STUDIES OF FLINT CLAYS AND THEIR ASSOCIATES

A THESIS

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL
OF CORNELL UNIVERSITY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY

SYDNEY LONGMAN GALPIN

Reprint from Transactions American Ceramic Society, Vol. XIV, P. 301, 1912

Reprinted from the Transactions of the American Ceramic Society. Vol. XIV.
[Paper read at Chicago, Ill., Meeting, March, 1912.]

STUDIES OF FLINT CLAYS AND THEIR ASSOCIATES.

By Sydney L. Galpin, Ithaca, N. Y.

INTRODUCTION.

Non-plastic fire clays have been recognized for many years as a type differing distinctly from the plastic fire clays, yet the investigation of their nature and origin has received but little attention. Their geologic occurrence and distribution in Maryland,[1] Pennsylvania,[2] Ohio,[3] Kentucky,[4] West Virginia,[5] Missouri[6] and Washington[7] have been briefly described by different authors; and they are also known to occur west of Pueblo in Colorado.[8]

Greaves-Walker[9] discusses the sedimentation of the Kentucky flint clays and concludes that they were deposited in basins of rather limited area. Hopkins[10] has argued from a study of some of the Pennsylvania fire clays that they were once the soil in which the flora of the coal beds flourished and that they owe their purity largely to the leaching action of the plant roots.[11] He also points out an explanation of flinty nature similar to Wheeler.

Wheeler[12] has described in detail the flint clays of Missouri. He considers them to be sediments deposited in limestone sinks and purified by the leaching of carbonated meteoric waters. Their non-plastic quality may be due to crystallization of kaolin-

---

[1] Md. Geol. Surv., Report on Allegheny County; Ries, Clays of Maryland, Md. Geol. Surv., Vol. IV, Pt. III.

[2] Hopkins, Clays of Western Pennsylvania, Ann. Rept. Penn. State College, 1897; Woolsey, Clays of Ohio Valley in Pennsylvania, Bull. 225, U. S. Geol. Surv.; Lines, Clays, and Shales of Clarion Quadrangle, Bull. 315, U. S. Geol. Surv.; Shaw and Munn, Foxburg Quadrangle, Bull. 454, U. S. Geol. Surv.

[3] Newberry, Geology of Ohio, Vol. III; E. Orton, Jr., Geol. Surv. of Ohio, Vol. VII, Part 1.

[4] Greaves-Walker, Flint Fireclay Deposits of N. E. Ky., Trans. A. C. S., IX, 1907; W. C. Phalen, Clay Resources of N. E. Ky., Bull. 285, U. S. Geol. Surv.

[5] Grimsley and Grant, W. Va. Geol. Surv., Vol. III, 1905.

[6] Wheeler, Clays of Missouri, Vol. XI, Mo. Geol. Surv.

[7] Shedd, Clays and Clay Industry of Washington, June, 1910.

[8] Personal communication, H. Ries.

[9] Loc. cit.

[10] Loc. cit.

[11] If this theory is correct it seems curious that many clays underlying coals are so impure.

[12] Loc. cit.

ite, because of their coarsely platy structure as seen under the microscope.

Others have made preliminary microscopic examinations which will be discussed later.

The investigations, upon which this paper is based, were undertaken with a view to determine if possible the nature of the differences between plastic and non-plastic fire clays. They were carried on partly in the field and in part at the geological laboratories of Cornell University.[13] The field work included a study of the refractory clays at the following localities: Strasburg, Ohio; Clarion, Pa.; Woodland, Clearfield County, Pa.; Mt. Savage, Md.; and Olive Hill, Ky. Many sections from these localities were also studied under the microscope.

DETAILED ACCOUNT OF OCCURRENCES.

In presenting the results of this investigation it seems best to give the details of the occurrence, petrography and other properties first; and then to explain the views or theories formulated as a result of these studies.

STRASBURG, OHIO.

The plastic and non-plastic clays of Tuscarawas County are found at several horizons in the Lower Productive Measures (Alleghany series). Probably the most important flint clay is that worked about two miles east from Strasburg by the National Fire Brick Company. The bed outcrops only near the crests of the higher hills and seems to be at the same horizon as Newberry's[14] No. 7 coal, which is thought to be the equivalent of the upper Freeport coal.

An unusually good exposure exists in the company's open-cut workings from which the accompanying sketch shown in Fig. 1 is taken. The clay bed consists of three divisions, *viz.*, a lower, No 1 grade fire clay; a middle, flint fire clay; and an upper, No. 2 grade fire clay.

---

[13] The author is pleased to acknowledge his indebtedness to Professors Ries and Gill for counsel and assistance in conducting the work, and to the National Fire Brick Co., The Harbison-Walker Refractories Co., The Union Refractories Co., The Olive Hill Fire Brick Co., and Mr. Wm. Ramsay, of Mt. Savage, Md., for courtesies and aid in obtaining materials.

[14] Geology of Ohio, Vol. III, p. 66.

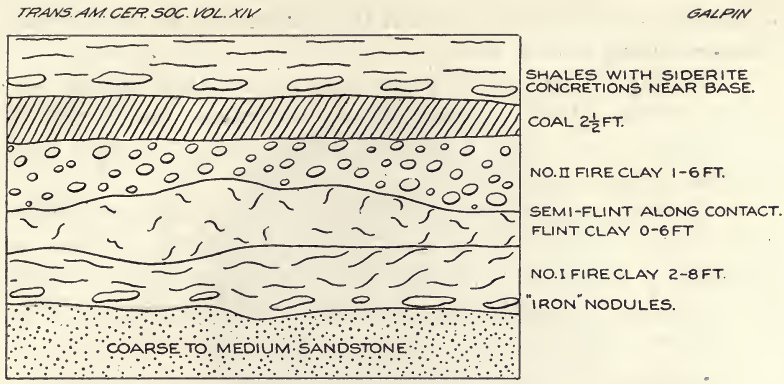


Fig. 1.—Section at Strasburg, Ohio.

The No. 1 fire clay is a gray laminated rock having an irregular hackly fracture. It shows some variation in color and texture, becoming more sandy toward the bottom, where occasional clay-iron stones may be seen. It is frequently contorted and always cut by a network of slickensided slip planes. Though hard when mined it becomes somewhat plastic when ground in a wet-pan. Its thickness is rather variable, due to "rolling up" in places and "squeezing out" in others. The clay rests upon an even sandstone floor but its upper boundary, though usually well defined, is irregular.

The flint fire clay has a massive appearance and is broken up into blocks by irregular joints, but slip planes so characteristic of the surrounding clays are wanting. It breaks with a clean conchoidal fracture, showing a light buff surface mottled by greenish gray lenticular markings, and lined in an irregularly concentric manner by bluish bands or ribbons. The latter seem to be generally grouped about bunches of small pyritic concretions. Upon exposure the clay breaks up into angular fragments stained by the decomposition of the pyrite. Carbonaceous material is locally present in quantities sufficient to produce a black clay. The thickness of the flint clay is decidedly variable, there being frequent marked swells and pinches. The boundary between the flint clay and the No. 2 fire clay is indefinite, the term "semi flint" describing the transition clay, as it is made up of lenses of flinty clay more or less surrounded by the slickensided and more plastic variety.

The No. 2 fire clay bears a close resemblance to the No. 1, but shows perhaps even greater contortion and variation in thickness. Its upper contact with the base of a three foot coal bed is even and regular.

The total thickness of the clay bed is fairly constant, variations of one kind being compensated by reciprocal changes in thickness of the others. The strata of the region show no signs of regional disturbance, indicating that the movements in the clay bed were of local nature.

MICROSCOPIC PETROGRAPHY OF THE STRASBURG CLAYS.

Section I.[15]—This represents the flint clay of this locality. With low magnification (40–80 dia.) one sees a fine more or less angular ground mass traversed by irregular veins usually under 15 microns in width, which are bordered by a brownish scum of limonite (?) and filled with material similar to the general ground mass. Numerous small pyrite crystals lie in this scum (see Plate I, Fig. 1) and a few are scattered through the clay. Spherical, radiated concretions of pyrite or marcasite (0.5–1 mm. dia.) are occasionally found.

Greater magnification (400–600 dia.) shows scattered angular quartz grains, a few scales of muscovite and rarely rounded zircons. None of the above exceed 10–15 microns in length. The bulk of the clay is made up of plates or grains less than 2 microns diameter, many of which show low interference colors in polarized light. From their similarity to determinable plates in other sections, they seem to be kaolinite. Sixty per cent. of the clay is estimated to be visibly crystalline, the balance being, in all probability, mainly colloidal in nature.

Section II.—This shows the contact of flint clay with the underlying semi-plastic fire clay.

The part of this section representing the "semi-plastic" clay is more coarsely and thoroughly crystalline than is that of the flint clay (Plate I, Fig. 2). Some areas of the "semi-

[15] Except where especially noted, these descriptions are of thin sections cut from the solid clay, and not of mounted powders.

PLATE I.

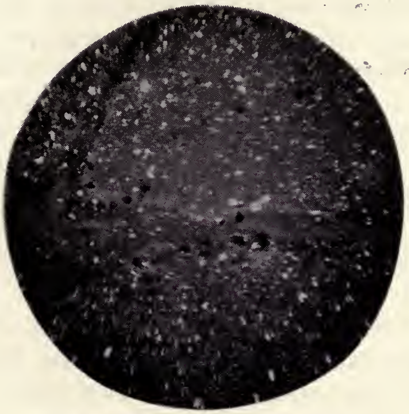


Fig. 1.—Section of flint clay, Strasburg, O., between crossed nicols. Dark spots are pyrite. Large light grains quartz, small ones partly kaolinite × 60.

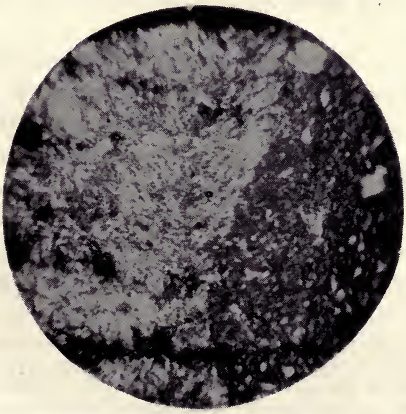


Fig. 2.—Section from Strasburg, O. Shows line of contact, the darker portion representing flint clay and the lighter portion the semi-flint clay with high development of the hydro-micas × 160.

plastic" are seen to be more highly crystalline than others, indicating varying stages of recrystallization. The platy grains are so interlocked and intergrown that there seems to be no doubt of their recrystallized nature. Most of these plates and aggregates resemble muscovite closely, except that they do not show as strong double refraction as that mineral. It was noted, however, that this property varies in different individuals, and that in a single section crystals may be seen which would form an unbroken series whose birefringence varies from that of muscovite to nearly or quite that of kaolinite. To distinguish these plates from muscovite and kaolinite, they will be mentioned as *hydro-micas* and discussed more thoroughly in a later paragraph.

Scattered through the felt of hydro-micas are occasionally columnar or fan-shaped aggregates of plates, showing low interference colors, low index[16] and the direction of greatest elasticity cutting across the plates. The optical character could not be determined in any of the plates in this section, but a similar plate in Section 14 gave a negative biaxial figure. These properties agree with those given by Iddings and Johannsen for kaolinite.

Hickling[17] has found the index of kaolinite in some of the English china clays to be nearer 1.56 than 1.54. Furthermore, A. B. Dick[18] describes one kaolinite which is optically positive rather than negative and whose mean index is about 1.563, while another he finds is negative. From this he concludes that there are two varieties of kaolinite. Among others who have described various forms of kaolinite crystals are Johnson and Blake,[19] who first used the term kaolinite, Merrill,[20] Reusch,[21]

---

[16] The index of similar plates in the powder of clay No. 1 was fixed at about 1.54 by the use of "index liquids." The strength of birefringence was determined by measuring the thickness of grains cut normal to the basal cleavage, by focusing on first the top and then the bottom of the grain, reading the difference on the micrometer head and correcting for index to give the true thickness. Knowing the thickness of a grain and its interference colors, the birefringence may be determined with fair accuracy.

[17] China Clay, Its Nature and Origin.

[18] Supplementary Notes on the Mineral Kaolinite, Mineralogical Magazine, XV, p. 124–7.

[19] Am. Jour. Sci., ii, XLII.

[20] Non-metallic Minerals.

[21] Neues Jahrb. fur Min., 1887, II, p. 70.

Rieke,[22] Cook,[23] Mellor[24] and Ries.[25] All of these investigators have recognized the peculiar sheaf and fan-shaped bundles of more or less hexagonal plates. It seems that there are then kaolinites of different optical properties, which may well represent simply different members of an isomorphous series, containing, perhaps, small amounts of alkalies or other elements in place of hydrogen in the theoretical molecule.

The prisms and fans of this section frequently show "ribs" or plates of higher index and birefringence intergrown with those of kaolinite (Fig. 2). These "ribs" show practically every grade of variation between kaolinite and muscovite.

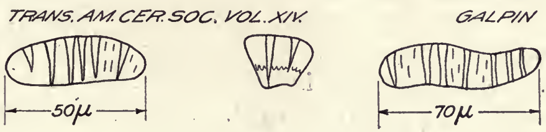


Fig. 2.—Sketch.

Irregular and often corroded quartz grains (under 80 microns dia.) make up about 15 per cent. of the crystalline material of the section. Zircon grains are frequently to be seen. Rather angular cloudy patches (under 100 microns dia.) are sometimes found and may represent the remains of decomposed feldspar fragments. Microscopic crystals (octahedral) of pyrite are abundant near the contact, where they were formed, probably as the result of the reduction of iron sulphate in solution by organic matter from the clay.

Section IV.—This was prepared from the powder of the upper fire clay (plastic); sixty to seventy per cent. of it seems to be in the form of small plates or scales, some of which are muscovite, but more show the lower interference colors of the hydromicas. No grains were seen which could be determined with certainty as kaolinite. Small quartz and zircon grains are present in slight quantities. The texture and mineral content of

---

22 Sprechsaal, XL, 1907.

23 Clay Deposits in New Jersey, N. J. Geol. Surv., 1878, pp. 280–281.

24 Trans. Eng. Ceram. Soc., Vol. VIII, 1908–9.

25 Md. Geol. Surv., IV, Pt. III.

the powder is similar to those of the powdered plastic clay from Mt. Savage (compare Section XIX).

Section VI.—Prepared from the powder of the "semi-flint" clay found between the upper plastic and flint clays.

The powder resembles that of the plastic clay except that some of the grains are not composed of a single flake or plate, but are made up of a large number of small plates still tightly bound together. (Compare with powders of Olive Hill semi-flint and Mt. Savage plastic clays.) Individual grains do not exceed 30 microns diameter. When lying flat in the section, their birefringence is very low and they may be distinguished from kaolinite only by their higher index of refraction. When on edge, the higher interference colors mark most of them as hydro-micas and muscovite. Only a few plates of kaolinite were seen. These show an index of refraction of about 1.54, and become dark in polarized light. A few quartz and zircon grains were also noted.

RESULTS OF DEHYDRATION TESTS.

The microscopic examination of these clays led to the belief that there should be decided differences in the water content of the flint, semi-flint and plastic clays. In order to test this view a 15 to 20-gram sample of each type was powdered, dried at 112° C. and then ignited to approximately constant weight, with the following results:

	Per cent. drying loss	Per cent. ignition loss	Per cent. total loss
Flint clay	0.8	12.3	13.1
Semi-flint clay	0.56	8.05	8.61
	0.5	7.87	8.37
Plastic clay	0.1[26]	7.33	7.43

For purposes of comparison a direct determination of the water in the plastic clay was made according to the Penfield method, giving: H_2O = 6.9%, other volatile matter (CO_2, SO_2, etc.) = 1.0 per cent., total loss = 7.9 per cent. This clay was taken for the Penfield determination because it contained con-

[26] Had been previously dried on a radiator.

siderable visible pyrite, and was expected for that reason to show a higher percentage of volatile matter, exclusive of water, than the other clays. It seems safe to conclude that with most of the clays tested, more than 90 per cent. of the ignition loss may be safely considered to be water.

The results were significant, in that they show the impossibility of much kaolinite in either the semi-flint or plastic clays. Commonly the low water content of a clay may be attributed to the presence of excessive amounts of anhydrous minerals, but microscopic evidence is against such an explanation in this case. Since the samples tested represent clays ranging from the middle toward the upper boundary of the bed, the results seem to throw some light on the geologic history of the clays, which consideration will be taken up later.

CLARION COUNTY, PENNSYLVANIA.

In this county, as in the region around Strasburg, Ohio, valuable fire clays exist at several horizons ranging from the Mercer to the top of the Alleghany series.[27] The clays investigated were collected at mines located from five to seven miles northwest of Clarion. Some specimens were taken from stock piles and others secured in the mine tunnels. The geologic relations at one of the mines is shown in the sketch (Fig. 3).

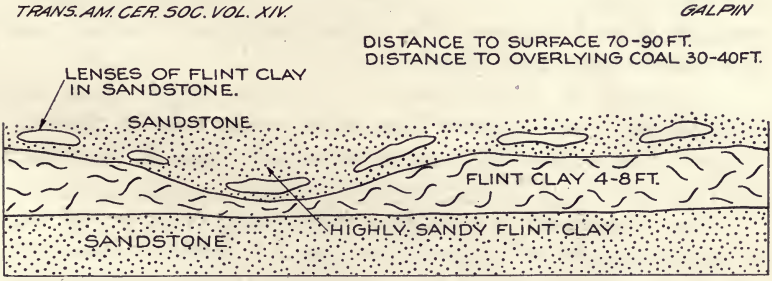


Fig. 3.—Section at Clarion, Pa.

The clay lying between massive sandstone beds is all nonplastic, and occurs in somewhat lenticular masses, which at times grade into sandstone if followed along the bed. The

[27] Bull. 315, U. S. Geol. Surv.; Bull. 454, U. S. Geol. Surv.

thickness varies from 0 to, perhaps, 16 feet. Variations of color and texture may be noted, mainly in crossing the bed vertically, but also in following it horizontally. The better grades of clay, usually found toward the middle of the bed, are of a cream or buff-gray color, and show a clean, smooth conchoidal fracture. All gradations from this type into a clayey sandstone of dull gray color and rough fracture may be found.

Although no coal lies directly above this clay, it seems probable that the horizon is that of the Lower Kittanning coal, which is sometimes missing in this locality.[28]

The strata of the region show only slight evidence of dynamic disturbance.

MICROSCOPIC PETROGRAPHY OF CLAYS FROM CLARION CO., PA.

Section VII.—This section is from a very smooth buff variety of the Clarion clay which shows a tendency to split into flat slabs. The type occurred as a layer 12 to 18 inches thick, but is now worked out.

Under the microscope, the clay is seen, in the main, to be finely crystalline, although the section is somewhat clouded by a limonite scum. In places, recrystallization of knots or bunches of kaolinite prisms has pushed the scum out into rims, which may be noted without magnification as brownish spots or circles upon the surface of the clay. Other than these recrystallization structures, the section presents a rather even and homogeneous appearance.

Kaolinite, in prisms under 50 microns length, fans, and vermicular forms, composes from 65 to 70 per cent. of the clay. "Ribs" of the hydro-micas are seen in only a few of the prisms and fans.

Rhombohedrons of siderite ($FeCO_3$) often 60 to 70 microns in length are evenly scattered through the section. They seem to have been among the first crystals to form after the sediments were laid down. Other less common minerals are quartz in badly corroded grains up to 90 microns length, zircon grains, rutile in needles, tourmaline grains, and a few small recrystallized plates of muscovite.

---

[28] Bull. 315, U. S. Geol Surv.

Section VIII.—This is slightly sandy flinty clay, and the section is similar to VII in general, but shows no siderite and contains more and larger detrital grains of quartz, zircon and tourmaline. Mica plates are slightly more abundant, many of them seeming to be recrystallization products.

Section IX.—This represents a variation which is so sandy that it is discarded at the mines. It comes from near the top of the bed (Plate II, Fig. 1). Quartz grains with very irregular outlines make up about 50 per cent. of the rock. The groundmass is similar to that of Sections VII and VIII, but shows little or no muscovite. The development of hydro-mica is more marked than in any of the foregoing clays from Clarion.

Section X.—A darker somewhat sandy phase of the Clarion clay, which is mottled with occasional black, waxy patches or lenses.

In general, this section resembles Nos. VII, VIII and IX, but has few of the spherical recrystallization forms. There is a larger amount of the brown or gray "scum" which may here be in the nature of organic matter. A section was cut across one of the black waxy lenses which under the microscope was seen to be clearer, extremely fine, crystalline material. The minerals could not be identified. It seems that contraction of the clay had opened slight fissures which were filled by this fine-grained material, probably from other parts of the same bed.

Section XI.—Typical flint clay, Clarion, Pa. This clay differs from No. VII mainly in showing no tendency to break or cleave in any one direction more than in any other. It is buff in color and has a medium conchoidal fracture.

Under the microscope, its structure resembles that of No. VII, but there are more of the recrystallization features, two generations being visible. (Compare with Sections XX and XXI.)

Kaolinite occurs abundantly, (1) filling the clear spaces in the recrystallization spots, (2) in prisms, and (3) in irregular felts throughout the section.

The prisms are frequently ribbed with hydro-micas. One or two instances were noted where a mineral grain determined

PLATE II.

Fig. 1.—Section of sandy flint clay from Clarion county, Pa., between crossed nicols. Shows edges of two corroded quartz grains. The long grain seen near the center of the section is a kaolinite prism. A few mica flakes may be seen as needle-like grains × 200.

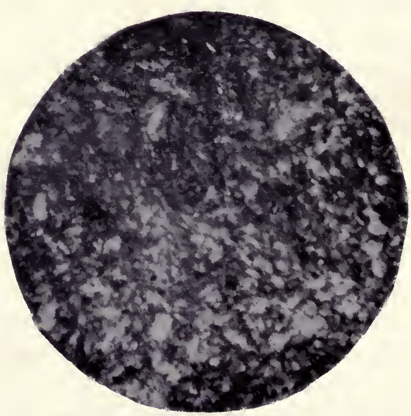


Fig. 2.—Soft clay, Woodland, Pa., between crossed nicols. Shows coarse mat of plates with scattered muscovite grains or flakes × 60.

as epidote, representing probably the recrystallization of traces of calcium with the silica and alumina, lay toward the center of one of these prisms and on either side of it, the ribs being developed to an especially strong degree. Some kaolinite fans were noted which were ribbed with plates showing the birefringence of muscovite. In all cases these plates are clear cut, sometimes extending beyond the kaolinite, and showing no evidence of decomposition into kaolinite. The evidence seems more to favor the view that the hydro-micas have developed with the kaolinite.

DEHYDRATION TESTS OF CLARION, PA., CLAYS.

Inasmuch as the various phases of the Clarion flint clay do not show much mineralogic difference, it was not expected that there would be so marked variation in their water content. Only two samples were dehydrated, one being the smooth buff clay described under Section VII and the other the sandy phase (Section IX). The results of these tests are given in the following table:

	Per cent. loss 112°	Per cent. loss ignition	Total
7 Flint clay.................	0.55	13.45	14.0
9 Sandy flint...............	0.03	12.17	12.20

The variation found is due mainly to the greater per cent. of quartz in the sandy clay. Carbon dioxide is responsible for some of the percentage loss in No. VII as it contains numerous grains of iron carbonate.

WOODLAND, CLEARFIELD COUNTY, PENNSYLVANIA.

The clay underlying the Mercer coal is economically the most important in this locality[29] although other horizons produce considerable amounts of refractory material.

Near Woodland this bed outcrops near the base of the hills and not many feet above stream level. It lies in a nearly horizontal position, but has been affected somewhat by the folding and faulting without changing the nature of the clay to any extent. The No. 1 mine of the Harbison-Walker Company

[29] Bull. 285, U. S. Geol. Surv., Clays and Shales of Central Pennsylvania.

is crossed by one fault whose throw varies from 8 to 40 feet. It extends in a northwest direction or normal to the axis of general folding in the region, and is said to continue at least two miles to the southeast where it is encountered in another mine.

An ideal section given in Fig. 4 may serve to show the occurrence.

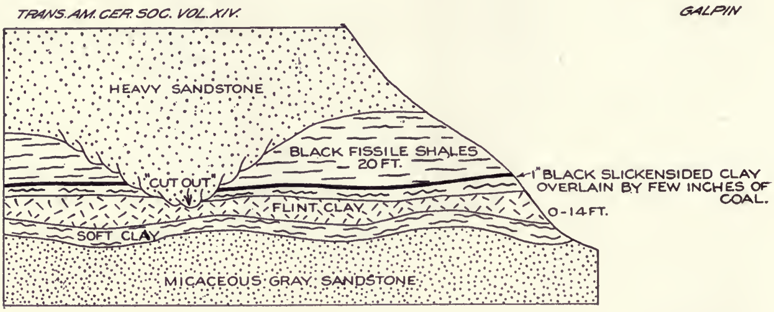


Fig. 4.—Ideal section at Woodland, Pa.

(1) The "soft" clay is a gray laminated rock with rough fracture and cut by numerous interwoven slip planes. It is fairly smooth but contains many flakes of mica which are quick to catch the eye. Though not truly plastic it is said to be a good bond clay. Its boundary with the flint clay is irregular and often difficultly determinable.

(2) The flint clay is also gray, often mottled with dark, irregular blotches, giving it the appearance of a breccia. The fracture is roughly conchoidal, and the mass is broken by irregular seams or joints whose sides are usually coated with limonite and sometimes clear tabular crystals of barite. The occurrence of barite with fire clays is somewhat unusual, but was noted also at Olive Hill, Ky. The crystals were probably deposited by the reaction of pyrite on solutions of barium hydrate or carbonate. The bed is variable in thickness, and to some extent in quality. One instance was noted where the clay is completely cut out by the overlying sandstone which appears to have settled and squeezed the clay out as its surface was crossed by a series of rough steps (Fig. 4).

Above the flint clay there is usually a thin layer of smooth black clay, with a few inches of coal at the top and over this some 20 feet of material called "Black Shelly." This is a dark shale which breaks up into thin planes on exposure to the atmosphere. The sandstone is normally found above this shale.

In one instance, a more plastic clay is found above the flint clay and it is interesting to note that water is reported more abundant in its vicinity.

MICROSCOPIC PETROGRAPHY OF THE WOODLAND CLAYS.

Section XIV.—"Soft clay," Woodland, Pa. This specimen is one of the most interesting of those examined microscopically.

With low powers (magnification 40 to 80 diameters) it is seen to be highly crystalline, and made up of a felt of mineral plates, which show a variation of from 5 to 200 microns in length or diameter. The clay is not microscopically homogeneous, that is, there are areas or patches which seem clearer than others (compare Section XV), and these often show slightly lower interference colors, although the felty structure is similar to other parts (Plate II, Fig. 2).

There are three prominent types of mineral grains: (1) Large plates 100–250 microns (though sometimes smaller) showing when on edge parallel extinction, and high interference colors. These plates are fairly evenly distributed through the section. Several determinations show that they are muscovite and may represent detrital material, although there is nothing other than their size to indicate this. Frequently these plates are bordered by an irregular growth of parallel orientation which shows lower index of refraction and lower order interference colors. These rims do not seem to be the result of weathering because of their irregular shape and also because the boundary between them and the muscovite scales is clean and well marked. The muscovite shows good cleavage cracks while few or none are to be detected in the bordering mineral. They, therefore, seem to be additional growth of hydro-mica upon the muscovite and indicate simply that crystallization of the border took place after the available alkalies for the formation of muscovite had been exhausted (Fig. 5).

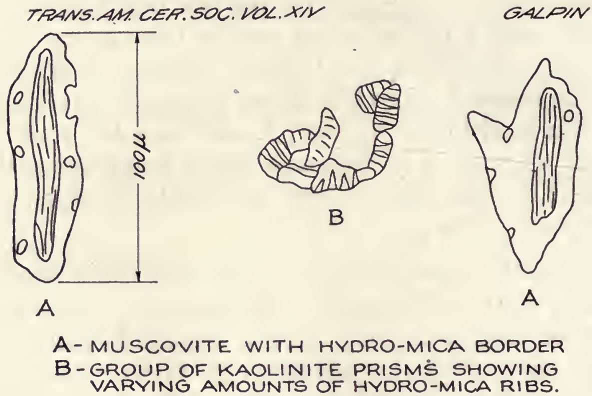


Fig. 5.—Sketches.

While conspicuous, these plates make up a small per cent. of the clay.

(2) Plates which are in general similar to (1) but smaller and of lower index and birefringence make up the bulk of the section. They usually lie in a confused felt-like mass, but sometimes show parallel orientation over considerable areas. (Compare Section XVII.) Occasionally they form fan-like aggregates closely resembling kaolinite but having usually higher index and birefringence. These are believed to be hydro-micas.

(3) Kaolinite in prisms, fans and plates is present. The commoner shapes are represented in accompanying sketches (Fig. 5, B).

"Ribbing" is always present to a considerable extent in these kaolinite prisms (Plate III, Fig. 1). Where any orientation could be detected the long direction of the prisms lay parallel to the direction of elongation of the mica plates, which would make the cleavage of one perpendicular to that of the other. The tendency sometimes noted, for crystal plates and prisms to lie with their long directions roughly parallel, probably represents movement within the clay under pressure.

Occasional groups or bunches of kaolinite prisms irregularly set together may represent the weathering of feldspar fragments, although it seems more probable that they are remnants of the

PLATE III.

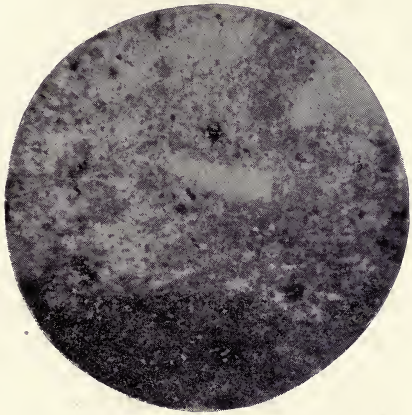


Fig. 1.—Soft clay, Woodland, Pa., by direct ight. Kaolinite prisms showing ribs of higher index of refraction × 300.

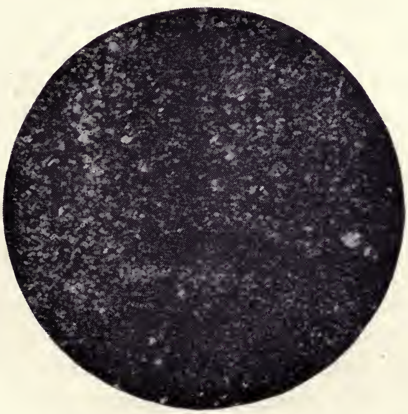


Fig. 2.—Flint clay, Woodland, Pa., between crossed nicols. Shows only the larger crystal grains which are mainly kaolinite, often "ribbed." A few bunches of the hydro-micas may be noted × 200.

knots or concretions of kaolinite so commonly seen in the more flinty clays.

Quartz and zircon in small grains are present but inconspicuous and probably rare.

Rounded tourmalines were noted but are unimportant. Rutile (?) needles of small size seem fairly abundant, sometimes so grouped that they suggest recrystallization products from the weathering of some mineral such as biotite. On the whole, there is, however, no definite evidence of detrital material other than quartz and zircon in this clay.

Section XV.—Mottled, or "conglomerate" flint clay, Woodland, Pa.

This section is composed largely of visibly crystalline material, although the largest individuals rarely exceed 20 microns in greatest dimension. The average size of grain is 5 to 10 microns although there is much finer material (Plate III, Fig. 2). The structure throughout is fairly uniform, but one notices that there are areas clearer than others which with slight magnification resemble sharp, irregular fragments embedded in a more turbid ground mass. With higher magnification, it may be seen that one part is much clearer than the other, although both seem equally well crystallized. The clear areas are found by comparison with the rock chip from which the section was cut to represent the dark patches which give the clay its brecciated or "conglomerate" appearance. Mineralogically there are some differences. The clear areas are composed almost entirely of kaolinite prisms and plates, while in the cloudy parts the incipient hydro-micas are more in evidence. Also in the cloudy areas knots and bunches of kaolinite sometimes occur, usually with a concentration of the limonite scum about them, as if it had been pushed out by the growing crystals. There are places too where this scum is puckered or drawn together about centers suggesting the contraction of a colloidal substance upon drying. The breccia-like structure seems due to a contraction in the clay not long after its deposition which formed irregular cavities or cracks. These were then filled through infiltration with purer material derived from the clay itself. The local variations in minerals noted in Section XIV may be explained as the metamorphic equivalent of these areas. The minerals in order of their importance here are (1) kaolinite, (2) hydro-micas, (3) quartz, (4) zircon, (5) tourmaline, (6) rutile, (7) mica.

The kaolinite is by far the most abundant, the lighter areas being made up of the small crystals of it.

The hydro-micas are present but do not show a marked development. They occur most often in radiate or fan-shaped groups of not more than 4 or 5 plates, each of which are seldom over 5 to 7 microns in diameter.

Quartz is scarce, as are also the other remaining minerals.

Section XVI.—"Semi-flint" clay from Woodland, Pa.[30]

Microscopically this resembles the "semi-flints" examined from other localities. It is of finer texture than No. XIV, but coarser than XV. Perhaps 90 per cent. of the section is visibly crystalline, kaolinite plates, prisms and fans with hydro-micas making up its bulk. Sharp sericitic plates are in evidence because of their higher index and interference colors. The section is considerably clouded by a scum of limonite.

Quartz grains are scarce. Rutile (?) needles (under 2 microns length) are present in large numbers and often grouped, suggesting the weathered residue from former biotite scales. Zircon grains were also noted but are not important.

The dehydration of two samples of Woodland clays gave the following results:

DEHYDRATION TESTS OF WOODLAND, PENNSYLVANIA, CLAYS.

	Per cent. loss at 112°	Per cent. ignition loss	Total per cent. loss
15 Mottled flint clay.........	0.39	13.3	13.7
14 "Soft clay"..............	0.39	12.11	12.5
	0.58	12.1	12.7

The differences here are not so great as those shown by the Strasburg, Ohio, clays, but the amount of kaolinite seen in Section XIV was greater than that of the other semi-flint clays.

That No. XIV owes its lower water content to the develop-

[30] This clay comes from the same bed as do Nos. XIV and XV, but from a point about 1½ to 2 miles southeast.

ment of hydro-micas seems probable since there is much of this mineral to be seen in the section, and greater amounts of quartz or other anhydrous mineral than in No. XV are not noted. The presence of hydro-micas up to 20 or 25 per cent. would produce about the reduction in dehydration loss here noted.

MT. SAVAGE, MARYLAND.

The fire clays are found outcropping toward the top of Savage Mountain and dipping steeply under its eastern slope. They are overlain by the Homewood sandstone of the Pottsville formation[31] which gives them a stratigraphic position similar to that of the Woodland, Pa., and Olive Hill, Ky., flint clays. This clay is underlain by a heavy conglomerate. The Mt. Savage coal is sometimes present above the clay[32] but in the mines visited by me no coal was seen.

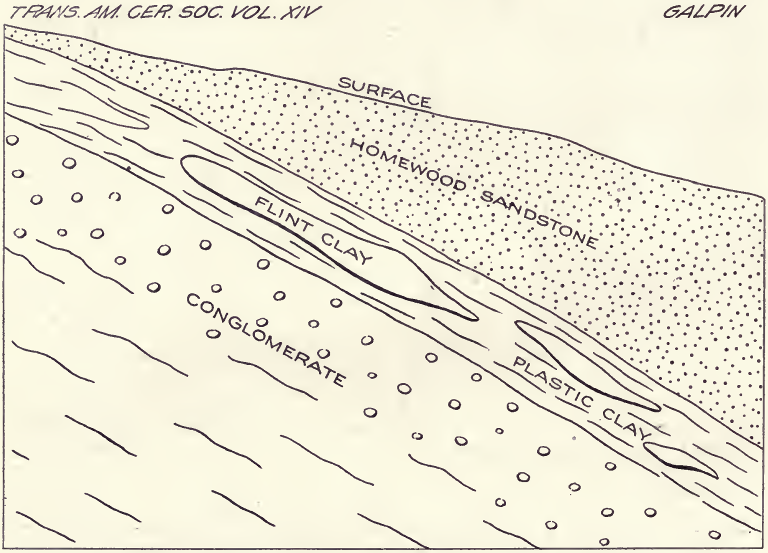


Fig. 6.—Section at Mt. Savage, Md.

The total thickness of clay shows a variation from 2 to 20 feet, made up of plastic and non-plastic material. The flint

[31] Md. Geol. Surv., Report on Allegheny County.

[32] Ries, Clays of Maryland, Md. Geol. Surv., IV, Pt. III.

clay is found toward the middle of the bed, swelling and pinching with great irregularity. Frequently it is represented only by lenticular masses which may be separated from each other along the dip by a distance of several feet. The surfaces of these lenses are plainly marked with slickensides, giving evidence of considerable movement along them. The clay in the lenses is usually greenish gray, sometimes mottled and broken into irregular chunks by cracks or joints along which oxides of iron have been deposited. Conchoidal fracture is not well developed, and in general appearance this clay is not so flint-like as the specimens from other localities.

The plastic clay is of a lighter color and soft enough to be broken up in the hands. There are at times parts which are black, due to the presence of organic material. These are usually toward the top of the bed where coal is said to be found in some cases. The proportion of plastic to flint clay is higher than in most other localities, and as far as our observation goes, the plasticity of the soft clay is greater than that of the soft clay from other localities visited. Because of the geologic structure of the region the clay is unusually wet, a fact which may have a direct bearing upon the development of the plastic clay, and which will be discussed later.

Section XVII.—Flint clay, Mt. Savage, Md.[33]

When examined under the microscope this clay is similar to No. XVI from Woodland, Pa., Few well defined crystal grains exceed 30 microns in greatest diameter, although there are frequently areas 200 to 300 microns across through which are grown many more or less distinct plates in parallel orientation. Often the spaces between the parts of one such group of plates are filled by another set of grains in different orientation from the former but parallel to each other. Such structures may well represent two or sometimes more intergrown crystals although it is not thought that they represent twins, since there is no apparent crystallographic relation between the position of the two sets. These areas are so irregular that they prob-

[33] While called a flint clay this more closely resembles, both under the microscope and in the hand specimen, the "semi-flint" clays of other districts.

PLATE IV.

Fig. 1.—Flint clay, Mt. Savage, Md., between crossed nicols. Shows development presumably by hydro-micas along a slip plane × 160.

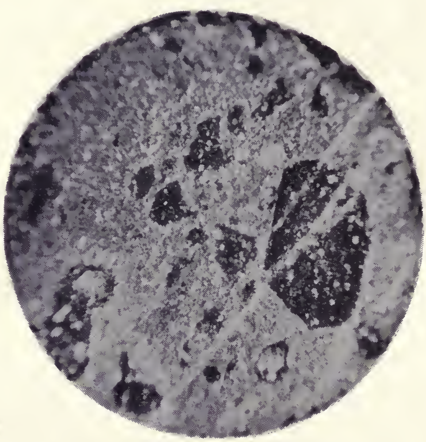


Fig. 2.—Semi-hard clay, Olive Hill, Ky., by direct light. Shows cloudy areas which may represent weathered feldspars × 80.

ably are not caused by the weathering of feldspar grains in situ, but represent instead intergrowths of rather large crystals.

The section is crossed by several cracks, which evidently represent slipping planes, as indicated by the drag of the minerals along them (Plate IV, Fig. 1). These cracks must have served as passageways for solutions for the reason that they are usually tinted strongly by limonite.

The determinable minerals are (1) kaolinite in plates, prisms and fans, more commonly "ribbed" by the hydro-micas; (2) hydro-micas in individual flakes or grouped in fan-shaped aggregates. The areas described above are composed of hydro-micas. This mineral apparently makes up from 50 to 60 per cent. of the clay.

Minute rutile needles are abundant, small zircon grains common, but prisms of tourmaline and grains of quartz are rare.

Muscovite scales are also rather rare and seldom exceed 15 microns length. An unusual reddish mineral was noted along the slickensides in one or two instances, which may be eucolite or eudialyte. The evidences are not satisfactory for certain identification.

Section XIX.—Prepared from powder of plastic fire clay, Mt. Savage, Md.

The powder was found to be made up of individual crystal plates and grains not exceeding 20 to 25 microns diameter, while much of the material was too fine to determine. It is interesting to compare this powder with that of a flint clay, and for this purpose a section of the "flint" from Strasburg, Ohio, was prepared. It was made up of irregular, angular grains up to 80 microns diameter. As both clays had been ground the same length of time in a ball mill, this difference is suggestive, and probably shows why the "soft" and semi-flint clays develop greater plasticity than do the flint clays as they are more readily reduced to very fine particles, and furthermore the platy structures of these particles would develop greater plasticity than would rounded grains of equal mass.

Only one plate of kaolinite could be identified in this section, but a considerable amount of the material was shown to have an index of about 1.54 by the use of index liquids, which indicates the presence of more in the section.[34] The one referred to was strongly ribbed by hydro-micas. The hydro-micas are the most common minerals, showing indices above 1.554 and in some cases running up to above 1.58, which would indicate that the composition was approaching that of muscovite, scales of which are also common in the section.

Rutile and zircon are present, the former being more frequently seen.

Dehydration tests on the Mt. Savage clays afford results quite similar to those of the Strasburg clays.

DEHYDRATION TESTS OF MT. SAVAGE, MARYLAND, CLAYS.

	Per cent. loss at 112° C	Per cent. ignition loss	Total per cent. loss
17 Flint clay...............	0.67	11.72	12.4
18 "Semi-flint".............	0.66	7.37	8.03
19 Plastic clay..............	0.87	6.33	7.2

It may be noted here that the Mt. Savage flint clay was compared microscopically with the semi-flints of other districts and the lower water content would seem to bear out the similarity. The "semi-flint" and the "plastic" clays show close agreement with similar varieties from Strasburg. The samples here tested were collected, as at Strasburg, ranging from the center of the clay bed toward the hanging wall.

OLIVE HILL, KENTUCKY.

The geology of this region has been described by Greaves-Walker[35] and also by W. C. Phalen.[36] The former has given such a detailed account of the occurrence of the clays that it seems necessary only to point out a few facts about the region. The following section from Phalen's report is characteristic:

[34] Quartz is also of about this index, but does not show the platy structure of kaolinite.
[35] Trans. A. C. S., Vol. IX, 1907.
[36] Bull. 285, U. S. Geol. Surv., Clay Resources of Northeastern Kentucky.

SECTION AT OLIVE HILL, KENTUCKY.

	Ft.	In.
Coal	...	2–6
No. 3 clay	1–9	...
Drab-flint clay	1–9	...
Semi-hard clay	1–5	...
Pink ore	...	18–20
Blue shale	...	4–8
Iron ore	...	...
Top of lower carboniferous limestone	...	...

There is, of course, considerable divergence from this section. In the "Burnt House" mine, for instance, flint and semi-flint clays only are found, while the roof is a massive sandstone. At the same horizon, and but a short distance from some of the "Burnt House" workings, is found the peculiar clay described by Greaves-Walker as "Aluminite" rock. It seems that there must be a transition from this into flint clay although the mine workings are not reported to show it. It is also possible that it may represent a more or less distinct lens.

The Olive Hill clay is correlated with the Mt. Savage, Md., and Woodland, Pa., clays, and, hence, would be at the Mercer horizon of the Pottsville.

The samples examined represent (1) *a*, typical flint clay, *b*, top of flint clay bed; (2) the semi-flint; (3) the aluminite varieties described by Greaves-Walker. All are found in or near the Burnt House mine.

(1*a*) (Specimen No. 21) is of buff color and shows a good conchoidal fracture. Small concretion-like spots may be seen. It is very similar in appearance to some of the Clarion, Pa., flint clays. Fractures in this clay are frequently lined with small plates of barite.

(1*b*) (Specimen No. 20). This clay is darker than No. 21 and shows its resemblance to the typical flint clay.

(2) (Specimen No. 22.) A smooth buff-gray clay cut up into interlocking lenses by slickensides. The central parts of these lenses are like the flint clay.

(3) (Specimen No. 23.) The aluminite is a buff or pinkish

rock of great toughness having a sharp but rough conchoidal fracture, the surfaces studded with oolites like those seen in bauxite, but of small size and seldom exceeding 1 mm. in diameter.

Section XX.—Clay from the top of the flint clay, Olive Hill, Kentucky.

Structurally this clay is similar to No. XI from Clarion, Pa. It is, however, richer in carbonaceous matter, which, along the cracks that served as pathways for solutions, had precipitated iron in the form of pyrite. Scattered through the clay are cloudy areas sometimes of circular outline and occasionally bearing remarkable likeness to the cross sections of feldspar fragments (Plate IV, Fig. 2). Crystallization of kaolinite prisms has formed clear patches in some of these areas, often producing radiate structures within, and more frequently about the periphery of the cloudy area (Fig. 7).

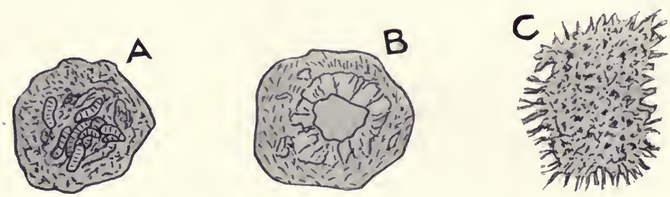


Fig. 7.—Types of structures characteristic of Olive Hill, Ky., clays.
a. An irregular mass of kaolinite prisms developed toward the center of a cloudy oolite.
b. Kaolinite grains or prisms producing radiate structure within oolite.
c. Radiating kaolinite crystals bordering an irregular clouded spot (possibly a weathered feldspar fragment).

Kaolinite is the most common mineral although hydromicas are to be seen, especially as ribs in the kaolinite.

Quartz, rutile, zircon and tourmaline are present in lesser amounts.

Section XXI.—Flint clay, Olive Hill, Kentucky.

This section closely resembles No. XX in mineralogical character, but is free from pyrite and contains much less carbonaceous material, and the structure is like that described in Section XI. There are traces of a sort of "mare's tail"[37] arrangement in the parts least crystallized. These structures are cut

[37] This term has been borrowed from meteorology where it is sometimes used to designate light wispy cloud structures.

by the concretionary and cloudy areas. It is thought possible that these structures were formed by movements during contraction of the colloidal jel, of which the clay was largely composed, as some of the water was squeezed from it by the weight of accumulating sediments above. Traces of such structures are to be found in all of the very fine-grained flint clays.

Kaolinite prisms (up to 70 microns length) show a great variety of bent and contorted forms. "Ribbing" by hydromicas is a prominent feature and is apparently responsible for much of the warping in the kaolinite prisms. Muscovite is practically absent.

Quartz may be seen in widely scattered corroded grains up to 400 microns diameter. Other accessory minerals are as noted in other sections.

Section XXII.—Prepared from powder of semi-flint clay, Olive Hill, Kentucky.

This section shows largely individual plates, but also many aggregate grains, indicating that the development of hydromicas in this clay is not as complete as in some of the semi-flint clays from other localities, for the development of hydromicas seems to accompany any movements in the clay which tend to loosen up the individual plates, resulting in more complete disintegration into individual grains upon grinding.

The main mineral seen is hydro-mica. No kaolinite was identified, but is doubtless present to some extent.

Muscovite is not common, and the same is true of quartz and the other common accessories.

Section XXIII.—Highly aluminous flint clay, Olive Hill, Kentucky.[38]

Here one sees numerous concretions or oolites (Plate V, Fig. 1) scattered through a fine-grained ground mass, which is similar to that of Sections XX and XXI, but for fewer kaolinite prisms and occasional patches of mineral grains which show a higher index than kaolinite, and a structure differing somewhat from that of mica. Careful determinations of elongation, extinction and birefringence together with comparison to known hydrargyllite (gibbsite, $(Al(OH)_3)$ lead to the conclusion that

[38] The aluminite of Greaves-Walker.

PLATE V.

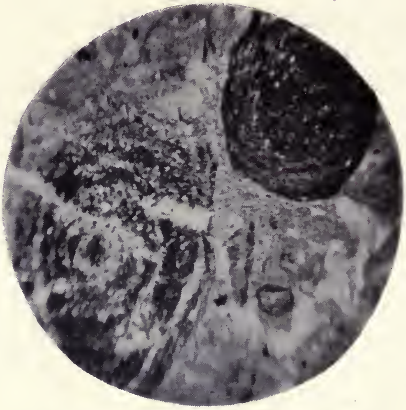


Fig. 1.—So-called "Aluminite," from Olive Hill, Ky., by direct light. Shows structure of oolites × 80.

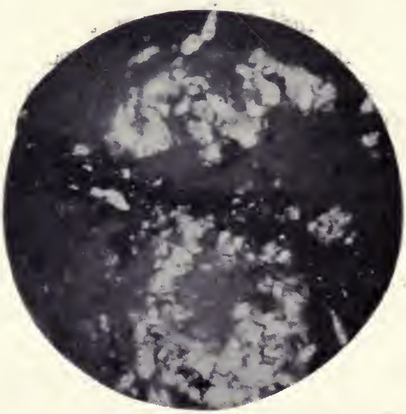


Fig. 2.—Section of "Aluminite" from Olive Hill, Ky., between crossed nicols. Shows hydrargyllite (gibbsite) recrystallized in central part of the oolite represented in Fig. 1 × 200.

these bunches are composed of grains of that mineral (Plate V, Fig. 2). It is more common in the oolites than in the ground mass. Here it is seen in nucleal groups and concentric bands separated by rings of cloudy, extremely fine-grained material which may be a bauxitic mixture.

Kaolinite prisms are rare in the oolites but are closely associated with the hydrargyllite in the ground mass. The hydrargyllite may represent the recrystallization of hydrous alumina which was present originally in the sediments.

This clay seems to represent an intermediate phase between kaolin and bauxite.

Dehydration of the Olive Hill clays gave the following results:

DEHYDRATION TESTS OF OLIVE HILL, KENTUCKY, CLAYS.

	Per cent. loss at 112° C	Per cent. ignition loss	Total per cent. loss
21 Flint clay.............	0.82	13.2	14.0
22 Semi-flint.............	0.96	11.7	12.7
23 "Aluminite"...........	0.4	13.0	13.4

The "semi-flint" shows similarity in water content to the Mt. Savage "flint" and the Woodland "soft" clay.

The aluminite, despite the lower amounts of kaolinite to be seen, shows a fairly high water content due to the presence of some hydrargyllite ($Al(OH)_3$).

OTHER CLAYS EXAMINED.

For purposes of comparison, a microscopic examination was made of the following clays:

Missouri flint clay (ground section).

Washed kaolin from Quebec (prepared from powder).

Washed Delaware kaolin (prepared from powder).

Halloysite from Alabama (prepared from powder).

Indianaite from Indiana (prepared from powder).

Tennessee ball clay (prepared from powder).

Plastic New Jersey fire clay (prepared from powder).

St. Louis fire clay, hard (prepared from powder).

St. Louis fire clay, soft (prepared from powder).

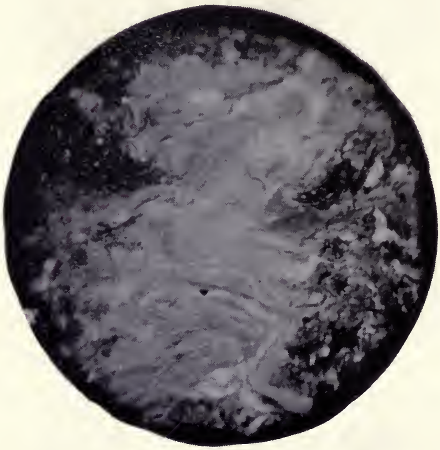
MISSOURI FLINT CLAY.

This is a cream-colored clay, having a fair conchoidal fracture and a more earthy luster than the other flint clays examined. The mode of occurrence has been briefly pointed out in the introduction to this paper.

Section XXIV.—Flint clay from Missouri.

This clay is structurally like Nos. XX, XXI and XI, but shows much greater development of the "mare's tail" feature (Plate VI). The texture is much finer than that of any other clay ex-

PLATE VI.



Section of Missouri flint clay between crossed nicols. Shows the mare's tail structure and the extremely fine grained crystalline texture × 300.

amined, there being comparatively few mineral grains of size sufficient for identification.

The minerals determined are (1) kaolinite prisms, occasionally somewhat "ribbed;" (2) minute scales of muscovite; (3) hydrargyllite (gibbsite) (?). Of this last mineral we cannot be certain as the grains were too small for identification. Their close resemblance to those seen in Section XXIII leads us to classify them as such, especially as the Missouri clays often show percentages of alumina higher than that of kaolinite.

Wheeler has noted in his work on the Missouri clays[39] that

[39] Mo. Geol. Surv., Vol. XI, 1897.

the water content of the flint clays often exceeds that of theoretically pure kaolinite, and suggests that it may be caused by the presence of some mineral such as pholerite, or possibly by the admixture of kaolinite and bauxite. The latter view seems more probable from the examination of a single slide and also from the fact that of the hydrous aluminous minerals, only kaolinite, muscovite, hydro-micas, and hydrargyllite were identified in sections of several of the eastern flint clays.

WASHED KAOLIN FROM QUEBEC.

While the greater part of this powder is composed of very small particles there are numerous crystalline grains which sometimes reach lengths of 50 to 60 microns. Many of these grains are platy, with low index of refraction and the optical properties of kaolinite usually seen. Two or three well developed fans of the same mineral were noted, but it is probable that most of these fans that exist in the crude kaolin are broken up during the process of washing. A few good tourmaline prisms were seen and occasional flakes of mica.

A chemical analysis of this kaolin showed it to be of almost theoretical purity. Its loss on dehydration was 14 per cent.

WASHED DELAWARE KAOLIN.

The powdered material is seen to be composed largely of clear transparent plates, the largest of which are as much as 100 microns across. Their outlines are usually irregular but some are seen which are hexagonal. Some of the smaller grains are more fibrous than platy. When mounted in a liquid having a refractive index of 1.54 their edges become indiscernible, showing that the index of the plates is close to that of the liquid. The interference colors range downward from grays of the first order. Extinction is nearly parallel and in some cases quite so. A few of the plates are of a slightly yellowish color. No fan or prism-like aggregates were noted, but may be present in the kaolin as the process of mounting would tend to break them down. The mineral is doubtless kaolinite.

Some mica-like flakes are present, as are also numerous small fibrous bunches which show the properties of the hydromicas. A few angular quartz grains were noted as well as some small grains taken to be zircon though not definitely identified.

HALLOYSITE FROM ALABAMA.

Numerous platy grains are seen in the halloysite powder, but when viewed with magnifications of 600–800 diameters, these grains seem to be composed of many smaller ones, the optical properties of which could not be determined although they seemed to be weakly doubly refracting. Some small plates of muscovite were the only grains which could be identified with certainty. The refractive index of the unidentified material seemed to be above 1.554, suggesting the possible presence of hydrargyllite.

Upon dehydration the halloysite lost 15.5 per cent. of its original weight.

INDIANAITE.

The powder is mainly crystalline in plates and grains ranging from 80 microns down. The plates often show a roughly hexagonal outline frequently elongated parallel to one of the diagonals. They have but slight effect upon polarized light. There are also fans or bunches of plates which in many cases show the "ribbing" so characteristic of the prisms in the flint clays. The double refraction is a little higher than that usually ascribed to kaolinite, but the agreement of other properties favors this mineral.

Quartz and zircon grains are present and also a very little greenish mica. Some sharply angular fragments, possibly of opal, have been noted. About 60 to 70 per cent. of the Indianaite seems to be made up of crystalline kaolinite or a very similar mineral.

TENNESSEE BALL CLAY.

This powder is composed of apparently crystalline granules too small to identify (less than 1 micron diameter). A few grains are present which seem to be zircons. Much of the material has a refractive index of about that of kaolinite and very likely is that mineral.

NEW JERSEY FIRE CLAY.

This powder is of finer grain than that obtained from any of the semi-flint clays. No grains were seen to exceed 15 or 20 microns. The coarser grains are frequently platy and occasionally show roughly hexagonal outline. Their index is below 1.554, but was not determined more definitely than that. They are thought to be kaolinite. Quartz and zircon grains were seen as well as a few muscovite flakes.

HIGHLY ALUMINOUS FIRE CLAYS FROM NEAR ST. LOUIS.

These two samples were sent by the Laclede-Christy Clay Products Co., both being obtained from Missouri. They have the following chemical composition, as determined by R. T. Hipp, Ceramist.

	178	165
SiO_2	45.45	31.89
Al_2O_3	38.92	51.57
Fe_2O_3	1.42	1.17
CaO	0.1	0.63
MgO	0.32	0.34
Alkalies	0.83	0.68
Water (combined)	12.35	12.99
TiO_2	0.49	0.49
	99.86	99.74

No. 178.—This is a hard gray clay (so-called flint clay) which, however, becomes plastic when ground.

The powder is composed of minute grains of crystalline appearance. The largest do not exceed 15 microns in diameter. Only a few grains could be determined among which were quartz in angular grains, mica scales and a few flat plates resembling kaolinite.

No. 165.—This is a soft clay, the sample examined being in small gray pellets, which are too hard to be crushed between the fingers.

Much of the powder is in a state of too fine division for purposes of identification, but there are numerous platy grains which sometimes measure 25 microns in greatest diameter. These grains are irregular or more rarely somewhat rhombic in outline. The refraction index is considerably above 1.54, and the birefringence is medium to high. Extinction seems to take place parallel to the diagonals of the rhombs, in which the longer diagonal is the direction of least elasticity. The prevalent angles in the rhombs are about 80°, although there is considerable variation from this angle.

It seems probable that these grains represent basal plates of hydrargyllite prisms.

The high percentage of alumina which the clay shows might in itself be taken as evidence of the presence of some hydrate of alumina, but if this excess is due to hydrargyllite the balance of the clay must be rather low in water content.

CHEMICAL TESTS.

Before making a microscopic examination of the flint clays it was thought that something might be learned concerning their constitution through their behavior towards acids. Accordingly several of the clays were powdered and digested with dilute H_2SO_4 for three hours. The residue was then filtered off and the iron and alumina precipitated with ammonia, filtered off, washed, ignited and weighed. Inasmuch as the iron present was never sufficient to more than tint the precipitate it was neglected. The precipitation was digested with HF, and again weighed, the figure last obtained being recorded as "soluble alumina."

The results are tabulated below:

Sample No.	1	21	22	23	4	Halloysite
% Al_2O_3 sol. in 15% H_2SO_4..	9.57	7.84	15.66	27.44	4.44	31.1

1, Flint clay, Strasburg, O.; 21, flint clay, Olive Hill, Ky.; 22, semi-flint clay, Olive Hill, Ky.; 23, "aluminite," Olive Hill, Ky.; 4, flint clay, Missouri; halloysite, Alabama.

Exclusive of the "aluminite" and halloysite, the solubilities shown are proportional to the readiness with which these clays are reduced to individual grains.

Washed Delaware kaolin was similarly treated, using concentrations of 10, 15, 20 and 25 per cent. H_2SO_4.

Strength of acid	10%	15%	20%	25%
% soluble Al_2O_3..................	4.46	4.55	5.1	6.5[40]

[40] These figures represent the average of two determinations.

It was concluded from these results and the microscopic examination that the solubilities in dilute H_2SO_4 are more an evidence of the fineness of the powders than of different mineral content except in cases such as the "aluminite" which has since been shown to contain ($Al(OH)_3$) and the halloysite, the mineral composition of which could not be determined because of its fine texture.

These results may have considerable bearing on the value of sulphuric acid as a reagent for use in rational analysis.

It may be seen from the foregoing data that the assumption that kaolinite is the basic mineral of all highly aluminous clays is in a few cases incorrect, as in the instance of those "soft" or semi-flint clays in which the development of hydro-micas is greatest. No evidence has been found, in this investigation, pointing to the existence of any other hydrous aluminum silicates as important minerals in the purer clays although a rather wide range of materials has been included. The presence of alumina in excess of percentages allowable for kaolinite may frequently be attributed to the existence of hydrargyllite in a clay, and it seems possible that diaspore (Al_2O_3, H_2O) may also occur at times.

Comparison of the flint clays and their associates with other highly aluminous clays, shows that the main difference is in texture. In the flint clays the kaolinite crystals are knit together so tightly that when the clay is crushed they break out in aggregates rather than as individuals. In the semi-flint clays, the crystals though larger than in the flint clays are not so tightly interlocked and so become separated on grinding, producing some plasticity. In the plastic clays, the crystalline particles are smaller and at the same time more or less separated, due either to considerable disintegration of a once crystalline clay, or to a lack of any great amount of original crystallization. Kaolins differ from the flint clays in having crystallized under conditions of less pressure, allowing a more open structure, which may account for the fact that they are frequently less pure than the flint clays because of infiltration of foreign matter. Any attempt, however, to do more than point out general causes for differences in the various clays, must be based upon a most intimate acquaintance with all of the different deposits, which it has not been the writer's good fortune to acquire.

THE NATURAL HISTORY OF THE FLINT CLAYS.

The origin and the nature of the flint clays have always excited interest, and yet but few attempts have been made to explain why or how they come to be so different from the plastic clays.

E. Orton, Sr.,[41] Wheeler[42] and Hopkins[43] have advanced the view that the flint clays owe their hard and non-plastic character to part or complete crystallization of kaolinite in them. The soft, semi-plastic and plastic clays associated with them are considered to be much less crystalline and finer grained. The investigations described in this paper have led to a theory of formation which agrees only in part with these earlier views.

The land surface from which the clay-forming sediments of carboniferous times were derived was presumably rather low and traversed by sluggish streams. The rank types of vegetation which flourished are taken to be evidence of a warm climate, perhaps even subtropical in nature. The rocks which were being disintegrated and decomposed were mainly sedimentaries of Devonian and Silurian age. The weathering processes which were then active were more or less such as are active at the present time in hot moist climates, producing lateritic soils[44] which were richer in alumina and iron than soils of temperate climates.[45] As these soils were carried away by streams to be deposited in bogs, swamps or lagoons, part of their iron content was dissolved by carbon dioxide, resulting from vegetable decay in the water. As the sediments were laid down they became the soil in which the coal-forming plants flourished and here

---

[41] Geol. Surv. Ohio, VII, Part 1.

[42] Geol. Surv. Mo., XI.

[43] "Clays of Western Pennsylvania," Ann. Rept. Penn. State College, 1897.

[44] Lateritic weathering has been shown by many investigators to result in a reduction of silica, alkalies and alkaline earths and a concentration of alumina. See M. Bauer Neues Jahrb. Min. Geol., 1907, p. 33–90; Chaubard and Lemoine, Compt. rend., **146,** p. 239–42. Others have found kaolinite to be formed also, E. C. Mohr, Bull. Dept. l'Agric. Ides. Neerld. No. 28; R. Lenz, Neues Jahrb. Min. Geol., 1909, II, 347.

[45] The deeply corroded quartz grains so frequently noted in the flint clays may be taken as a further evidence of lateritic weathering.

they were further purified by the leaching action of plant roots and the carbonated waters of the bogs.

It may be pointed out then that the sediments of the clay beds must have been rather free from iron, calcium, magnesium, potassium, and sodium when laid down, due to their having been reworked and to the fact that the waters of the carboniferous streams were probably unusually high in their content of carbon dioxide. If we consider, further, that these clays usually served as soil in which coal vegetation was rooted, further purification is to be expected for it has been shown that plant roots are very active in removing lime, potash, and also magnesia, soda and iron to lesser content.

It then seems probable that when first laid down these clays were very fine grained, hydrous aluminous silicates with varying amounts of hydrous alumina as a result of the lateritic weathering. The amounts of impurities were probably as low as at present, when consolidation began, for it does not seem possible that there could be much circulation of leaching solutions through the settling clay mass.

Every fine-grained sedimentary deposit must include a large per cent. of water when first laid down, and this would be especially true of a clay bed. As soon, however, as any pressure was brought to bear the pore water would begin to filter out, carrying with it some soluble material. Eventually only enough water would remain to fill the spaces between the component particles of the clay provided no changes took place in these particles. Changes, however, do take place since the equilibrium of the surface weathering zone is not the same as that of the buried deposit. Recrystallization[46] then sets in, resulting in a compacting of the mass; and in some cases the excess water collects in fissures and cracks formed by the contraction attendant upon recrystallization. These fissures, under increasing load of overlying sediments, become filled by the squeezing in of fine particles and colloidal material along with the water. The brecciated appearance of the Woodland, Pa.,

---

[46] According to Doelter (Min. Pet. Mitth., XXVIII, p. 557–9) amorphous substances (such as colloidal $Al(OH)_3$, etc.) may be made to crystallize by digesting at 60°–70° with water. It seems quite probable that the heat produced by decomposition in the overlying coal or peat was sufficient to bring about recrystallization in the underlying clay.

clay, and the dark waxy lenses frequently seen in other flint clays seem, in my opinion, to represent such changes. The filling material, as seen, usually contains fewer impurities than the surrounding clay. This may be explained on the ground that the small amount of alkali present, when the fine sediments were laid down, was taken up to form sericite and hydro-micas during the early stages of recrystallization. The hydrates of iron in the presence of a considerable amount of carbon dioxide formed siderite (as seen in Section VII); and it is of interest to note that sericitic scales are practically wanting and hydro-micas less common in this than in other flint clays due, it may be presumed, to the removal of the alkalies by the excess of carbon dioxide. When iron carbonate was not formed, most of the iron became enmeshed in the matte of growing crystals, remaining, as seen in many sections, as a sort of scum in the less altered parts of the clay. The fixation of these impurities left the material which filled the skrinkage cracks in a purer condition, so that on recrystallization a nearly pure kaolinite mass resulted. The noticeably white-burning character of the "dark" patches is explained on these grounds.

The crystallization of kaolinite and hydro-micas in the flint clays has gone on at about the same time as is indicated by the fact that many of the kaolinite prisms contain plates of the higher index mineral. From all the evidence I could gather through examination of numerous thin sections, there seems to be an isomorphous or nearly isomorphous series of minerals, ranging from kaolinite through to muscovite. Sometimes in a single prism there may be seen sections or plates whose optical properties vary between those of the aforesaid minerals as limits. Usually the plates of higher index are distributed through the central portion of a prism, indicating that the kaolinite continued to form after the available alkalies had been used in the growth of muscovite or the hydro-micas. There is not, however, any appearance of growth of the kaolinite at the expense of the micas. Hickling[47] has described kaolinite prisms from some of the English china clay deposits which show a variation from kaolinite to mica. He considers that there the musco-

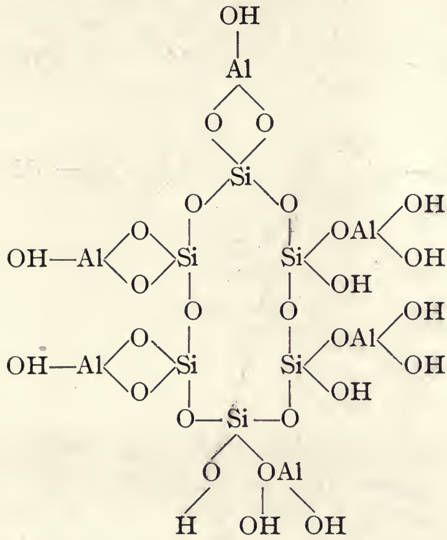
[47] "China Clay, Its Nature and Origin," Trans. Inst. Min. Engrs., Eng. XXXVI, p. 10, 1908–9.

vite represents a transition stage in the weathering of feldspar to kaolin, which is doubtless correct.

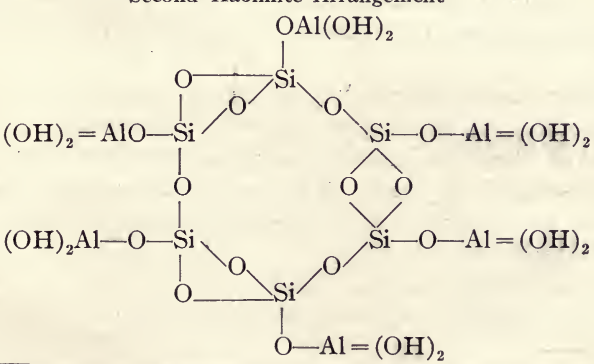
The apparent transition from sericite to kaolinite has been noted in other instances.[48]

Although the empirical formulae commonly used for the micas and kaolinite do not give great resemblance, it is possible to so construct them that they will show much similarity as follows:

Kaolinite $3(H_4Al_2Si_2O_9)$

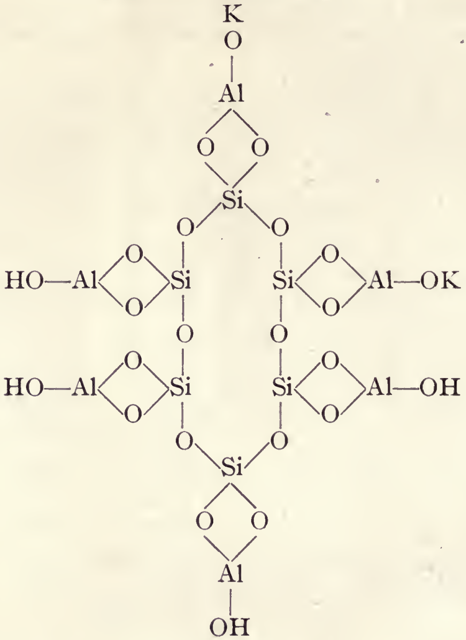


Second Kaolinite Arrangement



[48] V. Selle, Chem. Cent., 1908, **11**, 1903.

Muscovite $2(H_2KAl_3Si_3O_{12})$



Although such structural symbols are largely speculative, they are given because they are suggestive. The change from muscovite to kaolinite is accomplished through the replacement of two (KO) groups by two (OH) and the addition of $3H_2O$. In a molecule of the size postulated such an addition would not of necessity change either form or molecular volume to a great extent.

Mellor and Holdcroft[49] have classed muscovite chemically with kaolinite saying that in muscovite there appears to be an addition of three kaolinite groups where two (OH) are replaced by equivalent (KO) groups. They propose a formula for kaolinite, however, which joins all of the hydroxyl groups with the alumina thus:

$$\begin{matrix} (HO)_2 = Al - O.SiO \\ (HO)_2 = Al - O.SiO \end{matrix} \, O$$

[49] "The Chemical Constitution of the Kaolinite Molecule," Trans. Eng. Cer. Soc., Vol. X.

This arrangement is based largely on the fact that dehydration curves for kaolinite show no discontinuities of constitution.

Some other investigators have favored distributing three hydroxyl groups between both Si and Al. Among these are F. W. Clarke,[50] F. Hundeshagen,[51] W. Vernadsky,[52] G. Simmonds,[53] and W. Pukall.[54] P. Groth[55] and F. Ulffers[56] favor symbols similar to those of Holdcroft and Mellor.

The second kaolinite formula would conform somewhat to the ideas of the latter, but the objection is apparent that the substance should be hexagonal (trigonal) with such a symbol. In either case the possibilities of isomorphism between kaolinite and muscovite seem fair. On the other hand, it may be that isomorphism extends only to the complete replacement of K by H; and that with the addition of water a molecule is built up which, though not capable of forming isomorphous mixtures with the micas, is sufficiently similar to be oriented through contact with them. I am inclined to believe in complete isomorphism since the analyses of muscovites show considerable variation of hydrogen and alkali content, water frequently being present up to 6 or $6^1/_2$ per cent. often as an *addition* in part but occasionally *replacing* the alkali. To my knowledge, no mica has been reported in which the alkalies have been totally replaced, yet such an occurrence does not seem impossible or improbable except for the fact that alkalies are usually present to a slight extent where micas are forming. Such a mica would have the theoretical composition: $H_3Al_3Si_3O_{12}$, or in per cents., $H_2O = 7.5$, $Al_2O_3 = 42.4$, $SiO_2 = 50.1$.[57] There would then be two classes of micas showing water content in excess of the theo-

---

[50] "Constitution of the Silicates," 1896.

[51] Zeit. angew. Chem., Vol. XXI, 1908.

[52] Zeit. Kryst., Vol. XXXIV, p. 37, 1901.

[53] Jour. Chem. Soc., Vol. LXXXIII, p. 1449, 1903.

[54] Chem. Zeit., Vol. XXXIV, 610–13.

[55] "Tabellarische Uebersicht der Mineralien," p. 137, 1898.

[56] Jour. prakt. Chem. [2], LXXVI, p. 143, 1907.

[57] Brackett and Williams (Am. Jour. Sci., XLVII, ii, 21, 1891) have described a mineral which they call rectorite, having a theoretical composition of $H_2Al_2Si_2O_8$ (Al_2O_3 42.52 per cent., SiO_2 49.99 per cent., H_2O 7.4 per cent.), which is biaxial, strongly birefringent, with a refractive index *below* balsam (1.54). The properties of the hydro-micas are very similar to this mineral, except that the refractive index in them is considerably above that of balsam.

retical amounts: (1) the hydrated muscovites in which the excess water is in the nature of an addition, and (2) the hydro muscovites in which the water replaces alkalies. It seems probable that both types are represented in the flint clays, when the first recrystallization had taken place in the presence of an excess of water and a want of sufficient alkalies for the formation of muscovite only.

It is therefore suggested that the consolidation of the largely colloidal sediments took place partly as the settling of a colloidal gel, but mainly as a recrystallization of their hydrous aluminum silicates, with the formation of minute interlocking crystals of kaolinite and hydrated micas, resulting in the formation of the flint clays.

During and after the "setting" of the flint clays there were forces at work tending to break them down. These forces were (1) pressure, both from the weight of overlying sediments and from compressive movements of the earth's crust, (2) heat derived partly from chemical changes that were taking place in the coal measures and in part from the friction of rock structures as they became readjusted to accommodate the changing pressures. The effect of heat and pressure on the flint clays was, first, to break up the outer parts of the bed with numerous fractures along which there was some slipping, and, second, to cause a dehydration and metamorphism of the parts so broken up. The extent to which this action was carried depended upon the local conditions. The Clarion clay bed was apparently affected but little, probably because of the massive sandstone strata above and below which protected it from unequal local pressures. The clays at the other localities show varying amounts of metamorphism. At Mt. Savage, where pressures were probably most active, the flint clays often occur only as lenses, the original bed having been broken across in many places by the local faulting. The usual irregular boundary between the "flint clay" proper and the more or less plastic clay associated with it is also readily explained by this view. The metamorphism which accompanied the fracturing and faulting resulted in the development of hydro-micas mainly, especially in the parts where movement and friction were greatest. That the kaolinite has lost part of its constitutional water, especially the smaller crystals, seems certain from microscopic examination of the "soft" and semi-plastic clays; and the results of dehydration tests show rather conclusively that the water content of some of the clays is close to the theoretical amount required for a pure hydro-mica.

The clays of this metamorphic type are known at various localities as "soft," "semi-hard," or "semi-flint" and "semi-plastic" clays. They show greater plasticity than the true flint clays because the crystal prisms have been broken down largely into plates and the clay as a whole made more friable by countless small faults, so that with equal amounts of grinding the metamorphosed clay affords much more fine-grained platy material which will develop some, although not great plasticity.[58]

The development of truly plastic clays from the semi-flint varieties has sometimes been accomplished through weathering. After much of the overburden was removed and the pressure on the clay beds reduced, the fault planes began to open, allowing water to enter and begin the process of breaking down some of the mineral grains, at the same time usually to deposit some iron and traces of lime, magnesia and alkalies in the numerous capillary fissures. The continuation of this process for a sufficiently long time has produced rather plastic clays, which are at the same time less pure than the unweathered clays. Such clays are found at Mt. Savage and also at Strasburg, and at each locality the overburden is thin. At Mt. Savage, the drainage is such as to facilitate weathering processes.

It may be of interest to consider somewhat the interpretation which may be made of results obtained by others in experimenting with flint clays.

Wheeler[59] gives the fire shrinkage of the Missouri flint clays as ranging from 9 per cent. to 14 per cent.

---

[58] Cook ("Clay Deposits in New Jersey," p. 281), speaking of some kaolin clays, says: "Trituration, as rubbing between the fingers, breaks up the bundles and the mass is rendered thereby more plastic than in its original state." With the semi-flint clays the trituration was of a more rugged nature but equally effective.

[59] Loc. cit.

Purdy[60] records fire shrinkages for Olive Hill flint clay as 9 per cent. at cones 9–11 and 13.

Knote[61] gives fire shrinkage curves for Olive Hill flint and plastic clays, Clearfield County (Pennsylvania) flint and plastic clays, Mt. Savage flint clay and others.

At cones 11–13 they run as follows:

Clearfield County flint clay	5 4%
Mt. Savage flint clay	5.6–5%
Clearfield County plastic clay	6.2%
Olive Hill plastic clay	9.4–9%
Olive Hill flint clay	9%

If the Clearfield County flint clay tested was of the type described in this paper as "soft" clay, the increasing shrinkage noted by Knote is found in clays showing increasingly fine and interlocking grains. The Missouri clay being of finer texture than any of the others fits in well at the end of the groups. However, the variability of texture possible in any locality makes it difficult to do more than suggest that the differences in shrinkage in the flint and semi-flint clays depend, first, upon the amount of colloidal material present, and, second, upon the size of grain and texture of the crystalline parts.

Knote found also that changes in specific gravity of flint clays upon heating differed from those in plastic fire clays, the semi-flint clays showing intermediate variations. He further found that kaolins behave in this regard very much as do the flint clays, a fact which accords well with our finding that crystalline kaolinite is the principal constituent of these clays.

The "soft" and "plastic" clays derived from the flint clays should show varying degrees of difference in their physical changes upon heating, depending mainly on the extent to which metamorphism has acted in dehydrating the kaolinite, and weathering in breaking down the semi-plastic clays.

The porosity curves given by Knote (*l. c.*) show a lower porosity at all temperatures for the semi-plastic clay than for

[60] "Pyrophysical Behavior of Flint Clays," Trans. A. C. S., X, p. 365–79.

[61] "Some Chemical and Physical Changes in Clays Due to the Influence of Heat," Trans. A. C. S., Vol. X. Knote examined several of the flint clays under the microscope but does not emphasize their crystalline nature. It seems probable that he worked with the powders, which do not give as satisfactory results as do the rock sections.

the flint. This may be explained on the ground that the former have less constitutional water, and so upon dehydration would show less porosity, and that at higher temperatures their more micaceous nature would tend to reduce this absorption since Rieke[62] has found that muscovite cones become denser at cone 10.

It would seem also that the porous structures produced when the fragments of flint clay become dehydrated should make the material more refractory except in cases where gases containing fluxing elements come in contact with the clay.

Under such conditions it would seem that a less porous clay would have the advantage.

Those who are better acquainted with the uses of the flint clays may find other adaptations for the data obtained in this investigation.

SUMMARY.

From geologic occurrences, dehydration tests and microscopic examination the conclusions are drawn that:

(1) The flint clays have been formed by the setting and recrystallization of fine-grained largely colloidal sediments which have been purified mainly through the agency of carbon dioxide in the waters transporting and depositing them, and by the leaching action of plant roots. The products of recrystallization are mainly kaolinite, with minor amounts of hydrated micas.

(2) The "semi-flint" or "soft" clays have been derived from the flint clays through metamorphism by pressure and heat resulting in a conversion of much kaolinite into hydro-micas and the development of a completely microcrystalline structure of coarser texture than that of the original flint clay.

(3) The plastic fire clays associated with the flint clays have resulted from long weathering of the "semi-flint" or "soft" clays and are structurally more crystalline than the fire clays which have never been "set." They also differ from those clays in containing a high percentage of hydro-mica, kaolinite in all probability forming the base of other plastic fire clays.

---

[62] "The Effect of Muscovite upon Kaolin," Sprech., XLI, p. 577–83.

(4) The change from muscovite through hydrated or hydromicas to kaolinite may take place without destruction of the original structure, indicating the possibility of an isomorphous series embracing all of these minerals.

(5) Knowledge of the microstructure and composition of a clay may be used to explain and predict peculiarities in its physical and chemical behavior.