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Kaolin, Refractory Clay, Ball Clay, and Halloysite in North America, Hawaii, and the Caribbean Region

GEOLOGICAL SURVEY PROFESSIONAL PAPER 1306



Kaolin, Refractory Clay, Ball Clay, and Halloysite in North America, Hawaii, and the Caribbean Region

By SAM H. PATTERSON *and* HAYDN H. MURRAY

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*Geologic descriptions of kaolin
deposits occurring at 46 localities*



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Kaolin, Refractory Clay, Ball Clay, and Halloysite in North America, Hawaii, and the Caribbean Region¹

By SAM H. PATTERSON and HAYDN H. MURRAY²

ABSTRACT

The valuable types of kaolinitic clays occurring in North and Central America, Hawaii, and the Caribbean region are kaolin, halloysite, ball clay, and refractory clay. Most valuable deposits have formed by sedimentary processes, but a few are the result of hydrothermal activity, and some are residual accumulations of weathered rocks. The kaolinitic clays are widely distributed and occur in rocks of several different ages. Most refractory clay deposits are associated with coal beds; these deposits are called underclays. Most underclays are of Pennsylvanian age (Late Carboniferous of the European time scale), but a few are in Cretaceous and Tertiary rocks, and small deposits in Hawaii are of Holocene age. Most of the large kaolin and ball-clay deposits are in sedimentary rocks of Cretaceous age and younger. Hydrothermal kaolin deposits, which include most halloysite clays, are thought to have formed mainly in Cenozoic time, but the host rocks of some deposits are much older. Some residual deposits are related to the present land surface, and others are covered by younger rocks. They occur mainly on igneous and crystalline rocks.

INTRODUCTION

Valuable kaolin deposits occur at many places in North and Central America, a few have been found in the Caribbean region, and small deposits of scientific interest are located in Hawaii. White commercial kaolin occurs mainly in sedimentary deposits, but this type of clay also occurs in residual deposits formed by weathering and in hydrothermal deposits. Underclays, which form under coal or peaty material, are classified as sedimentary because virtually all are in sedimentary sequences. However, small underclay deposits in Hawaii formed by weathering of basalt in swamps, indicating that some underclays may have formed more by weathering and residual accumulation than by sedimentary processes. In this report, ball clay, a variety of kaolin, is included with the underclays because all but one minor occurrence of ball clay are closely associated with lignitic material. Commercial halloysite, another variety of kaolin, is found mainly in hydrothermal deposits, but this type of clay is also

recovered as a coproduct of kaolin from residual deposits.

Definitions

Kaolin.—The term “kaolin” is now variously used to mean a clay-mineral group, a rock (consisting of more than one mineral), and an industrial mineral commodity and interchangeably with the term “china clay.” The following definition of kaolin by Ross and Kerr (1931, p. 154) is probably the most widely accepted one:

“By kaolin is understood the rock mass which is composed essentially of a clay material that is low in iron and usually white or nearly white in color. The kaolin-forming clays are hydrous aluminum silicates of approximately the composition $2\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, and it is believed that other bases if present represent impurities or adsorbed materials. Kaolinite is the mineral that characterizes most kaolins, but it and the other kaolin minerals may also occur to a greater or lesser extent in clays and other rocks that are too heterogeneous to be called kaolin. * * *

Dickite and nacrite are two polymorphic forms of kaolinite that can be characterized in terms of two crystal-lattice structures, as Bailey (1963, p. 1196) described in his abstract as follows:

“1) direction and amount of interlayer shift, and 2) location of the vacant octahedral site in successive layers. Kaolinite and dickite have the same interlayer shift of $-\frac{1}{2}a$, when referred to a standard layer orientation. The two structures differ only in regard to the distribution of the vacant cation site in successive octahedral sheets and the consequences of this distribution in terms of symmetry, layer distortion, and Z-axis periodicity. In well-crystallized kaolinite the vacant site is the same in each layer. The structure is triclinic and may be right-handed or left-handed, because either of two octahedral positions, related by a mirror plane in an undistorted monoclinic structure, may be vacant. In dickite the vacant site alternates between these two positions in successive layers, creating a two-layer monoclinic superstructure that is a regular alternation of right- and left-handed kaolinite layers. Comparison of the two structures is facilitated by changing the standard orientation of the dickite unit cell to correspond to that of kaolinite. The interlayer shift in nacrite is $\frac{1}{2}b_1$ relative to the same axes as for kaolinite and dickite. The layer sequence is that of a 6R polytype, but the pattern of vacant sites reduces the symmetry to Cc and allows selection of a smaller

¹Contribution to International Geological Correlation Programme, Project 23—Genesis of Kaolins.

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two-layer unit cell. A modified system of polytype notation is suggested for describing the kaolins and other minerals in which the actual Z-axis periodicity or crystal system differs from that of the ideal trioctahedral polytype as a result of cation or vacancy ordering. * * *

The term "anaukite" is repeated in a few places in this article as used in old publications. Anaukite is described by Grim (1968, p. 68) as one of the problematical kaolin minerals that has a considerably higher silica-to-alumina molecular ratio than kaolinite.

When applied as a term for an economic clay commodity, the foregoing definition must be modified to include some indication of use and to account for the fact that most kaolin now marketed is beneficiated to improve its purity and whiteness. The following definition will apply to further discussions of kaolin in this report. Kaolin is a clay consisting of substantially pure kaolinite, or related clay minerals, that is naturally or can be beneficiated to be white or nearly white, will fire white or nearly white, and is amenable to beneficiation by known methods to make it suitable for use in whiteware, paper, rubber, or paint, or for similar uses. Many very large kaolin deposits are essentially pure and require little concentration during preparation for market. Some deposits are very impure, and the kaolin is recovered by washing. Most are slightly off-color and require leaching. China clay is an ancient term originating from the use of clay, later found to be kaolinitic, in porcelain tableware and art objects in China.

Halloysite.—Halloysite occurs in two forms: one has the composition $(\text{OH})_3\text{Si}_4\text{Al}_4\text{O}_{10} \cdot 4\text{H}_2\text{O}$, and the other, $(\text{OH})_3\text{Si}_4\text{Al}_4\text{O}_{10}$. Halloysite (10A)³ is a porcelainlike hard clay that dehydrates at or slightly above surface temperatures to a white or light-colored porous, friable, or almost cottony-textured material. Halloysite (7A) is similar to kaolinite in composition and mineral structure, but the hydrated form has a c-axis spacing greater than that of kaolinite. In older reports, the name "halloysite" is applied to the hydrated forms, and the dehydrated form is called "metahalloysite." However, some reports use the name "endellite" for the hydrated form and the name "halloysite" for the dehydrated form. Virtually all subsurface halloysite is halloysite (10A). Halloysite, like ball clay, is a variety of kaolin and is included with kaolin in most industrial classifications.

Ball clay.—Ball clays are defined by the American Society for Testing and Materials (ASTM) (1971) as sec-

ondary clays commonly characterized by the presence of organic matter, high plasticity, high dry strength, long vitrification range, and a light color when fired. Kaolinite is the principal mineral constituent of ball clay, and it typically makes up more than 70 percent of this type of clay. The minor differences between the light fired color required by this definition and the white required for kaolin provide little practical basis for distinguishing these two types of clay. Therefore, ball clay is actually a variety of kaolin, but it is treated as a separate type of clay because of its wide application in marketing and as a use term in the ceramics industries.

Refractory clays.—Refractory clays include several varieties of kaolinitic clays that are used in the manufacture of products requiring resistance to high temperatures. The quality and properties of refractory clays are expressed in terms of pyrometric cone equivalents, a method of designating fusion points (ASTM, 1971, p. 198): " * * * Pyrometric Cone Equivalent is defined as the number of that standard cone whose tip would touch the supporting plaque simultaneously with that of a cone of the material being investigated, when tested in accordance with the Standard Method of Test for Pyrometric Cone Equivalent (PCE) of refractory materials (ASTM Designation C24) of the American Society of Testing Materials. * * *"

The fusion points of products made from refractory clays range from just above PCE 19, the lower cutoff according to accepted definitions (Norton, 1968), to as high as PCE 36 (table 1). The refractory properties of kaolinitic clays are ordinarily classified according to suitability for heat service as low duty (PCE 19–26), moderate duty (PCE 26–31½), high duty (PCE 31½–33), and super duty (PCE 33–34). A few essentially pure kaolinite clays have fusion points as high as PCE 35, and some refractory kaolins and fire clays containing diasporite, boehmite, or gibbsite have PCE's as high as PCE 37.

The principal types included in the refractory clays are fire clay, kaolin, and ball clay. Kaolin and ball clay used in refractory products are referred to as refractory kaolin and refractory ball clay. The definition of fire clay used in this paper is essentially that of Norton (1968), who assigned this term to all clays that are not white burning and that have a PCE above 19. The term "fire clay," therefore, excludes most kaolin and ball clay because they burn white, but it does include kaolin and ball clay that are colored when fired. This classification of "refractory clay" as a group name and the threefold subdivision is by no means universally applied. Other reports, including earlier ones by the authors themselves, have used the terms "refractory clay" and "fire clay" interchangeably.

³In compliance with the recommendations of the AIPEA (Association Internationale Pour l'Etude des Argiles) Nomenclature Committee (Bailey, 1980), "halloysite (10A)" will be used to refer to the hydrated form and "halloysite (7A)" will be used for the dehydrated form. No angstrom indication will be made where halloysite is used as a general term, where both forms may be present, or where the hydration state is unknown.

TABLE 1.—*Temperature end points of American pyrometric cones*
 [Temperatures given are approximate and are applicable only when heated at
 specified rates (Norton, 1968)]

No. of cone	End point	
	°F	°C
18	2,714	1,490
19	2,768	1,520
20	2,786	1,530
23	2,876	1,580
26	2,903	1,595
27	2,921	1,605
28	2,939	1,615
29	2,984	1,640
30	3,002	1,650
31	3,056	1,680
32	3,092	1,700
32½	3,137	1,725
33	3,173	1,745
34	3,200	1,760
35	3,245	1,785
36	3,290	1,810
37	3,308	1,820
38	3,335	1,835

Saprolite.—Saprolite is decomposed weathered rock in which many if not all of the original minerals have been replaced by pseudomorphs consisting of other minerals. Textures and structures of the parent rock are preserved in saprolite, and little or no volume is lost as it forms. The term "saprolite" is now widely used in the literature on soil science and the geology of weathered rocks. It has essentially the same meaning as the term "lithomarge" used in India and the German term "Zersatz."

Underclay (seat earth).—Underclay is a type of clay normally underlying a coal bed or peat bed. Underclay is generally nonbedded and slickensided, fractures irregularly, and contains imprints of plant roots and other physical characteristics indicating formation as a waterlogged soil. Underclay has the same meaning as "seat earth" as used in England and is very similar to the German term "Tonstein." In this report, the term "underclay" is used according to the above definition. However, the term has also been used in a more general way for clay of almost any type or soil occurring below a unit of another lithology.

Types of Deposits

Kaolin in North America occurs in hydrothermal, residual, and sedimentary deposits. In some districts

and regions, all the kaolin is a single type. For example, all kaolin produced in Mexico is the hydrothermal type, all in the Spruce Pine district in the United States is residual, and all in the Georgia Coastal Plain is sedimentary. Both residual and sedimentary kaolin deposits are present in other districts, but no large deposits containing both hydrothermal and sedimentary types have been found. A few of the sedimentary clays in the United States have been mildly altered by hydrothermal solutions.

HYDROTHERMAL

Hydrothermal kaolin deposits form elongate pods, pipelike bodies, and irregular masses. Deposits tend to be aligned along joints, faults, pyroclastic beds, or other permeable zones that allowed movement of warm or hot solutions. Solubility of the host rock is a factor in determining the location of large replacement deposits, as dissolution is required to make space for the kaolin. An example is the halloysite body in the Dragon mine, Tintic district, Utah, that replaces limestone adjacent to a less soluble rhyolite intrusive rock. Many hydrothermal kaolin deposits are enclosed by halos of silica-enriched rock. Alunite, cristobalite, and other forms of silica including opaline material occur in many deposits, and metallic sulfide minerals are present in some. Pseudomorphs of the minerals forming the host rock are found in many deposits. The age of hydrothermal kaolin formation is not necessarily related to the age of the host rock. Most hydrothermal clay deposits are probably no older than Tertiary, though some are found in much older rocks.

RESIDUAL

Residual kaolin deposits in weathered rocks are generally at or very near the surface, except where formed during ancient weathering cycles and later buried by younger rocks. Most residual kaolin deposits have formed from granitic and gneissic and other types of crystalline metamorphic rocks. The age of kaolin formation is commonly controlled by the age of the present land surface rather than by the age of the parent rock. Residual kaolin deposits are generally irregularly shaped and grade downward into the parent rocks through partly altered, weathered saprolite zones. Residual boulders or blocks of parent rock enclosed by concentric layers of partly weathered rock are common in the least weathered parts of many deposits of this type.

All kaolin formed at the surface involves the removal of silica and other elements, and some downward movement of kaolinite undoubtedly took place in the formation of many of the sedimentary deposits. Therefore, such deposits as the underclays and ball clays that served as soils are in part residual.

SEDIMENTARY

In this report, all kaolin deposits in sedimentary rocks are considered the sedimentary type. Most kaolin deposits in this group are thought to have been formed by the transportation and deposition of kaolinite formed elsewhere. Underclay (seat earth) and ball clay, of which most deposits are varieties of underclay, are included with this type because with very few exceptions they occur in sedimentary rock.

The underclay and some kaolin deposits may have formed mainly by weathering in place from aluminous minerals in sedimentary rocks. Therefore, some of the deposits in this group are interrelated with the residual type. Many clays in the sedimentary group have undergone diagenetic changes and, therefore, may be considered to have formed by a process other than sedimentation. However, it is rarely possible to distinguish the characteristics of clay resulting from sedimentation from those formed after deposition, and no attempt is made to classify any of the deposits as diagenetic type.

Sedimentary kaolin deposits typically are ameboid tabular lenses that vary considerably in size. Many such lenses tend to have nearly flat or gently undulating upper surfaces and to extend convexly downward in the thicker central parts. Channel-fill deposits are common in some districts. One large blanket-shaped deposit in Georgia extends for more than 18 km, and for most of this distance it is 10–25 m thick.

UNITED STATES

History and Production

The sedimentary kaolins of the Coastal Plain of Georgia and South Carolina and the residual kaolins of North Carolina have been known since Colonial times. Smith (1929, p. 1) quoted from Sholes's chronological history of Savannah, " * * * 1741—Porcelain Clay was discovered in or near Savannah by Mr. Duchet, and china cups made. * * *" Probably even earlier, clays from New Jersey and Massachusetts had been used for lining pots and ladles used in making glass and iron (The Refractories Institute, 1979). In 1767, Josiah Wedgwood sent Thomas Griffiths to Macon County, N.C., to send a shipment of china clay to England (Goff, 1959). Minton (1922) recorded that " * * * As early as 1766 American clays from Georgia, Florida, and the Carolinas were being sent to England in considerable quantities. * * *" These clays were regularly imported and used by Wedgwood until 1768, when kaolin was discovered in Cornwall (Barton, 1966); this discovery ended the mining of the Georgia kaolins for more than a century. In 1876 (Smith, 1929, p. 1), the mining of the

sedimentary kaolins of Georgia was started again by Riverside Mills of Augusta in Richmond County. Mining of the Georgia kaolins has been continuous since that time. In addition to the original pottery in Savannah, a second pottery was established near Bath, Aiken County, S.C., at an early date. This plant was destroyed during Sherman's march to the sea in 1865 (Lang and others, 1940). However, kaolin mining was active again in Aiken County shortly after the Civil War and has continued with only minor interruptions until the present.

South Carolina has ranked as the second leading kaolin-producing State for several decades. Kaolin mining in North Carolina started in 1888 in Jackson County (Parker, 1946), and, in 1904, the earliest mines opened in the Spruce Pine district. The first kaolin operation in Vermont (Ogden, 1969) was in the early 1800's.

For most areas, production figures for kaolin in the late 1800's and early 1900's are difficult to trace. It is estimated that about 3 million tons was produced in Georgia before 1932 (Kesler, 1956), after which much better statistics are available. In 1972, total production in Georgia alone was nearly 4 million tons, and South Carolina, ranking second, produced more than 680,000 tons. Total kaolin produced in the United States in 1977 was 6,488,558 short tons (5,885,800 metric tons) (Ampian, 1977, table 5). Approximately 77 percent of this total was produced in Georgia, and 11 percent in South Carolina. In 1977, 894,277 short tons (811,200 metric tons) of ball clay was produced (Ampian, 1977, table 12), and more than one-half of this tonnage was produced in Tennessee. The 1977 output of fire clay, which was mainly kaolinite, was 2,965,607 short tons (2,690,100 metric tons) (Ampian, 1977, table 14). Missouri, Ohio, and Pennsylvania were the leading producing States.

Use

Kaolin has many industrial applications (Murray, 1963a), and new uses are still being discovered. It is a unique industrial mineral because it is chemically inert over a relatively wide pH range, is white, has good covering or hiding power when used as a pigment or extender in coated films and filling applications, is soft and nonabrasive, has low electrical and thermal conductivity, and costs less than most competing materials. Some uses of kaolin require very rigid specifications including particle-size distribution, color and brightness, and viscosity, whereas other uses require practically no specifications; for example, in cement, the chemical composition is most important. The better grades of kaolin make up most of the tonnage sold and,

of course, have the highest value. Many grades of kaolin are specially designed for specific uses, in particular for paper, paint, rubber, plastics, and ceramics.

The paper industry is by far the leading consumer of kaolin (fig. 1); approximately 50 percent of the total production is used in paper products. Much of the paper used in today's color picture magazines contains as much as 30 percent by weight of kaolin. Kaolin used in paper fills the interstices of the sheet and coats the surface, imparting smoothness, gloss, brightness, opacity, and printability (Bundy and others, 1965). Kaolin is less expensive than paper pulp and thereby effectively lowers paper-production costs, and it is cheaper or more efficient than other materials used in filling and coating. It is inert to the other ingredients in paper, is retained well between the paper fibers, and is available in large quantity, and the platy structure of kaolinite lends itself to the production of high-gloss papers. The low viscosity of kaolin at both high and low shear rates is a very important property, because at today's very high speed production rates the coating must be applied at high solids content and still impart the correct coating thickness and opacity to the paper. High-quality paper-coating kaolin flows readily when applied with very high speed coating equipment, giving the paper a smooth and even film.

The rubber industry uses large tonnages of kaolin as a filler or extender in both natural and synthetic rubber (fig. 1). Kaolin is incorporated in the latex mix to improve properties such as strength, abrasion resistance, and rigidity; furthermore, it lowers the cost. Through the years, two terms, "hard kaolins" and "soft kaolins" (Klinefelter and others, 1943), have become commonplace in describing types of kaolin used by the rubber industry. The hard kaolin, though distinctly softer than flint kaolin or flint clay, is a very fine particle-size kaolin that tends to improve the tensile strength of rubber and its resistance to tearing and abrasion. The principal uses of hard kaolin in rubber are in the production of footwear and cable covers. Soft kaolin lacks the reinforcing properties of the hard kaolins and is used to lower elasticity and improve abrasion resistance, particularly in such products as floor tile and soft rubber goods.

Kaolin is used as an extender in paints because it is chemically inert, has a high covering power, gives desirable flow properties, is low in cost, is white, and reduces the amount of expensive pigment required. In addition, it has very excellent suspension properties and is available in a wide range of particle sizes that can be used in many types of paints. For example, coarse-particle kaolins are used in paints where a dull or flat finish is required, and fine-particle kaolins are used in high-gloss paints. Large quantities of calcined

kaolin and water-beneficiated kaolin are used in interior flat wall paints and in metal primers. Water-beneficiated grades of kaolin disperse easily in water and are, therefore, particularly suited to latex paints. Some kaolin is chemically treated to make it organophilic or hydrophobic and thereby suitable for use in exterior oil-based paints. Calcined kaolin, because of its resistance to abrasion and its dry covering properties, is being used in increasing quantities by paint manufacturers. Calcined kaolin is an excellent extender for TiO_2 , the leading paint pigment, particularly in latex paint, and its use reduces costs and simplifies the formulation of the paint.

Kaolin is used extensively as a filler in plastics. The use of kaolin in plastics results in smoother surfaces, more attractive finish, dimensional stability, and resistance to chemical attack. Manufacturers of polyvinyl chloride (PVC) use kaolin as a reinforcing agent, and it makes the plastic more durable. Calcined and partially calcined kaolins are used as a filler in PVC wire insulation to improve electrical resistivity. In the manufacture of glass-reinforced polyesters, kaolin has helped eliminate flow problems that hindered production of large products, such as automobile body parts and boat hulls. The kaolin actually results in a stronger, more uniform part or body. Plastics are a major area of future growth for kaolin products. They are used extensively in vinyl floor coverings, and surface-modified kaolin gives improved dispersibility in certain plastic systems, which will greatly increase their usage.

Historically, kaolin was first used in ceramics, and this is perhaps still the best known application, even though the total tonnage sold for this use is small compared with that marketed for paper, paint, and rubber manufacturing (fig. 1). It is used in the manufacture of whitewares, wall tile, insulators, refractories, and in some face brick when a white color is desired. Specially designed grades having high green and dry strengths are available for use by whiteware manufacturers. The most important properties for this use are plasticity, strength, and fired color. Kaolin is used in insulators because of its properties of low conductivity, high dielectric constant, low power loss, plasticity, and fired strength. It is used in casting because of its excellent flowability, suspension properties, color, and water-release characteristics. It also is used in porcelain, again because of its excellent suspension characteristics and good color.

Kaolin has many other important applications, but the tonnages required are rather small in comparison with the aforementioned uses. Although the following list is not complete, it shows the extremely wide variety of products containing kaolin as a suspending agent, filler, extending agent, or a main constituent:

KAOLIN IN NORTH AMERICA, HAWAII, AND THE CARIBBEAN

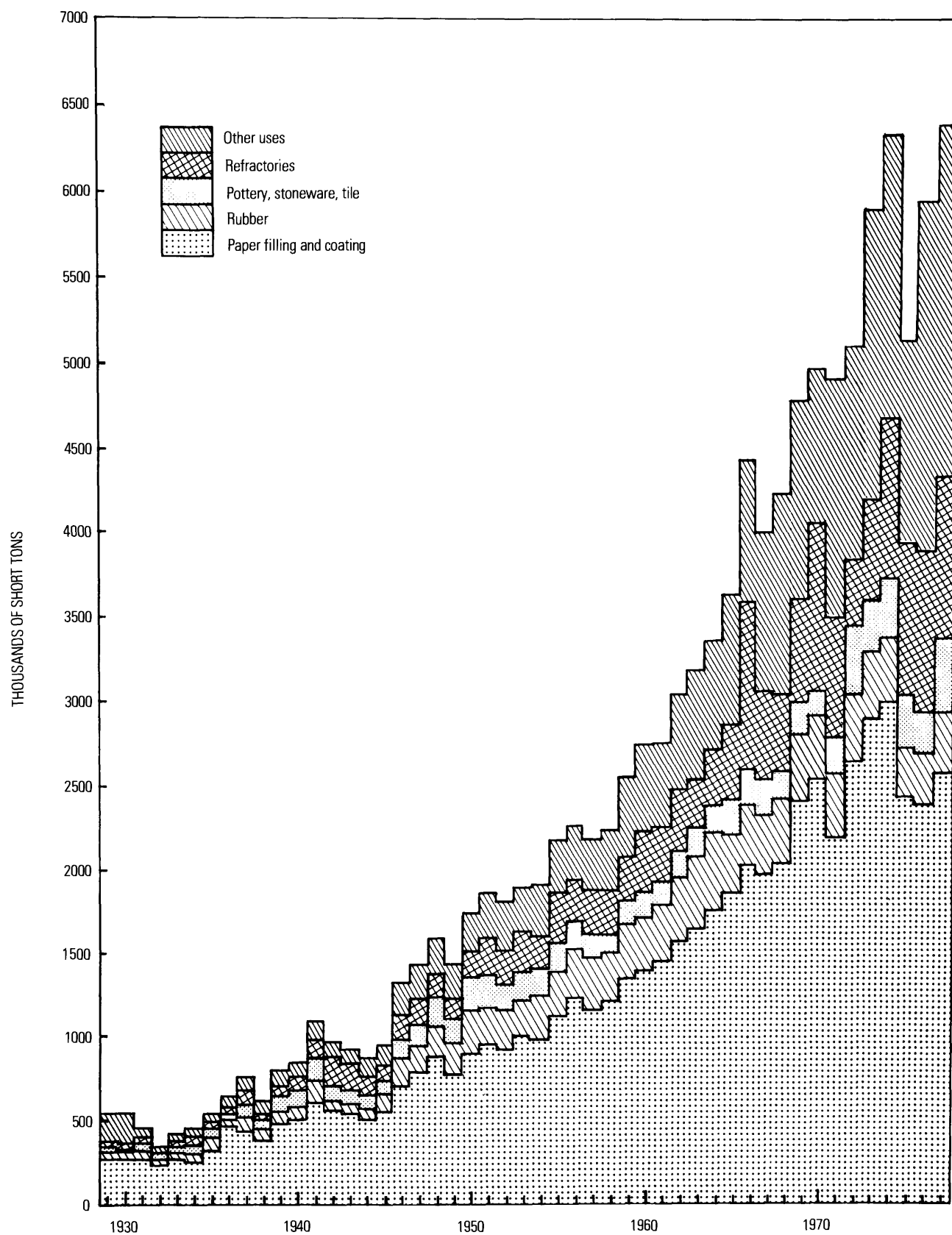


FIGURE 1.—Kaolin sold or used by producers for specified uses, 1929–77. [Compiled from U.S. Bureau of Mines Mineral Yearbooks. Short tons can be converted to metric tons by dividing by 1.1024]

ink
adhesives
insecticides
medicines
food additives
catalyst preparations
bleaches
adsorbents
cement
fertilizers
plaster
filter aids
cosmetics

chemicals
crayons
pencils
detergents
porcelain enamels
paste
roofing granules
sizing
foundries
linoleum
floor tiles
textiles

Sedimentary Deposits

Sedimentary kaolinitic clays are far more abundant and widely distributed in the United States than are the other deposit types (fig. 2, table 2). Kaolin, underclay, and ball clay occur mainly in sedimentary deposits.

ATLANTIC AND GULF COASTAL PLAINS

Many kaolin deposits are in sedimentary beds underlying the Atlantic and Gulf Coastal Plains. The largest

deposits are in the South Carolina–Georgia–Alabama belt, but other deposits are in districts in Florida, northwestern Alabama, Mississippi, southern Illinois, southeastern Missouri, Arkansas, and Texas. The ball clays that are grouped with the underclays in this report also occur in the Coastal Plains.

SOUTH CAROLINA–GEORGIA–ALABAMA KAOLIN BELT

Location

The South Carolina–Georgia–Alabama kaolin belt extends for a distance of nearly 400 km from the Aiken, S.C.–Augusta, Ga., district on the northeast to the Eufaula, Ala., district on the southwest (fig. 3). This belt contains estimated kaolin resources of 7 billion–10 billion tons and is the world's leading producer of sedimentary kaolin. More than 100 million tons have been mined in the six major districts shown in figure 3. The four districts located northeast of the Ocmulgee River (fig. 3) are the principal source of white clay having the properties required for the American usage of the term "kaolin" as an industrial mineral commodity. The Andersonville district, Georgia, is a center of production of light-gray to white refractory kaolin and kaolin

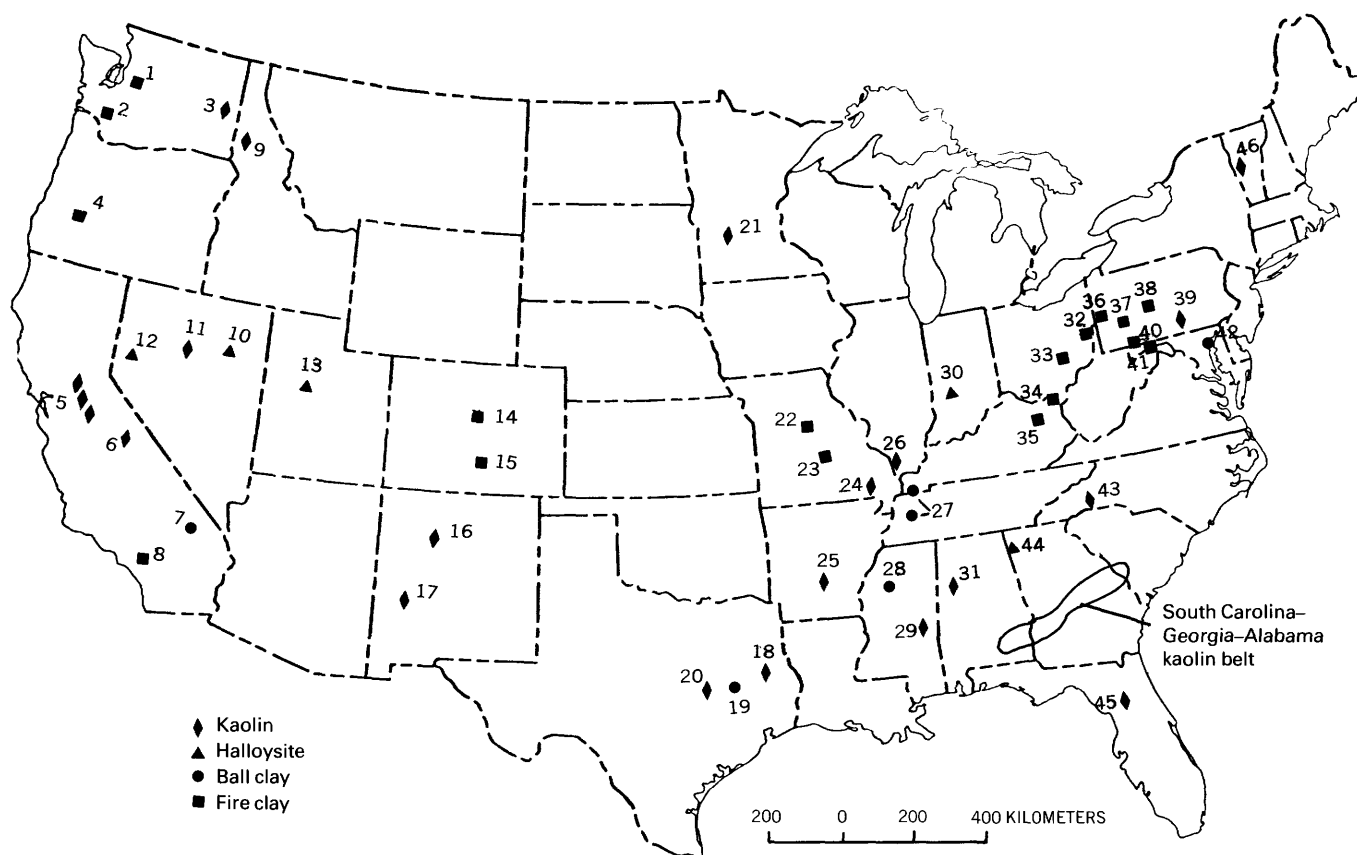


FIGURE 2.—Map showing kaolin, ball-clay, halloysite, and refractory-clay deposits in the United States. (Numbers refer to table 2.)

TABLE 2.—*Kaolin, refractory clay, ball clay, and halloysite found in the United States*

[Sed., sedimentary or transported; Res., residual; Hyd., hydrothermal; K, kaolin; H, halloysite; B, ball clay; Rk, refractory kaolin; Rf, fire clay, chiefly underclay. Numbers refer to figure 2]

Number	District	State	Type of clay	Age	Reference
1	King County -----	Washington -----	Sed., Rf -----	Eocene -----	Nichols, 1946
2	Cowlitz -----	do -----	Sed., Rf -----	do -----	Popoff, 1955
3	Spokane County -----	do -----	Sed., K, Rk -----	Miocene -----	Hosterman, 1969a
4	Hobart Butte -----	Oregon -----	Sed., Rf -----	Eocene -----	Allen and others, 1951
5	Ione -----	California -----	Sed., K, Rk -----	middle Eocene -----	Pask and Turner, 1952
6	Little Antelope Valley --	do -----	Hyd., K -----	Tertiary -----	Cleveland, 1962
7	Hart -----	do -----	Hyd., B -----	do -----	Kelley, 1966
8	Alberhill -----	do -----	Sed., Res., Rf -----	Paleocene -----	Cleveland, 1957
9	Latah County -----	Idaho -----	Sed., Res., K, Rk -----	Miocene -----	Ponder and Keller, 1960.
10	Bullion -----	Nevada -----	Hyd., H -----	Tertiary -----	Olson, 1964
11	Stoker -----	do -----	Hyd., K -----	Tertiary(?) -----	Do.
12	Terraced Hills -----	do -----	Hyd., H -----	Miocene and Pliocene --	Papke, 1971
13	Tintic -----	Utah -----	Hyd., H -----	Tertiary -----	Kildale and Thomas, 1957.
14	Front Range -----	Colorado -----	Sed., Rf -----	Cretaceous -----	Waage, 1961
15	South Central -----	do -----	Sed., Rf -----	do -----	Waage, 1953
16	Mesa Alta -----	New Mexico -----	Sed., K -----	Jurassic and Cretaceous	Reeves, 1963
17	Winston -----	do -----	Hyd., K -----	Tertiary -----	Patterson and Holmes, 1965.
18	Rusk County -----	Texas -----	Sed., K -----	early Eocene -----	Fisher, 1965
19	Troup -----	do -----	Sed., B -----	do -----	Stenzel, 1950
20	Kosse -----	do -----	Sed., K -----	do -----	Pence, 1954
21	-----	Minnesota -----	Sed., Res., K -----	Cretaceous -----	Parham, 1970
22	East Central -----	Missouri -----	Sed., Rf -----	Early Pennsylvanian --	McQueen, 1943
23	Ozark -----	do -----	Sed., Rf -----	Pennsylvanian -----	Keller, 1952
24	Glen Allen -----	do -----	Sed., K -----	Eocene(?) -----	Tennissen, 1960
25	Bauxite -----	Arkansas -----	Sed., Res., K, Rk -----	early Eocene -----	Tracey, 1944
26	Anna -----	Illinois -----	Sed., K -----	Eocene(?) -----	Grim, 1934
27	-----	Kentucky-Tennessee --	Sed., B -----	early to middle Eocene-	Olive and Finch, 1969
28	Panola -----	Mississippi -----	Sed., B -----	middle Eocene -----	Bicker, 1970
29	Kemper -----	do -----	Sed., K -----	Paleocene and Eocene-	Conant, 1965
30	Shoals -----	Indiana -----	?, H -----	in Paleozoic rocks ----	Callaghan, 1948
31	Hackleburg -----	Alabama -----	Sed., K -----	Late Cretaceous -----	Clarke, 1966
32	East Liverpool -----	Ohio -----	Sed., Rf -----	Middle Pennsylvanian-	Hosterman and others, 1968.
33	Tuscarawas -----	do -----	Sed., Rf -----	Early and Middle Pennsylvanian.	Do.
34	Oak Hill -----	do -----	Sed., Rf -----	Early Pennsylvanian --	Stout and others, 1923
35	Olive Hill -----	Kentucky -----	Sed., Rf -----	do -----	Patterson and Hosterman, 1962.
36	Beaver Valley -----	Pennsylvania -----	Sed., Rf -----	Middle Pennsylvanian-	Hosterman and others, 1968.
37	Allegheny -----	do -----	Sed., Rf -----	do -----	Do.
38	Clearfield -----	do -----	Sed., Rf -----	Early and Middle Pennsylvanian.	Foose, 1944
39	Mount Holly Springs --	do -----	Res., Hyd.(?), K -----	Tertiary(?) -----	Hosterman, 1969b
40	Somerset County -----	do -----	Sed., Rf -----	Middle Pennsylvanian-	Hosterman, 1972
41	Frostburg -----	Maryland -----	Sed., Rf -----	do -----	Waage, 1950

TABLE 2.—Kaolin, refractory clay, ball clay, and halloysite found in the United States—Continued

Number	District	State	Type of clay	Age	Reference
42	North East	do	Sed., B	Cretaceous	Knechtel and others, 1961.
43	Spruce Pine	North Carolina	Res., K	Tertiary(?)	Parker, 1946
44	Gore	Georgia	Sed.(?), H	in Devonian rocks	Broadhurst and Teague, 1954.
45		Florida	Sed., Res., K	Pliocene and Pleistocene.	Pirkle, 1960
46	East Monkton	Vermont	Hyd.(?), K	?	Ogden, 1969

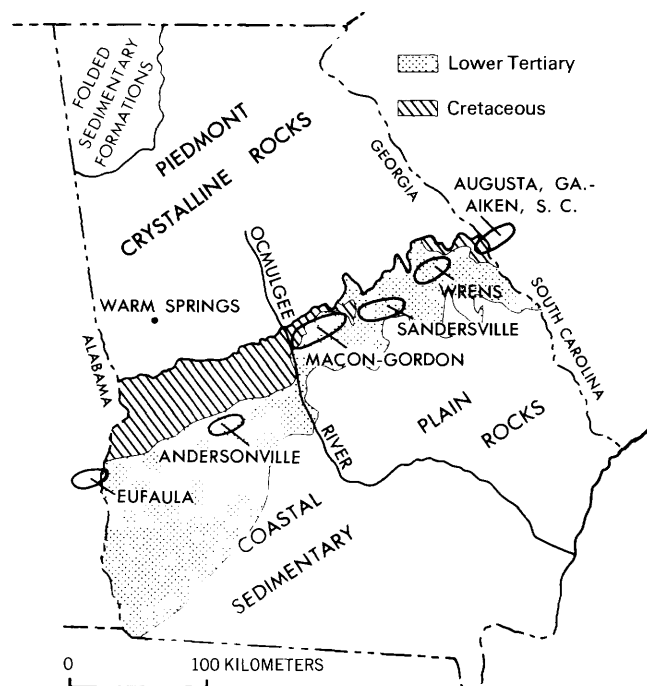


FIGURE 3.—Locations of the six major districts in the South Carolina-Georgia-Alabama kaolin belt.

used for making alum-type chemicals and bauxite. Similar refractory kaolin and bauxite are mined in the Eufaula district, Alabama. Kaolin and small bauxite deposits occur in the belt between the Andersonville and Eufaula districts (Zapp and Clark, 1965; Clark, 1965), but there has been no mining in this area for several decades. Kaolin is also known to occur between the Macon-Gordon and Andersonville districts, and deposits in this part of the belt may be very large; however, little information about these deposits is available, because the results of company drilling are privileged.

Occurrence and Age

All of the kaolin deposits in the South Carolina-Georgia-Alabama belt are in sedimentary beds, and,

except for a small outlier at Warm Springs (fig. 3), all underlie the Coastal Plains. The greatest inland overlap of Cretaceous and lower Tertiary sediments onto crystalline rocks is in the Wrens district (fig. 3). The kaolin deposits in the Wrens and other districts northwest of the Ocmulgee River are aligned along the landward edge of the overlap. The Andersonville district, Georgia, and the Eufaula district, Alabama, are 60–75 km south of the edge of the overlap. The small kaolin deposits in a downfaulted outlier of Coastal Plain sedimentary beds in the inactive Warm Springs district, Georgia, are about 35 km north of the edge of the overlap.

The kaolin deposits of Late Cretaceous age are in the Aiken-Augusta, the western part of the Sandersville, and the Macon-Gordon districts (fig. 3). The kaolin deposits of this age are in a wedge-shaped Cretaceous sand unit that is truncated updip by erosion and is known to be more than 335 m thick where penetrated by a well downdip. This unit rests unconformably on pre-Cretaceous crystalline rocks, and it is overlain by overlapping Tertiary formations. The Cretaceous beds consist chiefly of white to buff, crossbedded, irregular and channel-fill deposits of medium to very coarse, subrounded to angular quartz sand. Interstitial kaolinitic clay, kaolin balls, and white mica flakes are common in the sand. The only fossils known to be present in the unit are plant remains. The Cretaceous unit is dated by regional correlations and age of pollen. A pollen sample collected stratigraphically above a kaolin deposit in the Macon-Gordon district was found to be of Maestrichtian Age, and another from 70 m below the top of the unit was of definite Cretaceous age (Tschudy and Patterson, 1975). The kaolin deposits in the Cretaceous unit are generally lenticular or saucer-shaped bodies ranging greatly in thickness and extent. Some are as much as 12 m thick and more than 2 km long. Most deposits mined are in the upper part of the Cretaceous unit because of the cost of removing thick overburden.

Kaolin deposits of early Tertiary age occur in all

three districts northeast of the Ocmulgee River that contain Cretaceous kaolin and in the Wrens district. The Tertiary strata containing the kaolin are similar to the Cretaceous beds on which they rest unconformably. The lower Tertiary beds overlap the Cretaceous unit and extend onto crystalline rock at several localities. The lower Tertiary kaolin deposits tend to be larger than the Cretaceous deposits. One deposit in the eastern part of the belt, where thicknesses are 10–25 m, is 18 km long (Murray, 1976, p. 117).

The lower Tertiary strata in the Macon-Gordon district have been named the Huber Formation, which as defined by Buie (1978) includes all the strata between

the Cretaceous or older rock, upon which it unconformably rests (fig. 4), and the base of strata of Jacksonian Age (late Eocene). Lithologically, the Huber is typical of a tidal-flat environment of deposition. Channel-fill deposits are abundant, and most of the formation is intricately crossbedded. Ilmenite and other dark heavy minerals are abundant and are concentrated along bedding planes. Lignitic clays, which contain pollen, occur at many places, usually as single beds or as restricted lenses. Rounded boulders of pisolitic kaolin and gibbsitic kaolin, ranging in diameter from a few centimeters to more than 2 m, are present in the upper part of the formation at many places. Many of these

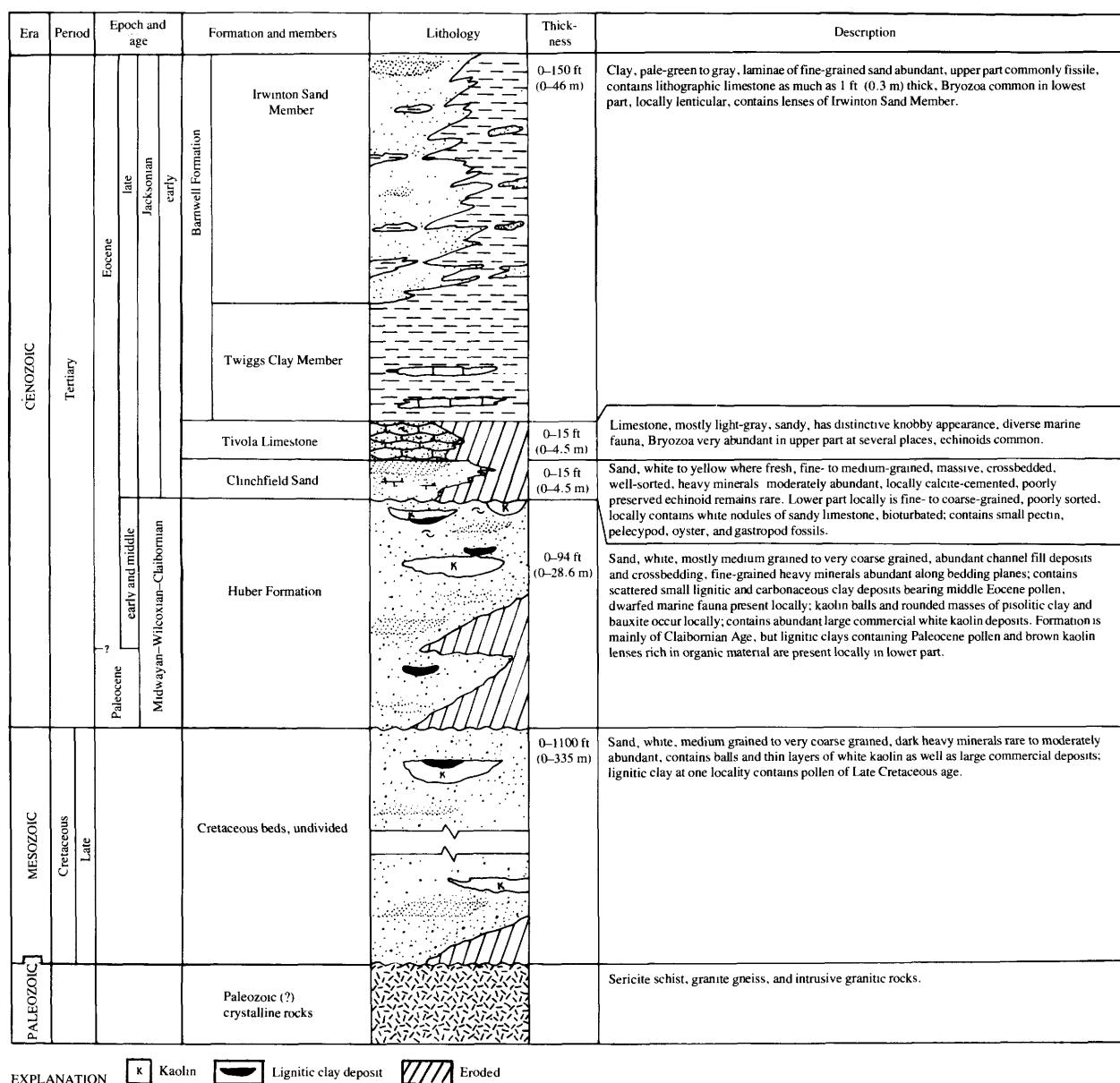


FIGURE 4.—Generalized geologic section, Macon-Gordon kaolin district, Georgia.

boulders are enclosed in sand, and they clearly indicate a high-energy environment of deposition. The upper parts of kaolin deposits in the Wrens district contain sponge spicules (fig. 5), and Scrudato and Bond (1972) reported that spicules are also present in deposits farther to the northeast.

The age of some of the kaolin in the Huber Formation is now known to be Claibornian (middle Eocene part), and some may be somewhat older Tertiary. The Claibornian Age is assigned on the basis of the discovery of pollen of this age below a clay deposit that is overlain by fossiliferous marine beds of Jacksonian Age (late Eocene) (Tschudy and Patterson, 1975). Diverse suites of small marine mollusks of early or middle Eocene age also occur in a stratigraphic position below commercial kaolin deposits at several localities (Buie and others, 1979). The possibility that some of the Tertiary kaolin may be older than middle Eocene is based on the identification of pollen from lignitic material in impure clays and kaolinitic sands (Tschudy and Patterson, 1975). A sample of drill core from a locality east of the

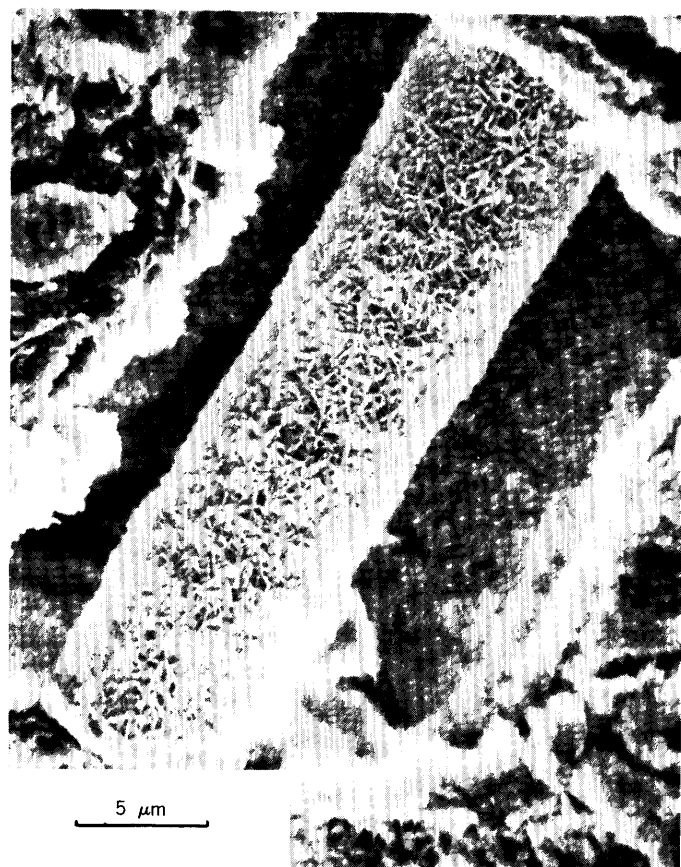


FIGURE 5.—Electron micrograph of kaolin of Eocene age from near Wrens, Ga., showing sponge spicule. (Micrograph by W. D. Keller, University of Missouri.)

Macon-Gordon district contained probable Wilcoxian (early Eocene) pollen. Definite Paleocene pollen were found in samples from three localities in one mine area in the district. This pollen is associated with dinoflagellates that are probably marine. The recognition of the older strata and the occurrence of Paleocene kaolin in the Andersonville district to the southwest make it seem likely that some of the valuable kaolin in the Macon-Gordon district and other districts to the northeast is older than middle Eocene.

At one locality, lignitic clay of Paleocene age located stratigraphically between kaolin deposits contains marine dinoflagellates. These fossils and the megascopic marine fauna of Claibornian Age indicate at least two intervals of marine or brackish-water deposition. Other intervals of marine deposition may have occurred during the approximately 20 million years when the Huber Formation was being deposited. However, during much of this time, this region was undergoing erosion, and neither marine nor continental sediments were being deposited.

Three types of tubular features or borings of animals are found in the Huber Formation. One type, found only in the kaolin deposits, is a peculiar spaghetti-like form; some of these tubes are branching and resemble Bryozoa, whereas others appear to be filled borings. Most are about 2.5 mm in diameter, and some are as much as 3 cm long. A second type of tubular feature is present in sand and clayey sand beds in the upper part of the formation. This type is commonly as much as 10 cm long. Most of these features are vertical, but they are oriented in various directions. Most are preserved only as clayey or slightly cemented sand fillings in unconsolidated sand. The third type consists of boring fillings called *Halymenites* in older reports (Eargle, 1955). This type is as much as 5 cm in diameter and is known to extend downward nearly 2 m.

Kaolin deposits of Paleocene age occur in the Andersonville and Warm Springs, Ga., and the Eufaula, Ala., districts (fig. 3). The ages assigned to the deposits in the two districts in Georgia are based on recent pollen studies (N. O. Frederiksen, oral commun., 1979). The deposits in the Eufaula district, like those at Andersonville, are in the Nanafalia Formation and therefore are the same age. The Warm Springs deposits have been exhausted, and little is known about them other than that they are associated with small gibbsitic bauxite deposits in a downfaulted block of sediments surrounded by crystalline rocks in the Piedmont region. They are of interest mainly because their geographic location strongly suggests that kaolin deposits were far more extensive in the region north of Andersonville before the extensive erosion of Paleocene and Upper Cretaceous beds.

The kaolin and bauxite deposits in the Andersonville district are in the Nanafalia Formation, which consists mainly of medium to coarse kaolinitic and micaceous sand (H. E. Cofer and J. P. Manker, written commun., 1979). The kaolin is in tabular lenticular bodies ranging from less than 1 m to about 15 m in thickness; some deposits extend over areas of several hectares. The bauxite is also in lenticular bodies, which typically are enclosed by bauxite kaolin that grades into kaolin. Most bauxite bodies are 1–3 m thick, and the maximum thickness of bauxite and bauxitic clay units is about 18 m.

The kaolin and bauxite in the Eufaula, Ala., district described by Clarke (1972) and Burst (1974) are remarkably similar to the deposits in the Andersonville, Ga., district. One difference in the geology of the two districts is that there is more evidence that sink-holelike depressions were, as postulated by Clark (1972, p. 83–88), the sites of bauxite formation in the Eufaula district than in the Andersonville district. The Clayton Formation, which underlies the Nanafalia Formation, is thicker, contains much more limestone, and shows more evidence of solution in the Eufaula district than in the Andersonville district.

Mineralogy

The kaolin deposits of Cretaceous and early Tertiary age in the districts northeast of the Ocmulgee River are quite similar in gross mineralogy. Kaolinite is by far the dominant mineral in these deposits and constitutes 90–95 percent of most clay mined. Trace amounts of smectite occur in many deposits, and this mineral makes up 30–40 percent of the kaolin at a few localities. Quartz is the most abundant nonclay mineral impurity in the kaolin, and amounts present range broadly. Most deposits mined are less than 5 percent quartz, but greater amounts are present in subeconomic kaolin, and very sandy kaolinitic beds contain more than 75 percent of this mineral. Ilmenite is the second most abundant nonclay mineral, and this mineral and very fine grained anatase contain the TiO_2 in the kaolin. Other minerals commonly present as accessories in kaolin are muscovite, biotite, magnetite, tourmaline, zircon, kyanite, monazite, goethite, leucoxene, graphite, and occasionally other heavy minerals.

The Cretaceous and lower Tertiary kaolin deposits northeast of the Ocmulgee River are similar in many ways, but they differ in several characteristics, including particle size, abundance of vermicular crystals, crystal perfection, and specific gravity (table 3). Although Cretaceous and lower Tertiary kaolins are similar in particle-size range (fig. 6), the older deposits sel-

dom are more than 65 percent $< 2\mu\text{m}$ particles, whereas the younger deposits generally are more than 90 percent $< 2\mu\text{m}$ particles. The Cretaceous kaolin contains appreciable quantities of vermicular crystals (fig. 7) that are as much as $30\mu\text{m}$ long. These relatively large crystals are in a fine matrix of kaolinite books and

TABLE 3.—*Characteristics of the Cretaceous and Eocene kaolin deposits in the Macon-Gordon district, Georgia*

General characteristics	Cretaceous	Eocene
Color -----	White to cream or buff; natural brightness high.	Mainly white to cream, buff, or gray; commonly has a slight greenish tinge that changes to a faint pinkish tint upon exposure; some deposits are very light gray; natural brightness moderate to low.
Fracture or parting.	Smooth; when dry, breaks easily into friable blocks having sharp angles and smooth flat or subconchoidal faces; commonly called "soft kaolin."	Mostly breaks into irregular chunks with rough or hackly fracture; commonly called "hard kaolin."
Tubular structures resembling borings or Bryozoa.	Absent -----	Common
Pisolitic texture.	Rare -----	Common in upper parts of deposits.
Particle size--	Generally 65 percent $< 2\mu\text{m}$; vermicular crystals and "books" common.	Generally more than 90 percent $< 2\mu\text{m}$; vermicular crystals scarce.
Crystal perfection.	Generally good -----	Generally poor
TiO_2 content-	About 1 percent -----	About 2 percent
Mineral impurities other than quartz sand.	Mainly mica, miscellaneous heavy minerals; fine-grained dark minerals are rare or unobservable in hand specimens.	Very fine grained dark heavy minerals moderately abundant and observable in most hand specimens.

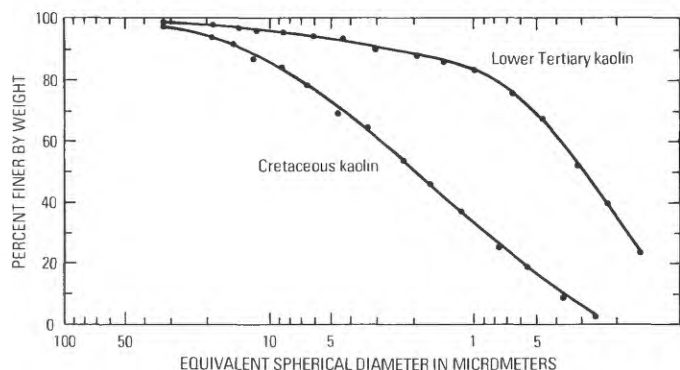


FIGURE 6.—Particle-size distribution of Cretaceous and lower Tertiary kaolins.

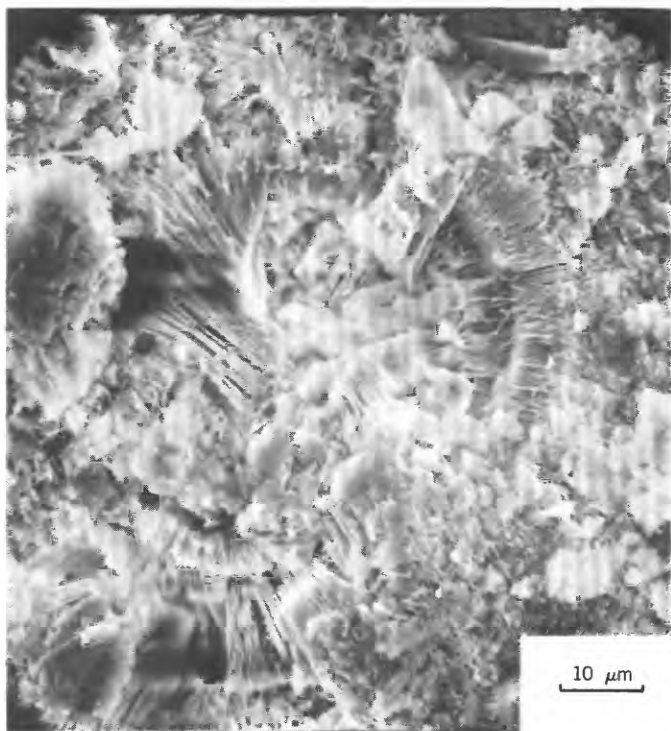


FIGURE 7.—Electron micrograph of kaolin of Cretaceous age from near Gordon, Ga., showing vermicular crystals. (Micrograph by W. D. Keller, University of Missouri.)

plates. Vermicular crystals are rare in Tertiary kaolin, which consists chiefly of thin plates with few thick books (fig. 8). In addition to the crystal characteristics shown in the electron micrographs, X-ray diffraction patterns of Tertiary kaolin show broad, diffuse prism reflections, indicating a poorly ordered crystal struc-



FIGURE 8.—Electron micrograph of kaolin of Eocene age from near Wrens, Ga., showing fine particle size. (Micrograph by W. D. Keller, University of Missouri.)

ture (Murray and Lyons, 1956), whereas the Cretaceous kaolinite shows sharp, distinct prism reflections, indicating a well-ordered structure. Klinefelter and others (1943) determined that the bulk specific gravity of the Cretaceous kaolin (soft) ranged from 1.32 to 1.55, whereas the bulk specific gravity of the Tertiary kaolin (hard) ranged from 1.61 to 1.79.

Except for the much greater abundance of gibbsitic bauxite bodies and the darker color, the kaolin deposits in the Andersonville district are similar to those northeast of the Ocmulgee River. Although most of the kaolinite in the Andersonville deposits is in the $<1\text{-}\mu\text{m}$ particle-size range, it also has a broad range of larger particles (H. E. Cofer and J. P. Manker, written commun., 1979). The books of coarse-grained kaolinite tend to be more perfectly ordered than the fine-grained clay matrix, and the coarser clay is generally most abundant in the bauxite and bauxitic clay.

Clay-mineral impurities in the Andersonville deposits include smectite, illite, and glauconite (H. E. Cofer and J. P. Manker, written commun., 1979). The iron content of kaolinite is thought to be the principal

cause of this kaolin being darker than kaolin in deposits to the northeast. Smectite is present in varying amounts throughout most of the Andersonville kaolin but tends to be most abundant in the upper parts of deposits that are overlain by marine beds. At places, nearly 50 percent of the upper few centimeters of clay is smectite. The glauconite in the Andersonville deposits was found in the sand fraction of a lens of dark-gray, lignitic clay, nearly 2 m thick, within a much thicker kaolin deposit. The glauconite occurs as abraded, lobate, and fragmented grains.

Nonclay minerals other than quartz in the Andersonville kaolin that were apparently deposited with the clay include muscovite, tourmaline, staurolite, kyanite, biotite, and zircon. Pyrite and siderite are common in parts of the kaolin. Both of these minerals formed diagenetically, as is indicated by their occurrence as euhedral crystals, fracture fillings, and concretionlike nodules.

Origin

Though geologists who have worked on the kaolin deposits in the South Carolina–Georgia–Alabama belt have some differing opinions, most agree that the clay was transported from weathered rocks located to the north and west. The principal source is commonly thought to have been weathered crystalline rocks in the Piedmont. However, there is some uncertainty as to whether or not the source of much of the kaolin may have been farther inland. Reasons for the uncertainty include lack of knowledge about how far the sedimentary overlap extended. The overlapping sediments may have extended much farther before erosion formed the present land surface, for the following reasons: (1) the existence of Coastal Plain sediments and kaolin in the Warm Springs outlier (fig. 3); (2) the occurrence of commercial kaolin near the edge of the overlap in the Wrens district, which is the maximum landward extent of conterminous Coastal Plain sediments; (3) the occurrence of boulders and cobbles of kaolin, some of which are pisolitic, at several places along the edge of the overlap; and (4) the dendritic drainage developed on the crystalline rocks in the Piedmont. Staheli (1976) pointed out that structurally controlled trellis drainage patterns would have developed on the folded and faulted crystalline rocks, if they had been at the surface when the drainage systems developed. He therefore concludes that present patterns have been superimposed on Coastal Plain sediments. Considering the four points in the foregoing outline, we conclude that the source of the kaolin can be, at best, little more than an opinion.

Sedimentary features in the kaolin and associated

beds make it clear that the Tertiary kaolin was deposited in a tidal-flat environment. Cretaceous deposits probably accumulated in a similar environment, but the evidence is less clear. The sedimentary features strongly suggest that, during early Tertiary time, the kaolin belt was a lowland much like the present Atlantic coast of Georgia. This coastal area is characterized by lengthy offshore bars, back bays, lagoons, salt marshes, and sluggish meandering streams having abundant oxbow lakes and intricately meandering distributaries. Advances and withdrawals of the seas took place in the kaolin belt in at least two, and probably several, intervals during early Tertiary time. Evidence for advances includes Paleocene glauconite in the Andersonville district, dinoflagellates in the Macon-Gordon district, and middle Eocene mollusks in the Macon-Gordon district. The sponge spicules in the kaolin in the Wrens and Aiken-Augusta district certainly indicate deposition in an aqueous environment, but it is not certain whether the sponges are marine or freshwater forms. Many of the tubular features in Tertiary kaolin are probably borings of littoral animals, but the identification is far too uncertain to provide acceptable evidence of depositional environments. Periodic emergences are indicated by the abundant plant remains, channel deposits, erosional contacts, and boulders and cobbles of kaolin in the Macon-Gordon district and the plant roots in kaolin in the Andersonville district. The bauxite also is evidence of emergence, if the conclusion that it formed by subaerial weathering is correct. The sporomorphs in the plant remains throughout the belt strongly suggest that the climate throughout the early Tertiary was subtropical.

We believe that the vermicular kaolinite crystals are authigenic and are the result of recrystallization influenced by moving subsurface water. We favor this origin over Hinckley's theory (1961) explaining vermicular growths as forming from mica and euhedral plates from feldspar. The following reasons are in opposition to the mica-parent idea for the vermicular forms: (1) The idea does not account for the abundance of vermicular crystals in the Cretaceous clay and their absence in Tertiary kaolin, as the kaolins of both ages are likely to have had the same source areas; (2) the Cretaceous kaolin, being older, has had considerably more time for recrystallization to take place; (3) the large vermicular crystals could not have withstood transportation even in an aqueous medium; and (4) the vermicular crystals in the Paleocene clay deposits in the Andersonville district occur almost exclusively in the bauxite and not in the associated fine-grained kaolin masses. It seems certain that the gibbsitic bauxite has undergone considerably more alteration and recrystallization than has the fine-grained kaolin.

The mineralogy and sedimentary characteristics of the kaolin and bauxite in the Andersonville district indicate that the deposits accumulated in a shallow estuarine environment and were altered during periods of emergence and submergence (H. E. Cofer, Jr., and J. P. Manker, written commun., 1979). The deposits accumulated as fine-grained kaolinitic sediments of widely varying purity that were transported by streams. The principal source was weathered crystalline rock to the north. Upper Cretaceous sedimentary formations also may have contributed kaolin, but this is uncertain because the presence of kaolin of Paleocene age in the Warm Springs district 60 km north of Andersonville suggests that Cretaceous beds may not have been exposed at the time of its deposition. Local basins of deposition were areas of shallow water between deeper distributaries in deltas of streams flowing into the estuary. Zones of root remains and carbonaceous material containing sporomorphs of land plants in kaolin deposits indicate emergences above sea level once during the period of kaolin deposition and again at the close of the interval. The gibbsitic bauxite is believed to have formed by weathering and leaching of kaolin during periods of emergence. Bauxitic clay enclosing the bauxite apparently formed in two ways. The clay on the sides of and below the bauxite represents incomplete stages of bauxite formation during weathering. The bauxitic clay above bauxite formed by resilication of gibbsite in silica-bearing water after submergence. The location of the larger kaolin deposits in the northern (landward) part of the district and the presence of glauconite interbedded with kaolin in the southern part of the district suggest that the principal centers of kaolin deposition were parts of the estuary having fresh or low-salinity water. At places in the southern part of the district and farther south, impure smectite associated with gypsum occurs at the stratigraphic position of the kaolin deposits; these minerals suggest deposition in saline water.

FLORIDA

Irregularly shaped, sandy kaolin deposits containing some quartz gravel are scattered throughout a narrow belt more than 200 km long in peninsular Florida (fig. 2, location 45). The deposits are near the surface in a problematical unit of clayey sand and gravel that is thought by some geologists to be part of the Citronelle Formation of Pliocene age and by others to be weathered Miocene beds. One raw sample of the kaolin for which composition data have been published (Pirkle, 1960, table 2) was 75–85 percent kaolin, 6–8 percent quartz, 5–8 percent hydrous mica, 2–3 percent iron-oxide minerals, and <1 percent smectite. However,

many of the deposits are known to contain considerably more than 8 percent quartz.

The origin of the Florida deposits is difficult to explain because of the absence of an obvious source of kaolinite and the abundance of coarse sand and gravel in the clay. Several theories have been advanced, including deposition in a deltaic environment and alteration of feldspar sand (Pirkle, 1960). We favor the idea that the deposits formed mainly by in-place weathering of older argillaceous sediments. Little can be mustered in support of this opinion except that Miocene beds of peninsular Florida are known to be rich in smectite, which Altschuler, Dwornik, and Kramer (1963) have shown conclusively weathers to kaolinite in the Florida phosphate region.

Kaolin has been produced intermittently in Florida (fig. 2, location 45) by hydraulic methods for more than 75 years. The total output is estimated to be nearly 2 million tons.

ARKANSAS BAUXITE REGION

In the Arkansas region (fig. 2, location 25), kaolin is abundant in residual and sedimentary deposits associated with the bauxite with which the kaolin intergrades, so that there are all degrees of mixture from fairly pure gibbsite rock to almost pure kaolin (Gordon and others, 1958, p. 87–88, 255). Kaolinite, where present in bauxite, occurs as white to gray masses of fine micaceous crystals in veins and veinlets cutting the gibbsitic masses and as cavity fillings. It also forms vermicular crystals or long accordionlike books, which in thin sections of bauxite have been observed to range in width from 0.005 to 0.7 mm. They frequently are contorted and have a characteristic wavy optical extinction. In pisolitic bauxite, kaolinite usually fills veinlets and cavities in the matrix; less commonly, it forms tiny veinlets that cut pisolites, or it fills their interiors. The kaolin deposits are scattered through the bauxite region, which is 40 km long and more than 10 km wide, and the total kaolin present is estimated to be more than 0.5 billion tons.

The residual kaolin deposits are in saprolite developed on nepheline syenite masses that are the principal parent rock of both the kaolin and the bauxite. The residual kaolin represents an intermediate stage of weathering between the syenite and bauxite. This kaolin and some of the bauxite show preserved textures of the syenite, and for this reason a few of the bauxite deposits are referred to as the granitic-textured type (fig. 9).

Electron micrographs (Gordon and others, 1958, fig. 28) of the clay in what is apparently the least weathered syenite show that the dominant mineral

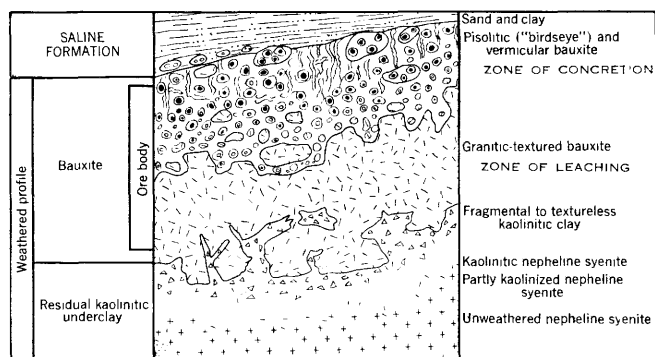


FIGURE 9.—Diagrammatic section of residual kaolin deposits in the Arkansas bauxite district. (From Gordon and others, 1958, fig. 36.)

developed in pseudomorphic replacement of nepheline and microcline is tubular halloysite. Hexagonal kaolinite crystals are present in pseudomorphs after feldspar that are probably intermediate stages of weathering between halloysite and gibbsite formation.

The largest kaolin deposits in the region are of the sedimentary type that commonly surround and grade into transported bauxite bodies through zones of bauxitic kaolin. The bauxite-kaolin deposits form lenticular bodies that have a maximum thickness of about 25 m, but in most places they are no more than 20 m thick. The bauxite-kaolin zone constitutes a facies along the upslope edge of the Berger Formation. Downdip the bauxite-kaolinite zone interfingers and grades into greenish and bluish sandy clay containing lignite. The Berger Formation is of early Eocene age, which dates the transported kaolin. The nepheline syenite and other rocks in the source areas are believed to have weathered to form kaolinite in both Paleocene and early Eocene time.

According to Tracey (1944), the typical sedimentary kaolin contains more than 35 percent alumina, less than 45 percent silica, and less than 5 percent iron oxide. In the transition through bauxitic clay to bauxite, the alumina increases and the silica decreases. In the bauxite, the alumina content is normally 45–60 percent and the silica <1–20 percent. The titanium oxide content of the clays is 1–4 percent, usually 2–3 percent. Crystalline siderite is the most abundant impurity. Siderite fills cavities in the bauxite and also forms disseminated pellets and granular aggregates. Siderite is most abundant, on the whole, in the lower bauxitic clays but also is abundant in other parts of some deposits, and a few deposits contain abundant siderite throughout. Aggregates and heavy concentrations of siderite are commonly of small extent. Limonite is present, probably as an oxidation and hydration product of the siderite. Biotite occurs rather sparsely in

the lower white clay. Tiny grains of a titaniferous iron mineral, probably ilmenite, are disseminated in the clays.

OTHER DISTRICTS IN THE COASTAL PLAINS

Very large deposits of sandy kaolin and kaolinitic sand of early Eocene age extend across Limestone and neighboring counties in Texas (Fisher, 1965). Light-colored kaolin and silica sand are recovered as coproducts by washing material from these deposits at Kosse, Tex. (fig. 2, location 20). This beneficiated kaolin is sold for use in special ceramic products, but it is not white enough to meet specifications for paper filler and coater clay. Sandy kaolin from near Kosse has also been used in making white portland cement, brick and tile, and pottery.

Kaolinitic clay deposits occur at several places in Rusk County, Tex. (fig. 2, location 18). These clays are in the upper beds of the Wilcox Group of early Eocene age. They are reported to have high plasticity and are mined at several localities to supply brick plants at Henderson (Fisher, 1965). Fisher also considered the clay in Rusk County to be a potential source of aluminum.

Appreciable tonnages of kaolin were mined in the Anna, Ill., district (fig. 2, location 26) when clay for crucibles and glass pots was produced in 10 mines during World War I (Lamar, 1948, p. 23), but there has been very little mining in the district in recent years. The kaolin in the Anna district was illustrated by Grim (1934, fig. 1) as occurring with sand in sinkhole depressions in Mississippian (Lower Carboniferous of the European system) limestone. The deposits are as much as 30 m thick and some are nearly 100 m in diameter. Minor amounts of lignite are in both the sand and the basal parts of clay deposits. The clay is overlain by red and white sand containing some clay pockets. Dr. Grim's petrographic studies and chemical analyses show that the kaolin is essentially pure. On the basis of X-ray analysis, Professor P. F. Kerr identified it as a member of the kaolinite-anauxite group (Grim, 1934, p. 663–664). The age of the kaolin at Anna is somewhat uncertain. Grim concluded, on the basis of its heavy-mineral content, that it is of either Late Cretaceous or early Tertiary age, and Lamar (1948) used Cretaceous(?) to indicate his uncertainty. In table 1 of this report, we use Eocene(?) for the age of this clay; this suggestion is based on the likelihood that the Anna kaolin is the same age as the Kentucky-Tennessee ball clay farther south.

Kaolin deposits that were mined in the early 1900's are near Glen Allen, Bollinger County, Mo. (fig. 2, location 24), and in nearby areas. This kaolin is thought to occur in sinkholes or other solution depressions in car-

bonate rock. Tennissen (1960) described some deposits as bedded and others as residual accumulations with chert and sand. He considered the deposits to be of Cretaceous age.

Kaolin deposits, many of which are associated with small high-silica gibbsitic bauxite deposits, are scattered through northeastern Mississippi. Deposits in several areas have been investigated, and typical ones in the Kemper-Pinedale area (fig. 2, location 29) will be discussed here. Conant (1965) found that the kaolin occurs in the uppermost part of Porters Creek Clay of Paleocene age and the lower part of the overlying Wilcox Formation of Eocene age. The two formations are separated by an unconformity representing an interval of weathering and erosion. The kaolin in Paleocene beds is residual, being preserved in weathered parts of the Porters Creek Clay (fig. 10) that were not eroded prior to the deposition of Eocene beds. The kaolin in the Eocene part of the Wilcox is mainly in channel-fill deposits. The lower strata in the fills commonly consist of kaolin conglomerate that was eroded and transported from the Porters Creek Clay. Presumably, massive kaolin in the channel-fill deposits also was transported from the Porters Creek Clay.

White kaolin occurs at a site known as Chalk Bluff several kilometers south of Hackelburg, Ala. (fig. 2, location 31). The deposit is in the upper beds of Late Cretaceous age assigned to the Tuscaloosa Group. This

kaolin is therefore approximately the same age as the Cretaceous kaolin in central Georgia located several hundred kilometers to the east. The Chalk Bluff deposit rests unconformably on weathered shale, part of the Pottsville Formation, which is of Westphalian Age of the European time classification. The upper parts of the deposit were eroded prior to the deposition of overlying beds, causing considerable variation in thickness. It is about 3 m thick at one mine and more than 8 m thick at another nearby mine (Clarke, 1966, p. 26). The $<2\text{-}\mu\text{m}$ fraction of a sample of this kaolin was 90 percent kaolinite, 5 percent chlorite, and 5 percent illite. It contained only a trace of quartz. Kaolin from this deposit is air floated and sold for use in pottery, glasses, carriers for insecticides, and pharmaceutical preparations.

DISTRICTS IN NORTH CENTRAL AND WESTERN UNITED STATES

MINNESOTA

The principal kaolin deposits in Minnesota (fig. 2, location 21) are in weathered rocks that are exposed in the Minnesota River valley between Granite Falls and Fort Ridgley State Park, a distance of 75 km (Parham, 1970). The deposits formed by humid tropical weathering during the latter part of the Mesozoic Era, probably early Late Cretaceous time. This weathering produced a kaolinitic residuum (fig. 11, unit 1), as much as 30 m

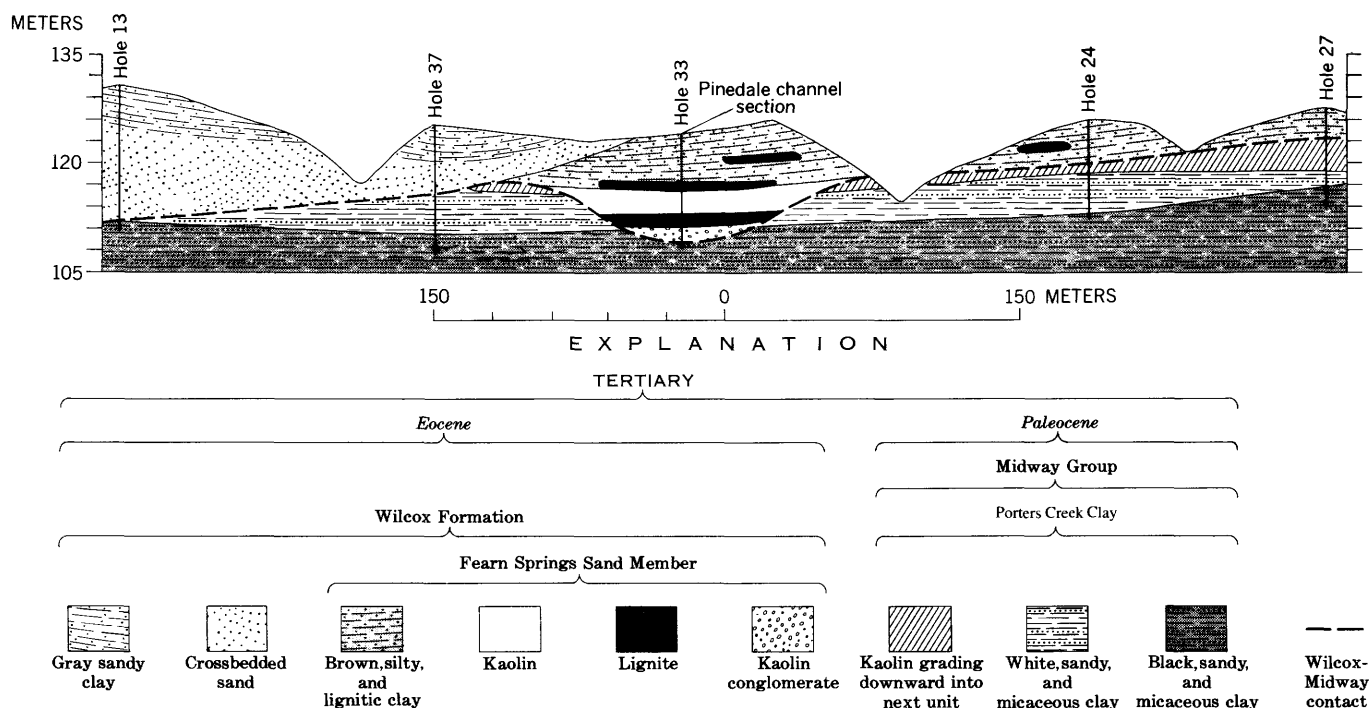


FIGURE 10.—Diagrammatic section of kaolin deposits in the Kemper-Pinedale area, Mississippi. (Modified from Conant, 1965, fig. 2.)

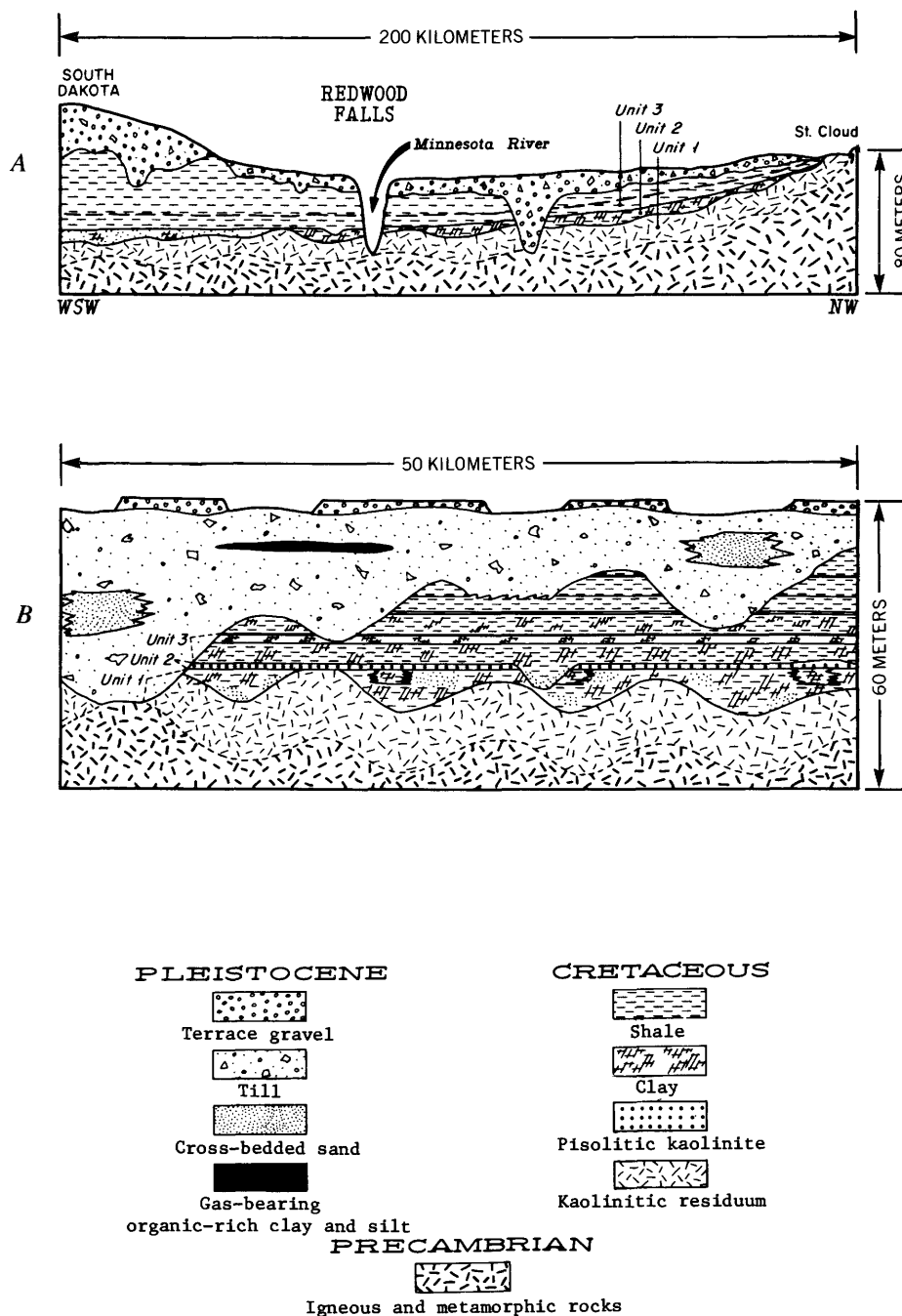


FIGURE 11.—Generalized sections illustrating: A, the regional geology of the Minnesota kaolin deposits and, B, the kaolin and associated beds along the Minnesota River valley. (From Parham, 1970, p. 8.)

thick, over much of Minnesota, mainly from Precambrian metamorphic and igneous rocks. The weathered zone is now covered by younger Cretaceous sedimentary rocks and Pleistocene glacial deposits except locally along the Minnesota River valley in southwestern Minnesota and between St. Cloud and Little Falls in the central part of the State. The sedimentary beds and glacial deposits overlying the residuum are 12 m or

more in thickness. The Cretaceous beds contain sedimentary kaolin deposits that have been reworked from the residuum.

The clay minerals of the residuum (fig. 11, unit 1) that were formed from weathering of felsic rock types are composed primarily of kaolinite. In the least weathered parts of the profile, the kaolinite has an irregular platy form. Tubular halloysite is present in

minor amounts, especially in the lower part of the weathering profile. Mafic rock types weathered first to montmorillonite and under progressively more intense weathering to kaolinite.

Two Upper Cretaceous units of kaolinitic sedimentary rocks (fig. 11, units 2 and 3) overlie the residuum. The lowermost of these (unit 2), which was derived from erosion of the weathered residuum and which also underwent tropical weathering, has a maximum observed thickness of about 15 m. It is composed of varying proportions of kaolinite and quartz, with trace amounts of halloysite. An iron-rich, kaolinitic, pisolitic clay 1–2.5 m thick that contains small amounts of gibbsite and boehmite occurs at the top of unit 2 in several places. Sedimentary rocks of unit 3 disconformably overlie unit 2 and consist of gray to black, organic-rich clays and shales, thick beds of lignite, and at least one thin bed of bentonite. Kaolinite is abundant in the basal part of unit 3 but grades upward into montmorillonite and illite, suggesting that the humid tropical climate under which units 1 and 2 had formed had been replaced by a more temperate climate by the time unit 3 formed.

LATAH COUNTY, IDAHO

The Latah County, Idaho, district (fig. 2, location 9) is located at the eastern edge of the Columbia Plateau physiographic province.

Three types of clay occur in the Latah district: residual clay derived from the Columbia River Basalt Group of Miocene age; residual clay derived from the granodiorite and related intrusive rocks of the Idaho batholith of Late Jurassic or Cretaceous age; and transported clay, an erosional product of the granodiorite and related intrusive rocks, deposited as part of the Latah Formation of middle or late Miocene age (Ponder and Keller, 1960; Hosterman and others, 1960). The two types of residual clay were formed during an interval of weathering called the "Excelsior weathering period" that occurred between flows of the Columbia River Basalt Group, when the land surface had a low to moderate relief and the climate was warm and humid with good oxidation conditions.

X-ray and differential thermal determinations on these clays show that kaolinite and halloysite (10A) are the principal clay minerals. The residual clay derived from basalt is composed of white halloysite commonly colored blue, gray, or black by ilmenite and occasionally stained brown by limonite or green nontronite. The residual clay derived from granodiorite and related intrusive rocks contains both halloysite (10A) and kaolinite, whereas the transported clay is predominantly kaolinitic. The latter two types of clay

are very similar in physical appearance—both are white and both contain abundant quartz grains and mica flakes—but the residual clay retains a relict granitic texture and is not bedded.

SPOKANE COUNTY, WASH.

The types of kaolin in Spokane County, Wash. (fig. 2, location 3), according to Hosterman (1969a) include (1) transported and a minor amount of residual clay in the Latah Formation of Miocene age, (2) bluish-gray residual saprolite formed on the Columbia River Basalt Group, and (3) white residual clay formed on pre-Tertiary igneous and metamorphic rocks. Transported kaolin and other clays and silts forming the shale and the sand that make up the Latah Formation were deposited in lakes believed to have formed by basalt flows damming rivers. The evidence for lacustrine deposition is the presence of diatoms and sponge spicules and many species of plant fossils found in Latah beds. The residual clay in the Latah Formation consists of kaolin formed by weathering of shale; this clay is overlain by transported kaolin. The age of the residual and transported kaolin and the saprolite on basalt is Miocene, because the Latah Formation, as well as the Columbia River Basalt Group with which this formation is interbedded, is of this age. Hosterman (1969a, p. 25) reports that, at the time weathering took place, the climate was temperate and the annual rainfall was 75–120 cm. This conclusion is based on the prolific fossil representation, which includes a large number of plant species that today live mainly where these climatic conditions exist. The age of the weathering that formed the kaolinite in the pre-Tertiary rocks is less clear, as weathering could have taken place well before emplacement of the Miocene Columbia River Basalt Group.

Five clay minerals have been identified by X-ray diffraction in samples from these deposits. Kaolinite is found in all types of clay, except residual clay derived from basalt. Halloysite (10A) is found primarily in the residual clay derived from basalt, and traces are found in the residual clay derived from pre-Tertiary rocks. Smectite and illite do not occur in residual clay derived from basalt but do occur in varying amounts in all other types of clay. Nontronite is found only in the residual clay derived from basalt.

The clays formed under similar physical, chemical, and bacterial conditions during Tertiary time. It is likely, therefore, that the mineralogic composition of the unweathered parent rock controlled the type of clay mineral produced during katamorphic alteration. The augite in basalt altered to nontronite, and the plagioclase (labradorite) to halloysite. The pre-Tertiary rocks contained feldspars and muscovite altered to kaolinite and ferromagnesian minerals altered to smectite.

The chemical composition of 220 samples determined by the X-ray fluorescence method indicates that the residual clay derived from basalt has an average Al_2O_3 content of 22 percent and individual samples as high as 39 percent; the Latah Formation clays, 20 percent and a high of 37 percent; and the residual clay derived from pre-Tertiary rocks, 20 percent and a high of 29 percent.

Analyses of fresh and partly weathered basalt and saprolite (table 4) show that the chemical changes taking place during the weathering are the leaching of Si, Fe, Ca, K, Mg, and Na. Al and Ti are the major elements concentrated, and H_2O is added.

TABLE 4.—Chemical comparison of unweathered Columbia River Basalt Group with saprolite derived from basalt

[From Hosterman, 1969a, table 2; data in weight percent. —, no data.
1, Average of 13 samples of Columbia River Basalt Group (Waters, 1955, p. 705); 2, one sample of Columbia River Basalt Group from sec. 3, T. 27 N., R. 44 E., Spokane County, Wash. (analysis by rapid-rock method; Paul Elmore, Samuel Botts, and Gillison Chloe, analysts, U.S. Geological Survey); 3, one sample of Columbia River Basalt Group from an outcrop on the road at Mica Creek, sec. 4, T. 23 N., R. 45 E., Spokane County, Wash. (analysis by X-ray fluorescence); 4, one sample of partly decomposed Columbia River Basalt Group from sec. 3, T. 23 N., R. 45 E., Spokane County, Wash. (same analysts as for 2); 5, average of six samples of residual clay derived from Columbia River Basalt Group from sec. 23, T. 24 N., R. 44 E., and sec. 3, T. 23 N., R. 45 E. (same analysts as for 2)]

	Unweathered			Partly decomposed	Saprolite
	1	2	3	4	5
SiO_2 ———	52.31	48.5	52	46.6	38.2
Al_2O_3 ———	14.38	13.0	15	20.6	30.4
Fe_2O_3 ———	2.47	8.8	19	4.8	2.8
FeO ———	9.95	7.3	—	3.5	3.3
MnO ———	.21	.29	.3	.07	.06
TiO_2 ———	2.10	3.3	3.7	5.8	8.7
CaO ———	8.37	8.4	8.8	6.7	.83
K_2O ———	1.26	1.0	1.7	.44	.09
P_2O_5 ———	.36	.82	—	1.2	.66
MgO ———	4.46	2.6	—	.28	.25
Na_2O ———	2.94	2.6	—	3.5	.18
H_2O^+ ———	.74	2.4	—	3.4	11.7
H_2O ———	.39	1.2	—	1.8	2.4
Total ———	99.9	100.2	100.5	98.7	99.6

^aTotal Fe is expressed as Fe_2O_3 .

The following mineralogical changes taking place as the basalt weathers are described by Hosterman (1969a, p. 17–18):

“* * * The katamorphic alteration of the Columbia River Basalt appears to have been controlled largely by ground-water movement. Most of the flows are vesicular and are cut by numerous vertical joints. It seems likely that surface water entered these joints but could not move freely until the basalt began to alter. Under the conditions of poor ground-water movement and poor drainage, the oxidation-reduction reactions probably proceeded at a slow rate, and the alkalies were not removed. The basaltic glass first altered to palagonite; subsequently, the palagonite and augite altered to nontronite which formed in vesicles and cracks. The formation of non-

tronite increases the permeability by removing some of the SiO_2 , Al_2O_3 , and Fe_2O_3 from the basalt surrounding the vesicles and cracks. Under these new conditions, ground water moved freely, oxidation took place, alkalies were removed easily, and plagioclase (labradorite) altered to halloysite. As more of the basalt became exposed to the oxidation process the early formed nontronite was replaced by halloysite. * * *

The alteration of nontronite to halloysite was observed in vesicles partly filled with clay; more massive accumulations along cracks remained unaltered. In the vesicles, greenish-yellow nontronite was replaced by white halloysite. Ilmenite is the principal resistant mineral in the parent basalt remaining in the saprolite. Disseminated fine grains of this mineral cause the gray color of the saprolite.

IONE, CALIF.

The principal deposits of high-alumina clay in California are in the Ione Formation of Eocene age, which crops out in a discontinuous belt bordering the western foothills of the Sierra Nevada Range (fig. 1, location 5). Most of the Ione clay that has been mined is near Ione, Amador County, but appreciable tonnages have been mined near Lincoln, Placer County. In recent years, deposits have been mined at Valley Springs, Calaveras County; Knights Ferry, Stanislaus County; Michigan Bar and Folsom, Sacramento County; and near Coopers-town, Tuolumne County (Cleveland, 1957, p. 136). These mines are scattered through a belt more than 190 km long. Most of the beds have an average thickness of about 5 m, but in places they are much thicker, as near Lincoln where the thickness is about 30 m. The Ione clay formed by the deposition of materials, including sand, transported from weathered rock higher in the Sierra Nevada Mountains to the east (Bates, 1945). The depositional environment is believed to have been lagoonal or deltaic. Because sand contents range from 20 to more than 50 percent, washing is required for the recovery of high-quality clays.

According to Bates (1945), the clay consists mainly of kaolinite, but an earlier report (Allen, 1929, p. 377–378) indicates that anauxite is present. On the basis of thorough differential-thermal-analysis (DTA) investigations, Pask and Turner (1952) concluded that some of the Ione kaolin is highly crystalline and some has a tendency toward halloysite, which presumably means it is disordered. These same authors report that PCE of the fire clay recovered from these clays ranges from 31 to 34.

MESA ALTA, N.M.

The Mesa Alta kaolin deposits (fig. 2, location 16) occur along the unconformity between Jurassic and Cretaceous sedimentary formations (Reeves, 1963).

The deposits are in an irregular bed <1–6 m thick. The clay ranges from pure white kaolin to very impure, commonly bluish, sandy material. An electron micrograph of the white type (Davis and others, 1950, pl. 5) shows that the kaolin occurs in subhedral and anhedral crystals. Though the origin of the Mesa Alta kaolin deposits is not adequately understood, it is likely that the clay has been transported from kaolinite formed by weathering of igneous rocks during the hiatus between the deposition of Jurassic and Cretaceous formations. The principal evidence for the igneous parent rocks is feldspar partly altered to kaolinite in granite pebbles in the sand overlying the kaolin. The clay probably was transported to local basins occupied by lakes or swamps. Some of the kaolin has been reworked, as is indicated by the presence of rounded clay pebbles at a few localities.

UNDERCLAYS

Underclays are more widely distributed and have a greater range in geologic age than all the other kaolinitic clays in the United States. They are most abundant in formations of Pennsylvanian age (Late Carboniferous of the European time scale) in the Appalachian Basin and in strata of this age in Missouri. The underclay deposits in Colorado are of Early Cretaceous age (Aptian), and those in Washington, Oregon, and California are of Paleocene and Eocene age. The small plastic-clay deposits in Hawaii of Holocene age also are underclays in the sense that they occur under peat.

Underclays also vary much more widely in mineral composition than do the other types of kaolin. Those discussed in this report consist mainly of kaolinite, but other large underclay deposits consist principally of mixtures of illite, chlorite, mixed-layer clays, minor amounts of kaolinite, and abundant nonclay impurities. The kaolinite ranges in crystallinity from very well ordered crystals to the extremely poorly ordered forms of the so-called fire-clay mineral. The underclay deposits in Hawaii are principally halloysite and apparently contain considerable quantities of noncrystalline matter. Diaspore and boehmite occur in some of the older underclay deposits. Gibbsite has been found in some deposits of Pennsylvanian age, as well as in Eocene deposits in Washington and the Holocene deposits in Hawaii.

A general relationship between mineral composition of the clays and thickness of the overlying coals exists in the United States. The purest kaolinitic underclays, including those containing diaspore, are restricted, with very few exceptions, to places where the overlying coal is no more than a few centimeters or at the most a fraction of a meter in thickness. On the other hand, the

thick coal beds that have been mined extensively tend to be underlain by impure underclays.

Another characteristic of underclays is that many of them contain fossil roots that prove they once served as soils. The most common root in deposits of Pennsylvanian age can be identified as that of the genus *Stigmara*, *S. ficoides* Brongniart. The best preserved fossils consist of a stout rootstock, usually now compressed to form a thin, coaly sheet, on which the points of attachment of roots, or scars at the points of former attachment, are spirally arranged. Rootstocks (fig. 12) are not as abundant as rootlets. The rootlets are commonly compressed into very thin, filmy ribbons that cut the rock at all angles. Occasionally the coaly film has been lost and only more obscure impressions remain. The rootstock of *Stigmara* was a spongy plant structure (fig. 13), and considerable volume must have been lost as the roots were reduced to coaly imprints.

In the following sections, several of the underclay districts of the United States will be discussed, and some of the others will be mentioned in an effort to show the wide occurrence of these deposits. The small

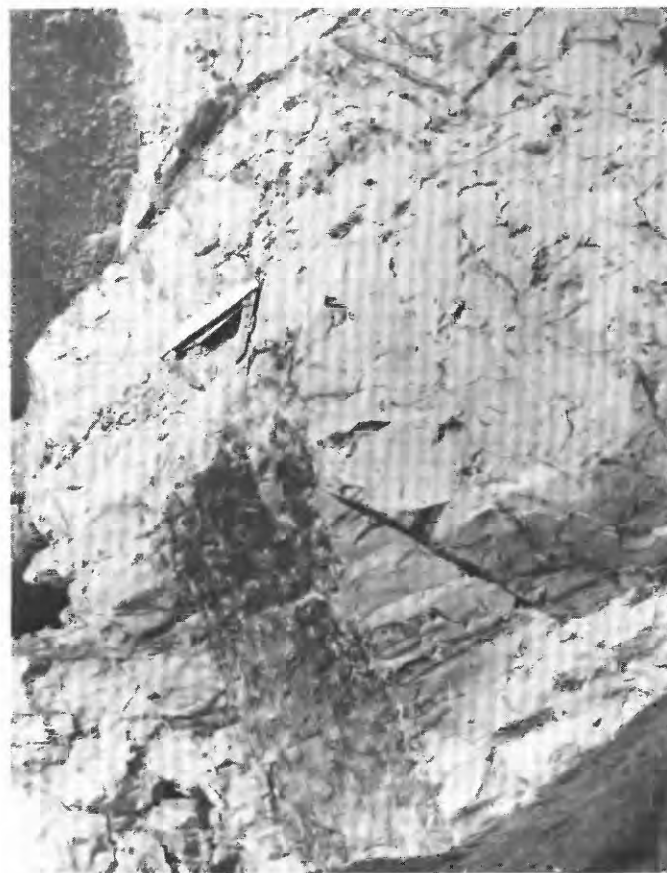


FIGURE 12.—*Stigmara* from the "Olive Hill" clay bed of the Lee Formation in Kentucky, showing main rootstock, attached rootlets (at right angles), and nodular root scars. Pocket knife is 7 cm long.

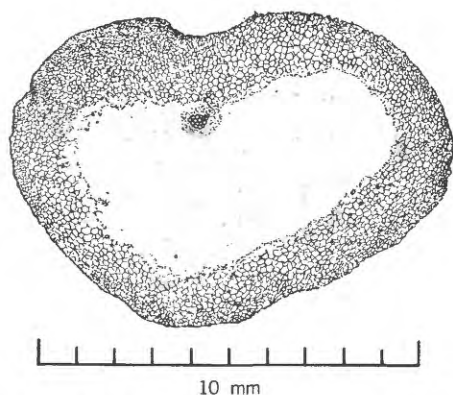


FIGURE 13.—Cross section of a petrified root of *Stigmara ficoides* Brongniart from a Pennsylvanian coal bed, Leslie County, Ky., showing delicate outer cortical tissue. The inner and middle cortex have broken down, leaving a large open cavity and a thin strand of conductive tissue. Shown about five times natural size. (Identified and drawn by J. M. Schopf, U.S. Geological Survey.)

deposits in Hawaii are included because of their youth and because they show that clay minerals form, iron is removed, and titanium concentrated in a swampy environment similar to that thought to prevail in a typical swamp in which plant material accumulated during Pennsylvanian time and later converted to coal.

CLEARFIELD, PA.

The principal fire-clay deposits in the Clearfield district, Pennsylvania (fig. 2, location 38), are in the "Mercer bed," which underlies the lowermost Mercer coal bed of Pottsville age (Foose, 1944). The deposits are lenticular and 0–7 m thick; major lateral variations commonly take place within distances of a few tens of meters. The varieties of clay and the alumina contents of the "Mercer" deposits also range broadly (table 5).

Plastic clay, containing <35 percent Al_2O_3 , is the most abundant type of clay in the "Mercer bed." The most abundant type of the much higher grade refractory material is flint clay, which breaks with a subconchoidal fracture and weathers into jagged fragments. Block clay is similar to flint clay in alumina content but lacks flinty characteristics and is much less resistant to weathering. Nodules 1–5 mm long occur in both flint clay and block clay.

The relationships of the types of clay in the "Mercer bed" vary considerably. At most places, the flint and nodule clays are in the middle part of the bed and are overlain by plastic clay. Locally the entire bed is plastic clay. Nodule clay, where present, is typically near

Table 5.—Types and alumina contents of clay in the "Mercer bed"
[From Foose (1944, table 2)]

	Percent of alumina
"Burnt" nodule clay —————	70–75
Rusty-brown, porous, cindery appearance.	
Fine-grained (or blue) nodule clay —————	60–65
Homogeneous appearance; all small nodules, finer grained and harder than green nodule clay.	
Green nodule clay —————	55 (approx.)
Coarsely nodular, rough fracture, usually greenish cast.	
Nodule-block clay —————	40–50
Gradation between green nodule and flint or block clay, nodules and nodular areas less than half of mass, scattered through block clay, greenish, fracture more blocky though still rough.	
Spotted flint —————	40–42
Few scattered small nodules in flint clay, fracture smooth conchoidal.	
Flint clay —————	38
Very hard, fracture smooth conchoidal with sharp edges and points, ringing flinty noise under hammer blow, weathers by breaking into smaller jagged fragments; never slacks down.	
Block clay —————	38
Softer than flint clay, fracture semiconchoidal to irregular blocky, no ringing sound when struck, weathers by crumbling into rounder granules than flint.	
Semiflint clay —————	35–37
Gradational from flint to soft plastic clay, present in minor amounts, hardness about same as block, fracture rough and irregular, not very conchoidal.	
Associated nonrefractory clays include:	
Slabby soft clay —————	30 (approx.)
Fracture slabby and irregular, slickensides very common.	
Soft (plastic) clay —————	25–30
Soft, fracture very irregular, chips and crumbles under little pressure. Slickensides common.	
Shaly clay or clay shale —————	20–30
Bedding evident, fracture shaly, siliceous.	

the middle of flint-clay units, and the contacts are gradational. Two beds of nodule clay separated by block clay have been found. Lateral gradations between types of clay are very common. At most places, the uppermost part of the clay is very carbonaceous, and coal layers 7–20 cm thick are locally present between different types of clay.

Kaolinite is by far the most abundant mineral in the "Mercer" deposits. According to Bolger and Weitz (1952), it forms the ground mass of the clay, and minor amounts are in large vermicular crystals in replacements of diaspore, scattered nodules of fine to coarse angular crystals, and veinlets of fine to medium crys-

tals. The kaolinite in vermicular crystals and in flint and nodular clays is very well crystallized, and that in the plastic clays tends to be very poorly ordered (Erickson, 1963).

Diaspore is the second most abundant mineral in underclay. It is mainly in aggregates of crystals forming nodules, but minor amounts are scattered through parts of the kaolin matrix and in the so-called second-generation vein deposits. Some of the nodular clay is more than 75 percent Al_2O_3 and more than 75 percent diaspore. Some of the diaspore is in the form of pisolite-like pellets having concentric spheroidal layering. Commonly, some of the internal layers of these structures are selectively replaced by kaolinite, and concentric layers are cut by veinlets of kaolinite.

Boehmite is the third most abundant mineral in the "Mercer" clay (Bolger and Weitz, 1952, p. 87). It forms crystals of <0.03 mm making up nodules in the clay and intermixed with diaspore in other nodules.

Impurities in the "Mercer" clay include minor amounts of quartz and flaky sericite, which tend to be most abundant in the lower parts of deposits (Foose, 1944, p. 567). The sericite was identified as 2M muscovite by Erickson (1963, p. 164–165), who described it as present in small aggregates and clear, sharply defined flakes as much as 2 mm long. Erickson found the sericite to be most common in plastic clay but absent in well-crystallized flint clay. Foose (1944, fig. 8) showed illite as being a primary mineral in the clay but did not discuss its distribution. Bolger and Weitz (1952, p. 89) stated " * * * Illite is an uncommon accessory mineral. It may have been the latest mineral formed, for it can be seen replacing the latest crystalline kaolinite along cleavage planes. * * * " Pyrite occurs as small grains in some of the clay and, in other parts, as nodules as much as 2.5 cm in diameter and as thin veins. Siderite occurs as rounded masses and lenticular bodies as much as 5 mm in diameter in the kaolin ground mass and as

replacements of kaolinite and diaspore in nodules. Most of the siderite is partly altered to iron oxide. Subhedral grains of tourmaline and anhedral grains of zircon are scattered through much of the clay. Iron oxide, mainly in the form of goethite, is present in minor quantities in the plastic, flint, and block clay and in much greater amounts in the burnt nodule clay, in which it causes the rusty appearance. Amounts of iron oxide in some of the nodules are several times the 2.17 percent listed for the analyzed sample (table 6), which was selected for its purity.

On the basis of a study of textural and structural features, Foose (1944, p. 575) identified paragenetic relationships of the minerals in the "Mercer bed." He considered that kaolinite was the first and chief mineral deposited and that minor detrital impurities, including quartz, tourmaline, and zircon, were deposited with it. A second generation of kaolinite is indicated by the vein deposits cutting the earlier bodies. A first generation of diaspore may have formed at the time of the second generation of kaolinite, but this relationship is uncertain. A second generation of diaspore is evidenced by veins cutting nodules formed earlier. Siderite formed contemporaneously with and later than the second-stage diaspore. Pyrite veinlets and iron oxides formed after the last diaspore stage. Bolger and Weitz (1952, p. 87), who recognized the presence of boehmite, believed that this mineral, as well as kaolinite, diaspore, and iron oxides, formed early from colloidal gels and that there were two additional stages of kaolinite and diaspore formation. Bolger and Weitz (1952, p. 93) summarized their more lengthy discussions of the origin of the "Mercer" clay as follows:

" * * * Study of petrography and field relationships has led to the conclusion that the source material of the Mercer was a colloidal mixture of hydrous aluminum silicates and aluminum hydroxides. These colloidal gels were transported into swamps by sluggish streams. The gels were then concentrated and crystallized to form kaolinite,

TABLE 6.—*Chemical analyses of varieties of clay in the "Mercer" deposits*
[From Foose (1944, table 3). —, no data]

Type of clay	Ignition loss	Al_2O_3	SiO_2	Fe_2O_3	$\text{K}_2\text{O} + \text{Na}_2\text{O}$	TiO_2	CaO	MgO	Total
"Burnt" nodule -----	14.40	75.72	4.0	2.17	0.38	2.75	0.10	0.25	99.77
Fine-grained nodule -----	13.88	61.52	—	—	—	—	—	—	—
Green nodule -----	13.50	54.50	26.76	.80	.95	2.26	.18	.30	99.25
Nodule-block -----	13.46	49.94	—	—	—	—	—	—	—
Flint -----	13.16	38.37	43.74	1.29	.96	1.72	.04	.28	99.56
Block -----	13.40	37.55	43.40	1.06	1.51	1.77	.13	.43	99.25
Semiflint -----	11.17	35.13	46.76	1.52	2.60	1.57	.18	.73	99.66
Slabby soft -----	8.76	30.99	52.62	1.63	3.21	1.28	.30	.75	99.54
Plastic (soft) -----	8.09	27.40	56.84	1.82	2.99	1.28	.30	.91	99.63

diaspore, and boehmite. After lithification, shrinkage cracks appeared, into which a silica-rich kaolinitic material was introduced, resulting in the replacement of diaspore by kaolinite. The silication of diaspore released free alumina, which recrystallized in voids as a later stage of diaspore. The process of cracking and crack filling continued over a long period until the mass was completely solid. Hardening took place before the deposition of post-fireclay sediments. * * *

Erickson's ideas (1963, p. 167) on the origin of the "Mercer" clay are more or less in agreement with those of Bolger and Weitz. According to his explanation, kaolinite and high alumina precipitates and gels accumulated in a coastal swamp environment under conditions of acid pH and negative Eh. Both mineralogical and chemical differences are explainable by differences in the nature and amount of sediment originally deposited rather than as responses to epigenetic leaching.

OLIVE HILL, KY.

Occurrence and Characteristics

The underclay deposits in the Olive Hill district, Kentucky (fig. 2, location 35), occur in the Olive Hill clay bed in the lower part of the Lee Formation, which is of early Westphalian Age as used in the European time scale. The coal that overlies the clay ranges from 0 to 25 cm in thickness, but in most outcrops it is only 7.5–15 cm thick. The coal extends over more than three-quarters of the area of the clay, and, in most places where it is absent, its stratigraphic position is marked by nearly black discoloration in the uppermost part of the clay or by a thin zone of carbon-rich black shale above the clay.

The "Olive Hill" clay bed consists of irregular lenses that rest on an undulating surface. Neither the lenses nor the areas in which the clay is missing show any regional alinement or preferred orientation. The maximum thickness of most lenses is less than 3 m, but in one old mine, now inaccessible, the bed is reported to be 7.5 m thick. The undulating surface on which the clay bed rests has a local relief of as much as 12 m. Although some of these undulations appear to reflect unevenness of the surface on which the clay was deposited, most of them probably formed after deposition of the clay, by differential compaction or other processes that caused slight warping of the rocks above and below the clay.

The "Olive Hill" clay bed is composed of three types of clay in irregular lenses of variable thickness and shape. About one-third of the bed is flint clay and the other two-thirds is chiefly semiflint clay and subordinate amounts of plastic clay, but all variations in hardness from flint to semiflint and from semiflint to plastic clay are present in different parts of the bed. Boundaries between one type of clay and another are ordinar-

ily sharp. Except for the superposition of one type of clay above another, the clay is essentially nonbedded. Typically, the flint clay overlies semiflint clay, but at many places the reverse is true, and at a few places the flint and semiflint clay are irregularly interlayered. Where plastic clay is present, it is ordinarily in the uppermost part of the bed, but there are many exceptions to this generalization.

Colors, nonclay minerals, soluble salts, organic materials, and fossils are similar in all three types of clays; the types of clay differ, however, in the type and crystallinity of the clay minerals and in certain physical properties such as resistance to high temperature, hardness, plasticity, resistance to erosion, and spacing of slickensides. Most of the clay is medium gray to brownish gray, but colors range from very light gray to almost black. Rusty iron stains are common along joints and in weathered outcrops. The content of non-clay minerals ranges from trace amounts to more than 50 percent in very sandy parts of the bed; lateral gradations from sand-free clay to very sandy clay within a few yards are common. Gypsum, the principal saline mineral present, occurs as crusts along joints. The plant-root fossil *Stigmara* is preserved as carbonaceous films in all three types of clay. Locally the main rootstock with rootlets attached (fig. 12) is preserved in flint clay, but commonly only the detached rootlets remain. The carbonaceous films seldom make up as much as 2 percent of the clay.

The flint clay in the "Olive Hill" clay bed is a hard, resistant, nonplastic refractory clay. It possesses flint-like characteristics of homogeneity and conchoidal fracture, but it is distinctly softer than true flint (SiO_2). Most high-grade flint clay has a Mohs-scale hardness slightly greater than 3; the clay intermediate between flint and semiflint clay is slightly softer. Flint clay will not slake in water and has no plasticity unless very finely ground, and then plasticity is developed to approximately the same degree as similarly prepared quartz. Flint clay is sufficiently resistant to erosion to form small benches in stream beds. It weathers to angular blocks which, in turn, break down into shardlike fragments having sharply curved knife edges and pointed corners. Slickensides are extremely rare in flint clay. Oolites are abundant in some of the flint clay but are not present in all deposits. The PCE's of high-grade flint clay range from 34 to 36.

Semiflint clay is intermediate between flint and plastic clay in physical characteristics and clay-mineral composition. It has a Mohs-scale hardness between 2 and 3, and it possesses very little natural plasticity except when finely ground. Nearly all semiflint clays contain abundant diversely oriented slickensides. Parting occurs mostly along the slickensides; and com-

monly, when fresh semiflint clay is subjected to a single rainfall, it breaks down into a rubble of irregular polyhedra having a slickenside on each face. Semiflint clays are seldom seen in natural outcrops except where they are protected by overlying flint clays or other resistant beds. However, some of the harder semiflint clays, which grade into the flint clays, are remarkably resistant to weathering. A good example is the semiflint clay that for many years has supported the footing of the bridge on a highway west of Elliotville, Olive Hill district. The semiflint clays consist chiefly of mixtures of kaolinite, illite, and mixed-layer minerals, and the kaolinite generally ranges from 60 to 80 percent or a little more. The PCE's of semiflint clays are mostly 31–33, and these clays are distinctly lower in heat-resisting properties than is good-quality flint clay. In a few places, semiflint clays are very refractory, and PCE's are as high as 34+ (table 7). The refractory properties of most semiflint clays are lower than those of flint clays chiefly because of higher contents of alkali-bearing clays such as illite and mixed-layer minerals.

Plastic clays consist of mixtures of kaolinite, illite, and mixed-layer minerals. Weathered plastic clay readily develops considerable plasticity when wet, but some grinding is required to develop maximum plasticity in the fresh clay. Abundant slickensides are present in the fresh plastic clay, but as weathering progresses the slickensides are sealed and the clay becomes a homogeneous mass. Natural exposures of plastic clay are exceedingly rare because it is soft and lacks resistance to weathering. Only a small amount of plastic clay is present in the "Olive Hill" clay bed. The few samples examined were very similar in mineralogical composition to the poorer quality semiflint clays. The content of illite and mixed-layer clay minerals was high; accordingly, the alkali content should be high and refractory properties should be relatively low.

Mineralogy

Kaolinite is by far the dominant clay mineral in the "Olive Hill" clay bed, and in places it makes up as much as 95 percent of the bed. The kaolinite in the flint clay is predominantly well crystallized. In the plastic clay and in some semiflint clay, the kaolinite has a poor degree of crystallinity similar to the "fireclay" kaolinite mineral of Brindley and Robinson (1947). Intermediate stages of crystallinity are present in most semiflint clays. Recognition of well-crystallized kaolinite is based on the narrow basal (001) X-ray diffraction peak at 7.1Å and the sharp peaks from the pyramidal and prismatic planes (fig. 14). Poorly crystallized kaolinite gives a broad (001) peak at slightly greater than 7.1Å, and the peaks from the pyramidal and prismatic

planes are diffuse. The degree of crystallinity of the kaolinite varies with the proportions of other clay minerals present in the clay. The well-crystallized kaolinite occurs only in clays that contain small amounts of other clay minerals, and therefore it is restricted to the flint clays. Poorly crystalline fire-clay kaolinite occurs only where appreciable amounts of illite and mixed-layer clays are also present. Kaolinite having intermediate crystallinity occurs in both the flint and semiflint clays that contain small amounts of illite and mixed-layer minerals. The conclusions regarding the crystallinity of the kaolinite are based on the criteria outlined by Brindley (1951, p. 46, 50–52). Our conclusions closely parallel those of Keller and others (1954, p. 19) and McConnell and others (1956, p. 279), who studied similar clays. The proportion of nonclay mineral bears no relation to the crystallinity of the clay, and well-crystallized kaolinite occurs in parts of the bed that contain as much as 50 percent quartz.

DTA curves of samples from the "Olive Hill" clay bed (fig. 15) appear to support the conclusion that kaolinite is the dominant clay mineral present and that the kaolinite in flint clay is more perfectly crystallized than that in plastic clay. The prominent endothermic peak resulting from the loss of hydroxyls is at approximately 600°C for flint clay (fig. 15, sample 25) and at only 580°C for plastic clay (fig. 15, sample 24). Also, the exothermic reaction for flint clays at about 975°C is intense and is completed within a temperature range of 25°C, whereas this reaction for plastic clays is much less intense and takes place over a temperature range of approximately 75°C. The DTA curves for semiflint clay (not illustrated in this report) are intermediate between those for plastic and flint clay. The higher energy required to drive the hydroxyl ion of the clay-mineral structure from the flint clay suggests that the hydroxyl ion is more tightly bound in flint clay than in plastic clay.

Illite is the second most common clay mineral in the "Olive Hill" clay bed. The amount ranges from a trace in the flint clay to about 40 percent in the plastic and the softer semiflint clays. Illite is recognized in X-ray diffraction traces by its basal (001) spacing at approximately 10Å (fig. 14). Weak second-order (002) peaks at 5Å and third-order (003) peaks at 3.3Å are also present in diffractometer traces of some samples. Only material that does not expand when treated with ethylene glycol is considered to be illite; if there is some expansion, the material is considered to be mixed-layer clay. In DTA curves, the presence of small amounts of illite is suggested by broad weak endothermic reactions between 100° and 200°C (fig. 15, samples 9 and 24) and by small endothermic reactions beginning between 450° and 500°C.

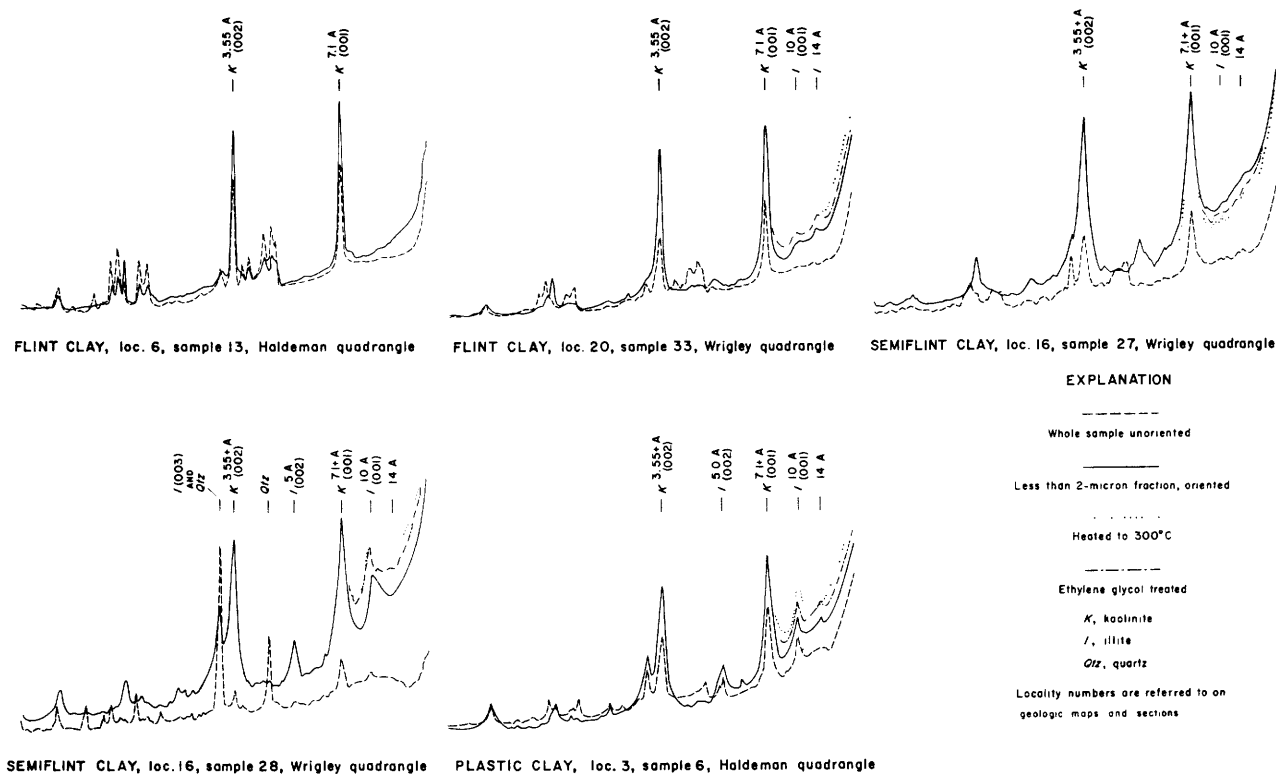


FIGURE 14.—X-ray diffractometer traces ($\text{CuK}\alpha_1$ radiation) of flint, semiflint, and plastic clays from the "Olive Hill" clay bed of the Lee Formation in the Wrigley and Haldeman quadrangles, Kentucky. Sample descriptions and locations in Patterson and Hosterman (1962).

Complex mixed-layer minerals are closely associated with the illite. Some of these minerals resemble smectite in that X-ray diffraction traces show a slight increase in intensity of the 14A peak when samples are treated with ethylene glycol. Smectite layers are most common in plastic clays and softer semiflint clays (fig. 14). Other mixed-layer clays consist of heterogeneous mixtures of minerals resembling chlorite, smectite, and probably vermiculite. X-ray traces of these clays have broad irregular bulges near 10A, and peaks are little changed by heat or ethylene glycol treatments. Efforts to improve the mineral structure of mixed-layer minerals by treatment with potassium ions were not successful. The structure of these minerals appears to be far more complex than that of some mixed-layer clays that are mostly potassium-deficient illites. Heterogeneous mixed-layer assemblages occur only in small amounts. They are probably present in all types of clay in the Olive Hill area, but they are most abundant, or at least most easily recognized, in the softer flint and harder semiflint clays.

The "Olive Hill" clay bed contains a very small amount of a clay mineral that is probably chlorite. In X-ray diffraction traces, this mineral has a funda-

mental basal spacing of 14A, and it does not swell when treated with ethylene glycol or collapse when heated to 300°C. Some doubt regarding the correct identification of this mineral remains, however, because it was neither destroyed nor enhanced by heat treatment at 650°C, and it was not destroyed by 3N hydrochloric acid treatment as are most chloritic clay minerals. Possibly the clay mineral here reported to be chlorite is a highly aluminous variety. Chlorite is most abundant in the softer flint clays and harder semiflint clays (fig. 14, samples 33, 27), but in none of the clay did the estimated amounts exceed 5 percent (table 7).

The materials other than clay minerals in the "Olive Hill" clay bed include allogenic minerals that were introduced during deposition of the clay, authigenic minerals that formed after deposition of the clay, and organic matter in the form of thin carbonaceous films. The allogenic minerals are quartz, zircon, tourmaline, garnet (which in the "Olive Hill" clay bed is probably almandine), ilmenite, and magnetite. The amount of quartz ranges from traces to approximately 50 percent. The other allogenic minerals are present only in trace amounts. The most abundant authigenic mineral is siderite, in amounts as great as 10 percent. Other

TABLE 7.—*Mineral composition and chemical analyses of clays from the "Olive Hill" clay bed of the Lee Formation in Kentucky, arranged in order of pyrometric cone equivalents*

[Samples located and described in Patterson and Hosterman (1962). Clay-mineral and non-clay-mineral compositions given in parts of 10. E, excellent; VG, very good; VP, very poor; Tr, trace; ---, no data. Chemical analyses in weight percent. Sample 1 analyzed by E. L. Prew, Alfred University, Alfred, N.Y., using standard methods; samples 13, 33, and 6 analyzed by P. L. D. Elmore, S. D. Botts, M. D. Mack, and J. H. Goode under supervision of W. W. Brannock, using methods like those of Shapiro and Brannock (1956). Summations rounded to nearest whole number. Samples for which TiO₂ only is given analyzed by Patterson and Hosterman using methods of Shapiro and Brannock (1953). * indicates sample contains organic matter that may cause FeO percentage to be in error]

Sample no.	25	13	33	9	27	1	6	24	28
Type of clay	Flint	Flint	Flint	Flint	Semi-flint.	Flint	Plastic	Plastic	Semi-flint.
Pyrometric cone equivalent	36	34+	34-	33+	33+	32½	32-	29-	29-
Clay minerals									
Kaolinite	9-9½	9-9½	9	8	7-8	7½-8	7	5½-6	5½
Illite	Tr	---	¼-½	½-1	Tr	Tr	1½-2	2	1½
Chlorite	½	---	---	Tr	---	---	---	---	Tr
Mixed-layer clay minerals	Tr	¼	¼-½	½	1-1½	1-2	½-1	1	½
Crystallinity of kaolinite	VG	E	VG	VG	VP	VG	VP	VP	VP
Nonclay minerals									
Quartz	---	---	---	½-1	Tr	Tr	Tr	½	2-3
Anatase	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr
Pyrite	---	---	---	Tr	---	Tr	---	---	---
Organic material	---	Tr	---	---	---	Tr+	Tr	---	---
pH index	6.0	4.9	5.5	4.3	5.5	4.1	4.4	4.8	6.5
Chemical analyses									
SiO ₂	---	45.0	45.5	---	---	39.0	45.4	---	---
Al ₂ O ₃	---	38.2	36.0	---	---	34.2	34.0	---	---
Fe ₂ O ₃	---	.46	.8	---	---	3.4	1.4	---	---
FeO	---	.19	.38*	---	---	---	.41*	---	---
MgO	---	.13	.36	---	---	.55	.69	---	---
CaO	---	.06	.08	---	---	.32	.11	---	---
Na ₂ O	---	.06	.10	---	---	.44	.24	---	---
K ₂ O	---	.30	1.0	---	---	2.57	3.1	---	---
TiO ₂	0.9	1.9	2.0	2.0	1.5	2.17	1.4	1.0	0.5
P ₂ O ₅	---	.01	.05	---	---	.24	.02	---	---
MnO	---	.00	.00	---	---	---	.00	---	---
H ₂ O	---	13.8	13.0	---	---	---	11.6	---	---
CO ₂	---	.05	.12	---	---	3.54	.26	---	---
SO ₂	---	.20	---	---	---	.72	---	---	---
S (total)	---	---	---	---	---	.29	---	---	---
Ignition loss	---	---	---	---	---	17.39	---	---	---
Sum	---	100.	99.	---	---	---	99.	---	---

authigenic minerals, present in minor amounts in samples studied in the laboratory, are pyrite, iron oxide minerals such as limonite, goethite, lepidocrocite, and hematite, and the soluble salts gypsum and iron sulfate. Traces of galena and sphalerite have also been reported in the clay bed; they are probably authigenic. Anatase is present in small amounts throughout the "Olive Hill" clay bed, but whether it was introduced at the time of deposition or formed after deposition is not known.

The allogenic minerals vary considerably in grain

size, roundness, and amount of alteration. Quartz forms both rounded and angular grains; most of the rounded grains are frosted and most of the angular ones are clear. Locally quartz grains are coated with an iron oxide mineral that is probably limonite. Grain size of the quartz ranges from very fine silt to medium sand. The quartz in plastic and semiflint clay is essentially unaltered, but many of the grains in flint clay are serrated and etched and partially replaced by clay minerals.

Most of the allogenic minerals other than quartz form rounded grains. Garnet and zircon grains are

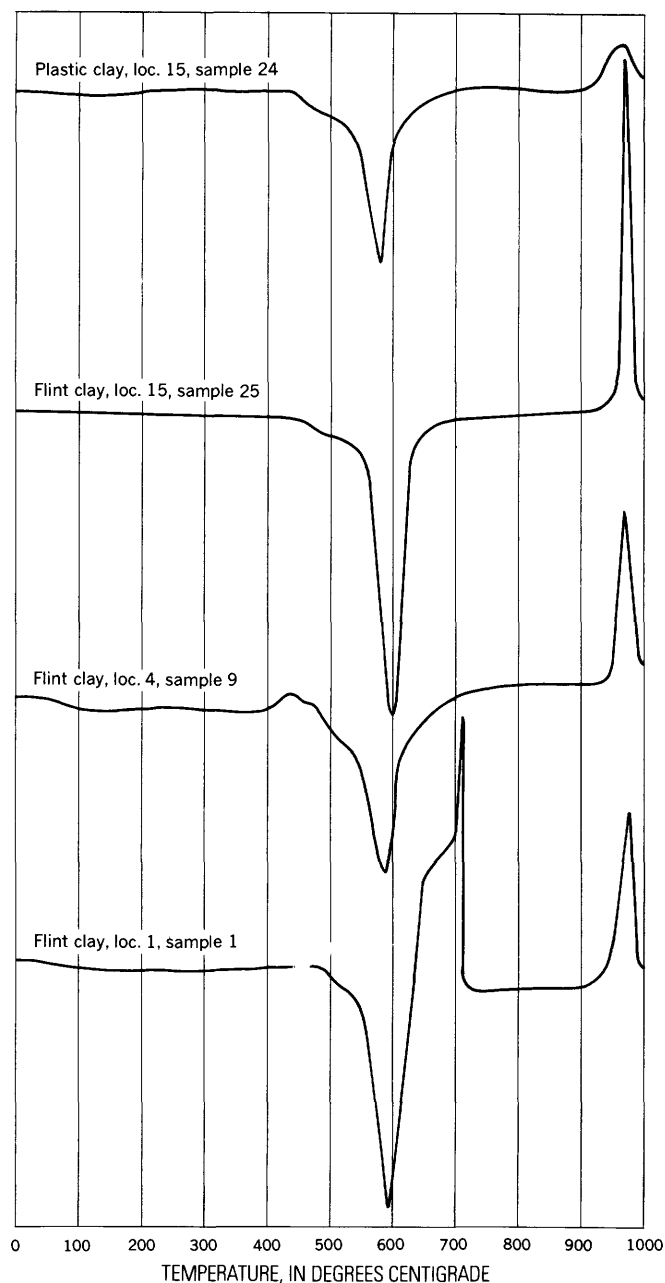


FIGURE 15.—Differential thermal analysis curves of clays from the "Olive Hill" clay bed of the Lee Formation in Kentucky. Sample descriptions and locations in Patterson and Hosterman (1962).

essentially unaltered. Most of the magnetite, however, is partly altered to limonite or hematite, and most of the ilmenite is coated with leucoxene.

The authigenic minerals, which apparently were formed at two different times, have a variety of crystal forms. Pyrite and siderite are scattered throughout the clay, and hematite, limonite, gypsum, and soluble salts are closely associated with joints in the clay. Probably

the pyrite and siderite formed long before the other minerals, which may be still forming by precipitation from ground water. Siderite occurs commonly as oolites, spherulites, and euhedral crystals, and, at the locality where it makes up 10 percent of the bed, it is in the form of nodular concretions as much as 3 mm in diameter and 1 cm in length. Many of the siderite concretions contain irregular inclusions of white kaolinite. Some of the pyrite occurs locally as small euhedral crystals disseminated throughout the clay, but most of it is in the form of small irregular nodular concretions. Most of these pyrite concretions are closely associated with carbonaceous films of *Stigmara*, suggesting that the pyrite was concentrated in the space originally occupied by a plant rootlet. Pyrite, in very fine particles, gives an exothermic reaction between 400° and 500°C in DTA (fig. 15, sample 9). Limonite and hematite occur as films along joints in the clay and as finely disseminated particles causing red, brown, and yellow discoloration of the clay adjacent to joints. The gypsum and soluble iron sulfate salts are chiefly in the form of films along joints. Iron oxides, gypsum, and soluble iron sulfate salts are present only in small amounts in most of the "Olive Hill" clay bed. The DTA curves give no indication that these minerals were present in any of the samples investigated, and the percentages of iron, calcium, and sulfur are low in the chemical analyses of most samples of these clays (table 7).

Anatase occurs in all samples of the "Olive Hill" clay bed examined in the laboratory (table 7) and appears to be present in essentially all parts of the bed; it probably contains nearly all the titanium present in the clay. Anatase was identified by the strongest X-ray diffraction peak at 3.51Å. Inasmuch as this peak is masked by the second-order basal (002) peak of kaolinite, it was necessary to heat the clay to 550°C for half an hour to destroy the kaolinite structure in order to recognize the presence of anatase. The strongest diffraction peak of anatase was weak for all samples, but the proportion of anatase indicated on the X-ray diffraction traces was probably sufficient to account for nearly all of the titanium, which ranges from 0.9 to 2.7 percent shown in the chemical analyses (table 7).

Anatase appears to be in very fine particles uniformly distributed throughout large bodies of the clay. The <2-μm fractions contained the same proportions of anatase as did the whole clay in samples investigated by X-ray methods. This observation and the absence of recognizable anatase in thin sections indicate that the mineral is present in very fine particles. The distribution of titania in the clay was investigated by chemical analyses of the type outlined by Shapiro and Brannock (1953). Samples were taken from opposite sides of blocks of flint clay and semiflint clay approximately

0.5 m in diameter. Samples from the same block contained essentially identical amounts of titania for each type of clay, though blocks from different localities differed within the range indicated in table 7.

The "Olive Hill" clay bed in one mine near Olive Hill, Ky., is reported by Greaves-Walker (1907, p. 470) to contain nodules and oolites of uncommonly high alumina content. He referred to the material as "aluminite"; it was later identified as gibbsite, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, by Galpin (1912, p. 324–329). Greaves-Walker reported as much as 48.5 percent alumina and a small amount of alkali and iron. Accordingly, the so-called aluminite was more valuable for refractory purposes than were parts of the bed that contain only kaolinite. During the present investigation a special effort was made to locate samples of gibbsite-bearing clay in the Haldeman and Wrigley quadrangles, but without success. The effort included X-ray examination of concentrated oolites from several localities within the clay bed. In all samples, the oolite concentrates contained only kaolinite of essentially the same composition as the enclosing nonoolitic clay.

Coaly organic matter appears to be abundant in the "Olive Hill" clay bed because black films and specks are conspicuous in hand specimens, but the total content of organic matter in the clay is low. Most of the carbonaceous films and specks are remains of detached rootlets of *Stigmara*, but locally nearly complete root systems are preserved by such films (fig. 12). The presence of organic matter is also indicated in some DTA curves by a sharp exothermic reaction between 650° and 720°C (fig. 15, sample 1). Of all samples investigated, sample 1 contained the most organic matter, and the exothermic peak shown by the curve of that sample is of the same order of magnitude as peaks obtained from a 2-percent mixture of coal from the bed overlying the "Olive Hill" clay bed in clay that contains essentially no organic matter. No organic matter was indicated in the DTA curves of most of the clays investigated, and organic matter probably makes up considerably less than 1 percent of most parts of the "Olive Hill" clay bed.

Origin

According to Patterson and Hosterman (1962, p. 79–81), stratigraphic, paleontological, mineralogical, and chemical evidence all support the conclusion that the clay deposits in the "Olive Hill" clay bed were formed by the alteration of ordinary fine-grained Pennsylvanian sediment in acid swamps. Some of the facts and observations pertaining to the origin of the clay are as follows:

1. The clay is a true underclay, as indicated by (a) the thin overlying coal bed, (b) abundant fossil plant roots, *Stigmara*, in the clay, (c) absence of bedding in the clay, (d) abundant slickensides in semiflint and plastic clays.
2. Root fossils indicate that the clay supported plant growth and, therefore, served as a subaqueous soil; however, evidence for a soil profile in the clay is absent.
3. The clay bed is discontinuous and consists of irregular lenses having no preferred orientation.
4. The kaolinite, illite, and mixed-layer clay minerals in plastic clays are similar to clay-mineral assemblages in Pennsylvanian shale enclosing the clay bed.
5. Proportions of kaolinite increase gradually from plastic to flint clay, and this increase is accompanied by a corresponding decrease in the amounts of illite and mixed-layer clay minerals.
6. Recrystallization of the kaolinite in flint clay is indicated by interlocking grains and by comparatively light-colored, large kaolinite grains in a dark-colored, very fine grained matrix. Semiflint and plastic clays show little evidence of recrystallization.
7. Some of the quartz grains in sandy flint clay are fresh, but others show evidence of solution and replacement by clay.
8. The clay bed contains no feldspar.
9. The titania content of most flint clay is about 2.0 percent; of semiflint, about 1.5 percent; and of plastic clay, 1.0–1.5 percent. Titania is one of the most stable of all chemical components, and, if it has not migrated, the increase in percentage from plastic to flint clay indicates a residual enrichment.

The shapes of the irregular lenses of clay, the relation of lithologic units within the bed, the presence of fossil roots, the absence of a soil profile, the lack of bedding, the overlying coal, and the marine or brackish-water fossils in the dark shale above the clay—all point toward an origin of the clay in coastal swamps. Clearly the irregularly shaped lenses of clay lack the orientation, continuity, and bedding that would be expected if they (1) formed by dissection of a blanket of sediment, (2) accumulated in channels, as did certain kaolin deposits of Tertiary age in Mississippi (Conant, 1965) or (3) formed in cutoff stream meanders as Kesler (1956, p. 553) has suggested for the kaolin deposits in Georgia. The irregular shapes and lack of orientation of the clay lenses, however, would be expected if the deposits accumulated in swamps in which bodies of water were irregular in shape and depth. Further evidence that the clay deposits formed in swamps lies in the root fossils in the clay and the overlying coal; this relation is remarkably in accord with the invasion of modern swamps by plants and with the accumulation of peat in

modern swamps, as described by Twenhofel (1950, p. 81–84). The best explanation for the absence of a soil profile seems to be that none developed because the clay was waterlogged at the time it served as a soil. The absence of bedding in the clay is probably due to the churning action of roots and to plastic flowage. The later gradation from pure clay to very sandy clay appears to be similar to the decrease in grain size away from shore in sediments in modern swamps diagramed by Twenhofel (1950). A sparse marine fauna, chiefly small *Lingula*, in the shale a short distance above the clay and the conformable relation of the shale and clay suggest that only slight subsidence was required to lower the clay below sea level. This, in turn, suggests that the swamps were located along coastal lowlands, a possibility that seems in accord with the evidence for deltaic deposition in the sandstone facies of the Lee Formation.

The clay appears to have formed by the leaching and alteration of ordinary fine-grained Pennsylvanian sediment in acid swamps, a theory similar in some respects to those proposed by Keller and others (1954) and by McMillan (1956). Inasmuch as the clay minerals in plastic clay do not differ greatly from those in the Pennsylvanian shale enclosing the clay bed, there is no reason to assume that special sedimentary sorting processes were involved. The three types of clay—plastic, semiflint, and flint clay—can be explained as representing progressive stages of leaching. According to this theory, kaolinite formed concurrently with the removal of alkalies and silica from illite and mixed-layer clays and certain nonclay minerals. Leaching of the clay is indicated by both direct and indirect evidence, but unfortunately little evidence supports the idea that kaolinite formed from other clay minerals, and nothing reveals what happened to the dissolved materials. The etched quartz grains and their replacement by clay minerals are convincing evidence that leaching took place. Also the absence of feldspars, which are present in many plastic underclay beds, is suggestive of leaching. The 50-percent increase in titania from plastic clay to flint clay seems to represent an expected increase in resistates with leaching. The root fossils provide another line of indirect evidence, for they clearly indicate that the clay supported plants, and alkalies and perhaps silica would be removed from any material that served as a soil. Perhaps most of the leaching took place while the rotted roots of many generations of plant growth provided channels for the acid waters to circulate through the sediments lying on the floors of the swamps. The materials removed by the leaching process and by upward diffusion into the overlying body of water were flushed away by sluggish movement of water through the swamps. The acidity of

the swamps is indicated by the present acid characteristics of the clay, by the overlying coal, and by organic material scattered throughout the clay. A suggestion that kaolinite formed from other clay minerals lies in the relation of the crystallinity of the kaolinite and its proportions to other clay minerals in the three types of clay. The kaolinite in plastic clay is a poorly crystallized fire-clay variety, and its proportion to other clay minerals is low. The flint clay is essentially pure, well-crystallized kaolinite. In the semiflint clay, the perfection of the kaolinite structure as well as the proportions present are intermediate between plastic and flint clays. This progressive increase in the perfection of the kaolinite structure as the amount of other clay minerals decreases seems more than a coincidence; it may represent a tendency for the crystal structure of kaolinite to become more perfect as the alkalies and silica are leached.

OTHER DISTRICTS IN EASTERN UNITED STATES

Underclay beds occur in Pennsylvanian coal-bearing strata at many places in the Appalachian region in the Eastern United States. All of these deposits are kaolinitic; however, many of them are not as pure as those in the Olive Hill and Clearfield districts previously described. Some of the deposits in the upper strata of the Pottsville Group or Formation (lower Westphalian, according to European general classification) include those in the following districts and beds: (1) Tuscarawas Valley, Ohio (fig. 2, location 33), "Brookville" bed (Hosterman and others, 1968, p. 180–181); (2) Oak Hill district, Ohio (fig. 2, location 34), "Sciotoville" bed (Stout and others, 1923). A few of the deposits in the Allegheny Group or Formation of Middle Pennsylvanian age (upper Westphalian of the general European classification) include the "Clarion," the widespread "Lower Kittanning," and younger beds. The "Clarion" bed is present in the East Liverpool district, Ohio (fig. 2, location 32), and nearby areas (Hosterman and others, 1968, p. 180) and in Somerset County (fig. 2, location 40) and nearby areas in Pennsylvania and Maryland (Hosterman, 1972). The "Lower Kittanning" bed occurs in the East Liverpool, Tuscarawas Valley, and Oak Hill districts, Ohio, and in the Beaver Valley district (fig. 2, location 36) (Hosterman and others, 1968, p. 180) and Somerset County, Pennsylvania. The younger underclays include the "Upper Kittanning" and "Bolivar" beds in Somerset County, Pa., and the nearby Frostburg district, Maryland (fig. 2, location 41) (Waagé, 1950).

MISSOURI

The fire-clay deposits in Missouri occur mainly in a large district in the east-central part of the State north

of the Missouri River (fig. 2, location 22) and in the Ozark region south of the river (fig. 2, location 23). All these clays are in sedimentary beds of Pennsylvanian (Late Carboniferous of the European time scale) age. Because of the presence of minor quantities of coal associated with some of the deposits, these clays are classed with the underclays in this report. However, the Missouri fire clays are not as clearly associated with overlying coal beds as are underclays elsewhere.

The most abundant clay mineral in the Missouri fire clay is kaolinite (85 percent or more in high-grade clay). Some very high grade fire clay contains appreciable amounts of diaspore, a mineral that is 85 percent Al_2O_3 . The fire clays are commonly classed as plastic, semiplastic, semiflint, flint, and superrefractory clays (burley and diaspore clays). McQueen (1943, p. 5-6) described the different clay types as:

“* * * (1) Plastic to semiplastic or semiflint fire clay, varies from soft to fairly hard, varies also in color and texture; grades imperceptibly into (2) flint fire clay, a hard, compact nonplastic fire clay. Flint fire clay is characterized by a conchoidal fracture and sharp splintery edges, and grades into (3) burley clay, so called because of the presence of ‘burls’ or shot-like particles (oolites) or small nodules (pisolites), which usually are highly aluminous in character. As the number and aluminous content of particles increase, this clay grades into (4) diaspore clay, which is usually a rough textured, compact clay of varying color and hardness, distinguished by a high alumina content. Diaspore clay is the designation used in Missouri for clay containing a minimum of 70 percent alumina (Al_2O_3). More recently, the grades of clay have been designated in Missouri as flint, less than 55 percent alumina, and diaspore, above 65 percent alumina. * * *”

East-central district.—Fire-clay deposits in the east-central district are scattered throughout an area of several hundred square kilometers. The fire clay occurs in the “Cheltenham Formation” of the Des Moinesian Provincial Series (Middle Pennsylvanian of the U.S. classification and Westphalian C and D of the European system).

The deposits in the “Cheltenham Formation” consist chiefly of plastic clays. The lower part of the “Cheltenham Formation” in the district is irregular in extent and thickness, and clay in this part of the formation chiefly forms sinklike structures. The middle part of the “Cheltenham” is a nearly continuous blanketlike deposit present over wide areas in Audrian, Callaway, and Montgomery Counties. In these counties, the bed has an average thickness of about 5 m. It yields the largest tonnage of plastic clays now produced in the district. The upper part of the “Cheltenham” is discontinuous and contains the least refractory clays of the district.

Flint and semiflint clays also occur in the east-central district but are less abundant there than in the southern district. Although deposits of these clays are scattered over much of the district, most deposits are out-

liers separated from the main mass of Pennsylvanian rocks in Callaway, Montgomery, and Warren Counties. The deposits occur in restricted circular or oval sinkhole structures in older rocks, many of which are steep-sided or even have one or more vertical walls.

Ozark district.—The Ozark district (fig. 2, location 23) is a large area south of the Missouri River and west of St. Louis County. It covers parts of Osage, Gasconade, Franklin, Maries, Pulaski, Miller, Crawford, and Phelps Counties. The clay is above conglomerate and sandstone at the base of the Pennsylvanian, which by their outcrops indicate the general area in which the clay deposits occur. Many of the scattered deposits are filled-sink structures (Keller, 1952; Keller and others, 1954). Most deposits are small, the typical ones containing about 15,000 tons. A few of the larger deposits are as much as 240 m long and 150 m wide and have a maximum thickness of about 8 m. Some smaller deposits are known to extend to depths of as much as 30 m. Flint and semiflint clays are the principal types found in these deposits; bedded plastic clay is not found in the district. Super heat-duty refractory burley and diaspore clays are associated with many deposits, and these high-grade clays have been mined extensively. The typical deposit containing diaspore consists of about 8,000 tons of flint clay, 250 tons of abrasive-grade diaspore, 750 tons of no. 1 grade diaspore, and 6,000 tons of no. 2 and no. 3 grades diaspore. Al_2O_3 contents of the diaspore clays are as much as 76.2 percent (table 8). As noted by Keller (1979), the diaspore deposits are depleted and the prospects for the discovery of more deposits are very poor.

TABLE 8.—Chemical analyses of Missouri fire clays, in percent

(From Keller and others (1954). 1, Diaspore clay, NE $\frac{1}{4}$ SE $\frac{1}{4}$, sec. 29, T. 41 N., R. 7 W., Maries County, Mo. (McQueen, 1943, p. 163); 2, Flint fire clay, SE $\frac{1}{4}$, sec. 19, T. 51 N., R. 1 W., Lincoln County, Mo. (McQueen, 1943, p. 47); 3, Semiflint fire clay, NW $\frac{1}{4}$, sec. 29, T. 47 N., R. 3 W., Warren County, Mo. (McQueen, 1943, p. 50); 4, Semiplastic fire clay, A. P. Green Fire Brick Co., Pit No. 4, Audrian County, Mo. (McQueen, 1943, p. 58); 5, Plastic “foundry” clay, A. P. Green Fire Brick Co., Pit No. 4, Audrian County, Mo. (McQueen, 1943, p. 64))

Sample no.	1	2	3	4	5
SiO ₂ -----	3.89	44.42	45.92	48.90	56.10
Al ₂ O ₃ -----	76.21	38.63	35.79	33.20	24.47
Fe ₂ O ₃ -----	.98	.55	.75	1.47	3.64
TiO ₂ -----	3.52	2.12	2.28	1.58	1.58
CaO-----	.08	.04	.06	.56	.61
MgO-----	.06	.10	.36	.34	1.11
Na ₂ O-----	.79	.30	.44	.10	.17
K ₂ O-----	.24	.12	.41	1.53	2.89
H ₂ O-----	14.56	13.90	13.06	11.55	8.39
Total -----	100.33	100.18	99.07	99.23	98.96

COLORADO

The principal kaolinitic clay deposits in Colorado are in the south-central (fig. 2, location 15) and Front Range (fig. 2, location 14) districts. Most of these clays are overlain by coal seams a few centimeters thick, and many of them contain carbonaceous imprints of plant roots resembling *Stigmara*. They, therefore, are classified as the underclay type.

South-central Colorado district.—The largest and most important clay deposits in Colorado are in Fremont, Pueblo, Custer, Huerfano, and Las Animas Counties in the south-central part of the State. These deposits are in the Glencairn Shale Member of the Purgatoire Formation and in the Dakota Sandstone, both of Early Cretaceous (Albian) age. The two formations are exposed in hogbacks at the south end of the Colorado Front Range and the east side of the Wet Mountains, and they also crop out in broad irregular belts farther east. The outcrops east of the mountains are particularly extensive in south-central Pueblo County, where nearly horizontal clay-bearing strata are cut by tributaries of the Arkansas River. The clay in the Glencairn Shale Member forms tabular lenses near the top of the member. At most places where this clay is mined, its thickness is 1.5–6 m. In the Dakota Sandstone, the clay is in a discontinuous unit of sandy clay, fire clay, and evenbedded sandstone in the middle part of the formation. These clay bodies are of various sizes, and they may be remains of a continuous bed that was dissected by erosion prior to the deposition of the overlying sandstone. Most of the Dakota Sandstone clay bodies that are mined are 1–2.5 m thick.

The fire clay in the Glencairn Shale Member is bluish gray to light bluish gray and plastic, and it parts with a blocky fracture. It is fairly uniform in chemical composition, has a silica-alumina ratio of about 3:1, and has fusible impurities of approximately 5 percent (Waagé, 1953). This clay is low grade to semirefractory but is commonly mixed with higher grade clays to obtain a more refractory product. Clay in the Glencairn Shale Member has been mined extensively in the Canon City district, in the hogback between Oil and Sixmile Creeks northeast of Canon City, and at Capers Spur in south-central Pueblo County.

Clay deposits in the Dakota Sandstone consist of an upper zone of plastic and semiplastic clay and a lower zone of flint clay. The plastic clay is light gray to blue gray and has a blocky to massive structure. It is compact and tough and parts with a splintery to rough-blocky fracture. The semiplastic clay is black and moderately hard and has a splintery to poorly developed conchoidal fracture. Semiplastic clay is the least common of the three types, and it occurs only locally be-

tween the plastic and flint clay. The flint clay is hard, light gray to light blue gray, and massive and has a well-developed conchoidal fracture. All three types of clay in the Dakota Sandstone are composed principally of kaolinite (Waagé, 1953, p. 38). The kaolinite in flint clay is fine grained, but plates, books, and vermicular crystals as much as 0.2 mm long occur in the plastic clay. Quartz sand is the principal impurity in the flint clay, and small lenses and pockets of sand are present in the clay at a few places. Scattered muscovite grains as much as 0.05 mm long and minor amounts of nontronite and organic matter also are present in some of the clay. The plastic and semiplastic clays in the Dakota Sandstone are of better grade than the clays in the Glencairn Shale Member, being white-burning semirefractory to refractory clay. Nonsandy plastic clay contains less than 5 percent of fusible impurities (Waagé, 1953) and has an average Al_2O_3 content of 29 or 30 percent. Most of this clay fuses at about PCE 29, and samples fusing up to PCE 31 are not uncommon. The flint clay is a white-burning highly refractory clay that fuses between PCE 31 and 36. It is fairly uniform in composition, and the only major impurity variation is in silica content, which is related to the amount of quartz sand present. The Al_2O_3 content of nonsandy flint clay is approximately 35 percent, and the fusible impurities are low.

Colorado Front Range district.—Refractory clay and clay shale deposits in the northern Front Range occur in the Lower Cretaceous South Platte and Lytle Formations of the Dakota Group, which is approximately equivalent to the Dakota Sandstone. These deposits extend south in a narrow belt from near Boulder, Boulder County, to the northwestern part of Douglas County. The largest and most abundant deposits are in the Van Bibber Shale Member of the South Platte Formation. Other deposits occur in the sandstone units overlying the Van Bibber, and a few scattered deposits are present near the top of the Lytle Formation (Waagé, 1961, p. 1). The best grade clays in the Van Bibber Shale Member are almost pure kaolinite (Waagé, 1961, p. 26), and probably this mineral is abundant in the other clays. Deposits of refractory clay and shale in the Golden area have been mined intensively since the 1860's, and many of the best grade and most cheaply mined deposits are exhausted.

KING COUNTY, WASH.

Six underclay deposits in King County, Wash. (fig. 2, location 1), about 30 km southeast of Seattle and 50 km northeast of Tacoma (Nichols, 1946), are in the Puget Group, which consists of formations of Eocene age (Vine, 1969). The underclay deposits range in thick-

ness from about 1 m to more than 10 m. The clay is mostly gray to black, but some of it is bleached to nearly white, and part of it is brown where weathered siderite is abundant. Most of the deposits consist of slickensided semiplastic clay, but parts of deposits are flinty material that has a subconchoidal parting. Small clay pellets and grains that are mostly about 10 mm in longest dimension and rounded, subrounded, or angular in form are scattered through the clay. Near the top of the clay, thin layers of carbonaceous clay containing small coal seams are less than 5 mm wide and several centimeters long. Other coal beds are found in the strata above and below the clay, and some of them are thick enough to be mined.

According to Nichols (1946), the clay is mainly kaolinite, as determined by DTA, X-ray, and petrographic methods. Boehmite is the second most abundant aluminous mineral, and minor amounts of dickite, diaspor, and gibbsite were thought to be present. Siderite, in the form of spherical, cylindrical, or dumbbell-shaped concretions that are about 1 mm in size, is locally the most abundant impurity. Small spherical concretions of pyrite occur sparsely.

According to Nichols (1946), one large sample of clay from one pit was estimated to be 51 percent kaolinite, 34 percent boehmite, and 14 percent limonite. It was 48.6 percent Al_2O_3 , 10.05 percent Fe_2O_3 , 24.0 percent SiO_2 , 0.5 percent MgO , 0.1 percent CaO , 0.12 percent Na_2O , 0.13 percent K_2O , 0.054 percent P, 0.02 percent S, 1.1 percent free H_2O , and 15.65 percent combined H_2O . This sample was exceptionally high in alumina; the average boehmite content of the clay is less than 10 percent.

Hydrothermal solutions have invaded the clay at one locality, as is indicated by the minor amount of realgar and chalcopyrite. Hydrothermal alunite is present in other parts of the Puget Group.

Nichols (1946) thought that the clay was deposited in a lacustrine environment and was transported from weathered rocks to the east. His opinion is supported by the following: (1) the presence of minute lamination and pellets of kaolinite in clay; (2) the fine-grained texture that suggests deposition as a clay; (3) the lack of quartz and mica that would be expected if the clay were a residual deposit formed by weathering of the Puget Group; (4) the sharp contact between the clay and the underlying strata. One of the clay deposits is underlain by a weathered zone, and Nichols implied that some of the kaolin in the lower part of this deposit is residual.

The origin of the boehmite is uncertain, as reported by Nichols (1946) as follows:

"* * * Several theories for the origin of the boehmite have been considered. They are: (1) the boehmite was deposited with the kaolinite;

(2) it was formed from the kaolinite in an Eocene weathering profile; (3) it was formed from the kaolinite in a profile developed on the present topography; (4) the boehmite was derived from the kaolinite by the action of ground water; (5) substances derived from the coal were responsible for the alteration of some of the kaolinite to boehmite; (6) two or more of the above processes were effective in the formation of the boehmite.

"There are several valid arguments which prove that the boehmite was not formed from kaolinite in a profile developed on the present topography. It suffices to say, however, that the boehmite is as plentiful in the high-alumina clay which is 200 feet below the surface as it is in clay which crops out at the surface. No definitive statement with regard to the origin of the boehmite can be made. * * *

COWLITZ, WASH.

The clay deposits in the Cowlitz district, Washington (fig. 2, location 2), are in two beds separated by strata as much as 30 m thick that consist of argillaceous silt layers interbedded with sand and carbonaceous materials (fig. 16). Both clay beds are tabular units varying considerably in thickness and composition. The lower bed, called the principal bed (Popoff, 1955; Nichols, 1945) is more than 15 m thick at most places, and the thickness of the upper bed is commonly somewhat less. The lower bed is underlain by waterlaid volcanic breccia; bedded sand capped by basalt is present above the upper bed.

The clay having the highest alumina content is in the basal 4–6 m of the principal bed. It is composed mainly of bluish-gray and gray, dense semiflint clay (Popoff, 1955, p. 18). White clay pellets are abundant in some seams in this clay, and siderite oolites and concretions are abundant in other parts. Only a minor amount of lignitic material is present. The upper part of the principal bed contains less alumina; it is gray or nearly black clay because it contains abundant minute particles of carbonaceous matter. This bed also contains lignite units, some of which are a meter or more thick.

According to Popoff (1955, p. 15), the Cowlitz clay deposits contain kaolinite, halloysite, gibbsite, smectite similar to beidellite, and nontronite, which were identified by DTA and optical methods. The gibbsite, which occurs in the white pellets in the lower bed, was found to be as much as 50 percent in selected specimens. One gibbsite-rich sample of the clay contained 49.3 percent Al_2O_3 , but representative samples contained 32–34 percent. Gibbsite was assumed to have formed by the leaching of silica by ground water carrying organic acids.

The upper clay bed in the Cowlitz district consists mainly of reddish-brown and greenish-blue semiplastic clay. It contains little more than trace amounts of lignite and lignitic clay. The average Al_2O_3 content of the upper bed is 31.6 percent.

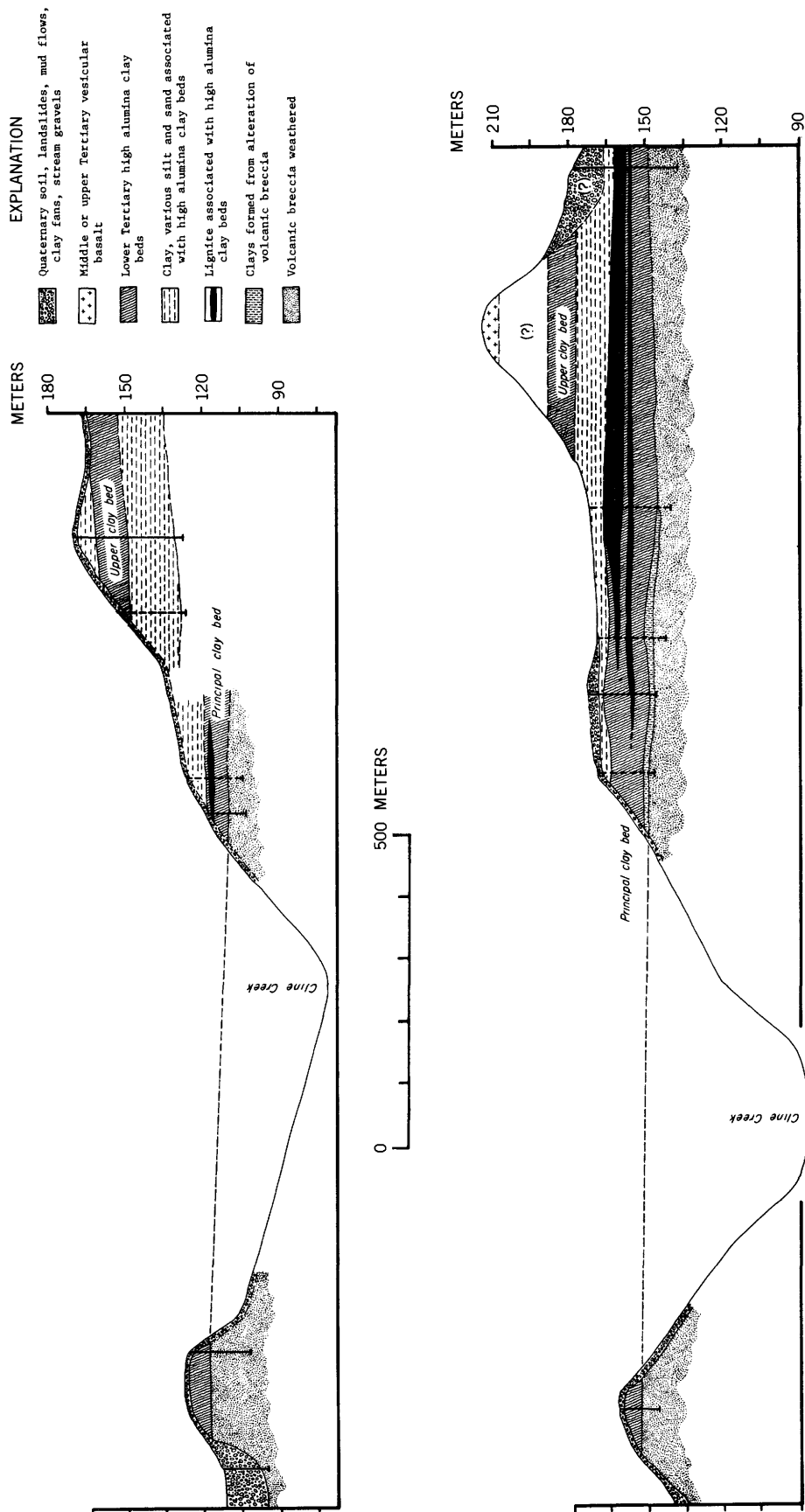


FIGURE 16.—Geologic sections of the Cowlitz kaolinitic clay deposits, Washington. (Modified from Popoff, 1955, fig. 4.)

HOBART BUTTE, OREG.

The Hobart Butte (fig. 2, location 4) is located about 25 km south of Cottage Grove, Lane County, Oreg. The kaolinitic deposits in this district are erosional remnants of more extensive deposits that are preserved in the higher parts of the butte. They are in the sedimentary Calapooya Formation of late Eocene and Oligocene age. The deposits are irregularly shaped and as much as 60 m thick (fig. 17). They consist of zones of massive clay or of mixed clay, sand, and pebbles (Allen and others, 1951). The sedimentary origin of the clays is indicated by zonation of flattened and reworked clay pellets, organic coating on pellets, and the presence of lignitic material, diatoms, and silicified wood. The kaolinite and associated sediments in the Calapooya Formation were probably transported from weathered rock at higher elevation to the east.

Kaolinite is the dominant mineral of the kaolin group in the Hobart Butte deposits (Allen and others, 1951), but minor amounts of dickite are present. The dickite apparently was altered from kaolinite or deposited along with additional kaolinite by hydrothermal solutions that invaded the deposits in late Miocene time. Minor amounts of sulfide minerals were introduced by the hydrothermal solutions. The clays are remarkably low in iron oxide (table 9). The analyses also show that no Mg, Ca, Na, or K is present; however, the analytical methods used may not have been sufficiently sensitive to recognize trace amounts.

TABLE 9.—Analyses of kaolinitic clays from Hobart Butte, Oreg., in percent

[From Allen and others, 1951, table 2; W. W. Brannock, analyst. 16G, Water-laid breccia in which the long axes of white fragments are aligned in one direction, and surrounded by dark-gray clay containing organic matter and appreciable iron. 16W, Bleached zone, 5 cm wide, in contact with clay represented by sample 16G, and retaining the same arrangement of fragments as 16G but in a white clay matrix. Some organic matter and ferric oxide have been removed by hydrothermal solutions]

Sample no.	16G	16W
SiO ₂ -----	50.80	50.91
Al ₂ O ₃ -----	33.45	33.67
Fe ₂ O ₃ -----	.81	.50
MgO-----	None	None
CaO-----	None	None
Na ₂ O-----	None	None
K ₂ O-----	None	None
H ₂ O (–110°C)-----	.61	.61
H ₂ O (+110°C)-----	12.11	11.97
TiO ₂ -----	1.92	1.99
Organic matter-----	.31	.16
Total-----	100.01	99.81

ALBERHILL, CALIF.

The Alberhill district and nearby areas in the northern Santa Ana Mountains (fig. 2, location 8) have been the major source of kaolinitic refractory clays in southern California (Cleveland, 1957, p. 136–138). In these areas, both sedimentary and residual clays occur in a single zone that apparently formed during Paleocene time. The complex sedimentary clays include (1) underclay-type fire clay underlying lignite, (2) hard pisolitic clay, and (3) sandy clay from which high-grade white or nearly white kaolin has been recovered by hydraulic methods. The commercial underclay ranges in thickness from about 1 m to more than 2 m. The best grades are flint clay having PCE's of 33 and 34. The lower grades contain disseminated quartz, lenses of sand, and some chlorite. Contacts between various grades are gradational; the quality of clays commonly changes considerably within short distances along the strike of beds. Most of the pisolitic material is in the upper parts of flint-clay units, and it tends to grade into light-colored hard clay.

The residual clays, which are as much as 34 m thick, are described by Cleveland (1957, p. 137) as grading "downward and laterally into weathered metasedimentary rocks of the Triassic Bedford Canyon formation and andesitic rocks of the Jurassic(?) Santiago Peak volcanics. Slaty cleavage, outlines of feldspar phenocrysts and of angular rock fragments, and hexagonal quartz grains are remnant structures that indicate that the residual clay was derived from slate, volcanic breccia, and hypabyssal igneous rocks respectively. * * *

HOLOCENE UNDERCLAY, HAWAII

Occurrence

Plastic clay deposits occur in swamp areas at several localities on Kauai, Hawaii, and deposits in five areas were investigated (Patterson, 1971). The deposits are of the underclay type and occur below peat layers and muds rich in organic matter. The swamps containing the clay are at altitudes of 120–1200 m and in belts that receive 250–500 cm of rainfall a year. The clay in Alakai Swamp is on rocks of the Waimea Canyon Volcanics, and the deposits at the other four localities are on the Koloa Volcanics. Alakai Swamp and one of those on the Koloa Volcanics are of the upland type that have been called summit swamps (Wentworth and others, 1940, p. 8); they are on narrow ridges surrounded by deep steep-walled valleys. The swamps in the other three areas are in gently sloping areas adjacent to highlands. Rainfall is the only water now reaching the swamps on the ridges. The preservation of swamps

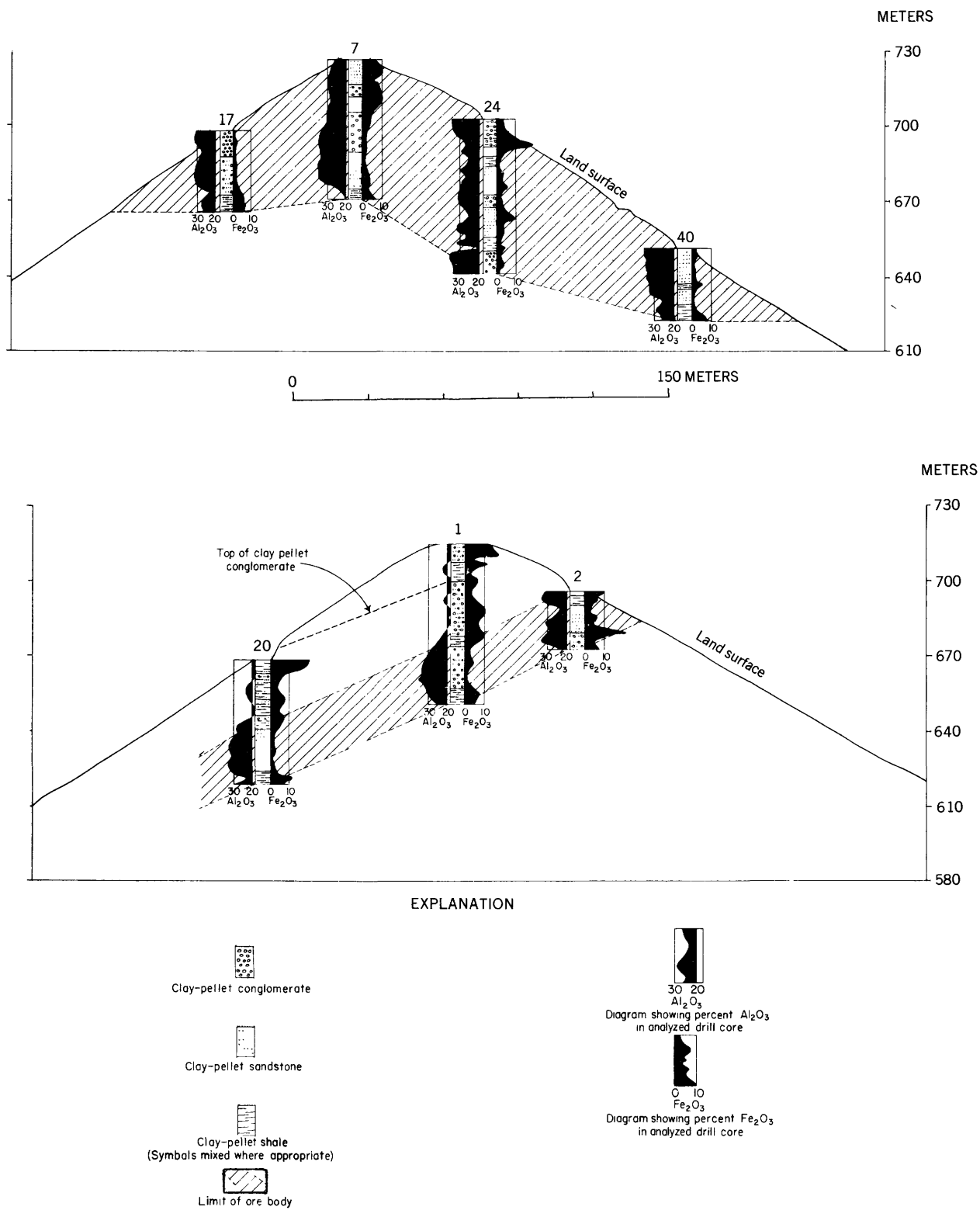


FIGURE 17.—Geologic sections of the Hobart Butte kaolinitic clay deposits, Oregon. (From Allen and others, 1951, pl. 2.)

under such conditions is partly due to the slow rate of evaporation caused by extended periods of rainfall and dense fog. Ground-water seepage probably contributes to the swamps in flat areas adjacent to highlands. Some of the swamps support only low-growing vegetation that consists, in part, of dwarfed forms of species that grow as large trees in the surrounding dense forest.

The clay deposits are young and are almost certainly still being formed. The oldest part of the Koloa Volcanics has been dated by the magnetic-reversal and potassium-argon methods as late Pliocene, but most of the basalt flows in it are Pleistocene. Therefore, some of the clay formed on Pleistocene rocks. The restriction of the clays to peat and organic-rich layers makes it certain that clay and the organic material are genetically related. Peat formation in Hawaii began at the close of the last glacial period, as determined by pollen analysis (Selling, 1948, p. 118), and that it is still in progress in areas having such heavy precipitation is a valid assumption. We may, therefore, conclude that much of the clay formed in Holocene time.

The plastic clays are light-colored, nonbedded, irreg-

ular lenticular deposits covered by a layer of peat or organic-rich mud. The clays and overlying organic layers are thickest in the central parts of the swamps and thin sharply toward the edges (fig. 18). Both commonly wedge out in the zone where the stunted swamp vegetation changes to normal forest growth. Several holes augered by hand in the central parts of swamps failed to penetrate the base of the clay at depths of 7 m. One power-auger hole penetrated 8 m of clay. Deeper holes were not successful because of poor sample recovery, but a few cuttings from greater depths indicate that maximum thicknesses are more than 9 m. All of the clay in the swamps is very plastic, and some water-logged deposits are almost fluid, as shown by the fact that a hand auger weighing about 14 kg sank under its own weight at several localities.

Most of the clay is light gray, but some is darker shades of gray, and parts of deposits in contact with the overlying peaty layers are ordinarily so rich in organic matter that they are almost black. Lower margins of deposits are commonly tan or brown and are richer in iron than middle and upper parts. Relict masses of

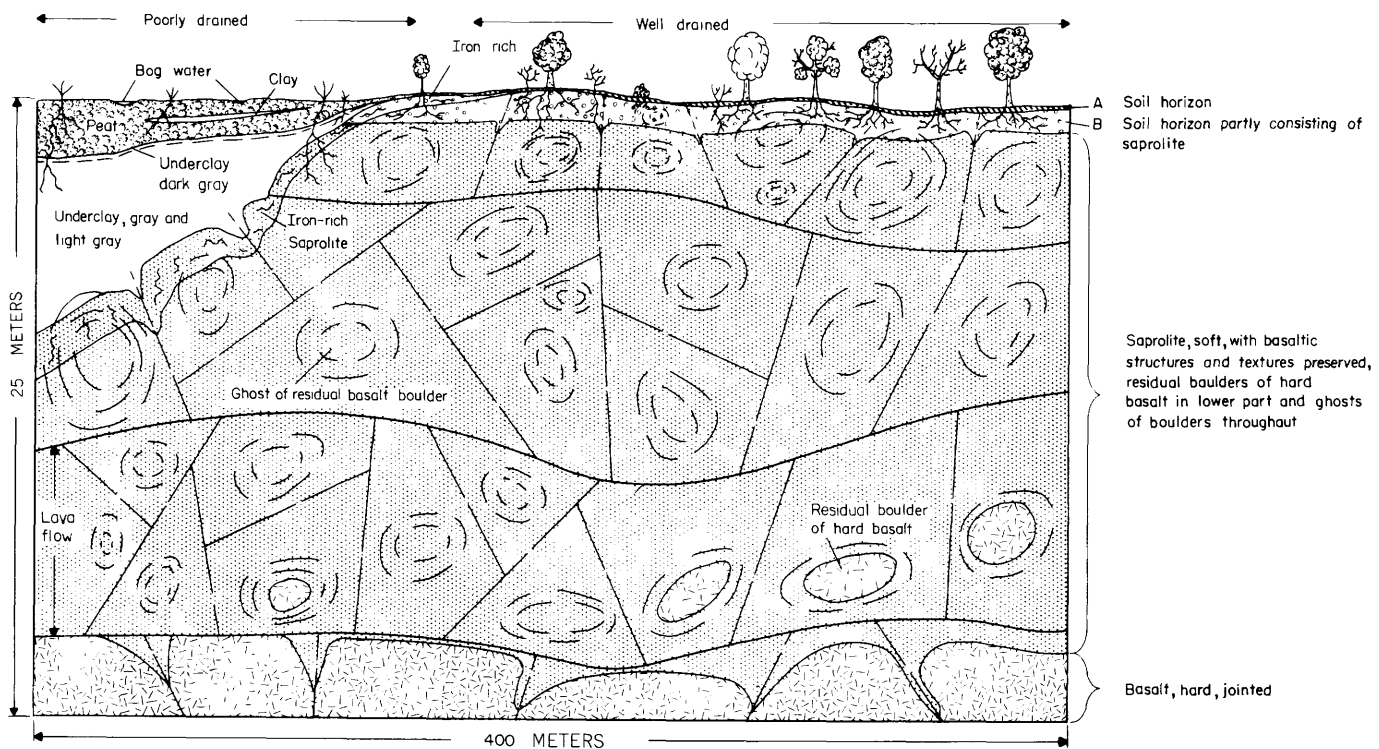


FIGURE 18.—Diagrammatic section illustrating the occurrence and nature of plastic clay deposits, Hawaii.

brown and gray saprolite are common near the base of deposits, and large residual boulders of nepheline basalt are scattered through parts of the clay in one swamp. The cores of these boulders are dark and hard rock, but their outer rims, 2–3 cm thick, are lighter colored and softer than the cores. Much of the iron has been leached from the boulder rims, and nepheline has been altered to clay minerals.

The clay in all the swamps investigated grades downward through saprolite from which much of the iron has been leached into iron-rich saprolite, which is the parent material of most of the clay. This saprolite is similar to the saprolite at depth in well-drained areas, except that it contains much more goethite in the form of veins and vesicle and vug fillings.

The pH of water in peat and clay, and of open-swamp water, was measured in the field; all are acid. One sample of swamp water had a pH of 3.5. Water from peat at five localities ranged in pH from 3.5 to 4.5; however, pH's as low as 3.2 have been recorded for water in this peat, and the water has been described as "extremely acid" (Cline and others, 1955, p. 573).

Mineral Composition

The plastic clay consists chiefly of halloysite (10A), gibbsite, illite, quartz, and anatase, and it contains traces of ilmenite and magnetite. Much of the clay probably also contains appreciable quantities of amorphous inorganic matter. The estimated ranges in abundance of these minerals and amorphous matter, expressed as parts of ten or trace, are as follows:

Halloysite (10A)	5–8
Illite	0–3
Quartz	0–2
Gibbsite	0–3
Goethite	Trace
Magnetite	Trace
Ilmenite	Trace to 1
Anatase	Trace to 2
Amorphous matter	0–4(?)

Halloysite (10A) is the most abundant mineral in the plastic clay, and in some samples it is the only one identifiable by X-ray methods (fig. 19). It is identified by its prominent 10A reflection from the 001 planes, while the natural moisture is still present (fig. 19A), and the collapse of this spacing to about 7A after the mineral converts to the less hydrous form (fig. 19B). Electron micrographs of the plastic clay (Patterson, 1971, fig. 12) show the presence of tubular structures characteristic of halloysite (7A), the halloysite (10A) having dehydrated during sample preparation or exposure required to obtain the micrograph.

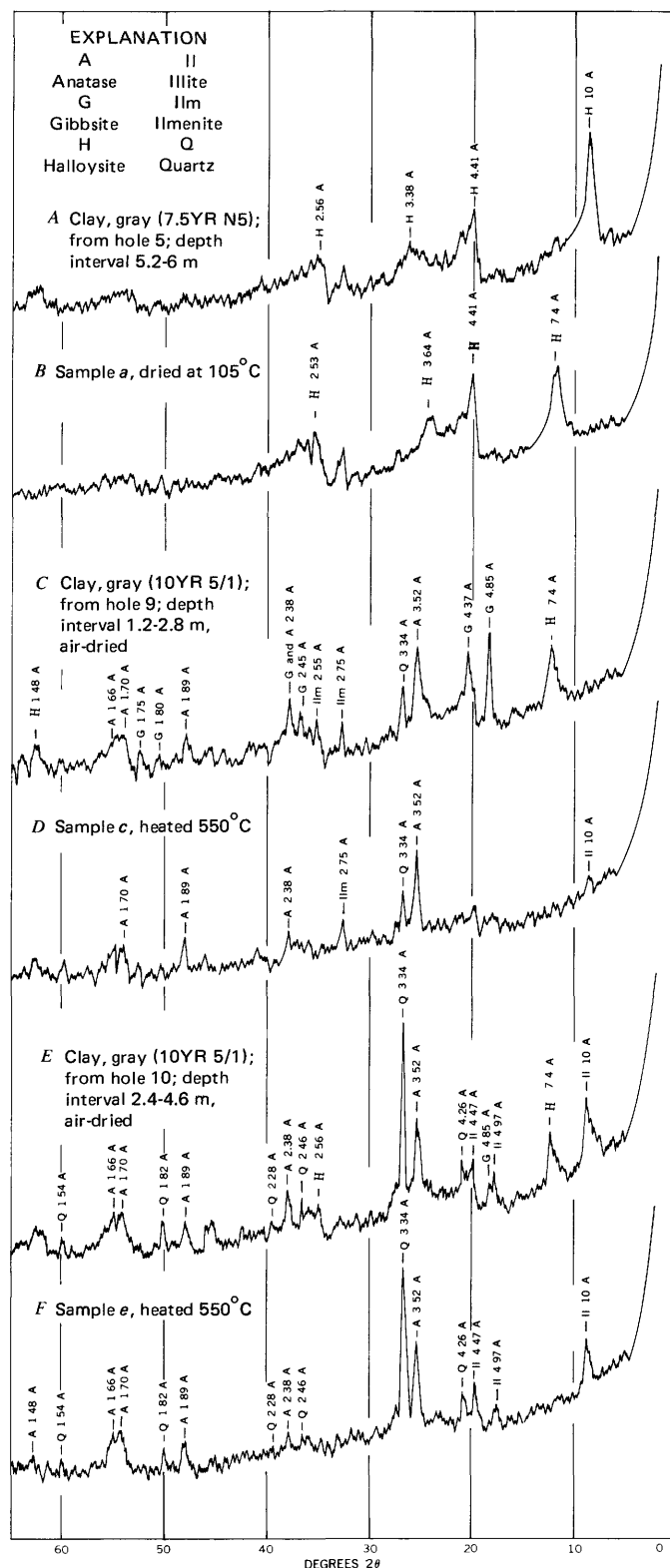


FIGURE 19.—X-ray diffraction traces of samples of plastic clay from Alakai Swamp, Hawaii, $\text{CuK}\alpha$ filtered radiation. Holes are located on map by Patterson (1971, pl. 5).

Illite is generally not abundant in the plastic clay, but it makes up as much as 20 percent of parts of some deposits. It is uncommonly abundant in a layer 2 m thick below the thickest peat penetrated in augering in Alakai Swamp and in a thin bed interlayered with peat and mixed peat and clay in another swamp. Illite was identified by its 10A peak in samples that had been dried to collapse the 10A peak of halloysite (fig. 19D-F). Illite probably contains nearly all the K_2O in the plastic clay, inasmuch as the sample richest in this oxide (table 10, sample 2; fig. 19E) also contains considerable illite and no other K_2O -bearing minerals were identifiable in this clay.

Quartz is present in sufficient quantities in much of the plastic clay to produce prominent X-ray reflections (fig. 19F). Most is extremely fine grained, similar to that found in the clay of the Koolau Volcanics on Oahu by Wentworth and others (1940, p. 25).

Gibbsite occurs as irregularly rounded grains and impure nodules, ranging from silt size (<0.0625 mm diameter) to more than 15 cm in longest dimension, scattered throughout most of the clay. However, in some zones gibbsite is absent, and in other zones small nodules are so abundant that the clay has a granular texture and is difficult to auger by hand.

Anatase is the principal titanium mineral in the plastic clay, and it is most abundant in the $<2\mu m$ fraction, but some is also present in the largest gibbsite nodules. The purest anatase found was sand-sized grayish-blue nodules that were concentrated in the heavy-mineral fraction separated by heavy liquid from a clay sample. These nodules were found to contain approximately 47 percent TiO_2 , and to consist chiefly of anatase, though trace amounts of ilmenite may be present.

Ilmenite is rare in most of the plastic clay, but a few zones contain as much as 10 percent. Most ilmenite grains are of fine-silt size, but a few grains are as large as fine sand.

Traces of goethite and magnetite were found in the silt and sand fractions separated from the clay. Neither mineral was sufficiently abundant in whole samples to be identified by X-ray methods.

Amorphous inorganic material is probably present in some of the clay because intensities of X-ray reflections from minerals in many samples are low, and estimated amounts of identifiable minerals are inadequate to account for the composition of whole samples. Also, the electron micrograph of the clay shows much finely dispersed material that is probably amorphous.

TABLE 10.—Chemical analyses of plastic underclay on the Waimea Canyon Volcanics and clay, typical saprolite, and fresh basalt from the Koloa Volcanics, Kauai, Hawaii, in percent

[LOI, loss on ignition; —, no data. From Patterson (1971)]

Sample no.	Waimea Canyon Volcanics		Koloa Volcanics			
	Plastic clay		Plastic clay		Typical Saprolite ¹	Fresh basalt ²
	1	2	3	4	5	6
SiO_2 ———	34.0	33.1	29.5	29.7	4.2	42.27
Al_2O_3 ———	34.8	26.7	34.6	32.7	29.6	10.90
Fe_2O_3 ———	2.2	2.2	1.8	.72	35.6	4.32
FeO ———	.67	1.5	.68	.44	.71	8.66
MgO ———	.06	.54	.10	.00	.10	12.77
CaO ———	.00	.00	.00	.00	$<.10$	11.67
Na_2O ———	.08	.22	.08	.07	.05	2.85
K_2O ———	.21	1.7	.28	.09	.10	.83
H_2O ———	6.8	6.1	10.8	15.0	21.7	{ ———
H_2O+ ———	13.5	9.3	12.6	11.9		
TiO_2 ———	7.5	17.5	8.9	7.6	5.4	2.69
P_2O_5 ———	.41	.31	.31	.98	.31	.69
MnO ———	.08	.16	.08	.08	.06	.13
CO_2 ———	$<.05$	$<.05$	$<.05$	$<.05$	$<.05$	——
LOI ———	23.6					——
Total ———	100	99	100	99	98	99

¹Sample from 1.3 to about 3 m below land surface.

²Average of 13 samples.

Chemical Composition

The plastic clays consist chiefly of Al_2O_3 , SiO_2 , TiO_2 , and H_2O (table 10); they are uncommonly low in Fe_2O_3 but rich in alkalis and several minor elements. The abundance of SiO_2 in surficial plastic clay deposits, which ranges from 29.5 to 34.0 percent in the samples analyzed (table 10, samples 1–4), contrasts sharply with the very low SiO_2 contents of saprolite near the surface in well-drained areas. Iron oxide, in very small quantities in the clay, is the most abundant component of most saprolite in well-drained areas. Titania is more abundant in plastic clay than in the saprolite; TiO_2 forms as much as 17.5 percent of the plastic clay (table 10, sample 2).

The alkali and alkaline-earth elements in the plastic clays vary considerably, but they tend to be more abundant in the clay than in saprolite. A comparison of the semiquantitative spectrographic analyses of plastic clays and saprolite from depths of less than 6 m shows that Mg, Na, and K all tend to be significantly more abundant in plastic clays in swamps than in saprolite in well-drained areas. The local concentration of K_2O is as great as 1.7 percent (table 10, sample 2) in clay formed on the Waimea Canyon Volcanics. This percentage of K_2O , though small, represents a considerable concentration, inasmuch as the nine rocks in the Waimea Canyon Volcanics that have been analyzed (Macdon-

ald, 1960) range from 0.22 to 0.47 percent K_2O , and the average is only 0.32 percent.

Two samples of plastic clay on the Koloa Volcanics and two on the Waimea Canyon Volcanics were analyzed for minor elements by semiquantitative spectrographic methods. The analyses suggest some differences in the behavior of minor elements during weathering in a swamp environment from that in typical well-drained areas. The minor elements concentrated in the clay are Sc, Ga, Nb, and V. Ce was found in all samples, and Ge was found in one sample of clay on the Waimea Canyon Volcanics. As neither element was found in any hard or weathered rock in well-drained areas, both may be concentrated by weathering under swamp conditions. Minor elements that are leached, but at a much slower rate than in well-drained areas, are Na, Mg, Ca, Co, Ni, Cu, Sr, Y, Zr, Ba, La, and Pb.

Origin

The plastic-clay deposits and associated saprolite both formed chiefly from parent rocks of similar composition and age. The plastic-clay deposits are restricted to swamps having peat or organic-rich layers, indicating that their origin is related to poor drainage conditions and decaying organic matter. Saprolite, which formed in well-drained areas, has a mineral content and a texture very different from those of the clay. Halloysite (10A), illite, quartz, and anatase are much more abundant—and gibbsite, goethite, hematite, and magnetite are less abundant—in the clay than in the saprolite. Textures of the parent rocks have been destroyed in the clay but are well preserved in the saprolite.

Plastic clay has formed from both saprolite and hard basalt. Clay formation from saprolite is indicated by the downward and lateral gradation of clay into saprolite and by residual lumps of saprolite in the lower parts of clay deposits. In one swamp, the residual nepheline basalt boulders have outer rims in intermediate stages of alteration to clay, indicating that the clay does form from the aluminous minerals in the parent rock. Weathering of basalt probably began shortly after the lavas cooled, as has been suggested for the rocks in well-drained areas. Probably some swamps in which the clay formed have always been areas of poor drainage, resulting from flow damming at the time the parent rocks accumulated. The thickness of the peat indicates that the swamps have existed for a long time, and the absence of evidence for any significant change in the swamp environment leads to the conclusion that both clay and peat are still forming today. The earliest date that can now be established for the beginning of clay formation is the close of the last glacial stage. This date is based on analysis of pollen (Selling, 1948, p. 118)

from near the base of the thickest peat that overlies clay on the Waimea Canyon Volcanics.

Part of the halloysite (10A) in the plastic clay probably formed in the swamps, and part has been preserved from a saprolite already rich in this mineral. Some of this clay formed in place and is probably still forming, as indicated by the several stages of replacement of nepheline by halloysite in the altered rims of residual boulders. Formation of part of the clay by preservation of the halloysite (10A) already present in the parent saprolite is indicated by the isolated masses in the lower parts of clay bodies and by the gradation of clay downward into saprolite. The preservation of the clay is due to the influence of the low-pH swamp environment; under these conditions, silica removal is impeded, but iron is leached efficiently.

Recent investigations by Jackson and others (1968) and Rex and others (1969) have established that the quartz in the plastic clay was introduced from a distant source by atmospheric transport.

The origin of the potassium-bearing illite in the plastic clay deposits is difficult to explain, because the traces of biotite in the volcanic rock on Kauai are inadequate to supply sufficient micaceous parent material, and the saprolite on which some of the clay formed must have already been leached of potassium. The problem is further complicated by the fact that one concentration of illite is under the thickest peat, whereas clay in the same stratigraphic position under thin peat in this swamp contains little or no illite. The relationship between abundance of illite and thickness of peat suggests that illite may form in a swamp environment. Such an origin of illite under surface conditions would be similar to the one suggested for mica in several Hawaiian soils by Swindale and Uehara (1966) and Juang and Uehara (1968). Another concentration of illite is in a thin bed interlayered with peat and mixed clay and peat in one swamp where the source of potassium may have been partly from decaying plant material. However, clays at both locations where illite is concentrated also contain angular quartz and a few euhedral microscopic grains of other minerals. The occurrences of these minerals suggest that an ash fall might have been the original rock of the bedded clay; therefore, an air-transported volcanic material, anomalously rich in mica and from an unknown source, might have been the parent of the illite.

BALL CLAYS

WESTERN KENTUCKY-TENNESSEE REGION

An extensive belt of deposits in the western parts of Kentucky and Tennessee (fig. 2, location 27) is the major domestic source of ball clay. The deposits, which

are found in lower, middle, and upper Eocene beds (Olive and Finch, 1969), are in sedimentary beds in the Mississippi embayment, a northern extension of the Gulf Coastal Plain. Deposits mined at one locality are of early Eocene age, but the clay in many other deposits is in the middle Eocene part of the Claiborne Formation or Group. The following discussions will be concerned only with the younger deposits.

The Kentucky-Tennessee ball clays occur in lenticular units, in which clay is interstratified with sand, silt, and lignite. Clay units range from less than 1 m to more than 5 m and are thinly laminated to thick bedded and massive. The aggregate thickness of clay in a single mine is as much as 10 m. The physical and ceramic properties of the clay in any given deposit commonly vary considerably, due to differences in mineral composition. Therefore the clays are selectively mined to meet product specifications. Mined bodies of clay range from about 100 m in longest dimension to deposits that are 800 m long and 300 m wide. Much of the clay is gray, and some of it is dark gray due to finely divided carbonaceous particles. Black carbonized imprints of fossil leaves, twigs, and other plant debris are common. Lignite and lignitic clay in discontinuous beds and lenticular units ranging from a few centimeters to nearly 3 m thick locally overlie the ball clay and are interbedded with it in a few places (Whitlatch, 1940).

The Kentucky-Tennessee ball clays of Claibornian Age are a mixture of clay minerals and nonclay impurities, and compositions vary greatly. Kaolinite is the dominant mineral present. Mixed-layer clays were found to make up 5–25 percent of the clay fraction of 11 samples studied (table 11). Illite is the second most abundant clay mineral, and smectite and chlorite are present in minor amounts in parts of deposits. Quartz is the major nonclay mineral and is found in amounts ranging from 4 to 43 percent in the 11 samples. Minor quantities of plagioclase, calcite, dolomite, and possibly potassium feldspar also are present.

Olive and Finch (1969, p. 14–15) offer the following explanation for the depositional environment of the ball clay:

“* * * Seeking evidence concerning environments of deposition, R. H. Tschudy (written commun., 1968) examined pollen assemblages obtained from the Claiborne Formation at localities shown in figure 1. Many assemblages contain taxa, such as freshwater algae and water fern, that indicate deposition in lakes and fresh-water ponds. Others contain large spores that are not likely to have survived long-distance transport. A clay sample from locality C-15 (fig. 1) yielded abundant hystrichospheres, a few dinoflagellates, and abundant plant tissue, which point to a marine or near-shore marine depositional environment. A sample from locality C-7 (fig. 1) contained much trash and a few hystrichospheres, which suggest a marine or brackish-water environment. The shapes and distribution

of the clay bodies and the ecologic information provided from a study of pollen assemblages suggest that the climate during Claiborne time was warm and humid with heavy seasonal rainfall; the terrain was a rather flat plain traversed by south- to east-flowing, meandering, low-gradient, aggrading streams that occupied broad flat shallow valleys. Flooding following seasonal rains caused shifts in the major channels and abandonment of channel segments, which became locales for accumulations of clay deposits and associated sediments. * * *”⁴

The foregoing comments on the depositional environment of the ball clay are plausible, but they provide no explanation of the origin of the kaolinite in the source area. Very little evidence can be mustered to support any proposed origin of the kaolin, because of the lack of knowledge of geography, geomorphology, and soils in the region in Eocene time.

TROUP, TEX.

The principal ball-clay deposits in Texas are in the Troup district (fig. 2, location 19). This clay is in the lower Eocene part of the Wilcox Group (Stenzel, 1950), which is separated from the overlying formation by a prominent undulating unconformity. The deposits are restricted to the higher parts of the Wilcox Group below this unconformity, which were once hills on the erosional surface existing prior to the deposition of the overlying formation.

The ball clay is described by Stenzel (1950) as being a tough clay, most of which has a subconchoidal parting and a uniform color of light bluish gray where fresh. This clay bleaches to nearly white with prolonged exposure to the sun. The deposits contain abundant carbonaceous tubes filled with ball clay that are fossil roots, proving that the clay once was a soil. The clay is cut by numerous inclined slippage planes having wavy slickensides. Displacement along such planes is not greater than 2 mm. The deposits typically grade downward into sandy lignitic clay and are overlain locally by thin zones of impure lignite.

According to Pence (1950), the clay near Troup is remarkably similar to the Tennessee ball clay. Kaolinite having imperfect crystallinity is the dominant clay mineral, and the deposits contain about 20 percent quartz. One incomplete analysis shows that the clay is 32.69 percent Al_2O_3 and 53.73 percent SiO_2 , and the PCE is 32.

OTHER BALL-CLAY DISTRICTS

Ball clay, which is mined by one company, occurs in the Panola, Miss., district (fig. 2, location 28). This clay is in the Zilpa Clay (Bicker, 1970), which is of middle

⁴Sample locations and figure 1 refer to Olive and Finch's report (1969).

TABLE 11.—*Description and X-ray mineralogic analyses of ball-clay samples from the Claiborne Formation, Tennessee and Kentucky*
 [Modified from Olive and Finch (1969, table 3) to conform with the recommendations of the AIPEA Clay Mineral Nomenclature Committee. Whole-rock analyses, in percent, calculated from X-ray diffraction data. Clay-mineral fraction, in percent, estimated from X-ray analyses, using methods described by Schultz (1964), except that total clay is reported as the difference between the sum of the nonclay minerals and 100 percent. Precision of determinations generally within 10 percent, —, no data]

Sample no.	Location	Lithologic description	Whole-rock analyses					Clay-mineral fraction						
			Quartz	Plagioclase	Potassium feldspar	Calcite	Dolomite	Total clay	Kaolinite	Illite ¹	Smectite	Mixed-layer clay	Chlorite	Proportions of smectite (M) and illite (I) in mixed-layer clay
12 -----	Paschall No. 5 clay pit, 4.1 mi northeast of Cottage Grove, Henry County, Tenn.	Brownish-gray ball clay-	4	-	?	-	-	96	70	5	-	25	-	I>M
13 -----	Etheridge mine, 4.3 mi east-northeast of Cottage Grove, Henry County, Tenn.	Pale-gray sagger clay---	23	?	-	-	-	77	83	6	-	11	-	I>M
14 -----	Scott mine, 2.35 mi southwest of junction of U.S. Route 641 and Tennessee Route 140 in Puryear, Henry County, Tenn.	Dark-gray wad clay----	34	?	-	1	-	65	79	14	-	7	-	I>M
15 -----	Clay pit, 0.4 mi southeast of Bell City, Calloway County, Ky.	White clay -----	34	1	-	1	1	63	67	9	-	24	-	I>M
16 -----	Lamkin clay pit, 2 mi west-northwest of West Viola, Graves County, Ky.	Pale-gray clay -----	20	-	-	-	-	80	70	22	-	8	-	-
17 -----	Middle of Powell pit, 1 mi southeast of Hickory, Graves County, Ky.	-----do-----	20	-	-	-	-	80	90	5	-	5	-	-
17 -----	Bottom of Powell pit-----	-----do-----	18	-	-	-	-	82	77	13	-	8	2	-
18 -----	Outcrop, 0.4 mi east of Wickliffe City limit, north side Kentucky Route 440, Ballard County, Ky.	Gray clay -----	43	?	?	?	?	57	61	8	16	15	-	M>I
19 -----	Outcrop, 3.8 mi east of Lovelaceville in Illinois Central Railroad cut, McCracken County, Ky.	Dark-gray carbonaceous, slightly silty clay.	31	?	-	?	?	69	68	9	3	20	-	I>M
20 -----	Outcrop, 0.75 mi south of Camelia, McCracken County, Ky.	White clay -----	26	2	-	2	?	70	76	9	-	15	-	I>M
21 -----	Outcrop, 0.9 mi north-northeast of Camelia, McCracken County, Ky.	Tan clay -----	23	-	-	-	-	77	72	18	-	10	-	-

¹Includes clay-sized mica, chiefly muscovite.

Eocene age, the same age as most of the deposits in the large Kentucky-Tennessee ball-clay district farther north. The "Panola" ball clay is remarkably similar in geologic occurrence and mineral content to the clay in the Kentucky-Tennessee district.

Deposits of white kaolin at Hart, Calif. (fig. 2, location 7), are classified by the California Division of Mines and Geology as ball clay (Kelley, 1966; Dietrich, 1928, p. 193-194). Though this kaolin is plastic and has some of the other physical properties of ball clay, it is of hydrothermal origin and, therefore, differs from the other ball-clay deposits in the United States, which are of sedimentary origin. It formed by the alteration of eruptive rocks that were high in alumina and low in alkali contents.

A ball-clay district at North East, Md. (fig. 2, loca-

tion 42), was active for many years. However, mining has ceased in this district, because much of the better grade clay is exhausted and most of the remaining clay is on land that is unavailable for strip mining. The ball clay in the North East district, which is in nonmarine beds of Cretaceous age (Knechtel and others, 1961), varies considerably in composition, and some deposits have little value because they contain too much quartz sand for industrial use. The clay fraction of most deposits is 60-80 percent kaolinite, and the rest is illite and mixed-layer clay.

Residual Kaolin Deposits

Residual kaolin deposits occur at many places in the Eastern United States and at several places in the

western part of the Nation. The residual kaolin in the Eastern States is mainly in weathered pegmatites and granitic igneous rock masses that are scattered through the Appalachian and Piedmont regions from Vermont and New Hampshire in the north to Alabama in the south. Many of these deposits were mined on a small scale in the last century. All are now (1980) inactive except the Spruce Pine district, North Carolina, and only this district will be discussed in this section of the report. Several of the districts in the other regions containing residual kaolin deposits have been discussed previously and will only be listed by name and parent rock type in this section.

SPRUCE PINE, N.C.

Numerous scattered deposits of residual kaolin occur in the Spruce Pine district, North Carolina (fig. 2, location 43). The deposits have formed by weathering of feldspathic rocks and contain high percentages of quartz and other resistant minerals (Parker, 1946, p. 42). High-quality kaolin containing 37 percent or more Al_2O_3 and less than 1 percent Fe_2O_3 is recovered by washing.

Sand (1956, p. 33), in reporting on the genesis of residual kaolins that included 12 samples from Gusher Knob, the principal mining area (table 12), and others from seven more locations in the Spruce Pine district, described the following alteration:

“* * * Hydrated halloysite predominated over kaolinite in all of these deposits. In individual samples the hydrated halloysite to kaolinite ratio varied from 30:1 to 1:1 with an average for the region of about 10:1. The feldspars, whether sodic plagioclase or microcline, weather to hydrated halloysite with plagioclase the first to decompose. This can be observed in the hand specimen of a partially altered perthite where the potash feldspar stands out in relief. Large, only slightly altered, microcline crystals were found next to completely altered plagioclase. However, in this region it was found that all feldspars alter to hydrated halloysite even though the rate of weathering differs. In only one sample, from the Woody Deposit, was the potash feldspar observed altered in small part to secondary mica. The primary mica was altered to vermicular kaolinite in all samples studied. * * *”

OTHER RESIDUAL KAOLIN DEPOSITS

Residual kaolin deposits discussed previously in this report, because they occur in districts where the principal deposits are sedimentary, include those that have weathered from the following rocks: (1) basalt in Spokane County, Wash., (2) nepheline syenite in the Bauxite district, Arkansas, (3) andesite, slate, and volcanic breccia in the Alberhill district, California, and (4) gneiss in the Minnesota kaolin district.

Weathering, the process that forms residual kaolin deposits, no doubt was active on many sedimentary kaolin deposits either before burial by younger rocks or near the present land surface much later. Therefore, many of the other kaolins, ball clays, and underclays are in part residual.

TABLE 12.—Bulk mineral compositions of saprolite in the Spruce Pine district, North Carolina, in percent
[Modified from Sand (1956, table 5). S.F., analysis of size fraction; T.S., point count of thin section; Tr, trace]

Deposit	Analysis	Parent rock	Quartz	Mica	Feldspar	Hydrated halloysite	Kaolinite
Gusher Knob ¹	S.F.	Granite	24.1	16.4	0.5	46.6	12.4
School Hill	S.F.	do	58.2	1.9	None	35.3	4.9
Fluken Ridge	T.S.	Pegmatite	22.4	.3	.8	73.7	2.8
Do	T.S.	Microcline	.4	1.3	.3	90.8	7.2
Do	S.F.	do	.7	7.0	4.7	74.4	13.1
Do	S.F.	Perthite	Tr	6.4	39.7	52.2	1.7
Do	S.F.	do	4.6	2.1	75.6	16.3	1.4
17-Acre Prospect	S.F.	Pegmatite	5.5	16.8	None	64.5	13.2
Do	S.F.	do	8.8	18.2	None	61.8	11.1
Do	T.S.	do	3.0	17.1	None	66.8	13.1
Do	S.F.	do	3.4	8.3	None	75.5	12.9
Do	T.S.	do	1.8	3.8	None	85.6	8.8
Do	T.S.	do	None	6.3	None	84.9	8.8
Carter Ridge	T.S.	do	None	2.9	None	84.3	12.8
Micaville	S.F.	Granite	4.4	14.8	None	78.0	2.7
Do	S.F.	do	29.9	39.7	.7	25.1	4.7
Do	S.F.	do	5.7	19.4	21.6	43.1	10.2

¹Average of 12 samples.

Hydrothermal Deposits

Hydrothermal kaolin deposits occur at several places in the Western United States, but only a few of these have been mined. The deposits in the Little Antelope Valley district, California, are the only ones consisting mainly of kaolinite that have been mined recently. Hydrothermal halloysite has been produced in the Tintic district, Utah, and at Terraced Hills, Nev.

LITTLE ANTELOPE VALLEY, CALIF.

The Little Antelope Valley clay deposits (fig. 2, location 6) are in an area of considerable geothermal activity in a range of low hills on the east side of the Sierra Nevada Range. The range of hills consists mainly of rhyolite flows, and the valley in which the clay is located was occupied by a freshwater lake in which tuff was deposited during Pleistocene time. Thermal springs, fumaroles, mud pots, and patches of warm ground are found at three localities in the district. Numerous vents along two northwest-trending faults about 1 km apart emit hot water and steam.

The deposits were described by Cleveland (1962); at the time his report was written, the largest of the Little Antelope clay deposits was exposed in an open-cut mine 210 m long. The cut extended into the hillside 100 m, and the working face was about 8 m high. The deposit was exposed along the principal fault for 600 m northward from the mine. The clay produced has been used as fillers in paint, plastics, rubber, and paper; as a whitener in paint and portland cement; and in stucco mixes. It had PCE's in the 30-34 range.

The kaolin varies considerably in mineral composition and other characteristics. Most of the kaolinite, the principal mineral, is well ordered, but some formed by alteration of tuff is described as "poorly crystalline" (Cleveland, 1962, table 4). Quartz, in amounts of as much as 20 percent, is the principal impurity. Cristobalite is present locally, and veins of opal and trace amounts of alunite occur at places. Noncrystalline matter that is presumably aluminous is abundant locally. Most of the clay is pale yellowish orange, but some is light gray to white. It ranges from hard to soft friable material (Mohs scale 1-4), contains megascopic and microscopic cavities, and has an earthy luster and specific gravity of about 2.5.

Chemical analyses (table 13) of the Little Antelope Valley kaolin indicate that it contains appreciably more silica and less alumina than theoretical kaolinite. Trace elements in this clay include Zr, Li, Ba, Mg, Ga, Pb, V, and Mn (table 14). Some of the trace elements, particularly Pb, V, and Mn, may have been introduced by thermal solutions.

TABLE 13.—Partial chemical analyses of kaolin from the Little Antelope Valley district and of theoretical kaolinite, in percent

(Modified from Cleveland (1962, table 3). 1, Sample from Little Antelope Mine. Analysis by Smith-Emory Company, Los Angeles, Calif. 2, Sample from Casa Diablo kaolin deposit. Analysis by Smith-Emory Company, Los Angeles, Calif. 3, Theoretical kaolinite. —, no data)

	1	2	3
SiO ₂	59.88	53.01	46.54
Al ₂ O ₃	28.67	31.13	39.50
Fe ₂ O ₃01	.48	—
MgO01	1.37	—
CaO01	.11	—
K ₂ O01	.06	—
Na ₂ O01	.59	—
TiO ₂	—	.20	—
SO ₃	0	.57	—
H ₂ O	—	—	13.96
Total	88.60	87.52	100.00

TABLE 14.—Semiquantitative spectrochemical analysis of clay material, Little Antelope Mine

(From Cleveland (1962, table 4), G. A. Ulman, analyst. Elements given in order of decreasing concentration)

Element	Concentration
Si	Major constituent
Al	Major constituent
Fe	1 percent (approx.)
Ti	Between 0.2 and 0.002 percent
Zr	Do.
Li	Do.
Ba	Do.
Mg	Do.
Ga	Do.
Pb	Do.
V	Do.
Mn	Do.

The kaolin in the Little Antelope Valley district clearly formed by hydrothermal solutions. Cleveland (1962, p. 20-21) stated that most of the alteration was by sulfuric acid, and he believed that the water in earlier intervals contained even more sulfur than it does now (table 15). Most of the altered host rocks are rhyolites, and the clay formed from older rhyolite is purer and of higher commercial value than the deposits from younger rhyolite and lacustrine tuff and tuff breccia. The typical alteration zone consists of a core of clay that grades outward into country rock or partly altered rock brightly tinted with iron oxide. Deposition of silica by the thermal solutions has caused local contamination of clay, and silicified zones several tens of meters in longest dimension are bypassed in mining.

TABLE 15.—*Partial chemical analyses of waters in the Little Antelope Valley district, California, in parts per million*

[From Cleveland (1962, table 2). 1, Hot Creek at Fish Hatchery; 2, Boiling Pot in Hot Creek Gorge; 3, Hot Creek at County Road (NE¼ sec. 19, T. 3 S., R. 29 E.); 4, Hot Springs on Little Hot Creek; 5, Casa Diablo Hot Springs. —, no data]

	1	2	3	4	5
Si —————			56.	—	—
Fe —————			.04	—	—
Ca —————	11.	11.	13.	—	—
Mg —————	12.	6.	4.8	—	—
Na —————	23.	119.	69.0	—	—
K —————			6.3	—	—
SO ₄ —————	8.	31.	21.0	—	—
Cl —————	11.	65.	37.0	7.25	—
B —————	.45	2.96	1.84	11.9	15.60
As —————			.10	—	—
F —————			1.7	—	—
Total —————	65.45	234.96	210.78	19.15	15.60

TINTIC, UTAH

Most of the catalytic-grade halloysite that has been mined in the United States came from the Dragon mine, Tintic district, Utah (fig. 2, location 13). The total production during the period 1931–62 was nearly 750,000 metric tons. The recorded output since 1962 is unavailable. However, the deposit is known to be exhausted, and another deposit in this district was being worked in the 1970's. The Dragon mine was originally operated for iron ore.

The halloysite bodies at the Dragon mine are located along conspicuous fissures at the northeast end of a monzonite porphyry stock (Kildale and Thomas, 1957). They are hydrothermal replacements of lower Paleozoic limestone near the contact with the porphyry and were known to extend from the surface to a depth of about 120 m. Layers of chert nodules that formed beds in the limestone before replacement are present in parts of the deposit. Outer edges of the deposit grade into limestone and masses of iron oxide containing very little clay.

The typical fresh clay is nearly pure halloysite containing very fine grained disseminated pyrite that is rarely sufficiently large to be observed in hand specimen. The purest halloysite is white and has a lustrous porcelainlike appearance, and this form grades into a duller white variety. Both 10A and 7A forms of halloysite are reported to be present, but virtually all the freshly mined clay was the hydrated type. Iron oxides were present in sufficient quantities to stain the clay near the surface and along fissures well below the surface. Manganese stains occur along fractures. An American Petroleum Institute reference sample from

the Dragon mine examined by Kerr and others (1950, p. 49) was 93.9 percent pure halloysite.

TERRACED HILLS, NEV.

Large deposits of hydrothermal halloysite in the Terraced Hills district, Nevada (fig. 2, location 12), have been mined intermittently for use in portland cement. The deposits range in thickness from about 3 m to more than 18 m (Papke, 1971). Most of the clay is grayish orange to light brown, but some is light gray. It has altered from andesitic tuff of Miocene to Pliocene age. The unaltered tuff commonly contains fragments of pumice and other volcanic rocks, including irregular beds of arkose or conglomerate arkose. Outlines or ghosts of the pyroclastic fragments are preserved in the clay. The clay is underlain by vesicular, locally porphyritic andesite and basalt flows and is unconformably overlain by thick basalt flows that are mostly fine-grained and dense.

The mineralogy of the deposits is described by Papke (1971, p. 72) as follows:

“* * * The clay bodies are composed of compact, brittle material with a dull to slightly waxy luster that slakes rapidly in water to form granules or small curved chips. Study of numerous samples by X-ray diffraction, differential thermal analysis and the optical microscope showed that the clay is composed principally of halloysite, hydrated iron oxides, and variable amounts of residual feldspar and residual or introduced quartz. About 1 percent magnetite is present in small disseminated grains. Montmorillonite was detected in a few samples.

“Most of the samples were cut from within 1 ft of an exposed face. The samples were stored in air-tight containers, except while being pulverized in a mortar and pestle, to prevent any change of hydration state. X-ray diffraction studies showed that all samples were mixtures of the fully-hydrated and dehydrated forms of halloysite. Portions of some samples were dried in air for 48 hr and examined again by X-ray. These contained a much higher percentage of the dehydrated form than did the original material. It is probable that the fully-hydrated form is the only type present in deeper, unexposed portions of the deposits. * * *”

The hydrothermal solutions that formed the clay rose along the high-angle faults occurring in the district and spread out in permeable and chemically favorable beds. The open-textured tuffs between less permeable flows formed a natural channelway for the hot solutions. The evidence that the solutions rose along faults is that near faults all the tuff is altered to clay, whereas farther away only the upper, more permeable part of the tuff has been altered to halloysite.

The hydrothermal process was selective, and fine-grained glass fragments are much more thoroughly altered than are fragments of crystalline rock. During the alteration of the andesitic tuff to halloysite, silicon, calcium, magnesium, sodium, potassium, and probably iron were removed and water was added. No silica-enriched halo was found above or surrounding the

deposits, as associated with hydrothermal halloysite elsewhere (Keller and Hanson, 1969). Therefore, the fate of the elements removed by the hydrothermal activity is unknown.

MINOR HYDROTHERMAL ALTERATION OF SEDIMENTARY CLAYS

Though only minor alteration of the clay by invading solutions took place, rare occurrences of hydrothermal activity in sedimentary clays have been found at Hobart Butte, Oreg. (fig. 2, location 4), by Allen, Loofbrow, and Nichols (1951) and in one deposit in King County, Wash. (fig. 2, location 1), by Nichols (1945). The clays at Hobart Butte were deposited in late Eocene and Oligocene time, and the hydrothermal activity was related to volcanism in the Miocene. The solutions deposited minor amounts of stibnite (Sb_2S_3), realgar (AsS), pyrite (FeS_2), scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), cinnabar (HgS), calomel (HgCl), and other minerals. They also either altered some of the kaolinite to nacrite or deposited this kaolin mineral. Realgar and stibnite occur as coatings of slickensides, fillings and replacements of porous material, coatings of pellets, and disseminated minute crystals. Well-formed pyritohedrons of pyrite are associated with the realgar. Scorodite occurs as green crusts and spherulites along crevices and replacements of the clay. The King County clay contains minor quantities of realgar and flakes of chalcopryite.

OTHER HYDROTHERMAL KAOLIN DEPOSITS

Kaolin and halloysite of hydrothermal origin occur in varying quantities in many mining districts of the Western United States. Many of these occurrences are associated with metallic minerals in mines that have long been inactive, and none of them have been adequately investigated. The Stoker deposit (fig. 2, location 11) and the Bullion district (fig. 2, location 10), both in Nevada, have been described by Olson (1964, p. 186).

*** The Stoker kaolin deposit, Pershing County, probably is the largest known kaolin deposit in Nevada. It may be traced for at least one-half mile along the base of the western flank of the Stillwater Range immediately north of New York Canyon. The body probably is on the order of a few hundred feet across. Bulldozed trenches have shown that it is as much as 25 feet [7.5 m] deep. The kaolin is thought to have been formed by hydrothermal alteration of a Mesozoic(?) phyllite. *** A large deposit of halloysite occurs in the Bullion (Railroad) mining district, *** Elko County, which originally was developed for silver, lead, copper, and gold in 1869. At the intersection of two large dikes of quartz porphyry on the north face of Bunker Hill, the porphyry has been almost entirely converted by hydrothermal processes to halloysite and other clays. The exact extent of the clay is unknown, but one adit which cuts the dike at an approximate angle of 45° is in clay for 350 feet [105 m]. This halloysite is reported to have potential value as a catalytic agent. ***

Large deposits consisting of a mixture of highly crystalline kaolinite and cristobalite occur in hydrothermally altered tuffs and other volcanic rocks along the Continental Divide about 22 km west of Winston, Sierra County (fig. 1, location 17), N.M. Parts of this deposit consist of rather uniform light-colored clay, but much of it contains appreciable vein quartz or other forms of silica and only partially altered volcanic rock. A few tons of clay from this deposit was used experimentally in making ceramic tile; the deposits have been explored in some detail and evaluations for use as paper coater are being made by private interests.

Problematical Kaolins and Deposits of Uncertain Origin

INDIANA HALLOYSITE

Halloysite (10A) was discovered at Shoals, Ind. (fig. 2, location 30), in 1874 (Callaghan, 1948), and small deposits have been found in several other places in the State. The best known deposits are in the Gardner Ridge mine area several kilometers northeast of Shoals. These deposits were mined intermittently on a small scale for use in floor tile and alum-type chemicals between 1880 and about 1930. They are of interest mainly because they are a problematical and uncommon occurrence of halloysite (10A).

The Gardner Ridge deposits are in irregularly shaped discontinuous bodies scattered along the unconformable contact between Mississippian limestone and Pennsylvanian sandstone (between Lower and Upper Carboniferous of the European classification). Isolated veins of halloysite (10A) and other veins extending from clay bodies occur in the overlying sandstone. In places the clay is disseminated and forms a matrix in the sandstone. The clay bodies range from about 1 m to a little more than 2 m in thickness. The larger bodies of clay mined are estimated to have contained only about 20,000 tons. The forms of clay present include glassy, banded, massive, and nodular, and some of it is plastic. It is described as white, grayish, some of it bluish and greenish, and parts of it are stained with manganese and iron oxide. The uppermost parts of the clay bodies are brown or mahogany. Though most of the clay is halloysite (10A), it is intermixed with allophane and contains minor quantities of alunite and gibbsite.

Callaghan (1948) reviewed the many theories offered to explain the origin of the Gardner Ridge halloysite deposits, pointing out that the most widely accepted theories are (1) the halloysite was introduced by solutions and (2) the deposits are ancient laterites consisting of residual material on limestone that have undergone considerable postburial changes. Among the

difficulties in explaining the origin of this uncommon type of deposit are the uncertainty of the source of the sulfur to form the alunite and the formation of gibbsite. It has been suggested that the gibbsite formed by the leaching of clay minerals by sulfuric acid that formed by alteration of pyrite in ground water. However, this theory is supported only by the negative evidence of the absence of pyrite in the overlying sandstone near the clay deposits and its presence elsewhere.

VERMONT KAOLIN

The largest known deposits in Vermont are located at East Monkton (fig. 2, location 46) in the west-central part of the State. Several attempts have been made to produce kaolin in this district since the late 1700's. Small tonnages were processed and used in refractory and other ceramic products, as a filler for soft rubber, and as a binder for animal feed, but the kaolin is too coarse grained to be used in paper making. The district has been inactive since the late 1960's, and the last processing plant, built in 1959, has been dismantled.

The kaolin occurs in the Cheshire Quartzite of Early Cambrian age as thin beds of quartz-rich clay and kaolinitic quartzite. Parts of the kaolin-bearing beds are cut by milky quartz veins as much as 10 cm thick.

The origin of the Vermont kaolin is not well understood because of uncertainty about the source of alumina. Early ideas included the weathering of graphic granite and feldspathic quartzite. Neither idea seems sound because no graphic granite occurs in the vicinity, and the Cheshire Quartzite contains very little feldspar. A graphic granite source rock also is improbable because most of the quartz grains associated with the kaolin are rounded (Ogden, 1969). Ogden favored the theory that the deposits formed by hydrothermal replacement by solutions from a deep-seated intrusion. Whether or not this explanation is correct is difficult to prove.

MOUNT HOLLY SPRINGS, PA.

The kaolin deposits in the Mount Holly Springs district, Pennsylvania (fig. 2, location 39), consist of sandy and silty clay (table 16) that formed on phyllite of Early Cambrian age (Hosterman, 1969b). They are mined for use in light-colored brick and white portland cement. Some clay is washed for filler applications. The whitest and best quality clay is in the upper parts of the deposits, and this clay grades downward into grayish-green and light-gray phyllite through a zone of yellow, pink, red, and brown variegated silty clay. The deposits have long been thought to be residual and to have formed by weathering. However, Hosterman (1969b) found that the deposits contain alunite, and he suggested that they were formed by hydrothermal alteration and later modified by weathering.

HALLOYSITE NEAR GORE, GA.

Halloysite of uncertain origin occurs near Gore, Ga. (fig. 2, location 44). According to Broadhurst and Teague (1954), the halloysite is in a bed less than 1 m thick within a chert formation of Devonian age. One sample from this bed was 37.30 percent Al_2O_3 , 42.20 percent SiO_2 , and 19.95 percent H_2O . This sample also contains trace amounts of iron, manganese, cobalt, titanium, and calcium. Several hundred tons of halloysite was mined in the Gore district in the early 1900's.

KAOLIN IN SINKHOLES IN THE APPALACHIAN REGION

Kaolin deposits in sinkholes, many of which also contain small bauxite bodies, are widespread in the Valley and Ridge province in the Appalachian region. The deposits are scattered from northwestern Georgia and northeastern Alabama to central Virginia, a distance of about 800 km. Gibbsite bauxite was mined from many of these sinkhole deposits until the mid-1900's,

TABLE 16.—Particle-size content (in weight percent), clay-mineral ratios, and content of SiO_2 , Al_2O_3 , and Fe_2O_3 (in weight percent) in clay from the Philadelphia Clay Co. deposit, Mount Holly Springs, Pa.

[From Hosterman (1969b, table 1). —, no data]

	No. of samples	Sand	Silt	Clay	Clay-mineral ratios			SiO_2	Al_2O_3	Fe_2O_3
					Kaolinite	Illite	Smectite			
White clay —————	30	6	24	70	9	1	—	71	19	0.4
Variegated silty clay —————	3	5	34	61	8	2	Trace	66	19	2.2
Weathered phyllite —————	5	7	33	60	1	7	2	56	18	6.3

and kaolin used in ceramics and aluminous chemicals also was mined on a small scale until the 1970's.

Most of the kaolin and bauxite in the sinkhole deposits occurs as subconical fillings of depressions in Paleozoic carbonate rock. The deposits are commonly elliptical or subcircular and are less than 100 m in maximum horizontal dimension; the greatest depth from the surface to the bottom of deposits is a little less than 60 m. A few deposits are elongate, and they probably are in solution chambers along joints. The higher grades of bauxite are ordinarily enclosed by concentric envelopes of clayey bauxite, bauxitic kaolin, and kaolin. The outer kaolin envelope is commonly separated from the carbonate wallrock by an envelope of cherty red clay. Collapse structures in some deposits apparently were formed by the slumping of bauxite as the carbonate rock was dissolved. The outer red clay zone in some deposits has been referred to as terra rossa (Knechtel, 1963) and is similar in composition to the typical residuum on limestone and dolomite in the region.

Problems of explaining the origin of kaolin and bauxite in the sinkhole deposits are much the same as those relating to the karst bauxites of Europe, Jamaica, and elsewhere. Although a great deal of work has been done and a voluminous geologic literature exists on the origin of karst bauxites, much remains to be learned about their origin. Though American geologists generally agree that most of the bauxite in the Valley and Ridge province formed in sinkholes, opinions differ as to the parent rock and explanations for the enveloping kaolin and cherty materials. Bridge (1950, p. 193, fig. 7) postulated that the kaolin and bauxite were derived from crystalline rock debris transported from igneous and metamorphic rocks in the Blue Ridge and Piedmont provinces east of the Valley and Ridge. Knechtel (1963) pointed out similarities between terra rossa associated with the sinkhole deposits and the cherty residuum on carbonate rock and suggested that the bauxite formed as acid water leached accumulations of residuum in sinkholes. Collapse of deposits after the bauxite formed may account for the present concentric envelopment of deposits and their low iron contents. The acidity of the water is suggested by scattered organic-rich layers in the upper parts of some deposits and by the fact that typical sinkholes on the present surface are swampy and rich in decaying organic matter. Knechtel (1963) suggested that the bauxite in the Valley and Ridge formed at many different times since the close of the Paleozoic Era. However, pollen of early Tertiary age has been found in one sinkhole deposit, and it seems likely that most of these deposits formed at approximately the same time as the kaolin in the Coastal Plains.

CANADA

Canada has large resources of low- to moderate-quality kaolinite clays, but large high-grade deposits, such as would be suitable for paper coater use, have not been found. The larger deposits are of the sedimentary type, but hydrothermal kaolinitic clays have also been found.

Probably the largest resources of kaolinitic clays in Canada are in the Whitemud Formation of Late Cretaceous age that extends across most of southern Saskatchewan and southeastern Alberta (fig. 20, location 3). The Whitemud clay is used in refractories and facebrick, and minor tonnages have been sold as ball clay (Brady, 1962). Brady found that the Whitemud clay is chiefly kaolinite and quartz, feldspar and mica are generally present, and smectite and chlorite are rare. Most of the clay is plastic, and PCE's of much of the clay are in the 20-32 range.

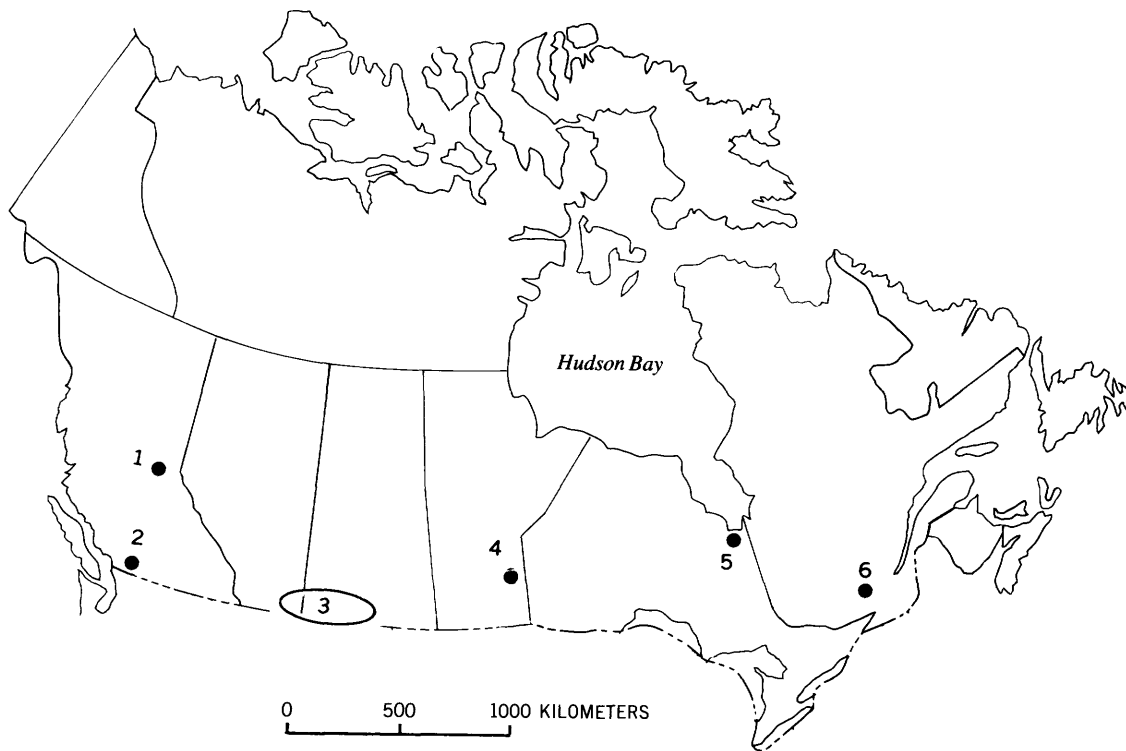
Small kaolin deposits occur at several places in Quebec and northern Ontario (Douglas, 1970, p. 222). The district that has produced the most kaolin is Saint-Remi, Quebec (fig. 20, location 6). About 25,000 tons of kaolin was mined in this district in 1942. Some was mined later, but apparently no mining has been done since 1946. The kaolin in Saint-Remi is of hydrothermal origin. It occurs in veinlike masses ranging from about 1 m to nearly 30 m across. The host rock is Precambrian quartzite.

Extensive deposits of kaolinitic clays occur in a Cretaceous sedimentary formation in the James Bay lowland, Ontario (fig. 20, location 5). This Cretaceous formation is a deltaic wedge-shaped unit of continental sediments that also contains lignite and silica sand (Vos, 1979). Significant tonnages of moderate-quality refractory kaolin are present.

Other clay deposits in Canada that are chiefly kaolinite include the fire clays at Giscome Rapids (fig. 20, location 1) and Sumas Mountain (fig. 20, location 2), B.C. (Brady and Dean, 1964), and a deposit at an unnamed location in Manitoba (P. Partridge, oral commun., 1977). Both deposits in British Columbia are in nonmarine sedimentary beds of Tertiary age. The Giscome Rapids clay has a PCE of 29, and the PCE of the Sumas Mountain clay is 31½. The clay in Manitoba (fig. 20, location 4) is a sand kaolin of pre-Pleistocene age and occurs as fillings of channels cut in Ordovician limestone.

MEXICO

Kaolin occurs in virtually every state in Mexico (Pasquera and others, 1969), mining is active in at least 9 districts (fig. 21), and the clay is used in several prod-



1. Giscome Rapids, British Columbia
2. Sumas Mountain, British Columbia
3. Approximate extent of Whitemud Formation, Saskatchewan and Alberta
4. Unnamed location, Manitoba
5. James Bay Lowland, Ontario
6. St. Remi, Québec

FIGURE 20.—Location of kaolinitic clay districts in Canada.

ucts. Most of the mining is by open-pit methods, but several mines are underground. The kaolin is processed at grinding plants equipped with hammer mills and air classifiers, but there are no kaolin washing plants in Mexico. Domestic kaolin is used as fillers in paper, rubber, and plastics; as extenders in paint; and in ceramic and refractory products. The production of kaolin in Mexico is greater than 100,000 tons per year, and approximately 25,000 tons of fine-particle-sized paper coating kaolin is imported annually.

Kaolin formed by hydrothermal alteration, by weathering, and by sedimentary processes occurs in Mexico. All the deposits mined are the hydrothermal type. Those formed by weathering tend to contain too much iron to be of value, and most of the sedimentary clays are impure. Most of the hydrothermal clays are related to upper Cenozoic volcanic rocks, but some formed from schists, and others are in volcanic pipes in limestone. A

few of the occurrences will be discussed in following sections.

The hydrothermal kaolin deposits near Ciudad Hidalgo, Michoacan, described by Kesler (1970), are in a region having numerous hot springs, fumaroles, and a few small geysers. The hot springs and other vents have white kaolin aureoles in which alteration and leaching has been so thorough that walking over them is unsafe. Orifices through which water and vapor emerge gradually shift due to slumping of ground as leaching proceeds. Accumulations of clastic kaolin that has been transported short distances overly some of the deposits.

The volcanic rock being altered to white clay near Ciudad Hidalgo consists of obsidian and rhyolitic breccia of the San Andres rocks, which are rich in silica and aluminum. The associated rocks of intermediate composition alter to dark clays having a high shrinkage

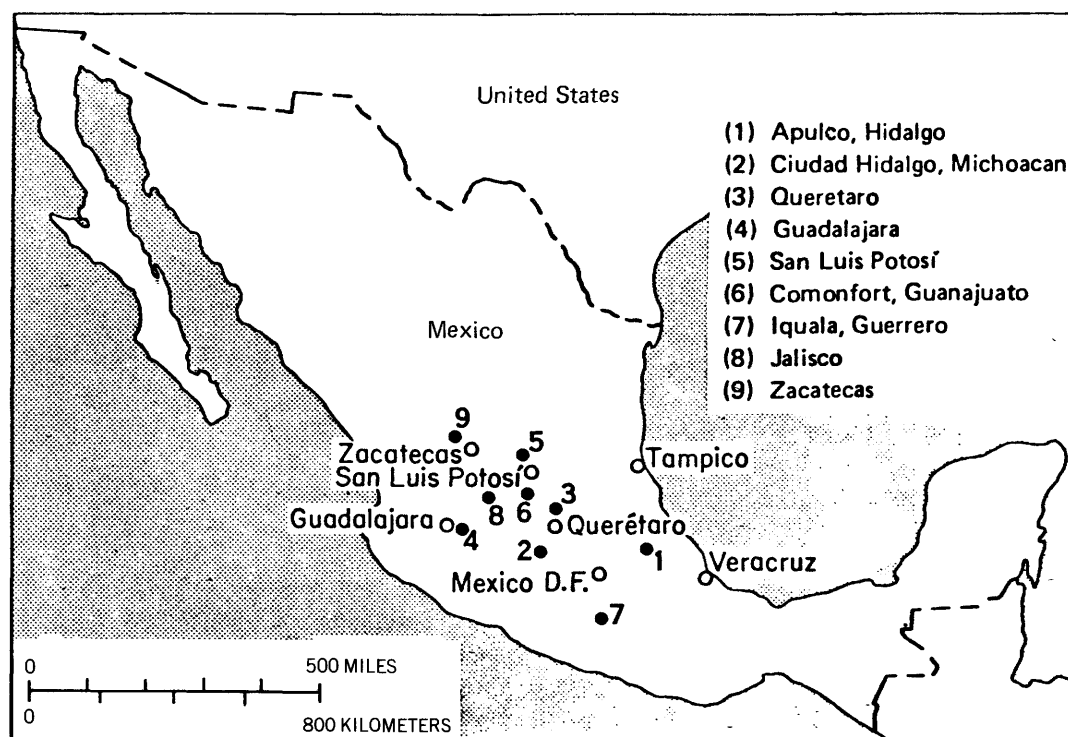


FIGURE 21.—Location of major kaolin mining areas in Mexico.

characteristic of smectite. The white alteration product is a variable mixture of kaolinite, cristobalite, and alunite containing trace amounts of mercury. The kaolin ranges from soft plastic clay to material that is moderately hard. The harder kaolin is sufficiently indurated to withstand water transportation, as shown by clastic kaolin in sedimentary beds overlying the San Andres volcanic rocks.

The kaolin clay at the General Zaragosa mine, located about 50 km northwest of San Luis Potosi, was formed by hydrothermal argillation of part of a fault block of rhyolite flow breccia and probably welded tuff (Keller and Hanson, 1968). Like most of the hydrothermal kaolin deposits in Mexico, the surficial rocks above the kaolin in this mine consist of a silica halo. The progressive stages in the formation of this clay were recognized by Keller and Hanson (1968, p. 223), as follows:

“* * * (a) Bleaching of the breccia matrix accompanied by mobilization of much of the iron, which was concentrated locally as spots of reddish oxide in the least altered areas. (b) Mobilization, and removal of considerable alkali and alkaline earth metals, in excess of that required to form montmorillonite; mobilization of silica, which was redeposited as fine anhedral quartz crystals disseminated within the montmorillonite and associated kaolinite-halloysite, or developed tripolitic, argillized rock peripheral to the clay ore body. (c) Further desilication of the silica and clay yielding relatively pure, but poorly ordered, kaolinite-halloysite as the most intense end product

of argillation. Much silica removed during intense argillation was reprecipitated as tripolitic clay, as minor cristobalite in microscopic globules and massive aggregates characteristic of colloform opal, and in vastly larger amounts as opal and chalcedony replacing the rock overlying the clay (forming a silica gossan). (d) Minor amounts of alunite are present at two places in the deposit, which are interpreted tentatively as being the most probable loci of rising solutions.”

A refractory kaolin deposit near Guanajuato, which formed from hornblende chlorite schist, is described by Hanson and Keller (1966) as occurring in hydrothermally altered zones along nearly vertical fractures and faults. The most refractory clay is chiefly kaolinite with variable amounts of finely crystalline quartz. The surficial rocks above the deposit consist of a halo of silica. The sequence of alteration that took place was as follows: (1) bleaching of the hornblende and chlorite accompanied by the oxidation of part of the iron, (2) leaching of alkali and alkaline earths accompanied by (3) partial desilication of the parent silicate minerals yielding kaolinite in flakes that tend to be oriented parallel to the chlorite in the schist, mobile silica, and finely divided quartz intermixed with kaolinite, and (4) final kaolinization and removal of silica and some iron.

Clay formed by hydrothermal alteration of volcanic pipes in limestone, described by Keller and Hanson (1969), occurs in the mining districts at Jasso Calera, which is near Apulco, Hidalgo (fig. 21), Zacatecas (fig. 21), and near Iquala, Guerrero (fig. 21). Typical pipes

cut bluish-gray Cretaceous limestone that has been faulted and tilted as much as 90° . The pipes are circular to oval in horizontal section, as much as 100 m in diameter, and one was found by drilling to be kaolinized to a depth of more than 100 m. Most of the parent material of the clay was volcanic pyroclastic and brecciated rock. The central part of a typical deposit consists of moderately well ordered kaolinite. Outer parts of deposits commonly contain halloysite (10A). The outer parts of most deposits also contain excessive amounts of iron and are bypassed in mining. A deposit in the Zacatecas district has a green powdery sand zone 15 cm thick at the contact of the clay and limestone. The material forming this zone was found to be a mixture of grossular and quartz. The grossular indicates that a high-temperature metamorphic reaction took place in the limestone near the margin of the volcanic pipe.

The total proven, probable, and possible reserves of kaolin in Mexico are estimated to be more than 500 million tons (Pasquera and others, 1969). These authors list the following five districts as containing more than 20 million tons of kaolin each: Jimenez, Chihuahua; Peron Blanco, Durango; Juventino Rosas,

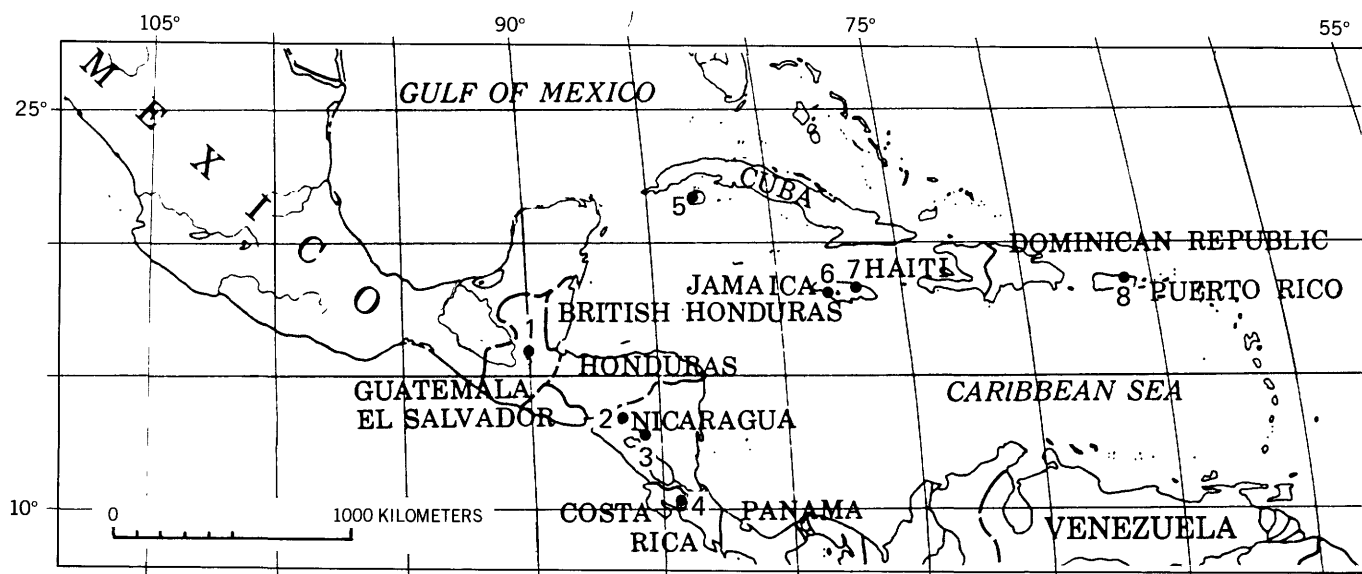
Guanajuato; Guayacocotla, Veracruz; and Ahualulco, San Luis Potosi. Eight other districts are listed as containing from 5 million to 20 million tons of kaolin each, and 45 more districts or occurrences are listed by name.

CENTRAL AMERICA

Kaolin deposits occur in most Central American countries (fig. 22); however, very few deposits have been investigated. The following incomplete information was found by the authors during the preparation of this report.

Costa Rica

White kaolin deposits occur at several places in Costa Rica (Castillo, 1965). Deposits are found along the Pan-American Highway between San Ramon and Esparta and between Robledal and Cartago. Deposits are reported to occur elsewhere, but little is known about them. Most of the kaolin mining in Costa Rica has been in the vicinity of Esparta (fig. 22, location 4). If estimates of the composition of kaolin in this vicinity



Central America

Guatemala

1. San Antonio la Pas

Nicaragua

2. Somoto

3. Esteli

Costa Rica

4. Esparta

Caribbean region

Cuba

5. Isle of Pines

Jamaica

6. Black River

7. Above Rocks

Puerto Rico

8. Carolina

FIGURE 22.—Location of kaolin districts in Central America and the Caribbean region.

(table 17) are correct, it may be fairly high grade. According to Castillo (1965, p. 43), most of the kaolin deposits in Costa Rica formed by hydrothermal alteration, but many deposits have been further altered by weathering.

Guatemala

As stated by Miller (1965, p. 32), "several deposits of clay are known to have been worked in Guatemala, but information on the size of deposits, composition and quality of the clays, production, and utilization is practically nonexistent. * * *" However, Miller noted that one clay deposit at San Antonio la Paz in El Progreso Province (fig. 22, location 1) was reported to be white clay of ceramic grade, and some of it was sold to manufacturers of paper, paint, rubber, and soap. It seems certain that the clay at San Antonio la Paz is kaolin.

Nicaragua

Several kaolin occurrences are noted and a few are located on maps in a summary report on minerals in Nicaragua (Zoppis de Sena, 1956). The principal occurrences are in the northwestern part of the country. Occurrences near Somoto (fig. 22, location 2) include white kaolin in weathered acid volcanic rocks in the Boqueron zone and alluvial kaolin at Asserradero Los Pinos. Kaolin has been found in the Achuapa area about 25 km west of Esteli (fig. 22, location 3). At this locality, white kaolin has formed from feldspar in weathered granite. Kaolin is also reported to occur near Dario.

CARIBBEAN REGION

Cuba

The largest and most productive kaolin deposits in Cuba are on the Isle of Pines (fig. 22, location 5), and three small deposits are shown to be present on the

metallogenic map of the main island of Cuba (Judoley and others, 1963). The deposit on Isle of Pines is called Rio del Cayejon, and the three small ones on the main island are McKinley, Kilometer 13, and Ponte Suelo Canaquay (Fen'ko and others, 1973). The kaolin occurs in weathered schist and gneiss. The small kaolin deposits in the Dumanekos district on the main island are in sedimentary beds of Cretaceous age.

Jamaica

The small kaolin deposits in Jamaica, summarized by Versey (1969), occur in alluvium along the Black River (fig. 22, location 6), in residual deposits in the vicinity of the village of Above Rocks (fig. 22, location 7), and in hydrothermal deposits at Jobs Hill. The alluvium along the Black River, which is in the southwestern part of Jamaica, has been transported from weathered Cretaceous tuffs. Some of the clay in this alluvium is in terrace deposits, but most of it underlies the flood plain. According to Versey (1969, p. 102), about 1 million tons of clay having the physical properties of ball clay could be recovered by washing this alluvium. The deposits in the vicinity of Above Rocks, which is in the east-central part of Jamaica, have formed by weathering of adamellitic rocks (quartz monzonite). The clay content of this rock is 20–25 percent. The deposits extend over an area of about 1 million m² and they probably have an average thickness of about 5 m. The white kaolin clay at Jobs Hill, which is near Above Rocks, is dickite formed by hydrothermal alteration or replacement of a series of red sands and conglomerates. Only a few thousand tons is known to be present.

Puerto Rico

The Carolina clay deposits (fig. 22, location 8), located in coastal lowlands about 12 km east of San Juan, contain the best quality kaolin in Puerto Rico (Cadilla, 1958). The clay is as much as 70 percent kaolinite, and the rest is mainly very fine grained quartz. The upper parts of the deposit are white, light bluish, and grayish white. Clay having these colors grades downward into

TABLE 17.—*Estimates of chemical composition of kaolin in Costa Rica, in percent*
[From Castillo (1965, table 3), based on spectrographic analyses by Octavio Durando]

Sample location	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	MnO	CaO	TiO ₂
Esparta	30–40	30–35	1–2	0.5–0.6	<0.1	0.01	<0.1	0.1–0.2
Between San Ramon and Esparta	70–80	30–35	1–1.5	.5–1.0	.05–.1	.01–.3	.1	1–2

brownish iron-stained clay at depth. The clay body extends over an area of about 1.3 km² and has an average thickness of about 4.5 m. Clay resources present are estimated to be about 12 million tons. Because of its high plasticity, the clay has been used in extruded heavy clay products and in ceramic art objects. Six samples tested by the Ceramic Department of the University of California had PCE's in the range 27–34.

The Carolina clay is sedimentary, having been transported from weathered rocks at higher elevations farther inland. According to Cadilla (1958, p. 8–10), the Carolina clay was deposited on a flood plain or delta by a stream draining upland areas of weathered tuff and volcanic rocks. The deposition of the clay probably took place in Pleistocene time. The clay is thought to have been all red when deposited, and weathering has leached the iron oxides from upper parts of deposits to form the white, light-blue, and light-gray clay. The reason for believing the clay was all originally red is that virtually all weathered rocks at nearby higher elevations are red.

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