CLAY MINERAL ALTERATION IN SOME INDIANA SOILS

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ABSTRACT

X-ray analyses of samples from thirteen soil profiles that were formed on glacial till, loess, and Mississippian limestones of Indiana indicate that (1) in some soil profiles chlorite of the parent material is changed completely to montmorillonite with intermediate stages of random mixed layers of chlorite-vermiculite-montmorillonite; (2) some of the illite of the parent material produces montmorillonite through random mixed layering of illite-montmorillonite, but the illite is not entirely altered in any profile; and (3) kaolinite may be produced as a weathering product, or it may remain unchanged from the parent material.

INTRODUCTION

For some time we have been studying the clay mineral alteration in soils of central and southern Indiana and we think it appropriate to publish the following data as a preliminary report. About 80 percent of Indiana is covered by glacial drift (Fig. 1), and thick loess deposits are found along some major streams. South of the glacial boundary (Fig. 1) limestone is a major rock type, and thick residual soils are developed on it. Our study includes surface soil profiles formed on till and loess of Wisconsin and Illinoian age and residual soil profiles developed on limestones.

1 Published with permission of the State Geologist, Indiana Department of Conservation, Geological Survey.
LABORATORY TREATMENT

Each sample was fractionated by sedimentation in water to remove the < 2 μm sizes, and standard X-ray practices were followed, using a General Electric XRD-5 unit and Ni-filtered copper radiation. Oriented samples were prepared and diffractometer data were obtained for untreated, glycolated, heated (400 °C and 450 °C), and potassium-saturated material.

![Figure 1](image.png)

**Figure 1.**—Index map of Indiana showing distribution of glacial deposits, loess, and Meramec rocks.

PRESENTATION OF DATA

Thirteen soil profiles, including three on Wisconsin till, four on Illinoian till, three on Wisconsin loess, and three on limestone bedrock, have been examined in detail, and one profile of each group will be discussed to illustrate the changes in clay mineral composition produced by weathering. After the clay minerals that are present in the profiles have been described, a mechanism will be offered to explain the data observed.

**Profile on Wisconsin till**

*Location: near Acton, SE $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 33, T. 15 N., R. 5 E., Marion County, Indiana*

The unaltered Wisconsin till contains well-crystallized illite and chlorite (Fig. 2). Chlorite starts degrading in the upper part of Zone V, and significant amounts of chlorite-vermiculite mixed layers develop in Zone IV.
Vermiculite, in the chlorite–vermiculite mixed layers, increases as degradation of chlorite continues. The mixed layers of chlorite–vermiculite become expandable in Zone III and II, and chlorite alteration reaches a maximum in the lower part of Zone I. The last remnants of chlorite in

ZONE I: Surficial soil horizon; vermiculite and chlorite–vermiculite mixed layers, and illite and degraded illite–montmorillonite mixed layers.

ZONE II: Chemically decomposed till; vermiculite and chlorite vermiculite mixed layers, and degraded illite and illite–montmorillonite mixed layers.

ZONE III: Oxidized and leached till; degraded chlorite and chlorite–vermiculite mixed layers, and partially degraded illite and mixed layered illite–montmorillonite.

ZONE IV: Oxidized but unleached till; partly degraded chlorite and chlorite–vermiculite mixed layers, and illite and degraded illite.

ZONE V: Parent till; well crystallized chlorite and illite.

Figure 2.—Diffractometer traces of samples taken from a soil developed on Wisconsin till (CuKα radiation). For each sample the top curve (A) is for an untreated oriented slide, the middle curve (B) is for the same sample after ethylene glycol treatment, and the bottom curve (C) is for the same sample heated to 400 °C.

chlorite–vermiculite mixed layers are detected in Zone II from a shoulder which develops at about 11.6 Å on the diffractometer trace when the sample is heated to 400°C. Upon heating, the vermiculite in the vermiculite–chlorite mixed layers collapses to about 10 Å while the chlorite in the mixed layers does not collapse, thus producing the 11.6 Å shoulder.

Illite is partially degraded in the upper part of the parent till, and significant amounts of illite–montmorillonite mixed layers are developed in the upper part of Zone IV (Fig. 2). In Zone III, illite is considerably de-
graded, and expandable mixed layers of illite–montmorillonite are developed. Further alteration of illite results in more expandable mixed layers, but some of the illite retains part of its original crystallinity and structural organization even in Zones II and I.

ZONE I: Surficial soil horizon; montmorillonite, montmorillonite-vermiculite mixed layers, and degraded illite and illite-montmorillonite layers.

ZONE II: Chemically decomposed till; montmorillonite-vermiculite mixed layers, highly degraded illite, and mixed layered montmorillonite-illite.

ZONE III: Oxidized and leached till; vermiculite, vermiculite-montmorillonite mixed layers, and degraded illite and illite-montmorillonite mixed layers.

ZONE IV: Oxidized but unleached till; vermiculite and chlorite-vermiculite mixed layers, and illite and degraded illite-montmorillonite mixed layers.

ZONE V: Parent till; degraded chlorite and chlorite-vermiculite mixed layers, and partially degraded illite and illite-montmorillonite mixed layers.

Figure 3.—Diffractometer traces of samples taken from a soil developed on Illinoian till (CuKα radiation). For explanation of A, B and C, see caption for Fig. 2.

Profile on Illinoian till

Location: spillway section, Brush Creek Reservoir, NE 1/4 SE 1/4 sec. 16, T. 7 N., R. 9 E., Jennings County, Indiana

Some of the illite and chlorite of the parent material are altered respectively to illite-montmorillonite and chlorite-vermiculite mixed layers, and degradation of these minerals continues progressively as weathering intensity increases upward in the profile (Fig. 3). We believe that the partly altered clay in the parent material has been inherited from the original sources of this till.
With increased alteration, chlorite structure is broken down in the upper part of Zone IV, and random mixed layers between montmorillonite-vermiculite and chlorite-vermiculite are developed. In Zone III, vermiculite, derived from chlorite, is partly transformed into montmorillonite, and the chlorite structure is completely lost. As alteration of vermiculite continues, more montmorillonite is formed and increases in abundance and crystallinity upward in the profile. In Zone I montmorillonite decreases considerably in abundance because of removal by eluviation or cation exchange by soil solutions, or both, to regrade the structure to vermiculite.

The alteration of illite produces illite-montmorillonite mixed layers. In Zone III illite is considerably degraded and montmorillonite is formed, but a part of the illite still remains unaltered in the illite-montmorillonite random mixed layers. In Zone II illite is highly altered and its identity is almost lost; at the same time montmorillonite increases in abundance and becomes better organized through intermediate stages of montmorillonite-illite mixed layering. In Zone I of the profile illite becomes distinct once again because most of the mixed layer clays and the montmorillonite have been removed downward by eluviation or have been regraded by cation exchange to form illite.

Profile on Wisconsin Loess

Location: 1 mile S.E. of Shawneetown Ferry Landing, Kentucky

Data are shown in Fig. 4 from a soil profile developed on Wisconsin loess a few miles southwest of the southwestern tip of Indiana, on the Kentucky side of the Ohio River. This profile is similar to loess profiles studied in Indiana but serves the purposes of this discussion better than the Indiana profiles because it contains fresher parent material and thus is more complete. The clay mineral alteration (Fig. 4) in this section (Leininger, Droste, and Wayne, 1958) is essentially the same as that in the previously described profiles developed on till. It is important to note that no unoxidized loess exists in this profile, and, as yet, we have not found any Zone V loess in Indiana. Clearly, the clay minerals in the upper soil zone on the Peorian loess (Wisconsin) are more thoroughly altered than in the upper zone of the profile developed on Wisconsin till (Compare Figs. 2 and 4).

Profile on Mississippian Bedrock

Location: 1 mile W. of Campdlsburff, center W. line, sec. 34, T. 3 N., R. 2 E., Washington County, Indiana

Thirty-three feet of soil derived predominantly from limestone within the Mitchell Plain (Tertiary erosion surface) was sampled with a mechanical auger. The bedrock at the bottom of the hole is St. Louis limestone. Field
evidence in the vicinity indicates that about 35 ft of St. Louis bedrock, and 120 ft of Ste. Genevieve limestone have been removed from the site by solution and erosion. An unknown thickness of Chester and Pennsylvanian limestones, shales and sandstones also may have been removed.

ZONE I: Montmorillonite and montmorillonite–vermiculite mixed layers, and degraded illite and illite–montmorillonite mixed layers.

ZONE II: Montmorillonite and montmorillonite–vermiculite mixed layers, and highly degraded illite and mixed layered illite–montmorillonite.

ZONE III: Vermiculite and vermiculite–montmorillonite mixed layers, illite and degraded illite–montmorillonite mixed layers.

ZONE IV: Degraded chlorite and chlorite–vermiculite mixed layers, illite and degraded illite–montmorillonite mixed layers.

ZONE V: Partially degraded chlorite, illite and mixed layered illite–montmorillonite.

Sand dunes within 6 miles of the hole indicate Pleistocene wind activity in the area; loess almost certainly is present in the upper part of the soil profile.

Samples were taken from the 0–3 ft interval and from each succeeding 5-ft interval down to a depth of 33 ft. X-ray diffractometer traces are shown in Fig. 5 for all samples except the 0–3 and 13–18 ft intervals. The runs indicate that illite decreases in amount upward from the base of the profile and that mixed layered material increases. In the upper 8 ft of the profile the 10 Å component is very greatly reduced, and material that expands to 17 Å is abundant. This completely expandable mineral is called montmorillonite in this report; it probably has been produced by thorough degrading of mica structures.
The kaolinite present throughout the profile is moderately well crystalized and increases in amount from the base of the profile through the 13-18 ft interval relative to the sum of the illite and the illite-montmorillonite mixed layered material. Kaolinite decreases in relative amount, how-

SOIL: Montmorillonite, degraded illite and mixed layered illite-montmorillonite, and kaolinite.

SOIL: Montmorillonite, highly degraded illite and mixed layered illite-montmorillonite, and kaolinite.

SOIL: Kaolinite, montmorillonite, and degraded illite-montmorillonite mixed layers.

SOIL: Degraded illite and mixed layered illite-montmorillonite, and kaolinite.

SOIL: Vermiculite-montmorillonite mixed layers, degraded illite and illite-montmorillonite mixed layers, and kaolinite.

Figure 5.—Diffractometer traces of samples taken from a residual soil developed on limestone (CuKα radiation). For explanation of A, B and C, see caption for Fig. 2.

ever, in the upper two intervals of the profile. It is known that kaolinite increases in abundance in the Mississippian bedrock of Indiana above the St. Louis limestone, and the increase of kaolinite in this profile may be the result of more abundant kaolinite in the parent rocks above the St. Louis limestone or may be due to the generation of kaolinite in the weathering process. The selection of the correct solution from these alternatives awaits more data.

The St. Louis limestone is known to contain a small amount of chlorite (Droste and Harrison, 1958), but the presence of this mineral or its altera-
tion products, or both, is almost completely camouflaged in this profile. The present authors feel, however, that some of the mixed layers and some of the montmorillonite may have been produced by chlorite degradation.

DISCUSSION

This study of thirteen soil profiles from Indiana yields essentially the same conclusions as a review of that literature (Barshad, 1955, 1959; Butler, 1953; Droste, 1956; Droste and Tharin, 1958; Frye, Willman and Glass, 1960; Jackson, 1959; Jackson and Sherman, 1953; Murray and Leininger, 1956; White, Bailey and Anderson, 1960) which describes the clay mineral alteration produced by weathering in materials of original composition similar to that of these soils. It is interesting to speculate on the mechanisms of these alterations. The following discussion is an attempt to explain the changes that have been observed on the diffraction diagrams.

Alteration of Chlorite

In all the profiles examined the chlorite group of minerals is the first to show changes in its structure under the influence of weathering. In order to suggest a mechanism to explain the changes observed in the chlorites, a few remarks concerning several of the features of chlorite structure will be helpful. It is generally believed that chlorite is a regular interlayering of mica-like (negatively charged) and brucite-like (positively charged) sheets. These sheets are held to one another primarily by electrical attraction and by hydrogen bonds between the hydrogens of the hydroxyls of the brucite sheets and the oxygens of the mica sheets.

The octahedral layer of the mica sheet may possess dioctahedral or trioctahedral coordination of \( \text{Mg}^{2+}, \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Fe}^{3+}, \text{Al}^{3+}, \text{Cr}^{3+} \), and other less common cations with oxygen and hydroxyl. The tetrahedral cations of the mica layer may have an \( \text{Al}:\text{Si} \) ratio of somewhat less than 1:3, as in ideal mica, to a ratio of 1:1. Though a large number of combinations of cations are possible in the mica sheet, the overall result is a negative charge for this layer.

The brucite sheet of the chlorite lattice is an octahedral coordination of \( \text{Mg}^{2+}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Al}^{3+} \), and other less common cations with hydroxyl ions. Because this layer must possess an overall positive charge, some trivalent cations must be present.

The kind and amount of substitution in the mica sheet (or brucite sheet) in large part govern the type of substitution in the brucite sheet (or mica sheet). For example, if the mica sheet has minimal substitution of Al for Si and an electrically neutral dioctahedral layer, the brucite sheet will have the lowest possible number of trivalent cations. Conversely, a high degree of substitution of Al for Si along with an electrically neutral dioctahedral
layer in the mica sheet will necessitate a large number of trivalent cations in the brucite sheet so that electric neutrality can be maintained. Of course, the excess of electrons in the tetrahedral layer of the mica sheet brought about by high Al substitution for Si can be balanced partly by trivalent cations in trioctahedral coordination in the octahedral layer of this sheet.

The crystallographic dimensions of chlorites differ in response to the wide variation in their compositions. Brindley, Oughton, and Robinson (1950), Kovalev (1956), and other authors have shown that the c-axis distance becomes greater with less substitution of Al for Si in tetrahedral positions. The greater c-axis distance may mean that the brucite layer “thickens” and thus is “stretched” in the c-axis direction. Kovalev (1956) indicated that the b-axis dimension depends on the cations in octahedral coordination. For example, a high population of ferrous iron causes an increase in the b-axis dimension, and thus a thinning of the brucite sheets results. This subject was discussed at an earlier conference (Bradley, 1959).

There is no doubt that the kind and amount of substitution in the tetrahedral and octahedral layers play some role in the nature and rate of weathering, and, ideally, one should know the details of these populations in order to be certain of the reactions occurring during alteration. We cannot obtain these data for the chlorite of our samples, because chlorite is not a dominant mineral in the clay-size fraction of the bedrock and soils of Indiana. Chlorite is known from all the Paleozoic systems and from all the major glacial deposits of Indiana, but in very few samples does it make up more than 30 percent of the clay minerals, and in most samples it makes up less than 15 percent of the clays. Although the chemical composition of the chlorite studied here is not known in detail, diffraction effects indicate that it is an iron-rich chlorite and has only a moderate amount of Al substitution in the tetrahedral layers.

Evidence shown in Figs. 2, 3 and 4 and gleaned from the literature previously cited indicates that in these profiles alteration begins in the brucite layer. This does not mean, however, that some changes do not occur in the mica layer at the same time. As mentioned above, the brucite layer has an overall positive charge produced by trivalent cations substituted for divalent cations in the octahedrons. As alteration proceeds, hydrogen ions (protons) become attached to externally opposed hydroxyls at the edges of the lattice. As each hydroxyl is changed to water, half of a divalent cation charge and one-third of a trivalent cation charge are no longer needed to balance the negative charge of the hydroxyl, and an excess of positive charge starts to build up. As proton addition continues, two, three, or four edge hydroxyls are changed to water, and the cation develops a hydration envelope. As hydroxyls change to water and become neutral, a certain amount of the octahedral cations go into solution and leave the structure. Only those cations necessary to balance the negative charge
of the mica layers remain in the lattice. The general scheme of a lattice gradually changing from one of cations in octahedral coordination with hydroxyls to one of cations surrounded by water continues throughout the brucite layer. It is worth mentioning that there probably is an "order of solubility" of the cations in the brucite layer; in general, it is thought to be Fe$^{2+}$, Mg$^{2+}$, Fe$^{3+}$, and Al$^{3+}$ in the weathering environment.

The destruction of all brucite sheets does not take place at the same time, and the alteration does not proceed at the same rate; therefore, a mixed layering of vermiculite can develop in the chlorite structure. This type of mixed layering has been called "heterogeneous" by Grim, Bradley and White (1957) and "segregated" by Harrison and Murray (1959). The smaller octahedral cations may be removed from the interlayer positions by base exchange reactions with calcium, sodium, potassium, and other cations. After the chlorite is thoroughly degraded (essentially all the hydroxyl changed to water), there is, at least in some soil profiles, a reorganization of the altered components of the brucite sheet, so that a better "stacked" vermiculite is formed. Jackson (1960) has suggested that this reorganization may result from polymerization of aluminoxydronium complexes. Continuous alteration of the components of the brucite sheet produces a structure that will expand completely with glycol and that gives the appearance of montmorillonite on a diffraction diagram. In the soils studied, the 14 Å mineral has not been altered beyond the "montmorillonite" stage; further alteration would bring about destruction of the mica sheet. (This subject is considered next in illite alteration.) It must be remembered that minor changes take place in the mica layer of chlorite at the same time that the brucite layer is being thoroughly altered.

**Alteration of Illite**

Those persons using the term illite usually mean the mica clay mineral as described by Grim, Bray and Bradley (1937). The octahedral layer of the structure may be dioctahedral or trioctahedral, and the mineral contains less potassium than "true" mica because there is less tetrahedral Al substitution for Si in this clay mineral than in mica. There also may be more water in illite than in mica, but mica polymorphs can be recognized in some samples of illite. This can only be true if some rather substantial grain interiors persist unaltered. The negatively charged mica sheets are held together by potassium ions, and the size of the potassium ions allows them to fit snugly into the cavities formed by the hexagonal loops of silica tetrahedrons.

It is generally agreed that biotite (trioctahedral) is altered more rapidly by weathering than muscovite (dioctahedral), and it follows that dioctahedral illites alter more slowly than trioctahedral illites. Serratosa and
Bradley (1958) and Basset (1960) have shown that in muscovites the proton of the hydroxyl groups of the octahedral layer is directed at a 45° angle toward the neighboring oxygens. These investigators reported that in biotites the proton of the hydroxyl of the octahedral layer is at the top of the hydroxyl and is directed into the cavity, where the potassium is located. The orientation of the octahedral protons of the hydroxyls in the biotite structure gives rise to a much more inhospitable environment for potassium than in muscovites. These proton orientation data and the fact that octahedral iron and magnesium are more easily removed from mica structures than is aluminum indicate why muscovite is more stable than biotite in weathering.

The initial alteration of illite usually is described as the removal of potassium ions and the introduction of water between the silicate sheets. Harrison and Murray (1959) have suggested that the mechanism is an exchange reaction (mass action) between potassium and hydronium ions. Garrels and Howard (1959), from laboratory work on muscovite in distilled water, represented the reaction by the simple equation,

$$K \cdot \text{mica} + H^+ = H \cdot \text{mica} + K^+,$$

and pointed out that the reaction also involves the loss of aluminum and silicon from the silicate sheet. If the interlayer, tetrahedral, and (or) octahedral ions released from the mica lattice are not removed from the environment, equilibrium conditions soon will be reached. As long as eluviation (leaching) removes the potassium, aluminum, and silicon ions from the environment of reaction, the lattice will continue to yield these ions. It is interesting to note that the ions “shed” by the alteration of chlorite may retard alteration of illite in the early stages of chlorite and illite alteration.

The protons that enter the interlayer positions and those present anywhere around the edge of the structure attack the oxygen and hydroxyls of the octahedral layer of the lattice. The mechanism envisioned is similar to the one discussed in the alteration of the brucite sheet of chlorite, but one difference is worth mentioning. Each oxygen of the octahedral layer in illite is also a part of the tetrahedral layer; therefore, a proton added to one of these oxygens to produce a hydroxyl ion involves an alteration of a bond in both the octahedral and tetrahedral layers. The change of a hydroxyl ion to water in the octahedral layer of illite is essentially the same reaction as described for the brucite sheet in chlorite alteration. The disruption of the octahedral coordination in illite to produce hydrated cations has a pronounced effect on the entire structure. The loss of the brucite layer in chlorite produces an expandable sheet silicate structure; the destruction of the octahedral layer in illite (and the mica portion of chlorite) produces oxides and hydroxides of the cations. The reorganization of the altered component of illite produces such minerals as kaolinite and the
hydrates of alumina, magnesia, iron oxides, and silica; the minerals produced are dependent on the population of the original mica layer.

Before the destruction of the octahedral layer of illite is completed, the illite may go through a number of intermediate weathering "stages." The minerals of these stages are formed through degradation of illite to produce mixed layers of several types. The intermediate products are in part dependent on the type of illite present in the parent material; iron-rich or magnesium-rich trioctahedral illite is likely to produce a vermiculite, and aluminum-rich dioctahedral types may produce a lattice that will expand to 17 Å with glycol and that will not go through a vermiculite phase. In some profiles it is difficult to interpret the alteration stages in the 10 Å mineral because the diffraction effects of chlorite and montmorillonite mask the details of the illite alteration. This problem certainly exists in the study of Indiana soils. No matter what the intermediate steps are, under suitable conditions of vegetation, time, climate, and topography, the illite in the parent material probably will develop a completely expandable lattice.

Such a completely expanding lattice has not yet formed in the soils studied, and it is not known what changes in the previously mentioned factors would be necessary to produce a totally expanding lattice. It is our feeling, however, that it is not just time, for old residual softs beyond the glacial boundary and on the highest erosion surfaces (Tertiary) in Indiana still contain significant amounts of nonexpandable 10 Å minerals. The fact that some illite of much of the bedrock and drift of Indiana is a 2 M muscovite-like clay mineral may be the reason that some of the 10 Å mineral is only partly altered by weathering.

All that can be said now is that the minerals producing the 10 Å and higher order peaks in the investigated till and loess of Indiana are several in number. Muscovite and biotite are present in the sand and silt sizes and very probably exist, at least in small amounts, in the clay size. Illite of unknown compositional and structural variation is also common. The combination of dioctahedral and trioctahedral lattices and the polymorphs of mica give rise to several rates of alteration in the 10 Å minerals: the more crystalline (better "stacked") forms change at a slower rate than the less crystalline forms. The uppermost zones of Indiana soils studied contain some 10 Å mineral that is only slightly altered, but lower in the same profiles a large amount of the 10 Å mineral is thoroughly altered.

CONCLUSIONS

Illite and lesser amounts of chlorite are present in the parent material from which almost all the soils of Indiana are formed. Moderate to large amounts of kaolinite are also found in some parent material. The soil-forming processes significantly modify the illite and chlorite to produce
an expandable suite of clay minerals culminating in a product that commonly is called montmorillonite. The process of chlorite alteration probably is characterized by several intermediate steps: (1) random mixed layers of chlorite and vermiculite, (2) vermiculite, (3) random mixed layers of vermiculite and montmorillonite, and (4) montmorillonite. In all the soil profiles studied the chlorite has been completely changed to one of the intermediate products or to montmorillonite. The illite alteration is not as thorough as that of chlorite, and the weathering products are: (1) random mixed layers of illite and montmorillonite, or random mixed layers of illite, vermiculite, and montmorillonite, (2) random mixed layers of vermiculite and montmorillonite, and (3) montmorillonite. In all the profiles studied some illite maintains its identity even in the upper soil zone. It is not known, however, what changes must occur in the weathering environment of these Indiana soils to bring about the total destruction of illite to produce a montmorillonite.

The increase of kaolinite content in the upper levels of some of the soils studied may result from an unequal distribution of kaolinite in the parent material or from an alteration of clays or other silicate minerals in the parent material.

The abundance of montmorillonite in the uppermost soil level is due to: (1) alteration of illite and chlorite in place and (2) “contamination” of the upper soil zone by loessial clays that alter readily to montmorillonite.

REFERENCES


