

# WEATHERING OF MIXED-LAYER CLAYS IN SOILS

By

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## ABSTRACT

The occurrence of mixed-layer clays was noticed in several New England soils; a particularly well developed mixed-layer sequence involving the weathering of randomly interstratified vermiculite and illite was intensively studied. Weathering of the interstratified system resulted in the formation of alumina in interlayer positions as evidenced by chemical and x-ray tests. The change in "apparent" spacing of the clay was found to be statistically correlated with sample depth which is in turn related to the intensity of weathering. The change in "vermiculite" spacing from 14.2 to 13.9 Å was also found to be correlated with depth. The diffraction effects of the interstratified mineral are discussed in the light of the Hendricks and Teller formula and Méring's refinement of the formula. The evidence points to the alumina being "brucitic" in character; this modifies the curves calculated by Brown and MacEwan for the randomly interstratified 10 to 14 Å mineral. The role of interstratification in the process of soil formation is discussed.

## INTRODUCTION

The importance of clay minerals in determining the physical and chemical properties of soils has encouraged soil scientists to investigate them; Jackson and Sherman (1953) have reviewed clay-mineral studies on soils. Many of the data obtained by investigators on clay-mineral weathering have been interpreted in terms of a monomineralic system, though the possible widespread existence of mixed-layer clays in soils was indicated by Jackson and others (1952).

The theoretical treatment of Hendricks and Teller (1942) and the curves subsequently calculated by Brown and MacEwan (1950) have been used to show the existence of these mixed-layer clays in soils and sediments. However, very little is known about the changes which these systems undergo upon weathering. It is the purpose of this paper to follow by x-ray and chemical treatments the changes observed in a randomly interstratified vermiculite-illite clay.

## EXPERIMENTAL

The clays were segregated from the coarser particles by centrifugation; the clays were subdivided into fine ( $<0.2\mu$ ) and coarse (2 to  $0.2\mu$ ) clay fractions. The x-ray unit consisted of a Norelco Geiger Counter Spectrometer, for oriented specimens, and a 114.59 mm circular camera for powder diagrams. Copper radiation was used.

Chemical analysis of the clay fractions was performed using the method of Corey and Jackson (1953). Potassium was determined with a model 52A Perkin Elmer flame photometer with 200 ppm lithium as internal standard; the colorimetric readings were made with a Beckman DU spectrophotometer.

The soil sample was originally obtained for soil-genesis studies; each sampling depth therefore represented a particular soil horizon. The samples were air dried, sieved through a 2-mm sieve and treated with hydrogen peroxide for organic matter decomposition.

### THE SOIL

The soil from which this sample is taken has been classified as a Paxton fine sandy loam and belongs to the Brown Podzolic great soil group. The solum extends to 25 inches; the *C* horizon is markedly different from the other horizons by its compactness. A brief description of the profile is included below.

<i>Horizon</i>	<i>Depth</i>	<i>Description</i>
<i>A<sub>p</sub></i>	0 to 8 inches	Very dark grayish-brown (10 YR 3/2) <sup>1</sup> horizon of fine sandy loam texture. Numerous grass roots and worm channels. Small pebbles 1 cm in diameter abundant. pH 5.8.
<i>B<sub>21</sub></i>	8 to 14 inches	Yellowish-brown (10 YR 5/8) fine sandy loam. Coarse fragments make up 5 to 10 percent of the mass with quartz, chert and hornblende schist predominant. pH 5.9.
<i>B<sub>22</sub></i>	14 to 19 inches	Light olive-brown (2.5 Y 5/6) fine sandy loam. Rock fragments of schist, diabase and granite make up 5 percent of coarse material. Many roots extend to this level but few penetrate deeper. pH 6.0.
<i>B<sub>3</sub></i>	19 to 25 inches	Olive (5 Y 5/4) gritty fine sandy loam. Same rock-fragment composition and distribution as above horizon. Material more compact than above horizons but friable when removed. pH 6.0.
<i>C</i>	25 to 45 inches	Olive-gray (5 Y 5/2) fine sandy loam. This horizon is compact. Pebbles up to 2 cm in diameter make up 25 percent by volume of this horizon. pH 6.2.
<i>D</i>	45 to 70 inches	Olive (5 Y 5/4) fine sandy loam; loose and crumbly. Water table at 70 inches. pH 6.4.

The soil is in a zone of humid cool temperate climate. Precipitation averages 40 to 45 inches per year with well-distributed monthly means of 3 to 4 inches. The winters are relatively long and cold and the summers are short and warm.

### RESULTS AND DISCUSSION

Owing to the weaker and poorly defined peaks of the fine-clay fraction which made it difficult to follow weathering changes accurately, data are reported for the coarse-clay fraction only. The general trend is similar for the two size fractions. From the chemical analyses (Table 1) it is seen that with increasing weathering intensity (surface proximity), potassium concentration is reduced and water and/or hydroxyls is added to the clay system. In addition the alumina content decreases and the silica concentration increases with depth.

<sup>1</sup> Color notation on moist soil using Munsell color charts.

TABLE 1 — PERCENTAGE ELEMENTAL COMPOSITION EXPRESSED AS THE OXIDE AND HEATING WEIGHT-LOSS DATA FOR THE COARSE CLAY FRACTION.

Element and temperature	Horizon and depth (inches)					
	<i>A<sub>p</sub></i> 0-8	<i>B</i> <sub>21</sub> 8-14	<i>B</i> <sub>22</sub> 14-19	<i>B</i> <sub>3</sub> 19-25	<i>C</i> 25-45	<i>D</i> 45-70
SiO <sub>2</sub>	34.6	34.6	38.9	45.1	42.0	42.8
Al <sub>2</sub> O <sub>3</sub>	32.1	31.5	28.8	27.8	27.9	27.3
Fe <sub>2</sub> O <sub>3</sub>	11.1	11.6	9.6	9.6	10.3	9.3
TiO <sub>2</sub>	0.90	0.98	0.73	0.60	0.42	0.43
K <sub>2</sub> O	1.96	2.29	2.73	3.58	3.92	4.45
MgO	2.58	2.94	3.59	4.30	4.24	4.08
200° C	5.20	4.12	4.58	2.24	1.56	0.72
300° C	4.77	4.70	3.43	1.95	0.89	0.43
400° C	2.82	3.54	3.10	1.56	2.32	2.80
600° C	3.75	1.55	2.47	2.88	3.54	3.72
900° C	1.12	1.50	1.05	1.26	1.39	1.78
Total	100.9	99.3	99.0	97.2	98.5	97.8

The chemical analyses (especially the K<sub>2</sub>O values), cation-exchange capacity, and x-ray data were used to arrive at an approximate mineralogical composition of the coarse-clay fraction (Table 2). The quartz and feldspar values were approximated from the very weak 4.2 and 3.2 Å maxima. The gibbsite content was estimated by x-ray patterns and confirmed with differential thermal analysis for the *A<sub>p</sub>* horizon only. Hematite is approximated from the free iron-oxide analysis. The chlorite estimation is based on a very weak maximum at 13.8 Å after the sample was heated to 550° C. The kaolin content is based on heating the sample to 450° C as recommended by Johns, Grim, and Bradley (1954).

The principal minerals in the clay fraction are illite, vermiculite, and a mixed-layer clay involving illite and vermiculite. Figure 1 illustrates the diffraction curves obtained from several samples that were x-rayed after calcium saturation and glycerol solvation.

TABLE 2. — SEMIQUANTITATIVE ESTIMATE OF THE MINERALS IN THE COARSE CLAY FRACTION.

Minerals	Horizon and depth (inches)					
	<i>A<sub>p</sub></i> 0-8	<i>B</i> <sub>21</sub> 8-14	<i>B</i> <sub>22</sub> 14-19	<i>B</i> <sub>3</sub> 19-25	<i>C</i> 25-45	<i>D</i> 45-70
Quartz	<5	<5	<5	<5	<5	<5
Feldspars	<5	<5	<5	—	—	—
Chlorite	<5	<5	<5	<5	<5	—
Illite	30	25	30	30	30	40
Interstratified illite-vermiculite	—	15	20	35	45	45
Vermiculite	30	20	15	10	5	5
Montmorin	—	—	—	—	—	—
Kaolin	10	10	10	10	10	10
Gibbsite	5	5	—	—	—	—
Hematite	10	10	10	7	5	5
Total	<100	<100	<100	<102	<105	<110

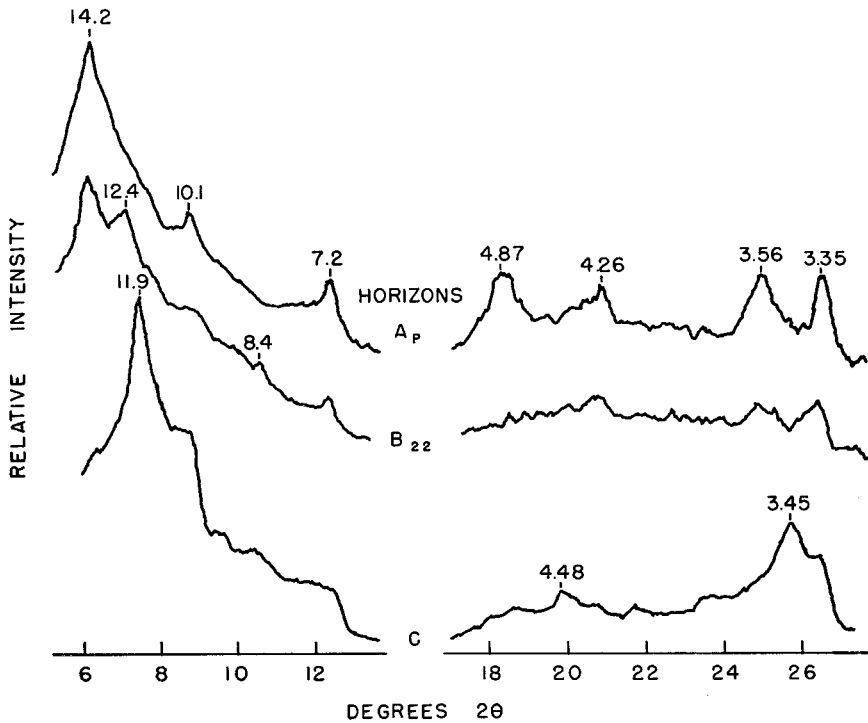


FIGURE 1.—Diffraction tracing of the coarse clay fraction of the  $A_p$ ,  $B_{22}$  and  $C$  horizons.

The identification of the interstratified component rests on the following tests. Firstly, the clay fraction was subjected to potassium saturation according to the method of Barshad (1948). The results of this and other tests are reported in Table 3. The 11.6 Å spacing of the mineral in the  $D$  horizon collapsed giving a strong 10.3 Å and a very weak 11.6 Å spacing after the Barshad treatment. The spacing which was slightly larger in the  $C$  horizon clay and which increased with proximity to the surface was not affected by this potassium treatment. The basal spacing of the interstratified component collapsed when the clay was heated in the furnace. The 11.6 Å spacing of the calcium-saturated clay from the  $D$  horizon collapsed at 300° C to 10.3 Å. Clay from each succeeding horizon above the  $D$  resisted collapse at higher and higher temperatures (Table 3); the basal spacing of clay from the  $A_p$  horizon collapsed to 10.5 Å when heated to 500° C and was not affected by the 300° C heating.

The above response of the mineral indicates that the hydrated component in the  $D$  horizon is vermiculitic but in higher horizons it becomes "chloritized" with increased weathering intensity. The behavior further suggests that the "chloritization" reaction is incomplete. This type of behavior has been noticed with several soils from New England and is closely related to iron and aluminum in interlayer positions. In order to test the hypothesis that the noncollapse of

the hydrated component is caused by iron and alumina, the clays from the different horizons were treated with sodium dithionite and sodium citrate for iron removal (Aguilera and Jackson, 1953) and then saturated with potassium using potassium chloride. The clays collapsed to lower spacings; the amount of decrease depended on the original spacings as shown in the last two columns of Table 3. Further tests with normal KOH plus KCl solutions (Brown, 1953) gave spacings which revealed the collapsed state of the mineral. The latter test together with the oxide-removal test indicate that alumina is responsible for the noncollapsible state of the hydrated mineral; the reason underlying the statement is based on the solubility of alumina at high pH and complexing of aluminum by citrate.

The idea that alumina prevented collapse became even more tenable when the citrate solution from the iron-reducing treatment was found to contain a large amount of alumina. The  $B_{22}$  horizon was selected because it was below the organic-matter zone and yet similar to the other samples. The material removed by the dithionite-citrate treatment contained 9.39 percent free  $Fe_2O_3$  and 6.23 percent free  $Al_2O_3$ . When sodium citrate was used without the reducing agent, the amounts of free iron oxide and alumina released and complexed were 0.90 percent and 2.10 percent respectively. It should be mentioned that the 6.23 percent free alumina represents two treatments with sodium dithionite-citrate and two washings with citrate whereas the 2.10 percent represents two washings with sodium citrate. Jackson and others (1954) report that the iron-removal

TABLE 3. — EFFECT OF CATION SATURATION, HEAT AND FREE OXIDE REMOVAL TREATMENTS ON THE 001/001 SPACING OF THE INTERSTRATIFIED MINERAL.<sup>1</sup> (IN ANGSTROM UNITS)

Horizon and depth (inches)	Calcium saturation				Potassium saturation	
	Air dried	300° C	400° C	500° C	Air dried	Air dried; free oxides removed
$A_p$ 0-8	14.2	14.0	14.0 and 11.9	10.5	14.2	12.6
$B_{21}$ 8-14	14.2-14.0	14.2-13.4 and 13.0-12.6	11.0	10.5	14.0	11.9
$B_{22}$ 14-19	14.2 and 12.3	11.9	10.9-10.8	10.5	14.0 and 12.4	10.9
$B_3$ 19-25	11.9	11.6	10.8-10.6	10.3	11.9	10.9
$C$ 25-45	11.9	11.4	10.8-10.6	10.3	11.9	10.6-10.3
$D$ 45-70	11.6	10.3	—	—	11.6 <sup>2</sup> and 10.3	—

<sup>1</sup> Dashes refer to the range in the diffraction maximum; *and* is used when two distinct maxima are observed.

<sup>2</sup> 11.6 Å spacing very weak in intensity as compared to the calcium saturated air dried sample.

treatment performed on a bauxite sample containing 81.1 percent gibbsite showed that only 3.05 percent  $\text{Al}(\text{OH})_3$  or 1.99 percent  $\text{Al}_2\text{O}_3$  was removed.

After removal of iron and aluminum by the dithionite-citrate treatment, cation-exchange capacity was determined for the clay of the  $B_{22}$  horizon. The untreated coarse-clay fraction possessed an exchange capacity of 27.0 meq per 100 g of sample based on the ignited weight; the treated sample exhibited an exchange capacity of 66.5 meq per 100 g of sample based on the ignited weight (the iron and alumina removed were added to the weight as the oxides for calculation). This may be interpreted to mean that the alumina was present as a neutralizing ion or was blocking the entrance of exchangeable ions. The gradual changes in properties noticed with heating and cation saturation tests would mean that the vermiculite-illite interstratification is changing to a chlorite-illite system or to a chlorite-vermiculite-illite system.

The absence of a peak at approximately 24 Å reduced the probability that this is a regularly interstratified system. The x-ray pattern for the lower horizon clay resembles the description for hydrobiotite (Walker, 1951). In order to follow the weathering changes more accurately the clay samples were x-rayed again by manually scanning  $2\theta$  at 0.1 degree intervals and at 0.05 degree intervals near the peaks. Using copper radiation, each sample was scanned from 6 to 9 and from 24 to 27 degrees  $2\theta$ . Each scanning was repeated five times.

The maxima obtained by the above method are shown in Table 4 and plotted in Figure 2. The graph of Figure 2 was plotted using the average Geiger counts for five measurements of each angular setting. The data in Table 4 represent the maxima derived from the frequency of occurrence of a setting representing the peak angle. The maxima obtained by the two methods are in close agreement.

The 001/001 and 003/004 maxima of the *D* horizon give similar values of

TABLE 4. — THE MEAN 00L SPACINGS AND STANDARD DEVIATIONS FOR THE INTERSTRATIFIED AND "VERMICULITE" COMPONENTS AS DETERMINED BY MANUAL SCANNING.

Horizon and depth (inches)	Interstratified		"Vermiculite"	
	001/001	003/004	001	004
<i>A<sub>p</sub></i>				
0-8	13.97 ± 0.04	3.508 ± 0.002	13.97 ± 0.04	3.534 ± 0.003
<i>B<sub>21</sub></i>				
8-14	13.67 ± 0.03	3.471 ± 0.003	13.91 ± 0.04	3.531 ± 0.004
<i>B<sub>22</sub></i>				
14-19	12.51 ± 0.03	3.455 ± 0.003	14.09 ± 0.04	3.534 ± 0.003
<i>B<sub>3</sub></i>				
19-25	11.81 ± 0.02	3.427 ± 0.003	14.11 ± 0.02	3.534 ± 0.003
<i>C</i>				
25-45	11.91 ± 0.03	3.449 ± 0.003	14.13 ± 0.04	3.549 ± 0.007
<i>D</i>				
45-70	11.61 ± 0.02	3.405 ± 0.003	14.24 ± 0.00	3.549 ± 0.004

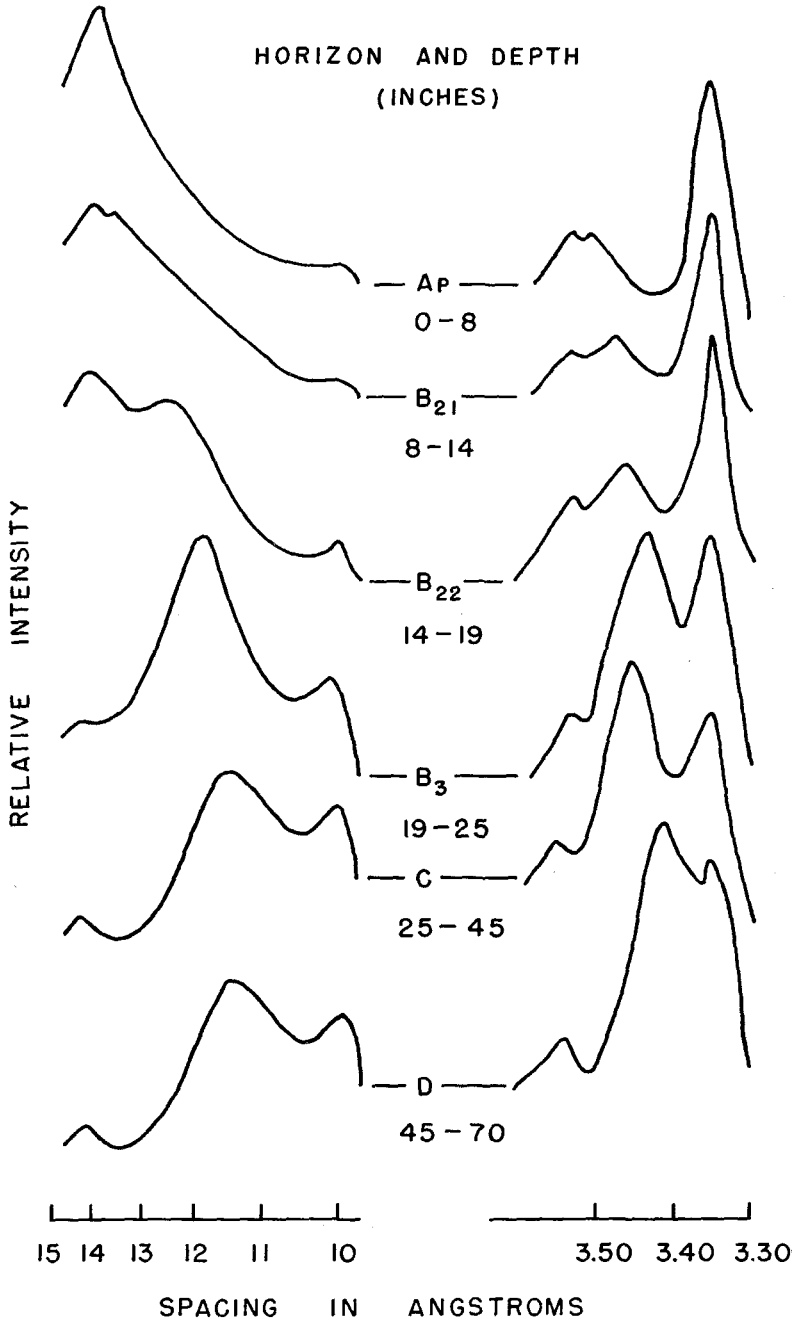


FIGURE 2.— Diffraction maxima in the 15 to 10 Å and 3.50 to 3.30 Å regions. Curve represents points obtained by averaging five independent Geiger-counter readings at  $0.1^\circ 2\theta$  intervals.

the amount of expanded component when the curves of Brown and MacEwan (1950) are used; thus the 001/001 gave 32 percent expanded component and the 003/004 gave 36 percent expanded component. It is reiterated here that the heating and potassium treatments revealed the mineral to be "ideal" vermiculite-illite in this horizon.

With increasing proximity to the surface, the interstratification changes in composition as revealed by the diffraction pattern (Fig. 2). The principal change involved is the increase in the hydrated component and decrease of illite. This change in spacing with depth is statistically significant.

The  $B_{21}$  and  $A_p$  horizons reveal the importance of investigating the higher-order spacings. The 003/004 spacing in the  $B_{21}$  horizon clearly shows the presence of the interstratified component closely related to that of the  $B_{22}$  horizon; the 001/001 spacing for the  $B_{21}$  clay is revealed by a strong reflection at 13.91 Å which would normally be assigned to vermiculite or chlorite, and a "hidden" spacing at 13.67 Å as shown in Figure 2. The x-ray powder pattern obtained on film revealed no evidence for an interstratified system; the 004 and 003/004 spacings appeared as one spacing at 3.52 Å.

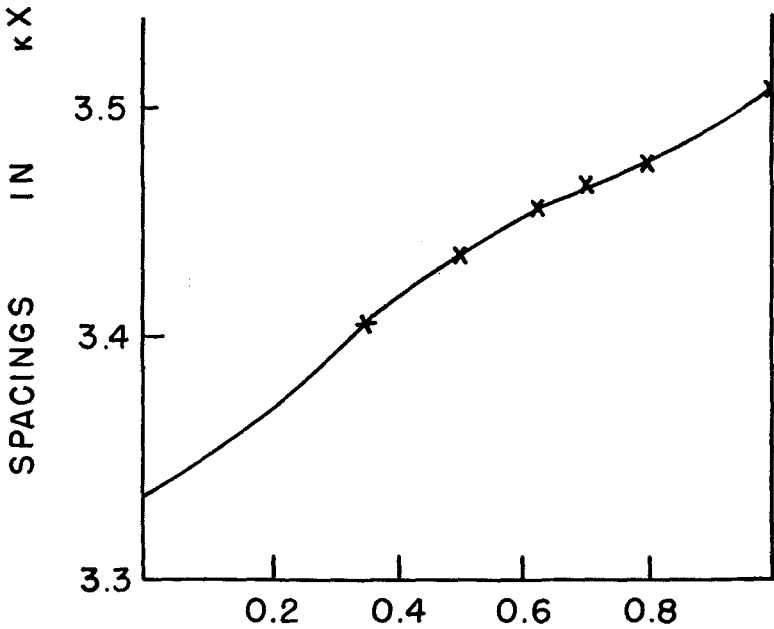
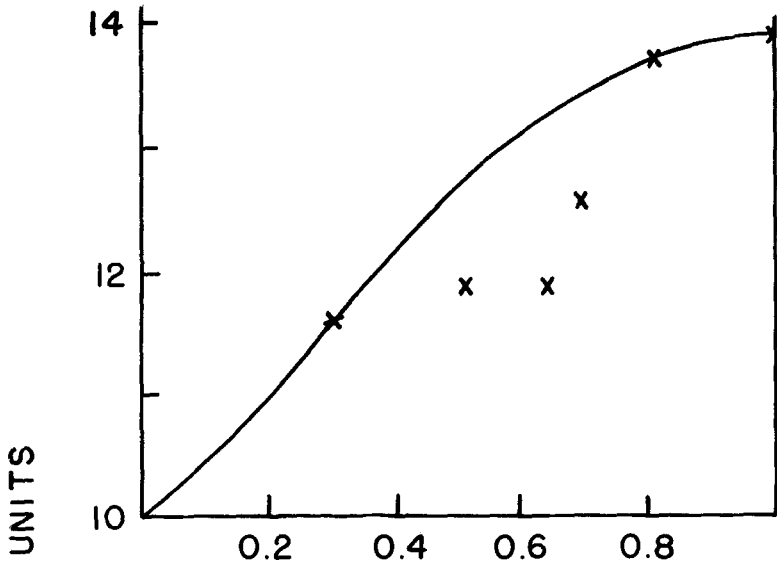
When the 001/001 and 003/004 spacings are considered for the  $B_{22}$ ,  $B_3$ , and  $C$  horizons, the degrees of hydration derived from the two separate spacings differ greatly (Fig. 3). One possible way of rectifying the difference between the two values is to consider the 004 spacing of the expanded component to be 3.55 Å. This would reduce the degree of hydration as calculated from the 003/004 curve. However, to achieve reasonable agreement between the 001/001 and 003/004 spacing with respect to the degree of hydration, the curve would have to be changed drastically from the original shape.

Another possible cause for the difference in the two values may be the use of curves which are not appropriate for the system under investigation. In particular the assumption in the Hendricks and Teller formula, that the layers have the same structure factor may invalidate the use of the curve. It has already been shown that the clays contain appreciable interlayer alumina. Méring (1950) has shown that the assumption involving the structure factor is not valid for interlayers of brucite in the mica-chlorite system. Thus Méring showed that a 50 percent distribution of mica and chlorite in a randomly interstratified system gave a spacing of  $11.7 \pm$  instead of  $12.5 \pm$  Å; the latter value being that of a mica-vermiculite system. Additional evidence that "chloritization" may be taking place is shown in the normal vermiculite spacing of 14.24 Å which was reduced to 14.09 Å in the  $B_{22}$  horizon. This change of the vermiculite spacing with depth in the profile was found to be statistically significant.

The interpretation of the weathering changes as outlined above has several important consequences in pedology. The occurrence of alumina in interlayer positions is related to potassium and phosphate fixation reactions. The presence of alumina in interlayer positions would prevent collapse of the structure and reduce potassium fixation. This situation would favor a relatively high degree of phosphate fixation since the alumina is in interlayer positions and is capable of taking part in exchange reactions.

Another mixed-layer structure thus far identified in soils but not reported herein is montmorillonite and illite. This association may prove to be very important in genetic studies of relatively acid soils of the northeastern states. Studies on several soils from New England have shown that the  $A_2$  horizon (the





FRACTION OF HYDRATED COMPONENT

FIGURE 3. — Comparison of the derived 001/001 and 003/004 spacings with the theoretical curves of Brown and MacEwan (1950).

gray, strongly leached horizon) of podzols contains montmorin interstratified with illite. Montmorins occurring under acid conditions may be closely related to interstratified minerals whereas the montmorins of basic systems may be monomineralic to a greater degree. The stability of the montmorin in the acidic and leached zone may be due to illite which serves to hold the layers together. However, studies being carried on in our laboratories have not come along far enough to make positive statements with regard to the process of podzolization. Much more must be learned about the characteristics of mixed-layer clays as well as monomineralic clays before positive statements can be made regarding the specific role of each clay in soils, but the evidence thus far gained appears to justify further research on clays in soils.

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