

FACTORS DETERMINING THE COLORS
OF RED AND GREEN SHALES

by

WILLIS DABNER WATERMAN

B. S., Kansas State College
of Agriculture and Applied Science, 1949

A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Geology and Geography

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1951

012-12-514

Spec
Coll.
LD
2668
T4
1951
W37

TABLE OF CONTENTS

INTRODUCTION 1

 Purpose of the Investigation 1

 Methods of Investigation 1

REVIEW OF LITERATURE 2

DESCRIPTION OF STRATIGRAPHIC UNITS SAMPLED 4

 Description of the Roca Shale 7

 Description of the Eskridge Shale 10

 Description of the Blue Rapids Shale 11

 Description of the Speiser Shale 11

 Description of the Wymore Shale Member of the Matfield
 Shale 12

 Description of the Blue Springs Shale Member of the
 Matfield Shale 13

 Description of the Holmesville Shale Member of the
 Doyle Shale 14

 Description of the Gage Member of the Doyle Shale 15

SPECTROGRAPHIC ANALYSIS OF SHALE SAMPLES 16

 Analytical Procedure 16

 Analytical Results 20

X-RAY ANALYSES OF SHALE SAMPLES 21

 Analytical Procedure 21

 Analytical Results 25

PETROGRAPHIC ANALYSES OF SHALE SAMPLES 30

 Analytical Procedure 31

 Analytical Results 33

MECHANICAL ANALYSES OF SHALE SAMPLES 34

Analytical Procedure 35

Analytical Results 36

CHEMICAL ANALYSES OF SHALE SAMPLES 45

 Analytical Procedure 45

 Analytical Results 46

DIFFERENTIAL THERMAL ANALYSES OF SHALE SAMPLES 47

 Analytical Procedure 48

 Analytical Results 50

OBSERVATIONS ON FIELD RELATIONSHIPS 60

SUMMARY OF ANALYTICAL RESULTS 61

CONCLUSIONS 63

ACKNOWLEDGMENTS 65

LITERATURE CITED 66

LIST OF ILLUSTRATIONS

Plates

I.	Map of Riley County, Kansas showing sample locations	6
II.	Generalized stratigraphic section of the Lower Permian System in Riley County, Kansas	9
III.	Spectrograms showing the similarity in chemical composition of three vari-colored shales	18
IV.	X-ray-diffraction exposures comparing the red and green zones of the Eskridge shale	23
V.	Densitometer record of red Eskridge shale	27
VI.	Densitometer record of green Eskridge shale	29

Figures

1-2.	Histograms showing the distribution of particle size of red and green Eskridge shale	39
3-4.	Cumulative-frequency curves of red and green Eskridge shale	40
5-6.	Histograms showing the distribution of particle size of red and green Speiser shale	41
7-8.	Cumulative-frequency curves of red and green Speiser shale	42
9-10.	Histograms showing the distribution of particle size of red and green Blue Springs shale member	43
11-12.	Cumulative-frequency curves of red and green Blue Springs shale member	44
13-18.	Thermal curves of untreated samples of the Roca and Eskridge shales	51
19-24.	Thermal curves of untreated samples of the Blue Rapids and Speiser shales and the Wymore shale member	52
25-30.	Thermal curves of untreated samples of the Blue Springs, Holmesville, and Gage shale members	53

31-36. Thermal curves of the Roca and Eskridge shales treated with cold hydrochloric acid 54

37-42. Thermal curves of the Blue Rapids and Speiser shales and Wymore shale member treated with cold hydrochloric acid 55

43-48. Thermal curves of the Blue Springs, Holmesville, and Gage shale members treated with cold hydrochloric acid 56

49-54. Thermal curves of the Roca and Eskridge shales treated with hot hydrochloric acid 57

55-60. Thermal curves of the Blue Rapids and Speiser shales and the Wymore shale member treated with hot hydrochloric acid 58

61-66. Thermal curves of the Blue Springs, Holmesville, and Gage shale members treated with hot hydrochloric acid 59

LIST OF TABLES

1. Mineral analyses of some shales in the Lower Permian System of Riley County, Kansas 34

2. Summary of quartile measures of mechanical analyses . . 37

3. Chemical analyses of Eskridge shale 46

INTRODUCTION

Purpose of the Investigation

This investigation was undertaken to determine the factors, both petrologic and environmental, which affect the colors in red and green shales. The conclusions reached through field observations and various laboratory analyses should indicate at least some of the geologic prerequisites necessary for the deposition of both red and green sediments within the same member or formation. The laboratory analyses were made to determine the lithologic basis for the color in the shales; the field observations gave indications of the environment which produced the lithologic cause. The data collected and the conclusions derived therefrom are contributed to the already vast store of information on sedimentary petrology.

Methods of Investigation

Inasmuch as this investigation was concerned with the factors influencing the colors of shales, it was decided early in the study that any method of analysis which would give information concerning the mechanical or chemical composition of the shales would be useful to the investigation. For this reason, every feasible method of analysis relative to the mineralogy, physics, or chemistry of the shales was employed.

The methods of analyzing the shale samples collected include the following: spectrographic analysis, X-ray analysis, petro-

graphic analysis, mechanical analysis, chemical analysis and thermal analysis. The results of each of these analytical methods were important to the investigation, and their combined results permitted an exhaustive study of the sediments.

The units sampled were studied in the field in an effort to ascertain the relative positions of the colored zones and the manner in which they were deposited. The types and numbers of fossils present in the shales were noted as a criterion of environment.

REVIEW OF LITERATURE

The literature reviewed in this study includes a survey of the methods of analysis used by previous investigators and a review of the results and field observations of those investigators. When the analytical procedures of other persons were followed, a review of their methods is given in the appropriate section of this report.

In the opinion of earlier investigators, the colors of sedimentary rocks are a function of chemical oxidation and reduction of the ferruginous and carbonaceous materials in the rocks. If the principal coloring agents, iron and carbon, were not present in sedimentary rocks, the rocks would in most cases be light in color because quartz and calcite are their predominant mineral constituents, and these minerals are intrinsically light in color. A. W. Grabau (1913, p. 478) states:

The color of clastic rocks depends to a very large extent upon the states of oxidation of its iron content,

on the absence or abundance of carbon. A low state of oxidation gives colors ranging from green to blue, while the higher states of oxidation are marked by yellow, orange, brown, or red colors. According to the carbon content, the color may vary from white, when no carbon is present, to various shades of gray to black. Abundant carbon in the strata will prevent oxidation of the iron and will reduce the higher oxides to the lower. Lack of carbon favors high oxidation.

Analyses of slates and shales made by Clarke (1924, p. 30) show that in red slate there is several times as much ferric iron (Fe_2O_3) as ferrous iron (FeO), the ratio in purple slates is about half that in the red, and ferrous iron predominates in green slates and shales. It is thought, therefore, that green and blue shades in the shales denote deposition under reducing conditions.

Glauconite, an additional coloring agent which is common in marine sediments, has been noted by Twenhofel (1926, p. 545). Twenhofel believes that the green shales in the Miocene and Oligocene of Texas owe their color to finely divided glauconite, a green hydrous potassium silicate. Glauconite is typical of the slightly reducing areas on the continental shelves and slopes.

The effect of climate on the coloring components of continental soils and sediments can cause marked changes in their primary colors. In this connection, the following excerpts from Barrell (1901, p. 233 to 290) as summarized by Hager (1928, p. 917) are given:

In cold, wet climates, carbonaceous material accumulates and tends to color the land and surrounding oceanic deposits gray or black. In hot, moist climates, oxidation is rapid and many bacteria are present. Dead vegetation, except where deposited under water, tends to be destroyed. The iron in the residual soils is thoroughly oxidized and dehydrated

to form red laterite. Streams from such areas make red land deposits and carry red loads to the ocean, but, when deposited there, the hematite is reduced by organic matter, and such oceanic deposits are gray beneath their surface.

The characteristics of intermittently rainy climates are those of extremely moist climates modified. In temperate climates of moderate rainfall, such as characterize the eastern half of the United States, there is generally sufficient humus in the soils and stream deposits to color them gray, brown, or black. The colder parts of the year tend to preserve this humus, where there is more iron in the parent igneous or sedimentary rocks than the amount of the decaying organic material present can reduce, this excess iron colors the soils and stream deposits. In the northern states, more of the iron is in the form of limonite and goethite, and yellow and brown shades are prevalent. Farther south, the sun's rays are hotter and red shades due to turgite and hematite are common.

In semiarid climates, the soils and alluvium tend to be light-colored, though less so than in arid climates.

In arid climates, oxidation is not active, due to the absence of water vapor in the air, though there is more oxidation in hot, arid climates than in cold. Disintegration rather than decomposition takes place, and the colors of the sediments are influenced to a large extent by the colors of the minerals derived from the parent rocks. Such deposits are generally light-colored, due to the presence of quartz, feldspar, and gray silicates.

DESCRIPTION OF STRATIGRAPHIC UNITS SAMPLED

The vari-colored shales which crop out in many places in Riley County, Kansas (Plate I) were sampled for this investigation because of the many red and green zones which are in contact in the region. All of the vari-colored shales sampled are assigned to the Council Grove and Chase Groups of the Wolfcampian Series, Lower Permian System (Moore, 1944, p. 147). A geologic column showing the stratigraphic position of the shales is presented on

EXPLANATION OF PLATE I

Map of Riley County, Kansas, showing sampling locations of the various shale units. Reprinted with the permission of the United States Geological Survey.

1. Roca shale.
2. Eskridge shale.
3. Blue Rapids shale.
4. Speiser shale.
5. Wymore shale member.
6. Blue Springs shale member.
7. Holmesville shale member.
8. Gage shale member.

PLATE I

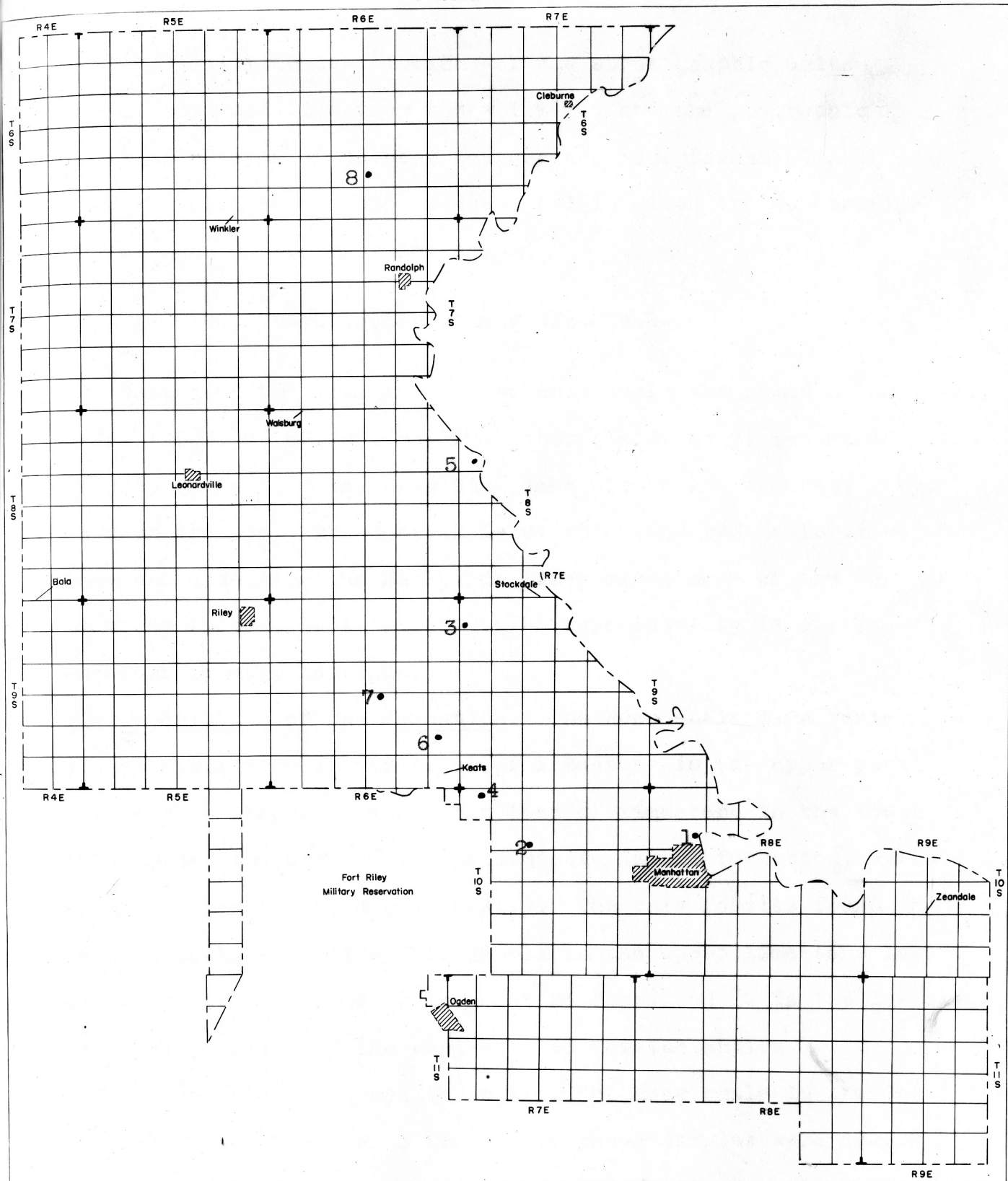


Plate II.

The following descriptions of the stratigraphic units sampled were modified from Mudge (1949), and the geographic location in terms of quarter quarter section, township, and range at which each shale was sampled is given in the description of each of the rock units.

Description of the Roca Shale

Naming of the Formation. The Roca shale was named by Condra (1927, p. 84, 86, 88) who later (1935, p. 8) separated the Roca shale from the Neva limestone with which it previously had been grouped. The Roca shale overlies the Red Eagle limestone and underlies the Sallyards limestone member of the Grenola limestone (Moore, 1951, p. 48). The type locality is Roca, Lancaster County, Nebraska.

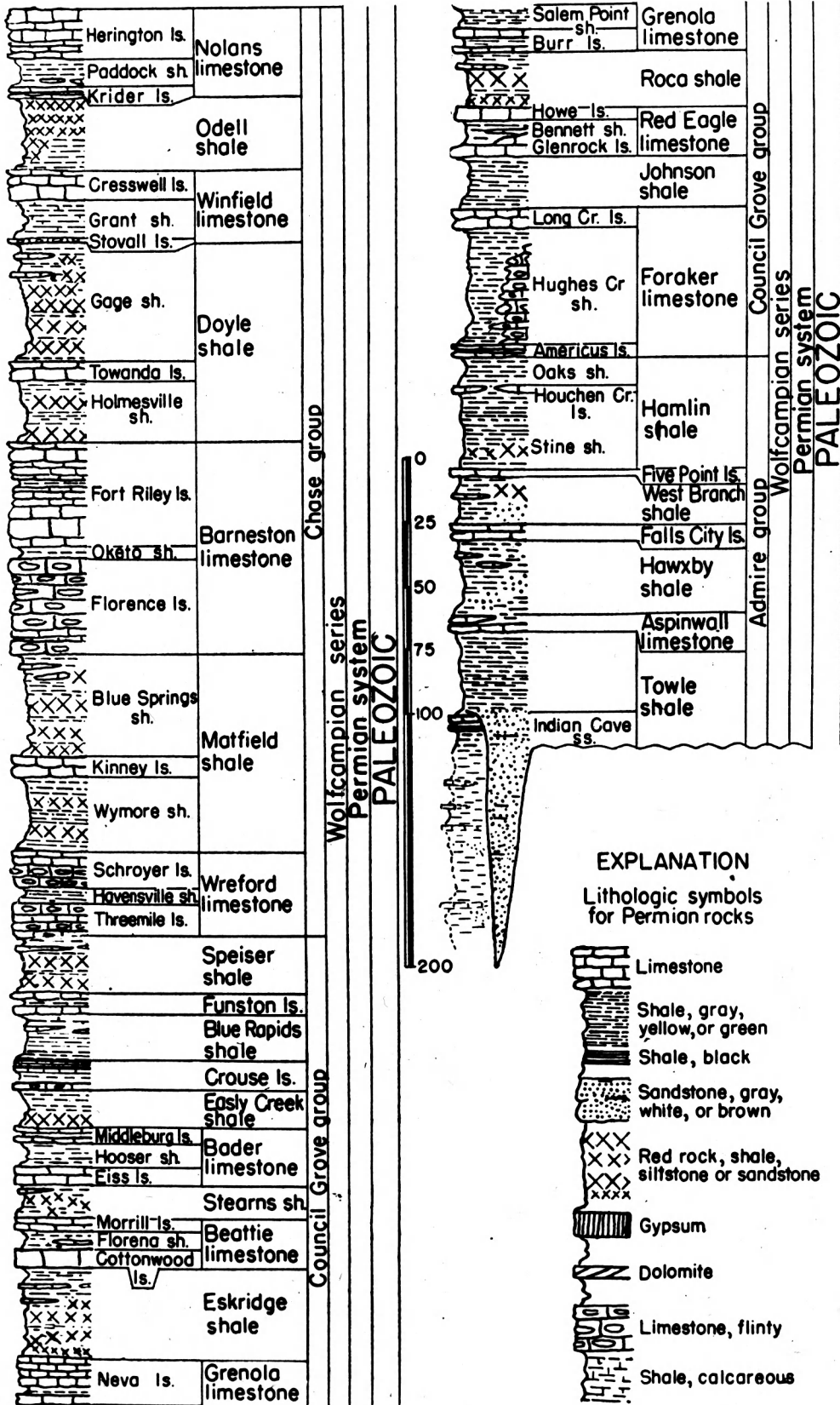
Description of the Formation. The Roca shale is a vari-colored shale with a thin layer of limestone in the upper part and, in some places, a very thin lens of limestone in the lower part. Green and gray shales predominate in the formation, while maroon and tan shales occur locally. The only fossils found in the Roca shale are crinoid columnals in the upper limestone layer. The thickness of this unit is about 24 feet, and it is the lowest, stratigraphically, of the vari-colored Permian shales.

Four samples were collected from the Roca shale in the SE $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 7, T. 10 S., R. 8 E. Two of these samples were taken from adjacent red and green zones about 4 feet below the base of the Sallyards limestone member of the Grenola limestone, and the

EXPLANATION OF PLATE II

Generalized stratigraphic section of the Lower Permian System in Riley County. Reprinted with the permission of the United States Geological Survey.

PLATE II



other two samples were collected at a level which is about 14 feet lower. The first pair of samples are designated as the Upper Roca samples and the second pair as the Lower Roca samples. In this unit, as in the other units sampled, the samples were obtained from zones as near as possible to the contact of the red and green shales.

Description of the Eskridge Shale

Naming of the Formation. The Eskridge shale was named by Prosser (1902, p. 709) from outcrops near Eskridge, Wabaunsee County, Kansas. Beede (1902, p. 181) defined the Eskridge shale as overlying the Neva limestone member of the Grenola limestone and underlying the Cottonwood limestone member of the Beattie limestone.

Description of the Formation. The Eskridge shale is predominantly shale with a few lenses of limestone. The shale beds vary from clay to silt which may be calcareous or noncalcareous, and the limestone lenses are hard, dense, massive, and somewhat argillaceous. Maroon, purple, green, and tan-gray zones constitute the lower three-fourths of the Eskridge shale, but the upper part is usually tan or gray. The common fossils, which are found only in some of the limestone lenses, are: Aviculopecten occidentalis, Myalina sp., Pseudomontis hawni, and ostracods; occasional brachiopods, plants, and insects are found in the shale. The average thickness of the Eskridge shale is about 35 feet.

A good exposure of the Eskridge shale was found in a road

cut in the SE $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 10, T. 10 S., R. 7E. and the samples collected there were from zones about 23 feet below the base of the Cottonwood member.

Description of the Blue Rapids Shale

Naming of the Formation. The Blue Rapids shale was named by Condra and Upp (1931, p. 22) who designated the type section as a road cut along Highway U. S. 77 about 1 $\frac{1}{4}$ miles north of Blue Rapids, Kansas. Condra and Busby (1933, p. 9, 6) defined the Blue Rapids shale as the middle member of the Bigelow limestone, but later discarded the Bigelow and redefined the Blue Rapids shale as a formation.

Description of the Formation. The Blue Rapids shale is principally gray to tan but contains maroon and green zones in the middle part. The shale is composed of thin-bedded to blocky silt and clay shale. Calcium carbonate stains and thin lenses of arenaceous limestone occur in the upper part. No fossils were observed in the Blue Rapids shale. The average thickness of this formation is about 20 feet.

Samples of the Blue Rapids shale were collected from a stream cut in the SW $\frac{1}{2}$ SW $\frac{1}{4}$ sec. 6, T. 9 S., R. 7 E. from a zone 14 feet below the base of the Funston limestone.

Description of the Speiser Shale

Naming of the Formation. The Speiser shale was named by Condra (1927, p. 232, 234) who designated the type locality as the W $\frac{1}{2}$ sec. 35, T. 1 N., R. 13 E., Speiser Township, Richardson

County, Nebraska. Condra and Upp (1931, p. 23) at first grouped the Speiser with the Blue Rapids shale and the Funston limestone as the Bigelow limestone; however, they later elevated each of the units to formation rank.

Description of the Formation. The Speiser shale is tan-gray, gray, green, purple and maroon in color. The shale beds are thin-bedded to blocky, silty to clayey, and generally calcareous. There is a persistent limestone a foot thick about 3 feet below the top and, in most exposures, there is also a second thin limestone just below the base of the Threemile limestone member of the Wreford limestone. The layers of limestone are hard, massive, and gray to gray-orange. The following fossils were found near the top of the formation: crinoid columnals, echinoid spines, Juresania nebrascensis, Derbyia Crassa, Chonetes granulifera, Dictyoclostus americanus, and trilobites. The average thickness of the formation is about 15 feet.

The Speiser shale was sampled in an old road cut in the NW $\frac{1}{4}$ NE $\frac{1}{4}$ sec. 6, T. 10 S., R. 7 E. Spot samples were taken from near the contact zone (about 4 feet below the base of the Threemile member) of adjacent red and green shales in an effort to obtain samples similar in all characteristics except color.

Description of the Wymore Shale
Member of the Matfield Shale

Naming of the Member. The Wymore shale was named by Condra and Upp (1931, p. 37). The type section is exposed in ravines on the west side of a creek 2 $\frac{1}{2}$ miles east of the south

side of Wymore, Gage County, Nebraska. The Wymore underlies the Kinney limestone member of the same formation and overlies the Wreford limestone.

Description of the Member. The Wymore is a calcareous, clayey but somewhat silty, blocky to thin-bedded shale. Tan-gray, gray-green, and maroon shales predominate in its lower part, and gray-green, olive drab, and local maroon shales compose the upper part. Two thin fossiliferous limestones are usually present in most exposures of the Wymore. The fossils found in the limestone beds are: Aviculopecten occidentalis, Myalina sp., and Orthomyalina subquadrata. The average thickness of this member is about 43 feet.

Samples of the red and green shale in the Wymore member were obtained from zones at levels of 1.5 and 9 feet, respectively, below the top of the member. The exposure sampled is in the NE $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 7, T. 8 S., R. 7 E.

Description of the Blue Springs Shale Member of the Matfield Shale

Naming of the Member. The Blue Springs shale was named by Condra and Upp (1931, p. 38). The type locality is at the base of the bluffs along the Blue River, southeast of Blue Springs, Gage County, Nebraska. The Blue Springs shale overlies the Kinney limestone member of the same formation and underlies the Florence limestone member of the Barneston limestone.

Description of the Member. The Blue Springs shale is both clayey and calcareous in most exposures, and its color varies

from maroon and green at the base to gray, green, and sometimes tan in the upper part. Lenses of hard, massive, tan-gray limestone commonly occur near the top of the member. No fossils were observed in this shale. The average thickness of the Blue Springs is about 28 feet.

This unit was sampled from adjacent red and green zones occurring about 10 feet below the Florence limestone in the SE $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 25, T. 9 S., R. 6 E.

Description of the Holmesville Shale
Member of the Doyle Shale

Naming of the Member. The Holmesville member was named by Condra and Upp (1931, p. 43). The type locality is $1\frac{1}{2}$ miles west and $\frac{1}{2}$ mile north of Holmesville, Gage County, Nebraska. The Holmesville was described as overlying the Fort Riley member of the Barneston limestone and underlying the Towanda member of the Doyle formation.

Description of the Member. The Holmesville shale member consists predominantly of shales but usually contains one or more thin lenses of limestone which are usually present in the middle or lower part of the member. The shales are silty with some clay intermixed, are generally calcareous, and are gray, gray-green, olive drab, and occasionally maroon in color. The maroon zone is usually in the middle part of the Holmesville but is absent in some exposures. The limestones are soft and usually argillaceous but locally may be dolomitic and arenaceous. These limestone lenses show evidence of penecontemporaneous folding in the northern part

of the outcrop area. The average thickness of the Holmesville member is about 19 feet.

Samples were collected from the Holmesville at a zone about 7 feet below the base of the Towanda and in the NW $\frac{1}{4}$ NE $\frac{1}{4}$ sec. 22, T. 9. S., R. 6 E.

Description of the Gage Member of the Doyle Shale

Naming of the Member. The Gage was named by Condra and Upp (1931, p. 45) from outcrops between one and two miles south of the west side of Wymore, Gage County, Nebraska. The Gage member overlies the Towanda limestone member of the same formation and underlies the Stovall limestone member of the Winfield formation.

Description of the Member. The Gage shale is predominantly maroon in the lower two-thirds and tan-gray to gray-green in the upper third. The maroon zone is mottled with green and contains some well-defined thin green lenses. This shale is composed of silt with some clay and is thin-bedded to blocky. The maroon zones are noncalcareous but the others are at least slightly calcareous, and thin limestone lenses occur in the upper part of the Gage in the eastern part of its outcrop area. The following fossils are generally present in the upper tan-gray to gray-green shales: Derbyia crassa, D. cymbula, D. hooserensis, crinoid columnals, Stenopora sp., echinoid spines, and Dictyoclostus americanus. The average thickness of this member is about 38 feet.

The Gage shale member was sampled at a stream cut exposure

in the NW $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 27, T. 6 S., R. 6 E. The sample was removed from a zone about 8 feet below the Stovall member where the maroon shales at the top grade into a gray-green layer below.

SPECTROGRAPHIC ANALYSIS OF SHALE SAMPLES

One of the methods chosen to determine the chemical nature of the shales was spectrographic analysis, because this method permits a rapid yet effective chemical comparison of the shales sampled. This investigation was concerned only with the physical and/or chemical differences producing color variations in the shales; therefore, this method of analysis was particularly suited to the purpose because it permitted the elimination of chemical elements common to the shales and the identification of any elements peculiar to individual samples.

Analytical Procedure

Of the eighteen shale samples previously described, six red and green shales from three stratigraphic units were selected for spectrographic analysis. The three stratigraphic units are the Eskridge shale, the Speiser shale, and the Blue Springs shale member of the Matfield shale. Selection of these units was based on the great contrast in color between the red and green zones of the shales.

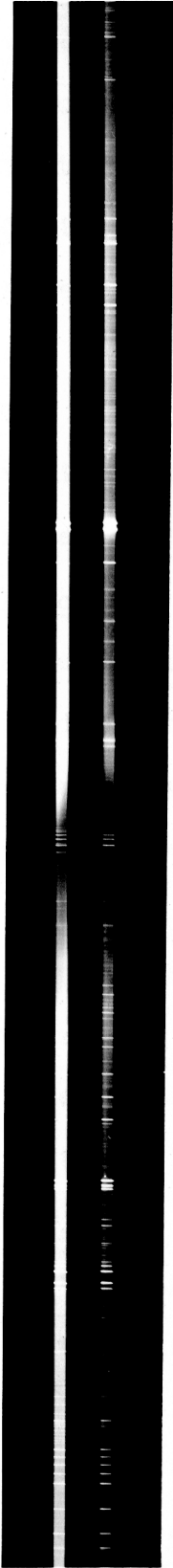
The spectrograms of the shales listed above are shown on Plate III in an arrangement which permits comparison of the red and green zones of each of the shales analyzed. The spectrograms were produced under the same conditions using the same spectrograph.

EXPLANATION OF PLATE III

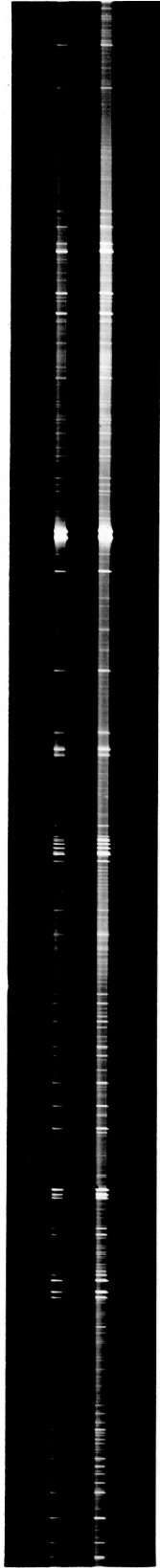
Spectrograms showing the similarity in chemical composition of three vari-colored shales. In each photograph the analysis of the red zone of the shale is shown on the left.

1. Spectrogram of red and green Eskridge shale.
2. Spectrogram of red and green Speiser shale.
3. Spectrogram of red and green Blue Springs member of the Matfield shale.

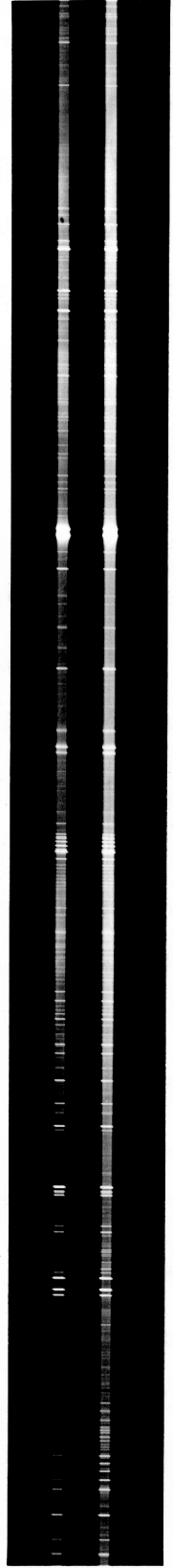
PLATE III



1.



2.



3.

Description of Equipment. The spectrographic procedure followed involved the use of a Rowland Grating Spectrograph manufactured by Applied Research Laboratories, Inc. The grating for light-dispersion is two inches long, is curved, and has 24,000 lines per linear inch. The focal length is 150 centimeters, and a 35 millimeter Eastman Process Film was used in the camera.

The light source used was a 110 volt-D.C. carbon-arc lamp with variable resistance and controlled amperage. Pure carbon electrodes were used throughout the analysis.

Description of Procedure. The electrodes were prepared for the powdered shale samples by drilling holes $3/16$ inch in diameter and $3/8$ inch in depth in one end of the electrode used as the anode. The cathode was sharpened, and the electrodes were placed in the electrode holder with the anode below and the cathode above. The holes drilled in the anodes were then packed with the shales to be analyzed. Because the shales are non-conductors, it was necessary to mix powdered carbon from the electrodes with the sample to insure a constant arc. The alignment of the slit, arc, and grating was checked before each exposure.

Factors upon which the quality of the spectrogram depended, such as the slit opening (100 microns), the slit length (2 centimeters), the distance between the slit and the light source (20 centimeters), and the separation of the electrodes (2 centimeters) were determined by computation.

The optimum exposure time (4 minutes) was determined by a

trial-and-error method. The standard photographic procedures of developing, fixing, hardening, washing, and drying of the film were followed, and the results of the analyses were determined through close examination of the projection-enlarged spectrograms.

Analytical Results

An examination of the spectrograms on the projection screen showed that the red and green zones of each of the shale samples contain the same elements in approximately equal concentrations. Further, the spectrograms of all three stratigraphic units are strikingly similar. This similarity can be seen even on small positive prints (Plate III). A comparison of the spectrograms of red and green shale with master spectrum cards and with each other revealed that not only are most of the common and rare earth elements present in the shales but also that there are no elements present in one shale which are not present in the others.

These results gave several indications of being important to this study. First, evidence that the same elements are present in all of the shales suggests that the presence or absence of one or more elements cannot account for the color variations in the shales. If the factor determining the color of the shales is a chemical one, then the color is due to the manner in which identical elements are combined as naturally occurring compounds or minerals. Secondly, the similarity of elements in the shales might also suggest that those shales were deposited

under similar conditions by the same geologic agent and that they were derived from like primary rocks.

The results of the spectrographic analysis suggested that a means of determining the physical structure of the shales would be significant to the study. X-ray analysis proved to be the most promising in this respect because it gives indication of alterations in the shales subsequent to their deposition.

X-RAY ANALYSES OF SHALE SAMPLES

X-ray-diffraction analyses were utilized to determine whether or not the less stable minerals of the shales, such as the clay minerals, had recrystallized because of such environmental factors as consolidation, induration, or weathering. Diffraction methods are unsurpassed in effectiveness in revealing changes in structure of materials. This method is also useful in confirming the differential-thermal determinations of the clay mineral present in a shale.

Analytical Procedure

On the assumption that the varied colors of all the shales are due to the same factor or factors, the red and green zones of only one stratigraphic unit (the Eskridge shale) were analyzed with the X-ray equipment. The X-ray photographs are shown on Plate IV.

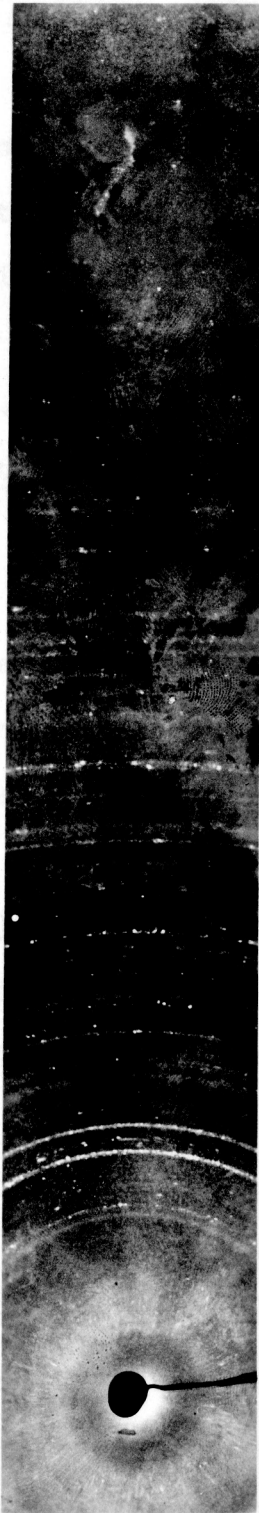
Description of Equipment. The equipment involved in the diffraction analyses included an X-ray-diffraction unit using a

EXPLANATION OF PLATE IV

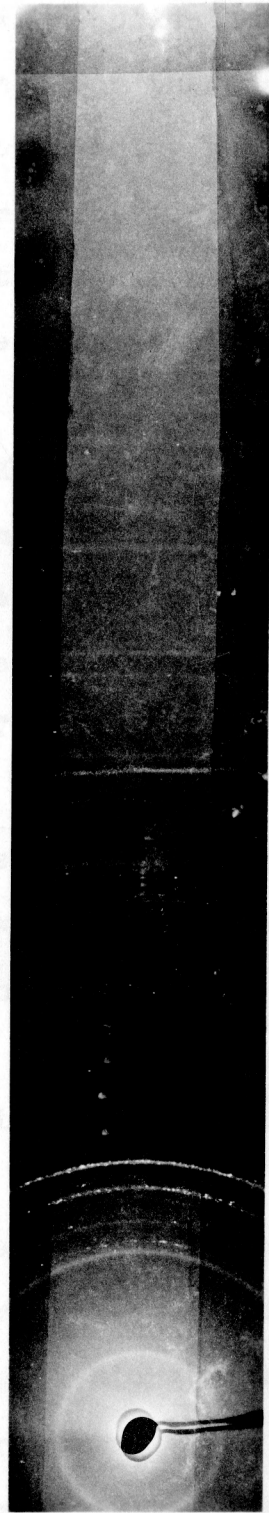
X-ray-diffraction photographs comparing the red and green zones of the Eskridge shale.

1. X-ray-diffraction exposure of red Eskridge shale.
2. X-ray-diffraction exposure of green Eskridge shale.

PLATE IV



1.



2.

copper-target tube and operating at a peak voltage of 30.1-k.v., and a Leeds and Northrup Recording Microdensitometer. The X-ray-diffraction unit is standard in many industrial applications; the densitometer is a photoelectric device designed for the analytical measurement of line density or photographic blackening and is coupled electronically to a Micromax Recorder. The function of the diffraction unit is to produce a diffraction pattern for each shale, and the densitometer permits a detailed examination of that pattern.

Description of Procedure. Analyses by X-ray-diffraction were made by the Hull-Debye-Scherrer powder method. This method reveals such important characteristics of the shales as (1) the relative size of the crystals, commonly called the "grain size"; (2) the absence or presence of any tendency for the crystals to orient themselves in a preferred manner (the absence of this condition is "random orientation" -- its presence, "preferred orientation"); and (3) any actual bending, twisting, or similar mechanical distortion of the crystals, commonly called "strain".

A detailed discussion of this method is given by Sproull (1946, Chap. 18). In brief, this method includes grinding a shale to powder and mounting the powder in a motor-driven, constant-speed, oscillatory device. The oscillatory device spreads the absorption edges, which are subtracted from the radiation by the sample and are characteristic of the sample, along a photographic film placed in position in a circular camera. The characteristic copper K radiation was used in the analyses. The

film is developed according to standard practices, and a densitometer record is then made directly from the X-ray exposures. From the exposed film and the densitometer record of that film, the results of the analyses of the shales were determined.

Analytical Results

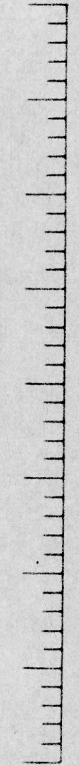
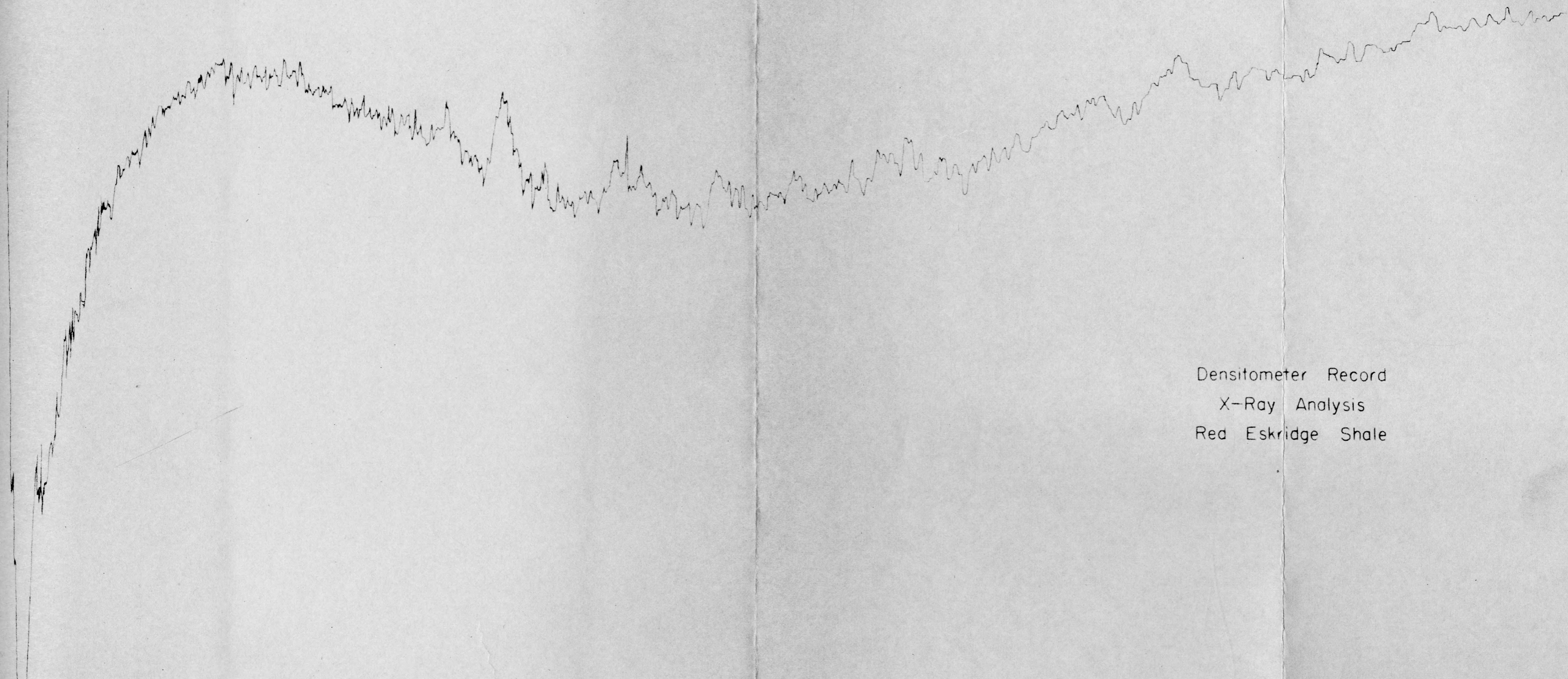
Comparison of the diffraction patterns yielded by the red and green shales give the following results: (1) the constituent particles of a red shale are in a more random orientation than those of a green shale, (2) a red shale is composed of smaller particles than a green shale or, at least, a red shale is reduced to smaller particles under the same conditions of grinding, (3) impurities are present in both shales and serve to mask or emphasize certain of the pattern lines, and (4) both shales show crystal distortion which may be due either to the grinding or compaction of the shales after their deposition.

From (1) and (2) above, a red shale shows evidence of being weathered more than a green shale. Lines which broaden, as in Fig. 1, Plate IV, indicate small particle size inasmuch as small crystals lack the resolving power to produce sharp rings. Lines which broaden and then "tail-off" indicate a randomness in intrinsic structure as differentiated from preferred orientation. This random orientation is shown in Fig. 2, Plate IV. These conditions are shown also on Plates V and VI, respectively. In the densitometer records, broadening of the lines is shown by an

EXPLANATION OF PLATE V

Densitometer record of red Eskridge shale.

Plate V



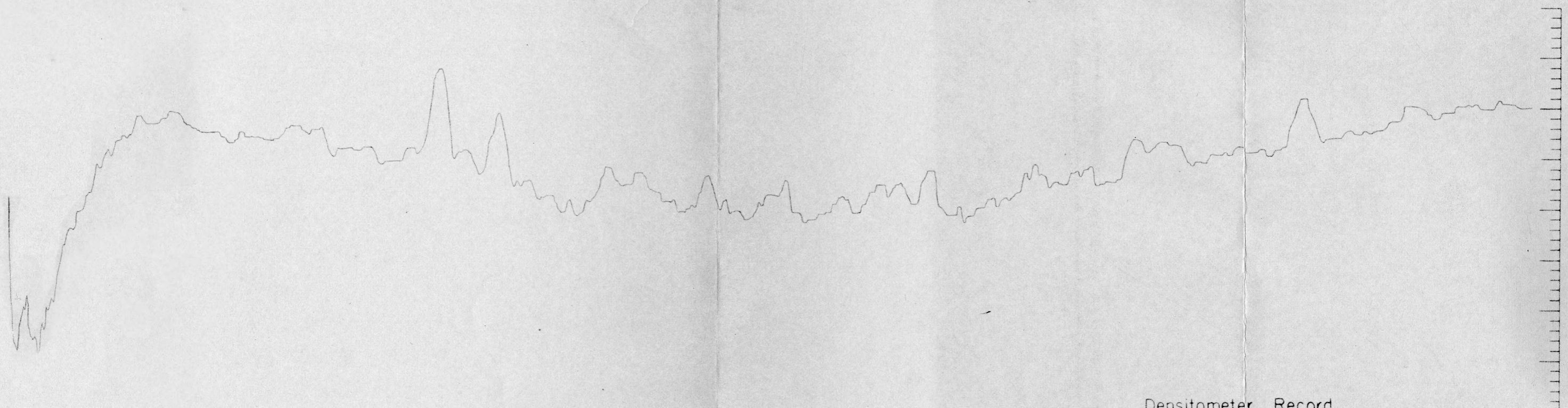
Densitometer Record
X-Ray Analysis
Red Eskridge Shale

EXPLANATION OF PLATE VI

Densitometer record of green Eskridge shale.

Den

Plate VI



Densitometer Record
X-Ray Analysis
Green Eskridge Shale

increase and subsequent decrease in amplitude of the peaks, whereas the "tailing-off" of the lines is evident where the peaks decrease in amplitude from an initial maximum peak.

The tendency toward a reduced particle or crystal size in red shale and, especially, the presence of preferred or original orientation in the green shale and random or altered orientation in the red shale is indicative of a structural change in red shale which is due to external causes. Weathering is considered the most probable geologic cause of the structural change in red shale because no differences in lithification or consolidation of these adjacent shales of the same formation were discernible in the field.

However, structural changes may have occurred in the shales for reasons other than weathering, such as recrystallization due to secondary replacement or metasomatic replacement. In an attempt to determine the exact cause of this physical change, each of the shales sampled was examined under a petrographic microscope.

PETROGRAPHIC ANALYSES OF SHALE SAMPLES

Detrital slides of the heavy and light fractions of the microscopic minerals were examined under a petrographic microscope to determine possible correlations between mineral content and the color of the shale. An effort was made to note the presence of stains on the detrital grains which might affect the color of the rock in the outcrop.

Analytical Procedure

The procedure involved in the petrographic analysis of the shales included the chemical treatment of the shales to remove soluble carbonates, the separation of the light and heavy mineral fractions, the preparation of the slides, and their examination under the microscope.

Description of Equipment. A petrographic microscope is an instrument designed to permit the identification of minerals by means of their optical properties. These properties are determined through the use of transmitted polarized or doubly-polarized light. The instrument is designed also for use as a conoscope to obtain the interference figures which further characterize a mineral.

Description of Procedure. Representative samples of the shales were dried in a controlled-temperature oven which maintained the temperature below the boiling point of water to avoid the loss of chemically combined water from the shales. From this dried sample, 800 grams of material was selected and placed in 16-ounce bottles, and 0.5 gram of sodium silicate per 50 grams of sample was added. The sodium silicate assisted in the dispersion of the shale particles. The bottles then were partly filled with de-ionized water and shaken in a machine for a period of two hours as a further aid to dispersion.

After shaking, the sample was allowed to stand for a period of 30 minutes to permit the settling of the heavier particles. The clay- and silt-size particles which remained in suspension

were removed by decantation and saved for mechanical, thermal, and X-ray-diffraction analyses.

The remaining material was washed repeatedly to remove adherent clay particles. The minerals to be examined were separated from the clay on the basis of the application of Stoke's law (Twenhofel and Tyler, 1941, p. 51) which is a mathematical statement of the settling rates of particles in a liquid medium.

The separated material then was treated with cold hydrochloric acid to digest the carbonates and was treated later with hot hydrochloric acid to remove a part of the iron oxide coating the grains. Enough of the stain remained on the grains to permit its identification.

Since the optimum grain size for mineral mounts is that size smaller than 1/8 millimeter and larger than 1/16 millimeter, only the fraction passing through the U. S. Series No. 120 sieve and retained on the No. 230 sieve was used in the petrographic analysis. The selected material was further divided into light and heavy mineral fractions by placing the material in bromoform and drawing off the heavy minerals that descended in the separation funnel. The bromoform used had a specific gravity of 2.75. The minerals of lower specific gravity, which therefore floated on the bromoform, were designated as the light fraction, and those which settled were termed the heavy fraction. These fractions were washed in alcohol after their separation to remove the bromoform.

Mineral mounts were made of both the light and heavy frac-

tions of the six shales sampled. Canada balsam, which has a refractive index of 1.537, was used as the mounting medium.

These slides were examined to identify the minerals present in each fraction and to determine the relative abundance of the minerals present. The minerals were identified on the bases of optical properties and other physical characteristics, and the physical characteristics which differed for the same mineral were carefully noted.

Analytical Results

The predominant minerals in the light fraction of the six shales sampled are quartz, chalcedony, orthoclase, microcline, and plagioclase. A rather large variety of heavy minerals was identified in the samples. Table 1 gives the percentage of light and heavy minerals present in the slides. The hornblende found in all of the slides was of the green variety, and in no instance was there any brown or basaltic hornblende identified.

No correlation between color and detrital mineral content can be made with the results obtained in the petrographic study; there are greater similarities between the different color zones of the same shale than there are between like colors of different shales. However, only in the red shales was there any hematite, and most of the grains in the red shales showed stains of hematite. No hematite was noted in the green shales, but a few of the grains in these shales were stained with a green material which could not be identified under the microscope.

Table 1. Mineral analyses of some shales of the Lower Permian System of Riley County, Kansas.

Minerals	: Eskridge : : shale : : red :	: Eskridge : : shale : : green :	: Speiser : : shale : : red :	: Speiser : : shale : : green :	: Blue : : Springs : : shale : : red :	: Blue : : Springs : : shale : : green :
Light fraction						
Quartz	28.5	2.0	19.5	1.0	11.3	20.4
Chalcedony	59.0	98.0	80.5	99.0	81.2	66.5
Orthoclase	8.5				5.0	8.5
Microcline	3.5				2.5	2.3
Plagioclase	1.0					2.3
Heavy fraction						
Zircon	16.3	50.0	28.5*	45.5	9.2	21.2
Topaz	6.7	10.0	2.1	31.5	6.9	2.5
Hornblende	1.0				9.1	8.8
Muscovite	28.0	37.5	8.4	6.5	69.0	50.0
Biotite	22.0		20.0			5.0
Garnet		2.5	1.0			
Tourmaline					2.3	3.8
Corundum	1.0		11.5	3.0		
Magnetite	10.4			13.5	3.5	8.7
Hematite	13.6					
Pyrite			5.5			
Ilmenite	1.0					
Coated (Hematite)			23.0			

* Inclusions in the zircon show pleochroic haloes.

MECHANICAL ANALYSES OF SHALE SAMPLES

Mechanical analyses of the shale samples were made to determine the quantity of material present in the various grain-size classes of the shale. The data collected in this analysis were arranged numerically to produce a frequency distribution of particle size of the sediments. The purpose of this analysis was to determine the effect, if any, of particle size on the color of the

sediments and to obtain evidence as to the mode of deposition of the shales.

Analytical Procedure

The hydrometer method of mechanical analysis as developed by Bouyoucos (1928, p. 233) was used in this investigation because the method is simple, rapid, and sufficiently accurate for this purpose.

In this method data are collected by reading a hydrometer placed in the suspension at various intervals of time and recording the readings as corrected for temperature. The histograms and cumulative curves shown on Figs. 1 to 12 were drawn from these data.

Description of Equipment. The Taylor hydrometer used in this analysis is an instrument calibrated to read grams of sediment per liter of the suspension. Two hydrometers which gave identical readings in the same suspension were used, and their readings were corrected for the temperature of the suspension because variations in temperature affect the viscosity of the suspending fluid.

Description of Procedure. The sample residue from the petrographic analysis of the shales was used in these mechanical analyses since it contained a complete suite of particle sizes less than 1/16 millimeter. This residue was decanted and dried, disaggregated with a mortar and pestle, and 50 grams of the material was again dispersed with sodium silicate and agitated for one hour. De-ionized water then was added to the dispersed

sample to bring the total volume of fluid to one liter.

The amount of material present in each of the size ranges shown in the histograms was determined by taking hydrometer readings at intervals computed from Stoke's formula. The beakers containing the suspension were shaken by hand after each reading to give independent readings for each size class.

The data collected were plotted as histograms for easy visual comparison of the shales, and also were plotted as a cumulative-frequency curve with the log diameter of the particle size against the cumulative weight of the sample. The results of this analysis were computed from the cumulative-frequency curve.

Analytical Results

The data obtained from the mechanical analyses and plotted as frequency curves are readily amenable to statistical methods of examination. Such statistical measures as quartiles, percentiles, and medians were used to compute the skewness, kurtosis, and coefficient of sorting of the samples. These values in turn are significant as indications of the degree of intermixing of size classes and, more particularly, of the admixtures of silt and clay in the shales. Further, the values give indication, of somewhat doubtful accuracy, of other characteristics of the shales, such as method or methods of transport of the sediment, and the gradation of sizes produced in the shales through their transportation and deposition. A summary of the quartile measures of the shales is given in Table 2.

The skewness or symmetry of the curves is the product of

the quartiles divided by the square of the median. This measure determines the dominance in the sediment of either silt or clay over the other. A skewness of less than unity, as in the case of the Eskridge shales, indicates a predominance of coarse over fine fractions. A skewness greater than unity indicates the reverse mixing of silt and clay, and this is shown by the Speiser shales and the green Blue Springs shale. The red Blue Springs shale gave a value near unity, and in this shale the amounts of silt and clay are approximately equal with only a slightly larger percentage of silt.

Table 2. Summary of quartile measures.

Shale	: Coefficient : of sorting	: Skewness	: Kurtosis	: Median
red Eskridge	3.58	.583	.364	.0150 mm
green Eskridge	2.82	.575	.288	.0145
red Speiser	2.41	1.410	.189	.0055
green Speiser	2.67	2.020	.276	.0079
red Blue Springs	2.33	.904	.254	.0135
green Blue Springs	2.17	1.372	.118	.0052

It is interesting to note that the skewness of the shales shows a correlation with the chroma or intensity of color of the shales. The writer at first believed that variations in the red and green hues of the shales were attributable to either the intensity of the oxidizing or reducing environment or the length of time those environments remained active. Whether or not this

is true, another explanation which is based on relative surface areas of particles per unit volume of the material now seems possible. Because the colors of the shales are apparently due to stains derived chemically from sediments basically alike, then equal amounts of stain in each of the shales is at least possible if oxidation or reduction is complete. If a shale is dominantly clay, then its surface area per unit volume is vastly greater than it would be if it were composed largely of silt. Since the alteration products or stains are visible only on the surface of the particles, the effectiveness of the stain is dependent on the area it must cover. Observations in the field give credence to this explanation. It was noted that shales that are especially clayey tend to have a color closer to neutral gray -- the color of the principal minerals composing the shale.

The sorting coefficient is the square root of the ratio of the quartiles. The values determined for the samples listed in Table 2 indicate a near-shore deposit inasmuch as those values agree with the average value of near-shore marine sediments (Pettijohn, 1949, p. 24). The values for these samples also indicate well-sorted sediments.

Kurtosis or "peakedness" is a measure of the quantity or percentage of sediment and the range of diameters or particles in the fraction of the maximum mass (Pettijohn, 1949, p. 25). Kurtosis is expressed as the numerical difference between the quartiles divided by twice the difference between the percentiles. The values obtained in this analysis are indicative of a single mode of transportation (Pettijohn, 1949, p. 22).

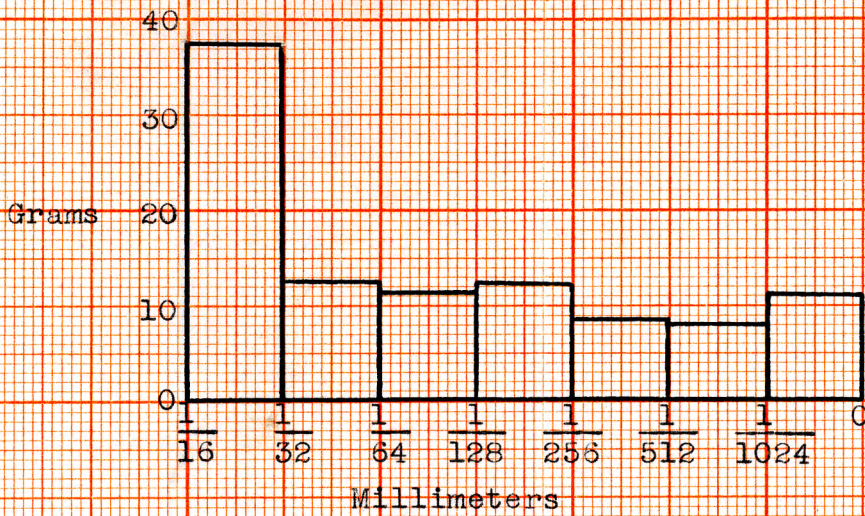


Fig. 1. Histogram showing the distribution of particle size of red Eskridge shale.

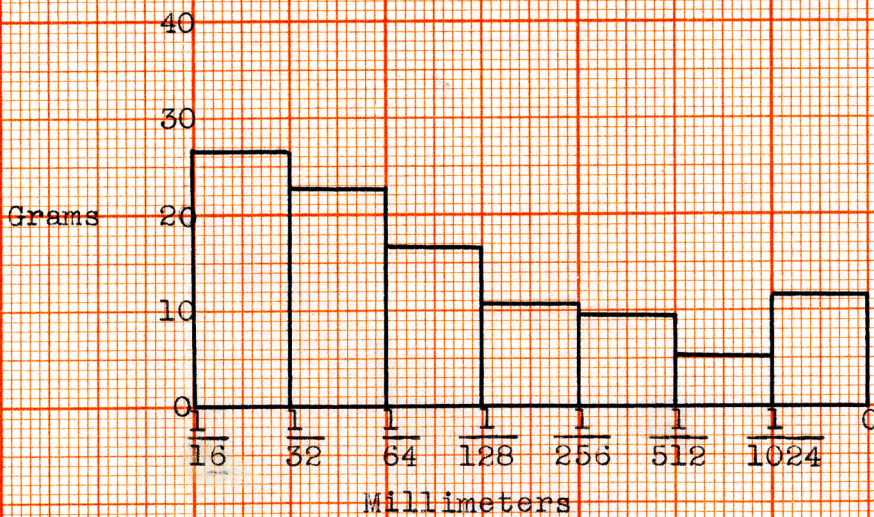


Fig. 2. Histogram showing the distribution of particle size of green Eskridge shale.

PRINTED IN U.S.A.

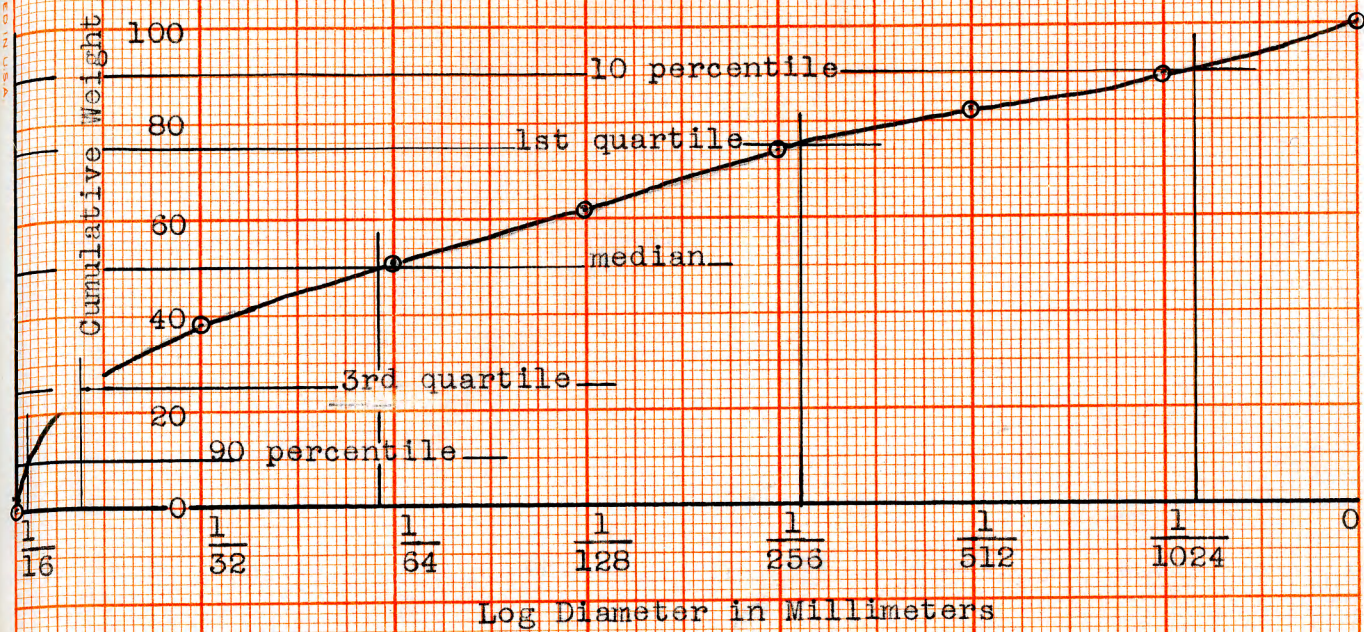


Fig. 3. Cumulative-frequency curve of red Eskridge shale.

EUGENE DIEZIGEN CO. NO. 346

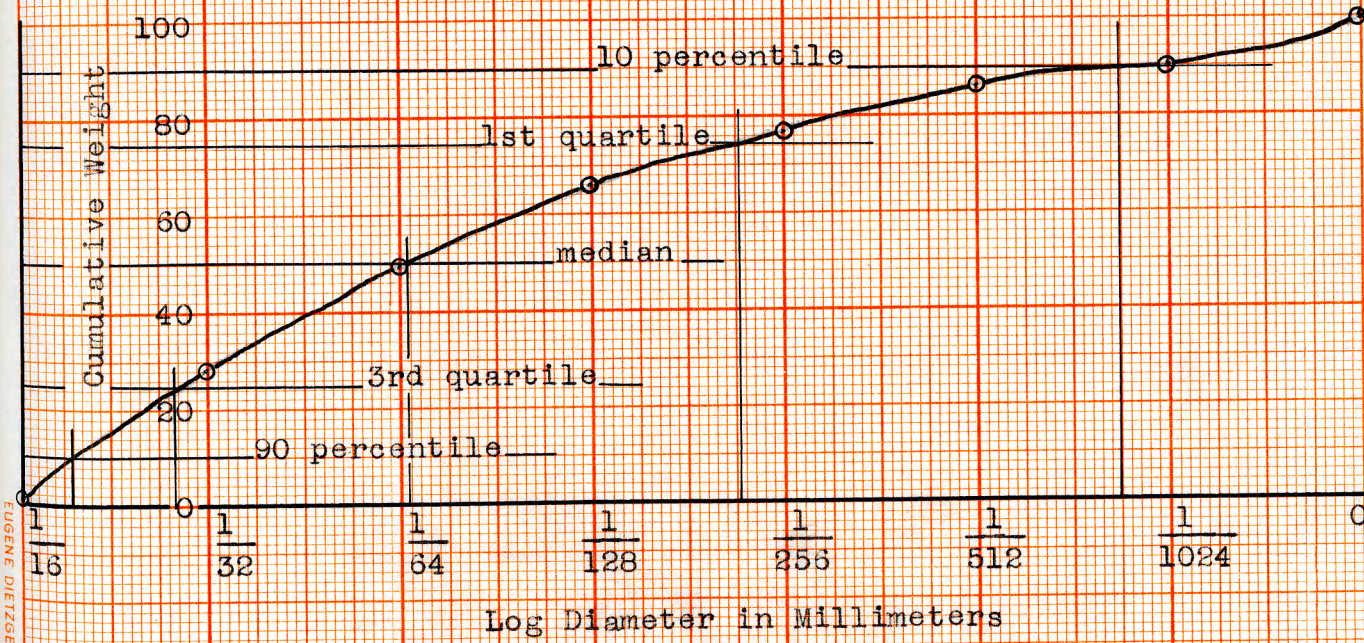


Fig. 4. Cumulative-frequency curve of green Eskridge shale.

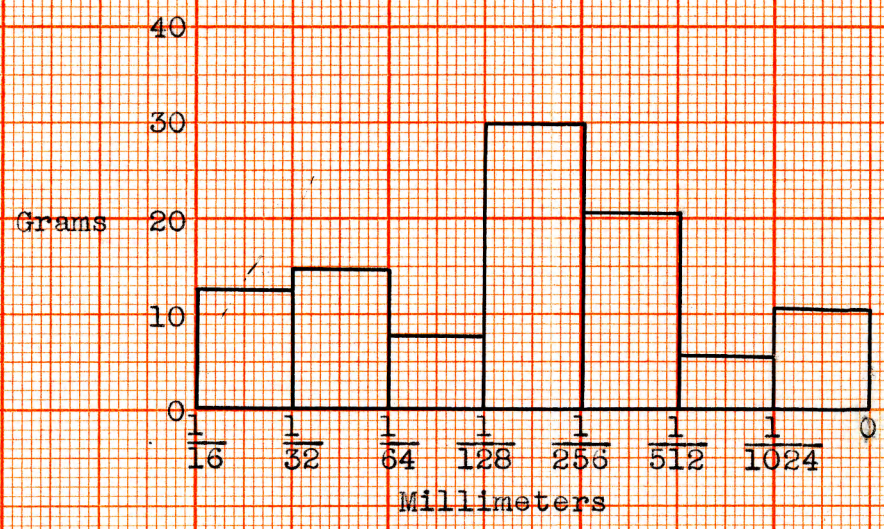


Fig. 5. Histogram showing the distribution of particle size of red Speiser shale.

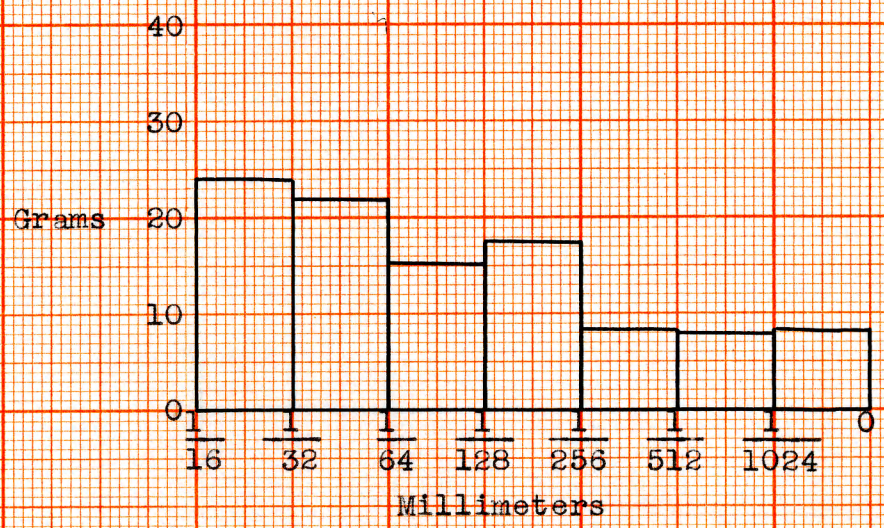


Fig. 6. Histogram showing the distribution of particle size of green Speiser shale.

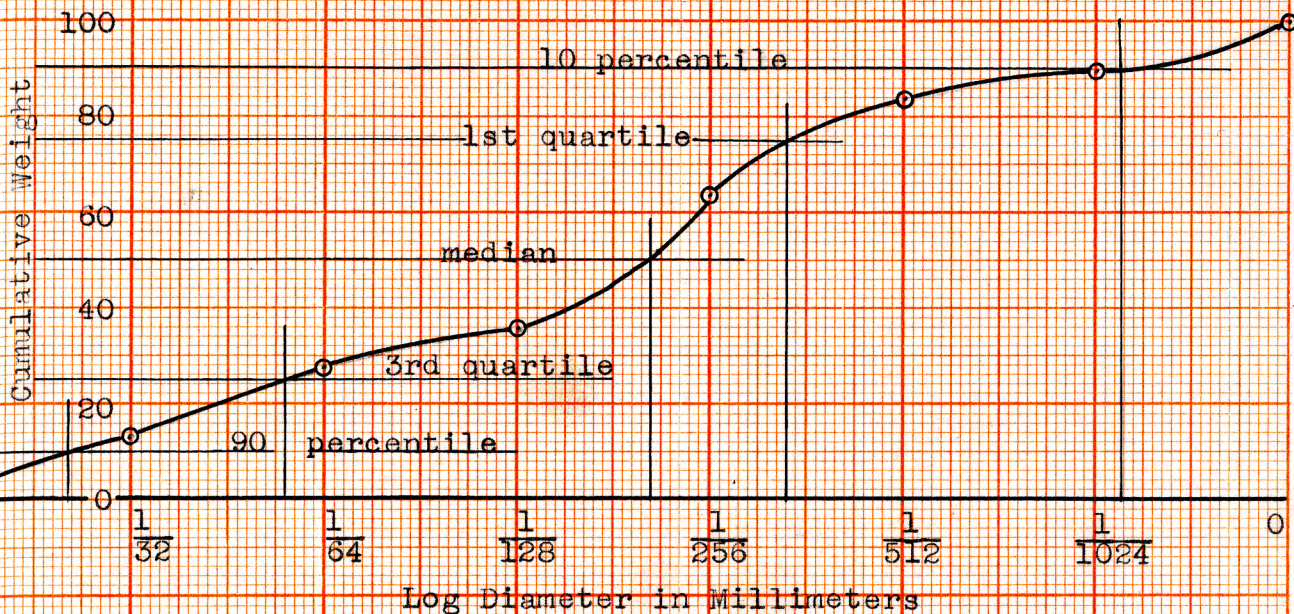


Fig. 7. Cumulative-frequency curve of red Speiser shale.

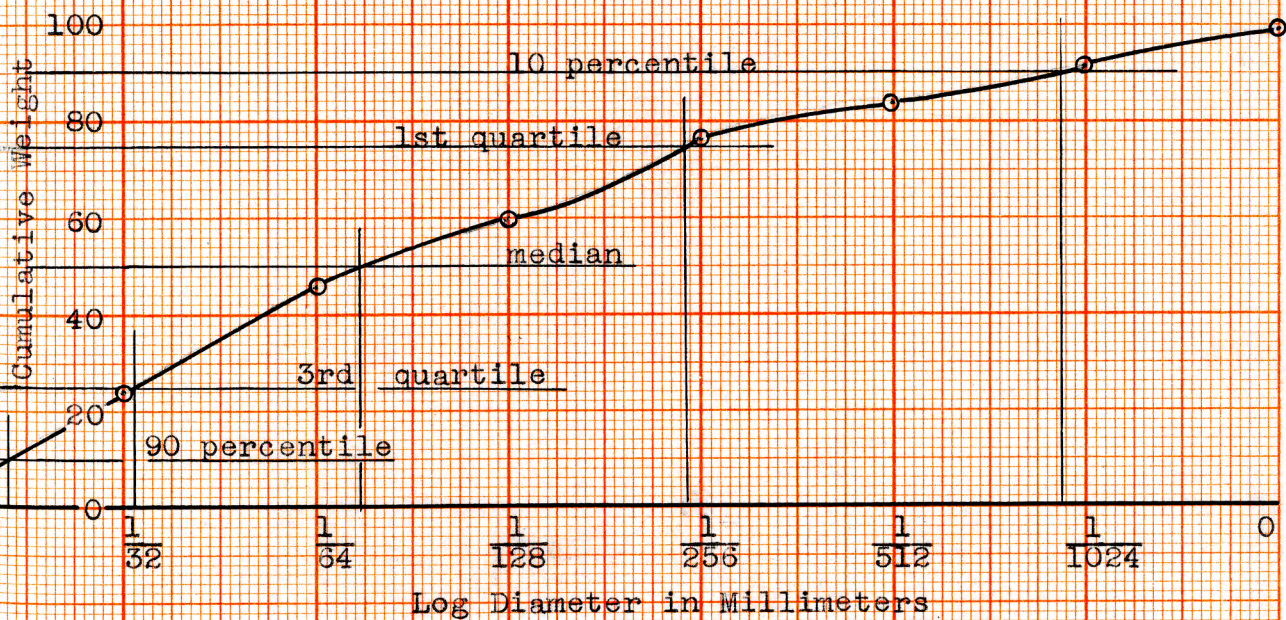


Fig. 8. Cumulative-frequency curve of green Speiser shale.

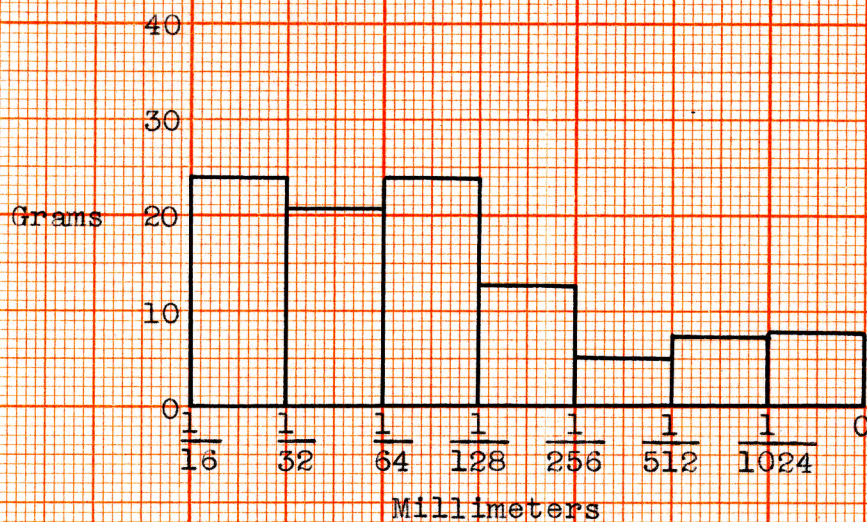


Fig. 9. Histogram showing the distribution of particle size of red Blue Springs shale.

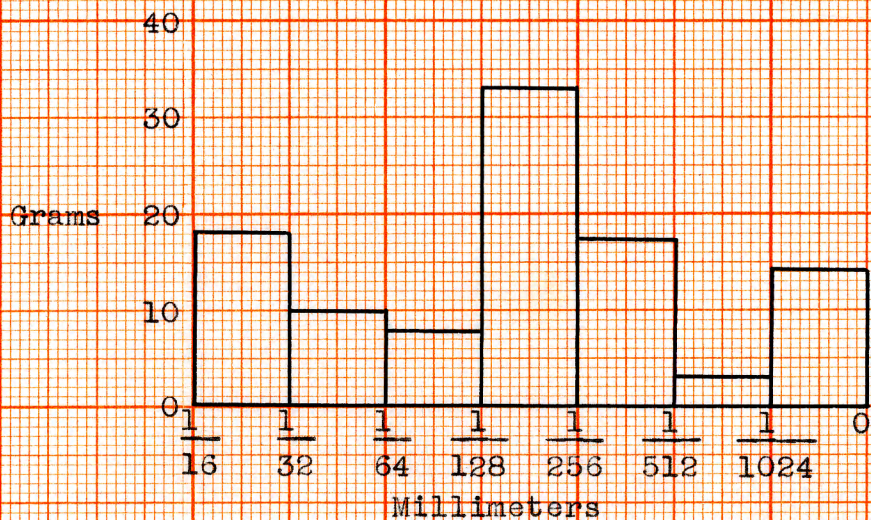


Fig. 10. Histogram showing the distribution of particle size of green Blue Springs shale.

PRINTED IN U.S.A.

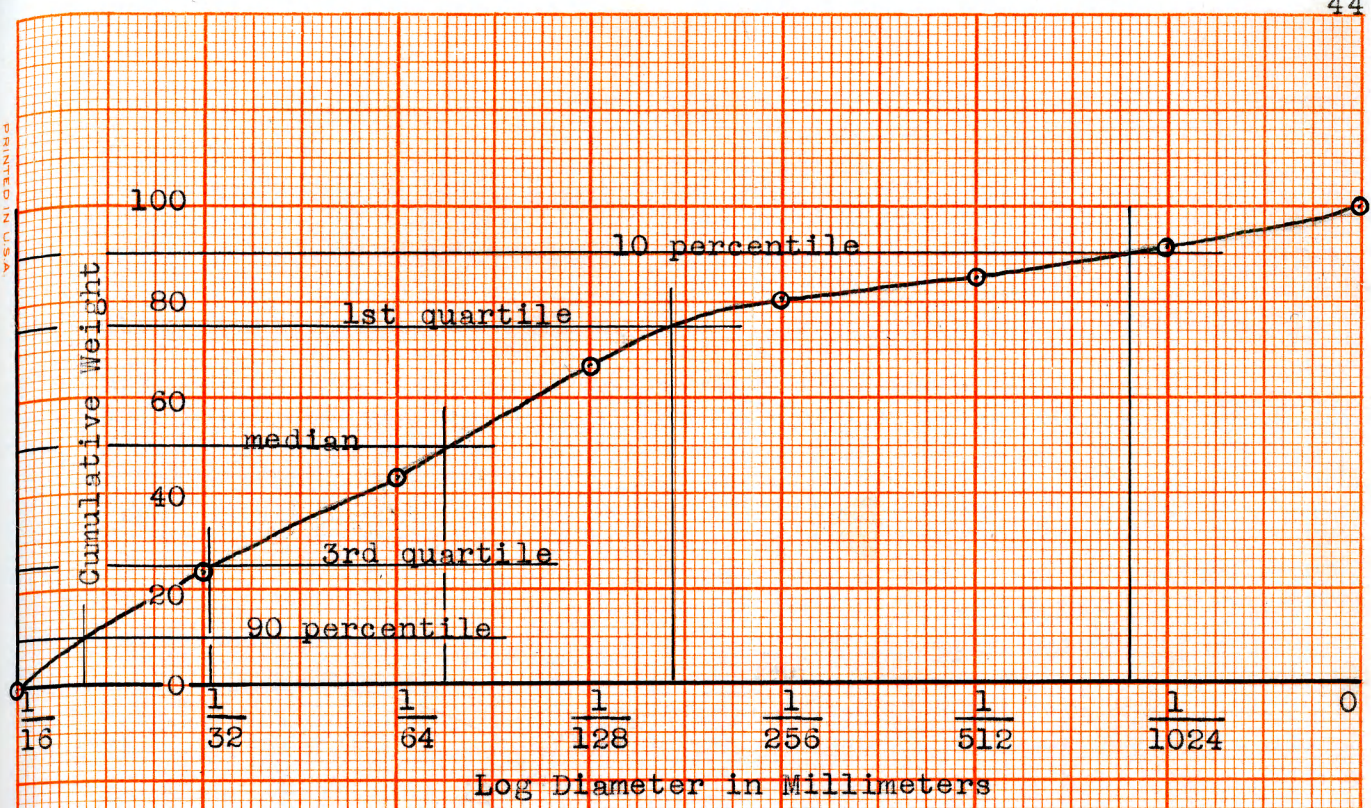


Fig. 11. Cumulative-frequency curve of red Blue Springs shale.

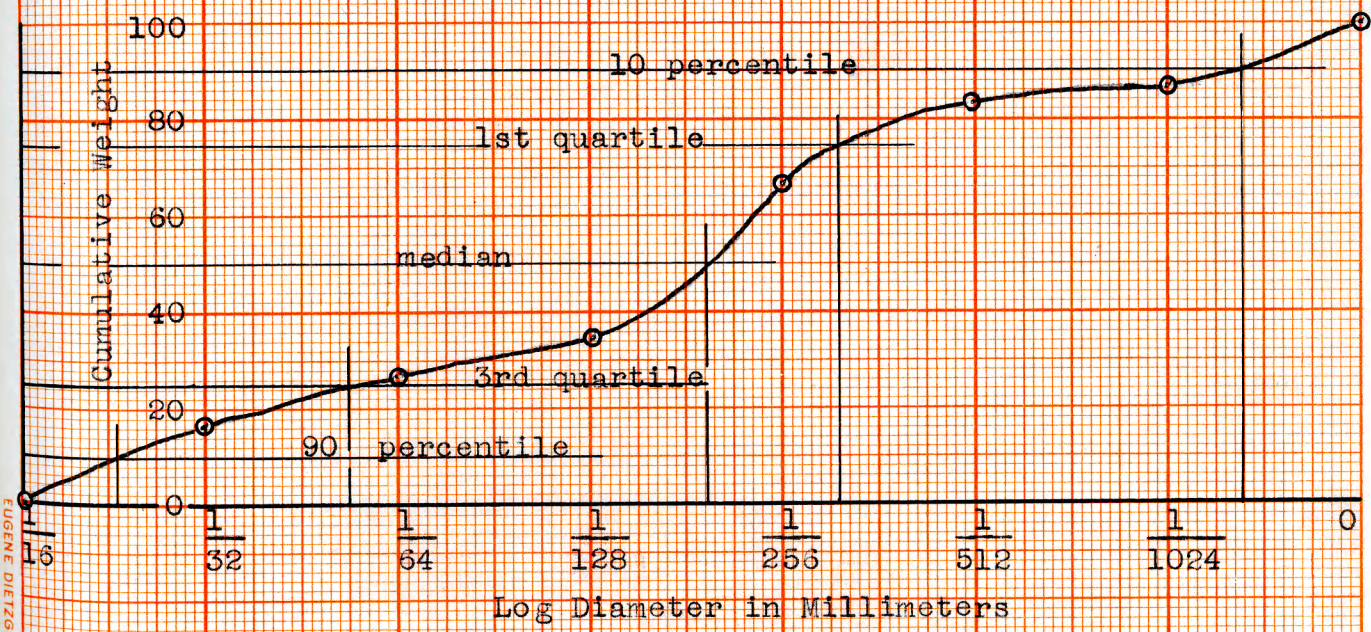


Fig. 12. Cumulative-frequency curve of green Blue Springs shale.

EUGENE DETZGEN CO. NO. 346

Because the mechanical composition of the shales seems to have at least some effect on the color of the shales where stains are the principal cause of color in the sediments, an effort was made to determine the nature of the stains through chemical analysis.

CHEMICAL ANALYSES OF SHALE SAMPLES

A quantitative chemical analysis for the determination of total ferrous iron and total iron present in the red and the green zones of the Eskridge shale was made by the Department of Agronomy, Kansas State College under the supervision of Dr. R. V. Olson.

Analytical Procedure

At the request of the writer, Dr. Olson conducted the analysis according to the methods of H. S. Washington (1930), which are particularly well suited to the analysis of rocks. In brief, the method depends on fusing the rock in platinum crucibles before the analysis is undertaken and, in the subsequent phases of the analysis, extreme care is used not to change the valence of the iron in the sample. The ferrous iron present in the shale was precipitated as ferric iron and, later in the analysis, the total iron of the sample was determined. Knowing the percentage of ferrous iron and total iron, the ratio of ferrous to ferric iron can be ascertained.

Analytical Results

The results of the chemical analysis of the two shales appear in Table 3. It will be noted that the percentage of total iron seems extremely low to color a sediment effectively; however, commercial clays must have a much smaller iron content than this or they will develop an objectionable color under the strong oxidizing conditions of baking.

Table 3. Chemical analyses of the Eskridge shale.

	Red Eskridge shale		Green Eskridge shale	
	No. 1.	No. 2.	No. 1.	No. 2.
	percent			
Ferrous iron*	0.10	0.08	0.10	0.10
Ferric iron*	0.24	0.24	0.41	0.41
Total iron*	0.34	0.32	0.51	0.51

* as Fe_2O_3 .

From the results of the chemical analysis, it is evident that the presence of iron in a shale does not alone explain its color inasmuch as the green shale contains more total iron than does the red shale. However, the determining factor relative to the color of the shales is the manner in which the iron is combined with other elements to form minerals. In the case of the red shale, it is probable that the ferric iron present is combined with oxygen as hematite, an effective coloring agent. Since ferrous oxide is relatively soluble, it is believed that a part of the total iron present in the green shales exists as a ferrous silicate.

Many of the ferrous silicates are green in color and might make staining agents perhaps as effective as hematite. The green silicate, chlorite, may be the coloring agent in those shales examined.

It is probable that the iron present in the shales at the time of their deposition was combined in the clay minerals, and it could have been in the bivalent or trivalent state or both. The clays are relatively stable minerals and would remain essentially unchanged until a change of environment was imposed upon them for a period of time of geologic significance. If the environment was an oxidizing one, iron from the clays could be expected to combine with oxygen from the atmosphere, or other source, to form hematite. If reducing conditions existed, it is chemically possible for chlorite, a hydrous ferrous silicate, to be produced from the iron and the excess of silica (as quartz) present in the shales. This formation of chlorite would be favored in the presence of water and magnesium, and magnesium is present in seawater.

DIFFERENTIAL THERMAL ANALYSES OF SHALE SAMPLES

Differential thermal analysis is a useful method for the study of those mineral groups which yield characteristic peaks in the differential thermal curves. The method is especially suited to both qualitative and semi-quantitative studies of the clay minerals.

Analytical Procedure

Thermal analysis is, in principle, a method of studying the thermal reactions of a sample when heated at a constant heating rate. These reactions are either endothermic or exothermic in nature, and they are due to the loss of either adsorbed water or water of hydration, changes in physical structure, or chemical decomposition.

Description of Equipment. The thermal apparatus used in this analysis is very similar to that used in other laboratories and has been described in detail in other papers such as those by Norton, F. H., and Grim, R. E. The sample to be analyzed is placed in a chrome nickel steel sample-holder which also contains the inert substance which is adjacent to but separate from the sample. Chromel and alumel couples are inserted into the sample and the inert substance, respectively, to record the e.m.f. generation that occurs when the loaded sample-holder is heated. Purified alundum, manufactured by the Norton Company, was used for the inert material.

The sample-holder was heated in an electric furnace at a rapid (increase of 33 degrees centigrade per minute) rate. The temperature interval recorded for these analyses was from 0 degrees to 1000 degrees centigrade, and this interval was continuously recorded through a platinum-rhodium temperature recording thermocouple.

The recorder of the differential thermocouples is a Leeds and Northrup "Speedomax" which is a high-speed, high-sensitivity,

electronic recorder with a maximum range of three millivolts. This recorder is synchronized with another recorder which produces the temperature record.

The equipment was frequently calibrated with the alpha-beta quartz change at 575 degrees centigrade, and reproducibility was checked also by analyzing samples of standard Georgia kaolinite after short periods of operation. This procedure permitted a correction of the "drift" which is inherent in all electronic devices.

Description of Procedure. All of the samples analyzed with the thermal apparatus were ground to a size which passed the U. S. Series No. 120 sieve and was retained on the No. 250 sieve. The alundum was also ground to this size. Care was exercised at all times to avoid contamination of the samples, and the procedures of filling the sample-holder, inserting the thermocouples, etc., were duplicated as nearly as possible for each analysis.

Three series of eighteen shales each were analyzed in all. The first of these series were analyses of untreated shales, and the thermal curves for this series are shown on Figs. 13 to 30. The second series, shales treated with cold hydrochloric acid, are included in Figs. 31 to 48; and Figs. 49 to 66 show curves of the eighteen shales when treated with hot hydrochloric acid. The shales were treated with cold acid to remove calcite and with hot acid to remove such other carbonates as magnesite and dolomite.

The thermal curves shown in the figures cited above are the deviations from a straight line plot of temperature differences

against temperature, and these deviations are dependent upon the nature of the heat change for their direction and amplitude. In plotting the thermal curves, the writer has followed the standard practice of plotting endothermic reactions below and exothermic reactions above the line of zero deviation.

Analytical Results

An examination of the thermal curves shown in Figs. 13 to 66 reveals that the clay minerals in each of the eighteen shales is an illite. Each of the curves shows the three distinctive peaks at approximately 160, 630, and 875 degrees centigrade. All three of these peaks resulted from endothermic reactions.

Although the curves of all the shales analyzed are somewhat similar, it will be noted that the curves for the red and green shales of the same member or formation are, in most cases, nearly identical. All of the shales, with the one exception of the Holmesville, were calcareous. The presence of calcite in the shales is shown by the peak of large amplitude which occurs at 925 degrees centigrade in the curves of the untreated shale samples. The presence of a double peak near the high-temperature end of the curves is indicative of magnesite or dolomite. The Blue Springs and Gage samples apparently contain small amounts of dolomite.

The differential thermal analyses have established that the same clay mineral is present in both the red and green shales; therefore, the clay mineral of the shale is not likely to be the cause of color variations in those shales.

Degrees centigrade

100

300

500

700

900

Fig. 13.
Lower Roca shale
Red

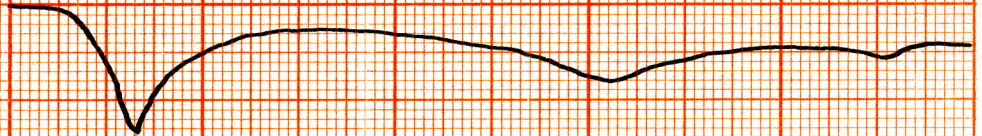


Fig. 14.
Lower Roca shale
Green

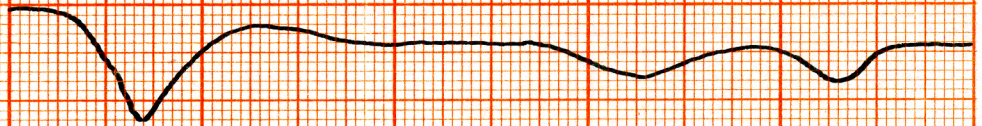


Fig. 15.
Upper Roca shale
Red

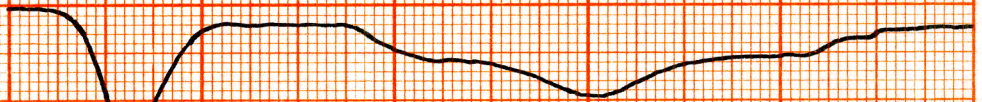


Fig. 16.
Upper Roca shale
Green

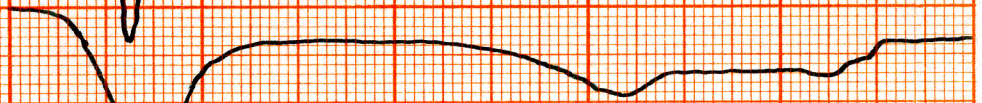


Fig. 17.
Eskridge shale
Red

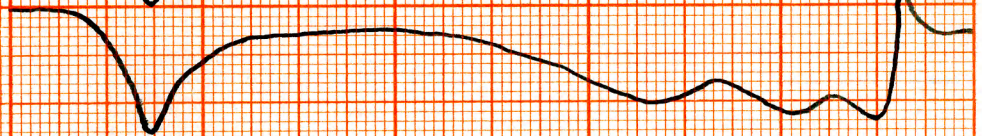
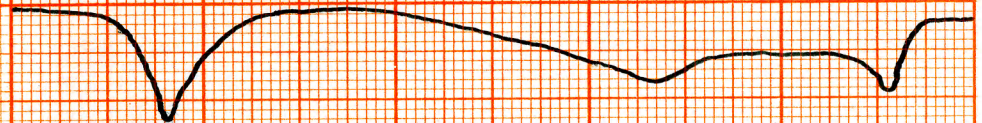


Fig. 18.
Eskridge shale
Green



100

300

500

700

900

Degrees centigrade

100 300 500 700 900

Fig. 19.
Blue Rapids shale
Red

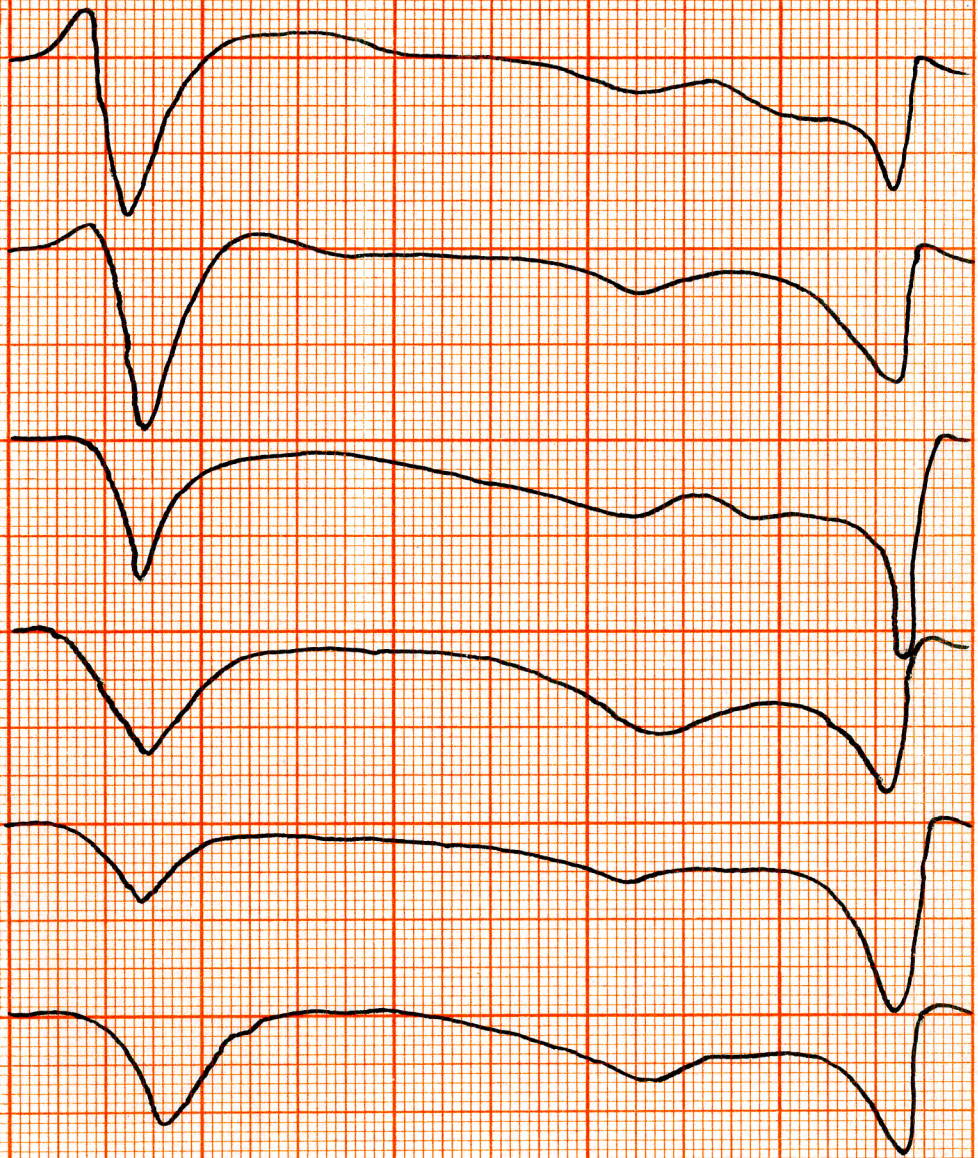
Fig. 20.
Blue Rapids shale
Green

Fig. 21.
Speiser shale
Red

Fig. 22.
Speiser shale
Green

Fig. 23.
Wymore shale
Red

Fig. 24.
Wymore shale
Green



100 300 500 700 900

Degrees centigrade

100

300

500

700

900

Fig. 25.
Blue Springs shale
Red

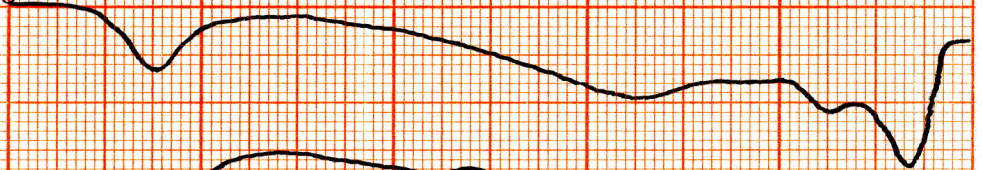


Fig. 26.
Blue Springs shale
Green

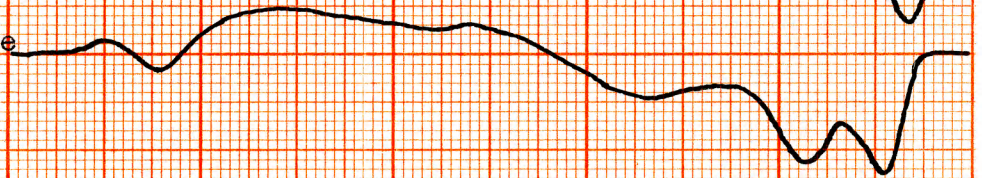


Fig. 27.
Holmesville shale
Red

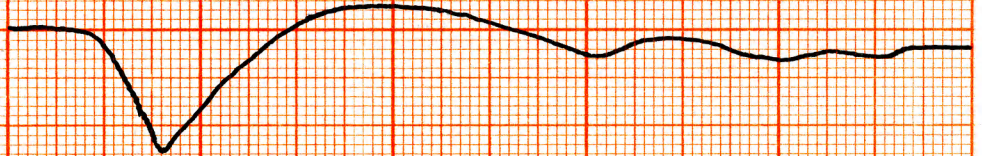


Fig. 28.
Holmesville shale
Green

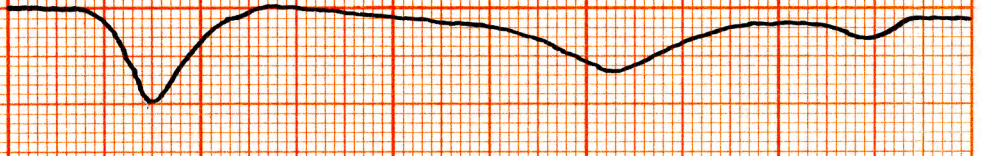


Fig. 29.
Gage shale
Red

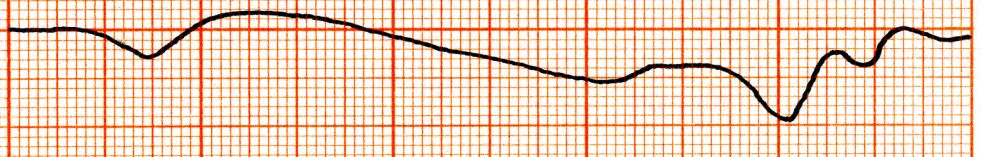
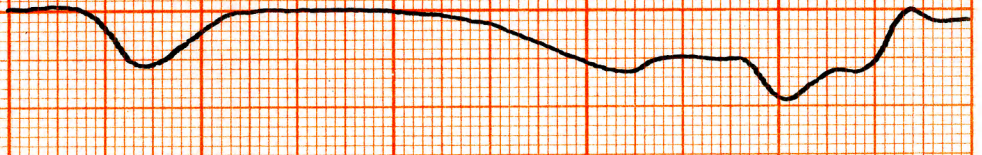


Fig. 30.
Gage shale
Green



100

300

500

700

900

Degrees centigrade

100

300

500

700

900

Fig. 31.
Lower Roca shale
Red

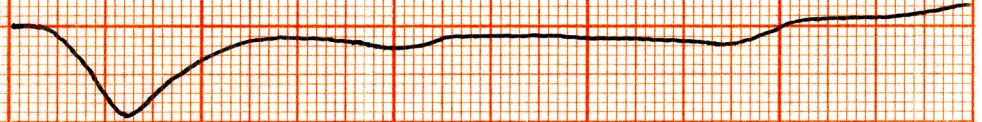


Fig. 32.
Lower Roca shale
Green

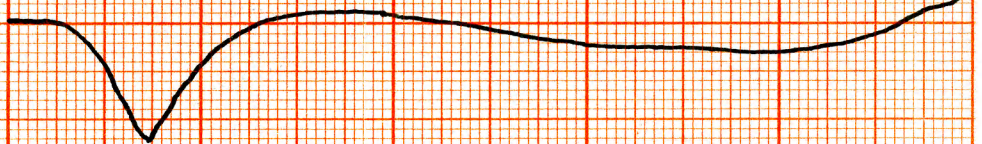


Fig. 33.
Upper Roca shale
Red

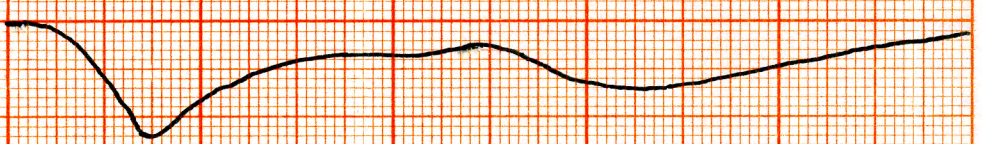


Fig. 34.
Upper Roca shale
Green

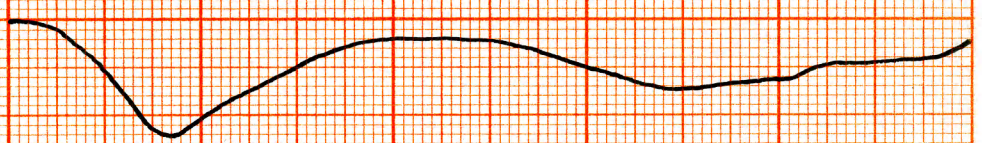


Fig. 35.
Eskridge shale
Red

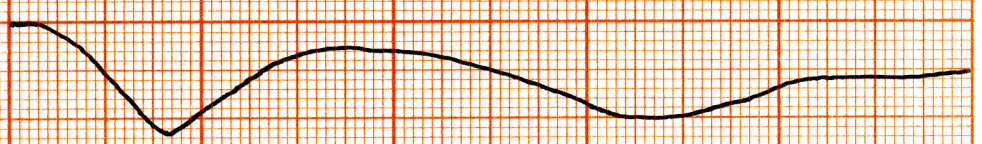
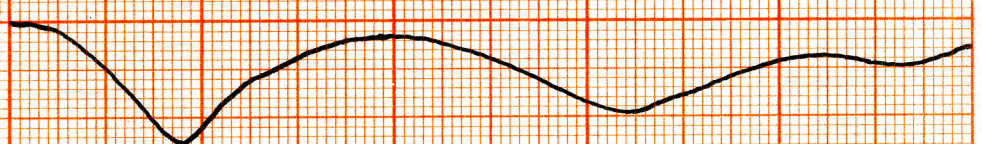


Fig. 36.
Eskridge shale
Green



100

300

500

700

900

Degrees centigrade

100

300

500

700

900

Fig. 37.
Blue Rapids shale
Red

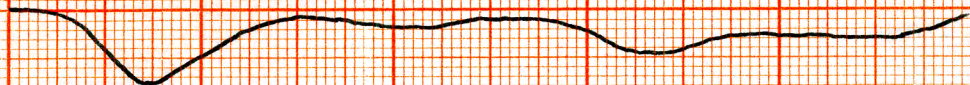


Fig. 38.
Blue Rapids shale
Green

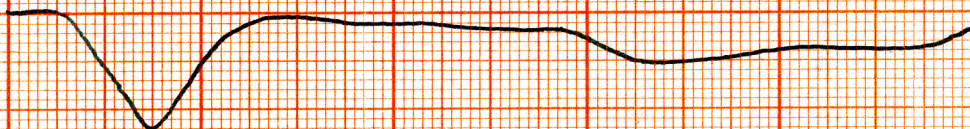


Fig. 39.
Speiser shale
Red

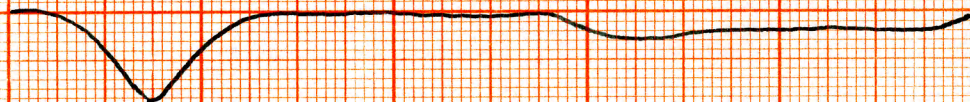


Fig. 40.
Speiser shale
Green

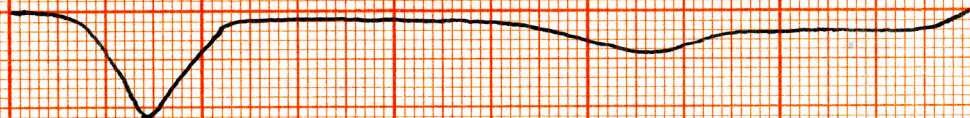


Fig. 41
Wymore shale
Red

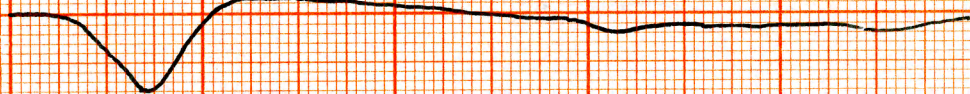
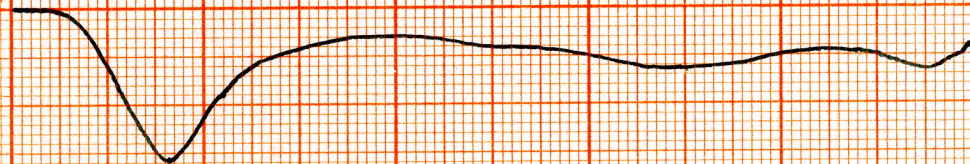


Fig. 42.
Wymore shale
Green



100

300

500

700

900

Degrees centigrade

100

300

500

700

900

Fig. 43.
Blue Springs shale
Red

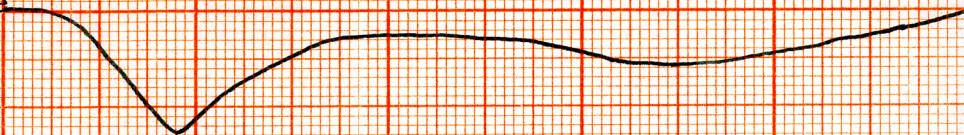


Fig. 44.
Blue Springs shale
Green

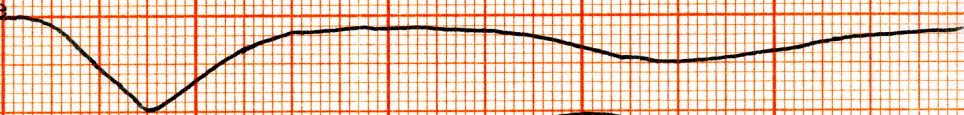


Fig. 45.
Holmesville shale
Red

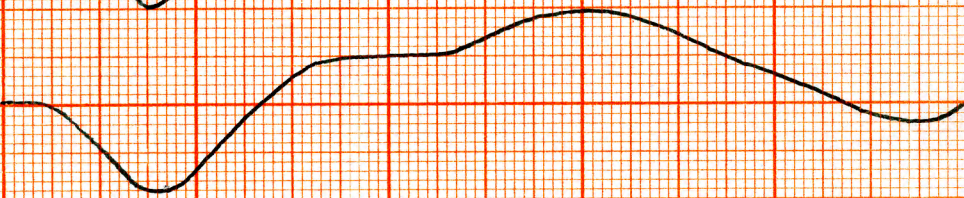


Fig. 46.
Holmesville shale
Green

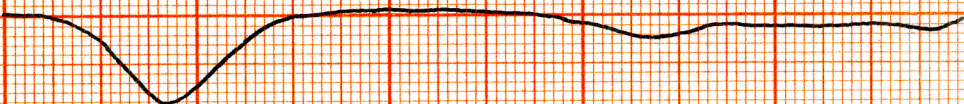


Fig. 47.
Gage shale
Red

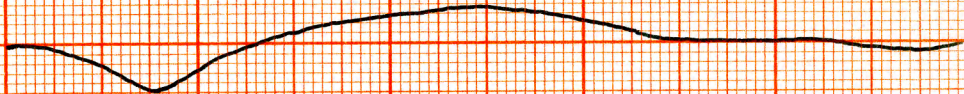
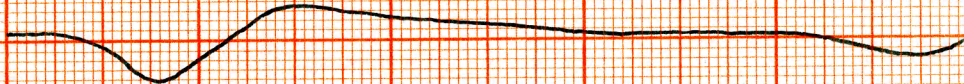


Fig. 48.
Gage shale
Green



100

300

500

700

900

Degrees centigrade

100

300

500

700

900

Fig. 49.
Lower Roca shale
Red

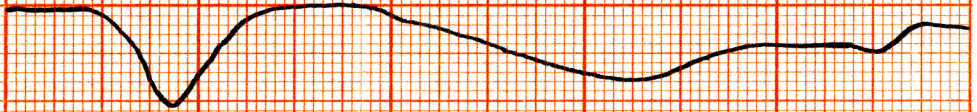


Fig. 50.
Lower Roca shale
Green

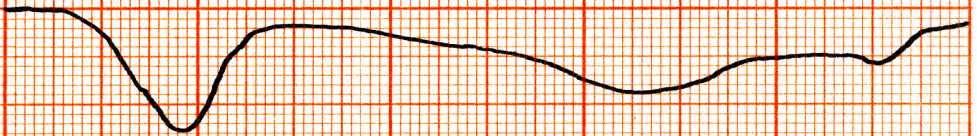


Fig. 51.
Upper Roca shale
Red

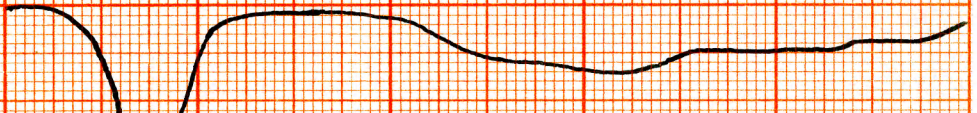


Fig. 52.
Upper Roca shale
Green

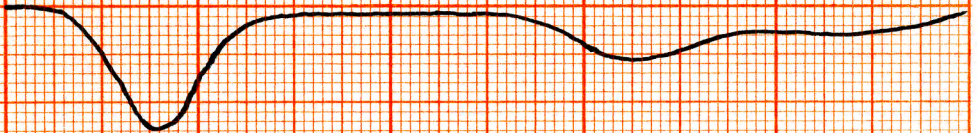


Fig. 53.
Eskridge shale
Red

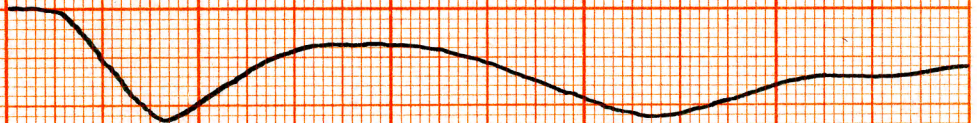
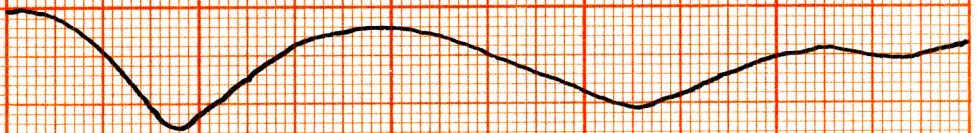


Fig. 54.
Eskridge shale
Green



100

300

500

700

900

Degrees centigrade

100 300 500 700 900

Fig. 55.
Blue Rapids shale
Red

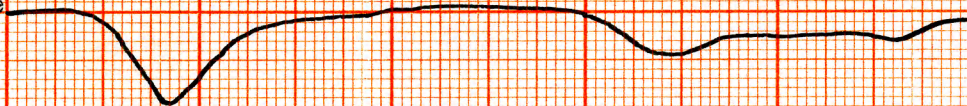


Fig. 56.
Blue Rapids shale
Green

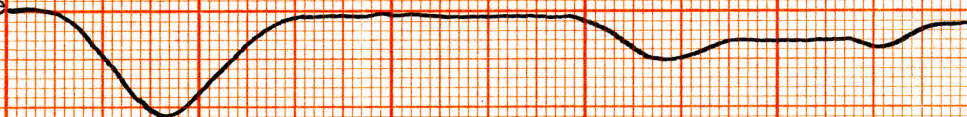


Fig. 57.
Speiser shale
Red

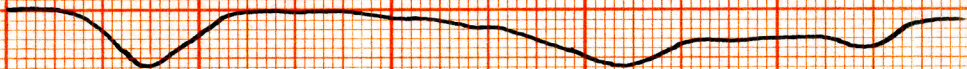


Fig. 58.
Speiser shale
Green



Fig. 59.
Wymore shale
Red

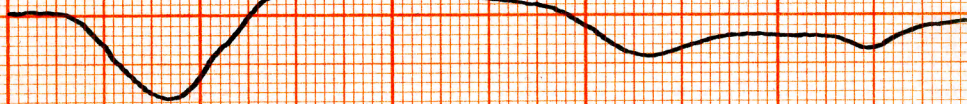
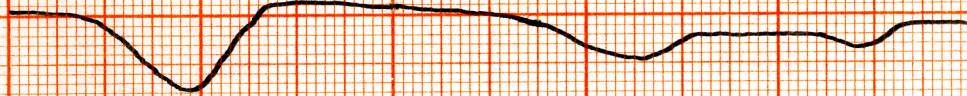


Fig. 60.
Wymore shale
Green



100 300 500 700 900

Degrees centigrade

100

300

500

700

900

Fig. 61.
Blue Springs shale
Red

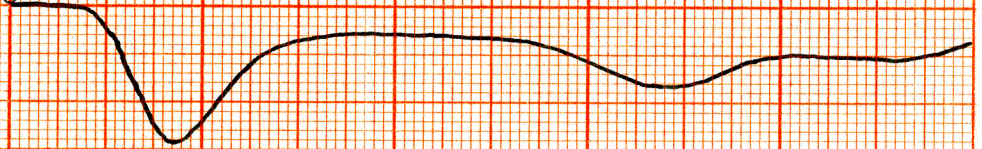


Fig. 62.
Blue Rapids shale
Green

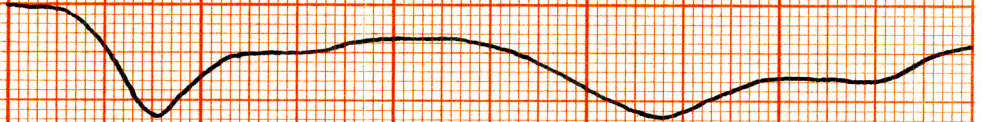


Fig. 63.
Holmesville shale
Red

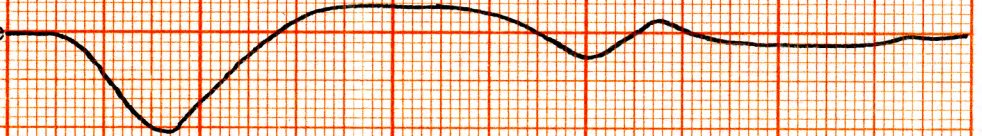


Fig. 64.
Holmesville shale
Green

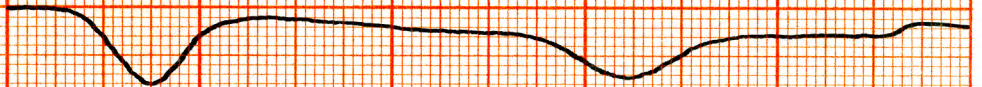


Fig. 65.
Gage shale
Red

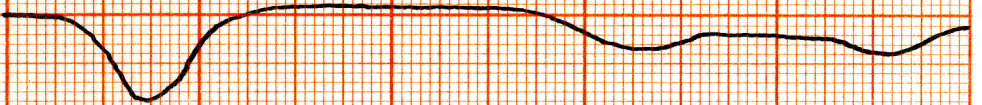
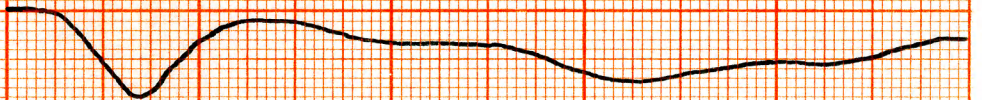


Fig. 66.
Gage shale
Green



100

300

500

700

900

OBSERVATIONS ON FIELD RELATIONSHIPS

The associations of the red and green shales sampled were noted during the collection of the samples, and further field notes were made at a later date from observations of vari-colored shales in the Sumner Group of the Permian System and the Wabaunsee Group of the Pennsylvanian System.

As has been mentioned, adjacent red and green shales were sampled wherever possible in an effort to obtain shales which were lithologically similar. These adjacent occurrences also gave more significance to such characteristics of the shales as their contacts and relative positions.

The red and green zones of some of the shale units are separated by irregular gradational boundaries, while in other units the contact is marked by an abrupt color change. Where gradational boundaries separate the shales, it was noted that the red color had a tendency to mask the green in such a way as to produce a maroon to purplish hue. In some cases the contact was mottled red and green, and it was thought that this condition is due to the mixing of partially lithified sediments by geologic agents shortly after a change of environment had caused an alternation of color.

Isolated green spots were noted at some places in the red shales, but on no occasion was the reverse observed to occur. These green spots in the red shales may be due to isolated reducing conditions caused by the decomposition of an organism embedded in the clay and silts from which the shale was formed.

The field evidence shows also that no definite statement can be made concerning the relative positions of the shales. Red shale was found to overlies the green in some places, but just as frequently the green shale was found in the higher position. Usually the green shale forms an outcrop which is somewhat more resistant to weathering, and from appearances the green shale contains a greater amount of carbonaceous material. Both the red and the green shale weather to a gray color which may be due to the removal of the stains through leaching.

SUMMARY OF ANALYTICAL RESULTS

The analytical methods employed in this investigation have developed some definite results and a number of indications which are valuable in explaining the color variations of the shales. Each of the methods of analysis has yielded information concerning the mechanical or the chemical composition of the sediments.

Spectrographic Analysis. The spectrographic analysis shows that no elements are present in red shales which do not also occur in approximately equal concentrations in green shales. This similarity in composition suggests that the colors of the shales must be due to valence differences of the intrinsic elements or, which may be the same thing, to dissimilar chemical combinations of those elements.

X-ray-diffraction Analysis. As was shown by the X-ray-diffraction analyses, red shale is characterized by a more random structure and a smaller crystal size than green shale. These

results indicate a structural difference between the shales which probably is due to weathering of the red shales.

Petrographic Analysis. The petrographic analyses reveal that the red stain present on detrital grains of the red shales is hematite and establishes the presence of a green stain, which may be a chlorite, in the green shales.

Mechanical Analysis. Statistical examination of the mechanical analyses has indicated that the shales are well-sorted, near-shore deposits. Further, there is an apparent relationship between the intensity of color and the clay-silt ratio of the shales.

Chemical Analysis. The chemical analyses show that there is ferric and ferrous iron present in both the red and green shales in a ratio that is opposite to the ratio expected if the state of the iron is solely responsible for the color of the shales. However, it is certain that a part of the iron is combined as minerals other than those staining the shales, and this presence of either form of iron in other relatively stable minerals of the shales would make the ferrous-ferric ratio unreliable as a criterion of the oxidizing or reducing conditions imposed upon the shales. The iron which is not combined as stains is undoubtedly retained by the original minerals.

Differential Thermal Analysis. The differential thermal analyses disclose that the same clay mineral, illite, is the major component of all of the shales examined.

CONCLUSIONS

The results of the analyses indicate that a mineral stain on the particles of the shales is the petrographic factor determining the color of the shales. The stains of both the red and green shales are alteration products or secondary minerals probably derived from the original clay minerals, and they apparently occur only on the surface of the particles composing the shales. The mineral hematite is undoubtedly the cause of color in the red shales; whereas the green shales are probably colored by a hydrous ferrous silicate mineral. This formation of minerals characteristic of either an oxidizing or a reducing environment can best explain the red and green color variations of shales. Moreover, this explanation does not require that the constituent iron of a shale be entirely of one valence or another.

The chemical conditions of oxidation and reduction necessary to produce the hematite or silicate stains are factors of the environment under which the shales were deposited or to which they were subjected subsequent to their deposition. The presence of organic material in the environment is conducive to the chemical reduction of the constituents, and the oxygen of the atmosphere is all that is required to produce conditions of oxidation.

Although insufficient evidence has been collected to definitely determine the environment under which the vari-colored shales were deposited, only an environment which is related to oxidation and reduction can effectively explain the alternation of color in the shales. From the field evidence it is thought

that the shales are littoral sediments inasmuch as these rocks show the stratification and contain the fossils of deposits related to marine conditions. The environment which might best induce alternate oxidation and reduction would be a subaerial plain of deltaic origin adjoining a sea fluctuating in level.

The subaerial plains (Twenhofel, 1950, p. 103) are frequently extensive deposits which may be quite flat, contain lakes and swamps, and are bordered on the seaward margin by lagoons.

The areas of the subaerial plains which were under water (lakes, swamps, and lagoons) would have an environment conducive to life if the water was not too saline, and in these areas there would be an accumulation of organic material with attendant reducing conditions. Particles collecting in the reducing areas might easily alter on the surface to a hydrous ferrous silicate which would effectively color the sediment.

Sediments which accumulated during flood conditions on the dry areas of the subaerial plains would owe their color to their exposure to the oxidizing conditions of the atmosphere. The rapid decay of organic matter under these conditions would inhibit its accumulation, and the dry conditions would permit no possibility of reduction of the iron of the oxide to which the red color is due. A fluctuation of sea level would explain the inconsistent relative positions of the shales as the normal onlap and offlap of advancing and retreating shorelines.

ACKNOWLEDGMENTS

The author wishes to extend his appreciation to Prof. A. B. Sperry, Major Instructor, and to Dr. Frank E. Byrne for their encouragement and sincere aid in preparing this thesis. Mr. V. C. Fishel and Mr. Carl F. Crumpton of the United States Geological Survey and Dr. R. H. MacFarland of the Department of Physics, Kansas State College, offered constructive criticisms and facilities for research which materially aided the investigation. Mr. Clyde Parkert ably advised the author during the X-ray analyses.

LITERATURE CITED

- Barrell, J.
Relation between climate and terrestrial deposits. Jour. Geol. 16:233-290. 1909.
- Beede, J. W.
The fauna of the Shawnee formation (Haworth), the Wabaunsee formation (Prosser), the Cottonwood limestone. Kans. Univ., Sci. Bul. 1. 1902.
- Bouyoucos, G. J.
The hydrometer method for making a very detailed mechanical analysis of soils. Soil Sci. 26:233. 1928.
- Clarke, F. W.
Data of geochemistry. U. S. Geol. Surv. Bul. 770. 1924.
- Condra, G. E.
The stratigraphy of the Pennsylvanian system in Nebraska. Nebr. Geol. Surv. 2d Ser. Bul. 1. 1927.
- Condra, G. E., and Upp, J. E.
Correlation of the Big Blue series in Nebraska. Nebr. Geol. Surv. 2d. Ser. Bul. 6. 1931.
- Condra, G. E., and Busby, C. E.
The Grenola formation. Nebr. Geol. Surv. Paper 1. 1933.
- Condra, G. E.
Geologic cross-section from Forest City, Missouri, to Du Bois, Nebraska. Nebr. Geol. Surv. Paper 8. 1935.
- Grabau, A. W.
Principles of stratigraphy. New York: A. G. Seiler, 1924.
- Hager, D. S.
Factors affecting color of sedimentary rocks. AAPG Bul. 12:901-938. 1928.
- Moore, R. C., Frye, J. C., and Jewett, J. M.
Tabular description of outcropping rocks in Kansas. Kans. Geol. Surv. Bul. 52. 1944.
- Moore, R. C., Frye, J. C., Jewett, J. M., Lee, W., and O'Connor, H. G.
The Kansas rock column. Kans. Geol. Surv. Bul. 89. 1951.
- Mudge, Melville.
The stratigraphy of Riley County, Kansas. Thesis. Kansas State Col. of Agr. & Appl. Sci. 1949.

- Pettijohn, F. J.
Sedimentary rocks. New York: Harper & Bros, 1949.
- Prosser, C. S.
Revised classification of the upper Paleozoic formations of
Kansas. Jour. Geol. 10:700-737. 1902.
- Sproull, W. T.
X-rays in practice. New York: McGraw-Hill, 1946.
- Twenhofel, W. H.
Treatise on sedimentation. New York: McGraw-Hill, 1926.
- Twenhofel, W. H.
Principles of sedimentation. New York: McGraw-Hill, 1950.
- Twenhofel, W. H., and Tyler, S. A.
Methods of study of sediments. New York: McGraw-Hill, 1941.
- Washington, H. S.
Manual of the chemical analysis of rocks. 4th ed. New York:
John Wiley & Sons, 1930.

FACTORS DETERMINING THE COLORS
OF RED AND GREEN SHALES

by

WILLIS DABNER WATERMAN

B. S., Kansas State College
of Agriculture and Applied Science, 1949

ABSTRACT

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Geology and Geography

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1951

This investigation was undertaken to determine the factors, both petrologic and environmental, which affect the colors of red and green shales. The occurrences of a number of vari-colored shales were observed in the field, and samples of these shales were analyzed in the laboratory by means of spectrographic, X-ray, petrographic, mechanical, chemical, and differential thermal analyses. Each of these methods contributed information concerning either the mechanical, chemical, or mineralogical composition of the shales.

The analyses indicate that the formation of secondary mineral stains on particles of the shales is the petrologic cause of color in the rocks. The mineral hematite stains the red shales, and the green shales studied are apparently colored by a ferrous silicate. The chemical conditions of oxidation and reduction influence the formation of these mineral stains, and the intensity of the color is affected by the clay-silt ratio of the shales.

The environment which might best induce alternate chemical oxidation and reduction to produce vari-colored shales within the same geologic member or formation would be a subaerial plain of deltaic origin adjoining a sea fluctuating in level. This environment contains accumulation areas for organic material with attendant reducing conditions and high, dry areas exposed to the oxygen of the atmosphere where oxidation is possible. Field observations on the stratigraphy and paleontology of the sediments also suggest a littoral environment for deposition of the shales.