

69-13,915

WU, Dah Cheng, 1939-
CLAY MINERALOGY AND GEOCHEMISTRY OF THE
UPPER FLOWERPOT SHALE IN MAJOR AND BLAINE
COUNTIES, OKLAHOMA.

The University of Oklahoma, Ph.D., 1969
Geology

University Microfilms, Inc., Ann Arbor, Michigan

THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

CLAY MINERALOGY AND GEOCHEMISTRY OF THE UPPER FLOWERPOT SHALE
IN MAJOR AND BLAINE COUNTIES, OKLAHOMA

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

DAH CHENG WU

Norman, Oklahoma

1969

CLAY MINERALOGY AND GEOCHEMISTRY OF THE UPPER FLOWERPOW SHALE

IN MAJOR AND BLAINE COUNTIES, OKLAHOMA

APPROVED BY

Charles M. Merriam
Bernard C. Huston
Dana B. Willis
Charles E. Harper
Arthur J. Myers

DISSERTATION COMMITTEE

ACKNOWLEDGMENTS

The writer is especially indebted to Dr. Charles J. Mankin who directed the thesis and gave invaluable suggestions and criticism.

Acknowledgment is also given to Drs. David B. Kitts, Arthur J. Myers, and Charles W. Harper who read the manuscript and offered valuable advice.

The author is grateful to Kenneth A. Sargent for his assistance in running the emission spectrographic analysis and Her Yue Wong for his help in the field work.

Thanks are extended to the Research Institute of the University of Oklahoma for its financial assistance.

The writer also desires to express his sincerest appreciation to his mother for her moral support and encouragement throughout the graduate program.

TABLE OF CONTENTS

	Page
LIST OF TABLES.	vi
LIST OF ILLUSTRATIONS	vii
INTRODUCTION.	1
Purpose of Investigation.	1
Location and Geologic Setting	3
Previous Investigations	3
Methods of Investigation.	4
STRATIGRAPHY.	6
El Reno Group	6
Flowerpot Shale	6
MINERALOGY.	11
Terrigenous Components.	11
Quartz.	11
Feldspar.	11
Rock Fragments.	16
Mica.	16
Heavy Minerals.	19
Clay Minerals	19
General Statement	19
Illite.	19
Chlorite and Swelling Chlorite.	21
Zonation of Swelling Chlorite	32
High Temperature Phases of Clay Minerals.	39
Authigenic Components	40
Gypsum.	40
Dolomite.	40
Analcite.	40
Definition.	40
Stratigraphic Distribution.	41
Origin.	43

	Page
PETROGRAPHY.	46
Shale.	46
Siltstone and Sandstone.	46
Dolomite	47
PIPETTE ANALYSES	49
General Statement.	49
Data and Interpretation.	50
TRACE-ELEMENT GEOCHEMISTRY	56
General Statement.	56
Variations in Trace-element Content between Coarser and Finer Size Fraction of Shale	57
Comparison of Trace-element Content between Red-brown Shale and Greenish-grey Shale.	60
Paleosalinity.	62
Correlations with Iron, Nickel, Cobalt, and Vanadium	64
CHEMICAL ANALYSES BY X-RAY FLUORESCENCE.	66
General Statement.	66
Data and Interpretation.	69
PROVENANCE AND ENVIRONMENT	74
Source	74
Environment.	76
CONCLUSIONS.	82
REFERENCES CITED	85
APPENDIX A. ANALYTICAL PROCEDURES AND TECHNIQUES.	89
Sample Preparation	89
Analytical X-ray Techniques.	90
Differential Thermal Analysis.	91
X-ray Fluorescence Analysis.	91
Emission Spectrographic Analysis	92
APPENDIX B. STATISTICAL AND MATHEMATICAL FORMULAE	95
Student's t Test	95
F Test	96
Correlation Coefficient.	96
APPENDIX C. MEASURED SECTIONS	97

LIST OF TABLES

Table		Page
1.	Vertical Stratigraphic Variations in "Swelling Chlorite Index" and "Sharpness of Illite" (Bulk Shale Samples).	22
2.	Vertical Stratigraphic Variations in "Swelling Chlorite Index" and "Sharpness of Illite" (Selected Less-than-one-micron Samples).	24
3.	Percentage of Different Size Fractions with Respect to the Total Weight of Clay and Silt	54
4.	Quantitative Trace-element Analyses of Shales.	58
5.	Chemical Analyses by X-ray Fluorescence (Less-than-one-micron Samples).	67
6.	Chemical Analyses by X-ray Fluorescence (Less-than-230-mesh Bulk Samples)	68
7.	Sodium-potassium Ratios of Bulk Samples (Less-than-230-mesh).	71
8.	Sodium-potassium and Magnesium-Aluminum Ratios of Clay (Less-than-one-micron).	72

LIST OF ILLUSTRATIONS

Figure		Page
1.	Index Map of Oklahoma Showing Location of Measured Sections.	5
2.	Columnar Sections	9
3.	X-ray Diffractograms of a Selected Sample (M-A-13) Showing Characteristics of Swelling Chlorite and Illite.	27
4.	X-ray Preferred Orientation Diffractograms of M-A-13 Showing Modifications of Swelling Chlorite with Heat Treatment in a Diffractometer Furnace (Less-than-one-micron Fraction)	28
5.	X-ray Preferred Orientation Diffractograms Showing the Presence of Swelling Chlorite at the Upper Portion of Measured Section M-A	34
6.	Differential Thermal Analysis Diagrams Showing the Presence of Swelling Chlorite at the Upper Portion of Measured Section M-A	35
7.	DTA Diagrams and X-ray Preferred Orientation Diffractograms of Two Selected Samples Below and Above the Presumed Boundary of Swelling Chlorite Occurrence in Measured Section B-D.	36
8.	DTA Diagrams and X-ray Preferred Orientation Diffractograms of Two Selected Samples Below and Above the Presumed Boundary of Swelling Chlorite Occurrence in Measured Section B-E.	37
9.	DTA Diagrams and X-ray Preferred Orientation Diffractograms of Two Selected Samples Below and Above the Presumed Boundary of Swelling Chlorite Occurrence in Measured Section B-F.	38
10.	DTA Diagram and Randomly-Oriented X-ray Diffractogram Showing the Presence of Analcite.	42

Figure		Page
11.	Histograms Showing Grain Size Distribution of Two Greenish-grey Shale Beds and the Intervening Red-brown Bed.	51
12.	Histograms Showing Grain Size Distribution of a Greenish-grey Shale Bed and the Overlying and Underlying Red-brown Shale Beds.	52
13.	Histograms Showing Grain Size Distribution of a Greenish-grey Spot and the Surrounding Red-brown Shale.	53
14.	Plot of B and V Concentration of the Flowerpot Shale Samples and Estimated Line of Separation Between Marine and Fresh Water Field, After Potter et al. (1963)	63

Plate

IA.	Greenish-grey Shale Interbeds in Red-brown Shale at the Basal Portion of Measured Section B-F.	2
IB.	Red-brown Shale Mottled with Greenish-grey Spots, Some with Dark Centers in Lithologic Unit B-E-2.	2
II.	Selected Photomicrographs.	12
III.	Selected Photomicrographs.	14
IV.	Selected Photomicrographs.	18

CLAY MINERALOGY AND GEOCHEMISTRY OF THE UPPER FLOWERPOT SHALE
IN MAJOR AND BLAINE COUNTIES, OKLAHOMA

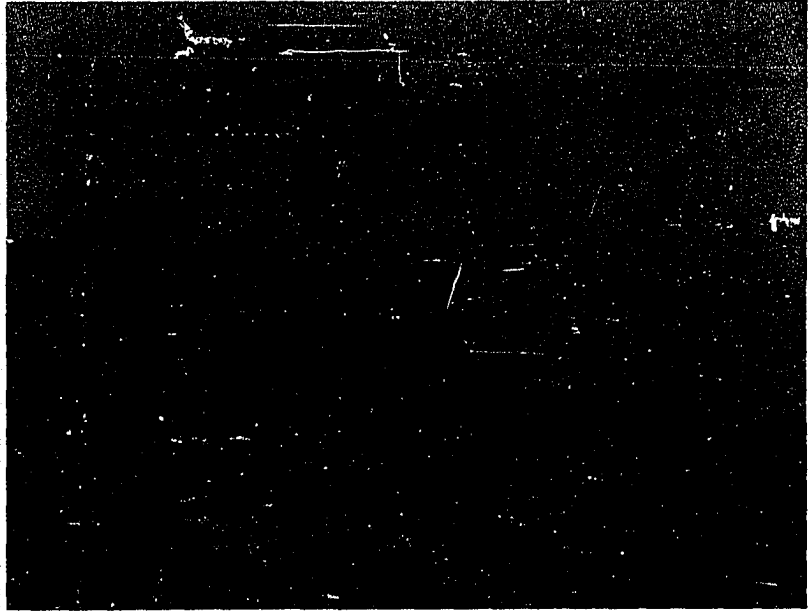
INTRODUCTION

Purpose of Investigation

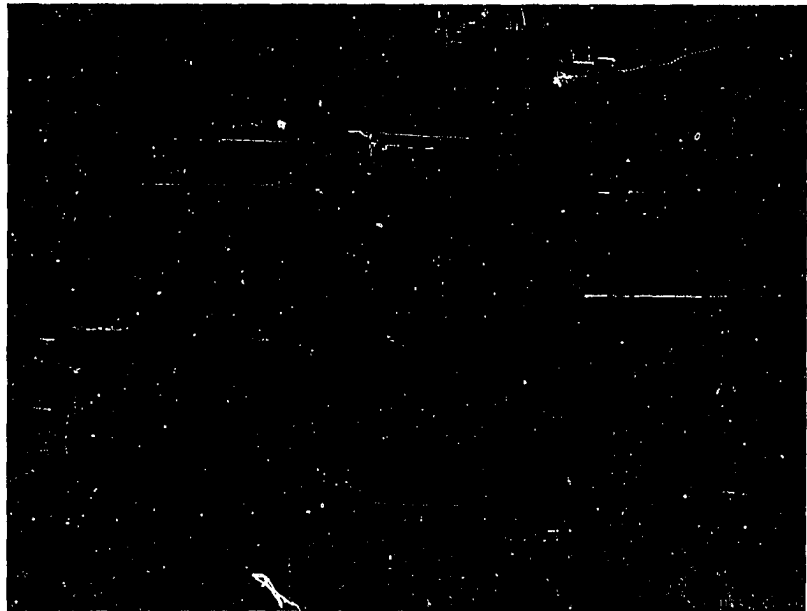
The excellent exposure of upper Flowerpot Shale in Major and Blaine Counties stimulated the writer's interest in detailed studies of vertical and horizontal variations in mineralogy and geochemistry of the shale. Although Fay (1964) has done stratigraphic and preliminary sedimentologic investigations on the shale, no detailed research on clay mineralogy and geochemistry of the Flowerpot Shale in this region has been carried out.

The study included a detailed examination of the geographic and stratigraphic distribution of the shale and mudstone sequence and variation in the mineralogy and chemistry of the sediments with particle size. The greenish-grey beds and spots in the red-brown shale have been thoroughly examined to infer their possible origin (Plate IA and IB).

The results of this investigation on upper Flowerpot Shale have provided additional information on lithology, location, and climate of the source area, as well as hypotheses on the environment of deposition.



A. Greenish-grey shale interbeds in red-brown shale at the basal portion of measured section B-F.



B. Red-brown shale mottled with greenish-grey spots, some with dark centers in lithologic unit B-E-2.

Location and Geologic Setting

The outcrop of the Flowerpot Shale extends northwestward from Canadian County, Oklahoma, to Barber County, Kansas. The present investigation is confined to the area of northern Blaine and Major Counties which are situated on the northeast flank of the Anadarko Basin. This region is bounded by the Anadarko Basin to the southwest, the Wichita Mountains to the south, the Arbuckle Mountains to the southeast, and the Nemaha Uplift to the northeast. The Wichita Mountains and the Arbuckle Mountains are prominent geographic features in the southern part of Oklahoma, whereas the Anadarko Basin and the Nemaha Uplift are well-known geologic features in the subsurface of southwestern and northcentral Oklahoma respectively.

Previous Investigations

The only stratigraphic and sedimentologic study on the Flowerpot Shale in Blaine and Major Counties to date was done by Fay (1964) who did a stratigraphic subdivision, particle size analyses, and petrographic study of the shale as a part of a research project published as Bulletin 98 of Oklahoma Geological Survey entitled "The Blaine and Related Formations of Northwestern Oklahoma and Southern Kansas." The petrography of the Upper Permian sequence in Kansas including the Flowerpot Shale was thoroughly studied by Swineford (1955). The Blaine Formation in northern Blaine County, which immediately overlies the Flowerpot Shale, has been investigated geochemically and mineralogically in detail by Everett (1962).

Methods of Investigation

The selection of measured sections depended upon the thickness as well as the quality of the exposure. Three sections in Major County and three sections in northern Blaine County, which are aligned somewhat along the outcrop strike of the shale (NW to SE) and spaced from 4 to 10 miles apart, (Figure 1) were measured. The thickness of the measured sections ranges from 72 feet to 196 feet. Successive channel samples were collected upward along cliff faces.

Minerals in the sample were identified by x-ray diffraction methods using both Siemens and Norelco units. A differential thermal analysis unit and an x-ray diffractometer furnace were used to complement the identification of clay minerals. A Siemens x-ray fluorescence unit was employed for quantitative chemical analysis of shale samples. Quantitative trace element analyses for boron, vanadium, nickel, and cobalt were performed using a Jarrel-Ash 1.5 meter Wadsworth Mount Grating Spectrograph.

In addition, thirty-one thin sections of selected samples including dolomite, siltstone, sandstone, and shale were examined with a petrographic microscope. Several shale samples were analyzed by pipette methods for comparison of their particle size distributions. The combination of decantation and high speed centrifugation methods was performed to collect the less-than-one-micron equivalent spherical diameter (esd) clay materials of 19 shale samples for analysis. A detailed description of techniques and procedures adopted in this project is included in Appendix A.

STRATIGRAPHY

El Reno Group

The El Reno Group, which was originally established by Becker (1929, p. 955) as the El Reno Formation, includes all beds from the top of the Hennessey Shale to the base of the Whitehorse Group, as recognized by the Oklahoma Geological Survey (Branson, C. C., 1960). Fay (1964, p. 12) stated:

In Blaine County, Oklahoma, the El Reno Group consists mainly of 750 feet of reddish-brown shale and evaporite beds of gypsum, anhydrite, and dolomite, divided (in ascending order) into the Flowerpot Shale (with the Chickasha Tongue in the middle), Blaine Formation, and Dog Creek Shale. The upper and lower contacts are here considered to be conformable.

There is a tendency for all the units in the El Reno Group to thin northward into Kansas.

Flowerpot Shale

The Flowerpot Shale was named by Cragin (1896, p. 24) for the highly gypsiferous varicolored shale overlying the Cedar Hills Sandstone and underlying the Medicine Lodge Gypsum at Flowerpot Mound, in Sec. 26, T. 32 S., R. 13 W., Barber County, Kansas. The name Flowerpot Shale is used for those rocks between the dolomite at the base of the Medicine Lodge Gypsum and the White Sandstone at the top of the Cedar Hills Sandstone as redefined by Norton (1939) and followed by subsequent

writers. Fay described the Flowerpot Shale in Blaine County as follows (1964, p. 14):

In Blaine County, Oklahoma, the Flowerpot Shale is 437 to 465 feet thick and may be subdivided into several distinct lithologic units. The upper 50 feet contains beds of gypsum, dolomite, and siltstone, some of which can be correlated over a distance of 200 miles. The next lower 40 feet is the typical Flowerpot type of reddish-brown silty clay shale with little or no gypsum, dolomite, or siltstone. The next lower 160 feet consists of alternating reddish-brown gypsiferous shales and light greenish-gray siltstones, the lower 115 feet of which grades southward in southern Blaine County into the Chickasha Formation and is termed the Chickasha Tongue, consisting of mudstone conglomerate, quartzose sandstone, siltstone, and interbedded silty clay shale. The remainder of the section below the Chickasha Tongue consists of 180 feet of reddish-brown silty clay shale with a few light greenish-gray siltstone beds.

This study concentrated on the upper 100 to 200 feet of the Flowerpot Shale in Major County and northern Blaine County. The six measured sections are described in Appendix C. The upper 70 to 80 feet of these measured sections are displayed (Figure 2) to show vertical and horizontal variations in lithology. The Medicine Lodge Gypsum tends to thin toward the southeast along the outcrop strike. The dolomite bed immediately underlying the gypsum also thins and is usually less than a few inches in thickness and is absent in many places in Blaine County. The highly gypsiferous shale in the uppermost portion of the Flowerpot Shale can be readily correlated from measured section M-A to measured section B-F. The first dolomite bed below the base of the Blaine Formation, though only a few inches thick can be easily traced from M-A to B-F over a distance of about 25 miles (Figure 2). The shale immediately below the dolomite bed, which is normally dark red-brown in the upper 1 to 2 feet and dark greenish-grey in the lower 3 to 4 feet in Major County, is physically and mineralogically different from the

Figure 2

- Measured Section M-A: NE $\frac{1}{4}$ SW $\frac{1}{4}$ SW $\frac{1}{4}$ Sec. 22, T. 22 N., R. 13 W., at the north side of highway 15, 6 miles west of the town Orenta, Major County.
- Measured Section M-B: SW $\frac{1}{4}$ NW $\frac{1}{4}$ Sec. 6, T. 21 N., R. 13 W., one mile east of Cheyenne Creek, Major County.
- Measured Section M-C: SE $\frac{1}{4}$ SW $\frac{1}{4}$ SW $\frac{1}{4}$ Sec. 24, T. 21 N., R. 13 W., 4 miles west of the town Fairview, Major County.
- Measured Section B-D: Center NE $\frac{1}{4}$ SW $\frac{1}{4}$ Sec. 10, T. 19 N., R. 12 W., 4.5 miles east of the town Longdale, Blaine County.
- Measured Section B-E: NE $\frac{1}{4}$ NE $\frac{1}{4}$ NE $\frac{1}{4}$ Sec. 26, T. 19 N., R. 12 W., one-half mile north of the town Ideal, Blaine County.
- Measured Section B-F: SW $\frac{1}{4}$ NE $\frac{1}{4}$ SE $\frac{1}{4}$ Sec. 23, T. 18 N., R. 12 W., north wall of Salt Creek Canyon, Blaine County.



Dolomite, argillaceous



Gypsum, massive or nodular



Shale, red-brown

Shale, red-brown,
slightly gypsiferous

Shale, greenish-grey

Shale, greenish-grey,
highly gypsiferous

Siltstone

Shale, red-brown, highly
gypsiferous

Sandstone, gypsiferous



Shale, red-brown, silty

Siltstone, argillaceous
red-brown and greenish-
grey, highly gypsifer-
ous or dolomiticShale, red-brown, intercalated
with thin greenish-grey shale,
highly gypsiferous

0 5 10
Vertical Scale in Feet

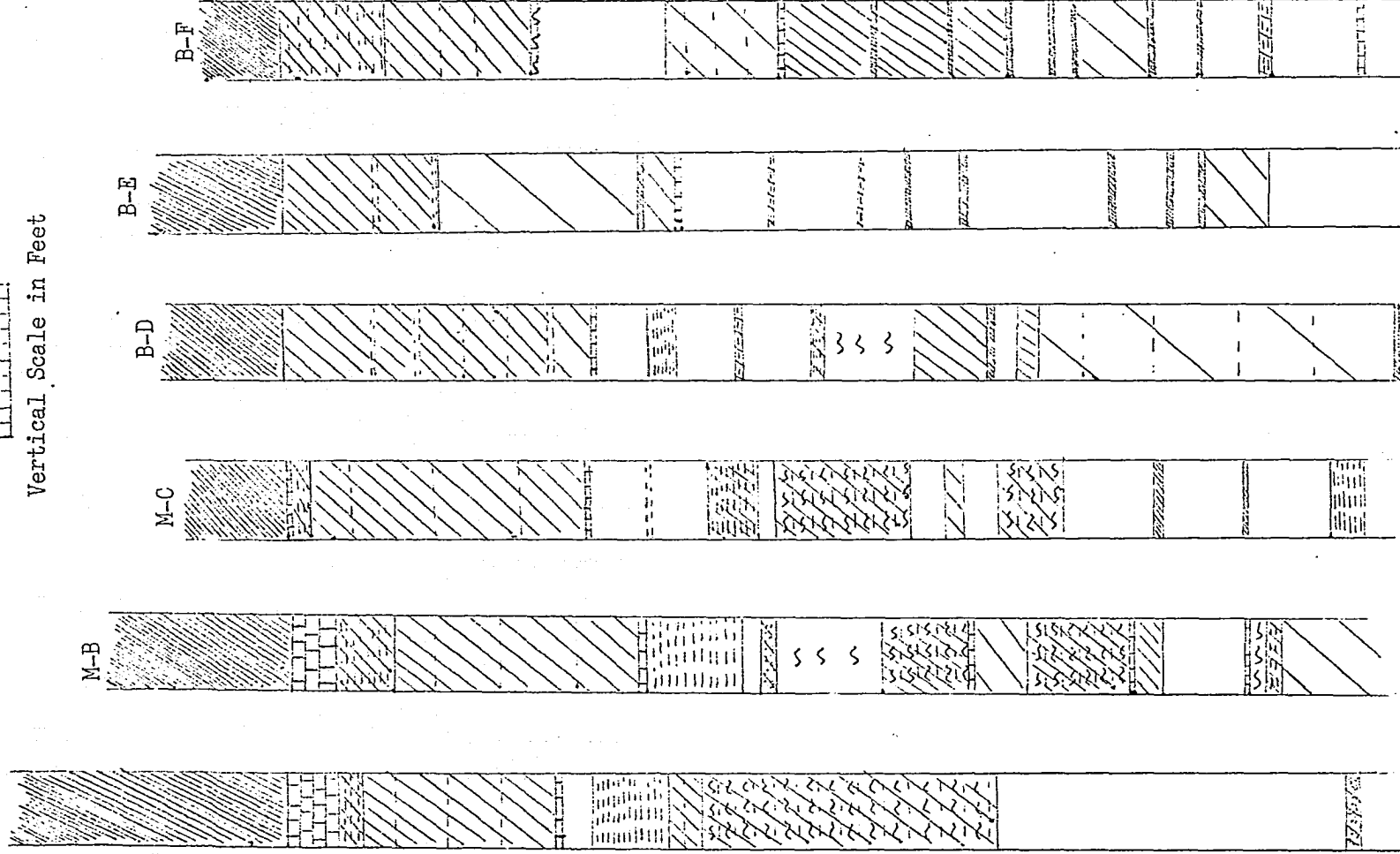


Figure 2. Columnar sections

common red-brown shale and greenish-grey shale of the remaining Flowerpot sequence. The shale loses its green color toward the south-east and grades into the common red-brown gypsiferous shale in section B-F.

The next lower portion of the sequence is composed essentially of red-brown and greenish-grey gypsiferous or dolomitic siltstones in Major County. The siltstones grade into red-brown silty shale or gypsiferous shale in Blaine County. The rocks below the siltstones consist mainly of red-brown shale intercalated with some nodular, thin gypsum beds. Below the illustrated portions of the sections, the rocks consist largely of red-brown gypsiferous shale in section M-A and red-brown shale intercalated with some light greenish-grey siltstones in section B-F.

MINERALOGY

Terrigenous Components

Quartz

Quartz grains in all thin sections examined range from medium silt size to very fine sand size. In general, the quartz grains are rather well sorted. The roundness of the quartz grains ranges from sub-angular to subrounded. Larger grains seem to show a better roundness than finer. They appear to be more angular than they actually are owing to partial replacement by dolomite or gypsum along selected surfaces (Plate IIA and Plate IIIB). This phenomenon is particularly apparent in some gypsum- or dolomite-cemented siltstones and sandstones.

The majority of quartz grains contain very few crystalline inclusions and vacuoles. Relatively straight extinction of most grains indicates that they are nearly strain free. In summary, most grains have the internal characteristics of igneous (plutonic) quartz (Folk, 1961). Pronounced or well developed quartz overgrowths was not observed.

Feldspar

The most abundant feldspar grains are orthoclase and plagioclase. Microcline is present in small quantities. Microcline is characterized by the gridiron twinning structure (Plate IIC). Plagioclase normally shows a conspicuous polysynthetic twinning of parallel, multiple bands

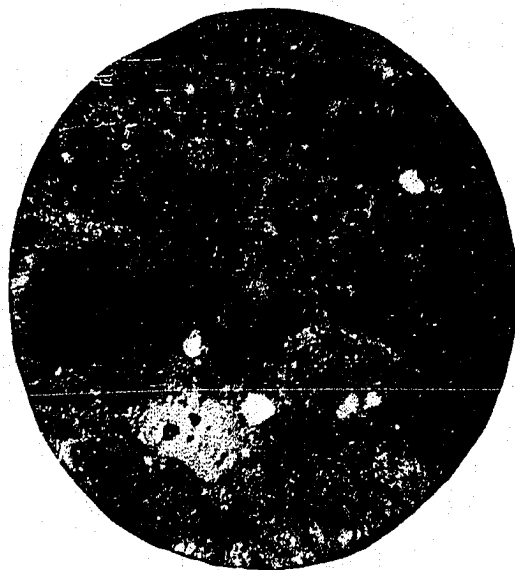
Plate II

Selected Photomicrographs

- A. A plagioclase grain with polysynthetic twinning (to the right of center) and a quartz grain (to the left of the center) are etched along the edges by dolomite. Thin section number 1735 Crossed nicols X183.
- B. Hematite-stained ooliths in quartz- and feldspar-bearing dolomitized oomicrite. Thin section number 1719. Crossed nicols X72.5.
- C. Microcline to the right of center showing gridiron structure in dolomite-cemented subarkosic siltstone. Thin section number 1732. Crossed nicols X183.
- D. An oolith showing concentric structure in quartz-bearing dolomicrite. Thin section number 1720. Crossed nicols X72.5.



A



B



C



D

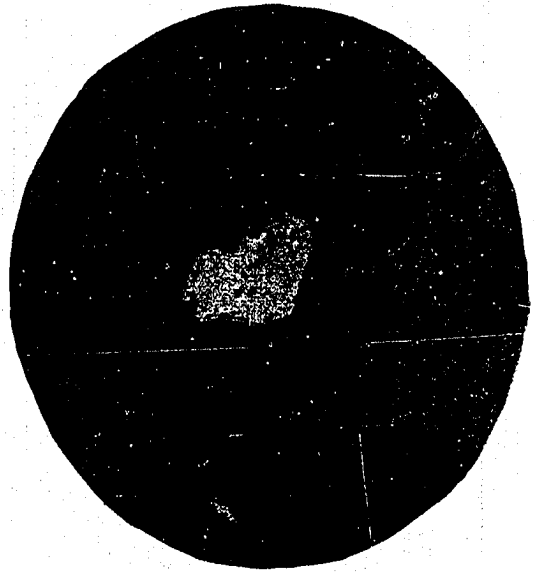
Plate III

Selected Photomicrographs

- A. A dolomite rhomb in gypsum-cemented subarkosic siltstone. Thin section number 1713. Crossed nicols X18.5.
- B. A quartz grain (center) etched along the edge by gypsum and big dolomite rhombs cemented together by gypsum. Thin section number 1725. Crossed nicols X183.
- C. Dolomite rhombs (black and grey) cemented together by gypsum. Thin section number 1725. Crossed nicols X18.5.
- D. An elongated flake of muscovite mica to the right of center in dolomite-cemented subarkosic siltstone. Thin section number 1732. Plane polarized light X72.5.



A



B



C



D

(Plate IIA, Plate IVA, and Plate IVC). Orthoclase has lower refractive indices than quartz and Canadian balsam. Some of the orthoclase grains show cleavages and cloudy surfaces due to incipient alteration. Orthoclase grains with Carlsbad twinning were found in two thin sections. Much of the feldspar is relatively fresh, but many degrees of weathering were observed. Feldspar grains are subangular to subrounded. Plagioclase seems to be more fresh and angular than orthoclase. Plagioclase grains etched and replaced by dolomite along the edges were observed in some sections (Plate IIA). Though feldspar was only positively identified in a few thin sections, it is present in almost all shale and siltstone samples as determined by x-ray diffraction.

Rock Fragments

A small number of metamorphic rock fragments such as chlorite schist and some fine-grained MRF's were found in siltstone and very fine-grained sandstone samples (Plate IVB and IVC). Sedimentary rock fragments such as chert, rounded carbonate, and gypsum grains also comprise a small percentage of the detrital grains.

Mica

Muscovite and a few biotite flakes, which are the common accessory minerals, occur as narrow lath-like crystals scattered in siltstone, sandstone, shale, and dolomite. Fine-grained muscovite (sericite) is present in nearly all thin sections examined and subparallel orientation of sericite is common in some shale and argillaceous dolomite samples. Biotite, which is green in color and strongly pleochroic, is present in a few thin sections. Swelling chlorite occurs

Plate IV

Selected Photomicrographs

- A. A plagioclase grain (center) with polysynthetic twinning in gypsum-cemented subarkosic siltstone. Thin section number 1713. Crossed nicols X72.5.
- B. An elongated subrounded chlorite-schist rock fragment surrounded by three quartz grains (white) to the upper left of center in fine-grained subarkose. Thin section number 1740. Crossed nicols X183.
- C. A fine-grained metamorphic rock fragment to the lower right of center and two plagioclase grains with polysynthetic twinning in fine-grained subarkose. Thin section number 1740. Crossed nicols X72.5.
- D. Dolomite composed of hematite-stained, rounded, dolomite grains. Thin section number 1737. Crossed nicols X72.5.



A



B



C



D

as irregular, light green, pleochroic flakes with low birefringence and low relief in some thin sections.

Heavy Minerals

The nonopaque heavy accessories such as tourmaline, zircon, rutile, and garnet were observed in thin sections of siltstone and sandstone. All occur as subangular to rounded detrital grains. The opaque heavy minerals include hematite, leucoxene, ilmenite, and magnetite.

Hematite is responsible for the red coloration of the shale. It stains clay and dolomicrite and also occurs as finely disseminated discrete particles. Concentration of hematite stains into red clusters and bands is common in shale, dolomite, and siltstone samples. Hematite coatings around detrital quartz and feldspar grains are either absent or insignificant.

Clay Minerals

General Statement

A total of 119 samples, among which 80 percent are shale samples, were studied by x-ray diffraction methods. Clay mineral identification was based upon x-ray diffraction characteristics of oriented clay aggregates and their response to solvation with ethylene glycol, heat treatment, and acid treatment. Differential thermal analyses were also performed as an identification aid.

Illite

The term illite was proposed by Grim, Bray, and Bradley in 1937 (Brown, 1961). It is a mica type clay mineral with a $10 \text{ \AA}^0$ c-axis spacing

which shows substantially no expanding-lattice characteristics. Illite differs from well-crystallized mica in having less substitution of aluminum for silicon in the tetrahedral layer. This results in a decrease in the charge deficiency and thus, in the amount of interlayer potassium. Some of the interlayer potassium may be replaced by hydronium ions (Brown and Norrish, 1952). Illite is normally finer in size and poorer in crystallinity than its mica counterpart.

Illite is present in all shale samples analyzed. It is one of the major constituents of the shale. The (060) reflection of the illite in the upper Flowerpot Shale ranges from 1.499 to 1.506 Å, which is characteristic of the dioctahedral type. With the exception of those shale specimens that contain a relatively high proportion of swelling chlorite, x-ray reflections between 1.53 and 1.55 Å, which fall into the (060) range of the trioctahedral structure, are either absent or very weak. The very weak peak in the range is most likely attributed to the presence of a small amount of chlorite in most shale samples. Some oriented clay aggregates show an asymmetrical 10 Å broad peak tailing toward the higher d-spacing. This is probably due to the small particle size, variation in the interlayer cation, and some slight interlayer hydration (Grim, 1968).

The polymorphism of illite was determined by comparison of the powder x-ray data with that of Yoder and Eugster (1955). Some specimens were pretreated with warm dilute hydrochloric acid to eliminate chlorite, swelling chlorite, dolomite and other contaminations so that polymorphism of illite could be firmly identified. In the less-than-230-mesh fraction of shale, the 2M type with a minor amount of 1M is the dominant mica

polymorphs, whereas the less-than-one-micron clay fraction contains only a 1M type of illite. It is probable that the 2M and 1M types of illite were derived from different sources.

The sharpness of the illite peak was defined as the ratio of the peak height of 10 Å peak to its width measured at one-half of peak height. The sharpness of illite in the coarser fraction is better than that in the less-than-one-micron (esd) fraction (Table 1 and Table 2). The phenomenon could be explained either by the poor crystallinity due to decreasing particle size or the degraded character of the finer illite particles. As shown in Table 1 and Table 2, no general rule of vertical variation in the peak sharpness of illite can be seen in any of the measured sections.

DTA curves of illite in the upper Flowerpot Shale show a pronounced endotherm at about 80 to 100 degrees centigrade. This corresponds to the loss of interlayer water (Grim, 1968). A second endotherm begins at about 400 degrees centigrade with a peak at about 540 degrees centigrade. This coincides with the loss of OH lattice water (Grim, 1968). Grim and Bradley (1940) showed that the loss of OH water in the illite studied by them is not accompanied by a loss of structure. The third slight endotherm at about 850 degrees centigrade correlates with the destruction of the illite structure (Grim, 1968). The exotherm at about 900 degrees centigrade coincides with the formation of a new mineral phase of spinel.

Chlorite and Swelling Chlorite

Structurally the chlorites are regular interstratifications of single biotite-type mica layers and brucite layers (Grim, 1968). The

TABLE 1.--Vertical stratigraphic variations in "swelling chlorite index" and "sharpness of illite" (bulk shale samples)

Sample No.	14.7 ^a	10H/10W ^b	Swelling of 14 Å Peak
B-F-48	0.95	17.4	o
B-F-44	1.56	12.9	o
B-F-41	0.86	6.6	x
B-F-37	1.45	8.0	x
B-F-28	0.98	19.0	x
B-F-22	0.81	11.8	x
B-F-17	0.82	11.9	x
B-F-16	1.21	16.9	x
B-F-12	0.73	11.0	x
B-F-10	0.73	2.2	x
B-F-7	1.36	10.6	x
B-F-2	1.25	14.8	x
B-F-1	0.66	18.5	x

B-E-24	0.90	11.8	o
B-E-22	1.26	12.1	o
B-E-20	0.91	13.1	o
B-E-18b	1.23	13.1	o
B-E-18a	1.16	14.4	o
B-E-4	0.57	26.7	x
B-E-1	0.74	17.1	x

B-D-27	1.47	6.3	o
B-D-20	1.79	8.7	o
B-D-19	1.46	10.6	o
B-D-14	1.20	12.3	x
B-D-9	0.97	12.6	x
B-D-7	1.06	13.0	x
B-D-6	1.00	9.3	x
B-D-5	1.10	9.8	x
B-D-4	1.00	19.8	x
B-D-3	0.75	6.2	x
B-D-1	1.00	9.6	x

^aindicates the peak height ratio of 14 Å peak to 10 Å peak.

^bindicates the ratio of 10 Å peak height to the width at one-half peak height.

Note: x indicates no swelling with treatment by ethylene glycol.

o indicates partial swelling resulting in splitting into two peaks.

TABLE 1.--(Continued)

Sample No.	14.7 ^a	10H/10W ^b	Swelling of 14 Å Peak
M-C-15	4.65	6.9	oo
M-C-12	1.63	4.7	o
M-C-11	1.20	6.3	x
M-C-7	1.28	3.2	x
M-C-5	1.20	6.1	x
M-C-2	0.96	6.3	x
M-C-1	1.17	14.8	x
M-A-19	2.33	12.7	oo
M-A-18	1.80	8.0	oo
M-A-14	3.83	15.6	oo
M-A-13	5.00	7.8	oo
M-A-12	1.20	22.0	oo
M-A-11	1.13	20.0	o
M-A-10	1.10	11.8	x
M-A-8b	0.67	10.0	x
M-A-8a	0.47	8.7	x
M-A-7	0.59	7.8	x
M-A-6	0.48	10.3	x
M-A-5	0.62	7.3	x
M-A-3d	0.56	10.8	x
M-A-3c	0.42	7.7	x
M-A-3b	0.75	12.0	x
M-A-3a	0.65	14.7	x
M-A-1	0.63	7.2	x

^a indicates the peak height ratio of 14 Å peak to 10 Å peak.

^b indicates the ratio of 10 Å peak height to the width at one-half peak height.

Note: x indicates no swelling with treatment by ethylene glycol.

oo indicates swelling to around 15.3 Å.

o indicates partial swelling resulting in splitting into two peaks.

TABLE 2.--Vertical stratigraphic variations in "swelling chlorite index" and "sharpness of illite" (selected less-than-one-micron samples)

Sample No.	14/7 ^a	10H/10W ^b	Swelling	
			14 ^o	7 ^o
B-F-41	0.82	2.7	x	x
B-F-28	1.00	1.5	x	x
B-F-20	1.43	2.2	x	x
B-F-15	0.88	2.4	x	x
B-F-14	1.33	2.6	x	x
B-F-10	1.20	2.2	x	x
B-F-1	0.50	1.3	x	x
B-E-18b	3.44	8.2	o	o
B-E-18a	2.38	5.8	o	o
B-E-8	0.60	1.8	x	x
B-D-21	2.75	3.4	oo	o
B-D-20	5.86	5.0	oo	o
B-D-14	1.29	3.9	x	x
M-A-19	2.54	3.8	oo	o
M-A-14	9.29	8.6	oo	o
M-A-13	10.45	7.0	oo	o
M-A-10	1.25	4.1	x	x
M-A-5	0.88	3.8	x	x
M-A-1	0.92	4.7	x	x

^aIndicates the peak height ratio of 14 Å peak to 10 Å peak.

^bIndicates the ratio of 10 Å peak height to the width at one-half peak height.

Note: x indicates no swelling with treatment by ethylene glycol.

oo indicates swelling to around 15.3 Å.

o indicates partial swelling resulting in splitting into two peaks.

many varieties of chlorite result from the kind and amount of substitution in the brucite layer and the tetrahedral and octahedral positions of the mica layer, and from the stacking of successive chlorite units. The most common substitution are aluminum and iron for magnesium both in the octahedral sites of mica layer and the brucite layer, and aluminum for silicon in the tetrahedral sites of the mica layer.

Chlorite is present in almost all samples of the upper Flowerpot Shale, but it normally is present in small amounts. The determination of chlorite is based on the presence of an integral series of diffraction peaks with a $14 \text{ \AA}$ periodicity. Upon heating to 600 degrees centigrade, the (001) peak increases in intensity and shifts to a smaller d-spacing, whereas the (002), (003), and (004) peaks decrease considerably in intensity. When treated with warm, dilute hydrochloric acid, no x-ray diffraction lines of chlorite persist. Chlorite does not swell after solvation with ethylene glycol with the exception of "swelling chlorite."

Swelling chlorite has been described as a mineral with a $14 \text{ \AA}$ spacing which does not collapse on heating and which expands slightly to between $16 \text{ \AA}$ and $18 \text{ \AA}$ following treatment with ethylene glycol (Grim, 1968). This spacing was regarded as due to a single-layer of glycerol molecules (thickness $4 \text{ \AA}$) between chlorite layers (thickness $14 \text{ \AA}$). Such swelling chlorites appear to be rather imperfect structures in which the brucite layers may be discontinuous, resembling islands between the mica layers and leaving channels through which glycerol may diffuse (Brown, 1961). Swelling chlorite-like minerals are present only at the top of the Flowerpot Shale. They normally occur in association with nonexpandable chlorite. The routine identification of the swelling

chlorite was based upon a more intense $14\text{ \AA}$ basal reflection than the subsequent lower orders of reflection on x-ray diffractograms. Upon treatment with ethylene glycol it expands from about $14.3\text{ \AA}$ to $15.3\text{ \AA}$ (Figure 3). The association of ordinary chlorite with swelling chlorite was verified by the maintenance of a nonexpandable peak at $14\text{ \AA}$ after solvation with ethylene glycol. When swelling chlorite exists in a greater amount, the nonexpandable $14\text{ \AA}$ chlorite peak is normally overshadowed by the broad, shifted swelling-chlorite peak upon solvation. However, the split of the $7\text{ \AA}$ peak into two peaks at about $7\text{ \AA}$ and $7.7\text{ \AA}$ on solvation could indicate the existence of some nonexpandable chlorite material. Montmorillonite, on the other hand, normally shows full expansion to about $17\text{ \AA}$ on treatment with ethylene glycol. Certainly the swelling chlorite is similar to vermiculite, but DTA and diffractometer furnace analyses do show that it has a closer affinity to chlorite. The $14\text{ \AA}$ peak of the swelling chlorite does not contract to $10\text{ \AA}$ on treatment with potassium acetate, although Weaver (1958a) found that clay vermiculites with a high surface charge density readily contract to about $10\text{ \AA}$ on K-treatment.

The less-than-one-micron (esd) clay material of the sample M-A-13 which shows prominent and expandable $14\text{ \AA}$ reflections on x-ray diffractograms was selected for analysis by the x-ray diffractometer furnace. The oriented clay sedimented on a platinum slide was heated for 25 minutes in the x-ray diffractometer furnace to 100, 200, 300, 400, 500, 600, 700, and 750 degrees centigrade. Nine diffractograms of the oriented clay slides are displayed in Figure 4 to show the successive changes upon heating at the aforementioned temperatures. The relative

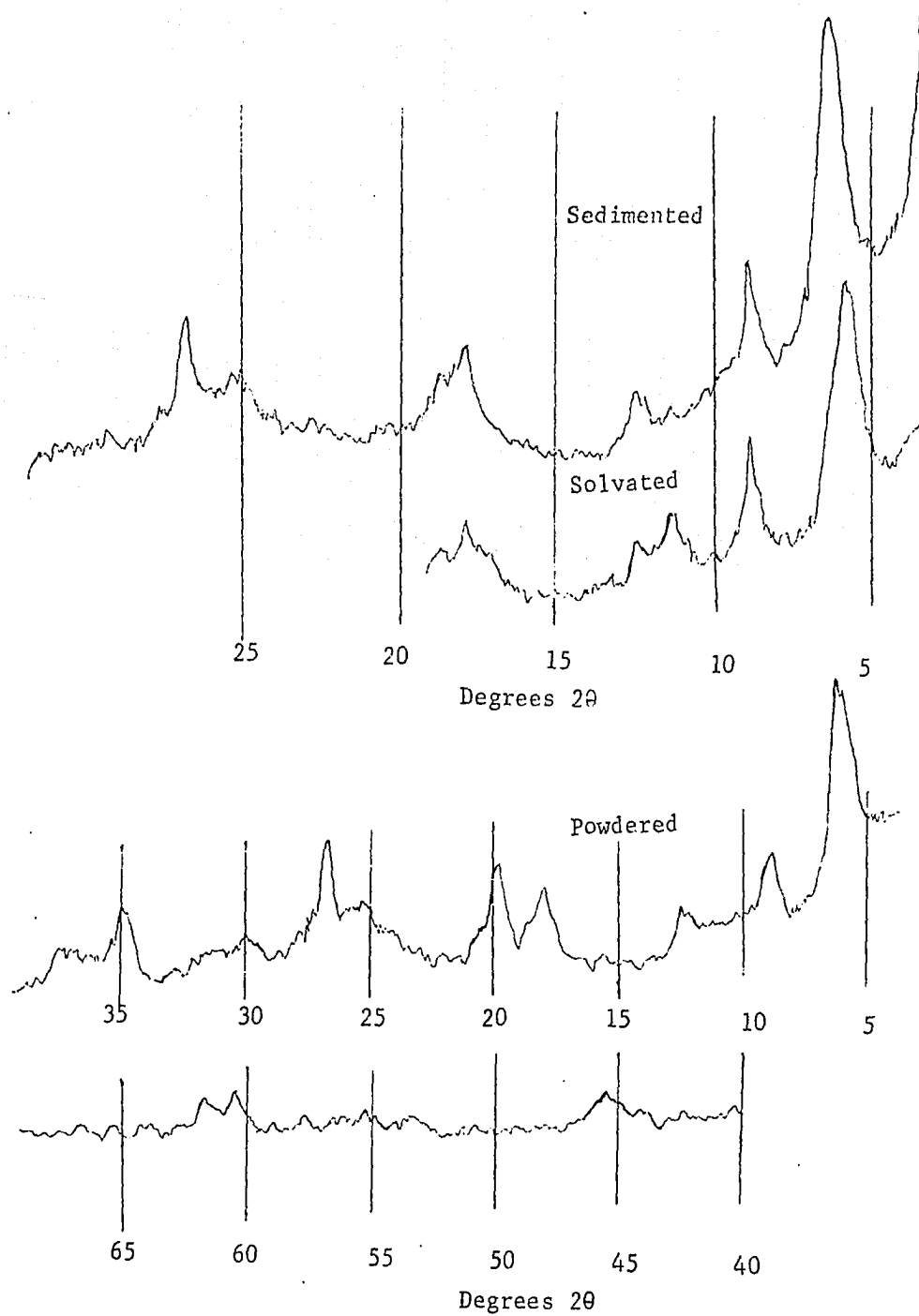


Figure 3. X-ray diffractograms of a selected sample (M-A-13) showing the characteristics of swelling chlorite and illite

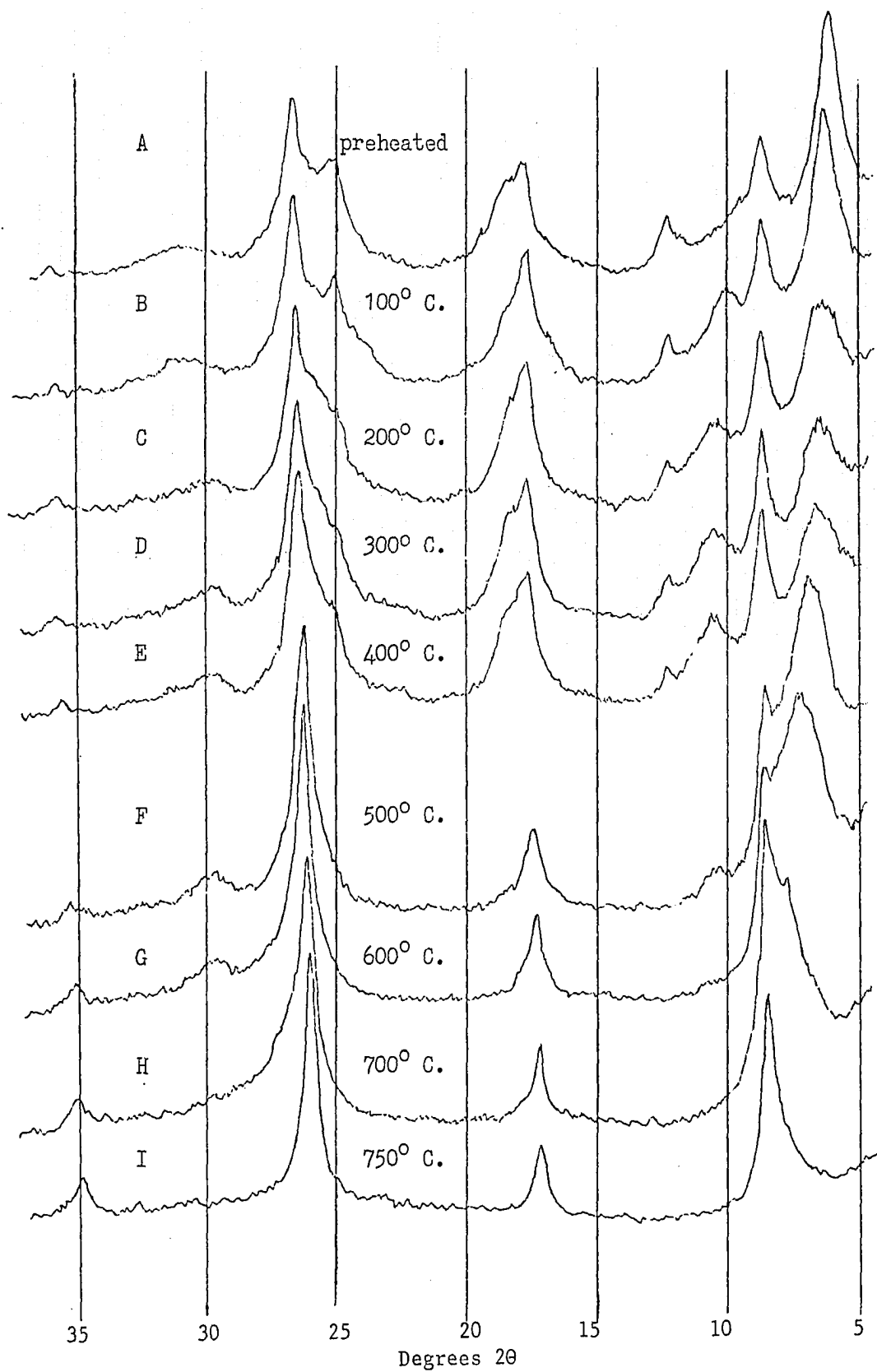


Figure 4. X-ray preferred orientation diffractograms of M-A-13 showing modifications of swelling chlorite with heat treatment in diffractometer furnace (less-than-one-micron fraction)

intensities and d-spacings of (001) reflections of the $14 \text{ \AA}$ material show no appreciable change below 100 degrees centigrade. An additional peak at about 10 degrees 2θ ($8.85 \text{ \AA}$) appears at around 100 degrees centigrade (Figure 4B). The $14 \text{ \AA}$ peak begins to decrease in intensity between 160 and 180 degrees centigrade. After heating to 200 degrees centigrade, in addition to having a broader and less intense $14 \text{ \AA}$ peak, the $8.85 \text{ \AA}$ peak shifts to about $8.35 \text{ \AA}$ (Figure 4C). No appreciable change occurs between 200 and 400 degrees centigrade (Figure 4D and Figure 4E). At about 485 degrees centigrade, the $14 \text{ \AA}$ peak begins to increase in intensity. At 500 degrees centigrade, the (001) peak increases considerably in intensity and shifts slightly to a smaller d-spacing, and (002), (003), (004) peaks disappear (Figure 4F). The $8.35 \text{ \AA}$ peak also decreases in intensity. After heating to 600 degrees centigrade, the $8.35 \text{ \AA}$ peak almost disappears and the (001) peak shifts to around 7.3 degrees 2θ (Figure 4G).

After modification by heating at 700 degrees centigrade, the (001) peak shifts to about 7.9 degrees 2θ and partially overlaps the (001) illite peak (Figure 4H). The temperature of complete collapse of the (001) peak is around 720 degrees centigrade. Upon modification by heating up to 750 degrees centigrade, the x-ray diffraction pattern shows only the (001) basal reflections of a $10 \text{ \AA}$ illitic material (Figure 4I).

According to the study by Gruner (1934), the structure of Mg-vermiculite resembles those of mica or talc between which are double sheets of water molecules occupying a space very nearly equal to that of a brucite layer in the chlorite structure. Because the octahedral

layers of mica sheets and the layers with Mg cations surrounded by water molecules are not spaced exactly at intervals of $d(001)/2$ and because the cation type and number are not expected to be evenly distributed between the two kinds of layers in Mg-vermiculite structure, the atoms in these layers (The oxygen ions and the cations) would not scatter waves exactly out of phase and thus, the atoms at octahedral positions make some contributions to the structure factor (F) of the (001) reflection. This is probably the reason that the (001) reflection of vermiculite is very strong in intensity. The strong $14 \text{ \AA}$ peak of the swelling chlorite in the Flowerpot Shale could be explained in a similar way. The interlayer positions of mica layers could contain a mixture of discontinuous brucite islands and water layers. The electrostatic forces between brucite layers and mica layers are probably not strong enough to keep from partial swelling upon solvation with ethylene glycol. Although the increased intensity of the $14 \text{ \AA}$ reflection and disappearance of other basal reflections after heating at 500 degrees centigrade coincide perfectly with the character of chlorite, the gradual collapse of the $14 \text{ \AA}$ peak toward $10 \text{ \AA}$ from 500 to 720 degrees centigrade is somewhat affiliated with vermiculite. The swelling chlorite-rich samples usually show an endothermic peak at about 580 degrees centigrade which partially overlaps the illite endothermic peak at 540 degrees centigrade (Figures 6, 7, and 8). The 580 degrees centigrade endotherm is characteristic of chlorite rather than vermiculite. The progressive removal of hydroxyl water and bounded water from the interlayer positions of mica layers may account for the gradual collapse of the (001) reflection from $14 \text{ \AA}$ to $10 \text{ \AA}$. Nevertheless, the (001) reflection for ordinary chlorite does not

collapse below about $13.9 \text{ \AA}$ with heat treatment and even at 700 degrees centigrade, only about two-thirds of the hydroxyls of the brucite layer have been removed and the magnesium atoms move away from their original position in a plane midway between the mica sheets to positions directly adjacent to the mica unit surface (Grim, 1968). Therefore, the collapse of the (001) reflection of the swelling chlorites from $14 \text{ \AA}$ to $10 \text{ \AA}$ may be explained as the complete dehydration of incomplete brucite layer. The mechanism of complete dehydration of brucite layers at 720 degrees centigrade is not clear; it could be due to the poor crystallinity and weak bonding forces of the discontinuous brucite islands. Some $14 \text{ \AA}$ layers perhaps start collapsing to $10 \text{ \AA}$ at a temperature as low as 100 degrees centigrade as demonstrated by the progressive enhancement of $10 \text{ \AA}$ peak with increasing temperatures (Figure 4).

The appearance of a broad peak at about $8.8 \text{ \AA}$ after heating the sample to 100 degrees centigrade may be due to the third order basal reflection of material with 26 to $27 \text{ \AA}$ periodic repetitions which could be a regular interstratification of $14 \text{ \AA}$ and probably a partially dehydrated $14 \text{ \AA}$ layer. The shifting of the peak to $8.35 \text{ \AA}$ at 200 degrees centigrade could represent further dehydration probably resulting in an interstratification of $14 \text{ \AA}$ and $11 \text{ \AA}$ layers. The disappearance of the peak at about 600 degrees centigrade may imply the collapse of the interstratified $14 \text{ \AA}$ layer to about $10 \text{ \AA}$. The hypothesis is based upon the assumption that there are regular alternations of $14 \text{ \AA}$ layers with mixture of water layers and poorly-crystallized brucite islands and $14 \text{ \AA}$ layers with relatively intact brucite structures. The trioctahedral nature of the swelling chlorite is demonstrated by the (060)

reflection at about $1.531 \text{ \AA}$ (Figure 3). Kaolinite is ordinarily not decomposed by the treatment of warm dilute hydrochloric acid. Acid treatment of some shale samples has proved the absence of kaolinite in the upper Flowerpot Shale.

Zonation of Swelling Chlorite

The swelling chlorite shows a very strong $14 \text{ \AA}$ peak and a weak $7 \text{ \AA}$ peak. Regular chlorite normally shows a stronger $7 \text{ \AA}$ peak than $14 \text{ \AA}$ peak on x-ray diffractograms. Thus, the ratio of the $14 \text{ \AA}$ peak height to the $7 \text{ \AA}$ peak height has been arbitrarily defined as the "swelling chlorite index." Values of the indices of selected shale samples from different stratigraphic levels were calculated based upon the x-ray diffraction peaks of oriented clay samples. The calculated figures of the indices are listed in Table 1 and Table 2 where the former contains those of bulk shale samples and the latter includes those of less-than-one-micron (esd) clay materials. As shown in the two tables, the swelling chlorite obviously concentrates at the top portion of the upper Flowerpot Shale. It is also evident that swelling chlorite tends to be highly concentrated in the 5 to 6 feet of dark greenish-grey and dark red-brown shale immediately underlying the first dolomite bed below the Blaine Formation. The change from illite-rich shale to swelling chlorite and illite-rich shale seems to be gradual and the presumed boundary ranges from about 30 to 45 feet below the base of the Medicine Lodge Gypsum. Swelling chlorites are also present in those argillaceous dolomites and siltstones that are above the aforementioned boundary. But the presumed boundary tends to become obscure toward the southeast along the outcrop strike of

the shale. No appreciable amount of swelling chlorite is present in samples collected above the presumed boundary at the measured section B-F which is the southernmost of the six sections measured (Figure 9). As shown in Figure 5, however, swelling chlorite showing a conspicuous $14 \text{ \AA}$ peak on x-ray diffractograms exists only at the top portion of measured section M-A. The corresponding DTA curves of swelling chlorite are characterized by the 580 degrees centigrade endothermic peak superimposed on the broad illite endothermic peak (Figure 6). The same phenomenon can be observed in measured sections B-D and B-E as shown in Figures 7 and 8.

Everett (1962) concluded that the chlorite of the Blaine Formation in northern Blaine County is predominantly iron-rich due to the presence of strong $7 \text{ \AA}$ and $3.5 \text{ \AA}$ order reflections and weak $14 \text{ \AA}$ and $4.7 \text{ \AA}$ order reflections. The presence of a 520 to 540 degrees centigrade endotherm on the DTA pattern was also used by Everett to support the conclusion that iron-rich chlorite was present. After carefully examining the x-ray and DTA data of his work on file in the X-ray Laboratory of the School of Geology and Geophysics at the University of Oklahoma, his evidence for the presence of iron-rich chlorite would seem to be questionable. The $14 \text{ \AA}$ peak is stronger than the $7 \text{ \AA}$ peak on almost all his x-ray diffractograms on file. The 520 to 540 degrees centigrade endotherm may represent the endothermic peak of illite. For a normal chlorite of either the iron-rich or magnesium-rich variety, one does not expect a stronger $14 \text{ \AA}$ reflection than a $7 \text{ \AA}$ reflection. The phenomenon could imply the presence of the same swelling chlorite as that found in the present study. As illustrated on his x-ray diffractogram,

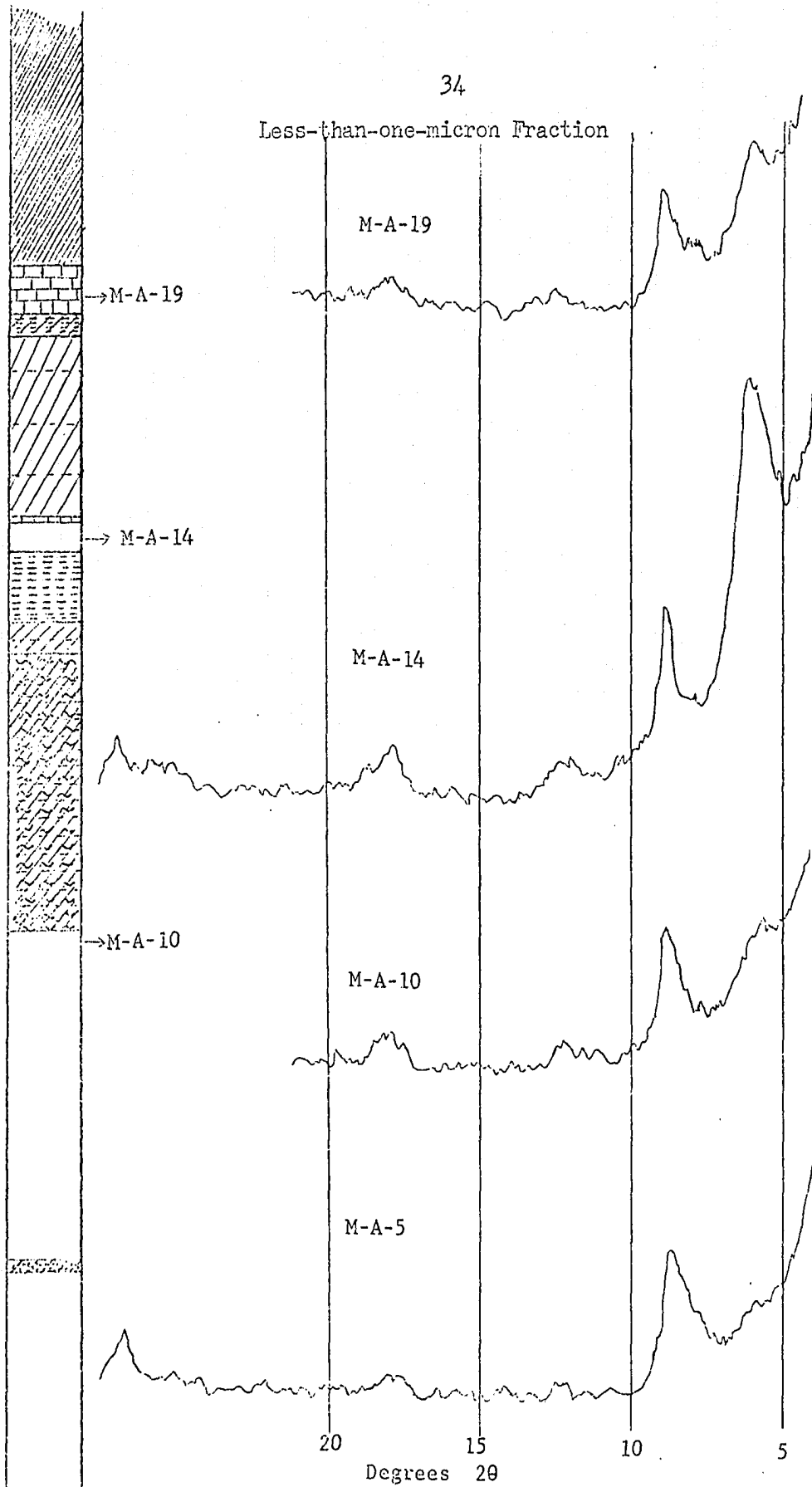


Figure 5. X-ray preferred orientation diffractograms showing the presence of swelling chlorite at the upper portion of measured section M-A

Less-than-one-micron Fraction

M-A-19

900 Degrees C.

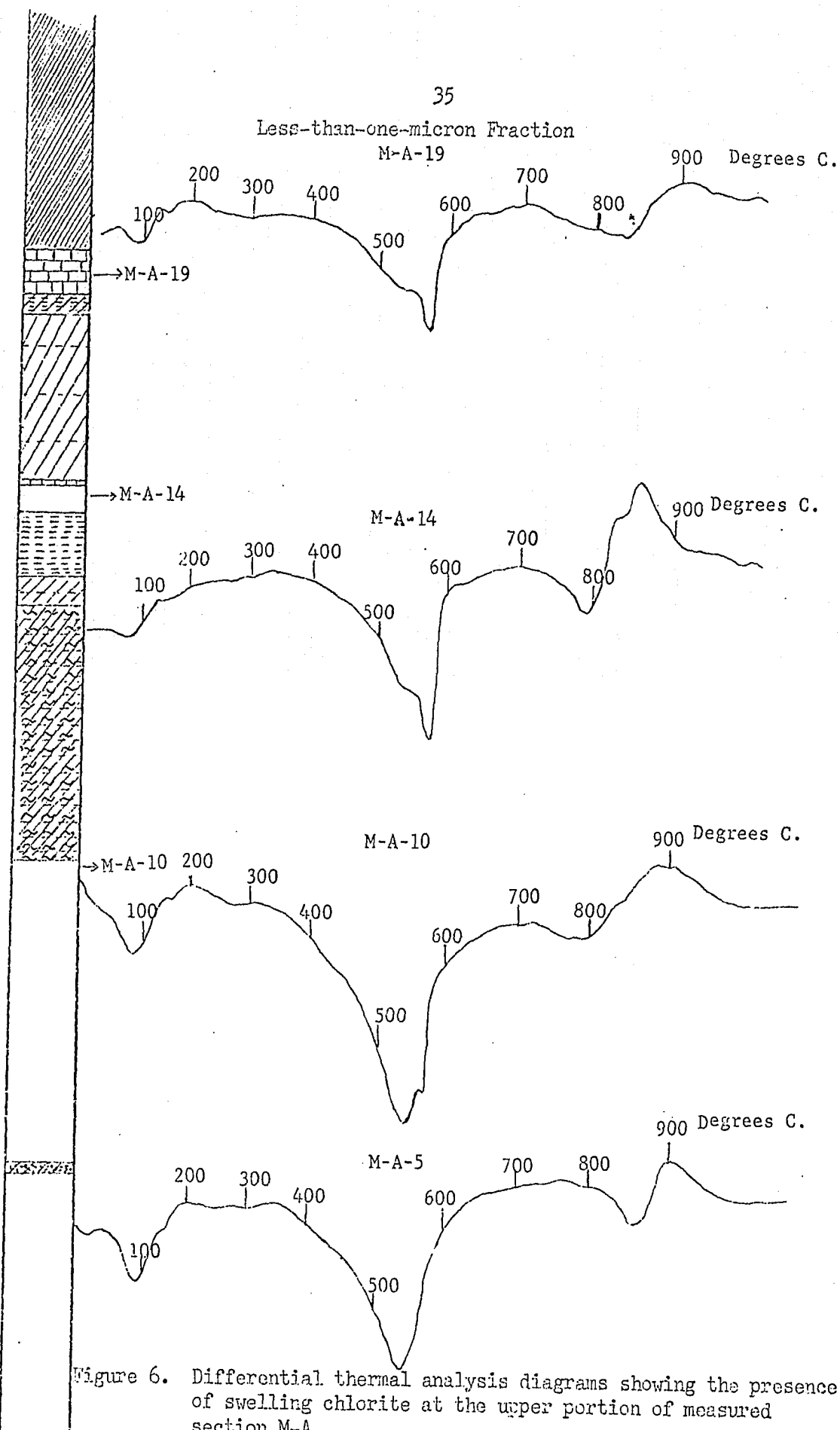


Figure 6. Differential thermal analysis diagrams showing the presence of swelling chlorite at the upper portion of measured section M-A

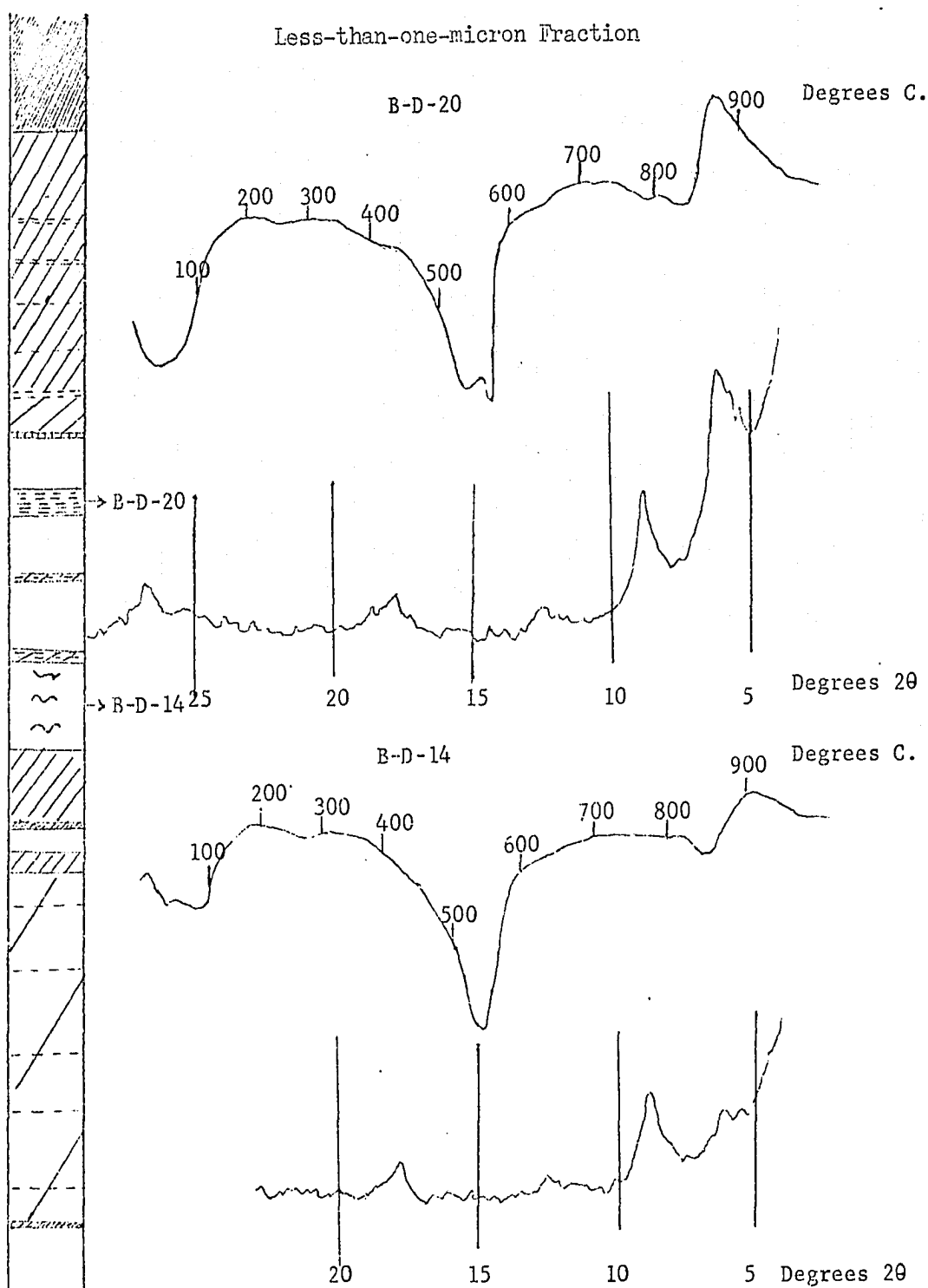
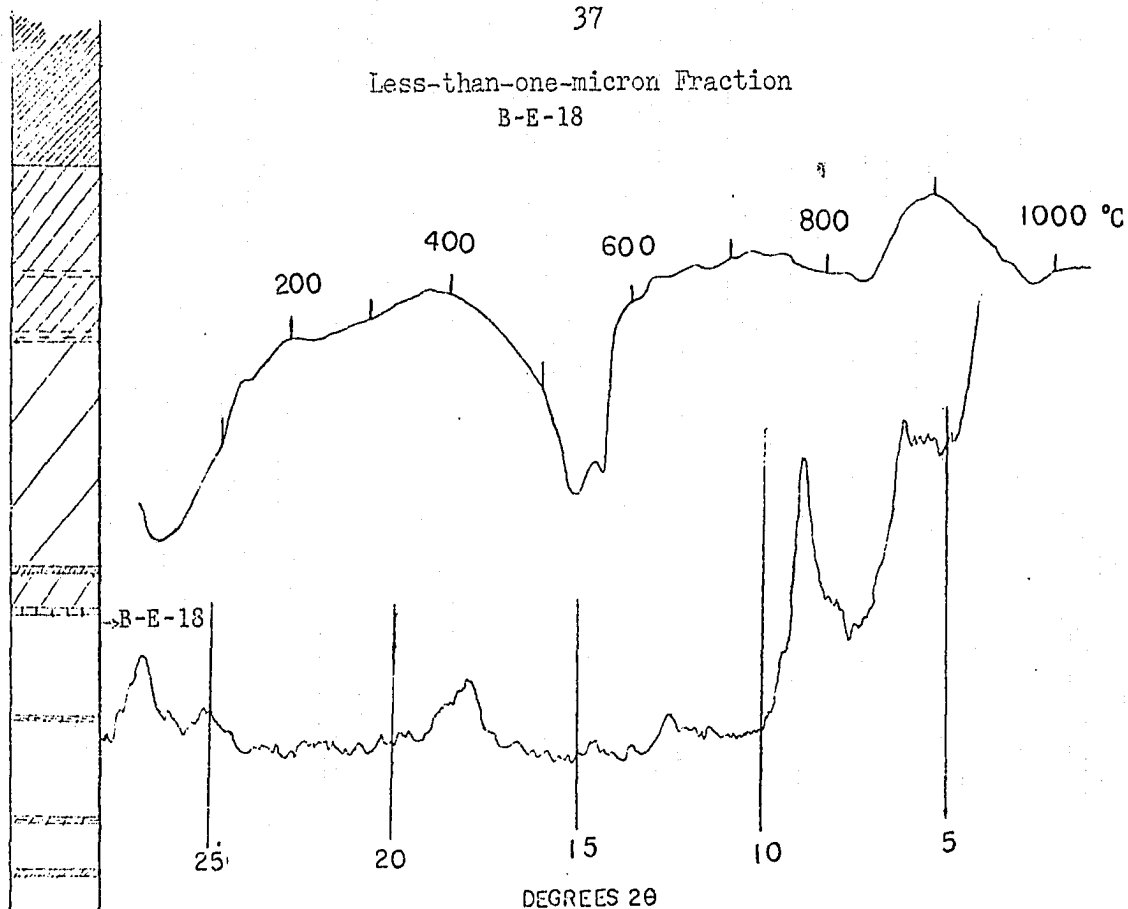


Figure 7. DTA diagrams and x-ray preferred orientation diffractograms of two selected samples below and above the presumed boundary of swelling chlorite occurrence in measured section B-D

Less-than-one-micron Fraction
B-E-18



B-E-8

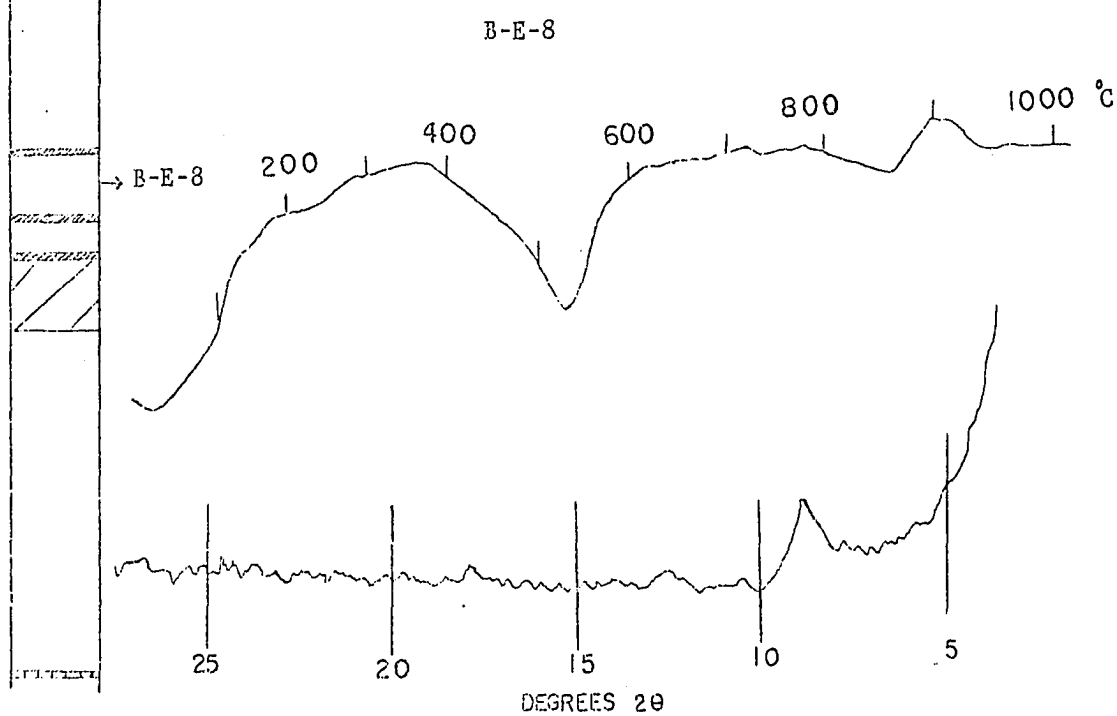


Figure 8. DTA diagrams and x-ray preferred orientation diffractograms of two selected samples below and above the presumed boundary of swelling chlorite occurrence in measured section B-E

Less-than-one-micron Fraction

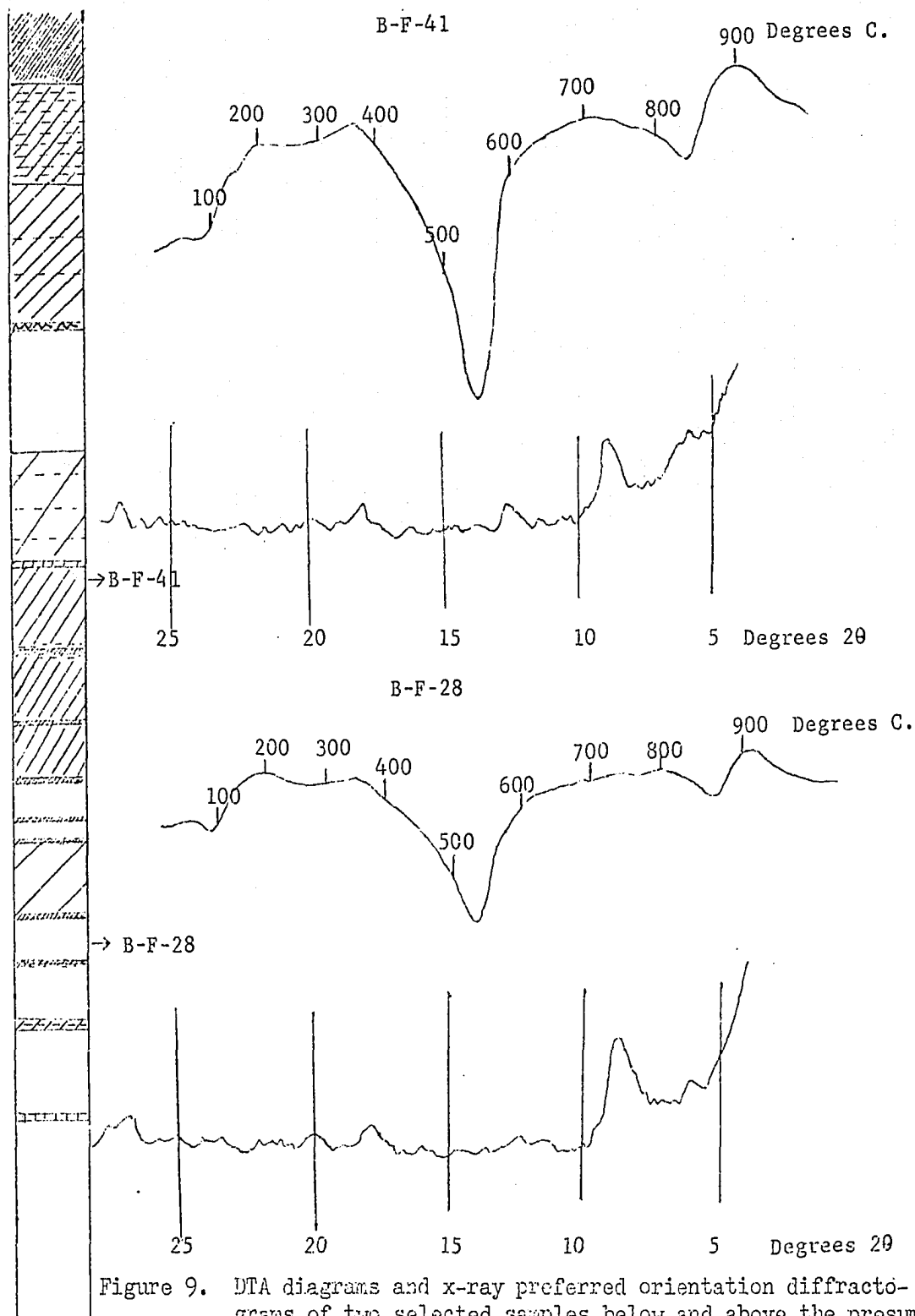


Figure 9. DTA diagrams and x-ray preferred orientation diffractograms of two selected samples below and above the presumed boundary of swelling chlorite occurrence in measured section B-F

the $14 \text{ \AA}$ reflection of some of his specimens such as U. S. 23 did expand to about $16 \text{ \AA}$ after treatment with glycerol. Some DTA curves of his Blaine Shale samples did show a peak at about 580 degrees centigrade which coincides with the swelling chlorite peak described in the present study. Hence, the swelling chlorite and illite-rich zone could probably extend into the Blaine Formation which immediately overlies the Flowerpot Shale.

High Temperature Phases of Clay Minerals

Less-than-one-micron (esd) fractions of clay samples and some bulk shale samples were heated to 1000 degrees centigrade for 12 hours in an oven and then, the high temperature products of the clay samples were identified by x-ray diffraction methods. The fired illite-rich shale consists of a spinel phase with the three principal peaks at $2.44 \text{ \AA}$, $1.43 \text{ \AA}$, and $2.87 \text{ \AA}$. Hematite shows more distinct reflections on the x-ray diffractograms after heating than before. For those samples containing a high percentage of swelling chlorite the mineral enstatite forms in addition to spinel. The enstatite is characterized by three principal reflections at $3.13 \text{ \AA}$, $2.86 \text{ \AA}$, and $2.49 \text{ \AA}$ compared to $3.17 \text{ \AA}$, $2.87 \text{ \AA}$, and $2.49 \text{ \AA}$ for the enstatite of ASTM card number 7-216.

On heating several illite samples, Grim and Bradley (1940) found spinel appearing in all of them at about 850 degrees centigrade and the spinel increased in amount and particle size up to about 1200 degrees centigrade. They also proposed that alumina, magnesia, and iron from the octahedral sheet goes into the formation of spinel, and that the silica from the tetrahedral layers and the alkalis form an amorphous

glass. Brindley and Ali (1950) showed that other high-temperature phases such as enstatite and spinel in addition to olivine formed when various chlorites were heated. The lack of olivine in the high temperature phases of the swelling chlorite is perhaps due to a relative deficiency in magnesium as compared to the ordinary chlorite.

Authigenic Components

Gypsum

Other than in the massive beds, gypsum occurs as fibrous cement in some siltstones and sandstones (Plate IIIA and IVB). Gypsum also forms selenite and satin spar veins parallel to and intersecting bedding planes. Gypsum was also found as cavity fillings in dolomite or as a matrix surrounding dolomite rhombs (Plate IIIC).

Dolomite

Other than in the bedded dolomite unit, dolomite occurs as a cementing material in siltstones and sandstones (Plate IIC). It is also present as rhombohedral crystals in some shales and siltstones (Plate IIIA). Veins and clusters of sparry dolomite are commonly found in the dolomicrite which is the most common dolomite type present in the upper Flowerpot Shale.

Analcite

Definition

Analcite (Analcime) is commonly included as a member of the zeolite group, but it has a higher temperature paragenesis than the other

zeolites and a close affinity to the feldspathoids. Analcite is defined by Deer, Howie, Zussman (1966, p. 389) as follows:

Analcite is cubic with $a=13.7 \text{ \AA}$ and 16 $(\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O})$ per unit cell. Its aluminosilicate framework is built of $(\text{SiAl})\text{O}_4$ tetrahedra linked in such a way that each corner oxygen is shared by two tetrahedra, the framework containing rings of six tetrahedra and of four tetrahedra respectively normal to triad and tetrad axes. A set of sixteen large cavities forming continuous channels are occupied by water molecules, whereas of [in] an adjacent set of twenty-four smaller cavities sixteen are occupied by sodium and the remainder are vacant. . . .

Stratigraphic Distribution

Analcite was identified by the presence of three major peaks at $5.60 \text{ \AA}$, $3.43 \text{ \AA}$, and $2.93 \text{ \AA}$ and some minor peaks on the randomly-oriented x-ray diffractograms (Figure 10). The DTA diagram of analcite shows a broad endothermic peak at around 280 degrees centigrade (Figure 10). As reported by Koizumi (1953), analcite (analcime) dehydrates so slowly and gradually between 200 degrees centigrade and 400 degrees centigrade that in DTA diagrams only a broad endothermic curve is obtained without a sharp endothermic peak. Analcite was found in the lower stratigraphic level of the measured sections B-D and B-F. In the measured section B-D, analcite occurs somewhere below the lithologic unit B-D-7 which is about 80 feet below the base of Medicine Lodge Gypsum. No analcite reflections were found on x-ray diffractograms of the samples collected above this level. The upper boundary of analcite occurrence in the measured section B-F is somewhere between 90 and 110 feet below the base of Medicine Lodge Gypsum. The lower boundaries of analcite occurrence are stratigraphically below the lowest units measured in sections B-D and B-F because x-ray detectable amounts of analcite

B-D-1 Bulk Sample

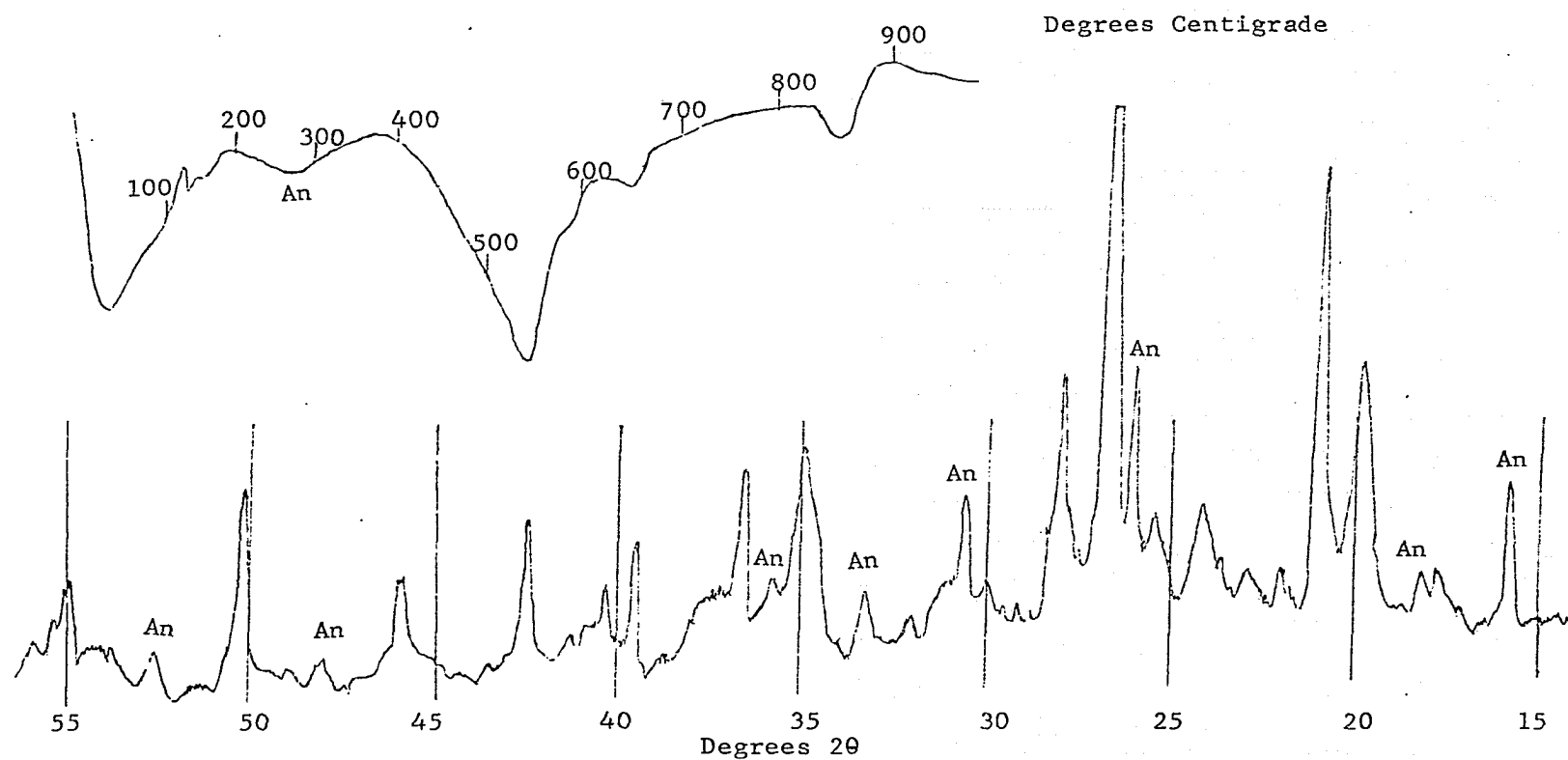


Figure 10. DTA diagram and randomly oriented x-ray diffractogram showing the presence of analcite

are present in the lowest unit of both sections. The exposed thickness of the measured section B-E is only 76.8 feet which is probably above the interval of analcite occurrence. This is perhaps the reason why no analcite was found in the section B-E which geographically lies between the measured sections B-D and B-E. No x-ray detectable amount of analcite was found in the three measured sections in Major County, even for those samples collected far below the level of the expected occurrence. As stated by Hay (1966, p. 12), "Zeolite forming less than 10 percent of a sample usually must be concentrated by heavy liquids or by hand-picking before they can be accurately identified by x-ray methods." Therefore, analcite reflections would probably not appear on the x-ray diffractogram if the analcite content is as low as 2 or 3 percent. Accordingly, failure to resolve analcite peaks on x-ray diffraction patterns does not necessarily mean the absence of analcite, but may merely indicate its presence in a small quantity.

Origin

Zeolites are rare as detrital constituents and thus, generally reflect only the depositional history of sedimentary rocks. Zeolites in sedimentary rocks may form by reaction of volcanic glass and aluminosilicate minerals in aqueous solutions and they may be also chemically precipitated. As stated by Hay (1966, p. 2), "Analcime is apparently a chemical precipitate in some saline alkaline lakes and extensive deposits of analcimic argillite and analcimolite possibly form in this way." Analcite could form as the altered product of plagioclase in a high sodium aqueous environment. As no analcite grains could be positively

identified under the petrographic microscope, they had to occur as very fine-grained particles associated with the clay matrix of shale. It seems unlikely that the analcite in the Flowerpot Shale was derived from detrital plagioclase grains. Furthermore, as no field and mineralogic evidence were found to prove that the analcite in the Flowerpot Shale formed as an alteration product of volcanic glass, the chemical precipitation of analcite should be considered as a possible alternative mode of origin. The chemical precipitation of analcite is a function of many factors, such as pH, salinity, and sodium availability. Laboratory data shows that mordenite may crystallize from a solution having a relatively low pH and analcime may crystallize at the same temperature from a solution which is similar except for a higher pH (Barrer and White, 1952; Coombs et al., 1959). A rather high average abrasive pH value of around 9 was observed for those analcite-bearing shale samples (pH of distilled water was 6.1 and clay-water ratio was 0.83 percent). Though abrasive pH may not have a significant relation to the real pH of the depositional environment, a high alkalinity should be expected in an environment where the evaporite-bearing Flowerpot Shale was deposited. Hay (1966) thought that an increase in salinity would lower the activity of water, possibly favoring a less hydrous phase such as analcime over the more hydrated phases. Trace-element studies of the upper Flowerpot Shale do imply a rather high paleosalinity. A high proportion of sodium cations is obviously important for the formation of the sodium zeolite, analcite. The presence of many evaporite beds in the upper Flowerpot Shale implies an arid condition with high evaporation. Hence, we would expect a high concentration of alkalies and alkaline-earth cations in the depositional

basin. Potassium may be fixed by illitic minerals. Calcium is mainly incorporated in dolomite and gypsum. Magnesium is essentially incorporated in dolomite and possibly in the clay minerals such as chlorite. The concentration of sodium ions could result in the deposition of analcite. Accordingly, the depositional conditions of the upper Flowerpot Shale seem to favor the chemical precipitation of analcite.

PETROGRAPHY

Shale

The great bulk of rock present in the upper Flowerpot Shale is red-brown shale mottled with greenish-grey spots. Apart from the color, there is no obvious difference between the greenish-grey spots and the red portion of shale. The red coloration in the shale is due to the presence of hematite staining and finely disseminated hematite particles. The staining coats all components of the shale. The hematite content is higher in the shale than in any other redbed rock-type and decreases in amount with an increase in silt. The detrital quartz and feldspar grains of silt size comprise generally less than 15 percent of the shale. Tiny muscovite (sericite) occurs as sparsely scattered flakes throughout. Swelling chlorites are present as light green, slightly pleochroic flakes and aggregate grains. Biotite occurs as green, pleochroic flakes. Very fine-grained illite commonly masked by hematite staining makes up the bulk of the clay matrix. Dolomite rhombohedra of silt size are found in places in some shale samples.

Siltstone and Sandstone

The siltstone and sandstone are commonly light greenish-grey and light red-brown in color. The lighter color is caused by the presence of less hematite and more quartz, feldspar, gypsum, and dolomite than in

the shale. The existence of organic materials with a consequent reduction of ferric iron to the ferrous state may also be a factor.

From the examination of the four thin sections of siltstone and sandstone, 1713, 1732, 1738, and 1740, the average size of detrital quartz and feldspar grains is shown to range from 0.05 to 0.07 mm in diameter. This is at the sand and silt boundary (average diameter is about 0.06 mm). The quartz and feldspar grains which are generally subangular to subrounded and well-sorted make up 50 to 55 percent of the rock (Plates IIC, IIID, IVA, IVB, and IVC). Feldspar which includes orthoclase, plagioclase, and a relatively small amount of microcline ranges in quantity from 5 to 15 percent in the siltstone and sandstone. Plagioclase is normally more fresh and angular than orthoclase. Rock fragments such as chlorite-schist and some fine-grained metamorphic rock fragments are present in small amounts. Accessory minerals present include tourmaline, zircon, apatite, rutile, garnet, leucoxene, magnetite, and ilmenite. Scattered muscovite, chlorite, and biotite flakes are common but in very small quantity. The cement, which generally makes up 35 percent or more of the rock, is essentially gypsum and dolomite. Some of the detrital grains are partly replaced by dolomite and gypsum along their edges. The siltstones and sandstones are classified as subarkoses (Folk, 1961).

Dolomite

The dolomite of the upper Flowerpot Shale is largely fine-grained, light grey to light tan, compact dolomite with varying amounts of silt and clay, and containing no fossils. Of the eleven thin sections

of dolomite examined, dolomicrite is the predominant dolomite type. The samples generally contain a few sparsely scattered silt-sized quartz and feldspar grains and some disseminated clay minerals such as illite. Hematite staining on the argillaceous dolomite is also common. Sparry dolomite aggregates and veins, which probably represent cavity and fissure fillings of secondary origin, are commonly found in the thin sections of dolomicrite. A few void-fillings of gypsum also exist in the dolomicrite. Thin section 1737 is composed of a coarse crystalline mosaic of dolomite grains ranging in size from 0.02 mm to 0.07 mm (Plate IVD). Because the dolomite grains are rounded and hematite-stained, they may represent recemented dolomite intraclasts. Coarse-grained dolomite rhombs which range in size from 0.1 mm to 0.8 mm and occupy as high as 50 percent of the rock by volume are well-cemented by fibrous gypsum in the thin section 1725 (Plate IIIC).

Thin section 1719 is particularly interesting because microcrystalline dolomite bands containing coarser-grained quartz, feldspar, and oolites alternate with those containing finer-grained, more angular quartz and feldspar. Oolites, which range in size from 0.1 to 0.2 mm, do not contain detrital grains as nuclei. Some of the oolites are hematite-stained (Plate IIB). A rounded intraclast of gypsum is also found in the thin section. It is obvious that the alternating bands indicate fluctuations of energy in the depositional environment. As only one of eleven dolomite thin sections examined displays this special feature, it should be considered that fluctuations of energy are exceptional rather than common conditions in the depositional environment where the Flowerpot dolomites were deposited.

PIPETTE ANALYSES

General Statement

Pipette analyses were performed to determine whether there is a difference in the size distribution between the greenish-grey shale and the underlying and overlying red-brown shale, and between the greenish-grey spots and the surrounding red-brown shale. Some of the greenish-grey beds in the upper Flowerpot Shale can be identified as siltstone or silty shale layers. These units have a coarser grain size distribution than the average mudstone and shale units in the Flowerpot Shale. The greenish-grey samples selected for the pipette analysis were those in which amounts of fine-grained silt were insignificant.

Ten to twenty grams of sample were obtained by dividing the crushed shale through a splitter. The split sample was then dispersed in a one-liter flask in distilled water and placed on a shaking table at low speed for four hours. As long as the shaking time remains constant, the effect of shaking on the decrease in particle size, if any, would not be significant. Larger than 4 phi (62 microns) particles were caught on the 230-mesh screen by wet sieving. Calgon (sodium hexametaphosphate) was added to prevent flocculation. A nomograph by Schweyer (1952, p. 10) which permits rapid graphical solution of Stokes' equation was used in determining the withdrawal depth and settling time in the pipette

analysis. For detailed procedures refer to the publication "Petrology of Sedimentary Rocks" by Folk (1961).

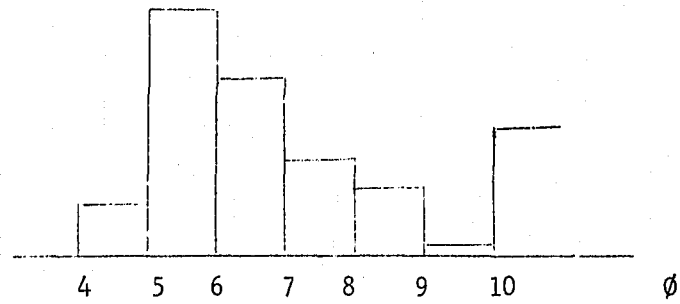
Folk (1961, p. 17) has commented that size analyses are commonly invalid for sizes finer than 6 or 7 phi because the settling velocity of such fine-size particles is affected greatly by the particle shape, degree of dispersion, and charge density and distribution on the particles. In this study, no detectable difference in clay mineral type, ratio, and composition were found between the red-brown and greenish-grey shales. Accordingly, these factors should affect the settling velocity of clay particles of both shale types to the same extent. Some of the particles that were caught on the 230-mesh sieve were examined with a binocular microscope and clay aggregates seem to comprise the bulk of the particles. The fact that few detrital grains coarser than silt size are present in the shale was confirmed by petrographic examination of some shale thin sections. Hence, sand-size materials were not considered important in the size analysis study.

Data and Interpretation

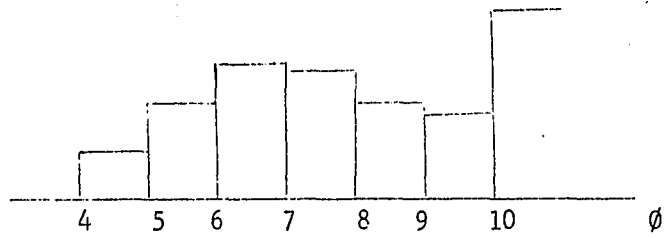
As shown in Figures 11 and 12, histograms of the greenish-grey shale tend to be skewed toward the coarse silt size as compared with those of underlying and overlying red-brown shales. As shown in Table 3, the greenish-grey shale bed contains a higher silt content (from 4 to 8 phi) than the overlying and underlying red-brown shale beds. However, the greenish-grey spots and the surrounding red-brown shale display similar size distribution histograms (Figure 13).

The chemical data of clay- and silt-sized materials of these greenish-grey and red-brown samples are shown in Table 6. M-B-2 (green)

B-F-16 Green



B-F-15 Red



B-F-14 Green

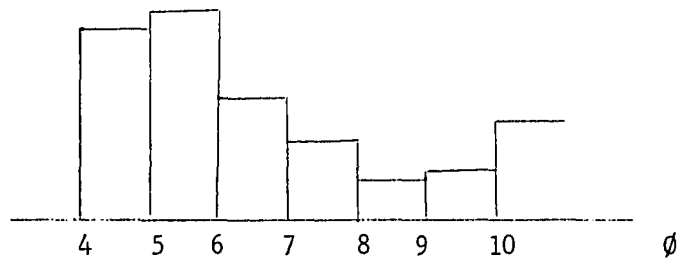


Figure 11. Histograms showing grain size distribution of two greenish-grey shale beds and the intervening red-brown bed

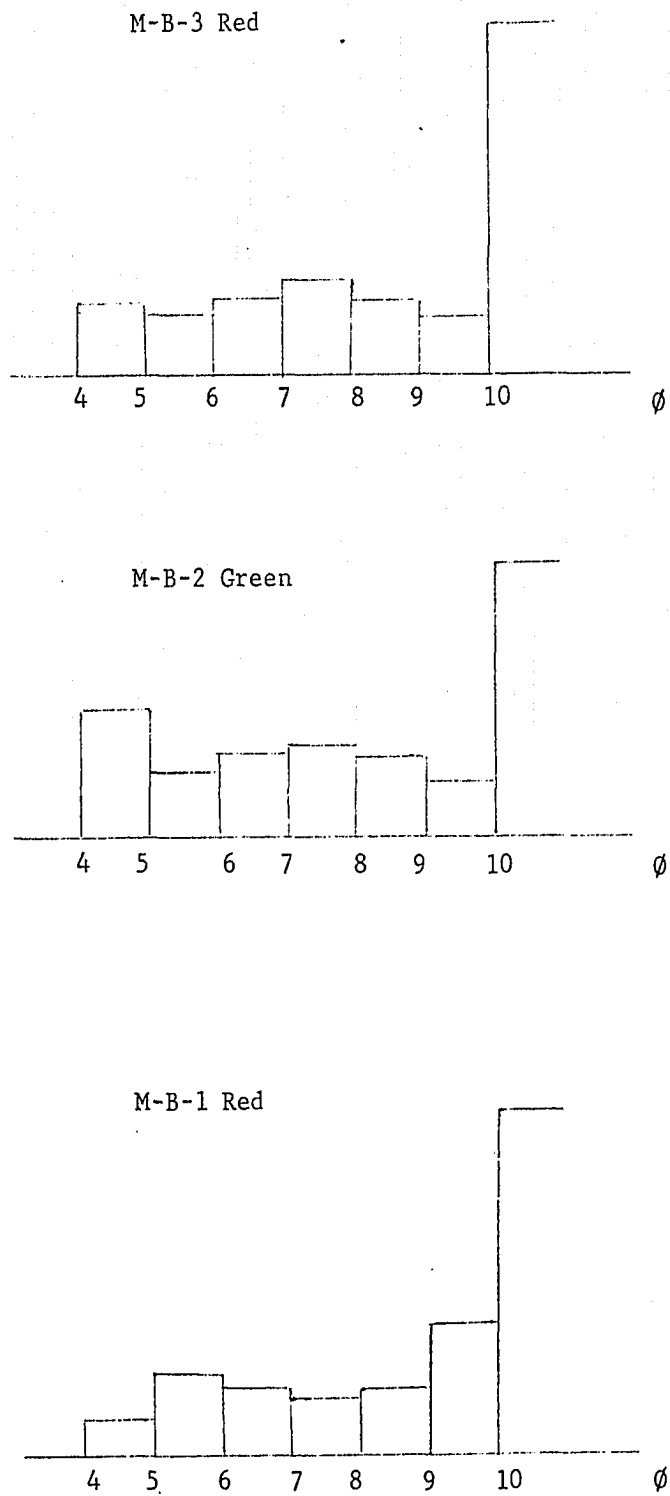


Figure 12. Histograms showing grain size distribution of a greenish-grey shale bed and the overlying and underlying red-brown shale beds

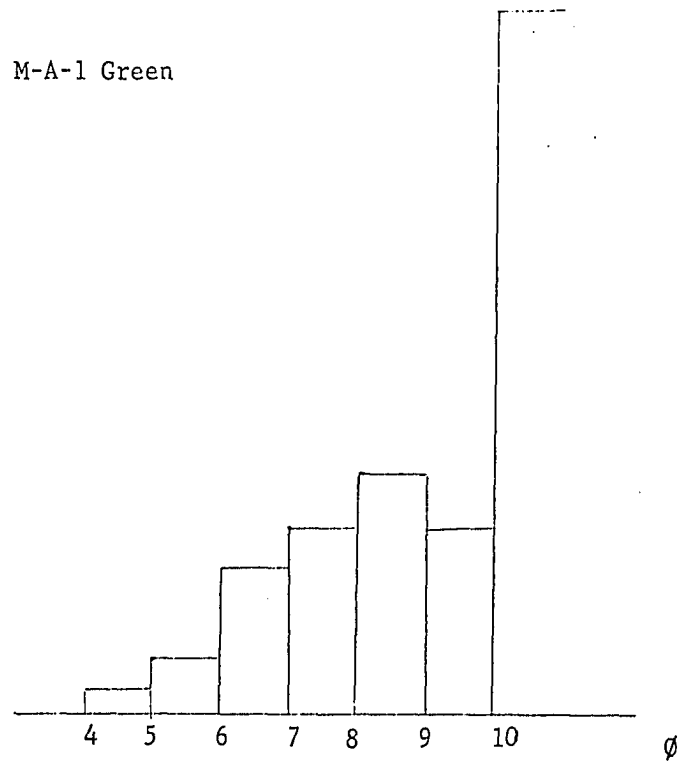
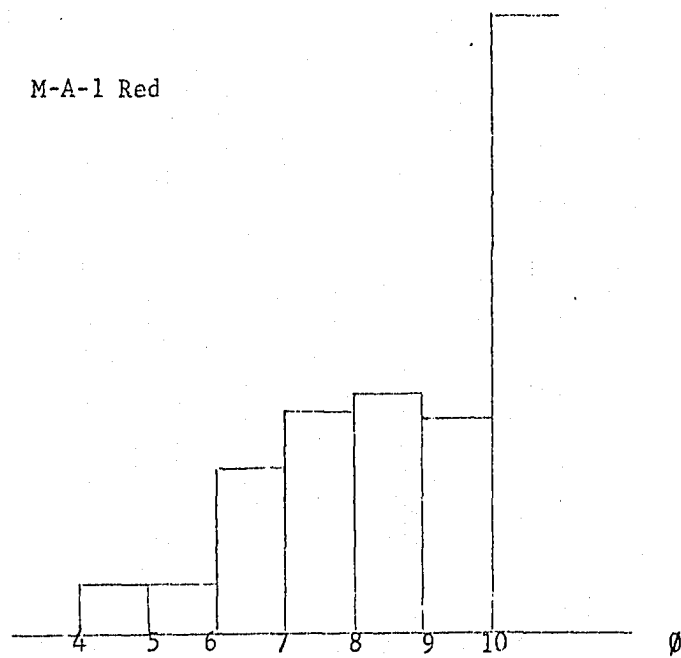


Figure 13. Histograms showing grain size distribution of a greenish-grey spot and the surrounding red-brown shale

TABLE 3.--Percentage of different size fractions with respect to the total weight of clay and silt

Sample No. Size in Phi	M-A-1 Green Spot	M-A-1 Red	M-B-1 Red	M-B-2 Green	M-B-3 Red	B-F-14 Green	B-F-15 Red	B-F-16 Green
4 to 5	1.57	3.17	4.37	16.72	9.21	24.68	6.19	6.69
5 to 6	3.66	3.17	10.37	8.55	7.79	26.77	12.39	31.86
6 to 7	9.41	10.57	8.73	10.89	9.92	15.47	17.34	22.82
7 to 8	12.03	14.27	7.10	11.66	12.04	9.82	16.52	12.20
8 to 9	15.69	15.32	8.19	10.11	9.21	4.76	12.39	8.65
9 to 10	12.03	13.74	16.92	7.00	7.08	5.95	10.73	1.18
Larger than 10	45.61	39.75	44.32	35.07	44.76	12.55	24.44	16.60
Total Silt	26.67	31.38	30.57	47.82	38.98	76.74	52.44	73.57
Total Clay	73.33	68.82	69.43	52.18	61.04	23.26	47.56	26.43

has a SiO_2 content of 59.15 percent compared to 50.12 percent for M-B-3 (red). B-F-14 (green) and B-F-16 (green), containing 67.54 and 69.52 percent of SiO_2 respectively, contrast with B-F-15 (red) with SiO_2 content of 60.66 percent. But the greenish-grey spot and the surrounding red-brown shale of M-A-1 possess a nearly identical SiO_2 content of 54.60 and 54.02 percent respectively. According to these data, the greenish-grey shale bed contains more silica than the overlying and underlying red-brown shale beds and this silica is probably in the form of free quartz. The thin section study of M-B-1 (red) and M-B-2 (green) confirmed this conclusion.

These greenish-grey silty shale and siltstone layers which are intercalated with the red-brown shale sequence might reflect episodes of slight increase of energy such as a slight increase in competence of the transporting currents. The greenish-grey spots scattered in the red-brown shale are not reworked shale fragments. Rather, they formed by reduction to the greenish-grey color due to the presence of organic material. The presence of dark organic material in the center of some greenish-grey spots and no textural, structural, or mineralogical difference between the greenish-grey spots and the surrounding red-brown shale support this explanation.

TRACE-ELEMENT GEOCHEMISTRY

General Statement

Quantitative analyses for the trace elements, boron, vanadium, nickel, and cobalt in 11 bulk shale samples and 13 clay samples were performed. Bulk samples were samples of the entire rock crushed so that they would pass through a 230-mesh U. S. Standard Sieve (4 phi). Clay samples are less-than-one-micron (esd) clay materials which were collected from dispersed clay suspensions by decantation and centrifugation methods (Appendix A).

There are several reasons in selecting these four elements for analysis. Boron is well-known as a potential paleosalinity indicator. Potter et al. (1963) found that a discriminant function based upon B and V alone can decisively separate marine and fresh-water sediments. The lower total iron content of the greenish-grey layers and spots was revealed by chemical analysis by x-ray fluorescence. Because V, Ni, and Co (transitional elements) are chemically similar to Fe, quantitative analyses of Co, Ni, and V may give a clue to the origin of the greenish-grey layers and spots.

The purpose of the trace-element study is threefold. The first is to examine the difference in the trace-element content between coarser and finer fractions of the same sample. The second is the comparison of

the trace-element content between the greenish-grey shale beds with the overlying and underlying red-brown shale beds. The third is to predict the paleosalinity based upon the boron and vanadium content of the shale samples.

Variations in Trace-Element Content between Coarser
and Finer Size Fractions of Shale

As described in Landergren (1958), Goldschmidt and Peters pointed out that the enrichment of boron in marine clay sediments was due to adsorption from sea water. The adsorption phenomenon should be affected by the size distribution of clay sediments. According to the experimental data on deep sea sediments by Landergren (1958), about 90 percent by weight of the bulk boron is bound to the size classes of less than 6 microns and 6 to 15 microns which are clay- and medium silt-sized materials. As shown in Table 4 and Figure 14, the less-than-one-micron clay fractions possess a higher boron content than the corresponding less-than-230-mesh fractions. Based upon eight pairs of samples, the statistical F test and Student's t test (Appendix B) were done to check the reliability of the conclusion.

Before doing the Student's t test to investigate the difference between the sample means, we should logically do a prior test to investigate whether the sample variances are sufficiently alike to warrant our assuming that they are independent estimates of the same population variances. Because the calculated value for F in this case is 2.20 which is less than the 5 percent level, the difference between the two variances is not regarded significant at the 5 percent level. The calculated value for t is 3.195 for 14 degrees of freedom. For 14 degrees

TABLE 4.--Quantitative trace-element analyses of shales

Sample No.	Concentration of Elements in Parts per Million (ppm)			
	B	Co	Ni	V
M-A-1 F	257	39	67	139
M-A-1 C	185	40	70	168
*M-A-1 C	210	54	112	590
M-A-5 F	218	41	70	123
M-A-10 F	210	42	68	134
M-A-10 C	173	33	54	108
**M-A-13 F	143	41	65	98
**M-A-13 C	129	39	66	117
M-A-14 F	221	43	72	116
M-A-14 C	158	38	68	111
M-A-19 F	218	30	60	143
*M-B-2 C	180	51	124	148
M-B-3 C	184	35	60	110
B-F-1 F	280	42	80	154
B-F-10 F	300	38	65	108
*B-F-14 F	245	38	80	270
*B-F-14 C	120	32	54	100
B-F-15 F	293	36	63	117
B-F-15 C	194	32	57	95
*B-F-16 C	124	59	65	118
B-F-20 F	237	36	72	142
B-F-28 F	254	38	64	113
B-F-28 C	188	31	53	90
B-F-41 F	210	41	70	127
B-F-41 C	200	42	70	124

F indicates less-than-one-micron material.

C indicates less-than-230-mesh material.

*Greenish-grey shale.

**Swelling-chlorite-rich dark greenish-grey shale.

of freedom, the critical value of t is 2.977 at the 0.005 level of significance. The calculated value falls in the rejection region. Therefore, we conclude that there is strong evidence to indicate a higher boron content in the clay fraction than in the clay and silt fraction. This means that if the mean boron content in both fractions were equal, the observed difference in boron content could arise by chance in less than one out of five thousand trials.

The distribution of boron in illite, kaolinite, and chlorite was studied by Frederickson and Reynolds (1960) and they report that boron seems to be preferentially associated with illite. Stubican and Roy (1961) demonstrated that synthetic phlogopite, muscovite, and saponite contain B^{3+} in tetrahedral sites. Degen (1965) stated that on geochemical grounds, boron should substitute for aluminum in the tetrahedral position (four-fold coordination). The higher boron content in the less-than-one-micron fraction may be explained in either of the following ways. 1) The clay minerals of the Flowerpot Shale are composed mainly of illite which is expected to concentrate in the clay-size fraction. 2) If substitution of boron for aluminum and silicon in tetrahedral sites (Harder, 1961) occurs preferentially at the surface of illite crystals, boron will be enriched in the finer sizes because there is a greater ratio of surface area to volume.

Cobalt and nickel also show a tendency to concentrate in the clay fraction. The data are not as conclusive as that of boron because of the presence of two exceptions (Table 4). The F test proved that the difference between the variances of coarser and finer fractions was not

significant at the 5 percent level for both cobalt and nickel. Based upon eight pairs of samples, the t test verifies that if the mean nickel and cobalt content in both fractions were equal, the observed difference in cobalt and nickel content could arise by chance in less than 5 percent of the trials. Although vanadium seems to show the same tendency as boron, cobalt, and nickel, the observed difference in the vanadium content between the coarser and finer fractions could arise by chance in more than 10 percent of the trials. Therefore, the significance of difference in the vanadium content between the two fractions cannot be established in a statistical sense.

Comparison of Trace-element Content between Red-brown Shale
and Greenish-grey Shale

As shown in Table 4, the greenish-grey shale seems to contain higher nickel, cobalt, and vanadium, and lower boron content than the overlying and underlying red-brown shales in the bulk (less-than-230-mesh) fraction and the clay fraction. The reverse trend between boron and the other three metal trace elements is interesting. The lower boron content in the greenish-grey shale compared to the red-brown shale could imply either a lower salinity or a dilution effect of silt-sized quartz. The fact that the greenish-grey shale contains a higher silt-sized quartz content has been verified by both chemical and size analyses. As pointed out by Potter et al. (1963), B, Cr, Cu, Ga, Ni, and V are significantly more abundant in marine than in fresh-water argillaceous sediments. So, we should also expect a slightly lower Ni, Co, and V content in the greenish-grey shale than in the red-brown shale, if the boron content

in the sample is proportional to paleosalinity. This discrepancy may be explained as follows:

1) The precipitation of cobalt, nickel, and vanadium sulphides or coprecipitation with ferrous sulphide in the greenish-grey shale under a reducing environment may account for it. But lack of sulphide minerals in these greenish-grey shale beds and the failure to form insoluble Co, Ni, and V sulphides in sea water (Krauskopf, 1956) seem to exclude this possibility.

2) It is a well-known fact that rare metals are commonly enriched in organic sediments. Based upon many studies on the concentration of rare metals in marine organisms, Krauskopf (1956) concluded that the metals V, Ni, and possibly Co are probably controlled largely by organic reactions. As stated by Mason (1967), vanadium and nickel may be extracted from sea water by organisms that utilize them in the form of metal-organic porphyrin compounds. The porphyrin compounds are exceedingly stable and have been recognized in shales, asphalts, and petroleum dating back to the Paleozoic. They are evidently able to withstand the ordinary processes of diagenesis. Goldschmidt, on the other hand, favored a concentration of trace elements during the decay of plant remains whereby the more soluble elements are leached out, leaving other elements retained either as insoluble compounds or as metal-organic complexes (Mason, 1967).

The presence of organic materials which reduce iron from the ferric to the ferrous state can also account for the greenish-grey color of the shale. The hypothesis that the iron oxides were removed was proven by the chemical data which show a considerably lower total iron

content in the greenish-grey shale than the red-brown shale (Tables 5 and 6). Antipathetic correlations between boron and organic carbon in the British Coal Measure sediments were demonstrated by Eager (1962). Curtis (1964) thought that an antipathetic relationship between organic carbon and boron concentration in sediments is expectable because the effective equilibrium for particles coated with organic "skins" is between the dissolved boron species and the organic phases. Therefore, the lower boron content in the greenish-grey shale compared with the red-brown shale could also be explained by the presence of more organic matter during deposition.

Paleosalinity

As suggested by Landergren (1945) and confirmed by the studies of Frederickson and Reynolds (1960), Nicholls and Loring (1962), and others, boron is a potential indicator of paleosalinity. According to the study by Potter et al. (1963), boron, nickel, vanadium, chromium, copper, and gallium are each more abundant in marine than fresh-water argillaceous sediments. As a result of statistical analysis of experimental data, Potter et al. (1963, p. 669) stated:

A discriminant function based on B and V alone and derived from 33 modern sediments decisively separated the modern marine and modern fresh-water sediments. When this discriminant function was applied to ancient sediments whose environment of deposition had been independently established by geologic evidence, 28 out of 33 sediments were correctly classified.

This implies that trace-element concentration in ancient shales is not seriously modified by postdepositional processes.

As shown in Figure 14, the estimated line of separation between marine and fresh-water fields duplicated the original separation line of

Potter et al. (1963) which was the line normal to the direction of maximum slope of the B and V discriminant function $X = 5.3415 x + 5.6928 y$ and through the midpoint between the logarithmic averages for the modern marine samples and the modern fresh-water samples. Although a direct application of this line for the interpretation of the present analytical data is not definitive, it is of value to compare the data directly. All the 24 samples including both the less-than-one-micron (esd) clay fractions and the less-than-230-mesh fractions fell well into the marine field without exception. Thus, marine environment with a possible higher than normal salinity is suggested for the upper Flowerpot Shale. The presence of evaporites and analcite in the upper Flowerpot Shale supports a high salinity environment too.

Correlations with Iron, Nickel, Cobalt, and Vanadium

Degen (1965, p. 244) stated, "Iron and manganese oxides and hydroxides are known for their ability to scoop up trace elements such as vanadium and nickel in amounts up to 1000 ppm (Krauskopf, 1955; Keith and Degen, 1959)." In the geochemical study of the Blaine Formation, Everett (1962) proposed that vanadium, chromium, cobalt, and nickel (the transition elements) are probably associated with the occurrence of iron. These elements would substitute in iron compounds and would be adsorbed onto the clay minerals with the iron or substitute for iron in the clay lattice. In order to test this hypothesis, the correlation coefficients between Ni, Co, and V respectively and the total iron content as determined by x-ray fluorescence of 22 clay and bulk samples were computed. These values are 0.13, -0.15, and 0.02 for Ni-Fe₂O₃, Co-Fe₂O₃, and V-Fe₂O₃ pairs respectively.

According to the definition of the correlation coefficient r , a value of $+1$ denotes a perfect functional relationship between the two, an increase in one of them being associated with an increase in the other. When the value of r is equal to -1 , we again have a perfect functional relationship, but this time, an increase in one of them is associated with a decrease in the other. When $r = 0$, there is no relationship between the two. The very low correlation coefficients between Fe_2O_3 and Ni, Co, and V respectively imply that Ni, Co, and V do not tend to vary with the increasing or decreasing total iron content in the shale. If the aforementioned hypothesis were correct, we should expect a tendency for increasing Co, Ni, and V with increasing Fe.

However, the correlation coefficients are equal to 0.45 between Ni and V, and 0.57 between Ni and Co. The fairly high positive correlation coefficients among Co, Ni, and V may suggest that they either have a similar association or mechanism of concentration in the shale. The hypothesis is supported by the similar chemical properties possessed by these three metal elements.

CHEMICAL ANALYSES BY X-RAY FLUORESCENCE

General Statement

Chemical analysis data of 19 shale samples on the less-than-one-micron (esd) clay fraction and 17 shale samples on the less-than-230-mesh fraction are shown in Tables 5 and 6 respectively. The main chemical components were quantitatively analyzed by the x-ray fluorescence method with the exception of H_2O^- and H_2O^+ where the former is the percentage of weight loss between room temperature and 120 degrees centigrade and the latter is that between 120 and 1000 degrees centigrade. The standards used for the quantitative x-ray fluorescence analysis are U. S. Geological Survey silicate rock standards, G-2, GSP-1, AGV-1, PCC-1, DTS-1, and BCR-1 (Flanagan, 1967). The analytical technique is included in Appendix A.

Based upon the Student's t test for comparison of mean Fe_2O_3 content (total iron expressed as Fe_2O_3) of six red shale and three green or grey shale samples of the upper Permian rocks in Kansas, Swineford (1955, p. 121) noted, "There is no evidence here that the populations are different."

It is more meaningful to compare the iron content between red-brown shale and greenish-grey shale on the same size clay fraction. The elimination of coarser-grained quartz, feldspar, and other coarse fraction iron-bearing minerals, whose existence in the sample would affect

TABLE 5.--Chemical analyses by x-ray fluorescence (less-than-one-micron samples)

No.	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MgO	CaO	K ₂ O	Na ₂ O	MnO	H ₂ O ⁺	H ₂ O ⁻	Total
B-F-1	45.15	17.61	0.75	15.55	4.51	0.67	5.03	0.58	0.10	7.06	3.70	100.71
B-F-10	45.86	17.98	0.95	13.98	4.67	0.82	5.26	0.32	0.10	7.47	3.65	101.06
*B-F-14	47.12	19.62	0.66	7.92	5.15	1.06	5.27	0.43	0.07	8.23	3.94	99.47
B-F-15	46.77	18.17	0.67	12.08	5.10	0.89	5.47	0.22	0.11	8.78	3.17	101.43
B-F-20	46.12	17.92	0.78	13.16	4.69	1.08	4.96	0.25	0.08	7.43	5.42	101.89
B-F-28	46.01	17.16	0.68	11.92	6.18	0.75	5.28	0.24	0.10	7.67	3.47	99.46
B-F-41	43.25	15.43	0.72	12.07	8.78	0.84	4.63	0.19	0.09	8.31	4.02	98.33
M-A-1	46.94	17.65	0.64	12.19	5.37	0.64	5.87	0.27	0.08	7.71	2.93	100.30
M-A-5	47.02	17.36	0.77	11.66	6.75	0.80	5.29	0.23	0.08	7.45	3.13	100.54
M-A-10	45.35	15.95	0.85	10.68	9.36	0.48	4.77	0.21	0.07	8.78	3.17	99.67
*M-A-13	43.64	12.54	0.67	7.82	17.16	0.78	3.18	0.13	0.08	9.61	4.68	100.29
M-A-14	41.83	10.54	0.65	13.24	14.70	0.77	3.27	0.17	0.08	9.00	3.39	97.64
*M-A-19	46.38	15.68	0.69	8.05	9.56	0.96	4.77	0.18	0.05	8.23	4.33	98.88
B-E-8	45.99	16.75	0.90	13.10	5.71	0.86	5.21	0.28	0.10	7.77	2.76	99.43
B-E-18a	42.82	14.00	0.65	11.43	11.25	1.61	4.26	0.18	0.12	10.46	3.08	99.86
B-E-18b	43.89	14.61	0.75	12.05	10.20	1.00	4.21	0.23	0.10	9.59	3.01	99.64
B-D-14	44.50	15.97	0.76	13.38	8.36	0.64	4.79	0.15	0.09	8.42	2.66	99.72
*B-D-20	43.61	14.43	0.71	7.53	13.11	0.74	3.92	0.22	0.08	9.32	3.81	97.48
B-D-21	43.15	13.87	0.68	13.24	10.75	0.76	4.02	0.17	0.09	8.64	3.24	98.61

*Greenish-grey color.

TABLE 6.--Chemical analyses by x-ray fluorescence (less-than-230-mesh bulk samples)

No.	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MgO	CaO	K ₂ O	Na ₂ O	MnO	H ₂ O ⁺	H ₂ O ⁻	Total
*B-F-14	67.54	7.79	0.74	2.02	4.38	4.44	2.05	1.41	0.21	6.72	0.97	98.27
B-F-15	60.66	11.45	1.06	6.89	3.89	1.77	3.18	1.27	0.09	5.95	1.76	97.97
*B-F-16	69.52	10.79	1.00	2.47	3.24	2.01	2.30	1.46	0.08	4.55	0.83	98.39
B-F-28	53.93	15.22	0.89	8.26	5.70	2.15	4.10	0.57	0.12	7.99	1.60	100.53
B-F-41	50.67	15.76	0.89	10.37	7.87	1.01	3.65	0.37	0.08	7.74	2.44	100.85
B-F-44	54.90	12.12	0.95	8.25	8.41	0.64	3.60	0.60	0.08	6.30	1.49	97.34
M-C-15a	56.82	11.22	0.98	8.97	9.26	1.25	2.60	0.82	0.08	5.89	1.32	99.21
M-C-15b	51.55	13.37	0.87	7.92	10.54	1.52	3.30	0.54	0.07	7.66	1.78	99.12
M-C-15c	50.80	14.34	0.87	9.07	11.09	1.60	3.58	0.37	0.08	8.58	2.34	102.72
*M-B-2	59.15	15.95	0.94	5.11	4.98	1.35	4.15	0.75	0.05	6.23	1.83	100.49
M-B-3	50.12	16.40	0.93	9.44	5.73	1.81	4.72	0.40	0.11	7.85	2.11	99.62
*M-A-1	54.60	19.27	1.01	6.46	5.49	0.59	4.88	0.83	0.07	6.75	2.49	102.44
M-A-1	54.02	18.06	0.99	9.09	5.24	0.53	4.74	0.75	0.07	6.32	2.39	102.20
M-A-11	48.79	2.94	0.97	2.09	4.69	13.06	1.39	0.77	0.09	4.68	4.96	84.43 ^a
*M-A-13a	52.02	10.60	0.89	6.51	12.20	1.06	3.30	0.63	0.10	7.97	1.82	97.11
*M-A-13b	49.79	11.05	0.85	7.53	12.70	0.95	3.57	0.66	0.11	8.23	2.06	97.50
M-A-14	50.09	12.64	0.86	9.88	11.54	0.64	3.46	0.57	0.09	7.20	2.40	99.37

*Greenish-grey color

^aThe low total in the gypsiferous siltstone due to the lack of SO₃ analysis.

the relative percentage of total Fe_2O_3 , should make the comparison more reasonable.

Data and Interpretation

The F test and the Student's t test on the mean Fe_2O_3 content of 13 red-brown shale and 4 greenish-grey shale samples were done. All samples are less-than-one-micron (esd) clay materials collected by standard sedimentation methods. The observed value of F with 12 and 3 degrees of freedom is 11.1 which is less than the critical value of $F = 14.3$ at 0.025 level. Therefore, we may conclude that the difference between the variances is not significant at the 2.5 percent level. The calculated value of the "t" statistic is 12.360 for 15 ($13 + 4 - 2$) degrees of freedom. For 15 degrees of freedom, "t" must not be less than 4.073 to be significant at the 0.05 percent level, and thus, we can conclude with confidence that the populations are different. The statistic shows that if the mean iron content between the red-brown shale and the greenish-grey shale were the same, the observed difference of total iron content between the two could occur by chance in less than 5 out of ten-thousand trials.

Student's t test for comparison of mean Fe_2O_3 content of 5 greenish-grey shale with 5 overlying or underlying red-brown shale samples on the less-than-230-mesh fraction was also conducted. We may also conclude that there is sufficient evidence to indicate that the red-brown shale has a higher total iron content than the greenish-grey shale at the one percent significant level.

The 6 red shale and 3 green shale samples used by Swineford (1955) as the basis of statistical comparison were scattered through a wide stratigraphic interval in the upper Permian section. In addition, her chemical data were a collection of analyses from several sources. It is questionable whether those samples can be assumed to have been drawn from similar populations with the same variance which is a required assumption for the "t" test. Nothing was mentioned concerning the testing of the equality of variances of the two populations.

The dark, greenish-grey shale underlying the topmost dolomite bed of the Flowerpot Shale (e.g., M-A-13) does not seem to contain a higher silt-sized quartz content than the red-brown shale because no conspicuous increase in silica content can be observed (Table 6). No difference in SiO_2 content is observed between the greenish-grey spot (*M-A-1) and the surrounding red-brown shale (M-A-1) (Table 6). However, the common greenish-grey shale beds such as *M-B-2, *B-F-15, and *B-F-16 show a 7 to 9 percent higher silica content than the overlying or underlying red-brown shale beds (Table 6).

According to Rankama and Sahama (1950, p. 432), the $\text{Na}_2\text{O}:\text{K}_2\text{O}$ ratio in argillaceous sediments has an average value of 0.36, and that in igneous rocks is 1.09. The average $\text{Na}_2\text{O}:\text{K}_2\text{O}$ ratio in the 17 upper Flowerpot Shale samples analyzed is 0.26, whereas the average ratio in the less-than-one-micron (esd) clay fraction of the 19 Flowerpot Shale samples analyzed is 0.05. The small average ratio in the clay fraction can be explained by the shortage of sodic plagioclase and the concentration of illite in the less-than-one-micron clay-sized materials. As

shown in Table 7, the bulk samples B-F-14, B-F-15, and B-F-16 display exceptionally high $\text{Na}_2\text{O}:\text{K}_2\text{O}$ ratio. This is due to the presence of analcime, a sodium zeolite, in these samples as confirmed by x-ray diffraction.

TABLE 7.--Sodium-potassium ratios of bulk samples
(Less-than-230-mesh)

Sample No.	$\text{Na}_2\text{O}:\text{K}_2\text{O}$
M-A-1	0.16
M-A-11	0.55
M-A-13a	0.19
M-A-13b	0.19
M-A-14	0.17
M-B-2	0.18
M-B-3	0.09
M-C-15a	0.32
M-C-15b	0.16
M-C-15c	0.10
B-F-14	0.69
B-F-15	0.40
B-F-16	0.64
B-F-28	0.14
B-F-41	0.10
B-F-44	0.17

Bulk sample M-A-11 which is a gypsiferous siltstone also shows a higher $\text{Na}_2\text{O}:\text{K}_2\text{O}$ ratio (Table 7). This is probably due to the presence of some sodic plagioclase which was identified in the thin section of the specimen.

The $\text{MgO}:\text{Al}_2\text{O}_3$ ratio in the clay fraction of the 19 Flowerpot specimens is also interesting. As shown in Table 8, a higher $\text{MgO}:\text{Al}_2\text{O}_3$

TABLE 8.--Sodium-potassium and magnesium-aluminum ratios of clay (less-than-one-micron)

Sample No.	Na ₂ O:K ₂ O	MgO:Al ₂ O ₃
M-A-1	0.05	0.30
M-A-5	0.04	0.39
M-A-10	0.04	0.59
M-A-13	0.04	1.37
M-A-14	0.05	1.40
M-A-19	0.04	0.61
B-D-14	0.03	0.52
B-D-20	0.06	0.91
B-D-21	0.04	0.78
B-E-8	0.05	0.34
B-E-18a	0.04	0.80
B-E-18b	0.06	0.70
B-F-1	0.12	0.26
B-F-10	0.06	0.26
B-F-14	0.08	0.26
B-F-15	0.04	0.28
B-F-20	0.05	0.26
B-F-28	0.05	0.36
B-F-41	0.04	0.57

is observed at the upper portion of the measured sections. This is attributed to the concentration of swelling chlorite near the top of the Flowerpot Shale as verified by x-ray diffraction. The average $\text{MgO}:\text{Al}_2\text{O}_3$ ratios and "swelling chlorite indices" of the swelling-chlorite-rich shale underlying the topmost dolomite bed of the Flowerpot Shale (Figure 2) are tabulated as follows:

Measured Sections	Average $\text{MgO}:\text{Al}_2\text{O}_3$	Average "Swelling Chlorite Index"
M-A	1.39	9.87
B-D	0.85	4.30
B-E	0.75	2.91
B-F	0.57	0.82

The "swelling chlorite index" was arbitrarily defined as the ratio of the $14 \text{ \AA}$ peak height over the $7 \text{ \AA}$ peak height on the x-ray diffractograms of oriented clay slides. All the above data were obtained from the less-than-one-micron (esd) clay fractions. According to the data, the swelling chlorite content of the swelling-chlorite-rich shale tends to decrease toward the southeast along the outcrop strike of the Flowerpot Shale (Figure 1).

PROVENANCE AND ENVIRONMENT

Source

Quartz is one of the major constituents present in the rocks of the upper Flowerpot Shale. Quartz grains which display straight to slightly undulose extinction and contain few vacuoles and microlites are most abundant. This type of quartz suggests a plutonic parent, especially a granitic source rock (Folk, 1961). However, it does not necessarily mean that these quartz grains have an immediate granitic parent. They may have undergone several times of recycling. Although the fresh and subangular plagioclase grains seem to be derived from a primary igneous source, the absence of euhedral and less stable heavy minerals would seem to exclude an igneous source as the main contributor. The presence of well-worn, stable heavy minerals such as zircon and tourmaline suggests the recycling of these grains from older sediments. It is believed that the fresh plagioclase grains in the siltstone and sandstone units could be derived from low-grade metamorphic rocks.

Most of the clay minerals are believed to be detrital rather than authigenic. The 2M polymorphs of illite which exist in the coarser fraction of the shale were probably derived from slightly metamorphosed sedimentary rocks. The 2M illite cannot be a weathering product because of its "high temperature" stability range (200-350 degrees centigrade at 15,000 psi water pressure) (Yoder and Eugster, 1955, p. 246). The 1M

polymorphs of illite which concentrate in the less-than-one-micron (esd) clay fraction of shale were probably derived from the sedimentary parent or weathering products of other rocks. The presence of chlorite-schist and other fine-grained metamorphic rock fragments in the siltstone and sandstone definitely indicates a metamorphic source.

According to Jordan and Vosburg (1963), the red shales and sandstones that belong to the middle and upper parts of the Hennessey Shale and the Flowerpot Shale grade downdip westward into evaporites in the subsurface. Specifically, strata of the upper Flowerpot Shale grade into salt in the subsurface to the west. This would imply that the terrigenous strata exposed on the outcrop could not have been derived from a western source. A northern source is considered to be insignificant because of the absence of any tectonically positive area to the north of this region during Permian time.

The closest positive tectonic areas to the south and southeast of the area are the Wichita Mountains, the Arbuckle Mountains, and the Ouachita Mountains. The Wichita Mountains are not considered as a major source for several reasons. They were mostly covered by the close of the Pennsylvanian Period (Becker, 1930). Stith (1967), who studied the Hennessey Shale in the Wichita Mountain area, pointed out the continuous deposition from the Wichita Formation into the Hennessey Shale, which underlies the El Reno Group, with little chance of reworking between formations. Fay (1964) demonstrated a general increase in the amount of sand southward and southeastward for the El Reno Group in the southern delta area. This would indicate that the clastics were probably supplied by erosion of the Arbuckle and Ouachita Mountain areas.

Deformation in the Arbuckles Mountains was of Late Pennsylvanian (Virgil) age according to Ham (1956, p. 425). The Ouachita Orogeny was mainly of Pennsylvanian age and migrated westward with time into the Permian (King, 1961). The late Precambrian or early Paleozoic interior zone of the Ouachita Mountains contains metamorphic rocks such as slate, phyllite, schist, metaquartzite, and marble, in the subcrop of Texas and southeast Oklahoma (Flawn, 1961). Hence, the metamorphic rock fragments, plagioclase, and possibly the 2M illite may be attributed to the erosion of the Ouachita structural belt, which is situated to the south and southeast. The clay minerals of the Ouachita structural belt and the adjacent foreland are composed essentially of illite and some chlorite (Weaver, 1961). Therefore, the illite and chlorite in the upper Flowerpot Shale were probably derived from the Ouachita Mountain area.

Environment

The presence of evaporites, such as gypsum and dolomite in the Flowerpot Shale, suggests that they must have been deposited under semi-arid conditions where evaporation exceeded runoff and a continuous supply of additional sea water was maintained. According to the study of Permian plant microfossils from the Flowerpot Shale in Greer County, Oklahoma, by Wilson (1962), the presence of an abundance of conifer pollen and several species of ephedran-like pollen indicates that the sediments of the Flowerpot Shale were deposited under warm arid or semi-arid conditions. The great quantity of spores and pollen in the shale indicates that the ancient land mass was not far distant. Accordingly,

a marine near-shore environment is proposed. It is difficult to find detrital grains larger than fine sand size in all the thin sections examined. The abundance of fine clastics in the Flowerpot Shale suggests a low energy environment. Ham (1960, p. 147) stated:

During Permian time most of eastern Oklahoma was a land area of low relief. It emerged persistently but slowly, providing fine-grained clastic sediments to the sea. At the same time the depositional basin, which extended through the western parts of Oklahoma and Texas into eastern New Mexico, was continually subsiding and receiving marine carbonates and evaporites.

A narrow, brackish-water zone around the perimeter of the sea is due to fresh-water entering with land-derived clastics. The brackish-water zone in southern Oklahoma is probably represented by the Tussey Delta of Permian age (Green, 1937, p. 1524). The delta was located somewhere in the Grady County area to the northwest of Arbuckle Mountains. As mentioned before, the main source areas of the upper Flowerpot Shale in Major and Blaine Counties are most probably the Arbuckle and Ouachita Mountains. Increasing competence of streams in the delta area, which was probably due to climatic changes such as increasing rainfall, could result in intercalations of some siltstone and fine-grained sandstone in the Flowerpot Shale.

As quoted in Curtis (1964), Bader (1962) pointed out that soluble organic matter is an important constituent of all terrestrial water. He also demonstrated that certain clay minerals will quickly and strongly adsorb up to 350 percent of their own mass of soluble organic matter from solution. The organic material which is responsible for the greenish-grey color of siltstone, silty shale and spots in the red shale was probably introduced by the streams in association with clay minerals

or in an organic colloid state. The remarkably, evenly spaced distribution of the greenish-grey spots in some of the redbeds supports the latter hypothesis. It is certain that some organic matters such as pollen and spores were carried in the depositional basin in suspension by water and wind. The general lack of a fauna which may be due to the penesaline conditions probably excludes the contribution of organic materials from marine organisms. The organic materials were oxidized and simultaneously ferric iron in iron oxides which occur as stains and finely disseminated discrete particles was reduced to the ferrous state and removed before the time of lithification. The circulation of intrastratal solutions along the more permeable siltstone and silty shale units may be responsible for the removal of the reduced iron oxides which result in the observed lower iron content of the greenish-grey beds.

The close association of gypsum with greenish-grey siltstone and silty shale may imply the secondary precipitation of gypsum from solution in the more permeable beds. Satin spars and selenite gypsum which commonly occur as veins crosscutting the bedding planes are evidently secondary in origin. The white, nodular gypsum beds in the upper Flowerpot Shale must have formed by hydration of anhydrite because it is common to find anhydrite nodules throughout the upper 100 feet or more of the Flowerpot Shale in the subsurface (Fay, 1964).

The micritic nature of dolomite beds implies a direct chemical precipitation from relatively quiet sea water, allowing microcrystalline carbonate ooze to precipitate to the bottom. The precipitate could either be high-magnesium calcite, aragonite or a form of dolomite depending upon environmental conditions. In present day environments comparable

to that suspected for the deposition of the Flowerpot Shale, no dolomite is found to precipitate directly from sea water. Accordingly, penecontemporaneous alteration from either high-magnesium calcite, aragonite, or protodolomite must be considered as the alternative.

Hematite in the red beds is not considered to have been produced chemically by precipitation from solution because such precipitation should have formed at least a few layers or stringers of comparatively pure iron oxide. The hypothesis that hematite forms after deposition owing to in situ alteration of iron-bearing detrital grains could only account for a portion of the hematite because no petrographic evidence was found to verify this hypothesis. In addition, the less stable iron-bearing minerals would be expected to be concentrated in the siltstone and sandstone units instead of the shale. The higher permeability of the siltstone and sandstone units would favor postdepositional alteration of the iron-bearing heavy minerals. Accordingly, if in situ alteration of iron-bearing detrital grains was the source of the hematite, a higher total iron content per unit volume would be expected in the siltstone and sandstone units. However, the opposite has been observed. Though some of the hematite was transported into the basin of deposition as coatings on sand and silt, most was probably carried mechanically as finely divided sediments and was, thus, distributed with detrital clay minerals. The concentration of hematite in the clay fraction was confirmed by the intenser red color and higher total iron content in the clay fraction than the clay and silt fraction.

It is believed that the great majority of clay minerals in the sedimentary rocks are detrital in origin (Weaver, 1958b). The absence

of kaolinite in the upper Flowerpot Shale may be explained as lack of intense weathering in the source area. The weathering in the source area would not favor the formation of kaolinite owing to the poor ground water circulation resulting in the preservation of alkali and alkaline earth ions.

Illite and chlorite, which are abundant in the Flowerpot Shale, may not be a good indicator of depositional or diagenetic environments because they are quite stable and are probably recycled. The swelling chlorite with an incomplete brucite layer at the top portion of the Flowerpot Shale may be the alteration product of chlorite formed by partial removal of the brucite layers and subsequent replacement by water. However, Keller (1964, p. 47) stated:

In summary, the following model is suggested for the reactions undergone by river-borne 3 layer, Ca-rich clays when poured into the ocean. The change in ionic concentrations in solutions pulls Ca from the exchange positions and tends to substitute Na, Mg, and K in that order of abundance. Because of the bonding energies of clays, reacting in the polyionic systems as described by Jarusov's rule, Mg is sorbed in a maximum exchange positions. The retention of Mg within the clay complex may be enhanced further in the alkaline environment of ocean water because $Mg(OH)_2$ can exist as brucite, a stable relatively insoluble mineral, whereas $Ca(OH)_2$, NaOH, and KOH are highly soluble at the concentrations in which they are present. Mg may return to the clay minerals to give rise to reconstituted chlorite and conceivably it could form chlorite anew or perhaps corrensite.

Accordingly, the swelling chlorite could also form by the addition of Mg^{2+} to degraded three-layer clay minerals in a high alkaline environment. The gradual decrease of swelling chlorite to the southeast toward the delta facies may be interpreted as a decrease of alkalinity due to the introduction of fresh water which halted the formation of stable $Mg(OH)_2$.

The occurrence of sedimentary analcime in the Flowerpot Shale suggests an environment of high alkalinity and high sodium content.

The existence of silt-sized, fresh, subangular to subrounded feldspar grains perhaps indicates an arid climate and tectonic quiescence at the source area.

The presence of a regular sequence: dolomite, gypsum, red shale, and green shale, in the Blaine Formation was interpreted by Ham (1960) as resulting from typical, simply cyclic deposition. The thin dolomite bed represents the beginning of a cycle due to transgression of the sea. Gypsum which is directly above the dolomite is considered to be precipitated as the water becomes concentrated through evaporation. Red shale and green shale which overlie the gypsum in a complete simply cycle are land-derived clastics which can be carried far from the shore during the time of regression. As proposed by Ham (1960, p. 149) the Blaine evaporite cyclicity results from "transgressions and regressions" which, in turn, are caused by eustatic changes of sea level probably due to the multiple glaciation during Permian time. The cyclic sequence is not well developed in the upper Flowerpot Shale, although some of the sequence may be explained as incomplete cyclic deposits. The thin evaporite beds intercalating in the Flowerpot Shale may be better explained by hypothesizing a fluctuation of rainfall. At the time of minimal rainfall, evaporation exceeding runoff under semi-arid conditions could result in the deposition of thin evaporites. When inflow or runoff exceeded evaporation during increased rainfall, the land-derived clastics would spread in a wider area and the precipitation of evaporites was retarded owing to the dilution effect of fresh water.

CONCLUSIONS

According to pipette analyses, the greenish-grey beds contain more silt than the overlying and underlying red-brown beds. A higher silt-size quartz content in the greenish-grey beds was confirmed by the comparatively higher silica content as revealed from the chemical analyses by x-ray fluorescence.

A higher vanadium, cobalt, and nickel content in the greenish-grey beds and spots is believed due to the presence of organic materials which contain a high proportion of these metal elements. The greenish-grey color of beds and spots must be attributed to the reduction of ferric iron to the ferrous state by the oxidation of organic matter. The removal of the ferrous iron from the greenish-grey spots and beds was verified by a lower total iron content in the greenish-grey shale than in the red-brown shale, as revealed from chemical analyses by x-ray fluorescence. The circulation of intrastratal solutions along the more permeable siltstone and silty shale units is believed to be responsible for the removal of the reduced iron oxides.

A marine environment with moderately high salinity is indicated by the trace element study of boron and vanadium. The existence of chemically precipitated analcite in the lower portion of measured sections B-D and E-F indicates an environment of high alkalinity and high salinity.

Clay minerals of the upper Flowerpot Shale include mainly illite with some swelling chlorite and chlorite. The swelling chlorite is present only at the top portion of the Flowerpot Shale and concentrates in the shale bed immediately underlying the topmost dolomite bed of the Flowerpot Shale. The swelling chlorite is believed to be either the alteration product of ordinary chlorite or an authigenic formation of incomplete brucite layers in the interlayer positions of degraded three-layer clay minerals. The absence of kaolinite in the upper Flowerpot Shale is probably caused by the shortage of this mineral in the source area.

Based upon the evidence from petrology, clay mineralogy, and stratigraphic trends, the main source area of the upper Flowerpot Shale could be to the south and southeast and most probably the Arbuckle and Ouachita Mountains.

The microgranular dolomite is considered to be a penecontemporaneous alteration product of precipitated carbonate oozes rather than secondary grain growth because of the fine grain size (less than 5 micron).

Hematite may have been derived from source area as coatings on clay particles and as fine discrete particles associated with clay minerals. Some climatic fluctuations, such as increase of rainfall, would allow coarser sediments (siltstone and fine sandstone) to be distributed.

In summary, the Flowerpot Shale was accumulated in a near-shore, marine environment under a semi-arid condition. The salinity

and alkalinity of the sea water was high and the energy of the environment was low.

REFERENCES CITED

- Bader, R. G., 1962, Some experimental studies with organic compounds and minerals: Graduate School of Oceanography, Rhode Island, Univ., Occasional Pub. 1.
- Barrer, R. M., and White, E.A. D., 1952, The hydrothermal chemistry of silicates, Part II, Synthetic crystalline sodium aluminosilicates: Jour. Chem. Soc., vol. 286, p. 1561-1571.
- Becker, C. M., 1929, Discussion, in Amer. Assoc. Petroleum Geologists, Bull., vol. 13, p. 955.
- _____, 1930, Structure and stratigraphy of southwestern Oklahoma: Amer. Assoc. Petroleum Geologists, Bull. vol. 14, p. 37-56.
- Branson, C. C., 1960, Proposed American standard of early Permian(?) rocks, a century-old controversy: Okla. Geology Notes, vol. 20, p. 229-235.
- Brindley, G.W., and Ali, S. E., 1950, Thermal transformations in magnesium chlorites, Acta Cryst., vol. 3, p. 25-30.
- Brown, George, 1961, ed., The x-ray identification and crystal structures of clay minerals: Mineralog. Soc. London, 544 p.
- Brown, George and Norrish, K., 1952, Hydrous micas: Mineralog. Mag., vol. 29, no. 218, p. 929-932.
- Coombs, D. S., Ellis, A. J., Fyfe, W. S., and Taylor, A. M., 1959, The zeolite facies with comments on the interpretation of hydrothermal syntheses: Geochim. et Cosmochim. Acta, vol. 17, p. 53-107.
- Cragin, F. W., 1896, The Permian System in Kansas: Colorado College Studies, vol. 6, p. 1-48.
- Curtis, C. D., 1964, Studies on the use of boron as a paleoenvironmental indicator: Geochim. et Cosmochim. Acta, vol. 28, p. 1125-1137.
- Deer, W. A., Howie, R. A., and Zussman, J., 1966, An introduction to the rock-forming minerals: New York, John Wiley and Sons, Inc., 528 p.

- Degen, E. T., 1965, *Geochemistry of sediments*: Englewood Cliffs, N. J., Prentice-Hall Inc., 342 p.
- Eager, R. M. C., 1962, Boron content in relation to organic carbon in certain sediments of the British Coal Measures, *Nature*, vol. 196, p. 428-431.
- Everett, A. G., 1962, Clay petrology and geochemistry of the Blaine Formation (Permian), northern Blaine County, Oklahoma: Okla. Univ., unpublished Master of Science thesis.
- Fay, R. O., 1964, The Blaine and related formations of northwestern Oklahoma: Okla. Geol. Survey, Bull. 98, 238 p.
- Flanagan, F. J., 1967, U. S. Geological Survey silicate rock standards: *Geochim. et Cosmochim. Acta*, vol. 31, p. 289-308.
- Flawn, P. T., 1961, The subsurface Ouachita structure belt in Texas and southeast Oklahoma, *in* The Ouachita System: Texas Univ., Bur. Econ. Geol., Pub. 6120, p. 65-82.
- Folk, R. L., 1961, *Petrology of sedimentary rocks*: Austin, Texas, Hemphill's Publishing Co., 159 p.
- Frederickson, A.F., and Reynolds, R. C., Jr., 1960, Geochemical method for determining paleosalinity: *Clays and Clay Minerals*, Natl. Conf. on Clays and Clay Minerals, 8th Proc., p. 203-213.
- Green, D. A., 1937, Major divisions of the Permian in Oklahoma and southern Kansas: *Amer. Assoc. Petroleum Geologists, Bull.*, vol. 21, p. 1515-1533.
- Grim, R. E., 1968, *Clay mineralogy*: New York, McGraw-Hill Book Co., Inc., 596 p.
- _____, Bray, R. H., and Bradley, W. F., 1937, Mica in argillaceous sediments: *Amer. Mineralogist*, vol. 22, p. 813-829.
- _____, and Bradley, W. F., 1940, Investigation of the effect of heat on the clay minerals illite and montmorillonite: *Journ. Amer. Ceramics Soc.*, vol. 23, p. 242-248.
- Gruner, J.W., 1934, Structure of vermiculite and their collapse by dehydration: *Amer. Mineralogist*, vol. 19, p. 557-575.
- Ham, W. E., 1956, Structural Geology of the Arbuckle Mountain region (Abs.): *Amer. Assoc. Petroleum Geologists, Bull.*, vol. 40, p. 425-426.
- _____, 1960, Middle Permian evaporites in southwest Oklahoma: *Internal. Geol. Cong.*, 21st, Copenhagen, Rept., pt. 12, p. 138-151.

- Harder, H., 1961, Einbau von bor in detritisch ton minerale: *Geochim. et Cosmochim. Acta*, vol. 21, p. 284-294.
- Hay, R. L., 1966, Zeolites and zeolitic reactions in sedimentary rocks: *Geol. Soc. America, Spec. Paper* 85, 130 p.
- Jordan, Louise, and Vosburg, D. L., 1963, Permian salt and associated evaporites in the Anadarko Basin of the western Oklahoma-Texas panhandle region: *Okla. Geol. Survey Bull.* 102, 76 p.
- Keith, M. L. and Degens, E. T., 1959, Geochemical indicators of marine and fresh-water sediments in *Research in geochemistry*, P. H. Abelson, ed.: New York, John Wiley and Sons, Inc., p. 38-61.
- Keller, W. D., 1964, Processes of origin and alteration of clay minerals in *Soil clay mineralogy*, a symposium, C. I. Rich and G. W. Kunze, eds.: Chapel Hill, Univ. North Carolina Press, p. 1-76.
- Kerns, R. L., 1967a, Particle-size separation of clays: *Okla. Geology Notes*, vol. 27, p. 167-174.
- _____, 1967b, Chemical analyses by x-ray fluorescence: *Okla. Geology Notes*, vol. 27, p. 201-210.
- King, P. B., 1961, History of the Ouachita System, in *The Ouachita System*: Texas Univ., Bur. Econ. Geol., Pub. 6120, p. 175-210.
- Koizumi, M., 1953, The differential thermal analysis curves and the dehydration curves of zeolites: *Mineralog. Jour. Japan*, vol. 1, no. 1, p. 36-47.
- Krauskopf, K. B., 1955, Sedimentary deposits of rare metals: *Econ. Geology*, 50th Anniversary Vol., p. 411-463.
- _____, 1956, Factors controlling the concentration of thirteen rare metals in sea water: *Geochim. et Cosmochim. Acta*, vol. 9, p. 1-32B.
- Landergren, S., 1945, Contribution to the geochemistry of boron: *Arkiv. for Kemi, mineralogi, o. geologi*, Bd. 19A, N:o 26, p. 1-31.
- _____, 1958, On the distribution to the geochemistry of boron on different size classes in marine clay sediments: *Geol. Foren. Stockholm Forhandlinger*, vol. 80, no. 492. p. 104-107.
- Mendenhall, W., 1963, An introduction to statistics: Belmont, Calif., Wadsworth Publishing Company, Inc., 305 p.
- Nicholls, G. D., and Loring, D. H., 1962, The geochemistry of some British carboniferous sediments: *Geochim. et Cosmochim. Acta*, vol. 26, p. 181-224.

- Norton, G. H., 1939, Permian redbeds of Kansas: Amer. Assoc. Petroleum Geologists, Bull., vol. 23, p. 1751-1819.
- Porter, P. E., Shimp, N. F., and Witters, J., 1963, Trace elements in marine and fresh-water argillaceous sediments: Geochim. et Cosmochim. Acta, vol. 27, p. 669-694.
- Rankama, Kalervo, and Sahama, T. G., 1950, Geochemistry: Chicago Univ., Chicago Press, 912 p.
- Schweyer, H. E., 1952, Sedimentation procedures for determining particle size distribution: Univ. Fla., Coll. Engineering, Engineering Progress, vol. 6, no. 6, Bull. ser. no. 54, 19 p.
- Stith, D. A., 1967, Petrology of the Hennessey Shale (Permian), Wichita Mountain area, Oklahoma: Okla. Univ., unpublished Master of Science thesis.
- Stubican, V., and Roy, R., 1961, Boron substitution in synthetic micas and clays, 10 p., in American Petroleum Institute Project 55, Fifth Annual Report: University Park, Pa., College Min. Ind., Penn. State Univ.
- Swineford, A., 1955, Petrography of Upper Permian rocks in southcentral Kansas: Kans. State Geol. Survey, Bull. 111, 179 p.
- Weaver, C. E., 1958a, Potassium fixation by expandable clay minerals: Amer. Mineralogist, vol. 43, p. 839-861.
- _____, 1958b, Geologic interpretation of argillaceous sediments pt. I, Origin and significance of clay minerals in sedimentary rocks: Amer. Assoc. Petroleum Geologists, Bull., vol. 42, p. 254-271.
- _____, 1961, Clay minerals of the Ouachita structural belt and adjacent foreland, in The Ouachita System: Texas Univ., Bur. Econ. Geol., Pub. 6120, p. 147-162.
- Wilson, L. R., 1962, Permian plant microfossils from the Flowerpot Formation, Greer County, Oklahoma: Okla. Geol. Survey, Circ. 49, 50 p.
- Yoder, H. S., and Eugster, H. P., 1955, Synthetic and natural muscovite: Geochim. et Cosmochim. Acta, vol. 8, p. 225-280.

APPENDIX A

ANALYTICAL PROCEDURES AND TECHNIQUES

Sample Preparation

Randomly-oriented powder slides were made by crushing the sample to less than 115 mesh and sieving the material directly onto a vaseline-coated slide or packing powders in an x-ray sample holder. Preferred orientation slides were prepared by dispersing the crushed materials in distilled water with an ultrasonic transducer and then, sedimenting the clay suspension on glasses slides or ceramic plates, dried in an oven at 60 degrees centigrade prior to x-ray analysis. This preparation enhances the (001) basal reflections by orienting the platy shape of clay minerals parallel to the slide.

The less-than-one-micron clay materials were collected by a combination of decantation and centrifugation methods. The crushed shale samples were thoroughly dispersed in one-liter beakers with distilled water, using an ultrasonic transducer. If the material flocculated, continued washing with distilled water was done until the clay remained in suspension. Then, the dispersed materials were permitted to stand free from disturbance for about 25 hours. This is the time needed for the larger-than-one-micron material to settle 10 cm below the surface in accordance with Stoke's law (density of particles taken as

2.7 g/cm³ and temperature at 25 degrees centigrade). A siphon hose was inserted into the beaker and the suspended material was decanted down to 10 cm. The same procedure was repeated on the decanted material to assume the complete elimination of larger-than-one-micron material. Then, the clay material was collected from the suspension by using a high-speed centrifuge at the speed of 12000 revolution per minute and a flow rate of 40 minutes per liter. These are the settings required to collect all the larger-than-1/20-micron (esd) material according to the calibration curves by Kerns (1967a).

Analytical X-ray Techniques

All the x-ray diffraction patterns were obtained with Norelco and Siemens x-ray diffractometers and recorders with nickel-filtered copper (K-alpha) radiation. The diffracted radiation was detected with a scintillation counter and the goniometer was operated at one degree 2θ per minute. Randomly-oriented powdered slides were scanned to determine gross mineral composition, to differentiate polymorphs of illite, and to distinguish dioctahedral from trioctahedral clay minerals based upon spacing of the (060) reflection. The oriented clays were examined before and after the sample was solvated in a saturated ethylene glycol atmosphere at 60 degrees centigrade for at least 4 hours. Heat treatments in a high temperature oven and diffractometer furnace were carried out to examine heating modifications of clay minerals. Hydrochloric acid treatment was employed to identify kaolin in the presence of chlorite. A detailed description of the analytical x-ray techniques is in chapter 1 of the book, X-ray Identification and Crystal Structures of Clay Minerals, edited by Brown (1961).

Differential Thermal Analysis

Samples were examined by differential thermal analysis on a Robert L. Stone Model DTA-13 M furnace and recorder assembly. The powdered samples were loaded in a stainless steel sample holder using nitrogen as the purging gas. The heating rate was 10 degrees centigrade per minute up to the maximum temperature of 1000 degrees centigrade.

X-ray Fluorescence Analysis

Quantitative x-ray fluorescence analyses were performed by using a Siemens x-ray unit with a chromium source tube, vacuum spectrometer, and a P-10 (methane 10 percent and argon 90 percent) gas flow counter. The heavier elements titanium, manganese, and iron were analyzed with a tungsten source tube and a scintillation counter. KAP, PET, and lithium fluoride were employed as analyzing crystals. A KAP crystal was used for the analysis of sodium, magnesium, and aluminum, PET crystal for silicon, potassium, and calcium, and a lithium fluoride crystal for titanium, manganese, and iron. A Siemens pulse spectroscopy was used for observing the energy distribution of the fluorescence x-rays so that the proper baseline and window settings could be established. Brickettes were prepared by thoroughly mixing a one gram powdered sample with 0.25 grams of Polyvinyl Alcohol (20 percent PVA) and pressed with a die to make a rounded brickette of one inch in diameter surrounded by PVA rims. The empirical curves for the analyses were constructed with the intensity in counts-per-minute as the ordinate and the weight percentage of element oxides as the abscissa. Most of the curves are straight lines. The weight percentage of an oxide in the unknown sample is readily

obtained by dividing the intensity in counts-per-minute by the slope of the straight line and plus or minus a constant value.

The requirements to obtain precise results by the x-ray fluorescence method are discussed in detail by Kerns (1967b, p. 205). The present study approximately followed Kern's procedures with minor variations. Analyses of the heavier elements, potassium, calcium, titanium, manganese, and iron may be reproduced to ± 2 ppt. The reproducibility of silicon and aluminum analyses may be as high as ± 5 ppt and ± 10 ppt may be obtained for magnesium and sodium determinations. Although the lower precision of the lighter elements could be partially due to a stronger absorption effect of the longer wavelength x-ray spectrum, the organic compounds KAP and PET, which were used as analyzing crystals for lighter elements, have been found to change d-spacing slightly but systematically with time, probably due to the gradual increase in temperature. Although the spectral line position was checked frequently and adjustments made, minor errors that would result from a shift of the spectral lines are still inevitable. An additional error has been imposed on the analysis of magnesium because no appropriate standard with a high magnesium content was available.

Emission Spectrographic Analysis

Standards with concentrations of 10, 25, 50, 100, 250, 500, and 1,000 parts per million for the four elements B, V, Ni, and Co were made with spectrographically pure compounds diluted with a silicate matrix which was approximately the composition of the shale. One part of standard or sample was thoroughly mixed with one part of graphite and two parts of SnO_2 were added as an internal standard.

Ignition of the sample was accomplished in a National AGKSP grade, L-4006 sample cathode at 9 amps with an analytical gap maintained at 6 mm for approximately 45 seconds. The counter electrode was a National AGKSP grade, L-4036. The analytical work was done, using a Jarrell-Ash 1.5 meter Wadsworth Mount, Grating Spectrograph. The film used was Eastman Kodak SA-1.

The spectral lines selected for intensity measurement were lines at 3185.3 Å for V, 3414.8 for Ni, 3453.9 for Co, and 3223.7 Å for Sn as the reference. The line chosen for B was at 2497.7 Å with the Sn line at 2408.1 Å as the reference. A Jarrell-Ash Console Microphotometer was used to read the transmission values of the spectral lines which are inversely proportional to intensity (opacity) of the lines. Then, the intensity ratio of the spectral lines of elements to the Sn reference line was read directly from the emulsion curve prepared empirically by John A. Schleicher (former geochemist of the Oklahoma Geological Survey) for this particular kind of film.

Empirical curves (straight lines) were constructed with the intensity ratio of the standards as the ordinate and the content of trace elements of the standards in ppm as the abscissa on a Sidel calculating board. The trace element content of the samples was read directly from the abscissa corresponding to the intersection of the intensity ratio and the empirical line.

Because the computation of the trace element content was based upon the ratio of the intensity of a spectral line with that of a nearby Sn line (internal standard of constant concentration), the ratio is not affected by variations in ignition time, ignition amperage, and

exposure time. Theoretically loss of sample due to careless loading of the electrode should also not affect this ratio.

The major error, if any, in the analyses probably results from the scatter of points for the standard samples from a straight line. However, the deviation was found to be insignificant in constructing the empirical lines for B, Ni, and V. The plotting of the points for the Co standard samples resulted in some scatter from a straight line. This required drawing a best-fit line through the points. However, it should not result in a deviation of more than ± 3 ppm of the Co content as reported.

The other possible error may have been the failure to maintain the same conditions in developing and fixing successive film strips. Nevertheless, this error is considered insignificant.

APPENDIX B

STATISTICAL AND MATHEMATICAL FORMULAE

Student's t Test (Mendenhall, 1963)

Inference concerning the difference between the means of two populations for a small sample size.

- 1) Assumptions: Both populations are approximately normally distributed and $\sigma_1^2 = \sigma_2^2$
- 2) Test: Null hypothesis: $U_1 - U_2 = 0$

Alternative hypothesis: $U_1 - U_2 > 0$ (one-tailed test)

$T = (\bar{X}_1 - \bar{X}_2) / S \sqrt{1/N_1 + 1/N_2}$ where S is a pooled estimate of

$$S = \sqrt{\left(\sum_{i=1}^{N_1} (X_i - \bar{X}_1)^2 + \sum_{i=1}^{N_2} (X_i - \bar{X}_2)^2 \right) / (N_1 + N_2 - 2)}$$

U : Population mean

$\bar{X}$: Sample mean

N : Sample size

σ^2 : Population variance

- 3) Rejection region: Reject if T is greater than $T_{\alpha}(N_1 + N_2 - 2)$,

where α is the tail area.

F Test (Mendenhall, 1963)

Test for comparing the equality of two variances.

1) Assumptions:

- A) Population I has a normal distribution with a mean of μ_1 and a variance of σ_1^2
- B) Population II has a normal distribution with a mean of μ_2 and a variance of σ_2^2
- C) Two independent random samples are drawn, N_1 measurements from population I, N_2 from population II

2) Test: Null hypothesis: $\sigma_1^2 = \sigma_2^2$

Alternative hypothesis: $\sigma_1^2 > \sigma_2^2$

$$F = S_1^2 / S_2^2 \text{ where } S_1^2 = \frac{N_1}{\sum_{i=1}^{N_1}} (X_i - \bar{X}_1)^2 / (N_1 - 1)$$

$$S_2^2 = \frac{N_2}{\sum_{i=1}^{N_2}} (X_i - \bar{X}_2)^2 / (N_2 - 1)$$

$\bar{X}$: Sample mean

N : Sample size

3) Rejection region: Reject if F is greater than or equal to

$F_{\alpha}(N_1 - 1, N_2 - 1)$ where α is the tail area.

Correlation Coefficient

The formula of the linear correlation coefficient is

$$r = \frac{\sum_{i=1}^n (X_i - \bar{X})(Y_i - \bar{Y})}{\sqrt{\sum_{i=1}^n (X_i - \bar{X})^2 \sum_{i=1}^n (Y_i - \bar{Y})^2}}$$

where $\bar{X}$ and $\bar{Y}$ are arithmetic means and n is the sample size.

APPENDIX C

MEASURED SECTIONS

Sections were measured with a hand-level and a steel tape along the cliff faces and channel samples were collected at variations in lithology or at a specific vertical interval, if the lithology was the same. As a maximum thickness of measured section was desirable, the lowest exposure of the Flowerpot Shale in the vicinity of the escarpment was selected for the starting point. In some instances, offset was necessary to avoid poor exposure and limited accessibility. But seldom was the offset a distance of more than 200 feet. However, the upper portion of all the measured sections are confined to the face of the escarpment.

The sample areas were designated by capital letters, M: Major County, and B: Blaine County. The measured sections from the north to the south were given by capital letters A, B, C, D, E, F, in order. Then, lithologic units were designated by numbers 1, 2, 3, . . . from the basal unit to the top unit. Collected samples adopted the same designation. For instance, M-A-15 means that the sample was taken from lithologic unit 15, measured section A, Major County. In order to differentiate the samples collected from the same lithologic unit, letters a, b, c, subfixed to the unit number in an ascending order from the lower to the upper can be seen in some tables of this thesis.

Thin sections are indicated at the end of the description of the individual unit from which they came. All thin sections are on file by accession number in the X-ray Laboratory, School of Geology and Geophysics, University of Oklahoma.

Section M-A

NE $\frac{1}{4}$ SW $\frac{1}{4}$ SW $\frac{1}{4}$ Sec. 22, T. 22 N., R. 13 W., on the east face of a butte capped by Medicine Lodge Gypsum, immediately behind the roadside park, at the north side of highway 15, 6 miles west of the town of Orenta, Major County.

Unit No.		Thickness (feet)
21	MEDICINE LODGE GYPSUM MEMBER Gypsum, white mottled light grey, fine-grained, massive .	16.0
	CEDAR SPRING DOLOMITE BED	
20	Dolomite, light grey, fine-grained, dense, massive, porous.	0.5
19	Shale, highly dolomitic, light greenish-grey, blocky. . .	2.5
	FLOWERPOT SHALE	
18	Shale, dark grey, highly gypsiferous, well-indurated (1730).	0.5
17	Shale, greenish-grey, highly gypsiferous, with a thin hematite layer at the top portion	0.8
16	Shale, red-brown, blocky, crinkly bedded, with some greenish-grey streaks and interbedded with many thin layers of satin spars and selenite.	11.0
15	Dolomite, light greenish-grey, fine-grained, dense, massive, blocky, locally with interlocking selenite crystals (1729)	0.4
14	Shale, dark red-brown, blocky	1.7
13	Shale, dark greenish-grey, blocky (1728).	4.3
12	Shale, red-brown and greenish-grey, gypsiferous	2.0
11	Siltstone, red-brown and greenish-grey, argillaceous, highly gypsiferous, alternating of red-brown and greenish-grey streaks, weakly indurated	17.0
10	Shale, red-brown, mottled with greenish-grey spots and streaks (partially covered)	20.0
9	Sandstone, very fine-grained, gypsiferous, greenish- grey, well-indurated (1740)	0.75
8	Shale, red-brown, blocky.	24.0
7	Shale, red-brown, intercalated with some thin satin spars	11.0
6	Shale and gypsum, white to greenish-grey.	0.4
5	Shale, red-brown, blocky, mottled with greenish-grey spots	26.0
4	Gypsum, white to greenish-grey, nodular	0.7
3	Shale, red-brown, blocky, mottled with greenish-grey spots	35.0
2	Gypsum, white to greenish-white, nodular.	0.35
1	Shale, red-brown, blocky, mottled with greenish-grey spots, some with dark centers (1726).	4.0
	Measured Total	178.9

Section M-B

SW $\frac{1}{4}$ NW $\frac{1}{4}$ Sec. 6, T. 21 N., R. 13 W., on the west end of a mesa capped by Medicine Lodge Gypsum, one mile east of Cheyenne Creek, one mile northeast of the curve in the section-line road, Major County.

Unit No.		Thickness (feet)
MEDICINE LODGE GYPSUM MEMBER		
34	Gypsum, white, mottled light-grey, fine-grained, massive, forming an escarpment.	10.0
CEDAR SPRINGS DOLOMITE BED		
33	Dolomite, light greyish-white, fine-grained, argillaceous, oolitic, somewhat friable, weathering light red-brown	2.5
FLOWERPOT SHALE		
32	Shale, greenish-grey, gypsiferous	1.0
31	Shale, greenish-grey, gypsiferous, well-indurated, containing some satin spar, forming ledge	2.5
30	Shale, red-brown, intercalated with much satin spar, mottled with some greenish-grey lenses and streaks.	14.0
29	Dolomite, grey, argillaceous, fine-grained, dense, gypsiferous at top (1739)	0.6
28	Shale, dark greenish-grey, blocky, intercalated with some red-brown layers (1715).	5.4
27	Shale, red-brown, blocky, mottled with greenish-grey spots	1.0
26	Sandstone, highly gypsiferous, light pinkish-grey, well-indurated, forming ledge (1738).	1.0
25	Shale, silty, red-brown, mottled with greenish-grey spots	6.0
24	Siltstone, highly gypsiferous, moderate to light red-brown, mottled greenish-grey, weakly-indurated, friable	5.0
23	Dolomite, argillaceous, light red-brown, mottled greenish-grey, dense, locally containing cavity-filling gypsum crystals (1737)	0.4
22	Shale, red-brown, intercalated with some greenish-grey lenses and thin satin spars	3.0
21	Siltstone, greenish-grey, weakly-indurated.	6.0
20	Dolomite, light red-brown, mottled greenish-grey, fine-grained, dense (1736)	0.25
19	Shale, red-brown and greenish-grey, containing some satin spars.	1.6
18	Shale, red-brown, blocky, mottled with greenish-grey spots	5.0
17	Dolomite, light red-brown, fine-grained, argillaceous, mottled greenish-grey (1735).	0.2

Section M-B--(Continued)

<u>Unit No.</u>		<u>Thickness (feet)</u>
16	Siltstone, gypsiferous, moderate red-brown, mottled greenish-grey.	1.0
15	Shale, silty, greenish-grey, blocky, well-indurated. . .	1.0
14	Shale, red-brown, blocky, containing some satin spars at the top and bottom portion.	9.3
13	Shale, red-brown, blocky	13.0
12	Shale, gypsiferous, greenish-grey.	0.4
11	Shale, red-brown, blocky	5.0
10	Shale, gypsiferous, red-brown, mottled greenish-grey . .	0.25
9	Shale, light red-brown, mottled with plenty of greenish-grey spots.	16.3
8	Shale, silty, greenish-grey.	0.2
7	Shale, red-brown, blocky	4.5
6	Gypsum, greenish-white, nodular.	0.4
5	Shale, red-brown, blocky	8.7
4	Gypsum, white, nodular	0.7
3	Shale, red-brown, blocky	5.0
2	Shale, silty, greenish-grey (1734)	1.0
1	Shale, red-brown, mottled with greenish-grey spots, blocky (1733).	3.0
Measured Total		135.2

Section M-C

SE $\frac{1}{4}$ SW $\frac{1}{4}$ SW $\frac{1}{4}$ Sec. 24, T. 21 N., R. 13 W., on the north face of the escarpment capped by Medicine Lodge Gypsum, at the south side of the section-line road where it makes a small bend around this escarpment, 4 miles west of the city of Fairview, Major County.

Unit No.		Thickness (feet)
MEDICINE LODGE GYPSUM MEMBER		
20	Gypsum, white mottled with light grey to red-brown streaks, fine-grained.	5.5
CEDAR SPRINGS DOLOMITE BED		
19	Dolomite, light grey, fine-grained, dense, oolitic, well-indurated	0.25
FLOWERPOT SHALE		
18	Shale, greenish-grey, gypsiferous, blocky.	1.0
17	Shale, red-brown, crinkly bedded, interbedded with thin greenish-grey streaks, selenite, and satin spar.	16.0
16	Dolomite, grey, dense, fine-grained, weathering light brown.	0.35
15	Shale, dark red-brown, blocky, with one thin greenish-grey interbed in the middle.	7.0
14	Shale, greenish-grey, highly gypsiferous	3.0
13	Shale, red-brown, blocky	1.0
12	Siltstone, red-brown, dolomitic, intercalated with plenty of greenish-grey streaks and lenses, moderately indurated (1732)	8.0
11	Shale, red-brown, blocky	2.0
10	Shale, red-brown, gypsiferous.	1.0
9	Shale, red-brown, blocky	2.0
8	Shale, red-brown, highly gypsiferous, intercalated with plenty of greenish-grey streaks and lenses	3.8
7	Shale, red-brown, blocky	5.3
6	Gypsum, white, argillaceous, mottled red-brown and greenish-grey forming prominent band	0.5
5	Shale, red-brown, blocky	4.7
4	Gypsum, white, nodular	0.35
3	Shale, red-brown, blocky	5.0
2	Shale, greenish-grey, silty, blocky.	2.0
1	Shale, red-brown, blocky, mottled with greenish-grey spot (1731).	3.5
Measured Total		72.25

Section B-D

Center NE $\frac{1}{4}$ SW $\frac{1}{4}$ Sec. 10, T. 19 N., R. 12 W., on the north face of the escarpment capped by Medicine Lodge Gypsum, 0.4 miles west of the section-line road and 0.2 miles south of a small creek, 4.5 miles east of the town of Longdale, Blaine County.

<u>Unit No.</u>		<u>Thickness (feet)</u>
MEDICINE LODGE GYPSUM MEMBER		
30	Gypsum, white, coarse crystalline, wavy bedded, selenitic, mottled red-brown to pinkish-white in the upper part and greenish-grey in the lower part, forming massive ledge.	7.0
FLOWERPOT SHALE		
29	Shale, red-brown, interbedded with plenty of satin spar.	5.0
28	Gypsum and shale, greenish-grey.	0.2
27	Shale, red-brown, with much satin spar.	2.0
26	Gypsum and dolomite, greenish-grey, well-indurated, forming ledge (1725)	0.4
25	Shale, red-brown, intercalated with much satin spar, mottled with greenish-grey streaks and lenses.	7.4
24	Shale, gypsiferous, greenish-grey, concentration of satin spar layers.	0.4
23	Shale, red-brown, with some satin spar (1723).	2.0
22	Dolomite, light grey, fine-grained, dense (1724)	0.25
21	Shale, dark red-brown.	3.0
20	Shale, dark greenish-grey.	1.3
19	Dolomite, argillaceous, greenish-grey, fine-grained, dense, (1722).	0.1
18	Shale, red-brown	3.6
17	Shale, greenish-grey, silty, well-indurated, containing many selenite.	0.3
16	Shale, red-brown, blocky	4.2
15	Shale, silty, greenish-grey, mottled red-brown, weakly indurated, forming prominent light colored band.	0.8
14	Shale, silty, red-brown (1721)	5.3
13	Shale, red-brown, containing much satin spar	4.3
12	Gypsum, white, nodular	0.2
11	Shale, red-brown, blocky	1.2
10	Shale, with quite a few of white satin spar.	1.3
9	Shale, red-brown, containing many greenish-grey streaks and lenses	21.0
8	Gypsum, white, nodular.	0.2
7	Shale, red-brown, blocky (1720).	16.0

Section B-D--(Continued)

<u>Unit No.</u>		<u>Thickness (feet)</u>
6	Siltstone, dolomitic, greenish-grey, mottled red-brown, well-indurated (1719).	0.2
5	Shale, red-brown, blocky.	17.5
4	Shale, highly silty, greenish-grey, forming prominent light colored band.	2.0
3	Shale, red-brown, blocky.	4.3
2	Gypsum, white, nodular.	0.2
1	Shale, red-brown, mottled with greenish-grey spots, some with dark centers.	6.4
Measured Total		118.05

Section B-E

NE $\frac{1}{4}$ NE $\frac{1}{4}$ NE $\frac{1}{2}$ Sec. 26, T. 19 N., R. 12 W., on the south face of the escarpment capped by Medicine Lodge Gypsum, at the "T-intersection" of section-line roads, one half mile north of the town of Ideal, Blaine County.

Unit No.		Thickness (feet)
MEDICINE LODGE GYPSUM MEMBER		
27	Gypsum, white, banded, fine to coarse-crystalline, mottled light red-brown to pale-pink, greenish-grey in the lower part, forming a massive ledge	7.5
FLOWERPOT SHALE		
26	Shale, red-brown, interbedded with plenty of white satin spar layers.	5.0
25	Gypsum and shale, greenish-grey and red-brown, well-indurated, thin-bedded, forming a ledge.	0.75
24	Shale, red-brown, gypsiferous, intercalated with some satin spars.	2.5
23	Gypsum and shale, greenish-grey.	0.6
22	Shale, red-brown, slightly gypsiferous (1717).	11.4
21	Gypsum, greenish-white, nodular.	0.25
20	Shale, red-brown, with some satin spar	1.7
19	Dolomite, light greenish-grey, dense, fine-grained (1718)	0.25
18	Shale, red-brown, blocky	5.0
17	Gypsum and shale, greenish-grey and red-brown.	5.0
16	Shale, red-brown	5.0
15	Shale, gypsiferous, greenish-grey.	0.2
14	Shale, red-brown	2.2
13	Gypsum, white, nodular	0.2
12	Shale, red-brown	3.2
11	Gypsum, white, nodular	0.25
10	Shale, red-brown	8.5
9	Gypsum, white to greenish-grey, nodular.	0.2
8	Shale, red-brown	3.0
7	Gypsum, greenish-grey to white, nodular.	0.25
6	Shale, red-brown, selenite veins along joints.	2.0
5	Gypsum, argillaceous, white, mottled greenish-grey (1716)	0.25
4	Shale, red-brown, with selenite veins across bedding	3.7
3	Shale, red-brown (partially covered)	10.0
2	Shale, red-brown, mottled with plenty of greenish-grey spots, some with black centers	7.4
1	Dolomite, argillaceous, greenish-grey, well-indurated, dense (1714)	0.1
Measured Total		76.8

Section B-F

SW $\frac{1}{4}$ NE $\frac{1}{4}$ SE $\frac{1}{4}$ Sec. 23, T. 18 N., R. 12 W., on the south face of the escarpment capped by Nescatunga Gypsum, the north side of Salt Creek Canyon, 2 miles east of highway 51 A, Blaine County.

Unit No.		Thickness (feet)
MEDICINE LODGE GYPSUM MEMBER		
52	Gypsum, white, mottled reddish-grey and greenish-white, fine to coarse crystalline, massive, forming a mappable escarpment.	4.5
CEDAR SPRINGS DOLOMITE BED		
51	Dolomite, light-grey, fine-grained, dense.	0.1
FLOWERPOT SHALE		
50	Shale, greenish-grey and red-brown, highly gypsiferous (partially covered).	6.0
49	Shale, gypsiferous, greenish-grey, red-brown at the top, well-indurated, forming a prominent ledge	0.7
48	Shale, red-brown, containing much white satin spar	1.8
47	Gypsum, white, hematite-stained, well-indurated.	0.1
46	Shale, red-brown, interbedded with greenish-grey layers and lenses, containing much satin spar	6.0
45	Siltstone, gypsiferous, greenish-grey, well-indurated, forming ledge (1713)	0.4
44	Shale, red-brown, mottled with greenish-grey spots	7.2
43	Shale, red-brown and greenish-grey, gypsiferous.	6.5
42	Dolomite, greenish-grey, fine-grained, dense (1712).	0.4
41	Shale, red-brown, containing lots of thin selenite	5.0
40	Gypsum and shale, white to greenish-grey	0.8
39	Shale, red-brown, containing much selenite.	3.5
38	Gypsum, white, nodular	0.2
37	Shale, red-brown	3.0
36	Gypsum, white, nodular	0.4
35	Shale, red-brown	2.0
34	Gypsum, white to greenish-grey, nodular.	0.2
33	Shale, red-brown	1.0
32	Gypsum, white to greenish-grey, nodular.	0.6
31	Shale, red-brown, containing some satin spar	4.3
30	Shale, dolomitic, light red-brown, mottled with greenish-grey spots, blocky.	0.3
29	Gypsum, essentially white satin spar layers.	0.4
28	Shale, red-brown	2.5
27	Gypsum, white to greenish-grey, nodular.	0.2
26	Shale, red-brown	3.3

Section B-F--(Continued)

<u>Unit No.</u>		<u>Thickness (feet)</u>
25	Shale, highly gypsiferous, greenish-grey and red-brown.	0.5
24	Shale, red-brown	5.3
23	Shale, highly dolomitic, silty, light red-brown, mottled with greenish-grey spots, some with dark centers.	0.25
22	Shale, red-brown, mottled with many greenish-grey spots, some with dark centers.	10.8
21	Shale, red-brown	11.0
20	Shale, red-brown, blocky	12.0
19	Covered, essentially red-brown shale	35.0
18	Dolomite, silty, greenish-grey, dense (1711)	1.0
17	Shale, red-brown	15.0
16	Shale, greenish-grey	0.5
15	Shale, red-brown, mottled greenish-grey.	3.7
14	Shale, greenish-grey	2.0
13	Shale, greenish-grey and red-brown	1.0
12	Shale, red-brown, blocky	6.0
11	Shale, silty, greenish-grey.	1.0
10	Shale, red-brown, blocky	8.0
9	Shale, silty, greenish-grey and red-brown.	1.5
8	Siltstone, greenish-grey	0.2
7	Shale, red-brown, blocky (1710).	5.4
6	Gypsum, white, nodular	0.5
5	Shale, red-brown	5.0
4	Siltstone, greenish-grey, well-indurated	0.2
3	Shale, red-brown, mottled with greenish-grey spots	5.0
2	Siltstone, argillaceous, greenish-grey, mottled red-brown, friable	1.5
1	Shale, red-brown, blocky	2.0
Measured Total		196.65