THE AMERICAN MINERALOGIST
JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 24 FEBRUARY, 1939 No. 2

ADSORPTIVE CLAYS OF THE TEXAS GULF COAST

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ABSTRACT

Numerous clay pits containing an abundance of material suitable for the clarification and purification of petroleum products are operated along the Texas Gulf Coastal Plain. Much of the original material has altered sufficiently to form adsorptive clay of usable quality. Optical, chemical, and *x*-ray studies indicate that the principal mineral constituent of the clays as mined is montmorillonite. Microscopic textures and structures, when well preserved, are significant of origin.

Many beds represent the result of alteration in situ of volcanic ash. However, substantial amounts of kaolinite, halloysite, and allophane occur in some deposits. In certain deposits alteration has been so complete as to obliterate direct evidence of the origin of the clay.

The waxy character of many moist clay layers is a convenient indicator in the field. Laboratory study shows that waxy clays contain more nearly pure montmorillonite than other types which are soft, granular, and kaolinitic. The luster may be attributed to unusual hydration characteristics of montmorillonite. Kaolinitic mixtures occur in the northeastern part of the clay belt, whereas the more nearly pure montmorillonite occurs in the southwestern part.

A review of the literature, correlated with field observations, indicates that the fuller's earths of eastern Texas formed during the Eocene, and Oligocene or Miocene epochs. Correlation of physical, chemical, and optical properties with adsorptive capacity has been attempted. The influence of mineralogical features on adsorptive capacity may be summarized as follows: impurities lower adsorptive capacity; microscopic structures and textures are apparently not related to adsorptive efficiency; the montmorillonite lattice structure permits high adsorption; amount and degree of alteration of original material to clay materially affect adsorptive capacity; origin by transportation of clay introduces granular impurities and lowers adsorptive power; high percentages of removable bases and water seem to accompany high adsorptive capacity; montmorillonite is the most highly adsorptive clay mineral studied.

INTRODUCTION

The clays described in this paper were collected during the summer of 1936 in connection with a program of clay-mineral study which has been carried on at Columbia University for a number of years. The specimens were collected by Dr. Paul F. Kerr who also provided notes concerning field occurrences. An attempt was made to obtain material from the then known occurrences of adsorptive clays of economic importance in Texas.

The deposits studied occur in at least six counties in Texas, along a broad crescent-like curve more or less parallel, and about one hundred miles from the Gulf Coast. All lie within a narrow belt which extends from the vicinity of the Louisiana border for about two hundred and forty miles southwest to Gillett, which is forty-three miles southeast of San Antonio. Similar clays are said to occur along the extension of this belt as far south as Mexico.

The deposits to be discussed may be listed as follows:

Zavalla	(1)	Bennett and Clark Deposit
Zavalla	(2)	Haralsen Deposit
Luce		Trinity Clay Products Company Deposit
Riverside	(1)	Continental Oil Company Deposit
Riverside	(2)	Texas Company Deposit
Fayette	(1)	Carr-Brown Tract
Fayette	(2)	Parker-Ivy Tract
Fayette	(3)	J. A. K. Tract
Fayette	(4)	Fleck-Darby Tract
Fayette	(5)	Lena Deposit of the Texas Company
Gonzales	(1)	Oscar Dubois Tract
Gonzales	(2)	Kent Dubois Tract
Gonzales	(3)	Gillett Deposit

GEOLOGIC OCCURRENCE AND HISTORY

The clay deposits included in the present study occur in a fairly narrow belt of Tertiary Gulf Coastal Plain strata. All are bedded and either flat lying, or exhibit a low angle of inclination. Structural disturbances are of minor importance. Localization of alteration, or lenticularity of deposition, however, limits the distance to which any one stratum may be traced. The deposits parallel the general strike of Tertiary strata and occur in the Jackson group (Eocene) and in the Catahoula formation (Oligocene or Miocene)[1] as mapped by the United States Geological Survey, the University of Texas, and various geologists and oil companies of Texas (Fig. 1).

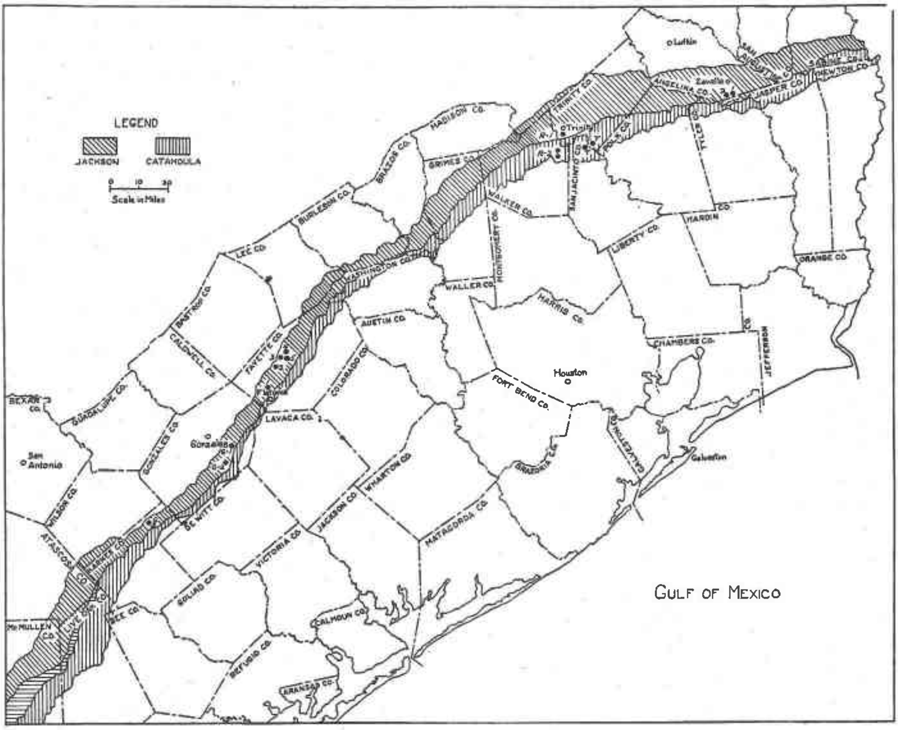


FIG. 1. Geographic and geologic distribution of the Texas Gulf Coastal clay belt deposits. (See reference 1.)

In Texas the Jackson group includes all uppermost Eocene strata above the top of the Claiborne group. The name Fayette is used as a formational name to include undifferentiated strata above the Yegua

(Eocene) and below the Catahoula, or, where present, the Frio (Oligocene or Miocene).[2] The Jackson group lies conformably upon the Yegua, and is overlain unconformably by the Catahoula and Frio formations.[3] No attempt has been made here to separate the deposits into the various members of the Jackson group designated by Renick.[4]

The Jackson group consists of shallow-water, marine, and beach deposits. The rocks include sand which is lignitic in places, and argillaceous and tuffaceous clays and tuffs. Frequently the beds are somewhat fossiliferous,[5] and in general dip southwestward.

The Catahoula formation is a member of the Gueydan group of Oligocene or Miocene age. It overlies the Fayette and Frio formations unconformably, and is overlain unconformably by the Oakville and Lagarto formations (Oligocene).[3,4] In east Texas the Catahoula is the only formation of the Gueydan group represented. Here it consists chiefly of sandstone and interbedded ash. In southwest Texas the Frio (Oligocene)[6] formation below, and Catahoula formation above, comprise the Gueydan group, which is largely made up of tuffs. Some authorities[2,7] have dropped the name Gueydan in favor of Catahoula group, which then includes the Frio and Catahoula formations. The age of the Catahoula has not been definitely determined, but it is commonly assigned either to the Oligocene or Miocene.

In the southwestern part of the clay belt economic deposits of waxy montmorillonite clays are found. In the northeastern part of the belt the clays have considerable admixed kaolinitic material. An interesting feature in connection with these deposits is the concentration of more nearly pure montmorillonite in the waxy clays. The other types of clay contain more kaolinitic material and are soft and more or less granular in structure. The waxy luster is believed due to the unusual hydration characteristics of montmorillonite. Waxy clays are not as thick as those containing kaolinitic material. In spite of appreciable amounts of kaolinitic material present in the northeastern clays, their adsorptive power is sufficient to make them economically useful as decolorizing agents[8,9,10,11] in petroleum refining.[12,13]

Igneous activity, which started in Yegua time, became more pronounced in the middle and late Jackson epoch,[7,14] and continued with even greater intensity in Catahoula time. Volcanic ash was deposited over a considerable area and was "picked up by streams which redeposited it along with muds to form the light-colored 'kaolinite' beds, which were sorted from the other sediments in such a way as to produce the chalky-looking fuller's earth deposits."[3]

On the basis of formational thickness and size of included volcanic boulders, it is believed that the source of volcanic ash was southwest of the present deposits. If this is true, it would be expected that more ash would occur in the southwest than at the localities where it is found at present. Although this condition is fulfilled in the Catahoula strata, some authorities do not believe it has been fulfilled in the Jackson strata. It has been suggested that the ash was ejected from volcanoes with considerable force, and then drifted for great distances northeast.[15] Streams eroded the deposits and then redeposited the ash in lenticles. Some of the material is believed to have been blown into dunes by winds. Although some of the fine ash probably traveled considerable distances, possibly from the Trans-Pecos region, the larger size and subangular shape of much of the coarser material in the Catahoula ash indicate that it could not have been transported far. Bailey[16] therefore, has suggested that some of the volcanoes were located in the near vicinity of the present deposits. This complex stratigraphy[17] is significant in view of the impure nature and irregular occurrence and distribution of the deposits studied.

DESCRIPTIONS OF INDIVIDUAL DEPOSITS

Zavalla Deposits

The Zavalla clays include two deposits: (1) the Bennett and Clark deposit, 9.3 miles south of Zavalla in Angelina County, and (2) the Haralsen property operated by Coen and Company, 2.6 miles west of deposit (1) in Angelina County (Fig. 2).

Both deposits show similarities in mineral constituents, optical properties, and structural characteristics. The clays are complex mixtures consisting of montmorillonite and kaolinite, together with about 25% of other minerals, principally quartz and feldspar. The texture is fine and laminations are distinct.

Zavalla (1)—The clay pit is located in strata mapped as belonging to the Jackson group of Eocene age. The clay beds of the deposit attain a considerable thickness, more than 20 feet of clay-bearing strata being exposed in places. It seems likely that the clay strata have a total thickness in the neighborhood of 30 feet (Fig. 3). The strata comprising this thickness, however, are far from uniform in quality.

The clay is for the most part bluish or greenish gray. It lacks the waxy appearance characteristic of most high grade bentonite, and the close-packed laminated structure present in many fulller's earths. In some places it grades into a black shale, and in the lower part of the clay layer there is a considerable amount of carbonaceous matter.

Examination in thin section shows that about 75% of the material is a complex mixture of at least two, and probably three, clay minerals.

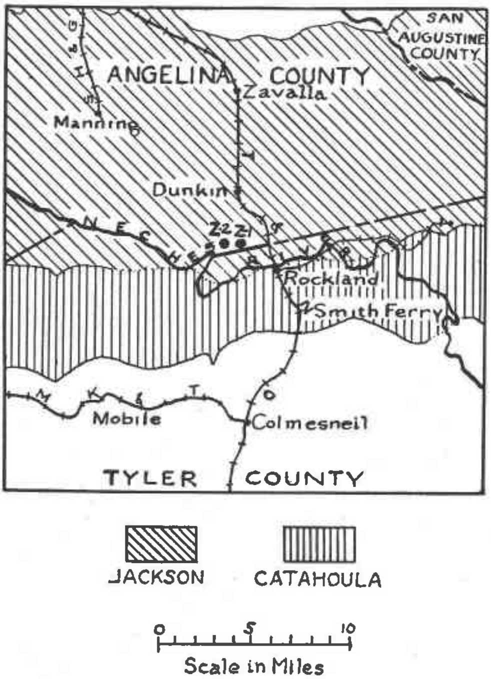
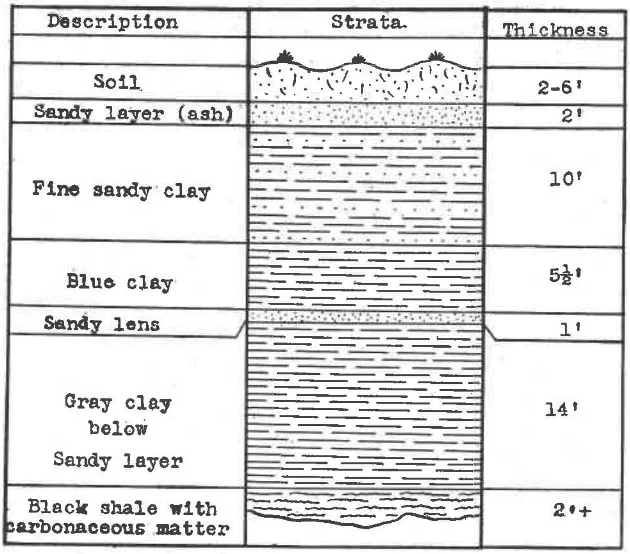


FIG. 2. Position of Zavalla clay deposits on the geologic map of Texas. (See reference 1.)



Description	Strata	Thickness
Soil		2-6'
Sandy layer (ash)		2'
Fine sandy clay		10'
Blue clay		5½'
Sandy lens		1'
Gray clay below Sandy layer		14'
Black shale with carbonaceous matter		2'+

FIG. 3. Generalized section of the Zavalla (1) pit.

About 25% of the material consists of glass and granular impurities, chiefly quartz, plagioclase, and muscovite. A small amount of pyrite occurs in streaks and patches sparsely scattered through the clay material. Limonite is present in very small amounts as surface stain.

The clay-mineral constituents include kaolinite and halloysite, occurring in relatively coarse grains and patches in a fine-textured matrix which appears to consist of a mixture of kaolinite, halloysite, and montmorillonite. Owing to the extremely fine texture of this mixture, the exact proportions of the constituents present are indeterminable, but from the nature of the *x*-ray and chemical data, it would appear that montmorillonite, if actually present, forms only a minor percentage of the mixture. Because of the intimate mixture of clay minerals it is difficult to determine the indices. The result of an approximate determination of the optical constants of the clay-mineral constituents is as follows: kaolinite $n=1.565\pm.003$ mean index, birefringence .005; halloysite $n=1.542\pm.003$ mean index, .003–.004 birefringence; montmorillonite $n=1.536\pm.003$ mean index, birefringence .022, 2V (−) small. The value given for the index of montmorillonite is within the range of published data, but owing to the intimate manner in which it is mixed with the other clay-mineral constituents, satisfactory determination of the indices is not feasible. This is also true of the birefringence given for halloysite which is high and may be explained as being due to the presence of admixed kaolinite. For all three minerals the elongation is (+), and the extinction slightly inclined to the cleavage.

The average grain size of both grit and clay particles, not including the coarse patches, is about .01–.02 mm. The clay particles are for the most part haphazardly oriented. The bedding is indistinct, both in hand specimen and in thin section. Some micro-faulting has taken place, shown by offset of the laminae. The streaks, patches, and veinlets of coarsely crystalline kaolinite and halloysite are sedimentary in origin and appear to be related to recrystallization along the micro-fractures in the clay.

In the clay bed described there is no trace of any structure which would indicate origin by alteration of a volcanic ash bed.[18,19] The structure and general character of the clay in thin section are characteristic of a normal fine-textured sedimentary deposit. However, just above the clay bed examined there is a two foot layer of sandy bentonite exhibiting vitroclastic structure. Although this should not be taken as evidence of volcanic origin of the underlying clay, it is at least suggestive that the main clay bed may be bentonitic in part, and has been so highly altered to clay, and contaminated by sedimentary material as to obliterate any original vitroclastic structure which might have been present. The sedimentary aspect of the clay may be due to reworking and redeposition of an original ash by stream action as explained in a subsequent section on origin.

X-ray diffraction patterns obtained from the raw blue clay show lines which correspond most closely to a mixture of kaolinite and quartz. It appears that the principal clay-mineral constituent is kaolinite. It is not surprising that in such a mixture the diffraction lines of halloysite and montmorillonite are obscured due to the stronger patterns given by both kaolinite and quartz.

Zavalla (2)—The Zavalla (2) deposit occurs in strata mapped as belonging to the Jackson group of Eocene age. In 1936 the clay bed was being mined by Coen and Company. Clay exposures in the pits were about ten feet in thickness. The upper five feet consisted of grayish white clay, and the lower five feet of blue clay. A hard, massive sandstone about four feet in thickness overlies the clay strata. Local operators at the pit have reported the presence of fossiliferous and lignitic strata beneath the clay (Fig. 4).

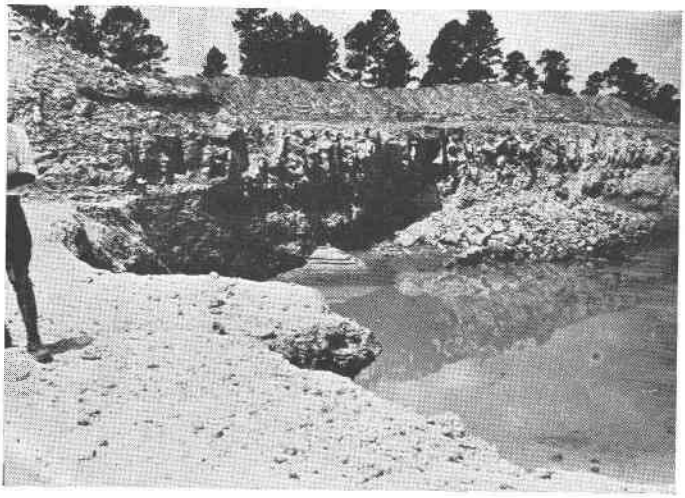


FIG. 4. A general view of the Zavalla (2) pit. The bench in the foreground marks the top of the clay.

Study of thin sections of the blue clay from the deposit shows that it is a complex mixture. The principal constituents appear to be montmorillonite and kaolinite. In addition there are impurities estimated at approximately 25% of the material. These range in size up to .1 mm. and consist chiefly of granular quartz and acid feldspar. Disseminated through the clay are minor amounts of pyrite cubes occurring as minute single cubes, and as clusters which are several millimeters in diameter. The pyrite is evidently of secondary origin. Numerous microscopic rosettes of gypsum occur in the clay, and appear to form several per cent of the material. Minor impurities include zircon, muscovite, and tourmaline. An unidentified isotropic mineral of high relief is present in small amounts.

The clay material is extremely fine-grained, average size of the particles being about .05 mm. For this reason accurate estimation of the amounts of kaolinite and montmorillonite present in thin section is difficult. The mean index of refraction of the montmorillonite is $n=1.525$, the birefringence .02. The value given for the index is high due to admixed kaolinite.

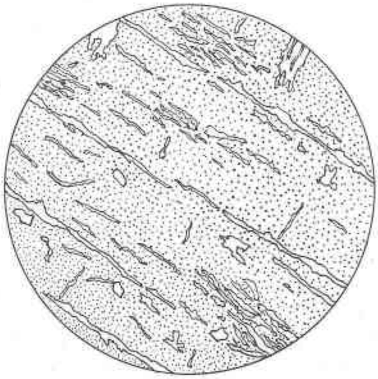


FIG. 5. Diagram illustrating oriented-shred structure of montmorillonite, thought to be the result of pressure-packing. ×25.

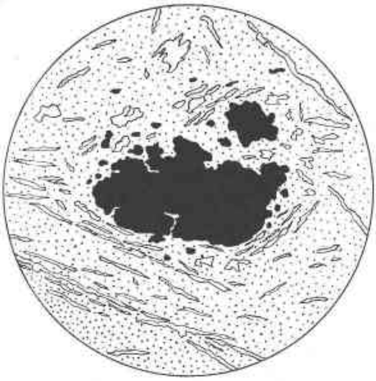


FIG. 6. Diagram showing arrangement of montmorillonite shreds around a pyrite crystal. ×25.

In the clay as a whole, a considerable percentage of clay particles is oriented sub-parallel to the lamination. The degree of this orientation, however, is variable from one lamina to another. Some parts of the sections show only rudimentary orientation, but exhibit a characteristic shred-like structure. This structure consists of shreds of montmorillonite crystals, or groups of crystals, aligned in a roughly parallel manner similar in appearance to aligned sericite flakes (Figs. 5, 6). It is believed that this structure is due to packing of clay particles, resulting from pressure-orientation.

Though massive in hand specimen, the material shows an indistinct lamination in thin section. Sections examined show no evidence of ash structure, the petrographic characteristics of the clay being those of a normal sedimentary deposit. However, it may be that this is a deposit in which the alteration and presence of sedimentary material have obscured all traces of original ash structure.

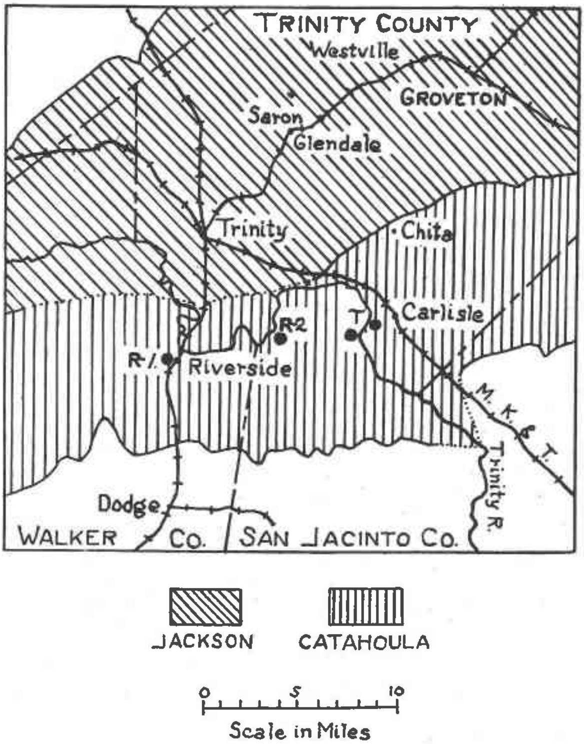


FIG. 7. Position of Trinity clay deposits on the geologic map of Texas. (See reference 1)

X-ray diffraction patterns of material from the deposit indicate that montmorillonite and kaolinite are present. In addition, lines due to quartz and feldspar impurities occur in the patterns.

TRINITY DEPOSITS

The Trinity clays include three deposits. The Luce deposit operated by the Trinity Clay Products Company is located at Luce, 12.5 miles southeast of Trinity, in Trinity and San Jacinto counties. Riverside (1), operated by the Continental Oil Company, is located one mile west of Riverside in Trinity County, Riverside (2), operated by the Texas Company, is located 5 miles northeast of Riverside in Walker County (Fig. 7).

The clays are in strata mapped as belonging to the Catahoula formation of Oligocene or Miocene age. In several ways the Trinity deposits are the most complex of the clays examined. They appear to include several types of clays. The Luce deposit consists of volcanic ash which has partly altered to bentonite, and shows well-preserved vitroclastic structure. The two Riverside deposits, however, are of doubtful origin. The petrographic features of the clays are those of ordinary sedimentary clays, but there is a possibility that they are bentonitic.

Luce Deposit—The clay section exposed in the pit at the Luce deposit consists of about four feet of sandstone caprock, beneath which are three feet of a hard, flint-like clay, followed by eighteen inches of soft, highly fractured clay, and five feet of coarse, laminated clay resembling fuller's earth in physical appearance. Sandstone occurs beneath the lowest clay layer of the deposit. It would appear, even from a brief field examination, that the clays of this deposit are lenticular and quite variable in character (Fig. 8).

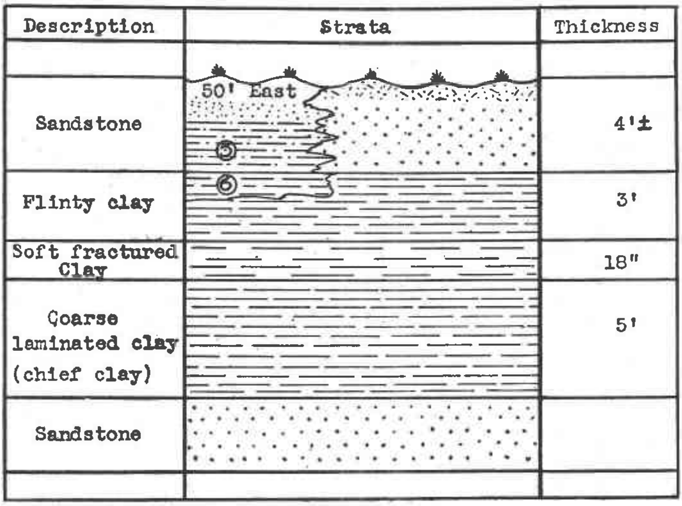


FIG. 8. Generalized section of the Luce deposit.

Representative material from the chief clay layer, and from the upper flinty layer was studied. Examination of thin sections of material from both clay beds indicates that they represent volcanic ash now partly altered to mixtures of halloysite and montmorillonite, with some unaltered glass. The halloysite represents sedimentary contamination.

A minor amount of grit, mostly quartz and feldspar, is present. In spite of the alteration, the structure of the original volcanic ash is clearly preserved in each case. In both beds the degree of alteration of ash to clay is variable from point to point, so that in places minute lenses or laminae of essentially unaltered ash may be seen; these are less abundant in the chief clay layer than in the upper flinty layer (Fig. 9).

The material as a whole is of complex composition. It consists of shard-shaped areas with a variable amount of interstitial coarsely crystalline montmorillonite, individual crystals of which may reach maximum diameters of .6 mm. The interstitial montmorillonite is evidently forming by alteration of the original glass shards, which can be seen to grade into the clay mineral in certain places. Although this montmorillonite varies in amount in different parts of the slides, it constitutes a fairly large percentage of the material. Vermicular crystals of what appears to be montmorillonite occur occasionally.

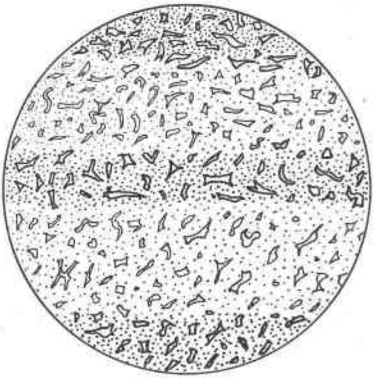


FIG. 9. Diagram of altered volcanic ash from the main clay bed at Luce, showing bedding and glass shards. ×25.

The relict shards have an average original length of .1 mm. and are of uncertain composition. Most of them are birefringent, but some are isotropic and may be partly altered glass.[20] They show moderate relief in the coarsely crystalline montmorillonite, and are thought to represent an intermediate product in the alteration of glass to montmorillonite, although they do not have the appearance of montmorillonite.

The clay appears to contain about 3–8% grit, mostly quartz and acid feldspar. The amount varies from one lamina to another, some laminae being practically free from impurities. A few lenticular areas are stained with limonite. In certain laminae oriented structure is poorly developed.

Material from the chief clay layer was found to consist of about 75%

of clay material, 20% unaltered ash, and 5% of grit. The clay material is variable in character and appears to consist principally of montmorillonite, but there is also a considerable amount of halloysite in streaks and patches irregularly distributed through the sections. Laminae consisting of nearly pure glass alternate with laminae almost completely altered to clay. The index of refraction of montmorillonite is $\alpha = 1.490 \pm .003$, $\gamma = 1.512 \pm .003$, birefringence .022, elongation (+), −2V small.

In material from the upper flinty layer, unaltered ash constitutes from 30 to 40% of the mixture. The remaining 60%–70% appears to be equally divided between montmorillonite and halloysite, except for a few per cent of grit. Some kaolinite may be present. The general character of the flinty layer is similar to that of the chief clay layer. However, in general the flinty material is somewhat more uniform and more regularly bedded. The indices of refraction are: $\alpha = 1.519 \pm .003$ and $\gamma = 1.539 \pm .003$; birefringence .020; −2V small. These values are high, probably due to admixed halloysite. The refractive index of halloysite is variable with $\gamma = 1.555$ maximum.

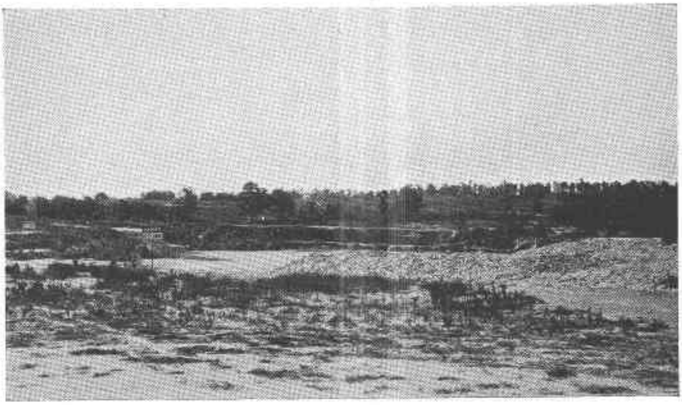


FIG. 10. Photograph of the fuller's earth bed at Riverside (1).

X-ray diffraction patterns obtained from the chief clay material show lines corresponding to those given by montmorillonte. Patterns obtained from the upper flinty layer, however, show additional lines characteristic of halloysite. These results confirm the conclusion, based on microscopic studies, that halloysite is present in considerably smaller amounts in the main clay bed than in the flinty layer.

Riverside (1)—The Riverside (1) deposit includes a number of clay pits which occur in strata mapped as belonging to the Catahoula formation. The clay strata are about 12 feet in thickness and dip about 2 or 3 degrees to the southeast. In general the beds exhibit a lenticular tendency. The overburden at the pits is small, varying from 0 to 10 feet (Fig. 10).

The fuller's earth just beneath the soil cover is quite hard. This is thought to be due to moisture loss. On the whole, the clay appears to be rather low grade, containing sand and light-colored nodular impurities.

In thin section the clay material has been found to consist of a mixture of several clay minerals, with an estimated 25% of granular impurities. The clay minerals present include kaolinite, halloysite, allophane (?), and montmorillonite. The principal impurities are quartz and feldspar, with minor amounts of opal, muscovite, glass or amorphous silica, limonite and scattered grains of a zeolitic mineral. These impurities are angular in character, the grains varying in size from one lamina to another.

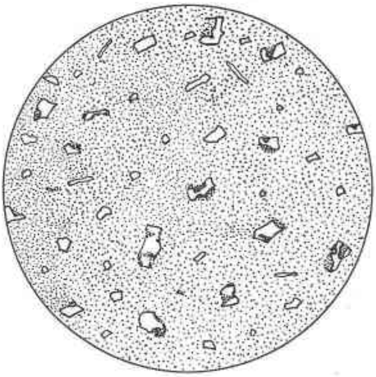


FIG. 11. Diagram illustrating replacement of angular quartz and feldspar grains by clay. ×115

Because of the intimate and complex mixture of the clay, the determination of optical constants of the various clay mineral constituents has not been found feasible.

An interesting feature in connection with the clay is the occurrence of pseudomorphs of clay after quartz and feldspar. In some cases clay has completely replaced angular grains of quartz and feldspar (Fig. 11).

The clay has a distinctive structure, but it does not fit well into any definite structural class. It resembles granular montmorillonite in appearance, although the true structure is perhaps flaky rather than granular. In hand specimen the material is massive, but in thin section it is arranged in well-developed laminae, consisting alternately of material with an average grain size of about .05 mm., and material with an average grain size of about .025 mm.

Orientation is variable from one lamina to another, and is not developed to a high degree except in the case of the finer bands which may be fairly well oriented.

The clay bed which was being worked in 1936 shows no trace of any structure which would suggest origin by alteration of an original volcanic ash. On the contrary, its characteristics are those of a fine-textured sediment. In numerous places in thin section, the montmorillonite occurs as grains, which resemble ordinary detrital grains, as if the clay represented a montmorillonite silt. In this case the granular structure may be a direct result of the mode of origin. If this is not a sedimentary clay, it at least contains a considerable percentage of material which was contributed by normal processes of sedimentation, probably in shallow water. Thin sections of associated clay from the same pit show a poorly-preserved vitroclastic ghost structure. The montmorillonite may have been derived by alteration of an impure water-deposited ash, but this is not clear in the sections examined.

It seems probable that the material from Riverside described by M. N. Broughton,[21] and collected by Dr. John T. Lonsdale, came from some clay bed or pit other than the ones examined in connection with this study. Broughton describes numerous glass shards and divitrified bubble walls not found in material recently studied.

Broughton refers to a letter received by Dr. John T. Lonsdale from Dr. Paul F. Kerr in connection with material submitted by the former for *x*-ray analysis. In his letter Dr. Kerr stated that the four samples submitted from Riverside and Lena do "not appear to be either a kaolin or a montmorillonite type of clay. The four samples appear to agree with the sedimentary clay type mentioned . . . in the *Journal of Sedimentary Petrology*.[22] This type of clay may not represent a valid mineral species. We have not yet determined whether it represents a distinct mineral . . . The *x*-ray patterns give numerous lines that do not resemble the lines of any other clay minerals." Further *x*-ray work supports these conclusions regarding the material sent to Dr. Kerr.

However, *x*-ray examination of the material collected by Dr. Kerr and studied in connection with this work, indicates that it consists of kaolinite and quartz. A few of the diffraction lines are somewhat weaker than those of standard patterns of kaolinite; this is probably due to the complex and impure nature of the material. The montmorillonite lines have been obscured by stronger lines of kaolinite and quartz. This *x*-ray evidence also supports the belief that the material from Riverside collected by Dr. Lonsdale came from some bed or pit other than the one described in this study.

Riverside (*2*)—The Riverside (2) deposit is made up of an upper and a lower fuller's earth stratum. The upper stratum is about 9 to 12 feet in thickness and appears to rest upon an ash bed. This clay layer contains considerable amounts of gypsum occurring in veinlets. The lower fuller's earth stratum beneath the ash bed is exposed along the creek just north of the pit. This lower bed contains veinlets of opaline or chalcedonic silica. The exposures examined occur in strata mapped as belonging to the Jackson group.

Thin-section examination of the clay material shows it to consist of a complex mixture of clay minerals with about 20% of granular impurities, chiefly quartz, acid feldspar, and muscovite. Some glass or amorphous silica is present as well as a small amount of limonite.

Two general kinds of clay material occur in the sections. One appears to be montmorillonite and consists of abundant minute flakes arranged roughly parallel to the lamination of the clay. The other type is more coarsely crystalline and forms patches, streaks, and irregular areas haphazardly distributed through the clay. This material appears to consist of a mixture of allophane, halloysite and kaolinite. These same minerals are probably present in considerable amount mixed with the fine-textured montmorillonite. However, the nature of the mixture does not make feasible accurate estimation of the amounts of different clay-mineral constituents.

The coarsely crystalline material gave the following indices: $\alpha = 1.519 \pm .003$, $\gamma = 1.543 \pm .003$, birefringence .024. It is not certain that this coarsely crystalline material, which exhibits undulose extinction, is homogeneous. Index determination of the finer material was unsatisfactory, the indices lying within the range given for the coarser material.

With respect to structural habit, the montmorillonite shows three types of material. The first two appear to correspond to different laminae and to be responsible for the lamination.

The first type forms the major portion of the sections. It consists of granular or flaky montmorillonite containing about 20% impurities, chiefly quartz, with some acid feldspar and muscovite. The average grain size, for both the clay mineral and impurities, is about .03 mm. This material resembles that of Riverside (1). It shows little tendency to orientation.

In the second type certain laminae in the clay consist of montmorillonite of the oriented-shred variety, showing fair to excellent orientation, parallel to the lamination. This material is considerably purer than the granular montmorillonite. It is extremely fine, the average grain size being about .01 mm. An estimated 5% maximum of impurities, all too fine to be identified definitely in sections is present, presumably of the same types as in the coarser material.

The third type of material resembles that of the Luce deposit. Patches of coarsely crystalline montmorillonite (?) in anhedral units or aggregate patches several millimeters in diameter occur in the sections. Single units showing undulose extinction may be as large as 1–2 mm. in length. These areas usually exhibit no relation to the lamination. In places they appear to follow cracks in the other types of material. The clay has been micro-faulted or brecciated, and the patches of relatively coarse montmorillonite (?) seem to be related in distribution to this disturbed condition.

The general structure of the clay is intermediate between the oriented-shred type and the granular type of Riverside (1). Traces of original ash structure are lacking, the material appearing to represent a sedimentary deposit. It appears that the material is too highly altered to clay to determine its origin with any degree of certainty. The presence of an interbedded ash exhibiting vitroclastic ghost structure in thin section, lends some slight support to a theory of bentonitic origin in part. However, the problem of origin is connected with the stratigraphic conditions of Tertiary time in Texas, and its solution seems to depend upon further detailed stratigraphic and microscopic work.

X-ray diffraction patterns of the clay material indicate the presence of montmorillonite, kaolinite, and quartz. From this and optical study, it is believed that montmorillonite, kaolinite, and halloysite are the principal clay mineral constituents with minor amounts of allophane.

FAYETTE DEPOSITS

The Fayette clays include five deposits situated in Fayette County:[23,24] (1) the Carr-Brown tract, 9.4 miles northwest of Flatonia; (2) the Parker-Ivy tract, 9 miles north of Flatonia; (3) the J. A. K. tract, 1.5 miles north of Muldoon; (4) the Fleck-Darby tract, 3.5 miles north of Muldoon and 1 mile west of Lena; and (5) the Lena deposit of the Texas Company at Lena (Fig. 12).

The deposits are aligned along the general northeast strike of the Tertiary formations of the area.[25] They are all Eocene in age, occurring in the Jackson group.[26] The general dip is southeast, but for the most part the beds appear to be flat-lying. There is a slight structural disturbance as indicated by minor faults, which are particularly evident in the Fayette (1) property.

The clays in these deposits prove on field examination to represent essentially two types of material. One is typical bentonite, which is yellowish and has a somewhat granular texture. The other is a somewhat waxy, chocolate-colored shale inclined to be more sandy than the bentonite. The sandy, chocolate-colored clays appear to be more widely distributed and to occur in thicker deposits than the yellow bentonitic clays. One would infer from field examination alone that the chocolate-colored material is usually an ordinary sedimentary shale, while, on the other hand, it would seem more likely that the yellow clays are bentonites.

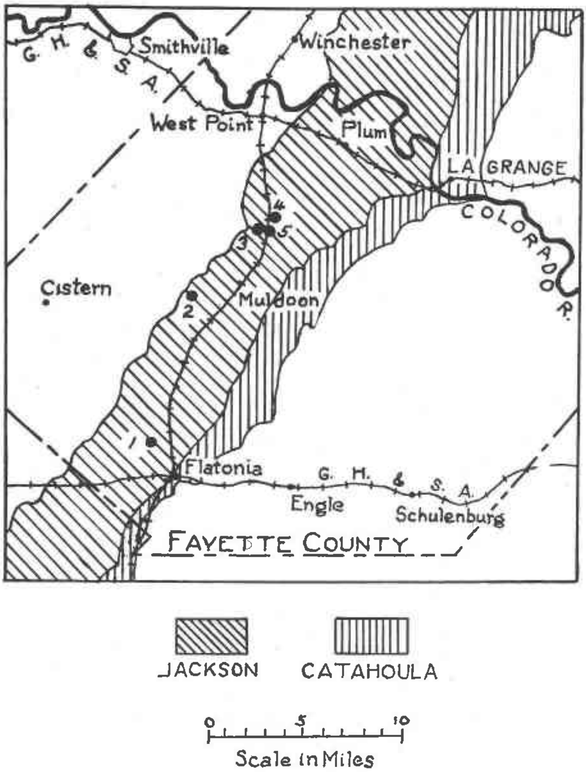


FIG. 12. Position of Fayette clay deposits on the geologic map of Texas. (See reference 1)

In the field, sandy ash beds several feet in thickness may be traced along small branches until they grade into bentonite. This is possible in several different places and it is assumed from this situation that the clays of the area were formed in localized alteration zones. It would appear that local geologic conditions are responsible for the alteration of the type observed. This situation is also suggested by the lack of uniformity of the alteration in certain places. In some of the beds, changes in texture and character of the clay may be observed within a few feet laterally and are even more apparent in vertical variations.

In several of the deposits opalized wood may be found in the strata immediately overlying the bentonite. The significance of this is not established, although it apparently indicates that if the clays were accumulated under marine conditions, they represent shallow water or near shore deposits. Marine fossils have been reported in the area discussed.

Another feature worthy of mention is the occurrence of gypsum in a number of places; this may indicate the action of sulphuric acid on the clay. It is not unlikely that the associated shale, which in some places contains abundant organic matter, could have supplied sulphur in such form that it would be readily converted to sulphuric acid. The action of this acid might easily account for the alteration of volcanic ash to bentonite. Unequal distribution of either the zones of solution, or the materials yielding sulphuric acid might explain the irregularity in distribution of the deposits.

The deposits exhibit similar mineralogic and petrographic characteristics. In all cases the clay-mineral constituent is montmorillonite,[27,28] which forms most of the material in the thin sections examined. The principal impurities are quartz, feldspar, muscovite, and in some cases glass. A variable but small amount of undetermined organic matter is present in all the sections. The texture is fine, and the orientation poorly developed except in the cases of Fayette (4) and Fayette (5), where it is good. Examination of the *x*-ray diffraction patterns from the deposits furnishes a check on the identification of montmorillonite as the clay-mineral constituent.

Fayette (1) and Fayette (2)—The clay bed at (1) is about 3 feet in thickness, the best exposures occurring along a small branch. The clay is waxy, yellowish, and rather uniform in character. It has the appearance in hand specimen of a slightly gritty bentonite. Judging from the operator's information concerning the results of drilling, there is a considerable area of "bentonite" underlying the property (Fig. 13).

The clay bed is cut off by faulting along the branch, but neither the total displacement of the clay, nor the effect of faulting on the overburden, was apparent on brief investigation.

The clay exposures along a small branch of (2) comprise the following section: sandy ash, containing opalized wood, overlying the clay beds, 3 feet of impure yellow bentonite above a 4-inch bed of chocolate-colored bentonite, a one-inch layer of yellow waxy bentonite, and 18 inches of chocolate-colored shaly material (Fig. 14).

In thin section the material from (1) and (2) consists of 90 to 95% of montmorillonite. The indices of refraction show an extreme variation,

FIG. 13. Photograph showing clay bed faulted against sandstone and shale.

FIG. 14. Photograph of upper clay bed stripped for mining.

presumably dependent upon the water content of the clay. The indices on air dried clay from Fayette (1) are: $\alpha = 1.477 \pm .003$, and $\gamma = 1.499 \pm .003$, birefringence .022. The indices on Fayette (2) are: $\alpha = 1.462 \pm .003$, and $\gamma = 1.483$, birefringence .021, $-2V$ small. These figures are as accurate as could be determined at present without standardizing the conditions of humidity under which the optical determinations were carried out. Impurities in (1) range from 5 to 10% whereas in (2) they represent only 2 or 3% of the material. In both deposits the chief impurities are feldspar, quartz, and muscovite. Chlorite, opal (diatoms), glass or amorphous silica, and limonite are present in varying but minor amounts.

The clay from (1) and (2) is fine-textured, the average particle size being .01 to .05 mm. Impurities are usually somewhat coarser. Orientation of the clay particles is either poor or lacking.

The material in thin section possesses a fine but poorly-developed bedding. Indefinite traces of vitroclastic structure are observable, and as these clays are similar to the bentonitic Fayette clays, it is believed that any definite evidence of original ash which might have been present was virtually obliterated by the extent of alteration. Associated with both deposits are fine ash beds exhibiting vitroclastic structure. The presence of diatoms and sponge (?) spicules suggests that the clays were deposited in lake or near-shore marine water.

X-ray diffraction patterns of (1) and (2) indicate that the clay mineral is montmorillonite.

Fayette (*3*)—The main bed at the J.A.K. tract is about 5 feet in thickness. The deposit has been opened and mined in a number of places, and probably contains the purest clay in the district. Material from this bed consists of a dense, pale, creamy yellow clay, apparently structureless in hand specimen.

Thin-section examination shows the material to consist of 50 to 60% montmorillonite. The indices of refraction of the montmorillonite are: $\alpha = 1.467 \pm .003$, $\gamma = 1.488 \pm .003$, birefringence .021, $-2V$ small. The remainder of the material is made up essentially of unaltered glass (30 to 40%), quartz, chlorite, feldspar, muscovite, and an occasional diatom.

The material is fine-textured, the average clay particle size being about .01 to .05 mm.; impurities are somewhat coarser. Orientation of the clay particles is poor or lacking, and when present is variable in character. The clay is finely, though indistinctly bedded and shows a well-preserved vitroclastic structure, indicating derivation from volcanic ash.

Some of the same material consists of 90 to 95% montmorillonite, the remainder being glass and sandy impurities. In this the vitroclastic structure has been almost completely destroyed, owing to the thoroughness of alteration. Thus, the extent of alteration varies from place to place in the same deposit.

Fayette (*4*)—Exposures of bentonite occur along a small branch about one mile west of Lena. The Fleck-Darby outcrops are covered with top soil and about 4 or 5 feet of a sandy, weathered, ash-like material. The bentonite bed appears to be impure, and is a little more than 4 feet in thickness. The upper portion consists of 3 feet of impure yellowish to yellow bentonite, a 4-inch chocolate-brown bentonite occurs near the bottom of the bed, and on the bottom there is a one-inch layer of bright yellow bentonite. Underlying the bentonite bed is an 18-inch layer of chocolate-colored sandy ash which appears to be stained bentonitic material (Fig. 15).

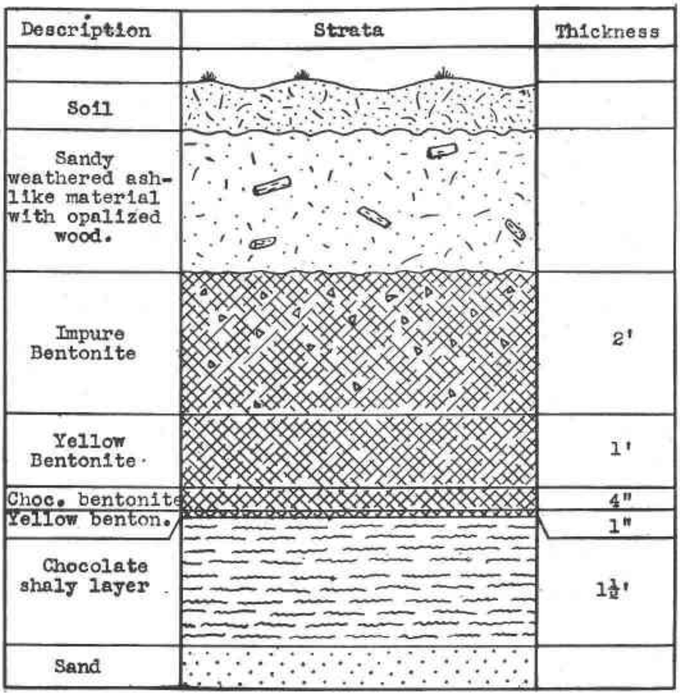


FIG. 15. Generalized section at the Fayette (4) deposit.

Opalized wood occurs in the sandy material over the bentonite, and it is thought that the dark stain of the bentonitic layer may be due in part to the presence of organic matter. While this deposit may be too variable to be of great interest from the economic standpoint, it provides an interesting sequence of materials.

Material from the chocolate-colored clay bed and from the chocolate-colored sandy ash was examined in thin section. The clay bed contains about 70% montmorillonite, 25% unaltered glass, and about 5% granular impurities, chiefly quartz with some muscovite, opal (diatoms), doubtful glauconite, magnetite, and limonite.

The material is fine-textured, clay particles ranging from .01 to .05 mm. in size. The material exhibits good orientation of the clay particles, is well-bedded and rather uniform in character. It represents an ash with preserved vitroclastic structure. It is probable that the original ash was deposited in lake or near-shore marine water, as suggested by the presence of numerous diatoms and sponge (?) spicules.

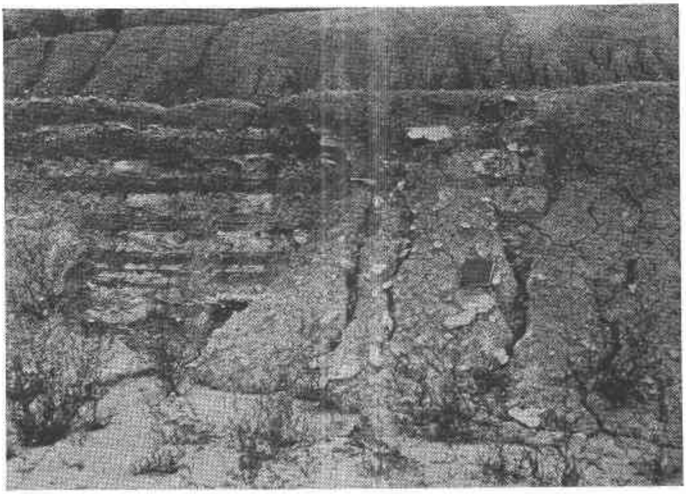


FIG. 16. Exposure in the old workings at Fayette (5) showing intercalated shaly and sandy strata. The loose slabs near the notebook are gypsum.

The chocolate-colored sandy ash contains approximately 80% montmorillonite. In comparison with the first sample, this shows a greater alteration to clay, and a higher percentage of the sandy impurities.

Fayette (*5*)—The most striking feature of the Lena deposit is the intercalation of impure clay with sandy layers, the outcrops of clay in the quarry resembling mixtures of sand and shale rather than the sequence one normally expects in a bentonite deposit. The best clay is a light chocolate brown, finely laminated material with occasional fine white streaks of sand (Fig. 16). A kaolin from the general vicinity of Lena has been described by Alexander Deussen.[29]

In thin section this material shows considerable contrast to the other Fayette County clays. Judging from *x*-ray patterns and determinations of optical properties, the clay mineral which forms an estimated 90 to 95% of the thin sections is montmorillonite. The indices of refraction show considerable variations, but fall within the range of published indices for montmorillonite. The values are $n=1.500$ mean index, birefringence .02, elongation positive, $-2V$ small. The impurities vary in amount and consist of quartz, muscovite, acid feldspar, opal (diatoms), chlorite, glass or amorphous silica, gypsum and limonite. It should be noted, however, that the percentage of impurities estimated from thin sections is undoubtedly low for the clay bed as a whole, since the material sectioned was free from the streaks of sand ordinarily present in hand specimen.

The texture is fine, the average clay particle size being under .1 mm. The fine texture and variability makes estimation of the amount of impurities uncertain.

The clay particles are well oriented and exhibit a well-developed lamination. Structurally, the clay is a borderline case between the oriented and oriented-shred types of montmorillonite, but is much closer to the latter, it being always possible to pick out the shreds which are the units of structure.

No indication of volcanic ash structure was observed in the specimen described. From field and microscopic study, this appears to be an ordinary sedimentary clay. It is possible that the absence of any indication of ash structure is due to completeness of alteration, but the presence of numerous diatoms suggests near-shore marine deposition, and the presence of numerous shreds of muscovite suggests at least considerable contamination by sedimentary material. Concentration of quartz in fine streaks parallel to the bedding is also strongly suggestive of ordinary sedimentary deposition. Nevertheless it is possible that in part the clay represents a highly altered and contaminated water-deposited ash. Associated interbedded strata, when not too highly altered, prove to be ash with well-preserved vitroclastic structures. The material from this deposit described by Broughton[21] was probably selected from one or more of these bentonitic layers, as it does not agree petrographically or by *x*-ray examination with the material examined in this work.

GONZALES DEPOSITS

The Gonzales clays consist of three deposits situated in Gonzales[23,26] and Karnes counties. Gonzales (1) and (2) were being operated by Coen and Company in 1936, and are located in Gonzales County. Deposit (1) is located about 6 miles from the town of Gonzales, and (2) is about 10 miles southeast of Gonzales. Gonzales (3) is located about ½ mile north of Gillett in Karnes County. All three deposits are in strata mapped as belonging to the Jackson group of Eocene age (Fig. 17).

In hand specimens the clays appear waxy and either yellow or chocolate-brown. In thin section the principal mineral constituent is montmorillonite, with quartz and feldspar the chief impurities. The material is fine-textured, poorly-oriented, and indistinctly bedded. The general structural aspect of the clays is bentonitic, but no definite evidence of volcanic origin is present in the sections.

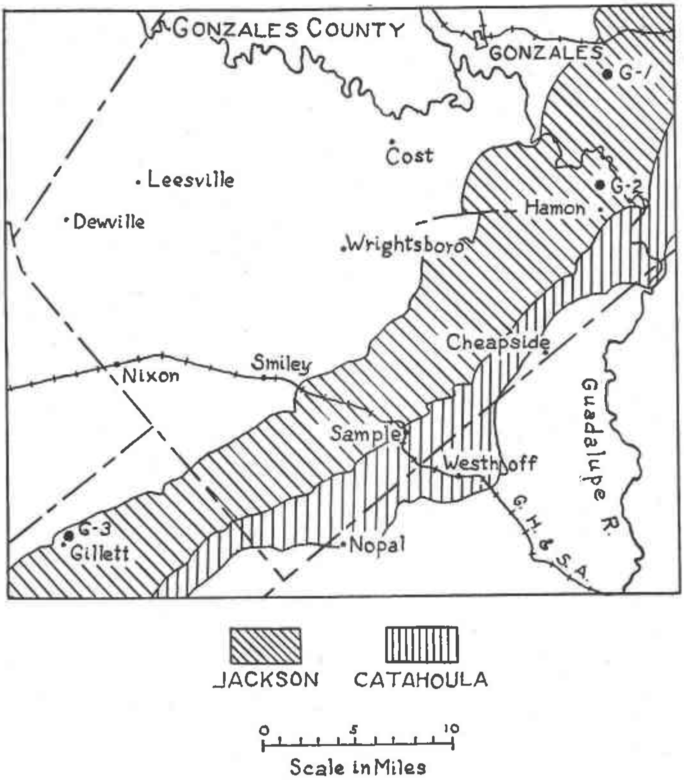


FIG. 17. Position of Gonzales clay deposits on the geologic map of Texas. (See reference 1)

Gonzales (1), (2), and (3)—Two different types of clay were being mined at (1). One is yellow, somewhat waxy, and has the appearance of a bentonite. This clay has a thickness of 2 to 3 feet, and occurs just beneath the soil overburden, which varies from 0 to 10 feet in thickness. The other is a variable layer of chocolate-colored clay which occurs below the yellow clay, and is about 5 feet thick. This bed furnished most of the clay in former operations. Fossil wood occurs in the soil cap above the "bentonite," and large pieces of vegetable matter are present, replaced by gypsum.

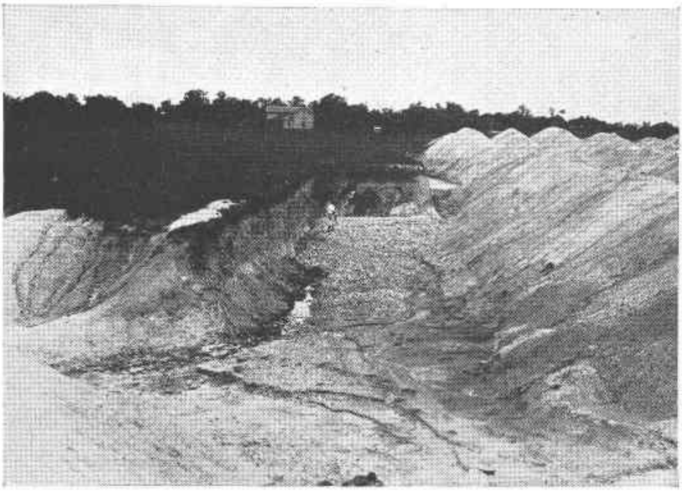
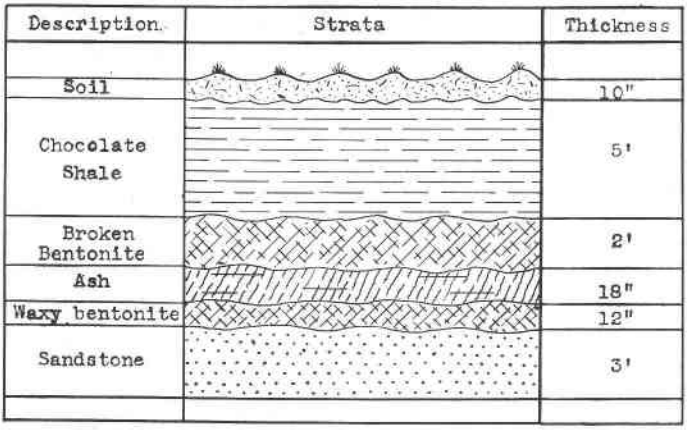


FIG. 18. Clay exposed in the open pit at Gonzales (2).



Description	Strata	Thickness
Soil		10"
Chocolate Shale		5'
Broken Bentonite		2'
Ash		18"
Waxy bentonite		12"
Sandstone		3'

FIG. 19. Generalized section at the Gonzales (2) deposit.

The clay at (2) is about 3½ feet thick and shows similar variation in color to (1), ranging from chocolate-colored clay to waxy yellow "bentonite." The clay is overlain by a chocolate-colored ash about 18 inches in thickness (Figs. 18 and 19).

The clay bed at (3) is about 5½ feet thick. It consists of a hard chocolate-colored clay resembling bentonite in appearance. Above the clay stratum is an 18-inch layer of ash.

Microscopic examination shows that montmorillonite constitutes 80 to 85% of these three clays. Indices of refraction of (1) are: $\alpha = 1.462 \pm .005$, $\gamma = 1.482 \pm .005$, birefringence .02. Refractive indices of (3) are: $\alpha = 1.468 \pm .004$, $\gamma = 1.493 \pm .004$, birefringence .024. In addition to montmorillonite, halloysite (?) occurs in streaks in the fine-textured montmorillonite matrix.

An isotropic substance making up approximately 15 to 20% of the area of the sections examined is distributed through the clay. Grit, chiefly quartz and feldspar, forms from 1 to 5% of the material. Minor amounts of muscovite, diatoms, glauconite, and limonite are present.

The clay is fine-textured, the average particle size being about .01 to .03 mm. Orientation of clay particles is poor or lacking. A peculiar system of lenticular fractures is developed in (1) when it dries. Along these fractures there is some tendency to orientation of the clay material.

The sections exhibit an indistinct bedding. No definite evidence of either sedimentary or volcanic origin is present, it probably having been destroyed by alteration. The general appearance of the clay and closely associated beds which exhibit vitroclastic ghost structures, is suggestive of volcanic origin. The presence of glauconite, diatoms, and muscovite indicate contamination by sedimentary material and possible deposition of ash in water.

SUMMARY OF *X*-RAY DATA

X-ray diffraction study was carried out with a powder camera[30,31] using molybdenum radiation. The width of arc was increased, yielding measurements of lines with large spacings. Numerous patterns were taken of clays from the various deposits described, and measurements of montmorillonite from selected samples were compared with those given by montmorillonite from Montmorillon, France, and from other localities. Measurements of the main clay at Luce, which is representative of the montmorillonite studied, are given in Table 1. Similar data by Gruner,[32] Hofmann, Endell, and Wilm,[33] and Nagelschmidt[34] are listed for comparison.

Table 1. *X*-ray Diffraction Measurements of Montmorillonite in Å

Gruner[32]		Hofmann, Endell and Wilm.[33]		Nagelschmidt[34]		Hagner Mont., Fr.		Hagner Luce, Tex.	
A.U.	Int.	A.U.	Int.	A.U.	Int.	A.U.	Int.	A.U.	Int.
15.0	8	15.2	s	15.3	vs	15.3	s	15.3	s
		7.36	w			7.37	vw	7.37	w
						6.01	vw?		
		5.05	w	5.15	s	5.16	vw	5.07	vw
4.45	3	4.32	m	4.50	vs	4.43	m	4.51	vs
						3.86	w?		
						3.38	w?		
		3.13	vw?	3.07	vs	3.09	w	3.07	w
2.81	?								
				2.61	vs				
2.535	2			2.55	vs				
2.43	?			2.41	w				
						2.340	s	2.345	vs
2.228	0.5	2.205	m	2.240	vw			2.239	vw
		2.197	vw	2.155	vw				
1.851	0.5			1.905	vw				
				1.708	m				
1.688	1	1.661	w	1.682	vs	1.690	s	1.676	s
1.643	1								
1.494	3	1.470	m	1.497	vs	1.496	s	1.496	vs
1.415	0.5								
1.285	1	1.273	w	1.292	m	1.287	m	1.287	s
1.241	0.5	1.225	w	1.247	m	1.240	m	1.240	m
		1.110	vw						
		1.021	vw					1.023	vw
		0.966	w	0.970	vw	0.975	w	0.972	w
		0.862	w	0.863	vw				

A.U.—Interplaner spacing in Ångstrom units.
Int.—Intensity
vs—very strong, s—strong, m—medium, w—weak, vw—very weak.

MINERALOGICAL FEATURES AND ADSORPTIVE CAPACITY

Adsorption in Clays

Adsorption has been defined by Robinson as depending upon "the change in interfacial tension produced by the presence of a dissolved substance in the liquid phase."[35] Many theories have been advanced in an effort to explain the mechanics of adsorption. Among the factors given as controlling adsorptive power are particle size, surface character, atomic structure, chemical composition, mineral composition, and a number of other physical and chemical factors mentioned below.

Evidence has been presented by Kelley[36] and others[37,38,39,40,41] to the effect that, other things remaining the same, the smaller the particle size,[42] the greater the adsorptive capacity.[43,44] Opinions are on record[45] suggesting that adsorption is a surface phenomenon.[46,47] Nutting has stated that "Clay particles (or oil sand grains) are potential bleaching agents for oil when their surfaces hold H or OH radicles adsorbed in a thin layer. When these are driven off by heating, open bonds are left which select from oil the darker, more basic constituents."[48] Flocculation,[49,50] adhesion tension,[51,52] porosity and density,[53], colloidal activity,[54,55] degree of saturation of the complex,[56,57,58,59] sesquioxide ratios,[44,60,61] bases present[62,63,64,65,66] and the effect of grinding,[67,68,50] appear to be most emphasized as physical and chemical factors influencing adsorption. Recent studies by Marshall,[69] Nagelschmidt,[34,70] Edelman,[71] Neulen,[72], Bragg,[73] Searle,[74] and others,[75,76] indicate by *x*-ray analysis that minerals possessing a loosely bound layer lattice built up of silicon-oxygen tetrahedra, have more adsorptive power than those which do not possess such a structure.[32,77] In general, clays with highest adsorptive capacity have certain similarities in chemical composition,[78,45b] principally a relatively high percentage of removable bases and water. The clay mineral montmorillonite, in certain occurrences, is the most highly adsorptive of the clay minerals.[79,80,81,82]

The Texas clays studied contain montmorillonite as the chief mineral and provide an unusual opportunity for observing a variety of physical occurrences of this mineral. The reason for variation in adsorptive capacity of montmorillonite in different occurrences is a matter of considerable interest, and of no little economic importance. It is hoped that the correlation of physical, chemical, and optical data of numerous montmorillonite-bearing Texas clays will contribute to the solution of this problem. It is felt that a somewhat detailed analysis is necessary if a correlation of important characteristics with adsorptive capacity is to follow. Where data on the Texas clays are insufficient, supplementary, physical, chemical and efficiency observations on other similar and important clays are substituted.

GRANULAR IMPURITIES

The unavoidable presence of small granular mineral impurities in the clays studied is believed to be one of the most significant features in connection with correlation of physical properties with adsorptive efficiency. Quartz, feldspar, and muscovite are the most abundant impurities, and are irregularly distributed in part in sandy streaks, and in part as disseminated grains in the purer clay. Because of the erratic distribution of these impurities, it is difficult to arrive at an accurate estimate of their average amount in any given clay bed as a whole, but they are judged to range from 2 to 25% in the deposits used for correlation of physical and chemical factors with efficiency.

Observations on impurities in the various clays indicate that adsorptive power increases with freedom from impurities. This may be shown for example by the relative efficiencies of two clays from Midway,[43] Florida. Midway 1 represents a purified fuller's earth in which particular care was taken to remove as much sand as possible before submitting it to efficiency tests. The efficiency rating of this clay is approximately eight points higher than that of Midway 1*a*, the same clay as Midway 1 but not purified. Commercial practice supports this conclusion. As far as bleaching power of clays is concerned, it seems that granular impurities largely represent inert matter (Table 2).

TABLE 2. IMPURITIES IN CLAYS STUDIED

Clay	Estimate % Impurities	Most Abundant Impurities
Polkville, Miss.	3	Quartz, feldspar, limonite.
Chambers, Ariz.	2– 3	Quartz, biotite, calcite, pyrolusite, glass.
Attapulgus, Ga.	5	Quartz, acid feldspar, muscovite, calcite.
Midway, Fla.	5–15	Quartz, acid feldspar, muscovite
Zavalla (1), Tex.	25	Quartz, feldspar, muscovite, kaolinite, glass or amorphous silica.
Luce, Tex.	25	Quartz, glass=20%.
Tehachapi, Calif.	20–25	Quartz, feldspar, biotite, zeolite and glass=20%.

Estimates include only principal kinds of impurities and are based upon samples of clays suitable for economic use.

CLOSELY BOUND IMPURITIES

In addition to granular impurities, clays often contain more tightly held, or difficultly separable, impurities such as zeolites, glass, or opal. From the standpoint of bleaching efficiency, kaolinite, allophane, and probably the halloysite present in certain northeastern Texas clays, might also be considered difficultly separable impurities. The effect of kaolinitic material on efficiency is taken up in the section on mineral composition. From the results listed in Table 2 it is inferred that zeolitic material and glass, or amorphous silica, possess little adsorptive power. This has been demonstrated by Nutting and others.

In both active and activable clays, closely bound impurities appear to affect the efficiency. The highest grade of activable clays, such as those from Chambers,[43,83] Arizona, and Polkville,[84] Mississippi are, on the whole, remarkably free from difficulty separable material. Among the naturally active clays, Midway,[43] Florida and Attapulgus, Georgia,[85,86] appear also to have greater freedom from such contamination. The latter, however, in virtually all commercial samples, contain fine inseparable material. This is not great in the case of the naturally active Zavalla (1) and Luce clays from Texas, or the naturally active clay from Tehachapi,[87] California.

As already stated, certain minerals[79,80,81,88] have adsorptive powers in much higher degree than others. Of the clay minerals, montmorillonite,[89] beidellite,[69c] and possibly halloysite[69a,71a,45b] are strongly adsorptive, whereas kaolinite[80,90] usually possesses little adsorptive capacity.

The Polkville, Mississippi, and Chambers, Arizona clays which possess high adsorptive power are relatively free from impurities and contain no kaolinitic material. On the other hand, the Zavalla (1) clay has a low efficiency rating, and contains chiefly kaolinite as the clay-mineral constituent. (See Table 5.) On the whole, the more kaolinitic clays of eastern Texas are generally admitted by producers to be less efficient than comparable naturally active montmorillonite clays of Georgia and Florida.

OPTICAL CONSTANTS OF ADSORPTIVE CLAYS

Optical constants of montmorillonite in the Texas clays may be compared with optical data derived from other montmorillonite clays. While there is some variation in the values for raw clays, they are in reasonably close agreement within the limits of error for the method used. Although no two samples yield exactly the same indices, most of them gave values within the same range. An exception is the montmorillonite from Zavalla (1), values for which are somewhat high compared with the others; this is probably due to the intimate manner in which it is mixed with kaolinitic material (Table 3).

The effect of activation on optical constants is to decrease refractive index values. It is believed that this may be due principally to acid treatment causing loss in weight per cent of MgO. Correns and Mehmel[91] have shown that there is a uniform loss in refractive index with loss in weight per cent of MgO. Experiments by Mehmel[92] indicate that loss of water results in an increase in refractive index up to 450°C. at which temperature refractive index values decrease. Similar results have been obtained on the clays studied. More recent dehydration tests carried out by Kelley[66] lead him to believe that the large losses in water content, due to loss of adsorbed water, occur at 180°C.; the other large losses that take place around 450°C. are believed to be due to loss of water in the crystal lattice.

TABLE 3. OPTICAL DATA

Clay	Raw			Activated		
	Ref. Index	Op. Angle	Biref.	Ref. Index	Op. Angle	Biref.
Polkville, Miss.	$\gamma=1.512$	(−) sm.	.02	$\alpha=1.476$ $\gamma=1.502$	(−) sm.	.026
Chambers, Ariz.	$\gamma=1.495$	(−) sm.	.02	$\alpha=1.472$ $\gamma=1.492$	(−) sm.	.02
Attapulgus, Ga.	$\alpha=1.511$ $\gamma=1.532$	(−) sm.	.021	$\alpha=1.498$ $\gamma=1.521$	(−) sm.	.023
Midway, Fla.	$\alpha=1.508$ $\gamma=1.529$	(−) sm.	.021	$\alpha=1.500$ $\gamma=1.520$	(−) sm.	.020
Zavalla (1), Tex.						
Kaolinite	$n=1.565$ mean		.005	not determined		
Halloysite	$n=1.542$ index		.003–4	not determined		
Montmoril.	$\gamma=1.536$	(−) sm.	.02	$\gamma=1.530$	(−) sm.	.02
Luce, Tex.						
Halloysite	$\gamma=1.555$ max.; variable	(−) sm.		not determined		
Montmoril.	$\alpha=1.490$ $\gamma=1.512$	(−) sm.	.022	not determined		
Tehachapi, Calif.	$\gamma=1.506$	(−) sm.	.02	$\gamma=1.487$	(−) sm.	.02

All values ± .003. Elongation positive. Extinction slightly inclined to cleavage.

In the clays studied the activated clay samples probably resorbed most or all of their water before index determinations were made. This may be seen in the chemical analyses made before and after activation (Table 4).

MICROSCOPIC STRUCTURES AND TEXTURES

Judging from the deposits studied, adsorptive efficiency varies regardless of microscopic structure and texture.[43] Lamination in the different deposits is variable, ranging from indistinct to well-developed. Orientation of clay particles and impurities ranges from clays having none to those with good orientation parallel to the bedding. The oriented shred-structure present in some clays and described as being due to packing, was at first believed to have some bearing on efficiency. However, no essential relationship could be found between degree of development of this structure and relative efficiency of clay.

X-Ray Data

X-ray diffraction patterns of material from the Texas clays were compared with other adsorptive clays of good quality. The patterns, together with petrographic and chemical data, confirm determinations of montmorillonite as the essential clay mineral constituent of the deposits studied.

Variations in amount of impurities, and presence of kaolinitic material are indicated by *x*-ray study. However, microscopic structures and textures appear to cause no significant differences in the patterns of montmorillonite.

X-ray diffraction patterns of activated clays, compared with those given by raw clays, indicate that activation causes no apparent change in the number or spacings of lines when ordinary molybdenum radiation is used. The diffraction lines are somewhat less clearly defined in patterns of activated clays, probably due to breaking up of particles during treatment.

These results would indicate that changes due to activation do not disturb the fundamental lattice structure. However, molybdenum radiation is inadequate to indicate small lattice changes. In view of the drastic chemical treatment during activation, and the fact that changes in water content[93,33,70b,94] and isomorphous replacements[75] have been suggested by *x*-ray studies with copper radiation, it seems likely that some changes take place within the lattice, and probably also in the bonds between layers.

Alteration and Origin

The adsorptive quality of an individual clay mineral may be considerably affected by the amount and degree of alteration. Progress of alteration depends chiefly upon kind of original material and the agents of alteration. "The crystalline inactive kaolin minerals appear to be the product of extreme weathering of many kinds of igneous rocks and are highly stable. The bleaching clays appear to be composed chiefly of the less stable and less completely weathered clay minerals. . . . Many or possibly all of the bleaching clays would go over to kaolins if sufficiently leached and given sufficient time to take on water of constitution. A few clays have been thus transformed (from bleaching to china clay) in the laboratory by water treatment alone."[45b] In general, however, the more original material left associated with clay, the less the efficiency. Therefore, in the case of bleaching clay, alteration of original material to clay should be rather complete, but not so extreme as to form kaolin. This is believed to be true of the deposits studied.

Clays from Attapulgus, Georgia, and Midway, Florida, consist of a mineral of the montmorillonite group believed to have formed as a weathering product of crystalline rocks and then transported and deposited in shallow water. These deposits are part of a widespread group of fuller's earths occurring in Georgia and Florida. Alteration has been rather extensive and complete, producing good quality naturally active clays.

The geologic occurrence of the Polkville, Mississippi montmorillonite has been described briefly by Bay,[84] who called attention to its good quality and efficiency on activation. The clay bed has since been opened and mined. The clay is believed to have originated by alteration in place of almost pure volcanic ash. Alteration has progressed so far that the original ash structure has been largely destroyed. The close similarity of the clay to other bentonite deposits in the vicinity is most suggestive of bentonitic origin. The presence of glauconite and marine fossils in associated strata, together with the composition and general character of the beds, suggests that the clay was deposited in near-shore marine water.

An interesting feature of the Polkville clay is the virtual absence of detrital material so characteristic of the Georgia-Florida clays. It is believed that this absence may be traced directly to differences in origin. Since it is believed that the Georgia-Florida clays represent sedimentary accumulation, detrital material is expectable. On the other hand, impurities in the Polkville clay would be derived either from the original ash, or from adjacent rocks by solution. As a result, impurities consist essentially of iron oxide stain, glass remnants, and occasional grains of quartz and feldspar. The Polkville clay, due perhaps, in large part to its origin and the completeness of alteration, is a very pure activable clay.

The presence of unaltered ash in the vicinity of the clay supports the belief that the Chambers[83,43] montmorillonite is probably bentonitic in origin. Any vitroclastic structure originally present has been destroyed by the high degree of alteration. The extent of alteration and small percentage of impurities has resulted in a good quality, highly activable clay.

The Zavalla (1) clay appears to represent a normal sedimentary deposit. However, it may be that alteration has obscured traces of original ash structure. The montmorillonite may be the result of alteration of volcanic ash, while the kaolinite, halloysite, and granular impurities represent sedimentary accumulation. This sedimentary material is believed to be largely responsible for the comparatively low efficiency of the clay.

The Luce clay represents volcanic ash now partly altered to a mineral of the montmorillonite group. In spite of alteration the structure of the original ash is clearly preserved. The halloysite present apparently reflects sedimentary contamination. This clay has a higher efficiency rating than Zavalla (1), probably because of a smaller percentage of sedimentary clay minerals and granular impurities. Also, the sedimentary clay mineral halloysite which is present, is said[69a,71a] to have greater adsorptive capacity than kaolinite, which is present in considerable amount in the Zavalla (1) deposit.

The Tehachapi[87] montmorillonite originated by alteration of a volcanic ash bed. Although the deposit is quite extensive, the clay does not compare in purity with Chambers or Polkville fuller's earths. This is believed to be due to insufficient alteration, leaving a considerable amount of residual ash and zeolitic material.

Thus, the amount and degree of alteration is presumably of importance in connection with the decolorizing efficiency of clay. It appears, from data available, that completely altered bentonite forms the best activable clay. At any rate, clays resulting from rather complete decomposition of volcanic ash appear to have superior qualities for acid treatment.[45b] Naturally active clays, on the other hand, may be less altered or less pure. Sedimentation evidently plays an important role in the origin of these clays in a number of instances, but not in all.

CHEMICAL COMPOSITION

Correlations of chemical composition with efficiency on the basis of a limited number of analyses are largely suggestive. However, the analyses in Table 4 indicate that the clays studied have a relatively high magnesia and water content.[78] Nutting has pointed out that bleaching clays "are characterized by high contents of loosely held water and by partial solubility in dilute ordinary acids, such as hydrochloric or sulphuric acid. The water is largely adsorbed water and is removable by heating to 200°C. . . . On the other hand, inactive clays, such as kaolin, retain almost all their water up to a red heat (500°C.). . . . Moderate dehydration to 200°C. is sufficient to develop the full bleaching power of the active clays, but heating to 600°C.–800°C. destroys that power; hence we infer that it is the water driven off between 50° and 200°C. that must be present in bleaching clays and must be driven off to induce bleaching power. Acid treated clays require similar heat treatment. . . . Before dehydration the kaolin minerals do not adsorb water or bleach oil, nor can

TABLE 4. CHEMICAL ANALYSES OF CLAYS STUDIED
(*Analyst*—Earl Emendorfer)

	Polkville, Miss.		Chambers, Ariz.		Attapulgus, Ga.		Midway, Fla.		Zavalla (1) Tex.		Luce, Tex.		Tehachapi, Calif.	
	Raw	Activated	Raw	Activated	Raw	Activated	Raw	Activated	Raw	Activated	Raw	Activated	Raw	Activated
SiO_2	49.59	58.66	50.03	55.70	53.42	63.46	52.92	64.73	60.21	66.50	52.53	59.81	58.95	71.07
TiO_2	1.11	.40	.84	.33	.52	.46	1.18	.49	.69	.60	.31	.33	.74	.20
Al_2O_3	15.07	16.15	15.00	13.13	10.06	8.65	9.41	8.18	21.33	17.04	22.86	19.01	9.92	8.38
Fe_2O_3	1.93	1.03	2.79	2.28	3.40	3.16	3.35	3.21	2.36	2.70	1.51	1.62	2.03	1.45
FeO	.09	.06	.13	.16	.18	.18	.30	.30	.20	.17	.11	.11	.26	.23
MnO	.01	.01	.01	.01	.02	.02	.03	.02	.01	.01	.04	.03	.01	.01
MgO	4.83	4.19	4.53	3.45	9.16	6.39	9.05	5.62	1.16	.81	2.16	1.27	4.64	2.22
CaO	1.39	.22	2.60	.31	1.29	.21	1.91	.41	.66	.15	1.30	.26	1.09	.52
Na_2O	.02	.05	.08	.12	.02	.02	.03	.02	.16	.13	.05	.13	.19	.43
K_2O	.15	.05	.12	.13	.64	.68	.98	1.00	1.13	1.12	.05	.31	.46	.60
P_2O_5	.03	.05	.02	.05	.12	.33	1.21	.46	.10	.05	.04	.04	.03	.04
H_2O above 110°C.	8.10	8.83	8.29	7.47	9.42	9.18	10.19	8.90	7.85	7.30	8.04	7.93	7.11	7.14
H_2O at 110°C.	17.76	9.48	15.63	15.77	11.83	6.78	9.06	6.05	3.75	2.69	10.98	8.35	14.28	7.19
CO_2	.01	none	.02	.01	.05	none	.11	none	.05	none	.04	none	.02	none
Cl	.02	.02	.01	.01	.03	.02	.02	.02	.03	.36	.03	.03	.01	.02
SO_3	.02	.79	.04	.72	.02	.19	.04	.26	.03	.02	.02	.59	.02	.60
Sum	100.13	99.99	100.14	99.65	100.18	99.73	99.79	99.67	99.72	99.73	100.07	99.82	99.76	100.10

Activated clays were acid treated and heated to 550°F.

they be activated by acid treatment."[455] Somewhat similar dehydration data have been published by Mehmel[92] and Kelley.[66]

Analyses of naturally active commercial earths from Attapulgus and Midway show relatively high lime, magnesia, and water, relatively low alumina, and a moderate amount of ferric oxide. Variations in the silica content are believed to reflect differences in degree of purity, rather than any essential difference in composition of the clay mineral. The percentages of other minor constituents show irregular variation, and are not considered to have any significant bearing on the problem of bleaching efficiency. The Midway clay is somewhat lower in alumina than the clay from Attapulgus, a difference which is not unusual in the montmorillonite group and may be attributed to isomorphism.

It is interesting to note that the activable Polkville and Chambers clays contain less magnesia, and a slightly higher alumina and water content than the Georgia-Florida clays. The inactivable Tehachapi clay contains less magnesia and slightly more lime than the Georgia-Florida clays, but agrees with them more closely in chemical composition than with the Polkville or Chambers clays.

The active Zavalla (1) and Luce clays show a higher alumina content and a lower magnesia, lime, and water content than any of the other clays studied. These differences in chemical composition presumably reflect the presence of kaolinitic material. Zavalla (1) also has a relatively high amount of potash, probably due to an appreciable percentage of muscovite.

Analyses of activated clays show a considerable increase in silica with a corresponding decrease, in most cases, of alumina, magnesia, lime, ferric oxide, and water at 110°C. The decrease, with the exception of Chambers, in water at 110°C. may be due to drying. This contrast is perhaps overemphasized in the table, since sufficient activated material was not available to permit the degree of purification that was possible with raw clays. Increase in sulphuric anhydride may be attributed to the acid used. Other small changes may be detected, and it is possible that acid treatment produces a structural change in clay which is evidently not great, as little change in diffraction lines is observable in an x-ray study, using molybdenum radiation.

In making the above comparisons it has been kept in mind that the clays analyzed, even after purification, were unavoidably contaminated with finely divided impurities. Reasonable allowance for the compositions and amounts of impurities has been made in the comparisons cited above.

SUMMARY

Many rocks and minerals possess adsorptive capacity in some degree, or can be made adsorptive by treatment with acid.[45b] However, most of these substances are of no practical value in refining oils, the commercial adsorbents being composed principally of the mineral montmorillonite. Recently bauxite[95] has been used successfully for oil decolorization, and under certain conditions is even more efficient than other commercial adsorbents, thus giving promise of its further use for this purpose.

Why some clays are naturally active and others neither naturally active or activable is a problem of considerable importance. At present little is known about these phenomena because of insufficient available standardized efficiency ratings. Also, "the ratings of active minerals according to their bleaching efficiency is obviously a quite arbitrary matter, because the relative bleaching power of any series of clays will be different for every test liquid used. . . . Even with a specific clay and test oil there is the question of which cut to choose as standard. . . . "[45b]

It has been suggested that the silica of active clays is more soluble than that of inactive clays. Also, that certain fuller's earths improve in efficiency with acid treatment "due to the removal of limonite, calcite, and possible hydrous alumina which may exert a clogging effect on the active minerals."[54] In the clays studied, with the exception of Attapulgus, little or no calcite or other carbonate was present in thin sections. The amount of limonite present was virtually negligible, occurring largely or entirely as surface stain. In Table 5 it may be seen that activable clays have a somewhat lower silica content than the naturally active clays. This is probably due to a greater freedom from impurities

TABLE 5. EFFICIENCY DATA

Clay	Decolorizing Efficiency*	Type
Polkville, Miss.	115.0	activable
Chambers, Ariz.	120.0	activable
Attapulgus, Ga.	30.0	naturally active
Midway, Fla.	33.0	naturally active
Zavalla (1), Tex.	60.0	naturally active
Luce, Tex.	95.0	naturally active
Tehachapi, Calif.	38.0	naturally active

After treating for 6 hours with 34 wt. % of 100% sulphuric acid (basis volatile free clay) in 8% solution.

* Commercial tests of acid treated clays based upon a standard acid treated clay =100%. Temperature 550°F., 20 minutes with steam.

containing appreciable silica. In any estimate of the significance of silica it should be kept in mind that small amounts of opal dispersed through montmorillonite may frequently escape detection.

Summarizing the data presented in this study it seems possible to offer the following suggestions in regard to correlation of mineralogical characteristics with adsorptive capacity. The presence of granular or inseparable impurities lowers the adsorptive capacity of a given clay. Strongly adsorptive members of the montmorillonite group possess an abundance of loosely held water. If any connection exists between microscopic structures, or textures, and adsorptive capacity it is yet to be established. *X*-ray data indicate that clay minerals with the montmorillonite lattice have a structure which permits a high degree of adsorption. The amount and degree of alteration of original material to clay appears to be related to adsorptive capacity. Montmorillonite clay reasonably free from coarse or closely held impurities while not normally active, may be activated to a high degree. Correlation between origin and adsorptive capacity appears either limited or doubtful, except that adsorptive clays originating by transportation of material tend to contain more granular impurities than those altering in place from volcanic ash, and seem to be active but poorly activable. High percentages of removable bases as well as water presumably accompany high adsorptive capacity. Montmorillonite appears to be the most highly adsorptive clay mineral.

ACKNOWLEDGMENTS

The writer is indebted to Dr. Paul F. Kerr of the Department of Geology, Columbia University, at whose suggestion this investigation was undertaken, and who has furnished valuable advice during the laboratory study and the writing of the manuscript. The chemical analyses were made by Mr. Earl Emendorfer. The writer is also indebted to Columbia University for fellowship assistance which has made this work possible.

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