Geochemical Investigations of Some Black Shales And Associated Rocks

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GEOLOGICAL SURVEY BULLETIN 1314-A

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By JAMES D. VINE *and* ELIZABETH B. TOURTELOT

CONTRIBUTIONS TO GEOCHEMISTRY

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The content and association of minor
elements in some black shales
deposited in various types of
geologic environments

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CONTENTS

ILLUSTRATIONS

TABLES

CONTRIBUTIONS TO GEOCHEMISTRY

GEOCHEMICAL INVESTIGATIONS OF SOME BLACK SHALES AND ASSOCIATED ROCKS

By James D. Vine and Elizabeth B. Tourtelot

ABSTRACT

The distribution of chemical elements in nine sets of samples of black shale and associated rocks was examined statistically to learn which elements accompany the major rock-forming constituents, such as detrital minerals, carbonate minerals, and organic matter. The rocks sampled range in age from Precambrian to Eocene and in environment of deposition from eugeosynclinal to carbonate lake. These and other differences in the samples result in varied minor-element distribution patterns.

Elements associated primarily with the detrital fraction of these sets include the major elements silicon, aluminum, and potassium and the minor elements titanium, boron, gallium, scandium, and zirconium. In any individual set, these elements generally show a small range in abundance. Those associated with the carbonate fraction show much greater ranges in abundance. Calcium and strontium together are associated with the carbonate fraction in eight sample sets; manganese is associated with the carbonate fraction in the Tacket Formation of Jewett, Emery, and Hatcher (1965), a black shale of Kansas, the Nonesuch Shale of Michigan and Wisconsin, and the Minnelusa Formation of South Dakota and Wyoming; and magnesium is associated with the carbonate fraction in the Minnelusa Formation and in the Tyler Formation of central Montana.

Minor elements associated with the organic matter in these sets tend to show a greater range of values within individual sets and a greater range of median values between sets than do those elements in the detrital fraction; their associations also tend to differ between sets. Elements associated with organic matter in the Tacket Formation of Kansas include chromium, molybdenum, silver, vanadium, and yttrium; those in the Heath Formation of central Montana include molybdenum, silver, vanadium, zinc, and possibly copper; and those in the Minnelusa Formation of South Dakota and Wyoming include lead, molybdenum, nickel, silver, and probably copper. The epigenetic enrichment of copper and silver in the Nonesuch Shale of Michigan and Wisconsin shows no association with major rock constituents, which indicates that the distribution was not lithologically controlled. The more mobile elements, chrom-

ium, cobalt, copper, lead, molybdenum, nickel, silver, uranium, vanadium, yttrium and zinc, should be given primary consideration in any search for "metal-rich" black-shale deposits, especially in the Heath Formation of central Montana, the Minnelusa Formation of South Dakota and Wyoming, and the Tacket Formation from the Pleasanton Group of Late Pennsylvanian age in Kansas.

INTRODUCTION

This is the fourth in a series of reports that discuss the chemical distribution of elements in black shale and associated rocks. Previous reports describe the distribution of major and minor elements (1) in shelf and eugeosynclinal black shales, grouped into sample sets 1–4 (Vine, 1966), (2) in black shales deposited in hypersaline, miogeosynclinal, and shelf environments, sample sets 5–8 (Vine, 1969); and (3) in black shales deposited in intracratonic trough and platform types of environments, sample sets 9–12 (Vine and others, 1969). This report discusses the geochemistry of nine more sample sets (13–21) of black shale and associated rocks deposited in diverse environments. The localities where the sample sets were collected are shown in Figure 1, and descriptions of the sets are summarized in table 1.

TABLE 1.—*Summary description of sample sets 13–21*

Set	Stratigraphic name	Age	State	Number of samples	Type of sample	Environment of deposition
13	Collier Shale, Mazarn Shale, Blakely Sandstone, Womble Shale, Bigfork Chert, and Polk Creek Shale.	Early Paleozoic	Arkansas	32	Outcrop	Eugeosynclinal.
14	Tacket Formation of Jewett, Emery, and Hatcher (1965).	Pennsylvanian	Kansas	19	do	Epicontinental shelf.
15	Heath and Tyler Formations and equivalents.	Mississippian and Pennsylvanian.	Montana and Idaho.	28	do	Intracratonic basin.
16	Nonesuch Shale	Precambrian	Michigan and Wisconsin.	20	Core	Near-shore shelf
17	Green River Formation	Eocene	Colorado	29	Quarry	Carbonate lake.
18	Sharon Springs Member of the Pierre Shale and upper part of the Niobrara Formation.	Cretaceous	Kansas	59	Cuttings	Epicontinental shelf.
19	Eagle Ford Shale and Buda Limestone.	do	Texas	28	Core	Do.
20	Unnamed equivalent to Health (?) Formation.	Mississippian	Wyoming	14	Outcrop	Intracratonic basin.
21	Minnelusa Formation (lower part).	Pennsylvanian	South Dakota and Wyoming.	22	do	Epicontinental shelf.

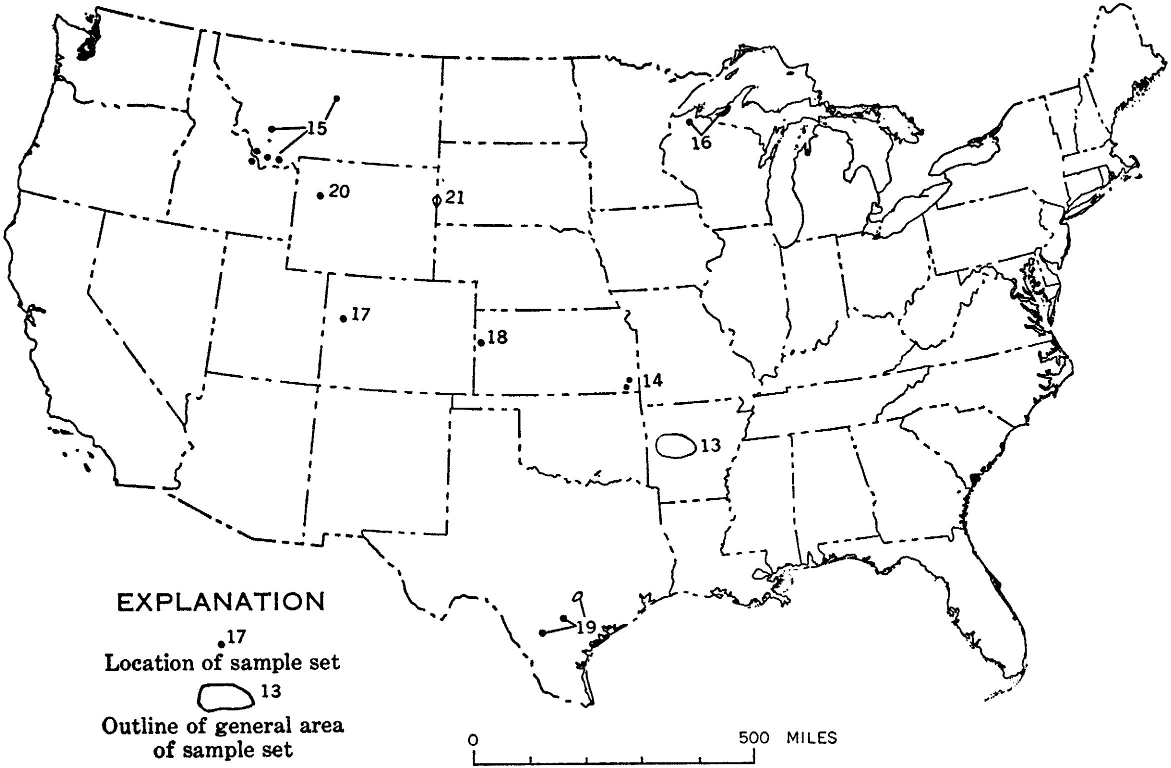

FIGURE 1.—Localities of black-shale sample sets 13–21.

The term "black shale" as used here and in our preceding reports includes a variety of dark-colored fine-grained sedimentary rocks deposited in marine or saline lake environments and composed of a mixture of detrital minerals, chemically or biologically precipitated minerals, and organic matter. The organic matter is commonly a minor but characteristic feature of these rocks, whose end members include claystone, siltstone, limestone, dolomite, anhydrite, chert, phosphorite, and coal. The fine-grained texture of these rocks makes definition of precise boundaries between the various types impractical, especially for field classification. Even with refined laboratory techniques, assignment of a specific name to each rock becomes rather arbitrary. Many of the sample sets include a wide variety of rock types, all included under the general term "black shale."

ACKNOWLEDGMENTS

The collection of sample sets 13–21 was greatly facilitated by the cooperation and helpful suggestions of colleagues familiar with the stratigraphy of specific areas. Philip J. Sterling and Charles G. Stone, geologists with the Arkansas Geological Commission, aided in the collection of the lower Paleozoic black shales from the Ouachita Mountains in Arkansas (set 13). Samples of the Heath and Tyler Formations in Montana (set 15) were collected in the company of Edwin K. Maughan of the U.S. Geological Survey, who was studying the stratigraphy of these rocks at that time. Core samples of the Nonesuch Shale (set 16) were collected by Walter S. White and the late James C. Wright of the Geological Survey for their studies of copper deposits in Michigan and were kindly provided to the writers for inclusion in this study. The samples of the Green River oil shale (set 17) were collected by James D. Vine and James G. Palacas of the Geological Survey from a quarry on an unpatented oil-shale claim held by John Savage of Rifle, Colo., with his permission. Drill cuttings of the Sharon Springs Member of the Pierre Shale and the upper part of the Niobrara Formation were provided by James R. Gill of the Geological Survey with the cooperation of the Kansas State Geological Survey. Core samples of the Upper Cretaceous shales of Texas (set 19) were provided by D. Hoye Eargle of the Geological Survey. J. D. Love of the Geological Survey suggested the section of the Upper Mississippian shales (set 20) in the Hoback Canyon, of western Wyoming. Computer programming and assistance were provided by R. N. Eicher, F. B. Sower, G. I. Selner, and George Van Trump, Jr.

DESCRIPTION OF SAMPLE SETS

LOWER PALEOZOIC SHALES OF ARKANSAS

Set 13 consists of 32 samples of black shale and siliceous shale collected from natural outcrops and roadcuts in the central Ouachita Mountains in parts of Pulaski, Saline, Garland, and Montgomery Counties, Ark. Samples were collected from the Collier Shale of Cambrian age and the Mazarn Shale, Blakely Sandstone, Womble Shale, Bigfork Chert, and Polk Creek Shale, all of Ordovician age, as shown in table 2. These rocks range in lithology from clay shale to siliceous

TABLE 2.—*Stratigraphic sequence of formations from which 32 samples of lower Paleozoic shales of Arkansas were collected*

[Description modified from Goldstein and Hendricks (1953)]

System	Formation	Thickness (feet)	Description	Number of samples
Ordovician	Polk Creek Shale	100–200	Shale, black, graphitic; contains graptolites.	4
	Bigfork Chert	500–700	Chert, hard, gray to black; black shale; dark-colored fossiliferous cherty limestone.	4
	Womble Shale	250–1, 000	Shale, black to green; contains thin layers of limestone and argillaceous sandstone.	13
	Blakely Sandstone	0–500	Sandstone, gray, quartzitic; some calcareous sandstone and minor amounts of black and green clay shale.	3
	—Unconformity—			
	Mazarn Shale	1, 000±	Shale, black and green, banded. Thin layers of gray sandstone, and in some areas thin lenses of bluish-black limestone.	7
Ordovician(?)	Crystal Mountain Sandstone	500–850	Sandstone, massive, light-gray, calcareous to quartzitic.	0
	-Unconformity-			
Cambrian	Collier Shale	200–500	Shale, black, graphitic; and dark-colored siliceous limestone. Some dense black chert.	1

shale and chert. All contain disseminated organic matter, and some are graphitic. The samples from the Polk Creek Shale and at least one sample from the Womble Shale contain graptolites. Bedding is commonly at a slight angle to the cleavage which formed during regional metamorphism. Metamorphic minerals, however, are not characteristic of these rocks. The Bigfork Chert was regarded by Goldstein and Hendricks (1953) as the oldest of the siliceous rocks characteristic of the Ouachita facies, but probably all these formations were deposited in or near the principal downwarp of the Ouachita geosyncline. Although the samples appear similar in hand specimen, this similarity may be due more to the metamorphic texture and structure of the rocks than to their environments of deposition.

BLACK SHALE FROM THE TACKET FORMATION OF JEWETT, EMERY, AND HATCHER (1965) OF KANSAS

Set 14 consists of 19 samples of black shale from the Tacket Formation in the Pleasanton Group of Pennsylvanian age in Labette and Neosho Counties, Kans. In this area, the Tacket Formation occurs at the top of the Pleasanton Group; it is overlain by the Hertha Limestone, which forms the base of the Kansas City Group, and is underlain by the Checkerboard Limestone of the Pleasanton Group. The Pleasanton Group forms the base of the Missouri Series, which lies unconformably on the Marmaton Group of the Des Moines Series. In contrast to the many thin black-shale units that overlie coal beds in the Pennsylvanian System, black shale in the Tacket Formation is associated primarily with limestone beds. It is a marine unit that was probably deposited in a shallow-water shelf not far offshore. In the area where the Tacket black shale was sampled, it is estimated to be at least 20 feet thick. Jewett, Emery, and Hatcher (1965, p. 8) reported that it is 40 feet thick near Parsons and ranges in thickness from 15 to 60 feet in southeastern Kansas. Natural exposures of this unit are very poor, but relatively fresh samples were collected from roadcuts. The 19 samples in set 14 represent channel samples from three roadcuts that include 27 feet of strata. The amount of overlap or duplication of strata in the three sections could not be determined because of limited outcrops.

BLACK SHALE FROM THE HEATH AND TYLER FORMATIONS

Set 15 consists of 28 samples collected from the Heath Formation of Mississippian age and the Tyler Formation of Pennsylvanian age in Montana and Idaho. The two formations were differentiated and described by Maughan and Roberts (1967, p. B7–B14). Near the Big Snowy Mountains in central Montana, these two black-shale units are locally superimposed and difficult to distinguish, although they are separated by an unconformity. In general, the black shales of the Heath Formation are associated with petroliferous limestone and gypsum, whereas those in the Tyler are associated with red shale and with sandstone beds that yield petroleum in several central Montana oil fields.

Of the 28 samples in this set, 18 were collected from outcrops in central Montana, chiefly from the flanks of the Big Snowy Range in Golden Valley and Fergus Counties. The remaining 10 were collected from outcrops of black shale of the Heath(?) Formation, in approximately the same stratigraphic position, much farther west, in Beaverhead County, Mont., and Lemhi County, Idaho. The black shale in these 10 samples was tentatively regarded by E. K. Maughan (oral commun., 1965) as correlative with the Heath Formation, although the correlation is not well documented. In the interpretation of the analytical data for these samples, four subsets were considered: 15A, 10 samples of the Heath(?) Formation from western Montana and adjacent parts of Idaho; 15B, 18 samples of the Heath and Tyler Formations from central Montana; 15C, 10 samples of the Heath Formation from central Montana; 15D, seven samples of the Tyler Formation from central Montana.

One sample of the Heath Formation from Central Montana was deleted from subset 15C because it contained an unusually large amount of organic carbon, which suggested that it is more closely related to coal than to black shale, and because the high carbon and low minor-element content seemed likely to bias the statistical correlations unduly.

NONESUCH SHALE OF MICHIGAN AND WISCONSIN

Set 16 consists of 20 drill-core samples from the "striped bed" of the Nonesuch Shale of Precambrian age in Michigan. The striped bed is a zone of interlaminated carbonaceous claystone and subordinate amounts of impure silty limestone 6–8 inches thick, which lies about 30 feet above the main zone of copper mineralization in the White Pine copper deposit, Ontonagon County, Mich. (White and Wright, 1954, figs. 5 and 6). According to James C. Wright (written commun., 1965), the striped bed is relatively uniform over the entire district and is the most organic rich, most limy, and most pyritiferous bed in the 50-foot-thick cupriferous sequence. He described the silt fraction as consisting chiefly of quartz and detritus from mafic lavas in a clay matrix that is altered chiefly to chlorite. Of the 20 samples in this set, 16 represent a 7-mile-long strip approximately normal to the presumed shoreline at White Pine and include two mineralized samples with visible chalcocite. Four samples represent other areas 15 to 70 miles from White Pine in western Michigan, and one sample came from an area 87 miles from White Pine, in Bayfield County, Wis.

OIL SHALE FROM THE GREEN RIVER FORMATION OF COLORADO

Set 17 consists of 29 samples of oil shale from the Green River Formation of Eocene age in the Piceance Creek Basin, Garfield County, Colo. Of these samples, 26 are large block samples collected from a quarry near Debeque, Colo., and three are outcrop samples collected from Cascade Canyon, about 14 miles north of Debeque. The quarry samples were collected from a stratigraphic interval of about 18 feet that includes the Mahogany marker bed about 3 feet below the top. The Mahogany marker bed is a distinctive bed of analcime about half a foot thick that is useful as a stratigraphic marker for the rich oil-shale zone known locally as the Mahogany ledge (Waldron and others, 1951). The Cascade Canyon samples were collected from approximately the same stratigraphic interval. In contrast to the depositional history of most of the other sample sets included in this study, the oil shale of the Green River Formation was deposited in a sodium carbonate-rich lake rather than in a marine environment. Moreover, the organic matter in these samples is a solid material called kerogen, which is largely convertible to oil on heating in a retort. The mineral matter is a fine-grained mixture of authigenic and detrital minerals, including quartz, dolomite, calcite, analcime, mica, and plagioclase, and minor amounts of pyrrhotite or pyrite. The rocks are characteristically laminated with an alternation of organic-rich and relatively organic-poor laminae.

UPPER CRETACEOUS SHALES OF KANSAS

Set 18 consists of 57 samples of drill cuttings collected at 5-foot intervals from the Sharon Springs Member of the Pierre Shale and the upper part of the underlying Niobrara Formation, both of Late Cretaceous age. These samples were collected in connection with a study of the type area of the Sharon Springs Member by J. R. Gill, W. A. Cobban, and L. G. Schultz (unpub. data) and include 44 samples from the Sharon Springs Member, ranging in depth from 0 to 220 feet, and 13 from the upper part of the Niobrara Formation, ranging in depth from 220 to 300 feet. Two samples from a nearby outcrop are included in set 18 for a total of 59. One of these surface samples is a phosphatic nodule; the other is a dark-gray shale. Gill, Cobban, and Schultz recognize three subdivisions of the Sharon Springs Member: a lower unit of soft dark shale 115 thick thick, a middle unit of hard organic-rich shale 90 feet thick, and an upper unit of hard slightly phosphatic shale about 10 feet thick. The entire member is marine and contains abundant vertebrate remains but relatively few mollusks. The shales are medium gray to black and are composed of clay minerals and quartz and minor amounts of pyrite, dolomite, and organic matter. The Sharon Springs Member contains many thin bentonite beds, rarely as much as 1 foot thick, and numerous carbonate rich concretions. The lower part of the member is transitional with the underlying Niobrara Formation, which is characterized by a greater content of dispersed carbonate minerals. In general, the samples consist of fine-grained detrital sediment with variable amounts of carbonate, either bedded or in the form of concretions, and thin interbeds of altered volcanic ash.

UPPER CRETACEOUS SHALES OF TEXAS

Set 19 consists of 28 core samples of the Eagle Ford Shale and Buda Limestone of Late Cretaceous age in southern Texas. The Eagle Ford Shale forms a consistently radioactive zone in the Upper Cretaceous formations that underlie the Texas coastal plain and is commonly used as a stratigraphic marker in subsurface logs. The core samples in set 19 are from cores collected by D. Hoye Eargle for his study of the radioactivity and uranium content of these rocks (Eargle and Hollingsworth, 1957). The samples for this study were selected from five drill cores from Guadalupe, Caldwell, Karnes, and La Salle Counties, Tex. Twenty-six samples are from the Eagle Ford and two are from the underlying Buda. They range in lithology from dark-gray laminated clay to limestone. Abundant shell fragments are present in the Buda Limestone samples.

UPPER MISSISSIPPIAN SHALES OF WESTERN WYOMING

Set 20 consists of 14 samples of dark-gray to black shale collected from an interval of shale and limestone nearly 70 feet thick that is exposed on the north side and about 1 mile east of the mouth of Hoback Canyon, Teton County, Wyo. The sampled interval lies directly above a unit identified as the Darwin Sandstone Member of the Amsden Formation in a stratigraphic section described by Wanless, Belknap, and Foster (1955, p. 22–29). The stratigraphic identity of the rocks is in question, however, for Sando and Dutro (1960, p. 125) reported fossils of Late Mississippian age in limestone beds interbedded with and overlying the dark shales, which indicates that these rocks may be approximately equivalent to the Heath Formation of the Big Snowy Group in Montana.

The rocks sampled range in lithology from soft black claystone to dark-gray fissile shale and carbonaceous brownish-gray siltstone. Limestone and sandstone beds in the sequence were not sampled, nor were any of the lower shales found to be interbedded with gypsum. The samples are weathered and include various secondary minerals associated with the weathering of carbonaceous rocks, including jarosite and limonite.

ASHED SHALE FROM THE MINNELUSA FORMATION OF SOUTH DAKOTA AND WYOMING

Set 21 consists of 22 ashed samples of black shale and associated rocks from the lower part of the Minnelusa Formation of Pennsylvanian age. The samples were collected from outcrops in the southern Black Hills of western South Dakota and eastern Wyoming. Black silty shale and carbonaceous limestone occur in thin beds 0.5–2 feet thick interbedded with sandstone. Some of the shale beds approximate an impure canneloid coal in composition (J. M. Schopf, written commun., 1951) and show as much as one-third loss on ignition. These black shales are commonly used as stratigraphic markers on subsurface well logs because of their persistently high radioactivity. Outcrops of the black shales are few, but they occur in several canyons in the southern Black Hills, including Hot Brook Canyon, about 2 miles northwest of Hot Springs, S. Dak., and in Redbird Canyon, about 10 miles southeast of Newcastle, Wyo. Of the 22 samples in this set, 16 were collected from three closely spaced outcrop areas in Hot Brook Canyon: four from Redbird Canyon, one from Frannie Peak about 4 miles west of Redbird Canyon, and one from Boles Canyon about 9 miles east of Newcastle. The samples were ashed because of their high loss on ignition, thereby reducing the matrix problems that sometimes arise during spectrographic analysis of organic-rich samples that are not ashed. Concentrations of uranium and other metals in these black shales have been reported previously by J.D. Love (written commun., 1951), by Duncan (1953), and by Davidson and Lakin (1961).

ANALYTICAL METHODS

The analyses on which this report is based were made primarily by the routine six-step emission spectrographic method, which is similar to the three-step method described by Myers, Havens, and Dunton (1961). Results for the six-step method are identified with geometric intervals whose boundaries are 1.2, 0.83, 0.56, 0.38, 0.26, 0.18, 0.12, 0.083 and so forth, and are arbitrarily reported as the geometric midpoints of these intervals, using the numbers 1, 0.7, 0.5, 0.3, 0.2, 0.15, 0.1, 0.07, and so forth. The precision of a reported value is approximately plus or minus one interval at 68-percent confidence, or two intervals at 95-percent confidence.

Quantitative spectrography was used in the analysis for minor elements in sample set 16. The results have an overall accuracy of ±15 percent except near the limits of detection, where only one digit is reported. The elements near the lower limits of detection in this set include boron, gallium, lead, silver, yttrium, and ytterbium. Chemical methods were used to determine arsenic, selenium, and sulfur in set 16 and selenium in set 20. Zinc in set 16 and nickel, chromium, and iron in set 17 were determined by atomic-absorption analysis. A beta-gamma scaler was used to determine equivalent uranium in sets 18, 19, and 20.

Separate analyses were made for total carbon and carbon in carbonate minerals following the methods outlined by Tourtelot, Huffman, and Rader (1964, p. D74). Organic carbon was calculated by computing the difference between total carbon and mineral carbon. The lower limit of detection for total and mineral carbon is about 0.02 percent. The approximate precision of the method is about 0.02 percent for samples containing small amounts of carbon. However, the precision may be reduced by a factor of about 10 for samples containing large amounts of carbon because of the necessity of using a smaller quantity of the sample in order to keep the evolved gas within the volume limits of the equipment. When subtracting mineral carbon from total carbon to determine organic carbon content, it is customary to show one less significant figure than is used for total or mineral carbon. Analyses for oil, gas, water, and ash were made on samples of oil shale in set 17 using the modified Fischer retort as described by Stanfield and Frost (1949).

STATISTICAL METHODS

Statistical analyses of the nine sets of chemical data were conducted by methods similar to those described in previous reports (Vine, 1966, 1969; Vine and others, 1969). The 5th, 25th, 50th, 75th, and 95th percentiles and the arithmetic and geometric means were calculated for each constituent. The coefficient of correlation was calculated for each pair of constituents after first making a log transformation to place the data in a more nearly normal frequency distribution. Because concentrations of some constituents in some samples were outside the limits of detection by the analytical methods used, some determinations by the analysts were reported as "greater than" or "less than" specified concentrations. These determinations were considered as given in the derivation of median and percentile concentrations and, where these were few in number relative to the determined concentrations, they were replaced by fairly arbitrary values in estimating log correlation coefficients. The only justification for this procedure is that the computed coefficients are not highly sensitive to the arbitrary values used.

Principal-component analysis of each correlation matrix was used to identify groups of associated elements, after substitution for indeterminate values. This technique, described by Harman (1960), has recently been applied to a variety of geologic problems, some of which were described by Imbrie and VanAndel (1964), Griffiths (1966), and Miesch, Chao, and Cuttitta (1966). The method involves constructing radial vectors for each constituent so that the cosine of the angle between any two vectors is equal to the coefficient of correlation. For two-factor analysis, the vectors are then rotated and projected onto a two-dimensional diagram on which axes that will best represent most of the data have been selected. Figure 2*A* shows an example of a vector diagram with a strong positive correlation between aluminum and titanium (the cosine of the small angle between these two vectors approaches +1). A strong negative correlation is shown between aluminum and mineral carbon (the cosine of the nearly 180° angle between these two vectors approaches −1). Little or no correlation is shown between aluminum and organic carbon (the cosine of the nearly 90° angle approaches 0). The vector for sodium is short, indicating that it is poorly represented in this two-dimensional diagram and probably has a low correlation with the other elements in the diagram. The vector for molybdenum shows a moderately strong correlation with organic carbon. Thus, when two elements plot close to each other near the unit radius a strong correlation is indicated, but when they have short vectors and plot close to each other near the center of the circle they may or may not correlate well.

In some sets where the vectors are short because they are poorly represented in two dimensions (the eigenvalues of the correlation matrices and communalities of variables on rotation indicate the probability of more than two principal components), it was desirable to use three-factor analysis to search for additional element groups. The interpretations from such three-dimensional diagrams are described but not illustrated. Even the three-component analysis sometimes fails to identify element groupings clearly where the coefficients of correlation have low levels of significance.

In the diagrams (figs. 3–11) illustrating the two-factor analyses of data for sample sets 13–21, the radial lines have been omitted for clarity, and only the position of the constituent within a circle of unit radius is shown. Figure 2*B* shows such an example, derived from the

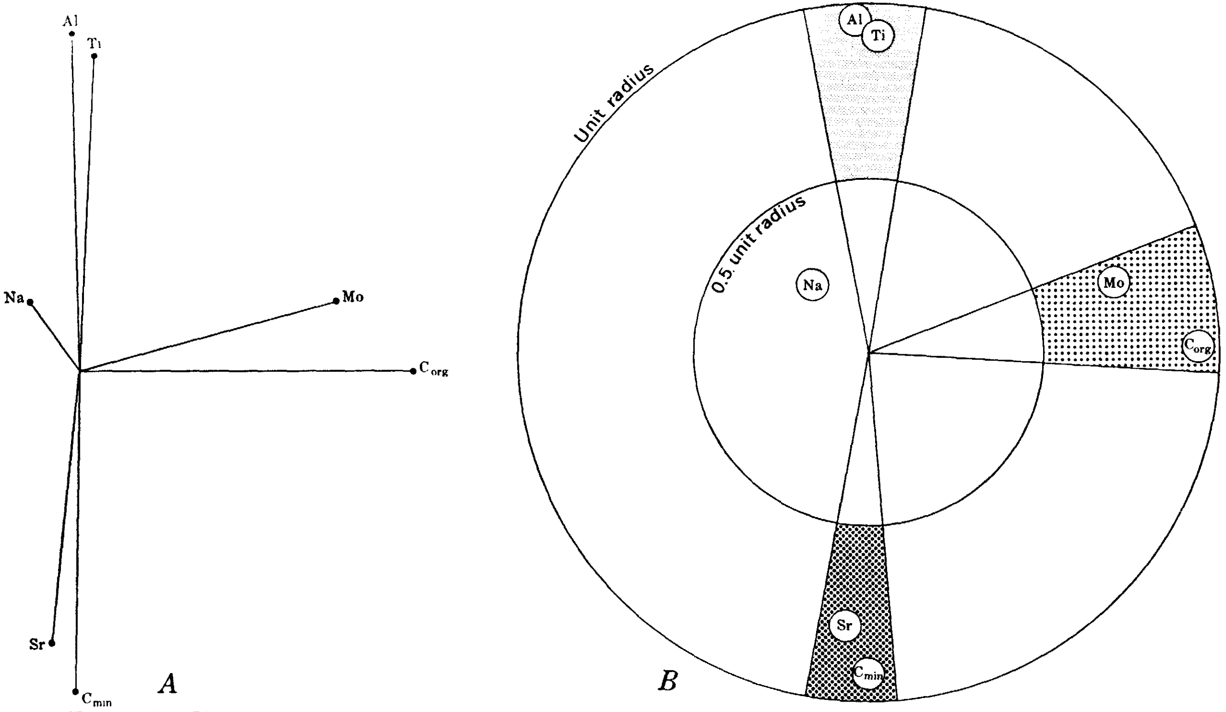

FIGURE 2.—Explanatory vector diagrams. *A*, Typical rotated two-dimensional vector diagram showing a direct relation between aluminum and titanium, an inverse relation between aluminum and mineral carbon (C_{min}), no relation between aluminum and organic carbon (C_{org}), and a poor representation of sodium. *B*, Diagram *A* without the vectors drawn but with the addition of a circle of unit radius and stippled segments to suggest geochemical groupings of constituents.

vector diagram in figure 2*A*. The stippled segments of each diagram were added to suggest possible geochemical groupings of the elements. The resultant groupings may reflect different physical and chemical processes during the depositional and postdepositional history of each rock unit.

The fact that the correlation data are part of a closed array complicates interpretation of the element groups. This problem, described by Chayes (1960), may be thought of as one of dilution. As an example, consider a set of samples that includes the major rock constituents, quartz, carbonates, and clay. Each of the end members, which are represented by the corresponding three lithologies, siltstone, limestone, and shale, contains only one of the three constituents; thus a built-in negative correlation must exist between at least two of the principal constituents. Also, a corresponding positive correlation may be imposed on a certain pair of minor elements that vary with a major constituent even where there is little geochemical association between the minor-element pair. The process of dilution, therefore, affects the magnitude of some of the correlations that appear on the vector diagrams, but the problem is basically one of interpretation.

DISTRIBUTION OF ELEMENTS IN THE SAMPLE SETS

The following sections describe the abundance and distribution of elements detected in individual sample sets. Table 3 lists percentile and mean values calculated from the spectrographic and chemical analyses of the samples. Data from table 3 are used in the following discussions of element abundances in the individual sets, and the results of factor analysis (fig. 3–11) form the basis for interpretation of element associations within the sets. Statements about "average" or "normal" element content imply that the content is close to the median value calculated from the median contents of sets 1–20 (Vine, 1966, 1969; Vine and others, 1969). (Set 21 is not included in the calculations because the samples were ashed prior to analysis.) The median values of most of the reported elements do not differ greatly from those of the average element contents in shale as listed by Turekian and Wedepohl) (1961, table 2). Exceptions are molybdenum and copper, both of which show medians for black shales that are considerably higher than the averages shown by Turekian and Wedepohl. Statements about relatively high concentrations of some elements also are based on comparisons of all values reported for the first 20 sample sets.

TABLE 3.—*Percentile and mean values in analyses of black-shale sample sets, in percent*

[Set: 13, Lower Paleozoic shales; 14, Tacket Formation; 15, Heath and Tyler Formations; 16, Nonesuch Shale; 17, Green River Formation oil shale; 18, Kansas Upper Cretaceous shales; 19, Texas Upper Cretaceous shales; 20, Upper Mississippian shale; 21, Minnelusa Formation. Six-step semiquantitative spectrographic analyses of sample sets 15, 16, 18, and 20 by J. C. Hamilton, of sets 13, 14, 17, and 19 by A. L. Sutton, Jr., and of set 21 by Harriet Neiman. Quantitative spectrographic analyses of sample set 16, indicated by asterisk (*), by Sol Berman. Analyses for total carbon by use of induction furnace, for mineral carbon by gasometric method, and for organic carbon by difference determined by I. C. Frost, E. J. Fennelly, and Dorothy Kouba. Zinc in set 16 and iron, chromium, and nickel in set 17 (analyses in parentheses) determined by atomic absorption method by J. D. Mensik and Claude Huffman, Jr. Selenium in sets 11 and 20 determined chemically by G. T. Burrow; sulfur in set 16 determined gravimetrically by E. J. Fennelly. Equivalent uranium in sets 18 and 20 determined radiometrically by Wayne Mountjoy, Lorraine Lee, and H. H. Lipp. Where many analyses for an element in a set are reported as indeterminate, the data for that set are omitted.]

Set	P_5	P_{25}	P_{50}	P_{75}	P_{95}	Arithmetic mean	Geometric mean
Silicon							
15	7	>10	>10	>10	>10	9.1	8.5
19	1.5	3	>10	>10	>10	5.2	4.4
21	.3	2	>10	>10	>10	7.4	5.4
Aluminum							
13	1	5	>10	>10	>10	7.8	6.6
14	2	5	7	7	7	5.8	5.4
15	2	3	7	>10	>10	6.3	5.3
16	5	5	7	7	7	6.5	6.4
17	3	3	5	5	7	5.0	4.8
18	2	7	7	>10	>10	7.2	6.7
19	.7	3	7	>10	>10	5.9	4.7
20	3	7	7	7	7	6.7	6.6
21	.2	2	7	>10	>10	6.0	3.4
Iron							
13	0.5	1.5	2	3	5	2.3	1.9
14	1.5	2	2	3	5	2.5	2.4
15	.7	1.5	2	3	5	2.5	2.1
16*	2.4	3.1	3.3	3.8	6.0	3.52	3.46
17	(1.2)	(1.5)	(2.0)	(2.2)	(2.8)	(1.94)	(1.88)
18	2	3	3	3	5	3.2	3.0
19	.7	1.5	2	3	5	2.5	2.1
20	1.5	2	2	3	7	2.7	2.5
21	.5	.7	2	3	5	2.6	1.9
Magnesium							
13	0.07	0.7	1.5	3	>10	2.3	1.1
14	.3	.5	.5	.7	1.5	.61	.56
15	.3	.5	.7	.7	1.5	.73	.64
16*	1.3	1.6	1.9	2.0	2.5	1.87	1.85
17	2	3	3	3	7	3.2	2.7
18	.3	1	1.5	1.5	2	1.3	1.1
19	.3	.5	.5	.5	.7	.54	.52
20	.3	.5	.7	.7	.7	.59	.56
21	.7	2	2	>10	>10	4.6	3.3

TABLE 3.—*Percentile and mean values in analyses of black-shale sample sets, in percent*—Continued

Set	P_{5}	P_{25}	P_{50}	P_{75}	P_{95}	Arithmetic mean	Geometric mean
Calcium							
13	0.01	0.02	0.07	0.2	7	1.1	0.12
14	.15	.5	1	2	7	1.7	.97
15	.3	1	2	>10	>10	4.5	2.3
16	5	7	>10	>10	>10	6.8	8.8
17	.15	>10	>10	>10	>10	----------	----------
18	1	1.5	2	7	>10	4.2	2.9
19	1.5	>10	>10	>10	>10	9.3	8.5
20	.07	.1	.15	.15	.3	.14	.13
21	.5	.7	2	>10	>10	4.8	2.8
Sodium							
13	<0.05	0.07	0.2	1	1.5	0.53	0.26
14	.5	.7	1	1	1	.91	.89
15	.07	.2	.2	.3	1	.35	.25
16	1.5	2	2	3	3	2.2	2.2
17	1.5	2	3	3	5	2.8	2.7
18	.7	.7	1	1	1	.92	.90
19	.3	.7	.7	.7	1.5	.73	.65
20	.05	.1	.15	.15	.2	.12	.11
Potassium							
13	<1	2	3	3	5	2.6	2.3
14	1.5	2	2	3	3	2.4	2.3
15	1.5	2	2	3	5	2.5	2.3
16	2	3	3	3	3	2.9	2.9
17	2	2	2	3	5	2.8	2.5
18	1.5	2	2	3	3	2.4	2.4
19	<1	1.5	2	3	3	2.0	1.8
20	1.5	5	5	5	5	4.3	4.0
Titanium							
13	0.07	0.15	0.2	0.3	0.5	0.22	0.17
14	.07	.1	.15	.2	.2	.15	.14
15	.07	.1	.15	.3	.5	.19	.15
16*	.26	.38	.44	.55	.71	.47	.46
17	.1	.15	.15	.2	.2	.16	.15
18	.05	.2	.2	.3	.3	.21	.18
19	.02	.07	.1	.15	.2	.12	.098
20	.3	.7	.7	.7	.7	.64	.63
21	.003	.03	.3	.5	.5	.28	.14
Manganese							
13	0.002	0.003	0.007	0.01	0.02	0.010	0.0068
14	.003	.007	.01	.02	.1	.017	.011
15	.002	.005	.01	.03	.1	.026	.013
16*	.092	.15	.23	.28	.52	.25	.23
17	.015	.02	.03	.05	.05	.034	.030
18	.01	.015	.02	.02	.07	.020	.018
19	.01	.015	.02	.03	.05	.025	.022
20	.001	.0015	.0015	.005	.03	.0057	.0027
21	.003	.005	.007	.01	.01	.0078	.0074

TABLE 3.—*Percentile and mean values in analyses of black-shale sample sets, in percent*—Continued

Set	P_{5}	P_{25}	P_{50}	P_{75}	P_{95}	Arithmetic mean	Geometric mean
				Silver			
13	<0.0001	<0.0001	<0.0001	<0.0001	0.00015	0.000076	0.000074
14	<.0001	<.0001	.0002	.0007	.001	.00040	.00023
15	<.0001	<.0001	<.0001	.0001	.0005	.00017	.00014
16*	<.0002	.0002	.0003	.0004	.0024	.00041	.00030
21	< .0002	<.0002	<.0002	.0002	.0007	.00020	.00012
				Boron			
13	<0.002	0.003	0.007	0.01	0.015	0.0077	0.0057
14	<.002	.002	.003	.003	.005	.0028	.0026
15	<.003	.007	.01	.015	.02	.0096	.0081
16*	.002	.004	.005	.006	.010	.0052	.0048
17	<.003	.005	.005	.007	.02	.0072	.0058
18	<.002	.007	.015	.015	.02	.012	.0098
19	<.002	<.002	<.002	.003	.02	.0048	.0027
20	.015	.02	.03	.03	.03	.027	.025
				Barium			
13	0.005	0.02	0.05	0.05	0.1	0.043	0.033
14	.015	.02	.02	.02	.03	.022	.021
15	.005	.007	.01	.015	.02	.013	.011
16*	.026	.050	.057	.064	.096	.059	.056
17	.05	.07	.07	.07	.1	.083	.070
18	.02	.03	.03	.05	.15	.045	.039
19	.001	.005	.007	.015	.2	.041	.0097
20	.005	.007	.007	.007	.007	.0066	.0065
21	.001	.003	.03	.03	.05	.026	.017
				Beryllium			
13	<0.0001	<0.0001	<0.0001	0.0001	0.0003	0.00011	0.000097
14	<.0001	<.0001	.0001	.0002	.0015	.00019	.00012
15	<.00015	<.00015	<.00015	<.00015	.00015	.00012	.00011
16	<.0002	<.0002	<.0002	<.0002	.0002	----------	----------
21	<.0001	<.0001	.00015	.0003	.0005	.00022	.00016
				Cobalt			
13	<0.0003	<0.0003	0.0005	0.001	0.005	0.0011	0.00056
14	<.0003	.0005	.0007	.001	.0015	.00081	.00068
15	<.0005	<.0005	.0005	.0007	.002	.00094	.00067
16*	.0010	.0014	.0017	.0020	.0024	.0017	.0017
17	<.0007	.0007	.001	.001	.0015	.00097	.00091
18	.001	.0015	.0015	.0015	.002	.0014	.0013
19	<.0005	<.0005	.0005	.0007	.001	.00062	.00056
20	<.0007	<.0007	.0007	.0007	.002	.00079	.00071
21	<.0003	.0003	.0005	.0015	.007	.0020	.00069

TABLE 3.—*Percentile and mean values in analyses of black-shale sample sets, in percent*—Continued

Set	P_5	P_{25}	P_{50}	P_{75}	P_{95}	Arithmetic mean	Geo- mean metric
Chromium							
13	0.0015	0.005	0.007	0.007	0.01	0.0065	0.0060
14	.007	.015	.05	.07	.1	.046	.035
15	.007	.01	.015	.02	.05	.019	.015
16*	.0036	.0050	.0052	.0062	.0080	.0056	.0055
17	(.0018)	(.0023)	(.0026)	(.0029)	(.0035)	(.0026)	(.0024)
18	.005	.007	.007	.01	.01	.0086	.0078
19	.002	.007	.01	.02	.03	.015	.012
20	.01	.015	.015	.02	.02	.016	.015
21	.0007	.003	.015	.05	.07	.032	.014
Copper							
13	0.0015	0.003	0.005	0.007	0.01	0.0054	0.0045
14	.002	.005	.01	.01	.015	.0091	.0079
15	.0015	.003	.003	.01	.015	.0056	.0043
16*	.0064	.0093	.012	.024	>1	.14	.021
17	.002	.003	.007	.007	.01	.0058	.0052
18	.002	.005	.007	.007	.02	.0072	.0063
19	.0007	.002	.003	.005	.007	.0036	.0029
20	.0015	.002	.003	.005	.015	.0039	.0031
21	.001	.0015	.005	.015	.05	.014	.0058
Gallium							
13	<0.0007	0.0015	0.002	0.003	0.005	0.0022	0.0018
14	.001	.0015	.0015	.002	.002	.0016	.0015
15	.0007	.001	.002	.005	.005	.0027	.0021
16*	.0006	.0008	.0010	.0011	.0013	.00098	.00096
17	<.0007	.001	.0015	.0015	.003	.0014	.0013
18	.001	.003	.003	.003	.005	.0030	.0027
19	<.0005	.0005	.001	.0015	.005	.0015	.0010
20	.002	.003	.003	.003	.003	.0029	.0028
Lanthanum							
13	<0.003	<0.003	<0.003	0.003	0.005	0.0027	0.0026
14	<.002	<.002	.003	.003	.005	.0026	.0024
15	<.003	<.003	.003	.005	.005	.0036	.0033
16	<.003	.003	.003	.005	.005	.0037	.0036
18	<.003	<.003	<.003	.003	.003	.0024	.0024
19	<.003	<.003	<.003	.003	.005	.0025	.0024
20	<.005	<.005	.005	.005	.5	.0043	.0042
21	<.003	<.003	.003	.007	.01	.0045	.0034
Molybdenum							
13	<0.0005	<0.0005	<0.0005	0.0005	0.002	0.00048	0.00039
14	<.0005	<.0005	.0015	.01	.02	.0050	.0018
15	<.0005	<.0005	.0005	.007	.02	.0042	.0014
16*	<.0004	.0010	.0012	.0013	.0025	.0012	.0011
17	<.001	.001	.0015	.002	.003	.0015	.0013
18	.001	.0015	.002	.003	.005	.0024	.0021
19	<.0005	<.0005	.0005	.002	.003	.0011	.00077
20	<.0007	.001	.002	.003	.01	.0027	.0019
21	.0003	.001	.01	.07	.3	.070	.012

TABLE 3.—*Percentile and mean values in analyses of black-shale sample sets, in percent*—Continued

Set	P_5	P_{25}	P_{50}	P_{75}	P_{95}	Arithmetic mean	Geometric mean
				Niobium			
15	<0.0015	<0.0015	<0.0015	0.0015	0.003	0.0014	0.0013
18	<.001	<.001	.001	.001	.0015	.0010	.00094
20	.0015	.0015	.002	.002	.003	.0019	.0019
				Nickel			
13	0.001	0.002	0.003	0.005	0.007	0.0035	0.0030
14	.002	.01	.015	.02	.03	.014	.012
15	.001	.005	.007	.01	.03	.0092	.0063
16*	.0016	.0023	.0027	.0032	.0048	.0029	.0028
17	(.0030)	(.0035)	(.0038)	(.0042)	(.0059)	(.0040)	(.0039)
18	.003	.005	.007	.007	.007	.0060	.0057
19	.0015	.003	.005	.005	.01	.0052	.0042
20	.0007	.001	.0015	.003	.007	.0021	.0017
21	.001	.003	.007	.02	.1	.026	.010
				Lead			
13	<0.001	<0.001	0.0015	0.0015	0.002	0.0013	0.0012
14	.001	.002	.003	.003	.005	.0027	.0025
15	<.001	.0015	.002	.002	.005	.0022	.0018
16*	<.002	.006	.011	.016	.026	.012	.0095
17	<.002	<.002	.003	.003	.005	.0027	.0024
18	.001	.002	.003	.005	.005	.0034	.0030
19	<.001	<.001	<.001	.0015	.002	.0011	.0010
20	<.002	.002	.003	.003	.01	.0035	.0029
21	<.001	<.001	.001	.005	.03	.0068	.0022
				Scandium			
13	<0.0003	0.0005	0.0007	0.001	0.001	0.00072	0.00064
14	.0005	.0007	.001	.001	.001	.00084	.00081
15	<.0005	.001	.0015	.0015	.002	.0013	.0012
16*	.0015	.0016	.0020	.0020	.0021	.0019	.0018
17	<.0007	<.0007	.0007	.0007	.001	.00073	.00070
18	.0007	.001	.001	.001	.0015	.00097	.00096
19	<.0005	.0005	.0007	.001	.0015	.00088	.00070
20	.0015	.002	.002	.002	.002	.0020	.0020
				Strontium			
13	<0.001	0.0015	0.003	0.003	0.07	0.0089	0.0035
14	.01	.015	.02	.03	.07	.024	.021
15	.007	.02	.02	.05	.15	.059	.033
16*	.014	.018	.020	.021	.029	.020	.020
17	.07	.1	.1	.15	.2	.12	.10
18	.015	.02	.03	.05	.2	.059	.037
19	.02	.07	.07	.1	.15	.088	.077
20	.005	.005	.007	.01	.015	.0083	.0078
21	.007	.015	.07	.3	.5	.19	.085

Table 3.—*Percentile and mean values in analyses of black-shale sample sets, in percent*—Continued

Set	P_5	P_{25}	P_{50}	P_{75}	P_{95}	Arithmetic mean	Geometric mean
Vanadium							
13	0.007	0.015	0.02	0.03	0.05	0.023	0.018
14	.007	.01	.05	.15	.2	.079	.041
15	.007	.01	.015	.02	.1	.028	.018
16*	.0090	.011	.012	.016	.024	.012	.010
17	.01	.01	.015	.015	.015	.014	.013
18	.02	.03	.03	.05	.05	.035	.034
19	.007	.015	.03	.03	.07	.029	.022
20	.01	.01	.015	.015	.02	.014	.013
21	.003	.01	.1	.3	.7	.23	.082
Yttrium							
13	0.001	0.001	0.0015	0.002	0.003	0.0017	0.0016
14	<.001	.001	.0015	.003	.007	.0022	.0018
15	.001	.002	.003	.003	.005	.0027	.0024
16*	.004	.004	.004	.005	.007	.0047	.0047
17	<.002	<.002	<.002	<.002	.003	----------	----------
18	.0015	.002	.002	.003	.003	.0024	.0022
19	<.001	.001	.0015	.002	.003	.0019	.0017
20	.003	.005	.005	.005	.005	.0049	.0048
21	<.001	<.001	.002	.005	.005	.0025	.0018
Ytterbium							
13	<0.0001	0.0001	0.00015	0.0002	0.0003	0.00018	0.00016
15	<.0001	.0001	.0002	.0003	.0005	.00025	.00023
16*	.0002	.0003	.0003	.0003	.0004	.00030	.00029
18	.0002	.0003	.0003	.0003	.0005	.00031	.00030
19	<.0001	.0001	.00015	.0002	.0003	.00019	.00016
20	.0005	.0005	.0005	.0005	.0007	.00053	.00052
Zinc							
14	<0.02	<0.02	0.02	0.05	0.1	0.033	0.012
15	<.03	<.03	<.03	.05	.2	.056	.029
16	(.0055)	(.0071)	(.0079)	(.0092)	(.015)	(.0087)	(.0085)
18	<.03	<.03	<.03	.03	.05	.027	.025
21	<.01	<.01	<.01	<.01	.02	----------	----------
Zirconium							
13	0.0015	0.005	0.01	0.015	0.02	0.010	0.0080
14	.0015	.003	.003	.005	.007	.0036	.0033
15	.003	.003	.005	.01	.015	.0079	.0060
16*	.007	.012	.013	.014	.017	.013	.013
17	<.002	.002	.003	.005	.007	.0039	.0035
18	.003	.007	.01	.01	.01	.0081	.0075
19	<.0015	.003	.005	.007	.01	.0050	.0042
20	.02	.03	.03	.07	.07	.044	.039

TABLE 3.—*Percentile and mean values in analyses of black-shale sample sets, in percent*—Continued

Set	P_5	P_{25}	P_{50}	P_{75}	P_{95}	Arithmetic mean	Geometric mean
			Total carbon				
13	0.20	0.58	0.86	2.28	4.20	1.58	1.05
14	2.51	5.58	8.99	13.24	18.80	10.19	8.31
15	.63	1.0	4.69	12.26	18.72	7.90	4.14
16	1.95	2.47	2.97	3.58	6.07	3.17	3.01
18	2.92	4.81	5.28	6.10	11.5	6.08	5.54
19	4.20	8.92	10.7	11.7	12.6	9.89	9.44
20	.19	.64	.81	1.12	2.06	---	---
21	.82	1.20	8.32	11.0	14.1	7.45	4.96
			Mineral carbon				
13	<0.01	0.03	0.05	0.08	2.28	0.35	0.072
14	<.02	.13	.19	.98	2.89	.69	.31
15	.02	.08	.33	3.43	5.0	1.51	.42
16	1.59	2.07	2.66	3.10	5.71	2.78	2.65
18	.15	.80	.97	2.23	7.93	2.15	1.16
19	.98	6.41	7.91	8.82	11.1	7.23	5.75
21	<.01	.08	.72	8.57	12.0	3.95	.68
			Organic carbon				
13	0.1	0.4	0.8	1.2	4.1	1.23	0.76
14	.7	3.3	8.9	13.1	22.4	9.49	6.78
15	.3	.9	2.2	7.6	15.6	6.39	2.92
16	<.1	.3	.4	.5	.9	.41	.36
18	1.6	3.3	4.0	4.4	5.1	3.84	3.54
19	.4	1.5	2.8	3.6	4.5	2.66	2.12
20	.2	.6	.8	1.1	2.1	.89	.74
21	<.1	<.1	1.0	2.4	14.0	3.50	.72
			Arsenic				
16	0.0013	0.0032	0.0036	0.0040	0.0044	0.0034	0.0033
			Sulfur				
16	0.64	1.01	1.15	1.25	1.53	1.12	1.10
			Selenium				
16	<0.00005	<0.00005	<0.00005	0.00005	0.0001	0.000042	0.000034
20	.00005	.0001	.0001	.0002	.0003	.00016	.00014
			Equivalent uranium				
18	0.001	0.002	0.002	0.003	0.003	0.0022	0.0020
19	<.001	.001	.001	.001	.003	.0013	.0012
20	.001	.002	.002	.002	.003	.0021	.0020
			Oil				
17	2.8	5.0	8.2	13.3	24.6	10.1	8.15

TABLE 3.—*Percentile and mean values in analyses of black-shale sample sets, in percent*—Continued

Set	P_{5}	P_{25}	P_{50}	P_{75}	P_{95}	Arithmetic mean	Geometric mean
			Gas				
17	0.2	0.9	1.9	2.7	5.1	2.26	1.95
			Water				
17	0.8	1.1	1.5	1.8	2.2	1.63	1.47
			Ash				
17	68.6	71.7	74.1	78.5	83.2	75.4	75.2
21	67	82	93	94	96	88.7	88.3

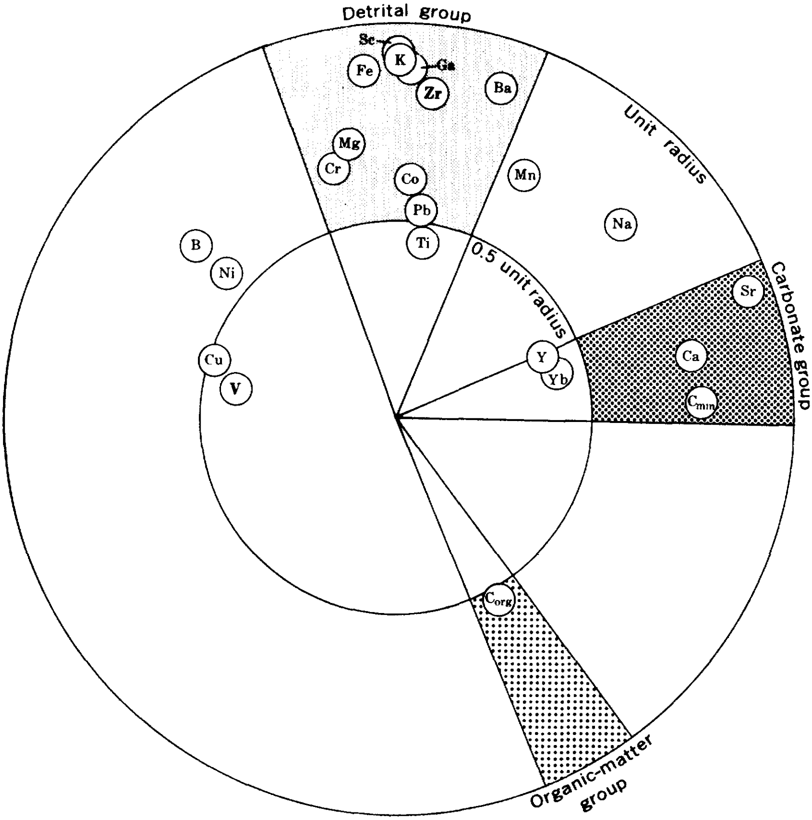

FIGURE 3.—Rotated two-dimensional vector diagrams showing principal components of the correlation matrix for set 13, lower Paleozoic shales of Arkansas. Abnormally abundant elements shown in bold type.

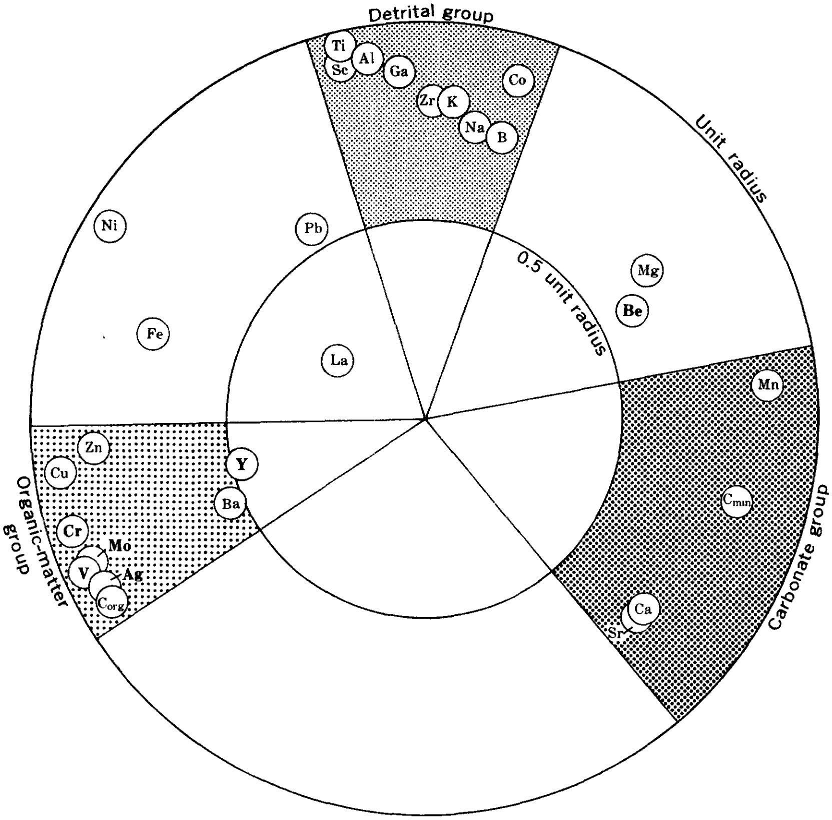

FIGURE 4.—Rotated two-dimensional vector diagrams showing principal components of the correlation matrix for set 14, black-shale from the Tacket Formation of Jewett, Emery, and Hatcher (1965) of Kansas. Abnormally abundant elements shown in bold type.

LOWER PALEOZOIC SHALES OF ARKANSAS

ELEMENT ABUNDANCE

The lower Paleozoic shales of Arkansas (set 13) are mostly fine-grained detrital or siliceous rocks, chiefly claystones and cherts that contain relatively minor amounts of either organic matter or carbonate minerals. The predominantly detrital nature of these geosynclinal rocks is reflected by their high content of silicon and aluminum. The reported analyses show that all 32 samples of this set contain more than 10 percent silicon and that 21 of the samples contain more than 10 percent aluminum. The medians of potassium, magnesium, iron, sodium, and titanium, listed in approximate order of decreasing abundance, are all 3 percent or less. The median content of calcium is

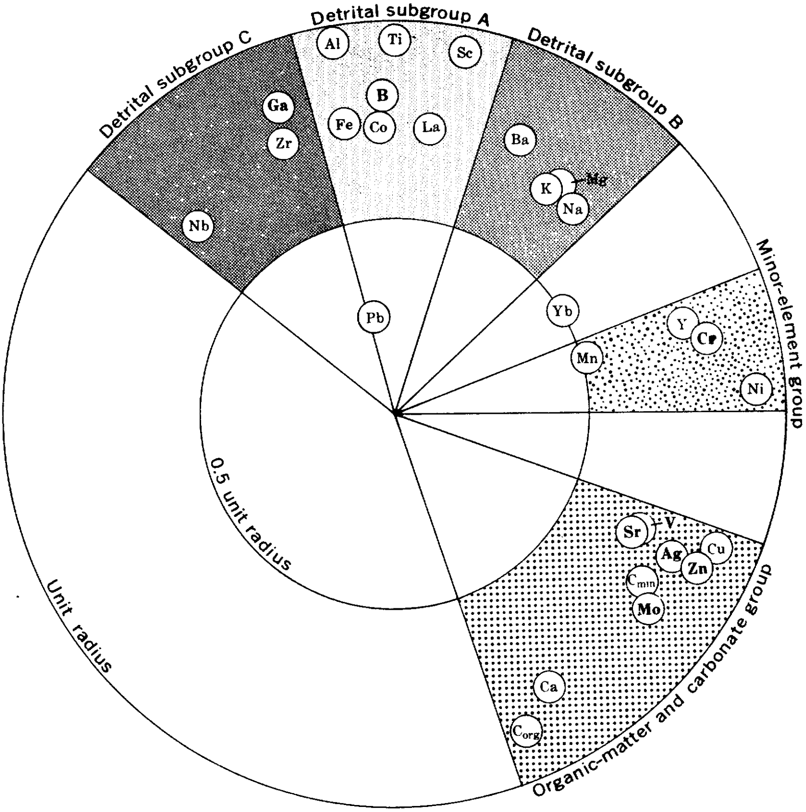

FIGURE 5.—Rotated two-dimensional vector diagrams showing principal components of the correlation matrix for set 15, black shale from the Heath and Tyler Formations and equivalents of Montana and Idaho. Abnormally abundant elements shown in bold type.

only 0.07 percent, but four of the 32 samples contain 5 percent or more. The median content of mineral carbon is similarly low (0.05 percent), but three samples contain more than 1 percent. The organic carbon content is also low; the median value for the set is 0.8 percent, and only one sample in the set has more than 5 percent. Of the minor elements, only vanadium and zirconium show any tendency to be locally enriched. The samples that contain 0.05 percent or more vanadium came from four formations: the Mazarn Shale, Blakely Sandstone, Womble Shale, and Polk Creek Shale. The samples with high zirconium content (0.02 percent) came from the Blakely Sandstone and Womble Shale. Most of the other minor elements are present in amounts that are average or less than average for black shales.

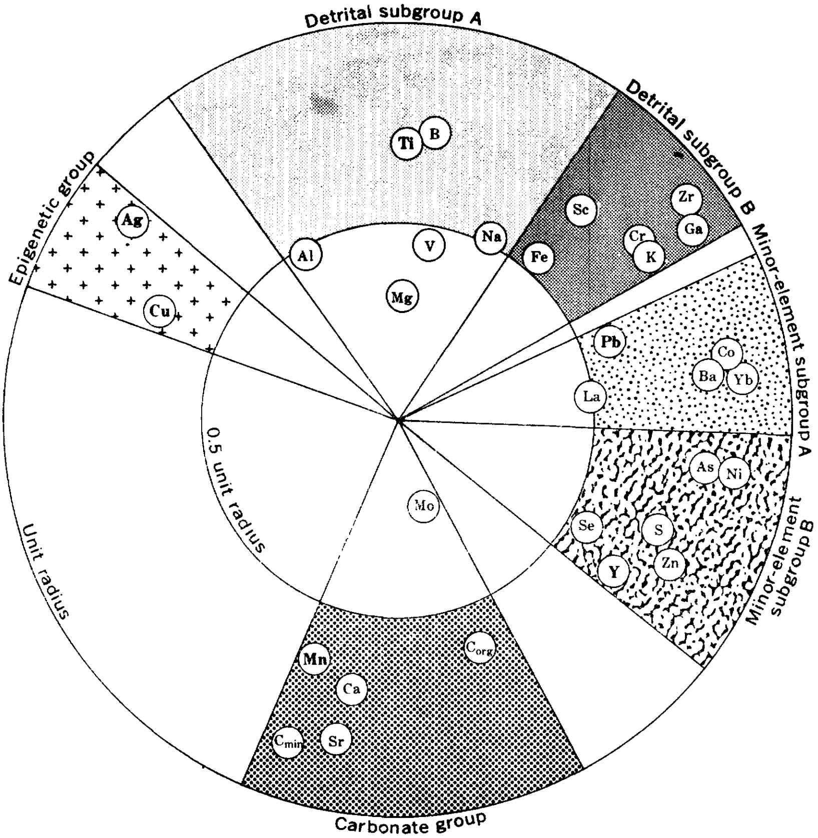

FIGURE 6.—Rotated two-dimensional vector diagrams showing principal components of the correlation matrix for set 16, Nonesuch Shale of Michigan and Wisconsin. Abnormally abundant elements shown in bold type.

ELEMENT ASSOCIATIONS

The two-factor vector diagram for the lower Paleozoic shales of Arkansas (fig. 3) shows three main groups of elements: a detrital group, a carbonate group, and an organic-matter group. No further subdivision of these groups was evident from a study of the three-factor analysis of the correlation matrix. Strong correlations exist between potassium, iron, magnesium, barium, gallium, scandium, and zirconium, and these represent the main part of the detrital group. Other elements less closely associated with the detrital group are manganese, boron, chromium, lead, cobalt (mostly with iron), and titanium. Organic carbon is inversely related to most of the elements in the detrital group. The carbonate group, consisting of calcium,

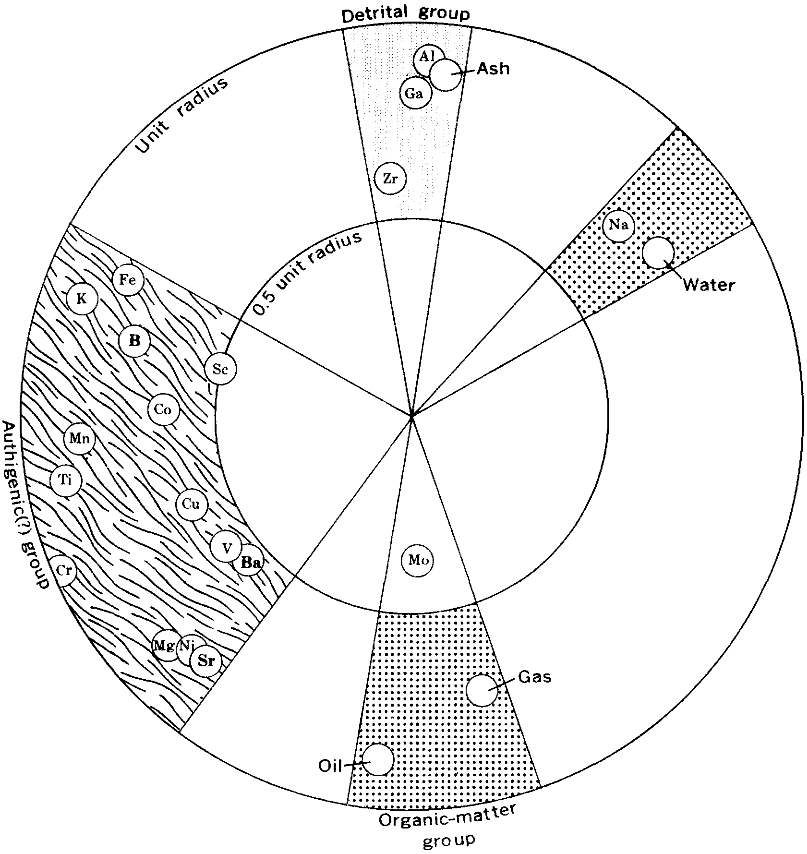

FIGURE 7.—Rotated two-dimensional vector diagrams showing principal components of the correlation matrix for set 17, oil shale from the Green River Formation of Colorado. Abnormally abundant elements shown in bold type.

mineral carbon, strontium, and probably part of the sodium, is a cohesive group that appears to be independent of the others. Several other minor elements do not fit neatly into any of the major groups. Yttrium and ytterbium show a positive correlation with organic carbon, and so also does vanadium, but the correlation is not strong enough to form a cohesive group of constituents. Nickel and copper correlate strongly with each other but appear to be independent of the other elements. Boron and titanium, while listed with the detrital group, are in large part independent.

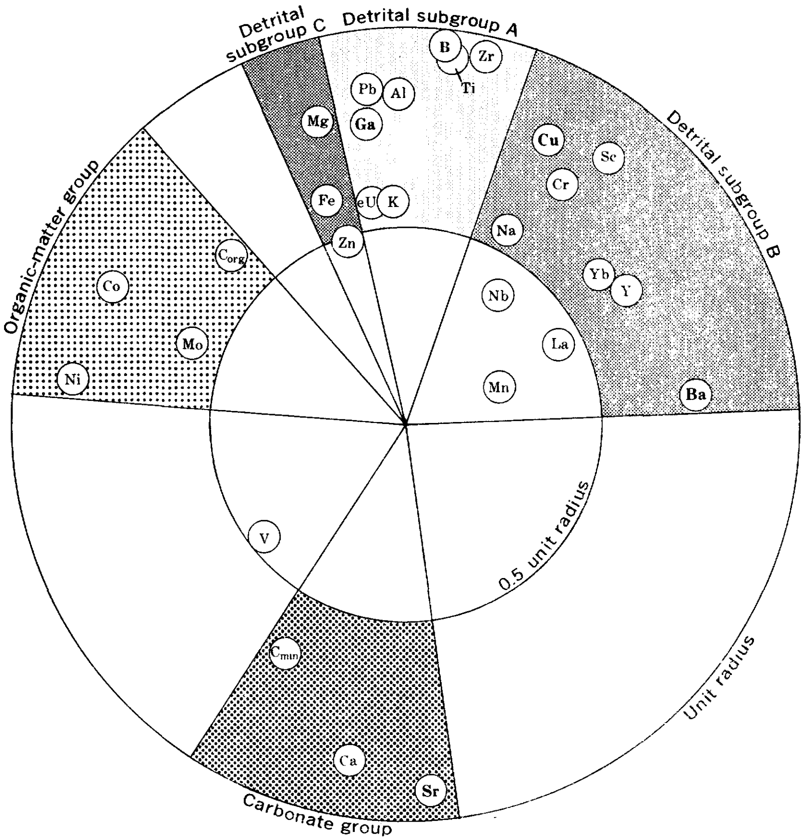

FIGURE 8.—Rotated two-dimensional vector diagrams showing principal components of the correlation matrix for set 18, Upper Cretaceous shales of Kansas. Abnormally abundant elements shown in bold type.

BLACK SHALE FROM THE TACKET FORMATION OF JEWETT, EMERY, AND HATCHER (1965) OF KANSAS

ELEMENT ABUNDANCE

The black shale of the Tacket Formation from the Pleasanton Group of southeastern Kansas (set 14) is an organic-rich detrital rock containing only minor amounts of carbonate minerals. Some samples also contain a small amount of phosphate. The major elements in the black shale include silicon, which exceeds 10 percent in all samples; carbon, which has a median of 9 percent; and aluminum, which is reported as 7 percent in 12 of the 19 samples. Iron, potassium, calcium, and sodium occur in approximately that order of decreasing abun-

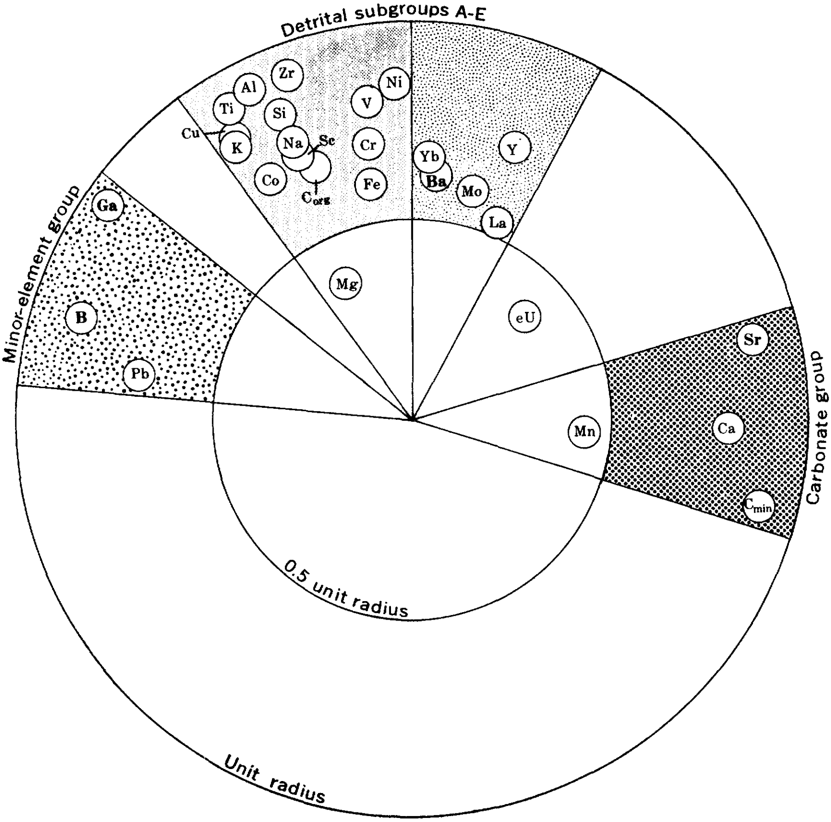

FIGURE 9.—Rotated two-dimensional vector diagrams showing principal components of the correlation matrix for set 19, Upper Cretaceous shales of Texas. Abnormally abundant elements shown in bold type.

dance, and all are less than 5 percent at the median level. Most of the carbon occurs as organic carbon and only a small amount as carbonate carbon. Minor elements that are unusually abundant in these samples from the Tacket Formation include beryllium, chromium, molybdenum, silver, vanadium, and yttrium; most of the other minor elements occur in at least average amounts.

ELEMENT ASSOCIATIONS

Three major groups of elements are evident from the vector diagram (fig. 4) constructed from the correlation matrix of set 14: (1) a detrital group of elements including titanium, scandium, aluminum, gallium, zirconium, potassium, sodium, boron, and cobalt, (2) a carbonate group consisting of mineral carbon plus calcium, strontium,

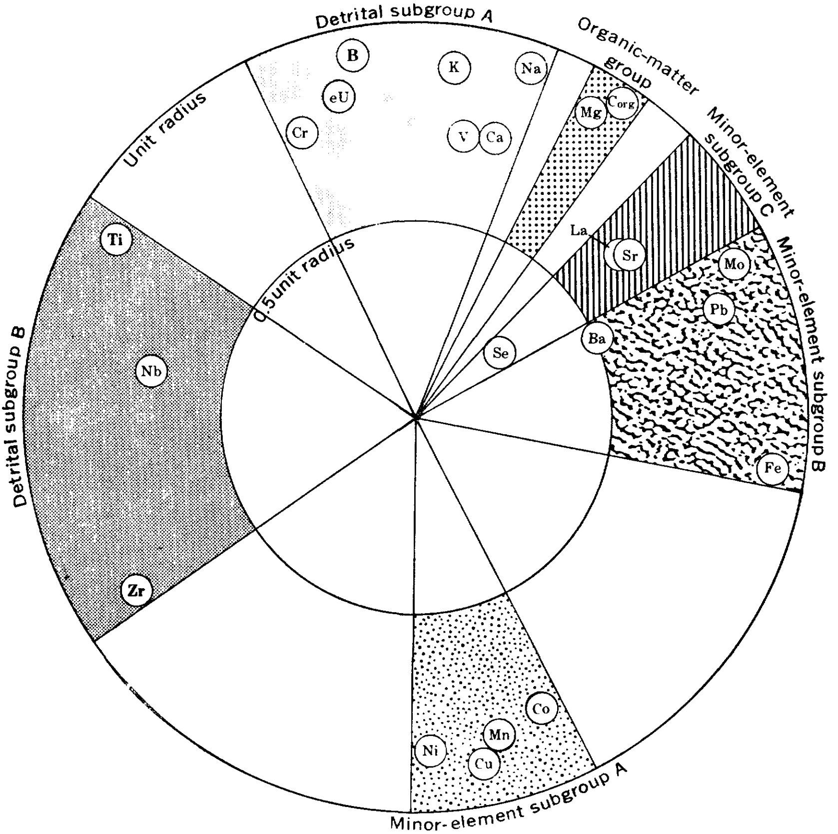

FIGURE 10.—Rotated two-dimensional vector diagrams showing principal components of the correlation matrix for set 20. Upper Mississippian shales of western Wyoming. Abnormally abundant elements shown in bold type.

and manganese, and (3) an organic-matter group consisting of organic carbon, zinc, copper, chromium, molybdenum, vanadium, silver, and possibly barium and yttrium. Several other elements fall outside the major groups; these include magnesium and beryllium, which fall between the carbonate and detrital mineral fractions, and nickel, iron, lead, and lanthanum, which fall between the detrital and organic-matter fractions. Lanthanum is so close to the center of the circle that it is probably independent.

BLACK SHALE FROM THE HEATH AND TYLER FORMATIONS

ELEMENT ABUNDANCE

The black-shale samples from the Heath and Tyler Formations (set 15) include a variety of fine-grained claystones and siltstones. Some of

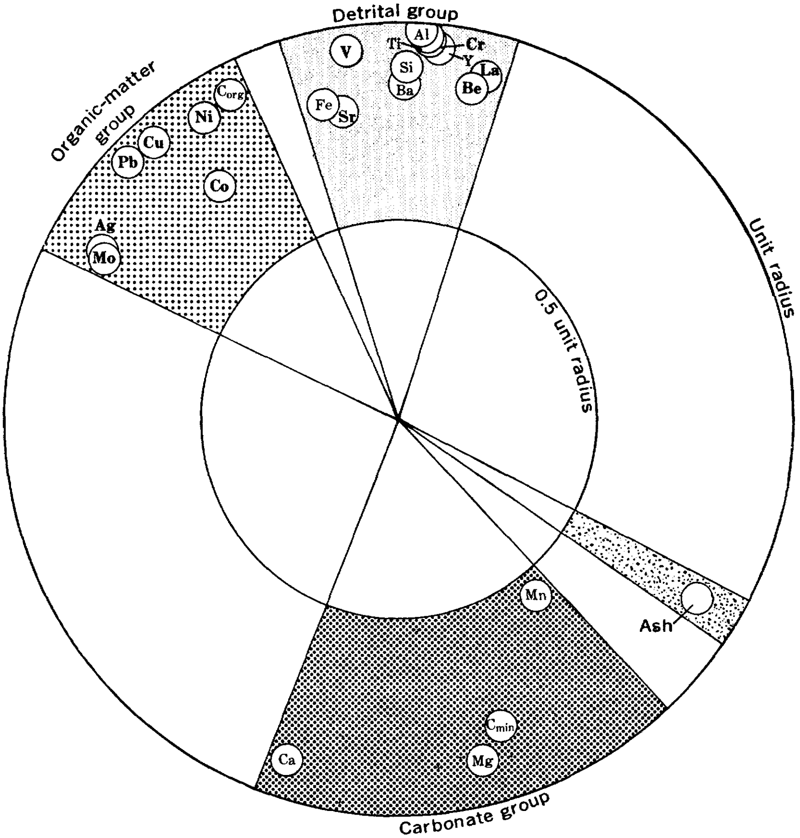

FIGURE 11.—Rotated two-dimensional vector diagrams showing principal components of the correlation matrix for set 21, ashed shale from the Minnelusa Formation of South Dakota and Wyoming. Abnormally abundant elements shown in bold type.

the samples contain abundant organic matter, and others, abundant carbonate minerals. About one-third of the samples are low in both organic matter and carbonate minerals. Analyses of the full set of 28 samples show silicon as greater than 10 percent in 22 samples and aluminum and calcium as greater than 10 percent in 10 samples. The median value of total carbon is 4.7 percent. Of the 28 samples analyzed, 13 contain 5 percent or more organic carbon, but only two contain 5 percent or more mineral carbon. Calcium, iron, and potassium have medians of 2 percent, whereas magnesium and sodium are each less than 1 percent at the median level. Many of the minor elements are abundant in one or more of the samples in set 15 relative to the other sets of black-shale samples. Elements that may be regarded as enriched include gallium, which is relatively high at the 75th-percentile level, and boron, chromium, molybdenum, silver, strontium, vanadium, and zinc, which all are relatively abundant in some samples. Lithium was reported as present in seven samples, cadmium in four, and cerium, with a value of 0.015 percent, in nine. In most black-shale samples these elements are below the lower limits of detection. Cobalt, copper, nickel, and lead are moderately abundant in some samples. The other reported elements, barium, beryllium, yttrium, ytterbium, lanthanum, scandium, and zirconium, occur in near-average amounts in this set.

ELEMENT ASSOCIATIONS

The two-factor vector diagram (fig. 5) for the full set of Heath and Tyler samples is not adequate to group most of the elements. Separation of the elements into the groups shown in figure 5, therefore, was supplemented with observations from three-factor analysis. Three detrital subgroups which lie within about a 90° arc on the two-factor vector diagram were distinguished: subgroup A, consisting of aluminum, titanium, scandium, iron, lanthanum, and cobalt; subgroup B, consisting of potassium, barium, magnesium, and sodium; and subgroup C, consisting of gallium, zirconium, and niobium. Three-factor analysis shows boron to be more closely related to subgroup C, although it appears to fall in subgroup A of the two-factor diagram. The remaining groups lie within an adjacent arc that also covers about 90°; these include a carbonate group, organic carbon, and two other groups of minor elements. The carbonate group consists of mineral carbon, calcium, strontium, and possibly manganese. Organic carbon is not very closely associated with any of the minor elements, but it is probably most closely related to a group that includes copper, silver, zinc, vanadium, and molybdenum. On the two-factor vector diagram the carbonate group, organic carbon, and copper, silver, zinc, vanadium, and molybdenum form a single group. A second group of minor elements, consisting of chromium, nickel, and yttrium, falls about halfway between the detrital group and the other elements. Lead and ytterbium appear to be unrelated to any of the groups.

Samples from the Heath and Tyler Formations were separated into several subsets (see p. A7) which were statistically analyzed separately in an attempt to find explanations for some of the unusual element groupings that were seen in the analysis of the full set (fig. 5). The resulting groups, as listed in table 4, suggest that the full set of 28 samples represents a statistically mixed population. Of particular significance are the association of silver, copper, zinc, nickel, chromium, molybdenum, and vanadium with organic carbon in the 10 samples from the Heath Formation in central Montana and the absence of that association in the seven samples from the Tyler Formation in the same area.

TABLE 4.—*Element groupings in subsets of set 15, samples from the*

[Da, detrital subgroup A; Db, detrital subgroup B; Dc, detrital subgroup C; Dd, detrital subgroup D;
B; I, independent]

Element	Al	Fe	Sc	La	Ti	Co	Ba	K	Mg	Na	B	Ga
Set 15, all 28 samples	Da	Da	Da	Da	Da	Da	Db	Db	Db	Db	Da	Dc
Subset 15A, 10 western samples	Da	Da	Da	Da	Db	Da	Db	Db	Dc	Da	Db	Db
Subset 15B, 18 central Montana samples	Da	Da	Db	Db	Da	Db	Db	Db	Db	Ma	Da	Da
Subset 15C, 10 Heath Formation, central Montana, samples	Da	Db	Db	Db	Da	Db	Db	Db	Db	Ma	Dc	Dd
Subset 15D, seven Tyler Formation, central Montana, samples	Da	Dc	Db	Da	Db	Db	Dc	C	C	I	Da	Da

NONESUCH SHALE OF MICHIGAN AND WISCONSIN

ELEMENT ABUNDANCE

The fine-grained detrital rocks of the Nonesuch Shale of Precambrian age in Michigan and Wisconsin (set 16) have a moderately high content of carbonate minerals and contain a minor amount of organic matter. Of the major elements (as determined by six-step spectrographic analysis), silicon is reported as more than 10 percent in all 20 samples and calcium is reported as more than 10 percent in 15 samples. Aluminum is reported as 7 percent in 15 samples and as less than that in the other five. Carbon, iron, potassium, sodium, and magnesium are all less than 5 percent but greater than 1 percent at the median level. Sodium, with a median content of 2 percent, is notably higher than in most of the other black-shale sample sets, and potassium, with a median of 3 percent, is also higher than average. The high sodium and potassium contents probably reflects the abundance and nature of the clay-mineral fraction of the rock. The mineral carbon content, which ranges from 1.59 to 5.71 percent, is much more uniform in set 16 than in most of the other sample sets. The organic carbon content is uniformly low, ranging from less than 0.1 to 0.9 percent. Of the minor elements (as determined by quantitative spectrographic analysis), copper, silver, lead, titanium, manganese, and yttrium tend to be abnormally abundant in some samples. Most of the other minor elements are present in amounts that are about average or less than average for black-shale samples.

ELEMENT ASSOCIATIONS

The elements detected in the Nonesuch Shale samples from Michigan and Wisconsin can be separated into four principal groups on the two-factor vector diagram (fig. 6): (1) a detrital group, (2) a carbonate group inversely related to the detrital group, (3) a minor-element group, and (4) an epigenetic group inversely related to the minor-

Heath and Tyler Formations and equivalents of Montana and Idaho

O, organic-carbon group; C, carbonate group; Ma, minor-element subgroup A; Mb, minor-element subgroup

Zr	Nb	Ag	Cu	Zn	Ni	Cr	Mo	V	C_{org}	C_{min}	Ca	Sr	Y	Yb	Mn	Pb
Dc	Dc	Ma	Ma	Ma	Mb	Mb	Ma	Ma	O	C	C	C	Mb	I	I	I
Db	Db	Ma	Ma	Ma	Ma	Dc	O	O	O	C	C	Ma	Ma	C	I	I
Da	Da	Ma	Ma	Ma	Ma	Ma	Ma	Ma	C	C	C	C	Db	Db	I	Da
Dc	Dc	O	O	O	O	O	O	O	O	C	C	C	C	I	Ma	I
Db	Db	Ma	O	Ma	Ma	Ma	Ma	Ma	O	C	C	C	Dc	Db	C	Db

element group. Further analysis of the correlation matrix, using three factors, indicates that the detrital group and the minor-element group can each be divided into three possible subgroups. The detrital subgroups are subgroup A, containing titanium, boron, sodium, vanadium, and possibly aluminum; subgroup B, containing potassium, chromium, gallium, scandium, and zirconium; and subgroup C, which is not distinguishable in figure 6, containing iron and magnesium. The minor-element subgroups are subgroup A, consisting of barium, cobalt, lanthanum, and ytterbium; subgroup B, consisting of nickel, selenium, sulfur, yttrium, and zinc; and subgroup C, which is not shown in figure 6, consisting of arsenic, lead, and part of the molybdenum. The carbonate group includes mineral carbon, calcium, strontium, manganese, and possibly organic carbon and part of the molybdenum. The epigenetic group consists of copper and silver. Although copper and silver occur as sulfides in the epigenetically mineralized samples, sulfur appears to be associated primarily with inversely related minor-element subgroup B, which may include some syngenetic sulfide minerals.

OIL SHALE FROM THE GREEN RIVER FORMATION OF COLORADO

ELEMENT ABUNDANCE

The oil shale from the Green River Formation of Colorado (set 17) is mainly a fine-grained marlstone (Bradley, 1964, p. A19) that contains unusually large amounts of solid organic matter and only minor amounts of detrital minerals. In most of the samples, carbonate minerals plus organic matter (kerogen) compose more than half the rock; the rest of the rock consists of quartz, analcime, mica, plagioclase, and pyrrhotite or pyrite, most of which were probably chemically or biologically precipitated. Analyses of the oil-shale samples show that silicon is greater than 10 percent in all 29 samples. Calcium is reported as greater than 10 percent in 28 samples, the one exception being a sample which is mostly analcime and came from the Mahogany marker bed. The presence of 8.2 percent oil and 1.9 percent gas at the median level indicates that organic matter is the next most abundant constituent, followed by aluminum, magnesium, sodium, potassium, and iron (5, 3, 3, 2, and 1.5 percent, respectively, at the medians). Such minor elements as titanium and zirconium, which are characteristic of the detrital fraction in most black shales, are much less abundant in the Green River oil shale than in most black shales and only slightly more abundant than in typical limestones. Of all the minor elements detected, only boron, barium, and strontium tend to be enriched in the oil shale. Even boron is not abundant in very many samples, although boron minerals from the saline facies of the Green River Formation in the central Piceance Creek basin have been identified (R. J. Hite, oral commun., 1966). Elements such as molybdenum, vanadium, chromium, copper, nickel, and silver, which commonly occur with organic matter and are locally enriched in some black shales, are not enriched in these oil-shale samples. Perhaps they have become uniformly dispersed throughout the oil shale where so much organic matter exists, or were dispersed by connate brines during consolidation of the oil shale.

ELEMENT ASSOCIATIONS

The Green River oil-shale samples were submitted for Fisher assay, which yielded data on the percent oil, water, gas, and ash at 900°C. These data were included in the correlation and factor analysis along with the six-step spectrographic analysis in place of the usual analyses for forms of carbon. The results, using data from Fisher assay, can be interpreted in much the same terms as the data from carbon analyses for the other sample sets. Four principal element groupings are evident on the vector diagram (fig. 7): (1) a detrital group that includes aluminum, gallium, zirconium, and ash, (2) a group that is probably composed largely of authigenic minerals, including carbonates, sulfides, and clay minerals, and includes potassium, iron, boron, manganese, titanium, cobalt, scandium, chromium, magnesium, nickel, strontium, copper, vanadium, and barium, (3) a group that shows an inverse relation to the detrital group, includes oil and gas and probably part of the molybdenum, and is thought to be equivalent to the organic carbon group of some other black-shale sample sets, and (4) a final group, sodium and water, which has an inverse relation to the authigenic mineral group. The analysis for water in the final group includes both free water and water from hydrous minerals, which makes interpretation of the group equivocal.

UPPER CRETACEOUS SHALES OF KANSAS

ELEMENT ABUNDANCE

The Upper Cretaceous shales of Kansas (set 18) range in lithology from detrital claystones that contain scattered small phosphate or carbonate concretions and moderately large amounts of organic matter, in the Sharon Springs Member of the Pierre Shale, to argillaceous limestone that contains large amounts of carbonate minerals, some detrital mineral matter, and relatively little organic matter in the Niobrara Formation. The 44 samples of Sharon Springs drill cuttings, the outcrop sample of dark-gray shale, and three of the 13 samples of Niobrara contain more than 10 percent silicon, whereas all the Niobrara samples and only two of the Sharon Springs samples, including the phosphatic nodule, contain more than 10 percent calcium. Aluminum is reported to be greater than 10 percent in 18 samples of the Sharon Springs but is less than 10 percent in all the Niobrara samples. Of the total 59 samples, 38 contain 5 percent or more total carbon, but of these only 10, including nine from the Niobrara, contain 5 percent or more mineral carbon, and only six from the Sharon Springs Member contain 5 percent or more organic carbon. Iron, magnesium, potassium, and sodium are all present in amounts of at least 1 percent but less than 5 percent at the median level. The median concentration of most of the minor elements is close to the average for black shales, but a few may be described as enriched at the 95th-percentile level. These include boron, gallium, strontium, and possibly barium and copper.

ELEMENT ASSOCIATIONS

Four principal groups of elements can be recognized in the two-factor vector analysis (fig. 8) of the correlation matrix for the Upper Cretaceous shales of Kansas. These groupings were verified by a three-factor analysis of the same data. Titanium, boron, aluminum, zirconium, gallium, lead, and possibly potassium and equivalent uranium form one group, detrital subgroup A. Detrital subgroup B includes the elements in the adjacent segment and consists of sodium, lanthanum, scandium, yttrium, ytterbium, copper, and possibly chromium, niobium, manganese, and barium. Iron, magnesium, and zinc form detrital subgroup C on the opposite side of subgroup A (fig. 8). An organic-matter group, adjacent to detrital subgroup C but unrelated to detrital subgroup B, includes organic carbon, molybdenum, cobalt, and nickel. A carbonate group including mineral carbon, calcium, and strontium is inversely related to detrital subgroup A. Chromium and niobium, although clearly detrital, appear to have associations with both detrital subgroups A and B. The distributions of barium and manganese, however, appear to be largely independent of each other and only in part associated with detrital subgroup B, with which they are listed. Vanadium is similarly independent, but is partly associated with the carbonate group.

UPPER CRETACEOUS SHALES OF TEXAS

ELEMENT ABUNDANCE

The 28 samples of Upper Cretaceous shales of Texas (set 19) are fine-grained carbonate-rich detrital rocks, chiefly claystone and marl, and contain low to moderate amounts of organic matter. Of the 28 samples, 25 contain greater than 10 percent calcium, 16 contain greater than 10 percent silicon, and eight contain greater than 10 percent aluminum. The median contents are iron and potassium, 2 percent; sodium, 0.7 percent; magnesium, 0.5 percent; titanium, 0.1 percent; and manganese, 0.02 percent. The median total carbon content is 10.7 percent; total carbon content at the 95th percentile is 12.6 percent. As would be expected from the high calcium content, mineral carbon makes up the major part of total carbon; at the median level, mineral carbon is 7.91 percent, and at the 95th percentile, 11.1 percent. The median of organic carbon is 2.8 percent, and at the 95th percentile it is 4.5 percent. Of the minor elements, boron, barium, gallium, and strontium are enriched at the 95th-percentile level. Silver was not detected in any of the samples, and beryllium was detected in only two. The other minor elements occur in near-average amounts.

ELEMENT ASSOCIATIONS

Three groups of elements can be recognized on the two-factor diagram (fig. 9): (1) a detrital group composed of silicon, aluminum, titanium, zirconium, potassium, copper, sodium, scandium, cobalt, organic carbon, iron, chromium, vanadium, nickel, yttrium, barium, lanthanum, ytterbium, molybdenum, and possibly magnesium, (2) a carbonate group composed of mineral carbon, calcium, and strontium, and (3) a minor-element group composed of boron, lead, and gallium. Manganese and equivalent uranium show no relation to each other or to any of the groups listed. Because so many elements occurred in the detrital group, a three-factor analysis was also run. Five closely related detrital subgroups were distinguished: subgroup A, silicon, aluminum, copper, and zirconium; subgroup B, potassium, titanium, organic carbon, sodium, and scandium; subgroup C, vanadium, nickel, and molybdenum; subgroup D, yttrium, lanthanum, ytterbium, and barium; and subgroup E, iron, cobalt, chromium and magnesium. Subgroups A, B, and C appear to be closely interrelated, and subgroups D and E are closely interrelated. The carbonate group is inversely related to the minor-element group and is not related to the detrital group. Organic carbon acts like a detrital element in this set, suggesting that most of the organic carbon was land derived.

UPPER MISSISSIPPIAN SHALES OF WESTERN WYOMING

ELEMENT ABUNDANCE

The Upper Mississippian shales of western Wyoming (set 20) are predominantly detrital rocks, chiefly claystones and siltstones that contain only minor amounts of organic matter and almost no carbonate minerals. Secondary sulfates occur on joint surfaces. Of the major elements in these black shales, the median contents of silicon, aluminum, and potassium are 5 percent or greater, those of iron and calcium are 1–5 percent, and those of carbon, magnesium, and titanium are slightly less than 1 percent. The median content of titanium (0.7 percent) is as high as the highest 95th percentile of the other black-shale sample sets. The minor-element content of these samples is very similar to that of average black-shale samples, with two exceptions: boron and zirconium. The median boron content of 0.03 percent is higher than that of most black-shale samples, and the median zirconium content of 0.05 percent is several times higher than that of most black-shale samples. Four of the 14 samples were reported to contain 0.07 percent zirconium, which is about three times the amount listed by Turekian and Wedepohl (1961) as the average for sandstone.

ELEMENT ASSOCIATIONS

The element groupings for the black shales of Late Mississippian age from western Wyoming are scattered on the two-factor vector diagram (fig. 10), but six groups can be distinguished from three-factor analysis of the correlation matrix. Detrital subgroup A consists of potassium, boron, equivalent uranium, sodium, calcium, vanadium, and chromium. Though largely independent, titanium, niobium, and zirconium are designated detrital subgroup B. A group that is composed of nickel, copper, manganese, and cobalt and that is inversely related to detrital subgroup A is designated minor-element subgroup A. Iron, lead, and molybdenum are unrelated to either detrital subgroup A or minor-element subgroup A and are designated minor-element subgroup B. Selenium is independent except for a correlation with lead. Minor-element subgroup C consists of lanthanum, strontium, and barium and is closely related to minor-element subgroup B. Organic carbon and magnesium, which fall between detrital subgroup A and minor-element subgroup C, form the organic-matter group. The dispersed nature of the element groupings in this set is due at least in part to the small range in values shown by analysis of the samples

ASHED SHALE FROM MINNELUSA FORMATION OF SOUTH DAKOTA AND WYOMING

ELEMENT ABUNDANCE

The carbonaceous rocks from the Minnelusa Formation of South Dakota and Wyoming (set 21) include lithologies ranging from black carbonaceous siltstone or claystone with abundant organic matter and little or no carbonate minerals to black dolomitic limestone with relatively few detrital minerals and little organic matter. The samples were ashed prior to spectrographic analysis because of the high organic content in some. Ash content ranged from 67 to 97 percent. Most of the reported major elements show a wide range in content. For example, the silicon content of the ashed samples ranges from 0.3 percent to greater than 10 percent; 14 of the 22 samples analyzed, however, contain more than 10 percent silicon. The median content of aluminum is 7 percent, and 10 samples contain more than 10 percent. Calcium content is greater than 10 percent in eight samples, and magnesium is greater than 10 percent in seven, but the medians for calcium and magnesium are only 2 percent each. In this set, potassium and sodium were not looked for, and the median content of iron is 2 percent. Fourteen samples contain 5 percent or more total carbon, and either organic carbon or mineral carbon is generally predominant. About one-third of the samples are rich in carbonate minerals, chiefly dolomite, as is indicated by their high magnesium content. Some of the minor elements are especially abundant in these black-shale and dolomite samples from the Minnelusa Formation. Unusually large amounts of molybdenum, vanadium, lead, and strontium occur, and cobalt, copper, lanthanum, silver, beryllium, chromium, and nickel are also enriched. These samples were all collected from weathered surface exposures, and possibly some of the more mobile minor elements have been enriched at the surface; whether all the high values can be thus explained is not known.

ELEMENT ASSOCIATIONS

In interpreting the element associations in set 21, the ashing prior to spectrographic analysis must be considered. Even though the ash content of the samples is high (average 88.7 percent), there tends to be some concentration of the elements in the ash. This concentration, however, is probably not great enough to significantly affect the coefficients of correlation. On the vector diagram (fig. 11), the elements fall into three main groups: (1) a detrital group composed of aluminum, silicon, titanium, chromium, vanadium, iron, strontium, barium, lanthanum, yttrium, and beryllium, (2) an organic-matter group, in the same quadrant as the detrital group, composed of organic carbon plus molybdenum, silver, lead, copper, nickel, and cobalt, and (3) a carbonate mineral group, inverse to the other two groups, composed of mineral carbon plus calcium, magnesium, and manganese. Ash is shown as a separate segment inverse to the organic-matter group. The association of strontium with the detrital group and its inverse relation to the carbonate group are unique to this set. Strontium shows its strongest correlation with vanadium, chromium, nickel, titanium, and aluminum.

SUMMARY

The nine sample sets of black shale and associated rocks described in this report are very diverse (table 1): They range in age from Precambrian to Eocene, their environments of deposition range from eugeosynclinal to shallow carbonate lake, and rocks sampled range from unweathered core to weathered outcrop; thus the geochemical distribution of elements also varies widely. Nevertheless, general behavior patterns for certain elements can be interpreted from the data.

The range in concentration of the elements detected in these nine sample sets of black shale and associated rocks is summarized in figure 12. The range and median of the set medians are shown for each element by a bar with open circles. Each of these is directly underlain by a second bar with solid circles that shows the range and median of the 95th percentiles for the nine sets. The minor elements are shown on the left in order of generally decreasing abundance, beginning with the most abundant minor element, vanadium. The major elements are plotted, also in order of decreasing abundance, on the right side of figure 12. For three of the major elements—aluminum, iron, and potassium—and eight of the minor elements—boron, cobalt, copper, manganese, nickel, scandium, yttrium, and zirconium—the lowest 95th percentile is equal to or greater than the median of the medians. This is not a geochemically cohesive group, for although it includes many elements that are commonly in the detrital group, it also includes several elements that are among the most mobile.

The elements that occur primarily with the detrital fraction show relatively small range in content within a single sample set, as shown in table 3, and include silicon, aluminum, potassium, titanium, and the minor elements boron, gallium, scandium, and zirconium. For most of these elements the concentration at the 95th percentile is commonly no more than one or two spectrographic steps greater than the median, and occasionally the median and the 95th percentile cannot be distinguished with available data; the range in concentration between sample

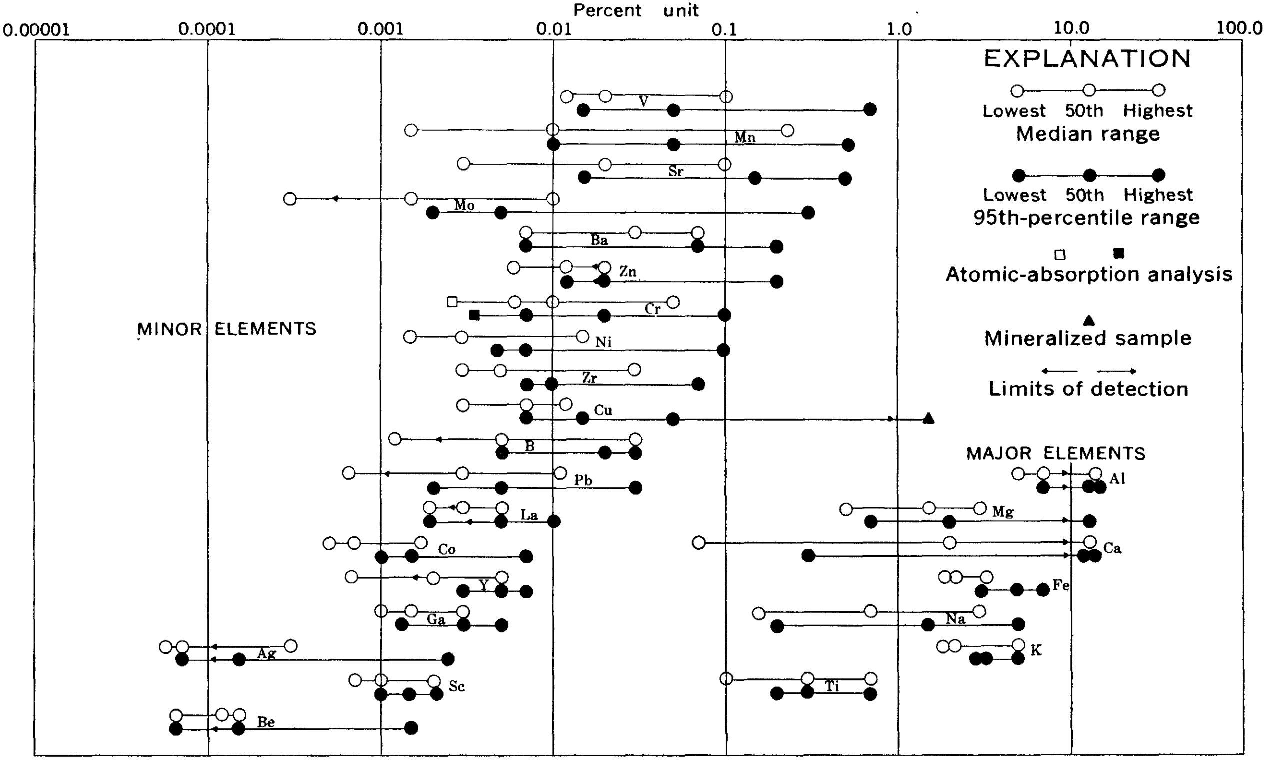

FIGURE 12.—Concentration range of chemical elements in nine sample sets of black shale and associated rocks.

sets is likewise small, as shown in figure 12. The highest 95th percentile is not significantly greater than the highest median for titanium, potassium, boron, and scandium. Silicon content was not shown in figure 12 because it is reported as greater than 10 percent in most of the samples.

Calcium and strontium are almost always associated with the carbonate fraction of the sample sets. A large range in their values in an individual sample set generally reflects a large range in carbonate content due to lithologic differences between the samples and does not reflect element mobility, as described in the following paragraphs. An exception to this general pattern of association of strontium with the carbonate fraction was found in the Minnelusa Formation (set 21), where strontium is unusually abundant and is associated with the detrital fraction. Its correlation with barium and iron suggests that strontium may occur as a sulfate and that it may have been epigenetically enriched. Manganese is associated with the carbonate fraction in the black shale from the Tacket Formation of Kansas (set 14), the Nonesuch Shale (set 16), and the Minnelusa Formatiton (set 21); magnesium is associated with the carbonate fraction in set 21 and in the Tyler Formation of central Montana (subset 15D). All four of these elements show a wide range in concentration between sample sets (fig. 12).

Minor elements associated with the organic matter of these sample sets commonly differ more than three spectrographic steps between the median and the 95th-percentile levels of abundance. These elements have greater mobility than do those that occur primarily with the detrital fraction. To whatever extent this mobility is real, it probably occurs during deposition, consolidation, and much later in the history of the rock, possibly even during weathering. The result during each episode is a local concentration of the elements. Content of these elements commonly varies directly with the amount of organic matter. Because organic matter is rarely a major constituent of these samples, the minor-element concentration is thought to be more a function of local physical and chemical controls in combination with the element mobility than of variations in lithology. The suite of chemically mobile elements varies from one sample set to another, but some of the same elements occur repeatedly. Chemically mobile elements in the black shale of the Tacket Formation of Kansas (set 14) include chromium, molybdenum, silver vanadium, and yittrium; those associated with the organic fraction of the Heath Formation in central Montana (subset 15C) include molybdenum, silver, vanadium, zinc, and possibly copper; and those having a similar association in the Minnelusa Formation of South Dakota and Wyoming (set 21) include lead, molybdenum, nickel, silver, and probably copper. These same mobile elements are evident in figure 12 by their extended ranges in concentration, especially between the highest median and the highest 95th percentile.

The greatest enrichment of minor elements among these nine sample sets occurs in the Nonesuch Shale of Michigan where copper and silver show no association with any of the major rock constituents. This occurrence is thought to reflect a definite secondary stage of mineralization and a distribution of the secondary elements that is not chemically controlled by variations within the rock unit.

Any search for "metal-rich" black-shale deposits of economic tenor should take into consideration the foregoing classification of the elements by association with major rock constituents. Elements that are sufficiently mobile to form epigenetic deposits or to be concentrated in association with organic matter are probably also those that possibly could occur in concentrations sufficiently high to form ore-grade deposits. Of the four sample sets that show a tendency to concentrate mobile elements, only the Nonesuch Shale of Michigan is known to contain commercially exploitable mineral deposits. The Heath Formation of central Montana, the Tacket Formation of Kansas, and the Minnelusa Formation of South Dakota and Wyoming may be worthy of additional study in the search for large low-grade deposits of mobile elements.

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