# LAYER CHARGE RELATIONS IN CLAY
# MINERALS OF MICACEOUS SOILS AND SEDIMENTS

*by*

## K. V. RAMAN and M. L. JACKSON

Department of Soil Science, University of Wisconsin,
Madison, Wisconsin

## ABSTRACT

MICACEOUS clays ("illites") of a number of sediments, subjected to quantitative mineralogical analysis, ranged in different samples from 58 to 65% of a dioctahedral mica of muscovite type, from 3 to 8% vermiculite, from 0 to 10% montmorillonite, from 2 to 12% quartz, from 0 to 4% feldspars, from 1 to 2% rutile and anatase, from 0.3 to 1.2% free iron oxides, and from 16 to 30% chlorite. The soil clays contained less mica (13 to 35%) but more vermiculite (13 to 16%), montmorillonite (6 to 14%) and chlorite (30 to 33%), besides kaolinite (3 to 8%) and amorphous material (6 to 15%). The presence of the various minerals was verified by X-ray diffraction. When the interlayer K of these micaceous clays was replaced by hydrated Na ions through treatment with 0.2 N sodium tetraphenylboron in 1 N NaCl, the analytically determined vermiculite and montmorillonite contents increased. The freshly produced vermiculites had an interlayer charge of 177 to 198 me/100 g. During this replacement of interlayer K in a 1 N salt solution, the pH of the equilibrium matrix solution was observed to increase instead of decreasing as would be expected if oxonium ($OH_3^+$) ions were associated with K in the interlayer space, thus precluding the possibility of interlayer $OH_3^+$. The calculated stoichiometric equivalent of the pH rise established a significant uptake of protons by the lattice as K was released.

Thermal analyses of vermiculites show 0.5 to 0.7% higher OH water content than the parent micas. Oxidation of ferrous iron in the silicate structure, suggested as a possible mechanism for lowering of layer charge during weathering of mica to vermiculite, accounted for about 66% of this in samples high in iron (16.0% FeO) and only 30% of this in samples fairly low in iron. The rate of extraction of K from muscovite with no ferrous iron was found to be pH dependent, increasing at lower pH values. The data indicate proton incorporation with structural oxygens of the silicate sheet to form OH as a charge reduction mechanism in weathering of mica, independent of and additional to that involving the oxidation of ferrous iron.

## INTRODUCTION

THE term "illite" was proposed (Grim, Bray, and Bradley, 1937) for the micas of argillaceous sediments which showed a broadened 10Å X-ray diffraction peak and contained about 6% $K_2O$. The interlayer K deficit was attributed to isomorphous substitution of oxonium ions for K in the mica lattice (Brown and Norrish, 1952). Attempts have been made to calculate an

"average formula" of $K-OH_3$ mica on the basis of elemental and thermal data (Mankin and Dodd, 1963); however, there is no direct evidence for the presence of oxonium in the samples that were studied. On the basis of X-ray diffraction, specific surface, and cation exchange data, the presence was shown of interstratified systems of mica with expansible layer silicates and chlorites in a number of micaceous deposits (Mehra and Jackson, 1959; Brindley and Sandalaki, 1963; St. Arnaud and Mortland, 1963; Weaver, 1965). Alexiades and Jackson (1965, 1966) found that mica, chlorite, vermiculite, montmoril-lonite, amorphous material, kaolinite, and quartz constituted an analytical total of very near 100% in a variety of micaceous samples including glaucon-ite.

It is the purpose of this paper to determine, for a number of micaceous clays of soils and sediments, (a) the complete mineralogical analysis by methods based on independent measurements of the different constituents, (b) the nature of the interlayer cations present, through sodium tetraphenyl-boron treatment, and (c) the cation exchange capacity, layer charge relations, OH-water balance, and weathering mechanisms.

## MATERIALS AND METHODS

The following micaceous materials were used for the study: clay from Blaylock formation from Beavers Bend State Park, Oklahoma (courtesy C. Mankin); clay lens of the Niagara dolomite at Marblehead quarry, near Fond du Lac, Wisconsin; glauconite of the Franconia (Cambrian) formation at Camp Randall Stadium excavation, Madison, Wisconsin; shale from New York (Ward's Scientific Establishment, Rochester, N.Y.); underclay from Fithian, Illinois; shale from southwestern Wisconsin; and three other clays. The latter three samples constitute a sequence of Illinoian till weathering: The Buffalo Hart till (considered to be the most micaceous of the Illinoian tills, Willman, Glass and Frye, 1963), the Sangamon paleosol developed on it during the interglacial period following the Illinoian, and the accretion gley deposit occurring in an adjacent toposequence depression and buried by Roxana silt at the Hipple School site.

In order to exclude the possibility of production of artifacts by cation exchange and other commonly used pre-treatments, the samples of sedi-mentary materials were washed and dispersed only in distilled water during the fractionation procedure; the soil samples were fractionated by standard procedures after removal of carbonates, organic matter, and free oxides (Jackson, 1956). The clay fractions consisting of particles of less than two microns in diameter were used. Total chemical analysis was carried out by HF and $HClO_4$ fusion (Jackson, 1958). Ferrous iron was estimated by titra-tion with $K_2Cr_2O_7$ after decomposition of the sample with HF and $H_2SO_4$ Cation exchange capacity (CEC) was determined by saturating the clay with Ca using $CaCl_2$, removal of excess salts, and displacing the Ca by $MgCl_2$, designated (CEC, Ca/Mg). For the determintaion of the exchange capacity

after K fixation, the same sample was saturated by washing with KCl, and dried at 110°C after removal of excess salt. The K then removed on displacement with NH$_4$Cl, designated (CEC, K/ /NH$_4$), was determined. For the calculation of vermiculite content from CEC data, an interlayer charge of 154 me/100 g was used as the basis for the vermiculite in the original specimen which has been aged long enough in nature for charge stabilization to occur. (Montmorillonite + amorphous material) was calculated on the basis of (CEC, K/ /NH$_4$ — 5)/1.05. These procedures for vermiculite and montmorillonite were those of Alexiades and Jackson (1965). Kaolinite and amorphous material were determined by the NaOH selective dissolution procedure of Hashimoto and Jackson; the montmorillonite percentage was calculated from the above by subtracting the percentage of amorphous material. Quartz and feldspars in the sample were determined by sodium pyrosulfate procedure of Kiely and Jackson. Details of these procedures are given in Jackson (1956). Rutile and anatase were determined by selective dissolution of silicates by cold HF (Raman and Jackson, 1965). For the thermal gravimetric analysis, a K-saturated sample was used and the percentage water loss between 300 and 950°C was calculated on the basis of the weight of the sample at 300°C (Alexiades and Jackson, 1966). The following hydroxyl water contents were assumed for the different minerals: dioctahedral mica = 4.5%; vermiculite = 5%; montmorillonite = 5%; chlorite = 14%; kaolinite = 14%; amorphous material = 8%.

For the depletion of K from the mica, and production of an expanded layer silicate, subsamples of the sedimentary micas were treated with a solution of 0.2 N sodium tetraphenylboron (NaTPB) in 1 N NaCl for varying periods of time, and the pH changes were recorded. At the end of appropriate time, the samples were removed by centrifugation and repeatedly washed with acetone and water to dissolve the precipitated potassium tetraphenylboron, after which they were used for other chemical analysis. In experiments in which refixation of K was to be avoided, 10 ml of a saturated solution of NH$_4$Cl was added to the suspension, before the acetone washing, to prevent K-fixation.

## RESULTS AND DISCUSSION

### *Exchange Capacity*

The CEC of the various materials varied widely from 14 to over 50 me/100 g. After depletion of K, the CEC was considerably higher than that of the original material (Table 1). Alexiades and Jackson (1965) proposed that the CEC values determined by Ca/Mg and K/ /NH$_4$ can be used for the calculation of per cent vermiculite and per cent montmorillonite. They also showed that the interlayer charge of new vermiculite, which probably equalled mica charge initially, falls rapidly on aging to stabilize around the value of 154 me/100 g.

TABLE 1.—CEC OF MICACEOUS CLAYS, ORIGINAL AND AFTER PARTIAL REMOVAL OF K BY NaTPB, ME/100 G OF SAMPLE

| Locality or origin | Original sample | | | K depleted by TPB | | | |
|---|---|---|---|---|---|---|---|
| | Ca/Mg (1) | K/ /NH$_4$ (2) | Diff. (3) | Ca/Mg (4) | K/ /NH$_4$ (5) | Diff. (6) | ILC* (7) |
| Beavers Bend | 13.9 | 4.2 | 9.7 | 50.0 | 5.9 | 44.1 | 34.4 |
| Marblehead | 14.7 | 5.2 | 9.5 | 55.0 | 7.3 | 47.7 | 38.2 |
| Camp Randall | 19.8 | 15.3 | 4.5 | 57.5 | 19.4 | 38.1 | 33.6 |
| New York | 17.3 | 4.8 | 12.5 | 55.0 | 7.0 | 48.0 | 35.5 |
| Fithian | 16.9 | 7.2 | 9.7 | 59.0 | 9.0 | 50.0 | 40.3 |
| Wisconsin | 26.6 | 11.5 | 15.1 | nd† | nd | nd | nd |
| Buffalo Hart till | 37.2 | 16.9 | 20.3 | nd | nd | nd | nd |
| Sangamon soil | 52.4 | 32.5 | 19.9 | nd | nd | nd | nd |
| Accretion gley | 51.7 | 27.7 | 24.0 | nd | nd | nd | nd |

\* ILC = Interlayer charge of new vermiculite; (7) = (6) — (3).
† nd = not determined.

The per cent vermiculite (Table 2) in the original sample was based on the lowered charge on the assumption that the mineral had aged sufficiently in nature for charge stabilization to occur. In making the analysis of the K-depleted sample (Table 2), the sum of mica, vermiculite and montmorillonite was assumed to be a constant. The mica was determined from K$_2$O analysis (as discussed in connection with Table 4, below); the new montmorillonite was calculated on the basis of the increase in CEC (K/ /NH$_4$) resulting from

TABLE 2.—PARTIAL MINERALOGICAL COMPOSITION OF MICACEOUS SAMPLES BEFORE AND AFTER K-DEPLETION AND LAYER CHARGE RELATIONS IN THE VERMICULITE COMPONENT PRODUCED BY K-DEPLETION

| Locality or origin | Percentage of minerals | | | | | | | Interlayer charge of new vermiculite | |
|---|---|---|---|---|---|---|---|---|---|
| | Original material | | K-depleted material | | | | | | |
| | Mica (1) | Verm. (2) | Mica + Verm. (3) | Mica (4) | New Mont.* (5) | Total Verm.* (6) | New Verm.* (7) | As me/100 g of sample (8)† | As me/100 g of vermiculite (9) |
| Beavers Bend | 60.9 | 6.2 | 67.1 | 40.8 | 1.5 | 24.8 | 18.6 | 34.4 | 184.9 |
| Marblehead | 62.6 | 6.1 | 68.7 | 41.3 | 2.0 | 25.4 | 19.3 | 38.2 | 197.9 |
| Camp Randall | 58.7 | 2.9 | 61.6 | 36.2 | 3.7 | 21.7 | 18.8 | 33.6 | 178.7 |
| New York | 64.6 | 8.1 | 72.7 | 42.5 | 2.0 | 28.2 | 20.1 | 35.5 | 176.6 |
| Fithian | 57.7 | 6.3 | 64.0 | 32.6 | 1.6 | 28.8 | 22.5 | 40.3 | 179.1 |

\* On the assumption that all the new montmorillonite (Mont.) and new vermiculite (Verm.) have come from mica; (6) = (3) — (4) — (5); (7) = (6) — (2).
† From Table 1.

the K-depletion; and the vermiculite, by difference. The interlayer charge of the freshly produced vermiculite, which had been partially aged in the K-depletion procedure employed, was then calculated (Table 2); it ranged from 177 to 198 me/100 g, values comparing favorably with the CEC for fresh vermiculites (Alexiades and Jackson, 1965).

### OH Water Content of Vermiculite

The chlorite component of clay was determined from total OH water content determined thermogravimetrically through allocation of water lost between 300 and 950°C. Since the OH water content of vermiculite and montmorillonite must be deducted to get the net for chlorite, the content of OH water in these minerals merits attention.

Two vermiculites of known (Alexiades and Jackson, 1965) mineralogical composition were selected for this study. The first sample was a biotite-derived vermiculite from Libby, Montana which showed a mineralogical analysis of 0.5% quartz, 28% trioctahedral mica, 64% vermiculite and 9% montmorillonite. The other sample was a phlogopite-derived vermiculite from Llano county, Texas, and showed a mineralogical analysis of 0.8% quartz, 1% mica, 3% montmorillonite and 95% vermiculite. Neither sample contained chlorite. The loss on heating (300 to 950°C) was 4.79% for the Montana sample and 5.09% for the Texas sample, on the 300°C base weight after K saturation. The former value has been corrected for weight gain through oxidation of the 0.58% FeO present, which takes place at such high temperatures and results in a weight gain of 0.11 g for each gram of FeO (Jackson, 1956). Allocation of water content of mica in the sample (4.0% $H_2O$ for the biotite-type mica of the Montana sample) gives a water content of 4.94% and 5.16%, respectively, for the montmorillonite and vermiculite components of the sample, values higher in amounts of OH water than the corresponding micas. A mean value of 5.0% OH water for vermiculites and montmorillonites has therefore been used in subsequent calculations herein.

### Thermal Gravimetric Analysis

Hydroxyl water lost between 300 and 950°C in K-saturated samples, calculated on the 300°C sample weight basis, ranged from 5.74 to 8.81% (Table 3). These values, which agree with many literature values for argillaceous micaceous minerals, are higher than the OH water content of micas or expansible layer silicates. Since the contents of mica, vermiculite, and montmorillonite have each been determined by independent measurements, the water content remaining after the allocation of the OH content of these minerals is allocated for chlorite. The presence of chlorite layers interstratified with the mica is established by the low angle diffraction after the samples were heated to 550°C (Fig. 1).

After removal of some of the interlayer K with NaTPB, the OH water content decreased slightly in all samples (Table 3). While these small differ-

TABLE 3.—THERMAL WATER LOSS BETWEEN 300
AND 950°C. PERCENTAGE ON 300°C BASIS

| Locality or origin | Percentage OH water | |
| --- | --- | --- |
| | Original | After K depletion for 81 days |
| Beavers Bend | 6.94 | 6.77 |
| Marblehead | 6.11 | 6.07 |
| Camp Randall | 5.82 | 5.77 |
| New York | 6.18 | 5.69 |
| Fithian | 5.74 | 5.72 |
| Wisconsin | 5.91 | — |
| Buffalo Hart till | 7.81 | — |
| Sangamon soil | 8.81 | — |
| Accretion gley | 7.79 | — |

ences do not affect to any appreciable extent the chlorite contents of the sample before and after K-depletion, such small losses can be taken as a measure of the limited amount of water molecules trapped in the interlayer structural position, (a) in empty hexagonal cavities, (b) $OH_2$ from brucite layer edges of chlorite, or (c) oxonium. The small magnitude of this loss in water also precludes the possibility of any appreciable chloritization reactions having occurred during the K-depletion, as discussed in detail below.

## Complete Mineralogical Analysis of the Micaceous Clays

A complete mineralogical analysis of the highly micaceous clays was carried out (Table 4). Ideal muscovite, $K_2(Al_2Si_6)Al_4O_{20}(OH)_4$, has a $K_2O$ content of 11.8% and biotite with equal amounts of $Fe^{2+}$ and Mg in the octahedral layer, $K_2(Al_2Si_6)Mg_3Fe_3O_{20}(OH)_4$ has a $K_2O$ content of 10.11%. $K_2O$ content of micas decreases with decreasing particle size as shown by Jackson (1956). For the calculation of the mica component, use of a $K_2O$ content of 10% was suggested to compensate for exchange of K from external planar surfaces (cleavage surfaces) as the crystals become very thin. The methods of mineralogical analysis adopted in this paper measure independently vermiculite, montmorillonite and chlorite components even in an inter-stratified system with mica. It was found that use of 10.6% $K_2O$ was a more quantitative basis for the calculation of dioctahedral mica in highly mica-ceous clays, in which the dioctahedral nature of the clay was established by an (060) X-ray diffraction peak at 1.49 to 1.50 Å. Besides mica, the samples also contain vermiculite, montmorillonite, chlorite, quartz, feldspars, rutile, anatase and free iron oxides. X-ray diffractograms of all these specimens showed a broad 10 Å peak, with asymmetry of the (001) peak on the low angle side, and asymmetry of the (003) peak toward the high angle side,

TABLE 4.—COMPLETE MINERALOGICAL ANALYSIS OF MICACEOUS CLAYS ($< 2 \mu$ FRACTION), PERCENTAGE ON 100° BASIS

| Locality or origin | Mica | Verm.* | Mont. | Chl. | Kaol. | Amor. | Quartz | Feld. | Rut. | Free iron oxides | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *Original samples* | | | | | | | | | | | |
| Beavers Bend | 60.9 | 6.2 | 0.0 | 29.3 | 0.0 | 0.0 | 1.8 | 0.0 | 1.5 | 0.6 | 100.3 |
| Marblehead | 62.6 | 6.1 | 0.6 | 21.7 | 0.0 | 0.0 | 2.4 | 4.1 | 0.9 | 0.3 | 98.7 |
| Camp Randall | 58.7 | 2.9 | 10.0 | 24.6 | 0.0 | 0.0 | 1.4 | 0.0 | 0.7 | 1.1 | 99.4 |
| New York | 64.6 | 8.1 | 0.0 | 20.5 | 0.0 | 0.0 | 1.9 | 0.6 | 1.9 | 1.2 | 98.8 |
| Fithian | 57.7 | 6.3 | 2.7 | 20.3 | 0.0 | 0.0 | 12.2 | 0.0 | 0.6 | 0.9 | 100.7 |
| Wisconsin | 61.5 | 9.8 | 5.1 | 16.3 | 0.0 | 1.4 | 2.6 | 3.8 | 0.6 | 0.6 | 101.7 |
| Buffalo Hart Till | 35.0 | 13.2 | 6.2 | 31.8 | 2.6 | 5.6 | 1.8 | 1.2 | 0.7 | † | 98.1 |
| Sangamon Soil | 13.1 | 12.9 | 12.2 | 32.9 | 8.4 | 14.9 | 1.6 | 0.6 | 0.9 | † | 97.5 |
| Accretion Gley | 19.5 | 15.6 | 13.6 | 30.6 | 3.4 | 8.7 | 2.8 | 1.6 | 1.3 | † | 97.1 |
| *K-depleted samples* | | | | | | | | | | | |
| Beavers Bend | 40.8 | 24.8 | 1.5 | 27.3 | 0.0 | 0.0 | 1.7 | 0.0 | 1.5 | 0.6 | 98.2 |
| Marblehead | 41.3 | 25.4 | 2.6 | 20.7 | 0.0 | 0.0 | 2.4 | 4.7 | 0.9 | 0.3 | 98.3 |
| Camp Randall | 36.2 | 21.7 | 13.7 | 23.4 | 0.0 | 0.0 | 1.3 | 0.0 | 0.7 | 1.1 | 98.1 |
| New York | 42.5 | 28.2 | 2.0 | 18.9 | 0.0 | 0.0 | 1.8 | 1.0 | 1.9 | 1.2 | 97.5 |
| Fithian | 32.6 | 28.8 | 4.3 | 19.6 | 0.0 | 0.0 | 12.6 | 0.0 | 0.6 | 0.9 | 99.4 |

*Verm. = Vermiculite; Mont. = Montmorillonite; Chl. = Chlorite; Kaol. = Kaolinite and Halloysite; Amor. = Amorphous material; Feld. = Feldspars; Rut. = Rutile and anatase.

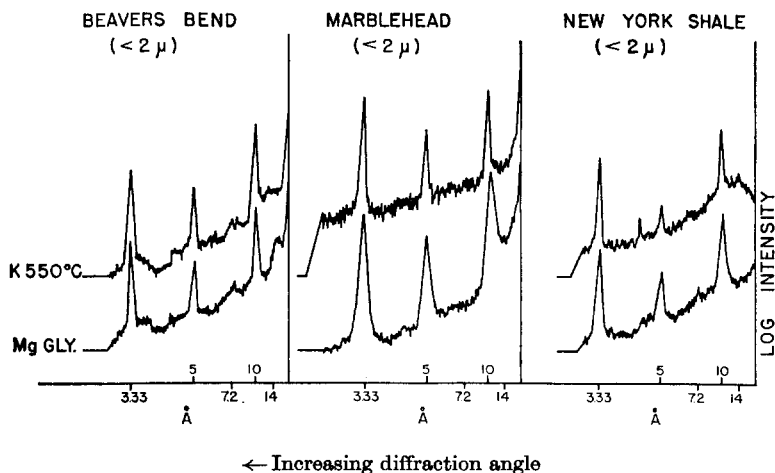† Free iron oxides were removed; the results are expressed on an iron oxide free basis as 100%.

← Increasing diffraction angle

FIG. 1. X-ray diffractograms of clay fractions ($< 2 \mu$) of representative samples. The diffraction in the vicinity of 14 Å after 550°C heating and the asymmetry of the (001) peak in the vicinity of 10 Å towards the low angle side, and of the (003) peak in the vicinity of 3.33 Å towards the high angle side indicate the presence of chloritic components.

indicating an interstratified system of mica with expansible layer silicates and chlorites. The persistence of such peak character even after K-saturation and heating to 300°C and 550°C reflected the chloritic nature of the components other than mica.

After treatment with NaTPB, the mica content of each sample decreased, with a corresponding increase in the content of vermiculite and montmorillonite. The chlorite content of the sample decreased very little, as discussed above. In the toposequence, the Buffalo Hart (Illinoian) till contained 35% mica while the weathered Sangamon soil contained only 13% mica. Both the Sangamon soil and the accretion gley had higher amounts of montmorillonite, kaolinite and amorphous material than the till (Table 4). From X-ray intensity measurements, the Sangamon soil was estimated to have 17% illite, 57% montmorillonite, and 26% kaolinite plus chlorite, while the weathered tills gave such poor X-ray patterns that no estimate was possible (Willman, Glass, and Frye, 1963). It is interesting to observe how the presence of amorphous material (and possibly free oxides of iron) affected the other minerals present in the sample, making their estimation by X-ray diffraction spurious and difficult.

These studies on the mineralogy of several micaceous clays confirm that "the mica of argillaceous sediments" is a discrete true mica component, occurring in association with numerous other minerals such as vermiculite, montmorillonite, rutile and anatase, quartz, and chlorite, which are also discrete determinable mineral components.

*Interlayer Cations*

Argillaceous sedimentary micas contain a lesser complement of interlayer potassium than ideal muscovite and higher amounts of water than theoretical. The oxonium ion which has the same crystallographic size as K was postulated to be present (Brown and Norrish, 1952; Mankin and Dodd, 1963) in the interlayer space. The postulate was based on formula calculations in which observed amounts of ignition water (assumed to arise from $OH_3^+$) were used to balance the charge of the silicate in micas of muscovite charge. This postulate regarded "illite" as "K-OH$_3$ mica" with nonexpanding properties.

The validity of this postulate was tested by equilibrating micaceous samples with sodium tetraphenylboron, which keeps the activity of K in the external solution very low and promotes the exchange of interlayer K with hydrated Na ions, producing a 14 Å component from the parent mica. The NaTPB–NaCl solution was adjusted to a pH of 7.0; potentiometric titration of this solution showed that it had only a weak buffering in the range of concentrations and pH used. On equilibration of the sample over a period of time, the pH of the equilibrium matrix solution increased (Table 5) as the layers were opened and reached a near steady value after about 3 days. Considerable exchange of Na for K took place as the layers opened up, as indicated by the chemical analysis (Table 4) and X-ray diffraction studies. Since the effect of the treatment was to exchange the interlayer K with hydrated ions from the external solution, there would have been an increase in the hydrogen ion activity of the external solution had there been any release of oxonium ions originally present in the interlayer space. The results show an increase in pH (or decrease in H-ion activity) when the layers open up. These results would therefore preclude the possibility of release of oxonium ions along with K from the interlayer space. From one-dimensional Fourier synthesis, Nelson (1956) concluded that micas of "illite" approach the composition of ideal muscovites, and that the interlayer positions were essentially anhydrous, in accord with our present findings based on an entirely different approach.

Oxonium is one of the most reactive ions known. It creates an intensely acid environment in its immediate vicinity. Oxonium clays convert into aluminum clays spontaneously on standing even under wet conditions for relatively short periods. Oxonium is therefore unlikely to remain in the interlayer space for long periods of time in soils and sediments, most of which date back to geologic era. Except for the underclays which may be deposited under acid conditions, most of the "illites" of sediments are found in marine deposits, which have a high salt concentration. Under such conditions, the pH of the system would tend to remain neutral as hydrolysis of cations would not occur to any appreciable extent. Since the environment is alkaline, or at least not acid enough for the presence of much oxonium ions, an abundance of oxonium ions in the environment of mica genesis is hardly to be expected.

TABLE 5.—pH CHANGES IN EQUILIBRIUM MATRIX SOLUTION ON TREATMENT OF MICACEOUS CLAYS WITH NaTPB.

| Locality or origin | pH values | | | | | |
|---|---|---|---|---|---|---|
| | Initial | 6 hr | 24 hr | 3 days | 20 days | 81 days |
| Beavers Bend | 7.0 | 7.9 | 8.1 | 8.1 | 8.2 | 8.2 |
| Marblehead | 7.2 | 7.6 | 7.6 | 8.4 | 8.4 | 8.4 |
| Camp Randall | 7.4 | 7.4 | 7.5 | 7.6 | nd† | 8.9 |
| New York | 7.2 | 7.5 | 8.5 | 8.9 | 9.1 | 9.3 |
| Fithian | 5.6 | 6.4 | 7.8 | 7.4 | 8.3 | 8.7 |
| Wisconsin | 6.9 | 8.1 | 8.4 | 8.3 | 8.2 | nd |
| Buffalo Hart till | 6.9 | 7.9 | 8.1 | 8.2 | 8.3 | nd |
| Sangamon soil | 7.1 | 8.1 | 8.4 | 8.3 | 8.2 | nd |
| Accretion gley | 6.9 | 7.8 | 8.0 | 8.1 | 8.3 | nd |
| NaTPB control* | | | | | | |
| (a) | 7.0 | 7.1 | 7.4 | 7.5 | nd | 7.9‡ |
| (b) | 7.0 | 6.8 | 7.4 | 7.6 | nd | nd |

  * Solution (a) was the original solution of 0.2 N NaTPB and 1 N NaCl used in this experiment, which after 200 days, had risen to pH 7.9 and then was readjusted to pH 7.0 by a very small droplet of dilute HCl for the shorter time controls; solution (b) was a freshly made similar reagent made of a new lot of NaTPB salt from the same supply house. The much less rapid rise in pH in the control solutions (a) and (b) with no clay present, as compared to the more rapid rise in pH in the presence of the micaceous clays establishes two points, namely, (1) that the clay is a proton acceptor, forwarding the release of OH in the solution faster than with the control, and (2) that the NaTPB solution offers little capacity for neutralizing oxonium (hydronium, $OH_3^+$) through its hydrolysis, thus supporting the conclusion stated in the text that no appreciable isomorphous replacement of K by oxonium occurs in the mica interlayer. The rate of pH rise in the presence of these clay micas was of the same order of magnitude as the pH rise in the presence of pure muscovite (Table 7).
  † nd = not determined.
  ‡ 200 days instead of 81 days.

The rise in pH resulting from treatment of the sample with NaTPB is significant. Even in the case of the sample of Fithian illite, which had an initial pH of 5.6, the pH rose sharply after 6 hr, and ultimately reached a value very close to that of the other samples. The liberation of OH to solution strongly suggests that some proton acceptor mechanism is at work in the system. Since very little hydrolysis of interlayer K or Na is to be expected in this system which has a high salt concentration (1 N NaCl and 0.2 N NaTPB) and since the mineral can be the only proton sink, hydroxylation of some of the oxygens in the mineral structure is indicated. Calculation of the stoichiometric relationship effect that this proton incorporation would have on the pH of the equilibrium matrix solution shows that in the concentrations of the suspensions used, the pH of the solution would rise to values above 10 and the OH water content of the sample would increase by

1.1% on lowering the charge from 250 me/100 g in muscovite to 159 me/100 g in vermiculite solely by this mechanism. This postulate is discussed below in the light of further evidence.

### *Lowering of Layer Charge in Mica by Oxidation of $Fe^{2+}$*

Since vermiculites and montmorillonites possess a much lower charge than the parent micas from which they are derived, it is evident that a charge reduction mechanism is operative simultaneously with the loss of interlayer K from micas. While no entirely satisfactory explanation is, as yet, available to account for this charge reduction, several postulates have been considered. Gruner (1934) suggested that the positive charges lost by removal of K are made up by oxidation of $Fe^{2+}$ to $Fe^{3+}$, or by substitution of $F^-$ or $(OH)^-$ for $O^{2-}$ to maintain electrostatic balance. From thermal analysis data, McConnell (1950) suggested that in montmorillonites, some silicate tetrahedra may have $OH^-$ instead of $O^{2-}$ and the second high temperature endotherm observed in DTA curves arises from OH groups bonded in this manner. Critical examination of the results of several published analyses of vermiculites and hydrobiotities by Foster (1963) led her to the conclusion that most vermiculites do not have sufficient ferric iron in their structure to account for the charge decrease that had taken place.

Samples with high, medium and low ferrous iron contents were weathered by treatment with sodium tetraphenylboron in 1 N NaCl. Changes in CEC, K-content, and ferrous iron content were determined (Table 6) after partial depletion of interlayer K which followed this treatment. The biotite sample lost 96 me/100 g of K from interlayers, while its CEC increased by 74 me/100 g, indicating a loss in layer charge of 22 me/100 g, out of which only 15 me/100 g is accounted for by the oxidation of Fe. This still leaves 34% of the charge decrease unaccounted for. For samples containing smaller amounts of ferrous iron much less of the layer charge decrease (50% for glauconite and 30% for the shale) is accounted for by the oxidation of iron (Table 6).

The data indicate that oxidation of ferrous iron does not account for all the charge loss accompanying K-depletion, even in samples such as biotite with high ferrous iron content. Some other charge reduction mechanism is operating simultaneously with loss of K to account for part of this lowering of charge in high-iron materials and most of it in low-iron samples.

### *Lowering of Layer Charge by Proton Incorporation*

Evidence for proton incorporation in the structure of silicate layers, by hydroxyl formation through proton reaction with oxygen during weathering of mica, is provided by the foregoing data which may be summarized as follows:

(a) During the depletion of K from micas by treatment with NaTPB, and exchange of interlayer K with hydrated Na ions, there is a rise in pH indicat-

ing a proton transfer from $H_2O$ to the mineral structure, leaving OH in solution (Table 5).

(b) A charge reduction mechanism, besides the oxidation of ferrous iron, is operating simultaneously with the loss of K from micas that accounts for part of the loss in charge in high-ferrous iron micas and for most of it in low-iron micas (Table 6).

TABLE 6.—RELATION OF K EXTRACTION TO FERROUS IRON OXIDATION AND CHARGE LOSS

|  | Spruce Pine Biotite | Camp Randall Glauconite | New York Shale |
|---|---|---|---|
|  | In me/100 g of material | | |
| Potassium content: | | | |
| Original | 194.0 | 131.8 | 145.1 |
| After NaTPB | 97.9 | 81.3 | 95.5 |
| Decrease | 96.1 | 50.5 | 49.6 |
| CEC, Ca/Mg: | | | |
| Original | 14.8 | 19.8 | 17.3 |
| After NaTPB | 88.7 | 57.5 | 55.0 |
| Increase | 73.9 | 37.7 | 37.7 |
| Loss of charge | 22.2 | 12.8 | 11.9 |
| Ferrous iron content: | | | |
| Original | 457.0 | 228.5 | 94.9 |
| After NaTPB | 442.3 | 222.1 | 91.3 |
| Decrease | 14.7 | 6.4 | 3.6 |
|  | Percentage of the charge loss | | |
| Charge loss, from $Fe^{2+} \rightarrow Fe^{3+}$ | 66.2 | 50.0 | 30.3 |
| Charge loss, other | 33.8 | 50.0 | 69.7 |

(c) During thermal analysis, vermiculites and montmorillonites of known composition show a higher OH water loss, by about 0.5 to 0.7% than the corresponding parent micas.

These facts lead us to conclude that a proton enters the structure of the mineral, forming an OH with the oxygens in the silicate sheet. The amount of protons so incorporated would equal the layer charge loss not accounted for by the oxidation of Fe. If the above conclusion is valid, the reaction occurring in that part of the material which has lost K can be represented by the equation
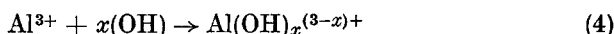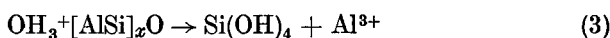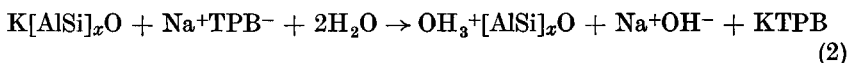
$$K[AlSi]_xO + Na^+TPB^- + H_2O \rightleftharpoons KTPB + [AlSi]_x(OH) + Na^+OH^- \quad (1)$$

in which O represents a structural oxygen and $[AlSi]_x$ represents the remainder of the aluminosilicate mineral. This reaction would result in the accumulation of NaOH in the external solution. If OH ions were removed, then the rate of the forward reaction should be more rapid; in other words, the reaction rate should be pH dependent. The validity of this conclusion was

tested by extracting K from muscovite ($< 2\ \mu$) using NaTPB–NaCl solutions at various pH levels from 5 to 8. Lower pH values were excluded to avoid chloritization reactions in the system. The interlayer K of dioctahedral micas can be extracted only with extreme difficulty (Table 7), so that even with buffered pH 5 NaTPB, less than 30% of the K could be extracted from the material during 30 days. In general, with decreasing pH, increasing amounts of K were extracted. There was, however, little difference between the amounts of K extracted by solutions of pH 7 and 8. The solution buffered at pH 5 extracted the largest amount of K.

TABLE 7.—RESIDUAL K IN MUSCOVITE AND pH OF THE EQUILIBRIUM MATRIX SOLUTION AFTER EQUILIBRATION WITH NaCl–NaTPB AT DIFFERENT pH LEVELS

| | Equilibration time | | | | | |
|---|---|---|---|---|---|---|
| | 1 day | | 3 days | | 30 days | |
| | pH | K (me/100 g) | pH | K (me/100 g) | pH | K (me/100 g) |
| NaTPB–NaCl: | | | | | | |
| pH 5 | 5.7 | 190.3 | 6.2 | 187.2 | 7.3 | 169.2 |
| pH 6 | 6.6 | 192.2 | 6.8 | 190.8 | 7.4 | 163.8 |
| pH 7 | 7.5 | 202.9 | 7.5 | 194.2 | 8.1 | 176.2 |
| pH 8 | 8.3 | 199.8 | 8.4 | 195.1 | 8.6 | 177.4 |
| NaTPB–NaOAc: | | | | | | |
| pH 5 | 5.0 | — | 5.2 | 185.6 | 5.3 | 154.7 |
| Distilled water | 6.8 | 216.2 | 7.1 | 214.1 | 7.2 | 213.7 |

These results prove that the K-release is pH dependent in a closed system involving dioctahedral mica. Similar observations on the pH dependence of loss of K from micaceous clays have been made (Rich, 1964). The pH dependence was attributed to replacement of mica K by $OH^{3+}$ ions formed by hydrolysis of the solution. Since $OH^{3+}$ is a very reactive ion, it will attack the structure of the clay, releasing $Al^{3+}$, which will polymerize into hydroxy aluminum compounds at pH values of 5 and above. This sequence of reactions may be written:

$$K[AlSi]_xO + Na^+TPB^- + 2H_2O \rightarrow OH_3^+[AlSi]_xO + Na^+OH^- + KTPB \tag{2}$$

$$OH_3^+[AlSi]_xO \rightarrow Si(OH)_4 + Al^{3+} \tag{3}$$

$$Al^{3+} + x(OH) \rightarrow Al(OH)_x^{(3-x)+} \tag{4}$$

Reaction (4) would produce a chlorite material from mica and take up $(3-x)$ charge per Al. Although, in many natural vermiculites, enough chlorite is present in the sample to account for this type of reduction in layer charge, many vermiculites are known which contain very little chlorite. According to

3

the chloritizing scheme, the sample of vermiculite from Texas with a CEC of 153 me/100 g and 5% other minerals (quartz, mica, etc.) should contain 70% vermiculite and 25% chlorite, if it is assumed that vermiculite has a layer charge equivalent of parent mica. The 25% chlorite should give an OH water loss of 6.36% (4.32% for the parent mica, phlogopite, and 13.0% for magnesian chlorite). From thermal gravimetric analysis, the vermiculite component of the sample (by cation exchange capacity procedure) is 95% and OH water loss between 300 and 950°C is 5.09%.

Also, in experiments with micaceous clays involving depletion of K with NaTPB, the thermal OH water loss (Table 3) is consistently slightly less than that present in the sample originally, as opposed to an increase expected from equations (2) to (4).

### Summary Observations on a Charge Reduction Mechanism during the Weathering

In a discussion on the water content of vermiculite, Bradley and Serratosa (1960) assume that the charge of vermiculite is the same as that of mica and, therefore, if any ferrous iron oxidation takes place in the system, a corresponding decrease in hydroxyls (H loss) should occur in order to maintain electrostatic balance. White (1958) showed that the layer charge of muscovite should be reduced to about $6.7 \times 10^4$ e.s.u./cm$^2$ (which is equivalent to 160 me/100 g) for expansion to occur. Structure analysis of vermiculite by single crystal techniques (Shirozu and Bailey, 1966) indicate that a phlogopite-derived vermiculite has an interlayer Mg content of 0.41 atoms per 4 tetrahedral sites. Interlayer exchange capacities of vermiculites from several different sources, measured by careful use of the experimental techniques of Alexiades and Jackson (1965), as well as the literature values compiled by them give a mean value of 154 me/100 g. Allowance of 5 me/100 g for external charge gives a CEC of 159 me/100 g. This would indicate that during the expansion (weathering) of mica, lowering of layer charge has occurred, while thermal gravimetric analysis (TGA) data show an increase in hydroxyls in vermiculite (rather than a decrease that would reflect OH → O in the structure).

Based on chemical and differential thermal analysis combined with X-ray investigations, Erdelyi and co-workers (1958) show that structural assignments of TGA values can be made other than the structural OH$_3^+$ assignment made by Brown and Norrish (1952). They assume that part of the oxygen atoms in the backbone elements are substituted by OH atoms in amounts equivalent to the alkali deficit in the dodecahedral positions. They assume that in hydrous micas the number of ions in the dodecahedral positions depends solely on the number of trivalent ions in the tetrahedral positions. Single crystal analysis of a Mg-vermiculite (Shirozu and Bailey, 1966) showed one Al to three Si, indicating no deviation of tetrahedral composition from ideal mica. The data presented here seem to indicate that proton incor-

poration in the basic silicate sheet operates as a co-mechanism for the net CEC charge loss of micas when K is lost. While no definite experimental evidence could be obtained to locate the positioning of this proton in the structure, positioning on the unshared oxygen of the tetrahedrons occupied by Al which is omorphously replaces Si, has been suggested (McConnell, 1950; Jackson, et al., 1952; Jorgensen and Rosenqvist, 1963). This supposition is in accord with the dictate of crystal chemistry whereby silicon atoms do not occupy tetrahedra with different ions other than oxygen.

## ACKNOWLEDGMENTS

## REFERENCES

ALEXIADES, C. A., and JACKSON, M. L. (1965) Quantitative determination of vermiculite in soils: Soil Sci. Soc. Amer. Proc. 29, 522–27.

ALEXIADES, C. A., and JACKSON, M. L. (1966) Quantitative clay mineralogical analysis, Clays and Clay Minerals: Proc. 14th Conf., 35–52.

BRADLEY, W. F., and SERRATOSA, J. M. (1960) A discussion of the water content of vermiculite: Clays and Clay Minerals, Proc. 7th Conf., Pergamon Press, London, 260–70.

BRINDLEY, G. W., and SANDALAKI, Z. (1963) Structure, composition and genesis of some long spacing, mica-like minerals: Amer. Min. 48, 138–49.

BROWN, G., and NORRISH, K. (1952) Hydrous micas: Mineral Mag., 29, 929–32.

ERDELYI, J., KOBLENCZ, V., and TOLNAY, V. (1958) Über Hydroparagonit, ein neuer Glimmermineral, sowie über seine Beziehungen zum Hydromuskovit, Natronillit und Brammalit: Acta Geologica, Acad. Sci. Hungary, 5, 169–86

FOSTER, M. D. (1963) Interpretation of the composition of vermiculites and hydrobiotites: Clays and Clay Minerals, Proc. 10th Conf., Pergamon Press, London, 70–89.

GRIM, R. E., BRAY, R. H., and BRADLEY, W. F. (1937) The mica in argillaceous sediments: Amer. Min. 22, 813–829.

GRUNER, J. W. (1934) Structures of vermiculite and their collapse by dehydration: Amer. Min. 19, 557–65.

JACKSON, M. L., HSEUNG, Y., COREY, R. B., EVANS, E. J., and VANDEN HEUVEL, R. C. (1952) Weathering sequence of clay-size minerals in soils and sediments. II. Chemical weathering of layer silicates: Soil Sci. Soc. Amer. Proc. 16, 3–6.

JACKSON, M. L. (1956) Soil Chemical Analysis—Advanced Course: Second Printing, 1965; Published by the author, University of Wisconsin, Madison, Wisconsin.

JACKSON, M. L. (1958) Soil Chemical Analysis: Prentice-Hall, Englewood Cliffs, N.J.

JORGENSEN, P., and ROSENQVIST, I. TH. (1963) Replacement and bonding conditions for alkali ions and hydrogen in dioctahedral and trioctahedral micas: Norsk Geol. Tidsskr. 43, 497–536.

MANKIN, C. J., and DODD, C. G. (1963) Proposed reference illite from the Ouachita Mountains: Clays and Clay Minerals, Proc. 10th Conf., Pergamon Press, London, 372–79.

McCONNELL, D. (1950) The crystal chemistry of montmorillonite: Amer. Min. 35, 166–72.

MEHRA, O. P., and JACKSON, M. L. (1959) Constancy of the sum of mica unit cell potassium surface and interlayer sorption surface in vermiculite-illite clays: *Soil Sci. Soc. Amer. Proc.*, **23**, 101–5.

NELSON, B. W. (1956) The illites from some northern Ohio shales: *Clays and Clay Minerals*, Proc. 4th Conf., Natl. Acad. Sci.—Natl. Res. Council Pub. 456, pp. 116–24.

RAMAN, K. V., and JACKSON, M. L. (1965) Rutile and anatase determination in soils and sediments: *Amer. Min.* **50**, 1086–92.

RICH, C. I. (1964) Effect of cation size and pH on K exchange in Nason soil: *Soil Sci.* **98**, 100–6.

ST. ARNAUD, R. J., and MORTLAND, M. M. (1963) Characteristics of the clay fractions in a chernozemic to podzolic sequence of soil profiles in Saskatchewan: *Canadian Jour. Soil Sci.* **43**, 336–49.

SHIROZU, HARUO, and BAILEY, S. W. (1966) Crystal structure of a two layer Mg-vermiculite: *Amer. Min.* **51**, (in press).

WEAVER, C. E. (1965) Potassium content of illite: *Science* **147**, 603–5.

WHITE, J. L. (1958) Layer charge and interlamellar expansion in a muscovite: *Clays and Clay Minerals*, Proc. 5th Conf., Natl. Acad. Sci.—Natl. Res. Council Pub. 566, 289–94.

WILLMAN, H. B., GLASS, H. D., and FRYE, J. C. (1963) Mineralogy of glacial tills and their weathering profiles in Illinois. Part I. Glacial tills: *Illinois State Geol. Survey* Circular 347.