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Bollinger County, Missouri"

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Introduction

The southeastern Kaolin district of Missouri comprises a number of counties, the most important of which are Cape Girardeau and Bollinger. Kaolin deposits are also known in Perry, Ste. Genevieve, Madison, Iron, Reynolds, Wayne, Carter, Ripley, Oregon, Shannon, Texas, Howell, and Ozark Counties.

This report is concerned only with the kaolin deposits in the Glen Allen-Lutesville area of Bollinger County. At the present time, no kaolin is being mined from this area, but during the early part of this century fairly large quantities of kaolin were produced for pottery manufacture in eastern Missouri.

Prospecting and mining have been carried on in only a small portion of the kaolin district. This is probably due to a decrease in demand for these kaolins as a result of unsuitable mining and processing methods employed in the past. The methods employed did not offer a uniform product to the ceramic industry. Underground mining methods were used in the past, and a costly operation was involved in extracting only the pure white material from the stained kaolins mixed in the same deposit. The kaolins also contained a large percentage of fine-grained free silica, which was not easily removed by washing and caused additional difficulty in processing the clays.

Topography and Drainage

The Glen Allen-Lutesville kaolin district is upland country and is nearly fully dissected. Most of the hills are well rounded and even crested. The upland surface bevels the southeastern regional dip of the strata. The area is well drained by Crooked Creek and Hurricane Creek and their tributaries. The water carried by these streams enters the Diversion Channel drainage ditch to the southeast and from there flows into the main drainage system of the Mississippi River.

Valleys in the area have reached the mature stage, having fairly steep valley walls and wide flood plains. The flood plain deposits are from 12 to 20 feet thick and contain large amounts of chert (Heller, 1943, pp. 5-6).

Stratigraphy

The kaolin district lies on the southeast flank of the St. Francois Mountains and is physiographically part of the Ozark region. The rocks exposed in the district are chiefly of Ordovician age, but Cretaceous rocks form a thin patchy capping on the higher hills of the district (Stewart, 1943).

The kaolin district is located on belts of the Ordovician Roubidoux, Jefferson City, and Cotter-Powell formations. The Roubidoux formation consists essentially of intercalated sandstones, sandy dolomites, and dolomites containing considerable chert. The lithology of the formation is variable, in that thick beds of sandstone grade laterally and vertically over relatively short distances into dolomite and sandy dolomites. Dolomites in the Roubidoux formation are mostly light gray, thick-bedded to massive, fine-grained, and dense. The thick-bedded sandstones in the Roubidoux are medium-grained, well-sorted, friable, and porous. The chert in the Roubidoux is of several varieties. The most common type occurs as nodules and lenses, and occasionally contains scattered sand grains and cavities filled with crystalline quartz. Conglomeratic white chert is present locally, and a persistent bed of brown oolitic chert occurs near the top of the formation.

The Jefferson City formation is very irregular and variable in lithology, ranging from finely crystalline, gray dolomite through tan, argillaceous dolomite, sandstone, chert, quartzite, and shale. Most of the argillaceous dolomites are thin-bedded. The crystalline dolomites are less argillaceous, and are both thin-bedded and thick-bedded. They are hard, dense, and have but little pore space. The sandstone beds of the Jefferson City formation are very irregular and discontinuous, varying in thickness from one inch to four feet. Chert commonly occurs as nodules and lenses in the dolomite. These nodules vary greatly in size, shape, color, and texture. Shale beds make up only a very subordinate part of the Jefferson City formation.

The Cotter-Powell formation is made up chiefly of dolomite, with subordinate amounts of chert, sandstone, and shale. Much of the formation is tan to gray, hard, finely crystalline dolomite, particularly in the lower part. In the upper part, argillaceous dolomite predominates.

The sandstone members of the formation are usually thin, except for a thicker basal unit. The sand is white, loosely consolidated, and medium- to fine-grained, although it may be highly colored by iron-oxide, very firmly cemented by silica, and somewhat coarser-grained.

Patches of Ripley formation of Cretaceous age (Heller, 1943, p. 58), which cap the higher hills in the district, are made up of clay, quartzite, and gravel. The clay is white to bluish-white in color, and many of the clay outcrops have Smithville fossils in them. The quartzite which forms large blocks capping the higher hills is white to gray in color, medium-grained, and very firmly cemented. The gravel beds are made up of well rounded quartz pebbles, which cover the surface of the ground.

Structural Geology

The regional dip of the Paleozoic rocks is about 1½° to the southeast, but there are depressed blocks, steep local dips, low domes, and shallow basins.

Around Marble Hill, there are seven areas where rocks of Middle Ordovician, of Lower and Middle Silurian, and of Lower Devonian age rest on and are associated with rocks of Lower Ordovician age. The rocks of the various formations are represented by jumbled blocks of various shapes and sizes. The blocks in the various fault areas show no definite alignment, but the general trend of each fault area is east-west. The fault areas as a group have a nearly northwest-southeast trend.

Heller (1943, p. 103) believes that the present position of the blocks in the fault areas is the result of terminal faulting which accompanied successive downwarpings of the embayment region. At the time of the faulting, the Lower Ordovician rocks, which now form the country rock in the area, were overlain by Plattin, Kimmswick, Girardeau, Brassfield, Bainbridge, and Bailey formations. Large blocks of these formations broke loose and dropped into the cracks that were forming simultaneously with the downwarping in the embayment region. Later, these blocks were covered by loose earth and in some places by Cretaceous clay, and have only recently been exposed by erosion. The faults have been dated by Heller (1943,

p. 104) only as post-Bailey in time.

Stewart (1945, p. 24) suggests that there was recurrent movement during post-Cretaceous time on these fault planes, as he found Cretaceous clays in the depressed blocks. These Cretaceous clays are found well below the normal level and were not exposed to weathering.

Occurrence of the Kaolin Deposits

In addition to the deposits of kaolin which have been mined in the past, many outcrops of kaolin have been reported in the Glen Allen and Lutesville area. Although most of the outcrops are small and not mineable, their presence indicates the distribution of the kaolin.

In general, the kaolin deposits occupy pockets and depressions in the underlying bedrock. However, this is not the case in all outcrops which have been reported. The deposits which have been worked in the past are limited in lateral extent, and usually grade into solid walls of chert, sand, sandstone, or dolomite. These deposits appear to occupy solution channels and sinkholes in the underlying formations. Some of the outcrops of the kaolin, too small for mining operations, often are found as bedded deposits and give no indication of occurring in depressions of any type, but appear to be highly weathered material which previously had been deposited upon the underlying bedrock.

The kaolin deposits usually grade upward into soft sand or chert rubble. This is also the case below the kaolin, except that in some of the mines, kaolin clay rested directly upon hard, firm dolomite.

In some cases, the kaolin appears as bedded deposits, formed under relatively quiet waters. In other cases, the kaolin is mixed with chert or sand, and the mass appears to be residual in character. The latter condition obtains for the majority of deposits. The sand associated with the kaolin is usually micaceous and unconsolidated, and is similar to that found in the Crowley's Ridge area farther southeast (Stewart, 1945, p. 25).

It is quite likely that the clay and sand were deposited during Cretaceous time in pre-existing depressions in the underlying bedrock, or were deposited upon the underlying formations and subsequently let down into depressions which developed after deposition of the clay and sand. At any rate, deposition of the clay was followed by supergene processes which promoted leaching of the material and development of the kaolin.

Locations of Kaolin Deposits near Glen Allen, Bollinger County

Name of Pit	Location			
Stevens	NW¼ NW¼	sec. 4	T. 30 N.	R. 9 E.
Bauscher	NW¼ NW¼	" 4	"	"
Snyder	SW¼ NE¼	" 4	"	"
Sharp	SE¼ SW¼	" 4	"	"
Slemmer	NE¼ SE¼	" 5	"	"
Sommers	NE¼ NE¼	" 7	"	"
Einwechter	NE¼ SE¼	" 9	"	"
Crawford	SW¼ NW¼	" 9	"	"
Reilly	NW¼ NW¼	" 10	"	"
McManus	NE¼ SE¼	" 10	"	"
Lutz	SE¼ NW¼	" 14	"	"
McClinick		" 14	"	"
Stemm	NW¼ SW¼	" 15	"	"

Locations of Kaolin Deposits (continued)

Name of Pit	Location				
Dobschutz	NW¼ NW¼	sec.	15	T. 30 N.	R. 9 E.
Waldo	SW¼ SE¼	"	15	"	"
Jones	SE¼ NW¼	"	15	"	"
Weasmer	E line	"	16	"	"
Smith	SE¼ NW¼	"	4	"	"
Cushman	NW¼ NW¼	"	17	"	"
Low	NE¼ NW¼	"	17	"	"
Pat Huskey	NE¼ NE¼	"	18	"	"
Lyley	NE¼ NW¼	"	24	"	"
Nenninger	center	"	22	"	"

Review of Important Mines

Stevens-Bauscher pit

These two pits occur in the same vicinity and were operated at the same time intermittently in the past. They consist of a series of clay pits which have been quite extensively worked. One shaft was sunk to about 100 feet, and a drift was driven into the hillside for about 150 feet. At present, the shafts are all collapsed and only depressions exist. These depressions are 10 to 12 feet deep. Some kaolin float is present around the pits, and a pile of reject kaolin, approximately 20 tons, still remains on the surface.

Snyder pit

This pit is about 15 feet across, but is now collapsed and filled with loose dirt and rock debris. A few small pieces of float are visible on the surface. This pit was not too extensively worked, although several test pits are present in the area.

Slemmer pits

Several shafts had been sunk to depths of 60 to 75 feet, and good kaolin had been mined from two different levels. At present, the pits are all caved in so that an examination is impossible. The pits extend along the east side of a ridge which runs northwest from the house. Float or test pit material is scattered at various places between pits, and it appears that fairly recent testing has been conducted.

Sharp pit

A series of three small pits occur along the south side of Highway 34 about 2½ miles southwest of Glen Allen. The pits are all caved in at the present time, but small dumps are still present. There is some kaolin showing in the dumps, but the quality cannot be ascertained. The pits are 10 feet, 8 feet, and 4 feet in diameter, respectively, and the largest is about 4 feet deep.

Weasmer pit-Stemm pit

These pits are very close together and appear to have been operated at the same time. There are several pits, but the bulk of the kaolin was mined from two main shafts. There were other small shafts here also, from which clay was mined at two levels. Some float or reject material is present near the main shafts and farther down the hillside.

Nenninger pit

Three shafts had been sunk in this area. At present, all three are caved in quite badly and only depressions filled with loose rock material remain. Reject kaolin is seen occasionally in the area, but no kaolin is exposed in the pits.

Pat Huskey pit

Seven pits were operated here, but all are badly caved at the present time. Some old mining equipment is still present near the workings, particularly parts of a windlass which was used to haul up the kaolin. A little float or reject material is scattered in the area, and small piles of mine waste remain.

Reilly pit

This pit is about 12 feet in diameter, and is located about 200 feet west of a gravel road. This pit has not been worked for many years, and is presently badly caved. At present, the pit is only 4 feet deep. Only a few tons of kaolin had been removed from this pit during its active period.

Lutz pit

The Lutz pit, located not far from Dry Creek School, was not a large producer in the past. The only indication of former mining operations is a pile of mine waste material. No pit was observed, and it is presumed that the pit is partly filled in with the mine waste, which consists of chert and dolomite.

Theories of Origin of the Kaolin Deposits

Wheeler (1896, pp. 161-166) has advanced the theory that the kaolin was derived from the decay and solution of limestones and dolomites. The limestones and dolomites may have originally contained white kaolin and fine sand or possibly feldspathic sand previously unweathered, and during solution and removal of the limestones and dolomites, the clay beds and

Analyses of Kaolin Clay in Glen Allen area

	1	2	3	4	5	6	7
SiO_2	76.38	43.62	79.04	72.30	85.20	85.98	87.46
Al_2O_3	16.18	40.29	14.12	18.94	8.11	7.67	5.37
Fe_2O_3	0.00	0.00	0.50	0.40	0.87	1.04	1.61
TiO_2	0.50	1.41	0.58	----	0.20	0.30	tr
CaO	0.48	0.07	0.05	0.68	0.32	0.32	nd
MgO	0.55	0.00	0.42	0.39	0.33	0.66	0.26
Na_2O	0.56	----	0.00)	0.42	0.16	0.00	----
K_2O	0.12	----	1.09)		0.67	0.54	----
MnO_2	----	----	----	----	----	----	----
P_2O_5	----	----	----	----	0.22	0.43	----
S	----	----	----	----	----	----	----
Moisture	0.23	0.01	----	----	0.10	0.13	0.58
Ign. loss	5.25	13.81	4.73	7.04	2.72	2.90	2.44
TOTAL	100.25	99.24	100.53	100.17	98.89	99.97	97.72

1. Sec. 15, T. 30 N., R. 9 E., D. M. Long, Analyst.
2. Sec. 18, T. 30 N., R. 9 E., D. M. Long, Analyst.
3. Bauscher pit - NW¼ NW¼ sec. 4, T. 30 N., R. 9 E., R. T. Rolufs, Analyst.
4. Near Glen Allen, Rissman, Analyst.
5. Center of W½ sec. 16, T. 30 N., R. 9 E., R. T. Rolufs, Analyst.
6. Center of N line, NW¼ NE¼ sec. 18, T. 30 N., R. 9 E., R. T. Rolufs, Analyst.
7. NW¼ NW¼ NW¼ sec. 6, T. 33 N., R. 10 E., R. T. Rolufs, Analyst.

Analyses of Kaolin Clay in Glen Allen area (continued)

	8	9	10	11	12	13
SiO_2	72.98	77.27	64.47	39.84	71.42	61.98
Al_2O_3	18.89	17.03	16.40	41.38	13.77	13.34
Fe_2O_3				0.97	1.71	1.00
TiO_2				0.38	----	----
CaO				0.83	0.64	0.84
MgO				0.45	tr	tr
Na_2O				0.26))	6.50	----
K_2O				0.45)		----
MnO_2				----	----	----
P_2O_5				0.08	----	----
S				0.07	----	----
Moisture	6.28	5.70	8.66	15.45	----	15.02
Ign. loss					5.84	3.92
TOTAL	98.15	100.00	89.53	100.16	99.88	96.10

8. Dobschutz pit - NW¼ NW¼ sec. 15, T. 30 N., R. 9 E., R. T. Rolufs, Analyst.
9. Stevens pit - NE¼ sec. 4, T. 30 N., R. 9 E., R. T. Rolufs, Analyst.
10. Stevens pit - NE¼ sec. 4, T. 30 N., R. 9 E., R. T. Rolufs, Analyst.
11. Bollinger County, H. W. Mundt, Analyst.
12. Near Lutesville, R. T. Rolufs, Analyst.
13. Near Lutesville, R. T. Rolufs, Analyst.

fragmental chert layers were left behind as insoluble residues. These residual materials were not disturbed much or intermingled with other sediments.

Orton (1907, pp. 62-64) ascribes another probable source to the kaolin. He believes that the kaolin may have been derived from the granite rock of the Pilot Knob district, located about 20 miles northwest of Glen Allen. Erosion of these mountains has been heavy, and much of the detrital material has been carried to the southwest toward the Mississippi Valley. During the Pleistocene period, probably the sands, clays, kaolins, etc., were carried off to the southeast and spread over the country in irregular strata. However, the deposits are found both over and under the cherty clay which appears to be ordinary residual matter left by solution of limestone. The lack of stratification of these clays tends to refute this hypothesis (Herold and Sedalia, 1954, p. 2).

A third hypothesis, brought forth also by Orton (1907, pp. 62-64), states that the presence of a large amount of purple, pink, and red stains in the kaolin is organic material which disappears during burning. This condition suggests that some chemical processes have been operating, probably in connection with decay of organic coloring matter in its place.

Age, Correlation, and Possible Origin

The kaolin clay deposits near Glen Allen occur within a topographic interval of about 200 feet, lying between 560 and 760 feet above sea level. Stewart (1945, pp. 23-25) discovered bones of a sauropod dinosaur a few miles north of Glen Allen and has given an Upper Cretaceous age to the clay beds which contained the bones.

Heller (1943, p. 57) mapped irregular beds of clay, quartzite, and gravel capping the higher hills in the Glen Allen area and states that the clays have reworked Smithville (Ordovician) fossils in them. Stewart (1945, p. 25) has also mapped small patches of white and red plastic clay, orange unconsolidated sand, and rounded sandstone boulders in the deeper highway cuts along hilltops. The bleaching of these outcrops gives them the appearance of having been deeply weathered. In areas where faulting or deep solution channels have allowed the Upper Cretaceous sediments to be brought down below the zone of surface weathering, the lithology is quite different, being more like the Cretaceous exposures in Crowley's Ridge farther to the southeast. The clays are dark brown to black and contain stringers of fine, micaceous sand, which is fine- to medium-grained, and white to orange in color. Stewart (1945, p. 25) has correlated these sediments in the Ozark area with Upper Cretaceous Ripley formation of Crowley's Ridge and has based this correlation on lithology, color, texture, and general appearance.

Stewart (1945, p. 25) suggests that Upper Cretaceous beds once covered a large part of the Ozark area than formerly was indicated, and that post-Tertiary erosion has removed the bulk of these sediments, leaving patches of clay, quartzite, and gravel capping the hills in the area. The kaolin deposits represent the upper weathered zone of the Riple formation.

Chemical and Physical Characteristics of the Kaolin Clay

From his study of the kaolin deposits of Bollinger County, Orton (1907, pp. 79-82) concluded that the clays were unusual kaolins. He noted that the proportions of kaolinite and silica in these clays ranged from 30 percent kaolinite and 70 percent silica to 60 percent kaolinite and 40 percent silica. The average contained 45 percent kaolinite and 55 percent silica.

The most fine-grained sample passed a 200-mesh screen completely, and 60 percent of the coarsest sample passed a 200-mesh.

The clays contain a large amount of very fine-grained silica which is not easily removed by washing. Since these clays contain less than 60 percent kaolinite, Orton suggested that they are not typical kaolins and should be marketed as siliceous clays, usable with a flux in whiteware bodies.

The kaolins generally are plastic and possess very low strength in the dry and fired conditions. Drying shrinkage and firing shrinkage are both low. They are open-burning, and the kaolins from Bollinger and Cape Girardeau Counties do not fire to a hard body at comparatively high temperatures, as do kaolins from other localities. The pink and purple stained clays, as well as the white, usually burn to a light gray or white color.

<u>Uses of Kaolin Clay</u> (Klinefelter and Hamlin, 1957, pp. 43-46)

The greatest market for kaolin clay is as a filler and coater for paper. Kaolins are excellent for these purposes because of such characteristics as controllable particle size ranges, softness of texture, freedom from abrasive impurities, chemical inertness, brightness, good ink absorption, ease of dispersion, ability to produce a high gloss, and economy. These characteristics are unmatched by any other filler or pigment.

The second largest consumer of kaolin clay is the rubber industry, where color, stiffening and reinforcing properties, and low cost are important features.

The third largest consumer of kaolin clay is the ceramic industry.

Here the important features are the refractoriness and the white or cream color on firing.

Requisite Physical and Chemical Properties of Kaolin Clay

Although many kaolins are pure enough to be used in their crude state for many purposes, most of them are refined or beneficiated before being used for specific products. Beneficiation processes (Ries, 1949, p. 233; Kellogg, 1947, pp. 343-350) include washing, screening, tabling and classification, settling, air separation, centrifuging, and flotation methods. At the present time, flotation methods are not used in benefication of kaolin, as good separation is achieved by the other methods.

After refining, the kaolin of commerce is nearly white or light cream. It feels soft and fluffy and will slake completely in a few minutes if placed in water. Commercial kaolin lacks the smooth unctuousness of a ball clay and does not throw or jigger very well. The water of plasticity for kaolins (25 to 40 percent) averages well below that of a ball clay (Klinefelter and Hamlin, 1957, p. 6).

Three essentials are required of kaolin clays to be used for paper fillers or coaters. The clays must be free from grit, as this cuts the screens of the rolls; they must have the proper degree of brightness or color; and they must have the proper fine sizing, as coarse particles clog easily.

For the rubber industry, kaolin clays must meet the same requirements as for the paper industry.

When used in the ceramic industry, kaolins should be graded or compared according to the particular use to which they are applied. The most important characteristic of the chinaware clays is their essential freedom from coloring impurities, which are usually compounds of iron, such as oxides, sulphides, carbonates, sulphates, and silicates. Occasionally manganese, with its browns and blacks, or titanium in the presence of iron-oxide, with its browns, also prevent clays from being used for chinaware. The amount of iron that can be tolerated depends not only on the purpose for which the clay is used, but also on the amount of lime and magnesia present, both of which tend to neutralize and reduce the coloring action of the iron. The maximum iron content should not exceed 2.0%.

Titanium oxide in the presence of iron-oxide can probably exceed 3.0% before objectionable brown tinges are observed after firing. Lime and magnesia in small amounts give additional strength to the fire body. Both lime and magnesia act as fluxes and shorten the vitrification range of the clay.

Sulphur causes acumming of ware, which develops a dirty white color and gives the ware an unattractive appearance. Sulphur also causes a lowering of the fusion point, bloating, bleaching, roughening of the surface of unglazed ware, and blistering and spalling of glazes.

Manganese dioxide is an effective coloring agent, usually producing browns and brownish-blacks. Phosphorus pentoxide usually acts as a flux, giving greater translucency to bodies, but less hardness and durability.

Alkalies, as potassium and sodium soluble salts, have an injurious effect on a clay's refractoriness. They form blebs and blisters on the surface when fired. Alkalies may range up to 5.0% for non-refractory purposes but in general refractory use should be less than 1.0%.

Free silica causes spalling and cracking, decreases tensile strength, and increases the vitrification range. However, free silica decreases plasticity, decreases drying and drying shrinkage, increases the ability to take a glaze, aids in brightening colors, and adds rigidity to the burned body.

In clays, alumina is found as kaolinite. During firing, alumina combines with silica to form mullite which has a melting point of about 1810° C., and it is this property that permits the kaolinite to be used in high temperature wares.

Purification of Kaolinite by Flotation (Kellogg, 1947, pp. 343-350)

Kaolins containing high percentages of fine-grained quartz, such as those occurring in Bollinger County, can be purified by flotation methods, after coarse sand is removed by washing. A fine fraction may be separated early by the addition of NaOH in an amount equal to 3 pounds per ton of solids to completely disperse the clay, after which the suspension is decanted from the settled solids.

The settled solids then form the flotation feed, to which is added distilled water until the pulp consistency is 10% solids. A dispersant, American Cyanamid reagent 651 (calcium lignin sulphonate), in the amount of 1 pound per ton, or reagent 653 (sodium lignin sulphonate) in the amount of 0.6 pound per ton, is then added to the pulp. Reagent 653 appears to give the best results when used in this flotation procedure. The pH of the pulp is then adjusted to about 3 by the addition of HCl, and the pulp is agitated for 5 minutes without removal of any froth which may form by the addition of the above reagent.

A collector (lauryl amine hydrochloride) is added in the amount of 0.16 pound per ton of solids, and the cell contents are agitated for half a minute. The froth is then removed and the products are filtered and dried.

By refloating the concentrate, without any additional reagents, an even purer kaolinite is produced.

Conclusions

Apparently the most injurious ingredients in the kaolins of Bollinger and Cape Girardeau Counties is the high percentage of very fine-grained free quartz. During active mining periods, this free silica was not removed sufficiently to provide high quality kaolin to a competitive market by the refining processes used at that time. In order for this kaolin to meet competitive specifications, it is essential that a method be employed whereby the kaolin can be refined economically. Currently, kaolin is separated from fine-grained silica by centrifuges and settling troughs, and there is a fairly recent process by which the separation can be made by flotation. Flotation methods are not used in present day beneficiation operations, however.

There appear to be fairly large tonnages of kaolin still to be found in southeast Missouri, and a detailed geologic study of the area might provide a good method for prospecting for the clay. Any large scale prospecting program could best be carried out by adequate financial backing, and modern methods of purification of the clay would need to be employed in order for the kaolin to meet industrial specifications.

According to Herold and Sedalia (1954, p. 2), the kaolin of the Glen Allen district is best suited for the manufacture of white pottery, porous and vitreous china, wall tiles, and electrical porcelain. In addition, the kaolins could probably be utilized in the unfired state in the paper industry, rubber industry, and paint industry.

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