Element Distribution in Some Shelf and Eugeosynclinal Black Shales

By JAMES D. VINE

CONTRIBUTIONS TO GEOCHEMISTRY

GEOLOGICAL SURVEY BULLETIN 1214-E

The content and association of minor elements in different black-shale environments

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1966

UNITED STATES DEPARTMENT OF THE INTERIOR

STEWART L. UDALL, *Secretary*

GEOLOGICAL SURVEY

William T. Pecora, *Director*

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C. 20402 - Price 20 cents

CONTENTS

ILLUSTRATION

TABLES

ELEMENT DISTRIBUTION IN SOME SHELF AND EUGEOSYNCLINAL BLACK SHALES

By JAMES D. VINE

ABSTRACT

Emission spectrographic analyses of 220 samples of black shale from Pennsylvanian rocks of the shelf area in the Eastern Interior coal province and from Ordovician and Silurian rocks of the western North America eugeosyncline have been compared. Some samples of both the shelf group and the eugeosynclinal group have high contents of vanadium, chromium, zinc, silver, and moderately high contents of nickel and copper. High molybdenum and nickel contents are characteristic of the samples from the shelf; high barium content is characterisic of the samples from the eugeosyncline.

INTRODUCTION

The significant enrichment of many minor elements in organic sedimentary rocks, including black shale, was emphasized by Krauskopf (1955). Since that time, much new information has been reported in the literature. Some of the data are tabulated by Wedepohl (1964, p. 308–311) in his discussion of the origin of the Kupferschiefer. A review of these and other similar published geochemical data on black shale suggests that many of the analyses are of samples selected because they were unusual in one or more respects. Moreover, the analyses are rarely identified with specific geologic environments in a manner that is adequate for making geochemical interpretations of significant volumes of black shale. This report includes a summary of chemical data pertaining to the distribution of elements in 220 samples of black shale from 2 geologic environments. The significance of the data is briefly interpreted with respect to the two contrasting environments of deposition.

Most workers (for example, Krauskopf, 1955; Wedepohl, 1964; Davidson and Lakin, 1961, 1962) have been interested in black shale because of the unusual concentration of minor elements, especially the metal concentrations of potential economic value. For this reason much of the literature tends to give a misleading impression of the quantity of black shale enriched in metals. Furthermore, the term "black shale" is somewhat misleading, for as it is defined by Swanson (1961, p. 69) and used here, it is not restricted to a single lithologic type of carbonaceous claystone, but includes many other dark-colored fine-grained rocks. Some, such as the Chattanooga Shale, are chiefly siltstone (Conant and Swanson, 1961, p. 43); but others, such as the graptolitic black shale in the Vinini Formation and equivalent units in Nevada, are siliceous mudstone (Ketner and Smith, 1963). The Kupferschiefer in Germany and the oil shale in the Green River Formation of Utah, Colorado, and Wyoming are marlstone (Wedepohl, 1964, p. 320–324; Bradley, 1931, p. 7). Pennsylvanian black shale in western Indiana is intermediate in composition between claystone and coal (Zangerl and Richardson, 1963, p. 105–106).

A classification for black shale could be constructed on a triangular diagram using siltstone for one corner, marlstone for another, and coal for the third. Alternatives possible are the substitution of claystone for siltstone, chert for marlstone, and sapropel for coal. More generally, the corners could be thought of as (1) fine-grained detrital minerals, (2) chemically or biogenically precipitated mineral matter, and (3) carbonaceous organic matter. As there are several possibilities for each corner within the general category, this allows a wide range of rock types to be included in the general name of black shale. By this definition, black shale includes all rock types of intermediate composition but not the pure end member. It may also be inferred that this wide range of rock types includes examples from many geologic environments, with possibilities for very different minor-element concentrations.

Such a classification finds further application in studying the distribution of minor elments in black shale. Thus, any specific element may occur principally in that fraction of a rock which is represented by an end member on the triangular diagram, or it may be included in two or more such fractions. For example, titanium may occur chiefly in the detrital-mineral fraction, but copper may be divided equally between the organic fraction and the chemically or biogenically precipitated fraction. Knowing which fraction of a rock contained the major share of each minor element facilitates determining whether each minor element was contained in the crystal lattice of a specific mineral or was held by chemical sorption. This, in turn, would lead to a better understanding of how certain elements become concentrated in some beds of black shale.

ACKNOWLEDGMENTS

Many individuals contributed directly or indirectly to the collection and analysis of the samples and the processing of the data used in the preparation of this report. R. H. Calvert, T. M. Kehn, and J. W. Palmer aided in collecting the samples in sets 1 and 2; Dr. Rainer Zangerl, of the Chicago Natural History Museum, donated the samples in set 3; J. P. Albers, Michael Churkin, Jr., R. R. Coats, K. B. Ketner, R. J. Kleinhampl, R. J. Roberts, D. C. Ross, J. F. Smith, Jr., and R. G. Yates aided in collecting the samples comprising set 4.

Spectrographic analyses for part of set 4 were made in the U.S. Geological Survey laboratory in Menlo Park, Calif., by Chris Heropoulos. The remainder of the analyses from set 4 and the other three sets were made in the U.S. Geological Survey laboratory in Denver, Colo., by J. C. Hamilton and A. L. Sutton, Jr. Carbon analyses were made by I. C. Frost. The analytical data were transcribed to data-coding and retrieval cards by Mary S. Niles and Patricia Zimmerman. Ralph Eicher provided the data transformation, control cards, and programing advice for the machine computations.

ANALYTICAL METHODS AND LIMITATIONS

A 6-step method of emission spectrographic analysis was used in both laboratories for all samples analyzed. This technique is similar to the 3-step method described by Myers, Havens, and Dunton (1961) except that in the 6-step method the operator compares the spectrogram of the sample with standard plates on which the amount of each element is increased by increments that are ⅙-order of magnitude instead of ⅓-order. The results are reported in percent to the nearest number in the series 1, 0.7, 0.5, 0.3, 0.2, 0.15, and 0.1, which represent approximate midpoints of group data on a geometric scale. The assigned group for 6-step results will include the quantitative value about 30 percent of the time. The analyst normally looks for 51 elements. This report discusses only 26 elements that were reported consistently from the samples of black shale and have a range of values adequate to allow valid statistical treatment. Other elements, for example ytterbium and neodymium, were reported in some of the samples but not with sufficient regularity to treat statistically. Silicon was reported in all samples in major amounts or in near major amounts, but too many values were reported in the category: "greater than 10 percent" for statistical treatment. The approximate lower limit of detection for the elements discussed is, in percent, as follows:

Element	*Approximate lower limit of detection (percent)*	*Element*	*Approximate lower limit of detection (percent)*
Al	0.001	Cr	0.0001
Fe	.0008	Cu	.0001
Mg	.0005	Ga	.0002
Ca	.005	La	.002
Na	.05	Mo	.0005
K	.7	Ni	.0003
Ti	.0002	Pb	.001
Mn	.0002	Sc	.0005
Ag	.0001	Sr	.0002
B	.002	V	.001
Ba	.0002	Y	.001
Be	.0001	Zn	.02
Co	.0005	Zr	.001

The content of organic carbon was determined by making separate analyses for total carbon and carbonate carbon and taking the difference according to the method outlined in Tourtelot, Huffman, and Rader (1964, p. D74).

STATISTICAL TREATMENT OF DATA

Analyses of the 220 black shale samples were coded and incorporated in a geochemical data storage and retrieval system employing IBM punch cards. From these cards a machine print-out of the analyses suitable for direct reproduction was prepared; this print-out has been released as an open-file report (Vine, 1965). These cards were then used as input for converting the analyses to a new format on another set of cards suitable for machine computation of grouped data. Because the spectrographic analyses are reported by 1/6-order class intervals, the carbon analyses were grouped in the same class intervals. Numerous univariate and bivariate statistics were computed including arithmetic and goemetric means, numerical and percent frequency for each class interval, and coefficient of correlation between all pairs of variables. It was not possible to obtain a complete set of univariate and bivariate statistics because the original data included a number of rejected observations (elements for which the analyst reported one or more values as "less than," "greater-than," or "not detected"). The data presented in this report are grouped into the percentile categories—5, 25, 50, 75, and 95—the 50 percentile being equivalent to the median, and the 25 and 75 percentiles being equivalent to the first and third quartiles, respectively. This grouping provides a suitable measure of central tendency, as well as of the range and nature of the data distribution. Table 1 lists these values together with the calculated values for arithmetic and geometric means for those elements having no rejected observations. Table 1 also lists the ratio, P_{95}/P_5 (the quotient of the 95 percentile divided by the 5 percentile), in order to provide a measure of the ranges for different elements.

TABLE 1.—*Percentile distribution of 27 elements in four sets of samples of black shale*

[Average abundance: A, shale;[1] B, pelagic sediment;[2] C, carbonaceous samples of Pierre Shale;[3] D, coal [4]]

Element	Set	Values, in percent, for indicated percentile					Arithmetic mean	Geometric mean	Ratio P_{95}/P_5	Strong correlation (negative correlations in parentheses)	Average abundance	
		P_5	P_{25}	P_{50}	P_{75}	P_{95}					Lithology	Percent
Al	1	7	7	>10	--------	--------	--------	--------	>1.4	--------	A	8.0
	2	3	7	7	7	>10	--------	--------	>3.3	--------	B	9.2
	3	1.5	3	3	7	7	--------	--------	4.7	Ga, Mg, K, Sr, Na, Ba, (C), Mn, Ti, Zr	C	7.75
	4	1.5	3	3	7	>10	--------	--------	>6.7	--------	D	--------
Fe	1	2	5	5	7	7	--------	--------	3.5	--------	A	4.72
	2	1	1.5	2	2	5	--------	--------	5	--------	B	6.5
	3	1.5	2	2	2	3	2.3	2.2	2	Mn, Ti, (C)	C	3.56
	4	.3	.7	1.5	2	5	1.7	1.3	17	Mg, Mn	D	--------
Mg	1	.7	.7	.7	1	1	.79	.77	1.4	V, Na, La, Ni[5]	A	1.5
	2	.3	.5	.7	.7	.7	.60	.56	2.3	Ga, Na, Ti, Sr	B	2 1
	3	.2	.3	.5	.7	1	.52	.48	5	Ga, K, Sr, Al, (C), Ti, Mn, Na, Ba, Zr, Sc.	C	.9
	4	.2	.5	.7	1.5	5	1.4	.95	25	Mn. Fe	D	--------
Ca	1	.05	.2	.3	.5	3	.53	.30	60	Ni, (Zr), Cu	A	2.21
	2	.02	.05	.1	.2	1	.27	.11	50	Mn	B	2.9
	3	.1	.2	.3	.5	1	.35	.27	10	--------	C	.72
	4	.05	.1	.3	3	>10	--------	--------	>200	--------	D	--------
Na	1	.7	1	1	1	1	.95	.93	1.4	V, Sc, Cr, Be, Cu, Ni, (Mn), Ti, K, Mg.[5]	A	.96
	2	.2	.5	.7	1	1	.84	.64	5	Mg, Ga, Ti	B	4
	3	.2	.2	.3	1	1.5	.56	.44	7.5	Ga, (C), K, Al, Ti, Mn, Zr, Sr, Mg, Ba.	C	.56
	4	.05	.1	.2	.3	1	--------	--------	20	--------	D	--------
K	1	2	3	3	3	5	2.9	2.8	2.5	Pb, Na, Sc	A	2.66
	2	1.5	2	2	2	3	--------	--------	2	--------	B	2.5
	3	1.5	2	2	3	5	.27	.24	3.3	Mg, Ga, Na, (C), Sr, Al, Ti, Mn, Ba, Zr.	C	2.32
	4	1	2	3	5	5	--------	--------	5	--------	D	--------
Ti	1	.15	.2	.2	.2	.2	.21	.20	1.3	Sc, Zr, Na [5]	A	.46
	2	.1	.15	.15	.2	.2	.16	.15	2	Ga, Zr, Sr, Mg, Ba, Na	B	.73
	3	.1	.1	.1	.15	.3	.14	.13	3	(C), Zr, Ga, Mg, K, Na, Sc, Al, Fe, Ba, Mn, Sr.	C	.35
	4	.05	.1	.2	.2	.3	.19	.15	6	Cr	D	.045
Mn	1	.005	.015	.015	.03	.15	.034	.021	30	(Na), (Cr), (V)	A	.085
	2	.0015	.003	.005	.01	.03	.0098	.0054	20	Ca	B	1.25
	3	.005	.007	.007	.01	.015	.0084	.008	3	Mg, Ga, Na, (C), K, Ti, Fe, Sr, Al, Ba, Zr.	C	.026
	4	.001	.002	.007	.015	.05	.012	.0064	50	Mg, Fe	D	--------

See footnotes at end of table.

TABLE 1.—*Percentile distribution of 27 elements in four sets of samples of black shale*—Continued

Element	Set	Values, in percent, for indicated percentile					Arithmetic mean	Geometric mean	Ratio P_{95}/P_5	Strong correlation (negative correlations in parentheses)	Average abundance	
		P_5	P_{25}	P_{50}	P_{75}	P_{95}					Lithology	Percent
Ag	1	------	------	------	<0.0001	0.0002	------	------	>2	------	A	0.000007
	2	------	<0.0001	0.0001	.0002	.0002	------	------	>2	------	B	------
	3	<0.0002	.0003	.0005	.0005	.0007	------	------	>3.5	------	C	------
	4	------	------	------	<.0001	.0005	------	------	>5	------	D	------
B	1	.002	.002	.003	.005	.005	------	------	2.5	------	A	.01
	2	<.002	.002	.003	.005	.005	------	------	>2.5	------	B	.03
	3	<.003	.003	.003	.007	.01	------	------	>3.3	------	C	.0145
	4	<.003	.005	.007	.01	.02	------	------	>6.7	------	D	.0096
Ba	1	.03	.03	.05	.05	.07	0.043	0.041	2.3	------	A	.058
	2	.02	.03	.03	.03	.07	.037	.033	3.3	Sr, Ga, Ti	B	.39
	3	.015	.02	.02	.03	.03	.023	.022	2	Sr, Ga, Al, Mg, (C), K, Na, Mn, Ti, Sc.	C	.063
	4	.02	.07	.1	.2	.5	------	------	25	------	D	------
Be	1	.00015	.00015	.0002	.0002	.0003	.00022	.00021	2	V, Cr, Ni, Na, Sc, Cu, La	A	.0003
	2	.00015	.00015	.0002	.0002	.0002	------	------	1.3	------	B	------
	3	------	<.00015	.0002	.0002	.0003	------	------	>2	------	C	------
	4	------	------	<.00015	.0002	.0003	------	------	>2	------	D	.00025
Co	1	.001	.001	.001	.0015	.002	.0012	.0012	2	------	A	.0019
	2	------	<.0002	.0003	.001	.001	------	------	>5	------	B	.016
	3	.0007	.0007	.001	.001	.0015	.001	.00097	2	Ni, Mo	C	.0014
	4	------	------	<.0007	.0007	.0015	------	------	>2	------	D	.00038
Cr	1	.007	.007	.01	.015	.015	.011	.010	2	V, Be, Na, Ni, Cu, (Mn), Sc	A	.009
	2	.007	.01	.015	.02	.03	.017	.014	4.3	V, Cu, Ni	B	.0093
	3	.01	.02	.03	.03	.05	.032	.029	5	V, Sc	C	.0125
	4	.003	.007	.01	.015	.03	.012	.009	10	Ti, V, Sr	D	.0020
Cu	1	.002	.003	.005	.007	.007	.0047	.0044	3.3	V, Cr, Na, Ni, Be, Ca	A	.0045
	2	.0015	.005	.007	.01	.01	.0064	.0053	6.7	V, Cr, Ni	B	.074
	3	.01	.015	.015	.015	.02	.015	.015	2	------	C	.008
	4	.0007	.003	.005	.01	.02	------	------	28.6	------	D	.0011
Ga	1	.002	.002	.002	.002	.003	.0022	.0022	1.5	(C) [5]	A	.0019
	2	.001	.0015	.002	.002	.002	.0019	.0018	2	Ti, Mg, Sr, Zr, Na, Ba, (C)	B	.0019
	3	.001	.0015	.0015	.002	.003	.002	.0018	3	Al, Na, (C), Ti, Mg, K, Zr, Sr, Mn, Ba, Sc.	C	.0017
	4	.0005	.001	.0015	.002	.003	------	------	6	------	D	.00041
La	1	.003	.003	.005	.005	.005	.0040	.0040	1.67	Be, Sc, Mg, Cr [5]	A	.0092
	2	<.002	.003	.003	.005	.005	------	------	>2.5	------	B	.014
	3	<.003	.003	.005	.005	.005	------	------	>1.67	------	C	------
	4	------	<.003	.003	.005	.007	------	------	>2.1	------	D	.00051

Mo	1	----------	<.0005	.0015	.003	.03	----------	----------	>60	----------	A	.00026
	2	<.0005	.0005	.005	.02	.03	----------	----------	>60	----------	B	.0045
	3	.015	.03	.03	.05	.07	.040	.037	4.7	Ni, Co, C	C	.0043
	4	----------	----------	<.0005	.001	.005	----------	----------	>10	----------	D	.00043
Ni	1	.002	.003	.007	.01	.015	.0071	.0060	7.5	V, Be, Cr, Cu, Na, Ca, Mg	A	.0068
	2	.002	.005	.007	.01	.015	.0077	.0060	7.5	V, Cu, Cr	B	.012
	3	.01	.02	.03	.03	.07	.032	.028	7	Mo, Co, Y, V	C	.0053
	4	<.0005	.0005	.0015	.005	.01	----------	----------	>20	----------	D	.0015
Pb	1	.0015	.002	.002	.003	.005	.0027	.0025	3.3	K	A	.002
	2	.001	.0015	.002	.003	.007	----------	----------	7	----------	B	.015
	3	<.001	.002	.003	.005	.007	----------	----------	>7	----------	C	.0019
	4	----------	<.001	.001	.0015	.003	----------	----------	>3	----------	D	----------
Sc	1	.001	.0015	.0015	.002	.002	.0016	.0016	2	Na, Ti, Be, La, V, Cr, K	A	.0013
	2	.0007	.001	.0015	.0015	.0015	----------	----------	2	----------	B	.0025
	3	.0007	.001	.001	.001	.0015	.0011	.0011	2	V, Zr, Ti, Cr, Mg, Ba, Ga	C	.0021
	4	<.0007	.0007	.001	.0015	.002	----------	----------	>2.9	----------	D	----------
Sr	1	.01	.015	.02	.02	.02	.021	.019	1	----------	A	.03
	2	.007	.01	.015	.02	.02	.015	.014	2.9	Ga, Ti, Zr, Mg, Ba	B	.071
	3	.003	.007	.01	.01	.015	.0097	.0087	5	Mg, Ba, K, Al, Ga, Na, (C), Mn, Ti, Zr.	C	.0115
	4	.003	.005	.01	.015	.05	.013	.0096	16.7	Cr	D	----------
V	1	.007	.01	.015	.02	.05	.018	.015	7.1	Be, Cr, Na, Ni, Cu, Mg, Sc, (Mn).	A	.013
	2	.007	.007	.02	.05	.05	.032	.022	7.1	Cu, Cr, Ni	B	.045
	3	.02	.07	.1	.15	.2	.12	.10	10	Cr, Sc, Ni	C	.04
	4	.005	.01	.02	.05	.2	.042	.023	40	Cr	D	.0035
Y	1	.002	.002	.003	.003	.005	.003	.0029	2.5	----------	A	.0026
	2	.001	.002	.002	.003	.003	----------	----------	3	----------	B	.015
	3	.0015	.002	.003	.005	.007	.004	.0034	4.7	Ni	C	----------
	4	.001	.0015	002	.002	.007	----------	----------	7	----------	D	.00077
Zn	1	----------	----------	----------	<.03	.07	----------	----------	>2.3	----------	A	.0095
	2	----------	----------	----------	<.05	.05	----------	----------	>1	----------	B	----------
	3	----------	<.05	.07	.15	.3	----------	----------	>6	----------	C	.015
	4	----------	----------	----------	<.03	.10	----------	----------	>3.3	----------	D	.0044
Zr	1	.005	.07	.007	.01	.01	.0075	.0071	2	Ti, (Ca)	A	.016
	2	.003	.005	.005	.007	.01	.0058	.0052	3.3	Ti, (C), Ga, Sr	B	.018
	3	.002	.003	.003	.005	.007	.0039	.0037	3.3	Ti, Ga, (C), Na, Sc, Mg, K, Al, Sr, Mn.	C	.021
	4	.003	.007	.007	.015	.02	----------	----------	6.7	----------	D	----------
C	1	1.5	3	5	10	15	7.3	5.5	10	(Ga)	A	----------
	2	.2	10	15	20	30	18	11.8	15	(Zr)	B	----------
	3	10	15	30	50	50	34.8	30.3	5	(Ti), (Ga), (Na), (K), (Mg), (Zr), (Mn), (Sr), (Ba), (Al), (Fe), Mo.	C	3.86
	4	----------	----------	----------	----------	----------	----------	----------	----------	----------	D	----------

---

[1] Average for shales, Turekian and Wedepohl (1961, table 2).

[2] Average of 22 samples of pelagic sediment cores from the eastern Pacific, Goldberg and Arrhenius (1958, table 9).

[3] Average of 14 samples of Pierre Shale containing more than 1 percent organic carbon; minor elements after Tourtelot, Schultz, and Gill (1960, table 205.1), major elements after H. A. Tourtelot (written commun., 1964).

[4] Average of 47 coal-bed columns from the Eastern Interior coal region, Zubovic and others (1964, table 7).

[5] Distribution of sample values not adequate for reliable correlation statistics.

Published values for the abundance of elements in some sediments and sedimentary rocks taken from four recent references are also listed in table 1. Included are the average values listed (1) by Turekian and Wedepohl (1961, table 2) for the abundance of elements in shales; (2) by Goldberg and Arrhenius (1958, table 9) for the abundance of elements in 22 samples of pelagic sediment cores from the eastern Pacific; (3) by Tourtelot, Schultz, and Gill (1960), table 205.1) for the abundance of elements in 14 samples of Pierre Shale that had more than 1 percent organic carbon; and (4) by Zubovic, Stadnichenko, and Sheffey (1964, table 7) for the average content of minor elements in coal beds from the Eastern Interior coal region. These published values are average (arithmetic mean) values; therefore, it is not statistically valid to make direct comparisons with the median values of table 1. Where both median and arithmetic mean values were calculated for the samples of black shale in this study, the arithmetic-mean values are usually greater.

Whereas values for the median and other percentile categories in table 1 are listed according to the same series of 6 numbers used in reporting the 6-step spectrographic analyses, the arithmetic and geometric means are rounded to two digits. This is not intended to imply greater accuracy for the arithmetic and geometric means than for the percentile categories. The second digit is retained because it is a useful indication of the skewness of the sample distribution.

In order to test the strength of association between various elements, the product moment coefficient of correlation was calculated for every pair of elements from every set, if there were no rejected observations (see table 2). The 99- and 99.9-percent levels of significance shown on the table for each set are quoted from Davies (1954, p. 276) and are based only on the number of samples. As this method assumes a normal frequency distribution of the sample data, it may give a misleading impression of the strength of association for element pairs that do not approach the ideal distribution, as for example, those elements having a range of three or fewer class intervals.

DESCRIPTION OF SAMPLE SETS

The chemical data that are the basis for this report are derived from the analyses of 220 samples of black shale divided into four sets that are individually summarized. Descriptions of individual samples, localities, and 6-step spectrographic analyses of all samples are tabulated in a separate report that has been placed on open file by the U.S. Geological Survey (Vine, 1965). Only the summary statistics and interpretation of the analyses are presented here. Three sets represent black shale associated with coal beds of Pennsylvanian age in the Eastern Interior coal province; the fourth set is composed of samples of graptolitic shale from the western and transitional facies of Ordovician and Silurian rocks in the Frazer belt (of Kay, 1947).

Sets 1 and 2 consist of core and outcrop samples, respectively, of black shale in the Tradewater and Carbondale Formations of the western Kentucky coal field (fig. 1). Each set includes numerous core or channel samples of black shale from beds 1 foot thick or more that lie directly above coal beds in a cyclic stratigraphic sequence. Both sets also include a few samples of black shale from below coal beds or between closely spaced coal beds. Although most of the beds of black shale are less than 3 feet thick, a few are thicker. Many contain brachiopods, conodonts, fish scales and fins, and other faunal remains similar to the black shales described by Zangerl and Richardson (1963).

The core samples comprising set 1 were taken from a group of four borings, drilled in connection with the Kentucky geologic mapping project at locations selected to provide the maximum stratigraphic and structural information in an area of poor outcrops and to aid in determining the thickness, grade, and reserves of coal. The complete sequence of black shales penetrated by these four borings is included in set 1. The set is probably representative of about 5 beds of unweathered black shale aggregating about 13 feet in thickness, at depths of less than 200 feet in the vicinity of Owensboro, Ky. Similar black shale probably underlies several quadrangles in the northern part of the Western Kentucky coal field.

The samples comprising set 2 were collected from all the readily accessible natural and artificial exposures of black shale in the areas near Owensboro and Madisonville, Ky., that were known to the U.S. Geological Survey field geologists mapping these areas in the spring of 1964. Set 2 is probably representative of about 10 beds of slightly weathered black shale that have an aggregate thickness of about 18 feet as they occur at or near the outcrop in the Western Kentucky coal field. Similar rock probably underlies much of the coal field.

Set 3 consists of a complete sequence of thin laminae split from a 12-inch bed of metal-rich black shale that lies above coal III–A in the Linton Formation of Parke County, Ind. (fig. 1). This bed was named the Mecca Quarry Shale Member by Zangerl and Richardson (1963); it was studied in great detail by them because it contains a remarkably well preserved fauna of Pennsylvanian sharks and other fish in association with invertebrate remains. Included in the report (Zangerl and Richardson, 1963, p. 99) are several spectrographic analyses of the shale that indicate unusually large amounts of vanadium, zinc, and several other metals. These first analyses were intended to aid in understanding the environment of deposition of the contained fossils, and it was probably not anticipated that they would be rich in metals.

TABLE 2.—*Correlation coefficients for element pairs in four sets of samples of black shale*

Level of significance:

Set	99.9 percent	99 percent
1	0.40	0.31
2	.49	.39
3	.52	.42
4	.38	.30

Element	Set	Al	Fe	Mg	Ca	Na	K	Ti	Mn	Ba	Be	Co	Cr	Cu	Ga	La	Mo	Ni	Pb	Sc	Sr	V	Y	Zr	C
		Al																							
Fe	1	------	Fe																						
	2	------																							
	3	0.37																							
	4	------																							
Mg	1	------	------	Mg																					
	2	------	------																						
	3	.77	0.48																						
	4	------	.42																						
Ca	1	------	------	0.31	Ca																				
	2	------	------	.27																					
	3	—.20	—.04	.02																					
	4	------	------	------																					
Na	1	------	------	.41	0.18	Na																			
	2	------	------	.63	.16																				
	3	.73	.37	.66	—.34																				
	4	------	------	------	------																				
K	1	------	------	.25	—.04	0.42	K																		
	2	------	------	------	------	------																			
	3	.76	.45	.80	—.19	.79																			
	4	------	------	------	------	------																			

Ti	1	------	------	.12	−.22	.42	.21										
	2	------	------	.57	−.20	.53	------	Ti									
	3	.57	.55	.73	−.21	.71	.74										
	4	------	.27	.04	------	------	------										
Mn	1	------	------	−.12	.14	−.47	−.19	−0.20									
	2	------	------	.38	.49	.13	------	−.19									
	3	.58	.61	.73	−.03	.70	.66	.63	Mn								
	4	------	.41	.53	------	------	------	−.13									
Ba	1	------	------	.26	.16	.36	.08	.20	−0.25								
	2	------	------	.47	−.11	.43	------	.56	−.14	Ba							
	3	.67	.37	.66	−.28	.60	.62	.54	.56								
	4	------	------	------	------	------	------	------	------								
Be	1	------	------	.35	.27	.54	.11	.28	−.37	0.33							
	2	------	------	------	------	------	------	------	------	------	Be						
	3	------	------	------	------	------	------	------	------	------							
	4	------	------	------	------	------	------	------	------	------							
Co	1	------	------	−.16	−.38	.19	.03	.29	−.21	−.11	0.18						
	2	------	------	------	------	------	------	------	------	------	------	Co					
	3	−.05	.24	.01	.30	.05	−.17	.06	.10	−.08	------						
	4	------	------	------	------	------	------	------	------	------	------						
Cr	1	------	------	.25	.20	.55	.05	.26	−.59	.24	.61	0.02					
	2	------	------	.36	.04	.43	------	.44	−.36	.32	------	------	Cr				
	3	.34	.08	.29	−.15	.14	.16	.26	.00	.27	------	.40					
	4	------	−.04	.11	------	------	------	.48	−.18	------	------	------					
Cu	1	------	------	.29	.40	.54	.36	.05	−.33	.33	.48	−.11	0.53				
	2	------	------	.34	−.19	.26	------	.35	−.43	.41	------	------	.71	Cu			
	3	−.06	.11	.09	.09	−.07	−.21	−.05	.01	−.07	------	.48	.51				
	4	------	------	------	------	------	------	------	------	------	------	------	------				
Ga	1	------	------	−.09	−.14	.06	.14	.38	.08	.24	.08	.17	−.11	−0.16			
	2	------	------	.67	−.10	.58	------	.78	.01	.58	------	------	.42	.39	Ga		
	3	.82	.47	.80	−.19	.82	.79	.81	.71	.70	------	.03	.31	−.10			
	4	------	------	------	------	------	------	------	------	------	------	------	------	------			
La	1	------	------	.40	.39	.32	.17	.09	−.23	.37	.44	−.12	.40	.39	0.11		
	2	------	------	------	------	------	------	------	------	------	------	------	------	------	------		
	3	------	------	------	------	------	------	------	------	------	------	------	------	------	------	La	
	4	------	------	------	------	------	------	------	------	------	------	------	------	------	------		
Mo	1	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	
	2	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	Mo
	3	−.26	−.18	−.23	.45	−.47	−.46	−.29	−.29	−.23	------	.56	.31	.49	−.37	------	
	4	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	

TABLE 2.—*Correlation coefficients for element pairs in four sets of samples of black shale*—Continued

Element	Set	Element																							
		Al	Fe	Mg	Ca	Na	K	Ti	Mn	Ba	Be	Co	Cr	Cu	Ga	La	Mo	Ni	Pb	Sc	Sr	V	Y	Zr	C
Ni	1	------	------	.40	.45	.50	.14	.09	-.36	.33	.58	.12	.53	.50	-.18	0.35	------	Ni							
	2	------	------	.25	.23	.25	------	-.01	.05	.18	------	------	.52	.53	-.01	------	------								
	3	-.14	-.18	-.15	.41	-.28	-.24	-.13	-.26	-.15	------	.62	.49	.45	-.16	------	0.78								
	4	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------								
Pb	1	------	------	.29	-.14	.33	.44	.25	-.36	.02	.12	.17	.09	.24	.08	.05	------	0.23	Pb						
	2	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------							
	3	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------							
	4	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------							
Sc	1	------	------	.34	-.05	.60	.41	.54	-.26	.36	.49	.24	.41	.37	.34	.43	------	.33	0.32	Sc					
	2	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------						
	3	.49	.41	.55	-.15	.48	.45	.61	.40	.54	------	.34	.61	.21	.58	------	.13	.17	------						
	4	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------						
Sr	1	------	------	.15	.37	.34	.10	.05	-.25	.21	.37	.01	.35	.39	.09	.35	------	.21	-.02	0.28	Sr				
	2	------	------	.51	-.03	.37	------	.60	-.03	.58	------	------	.35	.28	.64	------	------	-.02	------	------					
	3	.76	.48	.79	-.14	.70	.77	.58	.60	.78	------	-.09	.16	-.12	.72	------	-.35	-.23	------	.49					
	4	------	.00	.27	------	------	------	.02	-.02	------	------	------	.38	------	------	------	------	------	------	------					
V	1	------	------	.53	.26	.63	.33	.26	-.41	.30	.69	.07	.66	.59	-.09	.38	------	.59	.16	.43	0.28	V			
	2	------	------	.28	-.17	.33	------	.28	-.40	.43	------	------	.72	.74	.26	------	------	.62	------	------	.38				
	3	.35	.18	.41	.11	.22	.25	.43	.08	.26	------	.50	.87	.46	.37	------	.44	.55	------	.70	.22				
	4	------	-.14	.08	------	------	------	.08	-.03	------	------	------	.45	------	------	------	------	------	------	------	.15				
Y	1	------	------	.14	.37	.17	-.28	.29	-.03	.16	.37	-.10	.30	.19	.13	.32	------	.14	.08	.25	.28	0.04	Y		
	2	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------			
	3	-.30	.04	-.14	.41	-.18	-.18	-.06	-.24	-.30	------	.47	.15	.22	-.25	------	.51	.56	------	.06	-.26	.36			
	4	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------			
Zr	1	------	------	-.16	-.44	-.11	-.06	.46	.05	-.09	-.10	.22	-.12	-.27	.28	-.10	------	-.15	.07	.12	-.34	-.16	-0.02	Zr	
	2	------	------	.48	-.02	.42	------	.77	.03	.45	------	------	.10	.01	.60	------	------	-.27	------	------	.58	-.03	------		
	3	.57	.34	.66	-.07	.71	.61	.86	.52	.47	------	.10	.31	.01	.78	------	-.15	-.07	------	.68	.54	.51	-.04		
	4	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------		
C	1	------	------	-.19	.20	-.10	-.24	-.27	.16	-.21	-.19	-.06	.00	.25	-.55	-.12	------	.03	-.16	-.31	-.19	-.03	.04	-0.03	C
	2	------	------	-.42	-.26	-.24	------	-.43	-.36	-.09	------	------	.17	.29	-.25	------	------	.28	------	------	-.37	.24	------	-.70	
	3	-.62	-.53	-.76	.26	-.81	-.79	-.89	-.68	-.62	------	.04	-.12	.26	-.82	------	.53	.40	------	-.49	-.67	-.24	.21	-.74	
	4	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	

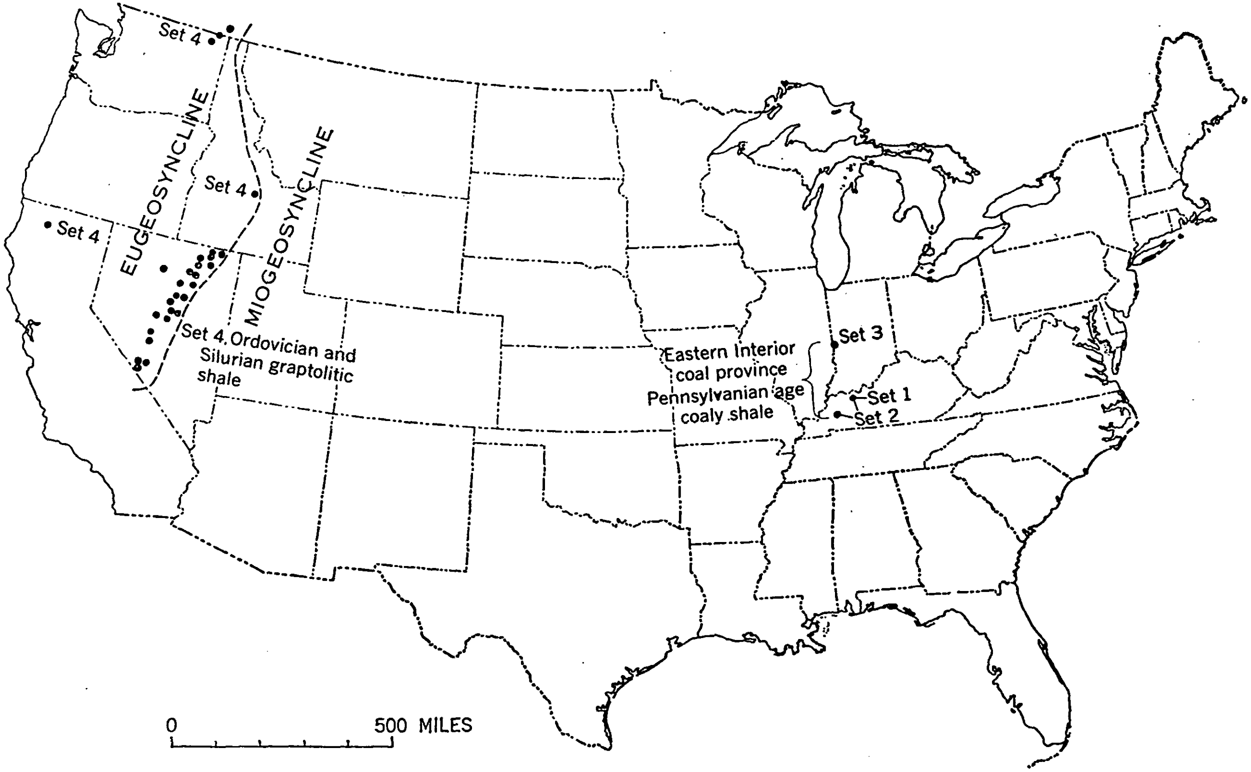

FIGURE 1.—Sample localities of black-shale sample sets and of individual samples in set 4. Set numbers refer to data in tables 1 and 2 and to Vine (1965).

The association of abundant well-preserved fossils with a metal-rich shale, however, may be evidence of a toxic environment. The Indiana III–A coal bed and the overlying black shale are recognized over much of the Eastern Interior coal province. Stratigraphic equivalents of the Mecca Quarry Shale Member in the Western Kentucky coal field are included among the samples of sets 1 and 2. Although the coal and black shale are widespread, the chemical composition of the black shale samples in set 3 may not represent more than a few hundred acres in the vicinity of the Mecca Quarry, Parke County, Ind.

Set 4 includes outcrop samples from widely scattered localities in California, Nevada, Idaho, Washington, and British Columbia collected from the graptolitic shale facies that was deposited in or marginal to the lower Paleozoic eugeosyncline of western North America. Several samples included in this set were collected from localities previously reported to be metal rich. One sample is from the locality described by Davidson and Lakin (1961) as the Comus Formation, Edna Mountains, Nev., and two were collected from the locality described by Davidson and Lakin (1962) as "Taylor Canyon, Elko County, Nevada." Other samples were collected wherever shale exposures of the Ordovician and Silurian "western" or "transitional" facies as defined by Roberts and others (1958) could be found. Roberts, Hotz, Gilluly, and Ferguson (1958, p. 2816) estimated that shale makes up 20–40 percent of the eugeosynclinal stratigraphic sequence in central Nevada. Many of the specific localities examined and sampled were suggested to me by colleagues in the U.S. Geological Survey or were located from published descriptions of black or graptolitic shale. They include several localities from which graptolitic fossils were collected by Ross and Berry (1963). Rocks of the graptolitic facies were deposited to the west of, and contrast markedly with, the miogeosynclinal rocks typical of eastern Nevada and Utah, which are largely carbonate rocks. The eugeosynclinal strata are characteristically siliceous (Ketner and Smith, 1963) and dark in color because of large amounts of included carbonaceous matter. Although there has been much speculation regarding the origin and environment of deposition including the depth of water in which the graptolitic shales were deposited, there is as yet no general agreement (Ross, 1961). However, many field geologists, including R. J. Roberts (oral commun., 1962), believe that the eugeosynclinal deposits accumulated in deep water, far from the continental shore. Ruedemann (1934) regarded most of the graptolites and such associated forms as the crustacean *Caryocaris* as being of planktonic origin. These rocks are therefore similar in many respects to the carbonaceous and siliceous rocks of the Monterey Formation of Miocene age in California that Bramlette

(1946, p. 50–51) thought were derived in large part from such planktonic organisms as diatoms and algae.

The samples making up set 4 are intended to be representative of the graptolitic shale facies of western North America. These rocks crop out in a region of complex structure, and the details of stratigraphic succession have not been worked out. Therefore, it is difficult to estimate the volume of black shale that is represented. Clearly, however, the 75 samples of set 4 represent a far greater volume of rock than do the 145 samples in the first 3 sets.

The environments of deposition for those samples collected from the shelf area and those samples collected from the eugeosynclinal area are in striking contrast. Whereas the samples of black shale in sets 1–3 may be regarded as characteristic of a near-shore shallow-water environment on the continental shelf, the samples of black shale in set 4 are probably characteristic of a deep marine environment remote from the influence of the continent. Furthermore, the composition of the organic matter preserved in the two environments is probably quite different. As pointed out by Vinogradov (1953, p. 134–135), pre-Devonian black shales did not include the humic decomposition products of lignin derived from the higher land plants, which had not evolved significantly until Devonian time. The organic matter preserved in the samples of sets 1–3 presumably includes abundant humic matter similar to the "liver mud" described by Spackman, Scholl, and Taft (1964, p. 28–29) derived from vascular land plants growing in the nearby coal swamps; in contrast, the organic matter preserved in the samples of set 4 is presumably sapropelic.

Each set of samples differs from the others in some significant respect that justifies separate statistical treatment. The samples comprising set 1 are less weathered than the other two sets from the Eastern Interior coal province. The samples comprising sets 1 and 2 are relatively large channel and core samples from several different beds, whereas the samples comprising set 3 are individual thin laminae from a single bed. Set 3 therefore represents a smaller scale of sampling. The samples comprising set 4 differ from the first three sets not only because they are from older rocks in a different environment of deposition, but because they had a wide geographic distribution. They represent a larger scale of sampling than the other sample sets. Therefore, whatever interpretation is given to the geochemical significance of the analytical data must consider these differences. Some of the more pertinent differences are outlined in the table below.

Set	Number of samples	Number of localities	Area or region	Sample description (generalized)	Degree of weathering	Age	Depositional environment
1	66	4	Western Kentucky.	0.5 ft coaly shale, drill core.	Unweathered.	Pennsylvanian.	Transgressive brackish or marine, shelf.
2	42	20	do	0.75 ft coaly shale, outcrop.	Slightly weathered.	do	Do.
3	37	1	Indiana	0.02 ft coaly shale, quarry:	do	do	Do.
4	75	51	Western North America.	1.0 ft siliceous shale, outcrop.	do	Ordovician and Silurian.	Eugeosyncline (abyssal slope).

SOURCES OF ERROR

No geochemical interpretation, especially one involving statistical treatment of data, should be attempted without recognizing the many possible sources for error. First, the plan of sample collection, if not random, may introduce a bias that is difficult to evaluate. Such a plan requires a geologic interpretation of the uniformity, areal distribution, and correlation of stratigraphic units that the samples are intended to represent. Because unweathered natural outcrops of black shale are rare, samples for this study had to be collected from a variety of artificial exposures and previously cored or quarried rock. The bias introduced into this study through failure to use truly random methods of sampling is probably no more significant than the errors common to most geologic investigations that attempt to represent any significant body of rock by a few chemical analyses of samples collected at natural outcrops, roadcuts, and similar exposures. Second, the precision and accuracy of the 6-step spectrographic method of analysis employed in this study is less than other more costly techniques. However, in trying to estimate a reasonable value for the abundance of a minor element in a given type of rock, as well as a range of values that might commonly be found, analysis of numerous samples by the 6-step spectrographic method is more informative than analysis of a few samples by a more precise method.

Perhaps the greatest danger with any geochemical interpretation is attributing to it greater significance than is warranted. This is especially true when one makes comparisons with data derived from samples collected for a different reason, analyzed by different techniques, and presented statistically using different measures of central tendency and dispersion. For this reason, comparisons with previously published data are not emphasized in this report. The new data are considered internally consistent enough to make valid comparisons between sample sets.

DISTRIBUTION AND ASSOCIATION OF MAJOR ELEMENTS

The distribution and association of individual elements can be determined from table 1, which shows for each set the percentile distribution of organic carbon and each of the 26 elements detected spectrographically, and table 2, which shows for each set the coefficient of correlation for element pairs. Two kinds of comparisons should be distinguished: (1) statements about strong positive or negative correlations between elements referring to coefficients of correlation having at least a 99-percent level of significance between element pairs in a specified sample set as shown in table 2 and (2) statements about direct or inverse variations between two elements in a series of sample sets, referring to the median content of one element that shows a set-by-set change which varies directly or inversely with the median content of another element as shown in table 1.

CARBON

Sufficient organic carbon to impart a dark-gray to black color to the rock is characteristic of all the samples studied. Analyses for organic carbon were made for all samples comprising sets 1–3 and for a few samples of set 4. The median organic carbon analyses for set 1 is 5 percent; for set 2, 15 percent; and for set 3, 30 percent. The median organic carbon analysis for set 4 is estimated to be about 2–3 percent. Of all the elements studied, organic carbon shows the greatest tendency to correlate negatively with most of the other elements, especially the other major elements. This tendency probably arises because no major element can vary independently of the others; the total element content must always approach 100 percent. Among the minor elements, copper and nickel show that most consistent positive correlation with organic carbon, and molybdenum shows the strongest positive correlation with carbon in a single set.

ALUMINUM

The median content of aluminum is greater than 10 percent for the samples in set 1, 7 percent in set 2, and 3 percent in set 3. The change in these three sets varies inversely with the median content of organic carbon. The median content of aluminum for the samples in set 4 is 3 percent, the same as set 3, which has the highest median carbon content. In set 4, however, the other major diluting element is presumed to be silicon, rather than carbon, as many of these samples are siliceous. The content of aluminum in all the samples of black shale is probably directly related to their clay mineral content. Consequently, of all elements studied except silicon, aluminum is the most characteristic element of the detrital mineral fraction. Other elements having a strong correlation with aluminum probably are more abundant in the detrital-mineral fraction than in the organic matter or in the biogenically and chemically precipitated fraction. Coefficients of correlation for aluminum were calculated only for set 3, where aluminum has a strong positive correlation with gallium, magnesium, potassium, strontium, sodium, barium, manganese, titanium, and zirconium and a strong negative correlation with organic carbon.

IRON

The median content of iron ranges from 1.5 percent in samples of set 4 to 5 percent in those of set 1 which have been weathered the least. Iron occurs in pyrite or its secondary alteration products in most of these samples, but it has no strong positive correlation with other elements, such as copper, zinc, molybdenum, nickel, or cobalt that might also be expected to occur in sulfide minerals. In set 3, iron has a strong positive correlation with manganese and titanium, both of which form common oxides with iron. A strong positive correlation of iron with magnesium in the samples of set 4 may indicate the presence of the mineral ankerite.

MAGNESIUM

The content of magnesium in samples of set 4 ranges from 0.2 percent at the 5-percentile level to 5 percent at the 95-percentile level; yet the median content of samples in all 4 sets is very close—0.7 percent in sets 1, 2, and 4, and 0.5 percent in set 3. Magnesium has a strong positive correlation with many elements; with sodium, gallium, titanium, manganese, and strontium, it shows such correlation in more than one set. Except for titanium, most elements with which magnesium correlates could occur in more than one fraction of black shale, but they appear repeatedly in combinations that are most readily interpreted as detrital.

CALCIUM

Although the content of calcium has the widest range of all the major elements, sets 1, 3, and 4 have the same median content of 0.3 percent, and set 2 has a median content of 0.1 percent. These median contents are significantly less than those for magnesium, which seems a little unusual. They are also significantly less than the average abundances in shale, pelagic sediment, and Pierre Shale (table 1, col. 13). The environment of deposition for most of the samples of black shale was probably too acid for calcium carbonate to be stable, and therefore calcium remained in solution. Calcium has a strong positive correlation with only a few elements: nickel and copper in set 1 and manganese in set 2; it also has a negative correlation with zirconium in set 1. This grouping of elements does not suggest any pattern of distribution that can be readily interpreted, except that calcium is nondetrital.

SODIUM

The median content of sodium ranges from 0.2 percent for the samples in set 4 to 1 percent for the samples in set 1. The occurrence of the highest median sodium content in the core samples from set 1 is in agreement with the findings of Gluskoter and Rees (1964) and Gluskoter (1965) in the Eastern Interior coal province that the chloride content of coal and the sodium chloride content of ground water associated with coal increases with depth. From this relation it may be inferred that part of the sodium in the core samples is derived from included pore moisture, or is lightly held in the mineral fraction by sorption or ion exchange. Probably a greater proportion of the sodium contained in samples from sets 2–4 is an essential part of specific minerals. Sodium has a strong positive correlation in sets 1–3 with magnesium and titanium, and in sets 2 and 3 with gallium, an element grouping suggestive of the detrital mineral fraction.

POTASSIUM

Potassium is consistently more abundant than sodium in the samples. The median content of potassium ranges only from 2 to 3 percent and the total range (ratio of P_{95}/P_5) is less than for sodium for 3 of the 4 sets. A strong positive correlation of potassium with the elements gallium, magnesium, and titanium as well as with sodium in set 3 indicates that potassium and sodium are geochemically similar. The highest median potassium content occurs in samples of set 1, like that of sodium, indicating that potassium too may be subject to weathering at the outcrop.

TITANIUM

The median content of titanium ranges from 0.1 percent for the samples in set 3 to 0.2 percent for the samples in sets 1 and 4. The corresponding arithmetic means calculated to two digits range from 0.14 to 0.21 percent titanium, means which appear to be significantly less than the average of 0.46 percent titanium in shale listed by Turekian and Wedepohl (1961, table 2). This divergence may be due to a greater proportion of detrital minerals in the shale samples used in compiling the data for average shale, as contrasted with a greater proportion of chemically or biogenically precipitated mineral matter and organic matter in the samples of black shale included in the present study. The median titanium content varies directly with the median aluminum content in the first three sample sets, but in set 4 the median titanium is relatively high and the median aluminum is low. This variation may be due to an origin for the detrital fraction of set 4 from mafic volcanic rocks rich in titanium. Goldberg and Arrhenius (1958, p. 189) suggested a similar explanation for the relatively high content of titanium in pelagic sediment. Perhaps the high titanium content relative to the aluminum content of the samples in set 4 is due to a contribution from biogenically precipitated titanium, as suggested by Cressman (1962, p. T13) for the relatively high titanium content of some other siliceous sedimentary rocks.

MANGANESE

The content of manganese in the 4 sample sets has a very wide range, from 0.001 percent at the 5-percentile level of set 4 to 0.15 percent at the 95-percentile level of set 1. The arithmetic-mean content of manganese calculated to two digits ranges from 0.0084 percent in samples of set 3 to 0.034 percent in samples of set 1, which is significantly less than the 0.085 percent manganese listed for the average shale by Turekian and Wedepohl (1961, table 2). The higher content of manganese in the core samples of set 1, like the correspondingly higher content of sodium, may be due to the greater degree of weathering that has removed the more soluble part of the original manganese from the samples of the other three sets. The manganese remaining in the more weathered samples may be that which is tightly held in resistant minerals, for in set 3 manganese has a strong positive correlation with several elements including magnesium, gallium, sodium, potassium, titanium, iron, aluminum, and zirconium, elements which presumably occur in the detrital fraction of the black shale.

DISTRIBUTION AND ASSOCIATION OF MINOR ELEMENTS

SILVER

The silver content of most of the samples of black shale is less than the 0.0001 percent lower limit of detection of the 6-step spectrographic method. The median value of 0.0005 percent in the samples of set 3 exceeds the 95 percentile of the samples in sets 1 and 2, but it is equal to the 95 percentile of samples in set 4. Thus, samples from the eugeosynclinal environment have local concentrations of silver as high as a single bed of metal-rich shale from the shelf environment. Although no coefficients of correlation were calculated between silver and other elements, because of insufficient data, inspection of the analyses suggests a probable positive correlation between high silver and high molybdenum, nickel, vanadium, and carbon.

BORON

In spite of the large variation in the proportions of detrital minerals and carbonaceous matter, the median boron content of the samples from the shelf environment, sets 1–3, is 0.003 percent. The 0.007 percent median boron content of set 4 indicates a significantly greater concentration of boron in the samples from the eugeosynclinal environment. Because several recent investigators (for example, Degens, Williams, and Keith, 1958) have considered the probability of boron being a salinity indicator, one might suspect that the greater content of boron in the samples in set 4 indicates a higher salinity environment for the eugeosynclinal samples. However, only the 0.02 percent boron at the 95-percentile level of samples in set 4 compares with the 0.03 percent reported by Goldberg and Arrhenius (1958) for boron in pelagic sediments. Furthermore, Zubovic, Stadnichenko, and Sheffey (1964, table 7) reported about three times as much boron in coal (0.0096 percent) as was found in black shale from the shelf environment. From this it would appear that a comparison of boron content in different rock types or environments cannot be used directly as a salinity indicator.

BARIUM

The contrast between set 4 and the other sets is even more marked for barium than for boron; the median content of 0.1 percent barium in the samples of set 4 exceeds even the 95-percentile value for the other samples. The samples from the eugeosynclinal environment are enriched in barium when compared with the samples from the shelf environment. Furthermore, barium shows a strong positive correlation with strontium, gallium, aluminum, magnesium, potassium, sodium, titanium, manganese, and scandium in set 3, such correlation suggesting that in this shelf environment what little barium is present occurs chiefly in the detrital-mineral fraction. Although coefficients of correlation were not calculated between barium and other elements for set 4, inspection of the analyses indicates a probable positive correlation between high barium and high vanadium but little or no correlation between barium and strontium. Inasmuch as the samples in set 4 include a relatively large proportion of chemically or biogenically precipitated mineral matter, it seems likely that some of the barium in these samples occurs as a discrete barium mineral precipitate, probably barite, as suggested by Goldberg and Arrhenius (1958, p. 188) for the occurrence of barium in Pacific pelagic sediments.

BERYLLIUM

The median content of beryllium is less than 0.00015 percent in the samples of set 4 and 0.0002 percent in the samples of sets 1–3, making beryllium one of the least abundant elements of the ones that are commonly reported in these samples of black shale. Furthermore, only 0.0002–0.0003 percent beryllium was found even at the 95-percentile level in these samples. In contrast to the above generalizations, Stadnichenko, Zubovic, and Sheffey (1961) found the beryllium content of coal to be highly variable, some beds containing as much as 0.0031 percent beryllium. Furthermore, they concluded (1961, p. 279–281) that most of the beryllium is associated with the organic matter of the coal and not with the extraneous ash. In the samples of set 1, even though beryllium has a negative correlation with carbon, it has a strong positive correlation with vanadium, chromium, nickel, copper, and lanthanum. As a group, these five elements are probably concentrated in, or associated with, the organic-matter fraction of black shale.

COBALT

The total range in content of cobalt in the samples of black shale is not large, but the 0.001 percent median cobalt content of samples in set 1 is about three times the median content of 0.0003 percent in samples of set 2. So much difference between two similar sets of samples seems unusual, unless as was suggested for the difference in content of sodium and manganese between sets 1 and 2, it is a reflection of the sample depth and degree of leaching or weathering near the surface. The only significant correlation data for cobalt are for the samples in set 3. There, cobalt has a strong positive correlation with nickel and molybdenum, as well as a positive correlation with vanadium, copper, yttrium, and probably chromium. As a group, these elements are probably associated with, or concentrated in, the organic-matter fraction of the black shale samples.

CHROMIUM

The arithmetic-mean content of chromium, calculated to two digits, ranges from 0.011 percent for the samples in set 1 to 0.032 percent for the samples in set 3. These amounts appear to be only slightly greater than the average content of shale, which, according to Turekian and Wedepohl (1961, table 2), is 0.009 percent. Chromium has a strong positive correlation with vanadium in all four sample sets and with copper, nickel, and scandium in two sets each. These elements, as a group, are not assignable to a specific fraction of black shale, but it is considered significant that vanadium, copper, and nickel, at least, are probably associated with the organic-matter fraction.

COPPER

The median content of copper in the samples of black shale ranges from 0.005 percent in sets 1 and 4 to 0.015 percent in set 3. Except for set 3, the arithmetic-mean copper content is very close to the 0.0045 percent listed by Turekian and Wedepohl (1961, table 2) for average shale. Even the 0.02 percent copper at the 95-percentile level of samples in sets 3 and 4 does not come close to the 0.074 percent listed by Goldberg and Arrhenius (1958, table 9) as the average copper content of 22 pelagic sediment cores from the Pacific. Moreover, copper is concentrated in economically significant amounts in other black shale units, such as the Kupferschiefer of Germany; so it is worth noting here that copper is one of the few elements that tends to correlate positively with carbon. Furthermore, copper has a strong positive correlation with vanadium, chromium, and nickel in sets 1 and 2 and a moderately strong positive correlation with these same elements plus molybdenum in set 3. As a group, these elements are probably among the most closely associated with the organic-matter fraction of black shale.

GALLIUM

The total range in content of gallium in the 4 sets of samples of black shale is from 0.0005 percent at the 5-percentile level of samples in set 4 to 0.003 percent at the 95-percentile level of samples in sets 1, 3, and 4. For all sets the median and arithmetic-mean contents of gallium are very close to the 0.0019 percent averages listed by Turekian and Wedepohl (1961, table 2) for shale and by Goldberg and Arrhenius (1958, table 9) for pelagic sediments. Gallium has an unusually strong positive correlation with aluminum, sodium, titanium, magnesium, potassium, and zirconium and a strong negative correlation with carbon in set 3. Goldschmidt (1954, p. 319) has emphasized gallium's close geochemical relation with aluminum, for which it readily substitutes, especially in clay minerals. Thus it is not surprising that gallium shows a strong positive correlation with those elements expected in clay minerals, as well as with other elements, such as titanium and zirconium, which occur in other minerals of the detrital-mineral fraction of black shale. When analyses for silicon and aluminum are not available, gallium is probably one of the most characteristic elements of the detrital-mineral fraction.

LANTHANUM

The median content of lanthanum is either 0.003 or 0.005 percent in all sample sets, and the highest content at the 95-percentile level is only 0.007 percent in set 4. These amounts are less than the average content of lanthanum in shale or pelagic sediment, but they are nearly one order of magnitude greater than the 0.00051-percent average content that Zubovic, Stadnichenko, and Sheffey (1964, table 7) found in coal beds of the Eastern Interior region. Together, these observations suggest that lanthanum is more closely associated with the detrital-mineral fraction than with either the organic fraction or the chemically or biogenically precipitated fraction of the black shale.

MOLYBDENUM

The molybdenum content is among the most variable of all the elements detected in the samples of black shale. The median content ranges from 0.0005 percent in samples of set 4 to 0.03 percent in samples of set 3. The samples of set 3 contain more molybdenum at the 5-percentile level than do the samples of set 4 at the 95-percentile level. Even more significant, perhaps, is the fact that the median contents of molybdenum in the samples of sets 1 and 2, which are more nearly typical of shelf environment, are 3–10 times greater than the median content of molybdenum in samples of set 4 from the eugeosynclinal environment. Correlation data were calculated for molybdenum only for the samples in set 3, where it has a strong positive correlation with nickel, cobalt and carbon. Furthermore, if the median content of molybdenum and the median content of carbon are compared in sets 1–3, a direct variation between molybdenum and carbon is evident. Coal from the Eastern Interior coal region (Zubovic and others, 1964, table 7) contained an average of only 0.00043 percent molybdenum, yet the molybdenum-rich samples in set 3 range from shale to coal in carbon content. The difference in molybdenum content between coal and black shale is probably due to the differing availability of molybdenum in a fresh-water coal swamp and in brackish or marine water adjacent to the strand line.

NICKEL

The total range in content of nickel from less than 0.0005 percent at the 5-percentile level of samples in set 4 to 0.07 percent at the 95-percentile level of samples in set 3 is the same as for molybdenum; but the range in content of individual sample sets is less than for molybdenum. The 0.0015-percent median content of nickel in set 4 is about one-twentieth that of set 3 and one-fifth that of sets 1 and 2, providing another example where samples from the shelf environment are much richer than samples from the eugeosynclinal environment. Correlation data were calculated for the samples in sets 1–3. Nickel has a moderate to strong positive correlation with vanadium, copper, and chromium in all three sets and also it tends to show a positive correlation with carbon. It is not concentrated in fresh water, however, for Zubovic, Stadnichenko, and Sheffey (1964, table 7) found an average of only 0.0015 percent nickel in the coal beds of the Eastern Interior region.

LEAD

According to data compiled by Wedepohl (1964, p. 308–311), lead is less commonly enriched in black shale than vanadium, chromium, nickel, and molybdenum; yet there is a marked enrichment of lead in the Kupferschiefer (Wedepohl, 1964, p. 332–334). The median lead content of sample sets 1–4 ranges from 0.001 to 0.003 percent. This is close to the amount in average shale and in the Pierre Shale (Tourtelot and others, 1960, table 205.1). Although the median content of lead in set 3 is higher than for the other sets, it may be significant that the 0.007-percent lead at the 95-percentile level is the same for samples in sets 2 and 3, suggesting that none of these samples contain unusual amounts of lead. Correlation data for lead are available only for set 1, wherein lead has a strong positive correlation with potassium and a moderately strong positive correlation with sodium and scandium. As a group, these elements suggest that at low concentrations lead is associated with the detrital-mineral fraction of the black shale.

SCANDIUM

Although scandium was detected in most of the samples of black shale, it has a limited range in content from less than 0.0007 percent at the 5-percentile level of set 4 to 0.002 percent at the 95-percentile level of sets 1 and 2. The median contents of scandium indicate no enrichment of this element with respect to average shale and a somewhat lower content than in pelagic sediment and the Pierre Shale (table 1). Correlation data calculated for sets 1 and 3 show that scandium has a moderate to strong positive correlation with sodium, vanadium, titanium, chromium, potassium, magnesium, and gallium in both sets and with zirconium, aluminum, barium, beryllium, lanthanum, and manganese in at least one set. As a group, these elements are not diagnostic of a single fraction, but they include several elements of the detrital-mineral fraction, as well as a few that are at least indirectly associated with the organic-matter fraction.

STRONTIUM

The median content of strontium ranges from 0.01 percent in samples of sets 3 and 4 to 0.02 percent in samples of set 1. For the samples in sets 2 and 3 where the correlation data are most complete, strontium has a moderate to strong correlation with magnesium, barium, titanium, sodium, gallium, and zirconium. In set 3 alone, it has a positive correlation with aluminum, iron, and potassium and a negative correlation with carbon. If this were the only information, it would indicate that in the shelf environment, strontium, like barium, is primarily associated with the detrital-mineral fraction of the black shale. However, in set 1, strontium has a moderate positive correlation with copper, calcium, beryllium, chromium, and lanthanum, indicating that in the unweathered core samples some strontium may be associated with nondetrital minerals.

VANADIUM

Of all the metals reportedly enriched in black shales, vanadium is probably the most common, yet many black shales contain no more than the average 0.013 percent vanadium that Turekian and Wedepohl (1961, table 2) listed for shale. Thus, the median content of 0.015 to 0.02 percent vanadium of the samples in sets 1, 2, and 4 is scarcely more than in average shale. The 0.1-percent median vanadium content of samples in set 3 is fairly typical of metal-rich black shale. At the 95-percentile level the samples from sets 3 and 4 both contain 0.2 percent vanadium; the highest 5 percent of the samples from the eugeosynclinal environment contain, then, as much vanadium as the highest 5 percent of a metal-rich bed in the shelf environment. Vanadium has a strong positive correlation with chromium in all sets, with nickel in the first three, with copper in the first two, and with scandium in the first and third. Vanadium and molybdenum have a moderately strong positive correlation in set 3, the only set for which the data were calculated. In sets 1, 2, and 3, the median content of vanadium has a direct variation with the median content of carbon, yet there is no strong correlation between vanadium and carbon. Thus, vanadium probably has an indirect association with the organic-matter fraction of the samples of black shale.

YTTRIUM

The yttrium content of the samples of black shale ranges from 0.001 percent at the 5-percentile level of sets 2 and 4 to 0.007 percent at the 95-percentile level of sets 3 and 4. Although not enriched in the black shale, yttrium, nevertheless, tends to have a positive correlation in set 3 with elements such as nickel and molybdenum, both of which are enriched in, and probably associated with, the organic-matter fraction of the rock. Yttrium has an insignificant or negative correlation with aluminum, gallium, titanium, zirconium, and other elements that occur chiefly in the detrital-mineral fraction of black shale; therefore it is probably chiefly associated with the nondetrital faction.

ZINC

The lower limit of zinc detection by the 6-step spectrographic method is about 0.02 percent, which was too high to disclose zinc in more than about 75 percent of the black shale samples of sets 1, 2, and 4.

However, at the 95-percentile level, the content of zinc is relatively high in all sample sets, ranging from 0.05 percent in set 2 to 0.3 percent in set 3. Were analyses available for all samples, they would probably indicate zinc to be one of the more characteristic elements of metal-rich black shale. Visual inspection of the analyses indicates that a high content of zinc frequently corresponds with a high content of such elements as vanadium, molybdenum, chromium, and nickel. Zinc probably occurs commonly in a separate mineral form, such as sphalerite, and is not directly attached to or associated with the organic-matter fraction of the rock. In this respect, zinc probably behaves much as does iron in pyrite.

ZIRCONIUM

The median content of zirconium ranges from 0.003 percent in samples of set 3 to 0.007 percent in samples of sets 1 and 4. The median zirconium content varies among the four sets of samples in a manner similar to that of titanium. Zirconium, like titanium, varies directly with aluminum in the first three sets, but not in set 4. However, neither a mafic source nor biogenic precipitation provides a suitable explanation for the relatively high zirconium in set 4; so this problem is unresolved. A strong positive correlation between zirconium and titanium was found in the first three sample sets, and between zirconium and gallium, sodium, scandium, magnesium, potassium, aluminum, and strontium in set 3. Zirconium also has a strong negative correlation with calcium in set 1 and with carbon in sets 2 and 3. Zirconium is one of the most characteristic elements of the detrital-mineral fraction of black shale.

SUMMARY AND CONCLUSIONS

1. A comparison of the analyses of core samples (set 1) with a similar set of samples collected in outcrops (set 2) reveals a significant difference in concentration of several elements that may be attributed to their relative susceptibility to weathering, leaching, and removal from the outcrop and subsequent concentration either in pore water or as a separate mineral precipitate at depth. The elements involved probably are sodium, potassium, manganese, iron, and cobalt.
2. Many elements tend to occur chiefly in either the detrital-mineral fraction, the organic-matter fraction, or the chemically and biogenically precipitated fraction. An element may occur at low concentration in all fractions of one set and at high concentration in one or more fractions of another set. The following groupings are admittedly based on incomplete correlation data and on esti-

mates of the major mineral constituents of black shale, and so should be regarded as provisional.

A. Elements primarily associated with the detrital-mineral fraction of black shale include silicon, aluminum, magnesium, iron (in part), sodium, potassium, titanium, manganese, barium (in low concentration), gallium, lanthanum, lead, scandium, strontium (in low concentration) and zirconium.

B. Elements primarily associated with the organic-matter fraction of black shale include silver, beryllium, boron(?), cobalt, chromium, copper, molybdenum, nickel, vanadium, and yttrium(?). Most of these elements are probably fixed or sorbed by the decaying organic matter at or a short distance below, the sediment-water interface at the time of accumulation. Some of them may be released, mobilized, and recombined in new ways as a result of the chemical changes that take place in the organic matter after burial. For example, magnesium-bearing chlorophyl pigments in recent sediments give way with increasing depth to vanadium and perhaps nickel compounds (Abelson, 1963). This change occurs at low temperatures in less than a few thousand years. It seems possible that part of the vanadium may also combine with such clay minerals as illite to form a clay mineral analogous to roscoelite mica.

C. Elements primarily associated with the chemical or biogenically precipitated mineral fraction include iron (in part), calcium, boron(?), strontium (in part) yttrium(?), and zinc. In addition, silicon in the eugeosynclinal shales is mostly chemically or biogenically precipitated. Thus, elements included in this group comprise the major mineral constituents of siliceous and calcareous shells. Strontium occurs in minor amounts in calcareous shells, and the elements iron, zinc, and barium form discrete sulfide or sulfate minerals associated with or replacements of microorganisms and fecal pellets. Boron and yttrium are included in this group, although without adequate criteria to exclude the possibility that they may also be associated with the organic-matter fraction.

3. Remarkably similar suits of minor elements are concentrated at the 95-percentile level of samples from both the shelf and eugeosynclinal environments. These elements are mainly those associated with the organic-matter fraction of the black shale or are biogenically precipitated; therefore, they may be regarded as characteristic of metal-rich black shale. They are listed here in approxi-

mately decreasing frequency of occurrence: vanadium, zinc, chromium, nickel, silver, barium, molybdenum, cobalt, yttrium, boron, and copper. Significant differences between the samples from the shelf environment and the samples from the eugeosynclinal environment are apparent, however. Molybdenum and nickel are relatively much more concentrated in the samples from the shelf environment, and barium is relatively much more concentrated in the samples from the eugeosynclinal environment.

4. Any future consideration of black shale as a potential commercial source of the contained metals would need to evaluate the following geologic factors.
   - A. The Pennsylvanian black shale beds in the Eastern Interior coal province are thin and comprise only a small part of the sedimentary sequence, but individual beds are flat lying and because they are locally removed during strip coal-mining operations, the cost of recovery would thereby be reduced.
   - B. The Ordovician and Silurian graptolitic black shale beds in the western eugeosynclinal region are locally thick, but the enclosing strata are almost everywhere so intensely deformed that systematic prospecting according to their stratigraphic position would pose difficult problems in correlation.

REFERENCES CITED

Abelson, P. H., 1963, Paleobiochemistry: Internat. Cong. Biochemistry, 5th, Moscow 1961, Proc., v. 3, p. 52–68.

Bradley, W. H., 1931, Origin and microfossils of the oil shale of the Green River formation of Colorado and Utah: U.S. Geol. Survey Prof. Paper 168, 58 p.

Bramlette, M. N., 1946, The Monterey formation of California and the origin of its siliceous rocks: U.S. Geol. Survey Prof. Paper 212, 57 p. [1947].

Conant, L. C., and Swanson, V. E., 1961, Chattanooga shale and related rocks of central Tennessee and nearby areas: U.S. Geol. Survey Prof. Paper 357, 91 p.

Cressman, E. R., 1962, Nondetrital siliceous sediments, *in* Data of geochemistry [6th ed.]: U.S. Geol. Survey Prof. Paper 440–T, p. T1–T23.

Davidson, D. F., and Lakin, H. W., 1961, Metal content of some black shales of the Western United States, *in* Short papers in the geologic and hydrologic sciences: U.S. Geol. Survey Prof. Paper 424–C, p. C329–331.

——— 1962, Metal content of some black shales of the Western Conterminous United States, *in* Short papers in geology and hydrology: U.S. Geol. Survey Prof. Paper 450–C, p. C74.

Davies, O. L., 1954, Statistical methods in research and production: New York, Hafner Publishing Co., 304 p.

Degens, E. T., Williams, E. G., and Keith, M. L., 1958, Application of geochemical criteria, Pt. 2 *of* Environmental studies of carboniferous sediments: Am. Assoc. Petroleum Geologists Bull., v. 42, p. 981–997.

Goldberg, E. D., and Arrhenius, G. O. S., 1958, Chemistry of Pacific pelagic sediments; Geochim. et Cosmochim. Acta, v. 13, p. 153–212.

Goldschmidt, V. M., 1954, Geochemistry: Oxford, England, Clarendon Press, 730 p.

Gluskoter, H. J., 1965, Composition of ground water associated with coal in Illinois and Indiana: Econ. Geology, v. 60, p. 614–620.

Gluskoter, H. J., and Rees, O. W., 1964, Chlorine in Illinois coal: Illinois Geol. Survey Circ. 372, 23 p.

Kay, Marshall, 1947, Geosynclinal nomenclature and the craton: Am. Assoc. Petroleum Geologists Bull., v. 31, p. 1289–1293.

Ketner, K. B., and Smith, J. F., Jr., 1963, Composition and origin of siliceous mudstones of the Carlin and Pine Valley quadrangles, Nevada, *in* Short papers in geology and hydrology: U.S. Geol. Survey Prof. Paper 475–B, p. B45–B47.

Krauskopf, K. B., 1955, Sedimentary deposits of rare metals, *in* Pt. 1 *of* Bateman, A. M., ed., Economic geology (50th anniversary volume, 1905–1955): Urbana, Ill., Econ. Geology Publishing Co., p. 411–463.

Myers, A. T., Havens, R. G., and Dunton, P. J., 1961, A spectrochemical method for the semiquantitative analysis of rocks, minerals, and ores: U.S. Geol. Survey Bull. 1084–I, p. 207–229.

Roberts, R. J., Hotz, P. E., Gilluly, James, and Ferguson, H. G., 1958, Paleozoic rocks of north-central Nevada: Am. Assoc. Petroleum Geologists Bull., v. 42, no. 12, p. 2813–2857.

Ross, R. J., Jr., 1961, Distribution of Ordovician graptolites in eugeosynclinal facies in western North America and its paleogeographic implications: Am. Assoc. Petroleum Geologists Bull., v. 45, no. 3, p. 330–341.

Ross, R. J., Jr., and Berry, W. B. N., 1963, Ordovician graptolites of the Basin Ranges in California, Nevada, Utah, and Idaho: U.S. Geol. Survey Bull. 1134, 177 p.

Ruedemann, Rudolf, 1934, Paleozoic plankton of North America: Geol. Soc. America Mem. 2, 141 p.

Spackman, William, Scholl, D. W., and Taft, W. H., 1964, Environments of coal formation in southern Florida, *in* Geol. Soc. America Guidebook, Field Guidebook to Environments of Coal Formation in Southern Florida, 1964: 65 p.

Stadnichenko, Taisia, Zubovic, Peter, and Sheffey, N. B., 1961, Beryllium content of American coals: U.S. Geol. Survey Bull. 1084–K, p. 253–295.

Swanson, V. E., 1961, Geology and geochemistry of uranium in marine black shales, a review: U.S. Geol. Survey Prof. Paper 356–C, p. 67–112.

Tourtelot, H. A., Huffman, Claude, Jr., and Rader, L. F., 1964, Cadmium in samples of the Pierre Shale and some equivalent stratigraphic units, Great Plains region, *in* Short papers in geology and hydrology: U.S. Geol. Survey Prof. Paper 475–D, p. D73–D78.

Tourtelot, H. A., Schultz, L. G., and Gill, J. R., 1960, Stratigraphic variations in mineralogy and chemical composition of the Pierre shale in South Dakota and adjacent parts of North Dakota, Nebraska, Wyoming, and Montana, *in* Short papers in the geological sciences: U.S. Geol. Survey Prof. Paper 400–B, p. B447–B452.

Turekian, K. K., and Wedepohl, K. H., 1961, Distribution of the elements in some major units of the Earth's crust: Geol. Soc. America Bull., v. 72, p. 175–192.

Vine, J. D., 1965, Spectrographic analysis of Paleozoic black shale samples: U.S. Geol. Survey open-file report, 5 p.

Vinogradov, A. P., 1953, The elementary chemical composition of marine organisms: Sears Found. Marine Research Mem. 2, 647 p.

Wedepohl, K. H., 1964, Untersuchungen am Kupferschiefer in Nordwestdeutschland. Ein Beitrag zur Deutung der Genese bituminöser Sediments: Geochim. et Cosmochim. Acta. v. 28, p. 305–364.

Zangerl, Rainer, and Richardson, E. S., Jr., 1963, The paleoecological history of two Pennsylvanian black shales: Chicago Nat. History Mus., Fieldiana. Geology Mem., v. 4, 352 p.

Zubovic, Peter, Stadnichenko, Taisia, and Sheffey, N. B., 1964, Distribution of minor elements in coal beds of the Eastern Interior region: U.S. Geol. Survey Bull. 1117–B, p. B1–B41.

U.S. GOVERNMENT PRINTING OFFICE:1966