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ABSTRACT

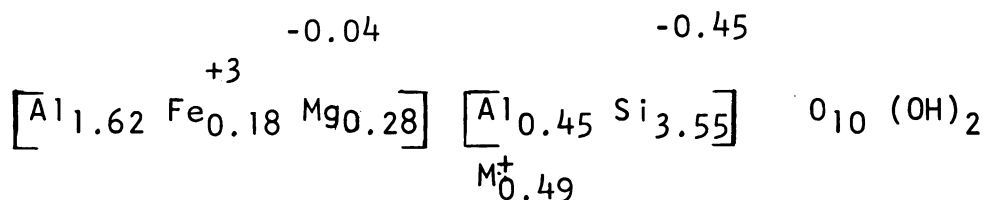
CHARACTERIZATION OF A MONTMORILLONITE IN A NORTHERN MICHIGAN PODZOL

by Gerhard John Ross

Illite, chlorite, interstratified chlorite-vermiculite and chlorite-montmorillonite have weathered in situ through a vermiculite stage to montmorillonite. This weathering sequence is prevalent in the sandy soils of Northern Michigan and results in accumulation of montmorillonite in the A₂-horizon of these soils in this area.

This montmorillonite is classified as a beidellite since it is dioctahedral and has a relatively high aluminum content and a high charge, most of which originates from substitution of Al for Si in the tetrahedral layer.

This beidellite interpretation is supported by data from the Greene-Kelly test, X-ray diffraction, differential thermal, infra-red, and chemical analyses. The formula for the beidellite is:



which has the high layer charge of 126 me/100g.

This beidellite has a strong tendency to fix potassium as is evident from a 40% reduction in cation exchange capacity when saturated with potassium, heated to 110°C, and resaturated with ammonium to replace potassium.

The acid dissolution technique (Osthaus, 1956) for determination of tetrahedral aluminum does not apply to the beidellite studied.

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NORTHERN MICHIGAN PODZOL

By

Gerhard John Ross

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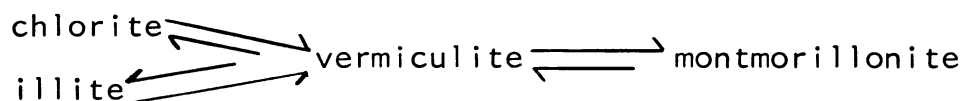
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1. INTRODUCTION

Franzmeier (1962), in his study of a chrono-sequence of Podzols in Northern Michigan, found that the layer silicates of the parent material are composed of kaolinite, chlorite and illite, but that montmorillonite is almost the only layer silicate present in the A₂-horizon of the soil studied. He postulated a weathering sequence in the 2:1 silicates as follows:



This sequence implies the removal of the brucite layer from chlorite and of the interlayer potassium from illite. Considering the structure of the chlorite and of illite, it follows that the montmorillonite formed would: (1) have relatively high substitution of Al for Si in the tetrahedral layer; (2) have relatively high cation exchange capacity predominantly originating in the tetrahedral layer; and (3) fall in the beidellite end of the montmorillonite-beidellite series.

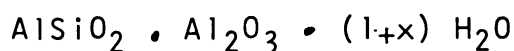
This investigation was designed to test the foregoing hypothesis. This was done by studies of the structure, chemical

composition, and reactions of the clay fraction from the A₂-horizon of these Northern Michigan Podzols, and by its comparison with structure, properties, and reactions of Wyoming bentonite, nontronite, and the clay fraction of the underlying soil and its parent material.

II. LITERATURE REVIEW

Montmorillonites - Structure and Classification

In 1897, Damour and Salvétat proposed the name montmorillonite for a clay mineral which had the approximate composition:



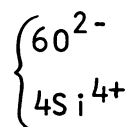
and which could be dehydrated reversibly at a low temperature. Ross and Shannon (1925) proposed the formula $(\text{Mg}, \text{Ca}) \cdot \text{Al}_2\text{O}_3 \cdot 5 \text{SiO}_2 \cdot n\text{H}_2\text{O}$ to account for the MgO and CaO which were present in all of the newer analyses. Later X-ray studies showed that Mg is frequently present as an essential constituent while Ca is not incorporated in the structure.

The structure of montmorillonites is based on that of pyrophyllite (Hoffmann, Endell, and Wilm - 1933, 1934). This mineral, as shown below, has the sequence of atomic planes perpendicular to the pseudo-hexagonal axes.

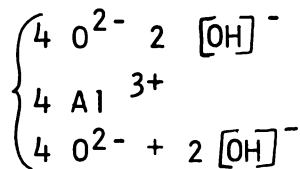
Pyrophyllite

Atomic planes

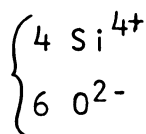
Silicate layer
(tetrahedral)



Gibbsite layer
(octahedral)



Silicate layer
(tetrahedral)



Combined, the atomic planes shown above form a neutral structure, which may be considered as one lattice layer. These layers may be extended indefinitely along a horizontal plane. Since each of these layers are neutral, there is only a small attractive force between them, resulting in the excellent cleavage of the mineral.

To account for the swelling characteristics and relatively large cation exchange capacity of montmorillonite, Hendricks (1942) and Marshall (1945) suggested that in some montmorillonites, such as Wyoming bentonite, negative charges arise from replacement of Al^{3+} by Mg^{2+} or Fe^{2+} in the octahedral layer. In other montmorillonites, such as beidellite and nontronite, negative charges are due to substitution of Al^{+} for Si^{+} in the tetrahedral layer.

The classification of montmorillonites is based essentially on their structural characteristics. Accordingly, dioctahedral and trioctahedral montmorillonites are recognized (Stevens, 1942, Ross and Hendricks, 1945). In dioctahedral montmorillonites only two-thirds of the positions in the octahedral layer are filled by ions in six-coordination, whereas in trioctahedral montmorillonites all positions are filled.

Arrangement of the dioctahedral montmorillonites according to the Si:Al ratio gives rise to the montmorillonite-beidellite series (Marshall 1935). The maximum ratio of 2.4:1 corresponds to that of montmorillite (Wyoming bentonite); the minimum ratio of 1.4:1 approaches that of beidellite (Black Jack Mine, Idaho).

The classification of dioctahedral montmorillonites in a single, continuous, isomorphous series has recently been challenged by Grim and Kulbicky (1961). From analytical data of 42 montmorillonites, they concluded that two different aluminous types were present, namely, Cheto- and Wyoming types. These types differ primarily in the larger amount of magnesium present in the octahedral layer of the Cheto types. Cation exchange capacities are also higher in the Cheto type montmorillonite.

Beidellite

Larsen and Wherry (1925) proposed the name beidellite for a clay mineral from Beidell, Colorado. Because this name was applied to many minerals distinctly different from the type mineral, Ross and Hendricks (1945) redefined beidellite as the aluminum-rich end-member of the isomorphous montmorillonite-beidellite series. However, X-ray diffraction

and thermal data showed that most of these beidellites were mixtures containing other minerals (Grim and Rowland, 1942).

Several mineralogists have discredited the name beidellite (Grim, 1953; Brindley, 1955; Frank-Kamenetskey, 1958; Ross, 1959). Others have included beidellite in their classifications (Mac-Ewan, 1951; Brown, 1955; Caillere and Henin, 1957; Mackenzie, 1957; Strunz, 1957). In 1959, Ross proposed that the use of the name beidellite be discontinued since there was no confirmed occurrence of a mineral with a structure and composition similar to that required by Ross and Hendricks' definition.

Because of the adverse criticism concerning the identity of beidellite, Weir and Greene-Kelly (1962) carefully re-examined a clay sample from the Black Jack Mine, Idaho. This sample was part of a specimen earlier analyzed by Shannon (1924) and listed as a beidellite by Ross and Shannon (1925). From X-ray diffraction, thermal data, chemical analysis, and electron micrographs, Weir and Greene-Kelly (1962) concluded that the B.J.M. clay mineral is composed of a single mineral species, and that it is a genuine end-member beidellite of the dioctahedral montmorillonites.

Greene-Kelly (1955a) suggested that montmorillonites and beidellites should be divided at the composition at which the lattice charges arising from octahedral and tetrahedral substitution equal one another. If the lattice charges due to tetrahedral substitution are greater than those due to octahedral substitution, the mineral should be named beidellite. If the reverse is the case, the mineral should be named montmorillonite. Greene-Kelly (1953b) also devised a test to distinguish between beidellite and montmorillonite. This test depends on the observation that Li-saturated montmorillonite collapses irreversibly when heated to 200-300°C., whereas beidellite similarly treated re-expands upon glycerol solvation.

Relationship With Illite And Chlorite

From their analyses of a large number of montmorillonites, Ross and Hendricks (1945) pointed out that as the beidellite end of the montmorillonite-beidellite series is approached there is a decided tendency toward the formation of mixed-layer type minerals containing potassium. In more fundamental terms the number of non-exchangeable interlayer ions,

essentially of potassium, increases with the increase in replacement of silicon by aluminum in tetrahedral coordination. According to the authors, this indicates that there may be a complete gradation between the beidellite-type clay minerals and moderately high potassium mica-like minerals.

Considering the structural similarity between montmorillonite and illite, White (1950) has postulated that if sufficient of the potassium ions could be removed from the illite without marked decomposition of the mineral, it should be structurally equivalent to a member of the montmorillonite series (beidellite); and Nagelschmidt and Hicks (1943) have stated that the replacement of all exchangeable bases by potassium in minerals of the montmorillonite group should lead to the formation of illite.

Foster (1954) calculated structural formulas for illites, montmorillonites, and beidellites and found that illites are characterized by a high total charge of 0.75 and 0.95 on the lattice layers, of which approximately two-thirds is in the tetrahedral layers. The total charge on the montmorillonites ranges from about 0.30 to 0.50 and is predominantly in the octahedral layer. Beidellites have

a total charge which is commonly lower than that found on the illites and higher than that on the montmorillonites. The origin of this charge is predominantly in the tetrahedral layers. Thus, as Foster (1954) pointed out, beidellite of all the montmorillonites has the composition of the clay that would be formed if the potassium in muscovitic illite were removed and replaced by exchangeable cations like sodium or calcium. However, at that time (1954) the natural occurrence of beidellite had not been authenticated.

The removal of the brucite layer from chlorite should result in an expanding clay mineral similar to that formed by the removal of interlayer potassium from illite. Both would be characterized by a high aluminum for silicon substitution in the tetrahedral layer and a high total tetrahedral charge. Ample evidence (cited in the next section) shows that chlorites in soils weather to montmorillonites. In the course of weathering and removal of the brucite layers, intermediate stages may be represented by regularly interstratified chlorite-montmorillonite (Bradley and Weaver, 1956), by randomly instratified chlorite-montmorillonite (Weaver, 1956a), or by swelling chlorite

(Lippmann, 1954). The fact that the resulting montmorillonites commonly are dioctahedral pointed to the existence of a naturally occurring dioctahedral chlorite. This existence has recently been confirmed. (Brydon, et al, 1961).

Weathering and Alteration of Illite and Chlorite in Soils

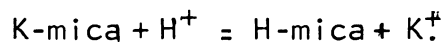
Murray and Leininger (1956) studied the changes in clay minerals of glacial tills under the influence of weathering. The three profiles studied represented immature, intermediate, and mature stages of weathering in a temperate climate. The results of their study showed that illite and chlorite change progressively to montmorillonite as the intensity of weathering increases. Droste (1956), in a similar study, also concluded that illite and chlorite of the parent mineral alter respectively to illite-montmorillonite and chlorite-vermiculite mixed layers. Further degradation of these mixed layers with attendant formation of montmorillonite continues progressively with increasing intensity of weathering.

These studies yield essentially the same conclusions as those given elsewhere in the literature (Barshad, 1955, 1959; Bayliss and Loughnan, 1963; Brydon, 1964; Butler, 1953;

Droste and Tharin, 1958; Droste, et al, 1962; Frye, Willman and Glass, 1960; Harrison and Murray, 1959; Jackson, 1959; Jackson and Sherman, 1953; Kodoma and Brydon, 1964).

Murray and Leininger (1956) postulated that the initiating mechanism for the change from chlorite and illite to montmorillonite is oxidation of ferrous iron in the octahedral layers. This oxidation causes a decrease in the net charge which weakens the bonds between the sheets and thus allows solutions to enter. These solutions may then remove iron, magnesium, and hydroxyl ions from chlorite and potassium from illite.

From X-ray analyses, Droste (1956), Droste, et al, (1962) and Bayliss and Loughnan (1963) concluded that illite is more resistant to weathering than chlorite. They explained this by assuming that the brucite sheet in chlorite is more accessible to leaching solutions than the potassium, which fits tightly in the hexagonal cavities formed by adjacent tetrahedral sheets of illite. Furthermore, alteration of chlorite may retard alteration of illite in the early stages of chlorite and illite alteration (Droste, 1962). This interaction is related to the reaction of illite with H^+ ions from water. Garrels and Howards (1959) presented this reaction by the equation,



They also pointed out that the alteration of mica also involves the loss of aluminum and silicon from the tetrahedral sheets. If these ions are not removed from the environment, equilibrium conditions soon will be reached. Such equilibrium conditions may be influenced by ions released from alteration of chlorite.

In an environment of intensive eluviation, potassium, aluminum, and silicon ions released from the lattice are continually removed resulting in formation of expanding clay minerals. Thus the intensive leaching conditions commonly present in A₂-horizons of podzols should be particularly conducive to weathering of chlorite and illite to montmorillonite. Brown and Jackson (1958) and Franzmeier and Whiteside (1963) showed that montmorillonite (apparently weathered from illite, vermiculite, and chlorite) is the dominant clay mineral present in the A₂-horizons of some Northern Wisconsin and Northern Michigan podzols. Brown and Jackson (1958) identified this clay mineral as a montmorillonite having many vermiculite characteristics, such as high charge, collapse to 14Å upon slight heating, and partial collapse to 10Å with potassium saturation.

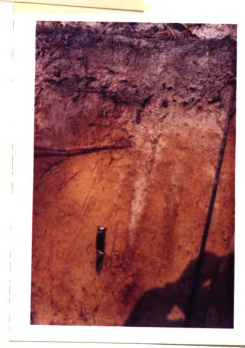
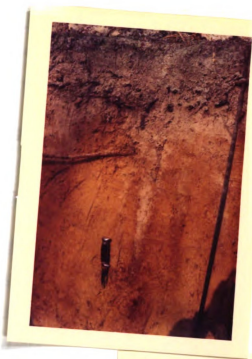
III. MATERIALS

Collection of Samples

Samples were collected from the A₂-horizons of soils at seven locations in Emmet and Cheboygan Counties, Michigan. The locations are shown in Figure 1. The X-ray tracings of the clay fraction ($<2\mu$) of each sample were examined for purity of montmorillonite in order to select the soil to be sampled for further study. The soil at location No. 1 was selected after examination of the X-ray tracings. A view of the soil profile at that site is shown in Plate 1.

A soil pit, about three by six feet, was dug and the profile described. The description was written according to standard conventions (Soil Survey Staff, 1951) except that the International Society Color Council - National Bureau of Standards (ISCC-NBS, Kelly and Judd, 1955) color names were used. Samples were taken from each horizon.

Samples of Wyoming bentonite, No. 25, from Upton, Wyoming, and of nontronite, No. 33a, from Garfield, Washington were used for comparison in the various studies.



Soil Profile Description

Deer Park Sand

Vegetation:

Red oak, aspen, red pine, white pine, paper birch,
red maple.

Physiography and Relief:

The soil described occurs on a low dune (3-5% slope)
along an old beach ridge.

Ground water: deep

Moisture: moist

Stoniness: none

Location:

NE 1/4 of SW 1/4 of SE 1/4 of Sec. 35, T38N, R1W.

Benton Township, Cheboygan County, Michigan

<u>Horizon</u>	<u>Depth (inches)</u>	<u>Description</u>
A ₁	0-1	Sand; brownish gray (10YR3/1); very weak, fine, granular; very friable to nearly loose; medium acid (pH 6.0); abrupt, smooth boundary.
A ₂	1-8	Sand; yellowish gray to very pale orange (10YR8/2); loose; very strongly acid (pH4.8); abrupt, irregular boundary with some tongues extending to a depth of 36 inches.
B ₂₁	8-15	Sand; light brown to strong yellowish brown (7.5YR5/6); very weak, fine, granular; very friable; strongly acid (pH5.5); abrupt, irregular boundary. This horizon is also adjacent to the A ₂ tongues.

B ₂₂	15-23	Sand; light brown to strong yellowish brown (7.5YR5/6); very weak, fine, granular; weakly cemented; slightly acid (pH6.3); gradual, wavy boundary. This horizon is most pronounced at the bottom of the A ₂ tongues where it may extend down to 36 inches.
B ₃₁	23-30	Sand; light brown to dark orange yellow (7.5YR6/6); very weak, fine, granular; nearly loose; slightly acid (pH6.3); gradual, wavy boundary.
B B ₃₂	30-40	Sand; light brown to dark orange yellow (7.5YR6/6); single-grain nearly loose; slightly acid (pH6.3); gradual, irregular boundary.
C ₁	40+	Sand; pale orange yellow (7.5YR8/4); single grain; loose; slightly acid; (pH6.5).

IV. LABORATORY PROCEDURES

Most of the procedures used in the identification and characterization of the clays in this study are described in detail in Soil Chemical Analysis - Advanced Course (Jackson, 1956) and in Soil Chemical Analysis (Jackson, 1958). Soil samples from the A₂ and C₁ horizons of the profile described above, and samples of Wyoming bentonite and of nontronite were analyzed in detail. Samples from the remaining soil horizons were prepared only for X-ray analysis.

Dispersion and Mineral Fractionation

The soil samples were air-dried and passed through a 2-mm. sieve. At least 1000 gm. samples were separated for subsequent analyses.

The soil samples were treated with H₂O₂ for removal of organic matter (Jackson, 1956, p. 35) and with NaOH for removal of amorphous material (Jackson, 1956, p. 529). Free iron oxides were removed from the soil samples by the sodium dithionite-citrate-bicarbonate method of Aguilera and Jackson (1953). All samples were dispersed by 5 minutes

boiling with 2% Na_2CO_3 (Jackson, 1956, p. 73). The <2 micron and <0.2 micron clay fractions were separated with a tube centrifuge (Jackson, 1956, pp. 140-141).

X-ray Diffraction

A Norelco X-ray unit with wide-range goniometer and Brown recorder, CuK_2 radiation (from a Cu target X-ray tube through a Ni filter) operated at 35 Kv. and 20 m amps. was used for scanning parallel-oriented samples on ceramic plates or glass slides. Powder diffraction patterns were obtained with a cylindrical X-ray diffraction camera with a diameter of 114.59mm. and X-ray photographic film mounted on its circumference.

To avoid quartz and feldspar reflections from ceramic plates, a prescribed amount of the clay from the A_2 -horizon was oriented on a glass slide (Jackson, 1956, p. 184). Suitable amounts of the clay from the other samples were deposited on ceramic plates according to the method of Kinter and Diamond (1956). This latter technique orients the plate shaped clay particles, so that the 001 planes of most of the clay minerals are in a position to diffract X-rays thus enhancing this reflection over that of an ordinary powder pattern.

X-ray diagrams were recorded for Mg-saturated, glycerol-solvated, parallel-oriented samples and for K-saturated specimens heated to 300°C and 550°C. Randomly oriented powder samples were prepared essentially according to the procedure outlined by Jackson (1956, p. 188). The powder sample was placed in a thin capillary tube of soft glass and X-rayed for approximately three hours.

The 060 reflections were determined from X-ray powder diagrams and from X-ray diagrams obtained from oriented flakes. The latter method has been discussed by Rich (1957). An oriented clay layer was deposited in a small aluminum dish by evaporation of sodium-saturated and dialyzed clay suspension. The oriented clay layer was peeled off the dish and mounted at right angles to the X-ray beam at the center of a diffractometer. Reflections were scanned in the range of 55-65°, 2 θ with CuK_2 radiation.

Greene-Kelly Test

A test devised by Greene-Kelly (1953b) was used to distinguish octahedrally substituted montmorillonite from

tetrahedrally substituted montmorillonite from beidellite and nontronite. Samples of the A₂-horizon fine clay, Wyoming bentonite, and nontronite were lithium saturated by adding IN LiCl under suction. Excess salt was removed by washing with distilled water, and the samples were heated to 250°C overnight. The samples were then saturated with glycerol and X-ray diagrams were recorded.

Differential Thermal Analysis

Differential thermal analyses of the clays were made using an instrument manufactured by the Robert L. Stone Company, Austin, Texas. The samples were heated at a rate of 13°C per minute to 1000°C. The fine clay of the A₂-horizon was thermally analyzed in air and in nitrogen gas to determine thermal effects due to oxidation of organic material.

Infra-red Analysis

This analysis was made using a Beckman IR7 infra-red spectrophotometer. Films of the Na-saturated clays, having parallel orientation of basal cleavage planes (001) were prepared by evaporating a suspension in aluminum dishes.

The films were mounted at right angles to the infra-red beam and scanned from 600 to 400 cm^{-1} . In the 800 to 2000 cm^{-1} region the samples were also examined after dissemination in KBr pellets at concentrations of 0.6 percent clay.

Total Specific Surface Area

This determination was made by means of the ethylene-glycol method as proposed by Bower and Geschwend (1952).

Cation Exchange Capacity and Its Reduction by Potassium Fixation

A method has been proposed to determine the vermiculite content in clay mixtures. (Submitted for publication by Jackson, M.L. and Alexiades in the Soil Sci. Soc. Amer. Proc). This determination is based on the reduction of CEC due to irreversible collapse of K-saturated vermiculite heated overnight at 110°C and subsequently saturated with NH_4^+ .

Cation-exchange capacity (CEC) is determined as follows: An aliquot containing a 100-mg. organic matter-free, iron oxide-free, CaCO_3 -free (Jackson, 1956) clay sample is placed

in a 20-ml centrifuge tube and washed three times with NaOAc of pH 5 (warmed in hot water bath each time) to insure freedom from Na_2CO_3 and CaCO_3 .

Ca saturation is obtained by washing five times with N CaCl_2 , washing once with H_2O and five times with 99% methanol and finally exchanging the Ca with Mg by five washings of 10 ml. each of N MgCl_2 solution (after 5 minutes of rotational shaking, the tube is filled with distilled water each time before centrifugation). The exchangeable Ca is determined on the extract diluted to 100 ml. with H_2O (approximately 0.5 N MgCl_2 solution) by means of flame emission at 5600 Å. The determined Ca is expressed as m.e. per 100 g. of the oven-dry sample, and is designated as CEC (Ca/Mg).

K saturation of a separate (or the same) 100-mg. sample is obtained by five washings with N KCl , removal of excess salt by washing once with water and five times with 99% methanol. The K saturated sample is dried from 99% methanol in an oven at 110°C . overnight. The unfixed K is exchanged with N NH_4Cl solution as follows. The clay is soaked five minutes with rotary shaking in the first washing, and triturated with a rubber-tipped rod in the

second washing. Subsequent washings (for a total of five) are carried out by rotating the suspended sample for five minutes each time and centrifugation. The displaced K is determined by flame emission at 7740Å. The determined K is expressed as m.e. per 100 g. of the oven-dry sample, and is designated CEC (K//NH₄). The difference between these two determined CEC values gives the interlayer charge of vermiculite (as developed below) and vermiculite percent is given by:

$$\% \text{ vermiculite} = \frac{\text{CEC}(\text{Ca/Mg}) - \text{CEC}(\text{K//NH}_4)}{153.9} \times 100 \quad (1)$$

The foregoing procedure was followed to determine total and reduced CEC of A₂- and C-horizon soil clays, Wyoming bentonite, and nontronite. Difficulties were encountered in determining Ca in 0.5 N Mg Cl₂ and K in 0.5 N NH₄Cl solutions by flame emission. These difficulties were avoided by determining Ca in 0.5 N Mg Cl₂ on a Perkin-Elmer Model 303 Atomic absorption spectrophotometer and by using 1 N NH₄Ac (pH 7), instead of 1N NH₄Cl, to exchange K which was then determined by flame emission on a Coleman flame photometer.

Hydration Properties

Oriented K, Na, Mg, and Ca-saturated samples of the 40.2μ clay fraction of the A₂-horizon, Wyoming bentonite, and nontronite were X-rayed when moist (100% R.H.) and after drying for 3 weeks at 40% R.H. and 20°C.

Acid Dissolution for Determination of Tetrahedral Aluminum

The acid dissolution method of Osthaus (1956) as modified (Brydon, et al, 1961) was used to determine tetrahedral Al. Ten 80 mg samples (larger samples if more clay were available) of A₂-horizon soil clay and 50 ml. of hot 30% HCl were added to Erlenmeyer flasks in a boiling water bath. The samples were treated for 5, 15, 30 minutes, 1, 2, 3, 4, 5, and 7 hours. After each treatment time the sample was immediately quenched in cold water. The supernatant solution was separated by centrifuge and added to a 200 ml. volumetric flask. The clay was washed twice with distilled water, and the washings were added to the flask. The aluminon method (Jackson, 1958, pp. 297-300) was used to determine Al. The dissolved Al was subtracted from the

total Al initially present. The logarithm of the undissolved Al was plotted versus time and the straight line obtained at 3 hours was extrapolated to zero time to obtain the value of tetrahedral Al.

Total Chemical Analysis

The semi-micro system described by Jackson (1958, Chapter 11) was followed for total chemical analysis of the clays. Total Si and Al were determined after fusion with Na_2CO_3 (Jackson 1958, Fig. 11-2, p. 280). The molybdosilicic acid colorimetric procedure (Jackson 1958, pp. 294-297) and the aluminon method (Jackson, 1958, pp. 297-300) were used for Si and Al, respectively. The HF decomposition procedure (Jackson 1958, Fig. 11-1, p. 279) was followed for elemental analysis of K, Na, Mg, Ca, and Fe. Both K and Na were determined by flame emission, using a Coleman flame photometer; Mg and Ca were analyzed using a Perkin-Elmer Model 303 atomic absorption spectrophotometer. Fe was determined using the o-phenanthroline method (Jackson 1958, pp. 389-391).

Calculation of Montmorillonite Formulas

The methods of calculation of mineral formulas used were essentially the same as those described by Ross and Hendricks (1945). The methods, including modifications, are explained and illustrated by a calculation of an analysis in the discussion of results.

Electron Microscope Examination

An RCA electron microscope was used to obtain transmission micrographs of $<0.2\mu$ clay particles from the Deer Park A₂-horizon. A Formvar specimen supporting film was formed essentially according to the method described by Jackson, 1956, p. 422. The clay suspension was treated with H₂O₂ to remove organic growth, washed with NaCl to remove H₂O₂ and dialyzed until free of solutes according to the rapid dialysis method (Jackson 1956, p. 423). The suspension was then sprayed onto the organic supporting film as a fine fog produced in a nebulizer.

V. RESULTS AND DISCUSSION

X-ray Diffraction Analyses of Clay Fractions

Figure 1 shows the locations of the soils from which the clay fraction ($< 2\mu$) of A_2 -horizons were obtained. Figure 2 shows the corresponding X-ray diffraction diagrams of oriented Mg-saturated, glycerol-solvated clay films. The strong peaks at $17.7\overset{\circ}{\text{\AA}}$ indicate that montmorillonite is the dominant clay mineral in the $< 2\mu$ clay fraction of the A_2 -horizons of all the sites sampled. Small peaks at about $31\text{\AA}$ in the X-ray diagrams of samples 1, 2, and 7 reflect regular interstratification of montmorillonite with chlorite or vermiculite.

The similarity of the X-ray diffraction diagrams obtained from the soils at the various locations, points to a uniform weathering sequence resulting in formation of montmorillonite in the A_2 -horizons of the sandy soils in this area of Northern Michigan.

Deer Park sand

The soil at location 1 was selected for further study. X-ray diffraction diagrams of the $< 2\mu$ clay fractions are

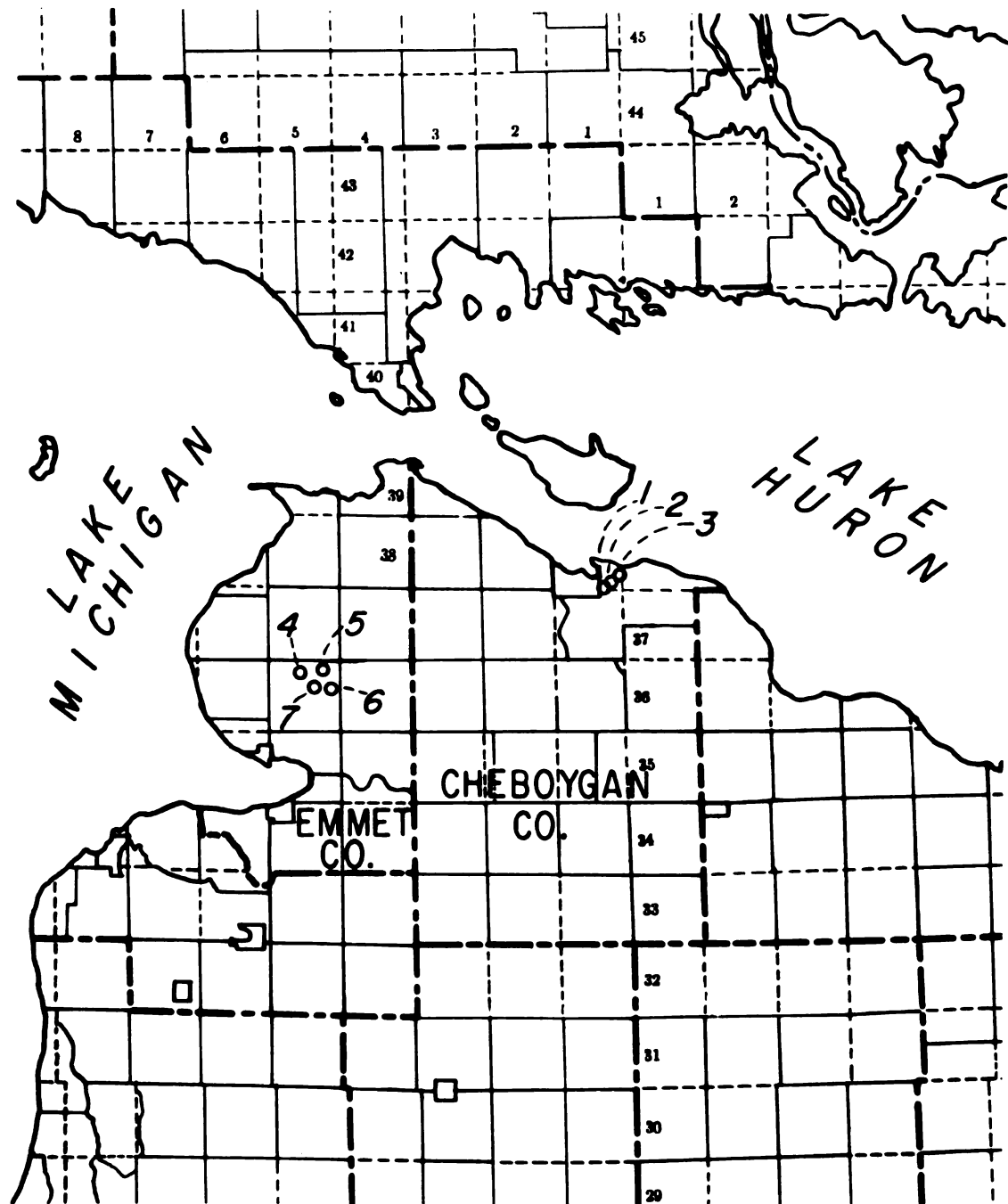


Figure 1. Locations of sites sampled in preliminary investigation

Figure 2. X-ray diffraction tracings of $< 2\mu$ clay fractions. Treatment: Mg-saturated, glycerol solvated. Samples taken from A_2 -horizons at correspondingly numbered locations shown in Figure 1. Scale factor is 8.

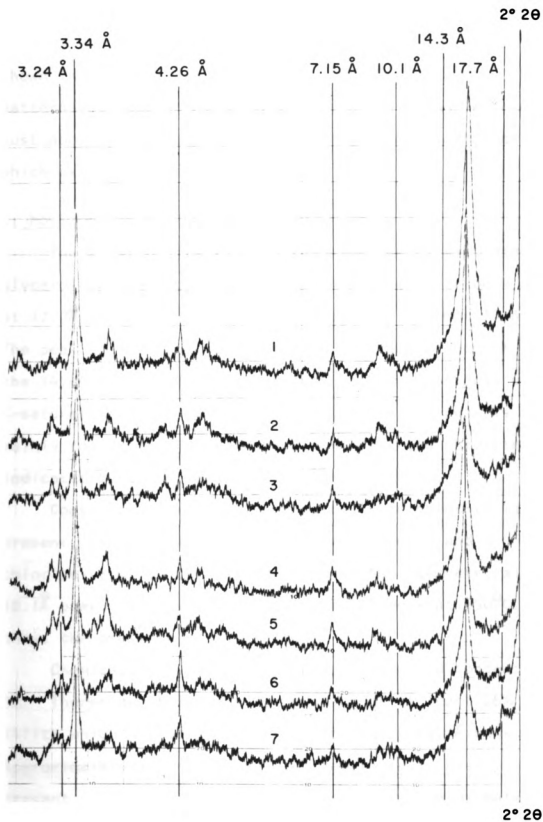


Figure 2

shown in Figure 3 for the A_2 , B_{22} , and C_1 horizons. The patterns designated A_2 (tongues) refer to a sample taken just above the lower boundary of tongues of the A_2 -horizon which extend to a depth of over 36 inches.

C_1 horizon

The X-ray diffraction patterns of the Mg-saturated, glycerol-solvated clay of the C_1 -horizon gives a peak at $17.7\text{\AA}$ which shows the presence of some montmorillonite. The peak at $10.1\text{\AA}$ indicates illite. Disappearance of the $14.4\text{\AA}$ peak and re-enforcement of the $10.1\text{\AA}$ peak upon K-saturation and heating show that the $14.4\text{\AA}$ peak is due mainly to vermiculite, although some discrete chlorite is indicated by this peak after heating to 300°C .

Considerable randomly interstratified chlorite is present, probably as chlorite-montmorillonite and chlorite-vermiculite, as indicated by the asymmetrical $10.1\text{\AA}$ peak. Disappearance of the $7.15\text{\AA}$ peak at 550°C shows the presence of kaolinite.

Chemical analysis of this clay gave a K_2O content of 3%. Therefore, this clay is composed of at least 26% illite which is not evident from the small $10.1\text{\AA}$ peak. Approximately 20% quartz and 10% kaolinite is also present. The remaining 40% is taken up in approximately

equal proportion by vermiculite, montmorillonite, and chlorite. Most of the chlorite present appears to be randomly interstratified with vermiculite and montmorillonite.

B₂₂ horizon

The X-ray diffraction patterns of the Mg-saturated glycerol solvated clay of the B₂₂ horizon shows a relatively strong peak at 14.3⁰Å and a small peak at 7.1⁰Å. Upon heating, the 14.3⁰Å peak shifts to a broad 10.1⁰Å peak, indicating Al-interlayering in vermiculite (Shawhney, 1960); at 550°C. the 7.1⁰Å peak disappears, indicating kaolinite. No discrete chlorite is shown to be present, but some chlorite, randomly interstratified with vermiculite, may contribute to the broadening of the 10.1⁰Å peak upon heating.

The presence of illite is not apparent from the X-ray patterns, but could be at least 25% according to chemical analysis of the clay fraction of a similar soil by Franzmeier (1962). The approximate amounts of other clay minerals are estimated as follows: vermiculite 35%, quartz 20%, randomly interstratified chlorite-vermiculite 15%, kaolinite 5%.

A₂ (tongues)

The X-ray patterns show strong peaks at 17.7⁰Å and 14.3⁰Å which collapse to 10.1⁰Å upon heating, indicating

that the clay in the tongues of this horizon is largely vermiculite and montmorillonite. Some kaolinite is also present.

Approximate quantities of the clay minerals present are estimated as follows: montmorillonite 30%, vermiculite 20%, illite 20%, (from chemical analysis of the $<0.2\mu$ fraction of the A_2 -horizon) quartz 20%, kaolinite 5%, and randomly interstratified chlorite-vermiculite and chlorite-montmorillonite 5%.

A_2 -horizon

The X-ray patterns of this horizon give a strong $17.7\text{\AA}$ peak which collapses to $10.1\text{\AA}$ upon heating indicating that montmorillonite is about the only layer silicate present in the clay of this horizon. However, chemical analysis shows that the $<2\mu$ clay of this horizon contains approximately 20% illite. Disappearance of the small $7.1\text{\AA}$ peak at 550°C . gives evidence of some kaolinite.

Approximate quantities of clay minerals estimated are: montmorillonite 55%, illite 20%, quartz 20%, kaolinite 5%.

Assuming that the intensity of weathering increases from the C_1 horizon upward to the surface of the soil, the horizons of the profile, shown in Figure 3, clearly illustrate the weathering sequence:

Figure 3. X-ray tracings of 2 clay fraction of the indicated horizons of the Deer Park profile. Treatments: 1) Mg-saturated, glycerol solvated; 2) K-saturated and heated to 300°C; 3) K-saturated and heated 550°C. Scale factor is 8.

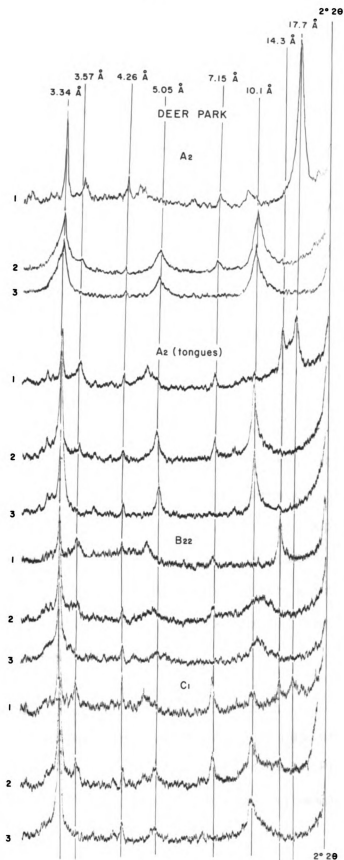
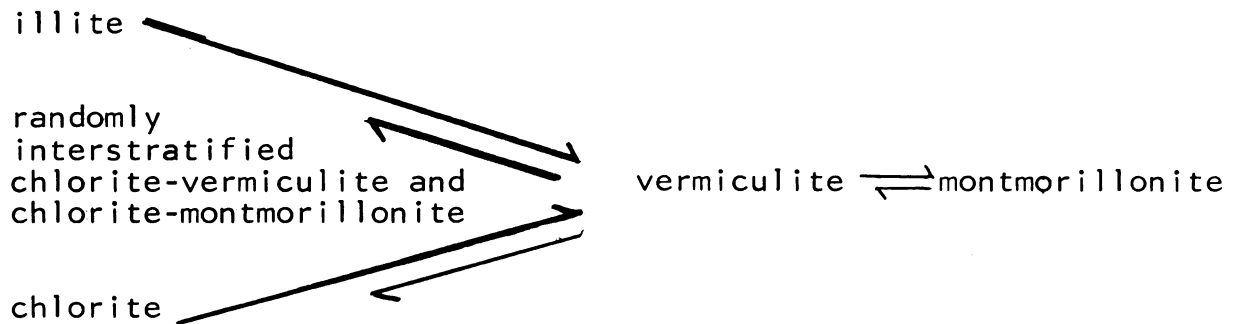


Figure 3



In the presence of adequate K, Al, and Mg, the reaction may be reversible.

Beavers, et al, (1954) concluded that the dominant montmorillonite component in the surface horizons of some Illinois soils is largely derived from loess blown in from the montmorillonitic soils and sediments of the Great Plains region. However, the clay mineral distribution in the Deer Park profile, especially the preponderance of vermiculite and montmorillonite in the A_2 tongues at depths near the upper boundary of the C_1 horizon, indicates that the montmorillonite in the A_2 -horizon of this profile has formed in situ and is not due to deposition of montmorillonite-rich, wind-blown material.

Clay fraction smaller than 0.2 microns

Figure 4 shows X-ray diffraction patterns of the fine clay obtained from the A_2 -horizon of Deer Park sand. X-ray patterns of the fine clays from Wyoming montmorillonite,

Figure 4. X-ray diffraction tracings of $< 0.2\mu$ clay fractions. Treatments: 1) Mg-saturated glycerol-solvated; 2) K-saturated and heated to 300°C ; 3) K-saturated and heated to 550°C . A is Wyoming bentonite; B is nontronite; C is A_2 -horizon clay; D is C_1 -horizon clay. Insets show 060 spacings of A, B, and C clays. Scale factor is 8.

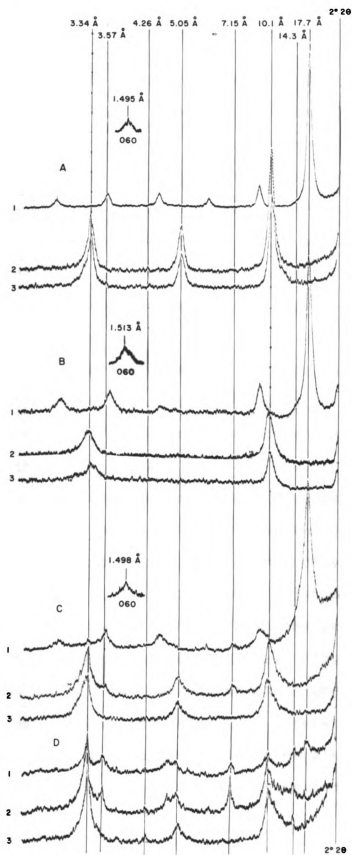


Figure 4

nontronite and the C₁-horizon of Deer Park and are included for comparison. All clay fractions are smaller than 0.2 micron. The A₂-horizon fine clay was deposited on glass slides to avoid quartz and feldspar reflections from ceramic plates. The other clays were oriented on ceramic plates.

As shown in Figure 4 the X-ray diffraction patterns of the A₂-horizon clay, nontronite, and Wyoming bentonite are similar and emphasize the dominant montmorillonite content of the A₂-horizon clay.

The X-ray pattern of the Mg-saturated, glycerol-solvated, A₂-horizon fine clay shows only little evidence of a 10.1Å peak for illite, although this clay contains 2.6% non-exchangable K₂O and thus at least 20% illite, as was determined by chemical analysis. Disappearance of the small 7.1Å peak at 550°C. indicates the presence of a small amount of kaolinite. Since this clay was deposited on a glass slide, the small 3.34Å peak shown in the Mg-glycerol X-ray pattern reflects the presence of a small amount of quartz in the fine clay. The symmetry of the 001 peak and the rationality of the higher orders of the 001 plane indicate the absence of interstratification.

The approximate amounts of clay minerals in the fine clay fraction of the A₂-horizon are estimated to be:

montmorillonite 70%, illite 22% (from chemical analysis), quartz approximately 7% and less than 3% kaolinite.

The X-ray diffraction patterns from the $<0.2\mu$ C₁-horizon clay appear similar to those from the $<2\mu$ C₁-horizon clay shown in Figure 3 and discussed in the previous section. The X-ray patterns of the smaller-size clay indicate less quartz and kaolinite, these two minerals commonly being more concentrated in the coarse clay fraction.

The (060) spacings shown in Figure 3 are near 1.50A and indicate that these clays are dioctahedral.

Randomly oriented powder samples

Table 1 shows X-ray powder data for the Mg-saturated A₂-horizon fine clay with interlayer glycerol. Calculated and observed values for beidellite, reported by Weir and Greene-Kelly (1962), are compared with values obtained for the fine clay of the A₂-horizon.

The diffraction data reported by Weir and Greene-Kelly include several reflections not observed in the powder diffraction patterns of the soil clay. Most of these reflections are also in addition to those observed for montmorillonites (MacEwan, 1961). However, Greene-Kelly

Table 1. X-ray diffraction powder data for Mg-A₂-horizon fine clay and Ca-B.J.M. beidellite with inter-layer glycerol.

d(calc.)Å (orthorhombic pseudo hexagonal)	d(obs.)Å Ca-B.J.M. beidellite	I	d(obs.)Å Mg-A ₂ - horizon-clay	I	hkl
--	17.57	10	17.70	10	001
4.48 } 4.35 }	4.42	10	4.45	10	{ 020, 110 021
3.99	3.95	10			022
3.56	3.54	10			023
3.15	3.17	2	3.33*	10	024
2.77	2.76	1			025
2.59 } 2.56 }	2.57	8	2.57	10	{ 200, 130 201
2.48	2.52	10			202
2.37	2.36	8	2.36	5	203
2.23 } 2.24 }	2.24	2	2.24	2	{ 204 040, 220
2.22 } 2.17 }	2.19	2			{ 041 042
1.695 } 1.687 }	1.693	6	1.693	6	{ 240, 310, 150 241
1.664	1.663	8	1.656	6	242
1.628	1.623	6			243
1.581	1.573	1			244
1.526	1.528	1			245
--	1.498	10	1.494	10	060, 330

d(calc.) ^o Å (orthorhombic pseudo hexagonal)	D(obs.) ^o Å Ca-B.J.M. beidellite	1	d(obs.) ^o Å Mg-A ₂ - horizon-clay	1	hkl
1.295	1.293	8	1.293	6	400,260
1.244	1.243	8	1.245	6	420,350,170
1.121	1.122	2			440,080
0.979	0.979	2			460,530,190
0.863	0.864	4			390,600

*Interpreted as quartz reflection

was able to index these additional reflections as the 021, 201, 041, and 241 series by reference to an orthorhombic pseudo-hexagonal unit cell. Calculated values of spacings for such a cell are given in the first column of Table 1 and the appropriate indices in the sixth. The scale of relative intensities (I) ranges from a minimum of 0 to a maximum of 10.

The agreement between calculated spacings and spacings observed for the B.J.M. beidellite and A_2 -horizon fine clay is good and gives evidence that the A_2 -horizon fine clay is a beidellite.

Application of Greene-Kelly Test

The X-ray diagrams in Figure 5 show that the Li-saturated Wyoming montmorillonite, when heated to 250°C. overnight, does not re-expand upon glycerol solvation but has reverted to an internally-compensated and non-expanding pyrophyllite-type mineral having an 001 spacing of 9.5A. Nontronite and the A_2 -horizon fine clay, similarly treated, expand to the 17.7A, 001 montmorillonite spacing.

The broadening of the peaks in the 10A, 5A, and 3.5A regions, shown in the X-ray pattern of the A_2 -horizon fine clay may be attributed to the presence of illite in the sample or the collapse of some layers to 9.5A or to both. However, the symmetry of the 001 peak indicates that such collapse has been negligible.

Figure 5. X-ray diffraction tracings of $< 0.2\mu$ clay fractions illustrating Greene-Kelly test. Treatments: Li-saturated, heated to 250°C , and then glycerol solvated. A is Wyoming bentonite; B is nontronite; C is A_2 -horizon clay. Scale factor is 8.

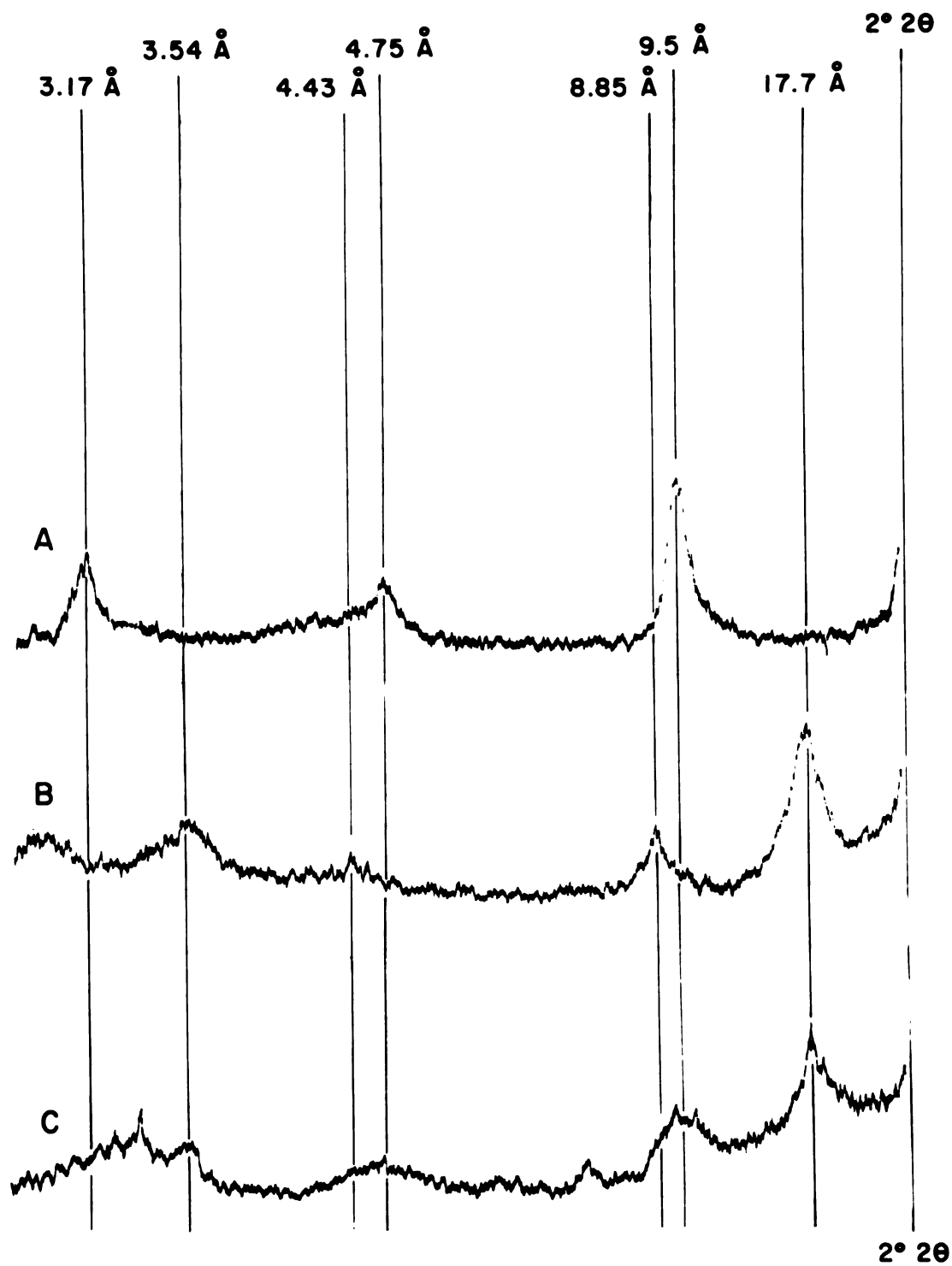


Figure 5

According to Greene-Kelly (1953), the positive test obtained in Wyoming montmorillonite indicates that in this clay mineral most of the charge is located in the octahedral layer. Upon dehydration, the predominantly octahedral charge attracts the small positive lithium ions into vacant octahedral sites, thus irreversibly reducing the charge with attendant loss of cation exchange capacity, surface area, and swelling properties.

A negative test indicates that most of the charge is located in the tetrahedral layer. Lithium ions are not retained in the octahedral layer, and no loss of cation exchange capacity, surface area and swelling properties occurs.

The test serves to distinguish octahedrally substituted montmorillonites from beidellites and nontronites. Such montmorillonites give a positive test; beidellites and nontronites give a negative test. Therefore, according to the test, the A₂-horizon fine clay is a beidellite. The dominant octahedral charge of Wyoming montmorillonite and the dominant tetrahedral charge of nontronite, which are known, confirm the effectiveness of the test.

Differential Thermal Analysis

Figure 6 shows differential thermal analysis curves for the fine clays of Wyoming bentonite, nontronite, and the A₂-horizon. The curve of the Ca-B.J.M. beidellite (Weir and Greene-Kelly, 1962) is included for comparison. The soil clay was heated in air and in N₂ to determine thermal effects due to oxidation of organic material. Table 2 contains data for peak temperatures.

All of the curves show the large low-temperature endotherm between 100°C. and 300°C. which is characteristic of minerals belonging to the montmorillonite group.

Wyoming montmorillonite gives an endothermic peak, due to dehydroxylation, at 740°C. and another at 915°C., due to breakdown of the dehydrated structure. Recrystallization to oxides and spinel gives an exotherm at 970°C.

The A₂-horizon fine clay heated in N₂, gives its main dehydroxylation peak at 560°C., a less pronounced endothermic peak at 830°C., and an exothermic peak at 960°C. The sample heated in air gives a broad exothermic peak at 380°C. which may be interpreted as being due to oxidation of organic matter remaining after the H₂O₂ treatment.

Nontronite gives a dehydroxylation peak at 530°C. and an exothermic peak at 985°C. The high temperature endotherm is absent which may be explained by simultaneous decomposition of the dehydrated structure and recrystallization to hematite or magnetite.

Figure 6. Differential thermal analysis curves of the $<0.2\mu$ clay fraction. A is Wyoming bentonite; B is A₂-horizon clay (heated in N₂); C is nontronite; D is A₂-horizon clay (heated in air); E is beidellite from the Black Jack Mine, Idaho (Weir and Greene-Kelly, 1962). All samples Na-saturated except E which was Ca-saturated.

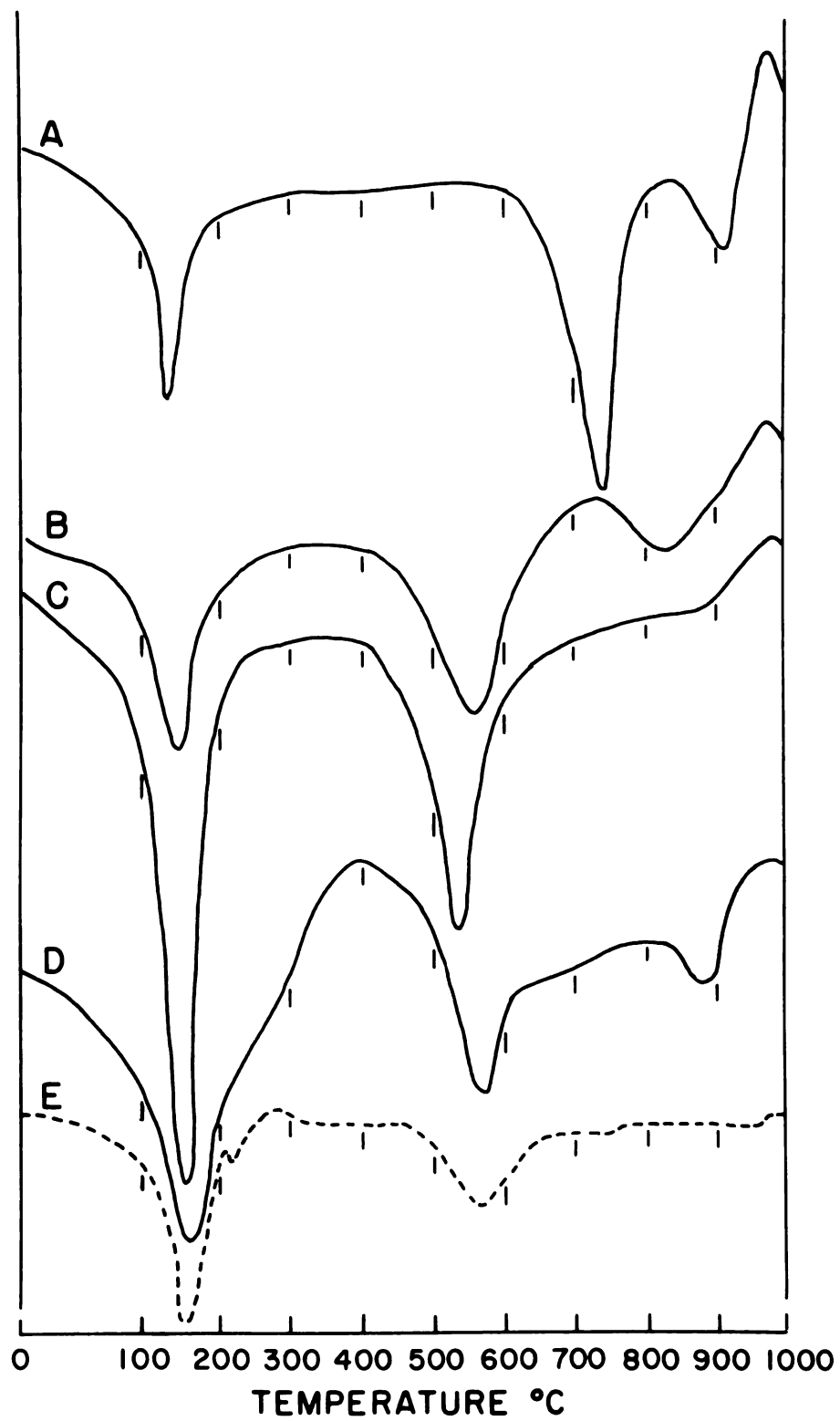


Figure 6

Table 3. Peak temperatures ($^{\circ}\text{C}$) in the differential thermal analysis of $<0.2\mu$ clays

Clay Mineral	1st End.	2nd End.	3rd End.	Exo.
Na-Wyoming montmorillonite	135	740	915	970
Na-A ₂ -horizon clay (in N ₂)	150	560	830	960
Na-A ₂ -horizon clay (in air)	155	565	880	980 (not distinct)
Na-nontronite	155	530	--	985
Ca-B.J.M. beidellite	140, 210	560	--	970

The differences in dehydroxylation endotherm temperatures have been attributed to variation in composition of the octahedral layer (Grim and Rowland, 1942; Kelley and Page, 1942). According to these authors the temperature of dehydroxylation increases from 420°C. to 650°C. to 890°C. as the composition of the 2:1 octahedral layer varies from high Fe to high Al to high Mg. However, in many studies (Greene-Kelly, 1961), including the one reported here, montmorillonites containing little Fe but much Al give a main dehydroxylation peak near to that of nontronite. It also seems to be established that the presence of Fe alone does not lower the peak temperature since the presence of 1.9 Fe ions per unit cell in an iron-rich montmorillonite from Japan does not alter the thermal curve (Sudo and Ota, 1952).

Greene-Kelly (1961), comparing thermal curves of several dioctahedral clay minerals belonging to the montmorillonite group, directs attention to the fact that all except octahedrally-substituted montmorillonites give their main dehydroxylation peak in the 500°C. region and all except montmorillonite owe their charge predominantly to tetrahedral substitution. The same conclusion may be drawn from a comparison of the curves in Figure 6. It seems logical, therefore, to correlate decrease in dehydroxylation temperature with increase in tetrahedral substitution.

Infra-red Analysis

Figure 7 and Table 3 show infra-red absorption data of the clays as indicated. The data obtained for the clays used in this experiment are compared to data taken from the literature for the clays marked with an asterisk. The broken curves in Figure 7 and the solid curves in Figure 8 are of samples examined as oriented films; the solid curves in Figure 7 are of samples disseminated in KBr pellets at concentrations of 0.6 percent before examination.

Although some progress has been made in relating variations in infra-red absorption to variations in structure and composition of clay minerals within the montmorillonite group, much uncertainty still remains. (Farmer and Russell, 1964). Therefore, except for the assignment of certain data to types of bonds and vibrations shown in Table 3, no attempt is made here to analyze in detail the structure and composition of the clays used in this experiment by means of their infra-red spectra. Instead, the data obtained in this analysis are compared to data from the literature for clay minerals having a well-known structure and composition. Thus agreement of data for the A₂-horizon fine clay with data for beidellite gives evidence as to the identity of the A₂-horizon clay. Agreement of data for Wyoming bentonite and nontronite with data from the literature for the same clay minerals indicates the reliability of the comparisons.

Figure 7. Infra-red analysis curves of the $<0.2\mu$ clay fraction. Treatments: Na-saturated and air-dried. Solid curves represent spectra from KBr pellets; broken curves represent spectra from films. A is Wyoming bentonite; B is A₂-horizon clay; C is nontronite.

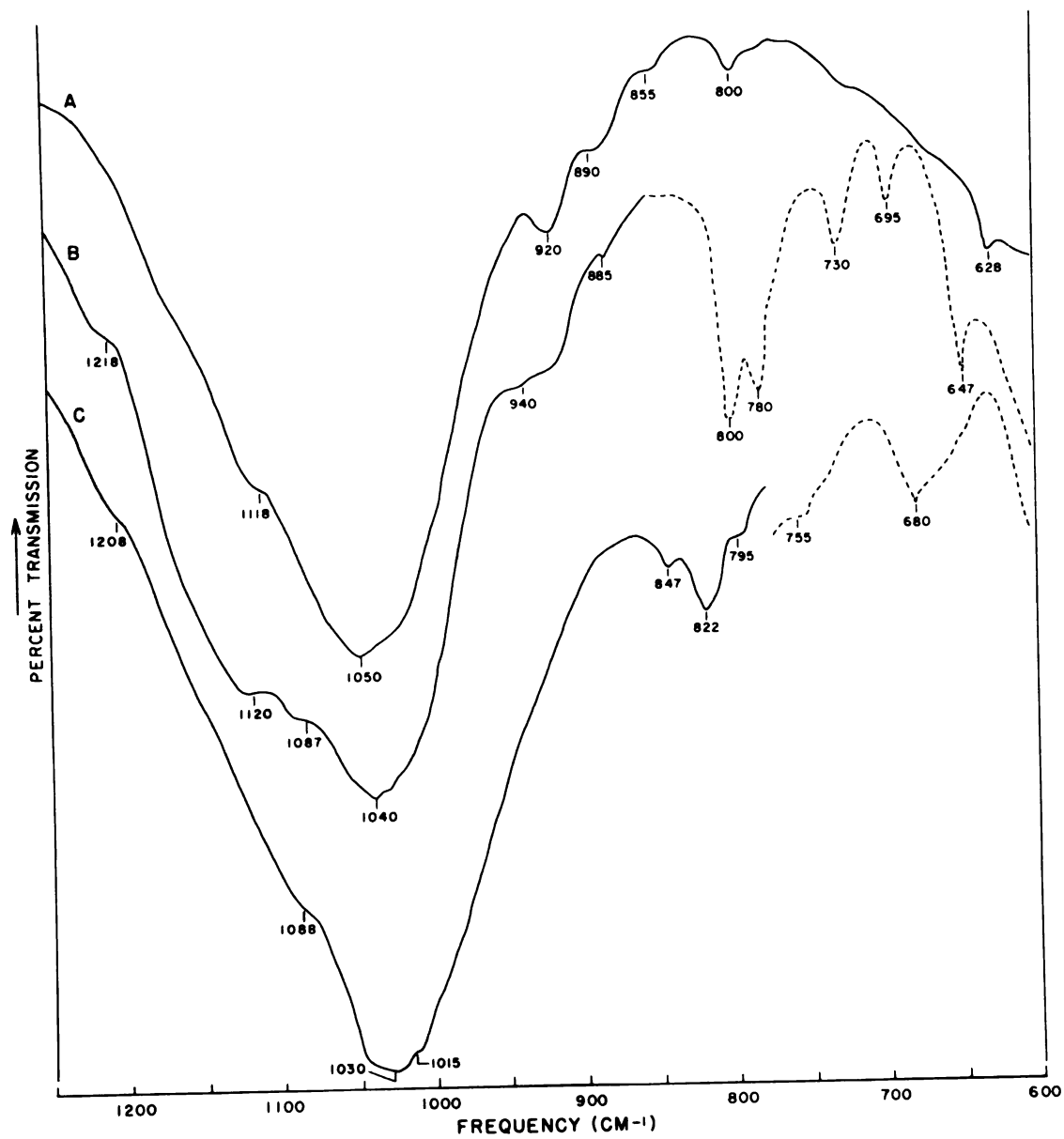


Figure 7

Figure 8. Infra-red analysis curves of $<0.2\mu$ clay fraction. Treatments: Na-saturated and air-dried. Curves represent spectra from KBr pellets. A is Wyoming bentonite; B is A₂-horizon clay; C is nontronite.

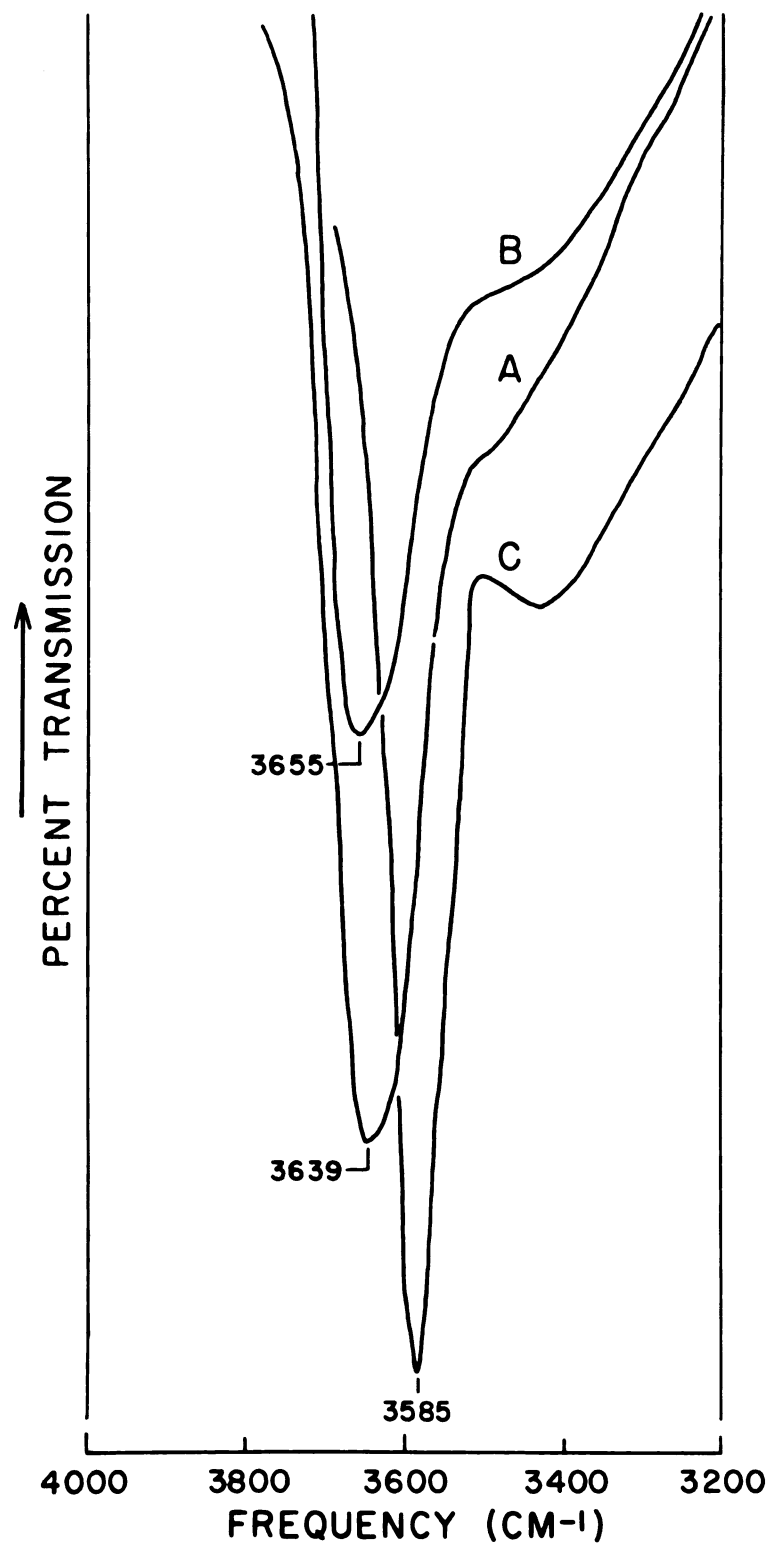


Figure 8

As shown in Table 3, good agreement exists between data obtained in this study and data obtained from the literature for Wyoming bentonite and nontronite. The absorption bands for the A₂-horizon fine clay, especially the strong Si-O peak at 1040cm^{-1} and the O-H peak at 3655cm^{-1} correspond to those given for beidellite in the literature. The doublet peak at 780cm^{-1} and 800cm^{-1} in the spectrum of the fine clay of the A₂-horizon indicates the presence of some quartz. This agreement provides evidence that the fine clay of the A₂-horizon is a beidellite.

Cation Exchange Capacity and its Reduction by Potassium Fixation

Table 4 shows the results of cation exchange capacity (CEC) and total specific surface measurements. The CEC were determined using Ca as the saturating cation and Mg Cl₂ as the replacing reagent.

The relatively low CEC of the C₁-horizon fine clay indicates that this clay contains some non-expanding clay minerals. The specific surface of this clay appears high, which may be due to incomplete removal by NaOH treatment of amorphous material having a large specific surface.

An experiment was carried out to investigate the potassium fixation capacity of the clays listed in Table 5. The clays were saturated with potassium, washed with methanol, and dried

Table 3. Frequency (Cm^{-1}) of the Infra-red Absorption Bands

	A2-horizon clay	Beidellite*	Wyoming		Nontronite	Nontronite*
			Bentonite	Bentonite*		
Si-O stretching	1120		1118	1120	1088	1091
	1087	1084	-	1080	1030	1034
	1040	1041	1050	1048	1015	1017
	-	1022	-	1025		
R-O-H bending	940	942	920	920	847	848
	885	872	890	890	822	818
			855	849	795	786
	800 quartz	819	800	800	755	753
	780 doublet	776				
	730	729				
	695	693				
O-H stretching	647					
	-	-	628	622	680	680
	3655	3660	3639	3632	3585	3564

58

*Data taken from the literature (Farmer and Russell, 1964)

Table 4. Cation-exchange capacity and total specific surface of $<0.2\mu$ clays

Sample	Cation exchange capacity me/100g.	Specific surface M ² /g.
A ₂ -horizon	91	730
Wyoming bentonite	87	1137
Nontronite	102	995
C ₁ -horizon	25	402

Table 5. Cation exchange capacity and 001 spacing of $<0.2\mu$ clays after K-saturation and heating to 110°C overnight and resaturation with NH₄

Sample	Cation exchange capacity me/100g.	Reduction in cation exchange capacity me/100g.	001 spacing (Å)
A ₂ -horizon	55	36	random inter-stratification of collapsed (10Å) and expanded layers
Nontronite	90	12	12.8
Wyoming bentonite	87	0	14.8
C ₁ -horizon	18	7	--

at 110°C. overnight. The cation exchange capacities were then determined by exchanging the K with NH_4Ac as replacing reagent. The values obtained are shown in column 1 of Table 5. The difference between the CEC values before (Table 4) and after this treatment (Table 5) gives the reduction of CEC shown in column 2, Table 5.

Samples of the clays were also oriented on ceramic plates, saturated with KCl, washed with 99% methanol to remove excess salt, and then dried at 110°C. overnight. After oven drying, the clay films were saturated with NH_4 by adding NH_4Cl under suction, washed with water to remove excess salt, and then X-rayed at 100% relative humidity. The 001 spacings are shown in Figure 9 and Table 5.

These data show that the reduction in CEC is correlated with a decrease in 001 spacings. The decreased CEC, therefore, may be attributed to incomplete expansion of K-saturated, oven-dried 2:1 swelling clays upon NH_4 saturation, resulting in incomplete replacement of NH_4 for K in the exchange reaction. Thus, under the conditions of this experiment, the K not exchanged by NH_4 may be designated as fixed K.

It is well known that vermiculite collapses irreversibly upon K saturation and drying. Therefore, the reduction in the CEC of the C_1 -horizon fine clay may be explained by the irreversible collapse of vermiculite shown to be present in

Figure 9. X-ray diffraction tracings of K-saturated, heated, and NH_4 resaturated clays. A is A₂-horizon clay; B is nontronite; C is Wyoming bentonite. Scale factor is 8.

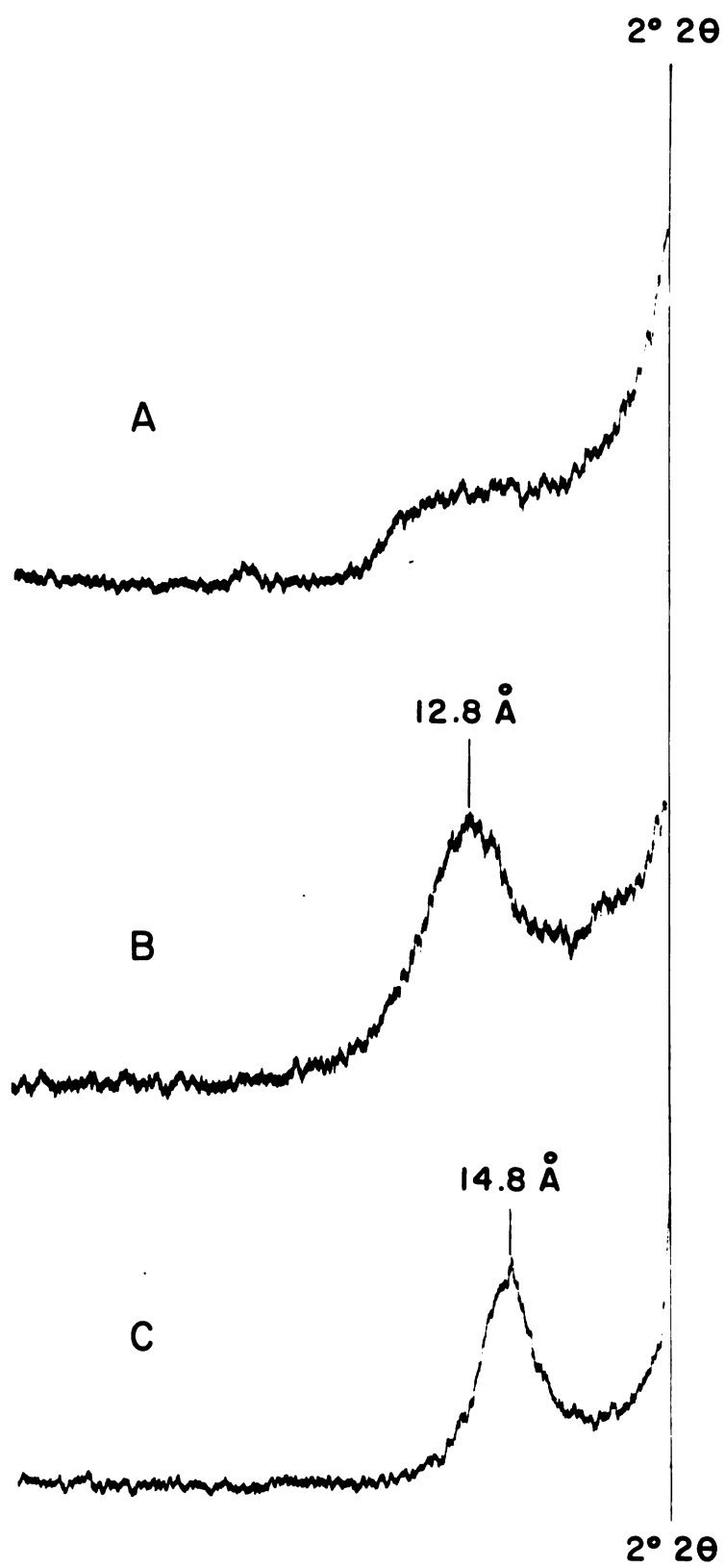


Figure 9

this clay by X-ray data (Figure 4). If the assumption is made that this irreversible collapse is restricted to vermiculite the amount of this clay mineral present in the sample could be calculated from the reduction in cation exchange capacity.

However, a comparison of the reduction in CEC of the fine clays from the A₂-horizon, nontronite, and Wyoming bentonite, shows that the CEC of Wyoming bentonite remains the same, whereas the CEC of the A₂-horizon fine clay and nontronite are reduced. Since these data were consistent in three repeated determinations, and since the X-ray tracings of neither the A₂-horizon clay nor the nontronite (Figure 4) indicate the presence of vermiculite in these clays, experimental error and irreversible collapse due to vermiculite cannot account for the reduced CEC values observed. Therefore, the assumption that K-fixation is restricted to vermiculite is in error and cannot be used as the basis for calculating the amount of vermiculite in the sample.

Further analysis of the data in Table 5 and Figure 9 shows that decrease of CEC and of 001 spacing occurs in the A₂-horizon clay and in nontronite which have high total and tetrahedral charge. The CEC of the Wyoming bentonite, which has a lower and predominantly octahedral charge is not affected by the treatment. Therefore, the logical conclusion is that

K-fixation and reduction in CEC is correlated with the source and amount of the charge on the clay mineral. The tetrahedral charge, being close to the interlamellar K ions has a greater capacity to fix these ions than has the octahedral charge which is farther removed from the interlamellar surfaces.

The higher total charge of the fine clay of the A₂-horizon may account for the greater reduction of its CEC as compared to that of nontronite.

Hydration Properties: Basal Spacings With Water

Figure 10 shows X-ray diffraction patterns at the relative humidities indicated for A₂-horizon soil clay, Wyoming bentonite and nontronite saturated with different cations. Table 6 contains the corresponding basal spacings in Angstrom units (Å).

Random interstratification due to interlayering of different "hydrates" with different spacings is shown in the broadening of the 001 peaks which are designated (br) in Table 6. Assuming that the broadened peaks resulted from random alternation of two different hydrates, the centers of the peak represent the approximate weighted mean of the spacings actually present.

Figure 10. X-ray tracings showing basal spacings of $<0.2\mu$ clay fraction at 100% and at 40% relative humidity. Treatments: Saturated with Na(1), K(2), Mg.(3), Ca(4). A is A₂-horizon clay; B is Wyoming bentonite; C is nontronite. Scale factor is 8.

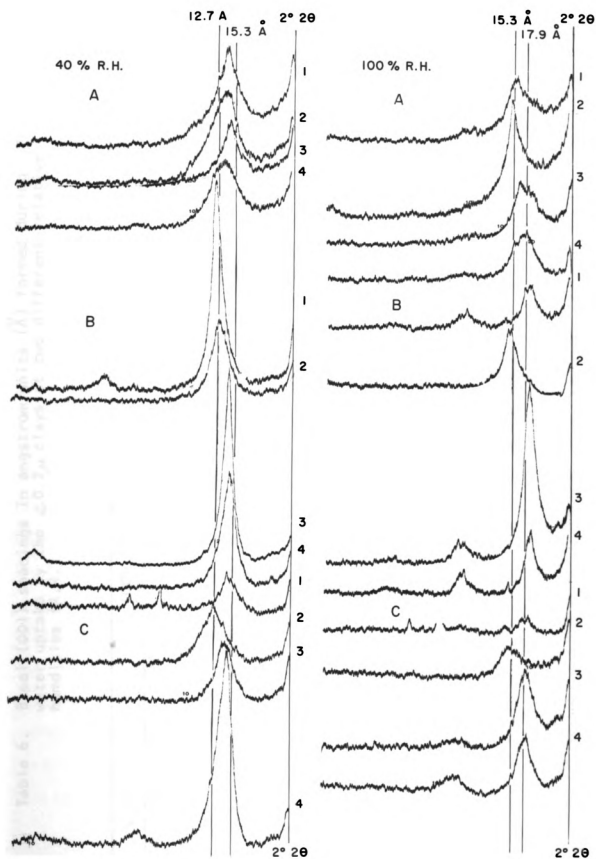


Figure 10

Table 6. Basal (001) spacings in angstrom units ($\text{\AA}$) formed during water uptake by the $<0.2\mu$ clays at two different relative humidities (R.H.)

Clay	100% R.H., 20°C				40% R.H., 20°C				
	Interlayer cation	Na	K	Mg	Ca	Na	K	Mg	Ca
A ₂ -horizon		15.5	15.0	15.8	17.7 br	14.1	13.8 br	14.5 br	13.9 br
Wyoming montmorillonite		19.2 br	14.8	18.8	18.9	12.4	12.8	14.5	14.3
Nontronite		18.4 br	14.8	18.1	18.4	14.3	12.6	14.0 br	14.5

The results show that at 100% relative humidity (R.H.) less water is absorbed by the Na, Mg, and Ca-soil clay than by the Wyoming bentonite and nontronite with the same ion species.

These results are in agreement with those of Marshall (1936) in his early studies on beidellite. He explained the limited swelling of beidellite as compared to that of montmorillonite, both having the same exchange capacity, by assuming that in beidellite the predominantly tetrahedral charge in the outer silica layers holds the units more closely together and limits the entrance of water and consequently the expansion as well. The predominantly octahedral charge in many montmorillonites is farther removed from the inter-lamellar surfaces and is not strong enough to prevent expansion and entrance of water.

This explanation would account for the difference in basal spacings between the soil clay and Wyoming bentonite but not between the soil clay and nontronite, which also has most of its charge in the tetrahedral layer but expands to a greater extent than the soil clay. Foster (1953) also found no correlation between differences in the source of charge and the degree of swelling. The smaller basal spacing of the K-clays at 100% R.H. may be explained by the tendency of 2:1

layer silicates to tightly absorb K ions, since they fit into the hexagonal cavities of the oxygen network of the silica sheets.

At 40% R.H., the basal spacing of some of the clays is close to $14.3\text{\AA}$ which indicates that two molecular layers of water are absorbed between the interlamellar surfaces of the clays. The basal spacings of Na- and K-Wyoming montmorillonite and of K-nontronite are close to $12.5\text{\AA}$ which indicates the absorption of one molecular layer of water.

Chemical Determination of Tetrahedral Aluminum in the $<0.2\mu$ Clay Fraction of the Deer Park A₂-Horizon

Because of the assumptions involved in the corrections for mica and quartz contents prior to the calculation of the structural formula of the fine clay of the A₂-horizon, a chemical method was used to determine the proportion of aluminum present in the octahedral and tetrahedral layers. Samples of the fine clay of the A₂-horizon were digested for the periods of time indicated in Figure 11. The percent Al₂O₃ left in the residue and the corresponding digestion times are given in Table 7. The semilogarithmic plot of these data are shown in Figure 11.

Table 7. Dissolution of aluminum of the $<0.2\mu$ clay fraction of the Deer Park A₂-horizon at various acid-treatment times

Treatment time	Percent Al ₂ O ₃ left in residue
0 minutes	27.9
5 minutes	24.6
15 minutes	24.2
30 minutes	20.4
1 hour	18.2
2 hours	14.7
3 hours	12.7
4 hours	10.5
5 hours	8.70
7 hours	6.06

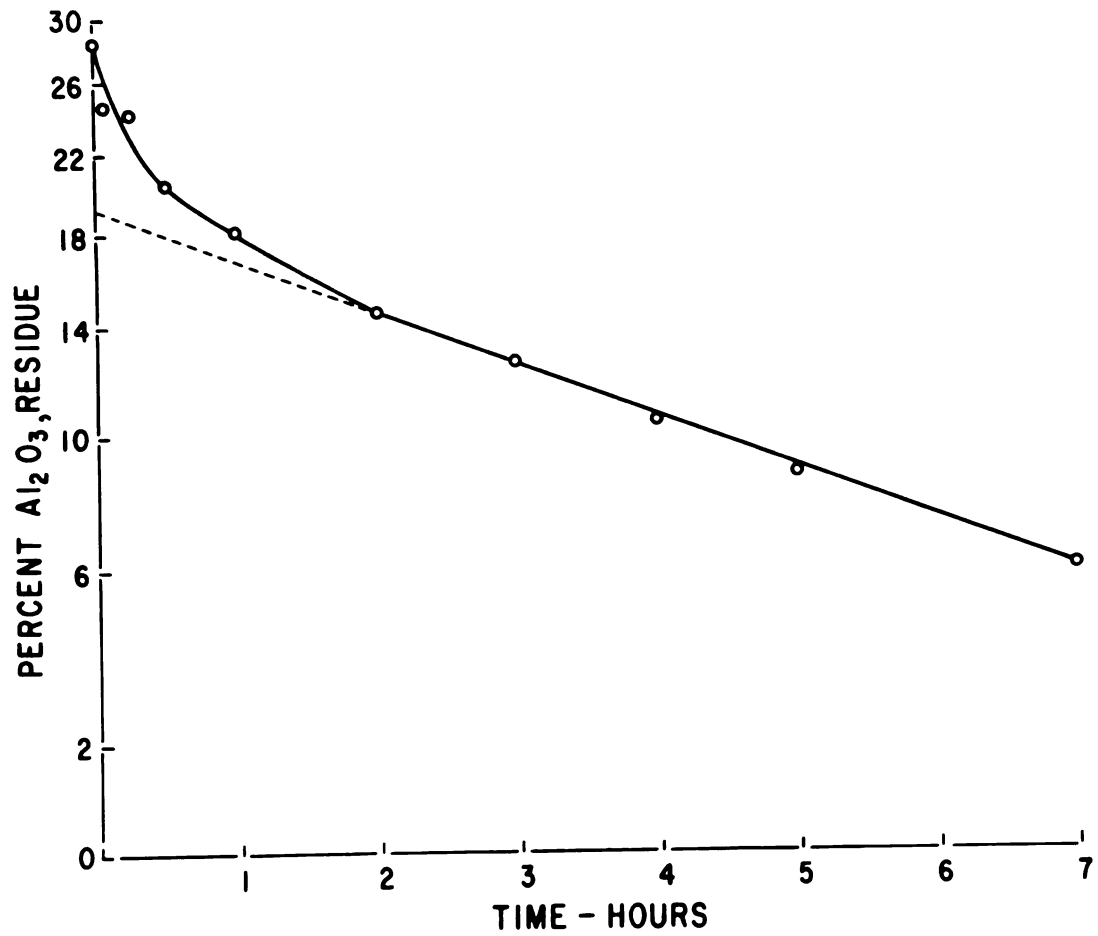


Figure 11. Dissolution curve for determination of the tetrahedral aluminum of the 0.2" clay fraction of the Deer Park A_2 -horizon

The curve shows two distinct slopes, which may be interpreted as two different rates of solution (Osthaus 1954). The steep slope represents mainly the relatively high rate of solution of octahedral Al; the less steep slope represents largely the relatively low rate of solution of tetrahedral Al. Extrapolation of the latter slope to zero time is believed to give the tetrahedral Al at the percentage where this slope intersects the coordinate axis.

In Figure 11 the slope intersects the axis at 19.2, which means that the Al in 19.2% of the total 27.9% Al_2O_3 is in the tetrahedral layer. Converted to gram atoms, this represents 3.76 Al ions in tetrahedral coordination and the remaining 0.17 Al ions in octahedral coordination. According to the results of this method, 94% of the Si ions in the tetrahedral layer have been replaced by Al ions, and scarcely any Al ions are left to occupy octahedral positions. Therefore, these results are entirely anomalous and must be rejected. Mackenzie (1960) also found that this technique did not apply to all the samples he investigated.

Although further investigation is necessary to identify the cause of these inconsistent results, the following explanation may be offered. Because the fine clay of the A_2 -horizon appears to be a weathered product (degraded illite and chlorite) it may be relatively unstable and have several

lattice defects. Such a clay treated with concentrated acid, could release tetrahedral as well as octahedral Al at a relatively rapid rate which would steepen the curve and give a slope intersecting the coordinate axis at an abnormally high value for tetrahedral Al.

Chemical Analysis of $\leq 0.2\mu$ Clay Fraction

The data in Table 8 are based on oven-dry weight which was obtained by drying the samples overnight at 110°C . The value for H_2O^+ is the total weight lost on ignition minus the H_2O lost below 110°C . The H_2O lost below 110°C was 6.6% for the A_2 -horizon clay, 8.1% for Wyoming bentonite, and 8.3% for nontronite. Since exchangeable bases were removed by washing with 0.05N HCl prior to chemical analysis, the CaO , K_2O and Na_2O were considered as impurities. The K_2O present in the A_2 -horizon clay was allocated to illite, using the theoretical muscovite formula. This would give the minimum amount of 22.7% of illite in the sample. Based on evidence of X-ray and infra-red analyses the amount of quartz present in the soil clay was estimated to be 7%. Assuming the quartz to be pure, 7% SiO_2 was allocated to quartz. The somewhat high value for total constituents in nontronite is allowable, since the microchemical system employed in the chemical analyses permits an over-all accuracy of $\pm 2\%$.

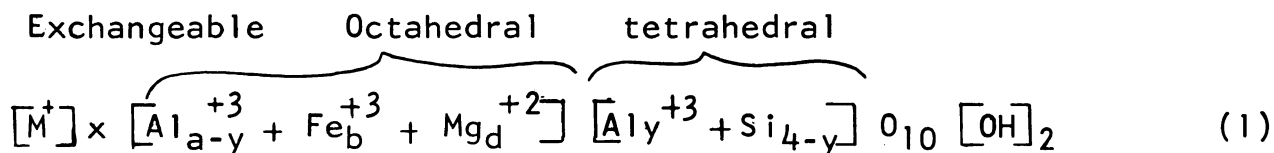
Table 8. Chemical analysis data in percent oven-dry weight of $< 0.2\mu$ clays

Constituent	A ₂ -horizon clay	Wyoming bentonite	Nontronite
SiO ₂	56.1	63.9	51.3
Al ₂ O ₃	27.9	21.7	6.38
Fe ₂ O ₃	2.60	3.52	35.1
MgO	2.10	3.58	0.10
CaO	0.11	0.07	0.61
K ₂ O	2.68	0.35	0.21
Na ₂ O	0.67	0.18	0.08
H ₂ O ⁺	7.3	7.6	8.6
Total	99.5	100.9	102.4

Calculation of Structural Formulas

The data for chemical analysis, cation exchange capacity, amounts of impurities, and crystal structure provide the basis for calculation of mineral formulas. The methods used to calculate the formulas were essentially the same as those used by Ross and Hendricks (1945) and may be explained as follows.

The basic formula containing the typical ions of the montmorillonite group is -



The subscripts a-y, b, d, y, and Si_{4-y} represent the proportions of cations in the formula and x represents the proportion of exchangeable cations. The total number of ions in octahedral positions equals (a-y) b+d and for dioctahedral minerals this should be close to 2 and not exceed 2.15. Thus

$$(a-y) + b + d \approx 2$$

The negative valence of O₁₀ + OH₂ = 22 and the ions in [Al_y⁺³ + Si_{4-y}] must equal 4.

Deriving the atomic proportions from the chemical analysis, let Al = A, Fe⁺³ = B, Mg = D, Si = Z, Al in tetrahedral positions = Y, O (oxygen) = R, and cation exchange capacity (equiv./100g.) = X; then

$$\left[\frac{M^+}{x} \right] \left[\frac{Al^{+3}}{A-Y} \quad Fe_B^{+3} \quad Mg_D^{+2} \right] \left[\frac{Al^{+3}}{Y} \quad Si_Z^{+4} \right] O_{10R} [OH]_{2R} \quad (2)$$

When multiplied by a constant k this equation is converted to the mineral formula (1).

Thus there are three unknowns: Y, k, and the number of $[Y \times k]$ of aluminum ions in tetrahedral coordination. From equations (1) and (2) it follows that

$$k [A \times 3 + B \times 3 + D \times 2 + Z \times 4 + X] = 22$$

or

$$k = \frac{22}{A \times 3 + B \times 3 + D \times 2 + Z \times 4 + X} \quad (3)$$

This equation expresses the condition that the sum of the positive valences, including the valences of the exchangeable cations, is 22.

From equations (1) and (2) it follows that

$$[Z + Y] \quad k = 4 \text{ or } \frac{4}{k} - Z = Y \quad (4)$$

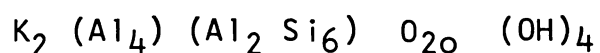
This equation requires that the atoms Si+Al, having tetrahedral coordination, equal 4. Since Z is obtained from the chemical analysis and k is defined by equation (3), Y x k can be calculated.

It also follows that

$$k [A + B + D - Y] = Z \quad (5)$$

where Z is the total number of ions in octahedral coordination. Since A, B, and D are given by the chemical analysis, and k and Y by equations (3) and (4), Z can immediately be calculated.

The method is illustrated by a calculation of the formula of the analysis obtained from the A₂-horizon fine clay. Before the soil montmorillonite formula can be calculated, however, the required SiO₂ must be allocated to quartz and the K₂O to the theoretical muscovite formula:



The theoretical composition of muscovite is:

SiO ₂	45.2%
Al ₂ O ₃	38.5%
K ₂ O	11.8%
H ₂ O	4.5%

The K_2O present in the soil clay is 2.68%. Therefore the amount of SiO_2 allocated to muscovite is:

$$\frac{45.2 \times 2.68}{11.8} = 10.3\%$$

The amount of Al_2O_3 assigned to muscovite is:

$$\frac{38.5 \times 2.68}{11.8} = 8.74\%$$

and the amount of water allotted is:

$$\frac{4.5 \times 2.68}{11.8} = 1.02\%$$

The amount of SiO_2 allotted to 7% quartz is 7%.

The cation exchange capacity assigned to muscovite and quartz is 10 me/100g. The cation exchange capacity for the 70% montmorillonite remaining in the clay fraction of the A_2 -horizon becomes

$$\frac{91 - 3}{70} = 126 \text{ me/100g.}$$

The adjusted elemental analysis of the soil montmorillonite is given in Table 9.

Substituting values for Z, A, B, D, and x in equation (3)

$$k = \frac{22}{.537 \times 3 + .046 \times 3 + .922 \times 4 + .074 \times 2 + .126}$$

or

$$\frac{22}{5.711} = 2.852$$

Table 9. Elemental analysis of A₂-horizon montmorillonite

Constituent	Percent (oven-dry weight)	Factor Mol - wt. no. of cations per mole	Atomic proportions and symbols
SiO ₂	55.4	60.06	0.922 = Z
Al ₂ O ₃	27.4	51.00	0.537 = A
Fe ₂ O ₃	3.71	79.92	0.046 = B
MgO	3.00	40.32	0.074 = D
H ₂ O ⁺	9.00		
CEC (equiv./100g)			0.126 = X

Substituting for k and Z in equation (4)

$$Y = \frac{4}{3.853} - 0.922 = .116$$

Substituting numerical values in equation (5)

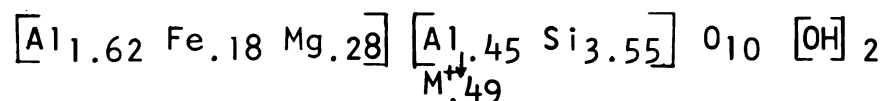
$$3.852 [0.537 + 0.046 + .074 - 0.116] = Z'$$

$$3.853 \times .541 = 2.08 = Z'$$

The mineral formula (1) is obtained by multiplying each of the above number of ions by their corresponding values, as follows:

$$\begin{aligned} a-y &= [A-Y] & k &= [0.537 - .116] & 3.852 &= 1.62 \\ b &= Bk & &= 0.046 \times 3.852 & &= 0.18 \\ d &= Dk & &= 0.074 \times 3.852 & &= 0.28 \\ y &= Yk & &= 0.116 \times 3.852 & &= 0.45 \\ 4-y &= 4 - 0.45 = 3.55 \end{aligned}$$

These values give the formula for the A₂-horizon montmorillonite as:



The layer charge (me/100g.) of this mineral is given by

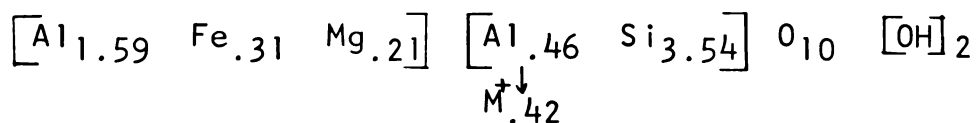
$$\left[\frac{\text{total negative charge} - \text{total positive charge}}{k \text{ (constant)}} \right] 1000 =$$

$$\left[\frac{22 - 21.51}{3.852} \right] 1000 = 127 \text{ me/100g.}$$

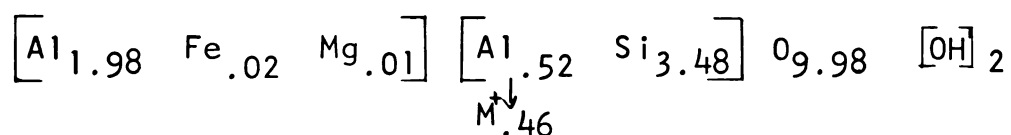
which is approximately the same as the cation exchange capacity of 126 me/100g. allotted to the soil montmorillonite before calculating the formula. There is a deficiency of $6.00 - 5.96 = 0.04$ positive charges in the octahedral layer which results in a net negative octahedral charge of 0.04. Thus the mineral formula shows that about 92% of charge in the soil montmorillonite is derived from substitution of Al for Si in the tetrahedral layer and 8% from substitution of Mg for Al and Fe in the octahedral layer.

Although this formula is an approximation of the actual composition and structure of the soil mineral (montmorillonite), it is consistent with the evidence obtained from the Greene-Kelly test, infra-red, and differential thermal analyses, which support the beidellite interpretation.

This soil montmorillonite is similar to a montmorillonite from Fairview, Utah, which was classified as a beidellite by Ross and Hendricks (1945). The formula for this clay mineral is:



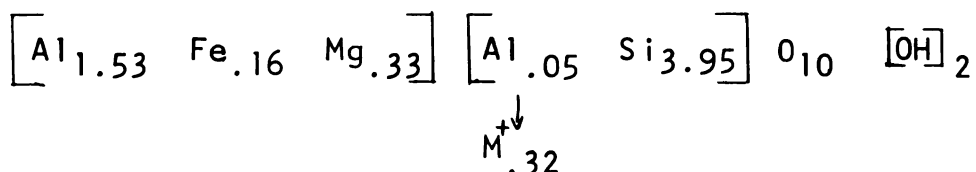
The formula for the beidellite from the Black Jack Mine given by Weir and Greene-Kelly (1962) is:



which agrees with the soil montmorillonite formula in the high Al for Si substitution in the tetrahedral layer and also in the high layer charge of 130 me/100g. It differs from the soil montmorillonite formula in the lower content of Fe and Mg in octahedral coordination. This difference may readily be explained by the reasonable supposition that the soil montmorillonite has formed from alteration of illite and chlorite which may contain considerable amounts of Fe and Mg.

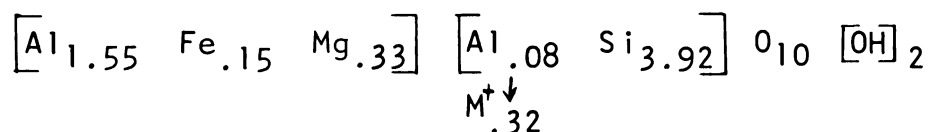
The formulas for Wyoming bentonite and nontronite were calculated in a similar manner. The small amounts of CaO, K₂O, and Na₂O were not entered into the calculations.

The formula calculated for Wyoming bentonite is:



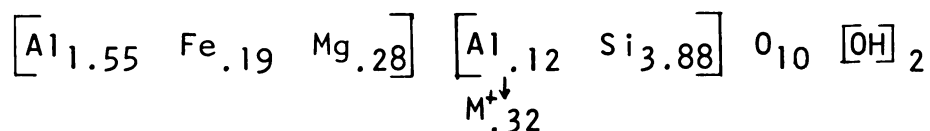
The sum of the cations in octahedral coordination, $\Sigma = 2.02$. Approximately 90% of the total cation exchange capacity or layer charge originates from substitution of Mg for Al and Fe in the octahedral layer and 10% from substitution of Al for Si in the tetrahedral layer. The layer charge calculated from the formula is 86 me/100g.

The formula shows that in this clay mineral nearly all the charge originates from substitution of Mg for Fe and Al in the octahedral layer. Thus this formula is also consistent with the results obtained in other analyses. The formula given by Kerr, et al. (1950) for Wyoming bentonite of the same locality (Upton, Wyoming) is:



with $\Sigma = 2.03$

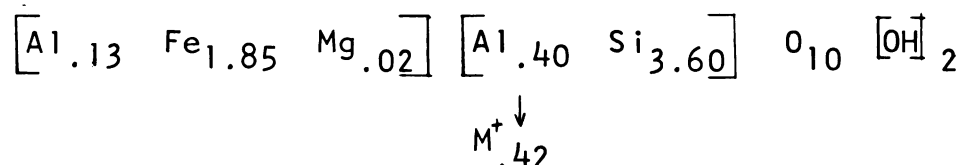
The formula given by Ross and Hendricks (1945) for Wyoming bentonite from Upton, Wyoming is:



with $\Sigma = 2.02$

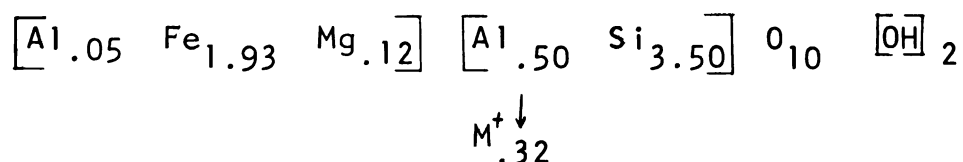
These formulas agree well with the formula calculated from the chemical analysis in this study.

The formula calculated for nontronite is:



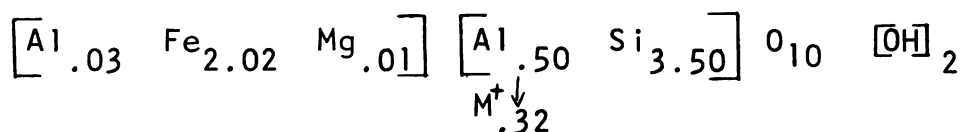
The layer charge calculated from the formula is 104 me/100g. Approximately 95% of the total charge originates from the tetrahedral layer and 5% from the octahedral layer. This agrees with the interpretations of the Greene-Kelly test, differential thermal analysis, and CEC-reduction studies.

The formula given by Kerr, et al. (1950) for a nontronite of the same locality (Garfield, Washington) is:



with $\Sigma = 2.10$

The formula calculated by the same authors for a nontronite from Manito, Washington is:



with $\Sigma = 2.06$

The substitution of Al for Si in the tetrahedral layer is slightly higher than that shown in the formula calculated from the chemical analysis in this study.

Formulas of the montmorillonites calculated from data of analyses made in this study are shown in Table 10. Formulas of montmorillonites obtained from data in the literature are included for comparison.

Electron Microscope Examination of the Fine Clay Fraction of the Deer Park A₂-horizon

The particles in the electron micrographs (Figures 12 and 13) show the characteristic features of nearly all the particles which were examined under the electron microscope, and these particles are therefore believed to be beidellite particles. The actual size of the particles shown range from approximately 0.1 to 1μ . They show a definite hexagonal shape and are very thin, especially along the edges. The dark spots on the crystals are probably iron-oxide coatings remaining after the iron-oxide removal treatment. The well-outlined shape of these beidellite particles is in contrast with the rather diffused and irregular outlines of other montmorillonites, such as Wyoming bentonite (Grim, 1953).

Table 10. Formulas for dioctahedral montmorillonites

Series	Sample and Locality	Tetrahedral Coordination		Octahedral Coordination			Equivalence of exchange cations M^+
		Si ⁺⁴	Al ⁺³	Al ⁺³	Fe ⁺³	Mg ⁺²	
Montmorillonites	Wyoming bentonite ² Upton, Wyoming	3.92	0.08	1.55	0.15	0.33	0.32
	Wyoming bentonite ¹	3.95	0.05	1.53	0.16	0.33	0.32
Beidellites	Black Jack Mine ³ Idaho	3.48	0.52	1.98	0.02	0.01	0.46
	No. Michigan ¹ (in Deer Park sand)	3.55	0.45	1.62	0.18	0.28	0.49
	No. Wisconsin ⁴ (in Hiawatha loamy sand)	3.65	0.35	1.40	0.45	0.15	0.50
Nontronites	Nontronite ² Garfield, Washington	3.50	0.50	0.05	1.93	0.12	0.32
	Nontronite ¹ Garfield, Washington	3.60	0.40	0.13	1.85	0.02	0.42

- 1 - Data obtained in this study
2 - Data from Reference Minerals A.I.P. (1950)
3 - Data from Weir and Greene-Kelly (1962)
4 - Data from Brown and Jackson (1958)

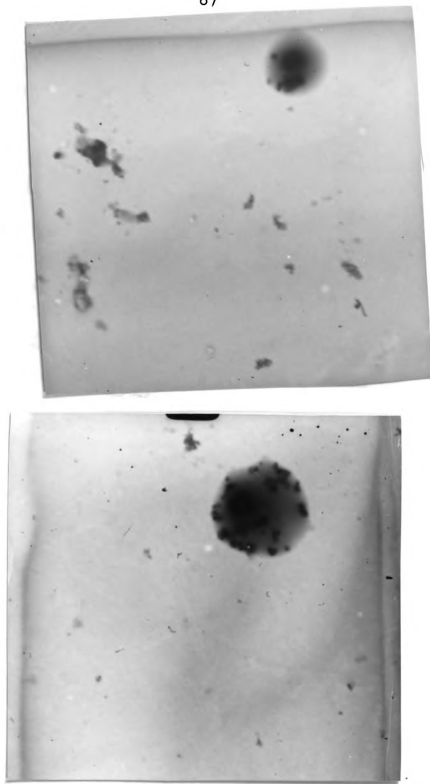


Figure 12: Electron micrographs of the fine clay fraction of the Deer Park A₂-horizon

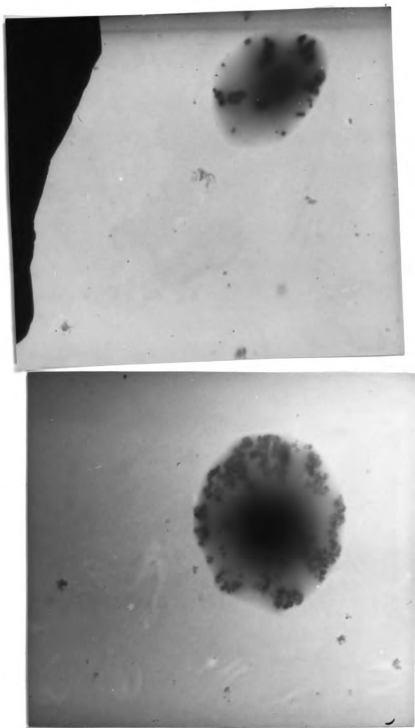
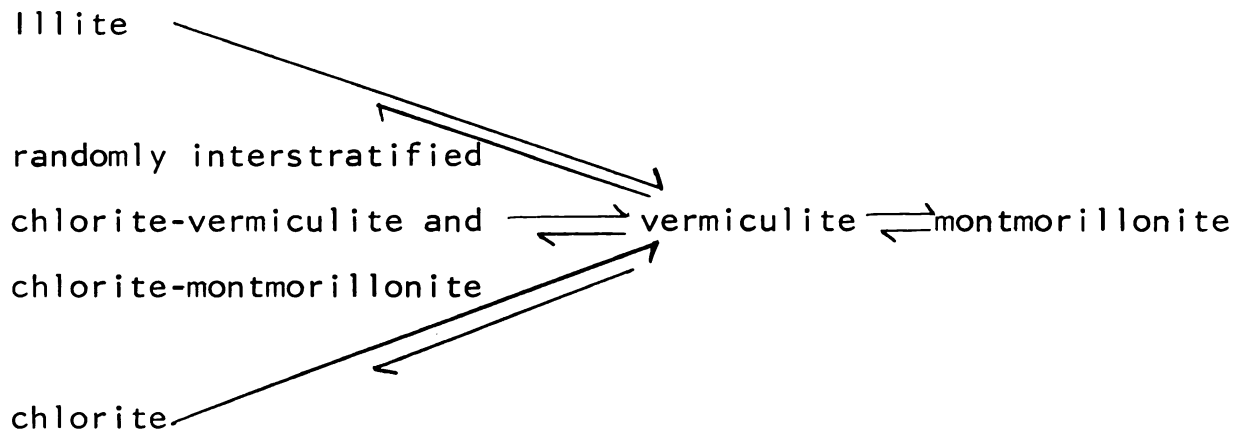


Figure 13. Electron micrographs of the fine clay fraction of the Deer Park A₂-horizon

VI. GENERAL DISCUSSION

X-ray diffraction tracings show that a montmorillonite is the predominant layer silicate in the $< 2\mu$ fraction of the A_2 -horizons of some sandy soils in Northern Michigan. The tracings of the $< 2\mu$ fraction of the Deer Park profile indicate that the montmorillonite has formed in situ and these tracings illustrate the following weathering sequence.



This weathering sequence is prevalent in Northern Michigan resulting in accumulation of montmorillonite in the A_2 -horizons of sandy soils of various ages as is evident in the Deer Park sand at location No. 1 (approximately 2250 years) and in the Blue Lake sand at locations No. 6 and 7 (approximately 10,000 years).

The 060 spacing and the structural formula indicate that this montmorillonite is dioctahedral. The structural formula also shows that over 90 percent of the total charge arises

from substitution of Al for Si in the tetrahedral layer and the remainder from substitution of Mg for Al and Fe in the octahedral layer. Greene-Kelly test confirms these charge relationships. Therefore, this material may be interpreted as a beidellitic member of the montmorillonite group.

Data from X-ray powder diffraction and differential thermal analysis of the fine clay of the A₂-horizon agree with those reported by Weir and Greene-Kelly (1962) for the typical end-member beidellite from the Black Jack Mine, Idaho. Data from infra-red analysis correspond to those reported for beidellite by Farmer and Russell (1964). These agreements provide additional evidence for the beidellite interpretation.

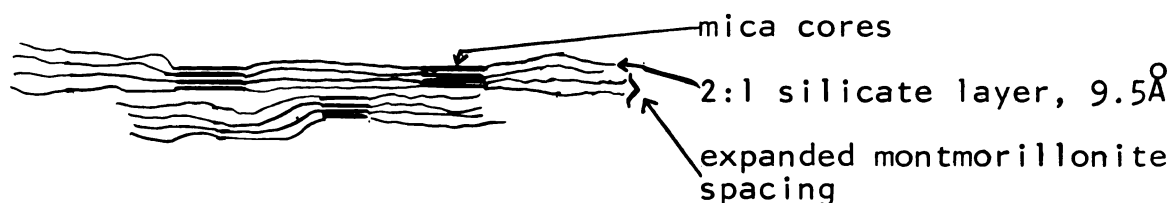
The K-saturation, heating, and NH₄-resaturation treatments reduce the cation exchange capacities (CEC) of both the fine clay of the A₂-horizon and nontronite but do not affect the CEC of Wyoming bentonite. This indicates a correlation of increased K-fixation with increased tetrahedral and total charge. Because none of the other analyses showed the presence of vermiculite in these clays, the determination of vermiculite in clay mixtures by the method of CEC reduction cannot be accepted, unless vermiculite is defined by this method alone.

Hydration studies show that at 100% relative humidity the fine clay of the A₂-horizon forms a somewhat smaller spacing with the Na, Mg, and Ca than do Wyoming bentonite and nontronite saturated with the same ion species. This smaller spacing may be related to high total and tetrahedral charge. The limited swelling of the fine clay of the A₂-horizon and also the tendency to fix potassium appear to be characteristic of beidellite in soils (Marshall 1936, 1949).

The chemical determination of tetrahedral aluminum by acid dissolution gave anomalous results. These may be related to relatively rapid dissolution of tetrahedral Al due to structural defects of the montmorillonite in the fine clay of the A₂-horizon.

Earlier beidellite interpretations have been questioned because X-ray diffraction and differential thermal analyses showed that in many cases the so-called beidellite was an interlayered mixture of illite and montmorillonite (Grim 1953). In view of the high illite content (22% calculated on a muscovite basis) the same doubt may be raised regarding the beidellite interpretation in this study. However, in this study X-ray diffraction analyses do not indicate random or regular interstratification of montmorillonite with illite as shown by the symmetry of the 001 peak and the rationality of the higher orders of the 001 plane.

The apparent absence of illite-montmorillonite interstratification may be explained by the presence of mica in montmorillonite as "cores." Such cores have been identified in electron micrographs by Venkata Raman and Jackson (1964) and in photomicrographs by Mortland (1958) of vermiculite in which the smooth surfaces of the mica cores could be distinguished from the rough surface of the surrounding vermiculite. A similar arrangement of unweathered mica cores in montmorillonite may be visualized according to the simplified diagram shown below.



Because there is a tendency for interlayer constancy of the sum of interlayer sorption surface and K-occupied interlayers, any given mica interlayer segment tends to remain completely filled with K or else becomes completely affected by interlayer swelling (Mehra and Jackson, 1959). If these conditions prevail, mica and montmorillonite are present as non-interstratified, discrete phases (Mortland, 1958).

This postulated arrangement of montmorillonite and mica may contribute to the tendency for K fixation, since the mica cores maintain alignment of the montmorillonite silica sheet cavities in which K may be strongly bonded. The presence of illite as mica cores also justifies the calculation of percent illite using the K_2O content of muscovite.

At this stage of weathering similar "islands" of chlorite may have weathered to expanding layer silicates, since chlorite appears to be less stable than illite under these weathering conditions (Droste, et al, 1962; and Bayliss and Loughnan, 1963). The apparent absence of vermiculite (commonly the first weathered product of mica) while mica is still present, indicates that this mica is very resistant to further weathering.

Weir and Greene-Kelly (1962) have recommended four requirements for the use of the name beidellite:

1. Beidellites are montmorillonite minerals, and the term should only be used as a species name for the appropriate member of the montmorillonite group.

2. The term beidellite should be used for the aluminum rich members of the montmorillonite-beidellite series of minerals, as proposed by Ross and Hendricks (1945), but the composition of the ideal end-member should be restricted to that of an exactly dioctahedral mineral, as proposed by MacEwan (1951) and Brown (1955).
3. Beidellites and montmorillonites should be divided at the composition at which the lattice charges from octahedral and tetrahedral substitution equal one another (Greene-Kelly, 1955).
4. Naturally occurring beidellite specimens should not ideally contain non-exchangable potassium.

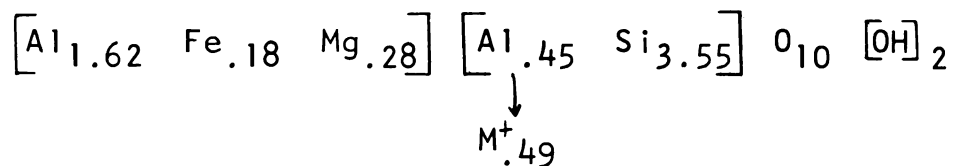
The first three of these requirements are fulfilled by the $<0.2\mu$ clay fraction of the Deer Park A₂-horizon, but the ideal condition in the fourth requirement is not satisfied. However, X-ray data indicate no interstratification of illite with montmorillonite, and considering the argument presented previously concerning the presence of illite as mica cores, the montmorillonite in this clay fraction may

be regarded as a discrete phase containing no non-exchangeable potassium. Therefore, the montmorillonite present in the $<0.2\mu$ clay fraction of the Deer Park A₂-horizon is classified as the species beidellite of the montmorillonite-beidellite series.

VII. CONCLUSIONS

1. Illite, chlorite, and randomly interstratified chlorite-vermiculite and chlorite-montmorillonite have weathered in situ through vermiculite to a dioctahedral montmorillonite in sandy soils of various ages over a relatively large area in Northern Michigan.

2. Because this montmorillonite mineral is rich in aluminum and has a high charge of which over 90 percent originates from substitution of Al for Si in the tetrahedral layer, it is classified as a beidellite of formula,



3. This beidellite has a strong tendency to fix potassium.

4. Vermiculite contents in clay mineral mixtures cannot be calculated from reduction in cation exchange capacities following K saturation, heating to 110°C., and resaturation with NH_4 .

5. The acid dissolution technique for determination of tetrahedral aluminum as used in this investigation does not apply to the beidellite studied.

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