

PEDOGENIC FORMATION OF MONTMORILLONITE FROM A 2:1–2:2 INTERGRADE CLAY MINERAL*

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Abstract—Montmorillonite was found to be the dominant clay mineral in surface horizons of certain soils of the North Carolina Coastal Plain whereas a 2:1–2:2 intergrade clay mineral was dominant in subjacent horizons. In all soils where this clay mineral sequence was found, the surface horizon was low in pH (below 4.5) and high in organic matter content. In contrast, data from studies of other soils of this region (Weed and Nelson, 1962) show that: (1) montmorillonite occurs infrequently; (2) maximum accumulation of the 2:1–2:2 intergrade normally occurs in the surface horizon and decreases with depth in the profile; (3) organic matter contents are low; and (4) pH values are only moderately acid (pH 5–6).

It is theorized that the montmorillonite in the surface horizon of the soils studied originated by pedogenic weathering of the 2:1–2:2 intergrade clay mineral. The combined effects of low pH (below 4.5) and high organic matter content in surface horizons are believed to be the agents responsible for this mineral transformation. The protonation and solubilization (reverse of hydrolysis) of Al-polymers in the interlayer of expansible clay minerals will occur at or below pH 4.5 depending on the charge and steric effects of the interlayer. A low pH alone may cause this solubilization and thus mineral transformation, but in the soils studied the organic matter is believed to facilitate and accelerate the transformation. The intermediates of organic matter decomposition provide an acid environment, a source of protons, and a source of watersoluble mobile organic substances (principally fulvic acids) which have the ability to complex the solubilized aluminum and move it down the profile. This continuous removal of solubilized aluminum would provide for a favorable gradient for aluminum solubilization.

The drainage class or position in a catena is believed to be less important than the chemical factors in formation of montmorillonite from 2:1–2:2 intergrade, because montmorillonite is present in all drainage classes if the surface horizon is low in pH and high in organic matter.

INTRODUCTION

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A 2:1–2:2 aluminum intergrade clay mineral with 14 Å spacing having some of the properties of vermiculite, chlorite, and montmorillonite has been studied intensively during the last decade. The mineral has also been referred to as dioctahedral vermiculite (Brown, 1953; Rich and Obenshain, 1955), chloritized montmorillonite (Sawhney, 1958; Frink, 1965), aluminum interlayered vermiculite (Douglas, 1965), intergrade chlorite-vermiculite-montmorillonite (Jackson,

1960), and chlorite-like intergrade (Weed and Nelson, 1962). This mineral, or perhaps more properly this series of similar clay minerals, is formed when aluminum, iron, magnesium, and perhaps other ions are precipitated in the interlayer space or when hydroxy polymers of these ions are adsorbed into the interlayer space of expanding 2:1 layer silicates. This process has been called "chloritization" because the end product of the phenomenon is chlorite, a 2:2 layer silicate. According to Sawhney (1958), a continuous chloritized montmorillonite series may exist in soils. The diversity of the reports concerning the character and composition of the mineral are a result of variation in the degree of chloritization, composition of the interlayer polymers, and layer charge characteristics of the parent mineral.

The 2:1-2:2 aluminum intergrade was first reported in soils by Brown (1953), and has been reported to occur in many soils of the eastern United States (Rich and Obenshain, 1955; Klages and White, 1957; Tamura, 1958; Sawhney, 1960; Weed and Nelson, 1962; Dixon and Jackson, 1962; Nash, 1963). The accumulation and heat stability (of characteristic X-ray diffraction peaks) of the intergrade normally is at a maximum in surface horizons and decreases with depth in the profile. Exceptions to this generalization have been attributed to poor drainage (Weed and Nelson, 1962; Sawhney, 1960) and to low pH (Sawhney, 1958). A possible inhibition of intergrade formation due to the complexing ability and other properties of organic matter has been suggested (Sawhney, 1960; Jackson, 1960; Weed and Nelson, 1962).

In this paper the clay mineralogy of certain soils in North Carolina with montmorillonite in surface horizons and 2:1-2:2 intergrade clay minerals in subsurface and subsoil horizons is examined and a mechanism is theorized for the pedogenic origin of the montmorillonite from 2:1-2:2 aluminum intergrade clay minerals.

METHODS AND MATERIALS

Soil sampling and characterization

Soil samples from two areas of the North Carolina Coastal Plain were used in this study. Three soils (Lakewood, Leon, and Wando soils) were sampled in Brunswick County, approximately one mile from the ocean along the inland waterway. Two catenas of four soils each were sampled in Wilson County, one on the lower Coastal Plain

and the other on the middle Coastal Plain. The soils of each catena include moderately well to very poorly drained soils. Some pertinent chemical, physical, and classification data of representative soils are given in Table 1. Soil pH was determined on samples with a soil:water ratio of 1:1, free iron by the citrate-dithionite method of Mehra and Jackson (1960), CEC_{8.2} and exchangeable aluminum by the method of Coleman, Weed, and McCracken (1959), total nitrogen by standard Kjeldahl, total carbon by the wet-combustion method of Mebius (1960), and particle size analysis by the sedimentation-pipette method of Kilmer and Alexander (1949).

Mineralogical analysis

The bulk soil samples were air dried and passed through a 2 mm sieve. The methods of Kunze and Rich (1959) were used with minor modifications to obtain K- and Mg-saturated silt and clay fractions. After organic matter was destroyed by hydrogen peroxide, the soil samples were dispersed in a mixing cup for 10 min with 1 per cent sodium hexametaphosphate as dispersant. Selected clay samples were fractionated into coarse clay (2.0-0.2 μ) and fine clay (< 0.2 μ) by high speed centrifugation. After saturation, a 2 ml suspension containing 50 mg of clay was allowed to dry on a glass slide to attain parallel orientation. Expansive properties of the Mg-saturated series were determined after ethylene glycol or glycerol solvation. The slides were irradiated by the X-ray beam of a GEXRD-5 diffractometer, using copper K α radiation. All X-ray diffraction patterns in Figs. 1-4 are for the whole clay fraction (< 2 μ).

RESULTS

A most striking mineralogical sequence occurs in the Lakewood Soil in Brunswick County (Fig. 1). Montmorillonite and swelling intergrade are the predominant clay minerals of the dark-gray Al horizon which has a low pH (3.9) and high organic matter content (2.2 per cent carbon). The term montmorillonite is defined operationally in this paper as the clay mineral component or smectite which exhibits a 14 Å spacing upon Mg-saturation at room temperature and expands to 17-18 Å upon ethylene glycol or glycerol solvation. A portion of the 14 Å clay fraction, a low stability 2:1-2:2 intergrade, did not expand with ethylene glycol solvation but readily collapsed with the montmorillonite to 10 Å upon K-saturation and heating at 350°C. At room temperature the major portion of the K-saturated clay sample collapsed to 11-12 Å with some low intensity broad peaks between 12-14 Å. A small amount of vermiculite may also be present in the sample.

*For more detailed soil descriptions, organic matter characterization and additional soil chemical and physical properties, refer to Unpublished Ph.D. Theses of R. L. Malcolm and W. D. Nettleton, N. C. State University, 1964 and 1966, respectively.

Table 1. General chemical and physical properties of representative soils

Soil horizon	Depth (in.)	pH	Exchangeable		Free iron	Nitrogen	Carbon	Sand	Clay
			CEC _{8.2}	Al					
			(me/100 g)		Percentage				
Wando (Typic Quartzipsamment, well drained) (Brunswick County, lower Coastal Plain)									
A2	0-2	4.7	4.1	0.5	0.30	0.044	1.62	96.9	2.2
B1	2-6	5.0	3.3	0.6	0.34	0.020	0.46	95.9	2.2
B2	6-16	5.4	3.0	0.4	0.30	0.014	0.25	96.5	1.8
B31	16-30	5.7	1.9	0.2	0.34	0.008	0.11	96.8	1.8
B32	30-60	5.6	1.4	0.2	0.35	0.003	0.07	97.1	1.1
C1	60-90	5.1	1.2	0.3	0.14	0.003	0.04	95.3	2.0
C2	90-108	5.4	0.5	0.1	0.07	0.000	0.02	99.1	0.8
Lakewood (Spodic Quartzipsamment, well drained) (Brunswick County, lower Coastal Plain)									
0	1-0	3.7	—	—	—	—	—	—	—
A1	0-3	3.9	11.8	1.7	0.05	0.045	2.19	98.0	0.8
A2	3-16	5.2	0.8	0.2	0.02	0.003	0.10	99.9	0.0
Bh	16-19	5.2	5.9	0.4	0.24	0.018	0.31	96.0	1.4
Bir1	19-33	5.4	2.4	0.3	0.09	0.008	0.14	97.6	0.5
Bir2	33-50	5.3	1.4	0.2	0.36	0.003	0.07	98.1	1.0
C1	50-100	5.9	0.4	0.1	0.02	0.000	0.01	99.4	0.0
C3	145-170	5.5	1.4	0.2	0.02	0.006	0.08	99.3	0.2
Unnamed (Typic Fragiaquilt, somewhat poorly drained) (Wilson County, middle Coastal Plain)									
A1	0-4	4.0	17.2	3.6	0.21	—	2.60 ^a	84.8	6.6
A2	4-8	4.3	10.9	2.8	0.22	—	1.21 ^a	57.1	11.2
B22gt	23-29	4.4	4.8	2.2	0.76	—	0.12 ^a	53.2	13.2
IIIC5	210-228	4.8	2.0	0.2	—	—	—	90.0	5.8
Portsmouth (Typic Umbraquilt, very poorly drained) (Wilson County, lower Coastal Plain)									
A1	0-10	4.5	13.9 ^b	3.6	0.01	—	2.5 ^c	57.1	10.9
B22gt	18-24	4.8	9.1 ^b	4.3	1.79	—	0.2 ^c	41.4	26.1
IIIC2g	80-90	4.8	10.0 ^b	6.6	0.39	—	0.1 ^c	45.7	26.6

^aDetermined by dry combustion.

^b< of exchangeable Ca, Mg, and K exchange acidity.

^cDetermined by wet combustion (Peech *et al.*, 1947).

The white bleached A 2 soil horizon was essentially devoid of crystalline clay minerals.

The mineralogy changes abruptly in the dark-brown Bh horizon which has a pH of 5.2 and 0.3 per cent carbon. The 2:1-2:2 intergrade is the dominant clay mineral. No traces of montmorillonite were found. The maximum formation of the intergrade, as indicated by heat stability, occurs in the Bh horizon where heat treatment at 550°C resulted in a sharp peak at approximately 12 Å with no resolution of a 10 Å peak.

The abundance of the intergrade clay mineral gradually decreases and the amount of montmorillonite increases with depth from the lower B in the C horizon. The clay in the C horizon, which expands with ethylene glycol, is believed to be

a mixture of montmorillonite and an expanding, poorly-formed 2:1-2:2 intergrade mineral. With increasing depth the 2:1-2:2 intergrade is less heat stable as indicated by increased resolution of the 10 Å peak and increased low intensity smudging of the diffuse peak between 14 and 10 Å. A small amount of vermiculite and mica are also present in the horizon. There is also the possibility that the clay fraction contains randomly interstratified vermiculite and mica in addition to the montmorillonite.

A relatively constant amount of kaolinite (approximately 25 per cent) and minor amounts of gibbsite and quartz are present in the clay fraction of all horizons.

The precursor of the 2:1-2:2 intergrade could

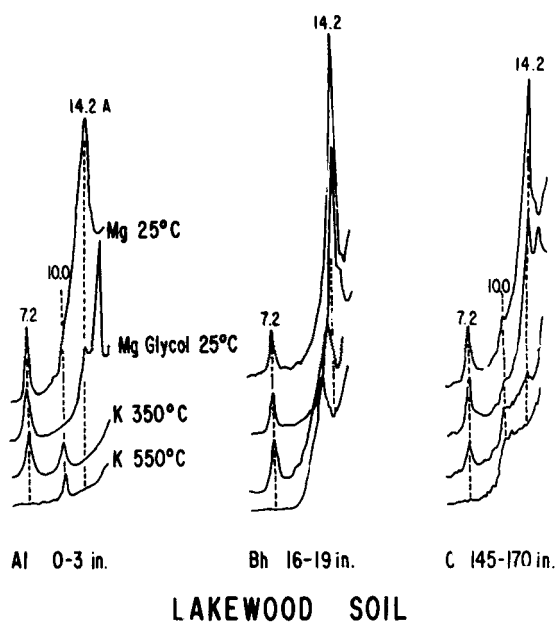


Fig. 1. X-ray diffraction patterns of clay fractions of the Lakewood soil.

be montmorillonite, vermiculite, or mica because all three minerals are present in the *C* horizon.

The well-drained Wando soil is a less well-developed soil which was sampled near, and is commonly associated with, the Lakewood soil. In contrast to the Lakewood soil, the Wando soil does *not* have a thin mat of organic matter covering the mineral soil, a low pH (below 4.5) in the surface horizon, a thick bleached *A* 2 horizon, a *Bh* horizon, or montmorillonite in the surface horizon (Fig. 2). A 2:1-2:2 aluminum intergrade is the predominant clay mineral in all horizons, with maximum intergrade formation in the *B* horizon. The intergrade also is well formed in the thin incipient *A* 2 horizon where the dealumination of the intergrade is beginning to occur. The pH of the *A* 2 horizon was 4.7 at the time of summer sampling and would probably approach pH 4.5 at some season(s) of the year. The intergrade is less well formed in the *C* horizon than *A* or *B* horizons as more of the 14 Å peak shifts toward 10 Å upon heating. Small amounts of vermiculite may be present in all horizons. Appreciable amounts of kaolinite are present in all horizons along with minor amounts of gibbsite and quartz.

The poorly drained soils of the catena in the middle Coastal Plain in Wilson County have clay mineralogy similar to the Lakewood soil with maximum relative accumulation of montmorillonite in the surface horizons and 2:1-2:2 intergrades

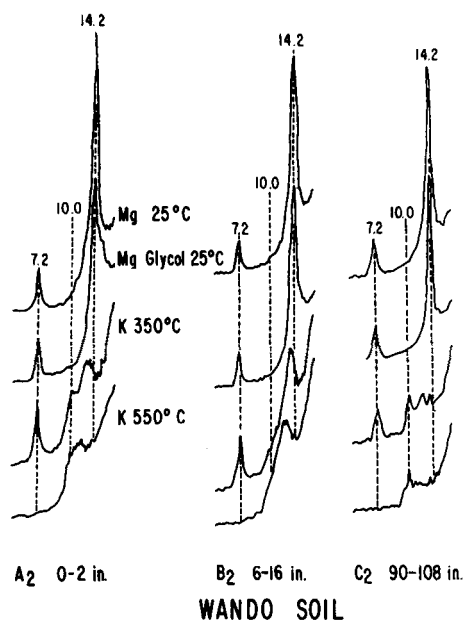


Fig. 2. X-ray diffraction patterns of clay fractions of the Wando soil.

in the subsurface and subsoil horizons. The surface horizons of the soils are below pH 4.5 and the subsurface and subsoil horizons near or above pH 4.5. The poorly drained soils of the catena in the lower Coastal Plain in Wilson County have a more diverse mineralogy but appear to have a mineral assemblage intermediate between the Lakewood and Wando mineral assemblages, i.e., the surface horizons contain both montmorillonite and a 2:1-2:2 intergrade clay mineral while *B* horizons are mostly 2:1-2:2 intergrade clay minerals with some montmorillonite. All horizons of the poorly drained soils of this catena from the lower Coastal Plains have a pH near or above 4.5. The surface horizons of all adjacent well-drained soils of both catenas in Wilson County contained predominately intergrade clay with no montmorillonite and were all above pH 5. The Norfolk soil is a typical well-drained soil of this area. An unnamed somewhat poorly drained soil and the Portsmouth soil representative of the respective conditions found in the wetter soils will be discussed.

The *A*1 horizon of a somewhat poorly-drained unnamed soil from the middle Coastal Plain with a low pH (4.0) and 2.6% organic carbon is predominantly montmorillonite (Fig. 3). Almost all of the 14 Å peak expanded to 18 Å upon glycerol solvation and readily collapsed to 10 Å upon K-saturation at room temperature. Heat treatment at 350°C produced a strong-sharp 10 Å peak. The

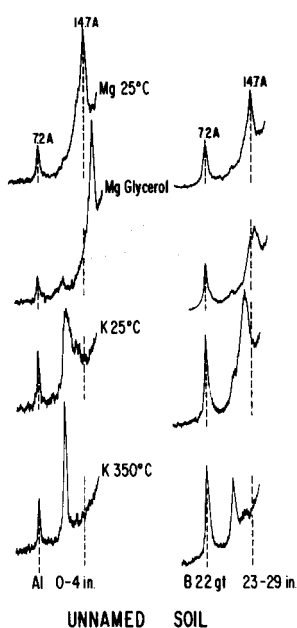


Fig. 3. X-ray diffraction patterns of the clay fractions of the somewhat poorly drained unnamed soil from Wilson County.

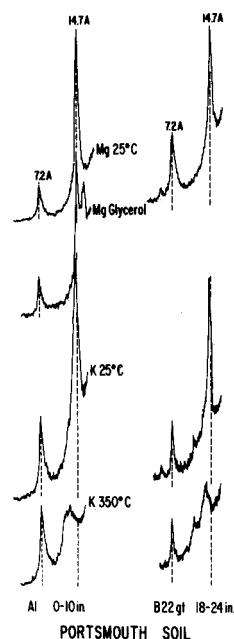


Fig. 4. X-ray diffraction patterns of the clay fractions of the Portsmouth soil.

14 Å clay in the *B22gt* horizon was a mixture of montmorillonite and a swelling poorly-formed intergrade. Upon glycerol solvation the 14 Å peak expanded to a broad peak from 14–18 Å and collapsed only to approximately 13 Å after K-saturation at room temperature. After heating to 350°C the 14 Å peak collapses to a broad 10 Å peak. The *C* horizon clays were kaolinite and illite with no montmorillonite or intergrade.

The clays of the solum of the very poorly-drained Portsmouth soil are predominantly of intergrade type (Fig. 4). The *Al* horizon with a pH of 4.5 and 2.5% organic carbon contained a small amount of expansible 14 Å material, presumably montmorillonite. The major portion of the 14 Å peak was an intergrade which gave a diffuse peak between 10 and 14 Å upon K-saturation and heating. The mineralogy of the *B* horizon was very similar to the *A* horizon except that the intergrade was slightly more heat stable. A small amount of vermiculite may also be present. Moderate amounts of kaolinite and small amounts of illite were present in the *A* and *B* horizons, with kaolinite becoming the predominant mineral in the *C* horizon. A moderate amount of illite was present in the *C* horizon also, with small amounts of quartz and montmorillonite. No intergrade mineral was present in the *C* horizon.

The presence of a swelling 2:1–2:2 aluminum

intergrade in addition to montmorillonite is indicated in the surface horizon of the Lakewood and the *B22gt* horizon of the unnamed soil by the weak broad 10 Å peak after K-saturation and heat. This peak is very weak when compared to the 18 Å after Mg-saturation and glycol or glycerol solvation. The swelling intergrade did not collapse to a uniform 10 Å spacing, but random collapse between 10 and 12 Å results in little reinforcement of the X-ray beam and poor resolution of the 10 Å peak. The strong sharp 10 Å peak after K-saturation and heating the clay from the surface horizon of the somewhat poorly drained wet unnamed soil suggests that the major portion of the 14 Å peak is montmorillonite with very little swelling intergrade clay.

DISCUSSION

The monomeric aluminohydronium ion is the fundamental acid ion in soil below pH 4.5. If the pH of the soil rises to 4.5, aluminum hydrolysis begins and is almost complete at pH 5. There is some evidence (Jackson, 1960) that hydrolysis may occur at a slightly lower pH when aluminum is held on exchange sites of expansible layer silicates due to a steric pinching effect. When aluminum precipitates as polymers in the interlayer of expansible minerals, the resultant mineral is called a 2:1–2:2 aluminum intergrade. Several inves-

tigators have synthesized aluminum and iron intergrades in laboratory experiments from montmorillonite and vermiculite (Rich, 1960; Shen and Rich, 1962; Hsu and Bates, 1964). These intergrades are heterogeneous in character as discussed previously, and loss of expansibility can be achieved when less than 10 per cent of the interlayer surface is covered with polymer (Frink, 1965).

Chlorite as well as montmorillonite and vermiculite have been postulated (Jackson, 1963) to be the precursor of aluminum intergrades in soil under conditions of natural weathering. In soil studies, Tamua (1958) and Douglas (1965) reported montmorillonite and vermiculite, respectively, to be the precursors of the intergrade. Mica was suggested as the precursor of the intergrade by Weed and Nelson (1963). It is now known if mica can weather directly to the intergrade or if intermediary phases of montmorillonite or vermiculite are necessary. In this study, montmorillonite is believed to be the dominant precursor in the Lakewood and Wando soils, although vermiculite and mica are minor possibilities because they are present in small amounts. Mica and/or montmorillonite is the precursor of the intergrade in the Wilson County soils.

The process of intergrade formation from montmorillonite or vermiculite is reversible in the laboratory and is believed to be so in soils. When synthetic interlayers are removed by chemical means such as acids or complexing agents, the parent expansible mineral is obtained. In soils or the laboratory, protonation (the reverse of hydrolysis) of the interlayer polymer would occur when the pH dropped below 4.5. This protonation would result in the solubilization or dealumination of the interlayer, and the mineral would once again become expansible.

The mineralogical sequence and associated chemical conditions in the soils studied support many of Jackson's postulates. The intergrade is apparently formed in the *B* and *C* horizons from montmorillonite or vermiculite where the pH is favorable for hydrolysis and then the intergrade is transformed back to montmorillonite in the surface where the low pH and high organic matter favor protonation or dealumination of the interlayer polymer.

Low pH and organic matter are probably of equal importance in the pedogenic formation of montmorillonite from 2:1-2:2 intergrades in the soils studied because the intermediates of organic matter decomposition (primarily fulvic acids) are the most common source of soil acidity (pH 4.5 and below), and because the properties of high organic matter and high hydrogen ion activity environments in soils are closely interrelated.

It is difficult to assess if low pH alone (below 4.5) without the influence of organic matter is an important or extensive mechanism in the pedogenic transformation of 2:1-2:2 intergrades to montmorillonite because few low pH environments are created in soils without the dominant influence of organic matter. Theoretically a source of protons at the low pH (below 4.5) and the 2:1-2:2 intergrade clay are all that is needed for the dealumination reaction and transformation to occur. At this low pH the aluminum polymer is thermodynamically unstable and protonation of the interlayer aluminum polymer would result in the formation of exchangeable aluminum species, subject to leaching, and an expansible aluminosilicate. This mechanism may also be functional in certain local or micro environments where sulfur oxidation is prevalent, as in oxidized soil materials from coastal marshes or in stripmine soil.

Likewise, organic matter alone above the critical pH of 4.5 may not bring about the transformation of 2:1-2:2 intergrade to montmorillonite. In most soils both the 2:1-2:2 intergrade and organic matter increase in amount with proximity to the surface, the maximum intergrade occurring where maximum accumulation of organic material is found. The critical point is that in such soils the pH is always above the critical pH for solubilization of the interlayer polymer.

Poor drainage alone is not responsible for the transformation because the process occurs in the well-drained Lakewood soil and the transformation does not occur in all poorly drained soils. For example, the poorly drained Plummer soil, a low Humic Gley with high organic matter content, exhibited a high degree of interlayering throughout the profile (Weed and Nelson, 1963). The critical point here again is that nowhere in the solum of the Plummer soil was the pH below the critical pH of 4.5.

Organic matter is believed to facilitate the removal of aluminum interlayers in several ways in addition to providing the acid environment or the source of protons for the protonation reaction. It is well established that organic matter, especially fulvic acids, form water-soluble complexes with Al, Fe, and other metals. The product of the protonation reaction, aluminum ion species in solution or on exchange sites, would be subject to complexation by fulvic acid and other mobile soil organic matter constituents. These water-soluble complexes would move downward in the profile in percolating water, thus removing the product of the protonation reaction. The continuous removal of product would keep the equilibrium shifted to the right, favoring the production of more aluminum ions at a maximum rate, K_1 .

The rate K_1 of this protonation reaction is believed to be very slow.

The organic matter may take a more active role in the solubilization of aluminum in a manner similar to the solubilization of iron from Triassic sands as reported by Coulson, Davies and Lewis (1960). The rate of iron solubilization by the polyphenols was ten times greater than with buffer solution at the same pH without polyphenols. The mechanism of this reaction is not known, but complex formation seems to be essential. Fulvic acids have phenolic carboxyl, and other reactive groups capable of complex formation and would be expected to act in a manner similar to complex polyphenols in solubilization of iron and aluminum sesquioxides.

By either mechanism the aluminum polymer would be readily accessible to fulvic acids or mobile soil organic matter. Other workers have shown that much of the aluminum interlayer polymer is near the edge of the clay particle. Electron micrographs of some of the clays in this study (Fig. 5)* show that clumps of amorphous material are on the surface and edges of the clay plates. These surface clumps of aluminum polymer would be expected to be readily available to fulvic acids in soil solution because the clay is dispersed throughout the sandy soils studied. In the surface horizons having montmorillonite the clay plates have fewer clumps of amorphous material and the edges of these are practically free of the material (Fig. 6).

The aluminum polymer within the interlayer would not be protected from solubilization by fulvic acids, because the fulvic acid-montmorillonite clay complex has a 14 Å spacing (Schnitzer and Kodama, 1966) which is essentially the same as the intergrade. The remaining portion of the polymer in the intergrade and the hydration of the portion of the platlet where the polymer was removed would prop the interlayer open for free movement of fulvic acids within the interlayer.

If organic matter is such an integral part of the dealumination process, there should be considerable amounts of organic matter in the soil and evidence of organic matter, aluminum, and iron movement. The composition of the O1, A2, and Bh horizons in the Lakewood and Leon soils provide strong evidence that a supply of organic matter is available and that considerable eluviation has occurred. The organic matter of the Bh horizon is readily extractable with acetylacetone

or sodium hydroxide and is composed of over 85% fulvic acids. The Bh horizon also has maxima of free iron and exchangeable aluminum suggesting that metal movement was associated with fulvic acid movement.

Soil water collected periodically from the Wilson County soils contained up to 0.07% organic matter, 0.2 ppm aluminum, and 3.4 ppm iron. The highest concentrations of aluminum and iron in soil solution occurred when the concentration of organic materials was highest. By paper chromatography it was determined that the water-soluble or mobile organic matter consisted of sugars, organic acids and polyphenols—all of which are capable of complex formation with aluminum, iron and other metals.

Soil conditions such as low pH or high organic matter content may prevent or inhibit intergrade formation. Such inhibition may well have occurred in certain instances and is surely preventing additional formation of intergrade in soils where the pH drops below 4.5. However, the dealumination theory is supported in this investigation because all the soil conditions necessary for the process to occur are present and the inhibition theory does not explain the presence of some intergrade in the surface horizon with a pH 3.9 or the apparent mineralogical sequence with decreasing pH and increased weathering.

Intergrade formation should be completely inhibited at a pH of 3.9, but a small amount of intergrade is present in the A1 horizon of the Lakewood soil. Aluminum hydrolysis should not occur at this low pH, therefore no intergrade could be formed. The swelling intergrade must be the last remnant of a well-formed intergrade which is undergoing dealumination because the pH dropped below 4.5 in the process of soil development.

In these soils weathering must have occurred over a long period of time before the formation of low pH conditions. During this initial weathering period, the inhibition theory could not apply and the intergrade which is a stable weathering product for the region probably would have formed in all horizons.

In support of these statements, there seems to be a sequence or evolution of soils and mineralogy with increased time on the coastal plain. Old soils or very youthful soils with a pH between 5 and 6 have maximum intergrade formation in the surface horizon. With decreasing pH and incipient A2 formation, such as is found in the Wando soil on the coastal dunes, dealumination apparently begins in the surface horizon. With time an acid litter mat forms on the soil surface, pH consequently drops to below 4.5 during the entire year, and the

*Electron micrographs were prepared by John L. Brown, Head, Electron Microscopy and Optical Laboratory, Georgia Institute of Technology, Atlanta 13, Georgia.

intergrade is transformed into montmorillonite in the acid soil surface. This situation occurs in the Lakewood soil which is approximately 1 mile back from the ocean.

With more time and lowering of the pH to below 4.0 in a Leon soil 50 miles inland (Duplin County), montmorillonite is weathered from the soil surface and only small amounts of crystalline clay mineral remain (Weed and McCracken, 1963). The weathering boundary moves downward in the soil and montmorillonite or poorly formed intergrade is in the upper *B* with maximum formation of intergrade in the middle to lower *B* horizon.

CONCLUSIONS

The decision table (Table 2) summarizes some of the evidence which support the conclusion that organic matter and low pH (<4.5) are jointly the principal agents responsible for the conversion of intergrade to montmorillonite. The surface horizon

and the Portsmouth surface horizon of 4.5 is mixed intergrade and montmorillonite. This Portsmouth surface horizon is believed to be a manifestation of incipient montmorillonite formation from the intergrade.

The critical amount of organic matter or mobile fulvic acids in the soil necessary for the conversion is not known, except that the organic matter must provide a pH of <4.5. Organic matter contributes to the conversion in many ways, in addition to providing an acid environment. These include a readily available supply of protons, the complexation of Al and Fe, and perhaps the active solubilization of Al and Fe polymers.

Drainage is not believed to be an important factor, because the conversion occurs in both well-drained and poorly-drained soils.

The theorized mechanism of intergrade dealumination is believed to be occurring and has occurred in the soils studied. It is believed to be a

Table 2. Decision table

<i>A</i> Horizon	Poor drainage	pH < 4.5	High organic matter	Predominantly montmorillonitic
1. Lakewood	no	yes	yes	yes
2. Leon (Brunswick County)	no	yes	yes	yes
3. Leon (Duplin County)	yes	yes	yes	yes
4. Unnamed soil	yes	yes	yes	yes
5. Portsmouth	yes	yes-no	yes	no
6. Wando	no	no	yes	no
7. Plumer	yes	no	yes	no
8. Norfolk	no	no	no	no

of the first four soils, which are predominantly montmorillonitic, have only high organic matter and low pH in common. Organic matter alone is not responsible for the conversion because many soils in addition to those listed in the table have high organic matter contents, but do not have montmorillonite in the surface horizon. From the table, it might be concluded that low pH alone could bring about the conversion, and may do so in some rare soil environments; but because organic matter is the agent responsible for the low pH in the soil studied, it is believed that organic matter and low pH are intimately associated in the conversion.

A pH of 4.5 seems to be the critical pH below which dissolution of the Al (Fe?) interlayer polymers occurs within the intergrade clay mineral. All horizons above this pH are devoid of montmorillonite and contain the intergrade; all horizons with a lower pH are predominantly montmorillonitic;

and the Portsmouth surface horizon of 4.5 is mixed intergrade and montmorillonite. This Portsmouth surface horizon is believed to be a manifestation of incipient montmorillonite formation from the intergrade.

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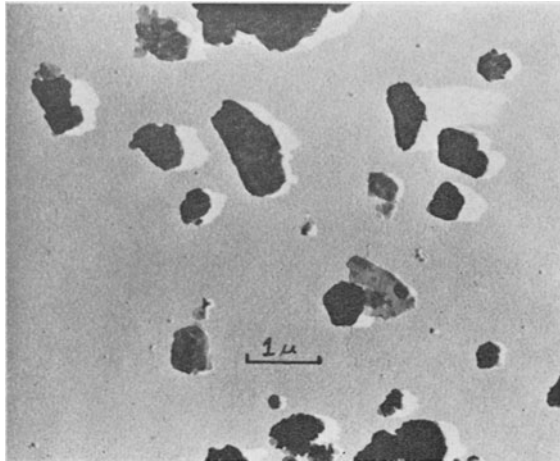


Fig. 5. Electron micrograph, 2-0.2 μ clay fraction of B22t horizon of somewhat poorly drained unnamed soil of the middle Coastal Plain.



Fig. 6. Electron micrograph, 2-0.2 μ clay fraction of A1 horizon of the somewhat poorly drained unnamed soil of the middle Coastal Plain.

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Résumé—Le montmorillonite s'est révélé le minéral d'argile dominant dans les horizons superficiels de certains sols dans la Plaine Côtière de la Nouvelle Caroline, tandis qu'un minéral d'argile interstratifié 2:1–2:2 dominait dans les horizons sousjacents. Dans tous les sols où on trouvait cette séquence de minéral d'argile, l'horizon superficiel avait un pH bas (inférieur à 4,5) et une teneur élevée en matière organique. Par contraste, les données obtenues dans les études d'autres sols de cette région (Weed et Nelson, 1962) montrent que: (1) le montmorillonite est rare; (2) l'accumulation maximum de l'interstratifié 2:1–2:2 a généralement lieu dans l'horizon superficiel et décroît avec la profondeur dans le profil; (3) la teneur en matière organique est basse, et (4) le pH n'est pas fortement acide (pH 5–6).

On présente la théorie que le montmorillonite dans l'horizon superficiel du sol a son origine dans le vieillissement pédogénique du minéral d'argile interstratifié 2:1–2:2. Les effets combinés de bas pH (inférieur à 4,5) et de la teneur élevée en matière organique dans les horizons de surface sont censés être responsables de cette transformation minéralogique. La protonation et solubilisation (inverse de l'hydrolyse) des polymères Al dans la couche intermédiaire des minéraux d'argile expansibles ont lieu à un pH égal ou inférieur à 4,5 selon la charge et les effets stériques de la couche intermédiaire. Un bas pH peut à lui seul provoquer cette solubilisation et de là la transformation minéralogique, mais dans le cas des sols étudiés, on considère que la matière organique facilite et accélère la transformation. Les produits intermédiaires de la décomposition de la matière organique fournissent un milieu acide, une source de protons et une source de substances organiques mobiles et solubles dans l'eau (surtout les acides fulviques) qui ont la capacité de rendre complexe l'aluminium solubilisé et de le déplacer vers le bas du profil. Cet enlèvement continu de l'aluminium solubilisé tend à fournir une pente qui favorise la solubilisation de l'aluminium.

La catégorie d'assèchement et la position dans la chaîne semblent être moins importantes que les facteurs chimiques en ce qui concerne la formation de montmorillonite à partir d'un intergrade 2:1–2:2, parce que le montmorillonite est présent dans toutes les catégories d'assèchement si l'horizon de surface a un pH bas et une teneur élevée en matière organique.

Kurzreferat—Montmorillonit wurde als vorherrschendes Tonmineral in den Oberflächenhorizonten gewisser Böden der Küstenebene von North Carolina gefunden, während in den darunter liegenden Horizonten ein 2:1–2:2 Übergangstonmineral vorherrschte. In allen Böden, wo diese Tonmineral-

folge festgestellt wurde, war das pH niedrig (weniger als 4,5) und der Gehalt an organischen Bestandteilen hoch. Im Gegensatz dazu erweisen die Ergebnisse der Untersuchungen anderer Böden dieser Gegend (Weed und Nelson, 1962) folgendes: (1) Montmorillonit tritt nur spärlich auf; (2) eine maximale Anhäufung des 2:1-2:2 Übergangsmaterials tritt normalerweise im Oberflächenhorizont auf und nimmt mit der Tiefe des Profils ab; (3) die Gehalte an organischen Bestandteilen sind niedrig; und (4) die pH Werte sind nur schwach sauer (pH 5-6).

Es wird die Theorie aufgestellt, dass der Montmorillonit im Oberflächenhorizont der untersuchten Böden durch paedogene Verwitterung des 2:1-2:2 Übergangstonminerals entstanden sein könnte. Dabei wird angenommen, dass die vereinigten Wirkungen des niedrigen pH (weniger als 4,5) und des hohen Gehaltes an organischen Bestandteilen des Oberflächenhorizontes für diese Mineralumwandlung verantwortlich sind. Die Protonisierung und Löslichmachung (Gegenteil von Hydrolyse) von Al-Polymeren in der Zwischenschicht quellbarer Tonminerale findet je nach der Ladung und der sterischen Effekte der Zwischenschicht bei pH 4,5 oder weniger statt. Ein niedriger pH Wert allein kann diese Löslichmachung und die sich daraus ergebende Mineralumwandlung verursachen, doch darf angenommen werden, dass in den untersuchten Böden die organischen Bestandteile die Umwandlung erleichtern und beschleunigen. Die Zwischenprodukte der Zersetzung organischer Bestandteile schaffen eine saure Umgebung, eine Protonenquelle und eine Quelle wasserlöslicher, beweglicher organischer Stoffe (vornehmlich Fulvinsäuren), die dazu fähig sind, das lösliche Aluminium in Komplexform zu bringen und es dem Profil entlang abwärts zu fördern. Diese dauernde Entfernung des löslich gemachten Aluminiums würde ein günstiges Verhältnis für die fortschreitende Löslichmachung des Aluminiums herbeiführen.

Die Entwässerungskategorie oder -lage in einer Reihe wird als weniger wichtig angesehen, als die chemischen Faktoren in der Bildung von Montmorillonit aus 2:1-2:2 Übergangsmaterial, da sich Montmorillonit in allen Entwässerungsklassen findet, wenn der Oberflächenhorizont ein niedriges pH und einen hohen Gehalt an organischen Bestandteilen aufweist.

Резюме—В прибрежной равнине Северной Каролины обнаружили, что преобладающим глинистым минералом является монтмориллонит в поверхностных горизонтах некоторых почв, а глинистый минерал промежуточного сорта 2:1-2:2 в подстилающих горизонтах. Во всех почвенных слоях, где была обнаружена эта последовательность глинистых минералов, поверхностный горизонт имел низкое pH (менее 4,5) и крупное содержание органических веществ. В противоположность этому, данные полученные из исследований других почв в этом же районе (Види Нелсон 1962) показывают: (1) что монтмориллонит встречается редко; (2) что максимальное накопление промежуточного слоя 2:1-2:2 обычно имеется в поверхностном горизонте и сокращается по мере увеличения глубины в профиле; (3) что содержание органических веществ не большое и (4) что значения pH являются только умеренно кислыми (pH 5-6).

Утверждают, что монтмориллонит в поверхностном горизонте исследуемых почв возник вследствие почвообразовательного выветривания глинистого минерала промежуточного сорта 2:1-2:2. Сочетание воздействия низкого pH (менее 4,5) и крупного содержания органических веществ в поверхностных горизонтах считают средствами, вызвавшими это минеральное преобразование. Протонодонорность и придание растворимости (противоположность гидролиза) полимерам Al в промежуточном слое вспучивающихся глинистых минералов происходит при pH 4,5 или менее, в зависимости от заряда и от пространственных эффектов промежуточного слоя. Это придание растворимости и, следовательно, и минеральное преобразование, может быть вызвано только низким pH, но предполагают, что в исследованных почвах органические вещества облегчают и ускоряют такое преобразование. Промежуточные разложения органических веществ предоставляют кислые окружающие породы, источник протонов, а также источник растворимых в воде мобильных органических веществ, которые обладают способностью комплексообразования растворимого в воде алюминия и передвижения его вниз по профилю. Такое непрерывное удаление растворимого в воде алюминия предоставит благоприятный градиент для растворения алюминия.

Считают, что для образования монтмориллонита из промежуточного слоя 2:1-2:2, класс дренажа или местоположение в цепи имеют меньшее значение, чем химические факторы, так как монтмориллонит присутствует во всех дренажных классах, если поверхностный горизонт имеет низкий pH и крупное содержание органических веществ.