

GEOCHEMISTRY AND MINERALOGY OF THE PERMIAN
RED BEDS AND RELATED COPPER DEPOSITS,
PAYNE, PAWNEE, AND NOBLE
COUNTIES, OKLAHOMA

By

RICHARD RALPH HEINE

//

Bachelor of Science

Oklahoma State University

Stillwater, Oklahoma

1973

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the Degree of
MASTER OF SCIENCE
May, 1975

SEP 12 1975

GEOCHEMISTRY AND MINERALOGY OF THE PERMIAN
RED BEDS AND RELATED COPPER DEPOSITS,
PAYNE, PAWNEE, AND NOBLE
COUNTIES, OKLAHOMA

Thesis Approved:

Zuhair Al-Shaieb

Thesis Adviser

Ray J. Starnes

John Trammell

N. N. Denton

Dean of the Graduate College

916333

PREFACE

This study attempts to delineate "red bed" copper mineralization in north-central Oklahoma using geochemical and field techniques. Copper distribution in stream sediments and bed rock was used as a guide for the tracing of mineralization to its source. Computer programs for trend surface and statistical analysis were used to prepare geochemical maps and to study relationships between spatial distribution of copper and clay minerals. Relations to other occurrences of copper in Oklahoma are discussed, and associations between copper occurrences and lithofacies of the host rocks within the study area are presented.

The writer wishes to express his gratitude and appreciation to Dr. Zuhair Al-Shaieb, thesis adviser, for his guidance, assistance, and many enlightening discussions. Special thanks are also due to Dr. Gary F. Stewart for his help with the depositional environments and Professor John W. Trammell for his constructive criticism of the manuscript. The author would also like to acknowledge Cities Service Minerals Corporation for allowing the use of atomic absorption spectrophotometry lamps for gold and silver analysis.

Finally, and most importantly, the author would like to thank his wife, Carol, and his son, Bobby, for their patience and understanding during the past two years.

TABLE OF CONTENTS

Chapter	Page
I. ABSTRACT.	1
II. INTRODUCTION.	2
Objectives and Methods	2
Previous Investigations.	4
Classification of Copper Deposits in Oklahoma.	5
Red Bed Type.	9
Copper-Shale Type	9
III. GEOLOGIC SETTING.	11
General Geology.	11
Structural Geology	13
IV. RELATION OF COPPER MINERALIZATION TO THE LITHOFACIES.	14
Distributary Channels.	14
Interdistributary.	17
Interdistributary Bay.	22
Tidal Flat	22
Shallow Marine	23
V. METHODS OF INVESTIGATION.	24
Sample Collection.	24
Stream Sediments.	24
Bed Rock Samples.	24
Sample Preparation	24
Stream Sediment and Bed Rock Samples.	24
Clay Mineral Content.	25
Statistical Procedures	25
Trend-Surface Analysis.	26
Factor Analysis	26

TABLE OF CONTENTS (Continued)

Chapter	Page
VI. RESULTS AND DISCUSSIONS.	28
Geochemical Maps.	34
Spatial Relationships of Copper and Clay Mineral Content of the Host Rocks.	43
Correlation of Clay Minerals and Copper	45
Copper cf. Clay in Shale.	46
Factor 1 (Kaolinite, Chlorite, and East-West Coordinate).	46
Factor 2 (Copper and North-South Coordinate)	46
Factor 3 (Illite and Chlorite)	46
Copper cf. Clay in Sandstone.	49
Factor 1 (Illite and Kaolinite).	49
Factor 2 (Chlorite and East-West Coordinate)	49
Factor 3 (Copper and North-South Coordinate)	49
Summary of Factor Analysis.	49
VII. SUMMARY.	52
SELECTED BIBLIOGRAPHY.	54
APPENDIX A. ANALYTICAL PROCEDURE FOR THE DETERMINATION OF COPPER CONTENT	56
APPENDIX B. COPPER CONTENT OF SANDSTONES.	58
APPENDIX C. COPPER CONTENT OF SHALES.	64
APPENDIX D. SILVER CONTENT OF SELECTED SAMPLES.	69

LIST OF TABLES

Table	Page
I. Types of Copper Deposits in Oklahoma.	8
II. Statistical Parameters for Copper Distribution in Stream Sediments and Bed Rock Samples.	33
III. Statistics for Trend Surface Analysis	41
IV. Factor Analysis	47

LIST OF FIGURES

Figure	Page
1. Index Map of Study Area.	3
2. Location Map of Oklahoma Copper Deposits	6
3. Columnar Section of Study Area	12
4. Channel Deposit.	15
5. Replacement of Carbon Film from Channel.	15
6. Replacement of Carbon Wood from Channel.	16
7. Nodule Containing Chalcocite, Malachite, and Azurite	18
8. Concretion Containing Chalcocite and Malachite	18
9. Pyrite Nodule from Channel	19
10. Replacement of Calcite Cement by Malachite	19
11. Gypsum Associated with Channel	20
12. Channels Overlying Interdistributary Shales.	20
13. Malachite Blebs from Interdeltaic Deposit.	21
14. Limonite-Rich Shale in Interdistributary Deposit	21
15. Distribution of Copper in Stream Sediments	29
16. Distribution of Copper in Shales	30
17. Distribution of Copper in Sandstone.	31
18. Distribution of Silver and Copper in Selected Samples.	32
19. Geochemical Stream Sediment Map.	35
20. Copper Distribution in Sandstone	36
21. Copper Distribution in Shale	37
22. Location of Copper Mineralization.	39

LIST OF FIGURES (Continued)

Figure	Page
23. Silver Distribution from Selected Samples.	40
24. Trend Surface Maps of Degrees 1 Through 4.	42
25. Residual Map for Copper in Bed Rock.	44
26. Distribution of Clay Minerals in Shale	48
27. Distribution of Clay Minerals in Sandstone	50

CHAPTER I

ABSTRACT

"Red bed" copper deposits in Payne, Pawnee, and Noble Counties, Oklahoma, are in deltaic, interdeltic-deltaic, and shallow marine environments. The deltaic facies includes copper-bearing distributary and interdistributary facies, and the interdeltic-deltaic facies consists of rocks deposited in tidal flats and interdistributary bays. The deltaic types predominantly occur in the middle part of the stratigraphic section, whereas the interdeltic-deltaic and shallow marine environments occur in the upper and lower parts of the column.

The mineralization commonly is replacements of carbonaceous material, disseminations of chalcocite, malachite, and azurite, and pyrite nodules containing chalcocite, malachite, and azurite. Minor quantities of covellite, tenorite, gold, and silver have been reported. The majority of the mineralized zones were located geochemically using stream sediments. Factor analysis clearly indicates that copper increases in a northerly direction. The residuals of trend-surface analysis of copper in bed rock coincide with known subsurface structural features.

CHAPTER II

INTRODUCTION

The area studied includes approximately 350 square miles in parts of Payne, Pawnee, and Noble Counties, Oklahoma (Fig. 1). It includes all or parts of T19, 20, 21, 22N, R3, 4, 5E. The largest city is Stillwater in the southwest corner of the study area. Other towns within the area are Glencoe, Lela, and Pawnee. Good roads make the area readily accessible, with 5 paved highways and a better-than-average system of secondary and section-line roads. County roads are generally graded with a surface of crushed rock. Many of these roads become temporarily impassable after heavy rains, especially where roads are built across shale outcrops. The Atchison, Topeka and Santa Fe railroad crosses the area in a north-south direction serving Glencoe, Stillwater, and Pawnee. The St. Louis and San Francisco railroad crosses the area in an east-west direction serving Lela and Pawnee.

Objectives and Methods

The main objectives of this study are: (1) to delineate the extent of copper mineralization by using geochemical and field methods, (2) to determine the relationships of copper mineralization to the lithofacies of the host rocks, and (3) to study relationships between the copper mineralization and the subsurface structure. Similarities to other Oklahoma copper deposits are discussed, and relationships to regional

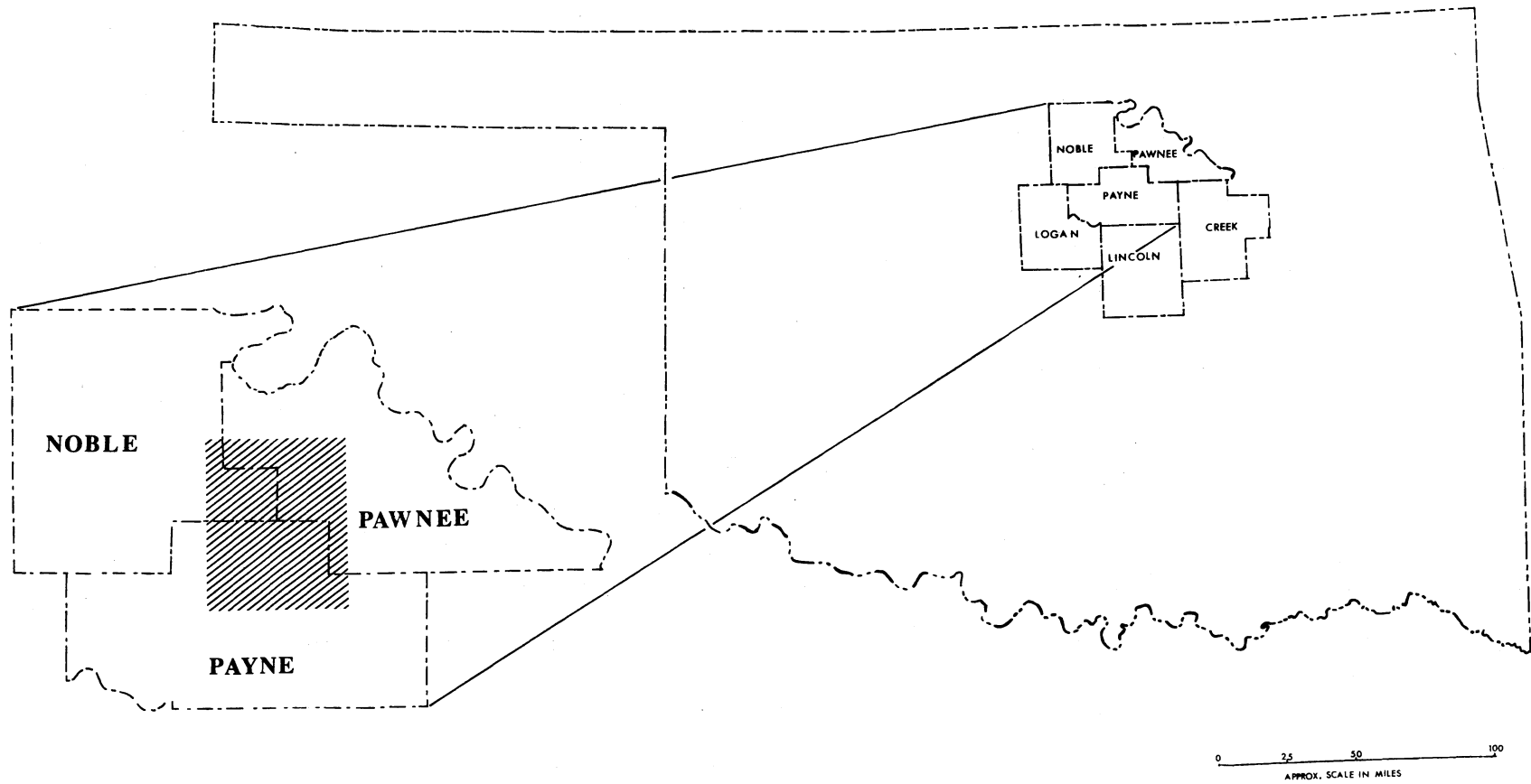


Fig. 1.-Index map of study area

geology are described.

Approximately 1,200 stream-sediment samples and 200 rock samples were analyzed for copper, and selectively for lead, zinc, and silver, using a Perkin Elmer 403 atomic absorption spectrophotometer. X-ray diffraction was used to determine the clay mineral composition of the -2 micron fraction of sandstone and shale. The data obtained were analyzed and interpreted by trend-surface and factor analysis, using an IBM 360 computer.

Previous Investigations

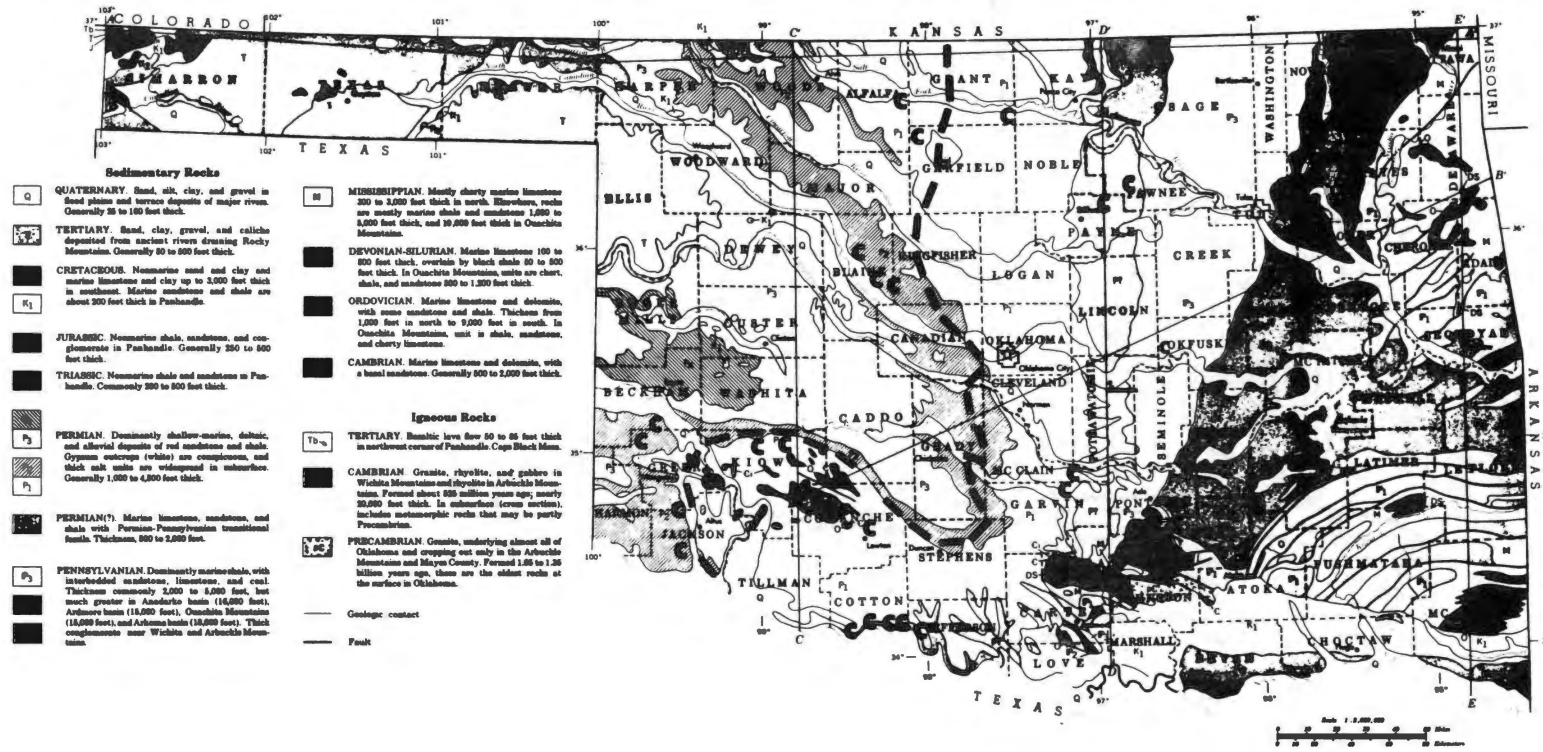
The earliest contribution to the economic geology of the area was made by Tarr (1910), who wrote a brief report on the occurrence of copper in northern Payne County. Fath (1915) and Rogers (1916) described polished sections of copper ores from the red beds of Oklahoma. Fischer (1937) described a Pawnee County deposit, which is probably one of the many found north of the town of Lela. Merritt (1940) also described the Pawnee County deposits north of Lela and reviewed the several theories of origin. The occurrence and value of radioactive minerals associated with some copper deposits were discussed by Branson and others (1955). Stroud reviewed the potential for production of copper deposits associated with the Permian red beds in Texas, Oklahoma, and Kansas. Ross (1972) mapped the surface geology of Payne County and prepared a structural geologic map of the shallow subsurface. The surface geology of Pawnee County was mapped by Greig (1959) and Noble County was mapped by Shelton (in press).

Classification of Copper Deposits in Oklahoma

Copper minerals in the Permian red beds of Oklahoma have been known since the time of the R. B. Marcy exploration in 1852. In the area that is now part of Jefferson County, Oklahoma, the Marcy party observed copper mineralization within beds of sandstone and shale of the Wichita Formation. Early development of these low grade, relatively unexplored copper deposits was hampered by uneconomic mining and milling techniques.

Prospect pits and tunnels have been used to explore some of the more promising outcrops in Oklahoma. Prior to 1965, processing of copper ores consisted of gravity separation and some hand cobbing. Some mine-run ore was shipped directly to the smelter.

The copper occurrences of Oklahoma are widely scattered throughout the north-central and southwest parts of the state. Age of the host rock ranges from Early Permian (Roca shale in central Oklahoma) to Middle Permian (Flowerpot Formation). The copper deposits show a sinuous belt with a north-south trend extending southward from Alfalfa and Grant Counties to Jackson and Greer Counties (Fig. 2). These deposits can be divided into two types; those representing interdeltatic or deltatic facies, and those comprising shallow marine or basinal facies. The copper in coastal environments is designated the "red bed" type whereas those found in the basinal or shallow marine rocks will be referred to as the copper-shale type (Table I). Because of the difference in economic potential of "red bed" and copper-shale types, a classification of the type encountered is of the uppermost importance. Even though they represent two basic groups, some care must be exercised in separating them because, in several areas, they co-exist.



GENERALIZED GEOLOGIC MAP (AFTER JOHNSON ET AL. 1972)

--- COPPER ZONE (AFTER STROUD ET AL. 1970)

C COPPER LOCATIONS (AFTER JOHNSON ET AL. 1972)

Fig. 2.—Distribution of copper deposits in Oklahoma

NR - Not Reported

LITHOLOGY

Sh - Shale
SS - Sandstone
Cgl - Conglomerate
LS - Limestone

LITHOFACIES

C - Distributary Channel
D - Deltaic, Interdeltaic-Deltaic
S - Shallow Marine

MODE OF OCCURRENCE

D - Disseminations
N - Nodules
R - Replacement of Carbonaceous Material
Rc - Replacement of Cement
S - Stains

MINERALOGY

N - Native Copper
C - Chalcocite
B - Bornite
T - Tenorite
Cr - Chrysocolla
M - Malachite
A - Azurite
Py - Pyrite

CARBONACEOUS MATERIAL

+ - Present
- - Absent

GENETIC TYPE

RB - Red Bed
D - Deltaic
ID - Deltaic-Interdeltaic
S - Shallow Marine
CS - Copper Shales

TABLE I
TYPES OF COPPER DEPOSITS IN OKLAHOMA

LOCATION	LITHOLOGY	LITHOFACIES	MODE OF OCCURRENCE	MINERALOGY	CARBONACEOUS MATERIAL	GENETIC TYPE
Blaine Co.	Sh	S	D, S	C, M	--	CS
Beckham Co.	Sh	S	D, S	C, M	--	CS
Jackson Co.	Sh	S	D, S	C, M	--	CS
Greer Co.	Sh	S	D, S	C, M	--	CS
Garvin Co.	SS	C	N, S	C	--	RB, D
Garfield Co. Location Uncertain	Sh, SS	NR	N	N	NR	RB
Cotton Co.	SS, Sh	C	N, S, R	C, Py, M, A	+	RB, D
McClain Co.	SS	C	N, S	M	NR	RB, D
Grant Co. Location Uncertain	Sh, SS	NR	D, N, R	M	NR	RB
Commanche Co.	SS, Cgl	NR	D, N, S	M	+	RB
Jefferson Co.	SS	NR	N, D, S, R	M	+	RB
Payne Co.	SS, Sh, LS	D, ID, S	N, D, S, Rc, R	C, Py, B, M, A	+	RB, DS, D, S
Pawnee Co.	SS, Sh, LS	D, ID	N, D, S, Rc, R	C, Py, B, M, A	+	RB, DC, D

Red Bed Type

The "red bed" copper deposits of Oklahoma occur in locally bleached areas within red-beds. The minerals occur in sandy shale, sandstone, dolomite, and conglomerate. Chalcocite and its oxidation products, malachite and azurite, are found as nodules of chalcocite and as replacements of wood and sandstone cement, and as replacements of pyrite concretions. Disseminations of chalcocite are sparse. Gypsum commonly occurs with the copper-shales.

One of the better known "red bed" copper deposits of Oklahoma is located near the town of Paoli in Garvin County (Shockey, Renfro, and Peterson, 1973). Host rocks for copper-silver minerals are channel-fill sandstones in the Permian Wellington Formation. The sandstone is greenish-gray, friable, well-sorted, and fine to medium grained. No carbonaceous material is associated with the copper minerals. In the surrounding area, the Wellington Formation is typically a red claystone or siltstone. The mineralization fronts occur at sharp oxidation-reduction interfaces which are marked by red-gray color changes within the sandstone. Copper minerals occur as nodules, replacements of the cement, and disseminations of chalcocite, malachite, and azurite. Native silver and minor amounts of lead, zinc, gold, and other elements are present. Uranium and other radioactive minerals are absent. Ore-grades are not continuous along the solution front but are concentrated along cutbanks in the paleochannel. Tenor is 0.75% copper and 6 ounce per ton silver.

Copper-Shale Type

Some of the largest and richest copper deposits in the world are of the copper-shale type. Their stratigraphic continuity is perhaps the

most striking feature that separates them from the "red bed" type. The mineralization is primarily in shales and sandy shales, although the minerals may also be in dolomite and evaporites. Disseminations of chalcocite, malachite, azurite, and replacements of finely disseminated pyrite and spores are common. Copper-shale mineralization is generally continuous and more uniform.

One of the better examples of the copper-shale deposits in Oklahoma is the Creta ore body in Jackson County. The copper is in the upper part of the Flowerpot Shale of the El Reno Group. It is believed that much of the Flowerpot Shale was deposited in a marine environment. The main evidence is gypsum, dolomite, and halite interbedded with the shales. A shallow marine environment has been postulated for rocks that contain the copper. The copper-bearing bed ranges in thickness from 6 to 16 inches. The principal ore mineral is chalcocite that replaces spores and disseminated pyrite. Surface staining of malachite and azurite is common. No mineral zonation has been reported (Lockwood, 1970).

CHAPTER III

GEOLOGIC SETTING

General Geology

The surface rocks of the study area are of Early Permian age¹, overlain locally by deposits of Quaternary age. Although most of the stratigraphic section is within the Wolfcampian Series, the upper 15 feet is considered a part of the Leonardian Series (Greig, 1959; Ross, 1972). The section, approximately 1100 feet thick, extends from the base of the Admire Group to within the lower 15 feet of the Wellington Formation. The gentle westward structural dip is responsible for the surface beds becoming younger in that direction and showing a strike of approximately north-south.

The section is characterized by a repetitious sequence of shales, carbonates, and lenticular sandstones (Fig. 3). The carbonates below the Eskridge Shale are continuous, fossiliferous limestones representing transgressive units as opposed to discontinuous, non-fossiliferous, nodular dolomites occurring above the Eskridge Shale formed during transgressions. These discontinuous dolomites thicken northward and show a change of facies to thin fossiliferous limestones and thick shales. Both the lowermost and uppermost parts of the section are predominately mud-

¹Some geologists believe that the Permian-Pennsylvania boundary should be placed at the top of the Herrington Limestone (Johnson, et al., 1972).

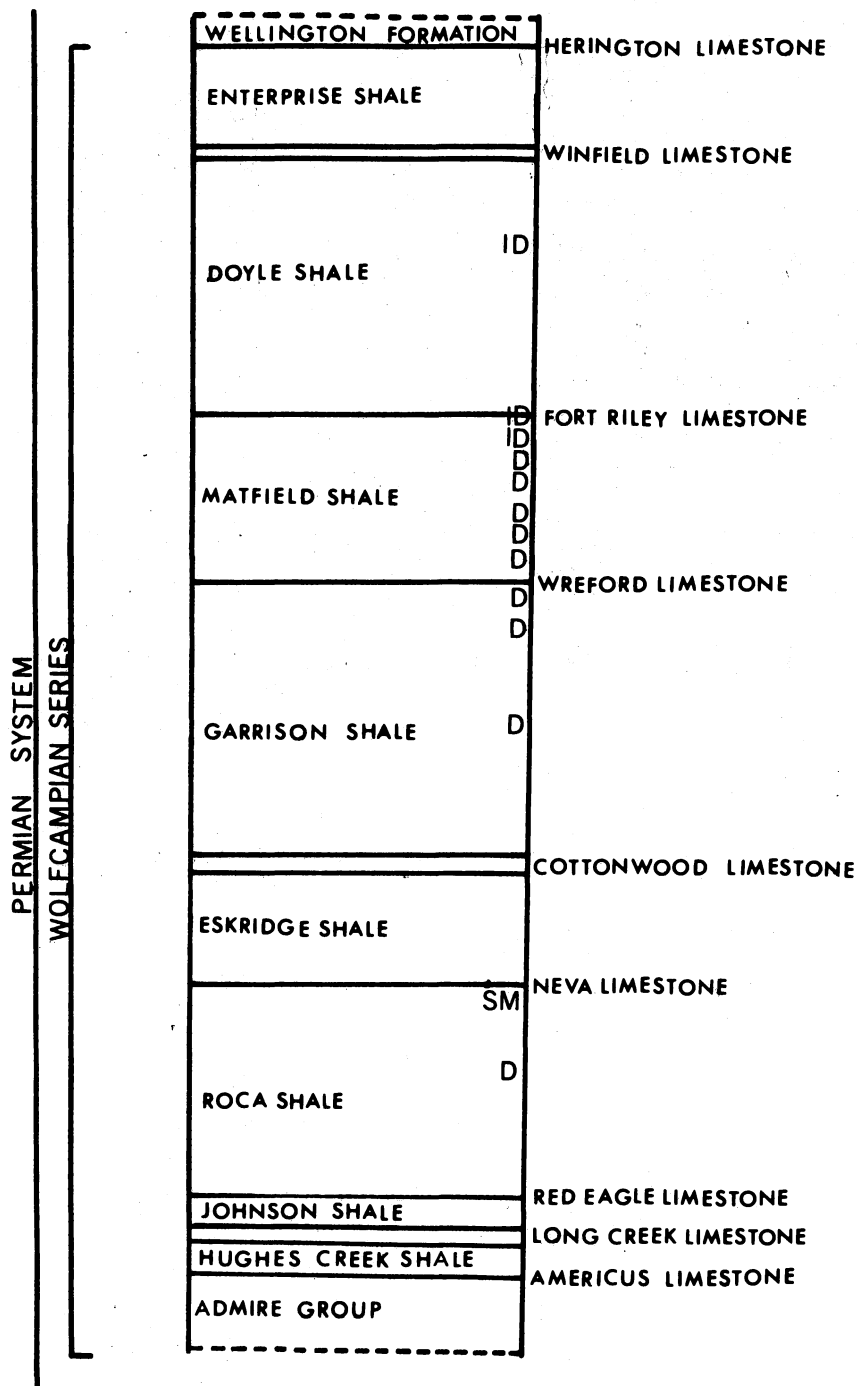


Fig. 3.-Columnar section of study area showing positions of deltaic (D), interdeltic-deltaic (ID), and shallow marine (SM) rocks that contain copper

stone; most of the formally named shale units contain abundant lenticular sandstones. The sandstones of Payne County are described as being fine- to very-fine-grained, feldspar-rich quartzarenites, with an average paleocurrent direction of N 50° W (Ross, 1972). In the Doyle, Matfield, and Garrison shales, sandstones decrease northward.

In general, sand deposition and arid climatic conditions become increasingly frequent with time. The area probably was part of the upper deltaic plain of sand-rich, tide-dominated deltas during regressions and the supratidal zone of carbonate tidal flats during transgressions. Influx of sand decreased during late Wolfcampian and Leonardian time with tidal flat conditions becoming more dominant.

Structural Geology

The principal structural feature of the surface rocks in the study area is the gentle, homoclinal, westward dip at 30 to 65 feet per mile (Greig, 1959; Ross, 1972). In Pawnee County, this homocline is interrupted locally by north-trending belts of en-echelon faults. Ross (1972, p. 45) described this homocline as having an undulatory surface of noses and saddles caused by local steepening and flattening of dip. Although the majority of the folds are generally less than a square mile in size, some seem to form subtle complexes 10 to 35 square miles in areal extent. The structures are generally not reflected at the surface except topographically by drainage anomalies.

No faults were observed in Payne County. Two sets of open joints, N 60° E and N 50° W with vertical dip, probably are extensional joints (Ross, 1972).

CHAPTER IV

RELATION OF COPPER MINERALIZATION TO THE LITHOFACIES

Copper-bearing rocks include shales, siltstones, sandstones, limestones, dolomites, and conglomerates. Most of these strata are interbedded and lenticular. "Red bed" copper occurrences are within the framework of deltaic, interdeltatic-deltaic, and shallow marine facies. The deltaic coppers occur in distributary and interdistributary units, whereas the interdeltatic-deltaic include tidal flat and interdistributary bay sequences.

Distributary Channels

Deposits are characterized by sharp erosional lower and lateral contacts, variable downstream paleocurrent directions, and initial dip representing bank slope. Channel-fill deposits show good sorting of sands and upward decrease in grain size. They are sand-rich with little or no shale. The trends of the deposits are perpendicular to the regional depositional strike of the coast line. In cross-section, channel-fill units are characteristically lens shaped, and cut out the underlying unit (Fig. 4).

The channels associated with carbonaceous material probably are braided tidal channel-fills (Ross, 1972). Most copper minerals in the channels have replaced carbonaceous material (Fig. 5, 6). Such deposits



Fig. 4.-Channel deposit showing typical lens shaped cross section. (O), oxidized, (R), reduced, Sec. 30, T18N, R2E

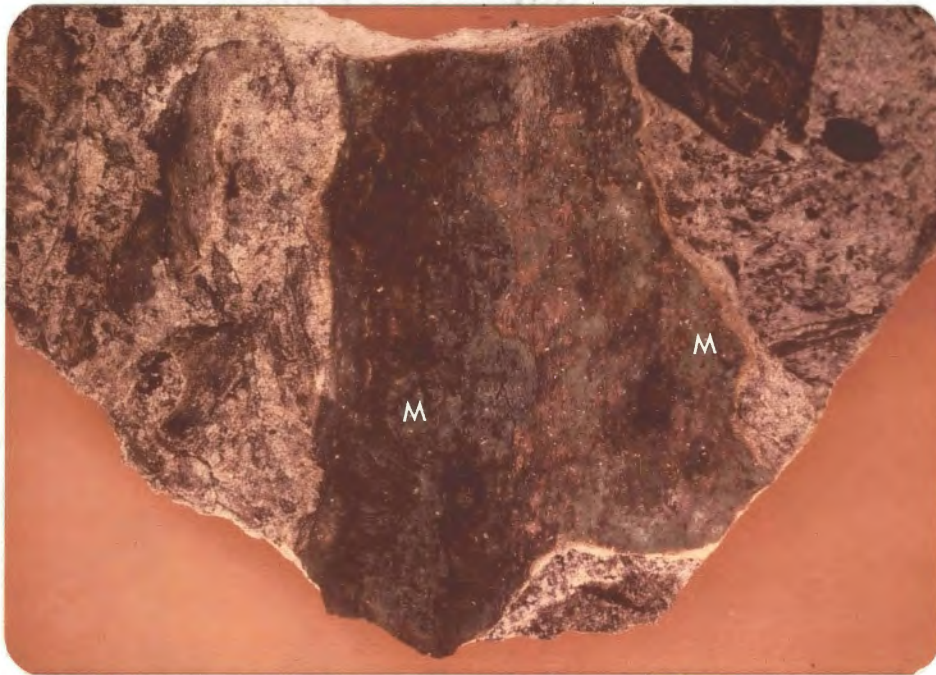


Fig. 5.-Carbonaceous plant material on bedding plane, replaced chalcocite with oxidation of malachite (M), Sec. 31, T20N, R4E



Fig. 6.-Replacement of carbonaceous wood by chalcocite (C), malachite (M), and azurite (A). From channel deposit in Sec. 23, T20N, R3E

are smaller and contain higher-grade mineralization than the other deposits. The higher-grade is probably due to the limited extent of the host rock, which permitted enrichment by the introduction of copper solutions. Most mineralization is malachite and azurite stains, although chalcocite disseminations or concretions also are present (Fig. 7, 8). Pyrite nodules are rarely found (Fig. 9). Rogers (1916) described the concretions in a Payne County channel deposit as being largely chalcocite, pyrite, and quartz with traces of covellite and silver. The chalcocite replaces the sandstone cement and, to some extent, the sand grains themselves (Fig. 10). Stratigraphically, the lowermost copper-bearing channel deposit which occurs in the Eskridge Shale was found to be the only unit that contained gypsum. The satin spar gypsum cut the beds in a red shale which underlay the paleochannel (Fig. 11). Copper in the distributary channels ranged up to 0.1 percent, whereas lead and zinc ranged in value from 5 to 50 parts per million.

Interdistributary

The interdistributary sequence consisted of shales interbedded with thin splay sands, some beds of which contain an occasional small-scale cross-bedding (Fig. 12). The beds range from a few inches to a few feet thick. The mineralization in this deposit occurs as blebs of malachite and azurite (Fig. 13). Like the channel deposits, the mineralization is scattered throughout the host rock as replacements of carbonaceous material and as disseminations of chalcocite. The copper is more continuous and more uniform in grade than in the channel deposits. The top few inches of this deposit are a limonite-rich layer of shale (Fig. 14). Limonite, which usually results from the weathering of iron minerals

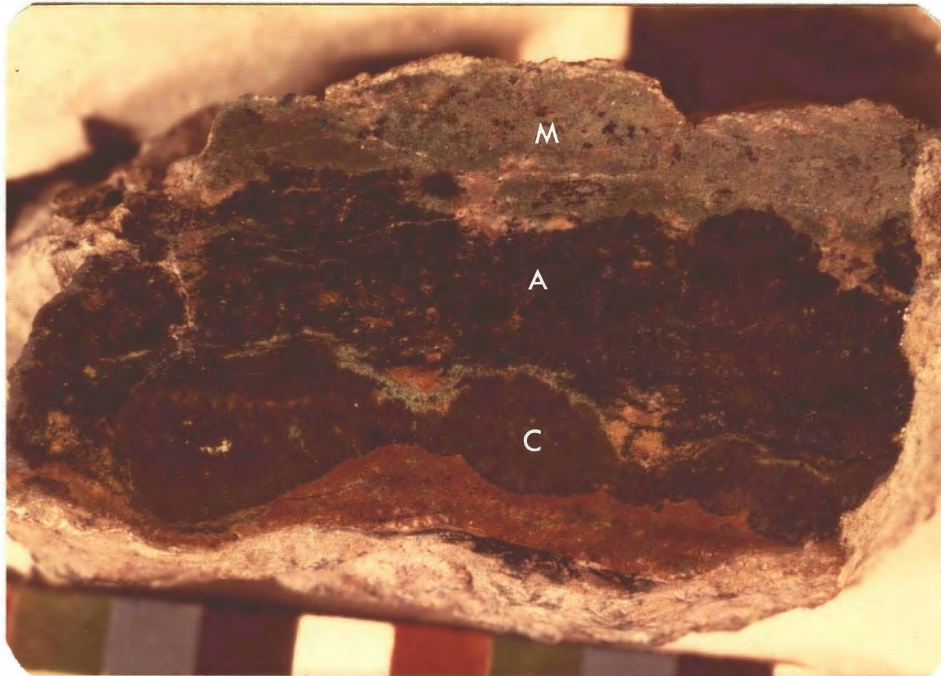


Fig. 7.-Nodule of chalcocite (C), malachite (M), and azurite (A). From channel in Sec. 19, T22N, R4E

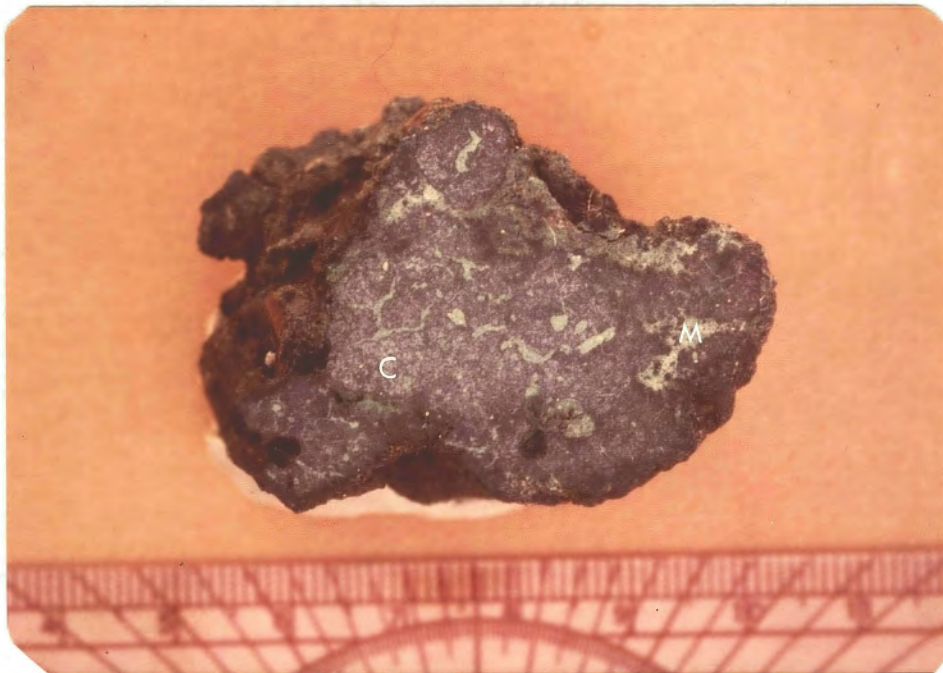


Fig. 8.-Chalcocite (C) nodule with malachite (M) in Sec. 23, T20N, R3E

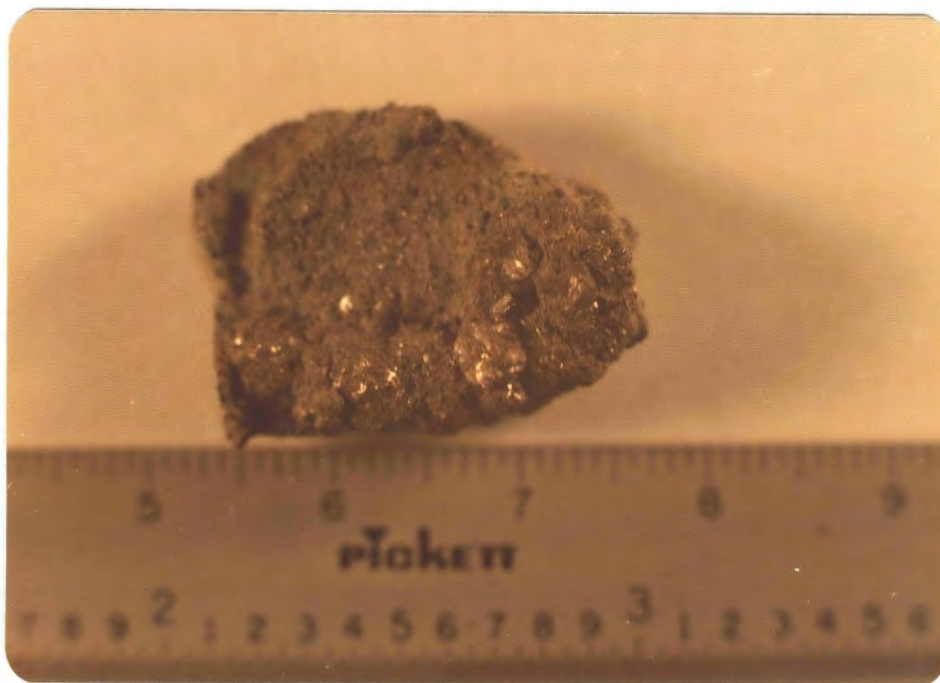


Fig. 9.-Pyrite Nodule from channel in Sec. 23, T20N,
R3E



Fig. 10.-Replacement of calcite cement by malachite (M)
from channel in Sec. 19, T22N, R4E



Fig. 11.-Satin-spar gypsum (G) cutting across bedding from Sec. 30, T20N, R5E



Fig. 12.-Channels (D) overlying interdistributary shales and splay sands (ID) from Sec. 2, T19N, R3E

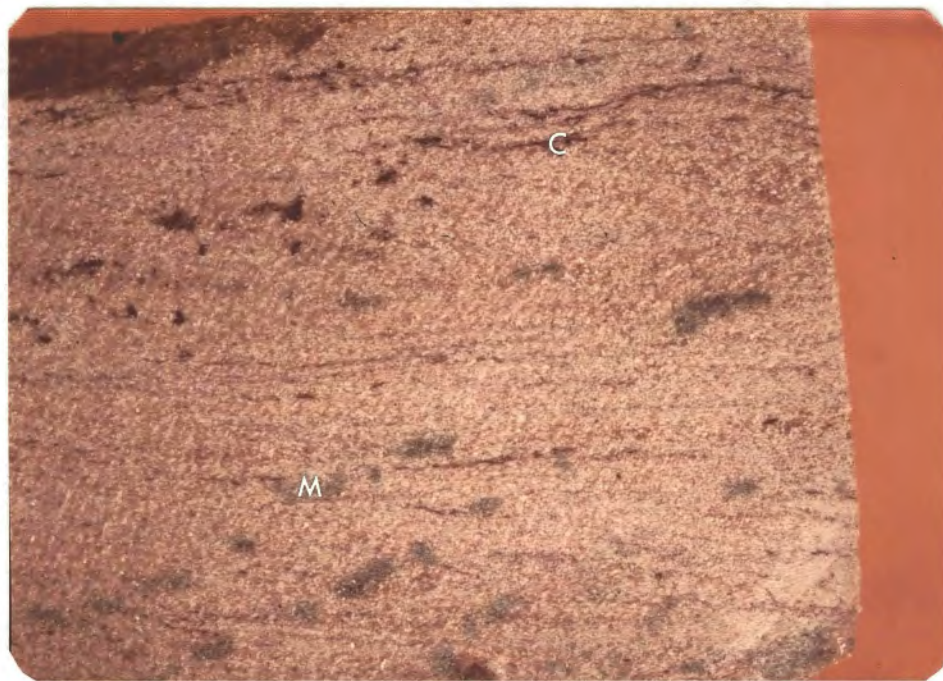


Fig. 13.-Spots of malachite (M) cutting carbonaceous bedding (C) in a thin splay sand from the interdistributary deposit in Sec. 2, T19N, R3E



Fig. 14.-Limonite-rich shale (L) in upper part of interdistributary deposit in Sec. 2, T19N, R3E

such as pyrite, probably was caused by slowly circulating, oxidizing ground water. Liesegang banding was also observed in the overlying sandstones, indicating possible fluid movement. The copper content of this deposit increases with depth and ranges from .02 to .2 percent. The lead and zinc range from 5 to 50 parts per million.

Interdistributary Bay

The sequence consists of fine-grained sandstone with such features as cutouts and small-scale cross-bedding. A lenticular clay-pebble conglomerate is contained in the sandstone. The conglomerate is cemented by sandy calcite.

The trend of this unit is approximately parallel to the regional depositional strike. This unit is sparsely fossiliferous, indicative of its marine or near-marine origin. The underlying red sandy shale contains carbonate concretions. Finely divided carbonaceous material and pyrite are restricted to the clay pebbles. The clay pebbles probably were derived from interdistributary material. Chalcocite and its oxidation products, malachite and azurite, are confined to the clay pebbles.

Tidal Flat

The tidal flat deposits form a wedge shaped body that is elongate parallel to the shoreline, but may be intersected by channels. Planer bedding and burrowed and mottled bedding are present. Finely divided plant remains and fragments of fossils are sparse. An upward increase in grain size, ripple marks paralleling the depositional strike, and glauconite-bearing sands are other features sometimes shown in these deposits. The lithology of the tidal flat environments in the study

area is sandy shale and fine-grained sandstone. Both contain carbonate-bearing concretions. At the northwestern locations, the concretions contained pyrite crystals which had subsequently been replaced by chalcocite surrounded by malachite stains. Chalcocite, malachite, and azurite are disseminated through the host rock and as staining along bedding and laminations. In these rocks, copper ranges from .01 to .3 percent and lead and zinc range from 5 to 25 parts per million.

Shallow Marine

Shallow marine environments are blanket-like and are flanked by marine fine-grained sediments on one side and coastal deposits on the other. The deposits commonly show gradational lower and lateral contacts, horizontal bedding, burrowing, medium-scale cross-bedding, and diverse paleocurrent directions. Glauconite, finely divided plant material, and marine fauna are common.

Copper in shallow marine environments within the study area occurs in two ways: as replacements of pyrite concretions by chalcocite and malachite, and as chalcocite- and malachite-bearing worm burrows in a fossiliferous limestone. The concretions are restricted to a zone 6 to 8 inches thick, underlying the fossiliferous limestone. Malachite, azurite and evaporites are absent.

CHAPTER V

METHODS OF INVESTIGATION

Sample Collection

Stream Sediments

Samples of silt and clay were collected from dry and wet drainages. To minimize the sampling of loess and bank material, all samples were collected from the centers of streams at depths of 3 to 4 inches. All samples were collected upstream from any possible source of contamination.

Bed Rock Samples

Rock samples were collected from the cleaned faces of outcrops, along drainages having anomalous stream sediment values. Each lithologic unit was sampled and described according to color, sedimentary structures, mineralogy, grain size, carbonaceous content, and visible copper mineralization.

Sample Preparation

Stream-Sediment and Bed-Rock Samples

All samples were dried within 10 hours of collection by placing them inside an oven on aluminum racks at 80^o centigrade. The samples

were then crushed to pass a ¼-inch mesh by using a jaw crusher, and the -80 mesh fraction was separated using a stainless steel sieve (Appendix A). Copper and, selectively, lead, zinc, and silver were analyzed using a Perkin Elmer 403 atomic absorption spectrophotometer (Appendices B, C, D). The precision of analysis was determined using the percent coefficient of variation computed using the following formula:

$$\frac{\text{Std. Dev.}}{\text{Mean}} \cdot 100 = Y_{1-n} \quad \text{and} \quad \frac{Y_1 + Y_2 \dots Y_n}{n} = \% \text{ Coef.}$$

The average percent coefficient of variation for all duplicates used was 2.2 percent.

Clay Mineral Content

Bed rock samples were also analyzed for their clay mineral content by X-ray diffraction. The -80 mesh fraction was mixed with water to form a slurry and centrifuged; -2 micron material was separated and put on porcelain slides. Clays were identified by methods described by Grim (1968).

Statistical Procedures

The over-all objective of the interpretation of exploration geochemical data is to distinguish anomalous metal patterns derived from mineralization from those derived from other causes. There are two major procedures of this type:

- (1) Univariate, which deals with data on single variables; and
- (2) Multivariate, which considers data on several variables.

Trend-surface analysis is employed in distinguishing anomalies from

background data and is thus a univariant method. Factor analysis is a method for identifying common underlying factors in many variables and is classified as a multivariant process.

Trend-Surface Analysis

Trend-surface analysis involves the fitting of mathematical surfaces to data by using the least squares method. Trend surfaces are curved or plane surfaces which represent regular trends. The difference between the estimated value of the trend surface and the observed value is called the residual. The trend surface may be regarded as the regional component while the residual is the local fluctuation from that component. Removal of the regional trend has the effect of amplifying the local component and making it conspicuous. The control locations are expressed by a numerical Cartesian coordinate system. From these data, a rectangular grid of points is created that control the contouring process.

Factor Analysis

Factor analysis is the method of determining interrelations of variables or samples in a set of apparently complex data by grouping the variables into associations on the basis of their mutual correlation coefficients. From these associations it may be possible to identify features within the data which may not be apparent from visual inspection. The factors necessary to account for variability of data are inferred from the correlation matrix. The extracted factors are ranked in order of decreasing importance in terms of the amount of the data variation accounted for by each factor, as determined by the eigenvalues

(the characteristic roots of the correlation matrix). The loading of each element onto each factor is determined from the eigenvectors computed with the eigenvalues. Ideally the loading close to a value of one should indicate a good representation of the factor, and the loading close to zero indicates a poor representation.

CHAPTER VI

RESULTS AND DISCUSSIONS

The frequency of copper in stream sediments and bed rock samples is illustrated as histograms (Figs. 15, 16, 17). The copper populations in stream sediments, sandstones and grey shales are approximately log normal and are positively skewed, whereas the histogram of silver derived from selected samples shows a bimodal distribution (Fig. 18). The geochemical threshold for an element is the upper limit of the normal background values. Values above the background are considered anomalous. The threshold value for a single element varies for each rock type, and a single value may be too high for some rocks and too low for others. Nevertheless, the arithmetic mean plus two standard deviations has been chosen as the geochemical threshold. Mean values, standard deviations, and thresholds calculated for copper in stream sediment and bed rock samples are shown in Table II. The copper content of 93 percent of the bed-rock and stream-sediment samples are below the geochemical threshold, whereas 7 percent of the bed-rock and stream-sediment values are above the threshold; and therefore, are anomalous. The range in values for the stream sediments was from 1.0 to 100 parts per million copper; the range for shales was from 3.0 to 2000.0 parts per million and 2.0 to 9000.0 parts per million copper for sandstones.

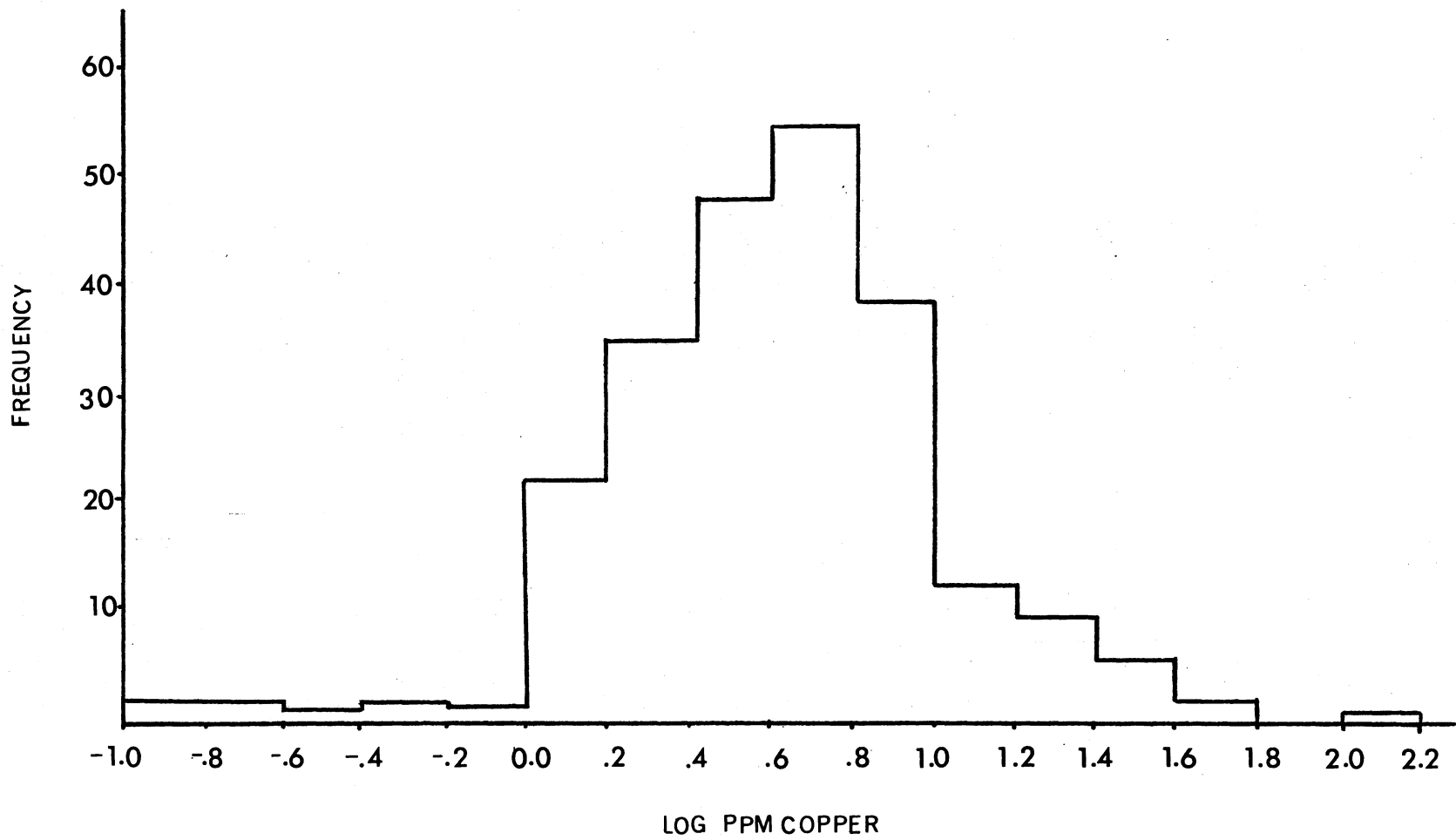


Fig. 15.-Distribution of copper (PPM) in stream sediments

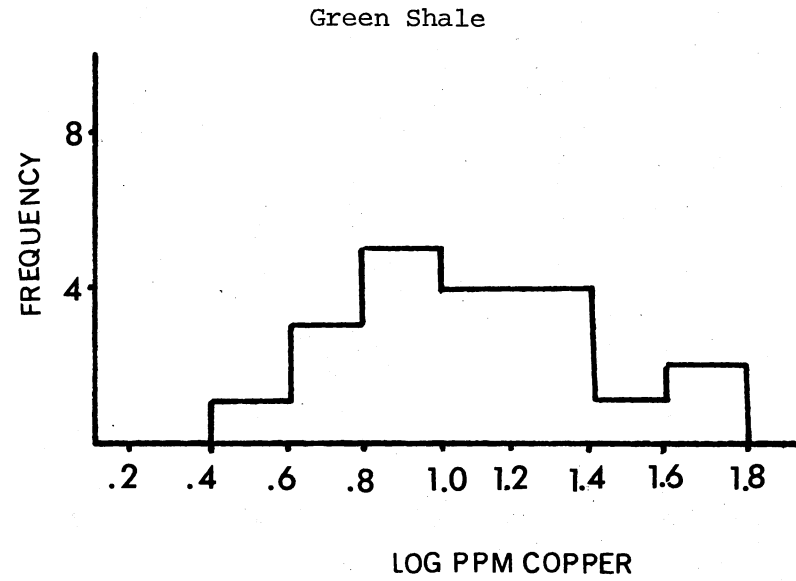
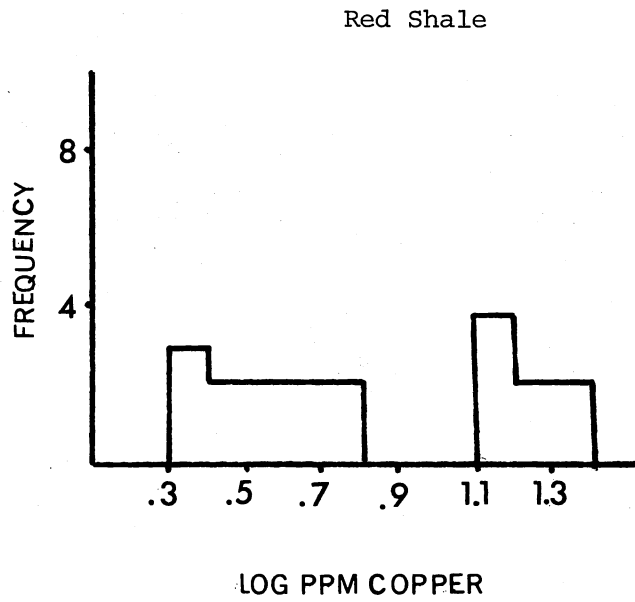


Fig. 16.-Distribution of copper (PPM) in shales

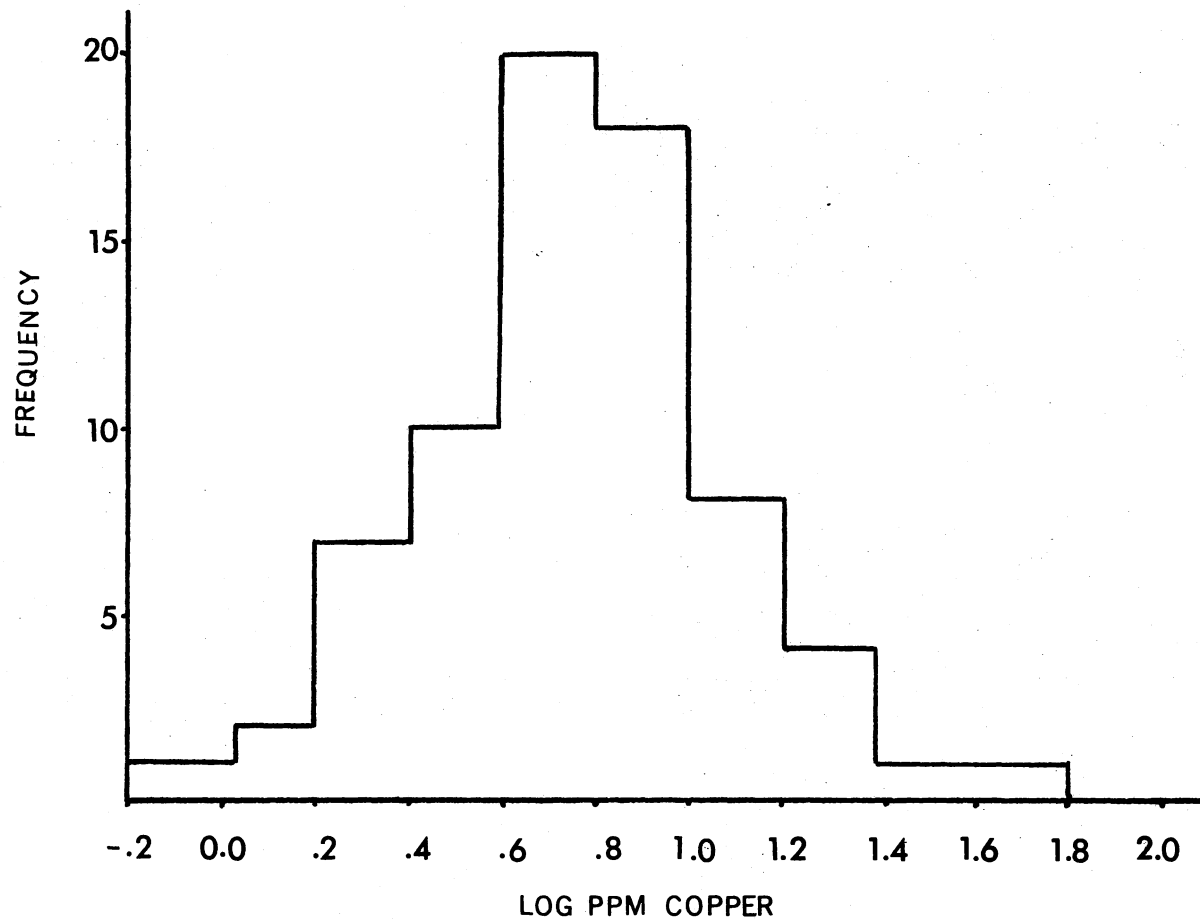


Fig. 17.-Distribution of copper (PPM) in sandstone

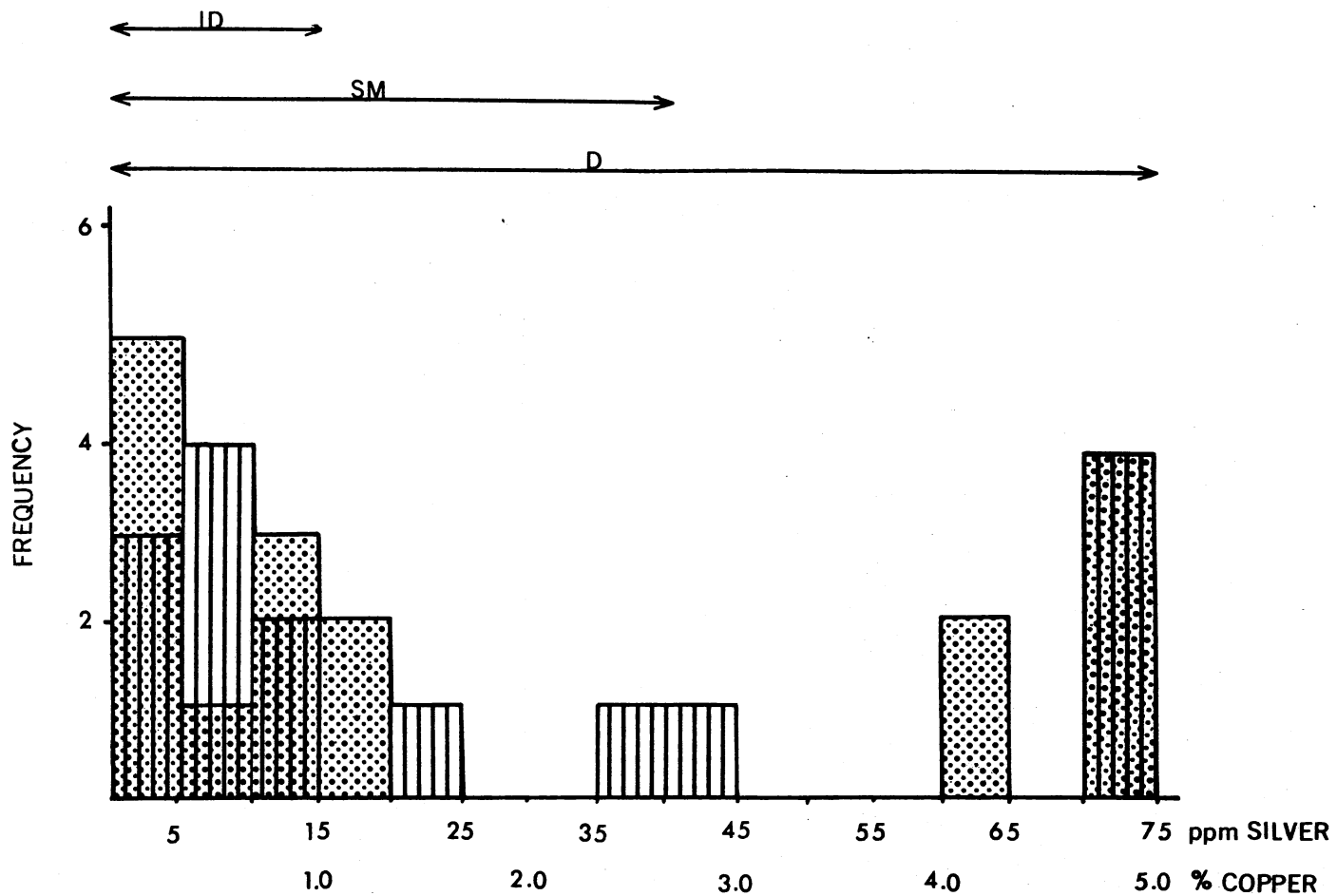


Fig. 18.-Distribution of silver (striped) and copper (stippled) in selected samples showing range of D-deltaic, SM-shallow marine, ID-interdeltaic-deltaic

TABLE II
STATISTICAL PARAMETERS FOR COPPER DISTRIBUTION
IN STREAM SEDIMENTS AND BED ROCK SAMPLES

	ARITHMETIC MEAN	STANDARD DEVIATION	THRESHOLD
Sandstone	5.6 ppm	2.0 ppm	24.6 ppm*
Red Shale	7.6 ppm	1.4 ppm	15.8 ppm*
Green Shale	10.0 ppm	2.3 ppm	54.9 ppm*
Stream Sediments	4.1 ppm	2.4 ppm	25.1 ppm*

*These numbers are antilogs of values computed on the basis of lognormal distributions.

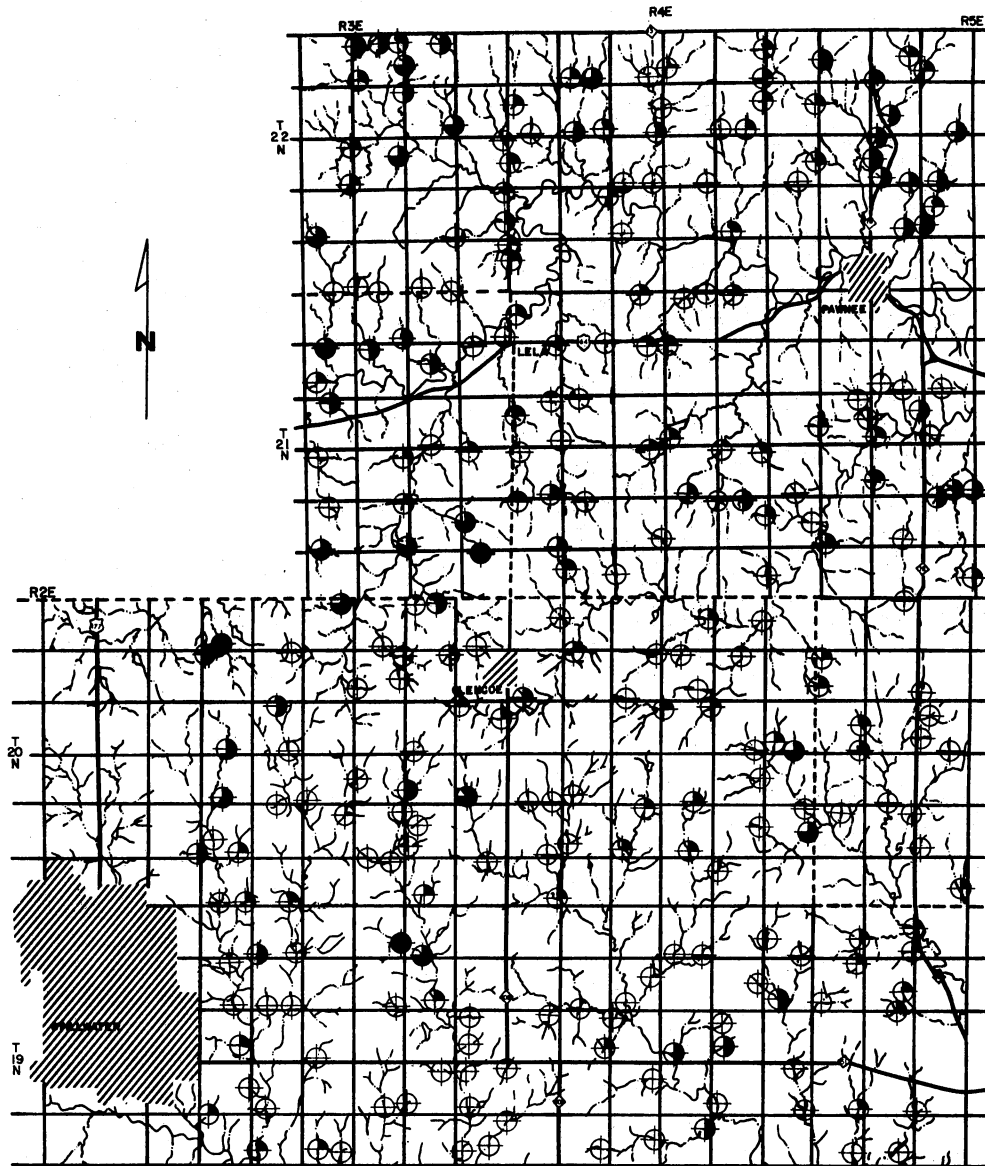
Geochemical Maps

The use of geochemical maps is the most powerful tool in the interpretation of spatially distributed data. Geochemical maps (Figs. 19, 20, 21) that illustrate the copper distribution in stream sediments and bed rock samples represent the purely objective approach (Levinson, 1974, p. 474). The maps show the location of each sampling point and its copper content.

Stream sediments can be anomalous for several reasons. Ore grains resistant to weathering and secondary ore minerals can be constituents of the stream sediments; clay minerals with adsorbed metal ions can remain in the stream sediments, especially if the current is not strong; and finally, anomalous constituents of ore metals in surface water can be fixed by organic material. In this way a stream-sediment anomaly is formed and gradually moves downstream. It can have considerable extent, making stream sediments very useful in regional geochemical prospecting.

Among the causes of contamination of stream sediments are industrial activities, dump sites, and agricultural activities. Copper contamination occurs in stream sediments northwest of the town of Glencoe where limestone and sandstone with approximately 75 parts per million copper were used for paving the section-line roads and as dump material to prevent further erosion along stream banks. In this area contamination was also derived from electrical equipment which was dumped in the drainage. In T19N, R4E, copper contamination averaging 100 parts per million was derived from oil field brines and recent construction activities in the drainage. The effects of chemical fertilizers, sprays, and other agricultural chemicals were found to be minimal.

Comparison of the stream sediment, bed rock, and copper location



EXPLANATION

COPPER ppm	SCALE 1:62500
⊕ < 5.1	1/2 0 1/2
⊗ 5.1-10.1	MILES
⊙ 10.1-20.1	
● 20.1-50.1	
● > 50.1	

Fig. 19.-Copper distribution in stream sediments

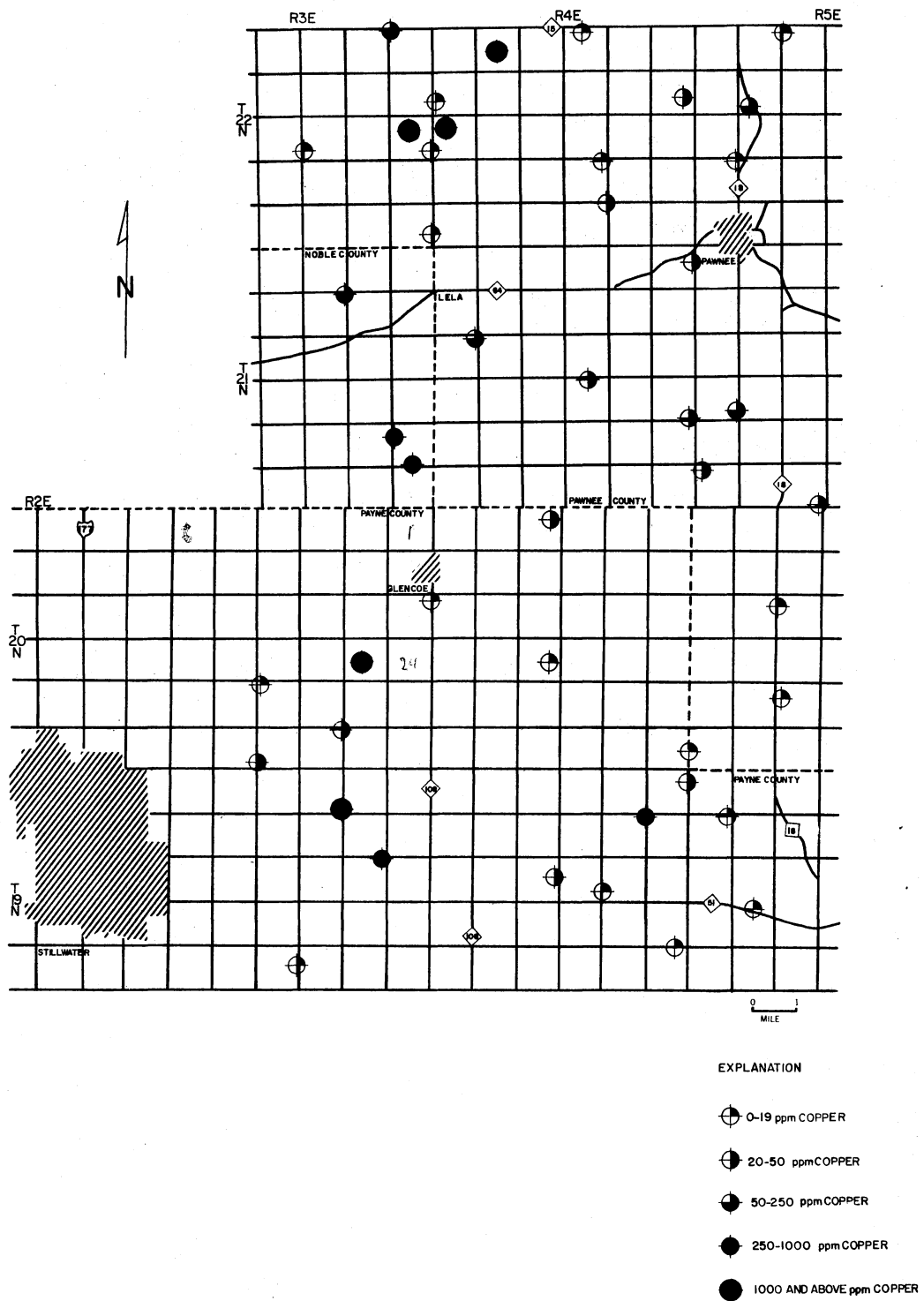


Fig. 20.-Copper distribution in sandstone

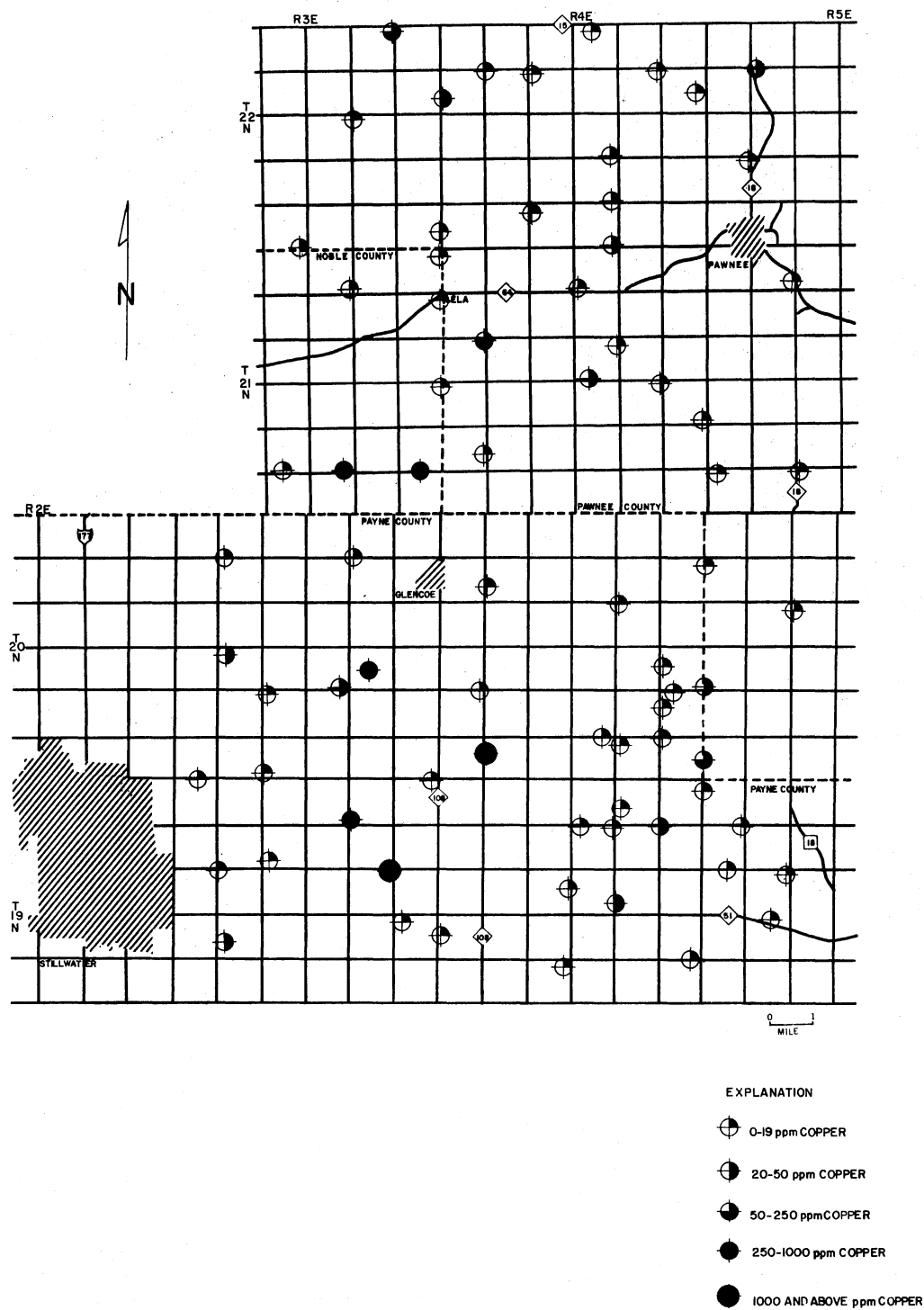


Fig. 21.-Copper distribution in shale

maps (Figs. 19, 20, 21, 22) suggests that virtually all anomalies on the stream sediment map are derived from sandstone and shale which underlie the study area. Geochemical sediment patterns show patterns that correlate positively with the bed rock and copper locations; especially pronounced is the northwest part of the study area where outcropping Fort Riley Limestone contains anomalously high copper values for approximately two miles along strike of its outcrop. Because of the limited extent of the copper-bearing channel-fill strata occurrences in the study area, most of the prospects are reflected by no more than one or two high sediment samples. Comparison of copper location (Fig. 22) and silver maps (Fig. 23) shows that the silver is dominantly a function of intensity of mineralization. This is also illustrated in Fig. 18. The average silver content for four distributary channel sandstone units is 50 ppm as compared to non-channel units, in which silver content averaged 12 ppm.

The trend-surface maps derived from the data in Figs. 20 and 21 illustrate the interpretive approach in geochemical mapping. In this study, first-, second-, third-, and fourth-degree trend-surfaces were fitted to the data. Goodness of fit, expressed as apparent total sum of squares, ranges from 22 percent for the first-order trend-surface to 54 percent for fourth-order trend-surface. Table III shows that all copper trends have confidence levels equal to or higher than 97.5 percent.

The linear surface for copper shown in Fig. 24A trends south-southeast and dips east-northeast. The copper increases west-southwest and decreases east-northeast. The curvatures of the higher order trends (Figs. 24B, 24C, and 24D) are approximately ridges, valleys, and partial

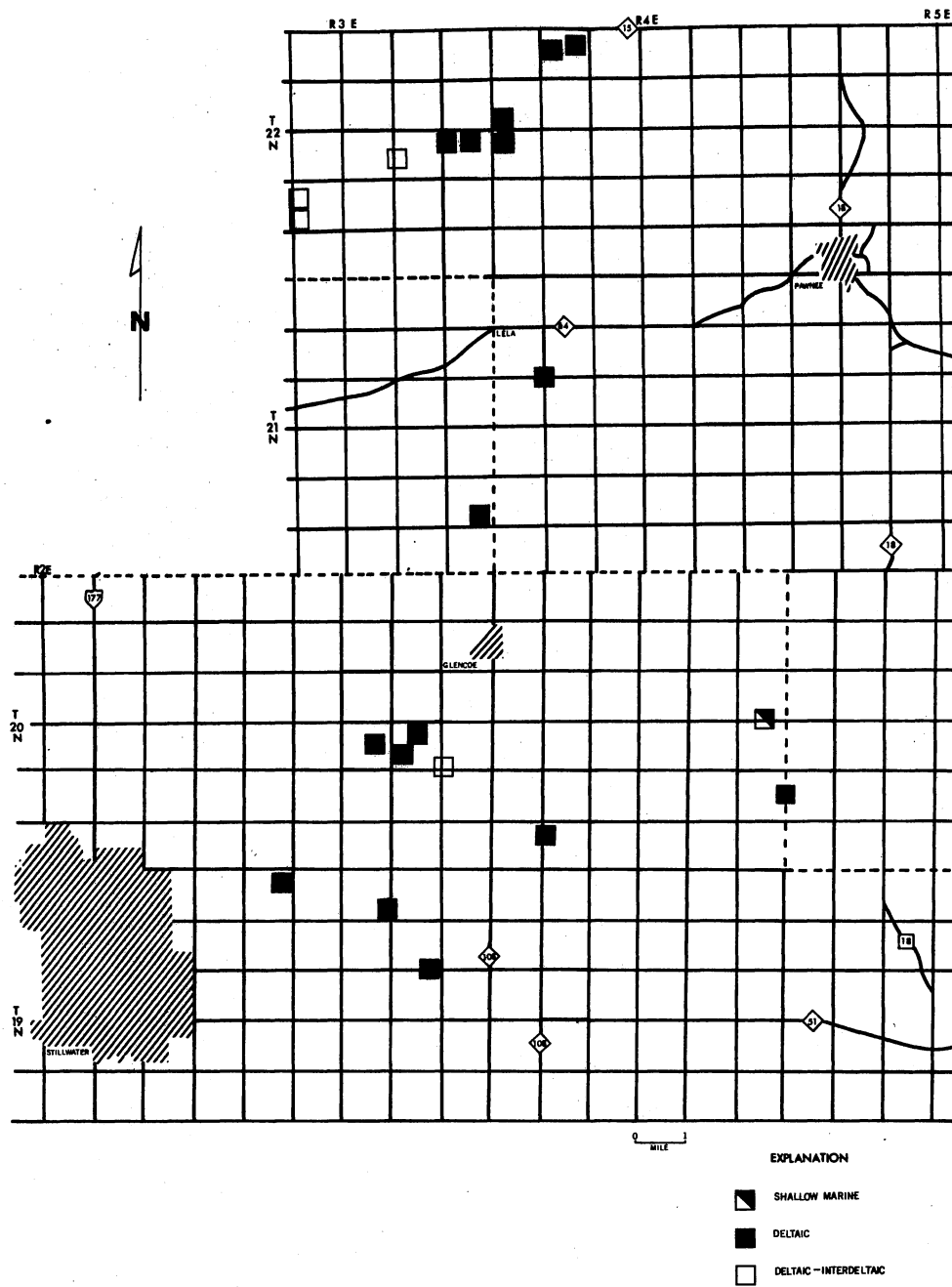


Fig. 22.-Location of copper mineralization according to host lithofacies

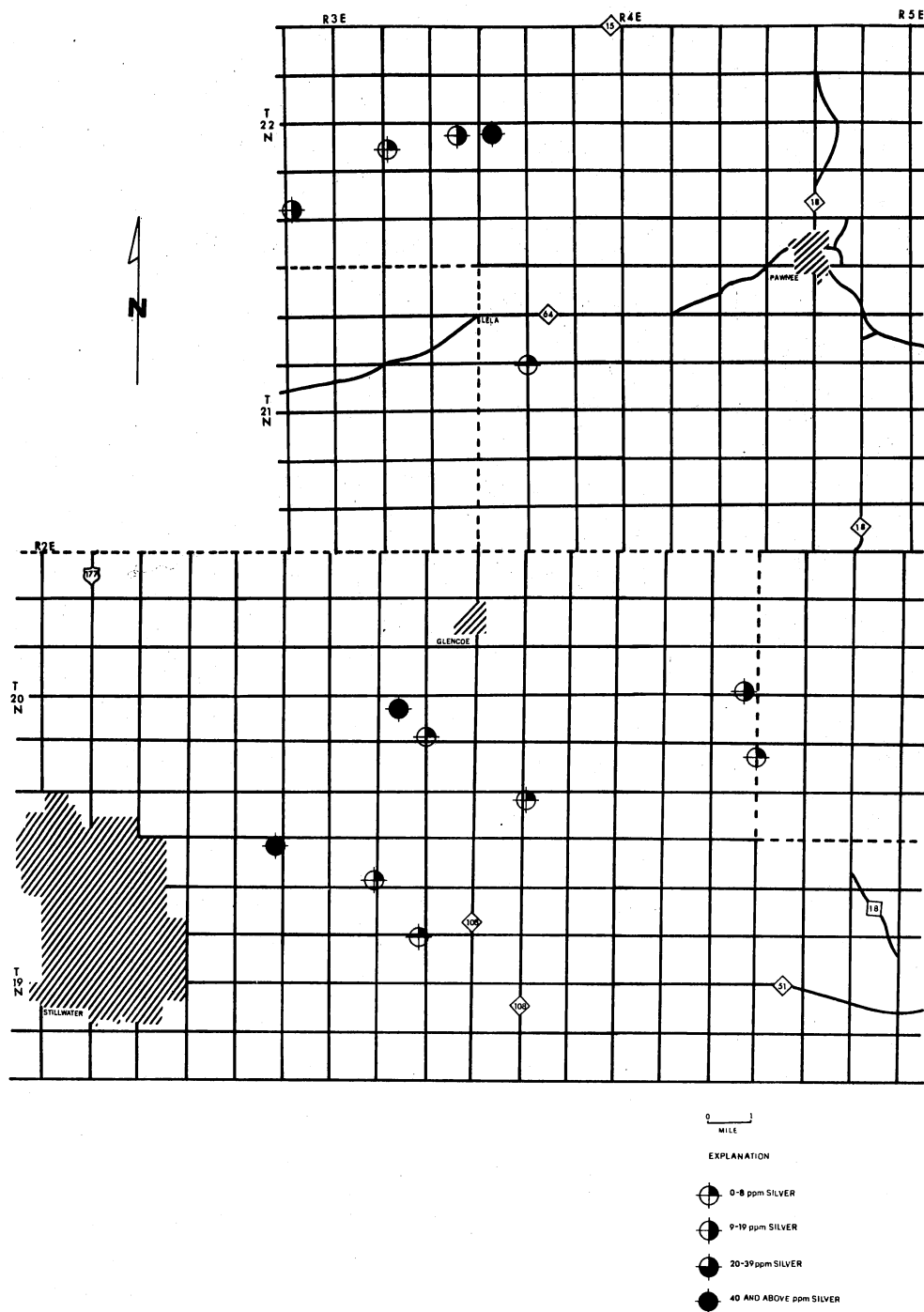


Fig. 23.-Silver distribution from selected samples

TABLE III
STATISTICS FOR GEOCHEMICAL TREND-SURFACE MAPS* FOR COPPER

	F TEST	CORRELATION COEFFICIENT	CONFIDENCE LEVEL
Trend 1	5.074	47.94	97.5
Trend 2	4.346	54.41	97.5
Trend 3	3.278	57.18	97.5
Trend 4	5.203	73.62	99.5

*Fig. 24.

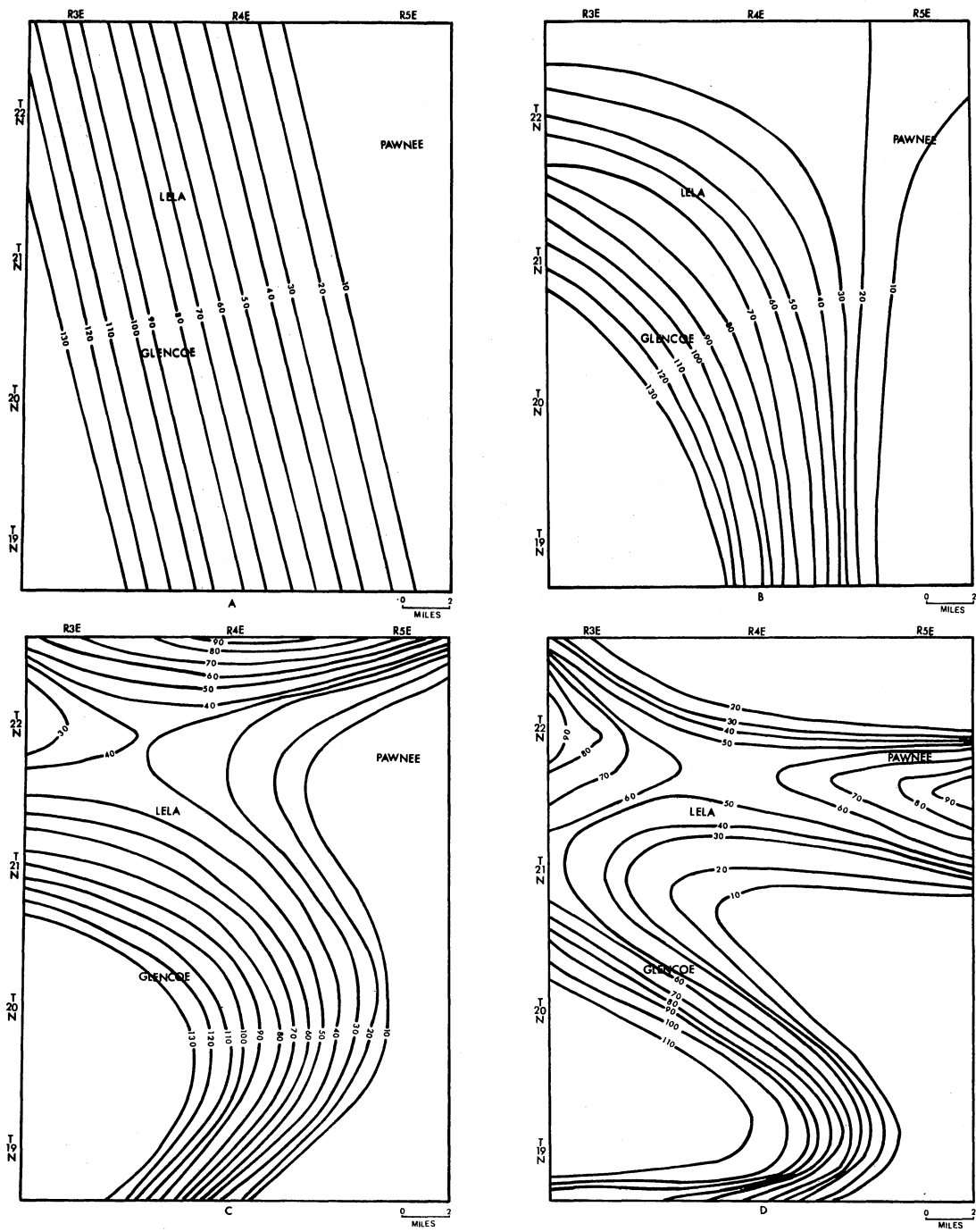


Fig. 24.-Geochemical maps showing trend-surfaces for copper in parts per million, (A) first order surface, (B) second order surface, (C) third order surface, (D) fourth order surface

positive ellipsoids where the known deposits and prospects seem to be clustered around their major axes.

The residuals or the deviations from the fitted linear trends describe principally the local geochemical fluctuations and also include the variability inherent in sampling and analytical procedures.

Examination of the residuals map (Fig. 25) reveals two important observations:

1. The high positive anomalous zones in the western part (Fig. 25) represent sites favorable for mineralization. This fact was verified by field examination. The only exception is to the northeast near Pawnee where no mineralization was observed.
2. The comparison between the residuals map and the subsurface structural-contour maps on the top of the Red Eagle Limestone of Early Permian age (Ross, 1972), and Checkerboard Limestone of Pennsylvanian age (Clare, 1961), indicates that all the high positive residuals coincide with some pronounced subsurface structural features. These features are described by Ross (1972, p. 45), as noses and saddles formed by local changes in the regional dip. This may indicate that the subsurface structure plays an important role in localization of copper mineralization. Feoktistov and Kochin (1972), proposed similar hypotheses for localization of sedimentary copper deposits in Dzhezkagan District, USSR.

Spatial Relationships of Copper and Clay Mineral Content

Illite, chlorite, and kaolinite are the major clay minerals in the

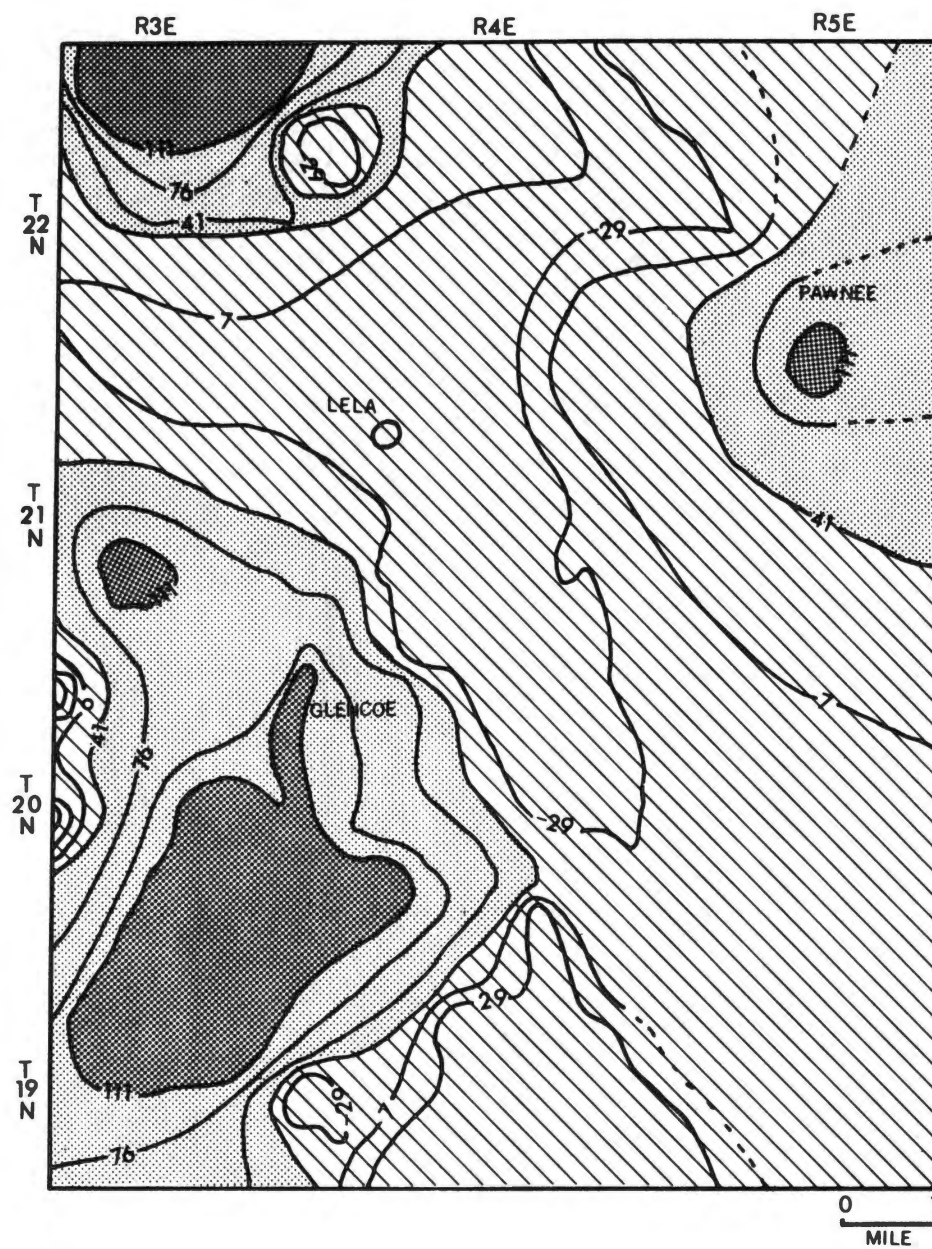
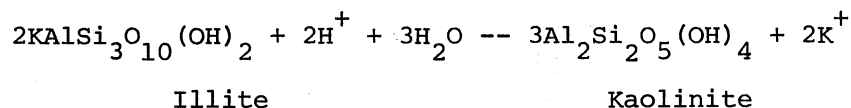


Fig. 25.-Geochemical map showing residuals of linear surface for copper

sandstones and shales of the study area. Most of the illite (2M poly-type) and chlorite is believed to be detrital rather than authigenetic, and is probably derived from the Ouachita structural belt (Weaver, 1961). The sub-angular quartz sand grains suggest that the distance of transportation was not great and, together with paleocurrent data, support the interpretation that the Ouachita structural belt was a prominent source area. The chlorite consists of two types, swelling chlorite and non-swelling chlorite. The swelling chlorite occurs in discontinuous masses within the eastern most and western most parts of the study area and is not included on the clay maps, whereas the chlorite, which is shown on the clay maps, occurs in both the eastern and western parts.

Kaolinite in both sandstones and shales is considered a weathering product. Glass (1958) stated that the majority of clay minerals in sedimentary rocks is thought to reflect the character of the source area and alteration effects, but not necessarily their depositional environment. Permeability contrasts within Pennsylvanian sandstones and shales in southern Illinois indicated that the increased relative kaolinite content of the sandstones implied a post-depositional formation of kaolinite; otherwise, the composition should remain similar for both sandstones and shales. The alteration was thought to be caused by reaction with ground water and can be shown by the following reaction:



Correlation of Clay Minerals and Copper

Factor analysis was used to examine spatial relationships between copper concentrations and post depositional changes of the host rock

(sandstones and shales). The percentage of the clay size fractions of approximately 100 samples of both sandstones and shales, along with the copper concentrations, and the north-south and east-west coordinates, were used as variables. The rotated factor matrix is shown in Table IV.

Copper cf. Clay in Shale

Factor 1 (Kaolinite, Chlorite, and East-West Coordinate)

The factor accounts for 38.81 percent of the data variability. High negative loading corresponds to kaolinite, while high positive loading corresponds to chlorite and east-west coordinate. This factor indicates that kaolinite is an alteration product of chlorite and also shows an increase of chlorite in an eastern direction with a corresponding decrease in kaolinite. Figure 26 shows the distribution of clay minerals in shales. The chlorite in the eastern part of the area ranges from 30 to 80 percent, whereas the content in the western part of the area ranges from 30 to 50 percent.

Factor 2 (Copper and North-South Coordinate)

This factor accounts for 31.59 percent of the data variability. High positive loading of both copper and the north-south coordinate indicate an increase in copper content in a northward direction.

Factor 3 (Illite and Chlorite)

The factor accounts for 29.61 percent of the data variability. The high negative loading of illite coupled with the positive chlorite loading indicates a partial change of illite to chlorite (swelling) post depositionally.

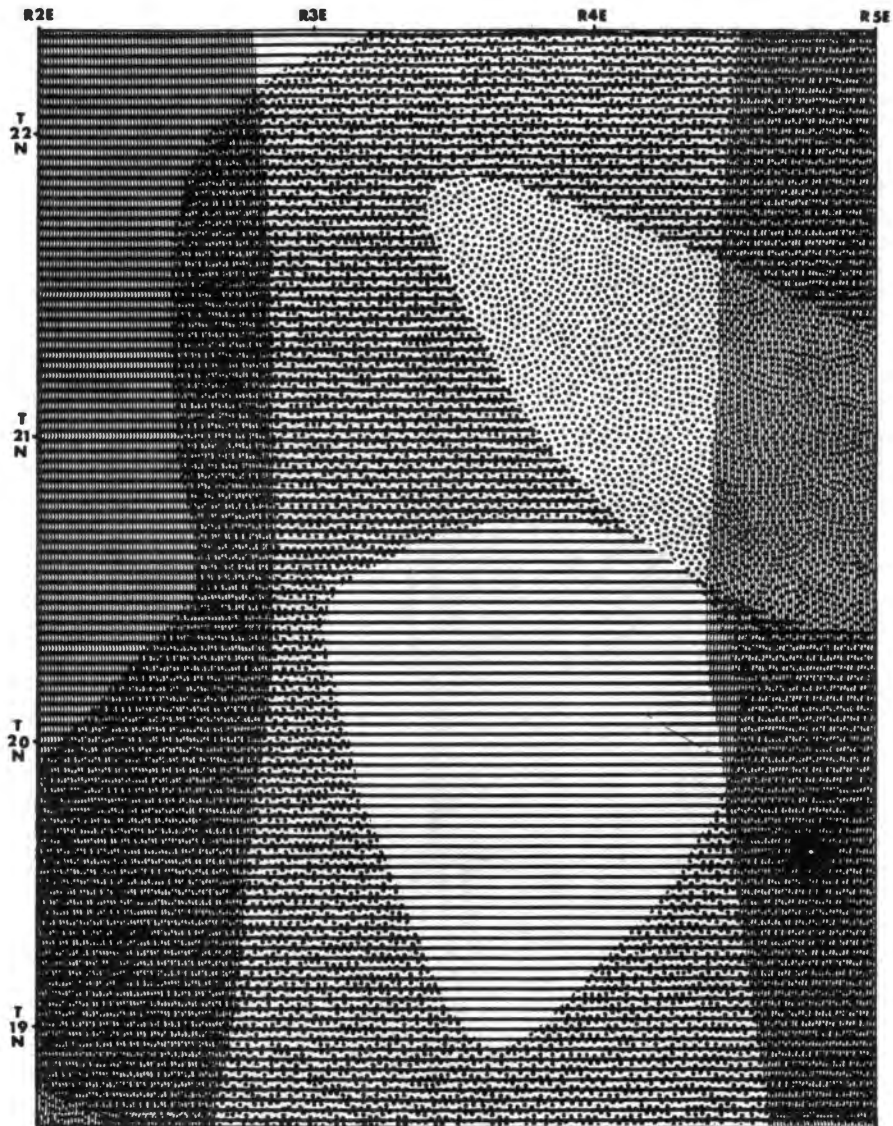
TABLE IV
FACTOR ANALYSIS

A. Copper cf. Clay in Shale

<u>Variables</u>	<u>Factor 1</u>	<u>Factor 2</u>	<u>Factor 3</u>
Kaolinite	-0.86789	0.24183	0.33357
Illite	-0.05620	-0.02712	-0.99342
Chlorite	0.81092	-0.16821	0.48468
Copper	-0.04623	0.82512	0.11132
North-South	0.01403	0.79975	-0.08838
East-West	0.61122	0.22092	0.11035

B. Copper cf. Clay in Sandstone

<u>Variables</u>	<u>Factor 1</u>	<u>Factor 2</u>	<u>Factor 3</u>
Kaolinite	0.88715	-0.33786	-0.05336
Illite	-0.92631	-0.18084	0.00392
Chlorite	-0.03724	0.84569	0.00275
Copper	-0.06309	-0.10306	-0.84362
North-South	0.12353	0.24689	-0.78453
East-West	-0.03247	0.72276	-0.10043



EXPLANATION

- ILLITE** 
- KAOLINITE** 
- CHLORITE** 

0 1
mile

Fig. 26.-Distribution of clay minerals in shales showing 30% or greater of the indicated clay minerals

Grim (1968) states that if the environment is alkaline, there is no leaching; and the water contains a high content of calcium and magnesium, conditions are favorable for the formation of chlorite rather than kaolinite.

Copper cf. Clay in Sandstone

Factor 1 (Illite and Kaolinite)

This factor accounts for 37.35 percent of the data variability. High positive loading corresponds to kaolinite, while high negative loading corresponds to illite. The factor is interpreted as the alteration of illite to kaolinite by ground water.

Factor 2 (Chlorite and East-West Coordinate)

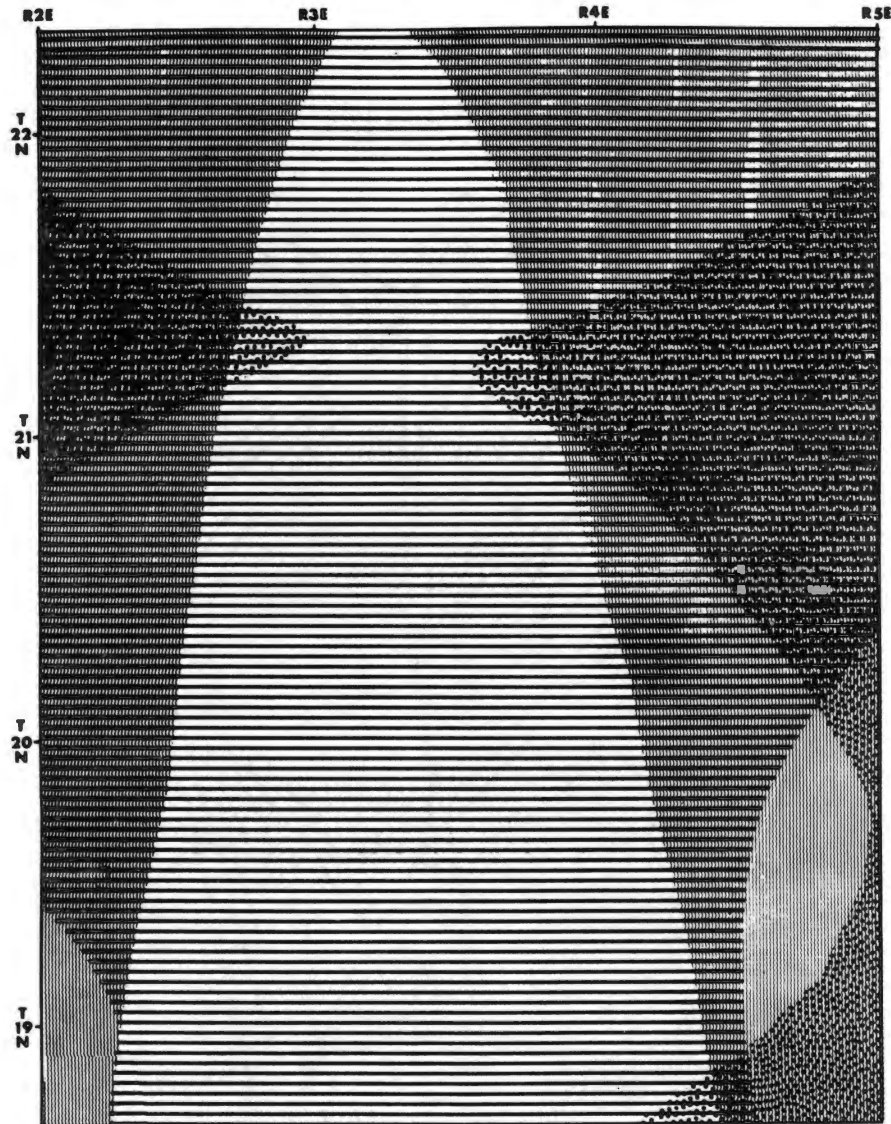
The factor represents 32.62 percent of the data variability. The high positive loadings for both chlorite and the east coordinate indicate an increase in chlorite eastward. Figure 27 shows the distribution of clays greater than 30 percent. In the eastern part of the map, the chlorite content increases from 30 to 60 percent; while in the western half, it is from 30 to 45 percent.

Factor 3 (Copper and North-South Coordinate)

The factor represents 30.03 percent of the data variability. High negative loading of both copper and the north-south coordinate indicates an increase in copper northward.

Summary of Factor Analysis

Copper concentration of both shales and sandstones increases in a



EXPLANATION

- ILLITE 
- KAOLINITE 
- CHLORITE 

0 1
mile

Fig. 27.-Distribution of clay minerals in sandstones showing 30% or greater of the indicated clay minerals

northward direction. This probably corresponds to a decrease in permeability (decrease in sand content; Ross, 1972). No direct relationship was found between clay mineral composition and copper concentration.

The increase in chlorite in shale and sandstone probably reflects nearness to the source area. The swelling chlorite, which occurs predominately in the western part of the mapped area, is believed to be formed post-depositionally. The kaolinite in both sandstone and shale is believed to be a weathering product of illite and chlorite.

CHAPTER VII

SUMMARY

The principal conclusions resulting from the study are as follows:

1) Two types of copper deposits exist in Oklahoma: (a) "red bed" coppers, primarily in deltaic or interdeltatic-deltaic environments, and (b) copper-shales which were deposited in shallow marine environments. The available data suggest that the "red bed" type is laterally less persistent and has a higher copper content than the copper-shales. The copper-shales occur primarily in the southwestern part of Oklahoma, while the "red bed" occurrences were found in the central part.

2) The sedimentary rocks of the Wolfcampian Series of the Lower Permian in North-central Oklahoma are favorable hosts for copper mineralization. Several areas of positive geochemical anomalies were located by using stream-sediment samples with subsequent bed-rock analysis. The stream-sediment survey is capable of producing results of great practical value in north-central Oklahoma.

3) "Red bed" occurrences of copper in the study area can be divided into three main categories according to sedimentary environment; (a) deltaic deposits (distributary and interdistributary), (b) interdeltatic-deltaic (interdistributary bay and tidal flat), and (c) shallow marine deposits.

4) Both shales and, to a lesser extent, sandstones show an increase in chlorite content in an eastern direction. Illite and most of

the chlorite were predominantly detrital, while kaolinite and swelling chlorite were weathering products. The copper content of both shales and sandstones increases in a northerly direction.

5) Carbonaceous material must be present in the host rock to provide a favorable reducing zone for the mineralization. A decrease in permeability seems to favor copper deposition in these reducing zones.

SELECTED BIBLIOGRAPHY

- Branson, C. C., A. L. Burwell, and G. C. Chase, 1955, Uranium in Oklahoma: Okla. Geol. Survey Min. Rept. 27, 22 p.
- Chuckhrov, F. V., 1973, On mineralogical and geochemical criteria in the genesis of red beds: Chemical Geol., v. 12, p. 67-75.
- Clare, P. H., 1961, Petroleum geology of Pawnee County, Oklahoma: Okla. Geol. Survey Circ. 62, Plate 4.
- Fath, S. E., 1915, Copper deposits in the "Red Beds" of southwestern Oklahoma: Bull. Econ. Geol., v. 10, p. 140-150.
- Feokistov, V. P., and G. G. Kochin, 1972, Certain distinctions in localization of stratified deposits of copper: International Geol. Review 10, v. 14, p. 1138-1146.
- Fischer, R. P., and J. H. Stewart, 1961, Copper, vanadium, and uranium deposits in sandstone -- their distribution and geochemical cycles: Bull. Econ. Geol., v. 56, p. 509-520.
- Fischer, R. P., 1937, Sedimentary deposits of copper, vanadium-uranium, and silver in southwestern United States: Econ. Geol., v. 32, p. 906-951.
- Glass, H. D., 1958, Clay mineralogy of Pennsylvanian sediments in southern Illinois: Clays and Clay Minerals, Fifth National Conference on Clays and Clay Minerals Society, Publ. 566, p. 227-241.
- Greig, P., 1959, Geology of Pawnee County, Oklahoma: Bull. Okla. Geol. Survey 83, 188 p.
- Grim, R. E., 1968, Clay Mineralogy. New York: McGraw-Hill Book Company, p. 536.
- Ham, W. E., and K. S. Johnson, 1964, Copper in the Flowerpot Shale (Permian) of the Creta area, Jackson County, Oklahoma: Okla. Geol. Circ. 64, 32 p.
- Haworth, E., and J. Bennett, 1901, Native copper near Enid, Oklahoma: Geol. Soc. of Amer., v. 12, p. 2-4.

- Hill, W. E., 1967, Copper in the red beds of south-central Kansas: Bull. Kansas Geol. Survey 187, p. 13-14.
- Johnson, K. S., Branson, C., Curtis, C., Ham, W., Marcher, M., and Roberts, J., 1972, Okla. Geol. Survey, Edu. Pub. 1, p. 1-8.
- Levinson, A. A., 1974, Introduction to Exploration Geochemistry: Applied Publications Ltd., 612 p.
- Lockwood, R., 1970, Geochemistry and petrology of some Oklahoma red bed copper occurrences: Unpublished Ph.D. Thesis, Univ. Okla., 125 p.
- Marcy, R. B., 1854, Exploration of the Red River of Louisiana in 1852: Exec. Doc., 33rd Cong., 1st Sess., pp. 391-393.
- Merritt, C. A., 1940, Copper in the "Red Beds" of Oklahoma: Okla. Geol. Survey Min. Rept. 8, p. 15.
- Renfro, A. E., 1974, Genesis of evaporite-associated stratiform metalliciferous deposits: a Sabkha process: Econ. Geol., v. 69, p. 33-45.
- Richard, L. M., 1915, Copper deposits in the "Red Beds" of Texas: Econ. Geol., v. 10, p. 634-650.
- Rogers, A. F., 1916, Origin of copper ores of the "Red Bed" type: Econ. Geol., v. 2, p. 366-380.
- Ross, J. S., 1972, Geology of central Payne County, Oklahoma: Unpublished M.S. Thesis, Okla. State Univ., 87 p.
- Shelton, J. W., 1973, Models of sand and sandstone deposits: a methodology for determining sand genesis and trend: Bull. Okla. Geol. Survey 118, 122 p.
- Shockey, P. N., A. R. Renfro, and R. J. Peterson, 1974, Copper-silver solution fronts at Paoli, Oklahoma: Econ. Geol., v. 69, No. 2, p. 266-268.
- Stroud, R. B., A. B. McMahan, and R. K. Stroup, 1970, Production potential of copper deposits associated with Permian red bed formations in Texas, Oklahoma, and Kansas: U.S. Geol. Survey Rept. of Invest. 7422, 103 p.
- Tarr, W. A., 1910, Copper in the "Red Beds" of Oklahoma: Bull. Econ. Geol., v. 5, p. 221-226.
- Woodward, L. A., W. H. Kaufman, O. L. Schumacher, and L. W. Talbott, 1974, Strata-bound copper in Triassic sandstone of Sierra Nacimiento, New Mexico: Econ. Geol., v. 69, p. 108-120.
- Weaver, C. E., 1961, Clay minerals of the Ouachita Structural Belt and Adjacent Foreland, in the Ouachita System: Texas University, Bur. of Econ. Geol., Pub. 6120, p. 147-162.

APPENDIX A

ANALYTICAL PROCEDURE FOR THE DETERMINATION
OF COPPER CONTENT

APPENDIX A

ANALYTICAL PROCEDURE FOR THE DETERMINATION OF COPPER CONTENT

All samples were placed in an oven on aluminum racks and dried thoroughly at 80° Centigrade for a period of eight hours. They were then broken to a ¼ inch size with a jar crusher, and the -80 mesh fraction was separated using a stainless steel screen.

Five grams of each sample were weighed and placed in teflon beakers, ten milliliters of aqua regia added, and the samples heated to 150° Centigrade for three hours. They were then filtered and diluted to 100 milliliters in volumetric flasks, and the resulting liquid aspirated into the atomic absorption spectrophotometer flame. Multiple readings were taken for each sample and the average recorded.

APPENDIX B

COPPER IN SANDSTONES

APPENDIX B

COPPER IN SANDSTONES

<u>Location</u>	<u>Sample No.</u>	<u>PPM Copper</u>
	<u>T19N R3E</u>	
NE $\frac{1}{4}$ S1 T19N R3E	RS40	0.9
SE $\frac{1}{4}$ S3 T19N R3E	RS2A	713.8
SW $\frac{1}{4}$ S12 T19N R3E	RS1	105.0
SW $\frac{1}{4}$ S12 T19N R3E	RS1B	1.6
SW $\frac{1}{4}$ S12 T19N R3E	RS1C1	27.0
SW $\frac{1}{4}$ S12 T19N R3E	RS1C2	162.0
SW $\frac{1}{4}$ S12 T19N R3E	RS1C4	140.0
SW $\frac{1}{4}$ S12 T19N R3E	RS1C4*	138.1
SW $\frac{1}{4}$ S20 T19N R3E	RS55	4.7
SW $\frac{1}{4}$ S24 T19N R3E	RS25A	2.8
NW $\frac{1}{4}$ S25 T19N R3E	RS25B	3.2
	<u>T19N R4E</u>	
SW $\frac{1}{4}$ S1 T19N R4E	RS30B	48.0
SW $\frac{1}{4}$ S2 T19N R4E	RS10	11.2
NE $\frac{1}{4}$ S10 T19N R4E	RS12A	5.2
NE $\frac{1}{4}$ S10 T19N R4E	RS12B	5.4
NW $\frac{1}{4}$ S10 T19N R4E	RS13A	4.4
NW $\frac{1}{4}$ S10 T19N R4E	RS13B	6.0

*Duplicate

<u>Location</u>	<u>Sample No.</u>	<u>PPM Copper</u>
<u>T19N R4E (Cont.)</u>		
SE $\frac{1}{4}$ S19 T19N R4E	RS11A	7.4
SE $\frac{1}{4}$ S19 T19N R4E	RS11C	7.4
SE $\frac{1}{4}$ S19 T19N R4E	RS11D	8.4
SE $\frac{1}{4}$ S19 T19N R4E	RS11E	15.0
SW $\frac{1}{4}$ S19 T19N R4E	RS19A	2.2
NE $\frac{1}{4}$ S16 T19N R4E	RS7B	8.0
NE $\frac{1}{4}$ S16 T19N R4E	RS7D	4.0
NE $\frac{1}{4}$ S28 T19N R4E	RS27A	3.8
NE $\frac{1}{4}$ S28 T19N R4E	RS27B	0.4
<u>T19N R5E</u>		
NW $\frac{1}{4}$ S6 T19N R5E	RS31B	6.8
NE $\frac{1}{4}$ S7 T19N R5E	RS21	6.0
SE $\frac{1}{4}$ S7 T19N R5E	RS21A	12.0
NE $\frac{1}{4}$ S17 T19N R5E	RS28A	4.6
NE $\frac{1}{4}$ S7 T19N R5E	RS28B	18.6
SE $\frac{1}{4}$ S17 T19N R5E	RS22A	8.8
SE $\frac{1}{4}$ S17 T19N R5E	RS22C	1.8
SE $\frac{1}{4}$ S17 T19N R5E	RS22D	3.0
NE $\frac{1}{4}$ S18 T19N R5E	RS24	1.2
<u>T20N R3E</u>		
NE $\frac{1}{4}$ S8 T20N R3E	RS53	4.5
NE $\frac{1}{4}$ S10 T20N R3E	RS46	2.2
SE $\frac{1}{4}$ S22 T20N R3E	RS51	23.1
NW $\frac{1}{4}$ S23 T20N R3E	RS34A	872.0

<u>Location</u>	<u>Sample No.</u>	<u>PPM Copper</u>
	<u>T2ON R3E (Cont.)</u>	
NW $\frac{1}{4}$ S23 T2ON R3E	RS34B	570.0
NW $\frac{1}{4}$ S28 T2ON R3E	RS52	5.0
NW $\frac{1}{4}$ S33 T2ON R3E	RS37A	16.8
NW $\frac{1}{4}$ S34 T2ON R3E	RS8A	7.2
NW $\frac{1}{4}$ S34 T2ON R3E	RS8A*	7.5
	<u>T2ON R4E</u>	
NE $\frac{1}{4}$ S7 T2ON R4E	RS35	4.1
NE $\frac{1}{4}$ S12 T2ON R4E	RS43A	7.0
NE $\frac{1}{4}$ S12 T2ON R4E	RS43A*	6.8
NW $\frac{1}{4}$ S14 T2ON R4E	RS44A	5.0
SE $\frac{1}{4}$ S24 T2ON R4E	RS18A	12.0
SE $\frac{1}{4}$ S24 T2ON R4E	RS18A*	10.6
NW $\frac{1}{4}$ S25 T2ON R4E	RS16A	4.4
NE $\frac{1}{4}$ S24 T2ON R4E	RS17A	2.4
SW $\frac{1}{4}$ S25 T2ON R4E	RS15A	2.0
NW $\frac{1}{4}$ S25 T2ON R4E	RS16B	6.4
SE $\frac{1}{4}$ S26 T2ON R4E	RS14A	4.0
NE $\frac{1}{4}$ S30 T2ON R4E	RS33A	9.0
NW $\frac{1}{4}$ S32 T2ON R4E	RS3	246.0
NW $\frac{1}{4}$ S32 T2ON R4E	RS3A	300.0
NW $\frac{1}{4}$ S32 T2ON R4E	RS3C	242.0
SW $\frac{1}{4}$ S33 T2ON R4E	PRS55	6.3
NE $\frac{1}{4}$ S34 T2ON R4E	RS9A	8.4
NE $\frac{1}{4}$ S34 T2ON R4E	RS9B	3.0

*Duplicates

<u>Location</u>	<u>Sample No.</u>	<u>PPM Copper</u>
	<u>T20N R4E (Cont.)</u>	
SE $\frac{1}{4}$ S36 T20N R4E	RS32A	38.0
SE $\frac{1}{4}$ S36 T20N R4E	RS32B	58.0
SE $\frac{1}{4}$ S36 T20N R4E	RS32C	88.0
	<u>T21N R3E</u>	
NE $\frac{1}{4}$ S1 T21N R3E	PRS1	8.1
SE $\frac{1}{4}$ S3 T21N R3E	PRS28	6.1
NE $\frac{1}{4}$ S12 T21N R3E	PRS20	7.0
SE $\frac{1}{4}$ S13 T21N R3E	PRS24	20.0
NW $\frac{1}{4}$ S19 T21N R3E	PRS19	6.2
SE $\frac{1}{4}$ S27 T21N R3E	PRS2	304.0
SE $\frac{1}{4}$ S28 T21N R3E	PRS61	4.7
SW $\frac{1}{4}$ S33 T21N R3E	PRS30	7.8
	<u>T21N R4E</u>	
SE $\frac{1}{4}$ S3 T21N R4E	PRS38	21.8
SE $\frac{1}{4}$ S14 T21N R4E	PRS18	4.4
SW $\frac{1}{4}$ S15 T21N R4E	PRS35	33.9
NW $\frac{1}{4}$ S15 T21N R4E	PRS36	12.4
NE $\frac{1}{4}$ S18 T21N R4E	PRS34	200.0
NE $\frac{1}{4}$ S30 T21N R4E	PRS18A	7.6
	<u>T21N R5E</u>	
NE $\frac{1}{4}$ S5 T21N R5E	PRS9	12.0
SE $\frac{1}{4}$ S24 T21N R5E	PRS17A	4.2
SE $\frac{1}{4}$ S29 T21N R5E	PRS15	3.2

<u>Location</u>	<u>Sample No.</u>	<u>PPM Copper</u>
	<u>T21N R5E (Cont.)</u>	
SW $\frac{1}{4}$ S30 T21N R5E	PRS16B	3.0
	<u>T22N R3E</u>	
NE $\frac{1}{4}$ S11 T22N R3E	PRS26A	121.6
NW $\frac{1}{4}$ S23 T22N R3E	PRS27	17.0
SE $\frac{1}{4}$ S36 T22N R3E	PRS22A	9.0
	<u>T22N R4E</u>	
SW $\frac{1}{4}$ S7 T22N R4E	PRS25	6.8
SW $\frac{1}{4}$ S9 T22N R4E	PRS14	2.1
NW $\frac{1}{4}$ S10 T22N R4E	PRS13A	14.4
SE $\frac{1}{4}$ S26 T22N R4E	PRS11A	5.2
NW $\frac{1}{4}$ S34 T22N R4E	PRS10B	16.0
NW $\frac{1}{4}$ S34 T22N R4E	PRS10C	8.2
	<u>T22N R5E</u>	
SW $\frac{1}{4}$ S11 T22N R5E	PRS12	6.6
NW $\frac{1}{4}$ S17 T22N R5E	PRS6	31.8
NW $\frac{1}{4}$ S17 T22N R5E	PRS6*	29.1
SW $\frac{1}{4}$ S17 T22N R5E	PRS7	3.5

*Duplicate

APPENDIX C

COPPER IN SHALES

APPENDIX C

COPPER IN SHALES

<u>Location</u>	<u>Sample No.</u>	<u>PPM Copper</u>
	<u>T19N R3E</u>	
NW $\frac{1}{4}$ S2 T19N R3E	RS5	8.4
SE $\frac{1}{4}$ S3 T19N R3E	RS2	806.2
SE $\frac{1}{4}$ S3 T19N R3E	RS2 (Unox.)	966.0
SE $\frac{1}{4}$ S3 T19N R3E	RS2B	206.0
SE $\frac{1}{4}$ S3 T19N R3E	RS2D	1,432.0
SE $\frac{1}{4}$ S3 T19N R3E	RS2C1	786.0
SE $\frac{1}{4}$ S3 T19N R3E	RS2C2	1,124.0
SE $\frac{1}{4}$ S3 T19N R3E	RS2C3	1,124.0
SE $\frac{1}{4}$ S3 T19N R3E	RS2C4	1,560.0
SE $\frac{1}{4}$ S3 T19N R3E	RS2C5	1,300.0
SE $\frac{1}{4}$ S3 T19N R3E	RS2C6	696.0
SE $\frac{1}{4}$ S3 T19N R3E	RS2C7	1,066.0
SW $\frac{1}{4}$ S12 T19N R3E	RS1D6	182.0
NW $\frac{1}{4}$ S27 T19N R3E	RS5	5.1
NW $\frac{1}{4}$ S27 T19N R3E	RS5*	5.4
	<u>T19N R4E</u>	
SW $\frac{1}{4}$ S1 T19N R4E	RS30	251.0
NE $\frac{1}{4}$ S16 T19N R4E	RS7A	5.2

*Duplicate

<u>Location</u>	<u>Sample No.</u>	<u>PPM Copper</u>
	<u>T19N R4E (Cont.)</u>	
SW $\frac{1}{4}$ S19 T19N R4E	RS19B	2.6
NE $\frac{1}{4}$ S25 T19N R4E	RS20A	5.6
NE $\frac{1}{4}$ S25 T19N R4E	RS20A*	5.9
	<u>T19N R5E</u>	
NW $\frac{1}{4}$ S6 T19N R5E	RS31A	46.0
SE $\frac{1}{4}$ S19 T19N R5E	RS22B	7.2
	<u>T20N R3E</u>	
NE $\frac{1}{4}$ S16 T20N R3E	RS45A	6.0
NW $\frac{1}{4}$ S23 T20N R3E	RS34A	2,214.1
NW $\frac{1}{4}$ S23 T20N R3E	RS34C	69.5
NW $\frac{1}{4}$ S23 T20N R3E	RS34C*	70.4
	<u>T20N R4E</u>	
SW $\frac{1}{4}$ S21 T20N R4E	RS37B	6.6
SE $\frac{1}{4}$ S36 T20N R4E	RS32D	11.0
	<u>T20N R5E</u>	
NW $\frac{1}{4}$ S4 T20N R5E	RS24A	8.6
NW $\frac{1}{4}$ S4 T20N R5E	RS24B	6.0
NW $\frac{1}{4}$ S4 T20N R5E	RS24C	6.4
NW $\frac{1}{4}$ S4 T20N R5E	RS24D	9.6
NW $\frac{1}{4}$ S16 T20N R5E	RS42B	12.4
NW $\frac{1}{4}$ S28 T20N R5E	RS41A	13.1

*Duplicates

<u>Location</u>	<u>Sample No.</u>	<u>PPM Copper</u>
	<u>T21N R3E</u>	
SE $\frac{1}{4}$ S3 T21N R3E	PRS28B	92.2
NW $\frac{1}{4}$ S25 T21N R3E	PRS30	267.0
NE $\frac{1}{4}$ S26 T21N R3E	PRS29B	222.0
	<u>T21N R4E</u>	
SE $\frac{1}{4}$ S1 T21N R4E	RS50	27.4
SW $\frac{1}{4}$ S15 T21N R4E	PRS3	33.2
NE $\frac{1}{4}$ S18 T21N R4E	PRS34	125.1
SE $\frac{1}{4}$ S24 T21N R4E	PRS17A	12.1
SW $\frac{1}{4}$ S27 T21N R4E	RS52	23.8
	<u>T21N R5E</u>	
NE $\frac{1}{4}$ S19 T21N R5E	PRS4	57.0
NE $\frac{1}{4}$ S19 T21N R5E	PRS4*	58.4
NE $\frac{1}{4}$ S21 T21N R5E	PRS24	13.0
SW $\frac{1}{4}$ S30 T21N R5E	PRS16A	25.0
	<u>T22N R3E</u>	
NE $\frac{1}{4}$ S11 T22N R3E	PRS26B	193.0
NW $\frac{1}{4}$ S23 T22N R3E	PRS27	2.7
SE $\frac{1}{4}$ S24 T22N R3E	PRS36	2,104.6
SE $\frac{1}{4}$ S36 T22N R3E	PRS22B	8.8
	<u>T22N R4E</u>	
NE $\frac{1}{4}$ S8 T22N R4E	PRS31	1,204.0
NW $\frac{1}{4}$ S10 T22N R4E	PRS13B	18.6

*Duplicate

<u>Location</u>	<u>Sample No.</u>	<u>PPM Copper</u>
	<u>T22N R4E (Cont.)</u>	
NE $\frac{1}{4}$ S11 T22N R4E	PRS11B	10.0
SE $\frac{1}{4}$ S18 T22N R4E	PRS24	14.6
NW $\frac{1}{4}$ S19 T22N R4E	PRS35	3,201.3
SE $\frac{1}{4}$ S22 T22N R4E	PRS32	17.1
SW $\frac{1}{4}$ S19 T22N R4E	PRS40	15.8
SE $\frac{1}{4}$ S27 T22N R4E	PRS33	2.7
	<u>T22N R5E</u>	
NE $\frac{1}{4}$ S8 T22N R5E	PRS5	6.6
SE $\frac{1}{4}$ S19 T22N R5E	PRS10A	10.0
SE $\frac{1}{4}$ S24 T22N R5E	PRS17B	47.6

APPENDIX D

SILVER CONTENT OF SELECTED SAMPLES

APPENDIX D

SILVER CONTENT OF SELECTED SAMPLES

<u>Location</u>	<u>Description</u>	<u>PPM Silver</u>
SE $\frac{1}{4}$ S3 T19N R3E	Disseminated Chalcocite	3.5
NE $\frac{1}{4}$ S5 T19N R3E	Carbonaceous Wood	70.5
NE $\frac{1}{4}$ S5 T19N R3E	Concretion	40.0
SW $\frac{1}{4}$ S12 T19N R3E	Malachite Blebs in Sandstone	9.0
NW $\frac{1}{4}$ S23 T20N R3E	Carbonaceous Wood	4.0
NW $\frac{1}{4}$ S23 T20N R3E	Concretion	11.0
NW $\frac{1}{4}$ S23 T20N R3E	Pyrite Concretion	15.0
SE $\frac{1}{4}$ S23 T20N R3E	Carbonaceous Wood	103.5
SE $\frac{1}{4}$ S23 T20N R3E	Concretion	75.5
NE $\frac{1}{4}$ S25 T20N R4E	Carbonaceous Wood	2.0
NW $\frac{1}{4}$ S32 T20N R4E	Carbonaceous Shale	7.0
SE $\frac{1}{4}$ S13 T20N R5E	Worm Borings	60.5
SE $\frac{1}{4}$ S13 T20N R5E	Pyrite Concretion	40.0
SE $\frac{1}{4}$ S13 T22N R5E	Disseminated Chalcocite	9.4
NE $\frac{1}{4}$ S19 T22N R3E	Carbonaceous Wood	130.5
NE $\frac{1}{4}$ S19 T22N R3E	Concretion	25.0
NE $\frac{1}{4}$ S22 T22N R3E	Clay Pebble Conglomerate	8.0

VITA

Richard Ralph Heine

Candidate for the Degree of

Master of Science

Thesis: GEOCHEMISTRY AND MINERALOGY OF THE PERMIAN RED BEDS AND RELATED COPPER DEPOSITS, PAYNE, PAWNEE, AND NOBLE COUNTIES, OKLAHOMA

Major Field: Geology

Biographical:

Personal Data: Born in Minot, North Dakota, November 18, 1949, the son of Dr. and Mrs. Ralph R. Heine.

Education: Graduated from Elk City High School, Elk City, Oklahoma, in May, 1968; completed the requirements for a Bachelor of Science degree in Geology from Oklahoma State University, Stillwater, Oklahoma, in May, 1973; completed requirements for the Master of Science degree at Oklahoma State University in May, 1975, with a major in Geology.

Professional Experience: Teaching assistant, Department of Geology, Panhandle State College, Goodwell, Oklahoma, spring, 1970; research assistantship, Oklahoma State University, summer, 1973; Junior Geologist, Cities Service Minerals Corporation, Salt Lake City, Utah, summer, 1974; Junior Member of the American Association of Petroleum Geologists.