# PART II. ECONOMIC GEOLOGY.

## The Silurian and Devonian Clays and Limestones of Eastern Kentucky,

WITH NOTES ON WAVERLY AND IRVINE CLAYS.

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#### PART II.

#### ECONOMIC GEOLOGY.

## The Chemical Characteristics of the Ordovician Rocks of Kentucky.

The High Bridge formations of Kentucky consist almost entirely of limestone with a high percentage of lime (more than 60 per cent. of calcium carbonate) and a low percentage of silica (less than 5 per cent.). Judging from the few analyses so far recorded, the Camp Nelson and Oregon divisions are distinctly more magnesian (from 10 per cent. of magnesium carbonate in the case of the Camp Nelson division to 36 per cent. in the Oregon) than the Tyrone division (2 per cent.), while the Tyrone division is distinctly more calcareous (95 per cent. of calcium carbonate, in place of 60 per cent., compared with the Oregon, and 80 per cent., compared with the Camp Nelson divisions).

The Curdsville bed, the lowest division of the Lexington formation, consists of crystalline limestone. This is followed by the argillaceous limestones and interbedded clay shales of the Logana bed, and the less argillaceous limestones of the Wilmore division; the Paris bed, which forms the top of the Lexington in by far the greater part of Central Kentucky, again is a crystalline limestone, with a high percentage of lime (often more than 90 per cent. of calcium carbonate). The percentage of silica, in the Lexington limestones formerly submitted to analysis is small, and while some of these limestones contained very little magnesium carbonate, others, referred to horizons here called Lexington, are accredited with 10 to 20, and even 35 per cent. of magnesium carbonate. The Perryville limestone, the Upper Birdseye of Linney, has not been studied as yet.

In the lower, or Greendale division of the Cynthiana formation, argillaceous limestones predominate, and these are interbedded with calcareous clays and clay shales, but in the upper, or Point Pleasant division the quantity of argillaceous material usually is distinctly less, and in some localities the Point Pleasant division contains 80 per cent. of calcium carbonate, and 12 per cent. of magnesium carbonate, with very little silica or alumina. Along the Ohio river, the quantity of silicious material in the limestones at the top of the Cynthiana formation is considerably greater (from 10 to 20 per cent.). The name for the lower of these subdivisions of the Cynthiana formation was suggested by J. M. Nickles; the upper division was named by Professor Orton.

For the lower and middle parts of the Eden division of the Cincinnatian series of rocks the name *Million* beds has been proposed. These consist chiefly of clay shale, limestone forming often less than a tenth, and very frequently less than a fourth of the section. These clay shales are distinctly calcareous (from 5 to 13, and even 18 per cent. of calcium carbonate), the silicious content is considerable (from 50 to 70 per cent.), and the quantity of alumina may equal or even exceed 12 per cent. The quantity of magnesia is usually small, sometimes less than 1 per cent. The limestones of this division usually are rich in calcium carbonate (88 to 96 per cent.) and usually are poor in silica, although occasionally layers with 10 to 16 per cent. of silica occur.

The limestones of the Lower Garrard or Upper Eden bed usually are accredited with a large percentage of silicious material (from 75 to 90 per cent.), with often less than 1 per cent. of carbonate of lime, but with 6 to 10 per cent. of alumina. Specimens not affected by weathering probably would show a greater per cent. of lime. For this part of the Upper Eden bed, the name *Paint Lick* bed is proposed.

The Fairmount bed, in the lower part of the Maysville division of the Cincinnatian series of rocks, contains usually a considerable quantity of rough irregular limestones with an abundance of fossil remains. The percentage of calcium carbonate is high (from 87 to 93 per cent.), while the percentage of silica usually is small (from 1 to 3 per cent.). In the eastern part of the State there is a recurrence of argillaceous, and more silicious limestones in the upper part of the Fairmont bed, reproducing conditions found in the Lower Garrard bed of Central Kentucky. For this phase of the Fairmount bed, the name *Tate* layer is suggested, from the very characteristic exposure about three miles west of Richmond. An equally good exposure is seen along the railroad, south of Maysville.

The limestones from the upper part of the Maysville division often contain 75 to 88 per cent. of carbonate of lime, and 6 to 14 per cent. of silicious material, with little alumina or magnesium carbonate. The clays, on the contrary, contain from 60 to 80 per cent. of silicious matter, from 7 to 10 per cent. of alumina, and from 3 to 15 per cent. of lime, being very variable as to their calcareous content. To the strata from the base of the Fairmount bed to the middle or top of the Arnheim bed, Prof. N. S. Shaler gave the name Kentucky river limestone.

The Lower Richmond or Waynesville bed, in the greater part of Kentucky, consists of indurated clay rock with a more shaly section at the base. West of the Cincinnati geanticline this is replaced by argillaceous limestone; and towards the Ohio river, on the eastern side of the geanticline, blue clays interbedded with a moderate quantity of thin blue limestones make their appearance.

The Middle Richmond or Versailles bed, in the southern and southeastern part of Kentucky, consists of a considerable quantity of argillaceous limestone interbedded with clay, often more or less indurated. West of the Cincinnati geanticline these limestones often are richly fossiliferous; and toward the Ohio river, on the eastern side of the geanticline, the section not only becomes richly fossiliferous, but the limestones interbedded with the clay are thicker, harder, less argillaceous, and deeper blue in color.

The Upper Richmond or Saluda bed, in all parts of Kentucky, is a distinctly argillaceous formation. Southward, and along the western side of the Cincinnati geanticline, a larger part of this section is strongly indurated and forms an argillaceous limestone. At Madison, Indiana, a sample of this rock, which also would be typical for the exposures in Kentucky as far south as Salt river, gave the following result on analysis:

Silica	19.80
Alumina	15.05
Water (dried at 212° F.)	.35
Water and loss	5.00
Lime	29.19
Magnesia	1.55
Carbonic acid	24.61
Oxide of iron	4.45

This suggests the presence of about 52 per cent. of calcium carbonate, 3.25 per cent. of magnesium carbonate, 5 per cent. of limonite, about 37.45 per cent. of clay, and only 2.35 per cent. of free silica. From this it may be seen that the rock is an argillaceous limestone, and that the term sandstone applied to this rock is incorrect. On the eastern side of the Cincinnati geanticline the upper part of the Saluda bed consists chiefly of soft clay, and northward, toward the Ohio river, clay forms a larger and larger part of the entire Saluda section.

From the upper part of the Richmond division of the Cincinnatian series of rocks, along Muddy creek, near Elliston in Madison county, the following analyses have been published:

2189.—Shelly limestone in the bed of Muddy creek; below the home of J. G. Covington, half a mile below Elliston. Of a dark umber-gray color; generally quite friable; some portions are compact.

Geological position: Richmond group. Collected by John Procter and referred by him to the Cumberland shales.

2190.—Impure limestone. From below the mill-dam on Muddy creek, southwest of Elliston. A pretty firm, fine-granular or compact rock of a handsome olive-gray color.

Geological position: From the upper twelve inches of the Richmond division. Collected by John R. Procter, from rocks which he referred to the Cumberland shales.

2191.—Impure limestone. From the same locality as the last. Rather darker colored than the preceding; color inclined to brownish; not so hard as the last.

Geological position: From eighteen to thirty inches below the massive bluff limestone (Brassfield or Clinton bed) of the Silurian on Muddy creek. Collected by John R. Procter from the top of the Richmond division, in rocks identified by him as Cumberland shales.

Analyses; rocks dried at 212 degrees F.:

	No. 2189	No. 2190	No. 2191
Siliceous residue	20.740	25.180	29.080
Alumina		17.656	21.256
Iron peroxide	10.330	3.700	4.120
Phosphoric acid		.204	.204
Water and loss	6.567	4.902	4.302
Lime carbonate	48.530	37.760	33.560
Magnesia carbonate	11.790	10.050	6.955
Potash	1.696	.458	.578
Soda	.347	.090	.045

These analyses suggest that none of the specimens contain more than 5 per cent. of free silica or sand. The rocks are essentially argillaceous limestones with 7 to 12 per cent. of magnesium carbonate, stained by relatively small quantities of limonite.

As far as may be determined from the analyses at hand, the Ordovician strata of Kentucky consist chiefly of calcium carbonate and kaolin. In the limestones, the calcium carbonate, of course, predominates. In some cases it forms more than 95 per cent. of the rock. But in other cases kaolin forms such a considerable proportion of the rock that the name argillaceous limestone is more appropriate. Magnesian limestones appear to be rare or absent in the Cincinnatian, but occur at various horizons in the Jessamine or Mohawkian series of rocks. Limestone containing considerable quantities of free silica or sand are rare apparently, except at the Garrard horizon, and in the lower part, of the Maysville division of the Cincinnatian.

In the clays there often is a considerable admixture of free silica or sand (from 20 to 50, and even 60 per cent.), the larger quantities occurring usually in the lower Garrard or *Paint Lick* bed and upper *Fairmont* or *Tate* layer. Magnesium carbonate occurs in small quantities, frequently forming less than 1 per cent., and rarely more than 4 per cent. of the clay. Calcium carbonate also usually forms only a small part of the clay, but it frequently forms as much as 5 per cent., and occasionally exceeds 8, and even 14 per cent. Where it is present in considerable quantities, the clay is likely to be more or less indurated, forming an argillaceous or clay rock.

In collating the various analyses of Ordovician rocks of Ken-

tucky so far published, it was noted that hitherto no systematic investigation of the chemical composition of the Ordovician rocks of the State had been attempted. The selections of samples for analysis appear to have been made at random. Sometimes many analyses have been made from practically the same horizon, while intermediate horizons have remained unknown. Moreover, it is no longer possible to identify with confidence the horizons from which many of the specimens analyzed were obtained; on this account they can not be used safely in forming opinions as to the general characteristics. chemically, of Kentuckian strata. This may be readily accounted for. At the time when most of these analyses were made, the knowledge of the stratigraphy of Ordovician strata was less advanced than at present. In consequence, it was difficult either to identify or to describe horizons from which samples were selected in such a manner that their relative position could be determined with exactness. Under these circumstances there was very little incentive to the systematic selection of material for analysis. Moreover, the demand for artificial cements was less imperative than to-day, and hence one of the possible uses of Ordovician strata did not invite investigation as much as at present.

The same indefiniteness as to horizons is characteristic also of the analyses of the Silurian rocks of Kentucky, hitherto made. A few analyses made in connection with the present survey, however, supplement those by former surveys, so that, while our knowledge of Silurian strata is still very fragmentary, it is, nevertheless, more definite than that of Ordovician rocks. The present paper is to be regarded only as preliminary to fuller investigations and shows merely the present stage of progress.

The preceding account of the chemical characteristics of the Ordovician rocks has been offered only in order to serve as a means of comparison with the Silurian strata, next to be described.

#### The Chemical Characteristics of the Silurian Rocks of Kentucky East of the Cincinnati Geanticline.

#### A. SILURIAN LIMESTONES.

No analyses of the limestones of the Brassfield bed and of the immediately overlying parts of the Crab Orchard bed have been made by the present Survey. A number of analyses, however, have been made by former geological surveys, and, although the exact horizon from which the samples, analysed were obtained can not be determined in several cases, in spite of their apparently very definite location, these analyses probably give a very fair idea of the general characteristics of the strata, in question.

2192.—Impure limestone; from below the mill-dam on Muddy creek, southwest of Elliston.

Geological position: From the bottom stratum of the Silurian, resting on the top of the Richmond division. This would place it at the base of the Brassfield bed. Collected by John R. Procter.

A granular limestone; somewhat cellular; containing some petroleum, which gives it a brownish color. It weathers ochreous.

2193.—Impure limestone; from below the mill-dam on Muddy creek, southwest of Elliston.

Geological position: Silurian. Top stratum, eight inches thick. Probably from the top of the Brassfield beds, although some of the Oldham limestones of the Crab Orchard bed also are exposed: at this locality.

An impure granular limestone; somewhat cellular; dark brownish-gray, somewhat mottled. Contains petroleum, the infiltration of which gave the dark color to the rock. When heated over the alcohol-lamp, the petroleum exudes from it. It weathers ferruginous.

2194.—Impure limestone. From just below the mill-dam on Muddy creek. Elliston.

Geological position: Second stratum from the top. Probably from the upper part of the Brassfield bed. Collected by John R. Procter.

It resembles the preceding, but is darker colored. It also contains petroleum and some iron pyrites.

2195.—Impure limestone. From below the mill-dam on Muddy creek, southwest of Elliston.

Geological position: Third stratum from the top. Probably from the upper part of the Brassfield bed. Collected by John R. Procter.

Resembles the preceding; rather finer-grained and harder; also containing petroleum. Exterior surface weathered ferruginous.

Analyses; samples dried at 212 degrees F.:

	No, 2192	No. 2193	No. 2194	No. 2195
Bitumen, water and loss	1.396	10.870	6.493	2.460
Siliceous residue	9.980	3.980	4.120	3.920
Alumina ?	11.360	9.960	5.960	12.360
Phosphoric acid		1	1	.140
Iron peroxide	3.500	3.900	3.566	4.460
Iron sulphide			.576	
Lime carbonate	45.700	50.860	50.960	51.200
Magnesia carbonate	27.475	20.100	27.972	25.124
Potash	.501	.276	.276	.287
Soda	.088	.054	.087	.049
Total	100.000	100.000	100.000	100.000
Percentage of lime	25.592	28.480	28.538	28.672
Of magnesia	13.083	9.608	13.319	11.899

796, 797.—Clinton Group limestones, from Bath county. Geological position: Exact position unknown; probably from the Brassfield bed, or the base of the Crab Orchard bed, beneath the Plum Creek clay.

	No. 796	No. 797
Silica and silicates	17.540	1.980
Alumina, iron and manganese oxides	9.020	11.408
Iron carbonate		3.095
Phosphoric acid	.117	.592
Sulphuric acid	.633	. 235
Lime carbonate	53.240	51.580
Magnesia carbonate	18.531	28,779
Potash	.444	.209
Soda	.212	Trace

973.—Magnesian limestone. Clinton Group, at Hillsboro, Fleming county. Dull, dirty-buff, impure limestone, with crinoid beads, small specks of mica, and brownish stains of oxide of iron.

Geological position: At very top of the Brassfield or Clinton bed, immediately below the Whitfieldella layer.

674.—Yellow red porous rock, over crinoidal limestone. A mile and a half east of Mount Carmel, Fleming county.

Geological position: Probably the base of the Crab Orchard bed, from the Whitfieldella layer or immediately above.

Analyses:

	No. 973	No. 674
Water and loss	1.858	1.802
Silica and insoluble silicates	10.880	2.880
Alumina	1.080	1
Iron oxide	11.073	1
Iron carbonate	5.155	\$12.240
Manganese carbonate	.421	11
Phosphoric acid	.848	.630
Sulphuric acid	.324	.337
Lime carbonate	42.680	71.700
Magnesium carbonate	25.358	9.931
Potash	.290	.341
Soda	.033	.139

A comparison of the analyses of the rocks from Muddy creek, near Elliston, in Madison county, shows a considerable uniformity in chemical composition. The rocks are evidently magnesian limestones. The total quantity of calcium and magnesium carbonate varies between 71 and 79 per cent., the quantity of the magnesium carbonate being about half that of the calcium carbonate. The total quantity of alumina and silicious matter varies between 10 and 20 per cent. The silicious matter probably is combined chiefly with alumina, so that there is little free silica or sand. The color of the rocks is due chiefly to iron.

The so-called Clinton limestones, from Bath county, present closely similar features. The total quantity of calcium and magnesium carbonate varies from 72 to 80 percent., the magnesium carbonate averaging to about half of the calcium carbonate. The color of the rock is due chiefly to iron. The relative quantity of silica and alumina differs, considerably in the two specimens. In sample No. 796 there may have been free silica or sand.

The specimen from Hillsboro, in Fleming county, shows similar features. The total quantity of calcium and magnesium carbonate is 68 per cent., the magnesium carbonate equalling roughly, half of the calcium carbonate. The quantity of iron is considerably greater than in the case of rocks undoubtedly from the Brassfield bed. This agrees with observations so far made in the field, according to which the more distinctly ferruginous layers begin with the layer containing large crinoid beads, at the top of the Brassfield bed, and these are followed by still more ferruginous layers immediately above the Whitfieldella layer, in the lower part of the Crab Orchard bed. The Hillsboro specimen probably contained free silica or sand. This also is in keeping with observations in the field, the crinoid layer, usually having a sandy appearance.

The horizon of the limestone from Fleming county is not definitely known. The chief notable features are the much larger percentage of calcium carbonate, and the correspondingly small percentage of magnesium carbonate.

A comparison of the limestones from the Brassfield bed and from the lower part of the Crab Orchard bed with the so-called Clinton limestones of Ohio shows that the latter contain a much larger percentage of calcium carbonate and a much smaller quantity of magnesium carbonate. This appears to be true especially of the more northern or northeastern exposures. For instance, at Centreville and Eaton the percentage of calcium carbonate is about 85, and that of magnesium carbonate about 12; while at Dayton, Brown's quarry west of New Carlisle, and Ludlow Falls the Clinton limestone contains from 91 to nearly 98 per cent. of calcium carbonate, and from 0.22 to 6.5 per cent. of magnesium carbonate. At all of these localities the quantity of silica is very small (1 per cent. or less). The quantity of alumina is even less.

### B. THE FERRUGINOUS, PHOSPHATIC, AND MAGNESIAN CONTENT OF SILURIAN ROCKS.

In Kentucky, the most characteristic feature of the Brassfield or Clinton bed, and of the immediately overlying limestones at the base of the Crab Orchard bed, below the Plum creek horizon, is the considerable increase of magnesium carbonate as contrasted with the percentage of this material in the limestones and clays of the Cincinnatian formations. This increase in the quantity of magnesium carbonate is accompanied by a corresponding decrease in the quantity of calcium carbonate.

The increase in the quantity of iron present, although ranging only from 3.5 to 4.5 per cent. when measured in the form of iron peroxide in the case of the Muddy creek limestones, also is noteworthy, since, at many point on the eastern side of the Cincinnati geanticline, this culminates at the base of the Crab Orchard bed in a distinctly ferruginous horizon, which at several localities is of commercial value. Analyses of ferruginous layers from several localities in Bath county show their value as ores.

2575.—Iron ore, from Carnel Rice, taken from the land of Captain W. G. Allen. Ore of a yellowish-brown color of the usual structure (oolitic) of the Clinton iron ore. Bath county.

Geological position: Near the base of the Crab Orchard bed, below the Plum creek horizon. Collected by W. M. Linney, June, 1885.

2576.—Iron ore from the Clinton group on the Purvis lands, in Bath county. Resembles the preceding, but, is reddish in color.

Geological position: From near the base of the Crab Orchard bed, below the Plum creek horizon. Collected by W. M. Linney, June, 1885.

2577.—Iron ore. Average sample from the lands of William Warren, near the head of Rose Bun, Bath county. Clinton Group. Ore of the structure of Clinton ore, of a reddish-brown color.

Geological position: Near the base of the Crab Orchard bed. Ferruginous layer below the Plum creek horizon. Collected by W. M. Linney, June 1, 1885.

Although the iron in the analysis is estimated as peroxide, some of it, in all these ores, is in the form of ferrous carbonate. These ores have a considerable proportion of lime and magnesia, which will aid in fluxing them, and a notable quantity of phosphoric acid, which will not prevent their profitable use in the production of merchantable iron. Analyses; samples air-dried:

	No. 2575	No. 2576	No. 2577
Water expelled at 212° F	1.143	.693	1.607
Carbonic acid, water, etc	10.863	11.283	8.445
Silica	7.160	7.800	6.960
Alumina	5.468	5.132	3.720
Phosphoric acid (P <sub>2</sub> O <sub>5</sub> )	1.202	1.138	1.010
Iron peroxide	47.630	51.430	58.570
Lime carbonate	16.560	13.080	15.160
Magnesia carbonate	9.974	9.444	4.528
Percentage of iron	33.341	36.001	40.999

1655.—Limonite with carbonate, said to be eighteen to twenty feet thick, from near Owingsville, on the road to Slate creek.

Geological position: From near the base of the Crab Orchard bed, below the Plum creek horizon. Collected by Philip N. Moore.

Of a fine oolitic structure. Colors varying from yellowish and reddish-brown to grayish-brown, with greenish-gray infiltrations in some parts.

Analyses; dried at 212 degrees F. :

Combined water	7.835
Siliceous residue	7.350= 7.560 of silica.
Alumina	8.346
Iron peroxide	39.063
Iron carbonate	11.479=30.734 of iron, total.
Phosphoric acid	.868 .379 of phosphorus.
Manganese peroxidenot est	timated.
Sulphuric acid	.185= .074 of sulphur.
Lime, carbonate	18.710
Magnesia	6.159

While the percentage of calcium carbonate and magnesium carbonate in these ferruginous layers may seem considerable, viewing them as ores, they are inconsiderable when compared with the quantities of these substances in ordinary Brassfield and lower Crab Orchard limestones. Considered as an ore, the total quantity of silica and alumina also is notable.

The composition and origin of these ores has not been fully investigated. They consist apparently of an intimate mixture

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of limonite, hematite and iron carbonate. Where hematite predominates the color is more strongly reddish or reddish-brown. It has been thought by some that the hematite was deposited in place, simultaneously with the calcium carbonate, as part of the original sediment. Water percolating slowly but for long distances through the ground, when coming in contact with rocks having a favorable texture and composition, may take considerable quantities of iron compounds into solution. These iron compounds are taken up probably chiefly in waters containing considerable carbon dioxide and hence are dissolved most frequently in the form of carbonates. If these carbonates enter the sea in areas where the water is comparatively shallow and little affected by currents, rich in vegetation and hence charged with acids derived from decaying plants, they may be precipitated as ferric hydrate or limonite, in accordance with the following reaction:

$$4FeCO_3 + 3H_2O + 2O = 2Fe_2O_3 \cdot 3H_2O + 4CO_2$$
.

This reaction is materially assisted by a class of bacteria known as iron bacteria, which are unable to exist without the presence of certain chemical substances of which iron carbonate is chief. When the iron carbonate has been taken up by the bacteria, or absorbed by them, it is oxidized and limonite is precipitated. Ordinarily, if the limonite remains where it is kept moist there is no further alteration, but at or near the surface in arid regions or in times of drought in humid regions, it may be dehydrated more or less and thus, pass into hematite.

The larger part of the hematite found in sedimentary rocks is due probably to segregation subsequent to deposition. The ore originally was distributed through a much greater mass of rock and subsequently was concentrated in some special layer or layers. Frequently this concentration takes place simultaneously with a replacement of original limestone deposits by the hematite. In these cases the iron compounds, widely distributed throughout the rocks, are dissolved by percolating waters in the form of iron carbonate and transported to other areas. If at any point these waters come in contact with other solutions rich in oxidizing materials, hematite, more or less hydrated, may be precipitated. The reaction is as follows:

$$2$$
FeCO<sub>3</sub>+O+water = Fe<sub>2</sub>O<sub>3</sub>+2CO<sub>2</sub>+water.

In the case of the ferruginous deposits in the lower part of the Crab Orchard bed, below the Plum creek horizon, on the eastern side of the Cincinnati geanticline, in Kentucky, there is no doubt of a considerable concentration of the hematite and other ferruginous material subsequent to the deposition of the original limestone. At some localities numerous fossil remains occur in the ferruginous material which originally, of course, consisted chiefly of calcium carbonate, but which at present are replaced, as a whole or in part, by hematite or by hematite mixed more or less with limonite and iron carbonate. A microscopical examination of the ferruginous rock reveals, moreover, that a large part of the rock consists of the comminuted fragments of various bryozoans and shells more or less replaced by ferruginous material. While a certain amount of precipitation of ferruginous material may have occurred at the time of deposition of the original sediments, there is no doubt that in their present form these ferruginous deposits are the result chiefly of concentration subsequent to deposition, accompanied by replacement of the original limestone.

All stages of concentration, between limestones slightly tinged with limonite, hematite, or iron carbonate and those in which the limestones have been replaced by sufficient of these materials to constitute ores, may be observed usually at the same locality. The ferrous carbonate in the rock is due to replacement of calcium carbonate and not, to original deposition.

The notable quantity of phosphoric acid recorded in the chemical analyses of these ferruginous rocks also is due to concentration subsequent to the deposition of the original limestones. This quantity is not large, but it is larger than in the non-ferruginous layers. The phosphates, as a rule, are dissolved by percolating waters near the surface where the rocks are weathering and are segregated at or just, below the level of the ground water. This segregation occurs most frequently in limestones. It has been suggested that this precipitation is brought about simply by the interchange of the bases in the phosphates and carbonate of lime thus brought together. It may have resulted also from the lowering of the solvent power of the percolating water due to loss of carbon dioxide. This would take place whenever a part of the carbon dioxide was used up in dissolving limestone or when a part of the carbon dioxide escaped from the ground waters due to relief of pressure on approaching the surface of the ground. The zone of the deposition of phosphates frequently is also the zone of the removal of calcium carbonate. It is closely associated with the zone of weathering. This raises the question whether the beginning of the period of deposition of the Crab Orchard bed may not have been a period of weathering of rocks in this and in closely contiguous areas. The sudden introduction of *Whitfieldella subquadrata* at and immediately above the horizon with large crinoid beads, at the very base of the Crab Orchard bed suggests some important change geographically. At this horizon the rock often is distinctly sandy. The tops of the limestone layers frequently are strongly wave-marked. Shallow water conditions, at least, appear to have prevailed.

Finally, the magnesian content of the Silurian limestones deserves some consideration. The quantity of magnesium carbonate in the specimens analyzed is not sufficient, in conjunction with the calcium carbonate, to form anything like a dolomite. Nevertheless, magnesium carbonate is an important constituent of the rock. The source of this magnesium is not organic. In the shells and skeletons of marine animals the quantity of magnesium carbonate usually is less than 1 per cent. Magnesium carbonate is present in sea water. It is present in larger quantities than calcium carbonate, but the calcium carbonate is largely taken up by sea animals in the construction of their shells and other hard parts, while but little magnesium carbonate is used in this manner. Under ordinary conditions magnesium carbonate precipitates much less readily than calcium carbonate, and is thrown down from solution later than the latter. It is not known to occur as a chemical precipitate in sea water, which is far from being saturated with this substance. Magnesium carbonate, in consequence, does not appear as an important original constituent of rocks. Hence the appearance of any considerable quantity of magnesium carbonate in rocks suggests the presence of the incipient stages of dolomitization, or of the partial replacement of the calcium carbonate of limestones by magnesium carbonate. This magnesium carbonate is supposed to be derived from the various magnesium containing minerals of the older rocks, or from the more or less dolomitic limestones of later age. In the more concentrated

areas, cut off from the general circulation of the sea, dolomitization may take place contemporaneously with the deposition of limestones, but as a rule dolomitization is believed to have taken place chiefly after the elevation of limestone deposits above the level of the sea, when the circulation of percolating waters throughout its mass is certain to be greater.

It has been noticed that magnesian limestones are more abundant among the older rocks of the earth. It may be that in these cases dolomitization has had a longer time to be operative. It has been noticed also that magnesian limestones are more abundant in faulted areas, where circulating waters had better opportunities to bring the magnesium carbonate into solution. In the case of the Silurian limestones of Kentucky no investigations were made as to the origin of the magnesian content.

Nothing is known of the chemical composition of the Oldham limestones in the lower part of the Crab Orchard bed beyond the few notes on the moderately ferruginous layers given in the earlier half of this bulletin. Several analyses have been made, however, by the present Survey, which give a fair idea of the general characteristics of the extensive layers of clay which form the major part of the Crab Orchard bed.

#### C. SILURIAN CLAYS.

#### 1. ANALYSES.

Most of the following analyses have been made for the present Survey, but several are appended which were made for the earlier surveys; as far as is possible from the information at hand, the geological positions of the samples collected by the latter are indicated in accordance with the revised classification.

2598.—Clay. From Panola, along Oldham branch, southeast of the railroad station; Madison county.

Geological position: Plum creek clay. A five foot clay layer at the base of the Crab Orchard bed, immediately above the Brassfield or Clinton limestones. Collected by A. F. Foerste, 1904.

#### Analysis, sample air-dried:

Moisture	
Ignition (combined water, etc.)	9.94
Silica	9.90
Alumina 1	8.15
Ferric oxide	5.57
Lime	4.02
Magnesia	3.32
Potash	5.32
Soda	.33
Titanium dioxide	.93
Sulphates	race

2600.—Clay. From Irvine, along the road an eighth of a mile north of Estill Springs, and an eighth of a mile south of James Harris; Estill county.

Geological position: Lulbegrud clay, collected from two to thirteen feet below the massive two-foot layer which forms the base of the Waco formation. This is the middle clay of the Crab Orchard bed. Collected by A. F. Foerste, 1904.

Analysis, sample air-dried:

Moisture	1.98
Ignition (combined water, etc.)	6.12
Silica	58.82
Alumina	18.14
Ferric oxide	4.83
Lime	.91
Magnesia	1.74
Potash	4.71
Soda	.36
Titanium dioxide	1.25
Sulphur trioxide	.12
Total	98.98

2187.—Clay shale or indurated clay. On the hill two hundred yards north of the home of Dr. Freeman, two miles southeast of Bobtown, on the east side of the Big Hill pike, north of Joe Lick creek.

Geological position: Collected by John R. Procter, and stated by him to occur beneath the Corniferous limestone. The

bed is six or more feet thick, and contains gypsum. Locality: R-S-21. Probably belongs to the Lulbegrud clay division of the Crab Orchard bed.

Generally in thin, soft, irregular laminae, of a light olive-gray color, irregularly varied with brownish yellow or ochreous. It contains gypsum in irregular crystals between some of the laminae. It is quite plastic with water. Burns quite hard, to a handsome light brick color.

Analysis, dried at 212 degrees F.:

Combined water, carbonic acid, and loss	5.871
Silica	48.780
Alumina	17.320
Iron peroxide	3.240
Lime sulphate	19.285
Magnesia	.496
Potash	4.768
Soda	.240

2170.—Indurated clay. From the farm of C. L. Searcy, near Elliston, west of Waco one mile; Madison county.

Geological position: Collected by John R. Procter and stated by him to occur beneath the Corniferous limestone and to form a bed ten or more feet thick, and to make good soil. At Waco the base of the great mass of clays forming the upper clay of the Crab Orchard bed occurs below the Devonian limestone. It may be that the base of this upper (Estill) clay is present also on the Searcy farm, although this clay is known to thin out eastward.

Analysis, sample dried at 212 degrees F.:

Combined water and loss	4.147
Silica	62.580
Alumina	22.940
Iron peroxide	3.760
Lime	.560
Magnesia	.425
Potash	5.280
Soda	.308

2599.—Clay. From Panola, at the railroad cut east of the station. Geological position: From the upper clay of the Crab Orchard bed, forming the main body of clays (Estill) above the Waco horizon. Collected by A. F. Foerste, 1904.

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#### Analysis, air-dried:

Moisture	2.20
Ignition (combined water, etc.)	7.80
Silica	54.33
Alumina	19.44
Ferric oxide	5.00
Lime	1.88
Magnesia	2.22
Potash	5.15
Soda	.31
Titanium dioxide	1.13
Sulphur trioxide	.39
- Total	99.85

2601.—Clay. From Irvine, on the hillside northwest of the home of James F. Harris, one mile north of town; Estill county.

Geological position: The upper or chief body of clay (Estill) in the Crab Orchard bed, overlying the Waco horizon. The specimens analyzed were a mixture of clays collected between twenty-seven and fifty-seven feet above the two-foot layer of limestone which forms the base of the Waco horizon. Collected by A. F. Foerste, 1904.

Analysis, sample air-dried:

Moisture	2.13
Ignition (combined water, carbon dioxide, etc.)	7.26
Silica	55.25
Alumina	20.79
Ferric oxide	4.40
Lime	1.51
Magnesia	1.04
Potash	4.95
Soda	.41
Titanium dioxide	1.16
Sulphates	Trace
	<u> </u>
Total	98.90

2619.—Crab Orchard. At the exposure south of the roadside well at the north end of the grounds belonging to the Crab Orchard Springs hotel, one mile north of the station, and a quarter of a mile south of Dix river.

Geological position: From the upper or chief clay (Estill) layer forming the greater part of the Crab Orchard bed. Col-

lected from the upper part of the section, fifty-five feet thick. These clays belong above the Waco horizon. Collected by A. Foerste, 1904.

Analysis, sample air-dried:

Moisture	1.69
Ignition (combined water, carbon dioxide, etc.)	7.86
Silica	54.48
Alumina	18.90
Ferric oxide	5.64
Lime	2.50
Magnesia	1.71
Potash	4.67
Soda, traces lithia	.38
Titanium dioxide	1.12
Sulphates and phosphates T	races
Total	98.95

2186.—Clay shale. On the road near Anderson Lake's house, three hundred yards west of Drowning creek, two miles southwest of Panola, a mile and a half northwest of Combs.

Geological position: Collected by John R. Procter, from the "Niagara Group." Either from the Lulbegrud clay division of the Crab Orchard bed, or from the upper clay (Estill) of this bed, above the Waco limestones; probably the latter. Locality, R-SE-21.

An olive-gray and brownish gray, somewhat firm shale, mottled in parts. Quite plastic with water when powdered. Calcines to a light brick color.

Analysis, dried at 212 degrees F.:

Con	abined water,	, carboni	c acid,	and	loss	16.221
Silie	ca					42.300
Alu	mina					20.840
Iron	n peroxide					4.120
Lim	ne					13.320
Pota	ash					2.387
Sod	a					.351

### 2. POSSIBLE USES OF SILURIAN CLAYS FOR THE MANUFACTURE OF CLAY PRODUCTS.

If attention be confined to the clays investigated by the writer, a considerable similarity in the chemical composition of the clays from the different horizons is noticed. The percentage of silica in these samples varies from 50 to 58 per cent; that of alumina, between 18 and 21 per cent.; that of ferric oxide, between 4.5 to 5.5 per cent.; that of potash, between 4.6 and 5.3 per cent.; that of soda, between 0.3 and 0.4 per cent. The percentage of lime and magnesia, however, is much more variable, the proportion of these substances being greatest in the case of the sample of Plum creek clay.

These samples of clay were selected with special reference to their availability for commercial purposes. Considerable care was taken to secure samples from localities where large quantities of these clays were available and to select the material in such a manner that an analysis of the mixture would give a very fair idea of the general characteristics of the clay as they would appear under ordinary methods of manipulation.

From these preceding analyses it is evident, of course, that they have no value as fire-clays. They contain too much of each one of the fluxing materials: potash and soda, ferric oxide, and lime, and magnesia. On this account they melt at too low a temperature and hence will not serve for brick intended to stand a high temperature.

They also have no value as stoneware clays, as the following table, giving the range of the percentage of the various constituents of good typical stoneware clays, will show:

	Maximum	Minimum	Average of eight analyses
Silica	72.10	45.00	64.08
Alumina	38.24	19.08	23.86
Ferric oxide	1.50	0.96	1.23
Lime	1.70	0.00	0.78
Magnesia	0.68	0.11	0.40
Soda	Trace	0.00	Trace
Potash	2.42	0.15	1.48
Oxide of lithium, with some soda	0.02	Trace	Trace
Titanium oxide	1.30	0.29	0.46
Water	14.80	6.25	7.78

A comparison of the analyses of the Silurian clays with this table indicates that the Silurian clays contain too great a percentage of fluxes. In place of a maximum of 2.4 per cent. of alkalies, as in good stoneware clays, the Silurian clays contain from 5 to 5.6 per cent. of potash and soda. In place of a maximum of 3.9 for the total quantity of ferric oxide, lime and magnesia, the Silurian clays contain between 7 and 13 per cent.

As far as may be determined from the analyses, these Silurian clays should be almost ideal for the average run of vitrified wares. This is well brought out by the following table, which indicates the range of variation of the principal constituents in a number of clays which have been found to be of value

for these purposes.

,	Maximum	Minimum	Average
Silica	75.00	49.00	56.00
Alumina	25.00	11.00	20.50
Ferric oxide	9.00	2.00	6.70
Lime	3.50	0.20	1.20
Magnesia	3.00	0.10	1.40
Soda and potash	5.50	1.00	3.70
Loss on ignition	13.00	3.00	7.00

In the Silurian clays here discussed, the percentage of silica varies between 54 and 59 per cent., except in the case of the Plum creek clay, where the proportion of silica is nearly at a minimum. The percentage of alumina varies between 18 and 21; that of ferric oxide between 4.5 and 5.5 per cent. The percentage of lime exceeds the maximum in the case of the Plum creek clay, but varies between 0.9 and 2.5 per cent. in the other cases. The magnesium also is in excess in the case of the Plum creek clay. The alkalies, potash and soda, on the contrary, are fairly high in the case of all of the clays (from 5 to 5.6 per cent.).

Clays of this description are used for sewer pipe, paving brick and other purposes, where the materials do not have to withstand high temperature. Clays of this class should be fine-grained and plastic, and should vitrify at temperatures as low as 2,130 to 2,210 degrees F. On this account the clays should contain a considerable amount of fluxing materials. However, to prevent complete fusion, there should not be much potash and soda, since in these cases there is frequently too little difference in temperature between the point of incipient fusion and that of complete fusion. The difference between these points should be about 150 to 200 degrees F., in order that the articles made from the clay may be raised to the temperature of incipient fusion or vitrification without any danger of the temperature rising sufficiently to approach complete fusion, which, of course, would cause the articles formed from the clay to lose their shape, stick together, and become altogether useless.

High-grade terra cotta work is now made from a mixture of fireclays which burn to a buff color. The Silurian clays here under discussion are not fire-clays, and they would not burn to a buff color. Clays containing 5 per cent. or more of iron burn to a deep cherry-red, unless under-burned, in which case the resulting ware loses in strength, and in fact may be worthless. There is no known reason, however, why the Silurian clays in question should not prove available for the lower grades of terra cotta.

On account of their large percentage of iron, these Silurian clays are not available for the manufacture of yellow and buff brick. They should, however, make excellent bricks of the common red variety. Brick clays should have a sufficient percentage of fluxes to reach incipient fusion at a little over 1,900 degrees F., and should burn hard at a temperature not over 2,000 degrees F. The Silurian clays here discussed have not been tested as yet as to their fusibility. It is probable that a good quality of pressed brick might be made out of these clays, but the color would be deep red and the brick would not be as hard as the pressed bricks made of more refractory material.

The clay from the C. L. Searcy farm shows a distinctly higher percentage of silica, and a distinctly smaller per cent. of lime, magnesia and iron than the clays collected by the writer. The clays from the Dr. Freeman and Anderson Lake localities are notable chiefly for the large quantities of calcium which they contain. In the case of the clay from the Dr. Freeman locality, the calcium is determined in the form of calcium sulphate, indicating the presence of considerable quantities of gypsum.

The use of the Crab Orchard clays for the purpose of manufacturing artificial cements should receive further attention. At present many of these artificial cements enter the market

under the name of Portland cements. Various materials may be used in the manufacture of these cements. Among these are marl mixed with clay, limestone mixed with clay, argillaceous limestone mixed with pure limestone, limestone mixed with shale, limestone mixed with slag from iron furnaces, and clay mixed with the calcareous waste left from the manufacture of caustic soda.

In order to give some idea of the sort of mixtures of limestone and clay that have proved to be of practical utility in the manufacture of Portland cements, the following analyses have been added. The first column in each table gives the ingredients of the limestone entering into the mixture, the second column gives the ingredients in the clay used, and the third gives the composition of the finished product, the so-called Portland cement.

Analyses of materials used by the Catskill Cement Company, at Smith's Landing, in Greene county, New York, and published by the New York Survey:

	Limestone	Clay	Resulting
Silica	1.54	61.92	22.48
Alumina	.39	16.58	6.52
Ferric oxide	1.04	7.84	4.46
Lime	53.87	2.01	62.93
Magnesia	.52	1.58	1.48
Alkalis		3.64	
Sulphur trioxide		Trace	1.30

The following analyses were published from an investigation of materials used by the Glen Falls Portland Cement Company, in Warren County, New York:

	Limestono	Clay	Resulting Cement
Silica	3.30	55.27	21.50
Alumina, ferric oxide	1.30	28.15	10.50
Lime	52.15	5.84	63.50
Magnesia	1.58	2.25	1.80
Alkalis			.40
Sulphur trioxide	.30	.12	1.50
Carbon dioxide	40.98		1
Organic matter and water	8.37		1

In the latter case the limestone and clay are dried and crushed separately. After being weighed on automatic scales, the materials are mixed dry and reduced to fine powder. This powder is then fed into wet mixers, where sufficient water is added to allow the mixture to be made up into bricks. The bricks are dried in tunnels heated by waste heat from the boiler, blowers being used to drive the heat through the tunnels. After drying, the bricks are burned in kilns, and the clinkers resulting from the brick are reduced to powder in mills constructed for this purpose. The powder is the finished product, the Portland cement.

The essentials in the manufacture of Portland cements are lime and silica. The lime is furnished by limestone or marls, and the silica is furnished by the clay. In burning, the lime and silica unite so as to form the compound  $3CaO.SiO_2$ . called tricalcic silicate. This compound, in large measure, supplies the hydraulic properties of the cements. The ideal Portland cement would consist, therefore, exclusively of tricalcic silicate, and would be composed entirely of lime and silica in the proportion of 73.6 per cent. of lime and 26.4 per cent. of silica.

Such an ideal cement, however, can not be prepared at present under conditions such as to make it a commercial product, since the heat required to cause pure lime and silica to unite can not be attained in any commercially useful kiln. In actual practice, therefore, it becomes necessary to select materials which, in addition to lime and silica, contain also other ingredients which will serve as a flux. The most important of these ingredients are alumina and ferric oxide, and when present in notable percentages they lower the temperature at which lime and silica will combine to a considerable degree. However, as the percentage of alumina and ferric oxide increases, the strength of the Portland cement decreases, so that considerable judgment must be used in the selection of materials.

In burning, the alumina is believed to combine with the lime so as to form dicalcic aluminate,  $2CaO.SiO_2$  and there is a possibility of a similar combination in the case of ferric oxide, forming the compound  $2CaO.Fe_2O_3$ . Owing to the relatively small percentage of ferric oxide in the materials used for Portland cements, it may be considered as producing about the same effect as alumina, and the two may be calculated together.

Owing to the necessity of having the fluxing materials, alumina and ferric oxide, present, in addition to the lime and silica, the necessary elements of Portland cement, before burning, may be said to be about 75 per cent. of carbonate of lime, and 20 per cent. of silica, alumina, and iron taken together. The remaining 5 per cent. will include the magnesium carbonate, alkalies, and sulphur compounds which may be present. Of the essential ingredients, the lime is usually furnished by the limestone, while the silica, alumina, and ferric oxide are supplied by the clay.

Some of the impurities found in the unburned materials may be regarded as useful to the cement. One of these is calcium sulphate, which, if present only in small quantities, retards the set of the cement. Magnesium carbonate is an undesirable impurity in the unburned mixture, and should form less than 3.5 per cent. of the latter.

For use as Portland cements the clays should carry not less than 55 per cent. of silica, and preferably from 60 to 70 per cent. The alumina and ferric oxide calculated together should not amount to more than one-half of the percentage of the silica. The value of the clay is greater  $Al_2O_3 + Fe_2O_3 = \frac{SiO_2}{8}$ . ratio of its ingredients approaches

The percentage of magnesia, and alkalies should be low, preferably not over 3 per cent.

From these statements it is seen that there is a possibility of the usefulness of the Crab Orchard clays for Portland cement, but that its usefulness can not be determined definitely until the composition of the available limestones is known, and the latter has not yet been determined.

#### 3. THE MINERAL WATERS AND SALTS OF THE CRAB ORCHARD BED.

Crystals of gypsum are common at certain horizons in the Crab Orchard bed. They are abundant in the Lulbegrud clay layer along the railroad southeast of Brassfield; also in the lower part of the upper or Estill clay of the Crab Orchard bed, above the Waco horizon, at Panola, north of Irvine, and at various other localities. The crystals occur in several forms. In a large number of cases the crystals are elongated parallel to the clino-axis, producing long negative pyramid and clinopinacoid faces and short unit prism faces, which give the crystals a sort of prismatic aspect. In another common form the crystals have a sort of elongate tabular appearance. In this case the crystals show twinning, the orthopinacoid being the twinning plane. The broad, flat faces are formed by the two clinopinacoids, while the two narrow faces on either side are formed by the unit prism faces. At one end there are four pyramid faces consisting of the two pairs of negative unit pyramid faces belonging to the twins. At the other end there is a corresponding re-entrant angle.

In a third group of crystals the gypsum assumes the familiar swallow-tail form of twins. In this case the orthopinacoid again is the twinning plane, but the greater part of the growth of the crystal is lateral, especially parallel to the clino-axis, rather than in the direction of the vertical axis. On the upper side of the twin the negative pyramid faces are well developed; on the other side the orthodome faces, *e*, round off apparently into the lower pyramid faces and thus form the peculiar reentrant angle which gives rise to the swallow-tail form. Sometimes this twinning takes place alternately first towards the right and then toward the left, producing a sort of arborescent or pagoda-like cluster. In these cases the elements of the cluster often have a more lenticular form.

Gypsum, or hydrous calcium sulphate, is not the only sulphate found in the Crab Orchard clays. As a rule, however, the other sulphates do not occur in sufficient quantities to show in an ordinary analysis of the clays. In an analysis of the waters obtained from the clays, on the contrary, some of these sulphates are readily detected, their ready solubilities causing them to form a much larger proportion of the solids dissolved in the water than of the solids forming the mixture of substances called clay. Among these sulphates is hydrous magnesium sulphate, also called epsomite or Epsom salt. This is a common substance in mineral waters. In the solid form it often occurs in mines and caves as delicate fibrous coatings on the walls or as minute crystals mingled with the earth on the floors of these underground passages. In Mammoth Cave it adheres to the roof of the cavern in loose masses like snow balls. It is very soluble in water. At 32° F. one hundred parts of water dissolve 25.76 parts of anhydrous sulphate and .265 parts for every additional degree rise in temperature. It has a rather disagreeable taste and is at the same time salty and bitter. It possesses purgative properties and occurs in the mineral waters of wells such as those of Epsom, in England, and Sedlitz, in Bohemia.

Another common ingredient of the waters obtained from the Crab Orchard clays is hydrous sodium sulphate or Glauber salt. This also is very soluble in water. One hundred parts of water at 32° F. will dissolve 12 parts of sodium sulphate, and at about 65° F. will dissolve about twice this quantity. The solution has a rather disagreeable, salty and bitter taste. It is well known as a purgative.

Potassium sulphate is much less soluble in water, only 11.5 parts being taken up by 100 parts of water at 65° F. It occurs in the waters of the Crab Orchard clays only in small quantities. Sodium chloride also occurs only in small quantities, especially when its ready solubility is considered, one part of salt dissolving in about 2.7 parts of water at almost any ordinary temperature.

The springs issuing from the Crab Orchard clays sometimes contain a sufficient quantity of salts in solution to be known as *licks*. This name dates back to the early history of the State of Kentucky, when herds of buffalo and deer still roamed through Kentucky forests and visited these springs in large numbers. A large number of the smaller streams originating among the Crab Orchard clays are still known as licks, the name often having been used not only for the springs but also for the streams fed by the springs. The quantity of mineral matter carried in solution varied, of course, in different springs. Among the springs or wells carrying the greatest quantity of magnesium sulphate and sodium sulphate in solution may be mentioned the Epsom well about a mile north of Crab Orchard Springs, on the western side of the Lancaster pike; the Foley well about half a mile northeast of Crab Orchard, on the Fall Lick road, two or three hundred yards beyond the cemetery; and the Sowder well, half a mile northwest of the Epsom well, along the road leaving the Lancaster pike a short distance south of the Dix river bridge. Analyses of the waters from these wells are given below.

Number of analysis	535 Epsom	536 Foley	538 Sowder
Silica	.060	.056	.021
Iron carbonate	Trace	Trace	Trace
Lime carbonate	.673	.912	.506
Magnesia carbonate	.116	.131	.375
Lime sulphate	.203	.185	1.566
Magnesia sulphate	3.454	3.520	2.989
Potash sulphate	.067	.170	.298
Soda sulphate	.774	1.013	.398
Sodium chloride	.081	.304	1.000

The medicinal virtues of the waters issuing from the springs or licks soon became recognized. At an early date the waters were evaporated and the ingredients, in a solid state, were sold under the name of *salts*, those from Crab Orchard enjoying a special celebrity. Their first manufacture dates from 1826, when a Mr. Reuben Dollins lixiviated the earth derived from the Crab Orchard clays, and boiled the solution obtained until the salts were thrown down. These were kept at the bar at the old Davenport hotel, in Crab Orchard, and sold at twelve and one-half cents a dose. Dollins afterwards boiled down the water from a spring. The manufacture of these salts, in the course of time, became a profitable business. It was carried on at all seasons of the year and gave employment to a number of families, who obtained their entire living from this industry. The salts became an article of trade and were used as medicine all over the country, especially in the Mississippi valley. It is interesting in this connection to note that at one time they had quite a reputation in the treatment of yellow fever, a groping in the dark for a remedy for this terrible scourge.

At a later time more concentrated solutions of these salts were obtained by digging pits into the clay. These were usually three to four feet wide, six to twelve feet long, and six to twelve feet deep. Generally the walls were planked up and the wells were covered in order to prevent the dilution of the water seeping into the wells by entering rain. Water seeping through the clay became impregnated with the salty materials in the shales, but on entering the pits were exposed to evaporation which resulted in a considerable concentration of the water in the well or pit before it was subjected to boiling. The water

was evaporated in large iron kettles or pans over wood fires. When the large part of the water had been removed, the final stages of evaporation were completed in smaller kettles over slower fire. The residue appeared very much like a mixture of coarse brown and white sugar. In the best brands, the salts were ground so as to give them a better appearance. From twenty to fifty gallons of water were required to make one pound of salt. These salts in the earlier stages of this industry brought as much as one dollar a pound, but at the time when Linney wrote his report on Lincoln county, in 1882, they sold for only fifteen cents per pound.

The following are analyses of two samples of salts as they were offered for sale by druggists in Louisville in earlier days, when this was still a thriving business.

1874. Crab Orchard Springs salts. Evaporated from the water secured at various springs.

1875. Crab Orchard Springs salts. Evaporated from water secured from various springs.

Analysis. Dried at 212<sup>0</sup> F.:

	No. 1874	No. 1875
Water of crystallization and loss	23.421	24.402
Silica	.124	.118
Ircn peroxide	.078	.028
Lime carbonate	.032	.018
Magnesia carbonate	.089	.036
Lime sulphate	2.149	1.795
Magnesia sulphate	54.842	60.627
Potash sulphate	2.707	2.814
Soda sulphate	13.566	8.260
Sodium chloride	2.954	1.874
Lithia sulphate	.038	.028

The area from which these Crab Orchard salts were obtained centered chiefly about Crab Orchard. Wells were operated as far west as Cedar creek, as far north as the Dix river, and up the Dix river valley, east of Crab Orchard, as far as the Crab Orchard clay bed was exposed. In all of these cases, as far as known, these wells or pits were opened in the great series of clays forming the upper part of the Crab Orchard bed, above the Waco horizon.

Similar mineral waters, however, occur also in the Lulbegrud layer, for instance at Kiddville, in Clark county. An analysis of the water of the Epsom well at Kiddville is here appended. It was an ordinary walled well at first, but afterward was enlarged so as to produce a pit 10 feet in diameter. For some reason this spoiled the well and operations were discontinued.

2471.—Magnesium mineral water. From a well at Kiddville, on the property of J. E. Groves. Collected by W. M. Linney, July, 1884.

Analysis. In 1000 parts of water.

Iron and manganese carbonates	.0024
Lime carbonate	.3740
Magnesia carbonate	.0191
Lime sulphate	3.2610
Magnesia sulphate	4.7776
Potash sulphate	.0490
Soda sulphate	.7118
Sodium chloride	.2120
Lithium chloride	.0130
Silica	.0100
Total saline matter	9.4299

The manufacture of Crab Orchard salts has practically come to an end. Its history, at present, is of interest chiefly in indicating the character of some of the ingredients of the clays not brought out by ordinary chemical analyses. The origin of these salts in the Crab Orchard clays has not been investigated. It is difficult to conceive of them as precipitates from the sea during the deposition of the clays. The proportion in which the various ingredients occur is so utterly different from the ratios of their occurrence in the sea. The following table, showing the proportion of the various ingredients dissolved in sea water and obtained by ordinary evaporation of the latter will illustrate this difference.

Chloride of sodium	77.758
Chloride of magnesium	10.878
Sulphate of magnesium	4.737
Sulphate of lime	3.600
Sulphate of potash	2.465
Bromide of magnesium	.217
Carbonate of calcium	.345

For the present it is desired merely to call attention to the fact that these Crab Orchard clays, where impregnated with considerable quantities of Epsom and Glauber salts, occur below or in the vicinity of great masses of Devonian black shale which often contain considerable quantities of iron pyrites. The decomposition of the iron pyrites often results in the production of various sulphates, and possibly some of the sulphates in the Crab Orchard clays may directly or indirectly have had this source.

The Crab Orchard clays may be traced northward into Ohio. Here they were identified by Professor Orton as the Niagara shales. In Highland county this shale, according to the analysis of Professor Wormley, is much more siliceous than the Crab Orchard clay; still farther northward in Ohio, however, the Niagara shale is replaced by a series of thin shaly fragile courses of limestone in which lime and magnesia carbonate predominate greatly. Analyses from these localities are added.

54 C	Highland county	Greene county
Silica	78.00	12.21
Alumina and iron	3.20	8.40
Lime silicate		8.48
Lime carbonate	11.40	34.42
Magnesia carbonate	6.50	30.87
Water combined		5.40
Total	99.10	99.78

#### 4. SILURIAN LIMESTONES ABOVE THE CRAB ORCHARD HORIZON.

In Ohio, the Niagara shales, stratigraphically equivalent to the Crab Orchard clays, are overlaid by magnesian limestones known as the Springfield and Cedarville limestones. These are followed by the Hillsboro sandstone, after which there is another series of magnesian limestones, the Greenfield or Monroe bed. Analyses of these rocks as they occur at Hillsboro and Greenfield are appended.

	Springfield limestone	Cedarville limestone	Hillsboro limestone	Greenfield limestone
Silica	13.30	.40	94.10	1.00
Alumina and iron	2.00	1.80	3.60	1.30
Lime carbonate	35.51	54.25	1.30	53.67
Magnesia carbonate Silicates of lime and magnesia.	49.87	43.23	.39	$\begin{array}{r}42.42\\1.44\end{array}$

Silurian limestones occur above the Crab Orchard clays north of the Licking river in Fleming and Lewis counties. These limestones have not been studied with sufficient care to determine their stratigraphical equivalency with the Ohio divisions, but the following analysis, taken presumably from the large exposures along the river at Vanceburg, is probably of Silurian age and is tentatively referred to the Greenfield or Monroe bed in the Upper Silurian.

2484.—Limestone. Probably from the neighborhood of Vanceburg. Geological position: Probably from the Greenfield bed at the top of the Silurian, at Vanceburg. Sent to John R. Procter by W. J. Richason, of Vanceburg.

A dull-gray, fine-granular rock, with faint lines of stratification. Analysis. Air-dried.

Moisture and loss	.547
Insoluble silica and silicates	8.850
Soluble silica	1.150
Alumina and iron oxide	2.490
Phosphoric acid (P <sub>2</sub> O <sub>5</sub> )	.143
Lime carbonate	48.790=27.322 lime.
Magnesia carbonate	
Potash	.490
Soda	.058
-	
Total	100 000

The following analysis appears to be from another Silurian locality, not visited. Judging from the location of this limestone in Lewis county, four miles from Clarksburg, the horizon should be immediately above the Crab Orchard clay.

1085.—Yellow magnesian limestone. Silurian. Salt Lick creek, four miles above Clarksburg, near Valley, Lewis county. Brownish buff porous limestone, full of fossil casts. Exterior surface soft, so as to be scratched by a nail.

Geological position: Probably Silurian, above the Crab Orchard shale horizon.

Water and loss	1.428
Silica and insoluble silicates	2.580
Alumina, oxides of iron and manganese	12.280
Phosphoric acid	.207
Sulphuric acid	.152
Lime carbonate	55.240
Magnesia carbonate	27.820
Potash	.167
Soda	.126

The Chemical Characteristics of the Devonian Rocks of Kentucky, East of the Cincinnati Geanticline.

A. DEVONIAN LIMESTONES.

#### 1. CHEMICAL ANALYSES.

The Devonian limestone has not been traced north of the Licking river. The following analysis of a bed of limestone immediately beneath the Devonian black shale, near Olympian Springs, in Bath county, probably represents the characteristics of one of the most northern exposures of the Devonian limestone in the State.

1989.—Ferruginous Magnesian Limestone, out of which flows the Chalybeate Spring, and which forms the bed of the Chalybeate Branch, about half a mile north of Olympian Springs.

Geological position: It lies immediately under Devonian Black shale, and probably represents the Devonian limestone. Collected by Robert Peter.

A crystalline-granular limestone; gray, of various tints, in the interior generally light gray; light ferruginous or brownish-ochreous on the exterior.
# Analysis. Dried at 212<sup>0</sup> F.:

Silica	.280
Iron carbonate	11.532
Phosphoric acid	.006
Lime carbonate	54.000
Magnesia carbonate	34.027
Potash	.143
Soda	.040
Total	100.028

In various parts of Clark and Madison counties, and even as far west as Boyle county, there is, a layer at the base of the Devonian limestone which contains, fish plates and fish teeth. This was correlated by the former geological survey of Kentucky with the Oriskany. They are here included in the Devonian series of limestones, occurring at their base. Owing to the presence of these fish remains, this thin layer of rock sometimes is rich in phosphoric acid, as the following analyses will show. It is the Kiddville layer.

2469.—Phosphatic rock. Stewart Mill, Lulbegrud creek, Clark county. About a mile and a quarter northeast of Indian Fields.

Geological position: Layer with fish remains, at base of the Devonian limestone. Collected by W. M. Linney, July, 1884.

A dark, brown-gray, conglomerate rock, containing many darkcolored fragments of fossil organic remains.

2470.—Phosphatic rock. From near Howard creek, Clark county. Probably west of Indian Fields.

Geological position: Base of the Devonian Limestone. Collected by W. M. Linney, July, 1884.

An impure, ferruginous limestone rock; gray-brown, with ochreous material in spots; contains, fossil impressions.

Analyses. Air-dried samples.

	No. 2469	No. 2470
Siliceous residue insoluble in acids Alumina and iron oxide not estimated	27.580	31.720
Phosphoric acid (P <sub>2</sub> O <sub>5</sub> )	9.710	1.842
Lime carbonate	21.380	33.980
Magnesia carbonate	3.055	11.185
Potash	.830	not estimated
Soda	.228	not estimated

Less than a mile from Stuart's mill, down Lulbegrud creek, is the Oil Spring, once a famous water resort. The following analysis is taken probably from a rock belonging to the top of the Devonian limestone at this locality. The dull buff color is very characteristic of the Duffin layer at this exposure.

889.—Rock with oil at base of Black shale, at the Oil Spring, about a mile east of Indian Fields, Clark county. A dark gray limestone with cavities lined with calcareous spar and impregnated with fluid bitumen. Weathered on the surface to a dull buff color.

Geological position: Probably the brecciated or Duffin layer, at the top of the Devonian limestone.

Bituminous matter, water, and loss	7.092
Silica and insoluble silicates	2.480
Alumina, oxides of iron and manganese	11.260
Phosphoric acid	.438
Lime carbonate	56.76
Magnesium carbonate	21.302
Sulphuric acid	.372
Potash	.193
Soda	.103

The following analyses were taken apparently from the base of the Devonian limestone, and from the upper part of this limestone, below the Duffin or brecciated layer.

2197.—Limestone, probably from the vicinity of Elliston, but locality not mentioned.

Geological position: From below the Cauda-galli horizon, at the base of the Corniferous limestone. Collected by John Procter.

A fine granular, brownish-gray rock. It gives the odor of petroleum when heated, and probably owes its brownish tint to a small quantity of this substance.

2199.—Impure limestone. Probably from the vicinity of Elliston, but the locality is not mentioned.

Geological position: Top of the Corniferous limestone. Total thickness fifteen feet, with intercalated beds of purer limestone six inches thick.

A tough, fine granular or compact rock. Samples from dif-

ferent levels are mixed; some are brownish-black, some umber colored, and some intermediate in tint.

Analyses. Dried at 212<sup>0</sup> F.:

	No. 2197	No. 2199
Bitumen, water, and loss	11.287	
Potash	.770	7.339
Soda	.149	
Siliceous residue	22.680	31.990
Lime carbonate	43.060	36.580
Magnesia carbonate	9.994	18.541
Alumina and phosphoric acid	9.420	4.010
Iron peroxide	2.640	1.540
Total	100.000	100.000
Percentage of lime	24.113	20.485
Percentage of magnesia	4.756	8.781

The only building stone known at the locality, from which the following analysis was taken, is of Devonian age.

947.—Building stone. Five miles from Irvine, on the Richmond pike, Estill county. Dark gray, fine grained limestone, with many small scales of mica.

Geological position: Probably Devonian limestone.

Silica and insoluble silicates	18.680
Alumina	.806
Iron oxide	2.360
Iron carbonate	4.321
Manganese, brown oxide	.480
Phosphoric acid	.374
Sulphuric acid	1.471
Lime carbonate	41.380
Magnesium carbonate	30.019
Potash	.482
Soda	.019

A careful study of the Devonian limestone has been made by the present survey at only one locality, at Duffin's cut, half a mile north of Junction City, on the Queen and Crescent railroad. Three samples were analyzed: One from the base of the

Devonian, one from the cherty part above the middle of the section, and one from the brecciated or Duffin layer.

2629.—Devonian limestone, lower 2 feet of section. A compact light gray limestone. The greater part of the sulphur is derived from iron pyrites. This limestone would probably make natural cement, as its analysis is very like that of the Louisville cement rock. Collected by Aug. F. Foerste, at Duffin cut, half a mile north of Junction City, Boyle county.

This limestone is overlaid by dense white limestone, 2 feet thick; baldly weathered limestone, 4 inches thick, quite fossiliferous; dense bluish white limestone, 2 feet 4 inches thick, dense bluish white limestone, 6 inches thick; and dense whitish limestone with considerable chert, 4 feet 8 inches thick. Of the last named part of the section the following analysis was taken.

2630.—Devonian limestone, from the chert part of the section, at Duffin cut. The greater part of the sulphur is in the form of iron pyrites, and the iron is mostly in the ferrous condition, although calculated as ferric oxide in the following statement of results.

Above this cherty limestone there is a dark gray rock, 6 to 8 feet thick, often having a sort of brecciated appearance. This is the Duffin layer and the analysis is given last.

2631.—Brecciated or Duffin layer. A dark gray stone with light, softer patches, giving it a brecciated appearance. It also contains some chert in small imbedded masses. The greater part of the sulphur is in the form of iron pyrites. For separate analyses of the white and dark gray parts of this sample see analyses No. 2632. and 2633 below. Collected at Duffin cut, half a mile north of Junction City, by A. F. Foerste, 1904.

	Base No. 2629	Cherty layer No. 2630	Duffin layer No. 2631
Moisture	.14	.09	.06
Ignition (combined water, volatile			
matter, and carbon dioxide	35.46	44.79	41.92
Silica	20.02	2.14	7.74
Alumina	3.23	1.24	2.73
Ferric oxide	1.36	2.34	2.04
Lime	24.06	31.96	29.66
Magnesia	14.62	17.84	14.65
Potash, soda, and lithia	Traces	Traces	Traces
Phosphorus pentoxide	.37	.06	.09
Sulphur trioxide	1.06	.45	.51
Total	100.32	100.91	99.40
Sulphur calculated from the sulphur		-	
trioxide Iron pyrites equivalent to total sul-	.42	.18	.20
phur	.79	.34	.38

Analyses. Air-dried samples. Devonian Limestones.

As a means of comparing the white component of the Duffin layer with the dark gray component, the following analyses are added. The white color is found in the small more or less angular blotches which give the brecciated appearance to the rock. The dark gray color is characteristic of the body of the rock, aside from the small light colored blotches just mentioned.

2632.—The white component of the Brecciated or Duffin layer, obtained by carefully breaking it out from the gray body of the rock. The white part appeared to constitute only about a fourth of the original rock. It was separated in a fair state of purity. The greater part of the sulphur is in the form of iron pyrites, and the iron is in the ferrous condition. This analysis resembles No. 2630 rather closely. Collected at Duffin cut, north of Junction City, Boyle county, by A. F. Foerste, in 1904.

2633.—The dark gray component of the brecciated limestone or Duffin layer, exclusive of the chert, obtained by carefully breaking it out. It was found impossible to separate the gray

entirely from the white. The greater part of the sulphur is in the form of iron pyrites and the iron is in the ferrous condition. From Duffin cut, collected by A. F. Foerste, in 1905.

	White blotches No. 2632	Dark gray body of rock No. 2633
Moisture	.05	.08
Ignition (combined water, volatile matter and carbon		
dioxide	44.42	42.46
Silica	3.18	6.86
Alumina	.76	1.40
Ferric oxide	3.62	2.94
Lime	31.04	29.58
Magnesia	17.22	16.25
Potash, soda, and lithia	Traces	.39
Phosphorus pentoxide	.06	.08
Sulphur trioxide	.26	.66
Total	100.61	100.70
Sulphur calculated from the sulphur trioxide	.10	.26
Iron pyrites equivalent to the sulphur	.19	.50

Analyses of components of Duffin rock. Air dried:

It is evident from the preceding analyses that the Duffin layer consists of a very typical dolomite, the ideal dolomite consisting of 30.4 per cent. of lime and 21.7 per cent. of magnesia. In the field, the Duffin layer often has a deep brown color and appears to be full of small angular fragments, chiefly less than half an inch in diameter. It then resembles a volcanic ash or tuff, but the chemical analysis is entirely against such an origin. The cause of the brecciated appearance has not been determined.

At some localities the Duffin layer appears to form a part of the Devonian black shale series; at other localities true limestones occur at horizons thirteen to twenty feet above the base of the black shale. Several analyses made under the preceding survey are added here, owing to the possibility of their affording a clue to some one interested in some special line of investigation. The precise horizon from which the rocks analyzed were obtained is not known, but is sufficiently indicated to afford a clue as to their probable location. 2198.—Bituminous limestone, from near Elliston.

Geological position: From above the Corniferous limestone. Bed, three to ten feet thick. Collected by John R. Procter. Possibly the brecciated appearing limestone or Duffin layer.

Generally of a dull, brownish-black color. Some pieces with bands of a lighter gray tint. It is a fine granular rock.

2200.—Limestone, on the road one mile south of Mrs. Susan Jane Embry. A little over two miles south of Waco, on the road to Brassfield, a lane turns off westward from the road and then angles off irregularly toward Searcy station; a short distance westward along this lane Mrs. Embry used to live.

Geological position: Intercalated with the so-called Black band or bituminous limestone. Collected by John R. Procter. Possibly the brecciated layer or Duffin layer.

A dull buff-gray, fine granular rock, with some little infiltration of hydrated iron oxide.

	No. 2198	No. 2200
<i>ā</i>		1
Water and loss		6.117
Bitumen, water, and loss, potash and soda	13.022	not estimated
Siliceous residue	20.990	18.190
Alumina and phosphoric acid	9.040	\$ 10.980
Iron peroxide	1.890	10.300
Lime carbonate	41.150	47.580
Magnesia carbonate	13.908	17.133
Total	100.000	100.000
Percentage of lime	23.044	26.645
Percentage of magnesia	6.384	8.158

Analyses. Dried at 212<sup>0</sup> F.:

888.—Limestone. From the base of the Black slate series, in Clark county. The dense calcareous portion of the gray black slate. Found also in Madison, Bath, Powell, Estill counties.

Geological position: Possibly the brecciated or Duffin layer.

## Analysis:

Bituminous matter, water, and loss	9.552
Silica and insoluble silicates	23.180
Lime carbonate	40.280
Magnesium carbonate	15.903
Alumina, iron oxides, manganese, and phosphates	9.460
Potash	.436
Soda	.164
Sulphuric acid	1.025

# 2. AVAILABILITY OF DEVONIAN LIMESTONES FOR THE MANUFACTURE OF NATURAL CEMENTS.

Among the preceding analyses, attention may be called to the small quantity of silica in the magnesian limestones from the Olympian Springs, and from the vicinity of the Oil well on Lulbegrud creek, northeast of Indian Fields. The small quantity of silica in the cherty part of the Devonian limestone in the Duffin cut, north of Shelby City, also is of interest, since here a much larger percentage of silica was expected. The question arises whether the segregation of silica in the cherty bands and nodules throughout certain layers of the limestone has not reduced the percentage of silica in the immediately surrounding matrix of limestone within which the chert occurs. There is no doubt, however, that by far the greater part of the chert must have entered the limestone from some extraneous source, since in some cases the quantity of chert, actually exceeds the total quantity of limestone, and often is large enough to necessitate some other origin than that of the limestone itself.

All of the Devonian limestones investigated are too strongly magnesian to be available for the manufacture of high grade Portland cement. The percentage of magnesium carbonate usually equals or exceeds 15 per cent. The layer at the base of the Devonian limestone at Elliston, which contains 10 per cent. of magnesium carbonate is only a couple of feet thick.

Moreover, most of the Devonian limestones are not likely to be of value in the production of natural cements. The total thickness of Devonian limestones in most parts of Kentucky, east of the Cincinnati geanticline, is altogether too small to make them available, especially since such a large part of even

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this comparatively small section of limestone is likely to be entirely too cherty to be of use commercially. Locally, however, considerable sections are known which are comparatively free from chert. Some of the localities near Elliston, and others several miles northeast of Waco, in Madison county, are known to be comparatively free from chert and yet to show about twenty feet of rock which might be commercially available. Other localities exist near Crab Orchard, and several of these are very favorably situated as regards railroad facilities. No chemical analyses have been made so far however.

Under the term natural cements a great variety of cements are included. In the manufacture of natural cements no attempt is made to remedy any of the defects of the natural rock. There is no mixture of materials, but whatever rock is selected for manufacture is burned without mixing or preliminary grinding. As in the case of Portland cement, the essential elements again are the lime, silica, alumina, and ferric oxide, but the rock is always burned at a lower temperature than Portland cements, the mass of the rock in the kiln is never hot enough to even approach the fusing or clinkering point which is essential in the manufacture of Portland cements. The lime combines with the silica, alumina, and ferric oxide, forming various silicates, aluminates, and ferrites of iron, but the natural cements set more rapidly than Portland cement and ultimately do not attain so high a degree of strength.

Limestones used for the production of natural cements invariably are clayey, containing from 13 to 35 per cent. of clayey material (alumina and silica), of which 10 to 22 per cent. is silica, while alumina and ferric oxide together may vary from 4 to 16 per cent. Since a great variety of clayey limestones will produce natural cement on burning, it is evident that rocks favorable for this purpose must be comparatively common and widely distributed. For this reason, also, natural cements are likely to be comparatively cheap and must find a market near home, usually within the boundaries of the State producing them.

In the production of these natural cements a much higher percentage of magnesium carbonate is permissible. In the limestones used for the manufacture of the so-called Louisville cements, the percentage of magnesium carbonate varies from

15.90 to 35 per cent. In fact, in the case of natural cements, the magnesium carbonate may be regarded as equivalent to an approximately equal amount of lime carbonate and the two may be calculated together, as far as their availability in the production of natural cements is concerned. This being the case, it is believed that the usefulness of Devonian limestone for the manufacture of natural cements deserves investigation, especially in the neighborhood of Crab Orchard, and in certain parts of Madison county.

# B. DEVONIAN BLACK SHALES.

The chemical composition of the Devonian Black shales is indicated sufficiently by the following analyses, one from Madison county, Kentucky, the other from the vicinity of Columbus, Ohio.

	Kentucky, Madison county	Columbus, Ohio
Bituminous matter, water, and loss	12.000	11.40
Silica	63.120	60.35
Alumina and iron peroxide	8.560	21.20
Phosphoric acid	.143	
Lime	6.261	2.95 = carbonate
Magnesia	2.034	3.33=carbonate.
Potash	1.363	
Soda, not estimated.		

## 1. THE MINERAL WATERS OF THE BLACK SHALES.

The black shale often contains iron pyrites, the decomposition of which results in the production of copperas. A general idea of the chemical composition of this copperas is afforded by the following analysis.

1083.—Saline efflorescence or copperas, from the Devonian Black slate, near David Mifford, 8 miles from Clarksburg, and 4 miles beyond Valley, Lewis county. Yellowish white.

Water and loss	48.762
Impurities	1.000
Aluminum sulphate	25.585
Iron sulphate	15.653
Magnesium sulphate	1.000
Alkaline sulphates	8.000

These sulphates go into solution in the waters percolating through the black shales, and issue at springs to which they may give a more or less distinct flavor. Many other substances are taken up, some of them in sufficient quantities to be readily detected on analysis. It has been stated that the table of contents of the waters from a mineral spring is but an index of the various geological strata through which its waters have passed and of the mineral bodies with which they have come in contact. In this sense, the Devonian black shales should be of special interest to the people of Kentucky, since a considerable part of the springs which are visited, more or less, for their medicinal virtues issue from the black shales. Among these may be mentioned the Fox springs, eight miles east of Flemingsburg, in Fleming county; the Olympian springs, in the southeastern part of Bath county; the Oil springs, about a mile northeast of Indian Fields, in the northeastern part of Clark county; the Estill springs, about a mile north of Irvine, in Estill county; Hale's well, about four southeast of Stanford, in Lincoln county; the Linietta springs, northwest of Junction City, in Boyle county; Alum springs, two miles farther west in Boyle county; the Sulphur springs, three miles, southeast of Lebanon, in Marion county; and numerous other springs, less, known but with waters containing the same ingredients.

For convenience, mineral waters may be divided into several classes. *Alkaline* waters are those which contain as principal ingredients the carbonates of the alkaline earths, calcium and magnesium, and the carbonates of the alkalies, potassium and sodium. Waters of this class usually contain considerable sodium carbonate and calcium carbonate, and, small amounts of the chlorides and sulphates. If much sodium carbonate is present, the water has a greasy touch. Such waters are regarded as diuretic, producing an increased flow of urine, and so may be of service in flushing the system and in helping to get rid of accumulated waste products. *Saline* waters contain as prin-

cipal ingredients the sulphates or chlorides of calcium, magnesium, aluminum, potassium and sodium. Sodium chloride is the most common ingredient of such waters, but magnesium sulphate (Epsom salt) and sodium sulphate (Glauber salt) occur in most waters of this class. Sodium carbonate, on the contrary, occurs only in very small quantity as a rule. Sodium chloride waters are said to be useful in stimulating the gastric mucous membrane, in increasing the appetite, and in getting rid of excessive amounts of secreted mucus. The best results are obtained in gastritis. Saline waters containing considerable quantities of magnesium and sodium sulphate are purgative. *Chalybeate* waters contain as their principal ingredients the salts of iron, especially iron bi-carbonate. On coming to the surface at the spring, this bicarbonate gives up the carbonic acid and takes up oxygen. It thus is changed to iron oxide which precipitates or settles as a brownishvellow sediment. This sediment is seen not only at the spring but also for some distance along the stream leading away from the spring. Such waters are often recommended for patients suffering from anemic or chlorotic conditions. Iron compounds, if taken in sufficient quantities, or for a long time, may cause constipation and other disturbances of the digestive system, but usually they occur in too small a quantity in the mineral waters to cause any injury.

Sulphur waters are those which contain a sufficient quantity of hydrogen sulphide to be readily recognized by the smell. The same gas is present in rotten eggs and hence waters containing sulphuretted hydrogen often are said to smell and taste like rotten eggs. On reaching the surface at the spring, much of the hydrogen sulphide escapes. When brought in contact with the oxygen of the air, the gas in part is dissociated into its elements and the sulphur is deposited as a white or whitish-yellow sediment upon surrounding objects, while the hydrogen unites with the oxygen to form water. Wells containing this deposit often are known as *white-sulphur* wells. When salts of iron are present, the free sulphur may unite with the iron to form black flakes of iron sulphide, resulting in a black sediment, and giving rise to the name *black-sulphur* wells. As far as known, hydrogen sulphide does not have any pronounced medicinal value when taken into the stomach. Waters contain-

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ing hydrogen sulphide in notable quantities usually are more or less saline and the medicinal virtues of these waters is due to their saline contents and not to the gas. The bad smell of the water is not an index of its medicinal value.

All of these classes of springs are represented among the springs issuing from the Devonian black shale, as may be seen by an examination of the following partial records of analyses, in which only the principal ingredients are recorded. Most of these analyses were made so long ago that a special report on the mineral springs of the Devonian black shale belt is now desirable. A report bringing together all available information on the mineral waters, of Kentucky, and accurately defining their mineral ingredients, would be of material assistance to physicians in recommending to their patients the use of waters from particular springs. In the following analyses the figures state the number of parts of the ingredients found in a total of 1,000 parts of water.

LOCATION, NAME AND CHEMICAL NATURE OF SPRING	Indian Fields, Clark County, Soda Spring, Alkaline, Saline	Olympian Springs, Bath County, Tea Water, Alkaline, Sa- line	Olympian Springs, Kitchen Well, Alka- line, Saline	Olympian Springs, Black Sulphur Water, Sediment nearly black, Alkaline, Saline	Olympian Springs, White Sulpnur Water, Alkaline, Saline	Junction City, Boyle County, Black Sulphur Water-sediment black, Alkaline, Saline, slight- ly Chalybeate	Alum Springs, Boyle County, Black Sul- phur Water, Alkaline, Chalybeate	Junction City, Lin- ney's Well, Black Sul- phur Water, Alkaline, Saline, with Epsom Salt	Fox Springs, Fleming County, White Sul- phur Water, Alkaline, Saline, with Glauber Salt	Indian Fields, Red Sulphur Water, Alka- line, Sallne, Calcareous	Alum Springs, Petro- leum Spring, Calcar- eous
No. of analysis	2474	1992	1991	1985	1986	2274	2275	2276	2658	2474 bis.	2277
Soda carbonate	.5266	.4479	.5431	.3247	.3113	.5089	.0870	.288	.0538	.033	
Lime carbonate		.0241	.0556	.0158	.0744		.0396	1.490	.0982	.156	.0151
Magnesia carbonate			.0277				.0216		.0430	.051	.0278
Iron carbonate						2600.	.0342				
Soda chloride	.0371	.0877	.1483	.1208	.1326	.1204		.247	.0427		
Magnesia chloride	.0159									.067	
Calcium chloride											.0086
Soda sulphate			.0208			.1841			.0460		
Potash sulphate			.0285			.0164		.192			
Lime sulphate	0.265	-		-				.267		.038	.0408
Magnesia sulphate								.160			

ALKALINE AND ALKALINE SALINE SPRINGS.

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LOCATION, NAME AND CHEMICAL NATURE OF SPRINGS. No. of analysis. No. of analysis. Soda sulphate. Lime sulphate. Potash sulphate. I of analysis. Soda sulphate. Potash sulphate. I on carbonate. I on carbonate.	Lebanon, Marion Co., Harrison Spring, from Waverly Bed, Epsom, Glauber Junction City, Boyle County, Knott's Spring, Glauber, Epsom.	Indian Fields, Grove's U. 49 81 01 Well, from Crab Orch- ard Bed, Epsom, Glauber 47 82 84 87 Well, from Crab Orch- ard Bed, Epsom, Glauber 47 80	Junction City, Fale's Epsom Spring Epsom, Chalybeate 82 73 12 10 20 647 70 10 10 10 10 10 10 10 10 10 10 10 10 10	Olympian Springs, Chalybeate Spring, Brownish-orange sedi- ment, Epsom, Glauber.	Junction City, Procter's $0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 $	County, Main Chaly- beate Spring, Ferrugin- ous-brown sediment, Epsom, Chalybeate 2 4 61   1 10 10 61 10	Olympian Springs, Bath
Lime carbonate		3.740	.198	.0890	.118	°.	8660
							0060

EPSOM AND GLAUBER WATERS.

LOCATION, NAME AND CHEMI- CAL NATURE OF SPRING	Junction City,Boyle County, Salt Well, Saline	Olympian Springs, Bath County, Salt Sulphur, Yellowish or Ochreeus Incrus- tation, Saline	Olympian Springs, Bath County, Salt Water, Saline	Indian Fields, Clark County, Oil Spring, Salime
No. of analysis	2280	1984	1990	2472
Soda chloride	13.878	4.8997	4.7121	.0973
Magnesia chloride Potash chloride		.1089	.1188	.0845
Lime carbonate	1.454	.1975	.1844	.1198
Magnesia carbonate	1.367	.0506		
Soda carbonate			.2241	
Lime sulphate				.0583

# SALT SPRINGS.

# ALUM AND CHALYBEATE SPRINGS.

LOCATION, NAME AND CHEMICAL NATURE OF SPRING	Junction City.Boyle County.Alum Water. Alum, Epsom	Junction City, Chaly- beate Well, Copper- as, Epsom, Glauber.	Indian Fields, Chaly beate Spring, Alum Chalybeate	Alum Springs, Boyle County, Old Chaly- beate Spring, Chaly- beate	Alum Springs, Phos- phorus Spring, Chalybeate
No. of analysis	2273	2270	2473	2271	2272
Alumina sulphate	5.3477		.0586		
Iron sulphate	2.6761	.1977		Contraction of the	
Potash sulphate	?	.0235	.0119	.0140	.0140
Lime sulphate	.4994	.2917	.0432		
Magnesia sulphate	.1350	.2250			
Soda sulphate		.1521			
Iron carbonate	1		.0192	.1862	.1654
Lime carbonate				.0199	.0307
Magnesia carbonate				.0093	.0133
Soda chloride	i		.0162	1 1	

In the case of the Alkaline springs, those in which sodium carbonate is the chief ingredient predominate. Springs of this type occur northeast of Indian Fields, and near the Olympian Springs. Those at Junction City and at Fox Springs contain not only sodium carbonate but also appreciable quantities of the sulphates of sodium and magnesium.

Some saline springs contain sodium chloride in quantities so much greater than that in which the other ingredients occur that the name salt springs or salt wells appears most appropriate. One well at Junction City, and two at the Olympian Springs are good examples of these wells. Magnesium chloride, and also the carbonate of sodium or magnesium, or both, also occur. A well containing a considerable quantity of salt occurred at the crossing of the Cincinnati Southern railroad over Green river, and another is found just east of the depot at Crab Orchard.

In one of the wells, at Junction City, the sulphate of soda or Glauber salt predominates, although the sulphate of magnesia or Epsom salt also occurs in considerable quantities. Usually the conditions are reversed and Epsom salt predominates very much. Wells of the latter class occur at Lebanon, Indian Fields, Junction City, Olympian Springs; and one at Fox Springs shows a slightly greater quantity of magnesium sulphate. The well at Lebanon issues from the base of the Waverly series, from the lower part of the Linietta or Bedford clay shales. The one at Indian Fields is in the Crab Orchard bed. The wells at Olympian Springs issue from the crevices in the Devonian limestone, at the base of the Devonian black shales. The water at Fox Spring issues from near the top of the limestone underlying the Devonian black shale. From this it may be seen that saline springs in which the sulphates of magnesia and sodium are the chief ingredients are more common in the ordinary clays of the Crab Orchard and Waverly beds, and in the accompanying limestones, than in the carbonaceous Devonian black shales.

Waters containing more or less alum and copperas are more common in the Devonian black shales than is indicated by the accompanying analyses. The analyses have not been made with the view of determining what percentage of the saline material is in the form of alum. The carbonate of iron occurs in small quantities in quite a large number of the springs which have been examined. In only two springs, however, is iron carbonate the chief ingredient, and both of these occur at Alum Springs, a short distance east of Junction City, on the Knoxville branch of the Louisville and Nashville railroad.

Such traces of life as have been found in the Devonian black shales have been chiefly of vegetable origin and on this account the bituminous matter in these shales is believed to be chiefly of vegetable origin. The large accumulations of oil at Ragland and Irvine may have had an entirely different origin. The mineral part of the shales does not show any close agreement with the materials forming the Crab Orchard clays, from which, indeed, they are separated in the greater part of the area under discussion by the Devonian limestone. As compared with the Crab Orchard clay, the black shales show more silica and lime, and less alumina and potash. The reasons for these differences have not been determined.

The Devonian black shales, in their original condition, are useful chiefly as road material. Although very little intelligence is shown usually in the use of this material for roads, during a large part of the year the black shale roads are in excellent condition. When greatly decayed and reduced to clay, the Black shale is serviceable for the manufacture of vitrified brick.

# The Chemical Characteristics of the Lower Waverly Rocks.

## A. LI:\IIETTA OR BEDFORD CLAY SHALES.

At the base of the Linietta or Bedford clay shales', at the bottom of the 'Waverly series of strata, phosphatic nodules occur yery frequently and over a wide area. Usually they are con11ned to a few inche.'S at the base of the series, although ranging sometimes for seyera 1 feet. They often contain fossil remains, mmall,v some shell or the fragment of some fish remain. The following analysis indicates at least the presence of cons,iderable phosphatic material. 2281.—Phosphatic nodules, Boyle county. Probably from the neighborhood of Junction City.

Geological position: From the base of the Linietta or Bedford clay shales, at the base of the Waverly series. Collected by William M. Linney, Oct. 17, 1882.

Shapes generally oblong, spheroidal or ovoid, somewhat flattened. Exterior of a dull brownish-gray color; interior darker and irregularly cellular. Some of them contained fragments of fossil bones.

On examination they were found to contain bituminous matter, ferrous carbonate, and a considerable proportion of phosphates, which in one analysis gave 29.10 per cent. of phosphoric acid ( $P_2O_5$ ).

At the base of the Waverly series of strata there is a great mass of clays, here called the Linietta clay, which occupies about the same horizon as the Bedford formation of Ohio and the New Providence shale of Indiana. Northward, toward the Ohio river, this clay section is replaced by arenaceous shales interbedded with fine-grained sandstones or *freestones*. The analyses of the Linietta clays are fairly represented by those cited below.

2597.—Linietta or Bedford clay. From Blue Lick, Madison county. From Berea, 1.5 miles on Kingston pike, then 1.5 miles east to junction with Blue Lick pike. Southwest of road corner. Geological position: 0 to 40 feet, at base of Waverly. Collected by A. F. Foerste, 1904.

Analysis of air-dried sample:

Moisture	1.75
Ignition (combined water, etc.)	4.29
Silica	65.58
Alumina	16.00
Ferric oxide	5.21
Lime	.03
Magnesia	1.25
Potash	3.89
Soda	.82
Titanium dioxide	1.13
Sulphates and phosphates	Traces
Total	99.95

2499.—Clay. On the land of John Pigg, three miles northeast of Berea, two miles south of Bobtown, near the road from Berea to Bobtown, at the Blue Lick. Locality: R-S-8. Geological position: Linietta or Bedford clay shale at base of the Waverly series. Collected by Moritz Fischer, August 16, 1884.

Analysis of air-dried sample:

Hygroscopic moisture	1.030
Combined water and loss	2.947
Silica	68.440
Alumina and iron oxide	20.180
Lime carbonate	.144
Magnesia carbonate	2.860
Potash	3.678
Soda	.740
Phosphoric acid (P2O3)	A trace
Total	100.000

Pulverized and kneaded with water, it would be plastic enough to be used for common pottery-ware.

2618.—Analysis of clay, Junction City, Boyle county, Ky. Geological position: Linietta or Bedford clay, at base of Waverly series. Blue Lick, northwest of Linietta Springs, northwest of Junction City about one-half mile. A. F. Foerste, 1904.

Analysis of air-dried sample:

Moisture	1.35
Ignition (combined water, etc.)	4.85
Silica	62.44
Alumina	17.87
Ferric oxide	6.31
Lime	.18
Magnesia	1.18
Potash	3.52
Soda	.77
Titanium dioxide	1.04
Sulphur trioxide	.19
Total	99.70

1873.—Clay. From the headwaters of Green river, on the land of Thomas W. Varnon. Bed two to four feet from the surface, and said to be forty-two to forty-five feet thick; resting on Black shale which is fifty feet thick. Salt water is found by boring at a depth of eighty-four feet, and some little petroleum in the sandstone. Collected by Senator Varnon.

Geological position: From the Linietta or Bedford clay shale, forming the base of the Waverly series.

Clay imperfectly laminated, of a dark olive-gray color. Burns to a gray-buff color. The considerable proportions of the iron oxide, lime, potash, and soda prevent this clay from being refractory in the fire; but while it is therefore unfit for the manufacture of fire-brick, it will yet answer well for ordinary pottery, terra cotta work, and tiles.

## Analysis, dried at 212 degrees F .:

Water and loss	5.705
Silica	61.580
Alumina	23.946
Iron protoxide	5.814
Phosphoric acid	Not Det.
Lime	.201
Magnesia	.850
Potash	1.542
Soda	.362
– Total	100.000

As compared with the Crab Orchard clay, these clays at the base of the Waverly series contain more silica, about the same amount of alumina and iron, and a less quantity of lime, magnesia, and potash. These clays contain too much iron to be serviceable as stoneware clays. They contain, however, enough iron and alkalies, and are sufficiently low in lime and magnesia to make excellent clays for vitrified ware, paving brick, sewer pipe and the like. They will burn to a cherry red color, and would serve also for the manufacture of ordinary brick. Owing to the larger percentage of silica, the Linietta or Bedford days should be more serviceable than the Crab Orchard clay for the manufacture of Portland cement. The clay from the Blue Lick locality, for example, conforms quite closely to the formula that the sum of the alumina and the iron oxide shall equal about a third of the silica, and the requirement that the silica shall equal at least 55 per cent., and preferably should be between 60 and 70 per cent.

#### B. UPPER LAYERS OF THE WAVERLY SERIES.

No attempt has been made to study the upper layers of the Waverly series in east-central Kentucky. In the vicinity of Vanceburg, on the Ohio river, at Alum Rock, the thickness of the arenaceous clay shales and interbedded sandstones, representing the Bedford formation of northern Ohio, is approximately 90 feet. This is overlaid in succession by Berea sandstone, 21 feet thick; thin black argillaceous Sunbury shale, 13 feet thick, and other shaly and sandy layers, representing the Cuyahoga shales. None of these overlying layers can be recognized as distinct formations in east-central Kentucky. The freestone layers at Irvine, and those quarried at Berea occur fully 350 feet above the top of the Devonian black shale. This, probably, is the horizon also of the Farmer station sandstone.

2429.—Sandstone. From the quarry near Farmer Station, on the Chesapeake & Ohio Railroad, thirty-five miles beyond Mount Sterling. Collected by W. W. Monroe.

Geological position: Probably from the upper part of the Waverly series, 350 feet above the base of the series.

A fine-grained sandstone of a handsome light gray color on the recently exposed surfaces, showing a few minute spangles of mica. Stained light ochreous and brownish on the weathered surfaces. Showing no fossil remains, except Taonurus cauda-galli on one of its surfaces. This rock was used in the construction of the court-house at Lexington in 1882. It is composed of fine grains of transparent, colorless quartz united by a cement composed of carbonates of iron, lime, and magnesia, with a little silicate of alumina.

## Analysis; sample air-dried:

Moisture and loss	2.514
Sand and insoluble silicates	93.128
Alumina, phosphoric acid and loss	1.188
Iron carbonate	2.336
Lime carbonate	.578
Magnesia carbonate	.256
Total	100.000

2498.—Plastic clay. From the land of Gordon Glasgow, on the slope of Bear Mountain, three miles southeast of Berea, Madison county.

Geological position: Collected by Moritz Fischer, July 1, 1884, and labeled as: Clay in the Waverly series, near the Conglomerate. This probably is a clay member of the Pennington shale, near the Rockcastle conglomerate, above the Lower Carboniferous limestone, and occurs about 600 feet above the base of the Waverly.

A light gray, plastic clay. Calcines to a light reddish color. This clay could be used for the manufacture of various kinds of common pottery ware, terra cotta products, and the like.

Analysis of air-dried sample:

Water and loss	20.014
Silica	48.000
Alumina	18.380
Iron peroxide	3.900
Lime carbonate	1.600
Magnesia carbonate	4.033
Potash	3.797
Soda	.276
– Total	100.000

# The Chemical Composition of the Irvine Clays.

Probably no class of clays in the central parts of Kentucky have aroused a wider interest for a longer time than those from the Irvine formation in various parts of Madison county. From no area of similar small size have we as many analyses. This is due to the fact that at an early date a fairly extensive production of common stone-ware was founded upon the use of this clay, and that this stone-ware industry is still in existence.

Stoneware differs from common earthenware chiefly in the fact that earthenware is burned merely until it reaches the stage of incipient vitrification but remains porous, while in the case of stoneware the clay is burned to vitrification so that the body of the ware becomes impervious to moisture. The color of the body may be reddish, buff, or bluish black, but this color frequently is concealed by a coating of salt glaze or slip. Stoneware is made usually from refractory or semi-refractory clays, the best results often being obtained by mixing different clays.

One of the clays is used to supply stiffness to the body in burning, while the other supplies the fluxing qualities and serves to bind the ware together. The fusible impurities must be of such a character as to cause the body to attain a state of incipient fusion while the slip or glaze at the same temperature will melt.

When the ratio of alumina to ferric oxide equals 7 to 1 the resulting stoneware is not colored red by the ferric oxide, but takes on a yellowish color, which becomes yellowish-white or nearly white as this ratio approaches 13 to 1. Clays of this kind could be used also for the manufacture of light or buff brick.

Chemical analyses usually show the following range of variation:

	Maximum	Minimum	Average of 8 analyses
Silica	72.10	45.00	64.08
Alumina	38.24	19.08	23.86
Ferric oxide	1.50	0.96	1.23
Lime	1.70		0.78
Magnesia	0.68	0.11	0.40
Soda	Trace		Trace
Potash	2.42	0.15	1.48
Water	14.80	6.25	7.78
	2000 C C C C C C C C C C C C C C C C C C		

Among the earlier analyses of the stoneware clays of Madison county are the following:

946.—Potter's clay. Four miles northwest of Irvine, on the Richmond pike. Light buff-gray, with stratified lines of reddish. Appears to be principally fine quartzose sand with a few minute sparkling specks of mica.

Geological position: Irvine formation.

Water expelled at red heat	4.400
Silica	71.780
Alumina	17.580
Iron oxide	2.420
Lime	None
Magnesia	.547
Potash	2.271
Soda	.322
Sulphuric acid	.112
Loss	.568

# 1122.—Potter's clay, near Waco. Geological position: Irvine formation. Analysis:

Water expelled at red heat	6.140
Silica	62.58
Alumina	21.98
Iron oxide	4.78
Brown oxide of manganese	Trace
Phosphoric acid	Not Est.
Sulphuric acid	.234
Lime	Trace
Magnesia	1.276
Potash	2.607
Soda	.500

In sample No. 946, the ratio of alumina to ferric oxide is about 7 to 1 and the clay should burn to a buff color. The percentage of silica is rather high, and the clay should prove more refractory than sample No. 1122. In the latter case the ratio of the alumina to ferric oxide is about 5 to 1 and the color of the burned clay should be darker.

Two additional analyses of the potter's clay at Waco were published in 1877.

1876a.—Potter's clay, quality No. 1. Light gray soft clay.

1876b.—Potter's clay, quality No. 2. Of a bluish-gray color.

Both clays from the neighborhood of Waco. These are good clays for ordinary stoneware.

No. 18764 No. 18765 Combined water and loss..... 7.020 10.531 59.976 56.960 Silica ..... Alumina, iron and manganese oxides, and phosphoric 27.640 28.740 acid ..... Lime carbonate..... .280 .200 .606 .752 Magnesia ..... 3.931 2.502 Potash ..... Soda ..... .547 .315 100.000 100.000 Total .....

Analyses; dried at 212 degrees F .:

These samples do not differ greatly from No. 1122, although the percentage of silica is less. Possibly the inferior quality of

the sample said to be of quality No. 2 was due to its vitrifying at a lower temperature, due to a smaller percentage of silica and a larger percentage of iron.

In 1879 two additional analyses were published, presumably from clay used for the manufacture of stoneware. Bybeetown is now known as Portland, and is still the seat of stoneware manufacture. The Oldham locality is believed to have been on the Bybeetown side of Waco.

2168.—Clay. From near Bybeetown or Portwood. Milton Barlow. Bed four feet thick, overlying Black shale.

Geological position: Probably from the Irvine formation. Collected by John R. Procter.

Clay of a light, warm drab-gray color. Irregularly and imperfectly laminated. Quite plastic. Burns to a delicate light reddish-cream color, nearly white.

2169.—Clay of workable thickness; on the road leading from Waco to R. Oldham; about a mile and a half from Waco.

Geological position: Collected by John R. Procter, and stated by him to occur probably below the Corniferous limestone. The exact locality not being known, this statement can not be verified, but, in this area, plastic clays with a very small percentage of lime are not known in Silurian formations.

A compact, clay, generally of a light, olive-gray color, stained irregularly with ochreous and ferruginous. Quite plastic. Calcines quite hard, to a handsome light brick color.

No. 2168 No. 2169 6.973 Water and loss..... 5.166 Silica ..... 62.560 64.566 20.160 24.780 Alumina ..... 4.200 Iron peroxide..... 1.800 .213 A trace Lime ...... .641 Magnesia ..... .317 3.2765.054 Potash ..... .294 Soda ..... Not Est. Total ..... 100.000 100.000

Analysis; sample dried at 212 degrees F.:

Regarding these clays, Dr. Robert Peter, the chemist of the Survey, made the following remarks:

These are good plastic clays for the manufacture of ordinary pottery ware, as well as for ornamental articles of terra cotta, for which they are adapted because of the pleasing tints which they assume on calcination. They owe these tints to their considerable proportion of iron oxide, which, together with their large proportion of potash renders them unavailable as fire-clays. This very circumstance, however, may fit them for stoneware and for superior kinds of hard-burnt, semi-fused, ornamental pottery in the hands of skillful workmen and artists.

The ratio of alumina to ferric oxide in sample No. 2168 is about 13 to 1, and the clay should burn to a nearly white color. In sample No. 2169, this ratio is about 5 to 1, and the clay should burn to a distinctly brick-red color. The percentage of potash is large, and the clay should flux at a distinctly lower temperature than any so far mentioned. This should cause it to be regarded as an inferior clay.

In 1884, the following analyses were published, showing that the interest in stoneware clay still focussed around Bybeetown and Waco, in Madison county.

2496.—Clay. From the land of James Walker Lewis, two miles southeast of Bobtown, about, one hundred yards to the left of the Big Hill pike, almost opposite the blacksmith shop.

Geological position: Bed four to five feet thick, resting on Silurian clay shale. Sample of the upper ten inches. Collected by Moritz Fischer, June 21, 1881. The Silurian clay shale at this locality is the Lulbegrud clay division of the Crab Orchard bed. The overlying clay, of which the analysis is given, probably belongs to the Irvine formation. Locality: R-S-22.

A laminated clay or soft shale, of a light gray color on the exterior; darker colored and brownish-yellowish-gray in the interior.

249i.-Clay. From the same locality as the preceding. Sample from ten to twenty inches below the surface. Collected by Moritz Fischer.

Geological position: Apparently from the Irvine formation, but the large percentage of lime is more suggestive of Silurian clays.

Darker colored than the preceding; of a light olive green color.

No doubt common pottery ware and terra cotta could be made of this clay, ground and properly tempered with water. It contains too much potash, lime, and iron oxide for a fire-clay.

Analysis of air-dried samples:

	No. 2496	No. 2497
Water, carbonic acid, and loss	8.091	15.548
Silica	59.000	42.560
Alumina and iron oxide	24.640	20.980
Lime	1.456	8.680
Magnesia	1.096	7.247
Potash	5.500	4.819
Soda	.217	.166
Titanic acid		Trace
Total	100.000	100.000

Sample No. 2496 contains 20.68 per cent. of alumina and 3.96 per cent. of iron peroxide.

As compared with other clays from the Irvine formation, the percentage of lime in sample No. 2496 is rather high, and the same may be said of the percentage of magnesia and potash. In this respect the clay approaches some of the Crab Orchard clays. The ratio of alumina to ferric oxide is about 5 to 1, and the clay should burn to a light brick-red color. It should fuse at a much lower temperature than the potter's clays hitherto mentioned, with the exception, perhaps, of sample No. 2169. Sample No. 2497 is utterly at variance with any other clay known in this part of Kentucky. It has a low percentage of silica and a high percentage of lime and magnesia compared with the clays so far investigated. It should not prove sufficiently refractory to make a good stoneware clay. The age of these clays is not definitely known.

Several analyses have been made for the present survey. The following analysis is taken from a sample of the clay used by the firm of D. Zittel & Son, manufacturers of common stoneware, about half a mile east of Waco. The clay is obtained from the McKinney farm, southeast of Waco.

2615.—Clay, Waco, Ky., on G. S. McKinney's land, Madison county, Ky.

Geological position: Irvine bed. Thickness, 3.5 to 5 feet.

# A. F. Foerste, 1904. From Waco, one-fourth miles south, one-fourth mile east. Pit on south side of road.

Analysis of air-dried sample:

Moisture	2.27
Ignition (combined water, etc.)	5.85
	63.76
Alumina	19.36
Ferric oxide	2.59
Lime	.40
Magnesia	.82
Potash	2.86
Soda	.47
Titanium dioxide	1.25
Sulphuric anhydride	Trace
Total	99.63

In this case the ratio of the alumina to the ferric oxide is about 7.5 to 1, and the clay burns to a light buff color. It is used at present for jugs, jars, churns, and the like, but apparently might be made useful also for architectural terra cotta, chemical stoneware, clay pipes, and the like, although not very refractory clay. In this respect it is surpassed by the white clay from the Adams farm, next to be described. This clay contains more alumina, and less ferric oxide, lime and magnesia. The percentage of alumina to ferric oxide is about 19 to 1, and the clay burns to a very light color. On this account it should be valuable for architectural terra cotta and for light colored pressed bricks, especially for those which are artificially colored or speckled by the use of manganese or other metallic oxides.

2635.—White clay, on the Adams farm, near Waco, Madison county. Color, nearly white, banded in places with brown. Found at the same locality as No. 2636.

Geological position: Irvine bed. Collected by A. F. Foerste, in 1904.

Analysis of air-dried sample:

Moisture	1.60
Ignition (combined water and volatile matter)	6.74
Diffed	61.00
Alumina	23.68
Ferric oxide	1.21
Lime	.20
Magnesia	.68
Potash	3.09
Soda	.43
Titanium dioxide	
Sulphur trioxide	frace
Total	)0.02

At present the Adams farm clay is used at the tiling factory, at Searcy Station, in the manufacture of roofing tiles. It is mixed with the clay which comes from the immediate vicinity of the factory, and probably serves to bind the latter together. The following analysis indicates the nature of the resulting mixture, consisting chiefly of clay obtained from the pit at the factory:

2634.—Tiling factory clay. Obtained north of the factory, at Searcy Station, about a mile southeast of Moberly. The sample consisted of broken, unburned roofing tiles. It was buff colored and uniform in appearance.

Geological position: Irvine bed. Chiefly alluvial. Directly above the Devonian black shale. Collected by A. F. Foerste, in 1904.

Analysis of air-dried sample:

Moisture	1.75
Ignition (combined water and volatile matter)	4.26
Silica	73.78
Alumina	13.23
Ferric oxide	1.24
Lime	.54
Magnesia	.82
Potash	2.27
Soda	.50
Titanium dioxide	1.25
Sulphur trioxide	Trace
Total	99.64

This clay mixture contains more silica and less alumina than any so far described. It is not used for stoneware, but only for roof tiling, drainage tiling and brick. The roofing tiles are burned to a light red color, but those so far put out appear underburned.

The following analysis shows the nature of the clay used at the Searcy roofing tile factory as fire-clay.

2636.—Fire-clay, used by Searcy at the roofing tile works. Obtained from the Adams farm, near Waco, Madison county. Samples mostly in the state of coarse powder, with some friable lumps. Buff colored, with some brown specks in the lumps. Found by going three-quarters of a mile north from Waco, then an eighth of a mile east, and finally an eighth of a mile south, past a cabin. Geological position: Irvine bed. Collected by A. F. Foerste, 1904.

Analysis; sample air-dried:

Moisture	1.52
Ignition (combined water and volatile matter)	3.56
Silica	81.54
Alumina	9.36
Ferric oxide	1.17
Lime	.10
Magnesia	.39
Potash	.56
Soda	.29
Titanium dioxide	1.25
Sulphur trioxide	
Total	99.74

The relatively small percentage of alumina should be noted. The point of incipient fusion of this clay has not been determined.

The following clay was analyzed for Mr. Searcy. It does not differ conspicuously from the stoneware clays previously cited. It probably belongs to the upper part of the Irvine formation, as far as may be determined from the analysis. No careful study was made of its position in the geological scale.

2616.—Alluvial clay, Waco, Madison county, Ky. Geological position: Alluvial clay. One-fourth mile south of Waco, and then one and one-eighth miles east, south of the road, on Grinstead farm. Black clay. A. F. Foerste, 1904.

Analysis of air-dried sample:

Moisture	1.72
Ignition (combined water, etc.)	3.38
Silica	5.82
Alumina 1	8.01
Ferric oxide	2.48
Lime	.22
Magnesia	.77
Potash	2.91
Soda	.46
Titanium dioxide	1.25
Sulphur trioxide	ace
Total	0.02

The next analysis gives the composition of the ordinary brick and tiling clay used by the Moberly Brick Company, and secured from the immediate vicinity of the plant, west of Moberly station. It contains a much larger percentage of ferric oxide than any clay here discussed, and evidently would not be useful for any other purpose than that for which it now is employed. It is chiefly an alluvial deposit.

2617.—Clay, Moberly, Ky., Madison county.

Geological position: Irvine formation. Chiefly alluvial. Used for brick and tile at the Moberly Brick Co. plant at Moberly.

Analysis, air-dried:

Moisture	1.98
Ignition (combined water, etc.)	4.20
Silica	74.36
Alumina	7.79
Ferric oxide	6.78
Lime	.14
Magnesia	.53
Potash	1.59
Soda	.49
Titanium dioxide	1.25
Sulphates and phosphates	Fraces
Total	99.11

# The Clay Industries of Madison County.

Only two stoneware potteries at present are in operation, one at Waco, and the other at Bybeetown, or Portwood.

The pottery half a mile east of Waco is known as the D. Zittel & Son pottery. They use the clay from the George McKinney farm, southeast of Waco. The clay bed varies in thickness from four to seven feet. In some parts of the pit the clay rests upon sand. In these cases it is considered better and will stand a little more fire. In other parts of the pit the clay rests upon the Black shale, and then is believed to be less refractory. No reason for this difference can be noticed on examining the clay in the pit.

Albany slip clay mixed with red lead and manganese is used as a glaze. The materials are obtained from the Bower Pottery Company, Louisville, Ky.

The articles made are as follows:

Jugs in 1 quart and <sup>1</sup>/<sub>2</sub>, 1, 2, 3, 4, and 5 gallon sizes.

Jars in 1 quart and <sup>1</sup>/<sub>2</sub>, 1, 2, 3, 4, 5, 6, 8, and 10 gallon sizes.

Fruit jugs, put up with lid so that they can be sealed. Used

chiefly for keeping sorghum. Put up in 2, 3, 4, and 5 gallon sizes.

Fruit jars, with lid, in 1 quart and in  $\frac{1}{2}$  and 1 gallon sizes. Used chiefly for fruit jams.

Pitchers, in 1 quart and <sup>1</sup>/<sub>2</sub>, 1, and 2 gallon sizes.

Churns, in 2, 3, 4, 5, and 6 gallon sizes. Supplied with lid.

Milk pans, in  $\frac{1}{2}$ , 1, and 2 gallon sizes.

Chambers, in  $\frac{1}{2}$  and 1 gallon sizes.

Flower pots, in 2, 3, 4, 5, 6, 7, 8, 10, 12, and 14 inch sizes.

The following analysis indicates the chemical composition of the Albany slip clay:

Free silica or sand	38.58
Combined silica	17.02
Alumina	14.80
Ferric oxide	5.85
Manganic oxide	.14
Lime	5.70
Magnesia	2.48
Potash	3.23
Soda	1.07
Phosphoric acid	.15
Water	5.18
Moisture and carbonic acid	4.94
Total	99.14

This clay not only fuses at a low temperature, but also produces a glaze of uniform color, and one which does not crack. Its fusibility may be lowered by the admixture of various metal compounds, as indicated in the following recipe:

Albany slip clay	63.30	to	70	parts.
White lead	25.30			**
Flint	6.30	to	7	**
Oxide of iron	.72	to	.79	
Oxide of manganese	.56	to	.61	"
Chromate of lead	1.27	to	1.40	ш.
Chromate of iron	.67	to	.73	**
Oxide of zinc	1.88	to	2.07	**

At Bybeetown, or Portwood, is located the pottery of J. E. Cornelison & Son. The clav is obtained on the road from Waco to Cobb Ferry, about a mile and a half east of the junction of this road with the road from Waco to Bybeetown. The pit is located northwest of the road corners, at which the road across Falling Brook joins the road from Waco to Cobb Ferry. The thickness of the clay bed in the clay pit averages about five feet. The clay overlies the Black shale. The clay is brought to the shop and put in a ring pit. This ring pit usually consists of a circular tub, between twenty-five and thirty feet in diameter, three feet deep, and lined with boards. In this revolves an iron wheel about six feet in diameter, and so geared that it travels from the center of the tub to its sides and then back again toward the center. This breaks up the clay thoroughly and tempers the clay in about six hours. This tempering is called pugging. The power used at the Bybeetown pottery is a single horse. The clay is taken from the pug tub to the cellar and there kept moist for further use.

The objects manufactured are chiefly jars, jugs and churns, in the following sizes:

Jars, 1 quart, <sup>1</sup>/<sub>2</sub>, 1, 2, 3, 4, 5, 6, 8, 11 gallons. Jugs, 1 quart, <sup>1</sup>/<sub>2</sub>, 1, 2, 3, 4, 5, 6, 8, 10 gallons. Churns, 2, 3, 4, 5, 6, 8 gallons.

The glaze used is a slip clay mixed with red lead and manganese. This is all stirred together, the slip clay being strained before mixing. The pottery is dipped into the mixture and dried before going to the kiln. The kiln used is a down-draft kiln, and coal is used as a fuel. The kiln is heated up slowly for about twenty-four hours and then raised to a white heat for twenty-four hours. A peep-hole is left to enable the operator to examine the interior of the kiln, and the state of firing is determined chiefly by the color of the ware, although test pieces also are used. Whenever the glaze is good on these test pieces the burning is considered sufficient. Then the kiln is allowed to cool for fifty hours. No Seger cones are used.

In addition to pottery, 4, 6, and 8 inch tiling also is manufactured.

At Searcy station, about a mile southeast of Moberly, the Lexington Tile Roof Company is situated. Here the Waco shingle tile is manufactured.

The chief clay used for this purpose is obtained directly north of the factory. At the pit about half a foot of soil is stripped off at the top, and the underlying clay layer, five feet thick, is taken out. This clay rests on the Black shale. For the manufacture of drain tile, brick, and shingles, the clay is dug, removed to the soak pit, and left over night. The next day the day is shovelled into the disintegrator, where any stones present in the clay are crushed until the fragments are reduced to a diameter of one sixteenth of an inch or less. From the disintegrator the clav is carried along a belt to the tile mill. Here the clay is pushed out of the tile mill, through the dies, where the proper thickness and width is given to the stream of clay which issues forth. From the tile mill the issuing stream of clay is carried forward by the machine to the cut-off table, where the clay, which already has the proper width and thickness, is cut off into the desired lengths. From the cut-off table the blanks or plates of clay, the future shingles, are carried forward and picked off by boys, who haul them to the shingle press.

Up to this point the manufacture of shingle tiles does not differ in any respect from the manufacture of bricks and drain tiling as carried on at the same factory, except that in each case a different die is used in order to give a different form to the stream of clay issuing from the die, and in each case the wires on the cut-off table are set at different points, so that the length appropriate to the particular object to be manufactured will be cut off. For the manufacture of shingle tiles the clay is heaped up usually about two days, moistened and covered with oil cloth, before it is run through the disintegrator, in order to become evenly moist.

From the cut-off table the clay plates are taken to the press, where they are pressed into shingles. In this machine the upper die is stationary and there are three lower dies, all of which are movable, only one die being used at a time. One of the clay plates is inserted into the machine and pressed. The lower die with the pressed shingle on it is then lifted up. A pallet or small board slightly larger than the shingle is placed on the shingle. Then die, shingle and pallet together are turned over and the die lifted off, the pressed shingle remaining on the pallet. In the meantime another clay plate has been inserted in the machine and pressed into the shape of a shingle, and is ready to be taken out and placed on a pallet. The shingles, still resting on the pallet, are carried off to the drying shed. The capacity of such a press is 4,000 shingles in one day of ten hours, ten men being employed in various ways.

The shingles are allowed to dry on the pallets for periods varying from two to five days, depending upon the weather. They are then skinned or trimmed. Trimming consists in rubbing off the rough edges of the clay shingles with the back of a coarse knife. Then the shingles are stacked up and taken to the kiln. Here they are set up on edge, eight shingles in each set, with fire-bricks between the sets. These fire-bricks are a little higher than the shingles and so take the weight. of the upper tiers of shingles from the tiers stacked up below. The fire-clay used is secured on the Adams farm, as is also, some of the clay which enters into the clay mixture used for the manufacture of the shingles.

The kiln used is a down-draft kiln. The shingles are heated for twenty-four hours, the fresh steam or water-smoke being let out at the top. No great heat is used during this time, the object being merely to drive off the water still present in the shingles. Then the heat is raised gradually for forty-eight hours until the shingles become white hot. Then the ovens are closed down, firing ceases, the fire-doors are cemented shut with clay, and for three days the kiln is allowed to cool slowly. It takes a day and a half to empty the kiln and another day and a half to fill the same again.

Three men can fill the soak-pit so as to supply enough clay for fifty squares per day. A square is equivalent to 100 square feet of roof surface, which in the present instance requires the use of 260 shingles. Fifty squares, therefore, would in this case be equivalent to  $50 \times 260 = 13,000$  shingles. Two men are needed at the disintegrator. One man is needed at the mill and to take care of the cut-off table. Two men serve as off-bearers, who wheel off the clay plates or blanks to which reference has been made in the preceding lines. One man works the lever at the press, one feeds the press, one dumps the pressed shingle onto the pallet, and one man, the offbearer, hauls the shingles to the drying room. At the drying room one man is kept busy as a skinner or trimmer. Two off-bearers are needed to fill the kiln, and one man sets up or stacks the shingles in the kiln. Two men are kept constantly employed in firing the
kiln, one serving as the day man, the other as the night man. The men firing the kiln are paid \$1.50 per day, and all others are paid \$1.00 per day. The man firing the kiln for this wage is given the higher sum of money because he is regarded as an expert. Similar wages are given for similar work at the potteries already mentioned.

The weight of a square of shingles, or of 260 shingles is about 650 pounds. The exposed surface of the shingles is 9.5 by 6 inches. In the process of burning the clay shrinks five-eighths of an inch to the foot and allowance must be made for this in constructing the die. No Seger cones are used in firing the kiln, the temperature being determined approximately by looking at the color of the brick through peep-holes left for this purpose on each side of the door in the front walls of the kiln. Shingles have been made at this factory for about two years. One of the churches at Irvine, in Estill county, is covered with this roofing tile. The shingles seem to be defective, owing to under-burning, and for this reason the use of Seger cones is recommended. They also have a tendency to open up irregular cracks on burning, and hence tests as to the proper mixtures to be employed should be made, but there is no reason why eventually, with greater experience, the manufacture of roofing tiles should not prove a success.

For purposes of comparison with clays from other localities, the following analyses are given. The clay from Vigo county, Indiana, was used formerly for roofing tile, but cracked in burning. The clay from Prospect Hill, in St. Louis county, Missouri, is used both for brick and for roofing tile. The clay (Chemung shale) from Alfred Center, in Alleghany county, New York, produces an exceptionally good quality of roofing shingle.

	Indiana, Vigo County	Missou <b>ri</b> . Prospect Hill	New York, Alfred Center
Silica	73.20	60.70	53.20
Alumina	13.38	18.22	23.25
Ferric oxide	2.19	7.58	10.90
Lime	.97	2.68	1.01
Magnesia	1.01	Trace	.62
Soda and potash		3.67	2.70

Since roofing tiles or shingles are to be used in order to shed water, their degree of porosity or permeability to water is of

the highest importance. The value of roofing shingles may be tested as follows: Heat the shingle to be tested to a temperature of 212 degrees F., then place on it a tin tube whose diameter is five inches and whose height is eight inches. This should be fastened to the tile by means of wax applied to the outside of the tube. Fill the tube with Water up to a level of four inches above the tile, and keep the water at this level by adding a few teaspoonfuls at a time until drops begin to appear on the under side of the tile or shingle. If these drops make their appearance in less than six hours, the roofing tile should be rejected. Tile burned to a higher degree of vitrification is, of course, more impervious to water.

In addition to the roofing tile or shingle, the Lexington Tile Roof Company manufactures also paving brick, eight and three quarters of an inch wide and long, and therefore having a hypotheneuse or diameter from corner to corner of one foot. The thickness of these bricks is two inches. They are intended for paths in gardens, sidewalks in villages, and the like. They are placed with their greater diameters parallel to the length of the walk, and the gaps thus left at the side of the walk are filled in with half bricks which have a triangular shape, fit in snugly, and are supplied in proper quantity with every order.

In addition to the paving brick, drainage tiling and common brick are manufactured. Several tests of different clays from the Waco area, made by the Boyd Company, of Chicago, at the request of the Lexingion Tile Roof Company, have demonstrated that a fine grade of pressed bricks can be manufactured from the different clays. These vary in color from a very light yellow to a distinct red. By a mixture of clays they secured a mottled brick giving a very pleasing effect. It is evident that the possibilities of these clays have by no means been exhausted. When the dams now under construction along the Kentucky river are completed, the question of cheap transportation from the eastern part of the Waco area should be considered solved.

Directly west of Moberly station is the plant of the Moberly Tiling Manufacturing Company. This is owned chiefly by William Tate. The clay is obtained at the factory. The layer is three feet thick and occurs immediately over black shale. Three or four inches of soil are stripped off at the top. They use the Little Warder press, made at Frankfort, Ind., by the Wallace

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Manufacturing Company. This turns out 5,000 tiles or 2,000 bricks per day. The cut-off table used is the Euring automatic clay cutter, manufactured by the I. D. Fate Company, at Plymouth, O. The tile truck wagon was made by the Arnold-Creager Company, at New London, O. The power for the press and cutter is supplied by a 30 horse-power engine. It requires more power to make the smaller sizes of tiling, four to six inches in diameter, than those of larger sizes. Labor is paid at the rate of \$1.00 per day, or 10 cents per hour.

### THE BEREA COLLEGE BRICK COMPANY.

The brick-yard run by Berea College for its own use and for the employment of some of the college students is situated about a mile north of town. The clay is obtained from a pit situated northeast of the brickyard. About three inches of soil are removed, and the underlying clay has a thickness of about three and a half or four feet. It overlies Black shale. A narrow track with cars is used to haul the clay from the pit to the plant. and then, by means of a cable run by steam, up an incline to the second floor of the building, where the bricks are made. At the top of the incline the clay is dumped from the car onto a platform, and then shovelled into the disintegrator. This consists of two large steel rolls, between which the clay passes. Any pebbles present in the clay are ground to small fragments. Water is added to the clay as it reaches these rolls in the disintegrator. From the disintegrator the clay drops into the pug mill. Here revolving blades mix the clay, and if necessary more water is added. In addition to mixing the clay, the blades push the clay forward into the brick mill. This is the Grand Automatic Brick Maker, manufactured by Jonathan Creagers' Sons Company, at Cincinnati, O.

The blades in the brick mill push the clay down into the arms of the brick mill, and these arms push the clay sidewise under the press. Here the press pushes the clay into the mold. Nine molds are used when the machine is in operation. Six bricks are made at a time in each mold. In front of the machine one man receives the mold and bumps it to the right and left so as to loosen the clay brick in the mold. Another man picks up the mold and places it on the turn-table, which is a sort of revolving wheel. The open side of the mold is placed against a pallet board and the mold is dumped, leaving the brick on the pallet board. Then the mold is put in the sander. The sander in use is made by the Wellington Machine Company, at Wellington, O. In the sander the mold is pushed through the sand, and on the other side another man picks up the mold and places it once more in the machine. In the meantime the other molds have been in use. The sand is shipped here from Cincinnati.

Nine pallet boards, with six bricks on each, are loaded on a truck and then are wheeled to the racks. Here they are taken off by a man and are put on the racks to dry. Between six to nine days are necessary for this purpose. The racks at the pallet yard have a capacity of 120,000 bricks. From the pallet yard the bricks are taken to the kiln. Three kilns are in use, one up-draft Morrison clamp kiln and two common up-draft kilns. The capacity of these kilns is 225,000, 200,000 and 200,000 bricks. The bricks are first fired for about four or five days to drive off the steam, usually called water smoke. After this has been driven off, the escape of the heat is cut off, the fires are increased, and in three or four days the brick comes to a red heat, and to a white heat in three and a half or four days additional. After this, all access of air is cut off, and it requires eight days for the kiln to cool.

The capacity of the yard when worked to its fullest extent is 2,000,000 bricks a year. It has been in operation about four years. The machinery for tile-making has been secured. Prof. S. C. Mason, at Berea, the Professor of Agriculture and Geology, is especially interested in this plant. Aside from its usefulness to the college, it is of great service to the students, who here get a practical knowledge of brick-making, which, with modifications, they can directly apply in the mountain districts from which so many come, doing by hand, of course, many of the things which here are made by machinery.

# Water Horizons.

The Devonian limestone is one of the chief water-bearing strata of east central Kentucky. Numerous fine springs issue from its horizon, and some of these have a wide reputation. One of these is the Buffalo spring, a quarter of a mile west of Stanford, along the pike to Hustonville. Another is situated about three and a half miles west of Crab Orchard, along the county road running east and west about a mile south of the railroad, east of the home of George Boone. Another spring is located about three miles southwest of Crab Orchard, near the headwaters of Cedar creek, north of the road leading to Chapel Gap (locality 17 CO-NE). The Moore spring, a mile and a third northeast of Waco, near the home of Tom Curtis, is one of the best known in that area. The Spout spring, four miles southwest of Clay City, is known for many miles. The spring southeast of the Oil springs hotel, about a mile northeast of Indian Fields, issues from the same horizon. These are only a few of many springs which could be mentioned, and which, collectively, demonstrate that the Devonian limestone is an important water-bearing stratum. This importance it does not owe to its thickness, since the Devonian limestone in most of this region does not exceed eighteen feet, and at many localities springs issue from this limestone where its thickness is less than six feet. But the overlying Devonian black shales are so abundantly traversed, at many localities, by minute cracks, that the ground waters percolating through their mass are enabled to reach the Devonian limestone horizon in sufficient quantities to feed numerous springs.

Over by far the greater part of east-central Kentucky, the Devonian limestones are underlaid by considerable quantities of Silurian clays, the most important of which belong to the Alger formation, but the Plum creek clay also is of importance. These clays soften up readily in the presence of abundant ground waters, and form a rather impermeable mass, arresting further downward progress. The slowly percolating ground waters accumulate above the Silurian clays, until they find an exit laterally as springs. The permeability of the Devonian limestones, no doubt, greatly assists in the ready egress of this water. Moreover, the numerous joints and vertical cracks, gradually widening under the influence of the slightly carbonaceous waters, usually provide channels for the ready exit of springs. The chief service of the Devonian limestone is the providing of a reservoir for the accumulation of the downward percolating ground water, and the providing of channels for its ready outflow.

These springs, at the horizon of the Devonian limestone, are most numerous where the overlying Black slates are not deeply covered by the soft Linietta clays, forming the base of the Waverly series. The latter act as a barrier, retarding the ready downward passage of percolating ground waters, thus preventing easy access to the Black shales and Devonian limestone beneath. The base of the Waverly series, therefore, is not a good water-bearing horizon in east central Kentucky.

For a somewhat similar reason, the Clinton, or Brassfield, limestone is not a reliable water-bearing horizon in this part of the State. Where it is thickly covered by the Plum creek, and especially by the Alger clays, the ground waters are held back and do not accumulate readily at this horizon. Although many springs issue at this horizon, they usually are of moderate size, and they often go dry in summer. This does not suggest the presence of important accumulations of water within the ground, at this horizon, and very little hope may be offered to those who may desire to secure a permanent and abundant water supply at this horizon in this part of the State, while the likelihood of striking an abundance of good water is much greater at the level of the Devonian limestones.

The Richmond formation, in by far the greater part of east central Kentucky, is an argillaceous deposit, often clayey at the top, with comparatively little limestone at any level, though often containing layers of indurated argillaceous rocks. As a matter of fact, few springs issue from Richmond strata in this part of the State. More frequently, the areas of outcrop of Richmond strata are marked by comparatively barren or bald spots, giving rise to such names as "Bald Hills." These names indicate that the Richmond is not a great water-bearing horizon, and that wells reaching the Richmond strata, without having found water, must be continued for at least 200 feet before the chances for a reliable water supply become much better.

The upper horizons of the Maysville division of the Cincinnatian series of rocks, on the contrary, contain much limestone,

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traversed by numerous crevices, and probably fairly permeable even where not cracked. At this horizon springs become numerous again, and the great thickness of the Maysville division affords the opportunity for many springs, at numerous localities, and at very different elevations.

There are no porous sandstones, in that part of east central Kentucky here under investigation, within reach of the well driller, and therefore this, the best medium, for the accumulation of ground waters, is absent. But in the absence of sandstones, the Devonian limestone is a valuable water-bearing stratum, and the Maysville limestones offer even a greater supply, while the Clinton, or Brassfield, limestone is uncertain, and the Silurian clays and the Richmond argillaceous strata offer no prospect.

Springs frequently issue from the Black shales, and some of these offer water which is very palatable, but, as has already been shown in that part of the report which deals on mineral springs, in the presence of iron sulphide, chemical reactions often take place which impregnate the waters with various kinds of salts, which may be very valuable for medicinal purposes, but which can hardly be recommended as parts of a steady diet. The quantity of these salts in solution depends, in part, considerably upon the rate of outflow. Where the streams issuing at the springs are at all rapid, the quantity of salt in solution usually is small. Where the rate of outflow is small, the quantity of material in solution often is great. It is evident that the rate at which the chemical changes producing these salts is taking place is too small to permit of the abundant impregnation of considerable quantities of ground water. Where the ground waters flow rapidly, the streams at their exits from the springs are relatively free from salts, at least in the great majority of cases.

The slow rate of percolation of ground waters through the Silurian clays readily accounts for the frequency with which wells sunk into these clays become impregnated with salts. In fact, in former days, these wells were sunk in the Alger clays for the express purpose of securing the brines for the manufacture of the Crab Orchard salts. Of course, natural evaporation was utilized to intensify the salinity of these brines, but the frequency with which the term "lick" is used in this part of Kentucky demonstrates the fact that Nature herself furnished many natural brines at some localities.

## Oil Horizons.

The same conditions which tended to make the Devonian limestone, in many parts of east central Kentucky, a great waterbearing stratum, have locally favored its acting as a reservoir for oil. Oil is lighter than water and tends to rise. Any oil which once reaches the level of the Devonian limestone is likely to be held back by the Linietta clay, at the base of the Waverly, if not by the Black shale, immediately overlying the Devonian limestone. At some localities in the northeastern part of the area here under investigation, this service would be performed very well also by the mass of greenish clays (Olentangy shale?), often six to eight feet thick, immediately underlying the Black shales. Here, again, the Devonian limestone, on account of its porosity acts as a reservoir. In quarrying this rock, cavities with small quantities of crude petroleum are not infrequent.

The source of this petroleum is a subject of considerable interest to the speculative geologist. The Devonian Black shales are known to be bituminous. In early days, oil was distilled from them, and when thrown into the fire, they undergo a sort of slow combustion, which, frequently, has led the observer to believe that a little further judicious search would lead to the discovery of a new coal field. When those Devonian shales are tilted, the more liquid bituminous material might slowly rise toward the crest of the incline, and, if held back by suitable impervious layers, might accumulate there. A considerable accumulation of oil, in that case, would not mean that the Black shales in general were heavily charged with oil, but that oil has gradually collected from over a very wide territory into some narrow space or pocket. This region of collection would be most pronounced along the most porous strata, where suitably covered by impervious layers.

It is the common opinion of geologists, however, that the general distribution of oil in the earth does not warrant the belief that all accumulations of oil have originated from such

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obvious sources as bituminous shales and coals, owing their bitumen to natural chemical changes of the remains of plant life, formerly inclosed within them. Some have sought for the origin of oil in the chemical changes resulting from the decay of animal life, while, recently, it has been suggested that considerable quantities of oil may have had an entirely inorganic origin. The opinion is gaining ground, from the enormous quantities of carbon dioxide given off from volcanic vents, that various metals known near the surface of the earth chiefly as oxides and sulphides, might occur, deep within the interior of the earth, as carbides, and later supply the carbon for mineral oils.

Whatever the truth may be, the thick mass of Silurian clays should be an effective barrier to the rise of oils from greater depths, and, in that case, the presence of considerable quantities of oil in the Devonian limestones should be due to local, rather than to general, conditions. Evidently, faults, if of sufficient throw, might occasionally enable oils to ascend through strata ordinarily impervious.

Oils are found in the Devonian limestones in the Ragland field, in the southeastern part of Bath county, and in the area east of Irvine, in Estill county. Gas is found at the same horizon in Menefee county. (The Oil and Gas Sands of Kentucky, by J. B. Hoeing, Bulletin No. 1, Kentucky Geological Survey.) It is probable that the oil and gas struck at the Caney creek well, in Morgan county, came from approximately the same horizon; not necessarily the Devonian limestone, but from limestone immediately beneath the Devonian Black shale and above the great mass of Silurian clays.\* If the very black shale at the depth of 1,028 to 1,035 feet is the Sunbury shale, then the combined thicknesses of the underlying Berea grit and Bedford shale should greatly exceed fifty-two feet, so that the estimate of 283 feet for the Black shale must include, at the top, a considerable quantity of the Linietta shale, at the base of the Waverly, corresponding, approximately, to the Bedford shale of Ohio. The soft blue shale immediately beneath the Black shale section, to which a thickness of thirty feet is assigned in the section, may correspond to the clay at the base of this Black shale in Bath county, possibly corresponding to the Olentangy

<sup>\*</sup>See foot note on following page.-C. J. N.

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shale of Ohio. At any rate, observations farther west suggest an increase, rather than a decrease, in the thickness of the Silurian clay section toward Morgan county, and these clays, therefore, are more likely to be 150 feet than thirty feet thick in Morgan county. If that be the case, the sandy limestone of the Caney creek well, in which oil and gas were found, may represent the limestones immediately beneath the Devonian Black shale in Lewis county. This would place their elevation among the Silurian limestones above the great mass of Silurian clays, rather than below, in the Clinton. This attempt to unravel the geology of a district from imperfect well records is largely guess work, but, whatever the truth may be in the case of the well in Morgan county, it is certain that elsewhere in that part of east central Kentucky here under investigation, the Clinton or Brassfield bed is not a source of oil or gas in commercial quantities, although little cavities, one or two inches in diameter, filled with black oil, are common at many localities, especially near the top of the Brassfield limestone, and in the Whitfieldella layer. \*

<sup>\*</sup>It is understood that Professor Foerste's remarks on oil and gas horizons are only tentative, and that they refer only to such observations as he had opportunity to make in the area traversed by him. As stated by him, the Silurian clays should act as a barrier to the upward passage of oils, but, of course, they can so act only when they are present, and over a large part of Eastern Kentucky they are entirely absent. It is not only in the Ragland field, and in the area east of Irvine, that oil is found in the Devonian limestone. Oil or gas is found, in larger or smaller quantities, in the Devonian (Corniferous) limestone wherever the latter is drilled through, unless the drilling is done far enough down a slope for salt water to occupy the horizon. The limestone is very often petroliferous on outcrop. It is important that there shall be no misunderstanding on this point, and that conclusions presented in the bulletin on oil and gas horizons shall not be discredited without ample evidence to support the criticism. The questions raised by Professor Foerste were, therefore, submitted to Mr. J. B. Hoeing, whose extended observations made in the especial study of our oil and gas horizons (fortified by a very large mass of data gathered before and since the publication of his Bulletin on Oil and Gas Sands of Kentucky, together with his intimate association with the drilling of the Caney creek well, in Morgan county, referred to by Professor Foerste, place him in a favorable position to discuss the subject. Mr. Hoeing says:
"In the Caney creek well the Corniferous was struck in its proper place at the base of the Black shale, and the Clinton was struck under the light shale. This was the case not only in that well, but in adjoining wells. Both formations gave oil and gas. Both give more or less oil or gas wherever struck in Eastern Kentucky, and both have been drilled through are easily recognized. The formation called Clinton in the Caney creek well is not above the Silurian clays; the drill does not show the latter

#### CLINTON OUTLIER ON AXIS OF CINCINNATI GEANTICLINE.

The thickness of the Clinton or Brassfield limestone on the eastern side of the Cincinnati geanticline, between Stanford and Crab Orchard, varies between 11 and 14 feet. On the western side, between Raywick and New Hope, it varies between 14 and 17 feet. Recently an outlier of this limestone, 14½ feet thick, was discovered about half way between the nearest outcrops hitherto known, east and west of the crest of the geanticline. It is located on Scrub Grass creek, a short distance beyond the home of Jim Jackson Edwards, about three miles southwest of Mitchellsburg. Overlying it is a layer of limestone, 1 foot thick, containing the large crinoid heads, *Whitfieldella* and *Stricklandinia triplesiana*. The Devonian limestone is 2½ feet thick. Opposite the home of J. J. Edwards it is 5½ feet thick, and the base is conglomeritic. This is the

this shale thickens rapidly from its western and southern outcrops in Clark and Powell to a deep trough of the shales in Bath, Menefee, Fleming, Mason, etc., and then thins again, still more rapidly, to the east and southeast and disappears entirely in all records before reaching the Big Sandy, on the east, and is quite thin to the southeast. The shales are not 150 feet in Morgan county (as Professor Foerste supposes); they have been drilled through repeatedly and shown to be from 30 to 40 feet thick. All evidence, obtained from a great number of wells, in addition to that on Caney creek, goes to show that the divisions in the Caney creek well record are correct. It should be borne in mind that the record of this well is not an imperfect one, but that a competent geologist examined each sample as it was bailed out of the well. The existence of the Berea or Sunbury shale in the Caney creek well is doubted by Professor Foerste, because he considers the interval as given between that and the Black Shale too small, and he assumes that the Linietta has been included with the Black Shale. The fact that the interval is less than it is elsewhere does not warrant such assumption, especially in this case, since all of the series, from the Berea shale down through the Berea grit, the Devonian shales and limestones, and the Niagara shales, are thinning rapidly from their exposures on the Ohio river south to the locality in question. The Berea shale and the underlying Berea grit have been followed from their outcrops on the Ohio river, in Lewis county, by outcrops and well records to the south and found to be thinning rapidly in that direction, but undoubtedly present over all that area. As to the Linietta or Bedford shale, it was repeatedly identified in the Oil Bulletin, and it is shown, in its thinned down section, in the Caney creek well as black shale directly above the Devonian Black Shale. This (Bedford) shale is readily recognized and differentiated from the Doutonian Black Shale, it direction, but undoubtedly preso

locality mentioned by Linney on page 37 of his Report on Nelson County. There is a strong unconformity between the Clinton and Devonian limestone. This outlier is interesting in showing a probable transgression of the Clinton, at least in Central Kentucky, across the area now occupied by the axis of the Cincinnati geanticline.