Mineralogy and Chemistry of the Hagerstown Soil In Missouri

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INTRODUCTION

Limestone soils occupy a large portion of Missouri south of the glaciated area. They show profile characteristics which sharply differentiate them from the loessial, glacial and alluvial soils to the north of the Missouri River. They differ widely amongst themselves both in appearance and fertility level. The experience gained in the previous study of a glacial soil (12) has now been applied to a limestone soil. In reporting this work it is therefore possible to devote less space to experimental methods and more to questions of soil genesis.

The Hagerstown soil was chosen for several reasons. It is derived from dolomitic limestone low in chert content; hence the profile does not include layers of chert which make pedological interpretation very difficult. The limestone formations which give rise to this soil are of relatively high uniformity and considerable thickness. The incidence of purely pedological factors should therefore become apparent on close study. This is of particular interest because limestone soils have always proved difficult to place in a genetic scheme of soil classification. The Hagerstown series occurs in Missouri and in other states to the east, in a region of transition from the gray-brown podzolic soils of the north, to the red-yellow soils of the south. It is not certain whether it belongs to either of these groups or whether it should be included with other limestone soils in an entirely separate grouping. The three alternatives all find support in the literature.

A considerable amount of chemical and mineralogical information is already available on soils of the Hagerstown series, mainly those in Pennsylvania, Maryland, Kentucky and Tennessee, with one example also from Missouri. Thus comparisons of our results with those found at other localities are possible.

GENETIC PROBLEMS OF THE HAGERSTOWN SERIES

Review of the Literature. The Hagerstown Soil Series has been classified by the United States Department of Agriculture Soil Survey (29) into two different Great Soil Groups. In Pennsylvania, Maryland, and Virginia it is classified as a Gray-Brown Podzolic, whereas in Kentucky, Tennessee, and Missouri it is classified as a Red Podzolic soil.

The type locality of the Hagerstown silt loam is at Hagerstown, Maryland. The broad limestone valley, extending from Pennsylvania through Maryland and into Virginia, is the largest area of Hagerstown soils (30). Other areas occur in central Kentucky and Tennessee and in the eastern Ozarks of Missouri. Marbut (40, 41) in 1910 and 1914 recognized the existence of the Hagerstown in the eastern Ozarks. He related the soils of this area to the geology and topography and stated that certain of the soils are "demonstrably derived" from the rocks underlying them. The names he gave are unmistakable. On the eastern border extending south from Perryville, he recognized the soil as being similar to the Hagerstown in the eastern United States. However, in and around the St. Francois Mountains, while the description of the soil is similar, he called the soil the Fredericktown. Two sub-divisions were the Caledonia and the Bismarck soils.

Marbut and co-workers at the United States Department of Agriculture(41) assigned the Hagerstown to the Limestone Valleys and Uplands Province. They describe the Hagerstown as prevailingly brown in color with a light brown to reddish brown subsoil. In some areas the subsoil is red or dull red.

Miller and Krusekopf (45) describe the Hagerstown in Missouri as red limestone land occurring in belts running north and south conforming to outcrops of limestone from which it is derived. The topography is undulating to hilly and the vegetation is hardwood forest although the majority of the land with no outcrops has been cleared. The soil is a brown, reddish-brown or yellowish brown silty clay grading into a heavy clay loam.

Since the Hagerstown has been classified as both a Gray-Brown Podzolic and a Red Podzolic soil, it is necessary to discuss the concepts of formation of these two Great Soil Groups as they are known today. The principal mechanism of formation of the Gray-Brown Podzolic is supposed to be illuviation and eluviation of clay material from the A to the B horizons of the profile, resulting in a characteristic clay-rich B horizon. The exact mechanism is not known.

Several concepts have been proposed for the development of the Red Podzolic soils and have been reviewed by Simonson (56):

a. Due to a changing climate, podzolization has set in upon a lateritic soil material; but there is evidence that laterization is going on now in these areas and the climate is not typical of a podzol.

b. "Tension Zones" are supposed to exist between the areas of the true laterite and the true podzol to give this type of soil. However, Red Podzolic soils are found in the tropics where no tension zone is apparent.

c. An intensive illuviation-eluviation process occurs whereby material is translocated from the A horizon; but the A horizon is too thin to give all the clay that is found in the B and C horizons in these soils.

Simonson has proposed that the dominant processes involved are formation of clay minerals in deeper horizons and destruction of these minerals in the upper horizons. He gives several reasons for this explanation. The zone of maximum clay is usually below the B horizon. In studies of the clay fraction of four Red-Yellow Podzolic soils (49) kaolinite was found to increase with depth to the C horizon, and depositional differences, or translocation of the materials from the A horizon down, were ruled out as possible causes of this increase. Since it

has been found that kaolinite is formed almost simultaneously with the disintegration of rock in the Piedmont region (4), Simonson thinks that formation of kaolinite is active in the C horizons of these four soils.

He postulates that the chief difference between the Red-Yellow Podzolic and Gray Brown Podzolic soils is that the clay minerals tend to disappear from the solums of the Red-Yellow Podzolic soils whereas they tend to accumulate in solums of the Gray Brown Podzolic soils. A preponderance of kaolinite has often been used to distinguish the Red-Yellow Podzolic soils, but there is evidence that this is not always the case.

On the other hand, Alexander and co-workers in 1939 (3), who made a chemical study of several Gray-Brown Podzolic and Red Podzolic soils derived from limestones, show that there is striking similarity among these soils. In all cases there was a continual increase in clay content down to, and including, the C horizon. The pH values of the soils were all low (from 4 to 5) in the B horizons, indicating rather extreme weathering conditions. However, in all cases, while the amount of free iron oxides varies from one soil to another, there was a uniformity of distribution in any one profile. The colors of the soils bore no relationship to the amounts of iron oxides. The Missouri Hagerstown has an A horizon similar to that in Pennsylvania, but the B and C horizons were reddish and more like the Dewey subsoil. Alexander and co-workers said they doubted that the Missouri Hagerstown was a true Hagerstown.

The results of their analyses of the Hagerstown sample taken near Hazel Run, Mo., are given in Table 1. While there are some variations from horizon

TABLE 1--ANALYSIS OF HAGERSTOWN SILT LOAM, HAZEL RUN, MO., AFTER ALEXANDER, BYERS AND EDGINGTON (3)

A_1 0- 4" light grayish-brown silt loam laminated
A2 4-16" light grayish-brown silt loam, light brown spots in gray laminated
B1 16-21" grayish brown silty clay, very granular
B2 21-31" brown silty clay, angular structure, black coating
C3 31-54" red silty clay angular blocky black coatings

	A_1	A_2	B_1	B_2	C_3
Sand	2.2	2.2	.9	1.0	1.4
Silt	81.8	79.9	68.5	60.2	60.8
Clay	14.6	16.9	30.2	38.9	37.8
pH	7.1	6.1	5.5	4.7	4.6
Total Soil					
SiO_2	80.64	80.96	75.96	72.32	74.14
Al_2O_3	8.42	8.65	11.55	13.97	13.15
Fe_2O_3	2.46	2.59	3.88	4.80	4.57
CaO	.54	.42	.43	.42	.29
MgO	.48	.46	.71	.84	.72
K_2O	1.94	1.95	2.03	1.81	1.75
Colloids					
SiO_2	45.51	46.49	46.71	46.74	46.12
Al_2O_3	24.75	24.96	26.54	27.15	28.52
Fe_2O_3	9.61	9.95	10.27	10.50	10.71
CaO	.96	.86	.77	.70	.68
MgO	1.70	1.75	1.97	1.62	1.06
K_2O	2.09	2.15	1.84	1.61	1.55
SiO_2/R_2O_3	2.50	2.50	2.40	2.38	2.21
SiO_2/Fe_2O_3	12.6	12.4	12.1	12.0	11.4

to horizon in the chemical analyses of the total soil, these are explained when one considers the variation in the amount of clay from horizon to horizon. The authors do not state whether the variation in clay content is an inherited or a genetic characteristic. Their analyses of the clay were similar in results to those obtained by Robinson and Holmes (52), who analyzed chemically the less than 0.3 micron clay from the Hagerstown in Fredericktown County, Md.

Jeffries and White (29) made mineralogical and chemical analyses of a virgin Hagerstown profile from State College, Pa. The total analyses were similar to other examples but there was more sand than in any of the other Hagerstown samples. There was an increase in clay with depth and a break in the mineralogical distribution at the bottom of the B_1 horizon, probably indicating two different parent materials. The variations in heavy minerals were small.

Morgan and Obenshain (48) studied a Hagerstown profile in southwest Virginia. They found small amounts of sand, a low pH, an increase in clay content to the C horizon where it was 75 percent, and a uniformity of iron oxide distribution from horizon to horizon.

McCaughey and Fry (34) in 1913 studied the mineralogy of soils from various parts of the United States. They found in the Hagerstown a predominence of quartz and potassium feldspars, as did Jeffries. On the basis of two different forms of quartz they concluded that there was a mixture of parent materials.

Alexander et al. (5) studied the minerals present in the less than 0.3 micron clay from the B_2 horizon of the Hagerstown analyzed in their earlier paper (3). On the basis of chemical analyses, X-ray diffraction and differential thermal analyses, they estimated 40 percent kaolin, 40 percent hydrous mica, 7 percent iron oxides, 5 percent quartz and no montmorillonite.

From these investigations certain facts are apparent regarding the characteristics of the Hagerstown soils. There is an increase in clay content down to the C horizon. In all samples except Jeffries' there is an extremely low content of sand. The pH of the soils decreases with depth to a rather low value in the B horizon. The amount of free iron oxides follows the distribution of the clay within the profiles and is rather uniform. The low pH suggests an acidic weathering of the soil and the low pH of the C horizon itself is significant. None of the investigators sampled below the C horizons and there are not enough mineralogical analyses to assign the Hagerstown to either of the Great Soil Groups according to Simonson's criteria.

Because of the similarities of the limestone soils studied by Alexander et al. (3), it is interesting to note that G. W. Robinson has devoted a chapter in his book (51) to soils associated with calcareous parent materials. He states that they are "grouped together for descriptive purposes, not necessarily because they form a major group in a world system." The limestone soils are divided into 1) the grayish or black rendzina-type soils and 2) the red or reddish-brown soils such as the terra rossa. Glinka is credited with the observation that while soft limestones produce rendzina soils, hard limestones produce the reddish soils.

Mohr and van Baren (47, p. 463) point out that there is no explanation in the literature for the considerable thickness of residuum apparently derived from a pure limestone. They believe that air-borne material is responsible in many, if not all, cases. Another baffling problem is the reason for the development of the reddish color of these soils. The total amount of free and combined iron may not be significantly different from the amount present in other soils, and yet the reddish color is dominant.

J. van Baren (60), in discussing the Limestone Soils of the East Indies, stated that the red color is independent of temperature, rainfall, orographic height, vegetation, and humus content. He concluded that the color of a limestone soil is independent of climate, and that the other properties of a limestone soil are solely dependent on the limestone and its properties.

Thus, limestone soils might be considered intrazonal soils, since similar soils are found in different climatic environments, and presumably are a function of parent material. At any rate, Robinson (51) has assigned the Hagerstown Series to the reddish-brown limestone soil group. This may account for the fact that the Hagerstown series has been classified into two different Great Soil Groups.

Jackson and Sherman (26) have made an exhaustive survey of the literature and have arrived at a geographic correlation, in which certain mineral suites in soil clays are divided into a series of weathering stages, which are, in turn, associated with the major soil groups. Fieldes and Swindale (17) suggest that the nature of the parent material must be used also in such a correlation. Grim (21, p. 340) has shown that the clay mineral composition of soils can be related to both the Great Soil Groups, i.e. to climate, and to the nature of the parent material. A greater emphasis was placed on the parent materials by Ross and Hendricks (54) than by any of the aforementioned authors.

Van Houten (61) has analyzed the clay minerals in some 40 soils and underlying sedimentary rocks across the United States. The dominant clay mineral in the soil differed from that of the rock in only a few cases. He pointed out that care must be taken that the effects of climate are distinguished from parent material in a discussion of the clay minerals of a given soil.

In the initial stages of geochemical weathering and in immature soils, the nature of the unstable minerals present determines the environment and the reactants. Unless this environment is quickly altered, the unstable minerals will determine the clay minerals formed (17). After a sufficiently long time, in a given macro environment, various parent materials will tend to give the same clay material, i.e., the zonality of clay formation becomes apparent. According to Grim (21, p. 343), "a significant condition in weathering is the presence of alkalis and alkaline earths in the environment of alteration, and the length of time they remain in the environment after their liberation from the parent materials." The dominant clay minerals found in calcareous sediments are illites and montmorillonites (21, p. 343). The weathering regime will be alkaline until the carbonates are removed. Following this, podzolization or laterization may occur,

depending upon the climate. Alexander *et al.* (5) studied a wide range of soils, including several derived from limestones in the eastern United States. Kaolinite, varying from 40 to 70 percent, and illite, varying from 10 to 40 percent were the major clay minerals formed in these limestone soils. No montmorillonite was found, but amorphorus and crystalline iron oxides, varying from 5 to 13 percent, were present.

Carroll and Hathaway (15) studied in detail a soil profile developed from the Lenoir limestone in Virginia. The rock contained hydrous mica with minor amounts of montmorillonite and kaolinite. In the soil, kaolinite was the dominant mineral with small amounts of chlorite in the surface horizons and illite in the horizons near the rock.

GEOLOGY OF THE MISSOURI
HAGERSTOWN REGION

The central core of the Ozark Region is composed of Pre-Cambrian igneous rocks. These are porphyries and granites with a variety of textures. Overlying these and lapping up to them in the St. Francois Mountain area are various rocks of paleozoic age. The first is the LaMotte sandstone of lower Upper Cambrian time which is arkosic or quartzitic. Next is the Bonneterre Dolomite which is normally 375 feet thick. The Davis shale overlies the Bonneterre and is in turn covered by the Eminence-Potosi limestone.

The lower part of the Bonneterre is sandy while the upper is coarsely crystalline, light gray in color, and has many vugs with dolomite and calcite crystals. Glauconite is an important impurity. Tarr (59) states that the glauconite is largely confined to the lower 50 feet but occurs in smaller amounts in the upper part. Dake (6), however, found that the Bonneterre Dolomite on the west side of the St. Francois Mountains in the Potosi-Edgehill Quadrangle was different from that on the east side. The lower portions consist of a crystalline fine-grained, buffcolored dolomite, sparingly mottled with gray, with a smooth weathering surface. The upper portions were more massive, more coarsely crystalline and a lighter gray color. It has numerous vugs and calcite crystals and the exposed weathered surfaces were cavernous and pitted. Numerous seams and splotches of green glauconite were found.

Buckley gives the description of the Bonneterre from cores taken from a well boring at Palmer on the west side of the Potosi-Edgehill quadrangle. His description is as follows, reading from the bottom up:

 0'— 18'—dark gray dolomite, with cavities, porous, no glauconite.
18'— 20'—dense dolomite, thin dark shale partings
20'— 44'—dark to light gray dolomite, medium grained, crystalline
44'— 98'—dark gray crystalline dolomite, medium grained, shale partings, stylolites
98'—108'—dark gray dolomite, porous or hard, fine grained, brown on weathered surfaces

108'—156'—dark gray porous, honey-combed and cavernous dolomite

156'—204'—very finely porous light gray dolomite, irregular layers and seams of green shale

204'—277'—light gray dolomite, irregular cavities, small pores lined with calcite

McQueen (39) divided the Bonneterre dolomite (as it occurred on the east side of the St. Francois Mountains) into several zones:

1. 0 to 35 feet above the LaMotte—dark gray, fine grained, silty or argillaceous dolomite, gives a red sandy soil on weathering.

2. Maximum thickness 150 feet—white or gray dolomite finely crystalline, compact and hard. Green clay occurs in small amounts as irregular masses filling vugs in the dolomite. It appears to be common to the top of the formation but may occur in others.

3. Massive, very dark brown, finely crystalline, hard and compact, rather pure but has organic matter giving dark color.

Allen (6) stated that the Bonneterre dolomite in places contains 40 to 50 percent glauconite. While many glauconites contain rutile needles, the Bonneterre glauconite does not and, in fact, there is a great scarcity of any of the heavy minerals in the Bonneterre.

It is apparent that the Bonneterre dolomite varies a great deal from place to place as well as within a column at any given site. On the east side of the St. Francois Mountains the lower part is sandy and has a very high proportion of glauconite incorporated in a fine grained dolomite. The upper portions are purer dolomite, varying from fine to coarse-crystalline with vugs containing dolomite and calcite crystals. Glauconite occurs in thin seams and partings throughout the formation. On the west side of the mountains, the lower part of the dolomite is generally a fine grained, porous, buff-colored rock with thin gray shale partings. The upper portions vary in texture and have irregular seams of green shale.

Hand specimens collected in this investigation from the country rock on the west side of the mountains contained, in splotches, a small amount of gray shale-like material. On the other hand, a drill core of Bonneterre dolomite, taken from the eastern portion, and obtained through the courtesy of Dr. C. S. Ross, was a rather uniform dark green in color.

FIELD CHARACTERISTICS OF THE HAGERSTOWN PROFILE

The Sampling Site.

In St. Francois County many examples of the Hagerstown silt loam occur, but because of the likelihood of loess contamination, it was decided to consider the area in southern Washington County and northern Iron County near the town of Caledonia. Although this area has not been covered by a detailed soil survey, the soils were very similar to those near Farmington. The Hagerstown predominates near the contact of the Bonneterre with the LaMotte Sandstone.

To the west, where the Davis outcrops occur, there is a sharp transition between the Hagerstown silt loam and a grayish-brown silt loam soil similar, if not identical, to the Lebanon. From its position it is a reasonable assumption that the Hagerstown in this area was formed from the residue of the middle of the Bonneterre formation. The Lebanon-like soil was considered to be derived from the residue of the upper part of the Bonneterre and probably part of the overlying Davis formation.

To obtain if possible, a Hagerstown profile derived entirely from the Bonneterre dolomite, sampling was done as near to the LaMotte Sandstone outcrops as possible. A favorable location was chosen at S.E. ¼, S.W. ¼, Sec. 19, T35N., R3E, 0.9 mile south of the Washington County line and ⅛ mile S.W. of highway 21. The elevation was 960 feet at the sampling site and decreased to about 880 feet at Saline Creek to the west and north. The slope to the north was 2.5 percent and to the west it was 3 percent. Outcrops of dolomite occurred on the slopes making them unfit for agricultural production but capable of supporting excellent forests. Hard maple was the predominant tree with several white and chinquapin oaks and some elm, hickory, ash, and red oak. The soil has developed under forest vegetation, but where no outcrops occur, it makes good farm land.

The sampling site was at the top of a low ridge having a horizontal surface, extending south and ultimately decreasing in height toward the south. To the N.E. and S.E. the topography is gently rolling with outcrops occurring on the lower slopes. These outcrops consist of Bonneterre dolomite and grade into the LaMotte Sandstone at Saline Creek to the north. The rock is a calcareous dolomite with vugs containing large calcite crystals, grading into sandy dolomite with grayish streaks at the contact with the underlying LaMotte. In the vicinity of this contact there was a very dark red soil.

The field containing the site was a rotation pasture consisting of sweet clover and lespedeza which had been seeded in 1953. There was evidence of erosion on the slopes but apparently only slight erosion had occurred at the ridge top.

The unconsolidated material was 100 inches thick at the site and was underlain by Bonneterre dolomite similar to that occurring in the outcrops.

There was good field evidence that the Hagerstown was derived from the Bonneterre. Since no chert was found, there could not be any contamination from the Potosi and Eminence limestone formations. The soil was underlain by the Bonneterre dolomite and, therefore, could not be derived from the LaMotte Sandstone. Since the LaMotte outcrops at the Creek, a short distance away, and since the dolomite fitted the description of the lower Bonneterre, there could only be a small thickness of Bonneterre dolomite under the sample site. A few miles to the west, the upper Bonneterre was found in the outcrops, followed by the Davis shale on which grayish-yellow soils were found. As will be seen, there was only a small amount of very fine sand in all of the horizons sampled and, therefore, it could not have been derived from the Davis formation. From these

considerations, it must be considered that the soil was derived from the middle and upper Bonneterre dolomite.

Description of the Profile.

Following is a description of the soil sample and two rock samples that were obtained with the assistance of Dr. M. E. Springer.

The Hagerstown Silt Loam

Location: S.E.¼, S.W.¼, Sec. 19, T35N., R3E, top of small knoll, level to 1 percent slope surrounded by 3 percent slope.

Native Vegetation: mixed hardwood including maple and ash.

Cover: Mixed sweet clover—lespedeza—grass pasture.

Parent Material: Bonneterre Dolomite

Climate: Mean annual temperature 54-56°F, 42-48 inches annual rainfall spread over all months of year.

Drainage: moderately good, both surface and internal.

Sample number, horizon, depth and description:

1. A_1 0— 7″ A dark-brown, friable, heavy silt loam with moderately developed fine-granular structure. 7.5YR 4/4   pH 6.3

2. A_3 7—10″ A reddish-brown, firm, silty clay loam with moderately developed coarse-granular structure. 5YR 4/7   pH 6.2

3. B_1 10—12″ A dark red, very firm silty clay with well developed fine sub-angular blocky structure. 2.5YR 3/6   pH 6.0

4. B_{21} 12—19″ A dark red, very firm, silty clay with well developed fine sub-angular blocky structure. 2.5YR 3/6   pH 4.6

5. B_{22} 19—25″ A dark red and yellowish-red, mottled, very firm, silty clay with moderately developed medium sub-angular blocky structure. Many medium-size concretions. 2.5YR 3/6 and 5YR 4/6.

         pH 4.8

6. B_{23} 24—33″ A mottled dark red and reddish-brown, very firm, silty clay with black coatings, a moderately developed medium sub-angular blocky structure, and numerous large concretions. 5YR 4/4 and 2.5YR 3/6.   pH 4.8

7. B_{24} 33—43″ A reddish-brown, slightly plastic silty clay, with poorly developed, medium sub-angular blocky structure, and numerous black coatings and large concretions. 5YR 4/4   pH 4.8

8. B_3 43—54″ A mottled yellowish-red and light brown, very plastic, waxy, clay, with poorly developed fine sub-angular blocky structure, and with numerous concretions and many black coatings. 5YR 4/6 and 7.5YR 6/4   pH 4.8

9. C   54—64″ A strong brown, very plastic, waxy clay with pinkish-gray

splotches and black coatings, and with a poorly developed fine sub-angular blocky structure. 7.5 YR 5/6, 7.5 YR 7/2   pH 5.6

10.   64—76″ A mottled dark brown, very dark brown and pinkish-gray massive, very plastic waxy clay. Material has shiny appearance as if little soil formation had occurred. 7.5 YR 4/4 7.5 YR 2/10, 7.5 YR 7/2   pH 7.0

11.   76—94″ Same as above   pH 7.3

12.   94—100″ A light gray to brownish-yellow disintegrated rock which crumbles readily.   pH 7.7

13.   A buff colored, rather uniform, porous dolomite with medium-sized grains taken at 100″ in the profile. The specimen concontained some red streaks but no seams of shaley material. It effervesced slowly with cold dilute HCl.

14.   A gray, slightly porous dolomite with some medium and some large-sized calcite and dolomite grains. Very thin seams of gray clay material were abundant. This specimen was taken on highway C, two miles west of highway 21.

Consecutive vertical samples were taken from the exposed face of the profile as the pit was dug. Volume weight cores were taken in triplicate down to 94 inches. Difficulty was experienced in getting a true core in the waxy clay horizons.

MECHANICAL AND CHEMICAL ANALYSES

Outline of Methods.

After the soil profile was selected, samples were taken of each horizon, of the underlying rock, and of a dolomite outcrop originating farther up in the geological column. The exchange chemistry and mechanical analyses were determined on each of the horizons. The carbonates also were determined. The carbonates were removed from the two rock specimens and the insoluble residue was separated into its various size fractions. Heavy minerals were separated from the very fine sand fraction and examined with the petrographic microscope; the proportions of light minerals were determined qualitatively with the X-ray diffractometer.

The clay fraction was examined by physical and chemical methods. The former methods were those normally used by clay mineralogists, and the latter was accomplished by determining the titration curves (42). Detailed methods are described in sections dealing with the various aspects.

A. Volume Weight (bulk density) Determinations.

The volume weight cores were brought into the laboratory and weighed immediately. After drying to constant weight, the volume weights were calcu-

lated and are shown in Table 2 along with the percent moisture. Volume weights were relatively constant down to the C horizon and decreased with depth below that horizon. The moisture content increased continually with depth, reflecting the increasing clay content shown by the profile description.

TABLE 2--VOLUME WEIGHTS OF THE HAGERSTOWN PROFILE

Sample Number	Horizon	Depth in Inches	Volume Weight	% Moisture
1	A1	0- 7	1.39	13.2
2	A3	7- 10	1.33	19.5
3	B1	10- 12	1.37	21.2*
4	B21	12- 19	1.40	23.0
5	B22	19- 25	1.45	23.6
6	B23	25- 33	1.40	25.3
7	B24	33- 43	1.46	26.3
8	B3	43- 54	1.43	31.1
9	C	54- 64	1.23	42.3
10	---	64- 76	1.13	44.1
11	---	76- 94	1.14	38.4
12	---	94-100	----	----**

*The B1 horizon was too thin to sample. The figures quoted are averages of the A3 and B21 horizons.
**Volume weights not taken since they are meaningless in this zone of free lime-stone.

B. Mechanical Analysis

(1) Pretreatment of soil and rock.

(a) *Soil samples:* The bulk soil samples were air-dried and sieved through a 10 mesh sieve. Triplicate 20-gm. samples were treated with dilute HCl and washed until free of salts and carbonates; organic matter was removed with H_2O_2.

(b) *Rock samples:* The rock specimens were cleaned and a portion was shattered to give small chips. Selected chips were crushed and sieved through a 10 mesh sieve. Several methods for dissolving carbonates were tried in order to obtain the insoluble residue without attacking the clay material too drastically. Treatments with carbonated water, with hydrogen saturated Amberlite and by electrodialysis were found too slow to be practical. Hydrochloric acid (1:1) was added dropwise to a stirred suspension of 100 gm. of the rock at 80 to 100° C. The pH was not allowed to fall below 3. Periodically the <5 micron material was decanted to avoid unneccessary contact with the acid. When all carbonates had been removed, the flocculated material was washed until it dispersed. A small amount of sodium carbonate was added to aid in the dispersion. The sample was separated into fractions as outlined below.

(2) Determinative Procedures.

After removal of organic matter, the soil samples were made slightly alkaline with sodium hydroxide and the total clay <2μ was removed by repeated sedimentation and decantation. The two silt fractions, 2-5μ and 5-20μ, were

removed in the same way, using the appropriate sedimentation times. The sands were wet-sieved on a 270 mesh sieve, then sieved dry into the different fractions and weighed. Since there was an abundance of iron coatings and concretions, the silts and sands were treated by Jeffries' method (28) to remove free iron oxides. The materials were reseparated and the residual fractions were reported in the mechanical analysis.

Aliquots of the clay suspension obtained from the first sedimentations were dried and weighed to get the percent clay. The <0.2 micron and the 2–0.2 micron clay were electrodialized to remove soluble cations and glycerine. The clays were diluted to 200 ml. volume and aliquots were taken to get the percentage fine and coarse clay. Table 3 shows the mechanical analysis.

The total weight of all the fractions was used as the basis for all calculations, rather than the washed, organic matter-free weight. Clay was removed before Jeffries' treatment and, therefore, contained free ion oxides. The other fractions were all carbonate and iron oxide-free. This conforms to the method used by Barshad for his profile calculations.

(3) Results.

It may be seen that the amounts of the different sand size fractions varied markedly from horizon to horizon (Table 3). To show the effect of the treatment, Table 4 was set up, giving the residue as percent of the original fraction. The values are very erratic with no uniformity in any one size fraction. However, the samples below the C horizon tend to have the lowest residue. While there is a loss in weight due to solution of the iron oxides, there will also be a gain in weight in the smaller fractions due to a liberation of fine particles entrapped in the concretions. Thus, a larger loss in weight would be expected in the coarser fractions than in the finer fractions.

The profile is characterized by a high clay content below the B_3 horizon. There is a continual increase in clay content down to the C horizon where it remains relatively constant down to horizon Number 12. The increase is primarily due to the <0.2 micron clay, since the 2–0.2 micron fraction increases only slightly and has rather uniform distribution. There is a small irregular variation in the different sand fractions but not enough to show a real change with depth. The silts decrease continually with depth and drop off sharply at the C horizon.

The A_1 horizon has a slightly coarser texture than any of the others. This may be due to loess contamination or to eluviation of clay to the lower horizons. The sample at 94-100 inches (Number 12) shows a high proportion of silt, particularly in the 2-5 micron fraction. During the mechanical separation, the suspensions of sample Number 12 appeared very micaceous. It was assumed that this was clay material from the rock which was not as well subdivided as in sample Number 11 above it.

(4) Discussion.

Variation in mechanical composition found between samples 13 and 14

TABLE 3--MECHANICAL ANALYSIS OF HAGERSTOWN PROFILE AS PERCENT OF RESIDUE FROM PRETREATMENT

Sample Number	Horizon	Depth in Inches	Size Fractions								
			2-1 mm	1-0.25 mm	0.25-0.1 mm	0.1-0.05 mm	50-20 micron	20-5 micron	5-2 micron	2-0.2 micron	minus 0.2 micron
1	A_1	0- 7	0.14	2.35	1.74	0.59	34.81	34.66	5.02	9.45	11.22
2	A_3	7- 10	.07	1.58	0.99	.33	30.54	30.25	6.07	13.63	16.53
3	B_1	10- 12	.06	1.17	.83	.31	25.76	29.50	5.91	17.83	18.63
4	B_{21}	12- 19	.05	1.34	.88	.39	29.22	28.70	6.12	18.13	20.06
5	B_{22}	19- 25	.08	1.63	.81	.19	22.95	27.64	6.00	26.21	14.45
6	B_{23}	25- 33	.05	1.51	.92	.32	20.54	23.50	5.33	20.47	27.36
7	B_{24}	33- 43	.27	1.31	.82	.33	16.88	18.58	4.98	25.47	31.38
8	B_3	43- 54	.19	1.05	.59	.31	10.75	12.88	4.52	30.18	39.53
9	C	54- 64	.06	.41	.62	.27	5.52	5.71	3.98	27.12	58.00
10	---	64- 76	.08	.82	.98	.38	3.77	7.27	3.51	26.29	56.91
11	---	76- 94	.02	.19	.26	.11	3.34	6.51	2.67	21.63	65.25
12	---	94-100	.22	.93	.98	.73	5.48	28.79	19.04	24.67	19.15
13	rock	100	0.00	5.42	12.36	10.13	1.47	14.82	13.77	19.93	21.58
14	outcrop	------	0.00	.05	.14	1.70	8.86	10.12	13.91	23.84	41.84

TABLE 4--EFFECT OF JEFFRIES TREATMENT ON THE VARIOUS
FRACTIONS OF THE HAGERSTOWN PROFILE; RESIDUE
EXPRESSED AS PERCENT OF ORIGINAL FRACTION

Sample Number	2-1 mm	1-0.25 mm	0.25-0.1 mm	0.1-0.05 mm	50-20 micron
1	12.1	49.2	70.3	51.7	94.3
2	11.0	50.6	72.6	52.5	93.2
3	15.4	46.8	64.1	41.1	95.8
4	10.9	46.6	66.2	54.7	95.1
5	15.8	47.4	42.1	15.8	92.8
6	13.8	64.0	57.2	29.4	89.3
7	46.9	55.2	48.6	24.0	85.3
8	35.4	44.6	30.4	20.3	74.8
9	24.2	22.2	20.2	9.6	89.0
10	46.8	64.5	41.3	14.4	75.2
11	20.0	35.4	15.3	4.7	67.7
12	69.7	58.1	39.2	30.3	84.5

shows that the Bonneterre dolomite gives residues of widely different character in different layers. Not only is the total sand greater in sample 13 below the soil than in sample 14 from an adjacent outcrop, but the proportions of the fractions as compared with one another are different. This extends also to the two clay fractions, 2–0.2μ and $<0.2\mu$. The appearance of similar but less extreme variations within the profile samples is thus not surprising. Down to 19 inches (samples (1-4) the ratios beween different fractions remain closely alike, so that uniformity of parent material might reasonably be inferred. Sample 5 (19-25 inches), however, differs markedly from those above in the following ratios: 1.0-1.25 mm sand/0.1-0.05 mm sand; 0.25-0.1 mm sand/0.1-0.05 mm sand; 2.0-0.2μ clay/$<0.2\mu$ clay. Samples 6, 7 and 8, although containing less sand and more clay, show similar ratios to those of samples 1 to 4. Samples 9, 10, 11, and 12 are all distinctive in two or more of these ratios. It must be concluded that the parent residues were non-uniform.

The question then arises whether the operation of pedological processes can be recognized or inferred. The ratio, coarse clay / fine clay, is helpful in this connection. Clay movement downward by simple eluviation normally affects the fine clay more than the coarse. But in the 19-25 inch layer (sample 5) there is a sharp increase in coarse clay and decrease in fine clay, compared with the overlying and underlying horizons, in all of which the fine clay slightly exceeds the coarse clay. Then at 54-64 inches we encounter a horizon with a much higher proportion of fine clay. The latter increases down to 94 inches, then decreases very sharply close to the rock, (sample 12).

The increase in coarse clay and decrease in fine clay at 19-25 inches clearly show that illuviation of fine clay such as characterizes gray-brown podzolic soils must here be absent or of entirely subordinate importance. Was fine clay transported to greater depths to be deposited at 54-94 inches? If so, why is there so little in the 94-100 inch sample? No clear answer to these questions can be deduced from the mechanical analyses alone. We shall return to them later in considering mineralogical and chemical evidence.

(5) Neutralization Capacity of Clay Fractions.

The cation exchange capacities (neutralization capacities in this case) were determined by averaging the values obtained from the titration curves with $Ca(OH)_2$ and KOH (section D under Mineralogy of the Clay Fractions). These values are shown in Table 5. The capacities of both the coarse and the fine clays were essentially constant down to sample 8 (the B_3 horizon) and then increased slightly to sample 12. Hydrous micas with some expanded layers and kaolinite have been established as the clay minerals on the basis of X-ray diffraction data. Kaolinite with an exchange capacity of 5 to 10 m.e. per 100 gm., and illite with 25 to 30 m.e. cannot account for the total exchange capacity. If the expanded mica layers have a capacity of about 100 m.e. per 100 gm., then a combination of 40 percent kaolinite, 40 percent illite, and 20 percent expanded layers would

give an additive cation exchange capacity of the proper order of magnitude. Other combinations were possible but this fitted the X-ray data of the coarse clays best. Considering the diffuse nature of the X-ray reflections from the fine clays, any calculated combination would be little better than a guess. The capacities of the fine and coarse clays were rather similar, indicating that the exchange capacity was not a function of particle size. Expanded layers are probably present and the fine clays may well contain more expanded material than is indicated by the X-ray results.

TABLE 5--THE NEUTRALIZATION CAPACITIES OF THE CLAY FRACTIONS IN MILLIEQUIVALENTS PER 100 GRAMS

Sample No.	Fine Clay <0.2 Micron	Coarse Clay 2-0.2 Micron
1	40	26
2	43	40
3	48	26
4	40	28
5	42	30
6	42	30
7	40	30
8	40	37
9	45	40
10	45	39
11	51	39
12	49	32

C. Chemical Characteristics of the Hagerstown Profile.

(1) Cation Exchange Properties.

A preliminary series of determinations of exchangeable Ca, Mg, K, and H were made using the rapid testing procedure of Graham (20). It was found that the sum of the cations did not agree well with the cation exchange capacities calculated from the contents of coarse and fine clay and their respective neutralization capacities. A more detailed study of the exchangeable cations and total exchange capacity was therefore undertaken. The ammonium acetate method was used for exchangeable Ca, Mg, K, and H; with direct distillation of the ammonium-saturated soil to give the total exchange capacity. Another value of the C.E.C. was obtained by the semi-micro potassium acetate method of Swindale and Fieldes (57). Thus, four values of the C.E.C. were available for comparison: two direct determinations; one comprising the sum of the Ca, Mg, K, and H released by ammonium acetate; and one calculated from the content of coarse and fine clay and their respective neutralization capacities. Table 6 contains these results.

The potassium acetate and ammonium acetate methods are in fair agreement except in samples 1 and 12. The sum of the replaceable cations gives values appreciably lower than the ammonia distillation. It is not likely that exchangeable Na (not determined) makes up much of this difference. Probably the exchange-

able H is underestimated in the titration procedure. The cation exchange capacity of the clay accounts for most of the total capacity except in samples 1 and 12. Since expanded micaceous minerals were present, it is quite likely that the silt fractions may have an appreciable capacity.

The failure of the rapid testing procedure was largely accounted for by the tenacity with which the clay held divalent cations. It gave low values for Ca and Mg in samples 8 to 11 which, as will be shown later, have very high bonding energies for Ca. The individual results for Ca, Mg, K, and H are given in Table 7. The proportion of exchangeable magnesium is high throughout and it exceeds calcium in samples 6 and 7.

TABLE 6--CATION EXCHANGE CAPACITIES OF HAGERSTOWN SAMPLES
AS DETERMINED BY DIFFERENT METHODS
(Milliequivalents per 100 gm. dry soil)

Sample	Depth	NH_4 Acetate Distillation	K Acetate Replacement	NH_4 Acetate Ca+Mg+K+H	C.E.C. of Clay
1	0- 7 inches	20.2	12.7	9.4	6.8
2	7- 10	14.2	13.0	9.2	12.5
3	10- 12	16.0	14.6	10.7	13.5
4	12- 19	17.1	15.3	11.0	13.1
5	19- 25	17.4	16.2	11.7	13.9
6	25- 33	20.4	18.7	13.8	17.6
7	33- 43	22.3	22.9	16.0	20.2
8	43- 54	30.1	30.0	20.0	27.0
9	54- 64	43.0	37.0	31.4	36.9
10	64- 76	47.5	42.2	30.6	35.8
11	76- 94	46.5	42.8	30.2	41.6
12	94-100	41.4	26.3	36.9	17.3

TABLE 7--EXCHANGEABLE CATIONS RELEASED BY N. AMMONIUM ACETATE
(Milliequivalents per 100 gm. dry soil)

Sample	Depth	Ca	Mg	K	H
1	0- 7 inches	6.25	2.49	0.28	0.43
2	7- 10	5.44	2.36	.19	1.18
3	10- 12	6.13	2.66	.20	1.70
4	12- 19	4.23	2.69	.21	3.83
5	19- 25	3.05	2.84	.19	5.65
6	25- 33	2.48	2.74	.23	8.30
7	33- 43	2.98	3.66	.26	9.15
8	43- 54	5.97	5.97	.29	8.09
9	54- 64	16.0	11.2	.33	3.83
10	64- 76	16.0	13.1	.39	1.06
11	76- 94	16.5	13.3	.33	----
12	94-100	21.5	14.2	.23	----

(2) Other Chemical Characteristics.

Three other determinations were made on all samples; soil-water pH, organic matter (wet oxidation) and available P_2O_5. The rapid methods described by Graham (20) were employed. Table 8 presents the results.

The pH figures were very uniform from 12 to 54 inches depth and indicated a highly unsaturated exchange complex. This is confirmed by the figures for ex-

changeable hydrogen. The layer at 64 to 76 inches was neutral and the lower samples were slightly alkaline as expected close to the limestone.

The organic matter content was low from the 12-inch depth downward. The available phosphorus, as determined with Bray's strong reagent, was very low throughout the profile.

TABLE 8--FURTHER CHEMICAL DATA ON HAGERSTOWN SOIL

Sample No.	Depth	pH	% Organic Matter	Available P_2O_5 Lbs./Acre
1	0- 7 inches	6.3	1.87	20
2	7- 10	6.2	0.98	17
3	10- 12	6.0	1.04	13
4	12- 19	4.6	0.57	22
5	19- 25	4.8	.33	16
6	25- 33	4.8	.42	15
7	33- 43	4.8	.33	22
8	43- 54	4.8	.45	16
9	54- 64	5.6	.37	18
10	64- 76	7.0	.62	16
11	76- 94	7.3	.50	28
12	94-100	7.7	.61	52

MINERALOGY OF THE SAND AND SILT FRACTIONS

Light Minerals.

The two fractions, 50-20μ and 20-5μ, of the profile samples were examined by X-ray diffraction using standard techniques (12). Quantitative determinations were not attempted, but broad conclusions about the proportions of different constituents were based on line intensities.

In the very fine sand fraction (50-20μ) quartz was the predominant constituent in samples 1 to 11. In all these samples feldspars and micas were detected in trace amounts. No other constituents were identified. The same result was found for sample 13, the residue of the limestone immediately below the soil profile. The residue of sample 14, the limestone outcrop, showed only quartz. Sample 12, the soil resting upon the limestone, was entirely different in mineral composition in the 50-20μ fraction. It contained no quartz but an intense mica pattern was obtained, accompanied by a strong 7.2 Å reflection. Part of the sample was extracted with hot 1N hydrochloric acid and part was heated to 340°, 450, 550 and 650° C. The acid treatment brought little magnesium into solution, so chlorites were absent. The 7 Å line diminished in intensity with heating and disappeared after the 650° C treatment. It was concluded that a mixture of a dioctahedral mica with kaolinite was present.

The mineral distribution in the 20-5μ fractions resembled closely that in the very fine sand. In samples 1 to 11 quartz was the predominant mineral with trace to minor amounts of feldspar and mica. The mica tended to increase in

amount slightly with depth. Kaolinite was identified in samples 9 to 12. Quartz was absent from sample 12, which consisted of mica and kaolinite. The residue from sample 13, the limestone immediately below the profile, also contained kaolinite and mica, but no quartz. Outcrop number 14 contained mica only in the 20-5μ fraction.

In summary it is clear that from the surface down to 94 inches the chief sand and silt mineral is quartz. Feldspars are present but of minor amount. Traces of mica were present from the surface down to 54 inches. Below this depth there was an increase in the mica content. Sample 12, at 94-100 inches consisted of a mixture of mica and kaolinite. The residue of the limestone immediately below it contained quartz, mica and kaolinite.

These results are certainly not consistent with the view that the high content of clay in samples 9 to 11 is due to clay formation from other minerals. The feldspars are present only in trace amounts, even where the soil reaction is neutral or slightly alkaline. Feldspar decomposition could not account for all the clay found. The mica content of samples 9 to 11 in the silt and sand, if extended through the overlying layers to the surface, would not provide sufficient parent material for the clay. We are forced to conclude that much of the clay is either inherited as such or is only slightly changed from finely divided micaceous minerals. There is no evidence that appreciable quantities have been produced by weathering of coarser mineral grains.

Heavy Minerals.

The very fine sand fraction (20-50 microns) isolated in the mechanical analysis was the coarsest material having an adequate amount of material for heavy mineral separations. This separation was done with the technique outlined by Jeffries (27) and s-tetrabromoethane adjusted to a specific gravity of 2.85 with nitrobenzene. There was a continual decrease within the size fraction down to the B_{24} horizon and a sharp increase at the C horizon. Since there is a decrease in the 20-50 micron fraction with depth, it is not surprising to find a marked decrease in the heavy minerals when expressed as percent of the total soil.

Portions of the heavy mineral fractions were mounted on microscope slides using Canada Balsam as the adhesive and reference index of refraction. A cursory examination of the slides showed that, with the exception of sample number 12, the minerals were nearly all cloudy, pitted and/or anhedral.

Quartz was found in all horizons and consisted of irregular grains showing a marked wavy extinction. Authigenic outgrowths were abundant and showed the same extinction position as the central crystal. All the quartz was cloudy, with opaque or gas-like inclusions, and the central crystals had a very high relief. Presumably, the central core was primary quartz carrying an iron oxide coating. The outgrowths which were not euhedral probably were formed in the dolomite.

The wavy extinction extending over the outgrowth might indicate that the whole is a remnant of a previous cycle in which metamorphism took place. However, no authigenic quartz was found in the light mineral fraction of any horizon.

Zircon was present as stubby or elongated crystals with one or both ends pyramidal. Inclusions were always present, sometimes as needles running along the crystal. Twinning was shown by only one crystal in the bottom horizon. The amount of zircon was rather uniform down the profile but doubled in sample number 12.

Rutile was the anhedral, fractured, amber-colored type. No euhedral or reddish grains were found. Fragments resembling broken glass were common. The amount of rutile was much more variable than the zircon, no regular distribution pattern being evident.

Bluish tourmaline was the only variety of this mineral species present. Usually the crystals were prismatic with irregular ends but a few crystals were anhedral. Red garnet was found throughout the profile and a few broken crystals of hornblende were found in the two surface horizons.

There were approximately equal amounts of zircon, rutile and tourmaline in all the horizons except number 12, and in every case but in number 12 the amount of each was less than 10 percent of the heavy fraction. In horizon 12 the zircon was greater than 10 percent and was about double the rutile or tourmaline.

There was an abundance of opaque minerals in the horizons above the C horizon. A sharp drop occurred at the C horizon and the amount decreased to only a few crystals in horizon 12. No euhedral crystals were found and the various sharp, rounded, massive or knoby forms were present in all horizons. An attempt was made to identify these minerals by oblique illumination but it was unsuccessful.

Spectrographic Determinations.

The evidence of the mechanical analyses, combined with the relative uniformity in species of heavy mineral, points to the presence of depositional differences in the original limestone residues from which the soil horizons were derived. These differences might be expected to show themselves also in varying ratios for pairs of the resistant heavy minerals and in somewhat varying particle size distribution for a given resistant mineral. Quantitative spectrographic methods had been worked out for boron, zirconium and titanium, which are characteristic elements of the resistant minerals tourmaline, zircon and rutile. Thus we decided to determine these elements in the two sand fractions 0.05- .01 mm and 0.1-0.25 mm. The results are in Table 9 in the form of ratios, which in absence of depositional variation should be constant for each column.

Considerable variation is shown in all the ratios examined; hence depositional variation is strongly indicated.

TABLE 9--RATIOS OF ZIRCONIUM, BORON, AND TITANIUM IN TWO SAND FRACTIONS OF THE HAGERSTOWN PROFILE

Hori-zon	0.05-0.1 mm			0.1-0.25 mm			Size Distribution $\frac{0.05\text{-}0.1 \text{ mm}}{0.1\text{-}0.25 \text{ mm}}$		
	B/Zr	B/Ti	Zr/Ti	B/Zr	B/Ti	Zr/Ti	B	Zr	Ti
1	0.0591	0.0162	0.275	0.135	0.0250	0.186	0.74	1.69	1.14
2	0.0523	0.0173	0.331	0.121	0.0264	0.218	1.55	3.58	2.36
3	0.115	0.0192	0.167	0.200	0.0267	0.133	1.92	3.33	2.67
4	0.0521	0.0173	0.332	0.100	0.0200	0.200	1.73	3.32	2.00
5	0.0500	0.0175	0.350	0.140	0.0191	0.146	1.67	4.67	1.82
6	0.1450	0.0169	0.375	0.257	0.0253	0.0986	1.50	8.57	2.25
7	0.0756	0.0189	0.250	0.300	0.0389	0.130	1.13	4.50	2.34
8	0.165	0.0275	0.167	0.380	0.0316	0.0833	1.74	4.00	2.00
9	0.550	0.0379	0.0689	0.642	0.0367	0.0571	1.43	1.67	1.38
10	1.14	0.100	0.0880	0.833	0.0652	0.0783	1.67	1.22	1.09
11	0.938	0.0714	0.0761	0.431	0.0363	0.0842	2.17	1.00	1.11
12	-----	-----		0.513	0.0514	0.100	----	----	----

MINERALOGY OF THE CLAY FRACTIONS

X-ray Determinations.

Various standard techniques were used which included the use of oriented and non-oriented specimens. Portions of the clays were saturated with K and Mg ions and thin films were prepared by drying a suspension of the clay on a glass microscope slide. The K-treated clays were heated, successively, to temperatures of 100, 350 and 550° C and diffraction patterns subsequently taken. The Mg-treated clays were solvated with ethylene glycol according to the method proposed by Brunton (11).

The Ca-saturated clay suspensions from the electro-chemical experiments were dried, ground through a 300 mesh sieve and examined by the powder method in order to observe prismatic reflections.

Coarse Clay: Representative X-ray patterns of the oriented films of the coarse clay (2-0.2 micron) using Cu radiation are shown in Figure 1. The gycolated Mg-saturated clays have an abundance of expanded micaceous layers, which collapse to 10 Å when K-saturated and heated to 100° C. The disappearance of the 7 Å and the 3.6 Å lines when the specimen was heated to 500° C indicates that kaolinite had been present and was reduced to an amorphous state.

Quartz is present in small amounts in the top eight horizons and in still smaller amounts in the bottom four horrizons, as judged by the 4.27 Å reflection. Kaolinite is constant in amount in all horizons but the bottom one (number 12). In it, the reflections are very sharp and intense; they indicate either an increase in amount or a more uniform crystalline material than in the other horizons. There were indications that traces of feldspars wre present throughout, as shown by small 3.2 Å peaks, but these peaks were not reproducible.

The chief differences in the coarse clay from horizon to horizon are in the expanded micaceous material (Figure 2). When it is Mg-saturated and glycolated, there is a partial expansion to 14-15 Å and to 17 Å. The 17 Å peaks indicate a montmorillonitic material, and the 14 Å peaks indicate a vermiculitic or mixed layer aggregate. The presence of chlorite was ruled out since all the layers collapse to 10 Å when K-saturated and heated to 100° C. Both the 17 and 14 Å reflections are present in the upper six horizons and only the 14 Å reflections appear in the lower six horizons. The proportion of expanded 2:1 layer silicates could not be determined.

The coarse clay fraction of the whole profile showed a very striking similarity, in general, in the amounts and kinds of clay minerals in each horizon. Kaolinite makes up possibly half of the material and the 2:1 layer silicates make up the remainder with minor amounts of quartz. The iron oxides were either not well crystallized or present in amounts too small to show distinctive and reproducible peaks in the X-ray patterns.

The non-orientated powder patterns of the coarse clay showed (060) reflections in this region (21). Since kaolinite was a major constituent in all the coarse
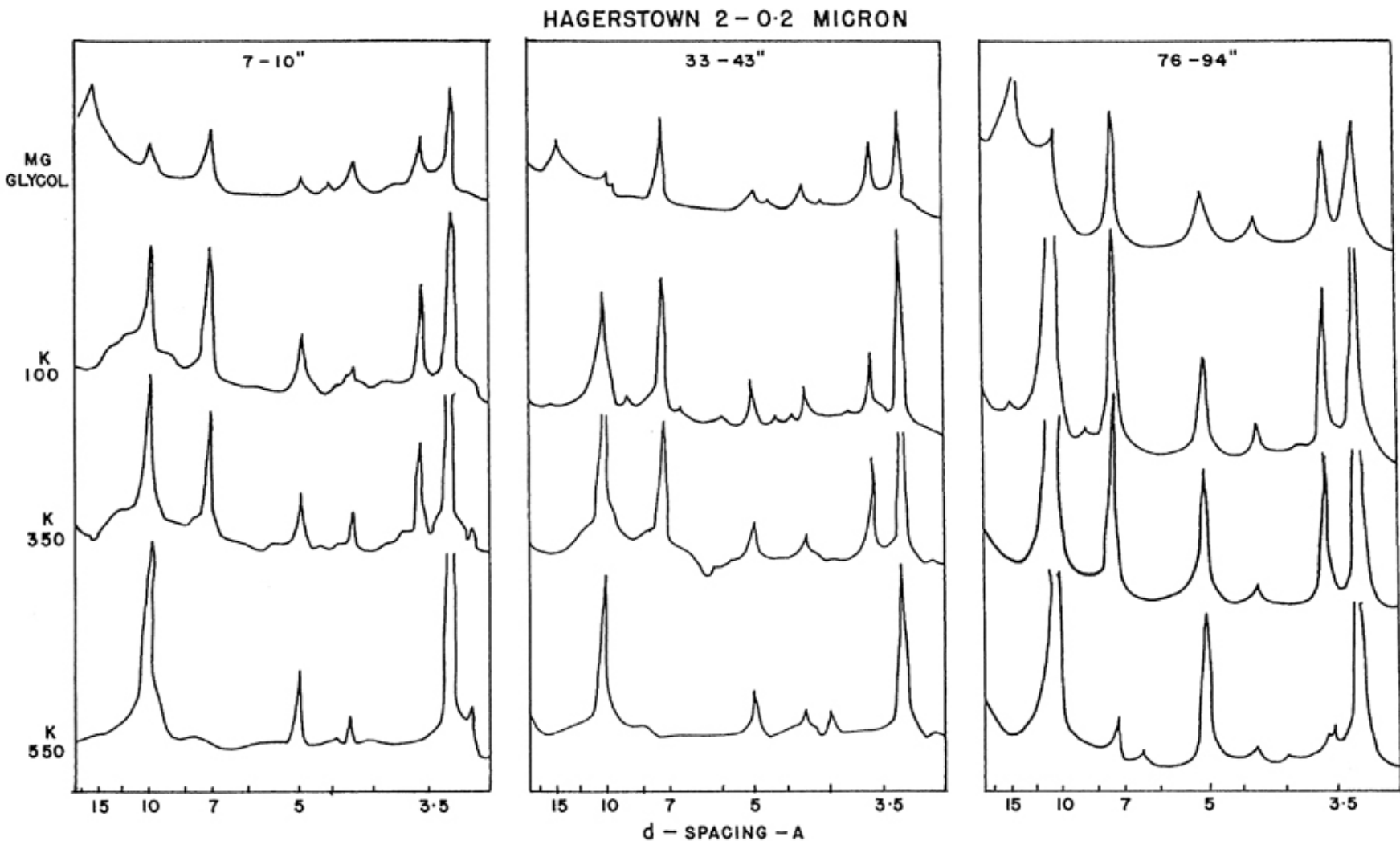
Fig. 1—X-ray diffraction patterns of oriented coarse clay fractions of three representative horizons of the Hagerstown profile.
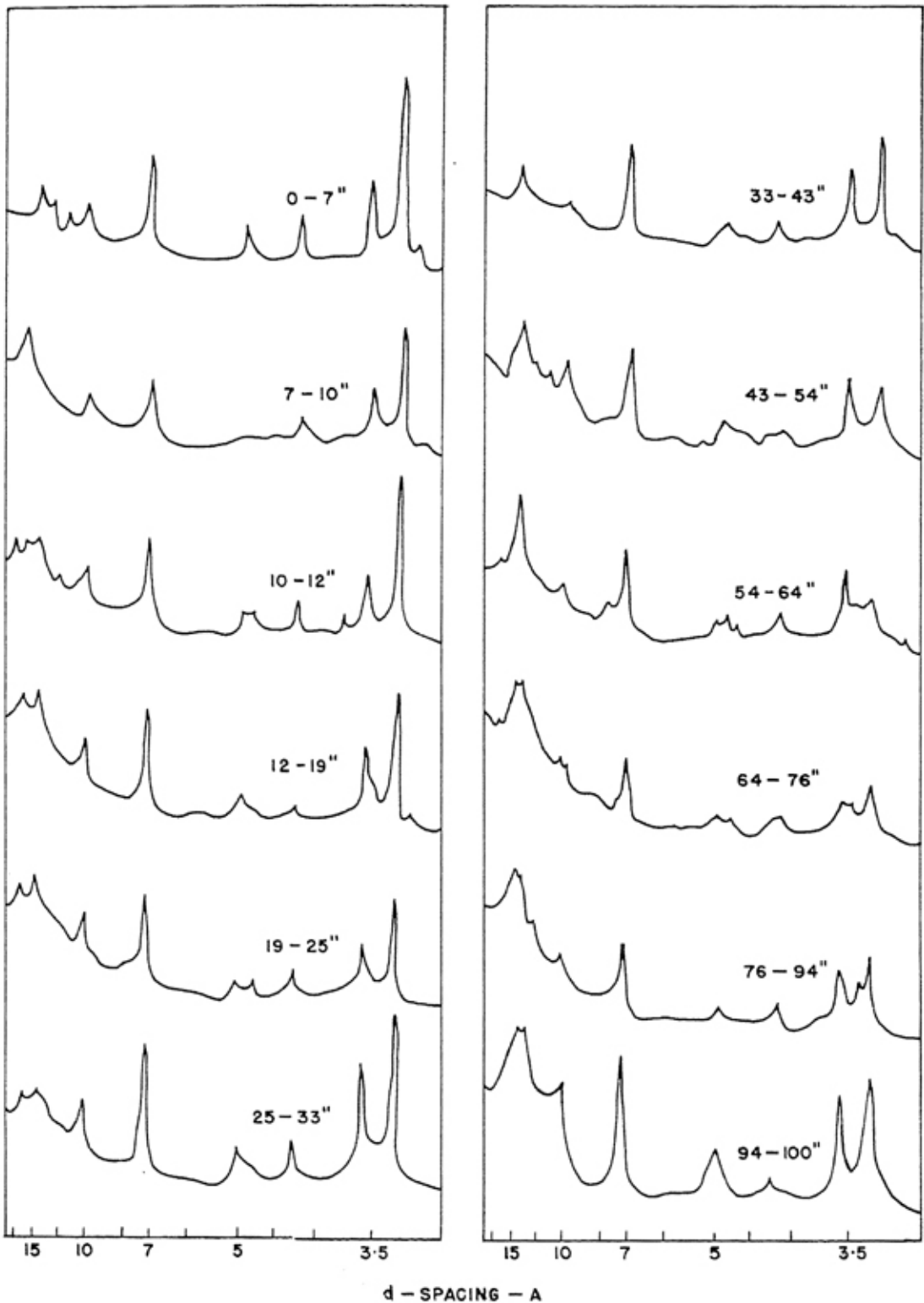
Fig. 2—X-ray diffraction patterns of oriented coarse clay fractions from all Hagerstown horizons. Magnesium clays expanded with ethylene glycol.

clays, it was impossible to state conclusively that the micaceous material was dioctahedral.

Fine Clay: The fine clay ($<$0.2 micron) consisted of kaolin and micaceous material (Figure 3). The oriented Mg-glycolated specimens of the top eight horizons gave a broad reflection zone extending from 15 to 20 Å with small peaks superimposed and with the peak position at about 17 Å. (Figure 4) In horizons 9, 10 and 11 there was a 14 Å peak along with 17 Å reflection. In the bottom horizon, there was a strong 14 Å peak and a weak 17 Å one. In situations of this kind it is virtually impossible to estimate, even qualitatively, the amounts of each mineral in the fine clays. On the basis of the K-clay patterns, the amount of kaolin was judged to be small.

The unoriented powder patterns of the fine clay, like the coarse clay, all gave (060) reflections at 1.49 to 1.50 Å. This reflection could not primarily have been due to kaolin in this case since only small amounts were present. It can be concluded that the micaceous material of the fine clay was dioctahedral. It seems probable that the micaceous material of the coarse clay was similar.

Comparison with Glauconites: It was pointed out in the section dealing with the geology of the sampling area that the Bonneterre dolomite varies from place to place. One of the differences was the color of the associated clay material. The clay mineral in the formation northeast of the St. Francois Mountains has been recognized as glauconite (53). It was clear that the clay in the rock near the sampling site should be examined to demonstrate whether or not it was glauconite. Before dealing with the analytical results, the characteristic features of glauconite will be discussed.

Although Ross (53) had described it earlier, Gruner (22) was the first to make a systematic study of glauconite. One of the samples he studied was from the Bonneterre dolomite near the town of Bonne Terre, Mo. He assigned this sample to the muscovite group with the following lattice parameters: $a_0 = 5.25$ Å; $b_0 = 9.10$ Å; $c_0 = 19.96$ Å. The X-ray pattern, shown in Table 10, will be discussed later.

Hendricks and Ross (24) made an elaborate study of glauconite, analyzing some 40 samples to get an average or ideal formula:

$$K_{.86} Al_{.36} Fe^{+3}_{1.06} Fe^{+2}_{.24} Mg_{.39} Si_{3.62} Al_{.38} O_{10} (OH)_2$$

The glauconites that they analyzed may be noted for their regularity in chemical composition. The average nonexchangeable K was 0.84 atoms per unit cell and was always less than 1. Si varied from 3.58 to 3.75 in the tetrahedral layer. Mg varied from 0.35 to 0.45 while the aluminum varied from 0.12 to 1.27 atoms per unit cell in the octahedral layer. The ratio of Fe^{+3} atoms to Fe^{+2} atoms in the octahedral layer was between 4.1 and 6.2. Glauconite is a heptaphyllite mica in which the octahedral ions are exceptionally constant, varying between 2 and 2.09.

Recently, Hoebeke and Dekeyser (25) have carried out a series of physical and chemical measurements of a glauconite sample from Belgium and compared
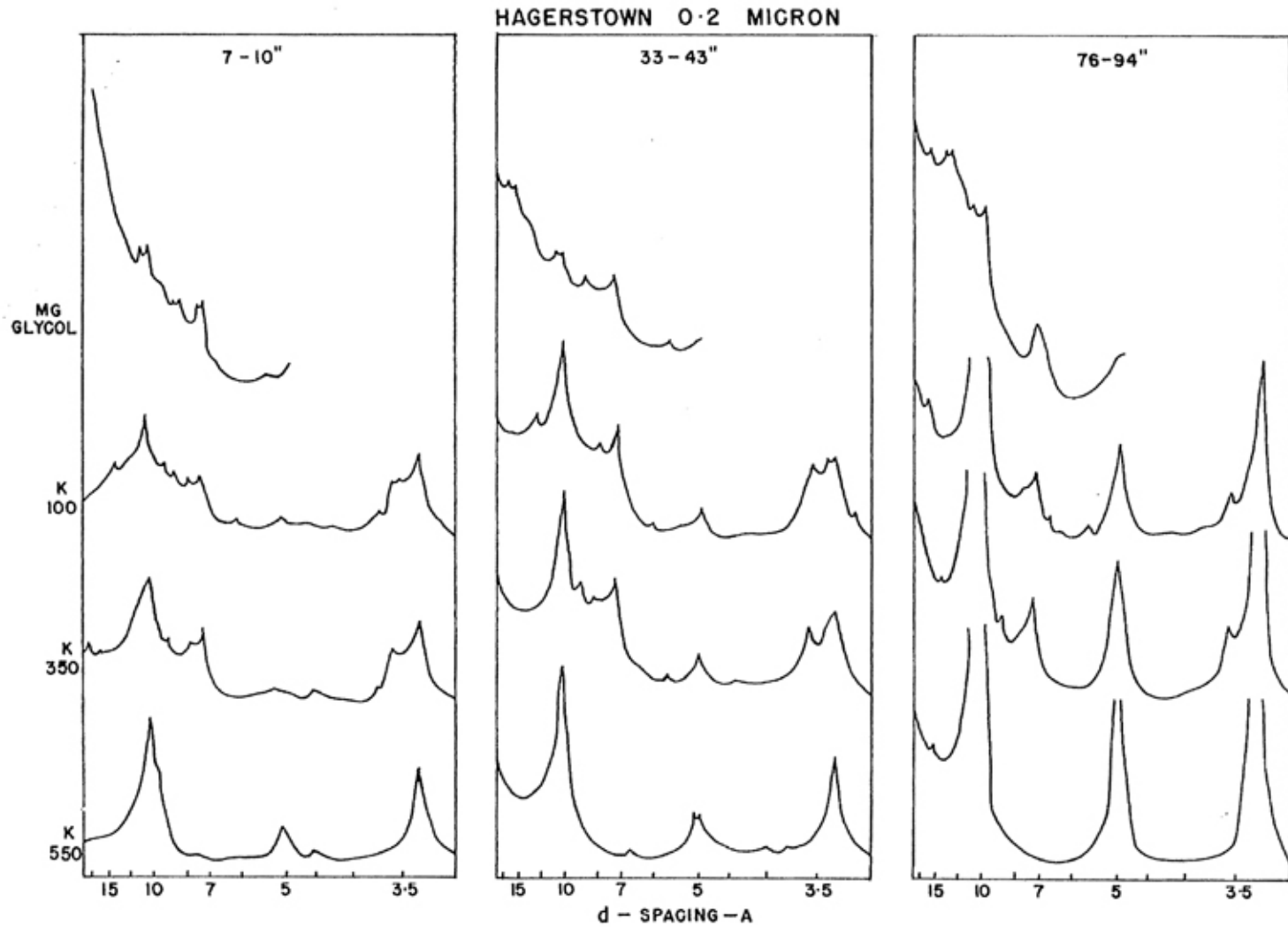
Fig. 3—X-ray diffraction patterns of oriented fine clay samples of three representative horizons of the Hagerstown profile.
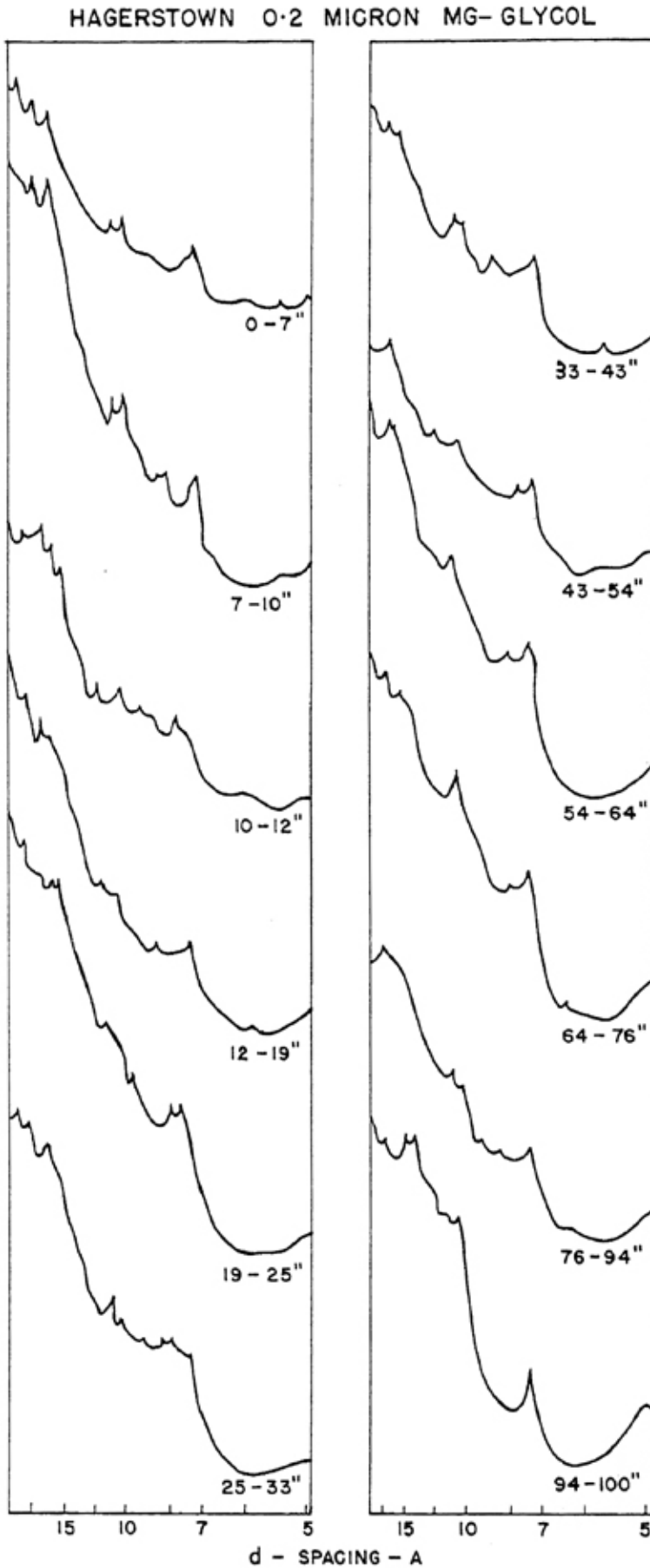
Fig. 4—X-ray diffraction patterns of oriented fine clay fractions from all Hagerstown horizons. Magnesium clays expanded with ethylene glycol.

the results with those of Gruner (22) and Hendricks and Ross (24). Thermal analysis indicated that oxidation of the ferrous iron and a change in color from green to brown occurred at 375°, and that the loss of lattice OH occurred at 585° C. At 975° C magnetite was formed but when the sample was pretreated with H_2O_2, hematite was formed instead. The X-ray diffraction patterns showed a similarity to muscovite and to the pattern published by Gruner (22). The mineral formula, as calculated from chemical analysis of the acid treated material, was rather similar to those cited by Hendricks and Ross (24). The ferric-ferrous ion ratio was 9 in contrast to the range 4.1 to 6.2 found earlier. The lattice charge was 0.84 whereas the external cations equalled 1.16 cation equivalents. A recalculation of the chemical analysis by the author gave a slightly different chemical formula with a lattice charge of 1.00 and 0.55 external cation equivalents. No explanation could be found for the discrepancy except that exchangeable hydrogen ions may have been present.

The most controversial part of their paper concerns the supposition of ferrous ions in the tetrahedral layer. By a series of subtle arguments they arrived at this hypothesis and attempted to prove it by differential rate of solution of the octahedral and tetrahedral layers in dilute HCl. At the time when the octahedral aluminium and ferric ions had been removed, the mineral was still green and all the ferrous ions were still present in the residue. Continued treatment bleached the residue. The fact that ferrous ions were much too large for tetrahedral coordination can be overcome as they claim that the small amounts of ferrous ions present would cause only a small average deformation.

In summary, it is found that glauconite is a green dioctahedral clay mineral, normally very fine-grained but occasionally occurring in microscopic crystals (24). Its chemical formula differs from muscovite in two respects.

First, in muscovite the uniform lattice charge of 1.00 per formula is due solely to the proxying of Al for one Si in every four in the tetrahedral layer. Glauconite has an average charge of 0.84 per formula, almost equally divided between the octahedral and tetrahedral layers.

Second, the muscovite formula, unlike that of glauconite, contains no appreciable ferric, ferrous or magnesium ions. Glauconite, on the other hand, has been classified as a member of the illite group since it has a similar X-ray diffraction pattern (22) and a similar lattice-charge distribution (24). The 060 reflection at 1.51 falls between that of a dioctahedral mica at 1.50 and that of a trioctahedral mica at 1.53 and is a consequence of the high iron content of the octahedral layer. It differs chemically from the typical dioctahedral illites (21) in that it has a high ferric ion content in the octahedral layer and an appreciable amount of ferrous ion in the lattice. Polymorphism of glauconite is difficult to establish, since the extinctions of the characteristic reflections may be governed by structural as well as geometrical factors (10). There is evidence that it may have a single-layer mica structure.

The concept of glauconite as a mineral species has recently been examined by Burst (13) who studied a series of marine deposits from the Gulf of Mexico. A wide series of compositions was found ranging from those formerly regarded as typical of glauconite to some which were very close to illite. On the basis of X-ray and chemical evidence the compositions were assigned to four groups. A clay mineral intermediate between glauconite and illite has been described by Keller (31) in an occurrence in the Morrison formation in Colorado.

A drill core of the eastern Bonneterre dolomite containing glauconite was obtained through the courtesy of Dr. C. S. Ross. The insoluble residue was obtained by warming the shattered sample with a strong potassium acid phthalate-HCl buffer at pH 3. The clay fraction of it and of New Jersey Greensand (Wards) were separated by mild trituration and sedimentation.

Oriented specimens were prepared on porous ceramic tile according to the method developed by Kinter and Diamond (32). This has the advantage over the glass slide technique in that various treatments can be given to the same specimen without altering it and, in so doing, the specimen variation is eliminated in the interpretation of the X-ray patterns.

X-ray patterns of the oriented specimens of the two glauconites are compared with those of the rock underlying the profile (sample 13) and the outcrop (sample 14) in Figure 5. The two glauconites showed very sharp 10 Å peaks, while samples 13 and 14 had rather broad peaks in the 10 Å region when dry and when glycolated.

Since the basal spacings of all four were over 10 Å, hydrated and expanded layers must have been present. The addition of the glycol decreased the spacing in all but the drill core specimen, indicating that hydrated layers had been present.

To determine if the acid treatment had any marked effect, the New Jersey Greensand oriented specimen was treated with hot O.1N acetic acid, followed by 0.1N sodium acetate and washed. The patterns of the sodium greensand, dry and glycolated, are also shown in Figure 5, and it is seen that there is no difference in peak position but there is a decrease in intensity and broadening of the whole peak.

The diffraction patterns of the fine clays (<0.2 micron) were similar to those of the coarse clays in shape and intensity of peaks. Kaolinite was present in both the fine and coarse fractions of sample 13.

The X-ray diffraction patterns of the non-oriented specimens were obtained with a 114.6 mm camera with Co radiation as sources. The data for the four samples listed above are compared in Table 10 with the d spacings of the Bonneterre glauconite recorded by Gruner (22). The h k l figures were assigned by Gruner on the basis of a muscovite structure. The three glauconite patterns agree reasonably well with one another, and also with the patterns published by Hoebeke and Dekeyser (25).
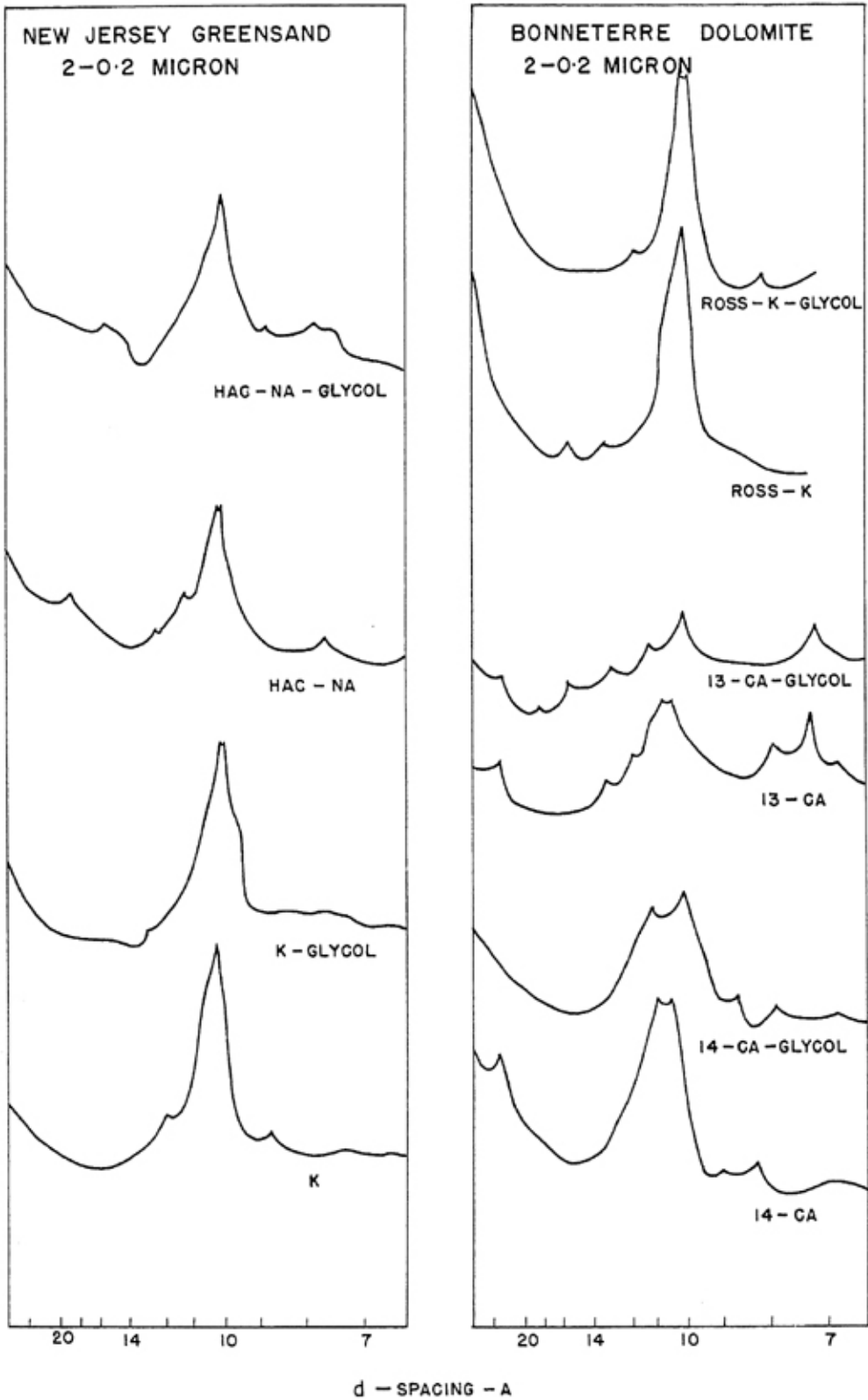
Fig. 5—X-ray diffraction patterns of oriented specimens of the coarse clay obtained from Bonneterre Dolomite and New Jersey Greensand.

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TABLE 10--X-RAY DIFFRACTION PATTERNS OF GLAUCONITE AND THE CLAYS FROM THE BONNETERRE DOLOMITE

h k l	(1) Glauconite		(2) Glauconite		(3) Glauconite		(4) 13 (2-0.2)		(5) 14 (2-0.2)	
	A	R.I.	A	R.I.	A	R.I.	A	R.I.	A	R.I.
002	9.94	1	10.16	5	10.06	10	10.06	4	10.37	8
			6.27				7.19	2		
110B	4.91	½	5.05	½	5.00	1	5.00	3	4.96	3
110	4.49	2	4.56	5½	4.56	9	4.52	5	4.51	10
			4.39	3	4.41	2			4.36	3
			4.15	1	4.15	½			4.15	1
024	3.67	2b	3.67	3½	3.67	3	3.67	5	3.66	4
							3.55	½	3.54	8
006	3.31	·3	3.16	10	3.34	6	3.37	2½	3.35	5
025	3.09	1b	3.08		3.10	2	2.98	3½	3.08	3
			2.91	½			2.92	1	2.88	
115	2.86	1	2.80		2.79		2.86	3		
	2.68	½	2.69	1	2.70	1	2.70	4½	2.69	1½
116	2.58	4	2.60	5	2.60	9	2.58	4½	2.58	9
133	2.40	2b			2.40	7	2.45	5	2.46	2
					2.271	2	2.35	4	2.39	5
040	2.256	½	2.225	9	2.225		2.252		2.248	3
	2.191		2.161		2.161	2	2.195	3	2.199	
043	2.141	1b	2.055						2.145	1
206	1.999	1b			1.998	2	1.977	2	1.998	1½
139B	1.823	½	1.899				1.927	3	1.899	4
	1.718	½	1.719	½	1.714	1	1.714	4	1.702	4
139	1.656	2b			1.660	3	1.695	3	1.667	4
			1.573	4			1.561	2		
			1.554							
060	1.516	4	1.518	4	1.516	7	1.509	3½	1.506	5
331	1.501	1	1.498		1.500				1.485	2
335	1.379	½	1.408	5						
2012	1.337	½b								
400	1.306	1	1.313	2	1.307	4			1.299	1
264	1.254	½	1.263	½			1.247	1	1.265	2
339	1.204	½	1.113	3	1.170	½			1.249	1
			1.050	4						

(1) Bonneterre glauconite, Gruner (22)
(2) Bonneterre glauconite from Ross, x-ray pattern by the author
(3) New Jersey Greensand
(4) Bonneterre underlying the soil profile
(5) Bonneterre clay from the outcrop rock specimen
R.I. Relative Intensity of lines.

The patterns of the clays from samples 13 and 14 appeared to be similar to the glauconite patterns but there are some significant differences. Characteristic kaolinite reflections were shown by sample 13, as was the case with the oriented specimens of this sample. The d spacing of the (060) reflection of glauconite (1.516 Å) is slightly different from that of samples 13 and 14 (1.509 and 1.506 Å). The (002) reflection at 5.0 Å has a lower intensity relative to the (001) and (003) reflections in glauconite than in samples 13 and 14.

The (060) reflection is close to 1.50 Å and the second order basal spacing is of the same intensity as the first and third order for the aluminous dioctahedral micas (10). On the other hand, if the octahedral layer is ferriferous, the (060) spacing is increased and the second order reflection is weak or absent (10). Glauconite, being ferriferous, conforms to the latter criterion. The clays in samples 13 and 14 presumably do not contain as much iron as the glauconites.

The lack of the green color in the rock samples 13 and 14 may be interpreted as being due to the small proportion of ferrous iron, according to the work of Hoebeke.

To check these interpretations, determination of free iron oxides, total ferric and ferrous iron was carried out on samples 13 and 14. The free iron oxides were removed by the sodium hydrosulfite method (46) and the ferrous iron was determined by the method of Shapiro and Brannock (55). The total iron was determined using o-phenanthroline. The results are shown in Table 11.

TABLE 11--THE FREE IRON OXIDES, TOTAL FERRIC AND FERROUS IRON IN THE COARSE CLAYS OF THE LIMESTONE RESIDUE FROM BELOW THE PROFILE AND FROM THE OUTCROP

Sample	Total % Fe_2O_3	Free Iron Oxide, % Fe_2O_3	Iron on Basis of Cleaned Residue		Fe^3/Fe^2
			% FeO	% Fe_2O_3	
13	36.1	32.1	0.81	5.90	5.7
14	10.85	7.38	0.64	3.74	4.5

The great amount of free iron oxide removed from sample 13 is surprising as there was five times as much of it as was apparently present in the clay lattice itself. The net Fe_2O_3 (total—free iron oxides – FeO) is certainly lower than most glauconites and is just above the range of values found in most illites (21). The amount of ferrous iron in both samples is extremely low compared to the amount found in the glauconites. If part of the free iron oxides were derived from the ferrous and ferric ions in the micaceous mineral lattice, the mineral could have been glauconite but, according to Hoebeke and Dekeyser (23), the ferrous ions are the last to be released on acid treatment.

The general conclusion, therefore, is that clay minerals are present throughout the profile; in composition they lie between illites and glauconites but closest to the illites.

Electron Microscopy.

The fine and coarse clays of all the samples were well dispersed with NaOH and diluted to 0.005 percent suspensions. Electron micrographs of the twelve soil clays were obtained through the electron microscope service of the University of Missouri Physics Department. Electron micrographs of the clays from the dolomites were taken by Mr. Maurice Patry of the Science Service, Canada Department of Agriculture at Ottawa.

Selected photographs of the fine clays of the soil horizons are shown in Figures 6 and 7. The clays of all the horizons except the lowest had a rather similar appearance. The particles were nearly all thin platelets with irregular but sharp edges and in some cases actually had hexagonal faces. Elongated thin laths were present in small amount down to 94 inches but predominated in the bottom horizon (94-100 inches). Needle-or rod-shaped particles were sparse. Small masses of opaque material, presumably iron oxides, were shown and local dark areas appeared on the larger platelets. These dark areas may have been zones of decomposition of the layer lattice, where the iron atoms of the lattice had been changed to free iron oxides at the surface of the platelet, or fine clay particles.

The coarse clays (Figures 8 and 9) also showed this speckled effect. These clays displayed a variety of forms in each horizon and portions were selected to show the best specimens, rather than to be representative of all the kinds in each horizon. In Figure 8a, a thick rounded particle is shown beside several thin speckled ones. A thinner rounded particle in Figure 8d may be compared with 8a. The long rod-like particle in 8f is possibly rolled up sheet, from the appearance of the lower end. The large thin platelet in Figure 9g is probably the most characteristic of all the horizons. In many cases overlapping of these platelets was clearly visible through the particle. The stacked aggregate of hexagonal platelets in 9h showed a marked similarity to published photographs of kaolin. Many particles were found in the profile similar to the one in Figure 9i; i.e., lath-like with a jagged termination. This one was unique in that an electron diffraction shadow was produced which moved along the particle as the focus was changed. Numerous thin euhedral speckled platelets are shown in 9l.

From the X-ray diffraction analyses, the coarse clay consisted of a substantial amount of kaolinite along with illite and expanded micas. The thin, irregular shaped, speckled platelets (Figure 8e and 9g) were considered to be illite or expanded micas and the thicker euhedral crystals (Figure 9h and i), kaolinite. However, the thin lath-like, speckled platelets were probably 2:1 layer silicates.

The fine clay of the underlying dolomite is shown in Figure 10a. This differs from most of the soil clays in that it has an abundance of very thin laths or "slivers" and some thicker laths and needles. Two fairly thin hexagonal platelets are also shown. If the soil clays were derived from material such as this, a substantial alteration of shape must have occurred. In Figure 10b, the shadow-cast image of a thin platelet from the coarse clay fraction of sample 13 is shown

underlying a small rod. This platelet has the same appearance as a sheet of muscovite and shows clearly the broken edge of part of the sheet. Small but thicker masses of material, possibly iron oxides, are also present.

The fine and coarse clay (Figure 10c and d) of the outcrop dolomite (Sample 14) demonstrate the lath-like and also fibrous nature of the illite material. The extreme thinness of these particles is shown in Figure 10c. Some of these platelets are made up of less than six 2:1 layers, as shown by the width of the shadows at the particle edges. The shredded appearance of the ends of the particles is shown only at high magnifications and so could have been missed in the photographs of soil clays.

The photographs of the New Jersey Greensand glauconite (Figure 10e) shows the characteristic irregular platelets with holes in them. These are probably due to the oxidation and removal of ferrous ions from the lattice and, if so, holes could be formed only if the lattice ferrous ions were segregated into zones.

The electron micrograph of the Bonneterre glauconite obtained from Ross is shown in Figure 10f. The material is platy in contrast to the bladed or fibrous nature of the clays obtained from the Bonneterre formation near the sampling site.
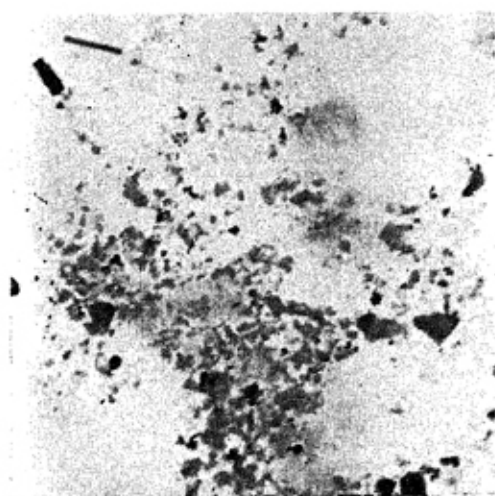
a. 0-7 inches
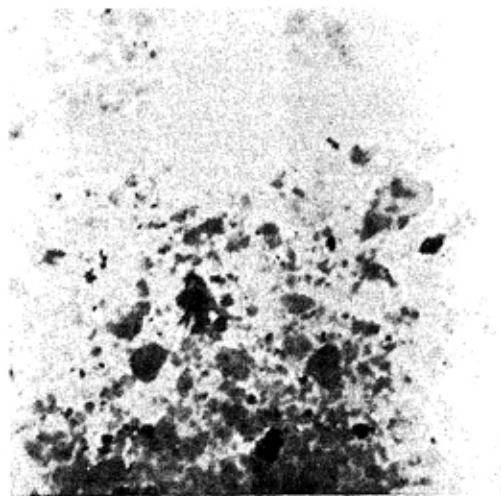
d. 12-19 inches
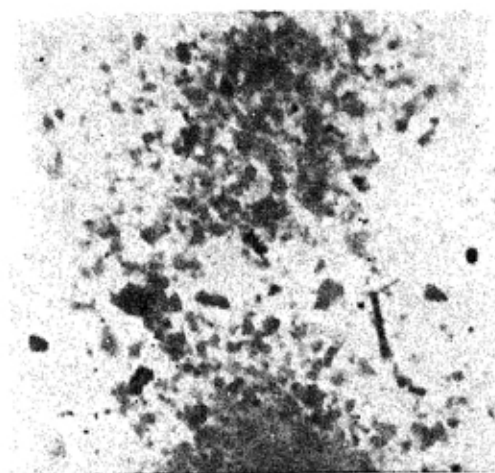
b. 7-10 inches
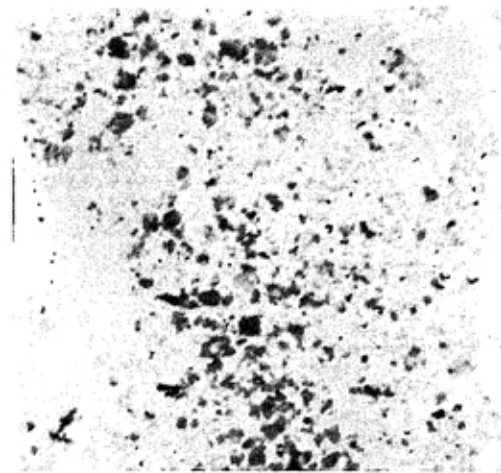
e. 19-25 inches

c. 10-12 inches
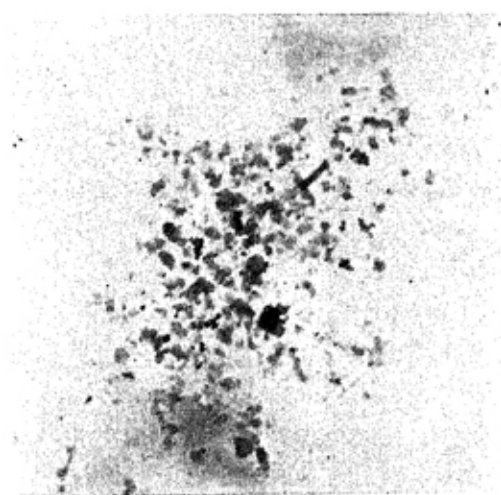
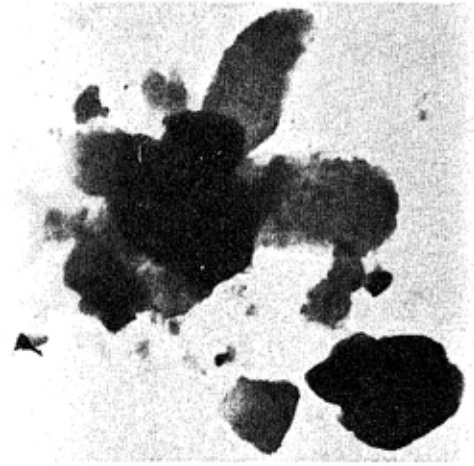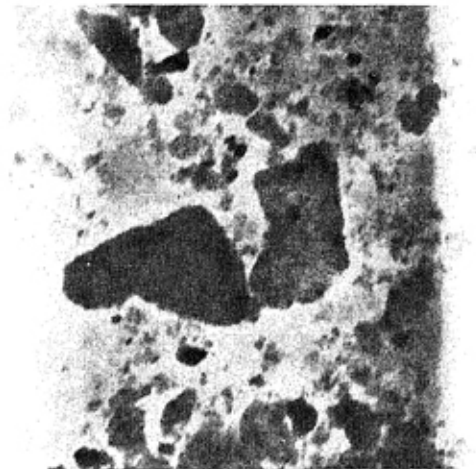f. 25-33 inches

Fig. 6—Electron micrographs of the fine clay fractions ($<0.2\mu$) of the Hagerstown soil horizons 0-33 inches. Magnification 4000-6000 as reproduced.
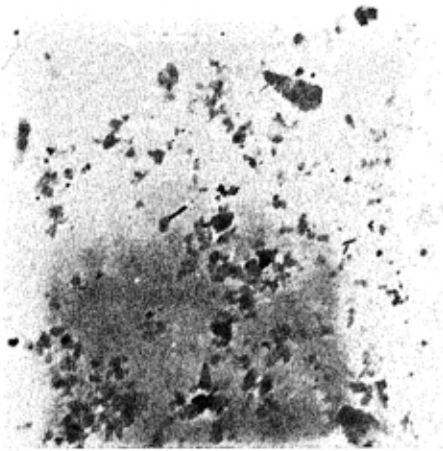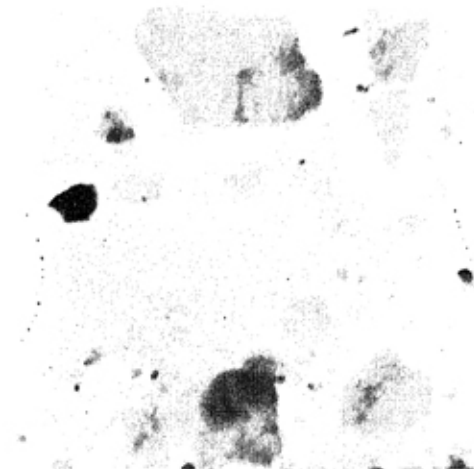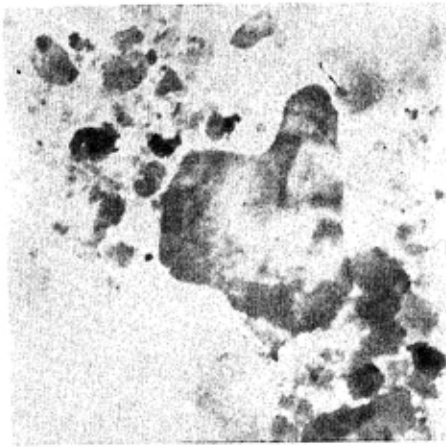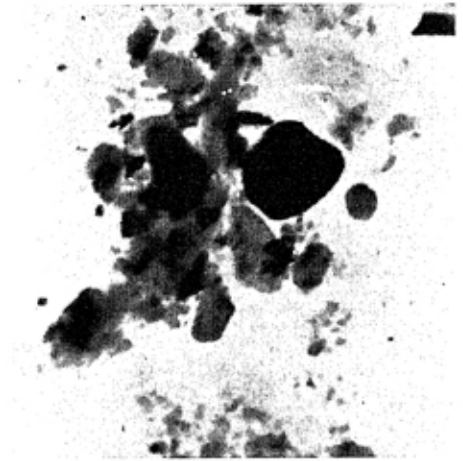
g. 33-43 inches
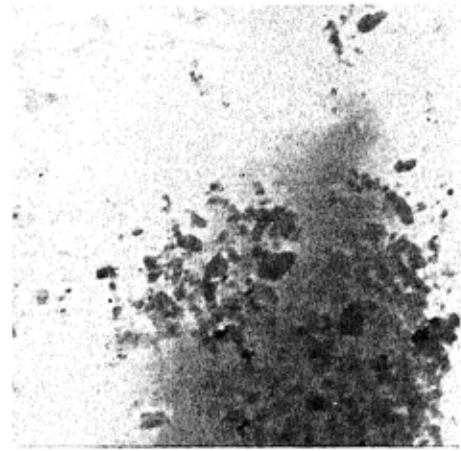
j. 64-76 inches
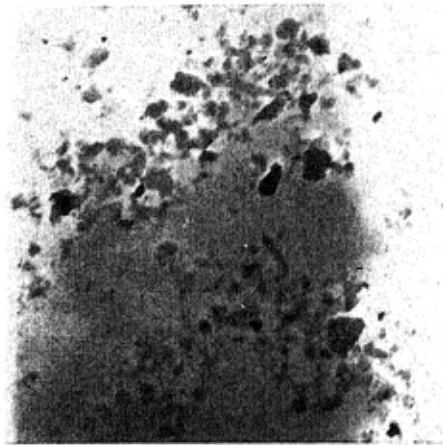
h. 43-54 inches
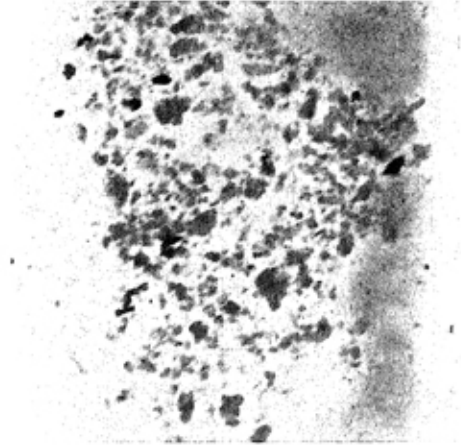
k. 76-94 inches
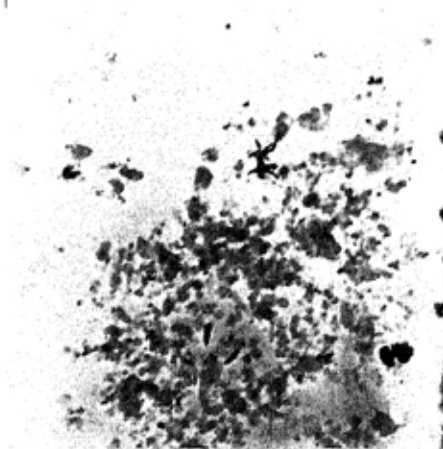
i. 54-64 inches
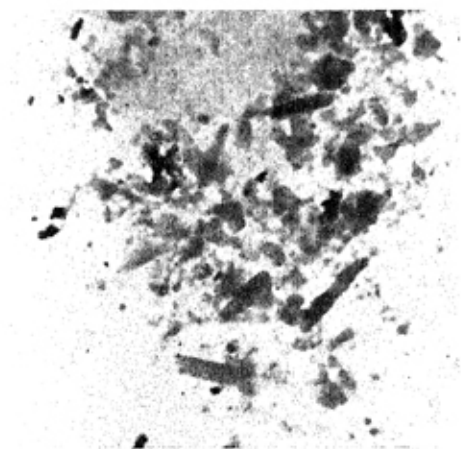
l. 94-100 inches

Fig. 7—Electron micrographs of the fine clay fractions ($<0.2\mu$) of the Hagerstown soil horizons 33-100 inches. Magnification 4000-6000 as reproduced.
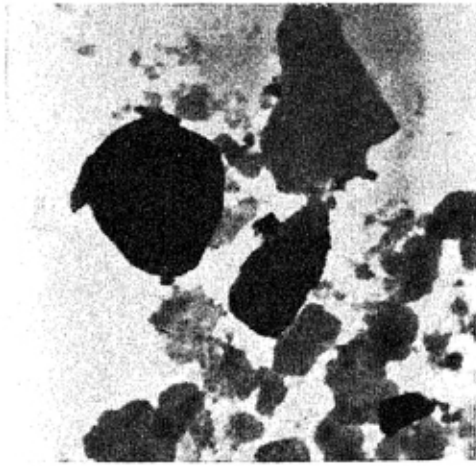
a. 0-7 inches

d. 12-19 inches

b. 7-10 inches

e. 19-25 inches

c. 10-12 inches

f. 25-33 inches

Fig. 8—Electron micrographs of the coarse clay fractions (2-0.2μ) of the Hagers-town soil horizons 0-33 inches. Magnification 4000-6000 as reproduced.

g. 33-43 inches

j. 64-76 inches

h. 43-54 inches

k. 76-94 inches
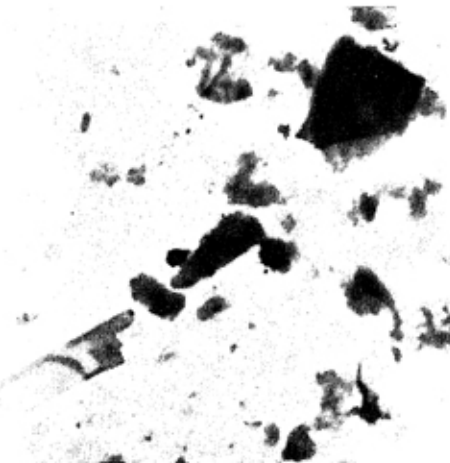
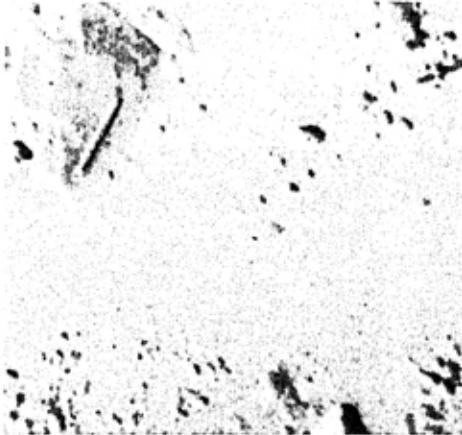i. 54-64 inches
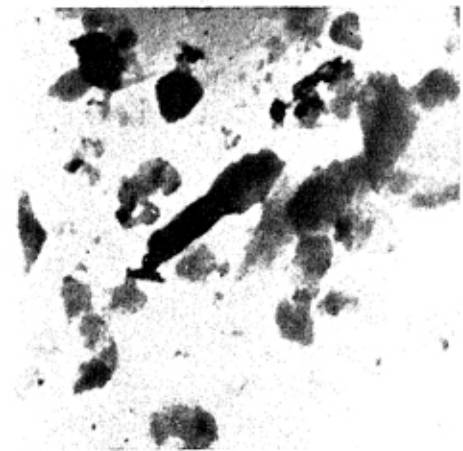
l. 94-100 inches

Fig. 9—Electron micrographs of the coarse clay fraction ($2\text{-}0.2\mu$) of the Hagerstown soil horizons 33-100 inches. Magnification 4000-6000 as reproduced.
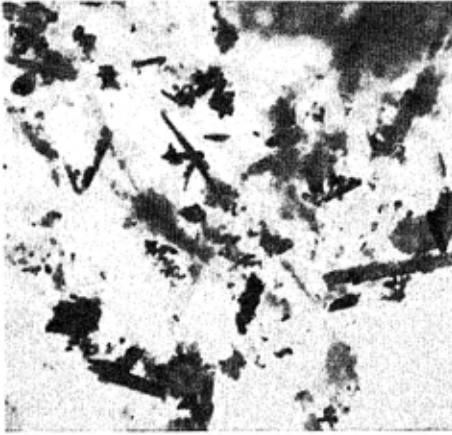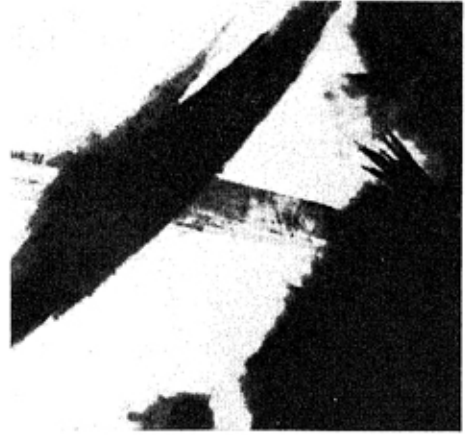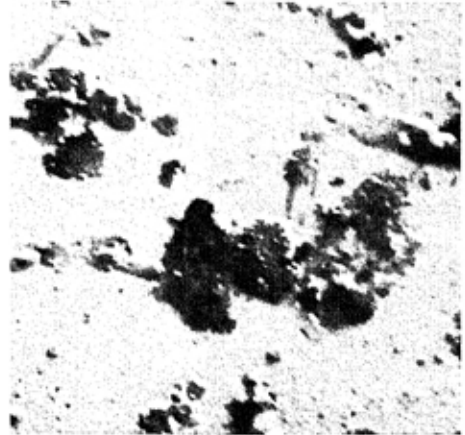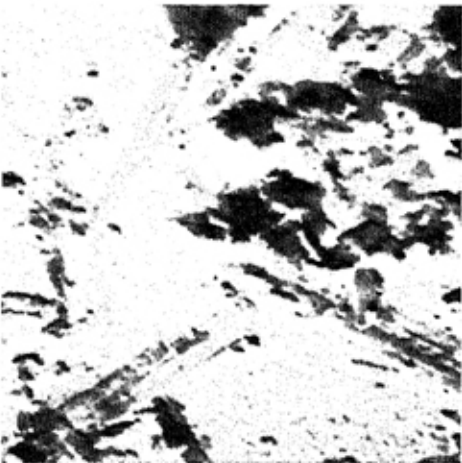
Fig. 10—Electron micrographs, magnification 6000-10,000, of the following: (a) Fine clay fraction ($<0.2\mu$) Bonneterre Dolomite (sample 13) underlying profile. (b) Coarse clay fraction (2-0.2μ) Bonneterre Dolomite (sample 13) underlying profile. (c) Fine clay fraction ($<0.2\mu$) Bonneterre Dolomite outcrop (sample 14). (d) Coarse clay fraction (2-0.2μ) Bonneterre Dolomite outcrop (sample 14). (e) Coarse clay fraction (2-0.2μ), Glauconite from New Jersey Greensand. (f) Coarse clay fraction (2-0.2μ) glauconite from Bonneterre dolomite sampled by C. S. Ross.

Differential Thermal Analysis.

The *Differential Thermal Analysis* was carried out by Mr. Richard Lake of the Department of Mines and Technical Surveys, Ottawa. The two patterns of the Ca-saturated coarse clays of samples 6 and 12 are shown in Figure 11. Both samples gave similar patterns. The first small endothermic peak at 150° C and the second larger endothermic peak at 570° C are typical of illite (21, p. 147). The lack of a third endothermic peak immediately before the exothermic one at 930° C is more a characteristic of the montmorillonites than of illites. The minor differences in the two curves are that the 570° C endothermic peak is sharper for sample 6 than sample 12 and the position of the final exothermic peak changes from 920° C in sample 6 to 960° C in sample 12.

Grim (21) states that the temperature of the final reaction is the only characteristic feature distinguishing glauconite from the other illites and this is supported by the results reported by Hoebeke and Dekeyser (25). In the illites quoted, the high temperature endothermic peak occurs below 900° C whereas with glauconites this peak is in the range 900-950° C. In the present case the peaks at 920° C and 960° C have no significance since the D.T.A. patterns of mixtures often bear no relation to the individual constituents (20, p.246).

Electrochemical Properties of Clay Fractions.

The fine and coarse clay fractions separated by the centrifuge and purified by electrodialysis were titrated individually with potassium hydroxide and calcium hydroxide. From the activity measurements, carried out as described below, cationic bonding energy curves and other derived quantities were calculated. These were compared with similar results previously obtained for known clay minerals. In this way the remarkable electrochemical properties of these clays were correlated with X-ray and chemical evidence as to their nature.

Methods

Preparation of the Clays: The less than 0.2 micron and 2-0.2 micron clays were electrodialyzed, dispersed by stirring, and made to a volume of 200 ml. Aliquots were dried and weighed to obtain the concentration of clay. Equal volumes of each suspension were pipetted into two 100-ml. volumetric flasks and CO_2-free 0.1004 N potassium hydroxide was added to one of the flasks in each case. The amount added was calculated to be equivalent to 90 milliequivalents per 100 gm. of clay for the fine fraction and 60 m.e. per 100 gm. for the coarse fraction. Both the H- and the K-suspensions were diluted to volume, mixed and allowed to stand with occasional mixing at least 48 hours or until the titration systems were made up. Increments of the K-clay suspension were pipetted into ten 25-ml. test tubes in duplicate and sufficient H-Clay was added to make the final volume 10 ml. Thus, a series of suspensions from zero K to 90 m.e. K per 100 gm. Clay was obtained. The test tubes were stoppered and shaken slowly overnight in a
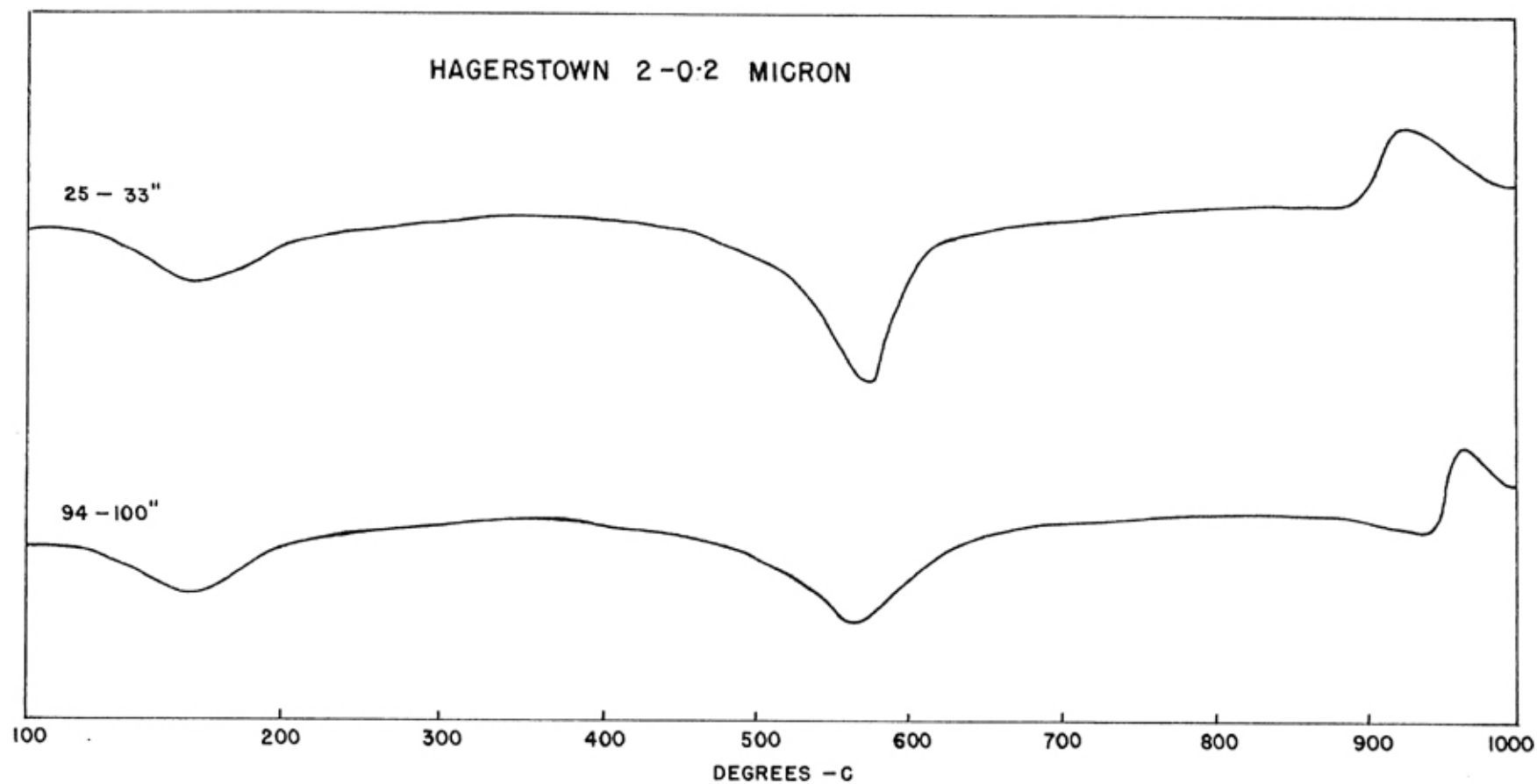
Fig. 11—Differential Thermal Analysis Patterns of Two Horizons of the Hagerstown Profile.

horizontal shaker. The Ca systems were made in a similar manner by adding CO_2-free 0.0419 N Calcium hydroxide to the electrodialyzed clays. The cation activities and pH values were measured on these systems.

Measurements

Two series of electrodes (42) were used: H-Wyoming bentonite membranes previously heated to 490° C for potassium determinations; Ca-bentonite membranes previously heated to 415° C for calcium. pH measurements were made on the same systems using a glass electrode and Beckman amplifier. Standard solutions of fixed composition ($a_K = .003$; $a_{Ca} = .0027$) were inside the electrode tubes, both in calibrations against known solutions and in the actual determinations. In the potassium calibrations, deviations from the theoretical potentials predicted by the Nernst equation were about –8% at $a_K = .00033$ and –13% at $a_K = .00011$. For calcium, slight positive deviations were found at $a_{Ca} = .0009$ and .0003 and good agreement at $a_{Ca} = .0001$. Calibration curves were drawn. In the clay systems the potentials were transformed into activities using these curves. Corrections for hydrogen ions were found necessary in some Ca systems. All measurements were made on duplicate clay systems, with two electrodes in each. One hour was allowed for equilibrium. The four measured potentials were corrected for asymmetry of the calomel half cells and of the clay membrane electrodes and for temperature variations from 25° C. The corrected values were averaged. Since very limited quantities of the clay fractions were available, measurements were made at only one clay concentration in each case. The concentrations ranged from 0.84 to 0.51% in the potassium series and from 0.7 to 0.30% in the calcium series. In such dilute systems the calculated cationic bonding energies would normally lie somewhat below the maximum values for given clays. To some extent they would be functions of concentration, but major differences in bonding characteristics should show themselves in spite of this.

Formulation of Data

Complete titration curve data can be used in a considerable variety of ways. Activities of cations or their negative logarithms, can be plotted against equivalents of base used. The fraction active, ($f = a/c$ where a is the measured activity and c the total concentration of the cation concerned) can also be plotted against amount of base. There is considerable advantage in the use of cationic mean free bonding energies, defined by $\Delta F = 1364 \log_{10}\frac{1}{f}$. (43) Many important cation differences in different clay minerals find expression in such curves (44). Because of the presence of a liquid junction at the contact of the saturated calomel half cell and the clay system, these data are classified as quasithermodynamic.

Strictly thermodynamic quantities can also be derived from the same set of measurements. In defining P_H, P_K, or P_{Ca} the liquid junctions are always present, but in differences such as $P_H - P_K$, $P_H - \frac{1}{2}P_{Ca}$, or $P_K - \frac{1}{2}P_{Ca}$ they are eliminated.

Unfortunately, these quantities are not highly characteristic for different clay minerals. The curves obtained when they are plotted against cationic composition follow the same general course in each case and are only slightly separated one from another. $P_K - \frac{1}{2}P_{Ca}$ is somewhat more favorable than the other two. Attempts to use them for characterization have proven disappointing, in spite of the advantages of their independence of clay concentration or of the presence of electrolyte impurity.

However, a fairly sensitive quantity appears when data for two separate titrations for K and Ca are combined in the following manner. From each titration the $P_H - P_K$ and $P_H - \frac{1}{2}P_{Ca}$ curves are determined. They are then subtracted at fixed P_H values; that is when $(P_H - \frac{1}{2}P_{Ca}) - (P_H - P_K) = (P_K - \frac{1}{2}P_{Ca})_s$. This quantity is given the suffix s (separate) to distinguish it from $(P_K - \frac{1}{2}P_{Ca})$ as determined on mixed K–Ca clays. $(P_K - \frac{1}{2}P_{Ca})_s$ expresses a thermodynamic difference between K–H and Ca–H clays when the complementary ion is hydrogen at a stated pH. It is given in calories per equivalent by multiplication by 1364. It varies somewhat with pH. Different clay minerals give well separated curves when $(P_K - \frac{1}{2}P_{Ca})_s$ is plotted against pH over the middle range, say from 5.5 to 7.5 Such data, calculated from Missouri titrations are plotted in Figure 16.

Results

Cationic Bonding Energy Curves: The curves for potassium are presented in Figure 12 for the coarse clay and in Figure 13 for the fine clay fraction. Samples 2, 3, and 7 are considerably lower in their bonding energy for potassium than samples 8-12, in both coarse and fine clay. The other samples vary somewhat between the two fractions. The $(\Delta F)_K$ values of samples 8-12 are high compared with those of clay minerals previously examined (44). Over a wide range of saturation they vary between 1400 and 1800 calories per mole. Putnam clay at 2.5 percent concentration also gives high values up to 1800 calories, but 1 percent systems fall lower. Arizona bentonite at 1.5 percent concentration is the only clay we have examined whose bonding energy for potassium rises as high as 2000 calories per mole. Considering that samples 1-12 were all at concentrations below 1 percent, high values (over 1500 calories) characterize 5 and 8-12 in the coarse fraction and 1,4, and 8-12 in the fine fraction.

Comparison of the calcium curves (Figures 14 and 15) with those of known clay minerals is even more striking. In all samples the bonding energy of calcium is much higher than has previously been found for Putnam clay (3000-3400 calories) and in many cases it exceeds 5000 calories per mol. Such values correspond to a dissociation of the order of 0.01 to 0.1 percent. The $(\Delta F)_{Ca}$ values previously found for illites were relatively low, around 2800 calories, and those for kaolinite and Wyoming bentonite were somewhat lower still. The highest value previously found for a clay mineral was 4200 calories for 1.5 percent Arizona bentonite. It is clear that in all horizons of this profile we have a consti-
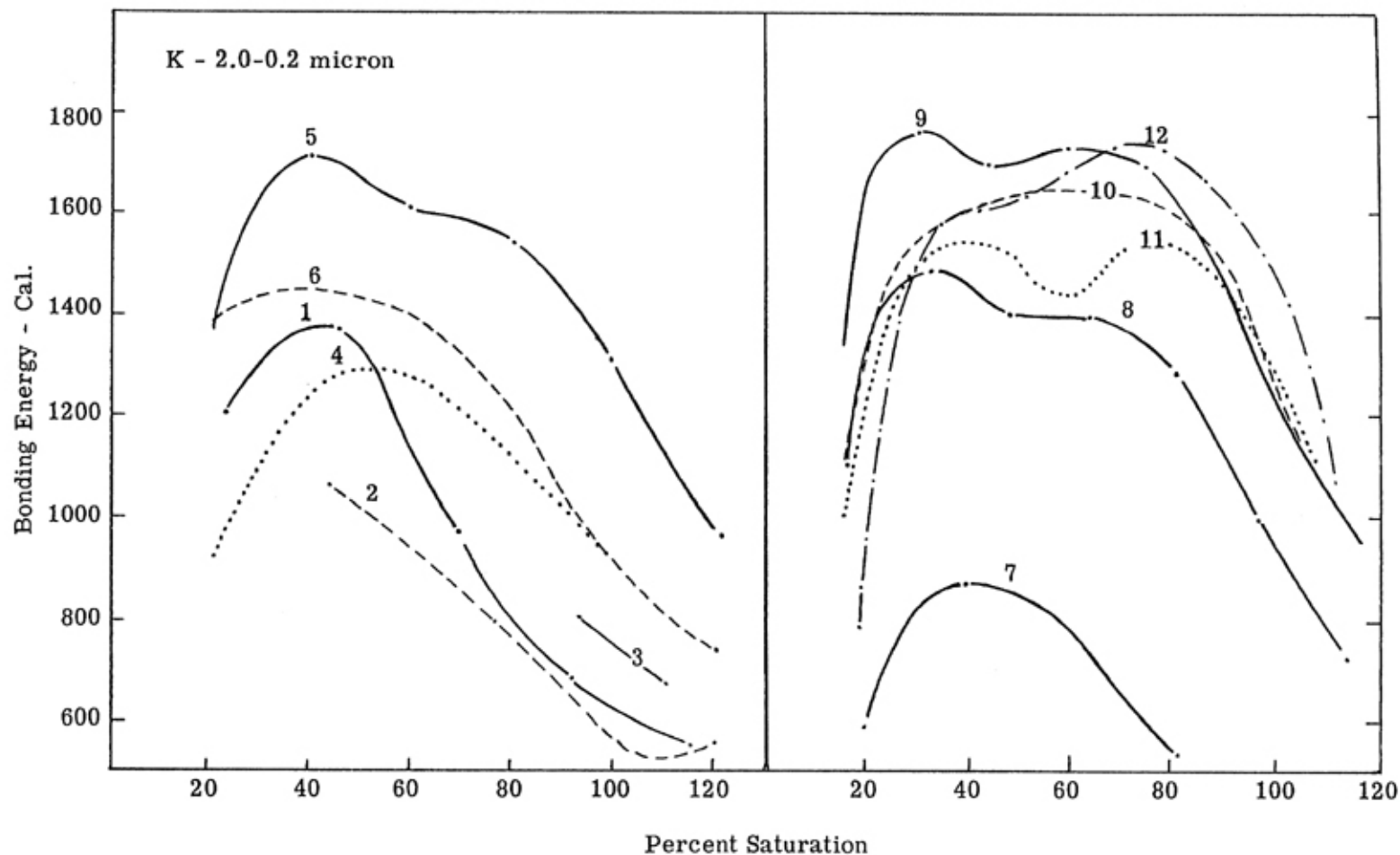
Fig. 12—Potassium ion bonding energy in relation to neutralization of coarse clay (2-0.2 micron, samples 1-12) with potassium hydroxide.

Fig. 13—Potassium ion bonding energy in relation to neutralization of fine clays (<0.2 micron, samples 1-12) with potassium hydroxide.

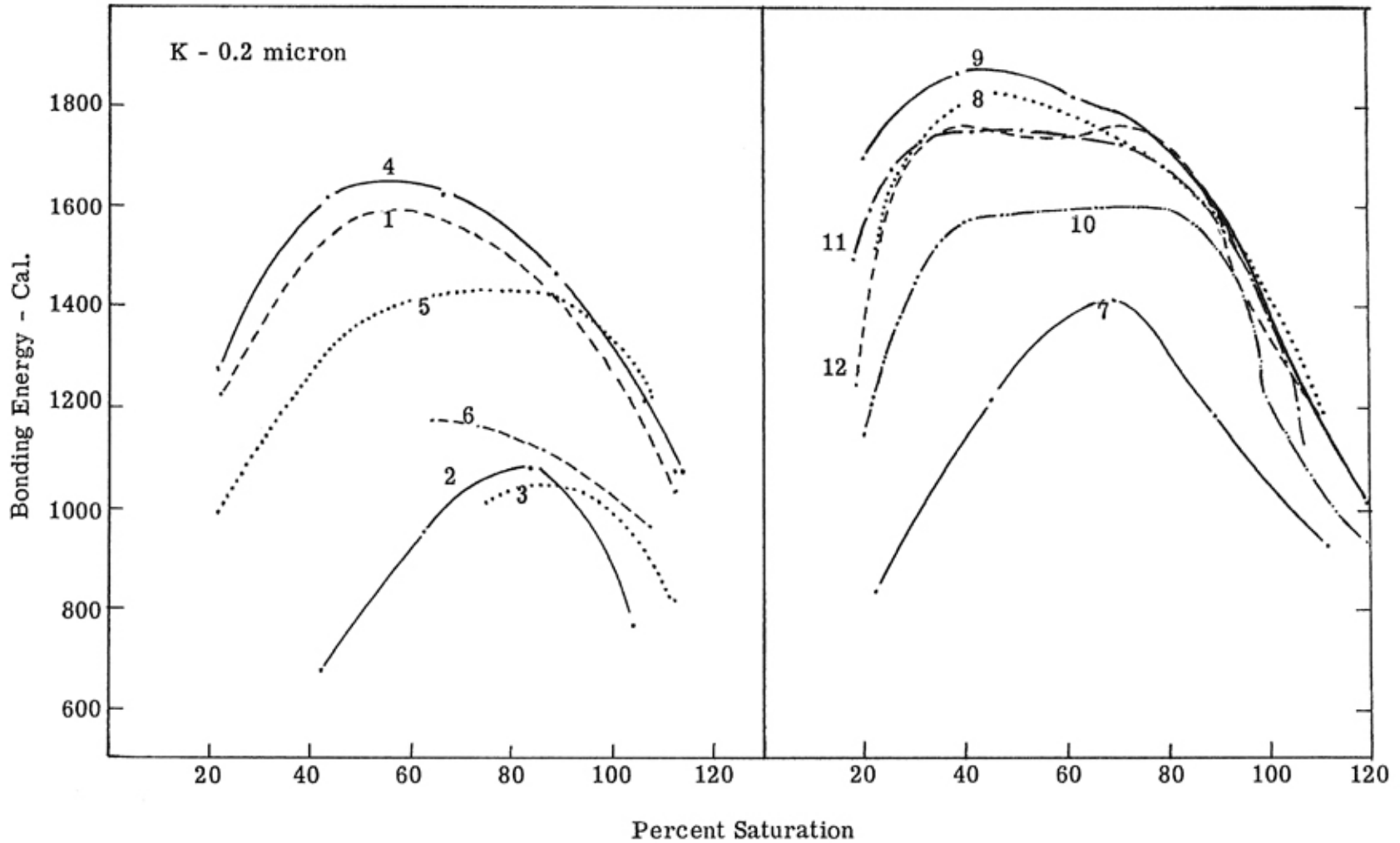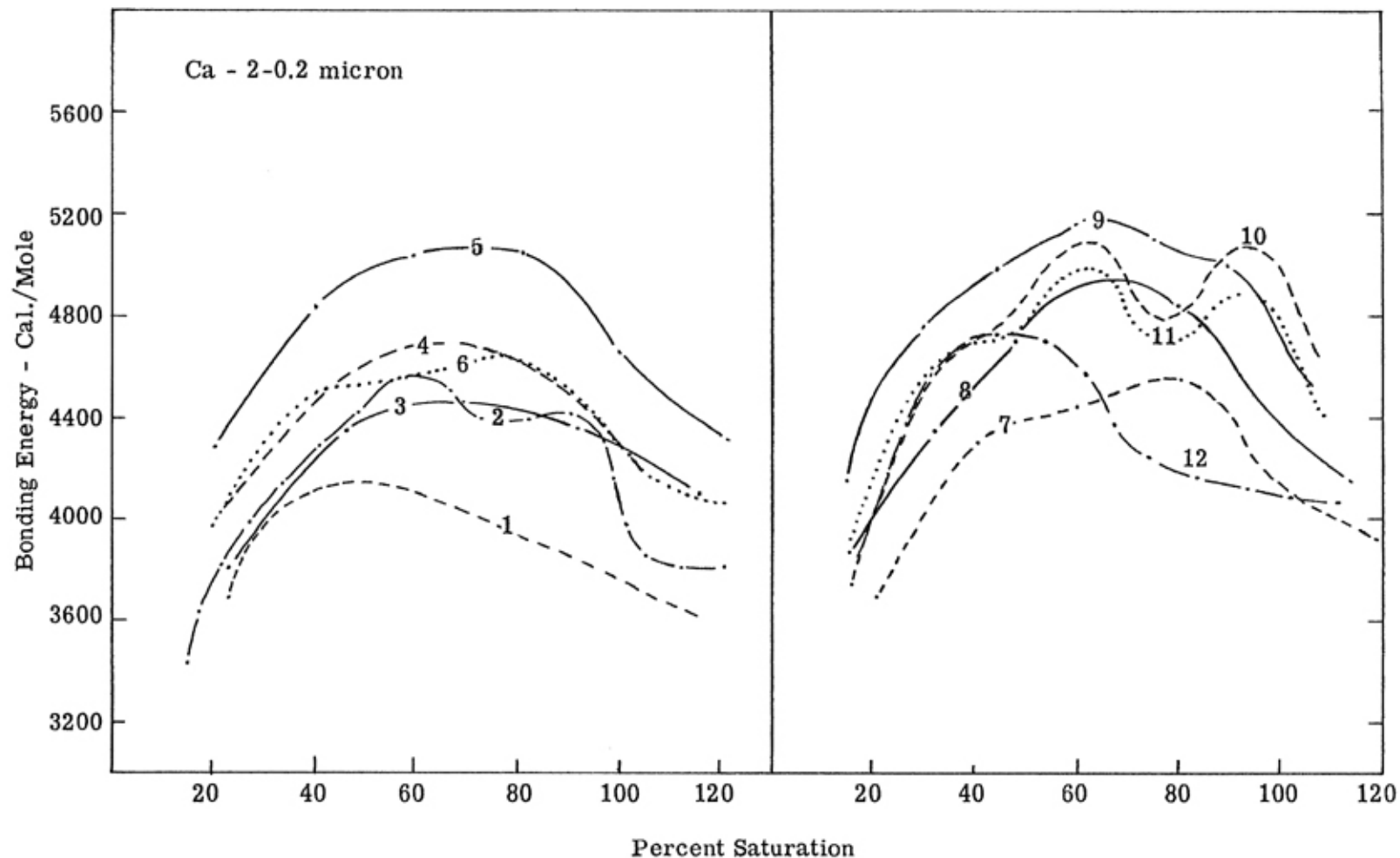Fig. 14—Calcium ion bonding energy in relation to neutralization of coarse clay (2-0.2 micron, samples 1-12) with calcium hydroxide.
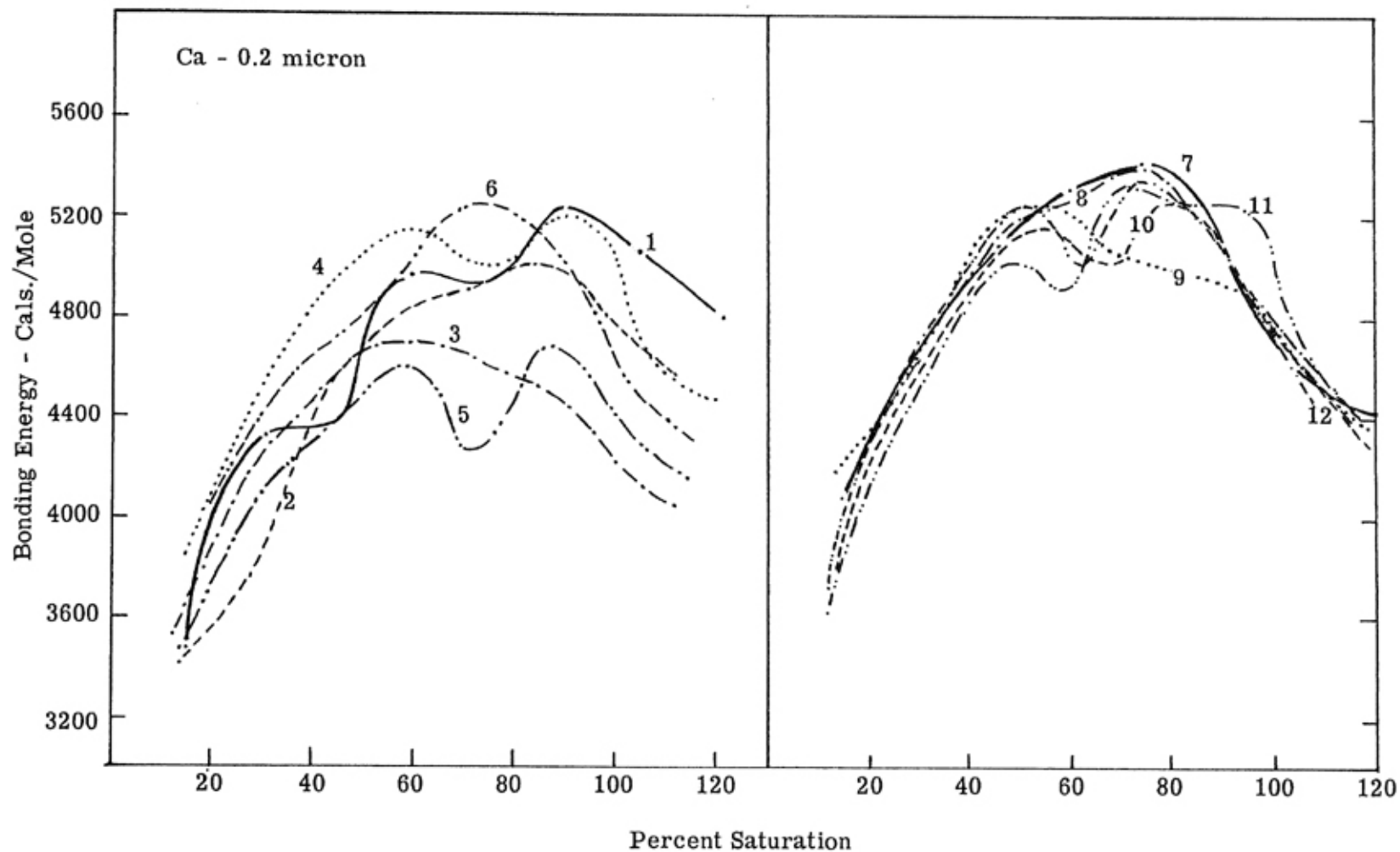
Fig. 15—Calcium ion bonding energy in relation to neutralization of fine clays (<2 micron, samples 1-12) with calcium hydroxide.

tuent with an extraordinary capacity for the bonding of calcium. In consequence, $(\Delta F)_{Ca}$ considerably exceeds twice (ΔF_K). This constituent apparently is most concentrated in samples 1, 6, and 7-12 of the fine clay, and in samples 5 and 8-11 of the coarse clay.

The quantity $(P_K - \frac{1}{2}P_{Ca})_s$: In Figure 16, this quantity calculated from data obtained in this laboratry is plotted against pH over the range 5.5 to 7.5. Here disturbing factors should be at a minimum. In general, $(P_K - \frac{1}{2}P_{Ca})_s$ falls with increasing pH, and in some cases fairly constant values are found at 7.0 and 7.5. The three clays of the montmorillonite group are well shown by this composite expression of their electrochemical properties. Wyoming bentonite gives values in the range 1.36-1.13. Arizona bentonite and Putnam clay fall close together in the range 1.1-0.6. The two illites, Maquoketa and Grundite, give values in the same range as those of Wyoming bentonite. Kaolinite gives much higher values throughout (1.62-1.25). The less common clay, attapulgite, also gives values in this range. Our sample of somewhat impure halloysite gives values from 1.17 to 0.95.

Any attempt to express the electrochemical properties of clays by a simple number is likely to prove inadequate by itself. Considering that three factors, namely, the strengths of bonding for hydrogen, potassium, and calcium are all involved in $(P_K - \frac{1}{2}P_{Ca})_s$, a primary mineralogical separation on the basis of cation exchange capacity and X-ray evidence is needed first. Then the range of electrochemical properties within the broad groups, montmorillonites, hydrous micas and kaolin minerals, can be expressed usefully through this number and its variation with pH.

The values for samples 1-12 coarse clay and fine clay are given in Tables 12 and 13. It is apparent that $(P_K - \frac{1}{2}P_{Ca})_s$ values higher than those of kaolinite are quite common in occurrence, particularly so in the coarse clay. When they are compared with the X-ray results, it becomes apparent that the high values must be ascribed to some other constituent besides kaolinite. In the fine clay fraction, samples 9 and 11 give higher values for $(P_K - \frac{1}{2}P_{Ca})_s$ than sample 12; yet the X-ray results show that 9 and 11 have less kaolinite than 12. Values ap-

TABLE 12--HAGERSTOWN FINE CLAY 2μ-0.2μ
$(P_K - \frac{1}{2}P_{Ca})_s$ from separate titration curves.

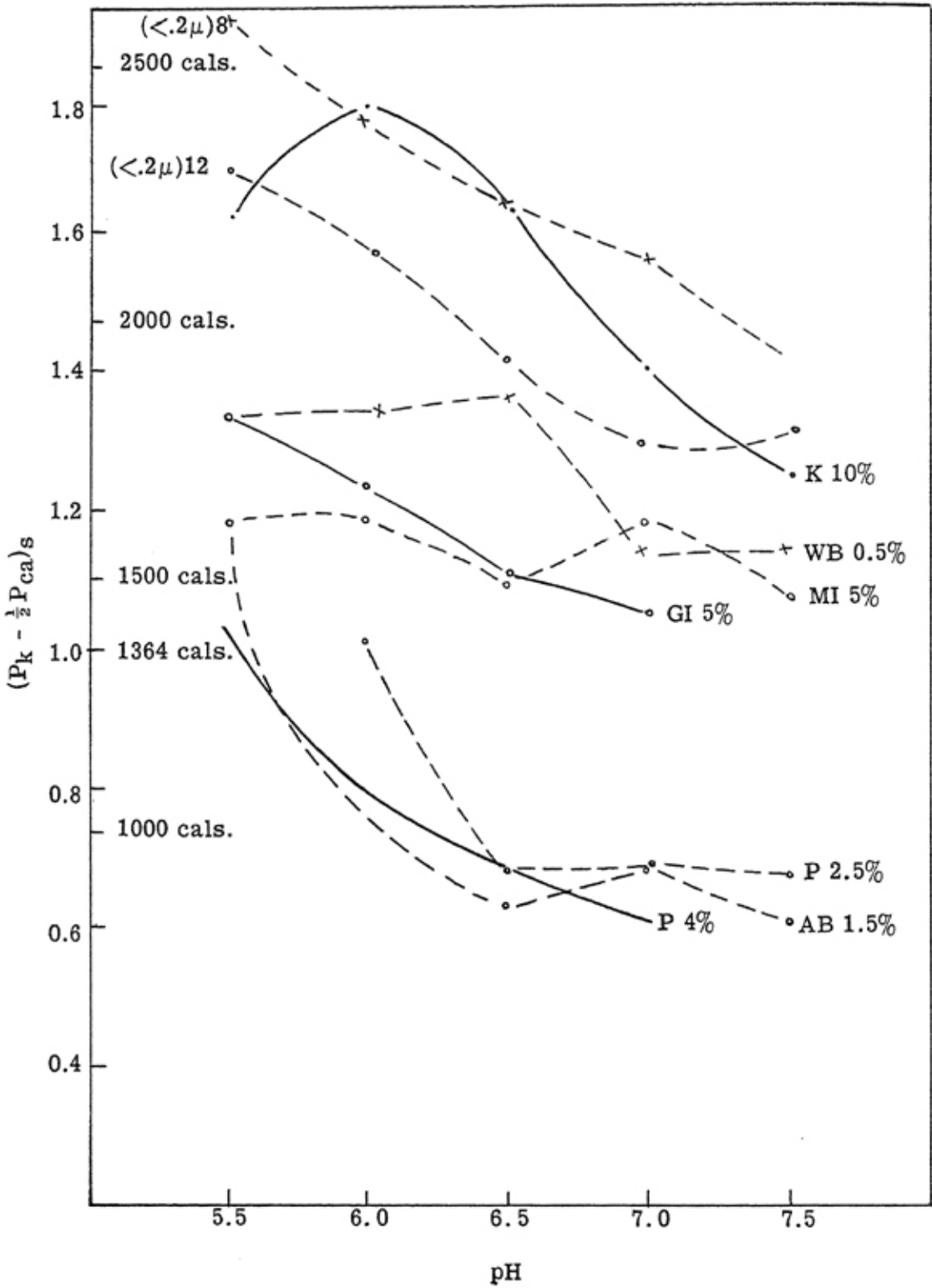| Sample No.	pH 5.5	6.0	6.5.	7.0	7.5
1	2.07	1.91	1.78	1.58	1.51
2			1.45	1.24	1.10
3				1.31	1.23
4		1.60	1.55	1.46	1.34
5		1.84	1.60	1.50	1.34
6		2.28	2.04	1.75	1.44
7	1.46	1.39	1.32	1.37	1.28
8		1.90	1.45	1.44	1.15
9	1.94	1.92	1.76	1.59	1.49
10	1.79	1.62	1.51	1.42	1.29
11	1.82	1.56	1.55	1.48	1.37
12	1.67	1.53	1.44	1.33	1.18

Fig. 16—$(P_K-\tfrac{1}{2}P_{Ca})_s$ plotted against P_H for various clay minerals.

TABLE 13--HAGERSTOWN FINE CLAY, $<0.2\mu$
$(P_k-\frac{1}{2}P_{ca})_s$ from separate titration curves.

Sample No.	pH 5.5	6.0	6.5	7.0	7.5
1	1.73	1.64	1.39	1.24	1.19
2	1.09	1.14	1.06	0.93	0.91
3			1.84	1.44	1.22
4	1.64	1.66	1.39	1.33	1.29
5	1.75	1.69	1.49	1.49	1.40
6			1.21	1.23	1.20
7	1.28	1.22	1.09	1.03	1.14
8	1.90	1.75	1.63	1.56	1.41
9	2.07	1.86	1.50	1.53	1.33
10	1.58	1.48	1.42	1.26	1.19
11	1.80	1.66	1.44	1.30	1.17
12	1.69	1.57	1.42	1.29	1.30

preciably higher than those of kaolinite occur both in the coarse and fine clays. They do not appear to be strongly correlated with the appearance of 17Å or 14Å spacings in the Mg-glycollated clays. Hence it must be concluded that a major constituent of most horizons of the Hagerstown profile (except possibly samples 2 and 7) gives high values of $(P_{K}-\frac{1}{2}{}_{ca})_s$; it shows high bonding for potassium and extremely high bonding for calcium; and is a dioctahedral mica containing more iron than typical illites.

This remarkable soil clay behaves electrochemically as a weaker acid than typical montmorillonites. It has a high bonding energy for potassium and an extremely high bonding energy for calcium and hydrogen. Under such circumstances the leaching process would have an extremely slow effect upon it. It seems possible that the absence of strongly marked pedological features in the soil profile is a consequence of the great chemical stability of this residual clay. It is very different from the Maquoketa and Grundite illites, which are from non-calcareous shales and have relatively low bonding energies for calcium. Further studies on electrochemical and structural features of the clays of limestone residues should be undertaken. The bonding energy relationships for the four cations, sodium, potassium, calcium, and magnesium, all of which are present during the marine synthesis of the clays, should be investigated.

DISCUSSION AND CONCLUSIONS

Several lines of evidence are in agreement on the presence of depositional differences among different layers of the Hagerstown profile. The mechanical analysis, the ratios of resistant heavy minerals and the X-ray evidence on the nature of the sand, silt and clay fractions all indicate this. It therefore becomes difficult to separate the operation of pedological factors from the effect of heterogeneity in the original limestone residues. The increase in clay content below the B horizon is a common feature of limestone soils and is very marked in this profile. From 54 to 94 inches depth the 2 micron clay averages 85 percent of the mineral soil. In the B horizon it increases steadily from 36 percent at 10-12 inches to 70% at 43-45 inches. It is possible that some clay was translocated

downwards, but the quantities involved are so great that in any case clay must have formed the major part of the original limestone residues. The X-ray evidence shows only minor variations in the mineralogical nature of the clay, which is chiefly a member of the illite-glauconite series which some expanded layers and a considerable amount of kaolinite. There is no evidence that pedological factors exerted much chemical influence on this clay except by extensive loss of exchangeable bases. Even the production of expanded layers by hydration of micas did not proceed very far.

The electrochemical evidence provides a reason for this stability, which otherwise would have seemed anomalous. The clays from all horizons except possibly the 7-10 inch and 33-43 inch layers of the profile contain a dominant constituent with an extraordinarily high bonding energy for calcium. From the proportion of exchangeable Ca and Mg still present in the strongly acidic layers it is evident that this high bonding extends also to magnesium. With some variations, a high bonding energy for potassium is also present. This would be expected from the illitic type of clay found, but the very high bonding for calcium is unlike that of the Maquoketa and Grundite illites from non-calcareous shales with which we have previously worked.

The clay residues from the Bonneterre dolomite, in virtue of this low dissociation of the major exchange cations Ca and Mg, are evidently very resistant to decomposition. If we take the mean free bonding energy of divalent cations on the Hagerstown clay as 5400 calories per mole, as against say 2700 calories for a normal illite, this would imply that loss of divalent cations by leaching would only be at one hundredth the rate of that of the normal illite. The great stability of this clay thus finds a reasonable chemical explanation. Whether this is a general feature of the clay residues from limestones remains for future research to determine.

The physical properties of the Hagerstown soil, which resemble those of kaolinitic soils in many respects, also follow from the electrochemical properties of the micaceous clay. The low dissociation of divalent cations would cause a low zeta potential and a high degree of sensitiveness to coagulation; thus the surface properties would come to resemble those of kaolinitic clays, but for entirely different structures.

Certain agricultural conclusions regarding this Hagerstown soil can be drawn from these results. Obviously, it will respond to adequate liming. The extremely high bonding energy for calcium will tend to immobilize the lime in those layers where it has been applied. Losses by leaching will be very small. If inadequate amounts of lime are applied the response is likely to be disappointing, since the plant will be competing for firmly held calcium.

The problems of classification of limestone soils are not solved by this investigation, but the weight of evidence certainly inclines toward the Hagerstown and soils like it being placed in a separate category. For reasons previously discussed they do not fit into the Grey-Brown Podzolic Soils, and there is no evi-

dence here for extensive clay decomposition and synthesis as postulated by Simonson for the Red and Yellow Podzolic Soils.

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