

# Clays and Shales of Indiana

INDIANA DEPARTMENT OF CONSERVATION  
GEOLOGICAL SURVEY BULLETIN 31



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# Clays and Shales of Indiana

By JACK L. HARRISON *and* HAYDN H. MURRAY

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INDIANA DEPARTMENT OF CONSERVATION

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# CLAYS AND SHALES OF INDIANA

By Jack L. Harrison and Haydn H. Murray <sup>1</sup>

## ABSTRACT

Modern concepts of clays as assemblages of discrete minerals form the basis for the first reevaluation of the clays and shales of Indiana since 1933. Brief explanations of the fundamentals of clay mineralogy and the major methods of investigation of clays enable the reader to understand more fully the data obtained.

Tabulated mineralogic, ceramic, and chemical data for 251 samples chosen from about 1,000 samples give a perspective of the types, properties, and locations of clays in Indiana. These data reveal that Indiana has large reserves of clay suitable as raw material for many types of products. The most notable reserves are several abundant clays and shales for manufacturing structural clay products and cement, the Pennsylvanian underclays for use in refractories and structural clay products, and certain shales, such as the New Providence Shale, for producing lightweight aggregate.

## INTRODUCTION

Clay is an abundant raw material that has an amazing variety of uses. The term clay is somewhat ambiguous unless specifically defined. As used in this report, clay is defined as a natural earthy fine-grained material composed largely of a limited group of crystalline minerals known as the clay minerals. Shale is defined as a rock composed of more than 50 percent clay.

During the past 30 years a new technology that has made possible a much more critical study and evaluation of clays has been developed. As the clay minerals are so fine grained that most particles cannot be resolved even with a high-power petrographic microscope, special techniques for studying the clay minerals, such as X-ray diffraction, differential thermal analysis, and electron microscopy, must be used. <sup>2</sup>

<sup>1</sup> Present address: Georgia Kaolin Company, 433 North Broad Street, Elizabeth, N. J.

<sup>2</sup> The following example gives some idea of the fineness of the clay minerals, most of which are finer than 2 microns (1 micron equals about 1/25,000 of an inch): A layer of clay minerals thinner than a human hair spread over a postage stamp consists of more than 10 billion particles.

At present most clay used in Indiana goes into making structural clay products, such as brick, tile, sewer pipe, flue lining, and conduit pipe. Some clay materials are much more suitable for these products than others, and some clays cannot be used at all. Certain types of clay are used for refractory brick, pottery, and insulators. No single clay material is satisfactory for all purposes, as the requirements for most products are specific.

#### PURPOSE AND SCOPE

This study of the clay resources in Indiana was made by the Indiana Geological Survey to describe more accurately those clays that are now being used commercially and to assess critically the reserves of clay and shale in Indiana for future use. The study encompassed two areas of investigation: a systematic laboratory evaluation of the mineralogy and the physical properties of ceramically important clays and shales and a geologic study of the character and distribution of rock formations that contain or are likely to contain potentially commercial clays and shales.

The geologic study, carried on during the summers of 1950 through 1955, consisted of stratigraphic measurements, lithologic descriptions, detailed sampling of outcrops, study of lateral areal lithologic variations, and correlations of the clay and shale beds. The mineralogic evaluation of about 1,000 samples was accomplished from 1952 through 1959 by using X-ray diffraction, differential thermal analysis, and the petrographic microscope. Certain physical properties, such as plasticity, shrinkage, fired color, fusion point, strength, absorption, and apparent porosity, were also determined for about 300 selected samples.

#### PREVIOUS CLAY STUDIES IN INDIANA

Because the clay industry in Indiana is economically important, various publications have been issued by the Indiana Geological Survey and its predecessors. The first comprehensive treatment, by Blatchley (1905), gave a brief treatment of the general geology of the clay deposits, detailed descriptions of clay deposits indexed by county, and a description of the active clay industries in 1904.

Logan (1919) described the geology, sample locations, and physical characteristics of what was then known as kaolin (later identified as the kaolin mineral halloysite). In part V of the "Handbook of Indiana Geology," Logan (1922) described the geology of the commercial clay deposits and reviewed the clay industries in the State in 1922.



A comprehensive study of the clay resources of Indiana by Whitlatch was published in 1933. The physical and chemical properties of clay and ceramic technology were described, and the geologic distribution of Indiana clays, the clay industries and their associated clay deposits, and some properties of certain undeveloped clay deposits were discussed.

Callaghan (1948) studied the endellite (halloysite) deposits in Lawrence County and described the geology and mineralogy in some detail. Murray (1955) and Harrison (1960) compiled directories of producers and consumers of clay and shale in Indiana, in which the geographic locations, product description, raw material used, and related information about each listing were given. Murray (1957) wrote a study of the use of certain Indiana underclays as bonding clays for specific use in foundries; Murray and Smith (1958) studied certain strategically located shale deposits and found several that could be used in manufacturing lightweight aggregate; and Harrison (1961) wrote a study of the refractory clays of Indiana.

#### ACKNOWLEDGMENTS

Appreciation is expressed to the many individuals and corporations who gave permission to collect samples from their properties. Special thanks are due Dr. Thomas F. Bates of The Pennsylvania State University for supplying copies of electron micrographs and for permission to reproduce them (pls. 1 and 2).

## CLAY MINERALS AND CERAMIC PROPERTIES

### MINERALOGIC COMPOSITION OF CLAYS

Clays are composed of clay minerals and nonclay minerals. Clay minerals are certain groups of hydrous aluminum, magnesium, and iron silicates that may contain calcium, potassium, or other ions. Both clay minerals and nonclay minerals influence the properties of a clay material. For understanding the relationships between clay minerals and the properties of a clay material, a short summary of the structures and compositions of clay minerals is necessary.

Any classification scheme tends to impose a certain rigidity, and as more information becomes available, revision of the scheme is necessary. Grim (1953, p. 27) proposed a tentative classification based on the crystal structures of various clay minerals. This classification is relatively simple and workable, and a version somewhat revised follows:

- I. Amorphous
  - Allophane group
- II. Crystalline
  - A. Two-layer types (structures composed of one sheet of silica tetrahedrons and one sheet of alumina octahedrons)
    - 1. Equidimensional
      - Kaolin group
      - Kaolinite, dickite, nacrite
    - 2. Elongate
      - Halloysite group
  - B. Three-layer types (structures composed of two sheets of silica tetrahedrons and one central dioctahedral or trioctahedral sheet)
    - 1. Expanding lattice
      - (a) Equidimensional
        - Montmorillonite group
        - Montmorillonite, saucanite
        - Vermiculite
      - (b) Elongate
        - Montmorillonite group
        - Nontronite, saponite, hectorite
    - 2. Nonexpanding lattice
      - Illite group
  - C. Regular mixed - layer types (ordered stacking of alternate layers of different types)
    - Chlorite group
  - D. Random mixed-layer types (random stacking of layers of two or three different types)
  - E. Chain- structure types (hornblende -like chains of silica tetrahedrons linked together by octahedral groups of oxygens and hydroxyls containing Al and Mg atoms)
    - Attapulgite, sepiolite, palygorskite

The structure and composition of each mineral shown in this classification are described briefly in the paragraphs that follow.

Allophane, the name applied to "any amorphous substance which may be present in clay materials as extremely fine material and which has an indefinite composition" (White, 1953, p. 634), is commonly considered to be composed of hydrated oxides of aluminum and silicon and also iron in many samples of allophane. It is commonly associated with halloysite and generally is glassy-looking when fresh. The purest material is colorless, but the mineral is also blue, pale green, brown, or yellow. Evidently, allophane is not completely amorphous because X-ray data indicate that it has a more ordered structure than glass has.

All layer clay minerals are composed of two fundamental subunits: silica tetrahedra and alumina octahedra. Silica tetrahedra are built of four oxygen atoms at the corners of a tetrahedron and a silicon atom at the center (fig. 1). Alumina octahedra are composed of six hydroxyl ions at the corners of an octahedron and an aluminum atom at the center. The oxygen atoms and hydroxyl ions are actually closely packed; the representation in figure 1, to illustrate the positions of the silicon and aluminum atoms, shows them at some distance.

Silica tetrahedra are united into unit layers by sharing oxygen atoms at the base of the tetrahedra; thus the ratio of silicon atoms to oxygen atoms in a unit layer is 1 to 2. Alumina octahedra are joined together into unit layers by sharing coincident hydroxyl ions. In alumina octahedral unit layers only two-thirds of the octahedra contain aluminum atoms; thus the ratio of aluminum to hydroxyl is 1 to 3.

The kaolin minerals are hydrous aluminum silicates and have the approximate composition of  $2\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ . Kaolinite is the most common of the kaolin minerals. The structure of kaolinite consists of a single silica tetrahedral sheet and a single alumina octahedral sheet combined into the kaolinite unit layer (fig. 1). These unit layers are stacked one on top of the other; variations in orientation of the unit layers in stacking cause differences in the kaolinite mineral itself and lead to the differentiation of the various minerals in the kaolin group. The details of the structure of the kaolin minerals were summarized by Grim (1953, p. 46-55).

Dickite and nacrite are identical to kaolinite in composition, but they differ from kaolinite in the manner in which the unit layers are stacked one upon the other. Dickite and nacrite are rarely found except in some hydrothermal deposits.

Halloysite is an elongate kaolin mineral that has two forms. One form has the same chemical composition as kaolinite; the other has an additional  $2\text{H}_2\text{O}$ . The hydrated form dehydrates to the other form irreversibly at temperatures of the order of  $60^\circ\text{C}$  or at lower temperatures when it is exposed to relative humidities less than about 30 percent. At present the terminology of these two forms is somewhat confused. Bates, Hildebrand, and Swineford (1950) proposed that the hydrated form of halloysite consists of rolled or curved kaolin unit layers; such a structure is consistent with what is seen on electron micrographs. On dehydration many of these tubes collapse and split or unroll. A representation of the hydrated halloysite structure is shown in figure 1.

Minerals of the montmorillonite group are composed of layers consisting of two silica tetrahedral sheets and a central alumina octahedral sheet. Because of substitutions of some aluminum for silicon in the silica tetrahedra, the lattice is always unbalanced

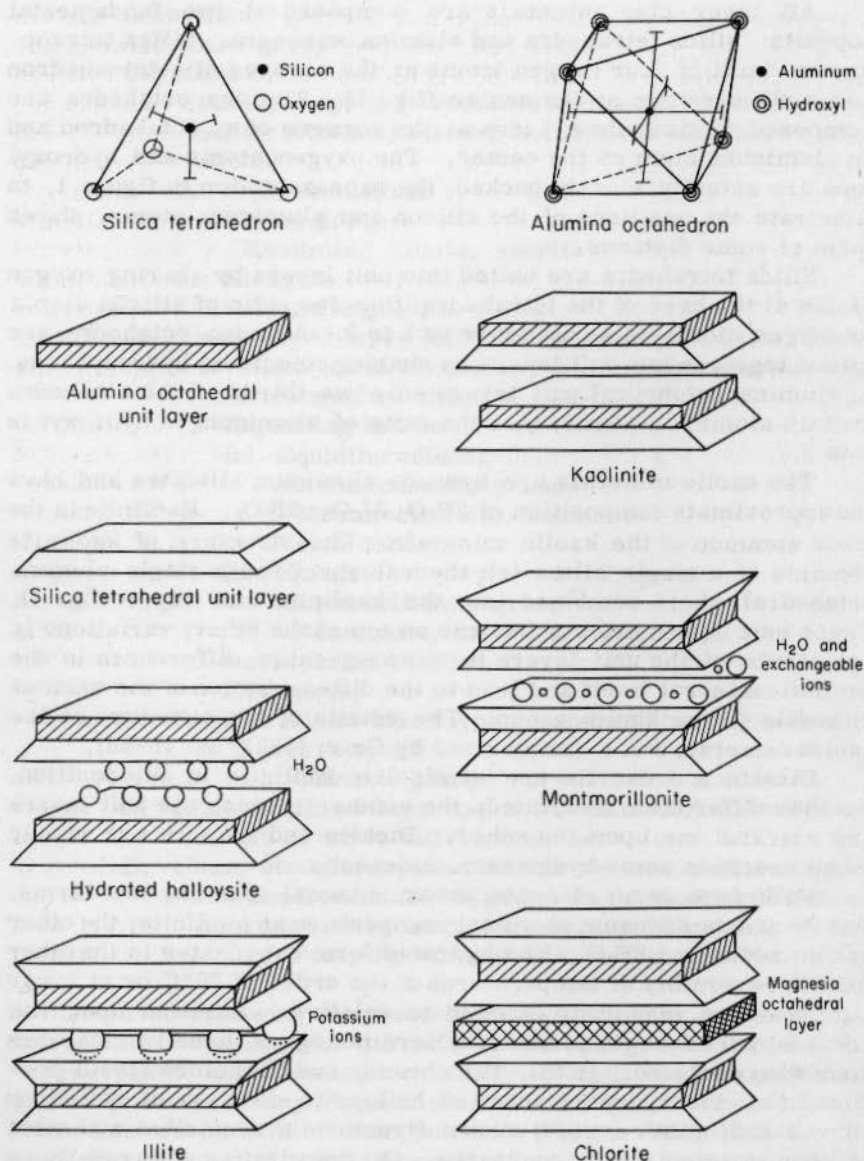


Figure 1.--Diagrams of a silica tetrahedron and an alumina octahedron, which are the fundamental building blocks of most clay minerals, and schematic representations of crystal structures of major clay mineral types.

chargewise. Also, because oxygen or hydroxyl planes are adjacent when these layers are stacked, the bonds are weak between the layers; therefore, water or other polar molecules can enter between the layers and cause expansion (fig. 1). Sodium, calcium, magnesium, iron, or other cations also can be present between the layers; these ions are generally exchangeable. There is a relationship between the thickness of the water layers and the type of exchangeable ion. The theoretical formula for the mineral montmorillonite is  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O} \cdot n\text{H}_2\text{O}$  (interlayer). But montmorillonite always differs from the theoretical formula because of substitutions in the lattice. These substitutions are the major basis for differentiation of the other minerals in the montmorillonite group. Sauconite results when aluminum is replaced by zinc. Both montmorillonite and sauconite are equidimensional.

Nontronite, saponite, and hectorite are elongate minerals of the montmorillonite group. Nontronite results from the replacement of aluminum by iron, and saponite and hectorite result from the replacement of aluminum by magnesium. Hectorite also contains lithium.

Vermiculite is an equidimensional expandable clay mineral. The structure consists of a unit layer made up of two silica tetrahedral sheets and a central magnesium and iron octahedral sheet separated by two layers of water molecules and adsorbed magnesium and calcium ions. Vermiculite differs from montmorillonite in that the unit layers of vermiculite will not expand as much as those of montmorillonite because the vermiculite layers show less randomness in stacking.

Illite is a general term for the mica-like clay minerals. The basic structure is a layer composed of two silica tetrahedral sheets and a central octahedral sheet. This structure is similar to that of montmorillonite except that more aluminum ions replace silicon in the tetrahedral sheet, a condition which causes a charge deficiency that is balanced by potassium ions. The potassium ions act as a bridge between the layers (fig. 1) and tie them together so that illites are nonexpandable.

Several rather common clay minerals of variable composition are species of the chlorite group; they are examples of regular mixed-layer types (fig. 2). The structure of all true chlorites consists of alternate mica layers and brucite layers. The brucitelike layer can be magnesium, aluminum, or iron hydroxide or a combination of all three. The mica layer is very similar structurally to illite discussed above. The structure of chlorite is shown in figure 1. The various members of the chlorite group are differentiated on the basis of the kind and amount of ionic substitution.

A group of abundant and therefore important clay minerals is the group known as random mixed-layer clay minerals (fig. 2). The clay minerals in this group are not mechanical mixtures of different

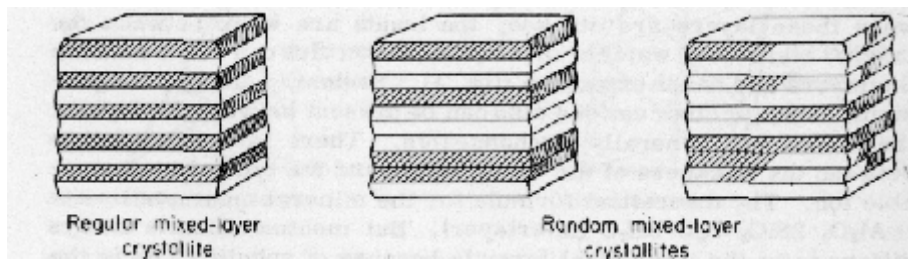


Figure 2, --Schematic representations of regular and random types of mixed-layer clay mineral crystallites.

species but are composed of two or more species interlayered in individual crystallites. The common mixed-layer clay minerals in sedimentary rocks and oil, are illite-montmorillonite, chlorite-vermiculite, and vermiculite-montmorillonite. The interlayering may be regular, as AB-A-B, etc. , where A and B represent individual species, such as mica and brucite in chlorite, or interlayering may be random, as A-B-B-A-B-A. etc. The randomness may also exist within the unit layers as well as normal to the unit layers (fig. 2).

The random types of mixed-layer clay minerals are the most abundant and commonly are intermediate products in the alteration of one clay mineral species to another. For example, under the influence of certain weathering conditions, illite tends to be altered to montmorillonite. The change is not instantaneous but is accomplished by the formation of an intermediate mixed-layer illite-montmorillonite. As weathering proceeds, the ratio of montmorillonite to illite increase, until all the illite is converted to montmorillonite.

The last group of clay mineral, to be discussed is the chain-structure type of which attapulgite, sepiolite, and palygorskite are examples. These minerals consist of double silica chain, linked together by octahedral groups of oxygens and hydroxyls containing Al and Mg atoms (Bradley, 1940). Sepiolite is also a hydrous magnesium silicate but differs structurally in certain details from attapulgite. Palygorskite is a name used in eastern Europe for a mineral that appears to be similar to attapulgite, a relationship that need, further study. No representatives of this group of clay minerals have been recognized in Indiana to date.

#### CHEMICAL COMPOSITION OF CLAY

Clay, vary widely in chemical composition and range from relatively pure, kaolinites to clay, that contain a wide variety of

chemical elements. Chemical analysis of clays can rarely be used alone to distinguish between clay mineral types, but it is a valuable supplement to other methods of identification, such as X-ray diffraction and differential thermal analysis, both of which are described in a later section. Kaolin minerals can generally be distinguished from montmorillonite, illite, and chlorite types of minerals by the  $\text{SiO}_2:\text{Al}_2\text{O}_3$  ratio. The ratio is 2:1 in kaolins and approximately 3:1 in the others. The clay minerals occur so rarely in monomineralic deposits, however, that chemical analysis is not a dependable method of identification. Attempting to calculate the mineral composition from bulk analysis alone is unwise because most clays contain more than one species of clay mineral or at least nonclay minerals. More significant is the fact that except for the kaolin minerals the composition of the different species varies according to the substitutions in the layers. Chemical analyses are important, however, as a general control in certain uses where specifications are required. For example, in certain types of ceramic uses iron content must be very low, and in some refractories the alumina content must be above a certain minimum. Many other chemical specifications could be cited that would give additional evidence of the value of chemical analyses for specific controls.

#### IDENTIFICATION OF CLAY MINERALS

*X-ray diffraction*- In the past 25 years X-ray diffraction techniques have become widely used, and considerable information based on these techniques has been published. X-ray diffraction patterns are directly related to the structure of minerals and therefore are an excellent means for identifying the different structural groups which characterize clay minerals.

In identifying clay minerals, the first order reflections from the basal planes are the most important. Figure 3 shows diffraction patterns of a sample prepared in both random and oriented mounts. Random mounts are prepared by packing powdered samples in suitable holders so that the fragments of the powders are not similarly oriented. Oriented mounts are preparations in which the clay flakes are nearly parallel; this condition is achieved by allowing the sample to settle out of water onto a glass slide. Distinction between montmorillonite, vermiculite, and chlorite on the basis of basal reflections is difficult for some samples. Certain types of chlorite are difficult to distinguish from kaolinite. Thus supplementary methods, such as heat treatment and application of organic liquids, are often necessary to make accurate identifications.

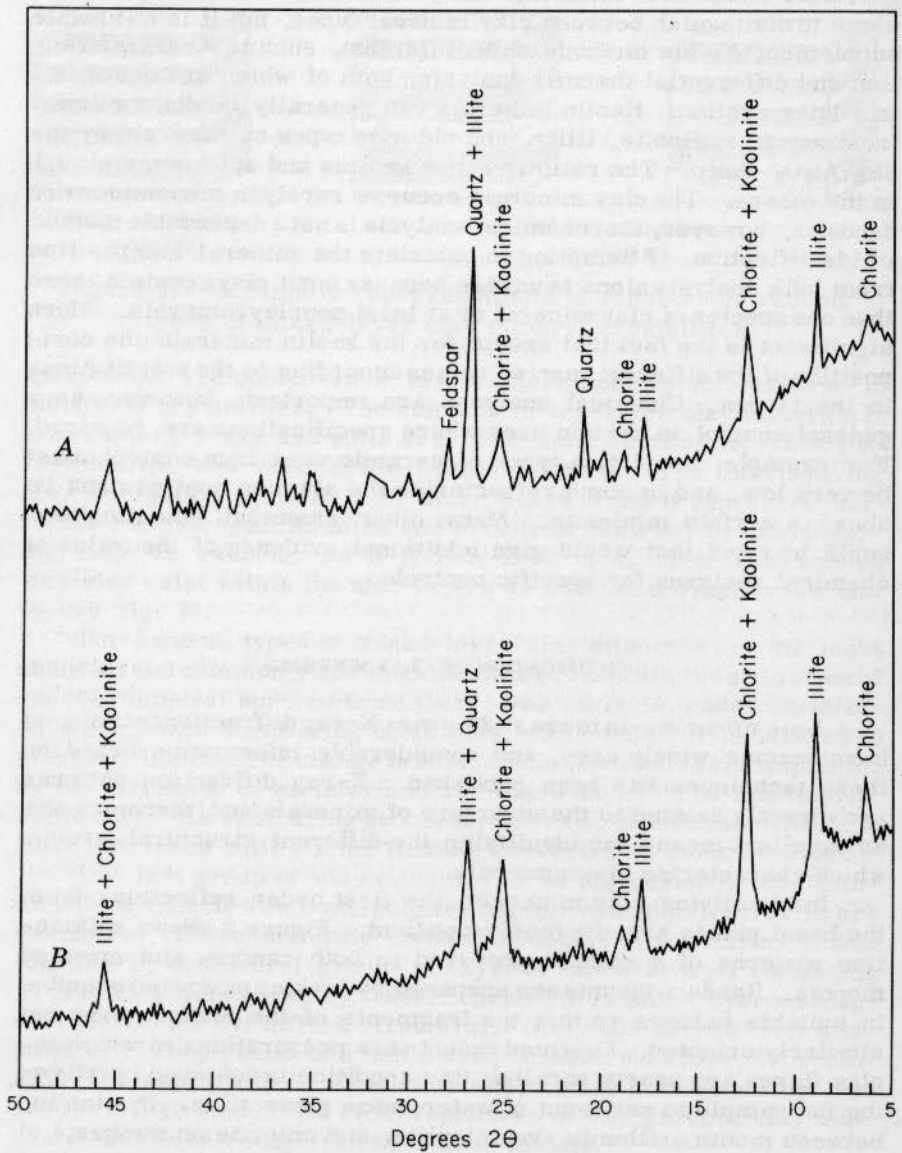


Figure 3.--X-ray diffraction patterns. A, Random mount of raw sample. B, Oriented mount of <2-micron fraction of same sample.



In addition to identifying the major structural groups of the clay minerals, careful X-ray diffraction work permits identification of structurally similar minerals of different chemical composition. Differences in the stacking arrangement of the unit layers in the clay minerals can also be detected. This is an important consideration for kaolinite because of its measurable effect on certain industrial properties. Information on crystal imperfection and shape and size of particles can be obtained by careful observation of the diffraction patterns.

Although many methods are used to identify and study the clay minerals, X-ray diffraction is probably the most widely used. With new techniques and developments the X-ray diffraction method, already rapid and precise, will be even more useful in clay mineral research in the future. In addition to the identification of the clay minerals in clay materials, quartz, calcite, pyrite, and other nonclay minerals can be identified.

*Differential thermal analysis.*-Another important tool in the characterization of clay materials is differential thermal analysis (DTA.). With suitable apparatus DTA determines and records the temperatures and intensity of thermal reactions. The clay material is heated at a controlled rate to an elevated temperature usually of the order of 1,000°C. The thermal reactions during which heat is absorbed or released are recorded. These reactions involve dehydration, oxidation, destruction of the crystal lattice structure, changes in crystalline phase, and others depending upon the material present in the sample. The temperatures of these thermal reactions, their intensity, and their general character provide information for identifying materials in the sample. Grim (1951) has covered the history, methods, and applications of DTA and calls attention to the experimental factors influencing the results.

DTA is not a very accurate or definitive method, but it is an important technique that is useful when it is used properly and in conjunction with X-ray diffraction, electron microscopy, and chemical analysis. Figure 4 shows idealized DTA curves of some clay minerals. The DTA. method has been used as a rapid, inexpensive, and accurate method for quantitative determination of amounts of specific minerals in relatively pure materials. In addition to usefulness as a method to aid in identifying the clay minerals, DTA is a precise method of determining the temperature of dehydration and the temperature and nature of high temperature phase changes.

*Electron microscopy.*-The electron microscope has proved to be a valuable tool in clay mineral research in the past 15 years. By electron microscopy many clay minerals have been shown to have morphologic characteristics that can be used to help in their identification. Detailed studies at high magnification have provided key

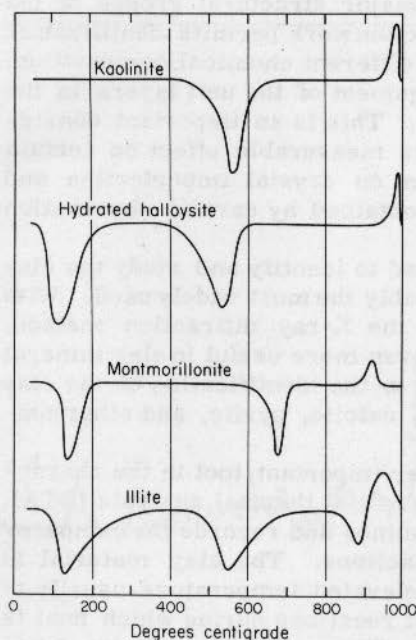


Figure 4.--Idealized differential thermal curves.

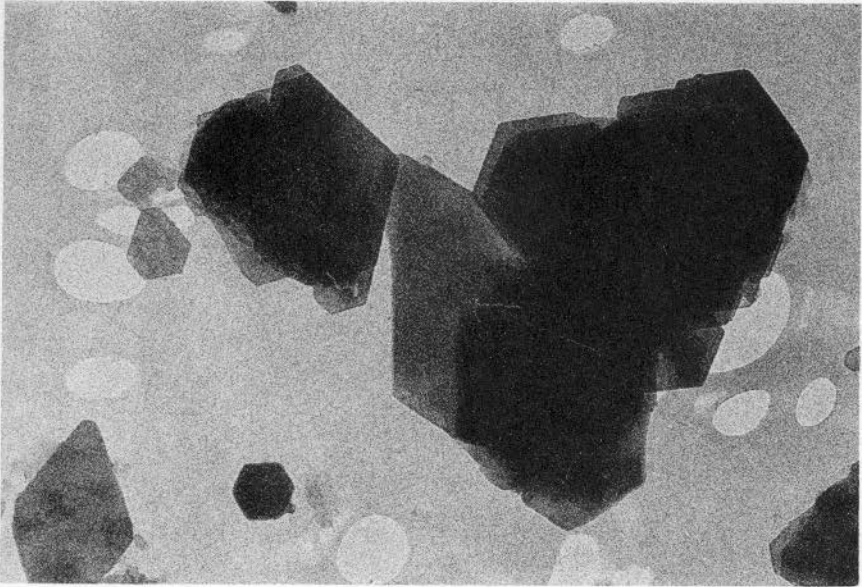
structural information that was not obtainable by other means. Bates (1955) has reviewed the usefulness of the electron microscope in clay mineral studies.

The common minerals in the kaolin group have a diagnostic morphology evidenced by electron micrographs of kaolinite and halloysite (pl. 1). Illite (pl. 2A) does not give as distinctive an electron micrograph as the kaolin minerals do. As the result of more precise and additional information, however, the illites would undoubtedly reveal certain distinctive morphologic variations. Electron micrographs of the montmorillonite minerals are difficult to interpret because the morphology is somewhat dependent on the way the sample is prepared. Montmorillonite generally gives a very thin indistinct appearance (pl. 2B).

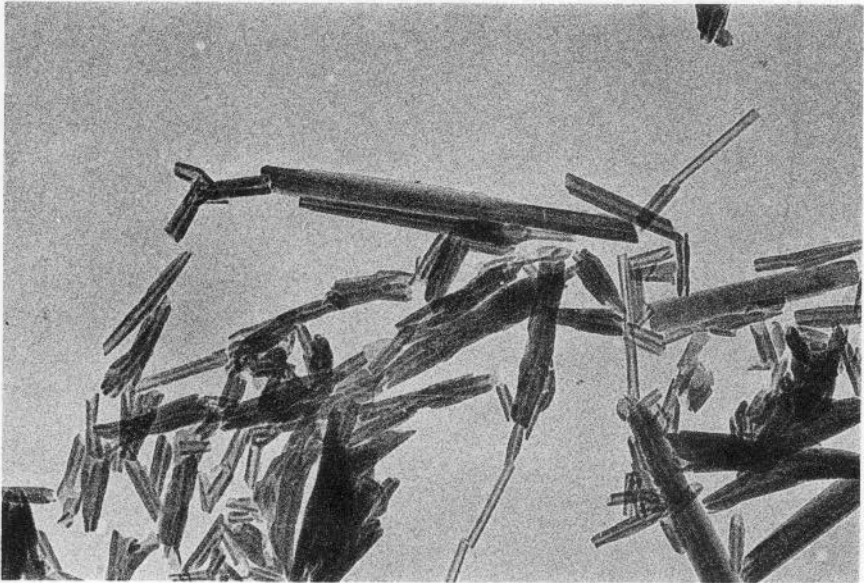
Recent studies of fired specimens of kaolinite have revealed the presence of small mullite crystals which appear to have a general hexagonal orientation inherited from the kaolinite crystal (Comeforo, Fischer, and Bradley, 1948; Comer, Koenig, and Lyons, 1956). This type of investigation can be very revealing in future studies of firing mechanisms and appears to be a promising research tool. The electron microscope is a good method of identifying the constituents of many clays and is even more valuable when it is used in conjunction with the other methods of identification.

*Light microscopy.*—The petrographic microscope, used in conjunction with the other identifying tools, can be of considerable value, but it cannot be used as the sole means of identifying most clay minerals. Grim (1955) pointed out several difficulties that are involved in determining optical properties.

Most oriented aggregates yield more precise optical values than the values obtained from random samples. Most nonclay minerals in a clay material can be detected with a petrographic microscope unless the particles of these minerals are as small as the clay minerals. Textural characteristics of a clay material can best



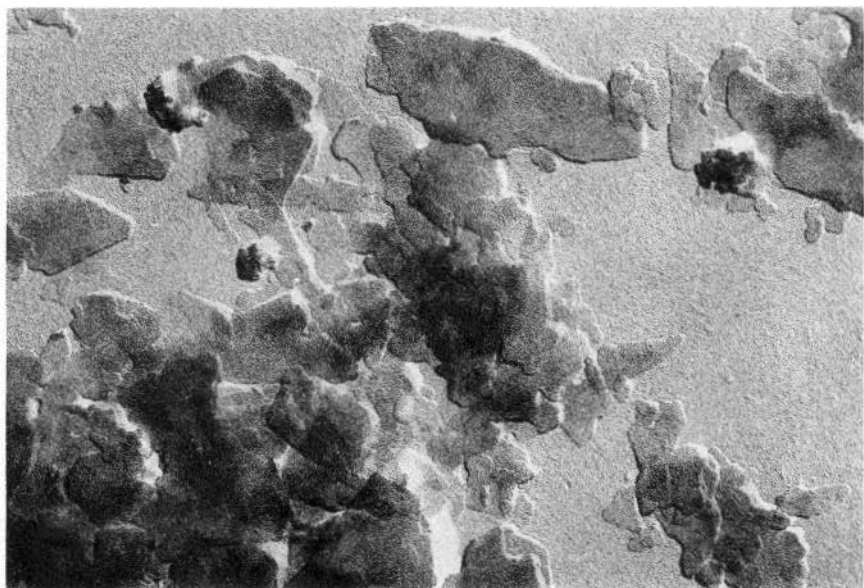
A. KAOLINITE ( $\times 35,821$ )



B. HALLOYSITE ( $\times 48,768$ )

ELECTRON MICROGRAPHS OF KAOLINITE AND HALLOYSITE

PICTURES FROM BATES, 1958, USED WITH PERMISSION.



A. ILLITE ( $\times 38,923$ )



B. MONTMORILLONITE ( $\times 37,632$ )

ELECTRON MICROGRAPHS OF ILLITE AND MONTMORILLONITE

PICTURES FROM BATES, 1958. USED WITH PERMISSION.

be revealed by a study of thin sections. Grim (1955) indicated that a preliminary study with the petrographic microscope would help in planning what other analyses should be made on a clay material.

The petrographic microscope is a valuable auxiliary method of study, but additional analytical data are required for complete identification of most clay minerals.

#### FACTORS WHICH CONTROL PROPERTIES OF CLAY MATERIALS

Five factors control the major properties of a clay material: clay mineral composition, nonclay mineral composition, organic material content, presence of soluble salts and (or) exchangeable ions, and texture. These factors must be known before a clay material can be completely characterized. Each is discussed briefly in the following paragraphs.

Clay mineral composition is exceedingly important in controlling the properties of a clay material. A small amount of montmorillonite in a clay material can exert a very strong influence, completely out of proportion to the amount present, on the physical properties of a clay. As will be pointed out later, each clay mineral has different properties dependent on its structure and composition.

Nonclay mineral composition may also be important in some clay materials. Certainly discrete fragments of calcite and pyrite are detrimental in ceramic clays. Quartz and other abrasive minerals are detrimental in kaolins used as coating pigments in the paper industry. These examples indicate that precise determination of the types and quantities of nonclay minerals is necessary before the use properties can be determined.

Organic material can occur as discrete fragments in clays or it can be adsorbed on the surface of the clay mineral particles. The total amount of organic material can be estimated by standard chemical procedures. DTA curves can be used to give a crude approximation of the amount of organic material. A small amount of organic material may have a large pigmentation effect, and some types of organic material have extremely high base exchange capacities. Grim (1953, p. 132) pointed out that, in general, organic material with a high base exchange capacity is found only in Recent sediments and soils.

Soluble salts and (or) exchangeable ions in a clay material can greatly affect its physical properties. Some salts flocculate the clay so that the clay is difficult to disperse in water. Ion exchange can affect the properties of clay; plasticity, drying properties, and firing properties can be altered by changing the exchangeable ion

carried by the clay. Properties of some clay materials can be explained by the presence of a certain soluble salt or a specific exchangeable ion.

Texture is also an important factor that affects the property of a clay material. It is defined as the grain to grain relationship in a clay and refers to particle size distribution, particle shape, and particle orientation. Particle size distribution in most clays is determined by wet methods of analysis, and great care must be exercised in the analytical procedure. Particle shape is best determined by the electron microscope. Particle orientation, important, for example, in producing lightweight aggregate from shales in which too much preferred orientation of the clay particles causes a weak aggregate particle, can be determined by petrographic microscope, electron microscope, and X-ray diffraction techniques.

Studies by Crane (1960) and Elberty (1960) contributed significantly to our knowledge of the effects of clay mineral composition on ceramic properties. Both investigators altered the clay mineral composition of synthetic mixtures of sand, silt, and clay of constant size ratio; they made standard physical tests of the ceramic bodies resulting from a specific firing routine. Table 1 is a summary of some results of both investigations. Most variations in the results are differences of degree rather than of kind, despite the fact that the two investigators used somewhat different raw materials.

Possibly some results of these studies are due primarily to the conditions of the experiments and only indirectly are the result of clay mineral composition. For instance, firing schedules were essentially the same for all mixtures in both investigations, a fact which caused the high kaolinite mixtures to be underfired and the high mixed-layer mixtures to be overfired. If all mixtures had been fired to optimum temperatures, some results obtained from fired bodies possibly would have been different. Also, there is the chance that some of the raw materials contained constituents that affected the results, although these constituents were not considered. For instance, the raw material used as a source of mixed-layer clay in both investigations contained a relatively large proportion of organic material. This organic material may have contributed some effects attributed solely to mixed-layer clay.

Despite these minor reservations, both investigations are important not only for their immediate results, but also as indications of what can be accomplished in increasing our knowledge of the influence of properties of raw materials on ceramic characteristics. Further basic investigations of this nature, taking other variables into consideration, will eventually lead to a more fundamental understanding of the ceramic behavior of clays.

Table 1.—*Effects of clay minerals on ceramic properties*<sup>1</sup>

Ceramic property	Kaolinite	Illite	Mixed-layer illite-montmorillonite	Montmorillonite
Plasticity -----	Increases (E)	Increases (E)	Increases (E)	No data
Drying shrinkage -----	Decreases	Increases moderately (C) Increases (E)	Increases greatly (C) Increases (E)	Increases greatly (C)
Dry crushing strength -----	Decreases (E)	Increases (E)	Increases (E)	No data
Firing shrinkage -----	Decreases	Increases	No correlation (C) Decreases (E)	Decreases (C)
Moisture expansion -----	No correlation (C) Increases (E)	No correlation (C) Decreases (E)	No correlation (C) Decreases (E)	No correlation (C)
Modulus of rupture -----	Decreases	Increases	No correlation (C) Increases (E)	Decreases slightly (C)
Fired crushing strength ---	Decreases	Increases	Decreases (C) Increases (E)	Decreases (C)
Water absorption -----	Increases	Decreases	Decreases (C) Increases (E)	No correlation (C)
Bulk density -----	Increases slightly	Increases slightly	Decreases slightly	Increases slightly (C)
Apparent porosity -----	Increases	Decreases	Decreases	No correlation (C)
Apparent specific gravity --	Increases	Decreases	Decreases slightly	No correlation (C)
Pyrometric cone equivalent -	Increases (E)	Decreases (E)	Decreases (E)	No data

<sup>1</sup>Designation in each column indicates effect of increasing proportion of a particular clay mineral on each ceramic property. (E) Represents result of investigation by Elberty (1960); (C) represents result of investigation by Crane (1960). No letter associated with result indicates agreement of two studies.

## CERAMIC PROPERTIES AND USES OF CLAYS

Clays used in the ceramic industry have wide variations in properties which restrict their use. Ceramics can be subdivided into several categories, and the properties of the clay which are most important for each type of product are discussed under the appropriate subdivision heading.

*Structural clay products.* -This is a broad category that includes brick, drain tile, sewer pipe, conduit tile, glazed tile, and terra cotta. The clays that can be used by the structural clay products industry vary in many properties in different parts of the country. But, in general, the properties of clays that are important in manufacturing structural clay products are plasticity, green strength, dry strength, drying and firing shrinkage, vitrification range, and fired color. These properties depend on the constituents of the clay material, their grain size, and texture.

As mentioned previously, most clays become plastic when they are mixed with varying proportions of water. They range from those which are highly plastic, called "fat" clay-s, to those of low plasticity, called "lean" clays. The cause of plasticity has been the subject of considerable controversy. Particle size and shape, type of clay mineral, soluble salts and adsorbed ions, organic matter, and amount and type of nonclay minerals are all known to affect plasticity. No standard test is prescribed for determining the plasticity of a clay; it is generally determined by feel. Plasticity in table 2 is an estimate of workability.

Green strength and dry strength are important in most types of structural clay products because the ware must be handled before it is fired. The green strength of a clay, the strength of clay after mixing with water but before drying, is closely related to plasticity. The dry strength can be determined by tension, compression, or transverse tests. Transverse tests are most commonly used. Strength depends on the proportion of fine particles, the shape of particles, the degree of hydration of the colloidal fraction before the sample is prepared, the way in which the test piece is formed, and the extent of drying before testing. A small amount of montmorillonite, which is a very fine-grained clay and is highly hydrated, increases the dry strength of most clays

Shrinkage, both drying and firing, is another important property of clays that are used for structural clay products. Drying shrinkage depends on the water content, the character of the clay minerals, and the amount of colloidal material in the clay. It is high in most very plastic or "fat" clays and thus tends to produce cracking and warping; it is low in sandy or "lean" clays, which thus dry to weak and porous bodies. Montmorillonite in relatively large



amounts (15 to 25 percent) causes excessive shrinkage and cracking and slow drying. Air shrinkage can be measured in either linear dimensions or volume.

The temperature range of vitrification or glass formation is another significant property of clays for structural products. Some clays have a very short vitrification range, and thus the temperature of the kilns must be closely regulated. Illites, montmorillonites, and chlorites vitrify at much lower temperatures than kaolins. Nonclay minerals, such as calcite, quartz, and feldspar, may lower the vitrification temperature by acting as fluxes.

Color is an important property of structural clay products. Several factors may determine color, but in most clays iron is the primary factor. The color of a product is influenced by the state of oxidation of the iron, the state of division and dispersion of iron minerals, the firing temperature and degree of vitrification, the proportion of alumina, lime, and magnesia in the clay material, and the composition of the fire gases during burning. The best white-burning clays contain less than 1 percent iron expressed as  $\text{Fe}_2\text{O}_3$ . Buff-burning clays contain between 1 and 5 percent  $\text{Fe}_2\text{O}_3$ , and their color depends on the relative amount of alumina and lime or magnesia. Red-burning clays contain 5 percent or more  $\text{Fe}_2\text{O}_3$ .

All types of clay and shale are used in the structural clay products industry, but in general these clays are not as pure or high grade as the clays used for some other industries that are discussed below. Shales of practically every geologic age are raw materials. Underclays of Pennsylvanian age, clays and tills of Pleistocene age, and soil clays formed on materials of various ages are also used. In general, underclays and some shales are best suited for glazed tile, conduit tile, and some grades of sewer pipe and brick. Shales and impure clays are used for common brick and drain tile.

*Refractories.*- All clays that have a fusion point above a pyrometric cone equivalent of 15 are considered refractory grade (American Society for Testing Materials, 1958, pt. 5, p. 277). Refractory clays generally are composed predominantly of kaolinite and commonly contain excess silica as quartz and only small amounts of other impurities.

The most widely used clay material for refractories is the material known as underclay, which is found underlying coal seams. Most underclays are plastic, but some are very hard and are known as flint clay. Flint clays are composed of essentially pure, relatively poorly crystalline kaolinite. In general, the refractoriness of underclays is proportional to the amount of alumina present and is reduced by the amount and types of impurities, such as iron and lime. Refractory underclays are often referred to as fireclays.

*Lightweight aggregate.*-Production and consumption of manufactured lightweight aggregate from clay and shale are rapidly increasing. Several products are marketed commercially under trade names, such as Haydite, Rocklite, Kenlite, and Gravelite. Firing is done in rotary kilns or sintering machines. The raw material is heated rapidly to a temperature between incipient and complete fusion. Bloating and vesiculation require constituents that release gas after fusion has formed a molten jacket around the particle to prevent the escape of the gas. The molten jacket must be viscous enough to retain the expanding gas. Several factors are important, most of which are based on chemical and mineralogic composition (Murray and Smith, 1958).

Shales and clays containing either illites, montmorillonites, or chlorite - vermiculite minerals are the most promising sources for lightweight aggregate. These minerals approximate the composition found by Riley (1951) to be most suitable for bloating. A large percentage of kaolinite causes the material to be too refractory for economic use.

*Bonding clays in foundry sands.*-Clays are used in the foundry industry to bind sands into desired shapes in which metals can be cast. In the past, and to a limited extent at the present time, natural deposits of sand and clay mixtures were and are used by foundries. These are called naturally bonded sands. In recent years synthetic mixtures of sand and clay have become more popular because by using mixtures of clean sand and specific types of clay the properties of the material can be more closely controlled. Some properties that can be partly controlled by using synthetic mixtures of clay and sand are green strength, dry strength, hot strength, permeability, flowability, and plasticity. The surface characteristics of the finished metal can also be controlled. Definitions of the above properties are given in the "Foundry Sand Handbook" (American Foundrymen's Society, 1952).

Clays used in foundries are bentonites and fireclays. Western bentonites from Wyoming and South Dakota are used extensively because these clays give the mold relatively high green, dry, and hot strengths. Only a small amount (3 to 5 percent) of western bentonite is needed to give sand a strong bond. Western bentonite is composed largely of sodium montmorillonite. Southern bentonites from Mississippi, Louisiana, and Texas are also widely used in foundries because of the exceptionally high green strength that these clay binders impart to the mold. Southern bentonites are composed largely of calcium montmorillonite. Fireclays are also used in many foundries in the North Central States because of economic considerations. These fireclays are composed mainly of the clay minerals kaolinite and illite;  
a p p r o x i m a t e l y   t w o   t o   t h r e e   t i m e s

as much fireclay as bentonite must be used to obtain equal strength. Because of the increased clay content in the mold, the surface character of the metal tends to be smoother. Grim and Rowland (1940) showed that the mineralogy of the clay material used to bond foundry sands controls the physical characteristics of the sands. They concluded that montmorillonite clays give the highest strengths.

*Portland cement.*-Large quantities of clay and shale are used in cement manufacture to add alumina and silica to the charge. Practically all clay or shale with average alumina and silica content and low magnesium and alkali percentage can be used in the cement industry. Commonly, this type of clay or shale can be found in the area in which the cement is being manufactured.

#### DETERMINATION OF CERAMIC PROPERTIES OF CLAYS

Ceramic tests were performed only on samples collected from commercial clay and shale pits. These tests consisted of determining the plasticity, slaking time, P. C. E. (pyrometric cone equivalent), percentage of linear drying shrinkage, percentage of linear firing shrinkage, percentage of volatile loss, percentage of apparent porosity, percentage of fired absorption, percentage of shrinkage water, percentage of pore water, fired color, hardness, crushing strength, and transverse strength (table 2).

Plasticity as reported in table 2 is a relative measure of the workability of the water-tempered samples. Slaking time was determined by the time required for disintegration of a small block of clay into its constituent particles when it was placed in water. Slaking time is a rough measure of the degree of lithification or hardness of a clay or shale. Pyrometric cone equivalence was determined by firing sample cones and standard cones in a Denver Fire Clay gas-fired P. C. E. furnace.

Briquettes formed by pressing tempered clay into a 1- by 1- by 3-inch metal mold were used for the remainder of the ceramic tests. The percentage of linear drying shrinkage was calculated from the difference in length of a test briquette before drying and after drying for 24 hours at 110°C, according to the formula:  $\frac{\text{wet length} - \text{dry length}}{\text{wet length}} \times 100$ . Dry briquettes were fired in a Harper

electric kiln in an oxidizing atmosphere. The heating and cooling cycles of the kiln were regulated to approximate the firing schedule of a continuous kiln. The percentage of linear firing shrinkage was calculated from the formula:

$\frac{\text{dry length} - \text{fired length}}{\text{dry length}} \times 100$ ;

volatile loss from the formula:  $\frac{\text{wet weight} - \text{fired weight}}{\text{wet weight}} \times 100$ ;

apparent porosity from the formula:  $\frac{\text{saturated weight} - \text{fired weight}}{\text{fired volume}}$

X 100; absorption from the formula:  $\frac{\text{saturated weight} - \text{fired weight}}{\text{fired weight}}$

X 100; shrinkage water from the formula:  $\frac{\text{wet volume} - \text{dry volume}}{\text{dry weight}}$

X 100; and pore water by subtracting the shrinkage water from the water of plasticity, which was calculated from the formula:

$$\frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} \times 100.$$

Fired color of the test specimens is given in approximate terms because fired color is altered by a change in firing conditions. The color indicated in table 2 was observed on the test briquettes fired to optimum temperatures. Hardness was tested by scratching the surface of fired briquettes with a steel knife blade. If the knife blade scratched the surface, the specimen was softer than steel, but if the briquette marked the surface of the knife blade, the specimen was harder than steel.

Crushing strength and transverse strength of fired specimens were determined by using a Southwark-Emery testing machine, type 60-TE-1003. For crushing strength tests, approximately 1-inch cubes cut from fired briquettes were crushed. Three trials for each sample were made, and the results were averaged. This average is given in table 2. To obtain transverse strengths, briquettes were placed upon knife edges, and pressure was applied by an inverted knife edge at a point midway between the upright knife edges. Two briquettes from each sample were tested; the average of the two results is shown in table 2.

#### GEOLOGY, MINERALOGY, AND PHYSICAL PROPERTIES OF SAMPLES STUDIED

About 1,000 samples of clay and shale were collected and analyzed for this study. Because many of the samples were taken from sites geographically close together and had similar properties, the results of tests on only 251 representative samples are included in this report. Mineralogic analyses were made for, all samples, ceramic analyses for samples of clays that have been or are being used for ceramic products, and chemical analyses for selected samples.

## SHALES OF SILURIAN AND DEVONIAN AGE

The oldest geologic system of rocks that contains clays of ceramic interest in Indiana is the Silurian. Older rocks in the State, such as Ordovician shales, may be found to be of use in the future as raw material for producing portland cement. These shales are generally too calcareous to be of other ceramic use (Whitlatch, 1933, p. 61). Owing to the scarcity of clays in rocks of the Silurian and Devonian Systems, the samples collected from rocks of these systems will be discussed together.

Both the Silurian and Devonian Systems are represented in Indiana primarily by a succession of limestones and dolomites. There are two shales in the Silurian sequence and one in the Devonian.

Silurian and Devonian rocks are exposed at the surface in Indiana in the southeastern part of the State (fig. 5). North of the Illinoian glacial boundary (fig. 5), glacial drift of varying thickness covers them, but in such places as creek and river beds, there is no glacial drift, and Silurian and Devonian rocks are exposed.

*Waldron Shale.*-The Waldron Shale is Silurian in age. It overlies the Laurel Limestone and is overlain by the Louisville Limestone (table 3). It ranges from less than 5 feet to as much as 12 feet in thickness along the outcrop. In a few places it is absent, and the Louisville Limestone rests directly on the Laurel Limestone.

Mineralogically, the Waldron Shale is composed of the clay minerals illite and chlorite, and there are significant amounts of kaolinite in some samples (table 2). The dominant nonclay minerals are quartz, dolomite, and calcite. Dolomite is commonly the most abundant carbonate mineral. All samples of the Waldron Shale studied contained major amounts of carbonate minerals.

The color of the Waldron Shale varies from green to gray. In some places it is massive and soft and lacks apparent bedding, but in other places it may be laminated and hard. The Waldron Shale is fine grained, and much of the quartz, calcite, and dolomite in the shale is as fine grained as the clay minerals are.

Because of the large proportion of calcite and dolomite in Waldron Shale, it has a low fusion point and a short vitrification range. For this reason, very little use has been made of the Waldron Shale as a raw material for ceramic products, and it is not being used now.

The fact that many samples of the Waldron Shale fire to a very white color may suggest a use for it in the future. The high proportion of calcium and magnesium apparently combines with the iron present to form colorless compounds when samples are fired.

*Mississinewa Shale.*-The Mississinewa Shale is Silurian in age. It overlies the Louisville Limestone and is overlain by the Liston

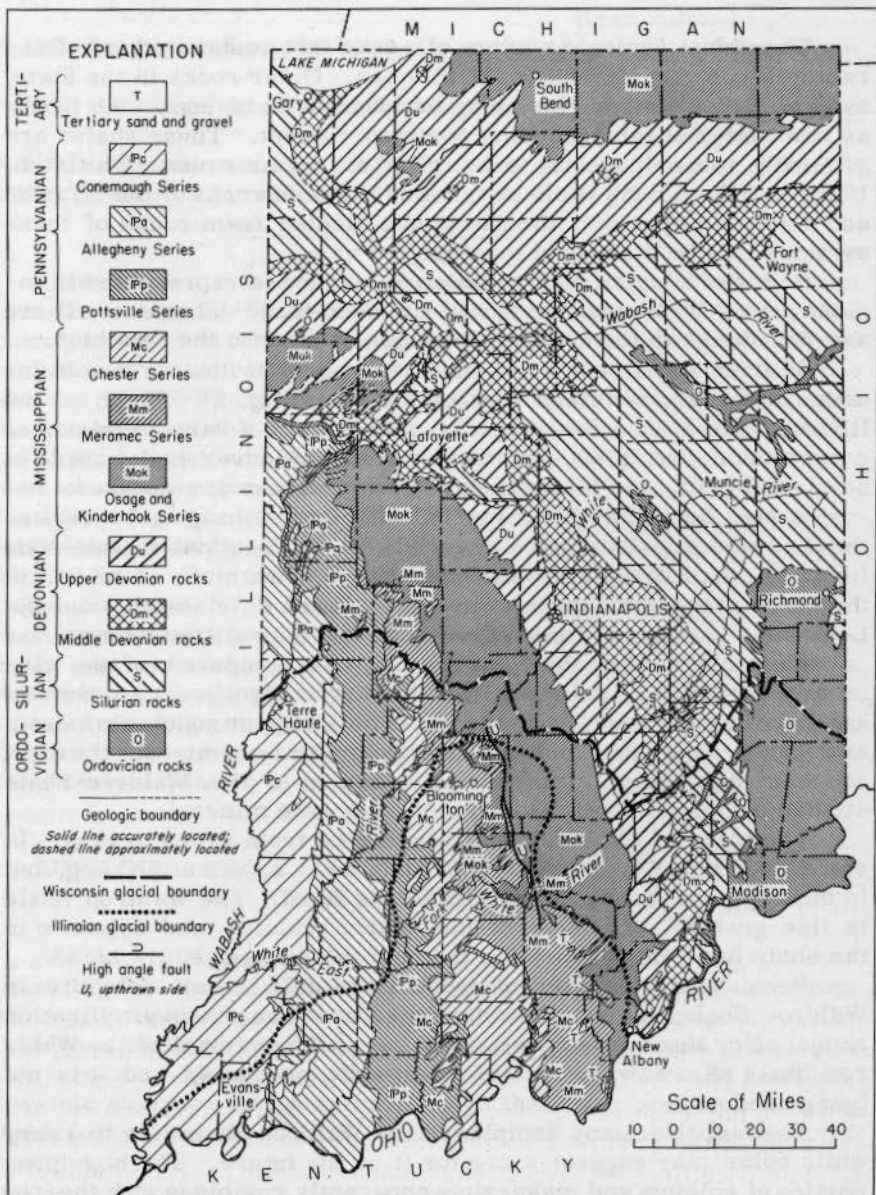


Figure 5. --Generalized geologic map of Indiana. From Indiana Geol. Survey Rept. Prog. 7, fig. 6.

Table 3.-*Silurian and Devonian rock units in Indiana*

System	Series	Formation
Devonian	Bradfordian Chautauquan Senecan	New Albany Shale (lower part)
	Erian	North Vernon Limestone
	Ulsterian	Jeffersonville Limestone Pendleton Sandstone Geneva Dolomite Kenneth Limestone
Silurian	Cavugan	Kokomo Limestone
	Niagaran	Unnamed Liston Creek Limestone Mississinewa Shale Louisville Limestone Waldron Shale Laurel Limestone Osgood Formation
	Albio	Brassfield Limestone

Creek Limestone. The Mississinewa Shale attains a maximum thickness of approximately 115 feet along the outcrop (Shaver and others, 1961).

The Mississinewa Shale is mineralogically similar to the Waldron Shale, except that samples of the Mississinewa Shale that were analyzed did not contain kaolinite. Dolomite was the dominant carbonate mineral in all samples analyzed. In many places Mississinewa rocks are dolomite rather than shale because dolomite constitutes more than 50 percent of the rock (table 2).

The Mississinewa Shale is gray to blue on a fresh surface and light brown when it has weathered. The shale is commonly massive, and bedding is not apparent. The Mississinewa Shale is dominantly fine grained, but in some places the nonclay minerals are silt or even sand, size, and thus the shale appears to be silty or sandy.

Like shale from the Waldron, shale of the Mississinewa has a low fusion point and a short vitrification range owing to the large proportion of carbonate minerals present. For this reason, the Mississinewa Shale is probably not suitable as a raw material for ceramic ware. It is used, however, for inorganic molded plastics which do not require high temperatures in their manufacture and was used in the past as a raw material for rock wool. Because of its short vitrification range, Mississinewa shale is not suitable for lightweight aggregate. The shale vitrifies before bloating takes place, and the molten jacket around each particle is not viscous enough to retain the gases released.

The only uses presently known for the Mississinewa Shale are those that do not require high temperatures during manufacture or use.

*New Albany Shale.*-The New Albany Shale is both Devonian and Mississippian in age because the boundary between these geologic systems is several feet below the top of the formation (table 3). The North Vernon Limestone of Devonian age underlies the New Albany Shale, and the Rockford Limestone of Mississippian age overlies it. The New Albany Shale ranges from about 80 to 150 feet in thickness along the outcrop.

The clay minerals making up the New Albany Shale are predominantly illite and chlorite, and kaolinite is present in a few samples (table 2). Quartz is the most abundant nonclay mineral and is associated with minor amounts of feldspar and small amounts of calcite, dolomite, and phosphate minerals. Pyrite is commonly present as fine to coarse crystals in concretions or disseminated in the shale.

The New Albany Shale is dark gray, dark olive green, dark brown, or black on fresh surfaces and weathers to light gray, brown, or maroon within a few years. The New Albany Shale is found in almost all places as a thin-bedded to fissile fine-grained shale. Some of its quartz and pyrite grains are large enough to be seen with the unaided eye.

Although at present the New Albany Shale is not being used ceramically, it might be suitable for making brick or tile if the fired color did not prove to be objectionable. Tests conducted to determine the bloating properties of New Albany shales (Murray and Smith, 1958) showed that these shales were definitely potential raw material for expanded shale lightweight aggregate.

Most black or dark-brown beds of the New Albany Shale contain large amounts of hydrocarbons; this material qualifies as an oil shale (Bell, 1948, p. 9).

#### SHALES OF MISSISSIPPIAN AGE

Mississippian rocks in Indiana are exposed in a band that trends northwestward-southeastward across approximately the middle of the State (fig. 5). The oldest (Kinderhook) rocks are at the east edge of the band, and the youngest (Chester) rocks are at the west edge. The northern extremity of the band of exposed Mississippian rocks is buried by glacial drift. Along the northern boundary of the State the uppermost bedrock is Mississippian in age, but a thick mantle of glacial drift covers it.



Table 4.-Mississippian rock units in Indiana

System	Series	Group	Formation
Mississippian	Chester		Kinkaid Limestone Degonia Sandstone Clare Limestone Palestine Sandstone Menard Limestone Waltersburg Sandstone Vienna Limestone Tar Springs Formation
		Stephensport	Glen Dean Limestone Hardinsburg Formation Golconda Limestone Big Clifty Formation Beech Creek Limestone
		West Baden	Elwren Formation Reelsville Limestone Sample Formation Beaver Bend Limestone Bethel Formation
		Blue River	Paoli Limestone Ste. Genevieve Limestone St. Louis Limestone
	Meramec		Salem Limestone Harrodsburg Limestone
	Osage	Borden	Edwardsville Formation Floyds Knob Formation Carwood d Formation Locust Point Formation New Providence Shale
	Kinderhook		Rockford Limestone New Albany Shale (upper part)

Rocks of the Mississippian System are assigned to four series in Indiana: Kinderhook, Osage, Meramec, and Chester (table 4). The only shale of the Kinderhook Series of economic interest is in the top part of the New Albany Shale, which was discussed as part of the Devonian System. Rocks of the Osage Series in Indiana consist of shales of economic importance and limestones. Meramec rocks are mostly limestones and dolomites except for a few thin shales of no ceramic value. Rocks of the Chester Series in Indiana are composed of limestones, sandstones, and shales. Several Chester shales could have some economic importance in the future, but at present they are not being used for ceramic products.

*Borden Group.*—The New Providence Shale at the base of the Borden Group and the Locust Point Formation, which overlies the New Providence Shale, are difficult to distinguish in the field because they are very similar lithologically. Because the other formations of the Borden Group are not economically important, except possibly in local areas, they are not discussed further.

Rocks of the Borden Group, which is assigned to the Osage Series (table 3), lie in a narrow band about 12 to 15 miles wide from New Albany on the Ohio River to just south of Lafayette (fig. 5). From the Illinoian glacial boundary northward, glacial drift of varying thickness covers the Borden shales, but they are exposed in spots about 30 miles northwest of Lafayette.

All lower Borden shales are similar mineralogically. They contain illite, chlorite, quartz, and feldspar (table 2). The feldspar content is low, generally less than 10 percent, and may be absent. The primary mineralogic difference between samples of lower Borden shale is variation in proportions of the above minerals. In addition, a few samples of New Providence shale contain kaolinite, but the amount of kaolinite is so small that it has very little effect on the properties of the shale. In addition to the minerals mentioned above, limonite concretions ranging in size from less than 1 inch to more than 1 foot are found in Borden shales.

The lower Borden shales are commonly coarse grained, the nonclay particles being of silt size. The color of the shales ranges from blue gray to brown, and there are gradations between. In most places these shales are massive to blocky on fresh surfaces, but on weathered surfaces they display definite partings and break out in small pieces. The lower Borden shales vary from relatively soft to very hard. In general, the fine-grained shales are soft, and the coarse-grained ones are hard.

Lower Borden shales have been used extensively as a raw material for brick, tile, lightweight aggregate, and inorganic molded plastics and as an ingredient in portland cement.

Most samples of lower Borden shale that were analyzed showed good ceramic properties (table 2). Most fired colors are shades of red or brown. Soluble salts formed during the firing process cause severe scumming in some samples. Crushing strength and hardness of samples tested are sufficient for almost any use for which other properties are suitable. Workability is variable but is good enough for most uses. Tests of samples of lower Borden shales to determine bloating, adsorption, and porosity indicated that most of these shales are suitable for lightweight aggregate.

The lower Borden shales have great potential as raw material for ceramic products. Factors limiting the usefulness of Borden shale in a particular area are primarily economic: markets, manufacturing facilities, and transportation.

*Chester shales.*—The rocks of the Chester Series consist of shales, sandstones, and limestones, which are relatively thin compared to formations of the underlying Meramec Series. This sequence of rocks is more variable in mineralogy, thickness, and physical properties, both laterally and vertically, than any of the rocks

discussed previously. In spite of this variability, several Chester shales have good ceramic properties and are sufficiently extensive vertically and laterally that they could have considerable economic importance.

Chester rocks crop out in a band west of the Borden rocks and are separated from them both areally and stratigraphically by limestones of Meramec age. The Chester outcrop belt extends from the Ohio River to a point about midway between Indianapolis and Terre Haute (fig. 5).

The Bethel Formation, formerly known as the Mooretown Sandstone, is the stratigraphically lowest formation of the Chester Series containing shale. The Bethel Formation consists of dark-gray shales and argillaceous sandstone 5 to 30 feet thick. Most Bethel shales are soft, and the grain size ranges from coarse to fine.

At present no ceramic products are being made from Bethel shale. Tests of bloating properties, adsorption, and porosity have shown that Bethel shale may be suitable for producing lightweight aggregate (Murray and Smith, 1958). A study of the mineralogy of the Bethel Formation in places where it is a shale suggests that it would be satisfactory for making brick and tile if color and crushing strength are adequate.

The younger Chester shales have not been used for ceramic purposes, but according to results of mineralogic analyses, they appear to be suitable for several ceramic products. Brick, tile, and lightweight aggregate could probably be made from many Chester shales. Ceramically significant shales of the Chester Series in addition to Bethel shale are shales of the Sample, Elwren, and Hardinsburg Formations. These formations are found both as sandstones and shales and also as all gradations between sandstone and shale.

All shales of the Chester Series are variable in physical properties and mineralogy, particularly in lateral directions. In many places a shale becomes a sandstone or limestone in less than a mile and in some places in not more than tens of feet. But Chester shales are similar to each other in lithology and mineralogy and are treated as a group in the following discussion. Samples of shale were collected and analyzed from the Sample, Elwren, Hardinsburg, and Tar Springs Formations.

The Chester shales of ceramic interest are gray, brown, or red and are generally soft and fine grained. The dominant clay minerals of Chester shales are illite, kaolinite, and mixed-layer illite-montmorillonite. Chlorite is present in some samples but in amounts less than 10 percent. Quartz is the only abundant nonclay mineral. There is less than 5 percent feldspar in about half the

samples. Calcite is never present in amounts greater than 5 percent, except in areas where a shale may be grading into a limestone. Information about samples of this type have not been included in this report.

No empirical tests were made of shales of the Chester Series, except for the Bethel shales. From the results of the mineralogic analyses, shales of the Chester Series should be promising for manufacturing drain tile or brick, and they may be suitable for lightweight aggregate. The relatively high kaolinite content should extend the vitrification range, and the quartz should restrict drying and firing shrinkage. The high illite and mixed-layer illite-montmorillonite contents would tend to increase plasticity and improve workability but might introduce shrinkage problems.

#### CLAYS ASSOCIATED WITH THE MISSISSIPPIAN-PENNSYLVANIAN UNCONFORMITY

After the deposition of the youngest Mississippian strata and before deposition of Pennsylvanian sediments had begun, a long period of erosion took place. Because erosion of Mississippian beds was progressively greater toward their northern extent in the area of Indiana or because younger Mississippian rocks were never present in the north, Pennsylvanian rocks overlie progressively older Mississippian strata from south to north along the exposure of the unconformity (fig. 5). In southern Indiana, therefore, Pennsylvanian strata overlie rocks of Chester age. At some localities the basal Pennsylvanian rocks overlie deposits composed essentially of halloysite and allophane.

Many small deposits of halloysite, which were called "kaolin" in the older literature, have been described (Logan, 1919, p. 100-127). but the largest known deposit is at Gardner Mine, about 30 miles south of Bloomington. The geologic relationships and physical properties of this deposit were described by Callaghan (1948) and Sunderman (1963). The deposit is composed primarily of allophane (p. 8) and halloysite. Minerals containing phosphorus are common, the most abundant of which is crandallite (Greenberg and Elberty, 1958).

The halloysite deposits at Gardner Mine, in Lawrence County, were used in the past for producing alum and as an ingredient in bone china and were mixed with underclay for refractories. The deposit has not been exploited commercially since the turn of the century. The halloysite has been explored several times since, but the use of Indiana halloysite has never been resumed.

## CLAYS AND SHALES OF PENNSYLVANIAN AGE

Rocks of the Pennsylvanian System in Indiana have been assigned to 11 formations (table 5). The lowest seven formations are the most important ceramically, for these are the formations that contain the important coals and associated underclays.

Pennsylvanian formations are stratigraphically complex because of common changes from one rock type to another over relatively short distances. In addition, the rocks of any one lithologic type are very similar mineralogically in all Pennsylvanian formations; thus only an expert stratigrapher can distinguish between the various formations.

Pennsylvanian rocks crop out in Indiana west of the Mississippian outcrop belt from the Ohio River to as far north as Lafayette and westward to the Indiana -Illinois boundary (fig. 5). North of the Illinoian glacial boundary glacial drift of varying thickness covers most Pennsylvanian rocks.

Pennsylvanian shales.-Many Pennsylvanian shales have been or are being used for ceramic products. Some products made from Pennsylvanian shales are brick, drain tile, pottery, and stoneware. In addition, these shales are mixed with underclays to alter the characteristics of the underclays to make them more suitable for manufacturing sewer pipe, brick, and stoneware.

Two general types of shale are found in the Indiana area of Pennsylvanian rocks: dark-gray to black fine-grained thin-bedded shale and light-gray silty relatively thick-bedded shale. Most black shales are not suitable for use as ceramic raw material because they contain large amounts of organic matter. But some black shales may be suitable for lightweight aggregate. Murray and Smith (1958) found that shales from the Linton, Dugger, and Shelburn Formations showed bloating properties.

The light- and medium-gray Pennsylvanian shales may have several desirable ceramic characteristics. Most of them are found in thick, relatively uniform beds. They have enough plasticity for good workability, and they fire to shades of red and orange.

Probably the most important general characteristic of the light-gray Pennsylvanian shales to the ceramic industry is their ability to improve the ceramic properties of underclays by increasing their plasticity, imparting a more pleasing fired color, and decreasing drying and firing shrinkage. A suitable shale can be obtained from many of the same pits as an underclay can.

Mineralogically, Pennsylvanian shales are characterized by relatively low quartz and feldspar content, abundant illite, approximately equal kaolinite and chlorite, and little or no mixed-layer clay minerals (table 2). The illite and chlorite have relatively high iron contents that impart a red or orange color to the fired clay.

Table 5.- *Pennsylvanian rock units in Indiana*

System	Series	Formation	Significant member
Pennsylvanian	Conemaugh	Unnamed	
		Mattoon Formation	Merom Sandstone Member
		Bond Formation	
		Patoka Formation	
		Shelburn Formation	West Franklin Limestone Member Busseron Sandstone Member
	Allegheny	Dugger Formation	Danville Coal Member (VII) Universal Limestone Member Coal VI
		Petersburg Formation	Alum Cave Limestone Member Coal V Coal IVa
		Linton Formation	Coal IV Colchester Coal Member (IIIa) Coxville Sandstone Member
		Staunton Formation	Coal III
	Pottsville	Brazil Formation	Perth Limestone Member Minshall Coal Member Upper Block Coal Lower Block Coal
		Mansfield Formation	

*Pennsylvanian underclays.*- Probably the most important rocks in Indiana for ceramic uses are the Pennsylvanian underclays. They are useful as raw materials for almost all ceramic products except high-quality porcelains, sanitary ware, and high-duty refractories. They are almost the only material in Indiana suitable for producing light-buff brick and tile.

Underclay is a unique rock type and is commonly found under a coal seam. If no coal overlies the underclay, field evidence usually shows that geologic conditions for coal formation existed but that either insufficient organic matter for coal formation accumulated or the coal was removed by erosion. Two types of underclays are found in Indiana. One is dark gray to black, very plastic, very fine grained, and contains a relatively high proportion of organic material. The other is light gray to almost white, less plastic than the previous type, and commonly coarse grained because of a high proportion of quartz and feldspar. Dark underclay is found at the top of a deposit, directly under coal, and is underlain by lightcolored underclay. Of course, gradations between these two general types of underclay are common, and the contact between them is in many places transitional rather than sharp. Further, an underclay may grade almost imperceptibly into an underlying shale.

Underclays are typically massive, that is, nonlaminated. Rarely are underclays in Indiana more than 5 to 6 feet thick. Most underclays that are more than about 10 feet thick are two or more underclays superimposed with a very thin coal between them. This is the result of slight oscillation of conditions of sedimentation suitable for the formation of underclays over periods long enough to accumulate a considerable thickness of underclay. Another possible mode of accumulation of unusually thick underclay beds is the deposition of underclaylike sediments in a relatively deep basin.

The mineralogic compositions of 110 samples of underclays are listed in table 2. The quartz and feldspar contents of these samples are quite variable, a reflection of the difference between dark- and light-colored underclays. The clay mineral content of Indiana underclays also is quite variable. Chlorite is a minor constituent or absent, and in some samples the mixed-layer clays are more abundant than in most Pennsylvanian shale samples. Kaolinite and illite range from equal amounts to predominantly kaolinite. In a few samples, such as those from the underclay below Coal IVa of the Petersburg Formation, the only major minerals are quartz and kaolinite.

Owing to the virtual absence of chlorite and pyrite and relatively low content of illite, the amount of iron in light-gray underclays is relatively low. This low percentage of iron is the cause of the light fired color of most underclays. The small amounts of calcium, magnesium, sodium, and potassium in most Indiana underclays account for their high fusion temperatures. Some underclays have a significant amount of soluble sulfate derived from oxidation of pyrite in or immediately beneath a coal. Soluble sulfate can cause efflorescence on fired clay bodies, but this efflorescence can usually be controlled by adding a chemical compound that will react with sulfate to produce an insoluble compound. A popular additive of this nature is a soluble salt of barium which reacts to form insoluble barium sulfate.

An advantage in the exploitation of underclays for raw materials is the fact that during mining of coal from a strip pit, underclay is commonly exposed. The cost of removing underclay is therefore relatively low, and the only remaining economic factors are quality and quantity of the clay, cost of transportation, and the market.

#### CLAYS OF PLEISTOCENE AGE

A few times during the Pleistocene Epoch (table 6) the northern part of Indiana was covered with thick ice sheets or glaciers (fig. 5). These glaciers carried tremendous amounts of sediments composed

Table 6.-Time-rock units of the Quaternary System in Indiana

System	Series	Stage
Quaternary	Pleistocene	Recent
		Wisconsin
		Sangamon
		Illinoian
		Yarmouth
		Kansan

of extremely diverse types of material. Parts of the rocks the glaciers passed over were incorporated in the ice so that fragments derived from rocks of many types were mixed and deposited.

This diversity of sediment composition has resulted in glacial deposits of quite variable composition. Furthermore, all ice-transported materials were not deposited in the same way. As the ice sheets melted, part of the contained sediment was carried along by meltwater streams, and the coarse fraction was deposited as valley fill. Sediment composed of fine particle sizes was carried along by the streams and deposited in sedimentary basins. The detrital material remaining in the ice was dropped in place as the glacier melted and formed the various types of glacial tills found today.

Valley fill or stream-laid deposits are commonly well sorted and of coarse particle size. Along margins of streams, where currents are slow, the particle size of sediments tends to be small. Lacustrine or lake clays which were deposited in relatively quiet water in basins are of uniformly small particle size. Glacial tills dropped by melting ice sheets are among the least sorted of all glacial deposits. Particle size in till ranges from boulder to clay-size particles, and these extremes of size can sometimes be seen in the same deposit. But where the glacier has passed over areas of fine-grained rocks, such as shales, near the site of deposition of the till, sediments tend to be fine grained.

Glacial deposits are commonly quite complex mineralogically because of the diverse rock types they are likely to contain (Patton, 1953). Although generalization of the mineral composition of glacial clays is difficult, several features are evident from a study of table 2. The quartz content of most glacial clays is high, and feldspar varies in amount from just detectable to 35 percent. The carbonate minerals, calcite and dolomite, are common in glacial sediments in Indiana, and the amount of total carbonate minerals can be as high or higher than 30 percent. Other minerals are present but



mostly in trace amounts undetectable by X-ray diffraction. The influence of these minor or trace constituents on the physical properties of the glacial material generally is negligible.

Illite is the predominant clay mineral in glacial sediments, but a mixed-layer illite-montmorillonite is abundant in some samples. Chlorite is present in most glacial materials but rarely in dominant amounts. If present at all, kaolinite is only a minor constituent.

Weathering drastically alters the mineralogic composition of glacial sediments, particularly at shallow depths and in permeable deposits above the water table. Two major alterations take place. Illite and chlorite are altered by the removal of potassium from the illite crystal structure and iron and magnesium from the chlorite; this alteration commonly results in the formation of mixed-layer clay minerals. Removal of calcite and dolomite by solution transforms many glacial sediments into a form suitable for ceramic use. Unfortunately, as weathering is commonly intense enough to remove carbonate minerals only in the upper few feet of a deposit, material suitable for ceramics is limited in thickness.

Because most samples of clays of Pleistocene age included in table 2 have been used as ceramic raw materials, they are not representative of glacial deposits in general but are indicative of the exploited deposits of this type. Even so, the physical properties shown in table 2, except pyrometric cone equivalent and fired color, are quite variable. The fired color of most samples studied was red or orange, but it was cream or buff in a few samples in which the lime content was relatively high.

Products commonly made from glacial clays are farm drain tile, low-grade backup brick, and clay flower pots. Specifications for these products are not stringent or are nonexistent, and thus the use of low-grade glacial clays is permitted.

#### SUMMARY

The ceramic industry in Indiana is in a favorable position with respect to reserves of clay raw materials. Producers of structural clay products in particular have adequate supplies of clay for years to come, although a suitable clay deposit may not be advantageously located near existing plants. Many rock units in Indiana contain shales and clays suitable for some ceramic uses. A large proportion of these clays and shales have not yet been used as ceramic raw materials. For example, shales of the Chester Series have been almost totally neglected by industry, even though they are promising sources of clay for many structural clay products.

This report does not include detailed analyses of all exposures of clays in Indiana but presents a general discussion of the types of clays found in Indiana and their suitability for ceramic products. An exploration program would be necessary to outline reserves of clay for specific needs. After an exposure of clay that seems to be suitable has been located, its extent can be most satisfactorily delineated by a well-planned drilling program. Samples collected during drilling should be tested to provide a sufficient characterization of the deposit.

Availability of raw material is only one factor of a manufacturing operation. Other factors, such as existence of markets, transportation, and fuel supply, are beyond the scope of this report, but they must be considered before any operation is begun.

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Table with columns for Sample No., Laboratory No., Location, County, Thickness (ft), Quartz, Feldspar, Calcite, Dolomite, Kaolinite, Illite, Chlorite, Mixed-layer, Plasticity, Slaking time, P.C.E., Linear drying shrinkage, Linear firing shrinkage, Volatile loss, Fired apparent porosity, Fired absorption, Shrinkage, Pore water, Fired color, Hardness, Crushing strength, Transverse strength, SiO2, Al2O3, FeO, TiO2, CaO, MgO, Na2O, K2O, MnO, P2O5, S, CO2, H2O, pH.