlayered montmorillonite but not for the Al-montmorillonite. This region, associated with OH-stretching, is where Weismiller *et al.* (1967) also observed absorption bands for interlayered montmorillonite.

Due to the varying degree and kind of interlayering, one would not expect a simple set of diagnostic techniques for characterizing such systems. Even with the techniques described, much is left to be done in order to characterize and properly identify interlayered minerals.

NATURAL INTERLAYERING

Incomplete "brucite" layers may occur in chlorites which are weathering or in vermiculites and smectites which are at some stage of chloritization. Although this report largely concerns the formation of interlayers, studies of trioctahedral chlorite weathering are instructive. Stephen (1952) proposed that the "brucite" layer of chlorite weathered so as to leave hydroxy-Al components in the interlayer space:

$$[Mg_4Al_2(OH)_{12}]^{2+} \rightarrow [Mg_3Al_2(OH)_{10}(H_2O)_2]^{2+} \rightarrow$$

$$[Al_2(OH)_4(H_2O)_8]^{2+}.$$

It is noted that the OH/Al ratio of 2 in the residue is frequently proposed for stable forms of fixed hydroxy-Al.

Acid soils

Hydroxy Al and Fe interlayers. Little evidence was found for naturally occurring interlayers composed largely of hydroxy-Fe groups. Apparently iron oxides are much more stable than hydroxy-Fe^{3+} interlayers. Experiments on synthesis (see section on "Synthesis of Interlayers") would confirm this. In order to maintain a positive charge and thus interlayer stability, a system too acid for phyllosilicate stability may be needed. Occlusions of $Fe(OH)_3$ in positively charged hydroxy-Al inter-

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Table 2. Theoretical* ratio of intensities of (002) or (003) and (001) X-ray diffraction reflections of dioctahedral and trioctahedral vermiculites in which the interlayer space is filled with Al^{3+} or hydroxy-Al groups

d(001), (Å)	Fractional coord. (z) H_2O, OH	Interlayer composition Al	OH	H_2O	OH/Al	Dioctahedral vermiculite-chlorite $\frac{I(002)}{I(001}\times 10^2$	$\frac{I(003)}{I(001)}\times 10^2$	Trioctahedral vermiculite-chlorite $\frac{I(002)}{I(001)}\times 10^2$	$\frac{I(003)}{I(001)}\times 10^2$
					Layer charge = 0·70				
	Variable d(001), constant OH + H_2O					$(Al_{1\cdot4}Mg_{0\cdot3}Fe_{0\cdot3})^a$ $(Si_{3\cdot56}Al_{0\cdot44})$		†$(Al_{0\cdot16}Mg_{2\cdot36}Fe_{0\cdot48})^b$ $(Si_{2\cdot72}Al_{1\cdot28})$	
14·81	0·4375	0·23	0·00	6·00	0·00	3·94	10·6	6·78	3·59
14·74	0·4373	0·47	0·47	5·53	1·00	5·26	12·8	8·27	4·26
14·67	0·4370	0·70	1·40	4·60	2·00	6·97	15·5	10·00	5·08
14·53	0·4365	1·17	2·80	3·20	2·40	12·40	23·4	15·10	7·31
14·18	0·4351	2·23	6·00	0·00	2·69	57·00	78·6	42·70	18·40
	Constant d(001), variable OH + H_2O								
14·18	0·4224	0·23	0·00	4·70	0·00	0·027	2·14	0·63	0·348
14·18	0·4238	0·47	0·47	4·49	1·00	0·035	3·22	1·28	0·644
14·18	0·4252	0·70	1·40	3·82	2·00	0·358	4·77	2·30	1·090
14·18	0·4281	1·17	2·80	2·94	2·40	2·810	10·32	6·08	2·720
14·18	0·4351	2·23	6·00	0·00	2·69	57·000	78·60	42·70	18·400
					Layer charge = 1·00				
	Variable d(001), constant OH + H_2O					$(Al_{1\cdot77}Fe_{0\cdot10}Mg_{0\cdot105})^c$ $(Si_{3\cdot05}Al_{0\cdot95})$		$(Al_{0\cdot15}Fe_{0\cdot01}Mg_{2\cdot83})^d$ $(Si_{2\cdot86}Al_{1\cdot14})$	
14·81	0·4375	0·33	0·00	6·00	0·00	4·03	13·8	6·12	6·79
14·77	0·4374	0·50	0·50	5·50	1·00	5·05	15·8	7·24	7·72
14·60	0·4368	1·00	2·00	4·00	2·00	9·60	24·5	11·90	11·40
14·39	0·4359	1·67	4·00	2·00	2·40	11·00	28·3	24·10	20·40
14·18	0·4351	2·33	6·00	0·00	2·57	74·50	122·0	54·80	41·40
	Constant d(001), variable OH + H_2O								
14·18	0·4224	0·33	0·00	4·70	0·00	0·0770	3·03	0·206	1·11
14·18	0·4235	0·50	0·50	4·46	1·00	0·0003	4·04	0·507	1·55
14·18	0·4267	1·00	2·00	3·22	2·00	0·9740	9·30	2·770	3·89
14·18	0·4309	1·67	4·00	1·74	2·40	10·9000	29·80	13·400	12·30
14·18	0·4351	2·33	6·00	0·00	2·57	74·4000	122·00	54·800	41·10

*Based on structure factor analyses using the powder L.P. factor and temperature factors of Shirozu and Bailey (1966); d(001) assumed to vary from spacings reported by Cotton (1965) for Al dioctahedral vermiculite to that of 14·18 for dioctahedral chlorite (Hayashi and Oinuma, 1964). Position of OH and H_2O in interlayer estimated from data presented by Shirozu and Bailey (1966).

†Cation composition of octahedral and tetrahedral sheets of 2:1 layer based on vermiculite analyses of: [a]Cotton, 1965; [b]Mathieson and Walker, 1954; [c]Unpublished data of H. G. v. Reichenbach and C. I. Rich; [d]Shirozu and Bailey, 1966; [anions = $O_{10}(OH)_2$].

layers appear to be more likely then those composed dominantly of hydroxy-Fe.

Although the occurrence of interlayers in expansible layer silicates has been reported for many different soils, the optimum conditions for interlayer development are not clear. However, in the view of the writer, the following conditions appear to be optimum: Moderately active weathering must be in progress or have occurred to furnish Al ions. Furthermore, the pH should be moderately acid, about pH 5·0, organic matter content should be low, and there should be frequent wetting and drying of the soil.

Effect of pH. One of the best developed dioctahedral chlorites formed in soil was found in the Bcc horizon of the Alberni soil, a Concretionary Brown Soil on Vancouver Island of British Columbia (Brydon, *et al.*, 1961). This horizon has a pH of 5·8, has 3·99 per cent organic matter, and contains abundant concretions (Clark *et al.*, 1963). The authors suggested that the climate of mild wet winters and dry summers has favored the development of this chlorite from montmorillonite.

Glenn and Nash (1964) proposed that the optimum pH for interlayer development is about 4·5. The Nason soil which contains vermiculite with

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well developed interlayers had a pH of 4·68 (Rich and Obenshain, 1955). The chlorite-like mineral described by Klages and White (1957) had a pH of 5·20.

Differences in optimum pH may depend on the mineral involved: Low pH (4·5–5·0) may be optimum for vermiculite, and a somewhat higher pH (5·0–6·0) may be optimum for montmorillonite. A lower pH may be necessary for interlayer formation in vermiculite because of the higher charge and need for hydroxy-Al species of smaller polymer size.

If a soil is extremely acid, the interlayer Al would be largely in the form of Al^{3+}, whereas as the pH approached 7·0 $Al(OH)_3$ would be more likely to precipitate outside the interlayer space.

Effect of organic matter. Organic matter may complex Al, or hydroxy-Al polymers may combine with negatively-charged organic matter in a reaction similar to that with clay (Rich and Obenshain, 1955). The ion product $(Al)(OH)^3$ is smaller for soils high in organic matter than for inorganic soils or for gibbsite (Clark and Nichol, 1965). Well developed aluminum chlorite occurred in the Alberni soil (Clark *et al.*, 1963) with an organic matter content of 3·99 per cent. In this case, the abundant iron in this Concretionary Brown Soil may have satisfied the organic complex.

Effect of soil depth (or horizon) and wetting and drying. Interlayers are generally developed best in the *A* but sometimes in the *B* horizons (Brown, 1953; Rich and Obenshain, 1955; Glenn, 1960; Johnson and Jeffries, 1957; Nash, 1963; Jones *et al.*, 1964; Singleton, 1965). Wetting and drying cycles may favor the *A* over the *B* horizon, but the *B* horizon may be favored by a lower organic matter content.

Alkaline soils

There is considerably less information on the development of interlayers in alkaline soils than in acid soils. One would expect that $Mg(OH)_2$ would be the principal interlayering component in such systems.

Whittig (1959) reports the formation of a vermiculite-chlorite principally in the B_{22} horizon of a Solodized-Solenetz soil which has a pH of 7·7. Jackson (1963*a*) and Volk and Jackson (1964) report that clay from a Chestnut soil (pH 8·4) is interlayered. This clay is similar to swelling chlorite (Stephen and MacEwan, 1951). The pH and the ease with which the interlayers were altered by H-resin treatment suggest that the interlayer contains considerable Mg.

Sediments

Although much of the evidence presented for natural interlayering comes from studies of soils, undoubtedly analogous processes are occurring in marine sediments to form chlorite. In soils, the process apparently involves primarily Al^{3+} and OH^- ions, whereas in marine sediments Mg^{2+} and OH^- probably are the dominant ions.

Studies of deep sea sediments by Biscaye (1964) indicate that chlorite is concentrated at high latitudes and imply a land-derived origin for this mineral. As a common constituent of low-grade metamorphic rocks and ancient shales, trioctahedral chlorite would persist only under weak weathering (Droste, 1956; Glass, 1958; Jackson, 1963*a*), but pedogenic dioctahedral varieties would be more persistent. The partially filled "brucite" sheet, consisting of hydroxy-Al, may be completed by $Mg(OH)_2$ in a marine environment. Nelson (1960, 1963), in a study of clay mineralogy along a salinity gradient in the Rappahannock estuary, noted the disappearance of dioctahedral vermiculite and the appearance of heat-stable chlorite. Nelson suggested that dioctahedral vermiculite, interlayered with hydroxy-Al, was the precursor of chlorite. Minerals similar to interlayered dioctahedral vermiculite were found by Brown and Ingram (1954) in the Neuse River of North Carolina. Powers (1954, 1959) noted chlorite genesis in the James River estuary and also noted a 5/1 Mg/K ratio for uptake of ions by clays recently sedimented in sea water. The increased hydrolysis of exchangeable Mg^{2+} ions compared to those in solution (Weiss *et al.*, 1964) may account for the chloritization at pH 7·0. Whitehouse and McCarter (1958) presented evidence indicating the alteration of montmorillonite to chlorite in artificial sea water.

In the tideland sediments near San Pablo Bay, California, chlorite formed under reducing conditions in which ferrous iron was active (Lynn and Whittig, 1966). Under these conditions hydroxy-Fe interlayers apparently form.

Dioctahedral chlorite

Since most of the natural 2:1 layer silicates that have been described as being interlayered are dioctahedral, the occurrence and nature of dioctahedral chlorite is pertinent to this discussion. Koizumi and Roy (1959) found a component in certain mineral syntheses that they suggested was an aluminous dioctahedral chlorite. Sudo and Hayashi (1956) and Sudo (1963) describe an aluminum chlorite in Japan. In Table 3 are listed the structural formulae proposed for four natural dioctahedral chlorites. The mineral may be interstratified with other phyllosilicates. Hayashi and Oinuma (1964) note three other occurrences of this mineral. It also has been found in hematite ores in Michigan (Bailey and Tyler, 1960).

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Table 3. Formulae for dioctahedral chlorites*

Formula	Reference
VI (Total) IV $(Al_{3\cdot2}Fe_{0\cdot4}Ti_{0\cdot1}Mg_{0\cdot8})(Al\,Si_3)\,O_{10}\,(OH)_8\,(K_{0\cdot2}X_{0\cdot2})$	Brydon *et al.*, 1961
VI IV $(Mn_{0\cdot004}Ca_{0\cdot110}Mg_{1\cdot175}Fe^{2+}_{0\cdot033}Fe^{3+}_{0\cdot345}Al_{3\cdot017})\,(Al_{0\cdot739}Si_{3\cdot261})\,O_{10}(OH)_8$	Hayashi and Oinuma, 1964
$Al_2\,[(OH)_2\,Si_4O_{10}]\,Al_2(OH)_6$ (Surmised formula)	Müller, 1961, 1963
VI IV VI (Brucite layer) $(Al_{1\cdot41}Ti_{0\cdot59})\,(Si_{3\cdot43}Al_{0\cdot57})\,(Al_{0\cdot86}Mg_{0\cdot93}Fe^{2+}_{0\cdot54}Fe^{3+}_{0\cdot15})\,O_{10}\,(OH)_8$	Jackson *et al.*, 1954
$(Al_{1\cdot68}Ti_{0\cdot32})\,(Si_{3\cdot38}Al_{0\cdot62})\,(Al_{0\cdot64}Mg_{1\cdot20}Fe^{2+}_{0\cdot44})\,O_{10}\,(OH)_8$	Jackson *et al.*, 1954

*A recent article by Eggleton and Bailey (1967) presents further information on the first three chlorites in this table, as well as on other dioctahedral chlorites.

Hayashi and Oinuma (1964) found that the dioctahedral chlorite from the Kamikita mine was more difficult to decompose by heating than trioctahedral chlorite. This is significant in view of the collapse of many interlayered minerals on heating to 300 or 550°C and supports the conclusion that such minerals are only partially interlayered.

Two of the formulae listed in Table 3 do not indicate the composition of the "brucite" sheet. Bailey (1966) described a dioctahedral chlorite in which the brucite layer is trioctahedral. This may be similar to the chlorite formed in a marine environment from partially interlayered dioctahedral vermiculite, a soil weathering product.

SYNTHESIS OF INTERLAYERS

Syntheses of interlayers have been attempted by precipitating hydroxides in the presence of clays, reacting clays with solutions containing partially neutralized Al^{3+} ions, acidifying clays with H-resins to induce Al release from the silicate structure and subsequent incorporation in the interlayer space, and boiling Al-saturated clays to increase hydrolysis.

The preparation of hydroxy-Al solutions of different OH/Al ratios may be accomplished by adding NaOH to $AlCl_3$ in solution. To avoid confounding the system with Na ions, one can dissolve Al metal in HCl (Treadwell, 1931), or in $AlCl_3$ (Barshad, 1960), or react OH-resin with $AlCl_3$ (Barnhisel and Rich, 1965). It should be pointed out that hydrolysis increases with dilution and a clear solution does not necessarily mean the system is polymer-free (Aveston, 1965).

Interlayering of montmorillonite

In an attempt to form chlorite from montmorillonite, Caillère and Hénin (1949, 1950) precipitated $Mg(OH)_2$ in the presence of this mineral. The X-ray diffraction pattern of the product was very similar to that of chlorite but was not as heat-stable as the natural mineral. Longuet-Escard (1950) also prepared similar materials, and Youell (1951) used an electrolytic technique to avoid the contaminating NH_4^+, Na^+, or other ions, involved in the normal precipitation.

In Table 4 are listed some of the methods by which attempts have been made to duplicate interlayering. Most of the work has been with cation-hydroxy-clay systems.

Slaughter and Milne (1960) prepared $Mg(OH)_2$-,

Table 4. Methods used for synthesis of interlayers

Method	Reference
(1) Precipitation of $Mg(OH)_2$, $Al(OH)_3$, etc. in the presence of clay	Caillère and Hénin, 1949, 1950; Lougeut-Escard, 1950; Slaughter and Milne, 1960; Carstea, 1965, 1967; Burner and Brydon, 1965.
(2) Electrolytic deposition of $Mg(OH)_2$	Youell, 1951.
(3) Repeated Al saturation and drying	Rich and Obenshain, 1955.
(4) Additions of hydroxy-Al solutions	Rich, 1960; Shen and Rich, 1962; Sawhney, 1960; Carstea, 1965, 1967.
(5) Boiling Al-saturated clay	Rich, 1960.
(6) Treatment with H-resin	Schwertmann and Jackson, 1964.
(7) Hydrolysis of $[Al(OR)]^{2+}[Si(OR)_2]^{2+}$ ions in interlayer position	Weiss, 1963.

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$Al(OH)_3$-, $Ni(OH)_2$-, and $Fe(OH)_3$- montmorillonite complexes by adding slowly and simultaneously NaOH and appropriate salt solutions to a dilute suspension while it was being stirred in a Waring Blendor. The first three reaction products gave rational X-ray diffraction patterns, whereas the $Fe(OH)_3$-montmorillonite complex did not. Evidence of hydroxide layers forming on both surfaces of the montmorillonite layers was obtained. According to these authors, a chlorite-like structure, that is, one "brucite" sheet between each montmorillonite layer, develops only upon association of unit layers through aging and dehydration. The observed (00l) intensities for the $Al(OH)_3$-montmorillonite complex were close to those calculated for a slightly deficient gibbsite sheet, that is, 3·75 vs 4·00 $Al(OH)_3$ groups per unit cell.

Interlayering in vermiculite

The laboratory synthesis of interlayers in vermiculite is much more difficult than in montmorillonite. Presumably this is due to less expansion of vermiculite and its greater negative charge and larger particle size, all slowing interlayer diffusion.

Brown (1953) saturated dioctahedral vermiculite with Al^{3+} ions, but this treatment failed to inhibit collapse of the mineral when it was subsequently saturated with K. Rich and Obenshain (1955) were successful in adding interlayers by repeatedly saturating a soil-derived dioctahedral vermiculite with Al^{3+}, washing free of salt, and drying. The clay also showed evidence of interlayering when it was Al-saturated and then titrated to pH 7·0. However, when Al-saturated trioctahedral vermiculite was titrated with NaOH, Al was removed from the interlayer space (Rich, 1960). Subsequently, partially neutralized $AlCl_3$ solutions were added to trioctahedral vermiculite (Rich, 1960) and montmorillonite (Shen and Rich, 1962), and interlayer Al-fixation was observed in both cases.

Hsu and Bates (1964*a*) added hydroxy-Al polymer solutions to vermiculite. The product, when K saturated, had a spacing of 13·8 Å at 25°C and 12·6 Å at 100°C. Kawasaki and Aomine (1965) titrated $AlCl_3$ in the presence of vermiculite and obtained similar results. Although Hsu and Bates state that 67 per cent of the charges are occupied by hydroxy-Al in their treated vermiculite, it collapsed to 10 Å on heating to 500°C.

Carstea (1967) was able to interlayer vermiculite with hydroxyl-Al so that a 13·4 Å spacing was maintained at 300°C. This was done with a solution having an OH/Al molar ratio of 2·43 and allowing the reaction to proceed for one year. During this time, the pH decreased from 4·6 to 3·9. Those interlayers formed at neutral and alkaline pH were less well developed and less stable.

The apparent general lack of heat stability of the hydroxy-Al interlayers in vermiculite may be explained not only by less interlayering caused by slower diffusion, but also be the isolation of the interlayer polymers due to fewer numbers (because of their lower OH/Al ratio). Both of these effects lead to more H_2O and a lower dissociation temperature. A low pH appears necessary for significant interlayer formation in vermiculite in a relatively short time because the higher the OH/Al ratio, the larger the polymer, and the slower the diffusion rate (Hsu and Bates, 1964).

Factors affecting interlayer formation

OH/cation ratio and pH. The stability of the interlayers is a function of a number of factors. Barnhisel and Rich (1963), working with an Upton, Wyoming Bentonite, found that when sufficient Al (16 meq/g) was present in the system to form a complete gibbsite sheet between each montmorillonite layer (Slaughter and Milne, 1960), interlayers were stable after 6 months only if the OH/Al ratio was 1·50 or less. Gibbsite was produced from the unstable interlayer material even at pH 4·0.

Carstea (1967) using a Santa Rita, New Mexico montmorillonite, also prepared interlayers similar to the method of Slaughter and Milne (1960) but at different OH/Al molar ratios. In contrast to the results of Barnhisel and Rich (1963), the interlayers prepared with a OH/Al ratio of 3·27 remained fairly stable for one year, although there was some decrease in stability during this time. Carstea also prepared interlayers at OH/Al ratio of 3·75, but these were less stable then those prepared in neutral or acid media.

Fe-OH interlayers prepared by Carstea were not nearly as distinctive as the Al-OH types and, furthermore, their stability to heating decreased at all OH/Fe ratios studied (2·64–3·75). Other workers also have obtained diffuse X-ray patterns in attempting to interlayer montmorillonite with hydroxy-Fe (Dion, 1944; Caillère and Hénin, 1949; Slaughter and Milne, 1960; Coleman *et al.*, 1964). Fe^{3+}-saturated montmorillonite is unstable in water (Page and Whittig, 1961) and H^+ ions released by hydrolysis may attack the clay, releasing Al^{3+} ions which then become exchangeable (Coleman and Thomas, 1964). Carstea (1967) found that Mg-OH interlayers in montmorillonite and vermiculite were formed only at high pH of about 10·0. Their stability decreased with time.

Amount of hydroxy-Al. Turner and Brydon (1965, 1967) observed that, if the amount of $Al(OH)_3$ precipitated was approximately one-half or less of that required for a complete gibbsite sheet for each interlayer space of montmorillonite, such interlayers were stable for at least 8 months.

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When more $Al(OH)_3$ was present, the interlayers were not stable.

Turner and Brydon (1967) found that when $Al(OH)_3$ was precipitated from $AlCl_3$ in the presence of montmorillonite, illite, or kaolinite, the reactions were quite similar except that more $Al(OH)_3$ was added to montmorillonite than to the other clay minerals before gibbsite formed as a separate phase. For amounts as small as 860 meq Al/100 g clay for montmorillonite (or about one-half that required for a complete gibbsite sheet between the montmorillonite layers) no separate gibbsite phase developed and the interlayers were stable for 8 months. For illite the minimum Al for stability was 130 meq/100 g. The ion product $(Al)(OH)^3$ for these two systems was $10^{-33\cdot0}$. In the case of kaolinite, when an amount of Al as low as 11 meq/100 g was precipitated, the $(Al)(OH)^3$ approached $10^{-33\cdot8}$, identical to that of gibbsite.

Anions. Most experiments on interlayering have been conducted with $AlCl_3$. When Singh and Brydon (1967) employed $Al_2(SO_4)_3$ rather than $AlCl_3$ for a source of Al^{3+} ions to be precipitated with montmorillonite, the interlayer material initially formed disappeared from the interlayer space and a crystalline basic aluminum sulfate formed within 240 days. The ion product $(OH)(Al)^3$ was $10^{-33\cdot6}$, slightly more than that for gibbsite ($10^{-33\cdot8}$).

The stability of hydroxy-Al interlayers in montmorillonite thus depends on associated systems that are competing for Al ions. Supersaturation can exist with respect to gibbsite, but once gibbsite is formed, interlayer material, approaching the OH/Al ratio of 3, is not stable. Even interlayer material with an OH/Al ratio of 2·2 was not stable in the presence of sulfate (Singh and Brydon, 1967).

Even Cl^- ions tend to inhibit the formation of gibbsite, but the presence of montmorillonite may negate this effect (Barnhisel and Rich, 1963). Hsu (1966) found that hydroxy-Al polymers, in a solution of $NaOH/AlCl_3$ molar ratio = 1·8–2·7, were meta-stable, but after two years a small amount of gibbsite formed. Gastuche and Herbillon (1962) and Hsu (1966) dialized gels of hydroxy-Al and thereby promoted the formation of gibbsite. Clay minerals with a negative charge repel anions and, like dialysis, remove anions from the site of $Al(OH)_3$ precipitation. Hsu (1966) proposed that the rate-determining step in gibbsite formation by neutralization of $AlCl_3$ is:

$$(\text{Initial polymer})^+Cl^- \rightarrow (\text{Initial polymer}^+ + Cl^-.$$

Effect of clay minerals on the hydrolysis of aluminum ions

The role of clay minerals in the hydrolysis of aluminum depends on the degree of neutralization, time of reaction, concentration of aluminum, and a number of other factors.

On theoretical grounds and experimental work, Frink and Peech (1963) concluded that the degree of hydrolysis would be less in the presence of negatively charged clay than in its absence. They proposed further, however, that more $Al(OH)^{2+}$ than H^+ ions would be adsorbed by the clay from an aqueous aluminum salt solution. Ragland and Coleman (1960), on the basis of their experiments, concluded that hydrolysis of Al ions increased in the presence of the clay. One important factor appears to be the strong afinity of clay minerals for hydroxy-cations (Barshad, 1960). Cotton (1965) studied the hydrolysis of Al as a function of the degree of cross-linkage in a synthetic cation exchanger, Dowex-50, and found that the degree of hydrolysis increased as the degree of cross-linkage (and charge density) decreased. One might infer that hydrolysis would be less in vermiculite than in montmorillonite, because of the higher charge density of the former. In the resin, pore size, which decreases with cross-linkage, may limit the polymer size. However, there is ample space in expansible layer silicates for the growth of polymers of large OH/Al ratio. Even in a clay with a charge density as high as that of muscovite, a polymer having an OH/Al ratio of 2·57 is possible.

Jackson (1960) proposed the idea of "steric pinching" in the interlayer space. For example, in the interlayer space of vermiculite, of 160 meq/100 g C.E.C. and saturated with Al^{3+} ions, the concentration of Al approaches 1 molar. In a clay with such a high C.E.C. there is a close approach of the ions and their coordinating water molecules. Thus, it is proposed by Jackson that there is a greater opportunity for hydrolysis and olation, resulting in a higher degree of polymerization.

The products of hydrolysis and neutralization are apparently much more complex than $Al(OH)^{2+}$, $Al(OH)_2^+$, and $Al(OH)_3$. Aveston (1965) proposes that $[Al_2(OH)_2]^{4+}$ and $[Al_{13}(OH)_{32}]^{7+}$ are the two principal hydrolysis products. Fripiat *et al.* (1965) suggest that hydrated $[Al_4(OH)_8]^{4+}$ and $[Al_7(OH)_{16}]^{5+}$ are likely hydrolysis products. Polymeric chain (Schofield, 1946) and ring-like structures (Jackson, 1960; Hsu and Rich, 1960; Hsu and Bates, 1964*b*; and Weismiller, 1967) either form in place or diffuse to negatively charged surfaces. These reaction products, because of their large size and high positive charge, become non-exchangeable and are effectively removed from the exchange system, except for their ability to release or accept protons in response to changes in pH or cation content of the associated solution.

The addition of salts may promote further hydrolysis of positively charged polymers (Coleman,

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1962) and release H_3O^+ ions. For example, on drying of an Al-saturated montmorillonite with $CaCl_2$, Al was hydrolyzed and HCl was evolved (Coleman *et al.*, 1960). Kaddah and Coleman (1967), working with Al-saturated trioctahedral vermiculite, showed that displacement of the Al with salt solutions promoted hydrolysis of the Al. Hydrolysis was greater where the Al was exchanged slowly, that is, in dilute solutions of the salt or in a solution of KCl which tended to collapse the layers at the edges of the mineral particles, thereby restricting exchange of the large hydrated Al^{3+} ion. Since protons are more easily displaced, hydrolysis was increased.

Fripiat *et al.* (1960) found that the first water molecules sorbed around exchangeable cations near clay surfaces have a degree of dissociation much higher than that about cations in solution. They proposed that in addition to the positive electrical field of the cation acting on the OH dipole of coordinating water, the negative electrical field, issuing from the surface oxygen of the silicate, promotes dissociation. Weiss *et al.* (1964) also suggest increased dissociation of interlayer Mg ions based on conductivity measurements of Mg-montmorillonite.

It is obvious that hydrolysis of Al^{3+} ions in water is a complex process. The hydrolysis and polymerization near clay surfaces is an even more complex problem.

A certain amount of hydrolysis in place must occur in the interlayer space. Basic monomers and small polymers may diffuse into the interlayer space, but hydrolysis must also proceed there in order to form a continuous "brucite" layer. The scarcity of fully chloritized expansible layer silicates in acid soils is evidence that the process is very slow or that it is limited by some other mechanism.

METHODS FOR REMOVAL OF INTERLAYER MATERIAL

Some methods (Table 4) employed for removing interlayers are based on the complexing ability of citrate or fluoride for aluminum and iron, the solubility of Al compounds at high pH, or the solubility of Fe and Al compounds at low pH. Other proposed methods are based on the selective destruction of hydroxy-groups on heating at different temperatures.

None of the proposed methods probably are able to dissolve interlayers without also attacking the silicate structure, and especially the separate amorphous material. Nevertheless, these techniques have been useful in determining, within limits, the composition and nature of the interlayer material.

Table 5. Reagents empolyed in removing interlayer material

Reagent	Reference
(1) KOH + KCl	Brown, 1953
(2) Heating at 400°C followed by boiling in NaOH	Dixon and Jackson, 1959
(3) NH_4F	Rich and Obenshain, 1955
(4) Na F	Glenn, 1960
(5) $NH_4 + NH_4Cl$ + HCl	Rich and Cook, 1963; Rich, 1966
(6) F-saturated resin	Huang and Jackson, 1966
(7) Acetic acid	Klages and White, 1957
(8) Citric acid	Klages and White, 1957
(9) Ammonium citrate	Klages and White, 1957
(10) Na-dithionite-citrate	Tamura, 1956, 1957
(11) Na-citrate	Tamura, 1958; Sawhney, 1960

Certain generalizations can be made from these studies: (*a*) In soils the degree of filling of the interlayer space is generally small (10–20 per cent), but sufficient to maintain K-saturated vermiculite or smectite at 14 Å, even at 110°C; (*b*) Artificially produced hydroxy-Al interlayers are more easily removed than those produced naturally; (*c*) No one method is suitable for all types of interlayers. The severity of the treatment depends on the degree of development and composition of the interlayer material.

NATURE OF INORGANIC INTERLAYERS

Composition

In acid soils hydroxy-Al appears to be the principal material forming interlayers. Quigley and Martin (1963) presented evidence supporting the presence of hydroxy-Fe interlayers in a soil clay. In cat clays of sediments, where reducing conditions are prevalent, Fe^{2+} ions may be important constituents of interlayers (Lynn and Whittig, 1966). Magnesium probably is the principal cation forming interlayers in alkaline soils and in most marine environments.

The copper vermiculites of Northern Rhodesia, described by Bassett(1958), apparently are analogous to hydroxy-Al vermiculites. This mineral ranges in copper content from 1·6 times that necessary for Cu^{2+} ions in the interlayer space of vermiculite to a Cu-chlorite. Since this Cu is probable in the interlayer space, varying amounts of OH are also present. Attempts to synthesize Cu vermiculite indicate that hydrolysis of the copper

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increases in the presence of the clay and that hydroxy-Cu is firmly adsorbed by the vermiculite.

A large number of ions probably could and do form interlayers, but because of their solubility and natural abundance Al^{3+}, Fe^{2+}, Fe^{3+}, and Mg^{2+} are of principal concern. In trioctahedral chlorites, the positively-charged "brucite" sheet nominally of composition $(Mg,Al)_3(OH)_6$ has important substitutions of Fe^{2+}, Fe^{3+}, Cr, Ni, Mn, or Li (Bailey and Brown, 1962). The insolubility of $Fe(OH)_3$ limits its availability except in very acid systems. Stable hydroxy-Mg interlayers would not be expected except in neutral or alkaline systems.

Hydroxy/cation ratio

The OH/cation ratio of interlayer material is a question that is largely unresolved. Attempts have been made to relate the change in the C.E.C. with the amount of Al added or removed from the interlayer space. One problem is whether all the added material enters the interlayer space or whether all the extracted material comes from interlayers. Another question is whether or not the OH/cation ratio of a given interlayer is constant.

Infrared analyses by Brydon and Kodama (1966) and Weismiller and Ahlrichs (1967) show that there are two kinds of OH^- groups in hydroxy–interlayers. Weismiller and Ahlrichs (1967) proposed that the inner and outer OH^- groups of gibbsite-like rings $[Al(OH)_2(H_2O)_2]_6^{6+}$ were responsible for the two frequencies. The 3695 cm^{-1} frequency was attributed to the stretching vibrations of inner OH^- groups, whereas the 3570 cm^{-1} frequency was attributed to the outer OH^- groups. The ratio of the two intensity bands was proposed as a measure of the OH/Al ratio of the interlayer material.

For a complete gibbsite-like interlayer about 16 meq Al/g of montmorillonite is required. Brydon and Kodama (1966) compared the observed and calculated intensities in X-ray diffraction analyses of montmorillonite with which 15 meq Al/g was precipitated. The observed intensities compared best with a system in which 11 meq Al/g was present in the interlayer.

Shen and Rich (1962) removed laboratory fixed hydroxy-Al interlayers from montmorillonite with HCl. The ratio of fixed Al to increase in C.E.C. by the HCl extraction indicated that the OH/Al molar ratio was 2·09, close to that found for fixed Al in Dowex-50 (Hsu and Rich, 1960). However, D.T.A. curves indicated the presence of interlayer OH after the HCl extraction, even though the original C.E.C. had been attained. This suggests that the remaining interlayer material has an OH/Al ratio of 3. Jackson (1963*b*) discussed the charge relationship of hydroxy-Al interlayer material and pointed out the significance of positively charged $Al\text{-}OH_2^{0.5+}$ edge groups and OH_2 for OH substitution in gibbsitic interlayers.

Frink (1965) reported that extractions of clay fractions of five New England soils with Na citrate for two hours increased the C.E.C., but no increase was observed with additional extractions. In contrast, the amount of Al extracted continued at the same rate for 2 more hours. That the Al continued to be removed from the interlayer space is indicated by the increase in collapsibility of the vermiculite, although Frink interprets this more as a change in blocking action at the edges of the mineral.

The writer has had a similar experience regarding the relationship of C.E.C. to Al extracted from several Virginia soil clays with a mixed NH_4F-NH_4Cl-HCl solution (Rich, 1966).

These experiments indicate that the OH/Al ratio in the same interlayer may be variable or that steric blocking of exchange reactions varies with the amount of hydroxy-Al in the system.

Location of hydroxy-polymers

Grim and Johns (1954) expressed the opinion that hydroxy interlayer "islands" were randomly dispersed in the interlayer space. This also has been the general concept of those working with interlayered soil clays. Dixon and Jackson (1962) and Frink (1965) expressed the opinion that the interlayer material in the soils studied was concentrated near the edges. In fact, Frink expressed the opinion that those he studied were more like "atolls."

All expansible layers in a mineral particle may not react in the same manner to hydroxy-Al. Barnhisel and Rich (1966) obtained regular interstratification of layers with and without hydroxy-Al in both vermiculite and montmorillonite. These systems were prepared in moist films of clay. In suspensions there is greater expansion and thus a larger proportion of the interlayer spaces are susceptible to Al fixation.

Amorphous components at edges of vermiculites and smectites probably inhibit exchange reactions, but the occurrence of pedogenic chlorite, the resistance to collapse of chlorite-vermiculite intergrades on heating, and the change in relative intensities are evidences for significant distribution of material throughout the entire interlayer space.

Extent of filling the interlayer space

The extent of filling of the interlayer space has been estimated by determining C.E.C. or surface area with glycerol or ethylene glycol (Rich and Obenshain, 1955; Shen and Rich, 1962; Dixon and Jackson, 1962). These methods can be criticized because the degree of exchange or solvation can be

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altered by material at the edges of the clay minerals.

Rich and Obenshain (1955) noted that glycerol sorption by naturally interlayered dioctahedral vermiculite was considerably slower than in similar clay which was only slightly interlayered. Diffusion rates would be expected to increase with interlayering. Thus, times for attaining maximum glycerol or ethylene glycol probably need to be increased for interlayered clays in area determinations.

The extent of interlayer filling undoubtedly varies from incipient interlayering to complete "brucite" sheets. In general, intergradient smectite-chlorite or vermiculite-chlorite in soils appear to have less than one-half of the interlayer space filled. Dixon and Jackson (1962) determined the Al released from the interlayer and calculated that in the 0–0·2 μ fraction of three soils approximately 40, 14, and 14 per cent of the expansible layers were filled. These soils gave X-ray evidence of significant interlayering. Glenn *et al.* (1960) also suggested that a small amount of aluminum is required to bond a relatively large number of silicate layers.

Interlayer filling of vermiculite appears to be less than that of montmorillonite, both under natural and laboratory conditions.

CONSEQUENCES OF INTERLAYER FORMATION

Effect on cation exchange capacity

The cation exchange capacity can be drastically reduced by interlayer formation (Clark, 1964*a*, 1964*b*). A consideration of C.E.C. with respect to interlayers might include (a) an evaluation of the measurement itself, (b) the role of interlayers in physical blocking of exchange, and (c) occupancy of exchange sites. The measurement of C.E.C. using buffered solutions may alter the interlayer material by adding OH groups, thereby lowering its positive charge. A C.E.C. higher than that obtained with an unbuffered salt would then be obtained (Clark, 1963; de Villiers and Jackson, 1967; Rich, 1962).

Steric blocking of exchange by hydroxy groups probably occurs, particularly in freshly prepared hydroxy precipitate-clay systems. Vermiculite, because of its generally large size and low degree of swelling, would be most susceptible to physical blocking of exchange. In natural systems and in synthethized products, after aging for a long time, steric blocking probably is less important because of reorganization and crystallization of the initial blocking material.

The occupancy of exchange sites by positively charged hydroxy groups is well established. In fact, the accepted structure of chlorite has a positively charged "brucite" layer. Intergradient, partially "chloritized" vermiculite and montmorillonite, would be expected to contain positively charged interlayers.

Most of the recent studies have been concerned with Al fixation. Dion (1944) concluded from his work that the adsorption of $Fe(OH)_2^+$ groups by montmorillonite reduced the C.E.C. of the clay mineral. Paver and Marshall (1934) found considerable Al and Fe retention by montmorillonite but significant C.E.C. reduction only for Al. The greater hydrolysis of Fe compared to Al apparently leads to its precipitation as $Fe(OH)_3$. Quantitative measurements of charge occupancy are needed. In these studies alteration and physical blocking effects should be fully evaluated.

Effect on ion fixation and selectivity

The fixation of K^+, NH_4^+, Cs^+, and Rb^+ by 2:1 layer silicates is related to the collapsibility of the silicate layers. The presence of hydroxy-cation islands tend to prop open the silicate layers and inhibit K fixation in vermiculite (Rich, 1960*a*) and in soil clays that contain vermiculite (Rich, 1960*b*) may affect the selectivity of ions (Rich, 1964; Rich and Black, 1964) by permitting entry of K-size ions into partially opened mica layers, without hindrance by collapse at the edges of the mineral.

Effect on swelling

Clays that do not swell like montmorillonite on ethylene glycol or glycerol solvation often do so once the interlayer material has been removed (Tamura, 1957).

The charged hydroxy-cation polymers may bond adjacent silicate sheets and inhibit expansion. That bonding is involved rather than a blocking action is supported by the occurrence of swelling chlorite (Stephen and MacEwan, 1951). The amount of negative charge on the silicate layers should determine the bonding of material in the "brucite" layer to the silicate layers. The swelling chlorites may have a low charge.

Effect on acidity

The hydroxy-Al (and perhaps hydroxy-Fe) are sources of acidity, e.g. "third range" acidity (Schwertmann and Jackson, 1963), or "pH dependent acidity (Clark, 1964; de Villiers and Jackson, 1967; Coleman and Thomas, 1964).

Clay mineral transformations

That transformations of vermiculites and smectites to chlorites occur in sediments and soils seems amply demonstrated. Partial interlayering with

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hydroxy-Al groups appears to be much more common than complete chloritization with hydroxy-Al. In fact, natural complete OH-Al "brucite" layers appear to be very rare. That chlorites with complete OH-Al "brucite" sheets may alter to kaolinite is a transformation that may account for the natural paucity or absence of complete OH-Al sheets in the interlayer space. This process was suggested by Glenn *et al.* (1960) and Jackson (1963). Evidence that montmorillonite ⟶ kaolinite alteration occurs in nature was presented by Altschuler *et al.* (1963). Poncelet and Brindley (1967) readily produced kaolinite from hydroxy-Al interlayered montmorillonite when it was treated in 1 *N* HCl at 220°C for 7 days. The authors suggest that single gibbsitic sheets apparently adsorb silica groups released from the montmorillonite by the HCl. An alternate method of transformation in soil clays, suggested by Glenn *et al.* (1960), is that one of the two silica sheets in chloritized montmorillonite is inverted. In this process there may be a reorientation of the bonds to form kaolinite.

Although chloritic intergrades often occur with kaolinite, as has been pointed out previously, other evidence from soil weathering studies often do not support the alteration of 2:1 silicates to kaolinite. Interlayering of expansible layer silicates generally increases as the soil surface is approached but kaolinite decreases. Where weathering is intensive, Al may be removed in solution or by formation of gibbsite so that a complete hydroxy-Al sheet does not develop.

Spyridakis *et al.* (1967) observed the formation of kaolinite from alteration products of biotite contained in a sand culture in which coniferous seedlings were grown. The authors proposed a biotite → hydroxy-Al interlayered vermiculite → kaolinite sequence. It is important to note that where organic material was included in the culture medium, kaolinite did not form. The organic matter may have complexed the aluminum released by weathering.

Sand (1956) reported that kaolin develops from muscovite during weathering. To form kaolinite from 2:1 layer silicates, it appears that an acid system, low in basic cations, is necessary to supply Al and Si groups and to prevent the formation of other minerals. A supply of Al in addition to that derived from local decomposition also appears to promote the reaction.

Layer silicates may promote the formation of gibbsite as has already been discussed. Other polymorphs of gibbsite also may be formed (Barnhisel and Rich, 1965). The partial formation of stable hydroxy-Al interlayers, on the other hand, may inhibit gibbsite formation. Jackson (1963*a*) describes this as an "antigibbsite effect".

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Résumé—Les vermiculites et les smectites en sols et sédiments sont souvent partiellement répartis en feuillets interstratifies ou "chlorées". Les silicates en couches expansibles dioctaédriques sont celles qui sont le plus souvent en feuillets interstratifies et l'hydroxy-Al apparaît être le principal composant du matériau non-interchangeable de la feuillet interstratifie.

Les conditions du sol les plus favorables pour la formation de feuillets interstratifies semblent être: un pH 4,6–5,8 modéré, de fréquents cycles d'humidité et de sècheresse, et une faible teneur en matière organique.

Dans les sédiments marins, une feuillet interstratifie d'hydroxy-Mg peut être importante. Des argiles dérivées du sol contenant des feuillets de "brucite" partiellement remplies d'hydroxy-Al peuvent être remplies d'hydroxy-Mg. Dans certains conditions, les feuillets interstratifies d'hydroxy-Fe peuvent être importantes.

Selon le rapport OH/Al et la teneur en Al 'dhydroxo-Al des feuillets interstratifies, le silicate de la feuillet expansible peut soit activer, soit retarder la formation de gibbsite. Les silicates en feuillets interstratifies de la feuillet expansible peuvent aussi être les précurseurs de kaolinite.

Kurzreferat—Vermiculite und Seifensteine in Böden und Ablagerungen sind häufig teilweise mit Zwischenschichten versehen oder "chloritisiert". Am häufigsten kommen Zwischenschichten in den dioktahedralen Silikaten mit Quellschichten vor und der Hauptbestandteil des nicht-austauschbaren Zwischenschichtmaterials scheint Hydroxy-Aluminium zu sein.

Die günstigsten Bodenbedingungen für die Bildung von Zwischenschichten sind scheinbar die folgenden: mässiges pH 5,6–5,8, häufige Nass-und Trockenzyklen, und niedriger Gehalt an organischem Material.

In Meeresablagerungen kann eine bedeutende Zwischenlagerung von Hydroxy-Magnesium vorkommen. Aus dem Boden stammende Tone, die teilweise gefüllte Hydroxy-Aluminium "Brucit" Schichten enthalten, können durch Hydroxy-Mg ausgefüllt werden. Unter Reduktionsbedingungen können Hydroxy-Fe Zwischenschichten von Bedeutung sein.

Je nach dem OH/Al Verhältnis und dem Al Gehalt der Hydroxy-Al Zwischenschichten können Silikate mit Quellschichten die Bildung von Gibbsit entweder fördern oder verzögern. Silikat-Quellschichten mit Zwischenschichten können auch Vorläufer von Kaolinit sein.

Резюме—В грунтах и отложениях вермикулиты и смектиты обычно переслоены частично или-же подвергнуты хлоритизации. Диоктаздрииеские расширяемые слоистые силикаты чаще всего переслоены и главной составляющей необменного прослоенного материала является гидрокси-Al.

Наиболее благоприятные грунтовые условия для образования прослойков вероятно: умеренное pH (4,6-5,8), частые циклы смачивания и сушки и малое содержание органических веществ.

В морских отложениях, прослаивание гидрокси-Mg может оказаться значительным. Полученные из грунта глины содержат слои брусита, частично наполненные гидрокси-Al, которые могут быть выполнены гидрокси-Mg. В восстановительных условиях важными могут оказаться прослойки гидрокси-Fe.

В зависимости от отношения OH/Al и от содержания в прослойках гидрокси-Al, расширяемые слоистые силикаты активируют или замедляют образование гибсита. Прослоенные расширяемые слоистые силикаты могут также являться предшественниками каолинита.

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