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A BRIEF STUDY
OF THE
CHEROKEE FORMATION OUTCROP
IN KANSAS

R2217
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APPROVED

A Thesis Submitted
to the Graduate Division in Partial Fulfilment of
the Requirements for the Degree
of Master of Science

Thesis Advisor

Chairman of Graduate Council

By

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KANSAS STATE TEACHERS COLLEGE

Pittsburg, Kansas

June, 1933

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J. A. Yates for criticisms and advice
given from time to time during the
progress of the work.

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a brief study of the rocks of the Cherokee formation at various horizons, (2) to attempt to show by chemical analysis the position of the land mass from which the sediments were derived, and (3) to see if it might be possible to divide the rock layers into definitely correlated beds on a basis of chemical analysis alone.

Nature of Study

The study of the rock formation was conducted by collecting samples at various places from the outcrop, usually upon the sides of strip pits. The samples were collected in such a manner as to get those having most bearing upon the three points to be considered. Ten of these samples are designated as the "X" series and were taken from approximately two to six feet above the Mineral vein west of Pittsburg. These samples were then analyzed according to the methods which are to be described in the analytical work; the percentages of the substances are reported in the oxide form. Also, the samples were treated with organic solvents and the amount of soluble material determined. The amount of volatile and combustible material was also determined.

CHAPTER I

INTRODUCTION

Purpose of Study

The Cherokee formation is one of the important rock formations of Kansas. There has been much work done upon the coal beds of this formation but so far as is shown by a search of the available literature, there has been no work carried on making a study of the rock beds of the formation by means of chemical analysis.

This paper is an endeavour to do three things: (1) to make a brief study of the rocks of the Cherokee formation at various horizons, (2) to attempt to show by chemical analysis the position of the land mass from which the sediments were derived, and (3) to see if it might be possible to divide the rock layers into definitely correlated beds on a basis of chemical analysis alone.

Nature of Study

The study of the rock formation was conducted by collecting samples at various places from the outcrop, usually upon the sides of strip pits. The samples were collected in such a manner as to get those having most bearing upon the three points to be considered. Ten of these samples are designated as the "M" series and were taken from approximately two to six feet above the Mineral vein west of Pittsburg. These samples were then analyzed according to the methods which are to be described in the analytical work; the percentages of the substances are reported in the oxide form. Also, the samples were treated with organic solvents and the amount of soluble material determined. The amount of volatile and combustible material was also determined.

CHAPTER II

DESCRIPTION OF FORMATION

Importance of Formation

Location

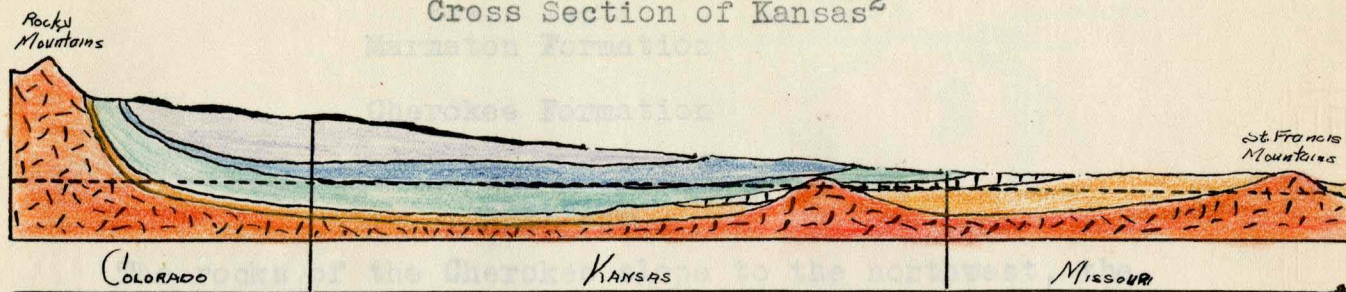
Cherokee Formation is the name given to the group of sandstones, limestones, shales, and coal beds outcropping in Southeastern Kansas between two lines extending in a northeast direction; the east most passing west of Baxter Springs, and toward Asbury, Missouri, and the line forming the west boundary of the outcrop passing through the vicinity of Cherryvale and Fort Scott. The formation is made up principally of sands and shales with the latter predominating; there are, however, occasional beds of limestone and coal. The rocks are not of any pure class but run from sands to limes and are found in all other combinations; the beds are very inconsistent and lensing is frequent.

The Southeastern part of the state is the only place in Kansas where the Cherokee outcrops. The outcrop is extensive and covers an area of approximately eight hundred sixty-five square miles in this part of the state; of this area we find five hundred forty square miles in Cherokee County, two hundred square miles in Crawford County, one hundred square miles in Labette County, and twenty-five square miles outcropping along the stream beds of Bourbon County.¹

¹ Erasmus Haworth, Special Report on Coal. pp. 21-22.

Figure No. I

Cross Section of Kansas²



- | | |
|----------------|---------------------------|
| ● Tertiary | ● Pennsylvanian |
| ○ Cretaceous | ▨ Mississippian |
| ● Permian | ● Cambrian and Ordovician |
| ● Pre-Cambrian | |

Pennsylvanian³

Virgil Series

Wabawnee Formation

Shawnee Formation

Peedee Formation

Missouri Series

Lansing Formation

Kansas City Formation

Bronson Formation

Bourbon Formation

² R. C. Moore and Kenneth K. Landes, Underground Resources of Kansas. p. 13.

³ Report of Sixth Annual Field Conference. Kansas Geological Society. 1932.

⁴ Erasmus Haworth, Special Report on Coal. p. 23.

Des Moines Series

Marmaton Formation

Cherokee Formation

Position

The rocks of the Cherokee slope to the northwest, the direction of the dip being given as N 69° 58" W,⁴ and since the topography is nearly flat the strike of the outcrop is approximately perpendicular to the dip. The amount of dip varies from about a foot six inches to about fifteen feet to the mile. The shales vary in thickness, the average being approximately four hundred fifty feet; the formation, however, tends to thicken to the southwest and thin out to the northeast.

Rocks of the Mississippian system form the foundation upon which the rock of the Cherokee formation is deposited. The Cherokee is separated from the Mississippian rocks by an unconformity representing a period of considerable erosion between the time of the deposition of the beds of the Mississippian system and the overlying Cherokee.⁵

At the western extremity of the Cherokee outcrop we find the rocks dipping under the younger layers of the Pennsylvanian period, namely, the Fort Scott limestone of the Marmaton group. The Cherokee is known to extend some distance west under this formation but tends to thin out as it reaches westward.⁶

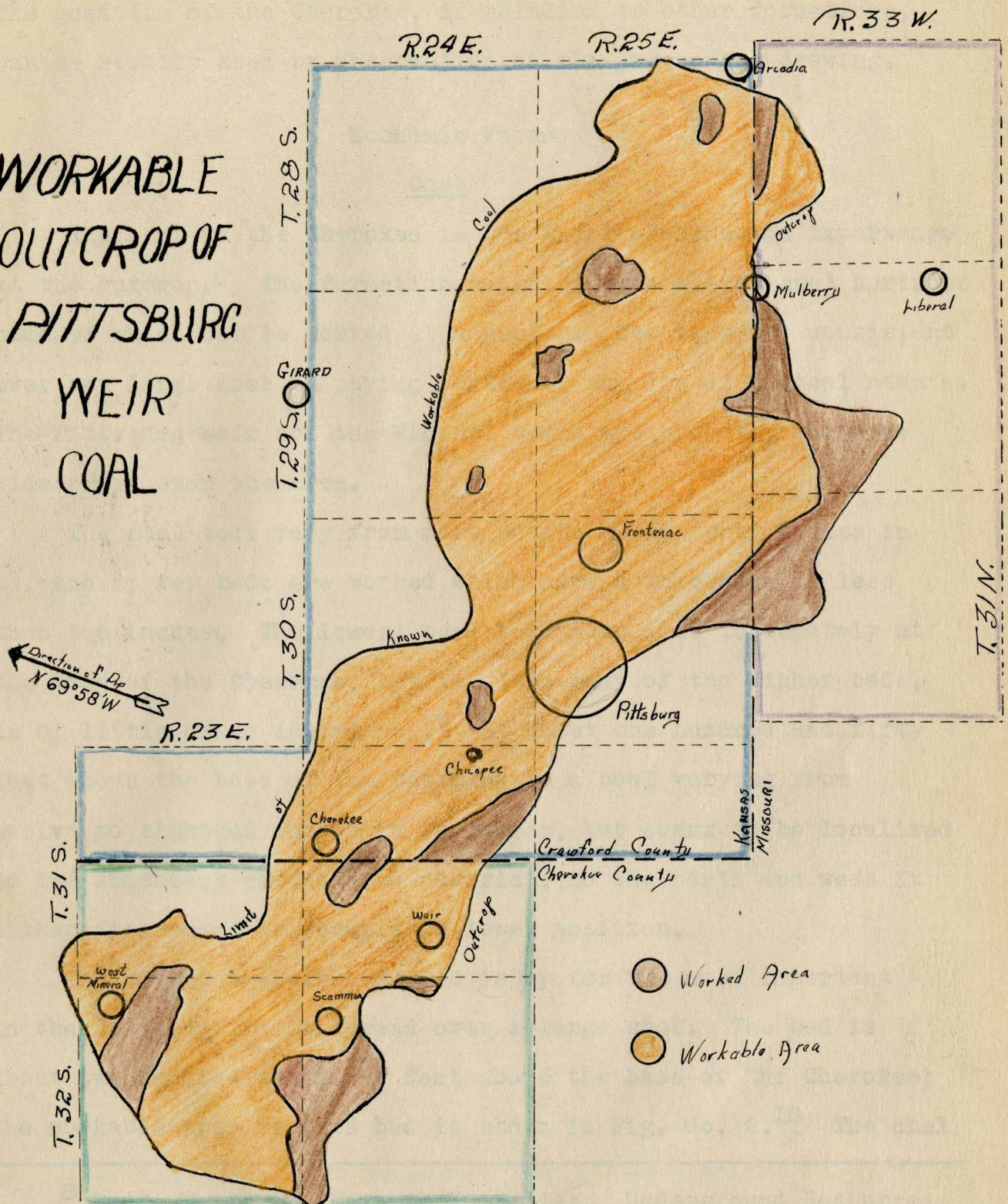
⁴ C. M. Young, H. C. Allen, Kansas Coal. p. 22.

⁵ E. R. Buckley, Geology of the Granby Area. Missouri Bureau of Geology and Mines. Vol. IV. p. 78.

⁶ Erasmus Haworth, Special Report on Coal. p. 23.

Figure No. 2

WORKABLE OUTCROP OF PITTSBURG WEIR COAL



The position of the Cherokee, in relation to other formations, can be readily seen by observation of the preceeding drawing.

Economic Value

Coal

The coal in the Cherokee is the thing of economic importance at the outcrop.⁸ The formation contains some eleven coal horizons some of which can be worked at a profit. Few beds are consistent over any large area in paying portions, but are of a local nature. The Pittsburg-Weir and the Mineral coals are probably the more widespread over the area.

The coal beds vary from mere sheets up to forty inches in thickness; few beds are worked which have a thickness of less than ten inches. The lowest coal bed known lies immediately at the base of the Cherokee, but it, like many of the higher beds, is of little or no importance.⁹ At about one hundred and fifty feet above the base of the Cherokee is a coal varying from twelve to eighteen inches in thickness, but seems to be localized to the southeast part of the district; to the north and west it either disappears or occupies a lower position.

The Pittsburg-Weir coal bed is by far the most important in the state, as it is spread over a large area. The bed is about two hundred and fifty feet above the base of the Cherokee; the workable area of this bed is shown in Fig. No. 2.¹⁰ The coal

⁸ R. C. Moore and Kenneth K. Landes, Underground Resources of Kansas. p. 25.

⁹ Erasmus Haworth, Special Report on Coal. p. 25.

¹⁰ C. M. Young and H. C. Allen, Kansas Coal. p. 70.

is of a good quality and varies in thickness from forty-three inches in the south to thirty-two inches in thickness in the north part of the district.

Oil

The Cherokee is very valuable as a reservoir for much of the oil and gas of the Mid-Continent field.¹¹ Oil and gas are found in the formation where it dips under the surface. The two principal oil and gas producing layers are the Bartlesville and Burgess sands, the former being about midway up in the formation and the latter at the base of the Cherokee where it rests directly upon the Mississippi limestone. Lenses of sand are present throughout the Cherokee, however, and in some cases contain oil and gas. The Cherokee produces oil in Cowley, Elk, Franklin, Labette, Linn, Miami, Neosho, and Rice Counties, in some quantities.

Natural Gas

The productive area for natural gas from the Cherokee formation is quite extensive. There is some production most everywhere the Cherokee is found as far west as McPherson County. The main gas fields or regions, however, may be divided into two areas: (1) beginning in Johnson County and extending southward into Chautauqua County are the "shoe string sands," and (2) farther west are the larger elongated sand bodies beginning in the northeastern part of Greenwood County and extending southward

¹¹ R. C. Moore and Kenneth K. Lander, *Underground Resources of Kansas*. pp. 93-115.

¹⁴ R. C. Moore and Kenneth K. Landes, *Underground Resources of Kansas*. p. 37.

¹⁵ C. R. Buckley, "Geology of the Granby Area," *Missouri Bureau of Geology and Mines*. Vol. IV. pp. 78-85.

through eastern Cowley County.¹² The "shoe string sand" region of eastern Kansas includes such important fields as the St. Paul string, the McCune string, the Bush City string, the Colony string, the Garnett string, and the Goodrich-Parker string.¹³ The important producing region of the western area is the Sallyards-Madison "shoe string" in Greenwood County. The Cherokee formation is the main gas producer in the eastern part of the state.

Asphalt

Exposures of asphaltic sandstone are present at various places in southeastern Kansas where the Cherokee outcrops.¹⁴ These deposits were formed by seepage of oil out of the outcrop of the oil sands. Apparently these outcrops are of little commercial importance except when used locally as road building material.

Metals

There are no metals of value found in the Cherokee itself. Some individuals have conceived the theory that the lead and zinc ores of the Joplin district leached down into the Mississippian from the younger rocks above; there has been considerable evidence brought forward to support the belief.¹⁵ There is a deposit of lead ore in the Pleasanton shales near Mine Creek, deposited in a fracture in the rocks and at various times it has been worked. Galena has also been reported as being found in

¹² Walter A. Van Wiebe, Oil Fields in the United States. p. 207.

¹³ Ernest R. Lilley, The Geology of Petroleum and Natural Gas. pp. 359-363.

¹⁴ R. C. Moore and Kenneth K. Landes, Underground Resources of Kansas. p. 37.

¹⁵ C. R. Buckley, "Geology of the Granby Area," Missouri Bureau of Geology and Mines. Vol. IV. pp. 78-85.

a limestone region to the west but the authority of this finding could not be definitely established. In support of the theory, may I also say that in observing the various shale samples under the ordinary microscope, on several occasions in studying sands from the lower Cherokee, there was observed what appeared to be small crystals of Galena. An attempt to isolate enough of these to get a definite chemical test for lead did not meet with success.

Conditions Under Which Formed

Climate

At the time of the formation of the Cherokee the climate on this continent was suitable for abundant vegetation. The atmosphere was very favorable to plant growth as it undoubtedly contained more carbon dioxide than it does today. The plants grew large and the great coal deposits were laid down in the swamps which were quite numerous. There were no destructive winds sweeping through the forest to disturb the vegetation, so it grew to enormous dimensions.¹⁶

Land Movements

The Cherokee was in the main coastal deposits, the rocks containing wave and ripple marks as well as showing the effects of shore currents.¹⁷ The sands are lenticular in nature and show markedly the effects of local conditions of deposition as well as the rhythmic movements of the land masses.

¹⁶ Alexander Winchell, Walks and Talks in the Geologic Field. pp. 183-188.

¹⁷ Erasmus Haworth, Special Report on Coal. p. 29.

Great elevations of the land masses along the coast line are not in evidence; apparently the coast line was low and of a very swampy nature. The sediments presumably came from the Wichita and other ranges to the southwest in Oklahoma as the rocks tend to thicken to the southwest and to thin out as we proceed to the northeast.

There were a number of swamps along this low lying coast in which was deposited the abundant vegetation in the form of carbonaceous shales or in some cases coal. Some of these swamps extended over almost the entire area causing such deposits of coal as the extensive Pittsburg-Weir beds; others were of a more local nature. It probably would have been difficult in many cases to tell where the land and seas really met.

The coal of Kansas is undoubtedly derived from the vegetation which lived in these swamps. In the coal we find decomposed vegetable tissue upon observation under the microscope. Leaves of plants are found in large quantities in the shales above the coal beds and in some cases we find tree roots in the beds below. The plants which supplied the vegetation for the Kansas coal beds were cryptogams in the swamps, with a few gymnosperms growing on the uplands.

The rock strata of the age show there was an elevation of a part of the land above the sea level, forming immense stretches of marshy country which was covered with a luxuriant growth of vegetation, where the coal beds were formed; but even at this period there were alternate elevations of the land above water level and depression below the level of the sea, as shown by the coal being in beds, alternating with marine rock strata.

Kedzie gives a very good description of the country during the Cherokee period in his following article:

"The indications are plain that this age was one of numerous changes of level; that all regions, over which the formations of coal was going on, were at long intervals of time depressed below the sea level, so that coal forming was for the time checked, and layers of marine rock were deposited; that when the land was again elevated to the condition of a marsh, the thick growth of vegetation and the making of coal began again, and thus there were formed alternate coal beds and marine rock layers."¹⁸

Fallen leaves and other dead vegetation constantly gathered over these great coal marshes, after long ages, making deposits of great thickness over which marine rocks were gradually deposited, producing a great pressure on the decayed vegetation below, forcing out the light gasses and leaving the deposits of coal.

Life

Flora¹⁹

The great marshy districts of the period were covered with a wonderfully dense growth of vegetation consisting of some three thousand different known species. The forests were both dense and extensive. The Calamites were the predominating rushes. The scale trees seemed to predominate in both size and number. They were a sort of evergreen, having small needle-like leaves. These trees frequently grew to one hundred feet or more in height and as much as twelve feet in diameter. The growth rings were absent except in those at the very close of the Pennsylvanian period showing an absence of seasons. Huge Calamites

¹⁸ W. K. Kedzie, Agricultural Geology. p. 34. 351-372.

¹⁹ J. W. Dawson, The Geological History of Plants. pp. 110-174.

or rushes grew to sixty feet in height and fifteen inches in thickness. Ferns also grew to unbelievable sizes and made growth very dense; some grew from the trees while others grew on the ground forming majestic trees themselves. Some of these ferns produced seeds but most were spread by spores. These forests grew up rapidly and were of very soft woods. The spores from these trees and ferns, when spreading, changed the green of the forest to a yellowish brown; some of the coals today are made up almost wholly of these spores which fell through the leaves of the dense forest foliage.

Lepidodendron and Sigillaria were the predominating trees, Calamites predominating among the rushes. The Lepidodendron tree was a tall tree whose trunk and limbs were covered over with seal-like impressions arranged in a diagonally winding series down the tree. The Lepidodendron has some features connecting it with the modern "ground pine," in other ways it is connected with tropical Cycads, having some properties of our modern trees and some of our typical ferns. The Sigillaria is similar to the Lepidodendron except the leaf scars were arranged lengthwise and more remote from each other. The Calamites were the predominating rushes.

Fauna²⁰

The Fauna of the Cherokee period does not seem as extensive as the plant life, yet it is quite extensive. The Pennsylvanian Age seems to be the dawn of the insect as well as its period of domination. Only one of the four hundred forms had a wing spread

²⁰ Schuchert, Charles. Historical Geology. pp. 351-372.

of under .38" and twenty over 4", the average wing spread being about two inches. At the close of the period the insects seemed to be declining, apparently having flourished in the warm, moist climate. There appeared, during the Pennsylvania period, eight hundred different kinds of cockroaches. Scorpions and spiders were present in primitive form, the spider not yet having the power of weaving its web.

The amphibian was the principal type of animal life. There were about eighty-eight species ranging in size from two inches to about twenty feet in length. Most of them were small creatures related to the living salamander. They were sluggish, living in or about the water, and were protected from their enemies by a coat of armor. A few primitive reptiles were known to be in existence, as well as some of the other forms of life.

The sea life of Cherokee time was mostly of the shell type and of cosmopolitan nature. The most important were the brachiopods, bivalves, gastropods, and cephalopods.

Charles Schuchert painted a very fine picture of a forest of this period when he wrote:

"In these forests of Pennsylvanian time might have been seen flying about the largest insects that have ever lived. Great 'dragon-flies' reaching a wing spread of twenty-nine inches. Huge cockroaches abounded everywhere in great variety, giants of four inches in length not being rare. As a rule, these insects were carnivorous, and did not transfer the pollen from one flower to another, with resulting cross-fertilization, as is so commonly done by living insects among present-day plants. The smaller insects were preyed upon by scorpions and spiders, the latter not making webs but living on the ground or in rotten logs, along with many myriapods, or thousand-legs. No insect of this time, so far as known, produced

chirping or other sounds, and the soughing of the wind among the trees was interrupted only by the croak of an amphibian in the marsh. Amphibians were common in the swamps, and it is probable that many small reptiles were running over the ground and about the trees. No large land animals, such as we know, and no birds were to be seen."²¹

Apparently about the only conflict occurring upon the continent during this period was the quiet struggle of the land and sea to gain domain over the region. We can observe by the record left in the rock that this struggle was not great at any time but was continually going on; it was this quiet oscillation of the land and sea which is largely responsible for the coal deposits of Kansas.

²¹ Schuchert, Charles. Historical Geology. p. 378.

Description of Samples

The Cherokee formation may be rather roughly cut into two types of formations with no definite dividing line between. The sediments of the lower parts of the formation seem to be of a more porous nature and to carry large quantities of sand and iron, the layers being subject to more local disturbances and appearing to have been deposited very close to the coast line where local conditions played a very important part. The upper portion of the formation, however, appears to be of a slightly more uniform nature and to carry larger amounts of lime and less sand, also to be of a more compact nature and to contain an abundance of organic material. The land, at the beginning of the period, must

CHAPTER III

SAMPLES OF FORMATION

Method of Sampling

The general method used in sampling was to clean off the face of the rock to be sampled with a stone mason's hammer, then to chisel down the face making a groove about two inches in width and several inches in depth. The rock chisled off was collected in canvas bags and labelled, these samples were later crushed to quarter inch size, quartered and then ground to pass a hundred mesh sieve. About twenty grams were placed in a tube for immediate use and about two hundred-fifty grams of the quarter inch size kept in labelled bottles for reference in future work. In all cases the analytical work was done on the material which had been passed through the hundred mesh sieve.

Description of Samples

The Cherokee formation may be rather roughly cut into two types of formations with no definite dividing line between. The sediments of the lower parts of the formation seem to be of a more porous nature and to carry large quantities of sand and iron, the layers being subject to more local disturbances and appearing to have been deposited very close to the coast line where local conditions played a very important part. The upper portion of the formation, however, appears to be of a slightly more uniform nature and to carry larger amounts of lime and less sand, also to be of a more compact nature and to contain an abundance of organic material. The land, at the beginning of the period, must

have been of higher elevation, more rugged and perhaps more unstable than at the close of the period.

The majority of the samples studied were from the upper portion of the formation. The samples were taken having the three points to be considered in mind. Ten of the samples were taken immediately above the Mineral coal vein (beginning at a distance of one foot above the vein and extending upwards for a distance of approximately six feet) and were collected in a line approximately parallel to the strike which happens to be presumably the direction from which the sediments came. These ten samples are graphed in the following chapter.

The ten samples discussed in the above paragraph were taken from five different pits. The rock seemingly was more porous at the south end of the section than at the north end, but the difference was very slight. The first break of consequence was the finding of a limestone layer beginning at the location of sample No. 6 and thickening slightly to the north. In the entire section small anticlines and synclines were observed and lensing was frequent indicating that the land was continually slowly moving during and following the deposition of sediments. At no time, however, was the land apparently far under the sea and in no case did it rise above the water level.

Something of the life of the period of deposition could also be read, but no study of this matter was made at this time. Notice was simply given to the fact that in the rock closely associated with large amounts of carbonaceous matter animal life, in the form of brachopods, crinoids, and a few gastropods, make up the principal

fossil remains, the Spirifer and Productus being pronounced. The deposits having more sand and less carbonaceous matter carried remains of flora in quantities, but few animal fossils; the sea water of these deposits were too muddy perhaps to be favorable to animal life.

The remaining ten samples which were analyzed in this work were selected from various places over the outcrop of the formation in this region. A description of these samples and their location can be secured from the description which is to follow.

Name and Location of Samples

The twenty samples discussed in this report were from various districts. The first ten were taken from above the Lightning Creek coal beginning at approximately two feet above the coal and extending upwards a distance of six feet. The samples were taken as follows:

1. Shale collected from a strip pit about three miles west and one-half mile south of the intersection of Broadway and Quincy Streets, Pittsburg; sec. 35, T. 30 S., R. 24 E.

2. Shale secured from a pit about one mile northeast of the location of sample No. 1. It was from the south end of the pit of the Commercial Fuel Company, on the south side of West Fourth Street; sec. 26, T. 30 S., R. 24 E.

3. Shale taken from the same pit as was No. 2, being northeast of it and at the north end of the pit; sec. 26, T. 30 S., R. 24 E.

4. Shale from the Commercial Fuel Company pit situated about one-half mile northeast of sample No. 3, but from the south end

of the pit on the north side of West Fourth Street; sec. 23, T. 30 S., R. 24 E.

5. Shale in the same pit as No. 4, but at the north end, approximately a quarter of a mile northeast of No. 4; sec. 23, T. 30 S., R. 24 E.

6. Shale from the Lone Star Coal Company pit northeast of No. 5, in the south end of pit; sec. 23, T. 30 S., R. 24 E.

7. Shale from the Lone Star Coal Company pit located about two hundred twenty yards north of sample No. 6; sec. 23, T. 30 S., R. 24 E.

8. Shale from the same pit as samples No. 6 and No. 7, but located south of West Twentieth Street, and in the north end of the pit about two hundred twenty yards north of the position of No. 7; sec. 23, T. 30 S., R. 24 E.

9. Shale obtained from the Eagle-Cherokee Coal Company about a mile and a half north of sample No. 8, from the south end of the pit; sec. 11, T. 30 S., R. 24 E.

10. Shale from the north end of the Eagle-Cherokee Coal Company pit and about two and one-fourth miles west of the Frontenac Road; sec. 11, T. 30 S., R. 24 E.

11. Shale consisting of the material immediately above the coal at sample No. 4; sec. 23, T. 30 S., R. 24 E.

12. Shale from the Jayhawk Coal Company across the state line in Missouri, north and east of Pittsburg. It was situated above the Pittsburg-Weir bed a distance of approximately six feet; sec. 7, T. 31 N., R. 33 W.

13. Shale located at the top of the Cherokee, immediately below the Fort Scott limestone of the Marmaton formation, five miles out on West Fourth Street.

14. Shale from the same stratigraphic position as sample No. 13, but on Broadway north of Arma.

15. Limestone found interbedded in the shale horizon of the first ten samples. This sample was taken at the same location as No. 7.

16. Shale found about a quarter of a mile east of No. 7, extending from a foot to six feet above the coal. A thin layer of limestone was found here two feet above the coal.

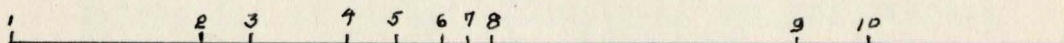
17. Sand outcropping as a hard layer above sample No. 4.

18. Sand located a half mile southwest of the Campus of Kansas State Teachers College, Pittsburg; sec. 31, T. 30 S., R. 24 E.

19. Shale immediately above the coal in mine (62½' deep) located a half mile west on air port road, and about two hundred yards north; sec. 16, T. 30 S., R. 24 E.

20. Sand located about one and one-half miles east of Broadway on Crawford-Cherokee County line; sec. 16, T. 31 S., R. 25 E.

Fig. 3 Relative distances between first ten samples



CHAPTER IV

METHODS OF ANALYSIS

Preliminary Work

Work by Others

There has been little work of value done in the analysis of shales. Work has been done by D. S. Hager²² upon the coloring matter, and by a number of men upon distillation and chemical treatment. I. G. Farbenind²³ did considerable work on the pressure and chemical decomposition of coals, oil shales and other carbonaceous solids. He used temperatures above two hundred degrees centigrade and a pressure of thirty atmospheres, in the treatment of shales with solvents in the presence of free halogens, or compounds setting free the halides.

The greater part of the work done in the way of an analysis of carbonaceous material seems to have been accomplished upon coal. Coal is analyzed as a selling factor as the purchaser wishes to know the value in comparison to other coals, this type of analysis being known as a proximate analysis. Considerable work has also been done in the treatment of coal with various solvents, active gasses, and distillation at various pressures and in different types of atmospheres.

²² Dilworth S. Hager, "Factors Affecting the Color of Sedimentary Rocks." Bulletin of American Petroleum Geologists. pp. 901-938.

²³ I. G. Farbenind, "Pressure and Chemical Decomposition of Coals, Oil Shales, and Other Carbonaceous Solids." British Patents 311,031.

²⁴ J. D. Davis and D. A. ... "Benzene-Pressure Extraction of Coal." Industrial and Engineering Chemistry. Vol. 21. pp. 1293-1298.

²⁵ Ibid. p. 1298.

Istvan Peter²⁴ found, after the extraction of coals with pyridine, a treatment with a mixture of ethyl alcohol and benzene does not give an additional extraction. While pyridine has a solvent action on the coal bitumen of ordinary temperature, the ethyl alcohol-benzene mixture acts only at high pressure. Both pyridine and pyridine-hydrochloride disperse the coal substance to a certain degree, which favors the view that pyridine acts on the coal not solely because of its basic nature.

J. D. Davis and D. A. Reynolds²⁵ extracted coal simply by the use of benzene as a solvent but used heat and pressure, which was impossible in the work performed in this paper; although the temperature itself was varied with not appreciable results. The work done by the above two men may be briefly summarized in the following four statements:

- "1. Solidity of the extract increases on continued extraction.
2. The ratio of solid bitumen to oily bitumen increases with continued extraction.
3. A bitumen that is soluble in benzene under the conditions of the extraction, but which precipitates from solution on cooling, is present in coal.
4. Removal of soluble substance from coal with either pyridine or benzene under pressure may cause its swelling property to either increase or decrease, depending upon the character of the coal."²⁶

It may be said that in securing the above given results the coals were extracted under pressure for a period of approximately eighteen hours at two hundred and eighty-five degrees centigrade.

²⁴ Istvan Peter, "Extraction With Pyridine." Chemical Abstracts. 1930. p. 3627.

²⁵ J. D. Davis and D. A. Reynolds, "Benzene-Pressure Extraction of Coal." Industrial and Engineering Chemistry. Vol. 21. pp. 1295-1298.

²⁶ Ibid. p. 1298.

Young²⁷ stated that the coals of Kansas have been extracted with such solvents as aniline, acetone, and phenol with the result that they lost their coking properties, but he does not describe the method used in the extraction or go any further into his results.

Organic Solvents

The preliminary work on this paper was done by use of sample No. 11. Many of the tests performed on this sample were not performed on any of the other samples, notably, the iodine test, and extraction with many of the organic solvents as well as the treatment with concentrated acids. This was the only sample which was given the distillation tests. Some thirty organic solvents were used on the preliminary, as shown below.

TABLE NO. I

Treatment of Sample No. 11 with Organic Solvents

No	Solvent	Per cent Extraction	No	Solvent	Per cent Extraction
1	Acetone	5.1	16	Ether, Diethyl	4.3
2	Alcohol Amyl	4.2	17	Ether, Petroleum	4.4
3	Alcohol Butyl	4.2	18	Ethyl Acetate	4.1
4	Alcohol Ethyl	4.5	19	Ethyl Iodide	4.3
5	Alcohol Methyl	4.8	20	Formaldehyde	4.5
6	Aniline	5.2	21	Furfural	4.1
7	Benzene	5.9	22	Gasoline	5.3
8	Bromobezene	4.2	23	Kerosene	5.5
9	Butyl Acetate	4.1	24	Olive Oil	3.9
10	Carbon Disulphide	4.2	25	O-Chlorotoluene	4.0
11	Carbon Tetrachloride	4.3	26	Pinene	4.7
12	Chloroform	4.2	27	Phenol	6.1
13	Cresol	5.2	28	Pyridine	6.7
14	Croton Oil	4.8	29	Toluene	4.8
15	Dimethyl Aniline	4.2	30	Xylene	5.0

²⁷ C. M. Young and H. C. Allen. Kansas Coal. p. 171.

The above results are given on the solubility of the sample placed in an extraction thimble in a test tube containing fifty cubic centimeters of the solvent, the amount of sample being one gram in each case. The whole was then placed in a bath at approximately twenty-five degrees centigrade for a period of ten days, at which time they were removed, dried and weighed and the results recorded in the table above. The thimble was then placed in a Soxhlet apparatus with one hundred cubic centimeters of the solvent and then extracted at the rate of about sixteen extractions per hour for approximately ninety minutes. The results of this extraction were very unsatisfactory, due principally to oxidization, so will not be definitely reported in this paper. Apparently the per cent of extraction with most solvents was unchanged but due to oxidization and polymerization of many of the solvents at higher temperatures these results were very unsatisfactory. The solvents in which increased solubilities were shown were pyridine, aniline, and phenol, but oxidation was pronounced in each case.

Solubility in Acids

The test sample was treated with eight of the common acids and the results were recorded. These determinations were made by treating one gram of the sample with fifteen cubic centimeters of the acid over a period of forty hours at a temperature of forty-five degrees centigrade. At the end of the treatment the residue was filtered in a Gooch crucible, washed free of acid with water, dried and weighed, the loss in weight being due to the material forming a gas or to its passing into solution.

TABLE No. II

Solubility of Sample No. 11 in Acids

Acid	Per cent Loss	Acid	Per cent Loss
Hydrochloric Acid	52.40	Hydrofluoric Acid	45.74
Nitric Acid	51.28	Formic Acid	44.62
Sulphuric Acid	49.84	Perchloric Acid	38.46
Phosphoric Acid	47.74	Acetic Acid	4.43

Treatment with Phenol

The treatment with phenol or carbolic acid, although not truly an acid, is discussed. The sample was treated with phenol under two sets of conditions, one at forty-five degrees centigrade for a period of forty hours, the extraction in this case being 7.11 per cent of the sample, the volatile part of the material amounting to 4.98 per cent.

The second treatment with phenol was carried on in a Soxhlet apparatus and the extraction was found to be 20.48 per cent while the combustible portion of the sample was found to be 21.76 per cent. The loss on ignition of the residue after the phenol extraction of the sample was 1.56 per cent. Treatment of the extraction liquor revealed no test for metals, so the conclusion was drawn that only organic material was extracted. The temperature used in this extraction was approximately one hundred and eighty degrees centigrade, and the extraction lasted over a period of approximately ten hours.

Treatment with Acetic Acid

Four of the samples were treated in the Soxhlet apparatus with glacial acetic acid for different periods of time, and it

was found the extraction varied. The extraction at ordinary temperature for a period of ten days seemed to extract only the volatile material, but when the sample was placed in a Soxhlet extractor the results were entirely different.

The test sample was placed in the tube and extracted for a period of ten days at twenty-five degrees centigrade, the percentage of extraction being 5.1 per cent, while the volatile matter was 5.0 per cent. This sample was then extracted for periods of half an hour in the Soxhlet tube, the maximum length of extraction being two and one-half hours. The percentage of extraction for the sample is shown in the table below.

TABLE No. III

Percentage of Extraction with Acetic Acid

Treatment at 25° C for 10 days	5.1%
Treatment in Soxhlet for 30 minutes	5.0%
Treatment in Soxhlet for 60 "	6.5%
Treatment in Soxhlet for 90 "	8.7%
Treatment in Soxhlet for 120 "	11.0%
Treatment in Soxhlet for 150 "	13.5%

The acid used for the extraction was filtered and evaporated to dryness and the residue taken up in hydrochloric acid and water. The residue was found to consist of large quantities of aluminum with traces of iron and calcium. The residue remaining in the thimble was then weighed and ignited. It was found that the loss upon ignition was practically the same as before treatment, with acetic acid, if the volatile material were subtracted it seemingly being taken away in the extraction.

Saturation Test

Shales and coals have been treated in various manners with halogen compounds, with some results, especially by the use of high pressures. In this test no attempt was made to determine the effect of iodine solutions at any pressure other than atmospheric. It was hoped that the iodine would attack the unsaturated bitumen within the shale if such existed, but no results were obtained in either case other than to show that the strength of the iodine solution was apparently unchanged.

Two different iodine solutions were used in this determination, iodine in solution in methyl alcohol and iodine in an aqueous solution of potassium iodide; neither of the solutions was standardized, but a blank determination was run in each case. It may be said here, however, that both solutions were approximately normal.

The procedure in each case was to take five grams of the sample and place it in a two hundred and fifty cubic centimeter iodine flask and to add fifty cubic centimeters of the respective iodine solutions to each of the samples as well as to each of the blanks. The flasks were then placed in a bath at approximately forty degrees centigrade and allowed to remain for a period of one hundred hours. Ten cubic centimeters of the solution were then pipetted off and titrated with approximately .1 N sodium thiosulphate. The same amount of titrating solution was needed in each case for the sample solution as was needed for the blank, so it was concluded that no reaction took place between the bitumen and iodine at the temperature and pressure used.

Distillation Test

The sample contained considerable carbonaceous material so a test was made by distillation. The method used was that used in the preliminary testing of oil shales at the Colorado School of Mines.²⁸ A diagram of the apparatus may be observed below:

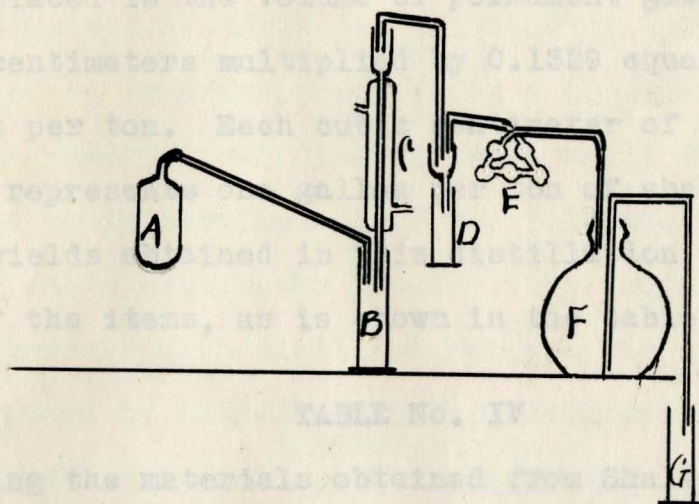


Fig. No. 4. Apparatus used in distillation of the shale.

- A. Retort
- B. Graduate cylinder for oils
- C. Condenser
- D. Graduate cylinder for oils
- E. Absorption bulbs for ammonia
- F. Carboy of water for gas
- G. Graduate to measure water

²⁸ Low, A. H. Technical Methods of Ore Analysis. pp. 291-294.

The shale is crushed to quarter inch size and the two hundred and forty-one gram sample is placed in the retort and heated carefully, the operation being ended when gas ceases to pass through the absorption bulbs. The amount of ammonia is determined by the Kjeldahl method, titrating into .2 normal sulphuric acid, each centimeter used being equivalent to 0.10954 pounds of ammonium sulphate per ton of shale. The volume of water displaced is the volume of permanent gasses and the volume in cubic centimeters multiplied by 0.1329 equals the yield in cubic feet per ton. Each cubic centimeter of oil or water collected represents one gallon per ton of shale.

The yields obtained in this distillation were not great for any of the items, as is shown in the table below:

TABLE No. IV
Showing the materials obtained from Shale Distillation

Product	Yield
Oil	
Light Oil	5 gal. per ton
Tar and heavy oils	8 gal. per ton
Water	3 gal. per ton
Ammonium Sulphate	.25 pound per ton
Gas	1000 cubic feet per ton

No attempt was made to analyze any of the oils or gasses. They were simply collected and the amount reported.

Analysis of Samples

The work upon the twenty samples of shales was run and is discussed in the order of color tests; insolubility, and sulphur

trioxide content; treatment with organic solvents, including acetic acid; and the regular inorganic analysis.

Color Test

The color test used for this work was one devised by Abrams and Harder for the detection of organic material in cement.²⁹ The sample was ground to about an eighth inch size and two hundred grams weighed into a container with one hundred cubic centimeters of three per cent sodium hydroxide solution and digested at room temperature for a period of twenty-four hours. The material was then filtered until the filtrate was clear. Ten cubic centimeters of the filtrate was then placed in a fifty cubic centimeter Nessler tube and diluted to fifty cubic centimeters with distilled water. The color value was then determined by comparison with a standard and reported in milligrams of tannic acid. (For preparation of standard see appendix.)

Insoluble Residue and Sulphur Trioxide

Tests for insolubility and sulphur trioxide were also used which are employed upon cement.³⁰ To find the insoluble residue treat one gram of the sample in a beaker with ten cubic centimeters of water and five cubic centimeters of hydrochloric acid and warm until effervescence ceases. Dilute to fifty cubic centimeters and digest on the steam bath until decomposition is complete. Filter the residue into a Gooch crucible containing a known weight of asbestos, and wash well with cold water.

²⁹ Griffin, R. C., Technical Methods of Analysis. p. 580.

³⁰ Ibid. pp. 573-574.

(Save washings for sulphur trioxide determination.) Digest the residue and asbestos in thirty cubic centimeters of five per cent sodium carbonate solution, keeping just below the boiling point for fifteen minutes. Filter into a Gooch crucible, wash with cold water then 1:9 hydrochloric acid, then again with cold water. The crucible is then ready to be dried and weighed, the loss in weight of the sample being the loss due to the treatment.

To the first acid filtrate above add water to make to two hundred fifty cubic centimeters heat to boiling and add ten cubic centimeters of ten per cent barium chloride solution, make up to five hundred cubic centimeters and place fifty cubic centimeters in a Nessler tube to be compared with a standard.

Organic Solvents

The work with the organic solvents was limited to benzene, methyl alcohol, and acetic acid. The sample was pulverized and one gram weighed into an extraction paper which was placed in a test tube with fifty cubic centimeters of the solvent and left in a bath at twenty-five degrees centigrade for ten days, at which time the extraction paper and sample were removed and weighed, the loss being the amount of the sample extracted.

Carbon Dioxide Determination

The amount of carbon dioxide in the various samples was determined by the methods of loss in weight and also gain in weight, the results checking very closely. The method of direct

weighing as used by Cloves and Coleman³¹ was perhaps the more accurate of the two methods, but the set-up is more exacting and it required more time than the method by loss in weight.

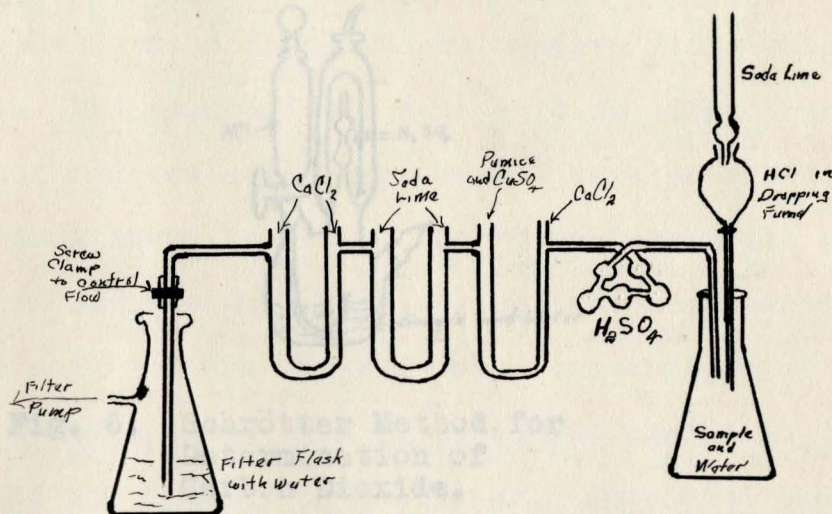


Fig. 5. Apparatus used in direct weighing of Carbon Dioxide

Several determinations were in progress at the same time. The Schrötter apparatus,³² as described in the same book, was the apparatus used in the determination by loss in weight. The results by this latter method are usually not so accurate as are those of the method of direct weighing, but in this case they were close enough together for the purpose intended.

³¹ Cloves and Coleman, Quantitative Analysis. pp. 121-127.

³² Ibid. p. 128.

Silicon Dioxide

The ash or residue remaining after ignition was fused with approximately ten grams of fusion mixture (sodium carbonate - potassium carbonate) and the fused mass transferred to a casserole where it was disintegrated in two hundred fifty cubic centimeters of water. The solution was made acid to litmus with hydrochloric acid and ten cubic centimeters were added in excess. The casserole was allowed to stand in the steam bath until evaporated to dryness. The residue was dissolved in one hundred cubic centimeters of hydrochloric acid and one hundred cubic centimeters of water was added. The

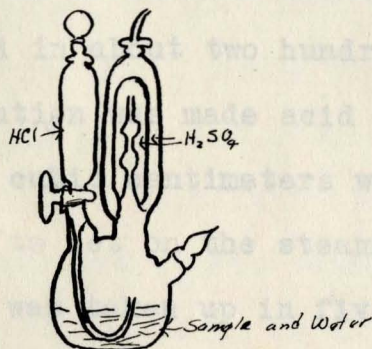


Fig. 6. Schrötter Method for Determination of Carbon Dioxide. The residue was washed in two normal hydrochloric acid and filtered. Evaporate the filtrate to dryness, take up in acid and water and filter as before, collecting

Volatile Material

To carry out this determination .5000 gram of the dry sample was weighed into a platinum crucible and the whole placed in a Skidmore iron crucible with a tight fitting cover. The iron crucible was then placed over a large Meeker burner and heated for a period of thirty minutes. The platinum crucible and contents were then removed and weighed. The loss in weight was reported as volatile material.

Combustible Material

The platinum crucible and contents were then placed over the direct flame of the burner and burned for a period of approximately two hours (until constant weight was attained after a short treatment in an atmosphere of dry carbon dioxide). The loss in weight from the original sample was reported as combustible material.

Silicon Dioxide

The ash or residue remaining after ignition was fused with approximately ten grams of fusion mixture (sodium carbonate - potassium carbonate) and the fused mass transferred to a casserole where it was disintegrated in about two hundred fifty cubic centimeters of water. The solution was made acid to litmus with hydrochloric acid and ten cubic centimeters were added in excess. The casserole was allowed to set on the steam bath until evaporated to dryness. The residue was taken up in five cubic centimeters of hydrochloric acid and one hundred cubic centimeters of water was added. This residue was then filtered and washed in two normal hydrochloric acid and finally in hot water. Evaporate the filtrate to dryness, take up in acid and water and filter as before, collecting the second yield of silica in a new filter paper. Ignite the filter papers in a platinum crucible and then add two or three drops of sulphuric acid. The crucible is then heated to a dull redness to constant weight. Add one cubic centimeter of six normal sulphuric acid and three to five cubic centimeters of hydrofluoric acid and evaporate to dryness on the steam bath. The crucible is now ignited to constant weight. The loss is the silicon dioxide.³³

Aluminum and Iron Oxides

The filtrate of the silicon dioxide determination was diluted to about two hundred and fifty cubic centimeters and made alkaline by addition of ammonium hydroxide, then boiled to drive off excess ammonia and filtered. The filtrate is saved for calcium oxide and

³³ Smith, George. Quantitative Chemical Analysis. pp. 85-88.

magnesium oxide determination. The precipitate was dissolved in hydrochloric acid and reprecipitated with ammonium hydroxide and again boiled to drive off excess ammonia, filtered and the precipitate ignited to constant weight as aluminum oxide and ferric oxide, the filtrate being added to the first filtrate.³⁴

Two procedures were used for finding the amount of ferric oxide present in the aluminum oxide and ferric oxide precipitate. The first method was a method of oxidization of the iron. The precipitate of aluminum oxide and ferric oxide was fused with sodium bisulphate and the melt taken up in dilute sulphuric acid and then heated until sulphur trioxide fumes were given off. The substance was dissolved in water and reduced by passing hydrogen sulphide through the solution, the hydrogen sulphide being boiled out while passing a current of carbon dioxide through the solution. This solution was titrated immediately with a standard solution of potassium permanganate.³⁵

The second method for the determination of ferric oxide in the sample was by a method of reduction of the iron. The aluminum oxide and ferric oxide precipitate was fused with fusion mixture and then dissolved in hydrochloric acid. The iron was completely oxidized by adding a few crystals of potassium chlorate and then evaporated to dryness to expell chlorine. The sample was taken up in fifty cubic centimeters of six normal hydrochloric acid, heated to boiling and quickly titrated with stannous chloride

³⁴ Scott, Winfred W. Standard Methods of Chemical Analysis. pp. 650-651.

³⁵ Ibid. pp. 651-652.

until the yellow color faded completely.³⁶
ignited and weighed.³²

Calcium Oxide

The determination of calcium was made in two different ways, one volumetrically and the other gravimetrically, both giving satisfactory results. The first method was carried on by making the filtrate from the iron and aluminum alkaline with ammonium hydroxide, then boiling and adding twenty cubic centimeters of a hot saturated solution of ammonium oxalate. The boiling process was continued until a good precipitate of calcium oxalate formed. After standing twenty minutes the precipitate was filtered. The calcium oxalate was dissolved in hydrochloric acid and water added to one hundred cubic centimeters, then reprecipitated as before, filtered and washed free from chlorides. The precipitate was decomposed by treatment with ninety cubic centimeters of three normal sulphuric acid, and made up to three hundred cubic centimeters then titrated with potassium permanganate at seventy degrees centigrade.³⁷

The gravimetric determination of calcium was much more rapid than the method preceeding and seemingly was as accurate. The filtrate from the iron and aluminum was heated to the boiling point, made alkaline with ammonium hydroxide, then alkaline molybdate solution was added at the rate of about one drop per second until an excess was present. The liquid was boiled until it became clear and then allowed to cool. The precipitate was

³⁶ Scott, Winfred W., Standard Methods of Chemical Analysis. pp. 221.

³⁷ Smith, George. Quantitative Chemical Analysis. p. 137.

filtered in a Gooch crucible, washed with hot water, dried, ignited and weighed.³⁸

PRESENTATION AND DISCUSSION OF DATA

Magnesium Oxide

The filtrates of the calcium precipitate were acidified with hydrochloric acid and concentrated on the steam bath to about one hundred and fifty cubic centimeters. To each filtrate was added ten cubic centimeters of a saturated solution of dibasic sodium phosphate. This solution was then boiled a short time, cooled, and made alkaline by the addition of ammonium hydroxide added drop-wise to secure complete precipitation. The solution was then set aside, cooled, filtered, ignited and weighed as magnesium pyrophosphate.³⁹

The several samples carrying magnesium were also run by washing the magnesium hydrogen phosphate in 1:9 hydrochloric acid, opening the filter paper and drying at room temperature for forty-five minutes to expell ammonia. The substance was placed in a dry beaker and tenth normal sulphuric acid added in an excess (using methyl orange indicator) the solution diluted to one hundred cubic centimeters and the excess of acid titrated with tenth normal sodium hydroxide.⁴⁰

³⁸ Wiley, R. C. "Separation of Calcium and Magnesium by Molybdate Method," Industrial and Engineering Chemistry. p. 127. April, 1933.

³⁹ Scott, Winfred W. Standard Methods of Chemical Analysis. pp. 652-653.

⁴⁰ Ibid. p. 256.

CHAPTER V

PRESENTATION AND DISCUSSION OF DATA

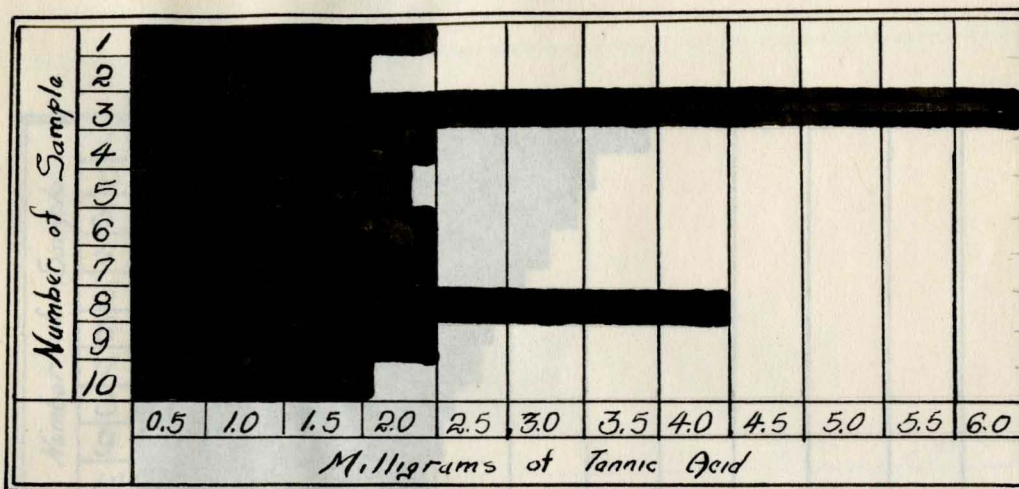
The table presented on the following page is the result of the application of the methods described in the preceeding chapter upon the twenty samples collected. The data of the entire analysis have all been placed in the one table so that the relationship between the samples can readily be observed.

The first ten samples, as has been stated elsewhere in this paper, are in a sequence line running for several miles in a south-southwest and north-northeast direction. It is from these that the basic conclusions of this paper are drawn, hence they shall be discussed in more detail than the last ten.

An observation of the table shows the great variety of rocks found within this one formation, and an observation in the field causes one to wonder that such variety is not more pronounced. It probably would be if the study had been more extensive. The rocks apparently range from almost a pure sand to almost pure limestone. The purest limestone of the formation is what is known locally as the Lightning Creek Lime, but as no analysis was obtained its true purity, at different points, is not known. However, it is known to become more impure to the southwest, finally disappearing.

Coloring Matter

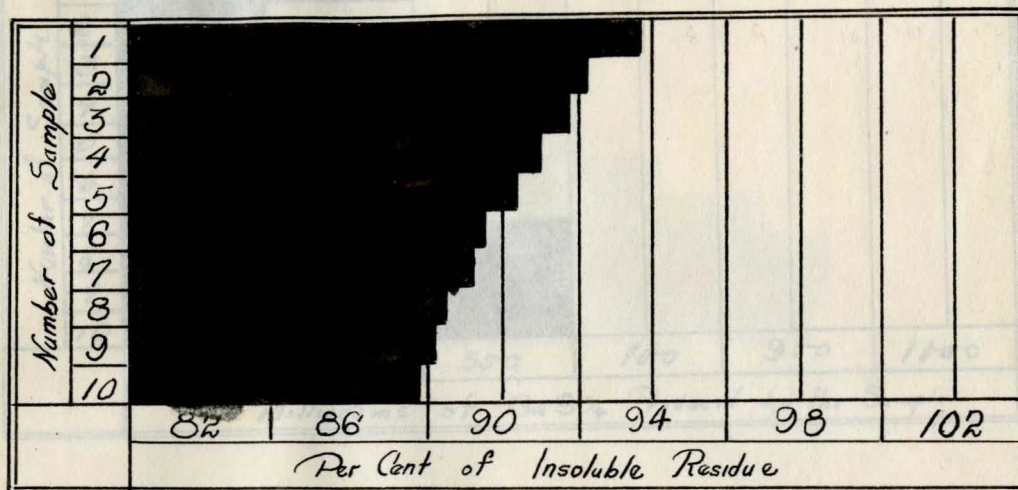
Graph No. I



This graph shows the relationship of the coloring matter in the shales as determined by the treatment of the samples with sodium hydroxide, reported in milligrams of tannic acid. It will be observed by a study of the table and graph that the location of the sample, apparently, has little relation to the color value imparted to the sodium hydroxide. This test, however, depends upon the existence, presumably, of certain bitumens and seems to have no relationship to the amount of combustible material as shown by ignition. Considering the fact of the above statement, the color test, as applied, apparently has little value as a means of classifying the shales, but seems to depend for its value upon some other factor other than the total amount of organic material present.

Insoluble Residue

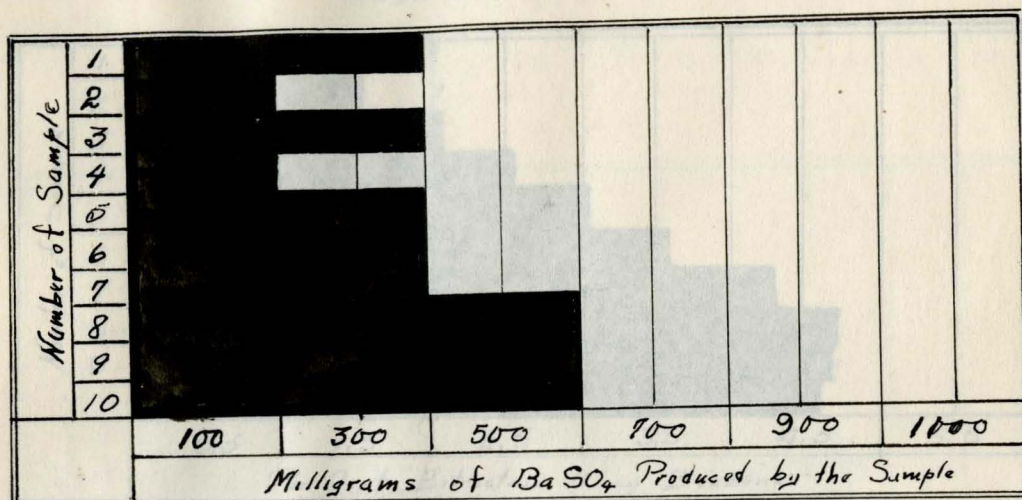
Graph No. II



The insoluble residue of the rock, as determined by treatment with hydrochloric acid and sodium carbonate, shows that the more insoluble rock is to the south and as one proceeds to the north a greater amount of soluble material is found. This fact would lead one to conclude that the rock to the south was probably closer to the land body and contained more of the insoluble sediments and sand particles from the shore while the rock farther north was formed less by sediments and more by precipitation of soluble substances, such as calcium carbonate.

Sulphur Trioxide

Graph No. III

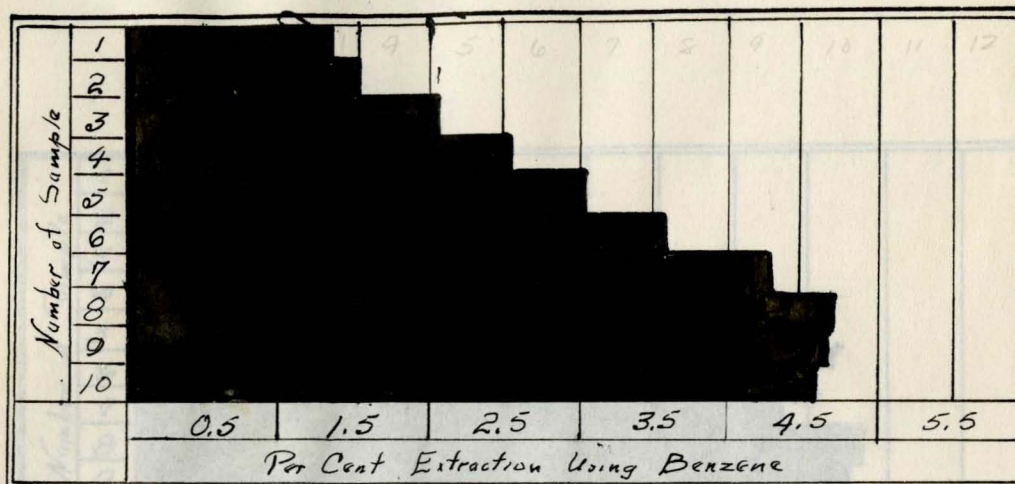


The origin of the sulphur trioxide is not known to the writer. The tests were slight in all cases. The sulphur is probably of organic origin, but there is no certainty. Seemingly, as shown by the comparative test, the content increased as one draws away from what is supposedly the position of the land mass which would lead one to believe that the deposit was from the sea water. However, this may be due only to the fact of the decrease in insoluble material, whether it is an error in sampling. It could be due to some local condition of deposition.

Solubility

Benzene

Graph No. IV

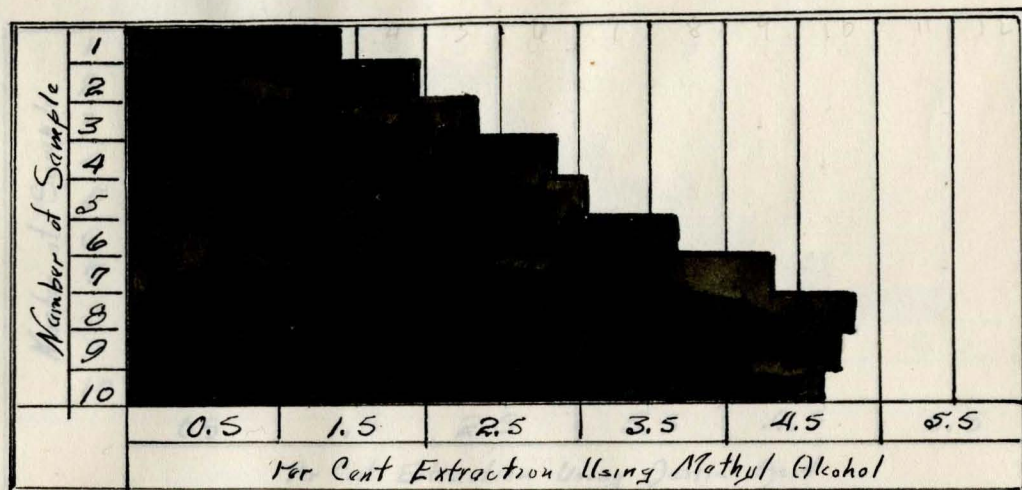


The extraction with benzene, as will be observed, increases as the samples get farther from the presumed land mass. This is supposedly due to the increase in organic matter up to the last two samples where both seem to decline. It cannot be definitely stated whether the decline is due to an actual decline in the general content of the strata or whether it is an error in sampling. It could be due to some local condition of deposition.

Methyl Alcohol

Graph No. V

Graph No. VI

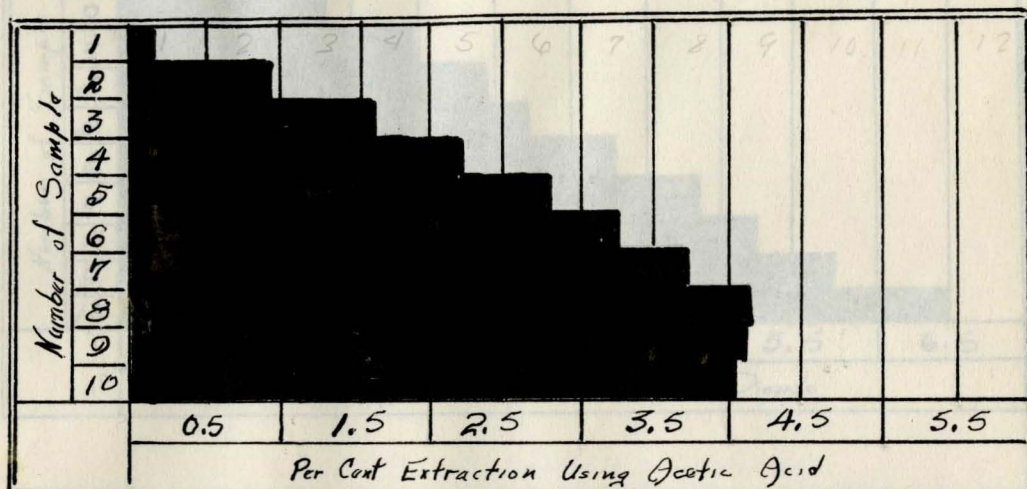


The methyl alcohol extraction declined on the last two samples, probably for the same reason as for the decline in the benzene extraction; but no definite statement can be made in either case. This extraction is only slightly below the benzene extraction and seems to bear out the same facts. Ignition of the extraction residues showed greater loss for the acetic acid than for the alcohol or the benzene.

Carbon Dioxide

Acetic Acid VII

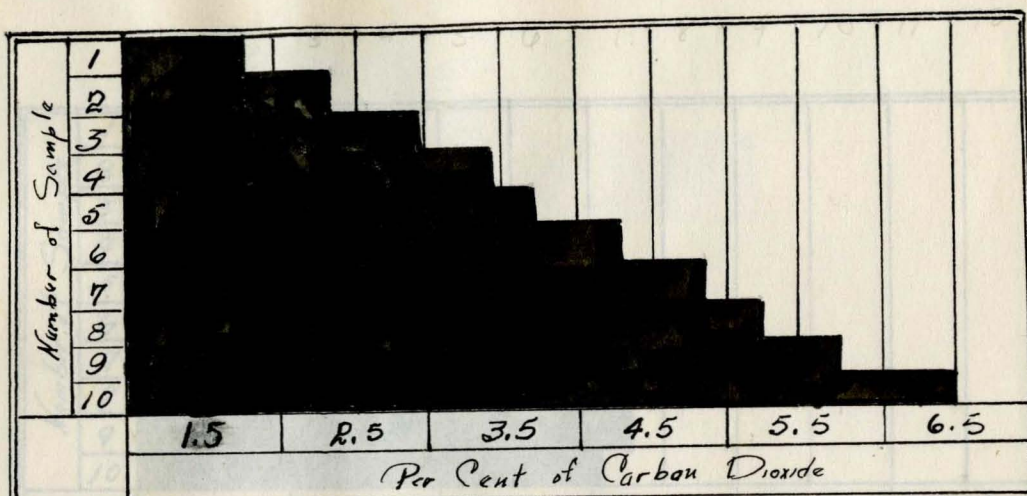
Graph No. VI



The carbon dioxide content of the rock increases markedly as we proceed away from the supposed position of the land mass. The acetic acid extraction has the same trend as the extraction with benzene and methyl alcohol, but seems to run approximately one per cent less in most all cases. There probably was something it did not extract which the other solvents extracted. Ignition of the extraction residues showed greater loss for the acetic acid than for the alcohol or the benzene.

Carbon Dioxide

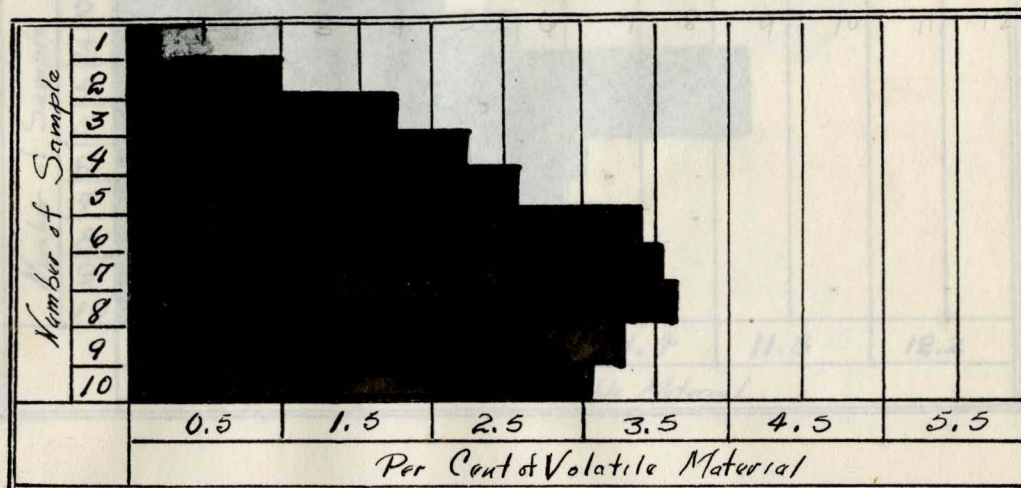
Graph No. VII



The carbon dioxide content of the rock increases markedly as we proceed away from the supposed position of the land mass. This fact is very strong evidence that the supposed position was the true position of the land and that the percentage of carbon dioxide increases as we proceed farther from the old shore line, due to the precipitation of Calcium Carbonate. being paid to the composition.

Volatile Material

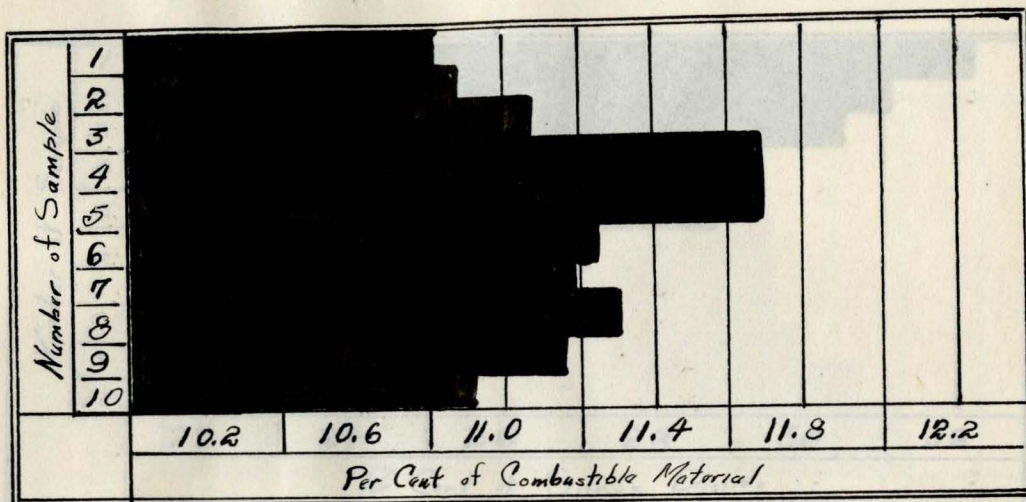
Graph No. VIII



The increase in volatile material runs in approximately the same trend as the extraction of the organic solvents with nearly the same percentage as the acetic acid extraction. Only the amount of the volatile matter was determined, no attention being paid to the composition.

Combustible Material

Graph No. IX

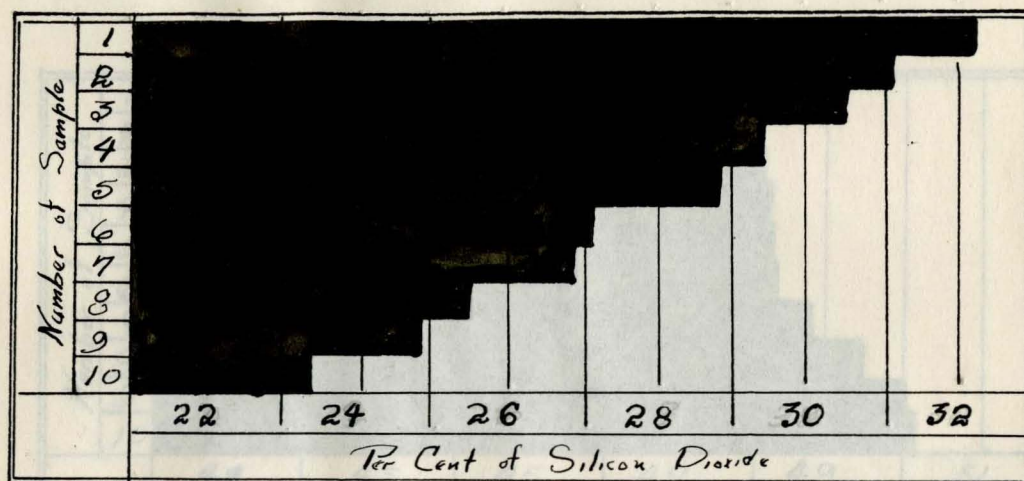


The amount of combustible material tends to increase from samples 4 and 5 after which it decreases except for the abnormality occurring in 8.

fact is strong support for the belief that the land mass was to the southwest during the deposit of the Cherokee formation, and that to the north and east we had a quiet, open sea.

Silicon Dioxide

Graph No. X

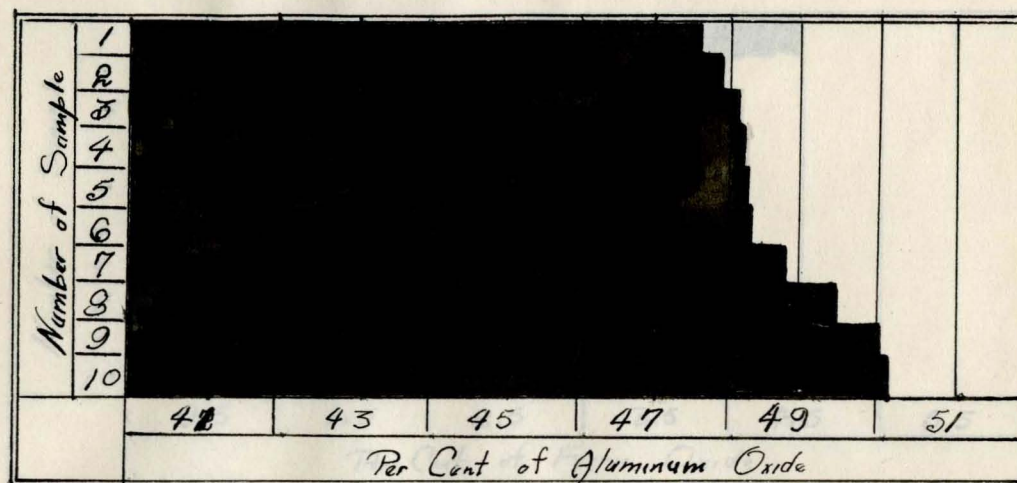


The percentage of silicon dioxide present decreases rapidly as we get farther away from the position from which the sediments are supposed to have been transported. This fact is strong support for the belief that the land mass was to the southwest during the deposit of the Cherokee formation, and that to the north and east we had a quiet, open sea.

rapidly as we went farther from the shore of the land mass.

Aluminum Oxide

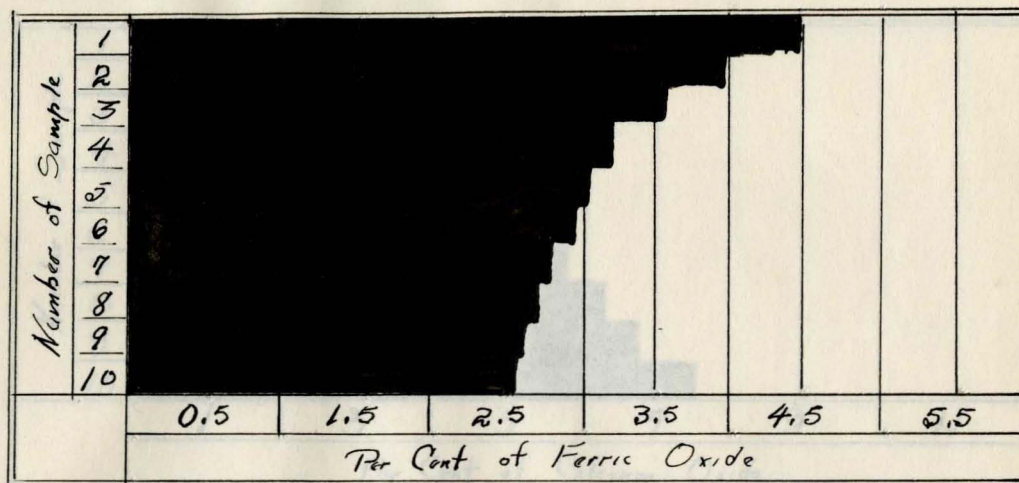
Graph No. XI



The aluminum oxide, which is one of the important constituents of fine muds, tends to increase as we draw away from the land mass. This fact with the decrease of the sand and increase in calcium carbonate shows that to the south sands were deposited. Farther north limes and oozes began to predominate. The limestone percentage increased more rapidly as we went farther from the shore of the land mass.

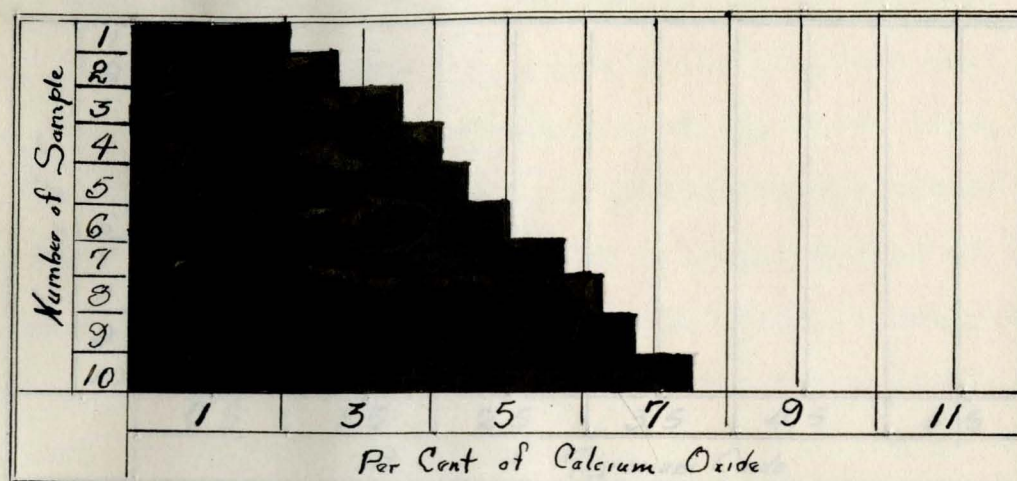
Ferric Oxide

Graph No. XII



The percentage of iron drops off as we leave the shore. The iron found was probably included as an impurity in the sand particles and decreased accordingly as the sand decreased, only much more rapidly, as the heavier sands containing the iron were deposited nearer the shore. This curve follows very closely the sedimentation curve. The calcium carbonate content of the rock decreases as we go toward land, first the coxes appearing, then the sands, as we proceed, nearer to the land mass.

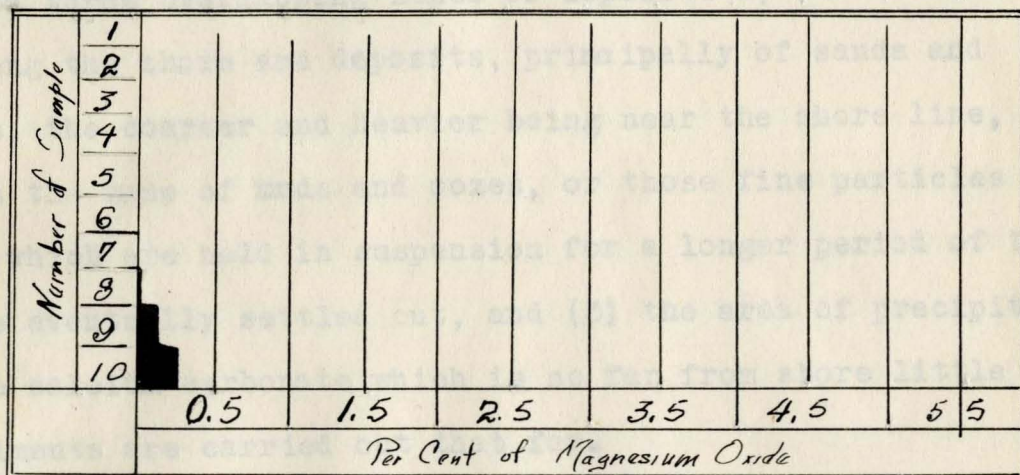
Calcium Oxide
Graph No. XIII



The limestone increasing as we draw away from the supposed land mass locates almost conclusively the position of the land mass at the time of the deposition of the rock strata. The purest of limestones are deposited where no material from a land mass reaches the place where deposition is occurring. The calcium carbonate content of the rock decreases as we go toward land, first the oozes appearing, then the sands, as we proved, nearer to the land mass.

Magnesium Oxide

Graph No. XIV



Apparently little magnesium oxide was formed in these rock layers, there being traces only as we proceed some distance from the shore lines.

The data shown in the table and the graphs show that undoubtedly the land mass, during the deposition of the rocks of the Cherokee formation, was to the south and west. This fact was the major thing which was hoped to be proven in this paper.

CHAPTER VI

The data, as found by the chemical analysis of the samples of rock, is very conclusive in the evidence that the land mass was to the southwest. This is especially true when we consider that all observations in the deposition of sedimentary layers point to three overlapping zones of deposition, as follows:

(1) along the shore are deposits, principally of sands and gravels, the coarser and heavier being near the shore line, (2) next is the zone of muds and oozes, or those fine particles of matter which are held in suspension for a longer period of time, but are eventually settled out, and (3) the area of precipitation of pure calcium carbonate which is so far from shore little or no sediments are carried out that far.

These resources could undoubtedly be distilled at a profit.

Location of Land Mass

The location of the land mass from which the Cherokee formation comes was undoubtedly to the southwest, as is shown by the chemical analysis and also by the facts concerning the geology of the beds.

The beds are known to thicken to the south and west, as well as to become more dominantly sandstone and to contain fewer lime layers. This is shown very decidedly in the analysis given, and upon applying the principles of sedimentation we find conclusive evidence of a southwest location of the dominating land mass. Local movements of the floor of the shallow sea, however, caused many irregularities in deposition throughout the entire period.

CHAPTER VI

CONCLUSIONS REACHED

Character of Formation

One of the three chief purposes for the work reviewed in the preceeding chapters was to make a study of the character of the rock making up the formation. The formation itself is of a very heterogeneous nature being of all gradations of sands, shales, and limestones. These beds themselves are not consistent, lensing frequently and continually changing in chemical composition. Some places coal of good quality is abundant and in other places apparently there is little or no organic material. Some few of the shales themselves are rich in carbonaceous material and in times of economic stress upon natural resources could undoubtedly be distilled at a profit.

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Correlation of Strata

It was one of the aims of this paper to be enabled to give the beds of the Cherokee some definite correlation and to be able to identify these beds on a basis of their analysis. The statement may be made now, however, that this task has met with failure. The outcrop of the Cherokee formation in Kansas, apparently, is so close to the original land mass from which sediments were constantly washed, and so near the shore that the currents and local shifting of the sea floor greatly affected deposition of sediments. The chemical composition of the rocks are apparently in no case in any wise consistent. The method of correlation, which is probably best for the Cherokee formation, is truly upon a lithological basis. Observations were made with the microscope and spectroscope but the work with the latter did not meet with any success, due to the difficulty of getting rid of the iron which is very detrimental when present in testing for other metals.

The results of the work, as a whole, were satisfactory. It was found that the formation was an admixture of carbonaceous material, sand, shales, and limestones in all varying degrees and combinations. The conclusion was reached that the land mass from which these sediments came was located somewhere to the southwest and presumably not so very far away. The attempt to give the different levels of the formation any stratigraphic standing on the basis of the chemical composition was unsuccessful.

SUMMARY

The three main lines of study in the paper were: (1) to make a brief study of the general character of the rocks making up the Cherokee formation, (2) to determine the approximate location of the land mass from which the greater part of the sediments of the formation were derived, and (3) to determine if the rock layers within the formation could be differentiated and classified upon a basis of their chemical analysis.

The work was carried on by giving the rocks a general chemical analysis, qualitative tests being made for heavy metals such as lead, zinc, copper, and silver, but none were found. The substances reported are the oxides of silicon, aluminum, iron, carbon, calcium, and magnesium. The rock was also extracted with benzene, methyl alcohol, and acetic acid and the amount of extraction determined. Observations were made with the microscope and spectroscope but the work with the latter did not meet with any success, due to the difficulty of getting rid of the iron which is very detrimental when present in testing for other metals.

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APPENDIX

Solutions

Organic Color Test Solution

Tannic Acid - Add ten cubic centimeters of a two per cent solution of tannic acid in ten per cent alcohol to ninety cubic centimeters of a three per cent solution of sodium hydroxide and let stand twenty-four hours at room temperature. Place 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 2.0, 3.0, 4.0, and 5.0 cubic centimeters of the solution in each of fourteen Nessler tubes and dilute to fifty cubic centimeters with distilled water. Each cubic centimeter of tannic acid solution used represents two milligrams of tannic acid.

Sulphur Trioxide Test Solution

Barium Sulphate - Weigh out 4.0000 grams of very finely divided barium sulphate into one hundred cubic centimeters of water and divide into colloidal dimensions. Place five, ten, fifteen, twenty, and twenty-five cubic centimeters of this solution into each of five Nessler tubes and dilute to fifty cubic centimeters with water. Each five cubic centimeters of the solution equals to two hundredths of a gram of barium sulphate on the basis of the weight of sample taken approximating 1.36 per cent sulphur trioxide.

Calcium Precipitation Solutions

Ammonium Molybdate - To a mixture of one hundred and thirty cubic centimeters of cold water and seventy-five cubic centimeters of concentrated ammonium hydroxide add fifty grams of molybdenum oxide and stir until dissolved. Add this slowly with constant stirring to a mixture of two hundred and forty cubic centimeters of concentrated nitric acid and five hundred and seventy-five cubic centimeters of distilled water. Allow to stand several days and decant the clear liquid, make ammonical with ammonium hydroxide immediately before using.

Ammonium Oxalate - Dissolve 35.0 grams of the ammonium oxalate crystals in one liter of distilled water.

Magnesium Precipitation Solution

Sodium Phosphate - Dissolve one hundred and twenty grams of dibasic sodium hydrogen phosphate crystals in one liter of water.

Standard Solutions

Potassium Permanganate - Dissolve 3.16 grams of the potassium permanganate crystals in one liter of water and standardize using sodium oxalate.

Stannous Chloride - Dissolve two grams of stannous chloride crystals in hot concentrated hydrochloric acid and make up to one liter. (Must be kept away from oxygen.) One cubic centimeter equals approximately 0.001 gram of iron, but it must be standardized against pure iron.

Sodium Thiosulphate - Dissolve 24.8 grams of sodium thiosulphate crystals in one liter of water and standardize using exactly one-tenth normal potassium dichromate.

Sodium Hydroxide - Dissolve 4.2 gram of stock sodium hydroxide in one liter of water. Titrate against standard acid.

Hydrochloric Acid - Mix 8.4 cubic centimeters of the concentrated acid with water to make one liter of solution. Standardize by titrating against dry sodium bicarbonate.

Sulphuric Acid - Mix 2.8 cubic centimeters of concentrated sulphuric acid with water to make one liter. Standardize by titrating against sodium bicarbonate.

Copper Sulphate-Pumice

This material is used in the determination of carbon dioxide by the method of direct weighing. It is prepared by placing small pieces of pumice in a normal solution of copper sulphate and then heating in an evaporating dish to dryness and finally entirely dehydrating the copper sulphate.

Chemicals

The majority of the chemicals used in this work were either "Mallinckrodt Chemicals" or "Bakers Analyzed." The purity of the products of these companies was a great help in the exactness of the work.

Treatment of Fibers

Extraction thimbles were treated with solvents used before they were used as containers for the samples. Filter papers were carefully selected for their specific purposes and treated when treatment was deemed necessary. The asbestos used was treated with both acid and alkali before use in all cases.

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