

# Element Distribution in Some Paleozoic Black Shales and Associated Rocks

By JAMES D. VINE

CONTRIBUTIONS TO GEOCHEMISTRY

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



**UNITED STATES DEPARTMENT OF THE INTERIOR**

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## CONTRIBUTIONS TO GEOCHEMISTRY

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### ELEMENT DISTRIBUTION IN SOME PALEOZOIC BLACK SHALES AND ASSOCIATED ROCKS

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By JAMES D. VINE

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#### ABSTRACT

The content of chemical elements in four sets of Paleozoic black-shale samples was determined, and the data were analyzed statistically in search of element associations that may have geochemical significance. Silicon, aluminum, titanium, zirconium, and gallium generally are the principal elements in the detrital mineral fraction of these rocks. Locally, boron, beryllium, scandium, and vanadium are also in the detrital fraction. Calcium, magnesium, and manganese are associated chiefly with the carbonate-mineral fraction, where present. Different groups of elements are associated with the organic-matter fraction of these rocks in the different sets of samples. In the hypersaline carbonate-rich detrital rocks of the Pennsylvanian Paradox Member of the Hermosa Formation of Utah, copper and zinc are associated with the organic matter, but neither element is highly concentrated in the rocks. The geochemical behavior of the minor elements in this evaporite basin is not known. Iron, cobalt, nickel, molybdenum, and uranium are associated with organic matter in the Devonian Chattanooga Shale of central Tennessee and northern Alabama, and uranium and cobalt tend to be enriched in this epicontinental shallow-sea deposit. Copper, nickel, vanadium, chromium, molybdenum, lead, and calcium are associated with organic matter in the Pennsylvanian black shales of southeastern Kansas and northeastern Oklahoma. Of these, vanadium, chromium, nickel, and lead seem to have been locally enriched in this brackish or marine shallow-water shelf environment. In the siltstones and phosphatic shales of the Permian Meade Peak Phosphatic Shale Member of the Phosphoria Formation, selenium, copper, molybdenum, chromium, nickel, and scandium are associated with organic matter in the detrital rocks; silver is more closely associated with the detrital mineral fraction; vanadium, zinc and lanthanum are associated with the organic matter in the more phosphatic shales; and yttrium is associated with phosphorite. All these elements except scandium are concentrated to an abnormally high degree in the Meade Peak Phosphatic Shale Member. The upwelling cold water that provided nutrients for an abundance of living organisms and that gave rise to the accumulation of phosphate along the margin of the Cordilleran miogeosyncline was probably also the source of the minor elements.

#### INTRODUCTION

The present report is the second in a series of reports describing the geochemical distribution of elements in black-shale deposits of differ-

ent environments and of different ages. The first report (Vine, 1966a) compared the element distribution in some shelf and eugeosynclinal black-shale samples grouped into four sets, numbered 1-4. The present report continues with the summary of chemical data pertaining to four more sample sets, numbered 5-8. The latter four sets represent four diverse environments of black-shale deposition; they are different mineralogically and were collected by different techniques. The samples were analyzed by a routine six-step spectrographic method for major and minor elements, and chemically for organic carbon and mineral carbon. The range in content of each of the elements determined is described, and the relations of the elements to different major constituents of the rocks are discussed.

Many fine-grained marine rocks are composed of various proportions of detrital minerals, chemically or biologically precipitated minerals, and organic matter. Refined laboratory techniques would be required to determine the proportions of each mineral species and to provide a means of interpreting the source of each. Therefore, the term "black shale" is used in a broad sense to include many dark-colored rocks that are not obviously classifiable as claystone, siltstone, limestone, dolomite, anhydrite, chert, phosphorite, or coal. These specific rock types commonly grade into black shale, and in some of the sets of samples, one or more end-member rock types are included. Where more than one end-member rock type was among the samples of black shale, the elements showed a much wider range in concentration. Furthermore, by including a few samples of the end-member rock types, the distribution of the minor elements with respect to the detrital mineral fraction, the chemically or biologically precipitated mineral fraction, and the organic-matter fraction can be more clearly defined.

#### ACKNOWLEDGMENTS

For their suggestions and encouragement in collecting the samples from southeastern Kansas, I thank F. C. Foley, State Geologist of Kansas, and various members of his staff. J. D. Love of the U.S. Geological Survey provided the necessary information to aid in collection of the Phosphoria Formation samples. J. I. Reese assisted in collecting these samples. The late Andrew Brown of the U.S. Geological Survey, at the time of his death in 1964, had an unpublished manuscript listing the locality and sample descriptions of the Chattanooga Shale cores. His locality and sample descriptions are included in the present report. O. B. Raup and R. J. Hite of the U.S. Geological Survey, as part of their studies of potash and other mineral commodities in the Paradox Basin, Utah, helped to obtain samples of the Paradox Member. E. B. Tourtelot and J. R. Keith assisted in the compilation of data.

Spectrographic analyses upon which this report is based were made by A. L. Sutton, Jr., and J. C. Hamilton, and most of the carbon analyses were made by I. C. Frost, all of the Denver laboratory of the U.S. Geological Survey. Other analyses were made in the Denver laboratory by E. J. Fennelly, G. T. Burrow, D. L. Skinner, Harriet Neiman, Wayne Mountjoy, J. D. Mensik, and Lorraine Lee. Uranium analyses of the Chattanooga Shale samples were made in the Washington laboratory of the U.S. Geological Survey by Carmen Hoy, Joseph Budinsky, B. A. McCall, J. H. Goode, J. Smith, and J. J. Warr.

M. S. Niles, P. A. Zimmerman, and Josephine Boerngen transcribed analytical data to punch cards. Computer programing and assistance was provided by R. N. Eicher, F. B. Sower, and G. I. Selner.

### SAMPLE SETS

Locality descriptions, listings of the individual stratigraphic intervals sampled, and analyses of individual samples for sets 5-8 are included in an open-file report (Vine, 1966b) available for consultation or reproduction at the libraries of the principal offices of the U.S. Geological Survey. Sample localities of sets 5-8 are shown in figure 1. Generalized descriptions of each sample set are given below.

Set 5 consists of 40 samples collected from outcropping black-shale beds of Pennsylvanian age in southeastern Kansas and northeastern Oklahoma. At least 13 different shale beds are represented by the 40 samples. The beds are dark gray to black, are fissile where even slightly weathered, and commonly contain fish scales, conodonts, and brachiopods. Phosphate nodules 1-2 cm (centimeters) across are especially characteristic of the Excello Formation of Searight and others (1953), but they also occur in many of the other beds. Typically, these black-shale beds are 1-3 feet thick, and they overlie a bed of coal and are overlain by marine limestone. Exceptions to this generalization are the Pleasanton Group, which is as much as 15 feet thick, and the Eudora Shale Member, which separates two limestone beds in the Stanton Limestone. The stratigraphic sequence of black-shale units and the number of samples collected from each unit are given in table 1.

Set 6 consists of samples from the entire sequence of black siltstone, phosphorite, dolomite, and limestone of the Meade Peak Phosphatic Shale Member of the Phosphoria Formation of Permian age. The member is exposed in a mine opening at Raymond Canyon in Sublette Ridge, Lincoln County, Wyo. The strata in this part of the western Wyoming fold belt are nearly vertical, strike approximately north, and dip to the east. The main adit extends along the strike of the beds. Open crosscuts perpendicular to the strike of the beds provide easy

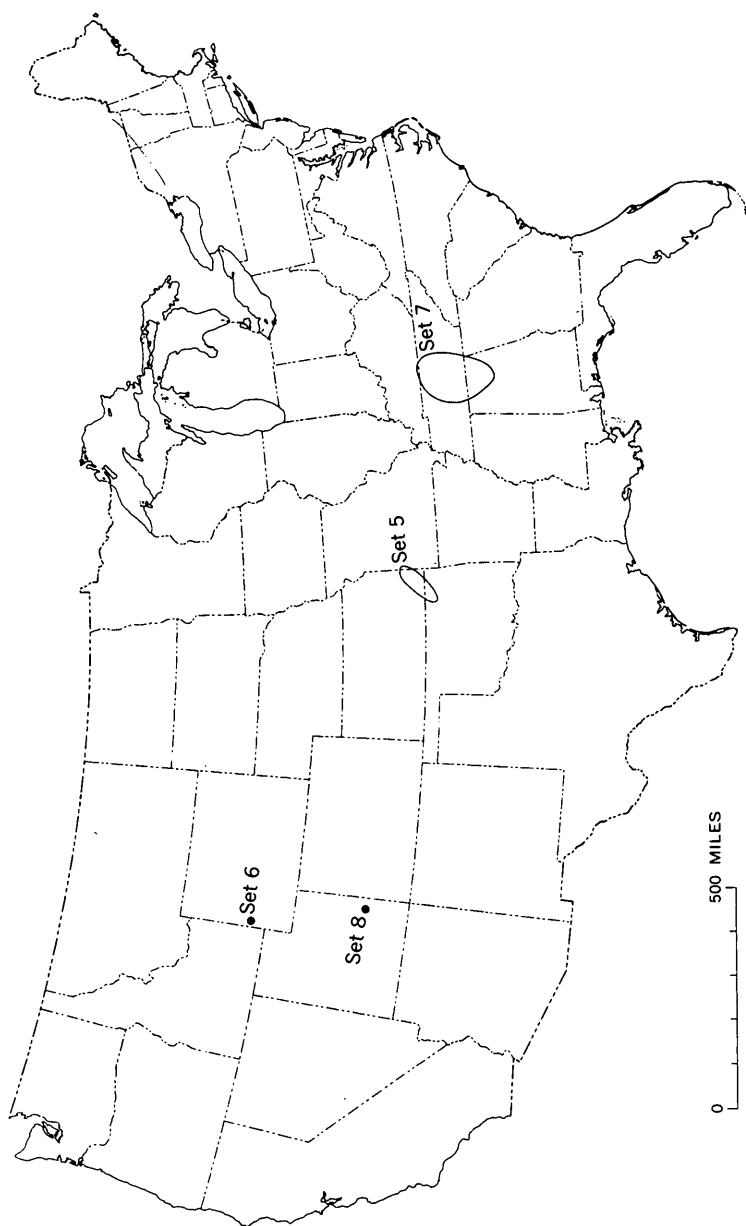


FIGURE 1.—Sample localities of black-shale sample sets 5-8. Set numbers refer to data in tables 2-11 and to Vine (1966b). Set 5, Pennsylvanian black shales, southeastern Kansas and northeastern Oklahoma; set 6, Permian Meade Peak Phosphatic Shale Member of the Phosphoria Formation, Wyoming; set 7, Devonian Chattanooga Shale, central Tennessee and northern Alabama; and set 8, Pennsylvanian Paradox Member of the Hermosa Formation, Utah.



ELEMENT DISTRIBUTION IN PALEOZOIC BLACK SHALES G5

TABLE 1.—*Stratigraphic sequence of black-shale units from which samples in set 5 were collected*

[The intervening members or formations that were not sampled are not shown]

System	Series	Group	Formation	Member	Number of samples
PENNSYLVANIAN	MISSOURI	LANSING	Stanton Limestone	Eudora Shale	2
		KANSAS CITY	Iola Limestone	Muncie Creek Shale	2
		PLEASANTON			3
	DES MOINES	MARMATON	Pawnee Limestone	Mine Creek Shale	1
				Anna Shale	2
			Fort Scott Limestone	Little Osage Shale of Jewett (1941)	3
		CABANISS SUBGROUP OF HOWE (1956)	Excello Formation of Searight and others (1953)		14
			Verdigris Formation of Smith (1928)		3
			Croweburg Formation of Abernathy (1937)		1
			Scammon Formation of Abernathy (1937)	Tiawah Limestone of Searight and others (1953)	3
			Tebo Formation of McQueen (1943)		3
		KREBS SUBGROUP OF HOWE (1956)	Bluejacket Formation of Howe (1956)		1
			Warner Formation of Howe (1956)		2

access to almost the complete thickness of the Meade Peak Member. As samples were collected underground, they are unweathered and show no evidence of the fissility characteristic of many of the silty beds in outcrop. The samples were collected from individual beds 0.4–8.5 feet thick and are intended to represent the various lithologies

present. Rock types in the Meade Peak Member grade into each other in all proportions. Viewed in thin section, many samples were found to contain recognizable amounts of carbonaceous matter, silt grains, phosphate oolites, and carbonate minerals. Pure siltstone, dolomite, and phosphorite are less common than the mixed lithologies. Mineral identification by X-ray diffraction of a number of samples showed major amounts of quartz, dolomite, and carbonate-fluorapatite, as well as minor amounts of calcite, mica, and feldspar and very small amounts of clay minerals. The stratigraphic sequence, petrology, mineralogy, and chemistry of the Meade Peak Shale Member at nearby Coal Canyon were described by Gulbrandsen (1960).

Set 7 consists of samples representing the complete section of Chattanooga Shale of Late Devonian age as penetrated in five core holes in the interior low plateau of central Tennessee and northern Alabama. These five cores were selected on the basis of availability and geographic distribution from about 75 cores drilled by the U.S. Geological Survey and the U.S. Bureau of Mines on behalf of the U.S. Atomic Energy Commission. The "standard section" of the Chattanooga Shale, as exposed in a roadcut near Sligo Bridge, 7 miles east of Smithville, De Kalb County, Tenn., was described by Conant and Swanson (1961 p. 24). There, the Chattanooga Shale consists of five major units: the Gassaway Member, at the top, comprises the three upper units, and the Dowelltown Member, at the base, comprises the two lower units. The upper and lower units of the Gassaway Member and the lower unit of the Dowelltown Member consist chiefly of black silty shale. The other two intervening units contain some gray as well as black laminae. The five cores were sampled, and the geologic units were identified by L. C. Conant, T. M. Kehn, Andrew Brown, and Lynn Glover, U.S. Geological Survey. In only one of the five cores, C-12, were all five units of the Dowelltown and Gassaway Members identified by the samplers. This core, 33.36 feet long, drilled near the standard section, was divided into 28 samples that range from 0.44 to 2.58 feet in length. In two cores, only the Gassaway Member was recognized. In the other two cores, both members were recognized, but the individual units were not. The 23 samples from core holes C-53, C-47, C-60, and C-65 represent a total thickness of more than 69 feet, and the individual samples range from 0.80 to 5.36 feet in length.

Set 8 consists of 25 core samples of carbonate-rich black shale from the saline facies of the Paradox Member of the Hermosa Formation, of Pennsylvanian age, taken from a drill hole near the crest of the Cane Creek anticline about 7 miles southwest of Moab, Utah. The saline facies, as defined by Hite (1960, 1961), consists of a sequence of at least 29 evaporite cycles (numbered from the top down). Each

complete cycle includes beds of black shale, limestone, dolomite, anhydrite, and halite. Southwestward, the limestone and dolomite beds tend to thicken and merge at the expense of the anhydrite and halite; the halite is thickest in the central and northeastern parts of the basin. The 30 or more beds of black shale, 10–40 feet thick, commonly extend the entire width of the basin. Of the black-shale core samples, 12 were collected from the interval between salt beds 3 and 4; nine were collected from the interval between salt beds 4 and 5; and four were collected from the interval between salt beds 2 and 3. Individual samples averaged about 0.1 foot thick.

The major minerals of several black-shale samples, as shown by X-ray diffraction analysis, are quartz, calcite, dolomite, and mica. Minor amounts of anhydrite and halite are present in some samples. In thin section, carbonate and mica grains less than 0.05 mm (millimeters) across can be distinguished, but most of the quartz is too fine grained to be readily visible. The samples have a nearly homogeneous texture, with a faint indication of lamination resulting from horizontal lenses of pyrite, calcite, and carbonaceous matter. Some calcite lenses are flattened whole brachiopod shells whose interior cavities are filled with pyrite and sphalerite.

The four sets of samples are markedly different in lithology, environment of deposition, degree of weathering, and age. The Pennsylvanian shales from southeastern Kansas and northeastern Oklahoma (set 5) were probably deposited in a transgressive shallow brackish-water or marine shelf north of the Ouachita geosyncline and adjacent to shore areas where coal swamps were forming. The presence of fish remains and phosphatic nodules suggests that life was abundant, but most of the organic matter in these rocks is too fine grained to be specifically identified. This organic matter probably consists of humic materials from the nearby coal swamps intermixed with marine plants and animals, all of which have been decomposed by the action of micro-organisms. These samples were collected from outcrops and, therefore, have been somewhat altered by weathering.

The Meade Peak samples (set 6) include phosphorite and dolomite, in addition to black siltstone; thus, they include a much wider range of lithologies than the other sample sets. In discussing the distribution of the carbonaceous rocks in the Phosphoria Formation, McKelvey and others (1959, p. 2, 23–24) suggested that the organic muds accumulated under reducing conditions near the east margin of the Cordilleran miogeosyncline in a relatively shallow marine shelf a considerable distance from land. Furthermore, they suggested that the phosphate and other chemical sediments in the Phosphoria were derived from upwelling cold oceanic waters, following a mechanism proposed by

Kazakov (1937) to explain the origin of nutrients required to support a tremendous bloom of plankton and nekton. The organic matter is therefore probably chiefly of marine origin, including mainly plankton and fish, but for most of the organic matter the specific organisms cannot be identified.

The Chattanooga Shale samples (set 7) are from a unit deposited in quiet marine waters on an intracratonic platform which was part of a broad epicontinental sea that extended westward from a geosyncline. The unit is thickest in eastern West Virginia. At times this inland sea spread as far west as New Mexico and Montana. The marine origin of the black shale is generally accepted on the basis of the conodonts, lingulid brachiopods, and other fossils present, and quiet water is generally inferred, owing to the uniform, thinly laminated character of the rocks. Some geologists have preferred the explanation that deposition in deep water sustained the stagnant environment necessary to preserve organic matter. Conant and Swanson (1961, p. 62) suggested, however, that the Chattanooga Shale was deposited in water only a few tens of feet deep, and this interpretation seems to be well documented. Plant material, including spores and sparse woody fragments, occurs throughout the Chattanooga (J. M. Schopf, written commun., 1953), but the proportions of terrestrial and marine organisms that have contributed to the carbonaceous matter are not easily determined. From a study of oil yield and uranium content of identifiable humic and sapropelic constituents in the Chattanooga Shale and its equivalents, Swanson (1960, p. 11, 12) estimated that each kind of organic matter comprises about half of the total organic matter in the rock. Breger and Brown (1963), however, concluded from a study of organic isolates that most of the organic matter in the Chattanooga Shale is related to coal and is of terrestrial origin. This latter conclusion is difficult to accept because of the widespread distribution of phosphate in the Chattanooga Shale, which suggests that a large area of shallow water supported abundant life.

The calcareous black-shale beds of the Paradox Member of the Hermosa Formation (set 8) were deposited in a deep hypersaline marine basin in Pennsylvanian time (Hite, 1960; 1961). The basin formed on the southwest margin of the ancestral Uncompahgre uplift, which provided a local source of clastic material. The finer fraction of the clastic material was intermittently spread across the entire basin as an euxinic mud between each of the 29 evaporite cycles of the saline facies. Microscopic examination of the organic matter indicates it occurs as thin films surrounding mineral grains. Oil and gas are reported to be commonly associated with the black-shale beds, which suggests that the organic matter was probably chiefly sapropel.

## CHEMICAL METHODS OF ANALYSIS

The analyses on which this report is based were done 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, and so on, and are reported arbitrarily as midpoints of these intervals, using the numbers 1, 0.7, 0.5, 0.3, 0.2, 0.15, 0.1, and so on. The precision of a reported value is approximately plus or minus one interval at 68 percent confidence, or approximately two intervals at 95 percent confidence. Separate analyses were made for total carbon and carbon in carbonate minerals after the methods outlined by Tourtelot, Huffman, and Rader (1964, p. D74). Organic carbon was calculated by taking the difference between total carbon and carbonate carbon. On some samples, several chemical analyses were made to determine the content of certain constituents—MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, Li, Zn, Cl, and S for set 8; P<sub>2</sub>O<sub>5</sub> and Se for set 6; and U for set 7. Radioactivity was measured for samples in sets 6 and 8 and expressed as eU (equivalent uranium), a measure of the radioactivity expressed as though uranium in equilibrium with its daughter products were the only source.

## STATISTICAL METHODS

Statistical analyses of the four sample sets were conducted in much the same manner as was described in a previous report (Vine 1966a). The 5th, 25th, 50th, 75th, and 95th percentiles and the arithmetic and geometric means were calculated for each variable, and the product moment coefficient of correlation was calculated for each pair of variables after first making a log transformation to place the data into a more nearly normal frequency distribution. Because the analyses commonly contain three types of indeterminate values (greater than, less than, and not detected), the substitutions given in table 2 were made in the data sets before correlations were calculated.

The substituted values are somewhat arbitrary, but they are slightly less than the lower limit of spectrographic or chemical determinations and are thought to introduce less bias in the estimation of correlation statistics than would be introduced by the exclusion of samples for which indeterminate values were reported. If more than 25 percent of the analyses for any element were reported as indeterminate values, the element was not used in the correlation studies.

The interpretation of geochemical associations in the rock units studied is based primarily on coefficients of correlation for each pair of constituents (tables 4, 6, 8, 10). The coefficients measure the degree to which log concentrations fit a straight line when plotted on a

TABLE 2.—*Substitutions made in data sets 5–8*

[&gt;, greater than; n.d. not detected; &lt;, less than]

Element	Number of samples	Reported value (percent)	Value substituted (percent)
Set 5 (40 samples)			
Ca-----	3	>10	15
K-----	1	n.d.	.5
B-----	2	n.d.	.0015
Be-----	1	n.d.	.00007
Co-----	5	n.d.	.0002
Ga-----	1	n.d.	.0007
La-----	1	n.d.	.0015
Mo-----	10	n.d.	.0002
Sc-----	1	n.d.	.0003
Set 6 (43 samples)			
Mg-----	1	>10	15
K-----	9	n.d.	.5
Ag-----	1	n.d.	.0001
Ga-----	1	n.d.	.00015
La-----	4	n.d.	.002
Sc-----	8	n.d.	.0003
Zn-----	6	n.d.	.015
Set 7 (51 samples)			
Al-----	8	>10	15
Set 8 (25 samples)			
C <sub>org</sub> -----	1	<0.2	0.15
eU-----	3	<.001	.0007

bivariate diagram, and the sign of the coefficient indicates whether the line of best fit has a positive or negative slope. If the bivariate-frequency distribution does not deviate markedly from the normal form, and if the data can be regarded as a random sample from the rock units represented, the statistical significance of the coefficients may be determined from published tables of critical values. (For example, see Davies, 1954, p. 276.) Tables 5, 7, 9, and 11 list the more significant correlations for each element. These coefficients of correlation can be viewed as an index of geochemical associations among the samples analyzed, even where ideal sampling of the rock unit was not fully realized.

Groups of associated elements are further identified from the correlation matrices by the use of principal-component analysis, a technique described by Harman (1960). The principal-component analysis

has recently been applied to a variety of geologic problems, some of which were described by Imbrie and VanAndel (1964) and by Griffiths (1966). The technique involves constructing radial vectors for each of the chemical constituents so that the cosine of the angle between any two vectors is equal to the coefficient of correlation. The vectors are then rotated and projected onto a two-dimensional diagram on which axes have been selected that will best represent most of the data in two dimensions.<sup>1</sup> In two-dimensional diagrams the relative lengths of the projected vectors are a function of how well each element is represented in the two-dimensional system. In the diagrams (figs. 2-5) the radial lines have been omitted for clarity, and only the position of the elements within a circle of unit radius is shown. The variously shaded segments of each diagram suggest possible geochemical groupings of the elements. The resulting groups of elements are thought to be the result of different physical and chemical processes in the depositional environment and subsequent alteration of each rock unit. However, the data are part of a closed array, a factor which complicates the interpretation of the groups. This problem, described by Chayes (1960), can be thought of as one of dilution. For example, the end members of such major rock constituents as detrital quartz, carbonate minerals, and clay can be regarded as pure siltstone, limestone, or shale that contains only one of the three constituents. A built-in negative correlation must necessarily exist between the dominant major constituent and the other two principal constituents. A corresponding positive correlation is imposed on some of the minor constituents that result entirely from the dilution process. The process of dilution is therefore a factor affecting the magnitude of any correlation coefficient given in tables 4, 6, 8, and 10.

### DISTRIBUTION AND ASSOCIATION OF ELEMENTS

The distribution and association of elements is described separately for each sample set because each set is different with respect to lithology, environment of deposition, and sampling technique. Consequently, each set is geochemically different. The amount of each element or other constituent in the sample sets is listed in table 3, and the coefficient of correlation calculated for each pair of constituents is listed in tables 4, 6, 8, and 10. The lists of element associations (tables 5, 7, 9, 11) and the vector diagrams constructed from the correlation data (figs. 2-5) aid in understanding and interpreting the element associations. In discussions of the relative abundances of the major elements, the elements normally detected by the six-step spec-

<sup>1</sup> Examination of the eigenvalues of the correlation matrices, and of communalities of variables on rotation into more than two dimensions, has failed to reveal more than two principal components with any acceptable degree of certainty.

trographic method and the chemically determined organic carbon and mineral carbon are considered. Where such elements as silicon, aluminum, calcium, magnesium, and phosphorus are reported in concentrations greater than 10 percent, the precise concentrations in the individual samples are unknown; but in some sample sets the median abundances can still be estimated (table 3).  $C_{min}$  (carbonate carbon) is a major constituent in two sets and is an insignificant constituent in the other two sets.

#### PENNSYLVANIAN BLACK SHALES FROM KANSAS AND OKLAHOMA

*Major elements.*—More than 10 percent silicon was reported from all but a few samples of black shale in set 5. Silicon is probably the most abundant element after oxygen. Carbon, with a median content of 15 percent, is probably the next most abundant element. The carbon is assumed to be chiefly of organic origin; mineral carbon content is negligible. The median contents of the other major elements are aluminum, 7 percent; potassium, 2 percent; iron, 1.5 percent; calcium, 1.5 percent; magnesium, 0.7 percent; sodium, 0.7 percent; and titanium, 0.1 percent.

*Minor elements.*—The minor-element distribution for the black shales in sample set 5 is similar to that in other black shales associated with coal beds in the Interior coal province. However, compared with the previously studied black shales from the western Kentucky coal field (Vine, 1966a), the 0.03-percent median chromium content is high. At the 95th percentile the contents of strontium, lead, vanadium, nickel, and zinc are also high. Conversely, the high molybdenum values that seemed to characterize the black shales from Kentucky were not found here.

TABLE 3.—*Element content in four sets of Paleozoic black-shale samples*

[Chemical analyses were made to determine  $MgO$ ,  $CaO$ ,  $Na_2O$ ,  $K_2O$ ,  $Li$ ,  $Zn$ ,  $Cl$ , and  $S$  for set 8;  $P_2O_5$  and  $Se$  for set 6; and  $U$  for set 7. Radioactivity was measured and expressed as  $eU$  (equivalent uranium) for sets 6 and 8. Parentheses indicate that content of element was recalculated to elemental form. All other analyses were made by the semiquantitative spectrographic method described on p. G9. See p. G3 for list of analysts]

Element or constituent	Set	Values, in percent, for indicated percentile					Arithmetic mean	Geometric mean
		$P_5$	$P_{25}$	$P_{50}$	$P_{75}$	$P_{95}$		
Si.....	5	7	>10	>10	>10	>10	-----	-----
	6	1.5	3	7	>10	>10	8.1	6.4
	7	>10	>10	>10	>10	>10	-----	-----
	8	1.5	>10	>10	>10	>10	12.2	11
Al.....	5	5	7	7	7	>10	-----	-----
	6	.3	1.5	1.5	3	3	1.8	1.5
	7	7	7	7	7	>10	7.9	7.6
	8	.7	3	5	7	7	4.7	4
Fe.....	5	.7	1	1.5	2	3	1.6	1.5
	6	.3	.7	.7	1.5	2	1.1	.92
	7	2	2	3	3	5	2.8	2.7
	8	.7	1	1	1.5	2	1.3	1.2



# ELEMENT DISTRIBUTION IN PALEOZOIC BLACK SHALES G13

TABLE 3.—*Element content in four sets of Paleozoic black-shale samples—Continued*

Element or constituent	Set	Values, in percent, for indicated percentile					Arithmetic mean	Geometric mean
		P <sub>1</sub>	P <sub>25</sub>	P <sub>50</sub>	P <sub>75</sub>	P <sub>95</sub>		
Mg.....	5	0.3	0.7	0.7	0.7	1	0.71	0.65
	6	.2	.7	1.5	3	7	2.5	1.5
	7	.7	.7	.7	1	1.5	.80	.78
MgO.....	8	4.9	5.6	6.9	9.5	17	8.6	7.9
(Mg).....		(3.0)	(3.4)	(4.2)	(5.7)	(10)	(5.2)	(4.8)
Ca.....	5	.15	.7	1.5	3	15	2.9	1.7
	6	5	>10	>10	>10	>10	-----	-----
	7	.015	.15	.3	.7	1	.51	.24
CaO.....	8	4	9.9	17	20	24	16	15
(Ca).....		(2.9)	(7.1)	(12)	(14)	(17)	(11)	(11)
Na.....	5	.2	.3	.7	.7	1	.64	.56
	6	.3	.5	.7	1	1.5	.80	.72
	7	.3	1	1	1	1	.90	.82
Na <sub>2</sub> O.....	8	.21	.42	.68	.97	5.9	1.2	.76
(Na).....		(0.16)	(0.31)	(0.50)	(0.71)	(4.4)	(0.89)	(0.56)
K.....	5	1.5	2	2	2	3	2.2	2.1
	6	.5	1	2	2	3	1.7	1.4
	7	3	3	3	3	3	3.2	3.2
K <sub>2</sub> O.....	8	.75	2.2	2.5	3.1	5	2.7	2.5
(K).....		(0.62)	(1.8)	(2.1)	(2.6)	(4.2)	(2.2)	(2.1)
Tl.....	5	.07	.10	.1	.15	.2	.13	.12
	6	.02	.07	.1	.15	.2	.11	.094
	7	.15	.15	.2	.2	.2	.19	.19
	8	.03	.07	.1	.1	.15	.084	.080
P.....	5	<.2	<.2	.5	.7	1.5	-----	-----
P <sub>2</sub> O <sub>5</sub> .....	6	1.5	7	15	30	30	17.5	13.5
(P).....		(0.65)	(3.1)	(6.5)	(13)	(13)	(7.6)	(5.9)
P.....	7	<.2	<.2	<.2	<.2	<.2	-----	-----
	8	<.2	<.2	<.2	<.2	<.2	-----	-----
Mn.....	5	.002	.007	.01	.02	.05	.014	.0095
	6	.0015	.005	.01	.015	.02	.011	.0086
	7	.005	.01	.01	.015	.03	.012	.011
	8	.01	.015	.015	.015	.02	.015	.014
C total.....	5	1.5	5	15	15	20	16	8.6
	6	3	7	10	10	15	9	8.3
	7	2	7	10	15	15	10	8.8
	8	3.3	4.9	6.7	7.8	9.9	6.4	6.1
C mineral.....	6	.7	1	3	5	7	3.2	2.2
	8	.99	2.9	4	6.2	9.1	4.5	3.9
C organic.....	6	1	3	5	7	15	5.8	4.6
	8	<.2	.8	2.1	2.9	3.4	2.0	1.5
Cl.....	8	<.7	1.5	2	5	7	-----	-----
S.....	8	<.1	<.1	.15	.7	3	-----	-----
Ag.....	5	<.0001	<.0001	.00015	.0002	.0007	-----	-----
	6	.0002	.0005	.001	.0015	.002	.00097	.00081
	7	<.0001	<.0001	<.0001	<.0001	.0001	-----	-----
	8	<.0001	<.0001	<.0001	<.0001	<.0001	-----	-----
B.....	5	.0015	.002	.003	.003	.005	.0031	.0030
	6	<.003	<.003	<.003	.005	.015	.0034	.0025
	7	.005	.007	.007	.007	.01	.0089	.0066
	8	.003	.005	.01	.015	.02	.010	.0090
Ba.....	5	.015	.02	.02	.02	.05	.025	.023
	6	.005	.007	.01	.015	.02	.012	.011
	7	.02	.02	.03	.03	.05	.030	.029
	8	.005	.015	.02	.03	.05	.023	.020
Be.....	5	.0001	.00015	.00015	.0002	.0002	.00018	.00017
	6	<.00015	<.00015	<.00015	<.00015	.00015	-----	-----
	7	.00015	.0002	.0002	.0003	.0003	.00024	.00024
	8	<.0001	<.0001	<.0001	.0001	.00015	-----	-----
Co.....	5	.0002	.0005	.0007	.001	.001	.00073	.00064
	6	<.0007	<.0007	<.0007	<.0007	.0007	-----	-----
	7	.001	.0015	.002	.003	.005	.0022	.0021
	8	<.0005	<.0005	.0005	.0005	.0007	-----	-----

TABLE 3.—*Element content in four sets of Paleozoic black-shale samples—Continued*

Element or constituent	Set	Values, in percent, for indicated percentile					Arithmetic mean	Geometric mean
		P <sub>5</sub>	P <sub>25</sub>	P <sub>50</sub>	P <sub>75</sub>	P <sub>95</sub>		
Cr.....	5	0.007	0.01	0.03	0.05	0.05	0.029	0.022
	6	.02	.07	.1	.15	.7	.15	.099
	7	.005	.007	.007	.007	.01	.0069	.0067
	8	.005	.005	.007	.02	.03	.013	.010
Cu.....	5	.002	.005	.007	.01	.01	.0070	.0062
	6	.003	.005	.007	.01	.03	.010	.0098
	7	.007	.01	.01	.015	.015	.012	.011
	8	.0007	.001	.002	.003	.005	.0022	.0019
Ga.....	5	.001	.001	.0015	.002	.002	.0016	.0015
	6	.0002	.0007	.0015	.002	.003	.0013	.0010
	7	.0015	.0015	.002	.002	.002	.0020	.0019
	8	.0005	.0007	.0015	.0015	.003	.0013	.0012
La.....	5	.002	.003	.003	.005	.005	.0038	.0037
	6	.002	.005	.01	.02	.07	.015	.010
	7	.003	.003	.003	.005	.005	.0037	.0037
	8	.001	.002	.003	.005	.005	.0030	.0026
Li.....	8	.0026	.0032	.0043	.0066	.0085	.0050	.0046
Mo.....	5	.0002	.0002	.001	.002	.005	.0017	.00095
	6	.001	.002	.005	.01	.02	.0074	.0049
	7	.0015	.003	.007	.01	.01	.0071	.0057
	8	<.0005	<.0005	<.0005	<.0005	.0007	-----	-----
Nd.....	6	<.015	<.015	<.015	.015	.03	-----	-----
Ni.....	5	.0015	.005	.01	.015	.02	.011	.0088
	6	.002	.01	.015	.02	.07	.020	.015
	7	.007	.007	.01	.01	.015	.0089	.0086
	8	.0015	.0015	.003	.005	.007	.0035	.0030
Pb.....	5	.001	.002	.003	.005	.01	.0041	.0033
	6	<.001	<.001	.001	.0015	.002	-----	-----
	7	.002	.002	.003	.003	.005	.0031	.0030
	8	<.001	<.001	.001	.001	.005	.0011	.00094
Sc.....	5	.0007	.001	.001	.0015	.002	.0012	.0011
	6	.0003	.0007	.0007	.001	.002	.00088	.00076
	7	.001	.001	.0015	.0015	.002	.0014	.0013
	8	<.0007	.0007	.0007	.001	.0015	-----	-----
Se.....	6	.002	.003	.007	.01	.015	.0070	.0056
Sr.....	5	.015	.015	.02	.02	.05	.022	.021
	6	.03	.07	.1	.2	.3	.13	.11
	7	.007	.01	.01	.015	.02	.012	.012
	8	.015	.02	.05	.07	.1	.046	.038
V.....	5	.007	.01	.015	.05	.07	.026	.019
	6	.007	.02	.05	.10	.2	.063	.042
	7	.015	.015	.015	.02	.05	.020	.019
	8	.002	.005	.005	.007	.01	.0060	.0056
Y.....	5	.0015	.002	.003	.003	.005	.0031	.0030
	6	.002	.007	.015	.02	.07	.020	.013
	7	.003	.003	.003	.005	.005	.0037	.0036
	8	.001	.0015	.0015	.003	.003	.0023	.0022
Yb.....	8	.0001	.0002	.0002	.0002	.0003	.00019	.00018
eU.....	6	<.001	.002	.005	.01	.02	.0071	.0044
	8	<.001	.001	.002	.003	.004	.0020	.0017
U.....	7	.0007	.003	.005	.007	.01	.0051	.0041
Zn.....	5	<.03	<.03	<.03	.05	.1	-----	-----
	6	.015	.07	.15	.3	1	.22	.13
	7	<.03	<.03	<.03	<.03	.03	-----	-----
	8	.0008	.0019	.0034	.0053	.011	.0048	.0035
Zr.....	5	.002	.003	.005	.007	.01	.0051	.0044
	6	.003	.005	.007	.01	.02	.0081	.0071
	7	.007	.01	.01	.01	.015	.010	.010
	8	.001	.003	.005	.007	.01	.0055	.0047

*Correlation data.*—The vector diagram (fig. 2) and the correlation coefficients and element associations (tables 4 and 5) suggest the possibility of grouping the elements reported from the Pennsylvanian black shales of Kansas and Oklahoma into four major groups. Elements in each group tend to have a strong positive intercorrelation. Chromium, nickel, copper, molybdenum, lead, vanadium, and calcium are thought to be associated chiefly with organic matter and are in the group that includes  $C_{org}$  (organic carbon). The group with organic carbon also tends to have a negative correlation with the group that includes titanium, zirconium, boron, gallium, and scandium. This second group contains many of the elements that commonly occur in detrital minerals, and so it may be regarded as a detrital-mineral group. In the third and

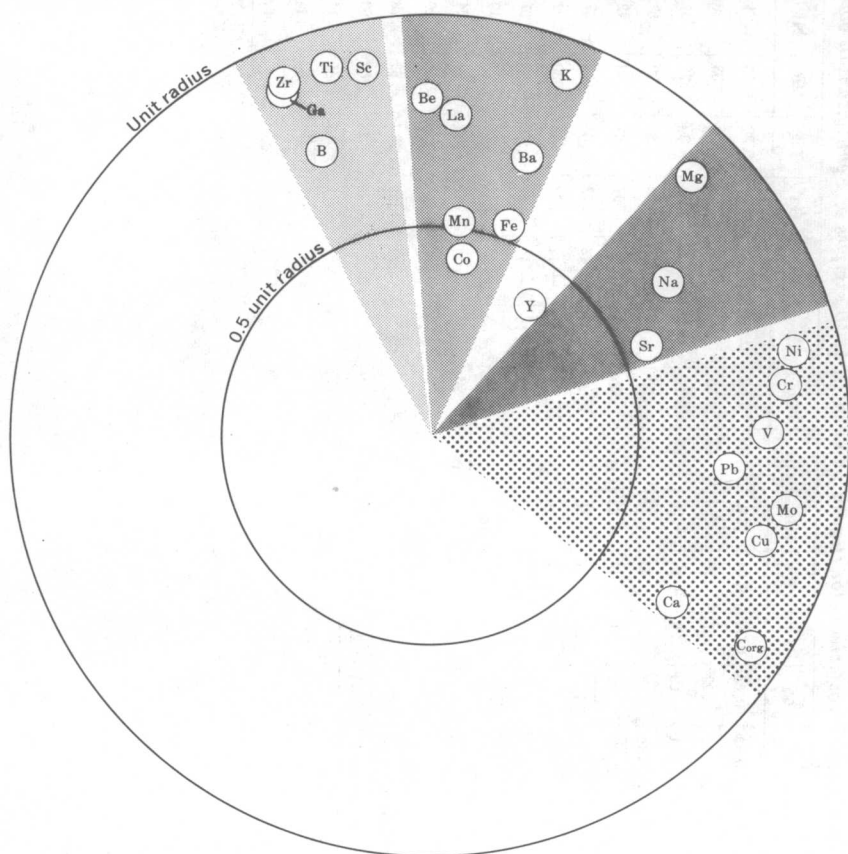


FIGURE 2.—Rotated two-dimensional vector diagram showing the principal-component analysis of the correlation matrix for set 5, 40 samples of Pennsylvanian black shales from Kansas and Oklahoma. Patterned areas suggest geochemical groupings of elements.

TABLE 4.—Correlation coefficients for element pairs in set 5, 40 samples of Pennsylvanian black shales from Kansas and Oklahoma

Fe	Mg	Ca	Na	K	Ti	Mn	B	Ba	Be	Co	Cr	Cu	Ga	La	Mo	Ni	Pb	Sc	Sr	V	Y	Zr	C
Fe	0.39	-0.18	0.04	0.43	0.55	0.36	0.04	0.42	0.35	0.17	0.14	-0.16	0.29	0.30	0.15	0.24	0.08	0.36	0.23	0.29	0.05	0.39	0.07
	Mg	.29	.59	.77	.29	.57	.26	.50	.44	.36	.53	.35	.24	.40	.33	.66	.22	.43	.49	.42	.27	.27	.05
		Ca	.26	-.11	-.60	.26	-.38	-.28	-.36	.15	.17	.59	-.53	-.30	.33	.37	.33	.51	.44	.23	.22	-.70	.52
			Na	.44	.13	.20	.33	.27	.22	.30	.44	.47	.20	.39	.32	.57	.45	.18	.24	.23	.19	.06	.23
				K	.63	.54	.46	.68	.63	.35	.35	.08	.57	.61	.08	.42	.10	.68	.34	.23	.38	.56	-.27
					Ti	.39	.57	.53	.64	.29	-.06	-.43	.78	.65	-.34	-.07	-.19	.83	.05	-.14	.20	.84	-.57
						Mn	.21	.19	.38	.52	-.12	-.12	.32	.20	-.30	.22	-.16	.37	.35	-.17	.20	.25	-.16
							B	.19	.59	.34	-.10	-.19	.77	.52	-.35	.01	-.21	.61	-.16	-.35	.05	.63	-.47
								Ba	.43	-.05	.35	-.11	.46	.60	.16	.19	.04	.40	.28	.30	.39	.51	-.19
									Be	.49	.09	-.17	.71	.47	-.14	.24	.07	.77	.06	-.03	.10	.66	-.31
										Co	-.13	.05	.30	.07	-.17	.29	.10	.41	.12	-.20	.07	.18	-.11
											Cr	.61	-.19	.17	.82	.78	.59	.02	.29	.82	.13	-.06	.46
												Cu	-.40	-.25	.67	.63	.59	-.31	.33	.51	.04	-.54	.56
													Ga	.57	-.45	-.14	-.19	.72	-.10	-.36	.10	.78	-.88
														La	-.08	.14	.00	.62	.25	.11	.49	.64	-.33
															Mo	.67	.61	-.26	.29	.89	.06	-.30	.60
																Ni	.62	.06	.29	.61	.10	-.12	.60
																	Pb	-.11	.19	.47	.01	-.34	.63
																		Sc	.10	-.08	.08	.79	-.60
																			Sr	.46	.48	-.10	.02
																				V	.18	-.12	.41
																					Y	.11	-.12
																						Zr	-.68
																							C

Level of significance:

95 percent	99 percent	99.9 percent
0.31	0.41	0.50

TABLE 5.—*Element associations in set 5, 40 samples of Pennsylvanian black shales from Kansas and Oklahoma*

[Elements are listed in order of increasing correlation coefficients. Regular type used where the level of significance exceeds 95 percent; boldface type where the level of significance exceeds 99 percent]

Negative correlation ←	Element	→ Positive correlation
Ca, C, Cu, Mo	Ti	Mn, Ba, Fe, B, K, Be, La, Ga, Sc, Zr
Ca, C, Cu, Pb	Zr	Fe, Ba, K, B, La, Be, Ga, Sc, Ti
C, Ca, Mo, Cu, V	Ga	Mn, Ba, La, K, Sc, Be, B, Zr, Ti
C, Ca, Cu	Sc	Fe, Mn, Ba, Co, Mg, B, La, K, Ga, Be, Zr, Ti
Ca, C	Be	Fe, Mn, Ba, Mg, La, Co, B, K, Ti, Zr, Ga, Sc
C, Ca, V, Mo	B	Na, Co, K, La, Ti, Be, Sc, Zr, Ga
	Ba	Cr, Y, Sc, Fe, Be, Ga, Mg, Zr, Ti, La, K
	Fe	Be, Sc, Mn, Mg, Zr, Ba, K, Ti
	Mn	Ga, Sr, Fe, Sc, Be, Ti, Co, K, Mg
	C	Na, Mg, Be, Y, B, Ga, Ba, K, Sc, Zr, Ti
	La	K, Ba, Sr, La
	Y	B, K, Mg, Sc, Be, Mn
	Co	Sr, Co, Cr, Y, Ni, Fe, Na, B, Mn, Zr, Ga, La, Be, Ti, Ba, Sc, Mg
	K	Mo, Cu, Co, Fe, La, V, Sc, Be, Sr, Ba, Cr, Mn, Na, Ni, K
	Mg	Mo, B, La, K, Cr, Pb, Cu, Ni, Mg
	Na	Cu, K, Mn, Ca, V, Y, Mg
	Sr	Pb, Mo, Ni, Sr, C, Cu
Zr, Ti, Ga, Sc, B, Be	Ca	C, Mg, Sr, Pb, Cu, Ni, Cr, Mo
Ga, B	V	Sr, Mg, Na, V, C, Ca, Pb, Cr, Ni, Mo
Zr, Ti, Ga, Sc	Cu	Ba, K, Na, C, Mg, Pb, Cu, Ni, Mo, V
	Cr	Na, Ca, Mg, C, Pb, Cu, Ni, Cr, V
Ga, B, Ti	Mo	Ca, K, Na, C, V, Pb, Cu, Mg, Mo, Cr
	Ni	Ca, Na, V, Cu, Cr, Mo, Ni, C
Zr	Pb	V, Cr, Ca, Cu, Mo, Ni, Pb
Zr, Sc, Ga, Ti, B, La, Be	C	

fourth groups the elements are not so easily interpreted because individual elements correlate positively with individual elements in the first two major groups. Some of the elements—for example, manganese, iron, and cobalt—are close to or less than 0.5 unit radius and do not really closely correlate with the other elements in their group. The fact that these two groups have strong ties to both the other groups may be due in part to the problem of the closed array. Mineralogically, these elements seem to represent a mixture of diverse components, such as phosphate nodules, clay minerals, and weathering products. Phosphate nodules may be enriched with strontium, yttrium, and lanthanum. Clay minerals may account for some of the potassium, magnesium, and sodium. Pyrite and weathering products such as hydroxides and sulfates probably account for most of the iron and such elements as barium, cobalt, and manganese.

#### PERMIAN MEADE PEAK PHOSPHATIC SHALE MEMBER OF THE PHOSPHORIA FORMATION

*Major elements.*—The samples from the Meade Peak Phosphatic Shale Member of the Phosphoria Formation that make up set 6 range in lithology from phosphorite, to carbonate rock, to siltstone. Therefore, the distribution of elements between several different rock components can be examined in set 6. Calcium is the major element in three of the principal rock-forming minerals—calcite, dolomite, and carbonate-fluorapatite—and it composes more than 10 percent of most of the samples. The other major elements, in order of decreasing

abundance, are phosphorus, silicon, potassium, aluminum, magnesium, iron, and sodium.

*Minor elements.*—A remarkable number of minor elements occur in abnormally high concentration in the Meade Peak Member, as was noted by Gulbrandsen (1960, p. 82). The concentrations of the following minor elements are especially high:

Element	Median	95 percentile
Ag-----	0.001-----	0.002
Cr-----	.1-----	.7
Ni-----	.015-----	.07
Se-----	.007-----	.015
Sr-----	.1-----	.3
V-----	.05-----	1.2
Y-----	.015-----	.07
Zn-----	.15-----	1.0

<sup>1</sup> Gulbrandsen (1960, p. 84) stated that the vanadiferous zone, 3.5 feet thick, at Coal Canyon, Wyo. contains an average 0.7 percent  $V_2O_5$  (equivalent to about 0.39 percent elemental vanadium).

Manganese, boron, gallium, molybdenum, scandium, and zirconium occur in concentrations more nearly typical of black shales and associated carbonaceous rocks. Other elements occur in relatively low concentrations in the Meade Peak Member. For example, the 95th percentile concentration of barium is only 0.02 percent, less than half the average concentration in shale, as reported by Turekian and Wedepohl (1961, table 2). Concentrations of beryllium, cobalt, and lead are also relatively low; yet these elements are among those that Krauskopf (1955, p. 417, 423) found to be commonly enriched in both black shales and phosphorites, and lead is among the elements he described to be markedly enriched in black shale (Krauskopf, 1955, p. 419).

*Correlation data.*—The range in lithologic types included in the samples of the Meade Peak Member is reflected in the correlation data (tables 6 and 7). However, most of the elements detected can be assigned to four major components represented by  $C_{org}$ ,  $C_{min}$ ,  $P_2O_5$ , and silicon. (see fig. 3.) These four components can be regarded as characteristic of four different end members of the Meade Peak lithologies and probably include all the more significant rock components, with the possible exception of sulfide minerals. The group characterized by silicon and including aluminum, titanium, zirconium, gallium, boron, barium, and iron is thought to represent the detrital end member. The phosphorite end member is characterized by  $P_2O_5$  and includes strontium, yttrium, and the radioactive elements expressed as eU (equivalent uranium). The carbonate end member, characterized by  $C_{min}$ , includes magnesium and manganese. It presumably includes calcium as well, but analytical data for this element are not available. The group characterized by  $C_{org}$  is made up of selenium, copper, nickel, scandium, molybdenum, and chromium, which show strong inter-correlations with each other and with  $C_{org}$ . They also show moderate

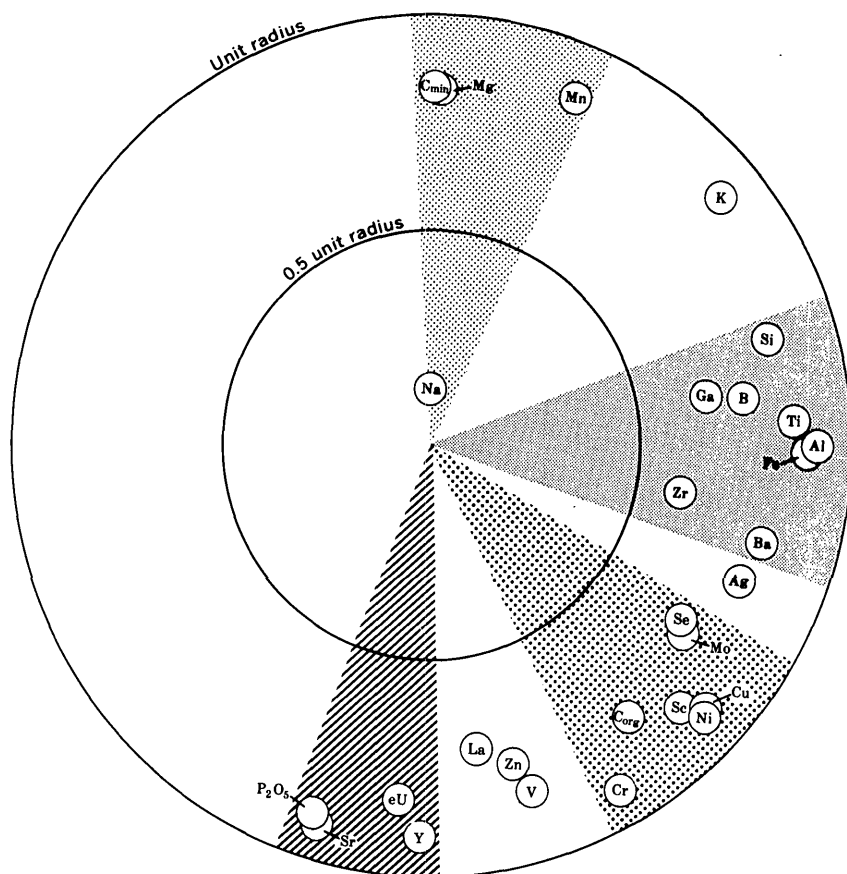


FIGURE 3.—Rotated two-dimensional vector diagram showing the principal-component analysis of the correlation matrix for set 6, 43 samples from the Meade Peak Phosphatic Shale Member of the Phosphoria Formation. Patterned areas suggest geochemical groupings of elements.

correlations with elements in the detrital groups. Vanadium, lanthanum, and zinc correlate strongly with each other and with *C<sub>org</sub>*; they also correlate moderately strongly with the elements in the phosphorite end member. Thus, the elements associated with organic matter tend to fall into several subgroups, according to whether they are more closely related to phosphorite or to siltstone. The carbonate end member tends to correlate negatively with the other groups, presumably because of the dilution effect of the carbonate rocks.

#### UPPER DEVONIAN CHATTANOOGA SHALE

*Major elements.*—In many ways the Chattanooga Shale samples of set 7 are typical of black shales in general. The content of most of the

TABLE 6.—*Correlation coefficients for element pairs in set 6, 43 samples of black shale, Phosphoria*

Si	Al	Fe	Mg	Na	K	Ti	Mn	Ag	B	Ba	Cr	Cu	Ga	La
Si	0.80	0.72	0.12	0.07	0.66	0.80	0.48	0.48	0.62	0.71	0.07	0.24	0.56	-0.15
	Al	.85	-.04	.15	.61	.84	.33	.64	.64	.80	.42	.57	.53	.06
		Fe	-.06	.09	.54	.84	.35	.60	.68	.75	.42	.58	.43	.16
			Mg	-.09	.59	-.13	.69	-.05	.02	-.39	-.56	-.39	.31	-.60
				Na	-.06	.18	.16	-.18	-.13	.20	-.10	-.05	-.28	-.21
					K	.54	.64	.49	.50	.33	-.12	.16	.67	-.42
						Ti	.30	.51	.63	.86	.27	.45	.41	.00
							Mn	-.05	.29	.12	-.43	-.25	.19	-.55
								Ag	.33	.47	.64	.77	.70	.40
									B	.63	.20	.37	.49	.05
										Ba	.46	.57	.27	.20
											Cr	.87	.13	.80
												Cu	.41	.62
													Ga	-.01
														La

Level of significance:

95 percent	99 percent	99.9 percent
0.30	0.39	0.49

<sup>1</sup> C<sub>t</sub>, total carbon.<sup>2</sup> C<sub>min</sub>, carbonate carbon.<sup>3</sup> C<sub>org</sub>, organic carbon.

major elements probably falls close to the median for black shales. Furthermore, the major elements, except for calcium, show a restricted range in values between the 5th and 95th percentiles (table 3). Presumably, this restriction reflects the remarkable uniformity of the Chattanooga Shale over a widespread area. Standard rock analyses for three outcrop samples of the Chattanooga Shale that are probably representative of the formation in central Tennessee were listed by Conant and Swanson (1961, p. 43).



*dolomite, and phosphorite from the Meade Peak Phosphatic Shale Member of the Formation*

Mo	Ni	Sc	Sr	V	Y	Zn	Zr	eU	P <sub>2</sub> O <sub>5</sub>	Se	C <sub>t</sub> <sup>1</sup>	C <sub>min</sub> <sup>2</sup>	C <sub>org</sub> <sup>3</sup>
0.38	0.28	0.42	-0.38	-0.01	-0.27	0.02	0.67	-0.15	-0.35	0.17	-0.10	0.08	0.01
.52	.58	.60	-.25	.19	-.01	.14	.57	.01	-.27	.48	.17	-.07	.37
.53	.56	.59	-.23	.15	.08	.07	.57	-.05	-.24	.61	.20	-.01	.39
-.27	-.39	-.55	-.68	-.62	-.73	-.49	-.36	-.77	-.62	-.30	.28	.87	-.32
-.13	-.28	-.03	-.23	-.15	-.14	-.28	.15	-.08	-.11	.11	-.25	-.09	-.17
.15	.15	-.03	-.63	-.27	-.57	-.19	.19	-.54	-.63	.21	.33	.53	.05
.43	.43	.57	-.34	.13	-.07	.03	.76	-.09	-.31	.38	-.04	-.10	.27
-.16	-.26	-.27	-.72	-.54	-.68	-.48	.11	-.62	-.73	-.08	.15	.77	-.39
.48	.70	.56	.10	.41	.28	.45	.21	.14	.16	.63	.38	-.14	.64
.42	.43	.45	-.32	.10	-.10	.07	.54	-.14	-.42	.31	.11	.02	.19
.49	.54	.69	-.04	.35	.16	.30	.79	.24	-.05	.40	-.20	-.36	.31
.55	.86	.75	.55	.66	.79	.65	.14	.53	.58	.68	.30	-.54	.82
.63	.85	.69	.34	.61	.57	.53	.27	.35	.31	.79	.41	-.41	.83
.35	.39	.28	-.19	.13	-.16	.14	.24	-.16	-.23	.31	.38	.14	.31
.26	.60	.67	.66	.49	.93	.50	.04	.49	.70	.38	.15	-.61	.56
Mo	.73	.51	.26	.69	.27	.56	.38	.38	.15	.52	.28	-.32	.57
	Ni	.68	.39	.69	.54	.66	.26	.47	.38	.68	.39	-.38	.84
		Sc	.36	.51	.65	.48	.59	.39	.34	.44	.01	-.57	.51
			Sr	.65	.78	.65	-.09	.75	.84	.13	-.08	-.69	.39
				V	.56	.79	.26	.74	.57	.45	.06	-.64	.60
					Y	.53	.03	.63	.81	.35	.05	-.67	.57
						Zn	.12	.66	.62	.32	.02	-.55	.53
							Zr	.19	-.15	.17	-.39	-.37	.05
								eU	.73	.19	-.32	-.76	.34
									P <sub>2</sub> O <sub>5</sub>	.18	-.12	-.65	.43
										Se	.48	-.21	.76
											C <sub>t</sub>	.38	.59
												C <sub>min</sub>	-.37
													C <sub>org</sub>

*Minor elements.*—Like the major elements, most minor elements in sample set 7 occur in concentrations fairly typical of black shales in general. The minor elements also show great uniformity over a wide area. Uranium and cobalt, however, are exceptions; they occur in greater concentrations than is typical of black shales. The median cobalt content of 0.002 percent is about three times greater than was noted in previously studied black shales. The median uranium content of about 0.005 percent is more than 10 times the concentration of

TABLE 7.—*Element associations in set 6, 43 samples of black shale, dolomite, and phosphorite from the Meade Peak Phosphatic Shale Member of the Phosphoria Formation*

[Elements are listed in order of increasing correlation coefficients. Regular type used where the level of significance exceeds 95 percent; boldface type where the level of significance exceeds 99 percent]

Negative correlation ←	Element	→ Positive correlation
eU, Sr, Y, P <sub>2</sub> O <sub>5</sub> , V, Sc, Zn, Cr, La, Cu, Ni, C <sub>org</sub> , Zr, Ba, Mo	C <sub>min</sub>	K, Mn, Mg
eU, Y, Sr, P <sub>2</sub> O <sub>5</sub> , V, La, Cr, Sc, Zn, Ba, Cu, Ni, Zr, Se, C <sub>org</sub>	Mg	Ga, K, Mn, C <sub>min</sub>
P <sub>2</sub> O <sub>5</sub> , Sr, Y, eU, La, V, Zn, Cr, C <sub>org</sub>	Mn	Ti, Al, Fe, Si, K, Mg, C <sub>min</sub>
	Na	
P <sub>2</sub> O <sub>5</sub> , Sr, Y, eU, La	K	Ba, Ag, B, C <sub>min</sub> , Fe, Ti, Mg, Al, Mn, Si, Ga
Mg, C <sub>min</sub>	Ba	Zn, Co, K, Y, Se, Cr, Ag, Mo, Ni, Cu, B, Sc, Si, Fe, Zr, Al, Ti
	Zr	Mo, B, Al, Fe, Sc, Si, Ti, Ba
C <sub>min</sub> , Mg	Si	Mo, Sc, Mn, Ag, Ga, B, K, Zr, Ba, Fe, Al, Ti
Sr, P <sub>2</sub> O <sub>5</sub>	Ti	Mn, Se, Ga, Mo, Ni, Cu, Ag, K, Sc, B, Zr, Si, Al, Fe, Ba
Sr, P <sub>2</sub> O <sub>5</sub>	B	Se, Ag, Cu, Mo, Ni, Sc, Ga, K, Zr, Si, Ti, Ba, Al, Fe
P <sub>2</sub> O <sub>5</sub> , Sr	Al	C <sub>org</sub> , Cr, Se, Ga, Zr, Cu, Mo, Ni, Sc, K, Ag, B, Si, Ba, Ti, Fe
	Fe	Mn, C <sub>org</sub> , Cr, Ga, Mo, K, Ni, Zr, Cu, Sc, Ag, Se, B, Si, Ba, Ti, Al
	Ga	Mg, Se, C <sub>org</sub> , Mo, Ni, Cu, Ti, Fe, B, Al, Si, K, Ag
	Ag	B, La, V, Zn, Ba, Mo, Si, K, Ti, Sc, Fe, Se, Al, Cr, C <sub>org</sub> , Ni, Ga, Cu
	C <sub>min</sub> Mo	Ga, Zr, eU, Si, Ti, B, Ag, Ba, Sc, Se, Al, Fe, Cr, C <sub>org</sub> , Zn, Cu, V, Ni
	Mg Se	B, Ga, Zn, Y, La, Ti, Ba, Sc, V, Al, Mo, Fe, Ag, Cr, Ni, C <sub>org</sub> , Cu
C <sub>min</sub> , Mg	Cu	P <sub>2</sub> O <sub>5</sub> , Sr, eU, B, Ga, Ti, Zn, Al, Y, Ba, Fe, V, La, Mo, Se, Ag, Se, C <sub>org</sub> , Ni, Cr
Mg, C <sub>min</sub>	Ni	P <sub>2</sub> O <sub>5</sub> , Sr, Ga, Ti, B, eU, Ba, Y, Fe, Al, La, Zn, Sc, Se, V, Mo, Ag, C <sub>org</sub> , Cu, Cr
Mg, C <sub>min</sub>	Sc	P <sub>2</sub> O <sub>5</sub> , Sr, eU, Si, Se, B, Zn, V, C <sub>org</sub> , Mo, Ag, Ti, Fe, Zr, Al, Y, La, Ni, Cu, Ba, Cr
Mn, C <sub>min</sub> , Mg	C <sub>org</sub>	Ba, Ga, eU, Al, Fe, Sr, P <sub>2</sub> O <sub>5</sub> , Sc, Zn, La, Mo, Y, V, Ag, Se, Cr, Cu, Ni
Mg, C <sub>min</sub> , Mn	Cr	Al, Fe, Ba, eU, Sr, Mo, P <sub>2</sub> O <sub>5</sub> , Ag, Zn, V, Se, Sc, Y, La, C <sub>org</sub> , Ni, Cu
C <sub>min</sub> , Mg, Mn	V	Ba, Ag, Se, La, Sc, Y, P <sub>2</sub> O <sub>5</sub> , C <sub>org</sub> , Cu, Cr, Sr, Mo, Ni, eU, Zn
C <sub>min</sub> , Mg, Mn	Zn	Ba, Se, Ag, Sc, La, Y, C <sub>org</sub> , Cu, Mo, P <sub>2</sub> O <sub>5</sub> , Cr, Sr, eU, Ni, V
Mg, Mn, C <sub>min</sub> , K	Y	Se, Zn, V, Ni, Cu, C <sub>org</sub> , eU, Sc, Sr, Cr, P <sub>2</sub> O <sub>5</sub> , La
Mg, Mn, C <sub>min</sub> , K	La	Se, Ag, Zr, V, eU, Zn, C <sub>org</sub> , Ni, Cu, Sr, Sc, P <sub>2</sub> O <sub>5</sub> , Cr, Y
Mg, C <sub>min</sub> , Mn, K	eU	Cu, C <sub>org</sub> , Mo, Sc, Ni, La, Cr, Y, Zn, P <sub>2</sub> O <sub>5</sub> , V, Sr
Mn, C <sub>min</sub> , Mg, K, Si, Ti, B	Sr	Cu, Sc, Ni, C <sub>org</sub> , Cr, Zn, La, V, eU, Y, P <sub>2</sub> O <sub>5</sub>
C <sub>min</sub> , K, Mg, B, Si, Ti	P <sub>2</sub> O <sub>5</sub>	Cu, Sc, Ni, C <sub>org</sub> , V, Cr, Zn, La, eU, Y, Sr

uranium in the average shale, as reported by Turekian and Wedepohl (1961).

*Correlation data.*—The correlation data (tables 8 and 9; fig. 4) indicate that most of the elements are associated with one of four major groups, only three of which are reasonably compact.

1. The group characterized by C<sub>org</sub> includes molybdenum, nickel, cobalt, uranium, and iron, all of which show strong positive intercorrelations. These elements may be directly associated with organic matter or with pyrite that is associated with organic matter.
2. The group that is characterized by aluminum includes magnesium, scandium, boron, strontium, beryllium, and chromium and, possibly, gallium and lanthanum. All these elements show a strong positive intercorrelation and are fairly typical of the elements associated with the detrital-mineral fraction of the rock.

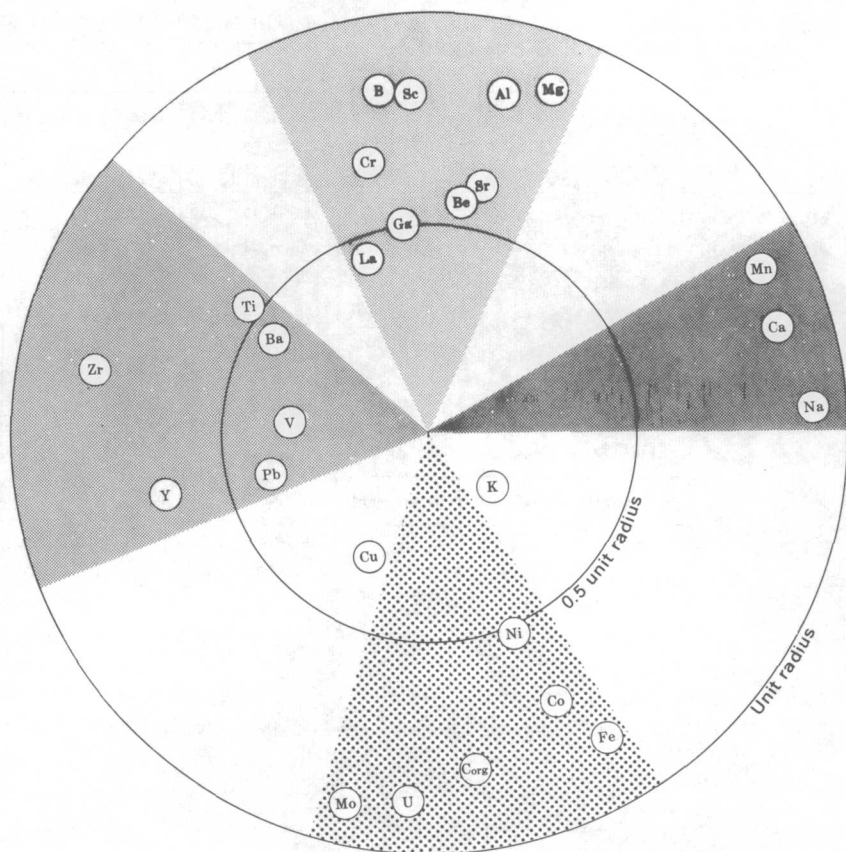


FIGURE 4.—Rotated two-dimensional vector diagram showing the principal-component analysis of the correlation matrix for set 7, 51 samples of Chattanooga Shale. Patterned areas suggest geochemical groupings of elements.

3. Calcium, magnesium, and sodium form a third group of unknown, possibly authigenic origin.
4. Zirconium is the most characteristic of a fourth group that may include heavy resistates. The principal elements of the organic group tend to correlate negatively with the principal elements of the detrital group.

#### PENNSYLVANIAN PARADOX MEMBER OF THE HERMOSA FORMATION

*Major elements.*—The samples from the Paradox Member of the Hermosa Formation are characterized by unusually large amounts of calcium and magnesium carbonates. The median carbonate mineral content is about 35 percent, and in some samples it is greater than 50

TABLE 8.—*Correlation coefficients for element*

Al	Fe	Mg	Ca	Na	K	Ti	Mn	B	Ba	Be	Co	Cr	Cu
Al	-0.44	0.79	0.28	0.18	0.00	0.16	0.36	0.56	0.10	0.43	-0.36	0.40	-0.30
	Fe	-.52	.16	.38	.21	-.16	-.03	-.74	-.22	-.28	.70	-.66	.15
		Mg	.38	.27	.00	.13	.56	.55	.01	.43	-.46	.59	-.23
			Ca	.84	-.07	-.36	.84	.15	-.15	.12	.05	.03	-.29
				Na	.06	-.33	.74	-.03	-.23	.19	.16	.00	-.16
					K	.00	.05	-.20	.00	.00	.38	.00	.18
						Ti	-.31	.08	.21	.15	-.23	.19	.14
							Mn	.28	-.18	.32	-.04	.17	-.15
								B	.30	.49	-.52	.66	-.18
									Ba	.30	-.01	.07	-.40
										Be	-.19	.43	-.16
											Co	-.52	.09
												Cr	.09
													Cu

Level of significance:

95 percent	99 percent	99.9 percent
0.28	0.36	0.45

percent. Described individually, these samples would be called limestones and dolomites. Potassium and sodium are generally present in normal concentrations, although a few samples contain abnormally large amounts of sodium. Iron, titanium, and manganese are present in relatively low concentrations; and organic carbon, with a median value of 0.5 percent, is considerably less abundant than in typical black shales.

*Minor elements.*—The median concentrations of most minor elements in the Paradox samples are low compared with those in other black-shale samples. Two notable exceptions are boron and strontium, which appear to be more abundant than in normal black shales. The high boron content may reflect the hypersaline environment (Degens

pairs in set 7, 51 samples of Chattanooga Shale

Ga	La	Mo	Ni	Pb	Sc	Sr	V	Y	Zr	U	C
0.33	0.33	-0.71	-0.30	-0.17	0.68	0.47	-0.05	-0.22	-0.01	-0.71	-0.69
-.46	-.31	.52	.26	-.09	-.50	-.30	-.35	-.17	-.40	.61	.55
.32	.26	-.76	-.17	-.15	.59	.39	-.06	-.27	-.16	-.79	-.57
.04	.16	-.31	.08	-.30	.12	.44	-.16	-.36	-.56	-.23	-.06
-.03	-.10	-.21	.10	-.30	.05	.23	-.23	-.56	-.71	-.08	.10
-.14	-.14	.00	.10	-.09	.00	-.09	-.49	.12	-.15	.08	-.05
.08	.08	-.29	-.45	.17	.36	.20	-.34	.06	.40	-.28	-.39
.13	.16	-.45	.13	-.37	.21	.31	-.20	-.42	-.45	-.40	-.18
.45	.26	-.62	-.29	-.13	.66	.52	.28	.02	.25	-.59	-.60
.29	.23	.02	-.28	-.07	.18	.16	.20	.26	.31	.03	-.23
.23	.19	-.41	-.30	.09	.54	.27	-.05	-.18	.00	-.31	-.32
-.35	-.21	.56	.34	-.18	-.42	-.22	-.36	-.06	-.28	.61	.36
.29	.11	-.46	-.08	.22	.54	.36	.16	.04	.14	-.50	-.34
-.35	-.34	.24	.35	.19	-.21	-.09	-.13	.19	.12	.19	.17
Ga	.04	-.40	-.25	-.02	.55	.04	.10	-.16	.01	-.33	-.19
	La	-.26	-.23	-.07	.20	.40	.05	.37	.29	-.33	-.43
		Mo	.41	.15	-.72	-.49	.11	.32	.04	.87	.73
			Ni	.19	-.43	-.24	.28	.08	-.31	.37	.46
				Pb	.05	.12	.08	.25	.09	.20	.25
					Sc	.44	-.13	-.15	.15	-.65	-.63
						Sr	-.14	.09	-.03	-.42	-.55
							V	.23	.16	.01	.06
								Y	.47	.24	.02
									Zr	-.10	-.28
										U	.79
											C

and others, 1957). The high strontium content, however, probably reflects the high calcium content, with which it is commonly associated (especially in evaporite minerals), even though it does not show a very strong correlation with CaO.

*Correlation data.*—A study of the correlation data (tables 10 and 11) suggests four principal groupings (fig. 5) for the constituents of the black shales in the Paradox. The first group consists of  $C_{min}$ , magnesium, calcium, and possibly manganese, the first three of which have a strong positive intercorrelation and a negative correlation with many constituents of the other groups. The second group is characterized by silicon, aluminum, vanadium, and titanium, all of which have a strong intercorrelation, and possibly also gallium, boron and

TABLE 9.—*Element associations in set 7, 51 samples of Chattanooga Shale*

[Elements are listed in order of increasing correlation coefficients. Regular type used where the level of significance exceeds 95 percent; boldface type where the level of significance exceeds 99 percent]

Negative correlation←	Element	→Positive correlation
Mo, U, C, Fe, Co, Ni, Cu	Al	Ca, Ga, La, Mn, Cr, Be, Sr, B, Sc, Mg
U, Mo, C, Fe, Co	Mg	Ga, Ca, Sr, Be, B, Mn, Sc, Cr, Al
Fe, Mo, C, U, Co, Ni	B	Mn, V, Ba, Ga, Be, Sr, Mg, Al, Sc, Cr
Mo, C, U, Ni, Fe	Be	Ba, Mn, Cr, Mg, Al, B, Sc
Mo, U, C, Fe, Ni, Co	Sc	Ti, Sr, Cr, Be, Ga, Mg, B, Al
Mo, Fe, Co, Cu, U	Ga	Cr, Ba, Mg, Al, B, Sc
C, Mo, U, Fe	Sr	Mn, Cr, Mg, La, Ca, Sc, Al, B
Fe, Co, U, Mo, C	Cr	Ga, Sr, Al, Be, Sc, Mg, B
Na, Ca, Mn, Fe, Ni, Co, C	Zr	La, Ba, Ti, Y
Ni, C, Ca, V, Na, Mn, Mo, U	Ti	Sc, Zr
C, Fe, U, Cu	La	Zr, Al, Y, Sr
Na, Mn, Ca	Y	Mo, La, Zr
Zr, Y, Ti, Pb	Na	Fe, Mn, Ca
Mo, Zr, Y, U, Pb, Ti	Mn	B, Sr, Be, Al, Mg, Na, Ca
Zr, Ti, Y, Mo, Pb, Cu	Ca	Al, Mg, Sr, Mn, Na
K, Co, Fe, Ti	V	Ni, B
V	K	Co
Cu, Ni	Ba	Ga, Be, B, Zr
Mn, Na, Ca	Pb	
Ba, Ga, La, Al, Ca	Cu	Ni
B, Cr, Mg, Sc, Ga, Al, Zr, V, La, Sr, Be	Fe	Na, Mo, C, U, Co
Cr, B, Mg, V, Al, Ga, Zr	Co	Ni, C, K, Mo, U, Fe
Ti, Sc, Zr, Al, Be, B, Ba	Ni	V, Co, Cu, U, Mo, C
Mg, Sc, Al, B, Sr, Cr, Mn, Be, Ga, Ca, Ti	Mo	Y, Ni, Fe, Co, C, U
Mg, Al, Sc, Cr, B, Sr, Mn, La, Ga, Be, Ti	U	Ni, Co, Fe, C, Mo
Al, Sc, B, Mg, Sr, La, Ti, Cr, Be, Zr	C	Co, Ni, Fe, Mo, U

iron. These may be regarded as the principal constituents of the detrital-mineral fraction. The third group with a strong positive inter-correlation includes  $C_{org}$  and the elements copper, zinc, nickel, chromium, lithium, lanthanum, yttrium, and ytterbium. A fourth group of uncertain geochemical significance includes barium, zirconium, sodium, and strontium. All these elements form soluble chlorides, and thus they may represent a group that has migrated in interstitial saline water. Potassium lies between this fourth group and the detrital group, which suggests a dual mode of occurrence.

### SUMMARY AND CONCLUSIONS

Conventional geologic and petrographic data were supplemented by statistical analysis of chemical data to determine the distribution and association of minor elements in several types of marine black shale. The results appear to be sufficiently unbiased to be consistent with accepted principles of sedimentary geochemistry despite the deviations from ideal sampling patterns and the use of much semiquantitative data.

The statistical analysis of data shows that most elements can be assigned to one of the three major rock-forming fractions: the detrital mineral fraction, the chemically or biologically precipitated fraction, or the organic-matter fraction. In some sets of samples two groups of detrital elements occur, and in some sets a separate group that may

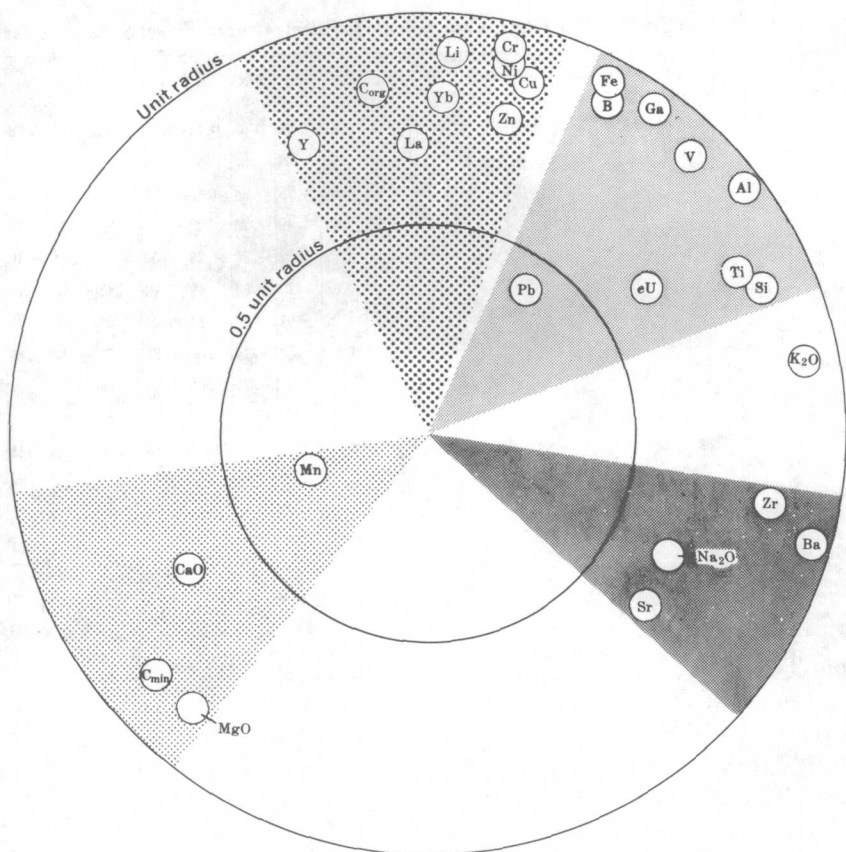


FIGURE 5.—Rotated two-dimensional vector diagram showing the principal-component analysis of the correlation matrix for set 8, 25 samples of black shale from the Paradox Member of the Hermosa Formation. Patterned areas suggest geochemical groupings of elements.

represent authigenic minerals is distinguished. The detrital-mineral fraction of these rocks generally includes silicon and aluminum (for which the data are incomplete), titanium, zirconium, boron, and, commonly, gallium, scandium, and beryllium. The Phosphoria and Paradox samples include carbonate rocks associated with the black-shale facies. In these sets calcium, magnesium, and manganese occur in a separate carbonate-mineral fraction inversely related to one of the other major mineral fractions. The organic-matter fraction correlates positively with the detrital-mineral fraction in these sets. The Chattanooga Shale samples and the samples of Pennsylvanian black shale from Kansas and Oklahoma did not include a significant carbonate-mineral fraction. In these sets the organic-matter fraction appears to

TABLE 10.—*Correlation coefficients for element pairs in set 8, 25 samples*

Si	Al	Fe	Ti	Mn	B	Ba	Cr	Cu	Ga	La	Ni	Pb	Sr	V
Si	0.86	0.64	0.65	-0.11	0.57	0.66	0.41	0.48	0.63	0.14	0.56	0.40	0.29	0.78
	Al	.80	.80	-.23	.71	.57	.65	.68	.82	.40	.70	.29	.27	.89
		Fe	.62	-.21	.86	.13	.86	.78	.88	.56	.81	.36	-.18	.84
			Ti	-.17	.56	.59	.47	.49	.78	.28	.46	.25	.34	.70
				Mn	-.39	-.18	-.22	.02	-.20	-.28	.09	.19	-.02	-.16
					B	.12	.83	.72	.83	.49	.72	.42	-.32	.70
						Ba	-.09	-.01	.28	-.14	-.01	.08	.70	.46
							Cr	.82	.79	.59	.86	.21	-.27	.70
								Cu	.79	.41	.89	.39	-.06	.72
									Ga	.48	.71	.40	-.02	.83
										La	.57	.06	-.30	.45
											Ni	.31	-.14	.74
												Pb	-.26	.37
													Sr	.21
														V

Level of significance:

95 percent	99 percent	99.9 percent
0.43	0.55	0.65

<sup>1</sup> C<sub>t</sub>, total carbon.<sup>2</sup> C<sub>min</sub>, carbonate carbon.<sup>3</sup> C<sub>org</sub>, organic carbon.

be inversely related to the detrital-mineral fraction. This apparent difference in the behavior of the organic-matter fraction is thought to be due to either the dilution effect or the closed-array problem and is probably not the result of a geochemical process.

Identification of the suite of elements associated with the organic-matter fraction of each set is of particular interest in this study. This suite is most clearly identified where the organic-matter fraction is inversely related to the detrital-mineral fraction. The suite includes copper, nickel, vanadium, chromium, molybdenum, lead, and calcium



of black shale from the Paradox Member of the Hermosa Formation

Y	Yb	Zr	eU	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	Zn	C <sub>1</sub> <sup>1</sup>	C <sub>min</sub> <sup>2</sup>	C <sub>org</sub> <sup>3</sup>	Li
0.12	0.46	0.76	0.46	-0.48	-0.57	0.72	0.37	0.39	-0.64	-0.61	0.21	0.29
.20	.58	.52	.58	-.48	-.83	.77	.23	.62	-.66	-.74	.35	.58
.43	.71	.20	.46	-.55	-.74	.51	.09	.58	-.47	-.77	.57	.83
.08	.41	.41	.60	-.42	-.61	.77	.27	.49	-.59	-.59	.14	.41
-.01	.02	.02	.09	.31	.47	-.28	-.26	.06	.40	.36	.09	-.20
.49	.58	.20	.33	-.73	-.71	.48	.13	.50	-.54	-.86	.55	.76
-.44	-.16	.77	.46	-.33	-.38	.82	.50	.05	-.64	-.37	-.27	-.22
.51	.73	.09	.41	-.41	-.73	.32	-.17	.65	-.23	-.66	.75	.84
.27	.60	-.01	.61	-.29	-.69	.40	-.26	.83	-.18	-.58	.71	.69
.27	.56	.23	.65	-.56	-.80	.69	-.03	.71	-.46	-.79	.60	.75
.63	.60	-.25	.13	-.17	-.51	.04	-.01	.46	-.11	-.30	.30	.71
.52	.78	.05	.48	-.27	-.63	.29	-.13	.74	-.17	-.53	.68	.73
.25	.19	.32	.29	-.36	-.19	.25	.01	.34	-.22	-.38	.31	.21
-.65	-.23	.33	.41	.34	-.19	.49	.14	.05	-.12	.18	-.32	-.41
.21	.54	.36	.61	-.38	-.85	.70	.06	.65	-.44	-.65	.47	.58
Y	.72	-.19	-.25	-.20	-.19	-.28	-.09	.27	.04	-.24	.47	.67
	Yb	-.02	.19	-.14	-.46	.04	.01	.52	-.14	-.35	.54	.78
		Zr	.31	-.50	-.22	.65	.56	-.05	-.71	-.45	-.21	-.14
			Ue	-.11	-.55	.73	-.18	.61	-.19	-.33	.37	.22
				CaO	.40	-.46	-.49	-.12	.80	.90	-.15	-.43
					MgO	-.68	.00	-.67	.48	.71	-.49	-.64
						K <sub>2</sub> O	.20	.37	-.62	-.63	.17	.16
							Na <sub>2</sub> O	-.37	-.77	-.33	-.60	-.07
								Zn	-.06	-.42	.64	.61
									C <sub>1</sub>	.79	.21	-.27
										C <sub>min</sub>	-.38	-.63
											C <sub>org</sub>	.63
												Li

in the samples of Pennsylvanian black shade from Kansas and Oklahoma, and uranium, iron, cobalt, molybdenum, and nickel in the samples of Chattanooga Shale. Iron, present in pyrite, is apparently closely associated with the organic matter in the Chattanooga Shale. Where carbonate minerals are absent, calcium can also occur with organic matter, perhaps as a calcium humate or a similar organic compound, which explains its association in the Pennsylvanian black shale. The other differences between the organic-matter fractions of these two sets probably reflect differences in availability of the elements in the two environments.

TABLE 11.—*Element associations in set 8, 25 samples of black shale from the Paradox Member of the Hermosa Formation*

[Elements are listed in order of increasing correlation coefficients. Regular type used where the level of significance exceeds 95 percent; boldface type, where the level of significance exceeds 99 percent]

Negative correlation←	Element	→Positive correlation
	Mn	MgO
V, Al, Ga, Fe, Cr, B, Cu, K <sub>2</sub> O, Zn, Li, Ni, Ti, Si, eU, La, <i>Cor<sub>g</sub></i> , Yb	MgO	Mn, C <sub>min</sub>
B, Ga, Fe, Al, Cr, V, Li, K <sub>2</sub> O, Si, Ti, Cu, Ni, Zr	C <sub>min</sub>	<b>MgO, CaO</b>
B, Ga, Fe, Na <sub>2</sub> O, Zr, Al, Si, K <sub>2</sub> O, Li	CaO	C <sub>min</sub>
	Pb	
<i>Cor<sub>g</sub></i> , CaO	Na <sub>2</sub> O	Ba, Zr
Y	Sr	K <sub>2</sub> O, Ba
<b>MgO</b>	eU	Si, Fe, Ba, Ni, Al, Ti, Cu, Zn, V, Ga, K <sub>2</sub> O
C <sub>min</sub> , CaO	K <sub>2</sub> O	B, Sr, Fe, Zr, Ga, V, Si, eU, Al, Ti, Ba
Y	Ba	V, eU, Na <sub>2</sub> O, Al, Ti, Si, Sr, Zr, K <sub>2</sub> O
CaO, C <sub>min</sub>	Zr	Al, Na <sub>2</sub> O, K <sub>2</sub> O, Si, Ba
MgO	La	V, Zn, Ga, B, Fe, Ni, Cr, Y, Yb, Li
Sr, Ba	Y	Fe, <i>Cor<sub>g</sub></i> , B, Cr, Ni, Li, La, Yb
MgO	Yb	Si, Zn, V, <i>Cor<sub>g</sub></i> , Ga, B, Al, Cu, La, Fe, Y, Cr, Li, Ni
MgO, C <sub>min</sub> , CaO	Al	Zr, Ba, Li, eU, Yb, Zn, Cr, Cu, Ni, B, K <sub>2</sub> O, Fe, Ti, Ga, Si, V
C <sub>min</sub> , MgO, CaO	Si	eU, Yb, Cu, Ni, B, Ga, Fe, Ti, Ba, K <sub>2</sub> O, Zr, V, Al
MgO, C <sub>min</sub>	Ti	Ni, Cr, Cu, Zn, B, Ba, eU, Fe, Si, V, K <sub>2</sub> O, Ga, Al
MgO, C <sub>min</sub>	V	La, Ba, <i>Cor<sub>g</sub></i> , Yb, Li, eU, Zn, Cr, B, Ti, Cu, Ni, K <sub>2</sub> O, Si, Ga, Fe, Al
C <sub>min</sub> , CaO, MgO	B	K <sub>2</sub> O, Y, La, Zn, <i>Cor<sub>g</sub></i> , Ti, Si, Yb, V, Al, Cu, Ni, Li, Ga, Cr, Fe
C <sub>min</sub> , MgO, CaO	Fe	Y, eU, K <sub>2</sub> O, La, <i>Cor<sub>g</sub></i> , Zn, Ti, Si, Yb, Cu, Al, Ni, Li, V, B, Cr, Ga
MgO, C <sub>min</sub> , CaO	Ga	La, Yb, <i>Cor<sub>g</sub></i> , Si, eU, K <sub>2</sub> O, Ni, Zn, Li, Ti, Cr, Cu, Al, V, Fe
MgO, C <sub>min</sub> , CaO	Li	Al, V, Zn, <i>Cor<sub>g</sub></i> , Y, Cu, La, Ni, Ga, B, Yb, Fe, Cr
MgO, C <sub>min</sub>	Ni	Ti, eU, Y, Si, La, <i>Cor<sub>g</sub></i> , Al, Ga, B, Li, V, Zn, Yb, Fe, Cr, Cu
MgO, C <sub>min</sub>	Cr	Ti, Y, La, Zn, Al, V, Yb, <i>Cor<sub>g</sub></i> , Ga, Cu, B, Li, Ni, Fe
MgO	Zn	La, Ti, B, Yb, Fe, Li, eU, Al, <i>Cor<sub>g</sub></i> , Cr, V, Ga, Ni, Cu
MgO, C <sub>min</sub>	Cu	Si, Ti, Yb, eU, Al, Li, <i>Cor<sub>g</sub></i> , V, B, Fe, Ga, Cr, Zn, Ni
Na <sub>2</sub> O, MgO	<i>Cor<sub>g</sub></i>	V, Y, Yb, B, Fe, Ga, Li, Zn, Ni, Cu, Cr

The elements associated with the organic-matter fraction in the Phosphoria and Paradox samples are not so clearly distinguished because of their relatively close association with the detrital-mineral fraction in both sets and with phosphate in the Phosphoria Formation. In contrast to the Paradox Formation, the abnormally high concentration of many minor elements in the Meade Peak Member of the Phosphoria Formation suggests that the upwelling cold, nutrient-rich water that was capable of supporting an abundance of living organisms and that provided a source for the phosphate may have also provided a renewable source of minor elements. The high concentration of such potentially toxic elements as selenium, molybdenum, and chromium seems to preclude the possibility of concentration as a part of the metabolic process of living organisms. As an alternative, the minor-element concentrations probably occurred while the organic matter—after death and partial decay—drifted to a final burial site.

Geochemical associations among the samples from the Paradox Member of the Hermosa Formation contrast sharply with those from the Phosphoria Formation. Although copper, zinc, and, to a lesser degree, several other minor elements show a tendency to correlate

with organic matter, none of these occurs in abnormally high concentration. Considering the volume of sea water that must have been concentrated by evaporation to produce the thousands of feet of saline minerals in the Paradox Basin, a question arises as to the fate of the associated minor elements, but the answer was not found within the scope of this study. The sparse organic matter in the Paradox samples is extremely fine grained; yet perhaps it was not sufficiently decayed prior to burial to produce optimum conditions for minor-element absorption.

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