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Mineralogical Study of Lindley Soil in Missouri

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J. E. BRYDON AND C. E. MARSHALL*

INTRODUCTION

Detailed chemical and mineralogical studies have been made of several soils from diverse parent materials in Missouri. These include the Putnam soil, derived from shallow loess (58)**, the Ashe soil from granite (27) an unnamed soil from diabase rock (27), the Tilsit soil from sandstone (23), the Marion soil from deep loess (23), the Grundy soil from moderately deep loess (23), and the gumbotil as a parent material (26). The general purpose in each case was to relate the processes of mineral weathering, clay formation and soil development to parent material, under the climatic conditions of Missouri.

The study reported here continues this general type of investigation, with special emphasis upon X-ray techniques. These techniques have been greatly improved in recent years. By their use it is now possible to make rapid quantitative determinations of the mineral species in the silt and sand fractions of soils. Previously, laborious optical methods had to be used. Study of the weathering products, that is, of the clay minerals, also has been greatly facilitated by these methods; although, as we shall see, fully quantitative determinations are not yet possible in all cases.

The Lindley soil, derived from glacial till, was purposely chosen because it would naturally inherit a highly complex mineral assemblage. It should provide a critical test of modern methods and the experience gained could be applied to other soils. For this reason the present report stresses procedures used in the X-ray investigation of soil fractions.

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The experimental material is taken from the M.S. thesis of J. E. Brydon entitled "A study of the mineralogy of a Lindley loam soil profile." The study forms part of the Department of Soils Research Project 6, "Heavy Clays."

**Numbers in parentheses refer to References listed in the back of the bulletin.

REVIEW OF X-RAY METHODS FOR SAND AND SILT FRACTIONS

The use of X-ray techniques for quantitative determinations in the coarser materials of soils began in 1947, when Whiteside (59) determined quartz, feldspars and free carbonates using a standard camera. The degree of blackening of the film at angular positions characteristic of a given mineral may be used to estimate the quantity of that mineral in a mixture, provided that the experimental conditions are carefully controlled and held uniform. The X-ray powder diffraction cone should be uniform so that the line produced on the photographic film is even. Whiteside presented films of the 2 to 5-micron fraction and the 40 to 50-micron fraction which showed, strikingly, the effect of large particle size. In the fine fraction, there were enough particles in random orientation to give diffraction effects in every possible direction. Brindley (61, Chapter I) points out that this property of the sample is extremely important and that care must be taken to avoid the production of effective large particles by an aggregation of smaller ones.

Whiteside also stated that the intensity of the primary X-ray beam and the quantity of the material exposed to the beam must be controlled. An accurate check of these factors may be obtained by the use of internal standards (18), i.e., the addition of a definite quantity of a crystalline material whose diffraction effects may be compared from one sample to another. The ratio of the density of the lines of the desired mineral to that of the internal standard was a linear function of the percentage of the desired constituent.

Jeffries (31) also outlined a procedure in 1947 for the qualitative estimation of the essential or major minerals in soils using a recording X-ray diffractometer. According to him, these minerals (quartz, feldspar, mica and the clay minerals) are the most abundant in sediments and may account for the mineral characteristics of soils. The X-ray diffractometer was proposed as a rapid means of obtaining the distribution of these minerals in soils. Focusing of the X-ray beam on the sample increases the intensity of the reflections and permits the exposure of a large area to the primary beam (31).

Difficulties arise in preparing specimens for the diffractometer as well as in the camera technique. To obtain a uniform exposed surface which is characteristic of the bulk sample, McCreary (33) has proposed a method of specimen preparation. The sample is sieved into the aluminum mounts, the powder tamped and pressed gently, and after covering with a glass slide, the holder is inverted and placed in the goniometer. Good reproducibility of the relative diffraction intensities of the components in synthetic mixtures was obtained using this method.

The intensity of the primary X-ray beam cannot be controlled more accurately in the diffractometer than with the powder camera method but the quantity of material exposed will remain essentially the same with the diffractometer. However, the variation in the relative amounts of the constituents of a sample at the exposed surface may be serious. Preferred orientation, which gives rise to spotty lines on the powder photographs, may cause large errors in the interpretation of the diffractometer patterns. The rotating specimen holder alleviates, at least partially, the latter difficulty (9).

With the advent of the Geiger-counter X-ray diffractometer in 1945, it was possible to measure the intensities with higher accuracy than with the photographic method. Klug, Alexander and Kummer (32) have investigated and established the accuracy and reproducibility with which quantitative analysis can be accomplished. From their work several points were apparent.

1. Quartz samples of different origin gave different intensities of the diffraction maxima.
2. Large particles decreased the intensity as measured by peak height and an upper limit of 5 microns was established for accurate measurement.
3. The measurement of heights gave better reproducibility than did the measurement of areas for 5-micron quartz when pure and when present in a mixture.
4. The accuracy of measurement is less if quartz is present in a mixture than if it is undiluted.
5. The measurement of the area under the peaks was more accurate for ground sodium chloride and was attributed to the presence of a wide particle size distribution. The measurement of peak heights was satisfactory only if the particles were greater than 0.1 micron or if the size distribution was identical from sample to sample.
6. Displacement of the specimen by 1 mm. in the X-ray beam gave the same angular position of the peak but the intensity varied a maximum of 20 percent. However, the benefits of a rotating sample holder were not

proved conclusively.

7. Specimens prepared by flowing a suspension onto a microscope slide with a binding agent were found to be too thin for optimum intensities and the thickness of the films was difficult to reproduce. Good reproducibility was obtained in all cases where the specimens were prepared as a powder pressed gently into the cavity of an ordinary microscope drop slide.

8. The different amounts of absorption by the components of a mixture made it necessary to adopt the use of an internal standard to compare the ratios of peak heights.

9. The precision was not good enough using the automatic recorder and a slower scanning speed did not increase the precision. For accurate work the intensities were measured by stepwise manual counting.

10. The response of the machine was found to change from day to day but in any one day the response was constant.

11. A standard curve was prepared by plotting the ratio of the intensity of the quartz line at 3.33 \AA to that of the internal standard (fluorite) at 3.16 \AA . This curve was a straight line down to 10 percent quartz and curved from 10 to 0 percent. In using the curve for samples containing more than 10 percent quartz, the error was rarely greater than ± 10 percent and usually less than ± 5 percent of the amount of quartz present.

The theoretical aspects of the absorption of X-rays by flat powder specimens were considered by Alexander and Klug in a later paper (1). Three cases were discussed; the more general one being a mixture of n components. The absorbing power of the desired unknown is not equal to that of the diluents and an internal standard may be added in order to construct a standard curve. The concentration now becomes proportional to the ratios of the peak heights of the internal standard to the desired unknown.

The variation of the X-ray diffraction peak intensities from quartz samples of different origin has been investigated by Pollack *et al.* (49). Mixtures were prepared using rock crystal quartz diluted with calcium carbonate and having 0.5 gm. fluorite per gm. of sample as an internal standard. Standard curves were constructed in the usual manner and the intensities of the quartz 3.35 \AA peaks in the various samples were compared with them. The standard working curve was found to vary from time to time but the differences obtained between rock crystal quartz and samples of cryptocrystalline quartz, flint, jasper, chalcedony, and others were striking. Only jasper contained crystalline impurities (hematite) and three possibilities were proposed to explain the other differences; viz., dilution by non-crystalline impurities, variations in diffraction intensity of

different varieties of silica and some inconsistencies in the method used. No amorphous material was apparent by optical examination of amethyst and chalcedony, and experimental errors were not sufficient to account for all of the variations. The authors concluded that, while the variation in the quartz samples was real, quartz could be used as an indicator mineral in studies of soil genesis where the parent material was uniform. They emphasized that quantitative analysis requires carefully standardized working conditions and frequent checking of standard samples.

In view of these considerations, it was proposed to adopt the method of Phillippe and White (47) to the analysis of quartz, microcline and albite in the silt and sand fractions of the Lindley silt loam profile. An explanation of the use of the term "albite" is necessary. Examination of the data published by the A.S.T.M. (3) indicates that the patterns of all the plagioclase feldspars are similar. When small amounts of these minerals are present in a mixture, only one strong reflection, the (040), is apparent and, therefore, it is impossible to state on this basis which mineral or minerals are involved. In view of the use in the literature of albite as the cause of the 3.20 Å peak (20, 47), the same terminology will be used in this investigation.

REVIEW OF X-RAY METHODS FOR CLAY FRACTIONS

In the identification of the clay minerals from the X-ray patterns of natural systems containing one or more minerals, the investigator has two alternatives. The first is to do X-ray determinations of reference or standard minerals which are likely to appear in the unknown sample. These must be treated in a manner identical with that used on the unknown since much depends on the uniformity of experimental technique used (61, Chapter XIV). A direct comparison of the unknown with the standards will serve to identify the material if the patterns are identical. The second alternative is to compare the list of interplanar spacings or d values and the relative intensities of the reflections with published data (3, 21, 61, and others). However, since the published data have been obtained from various sources which may appear to give contradictory results, the former alternative is preferable. Even this direct comparison has limitations, because of the variability of the reference materials, particularly where the clay minerals are concerned (61, Chapter XIV).

Kaolinite is the commonest clay mineral with a 1:1 type of lattice. There is, apparently, a slight degree of proxying of one cation for an-

other and no external cations or water molecules occur between the layers (50). The layers are held together with a hydroxyl bond strong enough to give rise to a large number of layers superimposed upon one another within a given particle. There is a high degree of regularity and the mineral gives a sharp X-ray diffraction pattern with a C axis spacing of 7 Å. The complete pattern has been published by Brindley (61, Chapter II).

Hydrous mica or illite has a 2:1 lattice similar to that of muscovite but with different and variable lattice substitutions. The muscovite and biotite micas have a slightly smaller basal spacing than illite, and the reflections from the prismatic planes are sharper and more regular. The large potassium ion which satisfies the excess negative charge due to lattice substitutions is situated between the layers such that it fits into the hexagonal holes of adjacent layers. This nice fit prevents expansion and exchangeability of the potassium ions and, therefore, the basal spacing remains fixed at about 10 Å. (61, Chapter V).

The minerals of the montmorillonite group have a lattice structure similar to the micas except that there is different lattice substitution, and a reversible expansion and contraction of the layers in the C axis direction depending on the water content (40, 51). Different amounts of expansion may occur simultaneously in the same sample, giving rise to a broad diffuse band on its X-ray pattern. This can be eliminated by introducing ethylene glycol (7) which is absorbed in two layers between the montmorillonite units, giving a basal spacing of 17 Å.

Because of the similarity of the structures, it might be expected that intimate mixing of layers of different minerals would occur within a single particle. Early workers reported mixed structures but it remained for the theoretical treatment to sort out the various possibilities (61, Chapter XI).

Mixed layer structures occur when minerals of different type (e.g. montmorillonite and illite) or a single mineral having different hydration states (montmorillonite) are interstratified. MacEwan (35) has stated that there are three main types:

1. *Regular Interstratification:* The diffraction effect of this type is due to the periodicity of the stacking; i.e., a new unit cell is effectively produced which contains a multiple of the individual layers. The best example of this type is chlorite in which brucite-like layers are mixed regularly with mica-type layers, giving a 14 Å basal spacing ($10 \text{ Å} + 4 \text{ Å}$) and an integral series of (001) reflections. In the hypothetical case of one water sheet between every third mica sheet, the "identity period" (35) will be 35.4 Å ($3 \times 10 + 5.4$) and there will be a series of higher orders at sub-multiples of 35.4 Å .

2. *Random Interstratification:* As a first approximation, this situation will give rise to a basal spacing corresponding to a weighted mean of the spacings of the constituent minerals (61, p. 108) but a non-integral series of higher order basal reflections will arise depending on the relative amounts of the two constituents which are present. The mathematical relationships for this type of interstratification have been worked out by Hendrickson and Teller (24) and developed further by Mering (42). The practical applications have been pointed out by MacEwan (35) and by Brown and MacEwan (15, 61). The latter authors have calculated a series of curves for the intensity of reflections as a function of $100/d$ where d is the measured basal spacing of the mixed layer structure. The alteration of the diffraction pattern by different proportions of the two-layer types will consist of a movement of peaks. There is not an exact straight-line relationship between the position of the peak and the relative proportions of the two types of layer; therefore, reference must be made to the curves. The direction of movement depends on the closeness of the (001) reflections of one type to those of the other. For example, a mixture of mica (10 Å) and vermiculite (15 Å) will have a peak intermediate between 10 Å and 15 Å, whereas a mixture of hydrous mica (10 Å) and glycolated montmorillonite (17 Å) will have a peak between the hydrous mica first order (10 Å) and the montmorillonite second order (8.5 Å) reflections. The theory is elegant in that it enables one to determine the proportion of each type of mineral simply by measuring the positions of the peaks and comparing them with the graphs, providing that the nature of the components is known and that it is only a type 2 interstratification.

3. *Zonal Segregation:* This situation occurs when zones of uniform constitution differing from the rest of the structure are present in a single particle and bands of various shapes occur depending on the constitution of the unit. An interesting case occurs when there is more water between one pair of layers in one position than in another in such a way that a mica with a uniform 10 Å zone in the center has expanded edges due to hydration. Since this type of interstratification may include the other two, the theoretical analysis is complicated and as yet has not been completely worked out.

Bradley (8, 9) has considered the first two types of interstratification and presented X-ray photographs giving examples. He suggests (9) that an assemblage intermediate between these two types would give scattering effects at very small angles which are unresolved from short wave length diffraction effects, but that the present theory does not give an adequate explanation. In 1953, Bradley (10) considered the scattering effects from mixtures of the first two types of interstratification within a single dif-

fracting unit or "coherently scattering domain." Theoretical scattering distribution curves and X-ray diffraction patterns of illite-chlorite-montmorillonite mixtures were shown. The mixtures were given various heat treatments and solvation to resolve the components.

Ideally, in X-ray diffraction of powder samples the specimen should have completely random orientation. Because of the micaceous character of the clay minerals and the small particle size, this is difficult to obtain and, consequently, the relative intensities of the basal reflections and the general reflections may vary. On the other hand, it is relatively easy to prepare a sample in which there is a well ordered orientation.

Bradley *et al.* (12) in 1937 produced this preferred orientation by the stress involved in smearing a clay paste on a 10 mm. glass tubing and drying it. This gave a "paper-like" sheet with good enough orientation to give interference figures under a petrographic microscope. These films were found to give several orders of the basal reflection which were sharp and more intense than the ones from powder specimens.

Nagelschmidt (45) obtained similar oriented aggregates by allowing clay suspensions to evaporate slowly on a flat surface in which case the basal planes were parallel to the plane of sedimentation. Strips were cut and mounted in the cameras and gave sharp basal spacings. Nagelschmidt states that the latter are the most useful characteristics for differentiating between the clay groups in mixtures when the grain-size is small. Jeffries (31) prepared mounts for the X-ray spectrometer by making a paste on a microscope slide of the dry clay with amyl acetate and allowing it to dry. Talvenheimo and White (54) used a sedimentation technique similar to that of Nagelschmidt to prepare specimens with preferred orientation for analysis with the X-ray spectrometer.

Nagelschmidt (44), in 1937, observed that dioctahedral and trioctahedral micas could be differentiated on the basis of the (060) reflection and the relative intensities of the basal spacings. The muscovite type gave an (060) peak at 1.50 Å with a strong second order basal reflection, whereas biotite gave an (060) response between 1.53 Å and 1.55 Å with the (002) peak weak or absent. Brown (61) has calculated the effects of substitutions of Fe in the octahedral layer of the micas and has plotted the basal spacing intensities against the amount of substitution in dioctahedral and trioctahedral micas. After determining whether an unknown mica mineral is dioctahedral or trioctahedral, it is possible to estimate the amount of substitution of Fe by multiplying the measured intensities by a factor of $1/\sin \theta$ and comparing these values with Brown's charts.

MacEwan (61) has shown that the (060) reflection may be used to calculate the a_0 and b_0 lattice parameters. The (060) spacing in Angstrom

units multiplied by six gives b_0 , and the a_0 parameter may be calculated from the relation $b_0 = a_0\sqrt{3}$. Obviously the c_0 dimension will vary according to the interlayer water content and the inter-layer cations, and it can be determined from the measurement of the basal spacings.

The effect of different exchange cations on the clay minerals has received a great deal of attention. Marshall (36) showed that the electrical birefringence of montmorillonite varied with the exchangeable cation and that the cations were distributed in the interlayer spaces. Illite and kaolinite have their exchangeable cations situated along the broken edges of the planar units. It has been found that the cations have no effect on the X-ray diffraction peak positions of illite and kaolinite but that the montmorillonite basal spacing varies considerably. Hendricks *et al.* (24) have shown that the basal spacing may have a uniform or a disordered distribution depending upon the exchangeable cations present.

Barshad (4) has investigated the effect of the interlayer cations on the lattice expansion of air-dry water-saturated and glycerol-saturated vermiculite and montmorillonite, and Talvenheimo and White (54), using a diffractometer technique, measured the effect of different cations on the diffraction maxima for bentonite. The results of these workers were similar. Barshad stated that interlayer expansion was not confined to montmorillonite but was a general property of the micas. The micas containing non-exchangeable K ions were non-expanding but, when K^+ was removed by chemical treatment, the lattice became expansive. Montmorillonite saturated with K retains interlayer water one molecule thick in the air-dry and wet state. It also holds glycerol only one molecule thick (14 Å).

Talvenheimo and White (54) showed that saturation with Ca or Mg ions intensified the basal spacings of air-dry montmorillonite, and attributed this to a higher degree of orientation of the water molecules which increased the preferential orientation of the montmorillonite layers. They found that 100 percent saturation with Ca ions was not needed to give good diffraction maxima. Saturation with Ca and Mg ions was found to alter the illite basal spacing but this alteration was attributed to an interstratification of illite and montmorillonite in the sample which they used. The position of the kaolinite peaks was unchanged and the intensity varied only slightly using the different cations. These authors proposed a set of experimental conditions for the analysis of general polycomponent systems of kaolinite, illite, and montmorillonite as follows:

The clay is saturated with Ca or Mg, solvated with glycerol, and deposited on microscope slides such that there is 5 mg. of clay per square inch. The suspension is dried at 8 percent relative humidity and analyzed.

The Ca clay used by Talvenheimo and White was prepared by adding small amounts of Ca Amberlite to the H clay, removing the Amberlite, and repeating until the clay suspension gave a neutral reaction. One drop of glycerol was added per 5 to 50 mg. of clay to solvate it; the suspension was allowed to stand for 12 hours. Their results showed that the ratio of mg. of glycerol to mg. of clay did not change the position of illite or montmorillonite spacing from 10 Å and 17.9 Å but it did change the intensity of the reflections. The greatest intensity of the illite occurred when no glycerol was present; for montmorillonite, it occurred when the gm. glycerol/gm. clay was 0.5. MacEwan (34), however, has shown that with glycol-clay complexes less glycol is needed if the clay is in a water suspension. He concluded that glycol molecules determined the expansion dimensions, with water molecules filling in the extra space.

Talvenheimo and White (54) prepared film specimens of varying thickness to obtain optimum diffraction characteristics. They stated that the diffraction of X-rays was a linear function of the number of reflecting planes until limited by the absorption and extinction of incident and reflected radiation. This "saturation thickness" was found to occur when each square inch of the film contained 5 mg. of clay.

After the clay suspensions had been placed upon the slides, these authors determined the effect of evaporating the suspension in atmospheres of various relative humidities. No changes were observed in the positions of the diffraction peaks but maximum intensities were obtained by drying in 10 percent relative humidity.

MATERIALS AND METHODS

Description of the Lindley Soil Series and the Soil Samples

The Lindley soil series extends from north central and northeast Missouri into Iowa (52) and consists of the rough, glacial, "white-oak" land along the streams (43). Nearly all of Missouri north of the Missouri river was covered by the Kansas glacier during Pleistocene time and, after receding, a mantle of drift of varying thickness remained. The northwest part of the state is underlain by Carboniferous rocks of which the lower beds are chiefly shales and sandstones and the higher beds, shales and limestones. Northeast Missouri is underlain by massive, crystalline, cherty Mississippian limestone. The overlying till consists of soil material from the north mixed with local ground up shales, sandstones, and limestones.

The Lindley loam varies in its physical properties from a fine sandy loam to a silty clay, depending on the till and the degree of erosion. The topography varies from gently rolling to hilly and erosion is excessive on

the steeper slopes. Only about 50 percent of the land is in cultivation due to the topography and it has low natural fertility because of its low organic matter and phosphorus content. The hilly topography has caused little horizon differentiation and, in some cases, severe erosion has exposed the subsoil.

The samples used in this investigation were collected from a site approximately 15 miles north of Columbia, Mo., in the northwest quarter, Section 18, Township 50, Range 13. The soil was located on a virgin, wooded region adjacent to worked-out coal strip mines. The parent material was considered to be till, with the possibility of a small amount of loess in the A₁ horizon. The origin of the till was indeterminable. Possibly, the parent material contained local limestone and shale mixed with the other transported soil materials. The topography of the area was sharply rolling but the sampling site was at the center of a rather level small knoll.

The surface soil to a depth of 3 inches was a grayish brown loam and had a single-grained structure. The B₁ horizon down to a depth of 18 inches was a granular yellowish-brown clay loam which graded into a slightly heavier B₂ horizon mottled with yellow and gray to a depth of 28 inches. The lower subsoil was yellowish-brown sandy clay, streaked and mottled gray. At a depth of 12 feet, calcareous concretions were clearly visible.

Seven samples were taken which were thought to be representative of the various horizons and subsoil variations. Colors were determined in the natural condition, using a Munsell Color Chart.

Description of the Samples:

#1	A - 0 - 3 inches	10YR4/3 grayish brown loam
#2	B ₁ - 6 - 18 inches	10YR5/3 yellowish brown clay loam
#3	B ₂ - 18 - 28 inches	10YR5/8 mottled yellowish brown clay loam
#4	5 feet	10YR5/6 mottled yellowish brown sandy loam
#5	7 feet	10YR4/4 mottled dark yellowish brown sandy clay
#6	12 feet	10YR4/2 mottled grayish brown sandy clay
#7	14 feet	10YR4/4 dark yellowish brown heterogeneous pebbly sandy clay

Subsequent to collection of the samples, lumps and aggregates were pulverized in a moist condition. The samples were air-dried. The dry soil was lightly ground so that all except the pebbles passed a 2 mm. sieve. It was then bottled and stored.

Mechanical Analysis

1. Procedure

Mechanical separations of the various fractions were made by means of sieves for particles greater than 50 microns in diameter. The pipette method (5, 48) was used for finer particles.

Duplicate 20-gram samples were treated with 50 ml. of 6 percent hydrogen peroxide and warmed gently on a steam plate. After standing overnight, 10 ml. of 30 percent hydrogen peroxide were added. The samples were then warmed on the steam plate until all action had subsided.

Following this oxidation of organic matter, the samples were cooled and enough normal hydrochloric acid was added to make the suspension acidic to pHydrion paper at a pH of four. After leaving overnight, the pH was adjusted again and the soil was filtered under suction on a Buchner funnel, using Whatman number 50 filter paper. The samples were washed free of soluble salts and basic exchangeable cations with 200 ml. of 0.01 normal hydrochloric acid.

Samples were transferred to milk-shake mixer cans with 0.02N sodium carbonate solution and stirred for 20 minutes to obtain maximum dispersion. The resulting suspension was washed through a nest of calibrated sieves, using a jet of hot distilled water. The sieves used and the corresponding sizes of their holes were:

- 30 mesh - 1 mm.
- 60 mesh - 0.25 mm.
- 150 mesh - 0.1 mm.
- 300 mesh - 0.05 mm.

Sieves were dried in an oven at 50° C and tapped to free any fine material clinging to them. The portion remaining on each sieve was transferred to weighed aluminum dishes, dried at 105° and weighed. The suspension passing through the sieves was transferred to a sedimentation cylinder and made up to one liter with more dilute sodium carbonate solution.

After shaking up the suspension, a 10 ml. pipette sample was taken at a depth of 10 cm. after a lapse of time calculated from Stokes' Law for the velocity of free fall of small particles. The time for free fall of the particles to a depth of 10 cm. was calculated for temperatures from 20° to 30° C and the proper time used according to the working temperature. These pipette samples were evaporated in a 50° C oven, dried at 105° C and weighed. Samples taken in this way were 0.02 to 0.005 mm., 0.005 to 0.002 mm., and less than 0.002 mm. equivalent spherical diameter. The 0.05 to 0.02 mm. fraction was recovered by transferring the suspension to a tall-form 600 ml. beaker and removing the less than 0.02 mm. e.s.d. ma-

terial by the beaker method. The remaining sediment (0.05 to 0.02 mm. e.s.d.) was dried and weighed. The weights of the coarse and fine silt and the clay were calculated and recorded.

The less than 2 micron e.s.d. fractions from the samples were electro-dialyzed to produce hydrogen clays. They were then dispersed by titrating with 0.1N sodium hydroxide, and separated into 2.0 to 0.2 micron and less than 0.2 micron fractions according to Marshall's (37, 38, 14) two-layer centrifuge method. After being centrifuged the clay was flocculated with saturated calcium hydroxide solution and washed until all the glycerol was removed. The clays were then mixed with coarse hydrogen-saturated Amberlite IR-120 in such a way that the exchange capacity of the Amberlite was at least ten times that of the clay. After leaving overnight the Amberlite was filtered off with fine rayon cloth and the resulting hydrogen-saturated clays were made to volume in a 250-ml. volumetric flask. Aliquots were taken to determine the solids by evaporation and to determine the exchange capacity. The amount of clay in each fraction was calculated to complete the mechanical analysis.

Moisture determinations were not made on the original samples but loss of weight after pretreatment was measured in separate samples. Duplicate 20-gm. samples were given the same pretreatment as the mechanical analysis samples up to and including the acid wash on the Buchner funnel. The washed soil was then transferred to weighed 100-ml. beakers, evaporated, dried at 105° C and weighed. The percentage of the material occurring in each fraction was calculated on this weight basis. The dried material was used as the source of the silt and sand fractions for mineralogical analysis, whereas the clay separated in the mechanical analysis was used for the X-ray analysis.

2. Results

Results of the mechanical analysis are in Table 1. All the samples gave a complete suite of particle sizes, thus confirming the presumed gla-

TABLE 1 -- MECHANICAL ANALYSIS OF THE LINDLEY PROFILE EXPRESSED AS PERCENT OF DRY SOIL AFTER PRETREATMENT

Equivalent in mm.	1 0-3"	2 6-18"	3 18-28"	4 60"	5 84"	6 144"	7 168"
2.0 - 1.0	0.52	4.90	6.63	2.37	2.89	4.18	23.19
1.0 - 0.25	2.96	5.55	6.48	7.20	8.53	8.77	11.70
0.25 - 0.1	4.41	6.72	5.85	8.65	11.58	10.91	9.49
0.1 - 0.05	5.97	6.46	6.40	8.26	11.44	10.50	8.40
0.05 - 0.02	29.00	19.25	19.52	14.10	13.70	14.04	10.84
0.02 - 0.005	15.08	13.12	12.98	13.70	13.58	10.98	10.23
0.005 - 0.002	4.35	4.11	10.31	11.39	9.47	12.81	0.81
0.002 - 0.0002	10.65	16.00	14.18	10.07	11.93	11.09	11.70
less than 0.0002	27.10	25.20	18.15	24.64	16.90	16.78	13.63

cial origin of the material. The top soil, however, (sample 1) contained less of the sand fractions and considerably more of the coarse silt (.05 to .02 mm.) than the deeper layers. This suggests admixture with loess, the bulk of which may well have been lost by erosion.

The ratios between the percentages of different sand fractions vary appreciably in different horizons of the profile, sample 7 being, as expected from field observations, considerably the richest in coarse sand particles. Sand lenses are not uncommon in glacial deposits.

No major clay accumulation was found in the profile, suggesting that at this site the soil was young in development. The mineralogical study confirmed this deduction, as will be seen later in the text.

Preparation of Soil Fractions and of Standards for Study

1. *Silt and Sand Fractions of the Lindley Soil*

The dried soil samples from the determination of the loss on pre-treatment with H_2O_2 were wetted and transferred to 600-ml. tall-form beakers. The suspension was made alkaline with sodium hydroxide and filled to a 10-cm. depth. The less than 2-micron clay fraction was removed by successive sedimentations and decantations and the liquid was discarded. The remaining silt and sand was treated to remove the iron oxides according to the method proposed by Jeffries (30).

The method depends upon the fact that nascent hydrogen, which is produced by the reaction of metallic magnesium in the presence of a solution of potassium oxalate and oxalic acid, reduces and dissolves the ferric iron in the sample. Following treatment, centrifuging, and washing, the clay-size material was again removed by successive sedimentation and decantation. The clean silt and sand mixture was separated into 2 to 5-micron, 5 to 20-micron, 20 to 50-micron, 50 to 250-micron, and greater than 250-micron e.s.d. fractions by sieving and successive decantations as outlined in the procedure for mechanical analysis.

The procedure used for specimen preparation was the one given by Phillippe and White (47) and Graham (20). Sodium fluoride was mixed with the samples as an internal standard to compare with known mixtures of quartz, microcline, albite and sodium fluoride. Additions of 250 mg. of powdered sodium fluoride were made to each gram of sample. The samples were mixed by grinding in a mechanical grinder equipped with a mullite mortar and pestle. The finest fraction tended to ball up after a short mixing time due to its hygroscopicity. To get good mixing, these samples were dried and ground three times for 10 minutes.

A longer grinding period was necessary for the coarser silt and sand-size fractions since it was desirable to have a particle size of less than 5-

micron e.s.d. to get optimum X-ray diffraction characteristics (1). The grinding and mixing was assumed to be satisfactory when the material appeared to ball up as in the 2 to 5-micron fraction. The samples were then bottled, dried and stored.

2. *Standard Quartz-Feldspar Mixtures*

The set of standard mixtures supplied by Dr. E. R. Graham were composed of optically pure feldspars obtained from Ward's (56) and a sample of Arkansas crystal quartz obtained from Dr. W. D. Keller. These mixtures contained the following proportions of each mineral to give 1 gm. of sample.

	<i>Percent Quartz</i>	<i>Percent Albite</i>	<i>Percent Microcline</i>
a	100		
b	90	5	5
c	80	10	10
d	70	15	15
e	60	20	20
f	50	25	25

Two hundred and fifty mg. of powdered sodium fluoride had been added to each sample as an internal standard. Mixing was accomplished by grinding for two hours in a chemical grinder with intermittent oven-drying periods.

3. *Clay Fractions of the Lindley Soil*

Enough of each suspension of hydrogen-saturated clay to give a total of 500 mg. of clay was removed with a pipette and placed in each of two 150-ml. Erlenmeyer flasks. From the known exchange capacity per 100 gm. clay, the proper amount of 0.413N potassium hydroxide was added to one flask in order to obtain a potassium-saturated clay. Similarly, a calculated amount of powdered magnesium oxide was added to the other flask to obtain a magnesium-saturated clay. The suspensions were brought to a boil and heated for ten minutes to enhance the exchange reaction. All except two of the magnesium-saturated clays had a final pH near 7.0.

The suspensions were transferred to 100-ml. volumetric flasks, made to volume with distilled water, and the resulting 0.5 percent suspensions were stored in Erlenmeyer flasks.

The procedure used for X-ray specimen preparation was essentially that proposed by Talvenheimo and White (54) and consisted of the preparation of clay films on microscope slides which could be used directly. Since standard microscope slides were too long to fit the X-ray equipment, the slides were cut in half by scratching with a file and breaking

them. Gummed labels were placed on one end of the surface and a thin film of DeKhotinsky vacuum stopcock grease was placed on the slide along the edge of the label. After several trials, this was found to be the most satisfactory material to prevent liquid from running over the label. Desiccators were prepared with a saturated zinc chloride solution in the bottom to give an atmosphere of 10 percent relative humidity (54). Each of the prepared slides was placed in one of the desiccators and the suspensions were deposited on the slides in such a way that there was 1 ml. per square inch of exposed surface. The desiccators were covered and left until all the liquid had evaporated from the specimens.

4. *Reference Clay Minerals*

Three clay specimens included in the American Petroleum Institute Project 49 (2) were chosen as reference minerals. The kaolinite (sample number Hg) was a well-crystallized specimen from Mesa Alta, N. M., as supplied by Wards Natural Science Establishment (56). The reference specimen of illite (21) was from Fithian, Ill. (Ward's sample H-35). This was a dioctahedral mica. The montmorillonite was Ward's bentonite, sample H-28 from Little Rock, Ark. (51), a reasonably pure specimen with X-ray diffraction and chemical characteristics of a calcium-saturated montmorillonite. The respective cation exchange capacities, as given in A.P.I. report No. 49 (2), are: kaolinite Hg, 6.8 m.e./100 gm.; illite H 35, 25 m.e./100 gm.; montmorillonite H28, 92 m.e./100 gm.

The kaolinite, illite, and montmorillonite samples were disaggregated by gentle trituration in water with a mortar and pestle. The slurries of kaolinite and illite were made alkaline with sodium hydroxide and stirred in a milkshake mixer for 20 minutes. The coarse material was separated and discarded by successive 24-hours, 10 cm. sedimentations and decantation of the suspended material. The montmorillonite sample was washed with 0.02N sodium carbonate solution in the centrifuge until dispersion occurred in order to remove exchangeable calcium. It was then made alkaline with sodium carbonate and stirred in the mixer for 20 minutes. The coarse material was removed as outlined for kaolinite and illite. By calculation, these samples were less than 1.15 microns e.s.d.

These clay suspensions were then handled in a manner identical with that used for the clays from the Lindley soil. Exchange capacities were determined and specimens of the K- and Mg-saturated clays were prepared for X-ray examination.

X-ray Diffraction Procedure

1. *General*

X-ray analysis is based on the diffraction of rays of suitable wave

length by atomic planes according to the Bragg equation $n\lambda = 2d \sin \theta$. The fundamental theory has been described in treatises by Bragg (13), Buerger (16), and Bunn (17). The characteristic reflections are measured as a function of the angle from which the interplanar spacings may be calculated. The intensity of the reflection is also important, since it is determined by the characteristics and number of atoms in the given plane.

For a fine powder with completely random orientation of particles, a single reflection forms a conical surface. In the instrument employed here, the measuring device was a Geiger-Muller tube, mechanically operated so as to intersect possible reflection cones in an arc from 3° to about 150° . Since the Geiger tube was operated at an angular speed twice that of the sample, the angles marked on the recording paper corresponded to Bragg angles 2θ . Published tables (53) can be used to convert them to d/n values in KX or Å units.

The pattern showing the interplanar spacings and reflection intensities was characteristic of a crystalline species and could therefore be used for identification. In mixtures of two or more crystalline materials, the characteristic patterns are superimposed and, ideally, the intensities of reflection relative to those of a pure sample may be used for quantitative determination.

2. Operation of the Unit

A copper-anode X-ray tube was used in a North American Philips X-ray Diffractometer (60) and the diffraction patterns were recorded with a Brown recorder. The unit was adjusted to 35 kilovolts and 15 milliamperes across the X-ray tube. It was allowed to "warm up" 20 to 30 minutes or until the current remained constant. The radiation was collimated by passing through slits giving a 1° beam arc before impinging on the sample. A nickel filter on the Geiger tube absorbed most of the continuous X-radiation but transmitted the characteristic Cu K and K radiation with an average wave length of 1.5418 \AA . The Geiger tube was operated at a scanning speed of 1° per minute. The impulses were recorded at various counting rates, depending upon the material and the information desired. The chart speed in all cases was 1 cm. per minute. The performance of the unit was checked periodically by scanning the strong quartz reflection at 26.6° .

The reference clay minerals and the Lindley samples of 2.0 to 0.2-micron and less than 2-micron e.s.d. were all prepared as thin films on glass microscope slides. These slides were placed in the diffractometer and exposed to X-rays over various ranges of the angle 2θ . The time was constant and the scale factor was set at various values to get a good on-scale pattern. For the reference minerals, the counting rate was decreased to

keep the peaks from going off the paper. In one case a setting of 32 - 0.6 - 2 had to be used.

The patterns produced were indexed with the corresponding interplanar spacing and the unknowns checked against the reference patterns. The intensities of the reflections of the unknown samples were compared to get the relative amounts of the clay minerals present.

The standard quartz-feldspar mixtures and the Lindley samples, after having been mixed with the sodium fluoride, were packed into aluminum holders according to the method of McCreery (33). The sodium fluoride peak at 2.32 Å and the quartz peak at 3.35 Å were run at a setting of 16 - 1 - 4.

The intensities of the reflections were measured as peak heights. The ratio of the height of the quartz peak to the sodium fluoride peak of the standards was calculated and plotted against the percent quartz in the sample. The peaks were run four times on the same mount and run two days in succession. The sample mounts were remade five times and the procedure repeated. Ratios in all these cases were plotted, giving a scatter diagram. The height of the quartz line was plotted directly against percent quartz in the standard to give a comparison. This procedure was repeated for the albite and microcline peaks, using a setting of 2 - 1 - 8. The line of best fit was constructed on the resulting scatter diagram, giving the relationship between peak height and percent composition.

The peaks of the unknown were run three times or more to get checks on each sample mount and the mount was remade twice or more until checks were again obtained. The peak heights were averaged and the points on the standard curves determined which corresponded to these peak heights. These points then gave the percent quartz, albite and microcline in the unknown sample. A table was then constructed giving the percent of these minerals in each sample.

3. Results with Standard Quartz-Feldspar Mixtures

The equations of the straight lines connecting peak heights (y) and percentages of known mineral species (x) were:

$$\text{For quartz } y = 1.20 + 1.91 x$$

$$\text{For microcline } y = 2.34 + 0.358 x$$

$$\text{For albite } y = 2.76 + 0.55 x$$

The quartz data were for mixtures containing 50 to 100 percent quartz. Those for albite and microcline each covered the range 5 to 25 percent. It will be noted that the sensitivity of the method was greatest for quartz and that microcline gave a less prominent peak than albite.

4. Results with Reference to Clay Minerals

H-9 Kaolinite: The X-ray diffraction patterns of kaolinite did not change when the sample was saturated with K, Mg or glycol. This conformed to the established concepts of its structure and X-ray diffraction characteristics (21, 61, Chapter II). The basal (001) spacings were the only ones obtained, giving $d(001) = 7.20 \text{ \AA}$, $d(002) = 3.58 \text{ \AA}$, and $d(003) = 2.51 \text{ \AA}$. Well-crystallized kaolinite should give $d(001) = 7.14 \text{ \AA}$, and poorly crystallized and fine-grained kaolinite have been found to vary from 7.20 \AA to 7.3 \AA . Brindley (61, Chapter II) states that this may be due to a small degree of hydration but, when the same slide was heated to 500°C and soaked for 30 minutes, the position of the peak did not change. This effect may also be due to the use of a high time constant in running the sample since it was observed that quartz peak was displaced slightly toward higher angles (2θ) at higher time constant values.

The (001) spacings decreased in intensity linearly from (001) to higher orders. This is in agreement with the published values (61, Chapter II). Kaolinite decomposes to an x-amorphous state at a temperature somewhat less than most chlorites. This has been used as a diagnostic criteria for their separation in mixtures (61, Chapter II). However, Bradley (11) has emphasized that some chlorites will decompose at lower temperatures and that extreme caution has to be used in using this criterion. The heating treatment in this case reduced the height of the kaolinite peaks but did not remove them completely.

H-28 Montmorillonite: The potassium saturated sample gave a pattern consisting of essentially one peak or band, the basal spacing, ranging from 11.05 \AA to 11.95 \AA . This was attributed to a mixture of minerals of (001) at 10 \AA and 14 to 15 \AA , and may have been either of two cases of mixed-layering cited by Brown and MacEwan (61, Chapter XI). If there is segregation of the minerals into zones, bands will occur whose shapes depend on the distribution of the various hydrates. Since the X-ray reflection occurred in a rather definite peak, it was assumed that this was a case of random interstratification of different hydration states.

When glycol was present in the K-saturated clay, the peak was at 17.0 \AA . Barshad (4), however, found that a K montmorillonite, when solvated with glycerol, had a basal spacing of 14 \AA or an interlayer expansion one glycerol molecule thick. The second peak was at 8.67 \AA and, since this value was slightly higher than the calculated montmorillonite, $(002) = 8.5 \text{ \AA}$, it was thought that a small amount of random interstratification had occurred.

The Mg-saturated clay, examined at the same counting rate as the K-clay, gave a peak which went off the scale at about 15 \AA and did not

give an (002) peak. When saturated with glycol, the peak shifted to 17 Å and a counting rate of 32 - 0.6 had to be used to bring it on scale. The (002) was in the calculated position and indicated that there was essentially no mixing of hydrates according to the Brown-MacEwan interpretation. It was therefore concluded that when a Mg-montmorillonite is saturated with glycol, there is essentially no occurrence of a collapsed lattice.

Another K-montmorillonite slide having no glycol present was given the heat treatment used for kaolinite (500° C for 30 minutes). The pattern showed that essentially all the interlayer water was removed, since the lattice had collapsed to 10.05 Å. Broad (002) and (003) peaks were apparent at 4.98 Å and 3.28 Å, respectively. It was also observed that the (003) reflection was more intense than the (002).

H-35 Illite: The potassium-saturated illite gave a pattern showing the (001), and (002), and (003) peaks at 10.40 Å, 5.01 Å, and 3.35 Å, respectively. The spacing for the (001) was slightly greater than that reported in the literature (61, Chapter V) and this could be reconciled by examination of the broadening of the peak. There was some random mixing of the 10 Å layers with hydrated layers which showed up as a broadened peak tailing off toward lower angles. Talvenheimo and White (54) had evidence for the occurrence of mixed layering in their sample of Fithian illite. Mg-saturated illite gave a sharper (011) peak at a slightly more collapsed position, 10.16 Å. As with K-illite, the (002) and (003) reflections were apparent at 5.01 Å and 3.35 Å, with the (003) slightly more intense than the (002). Upon saturation with glycol, the spacing did not change from 10.16 Å but the intensity was decreased. When the K-illite was heated, the peaks were much more intense than those of the K-montmorillonite. The (001) spacing was 10.16 Å as compared to the unheated sample, 10.40 Å, and was the same as the Mg-illite and the heated K-montmorillonite. The (002) and (003) of the heated sample were also in the same positions as in the unheated sample.

Mixtures of the Reference Clay Minerals: Mixtures made by pipetting aliquots of the suspensions of the Mg-saturated pure minerals were run in the same manner as the other samples. The diffraction pattern of the mixture of 25 percent quartz, 25 percent kaolinite, 25 percent illite, and 25 percent montmorillonite was a composite of the patterns of the individuals. The strong quartz peaks were at 3.35 Å and 4.29 Å and the first and second order kaolinite peaks were at 7.20 Å and 3.59 Å. The illite and montmorillonite peaks were not apparent but there was a plateau extending from 10.16 Å to 11.63 Å, followed by a series of peaks up to 15 Å. This was thought to be a situation where zoning of the various hydrates of montmorillonite occurred randomly mixed with illite. When the sam-

ple was saturated with glycol, the montmorillonite and illite peaks were resolved into their proper positions, 17.3 Å and 10.28 Å. However, there was a low plateau extending from 8.59 Å to 9.51 Å. The former d spacing corresponds to a calculated (002) of montmorillonite. This plateau may be explained by a random type of mixing giving diffraction effects between the (001) of illite and the (002) of montmorillonite. The broad base of the 3.35 Å peak probably corresponded to the (003) reflection from illite since it remained in the mixture containing no quartz.

The pattern of the mixture, 25 percent kaolin, 25 percent illite, 50 percent montmorillonite, had an intense, pronounced peak at 14.5 Å which extended down to a small shoulder occurring in the 10 Å region. When this sample was treated with glycol, the peaks were adequately separated and the montmorillonite (001) peak at 17.5 Å went off the chart. The 10 Å illite peak was not well outlined. A broad peak occurred at the montmorillonite (002) position and two peaks were apparent, 5.72 Å and 3.36 Å. If the 10 Å peak had been shown to be more highly developed, the 3.36 Å peak could have been accounted for as the (003) mica peak. To correspond to the (005) montmorillonite peak, a shift to 3.5 Å would be needed. The peak at 5.72 Å corresponded to the (003) spacing of montmorillonite. Similarly, the (002) of montmorillonite occurred at 8.67 Å. It was concluded that this sample contained a random mixed-layering of montmorillonite and illite since the higher orders of both showed up, and since there were spurious diffraction effects between the montmorillonite (002) and the illite (001) peaks.

The theory of mixed layering is invaluable in that the occurrence of bands of plateaus and displaced peaks can be analyzed or at least recognized. The occurrence of these effects in the patterns of the pure minerals and in the synthetic mixtures was surprising and it would appear that the complete absence of mixed layering would be the exception rather than the rule.

RESULTS ON LINDLEY SOIL FRACTIONS

X-ray Examination of Sand and Silt

The five fractions were run on the diffractometer under conditions identical to those of the standards. The results of the quartz determination are given in Table 2. The peak heights of four repetitions of the same specimen mount were averaged with those from two or three separate mounts and the corresponding percent quartz was selected from the standard curve.

The most striking aspect of these figures was the fact that the amount

. TABLE 2 -- QUARTZ CONTENT OF THE SILT AND SAND FRACTIONS OF THE LINDLEY LOAM PROFILE

Sample Number	Percent Quartz in the Fractions				
	0.002 to 0.005 mm.	0.005 to 0.02 mm.	0.02 to 0.05 mm.	0.05 to 0.25 mm.	0.25 mm.
1	40	71	77	85	69
2	53	65	82	90	78
3	51	75	86.5	87	70.5
4	36	63	80.5	86.5	77
5	31	66	79	83	74
6	37	57	79.5	82	60
7	--	34.5	66.5	58	44

TABLE 3 -- ALBITE CONTENT OF THE SILT AND SAND FRACTIONS OF THE LINDLEY LOAM PROFILE

Sample Number	Percent Albite in the Fractions				
	0.002 to 0.005 mm.	0.005 to 0.02 mm.	0.02 to 0.05 mm.	0.05 to 0.25 mm.	0.25 mm.
1	2.8	6.1	7.4	3.5	2.9
2	2.2	4.0	4.0	5.8	3.2
3	1.4	4.2	12.2	3.9	4.8
4	1.0	4.6	6.0	4.1	9.7
5	1.3	4.0	11.4	5.0	7.0
6	1.8	2.8	5.4	6.4	7.3
7	---	2.1	7.5	4.3	7.1

TABLE 4 -- MICROCLINE CONTENT OF THE SILT AND SAND FRACTIONS OF THE LINDLEY LOAM PROFILE

Sample Number	Percent Microcline in the Fractions				
	0.002 to 0.005 mm.	0.005 to 0.02 mm.	0.02 to 0.05 mm.	0.05 to 0.25 mm.	0.25 mm.
1	5.0	8.0	8.9	7.4	5.8
2	4.6	7.2	6.2	6.3	6.0
3	3.4	6.0	11.2	6.0	10.9
4	3.6	8.1	8.7	7.4	16.5
5	3.2	5.4	11.1	5.6	9.1
6	3.9	4.3	8.0	6.7	16.2
7	---	2.4	8.4	4.2	5.5

in the 2 to 5 micron fraction was low; in all but two cases it was less than one-half of the amount in the 0.05 to 0.25 mm. fraction. There was a gradual increase up to a maximum in the .05 to .25 mm. fraction in all of the samples except 7. These differences were too large and too regular to be attributed to experimental error.

The feldspar contents of the different size fractions are reported in Table 3 (Albite) and Table 4 (Microcline). These figures were obtained in the same manner as the quartz values by reference to the respective standard curves.

Both albite and microcline were present in smaller amounts in the 2 to 5 micron fractions than in the coarser fractions of all the samples.

TABLE 5 -- QUARTZ-FELDSPAR CONTENT OF SILT AND SAND FRACTIONS OF THE LINDLEY LOAM PROFILE

Sample Number	Summation Percentage in the Fractions				
	0.002 to 0.005 mm.	0.005 to 0.02 mm.	0.02 to 0.05 mm.	0.05 to 0.25 mm.	0.25 mm.
1	47.8	85.1	93.3	95.9	77.7
2	59.7	76.2	92.2	102.1	87.2
3	55.8	85.2	109.9	96.9	86.2
4	40.6	75.7	95.2	98.0	102.2
5	35.5	75.4	101.5	93.6	90.1
6	42.7	64.1	92.9	95.1	83.5
7	---	39.0	82.4	66.5	56.6

This is in line with the findings of Marshall (39) and Truog *et al.* (55) who showed that the amount of feldspars increased with increasing size from 2 to 10 microns in five different soils. The maximum amount occurred in the 0.02 to 0.05 mm. and 0.05 to 0.25 mm. fractions in all the samples except one (number 6) where it occurred in the greater than 0.25 mm. fraction.

There was no big difference in the feldspar contents between the same size fractions from the different horizons. However, the two surface horizons had a slightly larger amount in the 2 to 5 micron fraction than did the underlying material. Mixture of loess with the till and a low degree of pedochemical weathering were suggested by these results.

The sums of the quartz, albite, and microcline contents of each fraction were calculated. They are listed in Table 5. Several fractions had a total of over 100 percent but the 0.02 to 0.05 mm. fraction of sample 3 was rerun several times without altering the results. A very striking aspect of these figures is the low total obtained in the fine fractions. Inspection of the complete diffraction patterns showed that no peaks were apparent other than those of quartz, albite, microcline, and sodium fluoride. There may have been small amounts of the clay minerals present which would not be resolved on the X-ray patterns but it would be difficult to attribute 50 percent of the fine fraction to this effect.

X-RAY EXAMINATION OF LINDLEY CLAY FRACTIONS

Coarse Clay (2 to 0.2 micron)

The X-ray diffraction patterns showed that kaolinite, illite, montmorillonite, quartz and feldspars were present. Because of the presence of illite, whose third order reflection comes in the same position as quartz, it was difficult to assign a definite value for the amount of quartz. The coarse clays were run at a lower counting rate than the fine clays and the intensities multiplied by the amplification factor were compared to give a

rough estimate of the amounts present. When this was done, it was found that the sum of the montmorillonite, illite, and kaolinite in the coarse clay fraction was greater than 100 percent. Two reasons were suggested for this phenomenon: the clay minerals in the coarser fraction were better crystallized and gave stronger reflections for a given amount present and, because of the nature of the mixing, the shapes of the peaks of montmorillonite and illite were not proportional to the amount in the less than 0.2 micron fraction. Therefore, the amounts of the minerals could only be relative to one another within the coarse fraction.

The maximum amount of kaolinite occurred in Sample 4 and the maximum amount of illite was in Sample 6. Table 6 gives the relative intensities of the peaks from these two minerals.

These intensities were obtained by multiplying the peak height by the amplification factor used when the pattern was made. Montmorillonite occurred in significant amounts in all but Sample 7. However, it was not included in Table 6 because the shapes of the peaks differed greatly. A different manner of stacking and/or a different degree of crystallinity, or non-uniform separation of the two size fractions could account for this effect.

TABLE 6 -- RELATIVE AMOUNTS OF THE MINERALS IN THE 2 TO 0.2 MICRON FRACTION OF THE LINDLEY LOAM
(expressed as equivalent peak heights in mm.)

Sample	Kaolinite	Illite	Quartz
1	13	13	23
2	28	12	30
3	32	12	28
4	46	16	21
5	34	24	18
6	34	30	20
7	20	12	18

Fine Clay (< 0.2 micron):

Sample 1. The pattern of the K-saturated clay showed that in addition to the micaceous material there was a small amount of kaolinite. The (001) reflection at 7.31 Å indicated that it was a poorly crystallized type with the probability of some interlayer water. If this explanation is valid, then the Brown-MacEwan curves could be used, showing that there was approximately 10 percent of the kaolinite in the hydrated state. The possibility of chlorite was ruled out because there was no chlorite (003) peak at 4.7 Å and there was no apparent 14 Å peak on the pattern of the heated K-clay. The (001) and the (002) reflections of kaolinite were the same in the K- and the Mg-saturated samples.

In the K-clay pattern there was a series of peaks from 10.4 Å to 17.0 Å at the top of a plateau and peaks at 5.01 Å and 3.36 Å. The plateau was similar to that obtained with the reference clay mixture of 25 percent montmorillonite and 25 percent illite. The 5.01 Å and 3.36 Å reflections corresponded to the (002) and (003) from the 10 Å mica as in the reference materials. The Mg-saturated sample gave a broad peak at 15 Å extending from about 9 Å to 20 Å, indicating a mixture of micaceous minerals in various hydration states. The 5 Å peak became much broader and lower with a position at 4.93 Å. This was thought to be the (003) reflection of the 15 Å montmorillonite. The 3.33 Å peaks almost disappeared but, since there was a slight shoulder on the basal spacing at the 10 Å position, the small 3.33 Å peak could have been the (003) spacing of illite.

The Mg-clay saturated with glycol gave a pattern having a high, wide montmorillonite peak which fell off to a plateau extending from 7.97 Å to 11.33 Å with a small peak at 9.94 Å. This peak corresponded to the curve for random interstratification given by MacEwan and Brown (61) for the case of a 70 percent montmorillonite and 30 percent illite mixture. Apparently this was not a strict case of true random interstratification since the plateau indicated a zonal mixture giving X-ray interference phenomena between the illite (001) and the montmorillonite (002).

After the heat treatment, the micaceous layers collapsed to 10.28 Å with the peak tailing off toward low angles. This phenomenon has been attributed by MacEwan (35) to the presence of non-clay mineral material in the interlayer position which prevents the complete collapse. The (002) and (003) were present at 5.04 Å and 3.33 Å, respectively. The kaolinite lines at 7.25 Å and 3.59 Å were markedly reduced but were still present.

Sample 2. The K-saturated clay gave a pattern very similar to that from Sample 1, except the kaolinite peak was slightly larger. This probably meant that there was slightly more kaolinite present and/or it was better crystallized. The heated sample showed diminished peaks and broadening of the 10 Å peak and the mica (003) more intense than the (002). The glycercol-saturated Mg-clay had a slightly sharper montmorillonite (001) peak but the plateau from 8 Å to 11 Å was more uniform and lower than Sample 1.

Sample 3. The K-clay gave a pattern with the same broad (001) mica band but the (002) was absent and the (003) was not as intense as in Samples 1 and 2. The kaolinite peaks were only slightly more intense than Sample 2. The pattern for the Mg-clay showed the strong 15 Å peak and a well developed 5.00 Å peak while the 3.35 Å peak was absent. The montmorillonite (001) peak, when glycolated, was very sharp, and the

(002) peak at 8.42 Å was moderately well developed. There appeared to be a smaller amount of illite present than in the first two samples. The heated K-clay gave an (001) peak at 10.16 Å with the (003) stronger than the (002). The basal spacing peak tailed off to low angles as in the other cases. In spite of this, the position of the heated mica (001) peak and the sharpness of the montmorillonite (001) and (002) peaks suggested that there was less amorphous interlayer material and that the montmorillonite was crystallized better than in the first two samples.

Sample 4. The pattern from the K-clay showed sharp kaolinite peaks; the mica showed (003) but no (002) and the micaceous material showed a (001) band. However, the 10 Å peak is well defined as compared to the previous samples. The Mg-clay gave the same type of pattern as previously with montmorillonite (001) and (003), the kaolinite peaks present and the 3.35 Å peak missing. The heated sample had mica (001) at 9.93 Å with the (003) more intense than the (002). In this case the kaolinite (002) peak at 3.59 Å was removed by the heat treatment and the (001) peak was diminished. The glycolated Mg-clay gave a sharp (001) peak and a plateau similar to Sample 3. The fact that there was a sharper peak from K-saturated clay, and that there was lower mica (001) spacing from the heated sample would indicate that the montmorillonite was well crystallized.

Sample 5. The K-clay gave a pattern very similar to that from Sample 4 except that the 5 Å and 3.35 Å peaks were more pronounced. The pattern from the Mg-clay showed a more pronounced 10 Å shoulder and the kaolinite (001) peak was sharper than in Sample 4. The kaolinite peaks were diminished to almost nothing and the mica (001) peaks were sharper in the heated sample than in Sample 4. The glycolated Mg-clay showed a very sharp montmorillonite (001) peak with the same type of plateau in the 8 Å to 10 Å region as in all the samples. The sharper second and third order mica peaks and kaolinite peaks indicated that the clay minerals were better crystallized in the lower horizons than in those nearer the surface.

Sample 6. The kaolinite peaks were more intense in this sample than in any previous ones and disappeared completely upon heating the K-clay sample. The glycolated sample gave a pronounced 10 Å peak along with the first and second order montmorillonite peaks. When the pattern given by the prepared glycolated mixture of 25 percent kaolinite, 25 percent illite, 25 percent montmorillonite and 25 percent quartz was compared with that given by the glycolated #6 Mg-clay, the two appeared very similar. However, there was no quartz found in the #6 sample and it was run at a higher counting rate (16 - 0.6 - 2) than the mixture (4 - 1 - 4). If

Sample 6 were run at 4 - 1 - 4, the heights of the peaks would be approximately 2.4 times as high as they were in the present chart.

A number of theoretical reasons may be offered to explain this anomaly. Certainly the degree of crystallinity of the reference clays was different from the unknowns. The reference clays were less than 1.5 micron e.s.d. as compared to the less than 0.2 micron size of the unknowns, but an increase in size in this range and an increase in crystallinity, as would be expected with the reference materials, usually tends to increase the diffraction effects rather than repress them (61, Chapter I). The reference illite and montmorillonite clays might have been broken down more readily by the preliminary treatment than the soil clays. In that case, 25 percent of each would not present. There might have been a major source of error in the preparation of the slides; i.e., the montmorillonite formed a layer over the kaolinite and quartz such that X-rays were absorbed by the montmorillonite before or after the diffraction effects occurred. This effect was not apparent in the coarse clay patterns but may have happened in the mixtures due to a possible larger absorption power of the reference montmorillonite and illite. Different isomorphous replacements of the constituent atoms in the micaceous materials may also change the diffracting power of the minerals (61, Chapter I).

Sample 7. The K-clay had the same type of pattern as the other samples but the intensities of all the peaks were much smaller. The Mg-clay gave an extremely low montmorillonite peak and all the others were small. The heated sample showed the mica first, second, and third orders, and the kaolinite peak was removed. The glycolated sample also showed poorly defined peaks of montmorillonite, illite, and kaolinite. The characteristics of the patterns were such that no definite amounts could be assigned to the clay minerals. However, there is probably a majority of montmorillonite with minor amounts of illite and kaolinite.

Clay mineralogists are agreed that a quantitative analysis of clay minerals is inaccurate at the present stage of our knowledge. Figures for the amounts of clay minerals in the fine fraction are in Table 7 and must be regarded as no better than semi-quantitative.

TABLE 7 -- DISTRIBUTION OF CLAY MINERALS IN THE LESS THAN 0.2 MICRON FRACTION OF THE LINDLEY LOAM

Sample	Percent Kaolin	Percent Illite	Percent Montmorillonite
1	15	25	60
2	15	20	65
3	15	15	70
4	15	15	70
5	20	15	65
6	25	25	50
7	low	low	medium

Results with Randomly Oriented Specimens:

Dry and glycolated, randomly oriented powder specimens were used to obtain additional X-ray data. A sample of Ca-saturated, less than 2-micron clay from Sample 3 was prepared. Specimens were made in the aluminum holders according to the method of McCreery (33) and X-rayed over a range of 65 degrees 2θ . The patterns obtained are shown in Figure 13. The characteristic clay mineral basal spacings were resolved very poorly compared to those of the oriented specimens. The strongest line, at 3.35 Å, and a weaker line, at 4.29 Å, were due to quartz. There were no strong basal reflections for the clay minerals from the dry specimens but, when glycolated, montmorillonite peaks were apparent at 18.03 Å and 8.58 Å. The 7.20 Å kaolinite peak was not well developed in either pattern and no illite peak was shown. When the complete pattern was indexed, it was shown to contain the following montmorillonite (hk) reflections: 4.48 Å (02,11); 2.56 Å (20,13); 1.675 Å (31,24,15); and a doublet, 1.508 Å and 1.499 Å (06,33). The latter double peak was superimposed on a single broad peak and suggested that the mica mineral (montmorillonite in this case) was dioctahedral (61).

The heated K-saturated, less than 0.2-micron clay fractions, when run as oriented films, gave patterns in which the third order was always twice as intense as the second order reflection. Using Brown's chart (61, Chapter V) as an approximation, this fact showed that there was little ferric iron in the octahedral positions of the montmorillonite. Therefore, since it was dioctahedral, it was populated mainly by aluminum.

Profile Differences in X-ray Diffraction Results:

The patterns of the two clay fractions of the seven samples obtained from the solvated Mg specimens were set up together for comparison. The height and shape of the beidellite (001) peaks at 17 Å varied from sample to sample in the fine fraction. In general, the peaks were sharper at lower depths within the profile. There appeared to be an increasing amount of alteration and mixed-layering in the fine fraction from the lower depths toward the surface. A sharp illite 10 Å peak was apparent only in Sample 6 (12 feet) and above this the illite was incorporated in some manner with the beidellite. The kaolinite peak becomes sharper and higher with depth of Sample 6.

As in the fine fraction, the beidellite peaks became sharper and stronger with depth in the 2 to 0.2-micron fraction. There was no indication of mixed-layering with the illite in any of the samples. This would indicate that the particles must be exceedingly small in order to mix intimately and give the characteristic mixed-layer diffraction effects. The

illite 10 Å peak itself became better defined with depth in the profile as did that of montmorillonite.

The kaolinite peaks increased in intensity with increasing depth in the fine fraction but in the 2 to 0.2 micron clay the maximum occurred in Sample 4 (5 feet in depth). There was a definite increase in the coarse fraction from the surface down but there was very little difference in Samples 4, 5 and 6.

Other Determinations on Clay Fractions

Differential Thermal Analysis:

A differential thermal analysis diagram was made on the same sample that was used to obtain the powder X-ray diffraction pattern. The diagram, Figure 14, was made by E. C. Woodruff, using the D.T.A. equipment in Dr. W. D. Keller's laboratory. There were three main characteristics of the curve. The low temperature, endothermic peaks corresponded nicely to the established characteristics of Ca-montmorillonite with peaks occurring at 150° C and 225° C (21). The next endothermic peak, occurring at 560° C, was at a lower temperature than most montmorillonites and occurred at a temperature characteristic of some illites. The high temperature phase change was characterized by an S-shaped curve beginning about 850° C with the maximum exothermic peak occurring about 940° C. The lack of a pronounced endothermic peak in this region showed that the material probably was not trioctahedral (21). Also, since no distinct shoulder appeared at the top of the exothermic peak, there would be substitution of Al for Si in the tetrahedral layer.

The complete pattern showed such a similarity to that of Putnam clay (57) that it was concluded that the same type of clay mineral was present here. The X-ray diagrams indicated that the mineral was dioctahedral and the D.T.A. patterns that there was substitution in the tetrahedral layer. Since the illite was present in small amounts, its characteristics would not have shown up in the D.T.A. pattern and, therefore, the pattern must be attributed to the montmorillonite type mineral.

The overall D.T.A. pattern was similar to those published by Westcott for clays from Putnam subsoil, loess, gumbotil and type beidellite and was almost identical with the loess clay pattern. From all indications, beidellite was the montmorillonite type of clay mineral in these samples.

Determination of Cation Exchange Capacity:

Duplicate 25 ml. aliquots of the hydrogen clay suspension were titrated to pH 7.5 with a 0.0413N potassium hydroxide solution, using a Beckman pH meter. One ml. of saturated potassium chloride solution was

TABLE 8 -- CATION EXCHANGE CAPACITIES OF THE LINDLEY CLAYS AND OF THE REFERENCE CLAY MINERALS

Lindley Sample	2.0 to 0.2 micron	< 0.2 micron
1	30.3	56.8
2	34.3	57.5
3	39.1	61.1
4	24.8	56.5
5	23.9	50.8
6	28.1	47.2
7	15.0	36.9
	<u>Experimental</u>	<u>Literature</u>
Kaolinite H-9	4.07	6.81
Illite H-35	36.1	25.0 ¹ 35.5 ² 24.7 ³
Montmorillonite H-28	71.0	92.0 ¹

¹ A. P. I. Reports (2)

² Grim (22)

³ Ormsby (46)

added and the samples were set aside for 1 hour. The suspension was then titrated to pH 7.0 and the exchange capacity (neutralization capacity in presence of salt) per 100 gm. was calculated from the total milliequivalents of potassium hydroxide and from the concentration of the clay suspension.

The cation exchange capacity of the clays is given in Table 8. The exchange capacities of the coarse fractions were just slightly lower than that of the reference illite, and the exchange capacities of the fine fraction were between those of the reference illite and montmorillonite. If only these two minerals were present, it would be possible to offer a semi-quantitative estimation of the two constituents by considering the exchange capacities of the two references and the unknown (46). It was considered very probable that some quartz and kaolinite were present in the coarse clay and that some kaolinite was present in the fine clay. Therefore, the estimation would be valueless. However, the exchange capacity of the fine clays was sufficiently close to the value for montmorillonite that it is likely that the majority of samples 1 to 5 were members of the montmorillonite group. This is in agreement with the results of the X-ray diffraction analysis.

A comparison of the three cation exchange capacities for illite which were taken from the literature indicated the large variations which were encountered. The methods of analysis were all different. Titration curves were used in the A.P.I. reports (2), Grim *et al.* (22) used the ammonium distillation method, and Ormsby and Sand (46) employed Bower and Truog's method (6), estimating the replaced manganese. However, analyses carried out by one method and by one operator should be comparative.

Electron Microscope Examination.

Samples of fine clay (< 0.2 micron) from samples 1 and 4 and of coarse clay (2 micron - 0.2 micron) from sample 4 were examined at primary magnifications around 5000 and compared with the three reference clays. Kaolinite was recognized by its hexagonal outline in both coarse and fine clay. In the coarse clay, euhedral particles, highly opaque to electrons, were assumed to be quartz. Illite was recognized as rather large plates of uniform thickness. The fine fraction contained considerable material resembling either finely divided illite or beidellite. No rod-shape or tubular particles resembling halloysite were found, nor were there striated laths of the nontronite type.

CONCLUSIONS

From the mechanical analysis it was immediately apparent that the parent material of the different horizons was not uniform in texture. The surface layer (0 to 3 inches) and the layer at 14 feet were both appreciably different from the intervening layers, the former containing more silt and the latter more of the coarser grades of sand. There were smaller differences among the intermediate layers. The lack of well marked accumulation of clay in the subsoil strongly indicated that the whole profile was at an early stage of development. This could possibly be explained by the removal by erosion of overlying loess, traces of which can possibly still be detected by the high silt content near the surface. The original till was presumably calcareous, since it must have been derived largely from local limestones and shales. It has weathered sufficiently to have lost its carbonates, but no other deep seated changes are apparent.

X-ray examination of the sand and silt fractions showed little variation in composition with depth. Quartz, microcline and plagioclase feldspar were recognized throughout. Their sum accounted for around 100 percent of the material coarser than 5 microns. In the fine silt (5 microns to 2 microns), only about 50 percent was thus accounted for, yet no other constituents were definitely identified. It seems possible that 10 Å micas were present. Characteristically, they give a (.003) reflection in the same position as a strong quartz line at 3.35 Å. The 10 Å line might well be of extremely low intensity in a randomly oriented specimen such as that examined. In this fraction also, the peaks characteristic of quartz and the feldspars were broadened, suggesting that peak heights might afford low estimates of quantity.

It is interesting that microcline showed itself, not only throughout the sand and silt, but also in small amount in the coarse clay (2 to 0.2

micron). Its abundance attained a maximum in the 0.05 to 0.02 mm. fraction. Albite was not detected in the coarse clay and did not attain 3 percent in the finest silt (5 to 2 microns). The maximum content was found also in the 0.05 to 0.02 mm. fraction. Quartz constituted over 20 percent of the coarse clay (2 to 0.2 micron) and 30 to 50 percent of the finest silt (5 to 2 microns), with a maximum of 80 - 90 percent in the 0.25 to 0.05 mm. fraction (sample 7 alone excepted). If we apply Jackson's concept (27, 28, 29) that easily weathered minerals will be found, if at all, as coarser particles, while more resistant minerals will show themselves also in finer fractions, then the results indicate that the order of weathering is albite > microcline > quartz. This, in fact, is the commonly accepted order. The presence of microcline in the coarse clay throughout the profile strongly reinforced the conclusion that soil development was present at an early stage.

The clay fraction showed little variation in properties throughout the profile. It was essentially a mixture of a beidellite-like member of the montmorillonite group with kaolinite and illite; quartz and traces of feldspar were present in the coarser fraction. In the surface and subsurface horizons, the X-ray results indicated a higher proportion of mixed-layer clay. The deeper samples contained somewhat more perfectly crystallized material.

In general, this study has clearly demonstrated the great value of X-ray methods in elucidating the whole mineralogy of the soil. Complex mixtures of finely divided minerals can be analyzed, semi-quantitatively at least. The method is of great promise in enabling us to follow changes from primary rock minerals to products of weathering as the latter accumulate. Thus, many problems of soil formation and development become amenable to accurate evaluation. By combining these techniques with chemical studies of the exchange reactions of soil colloids, the whole relationship between the past history and the present agricultural value of our soils should become apparent.

SUMMARY

1. Seven samples were selected from a 14-foot profile of the Lindley loam. Quartz, albite and microcline were determined quantitatively in the silt and sand fractions and the clay mineral distribution was estimated in two clay fractions.
2. Mechanical analysis showed that the surface soil was contaminated with loess. There was only slight clay accumulation in the B horizon, indicating that pedologically this was a young soil.
3. There were no large differences between horizons in the amounts of

- quartz, albite and microcline in the silt and sand fractions.
4. From the distribution of the minerals with variation in particle size, the order of weathering was deduced to be albite, microcline, quartz.
 5. Beidellite-like clay was found to dominate the fine clay fractions from all horizons. Kaolinite and illite were also present. The illite occurred as a mixed-layer mineral with beidellite in the two uppermost layers of the profile.
 6. The coarse clay fraction contained quartz, kaolinite and illite, with some beidellite and traces of microcline. The kaolinite and illite peaks were less well shown by the two uppermost layers than by the underlying horizons.
 7. It was concluded that the techniques used were likely to be of great value in further studies of the mineral composition and mode of formation of Missouri soils.

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