SOME ANALYSES OF SOIL MONTMORIN, VERMICULITE, MICA, CHLORITE, AND INTERSTRATIFIED LAYER SILICATES[1]

By

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ABSTRACT

Analyses were made of 12 clay fractions and one silt fraction taken from 10 different soil horizons and clay deposits. The analyses presented were selected to represent a wide variety of analytical problems with materials containing 2:1 layer silicates, 2:2 (chlorite) layer silicates, varying amounts of 1:1 layer silicates, and in some cases with appreciable amounts of quartz, feldspars, gibbsite, hematite, magnetite, and (or) anatase.

The analyses were performed by x-ray diffraction, specific surface, integral heating weight loss, and elemental analyses. The x-ray diffraction analyses included both wedge-powder (film recorded) and oriented (Geiger counter recorded) techniques. Vermiculites of soils were found to vary in the degree to which K-saturation would close the interlayer space, but vermiculite is established by: (a) a 14 A spacing when solvated (even with glycerol); (b) closure of the interlayer spacing on heating to 500° C; and (c) an interlayer surface of about 800 m^2 per gm. In the absence of adequate criteria, vermiculites can be mistakenly identified as chlorites.

The data obtained from the various techniques were combined by a system of allocation so that the minerals reported represented a unique fit of all the data. The specific surface measurement, including the measurement of interlayer surface, is a key criterion in the allocation. Interstratified ("mixed layer") layer silicates are determined as the individual component minerals.

The beidellite of Iron River and Putnam soil clay finer than 0.08 microns is extensively interstratified with chlorite, mica, and vermiculite. No discrete x-ray crystalline zones of any of the latter three minerals were observed, but a 19.6 to 19.2 A spacing may be indicative of a superlattice of these materials and beidellite with mica and chlorite at the electron density nodes. A titaniferous ceramic clay contains 43 percent mica (as determined by allocating the 5.03 percent K_2O to muscovite), 20 percent kaolinite (water loss in 300-525°C range), 21 percent TiO_2 and 17 percent of other constituents (by elemental and surface analysis). This occurrence of the full complement of K_2O in clay micas (both biotite and muscovite type) is general for the various clays examined, when the interlayer surface is calculated to halloysite, vermiculite, and montmorin. A general occurrence of interstratification of layer silicates is proposed.

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INTRODUCTION

A single type of analytical technique, such as x-ray diffraction or differential thermal analysis, often yields important *qualitative* information as to the more abundant mineral or minerals of polycomponent clays, but a combination of several analytical methods is essential for a *quantitative* mineralogical analysis. While performing the analyses presented herein the authors have been impressed by the fact that one or two criteria, which are indicative qualitatively, often give a completely distorted view of the quantitative mineral content. This is especially true of the x-ray diffraction technique which, while indispensable for qualitative identification of layer silicates, is virtually without quantitative reliability because of the general occurrence of interstratification ("mixed layer" structure) among the 2:1 and 2:2 (chlorite) layer silicates. This interstratification is of the type referred to by Gruner (1934) as "meta-crystalline". Use of specific surface, integral heating weight loss, and elemental analyses together with qualitative x-ray diffraction and differential thermal analyses permits a decisive quantitative analysis of the minerals present.

The objectives of this paper are:

a. To present some representative analyses of soil mineral colloids containing representatives of the main classes of layer silicates, namely montmorin series, vermiculite, micas (illite), and chlorite, and interstratified mixtures of these, with and without kaolin.

b. To illustrate the residue mechanism of chemical weathering in the system Hydrol Humic Latosol (mostly hydrous oxides) to titaniferous ceramic clay (abundant in micas).

c. To present, through a system of allocation of several types of analytical data, evidence of the occurrence of random interstratification of different layer silicate series in clays generally.

The soils employed are identified within the respective sections in which data are presented. The literature is reviewed in the sections to which it pertains.

EXPERIMENTAL PROCEDURES

The mineral colloid fractions were separated by the procedure of Jackson, et al. (1950), with iron oxide extraction by the procedure of Aguilera and Jackson (1953). The criteria for the analyses reported herein include x-ray diffraction analysis with various exchange saturation, solvation, and heat treatments (Jackson, et al., 1955); internal and total surface measurement (Vanden Heuvel and Jackson, 1955); elemental analysis (Corey and Jackson, 1953); and integral heating weight loss analysis; followed by allocation to mineral components on the basis of the combined data. The system of allocation, details of which are to be published elsewhere, is based on allocation of water and hydroxyl (as a function of temperature) and of elements (particularly K, Ca, and Na) to feldspars and micas, on the basis of the qualitative indication on the x-ray diffraction patterns, within the limits of vermiculite and montmorin set by the specific interlayer surface.

The diffraction analyses were carried out on three specimens, two flat (oriented) specimens and one wedge-powder specimen. Of the two flat specimens, one was exchange saturated with Mg and dried from water at room temperature in the presence of glycerol (weight equal to the colloid) and a second was exchange saturated with K or NH_4 and dried at room temperature from water in the absence of glycerol; they were x-rayed with the General Electric XRD-3 generator and Geiger counter recorder, with copper radiation filtered with Ni. Each flat specimen was then heated at various temperatures up to 500°C and further x-radiated; changes in diffraction intensities of a specimen of a given cation saturation resulting from heat treatment are therefore attributable to the heating (use of the same mount eliminates any possibility of variation in particle orientation as might occur between different mountings). The wedge-powder x-ray diffraction patterns (General Electric XRD-1, with Fe radiation) were made by the White, et al., procedure[1] in which the Mg colloid is solvated with glycerol dissolved in a benzene-ethanol solution.

COLLOIDS CONTAINING MUCH OF THE MONTMORIN SERIES MINERALS

Analyses of soil and clay colloids containing much montmorin (term after Correns; if preferred, this may be read "montmorillonite isomorphous series" which consists of 2:1 layer silicates with an 18 A diffraction spacing when dried in the presence of glycerol) are illustrated with six samples. These analyses illustrate an effective technique for the evaluation of the several associated layer silicate species by allocation of the several types of data. The fact that soil mineral colloids are generally polycomponent has been emphasized earlier (Byers, et al., 1935; Jackson, et al., 1948).

Ahmeek Loam, A_1 Horizon

The Ahmeek loam soil is a Brown Forest soil from northern Wisconsin (location described by the U. S. Department of Agriculture, 1952). The 2-0.2 micron size fraction from the A_1 horizon gave a relatively intense 18 A diffraction spacing (Fig. 1, A) when the sample was dried at room temperature in the presence of glycerol. Drying of this specimen at a steam hotplate temperature caused the volatilization of considerable glycerol and a shift of the basal spacing to 14 A, thus coinciding with that of the vermiculite present. This shift of spacing from 18 to 14 A has been noted commonly in our laboratory with soil beidellites from many localities (with the Hagerstown colloid, Fig. 3 below, for example), although the shift does not occur with many other soil montmorins and with most

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[1] Manuscript to be published (essentials reviewed by Jeffries and Jackson, 1949).

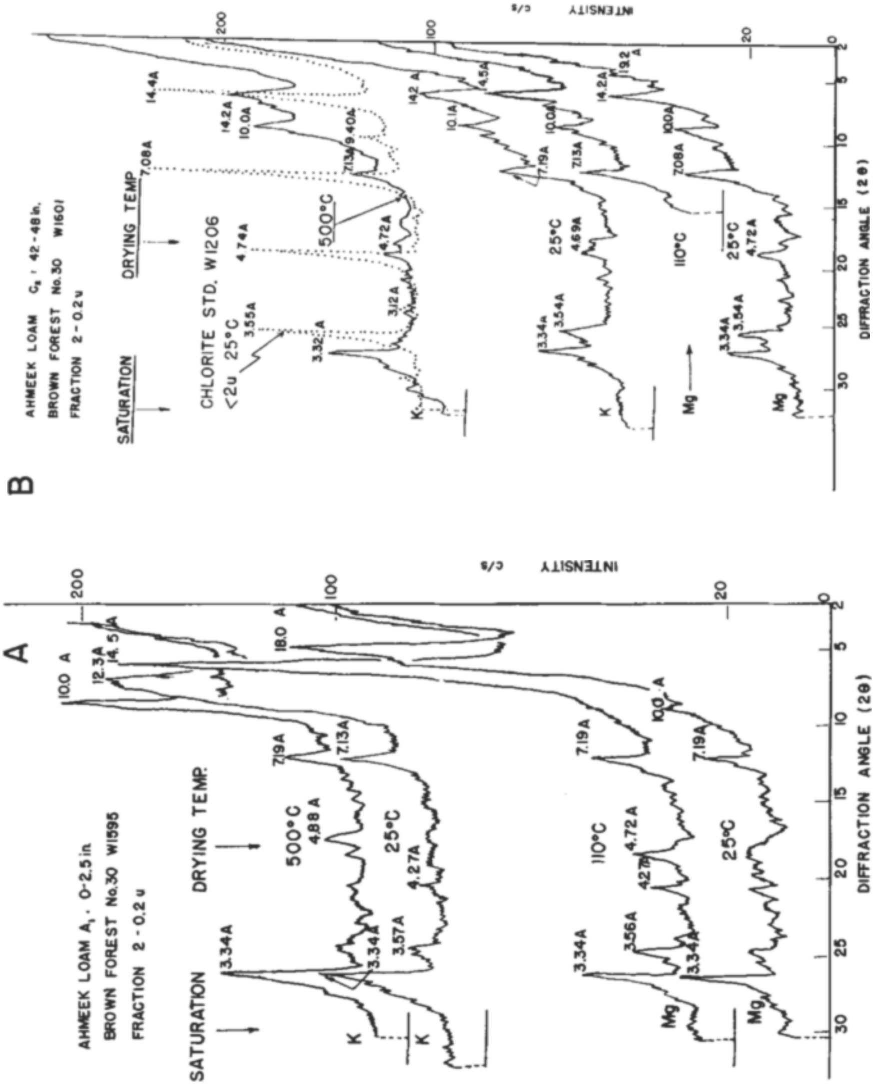

FIGURE 1. — X-ray diffraction patterns of coarse clay from Ahmeek loam; (A) A_1 horizon, showing the shift of basal beidellite 18 A spacing as a result of 110°C drying even in the presence of glycerol; (B) C_2 horizon, which show the retention of 7.2 and 14 A spacings of chlorite on heating to 500°C, thus differentiating the spacings from those of vermiculite or kaolin. The zero intensity base lines are shifted vertically for the successive patterns as indicated with a bar at left.

TABLE 1. — SOIL AND CLAY FRACTIONS ANALYZED, SPECIFIC SURFACE MEASUREMENTS, AND K_2O CONTENTS

	Soil	Size fraction, microns	Percent of soil	Specific surface measurements				Percent K_2O
				Glycerol mgm/50mgm	External* mgm/50mgm	External* m2/gm	Interlayer† m2/gm	
1	Ahmeek lo., A_1 horizon (N. Wis., W1595)	2-0.2	4.36	4.78	0.65	25	205	2.83
2	Ahmeek lo., C_2 horizon (N. Wis., W1601)	2-0.2	2.75	4.81	0.65	25	250	3.04
3	Iron River lo., A_2 horizon (N. Wis., W1587)	<0.08	9.1**	13.8	4.7	180	450	1.67
4	Hagerstown si. lo., B horizon (C. Pa., W1632)	<0.08	6.7	16.0	4.7	180	—	—
5	Putnam si. lo., B horizon (C. Mo., W1075)	<0.2	—	11.6	2.4	90	405	1.64
6	Beidellite (Nashville, Ark., W1020)	<0.2	—	22.2	2.4	90	685	0.77
7	Montmorin (Upton, Wyo., W1021)	<0.2	—	23.3	2.4	90	725	0.25
8	Hilo, B_1 horizon	2-0.2	27.6	—	—	—	—	0.76
	(Hawaii, 49-955)	<0.2	57.9	—	—	—	—	0.25
9	Titaniferous ceramic clay	20-2	46.2	—	—	—	—	1.30
	(Hawaii)	<2	48.2	3.3	1.2	45	40	5.03
10	Davidson soil, A horizon	2-0.2	6.0	3.2	0.65	25	140	1.30
	(Ala., W1638)	<0.2	3.9	7.4	2.4	90	140	0.47

* Calculated by method reported by Vanden Heuvel and Jackson (1954).

** Percentage of the clay fraction; the clay makes up 6.18 percent of this sandy loam soil.

† Sum of that of the montmorin and vermiculite components.

montmorins from bentonites. The controlling factor is believed to be related to the layer charge and this is proposed as a possible means of subdividing the montmorins into two classes. These data show the necessity for restricting the drying temperature to room temperature for the x-ray diffraction test for the montmorin series (including beidellite).

The presence of some chlorite in the Ahmeek A_1 colloid is indicated by the persistence of the 7.2 A spacing after heating to 500°C. On the basis of allocation of surface and elemental analyses (Tables 1 and 2) with consideration of the powder pattern which clearly reveals quartz and feldspars, the minerals present were calculated (Table 3). The disproportionality of the montmorin and vermiculite diffraction intensity (Fig. 1, A) to that of the other components is attributed to the occurrence of these two constituents (a) in large crystals and (b) with little interstratification.

The chlorite formula derived by the Marshall (1935) type calculations is:

$$(Si_{3.43}Al_{0.57})\ (Al_{1.41}Ti_{0.59})(Al_{0.86}Mg_{0.93}Fe^{2+}_{0.54}\,Fe^{3+}_{0.15})O_{10}(OH)_8$$

in which the total brucite cations = 2.48. The mica formula is:

$$K_{1.00}\ (Si_{3.00}Al_{1.00})\,(Al_{0.98}Mg_{0.50}Fe^{2+}_{0.29}\,Fe^{3+}_{0.08}\,Ti_{0.31})\ O_{10}\ (OH)_2$$

in which the octahedral cations = 2.16. The 3:1 Si to Al ratio is not inherent in the method of calculation. The vermiculite plus montmorin average formula is similar to that of the mica except for $X_{0.54}(Si_{3.50}\,Al_{0.50})$ in the first three terms.[1] Intermediate octahedral cation values are expected because of the heterogeneous sources of the colloidal mineral particle population.

Iron River Loam, A_2 Horizon

An x-ray diffraction maximum at 19.6 A was found (Fig. 2) with the colloid less than 0.08 microns separated from Iron River loam, A_2 horizon, a Podzol soil of northern Wisconsin (U.S.D.A., 1952). The 19.6 A spacing is noted in the sample which was Mg saturated and dried at room temperature; an inflection at 10 A spacing (arrow, Fig. 2) indicates some mica, the presence of which is confirmed by a K_2O content of 1.67 percent. The diffraction background is high. It is well known that K or NH_4 saturation of any montmorin, followed by drying from water at room temperature in the absence of glycerol, allows the crystal layers to come together to 11.5 to 13.5 A as observed in this material. According to Walker (1951, p. 203), a vermiculite spacing may decrease to 10.5 A when mineral is NH_4 saturated.

Ammonium versus potassium saturation for the heated specimen.—When the sample was heated to 500°C, a clearly defined diffraction maximum at 10 A was obtained when the sample had been previously saturated with ammonium, and a less distinct one was obtained when it was previously

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[1] X refers to equivalent of exchangeable cations.

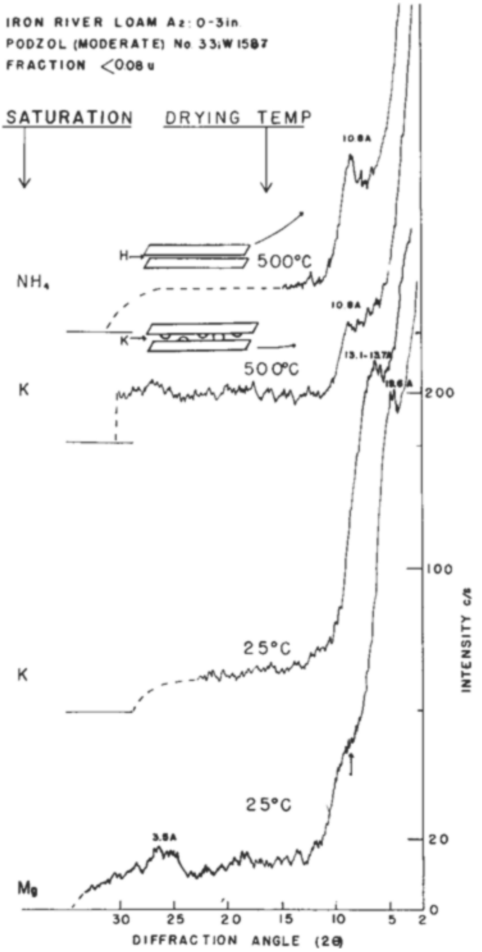

FIGURE 2.—X-ray diffraction patterns of the fine clay of Iron River loam, A_2 horizon. A high background occurs in association with the 19.6 A spacing associated with a superlattice. Drying at 500° C with ammonium saturation gave a more clearly defined 10 A maximum than drying with K saturation.

saturated with K. This is interpreted as an indication that the K ion holds the crystal layers apart somewhat (illustrated in Fig. 2) because the layers have rotated at random around the Z-axis, so as to lose the correspondence of opposing holes in the surfaces of the layers. The ammonium saturated material becomes hydrogen saturated during heating, and this ion would not hold the layers apart appreciably. The coming together of many layers to 10 A on heating disqualifies the material as a "swelling chlorite" (Stephen and MacEwan, 1951). Although the heating tests on the Iron River colloid indicate that ammonium saturation is preferable to potassium saturation, tests with other materials indicate that ammonium is not consistently superior.

A quaternary interstratified system. — The low intensity 10 A diffraction maximum on heating the Iron River colloid (Fig. 2) proves the presence of some chlorite, the brucite layer of which holds some layers apart after heating. Interstratification is intimate enough to prevent either a 14 or a 7 A diffraction maximum to be formed. The mica content is 17 percent (from the K_2O analysis) and the chlorite content is 15 percent (Table 3) based on the allocation of interlayer surface (Table 1) to montmorin (37 percent) and vermiculite (31 percent). An intense (*hk*0) diffraction maximum at 4.45 A observed in the film-recorded pattern (not shown) proves the predominance of layer silicates rather than truly amorphous materials. The system is therefore appropriately termed a *complexly interstratified mixture of layer silicates.* It is probably in part quaternary interstratification. Essentially the same characteristics are found in the Putnam and Ahmeek C_2 colloids (below) and in many other soil colloids that have weathered from micas.

Possible structure. — Although not a premise to the above conclusion on interstratification, one possible structural possibility to account for the increase in basal spacing to 19.6 A and the broadening and low intensity is the occurrence of a "superlattice" of which the 19.6 A spacing is a higher order. Nodes of electron density may be formed by mica and chlorite assemblages, while the electron density internodes would be formed by vermiculite and montmorin sequences. A sequence of 5Mt+

TABLE 2. — ELEMENTAL ANALYSIS AND HEATING WEIGHT LOSS DATA ON CLAY FRACTIONS STUDIED, PERCENTAGES AS OXIDES

Soil	Ahmeek loam		Ti Ceram. clay		Davidson	
Horizon (and No.)	A_1(1)	C_2(2)	—(9)		*A*(10)	
Size fraction, microns	2-0.2	2-0.2	20-2	<2	2-0.2	<0.2
SiO_2	63.9	51.5	19.6	35.4	43.3	35.3
Al_2O_3	19.7	25.7	14.4	24.7	33.6	37.5
FeO	2.08	1.52	2.74	0.35	—	—
Fe_2O_3	1.29	4.56	13.9	6.70	2.82	2.63
TiO_2	2.48	1.68	37.4	20.6	2.02	0.54
MgO	1.21	3.29	1.29	1.66	1.79	1.37
CaO	0.24	1.38	—	—	0.08	0.05
K_2O	2.83	3.04	1.30	5.03	1.30	0.47
Na_2O	0.87	1.05	0.38	0.97	0.30	0.20
H_2O, 110-300°C	3.28	1.02	5.51*	2.42*	4.62	6.53
400-500°C	—	—	0.71	3.67	9.80†	11.4†
to 900°C**	4.96	7.26	1.90	2.00	2.07‡	3.50‡
Total	102.8	102.0	98.2	103.1	101.7	99.5

* 110-400°C

† 300-525°C

** From temperature of previous loss entry, corrected for ferrous iron oxidation.

‡ Uncorrected for ferrous iron oxidation, since iron content is low.

2Vm+2Chl+1Mi, for example, gives a 156 A spacing of nodes of which the eighth order is 19.5 A; also, a sequence of 3Mt+1Chl+1Mi gives a spacing of 78 A of which the fourth order is 19.5 A. These and related layer assemblages would be expected to follow a probability distribution around the mica nucleus rather than a regular sequence. Their complexly interstratified system is similar to but more complex than the Hendricks and Teller (1942) binary randomly interstratified systems. The occurrence of long (2 to 24-layer) unit cell sequences in micas was previously proposed by Hendricks (1939) and such structural units, accompanied by a periodicy of ionic substitution, might result in similarly spaced preferential weathering planes which grow to form the internodes. It is suggested that the nodes around a mica-chlorite nucleus reflect the mica-to-chlorite-to-vermiculite-to-montmorin weathering sequence (Jackson, et al., 1952); Jackson and Sherman, 1953), wherein the weathering is more extensive (to montmorin) the further from the mica node. Chlorite formed adjacent to mica layers would be the "aluminous chlorite" of Jackson and Sherman (1953, p. 236). A distribution of metallic cation saturation, pH, and Mg activity would be expected to follow in phase with the electron density nodes on a "superlattice" unit cell scale, the weathering sequence thus following in consequence. Such a "superlattice" system would represent a *fourth* recapitulation of the weathering sequence of Jackson, et al. (1948).

Another possible source of a 19.5 A spacing would be the presence of two loosely packed brucite layers between some pairs of 2:1 layers. Either the "superlattice" or the double brucite layer mechanism suggested provides a correlation of the relatively low glycerol sorption (Table 1) with the basal spacing higher than that of pure montmorin (which might lead to expectation of more than normal glycerol sorption). Either allows for a high background and line broadening without requiring an excessively fine particle size (which is precluded by the low specific surface).

TABLE 3. — MINERAL CONTENT OF SOIL AND CLAY FRACTIONS
BASED ON ALLOCATION OF COMBINED DATA

Soil or clay fraction	Minerals present expressed in percent*											
	Fl	Qr	Mi	Chl	Vm	Mt	Kl	Gb	Gt	Hm	Ma	An
1. Ahmeek, A_1, 2-0.2μ	19	35	10	10	13	13	0	0	n.d.	n.d.	0	0
2. Ahmeek, C_2, 2-0.2μ	21	20	20	17	6	16	0	0	n.d.	n.d.	0	0
3. Iron River, A_2 $<0.08\mu$	0	0	17	15	31	37	0	0	n.d.	n.d.	0	0
5. Putnam, B $<0.2\mu$	0	0	15	30	14	41	0	0	n.d.	n.d.	0	0
6. Beidellite, Ark. $<0.2\mu$	0	0	7	0	0	93	0	0	n.d.	n.d.	0	0
7. Montmorin, Wyo. $<0.2\mu$	0	0	0.5	0	0	99	0	0	n.d.	n.d.	0	0
9. Ti Ceram. clay, 20-2μ	0	12	11	0	5	0	2	13	8	0	9	37
Ti Ceram. clay, $<2\mu$	0	5	43	0	5	0	20	0	6	0	1	21
10. Davidson, 2-0.2μ	0	5	15	5	10	8	52	5	n.d.	n.d.	0	0
Davidson, $<0.2\mu$	0	0	6	5	7	12	55	15	n.d.	n.d.	0	0

* Fl—feldspars; Qr—quartz; Mi—micas; Chl—chlorites; Vm—vermiculites; Mt—montmorin series; Kl—kaolin family; Gb—gibbsite; Gt—goethite; Hm—hematite; Ma—magnetite; An—anatase; n.d.—not determined — reported percentages are on samples from which free Fe_2O_3 was extracted.

Hagerstown Silt Loam, B Horizon

The Hagerstown silt loam, *B* horizon, a Gray-Brown Podzolic soil, was sampled from the profile near Zion, Pa. (a few miles northwest of State College, displayed during the National Soil Science Society Meetings, in 1951). The Hagerstown soil colloid of less than 0.08 microns gave a distinct 18 A montmorin diffraction spacing (Fig. 3). This fine clay fraction makes up 17.7 percent of the total clay and 6.7 percent of the soil and thus is a very important component of the soil. The surface measurement (Table 1) is also high and thus corroborates the interpretation of a high beidellite content.

Importance of size segregation. — X-ray diffraction patterns are shown also (Fig. 3) for the Hagerstown fine silt (5-2 micron), coarse clay (2-0.2

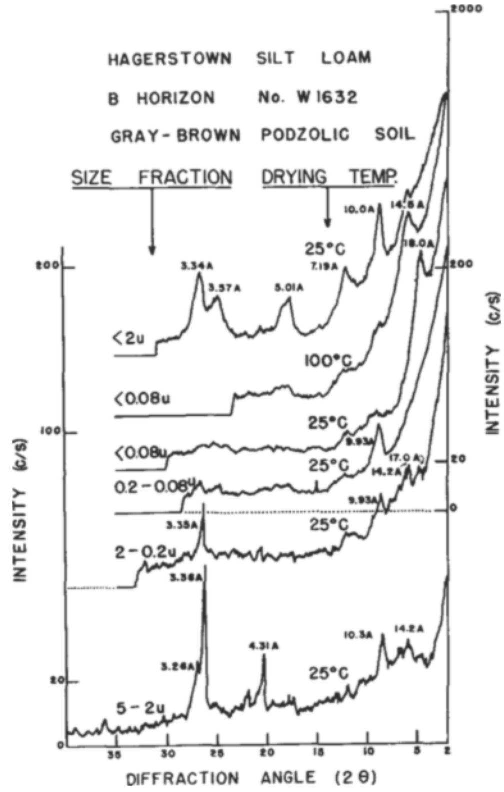

FIGURE 3. — X-ray diffraction patterns of fractions from Hagerstown, *B* horizon. The presence of beidellite (18 A spacing when Mg saturated and dried from water in the presence of glycerol) can only be shown when the less than 0.08 fraction is separated from the rest of the clay fraction. The other fractions contain mainly mica and quartz. Dotted lines lead to the appropriate intensity scale for the respective zero base lines.

micron), medium clay (0.2-0.08 micron) and total clay (less than 2 micron) fractions to illustrate the advantage of separation of the fine clay fraction (less than 0.08 micron) in order to detect the beidellite (18 A in the presence of glycerol) in this soil. Because of its low 18 A diffraction intensity, the beidellite cannot be detected in the diffraction pattern of the total clay, less than 2 microns (upper curve in Fig. 3). The need for segregation at a small size such as 0.06 or 0.08 micron to detect beidellite in some soils was pointed out by Bray (1937). The occurrence of otherwise undetected amorphous mineral colloid in the less than 0.08 micron fraction has been reported in the kaolinic Chester soil clay (Pennington and Jackson, 1948) and in the vermiculitic Omega soil clay (Jackson, et al., 1955). Separation of the mineral colloids at the 0.08 and 0.2 micron limits is included as one of the necessary criteria for soil mineral colloid identification and characterization (Jackson, et al., 1955).

Mica diffraction enhancement. — The intensity of the 10 A diffraction maximum is greater in the sample of total clay of Hagerstown than in any of its clay subfractions (Fig. 3). This phenomenon has been noted in other soils (Jackson, et al., 1955) also, and is attributed to the enhancement of orientation of the coarse clay mica crystals by the presence of fine colloidal (non-mica) particles. These observations are being tested with other materials.

Putnam Silt Loam, B Horizon

The Putnam silt loam, *B* horizon (kindly furnished by Dr. C. E. Marshall) is a grassland Planosol developed on loess, the sample being obtained from the Sanborn field of the Missouri Agricultural Experiment Station. The results with Putnam colloid were compared with those from a beidellite (kindly furnished by C. S. Ross) from Nashville, Arkansas, and with the colloid of Wyoming bentonite (kindly furnished by the American Colloid Co., Chicago, Ill.) from Upton, Wyoming. In each case, the finer than 0.2 micron size fraction was studied.

The basal spacing of the Putnam colloid (Fig. 4) was found to be 19.2 A as compared with 18 A for the usual montmorin. The intensity of diffraction of the Putnam colloid is less than one-tenth that of the Arkansas and Wyoming montmorins (Fig. 4) and shows a much broader first order peak. These characteristics of the Putnam colloid are similar to those of the Iron River colloid (above). The contents of mica and montmorin are similar, but more chlorite and less vermiculite are present (Table 3). The lower basal diffraction spacing of 19.2 A in Putnam colloid, compared with 19.6 A in that of Iron River may arise from the slightly different proportion of these layer silicate constituents in the complexly interstratified system.

Randomness and heating changes. — No higher orders are apparent in either the Putnam or Arkansas sample, and this is taken as indicative of randomness in the basal spacing distribution in both samples. The beidellite

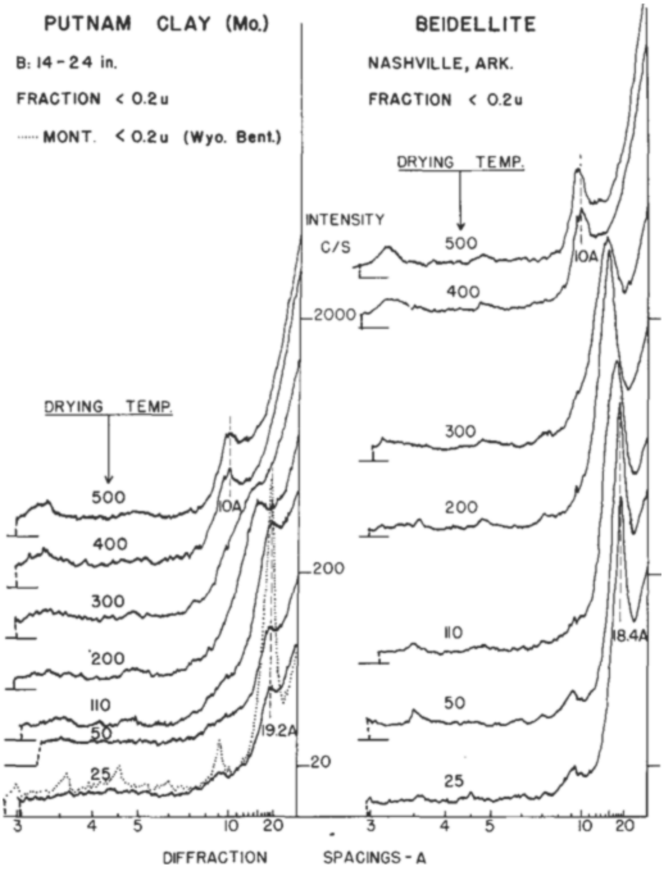

FIGURE 4.—X-ray diffraction patterns of fine clay from Putnam, *B* horizon, in comparison with those of beidellite and a montmorin from Wyoming bentonite.

(randomness through distribution of only 7 percent mica) has nearly as strong an 18 A diffraction intensity as the Wyoming montmorin, but the latter shows six distinct orders (has no randomness). It will be noted that the Putnam colloid maintained its 19 A spacing through the 110°C temperature (stabilized by vermiculite) whereas the 18 A spacing of Arkansas beidellite (not so stabilized) decreased appreciably at the same temperature (cf. the more extensive decrease with Ahmeek A_1 and Hagerstown colloids wherein the montmorin is in large zones as shown by sharp 18 A peaks). The occurrence of only a low 10 A peak in the heated Putnam samples confirms the presence of chlorite and the other constituents shown in the analysis (Table 3).

A COLLOID CONTAINING MUCH MICA AND CHLORITE

Ahmeek Loam, C_2 Horizon

The x-ray diffraction patterns of the coarse clay fraction of Ahmeek loam C_2 horizon (42-48 inches, Fig. 1, B) clearly reveal the presence of mica (illite, 10 A spacing unchanged by heating to 500°C) as well as chlorite (14 and 7.2 A spacings which remain unchanged on heating to 500°C). The small maximum at 19.2 A shows that some montmorin is present, interstratified with chlorite and mica in the superlattice or other complexly interstratified system (as above), but the vermiculite content is lower (Table 3). This maximum disappears as a result of heating to 110°C, as does that of the montmorin in the surface of this soil (Fig. 1, A).

The diffraction intensity of this soil chlorite is low compared with that of standard chlorite ground and fractionated at 2-0.2 microns (Fig 1, B). In addition, the background in the region from 7 to 20 A is much lower for the standard chlorite than in the soil colloid of the same size fraction. These observations are taken to indicate the probable interstratification of some vermiculite and montmorin spacings in zones too small to be x-crystalline among the chlorite and mica x-crystalline zones. Because this is a coarse clay fraction from which the particles less than 0.2 microns in diameter had been removed after thorough dispersion, the high background cannot be attributed to particle size effect, except insofar as randomness along the Z-axis of single ultimate grains is truly a one-axis particle size effect.

The chlorite formula for the material is $(Si_{3.38}Al_{0.62})\ (Al_{1.68}Ti_{0.32})\ (Al_{0.64}Mg_{1.20}Fe^{2+}_{0.32}Fe^{3+}_{0.44})\ O_{10}\ (OH)_8$ in which brucite cations = 2.50. The mica present has the formula:

$$K_{1.00}\ (Si_{3.01}Al_{0.99})(Al_{1.00}Mg_{0.67}Fe^{2+}_{0.16}Fe^{3+}_{0.23}Ti_{0.16})\ O_{10}\ (OH)_2$$

in which octahedral cations = 2.22. The vermiculite plus montmorin average formula is similar except for $X_{0.37}$ $(Si_{3.58}Al_{0.42})$ in the first three terms. The departure from full dioctahedral or trioctahedral systems is expected because of the heterogeneous sources of the colloidal mineral particle population.

Geochemical Relationships

The depth function (Jackson, et al., 1948) of the weathering sequence is illustrated by the Ahmeek loam profile including the various horizons from A_1 to C_2, of which only the coarse clay fractions of two horizons are considered here. The weathering stages advance from much ordered chlorite and mica (stages 4 to 6) in the subsoil to much ordered vermiculite and montmorin (stages 8 and 9) in the surface. In the C_2 horizon the mica and chlorite are largely in x-crystalline zones with vermiculite and montmorin split up in x-amorphous zones (Fig. 1, B); in the A_1 horizon the vermiculite and montmorin zones have grown large enough to be highly x-crystalline (Fig. 1, A). The percentage changes (Table 3) are much less radical than the diffraction patterns indicate.

Similarly, the percentage of feldspar species and quartz change systematically as follows:

	A_1 horizon	*C_2 horizon*
Feldspars		
Anorthite	1	7
Albite	8	9
Orthoclase	10	5
Quartz	35	20

The anorthite and albite decrease in the A_1 horizon in accord with the weathering sequence depth function (Jackson, et al., 1948; Jackson and Sherman, 1953) while quartz and the more resistant feldspar, orthoclase, increase. The occurrence of much feldspars in the clay fraction is not common in fine-textured Wisconsin soils; it is attributed to the sandy texture and youthful weathering stage in this soil.

Increase of quartz in the A_1 horizon relative to the C_2 horizon (seemingly contrary to the weathering depth function) is common for the coarse clay fraction and is caused by (a) the size function and (b) the residue mechanism of weathering, the layer silicates having weathered out into the finer fraction. The weathering sequence "quartz to mica" (stage 6 to 7) applies best for the finer clay fractions, and applies better for size fractions "less than" a given diameter than to coarser fractions from which the layer silicates resulting from weathering have been removed.

VERMICULITE AND MICA IN A HYDROL HUMIC LATOSOL IN RELATION TO MICA AND KAOLIN IN A TITANIFEROUS CERAMIC CLAY OF HAWAII

Hilo, a Hydrol Humic Latosol

The mineral colloids of the Hilo and Akaka family of the Hydrol Humic Latosols of Hawaii contain (Tamura, et al., 1953) predominantly amorphous (allophane) materials, with some crystalline minerals including gibbsite, goethite, anatase, and a small percentage of mica. These analyses were made separately on the untreated 2-0.2 and less than 0.2 micron fractions. The powder diffraction patterns of these colloids recorded on film show but faint evidence of vermiculite and mica. The B_1 horizon of Hilo was further examined in the present study by means of the flat oriented sample technique applied to the mineral colloid after preconcentration of the 2:1 layer silicates by the iron oxide extraction procedure. The iron oxides extracted constituted 25.8 percent of the sample. Analyses of aluminum in the extract solution showed that only 2.75 percent of $Al(OH)_3$ was removed, and thus the Aguilera and Jackson (1953) procedure is shown not to attack the aluminous components very much. (A

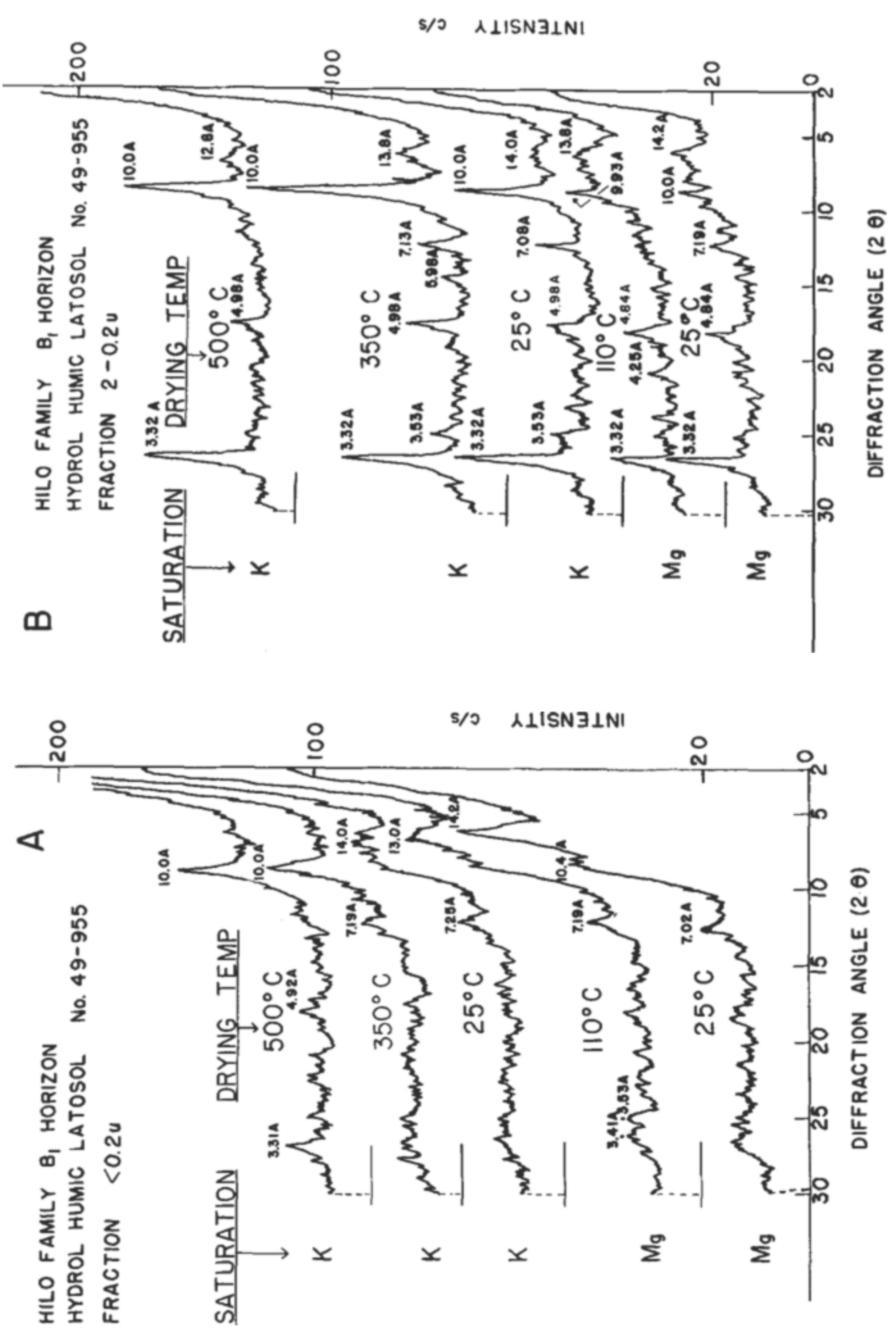

FIGURE 5. — X-ray diffraction patterns of the clay fractions from the Hilo family of the Hydrol Humic Latosol group; (A) less than 0.2 micron fraction, containing much vermiculite and mica; (B) 2-0.2 micron fraction containing much interstratified material.

control test of the procedure on a bauxite sample containing 81.1 percent gibbsite also showed that only 3.05 percent $Al(OH)_3$ was dissolved.)

The x-ray diffraction results for the Hilo fine clay (less than 0.2 microns, Fig. 5, A) show an abundance of vermiculite with some kaolin. The Mg saturated and glycerol solvated coarse clay fraction (Fig. 5, B) shows broad weak diffraction maxima over a range from 14 A to 10 A; its change to a strong 10 A maximum on heating establishes rather conclusively that the sample contains 2:1 layer silicates with various spacings randomly distributed and that the results cannot be explained by fineness of particle size. Potassium saturation of the specimen markedly enhanced the 10 A diffraction maximum without heating (the "Barshad effect"), indicating closure of some of the expanded interspaces. Barshad (1948) noted closure of 14 A spacings of Mg-treated biotite to 10 A on resaturation with K. Some quartz and kaolin are present, in agreement with Tamura, et al. (1953); further detailed study is being given to the vermiculite and other interstratified layer silicates of this clay on the basis of the present findings. A 14 A spacing (heat-shifted to 10 A, thus of vermiculite) was reported in an aluminous (gibbsite, boehmite) Latosol from Haiti by Aguilera and Jackson (1953), after the extraction of iron oxides.

Titaniferous Ceramic Clay

The titaniferous ceramic clay (kindly furnished by G. D. Sherman of the Department of Soils and Agricultural Chemistry, University of Hawaii) is a product of extreme tropical leaching under reducing conditions in the presence of acid surface organic matter. The annual rainfall is several hundred inches.

The analyses. — The diffraction patterns of the clay fraction (Fig. 6) show that the material is very high in kaolin and illite with some interstratification (11.3 A spacing in lower curve). It was found that K saturation (as compared with Mg saturation) enhanced both the 10 A and 7.2 A diffraction maxima in the sample dried at room temperature. This enhancement may be attributable in part to increased basal orientation of the particles in the K saturated specimen, but the loss of the 11.3 A spacing proves that some "Barshad effect" closure occurred, enhancing the 10 A diffraction. The 7.2 A maximum remained constant in intensity in the K saturated specimen on heating from 25 to 350°C, while the 10 A maximum increased progressively. Heating of the K-saturated specimen to 400°C increased the diffraction intensity of both the 10 A and 7.2 A maximum as compared with the 350°C heating. It lowered the background under the 10 A maximum, indicating decrease in randomness of basal spacings with dehydration of vermiculite and (or) montmorin interlayers interstratified in the mica. The increase of the 7.2 A maximum is attributed to expulsion of water from the small amount of hydrated halloysite present (confirmed by a few rods appearing in electron micrographs). Brindley (1951, p. 55) described trapping of a portion of halloysite water

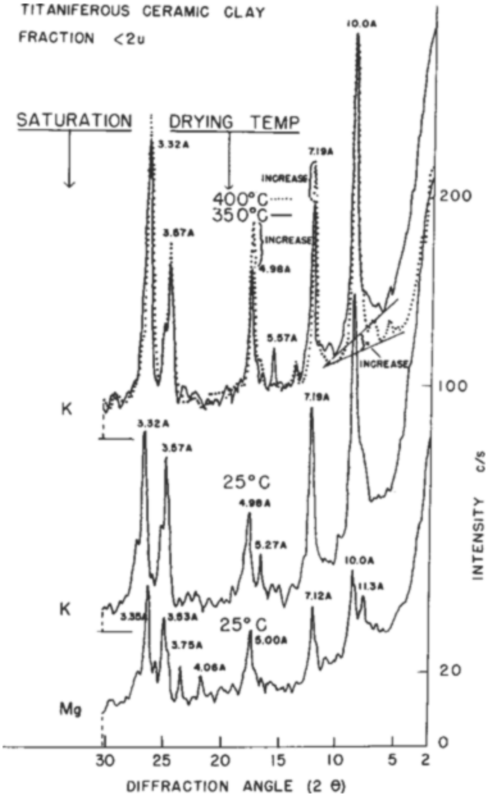

FIGURE 6.—X-ray diffraction pattern of titaniferous ceramic clay fraction less than 2 microns. The marked increase in the 7.2 and 10 A spacings on heating to 400°C, together with lowered background, indicate expanded interspaces in both the 1:1 and 2:1 components. The 5.05 percent K_2O content must be allocated to mica containing 11.8 percent K_2O when the kaolin, titanium (anatase) and interlayer surface components are weighed with the elemental data.

during dehydration until a temperature of 350 to 400°C was reached. In the present case, the water expulsion from halloysite allows the halloysite diffraction to augment that of kaolinite (strong 7.19 A spacing before heating). Interstratification of a few hydrated layers in the kaolinite would of course also produce the diffraction intensity changes noted (Fig. 6).

Calculation of the surface to vermiculite (5 percent), 400-500°C water loss to kaolin (20 percent), TiO_2 to anatase (21 percent), and suitable allocation of the other constituents gives 43 percent mica (Table 3). Since the total K_2O content is 5.03 percent, the mica has 11.8 K_2O or an amount equal to the full theoretical formula for muscovite. This is a significant finding when considered in relation to the firm qualitative and quantitative basis for the amounts of other constituents reported. A similar allocation shows 37 percent anatase, together with other constituents (Table 3), in the silt fraction.

Related geochemistry. — The question has been raised: What is the source of the mica in this extremely weathered titaniferous-illite-kaolin formation? The titanium content (Table 1) corresponds to the most advanced stage of chemical weathering (Jackson, et al., 1948; Jackson and Sherman, 1953), while mica in large amounts is not ordinarily associated with the anatase stage of weathering. The finding of a small but distinct residue of mica, kaolin, and vermiculite in the Hydrol Humic Latosol after removal of the iron oxides suggests that the mica of the titaniferous ceramic clay is a residue remaining after the free oxides and hydroxides have been leached out by the combined action of acidity and chelation by organic acids. The predominance of the residue mechanism in causing mica accumulation in soils has been advocated by Grim (1942). The kaolin and vermiculite contents of the two materials suggest that the vermiculite largely weathered to kaolin. The mica concentration process has already begun in the Hydrol Humic Latosol, since the iron oxide content is only half that in the Ferruginous Humic Latosol (Tamura, et al., 1953). Titanium is less subject to leaching though it apparently leaches somewhat (Sherman, 1952).

On the basis that good oxidation and open drainage have a positive sign (Jackson, et al., 1948) in the weathering function, leaching in the presence of an organic layer and reducing conditions has a negative functional sign. The weathering reactions, and therefore the weathering sequence, are reversed (advanced, oxide stages removed; early stage, mica left as a residue).

COLLOIDS HIGH IN KAOLIN AND GIBBSITE

Application of the method of allocation to colloids high in gibbsite and kaolin (both kaolinite and hydrated halloysite) provides a more severe test of its applicability than the above colloids, because of the increased variety of water loss energies, specific surface, and elemental sources. Pearson and Ensminger (1949) reported analyses of high kaolin with some gibbsite in the clay of Davidson soil of Alabama. They observed an unidentified diffraction maximum at 14.3 A, indicating the presence of some 2:1 and (or) 2:2 layer silicates, and a relatively high cation exchange capacity of 30 to 45 meq per 100 g. Dr. R. W. Pearson kindly furnished the authors a Davidson soil sample from Alabama similar to the one reported in 1949 for purposes of further analysis and test of our methods. The "free" iron oxides (2.9 percent Fe_2O_3) were removed and excluded from the following analysis.

Davidson Soil, Fine Clay

The diffraction patterns of the colloid finer than 0.2 microns (Fig. 7 A) show much kaolinite and some halloysite (increased 3.55 A diffraction intensity on heating), some gibbsite, and the 14 A diffraction maximum in accord with Pearson and Ensminger (1949). Saturation with K shifted the spacing to 13.8 A (a bit of "Barshad effect" in the interstratified vermiculite). Heating to 500°C decreased the spacing to 12.3 A, showing the presence of chlorite with interstratified vermiculite and (or) montmorin. The presence of chlorite is established by failure of the 10 A diffraction maximum to be resolved by heating to 500°C.

Allocation of the low temperature water loss to gibbsite, halloysite, and vermiculite, the K_2O to mica, the interlayer surface to vermiculite and montmorin and the other elements and water loss accordingly gave the mineral content reported in Table 3. The distribution of elements is such that the percentage of each component is certain within narrow limits. The montmorin is definitely established by the surface allocation between that mineral and vermiculite. The presence of the vermiculite and montmorin explains the relatively high exchange capacities observed by Pearson and Ensminger (1949), although the presence of montmorin was not detected by diffraction methods in either their study or ours because the

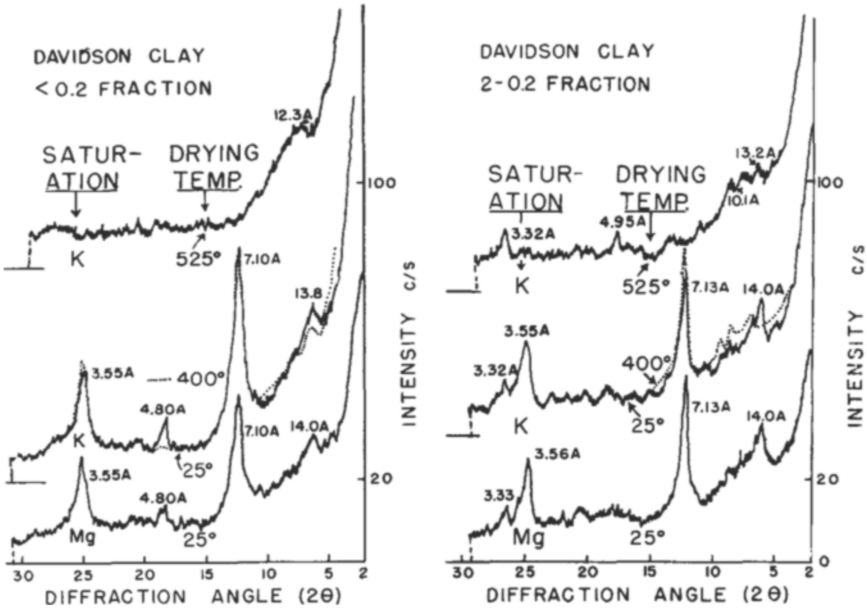

FIGURE 7.—X-ray diffraction patterns of (A) fine clay fractions, and (B) coarse clay fractions, of Davidson clay soil showing abundant kaolin and presence of interstratified layer silicates including vermiculite and (or) montmorin with chlorite.

montmorin, like the mica present, is entirely interstratified in zones too limited to show their diffraction maxima.

Davidson Soil, Coarse Clay

The x-ray diffraction patterns of the coarse clay (2-0.2 microns, Fig. 7 B) show much kaolin and the 14 A diffraction maximum, in accord with Pearson and Ensminger (1949). Rise of the kaolin 7.13 A maximum on heating to 400°C establishes the presence of some halloysite, and the shift of the 14 A diffraction maximum shows that some vermiculite and (or) montmorin are interstratified with chlorite. Heating to 500°C shifted the 14 A spacings to a range of 10 to 14 A; this establishes the presence of some chlorite with the vermiculite and (or) montmorin.

Allocation of all the low temperature water to halloysite was not permissible, from the elemental analyses. The presence of about 5 percent gibbsite was indicated although no gibbsite diffraction maximum was noted for this fraction. Again, as for the fine clay, the allocation of interlayer surface, water, and elements gave the mineral composition shown in Table 3, within surprisingly narrow confidence limits. The montmorin, as in the fine clay, is interstratified and thus does not show a discrete diffraction maximum.

OCCURRENCE OF INTERSTRATIFICATION IN LAYER SILICATES GENERALLY

A comparison of the intensities of the diffraction maxima of pure specimens with those of soils and many sediments shows a radically higher intensity of the diffraction maxima of the pure specimen material. The presence of fine particle size, crystal defects, and of amorphous materials could in part explain the lower basal diffraction intensity. However, the frequent rise in 10 to 7 A diffraction intensity on heating could scarcely occur except through decrease in randomness of the Z-axis spacings through removal of water layers. Also, the composition and properties of the soil colloids and the general persistence of a fairly strong 4.45 A (*hk*O) diffraction line in powder diffraction patterns (film recorded, not shown) suggest that they are layer silicates which have much x-amorphous (randomly spaced) material distributed along the Z-axis, i.e., that the materials are interstratified. The fact that the simpler binary (2-component) randomness (Gruner, 1934) occurs commonly to give the Hendricks and Teller (1942) intermediate spacings, for example the 11.3 A spacings in Figure 6, is also in accord with the expectation of not uncommon occurrence of ternary, quaternary (mica-montmorin-vermiculite-chlorite), and greater randomness (binary-binary systems, etc.) through interstratification along the Z-axis. In this way, much or all of the basal diffraction is reduced to a general low angle scatter consisting of a merging of the broadened maxima of virtually all spacings. The common occurrence of a definite though broad diffraction maximum at approximately 3.5 A (corresponding to 005 of 18 A, 004 of 14 A, 003 of 10 A, and 002 of 7 A spacings) points to the occurrence of these Z-axis spacings in x-amorphous zones. Each x-amorphous zone has too few repetitions to show a distinct maximum, but the sum total of their scattering is responsible for the high intensity of low angle diffraction background. The specific surface measurements do not allow fine enough particle size to permit the high background to be attributed to ordinary particle size effects alone. (Randomness or interstratification along the Z-axis *is a one dimensional fine-particle size effect.*) Excessively broadened diffraction maxima and high backgrounds were in fact correlated with lower specific surface than that of some of the samples with high sharp diffraction maxima. The broadening has therefore been attributed to interstratification of low surface minerals, such as micas and chlorite with high surface minerals such as vermiculite and montmorin.

Even with the relatively intense 10 A diffraction maximum for illite in the titaniferous ceramic clay, the intensity was markedly increased by heating in increments up to 400°C. This fact indicates closure of spacings greater than 10 A due to interstratified vermiculite or montmorin with consequent decrease in randomness along the Z-axis in the assemblages which contain much relatively pure mica. Increases in the 7.2 A diffraction maximum of this sample on heating similarly indicate decrease in randomness of the halloysite spacings.

Hendricks and Alexander (1941) showed the presence of up to 20 percent montmorin in illite (Grim, et al., 1937) and in the Ordovician bentonite from High Bridge, Kentucky, based on the exothermic peak at 235-250°C obtained in differential thermal analysis (Hendricks, et al., 1940). This was confirmed through hydrogen-cerous competitive exchange studies. The cerous fraction was 0.06 for sericite (mica ratio), and on the order of 0.9 for montmorins. The fraction was 0.30 for a glauconite (greensand, New Jersey), and 0.22 for the type illite referred to above. The fraction was about 0.9 for Ordovician bentonites (micaceous) and glimmerton (Maegdefrau and Hofmann, 1937) ; the similarity of the ratio for these micaceous materials to that of montmorin was explained by the presence of montmorin in them in appreciable amounts. The montmorin component would dominate the ratio because of the low exchange capacity of the true mica component. Interstratification of montmorin with mica spacings was shown in illite from Pennsylvanian underclay (Jackson, et al., 1952, Fig. 1, b). Complex interstratification with clearly defined diffraction maxima shown for mica and vermiculite and their intermixtures in a single crystal were shown also (Jackson, et al., 1952, Fig. 1, a) and the occurrence of open interspaces (montmorin and vermiculite) in micaceous layer silicate clays was explained by the preferential weathering plane principle. These findings are in accord with the present findings of the rather general occurrence of interstratification of different 2:1 and 2:2 (chlorite) layer silicates in clays. Partially dehydrated halloysite accounts for Z-axis spacing randomness in the 1:1 layer silicates encountered in this study.

SUMMARY

Allocations of the necessary analytical data (including diffraction, thermal, surface, and elemental data) show the polycomponent nature of clays generally, and also the general occurrence of interstratification in layer silicates. The interstratification may possibly involve a "superlattice" which reflects the mica-to-chlorite-to-vermiculite-to-montmorin weathering sequence.

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