

# Element Distribution in Some Trough and Platform Types of Black Shale and Associated Rocks

By JAMES D. VINE, ELIZABETH B. TOURTELOT, and JOHN R. KEITH

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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### ELEMENT DISTRIBUTION IN SOME TROUGH AND PLATFORM TYPES OF BLACK SHALE AND ASSOCIATED ROCKS

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#### ABSTRACT

The distributions of some chemical elements in four sample sets of black shale and associated rocks were examined statistically. Pennsylvanian black shales deposited in a rapidly subsiding trough in central Colorado show few unusually high concentrations of minor elements, except lead, that can be attributed to adsorption by organic matter. High concentrations of boron, beryllium, gallium, lead, and possibly lithium may be related to Precambrian source rocks that are rich in the same elements. Minor elements in upper Paleozoic black shales of the Ouachita geosyncline show little or no association with organic matter. Local high concentrations of gallium and zirconium are associated with the detrital mineral fraction. High concentrations of barium show no association with major rock constituents, and barium may have been authigenically redistributed. Samples of shale from the Cherokee Group in the Western Interior coal province contain large amounts of silver, chromium, lead, vanadium, and zinc associated with organic matter and carbonate minerals. These elements may have been concentrated syngenetically by adsorption from sea water on decaying organic matter in a shallow-water platform environment. Samples of black shale and associated rocks from the Houy Formation of Devonian and Mississippian age in central Texas show unusually high concentrations of many minor elements, including cobalt, copper, molybdenum, nickel, lead, thallium, vanadium, and zinc. Of these, all but vanadium occur in close association with organic matter and pyrite. A very slow rate of deposition may have contributed to the concentration of these elements from sea water. However, many of these elements are toxic and could not coexist in abundance with living organisms. Some later addition of elements may have occurred.

#### INTRODUCTION

The present report is the third in a series of reports describing the geochemical distribution of elements in black shale and associated rocks. The first report (Vine, 1966) describes the element distributions in some shelf and eugeosynclinal black shale samples grouped into into four sets numbered 1-4. The second report (Vine, 1969) describes

the geochemistry of four more sample sets, numbered 5-8, representing black shales deposited in a hypersaline marine basin, in a miogeosyncline, and in two shallow shelf environments. The present report describes the distribution of major and minor elements in sample sets 9-12 (fig. 1) which represent black shale and associated rocks deposited in intracratonic trough and platform environments.

The term "black shale" as used here, as in previous reports (Vine, 1966, 1969), indicates dark-colored fine-grained marine sedimentary rocks composed of a mixture of detrital minerals, chemically or biologically precipitated minerals, and organic matter. End members include claystone, siltstone, limestone, dolomite, anhydrite, chert, phosphorite, and coal. Definition of precise boundaries between black shale and these end members is impractical because of the difficulty and expense of determining the exact mineralogic composition of fine-grained rocks, even with modern laboratory techniques. Therefore, samples approaching the composition of end members have been included in the study. This has increased the range in content of many constituents, thereby providing the bivariate statistics that are useful in interpreting the distribution of minor elements among different fractions.

#### ACKNOWLEDGMENTS

Samples were collected from many areas unfamiliar to the authors, and the information and guidance given by colleagues familiar with the stratigraphy of specific areas are gratefully acknowledged. C. T. Wrucke, U.S. Geological Survey, guided the senior author to outcrops of the Belden Shale in central Colorado. N. F. Williams, State Geologist of Arkansas, and his staff members, P. J. Sterling and C. G. Stone, accompanied the senior author in the field and directed him to outcrops of Paleozoic black shales in the Ouachita Mountains. V. E. Swanson, U.S. Geological Survey, provided the core of the Houy Formation that was sampled. D. R. Baker, formerly with the Marathon Oil Co. Research Center, Littleton, Colo., in cooperation with the company management, provided samples from cores of Pennsylvanian black shale from southeastern Kansas and northeastern Oklahoma.

The spectrographic analyses upon which this report is based were made by A. L. Sutton, Jr., and J. C. Hamilton of the U.S. Geological Survey. The other analyses were made by G. T. Burrow, I. C. Frost, W. D. Goss, Claude Huffman, Jr., H. H. Lipp, J. D. Mensik, and Wayne Mountjoy, all of the U.S. Geological Survey.

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

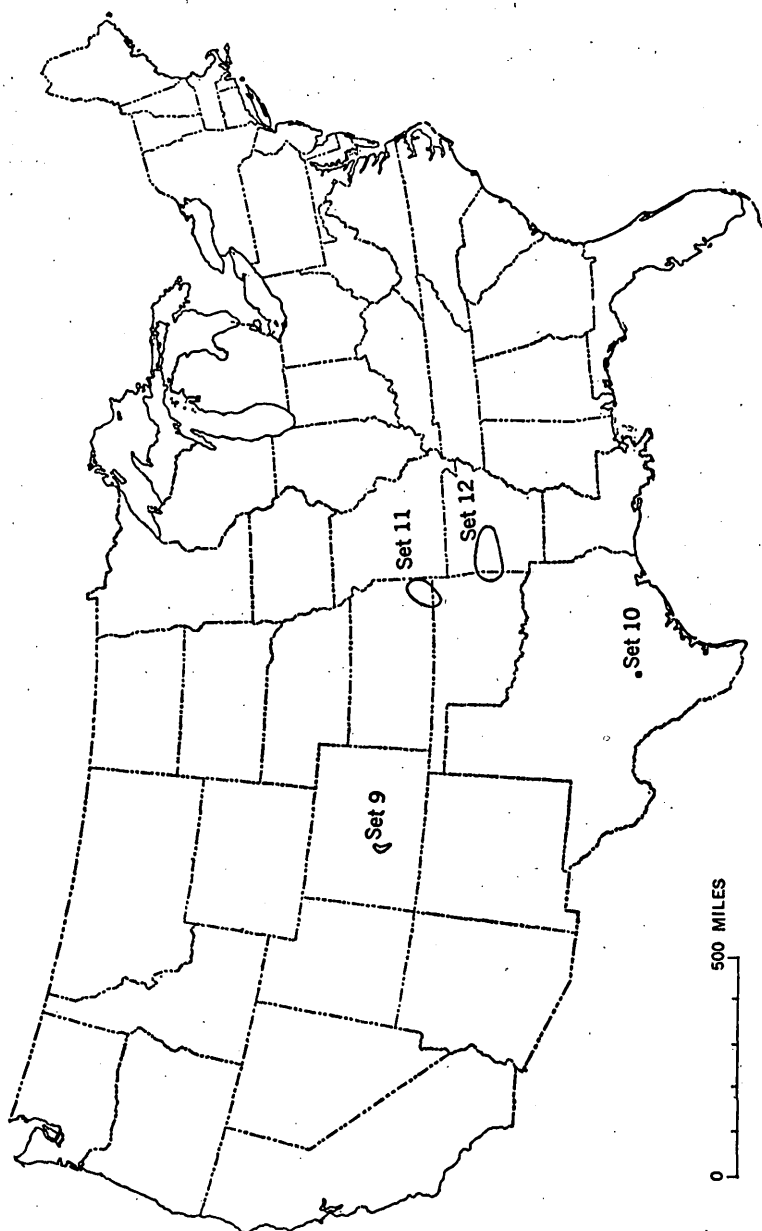


FIGURE 1.—Sample localities of black shale sample sets 9-12. Set numbers refer to data in tables 2-10.

## SAMPLE SETS

## BELDEN SHALE FROM COLORADO

The Belden Shale samples from Colorado, set 9, consist of 43 samples collected from outcrops of the Belden Shale of Pennsylvanian age and from the lower gradational part of the Minturn Formation, also of Pennsylvanian age, in Park, Chaffee, and Fremont Counties, Colo. About half the samples were collected from exposures in the canyon of the Arkansas River, 5-7 miles southeast of Salida, Colo. (Chronic, 1960, map, p. 113). The remainder were collected from various exposures north of the river to a point in the Mosquito Range west of Fairplay. Among the areas sampled were Trout Creek Pass, Chubb Park, Kaufman Ridge, Salt Creek, Weston Pass, and Mount Sherman. The samples are mostly channel samples representing 1-5 feet of stratigraphic thickness, but a few are grab samples representing only a few inches of strata. Generally, each sample represents a different bed, but equivalent beds in different sections are probably included; detailed correlation between areas was not attempted. The rocks sampled are chiefly medium-dark-gray to black arkosic siltstones containing varying amounts of calcite and clay minerals in the matrix. Petrographic descriptions of Pennsylvanian clastic rocks in this area by Gould (1935) indicate that they are first-cycle detrital sediments shed from the ancestral Rocky Mountains into a narrow marine trough in Pennsylvanian time. Anhydrite and halite occur to the northwest, in Eagle Basin, and beds of gypsum have been reported in the area sampled. The presence of saline springs in the vicinity of Salt Creek further suggests the occurrence of evaporite minerals in subsurface Pennsylvanian rocks.

The stratigraphy and nomenclature of Pennsylvanian rocks in central Colorado are complex and controversial. The name Belden Shale Member, as defined by Brill (1942), was applied to the lower member of his Battle Mountain Formation. He described the Belden as 100-200 feet of black and dark-gray carbonaceous shale and argillaceous limestone with thin beds of dark-colored sandstone overlying the Leadville Limestone in the vicinity of Gilman, Colo., and later raised the unit to formation rank (Brill, 1944). The coarser clastic rocks overlying the Belden were redefined and subdivided into the Minturn Formation and the Maroon Formation (Tweto, 1949). Chronic (1964, p. 109) indicated that in the southern part of the Mosquito Range the Belden Shale ranges in thickness from 500 to 3,000 feet. The variation in thickness of the Belden as reported by Brill and Chronic probably is partly due to the difficulty of defining a boundary, where no key beds have been traced, between the Belden Shale and the overlying Minturn Formation.



The stratigraphic section near the Arkansas River was described by Brill (1952). In the text (p. 812) Brill stated that the Belden type of lithology extends from Eagle Basin on the north to Huerfano Park on the south, but in the detailed section (p. 864-879) he showed 4,200 feet of Minturn Formation directly underlain by 157 feet of the Kerber Formation. Kerber Formation is the name applied to partly non-marine basal Pennsylvanian strata in the Bonanza mining district of Saguache County, Colo. The samples collected for this study from the Arkansas River section include dark-colored shales and siltstones from the lower 280 feet of Pennsylvanian strata which are probably nearly equivalent to the Belden Shale but which may include some nonmarine beds.

#### HOUY FORMATION FROM TEXAS

The Houy Formation samples from Texas, set 10, consist of 51 core samples of black shale and associated limestone and chert from the Houy Formation of Middle (?) Devonian to Early Mississippian age in Kendall County, Tex. (Cloud and others, 1957). Small samples were chipped from the core every few inches throughout an interval of 15 feet, representing the complete thickness of the Houy Formation and the overlying Chappel Limestone, about 3 feet thick.

The Doublehorn Shale Member of the Houy Formation is similar to, and probably in part equivalent to, the Chattanooga Shale of Tennessee, the Arkansas Novaculite in Arkansas, and the Woodford Chert in Oklahoma. The distribution of the Chattanooga Shale and its equivalents, including the Doublehorn Shale Member of the Houy Formation, is shown on a map by Conant and Swanson (1961, pl. 14). They infer a restricted epicontinental sea in Late Devonian and earliest Mississippian time that extended diagonally across the continent from Texas and New Mexico in the southwest to New York and Michigan in the northeast, and bounded by extensive land areas, including some, such as the Ozark highland, that extended well into the seaway. Except for deltaic sandstones in the Appalachian geosyncline, much of this sea was characterized by deposits of black shale and associated siliceous rocks. The Houy Formation was probably deposited in a local embayment in central Texas, adjacent to inferred land areas on the south, east, and northeast. Like many of the black shale units deposited during Late Devonian and earliest Mississippian time, the Houy Formation represents a relatively thin deposit for the time interval involved. Deposition probably occurred in quiet water on a shallow marine platform. An abundance of life in the sea is inferred because the supply of chemically or biologically precipitated mineral matter appears to have exceeded the supply of detrital mineral matter throughout much of the time.

Bioclastic carbonate rock occurs in the Chappel Limestone, and it also occurs in the upper part of the Doublehorn Shale Member of the Houy, which contains some fragments of brachiopods and crinoid stems largely replaced by pyrite. These units also contain scattered 1- to 2-cm nodules that may be coprolitic in origin. The nodules have an exterior rind of pyrite and an interior composed of radiolarian or other organic hash replaced by apatite. Conodonts also occur in black silty shale, but the most abundant fossils are the spore coats of *Tasmanites*, translucent yellow fragments of which occur throughout the shale. In cherty laminae, the *Tasmanites* are commonly preserved as spherical bodies with the interior cavity replaced with chalcedony. The inferred proximity to extensive land areas suggests that the organic matter in the Doublehorn Shale Member may also include a considerable amount of land-derived humic degradation products. This may account for the wide range in the appearance of the organic matter in thin sections of the shale. The organic matter, which contains many yellow objects, chiefly spore coats, is mostly opaque, but some is reddish brown.

#### CHEROKEE GROUP FROM KANSAS AND OKLAHOMA

The Cherokee Group samples from Kansas and Oklahoma, set 11, consist of 47 core samples of gray to black shale and siltstone and black phosphatic shale from four well cores through the Cherokee Group in Greenwood County, Kans., and Osage and Craig Counties, Okla. Baker (1962), who provided these samples, distinguished three types of shale: (1) grayish-black to black carbonaceous clay shale which contains phosphatic nodules and marine fossils, including conodonts and inarticulate brachiopods; (2) greenish-gray to medium-gray nonfossiliferous clay shale; and (3) medium-dark-gray silty shale which contains coaly plant fragments. All three types of shale are probably shallow-water marine shelf deposits, and the color differences probably reflect differences in the amount of oxygen and organic matter available during sediment accumulation. In this set, each of 38 samples was split from the crushed core of a 3- to 5-foot-thick bed. Of these, 17 are of the first lithologic type, 17 are of the second type, and 4 are of the third type. The remaining nine samples in the set are composite samples that were prepared by mixing equal parts from the crushed core of several beds of the same type of lithology. Of these, four are of the first lithologic type, four are of the second type, and one is of the third type. Individual and composite samples were analyzed in the same manner and were given equal weight in the statistical treatment.

Oil is recovered from shoestring sandstones in the Cherokee Group in this part of Kansas and Oklahoma. The Cherokee Group is a cyclic sequence that includes limestone, coal, and underclay, as well as sandstone and shale. The limestone beds contain marine fossils that probably represent the most northerly transgression of the sea on a broad shelf. The coal beds probably represent the most southerly regression of the sea. The shale beds probably represent shallow marine deposition intermediate in position between coal and limestone. The shoestring sandstones occur only locally and have been interpreted as river channels (Cadman, 1927) and as beach bar deposits (Bass, 1936). Their shape and their stratigraphic position above shale indicate that they are more likely beach bar deposits. The Cherokee Group in this area ranges in thickness from about 265 to 375 feet and is correlative with rocks exposed to the east that range from the basal Pennsylvanian to the top of the Excello Formation of Searight and others (1953). As many as 18 individual formations, defined as all the strata from the top of one coal bed to the top of the next higher coal bed, have been recognized in scattered surface exposures, and many of these same units can be identified in the cores (Baker, 1962, p. 1627).

The samples in set 11 represent part of the same stratigraphic interval as the samples in set 5 (Vine, 1969), but they are different in that they are more variable in color and organic carbon content and are unweathered core samples instead of partly weathered outcrop samples. They also differ in that each bed was not subdivided into upper, middle, and lower parts as was commonly done in set 5. In general, these samples represent the noncarbonate fine-grained marine facies of the intertonguing marine and nonmarine sequence of coal-bearing strata in the Pennsylvanian shelf area north of the Ouachita geosyncline.

#### UPPER PALEOZOIC BLACK SHALE FROM ARKANSAS AND OKLAHOMA

The upper Paleozoic black shale samples from Arkansas and Oklahoma, set 12, consist of 30 outcrop samples of upper Paleozoic shale from Arkansas and Oklahoma. They include 20 samples of dark-gray to black shale and argillite from the Stanley Shale in Montgomery, Pulaski, Hot Spring, and Garland Counties, Ark.; seven samples of Atoka shale from Logan, Sebastian, and Scott Counties, Ark., and Pittsburg County, Okla.; two samples of black shale from the Arkansas Novaculite in Montgomery and Pulaski Counties, Ark.; and one sample of black shale from the Jackfork Sandstone in Perry County, Ark. These samples have much in common even though they are from several different formations. They are all taken from thick detrital sedimentary sequences deposited in the Ouachita geosyncline.

The Arkansas Novaculite, almost 1,000 feet thick, is chiefly siliceous mudstone (novaculite). The black shale samples from this formation were collected from the middle unit of Hass (1951), 347 feet thick, which contains abundant dark-colored shale interbedded with siliceous mudstone. This middle unit is regarded as the stratigraphic equivalent of the uppermost Devonian and lowest Mississippian Chattanooga Shale of Tennessee (Hass, 1951, p. 2536) and the Doublehorn Shale Member of the Houy Formation in Texas (Cloud and others, 1957, p. 812). It is lithologically similar to the Doublehorn as described on pages H5, H6.

The Stanley Shale overlies the Arkansas Novaculite and consists of as much as 11,000 feet of dark-colored shale and siltstone. In many parts of the Ouachita Mountains the shales have been metamorphosed to argillite or slate, some of which is suitable for roofing material. Northwest of Little Rock, the upper part of the formation is considerably fractured and sheared so that bedding is obscure or lacking. The samples collected from this formation are chiefly medium-dark-gray to dark-gray silty shale or quartzose siltstone with variable amounts of clay minerals including illite and chlorite. Although the samples are dark, in thin section they show little opaque carbonaceous matter.

Some samples were collected at artificial exposures in the vicinity of barite deposits near the base of the Stanley Shale, but ore beds were not sampled. Because megafossils are sparse and poorly preserved in the Stanley, its age and stratigraphic correlatives have been the subject of controversy for some time. On the basis of conodonts from the lower part, however, Hass (1950) suggested that at least the lower part of the Stanley Shale may be of Mississippian age and correlative with the Caney Shale of Oklahoma and the Barnett Shale of central Texas. The Stanley Shale was probably deposited during a period of rapid downwarping of the Ouachita geosyncline, but there is little evidence other than the dark color to suggest environmental conditions at the time of deposition. Moreover, little information exists about the nature of the organisms that contributed to the accumulation of carbonaceous matter in the rocks.

The Jackfork Sandstone, which conformably overlies the Stanley Shale, consists of as much as 8,700 feet of sandstone and dark shale that probably represents a continued rapid downwarping of the Ouachita geosyncline and introduction of a greater proportion of coarse clastic material. The one sample of black shale from this formation was collected from a middle shale unit and is megascopically similar to many of the samples of Stanley Shale. The age of the Jackfork Sandstone, like that of the Stanley Shale, has been controversial partly because fossils are sparse and poorly preserved. Miser and

Hendricks (1960) reviewed the evidence, chiefly fossil plant material and field relationships, and concluded that the Jackfork Sandstone should be assigned a Mississippian age and that the overlying Johns Valley Shale should be assigned to both the Pennsylvanian and Mississippian Systems.

The Atoka Formation of Middle Pennsylvanian age overlies the Johns Valley Shale of Mississippian and Pennsylvanian age in parts of western Arkansas and eastern Oklahoma. In other areas it lies on other named units of Early Pennsylvanian (Morrow) age. Reinemund and Danilchik (1957) described 11,800 feet of strata of the Atoka Formation in the Waldron quadrangle, Scott County, Ark., where the base is not exposed. They estimated that the Atoka may be as much as 19,000 feet thick locally in the Ouachita geosyncline. The Atoka thins rapidly northward and is not present in the outcrop area of southeastern Kansas, although it is represented by as much as 500 feet of strata in the subsurface of southwestern Kansas. The Atoka consists of dark-gray fissile clay shale with interbedded siltstone and sandstone. Most samples collected from this unit are dark-gray clay shale.

#### ANALYTICAL METHODS

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, 0.083, and so forth, and are arbitrarily reported as 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. 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 taking the difference between total carbon and mineral carbon. Several chemical analyses were made on samples from set 10, including  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , zinc, and sulfur. Silver and zinc were determined in samples of set 11 by atomic absorption analysis.

#### STATISTICAL METHODS

Statistical analyses of the four sets of chemical data were conducted in the same manner as described in the previous reports (Vine, 1966, 1969). The 5th, 25th, 50th, 75th, and 95th percentiles and the arithmetic and geometric means were calculated for each constituent, and the

product moment coefficient of correlation was calculated for each pair of constituents 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), correlation coefficients were calculated after certain substitutions were made in the data sets (table 1).

The interpretation of geochemical associations in the rock units studied is based primarily on coefficients of correlation for each pair of constituents (tables 3, 5, 7, 9). The coefficients measure the degree to which log concentrations fit a straight line when plotted on a 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, Davies, 1954, p. 276). Thus, in tables 4, 6, 8, and 10 are listed 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 the conditions for ideal sampling of the rock unit are not fully satisfied.

Groups of associated elements are further identified from the correlation matrices by the use of principal-component analysis. This technique, described by Harman (1960), has recently been applied to a variety of geologic problems. Some of these applications are described by Imbrie and Van Andel (1964) and by Griffiths (1966). The method involves constructing radial vectors for each chemical constituent such 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 the axes have been selected that will best represent most of the data in two dimensions.<sup>1</sup> In these 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 patterned segments of each diagram suggest possible geochemical groupings of the elements. The resulting groups of elements probably reflect different physical and chemical processes in the depositional environment and subsequent alteration of each rock

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<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 the presence of more than two principal components with any acceptable degree of certainty.

# ELEMENT DISTRIBUTION IN SOME TYPES OF BLACK SHALE H11

TABLE 1.—*Substitutions made in the data sets*

[>, greater than; n.d., not detected; <, less than]

Element	No. of samples	Reported as (percent)	Value substituted (percent)
Set 9 (43 samples)			
Al.....	28	>10	15
Fe.....	1	>10	15
Ca.....	7	>10	15
K.....	1	n.d.	1
B.....	1	n.d.	.0015
Be.....	2	n.d.	.00005
Co.....	1	n.d.	.00003
La.....	3	n.d.	.0015
Pb.....	8	n.d.	.0003
Zr.....	1	n.d.	.0015
C <sub>min</sub> .....	7	<0.01	.007
Set 10 (51 samples)			
Fe.....	9	>10	15
Ca.....	10	>10	15
K.....	6	n.d.	.5
Ag.....	21	n.d.	.00005
B.....	25	n.d.	.0005
Co.....	1	n.d.	.0003
Ga.....	8	n.d.	.0003
Ga.....	4	<0.0007	.0005
La.....	16	n.d.	.001
Mo.....	4	n.d.	.0002
Mo.....	4	<0.0005	.0003
Pb.....	5	n.d.	.0005
Sc.....	30	n.d.	.00015
Tl.....	30	n.d.	.0015
Y.....	1	n.d.	.0007
Yb.....	1	n.d.	.00005
Yb.....	14	<0.00015-0.0007	.00007
Zr.....	1	n.d.	.0015
C <sub>org</sub> .....	5	<0.1	.07
Set 11 (47 samples)			
Al.....	4	>10	15
Be.....	14	n.d.	.0001
La.....	3	n.d.	.0015
Mo.....	27	n.d.	.0002
Pb.....	1	n.d.	.0005
Set 12 (30 samples)			
Na.....	2	n.d.	0.02
K.....	1	n.d.	.5
B.....	3	n.d.	.001
Be.....	2	n.d.	.00007
Co.....	3	n.d.	.0005
Ga.....	2	n.d.	.0005
La.....	2	n.d.	.001
Nb.....	3	n.d.	.0005
Pb.....	3	n.d.	.0005
Sc.....	1	n.d.	.0002
Yb.....	1	<0.0003	.0002
C <sub>min</sub> .....	3	<0.01	.005

unit. A factor complicating the interpretation of the groups, however, is that the data are part of a closed array. This problem, described by Chayes (1960), may be thought of as one of dilution. For example, consider major rock constituents such as detrital quartz, carbonate minerals, and clay. The end members of these three components may be regarded as pure siltstone, limestone, or shale containing only one of the three constituents. A built-in negative correlation must necessarily exist between a dominant major constituent and the other two principal constituents. A corresponding positive correlation is imposed on some of the minor constituents that results entirely from the dilution process. The process of dilution, therefore, is a factor affecting the magnitude of any of the correlation coefficients in tables 3, 5, 7, and 9.

### DISTRIBUTION OF ELEMENTS

The distribution of elements is described separately for each of the four sets of samples because each set is different in lithology: the stratigraphic units represented by the four sets accumulated in different environments of deposition, and each was sampled according to different sampling patterns. The concentrations of each element or constituent are listed by percentiles in table 2, and coefficients of correlation that were calculated for each pair of constituents for each sample set are listed in tables 3, 5, 7 and 9. Where less than half of the values are listed as indeterminate values (greater than, less than, not detected), it is possible to give the median and some of the percentiles.

TABLE 2.—*Element concentration in four sets of Paleozoic black shale samples*

[Chemical analyses were made to determine  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , Zn, and S for set 10; Ag, and Zn for set 11. All other analyses except carbon were made by the six-step spectrographic method. Total carbon was determined by induction-furnace method, mineral carbon by acid extraction, and organic carbon was calculated by difference. Parentheses indicate content of element recalculated to the elemental form. See p. H2, H9 for discussion and list of analysts]

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>		
Si.....	9	5.0	>10.0	>10.0	>10.0	>10.0		
SiO <sub>2</sub> .....	10	19.4	36.4	45.6	69.0	93.0	50.3	48.6
(Si).....		(9.0)	(17)	(21)	(32)	(43)	(23)	(23)
Al.....	9	3	7	>10	>10	>10		
Al <sub>2</sub> O <sub>3</sub> .....	10	1.27	3.02	4.36	5.44	8.41	4.6	4.1
(Al).....		(.68)	(1.6)	(2.3)	(2.9)	(4.5)	(2.4)	(2.2)
Al.....	11	5	7	7	7	>10	7.2	7.1
Al.....	12	2	>10	>10	>10	>10		
Fe.....	9	2	2	3	3	5	3.3	2.9
Fe <sub>2</sub> O <sub>3</sub> .....	10	1.5	5.61	9.60	13.1	19.8	10	8.0
(Fe).....		(1.0)	(3.9)	(6.7)	(9.2)	(14)	(7.0)	(5.6)
Fe.....	11	2	3	3	5	5	3.6	3.4
Fe.....	12	.7	3	5	5	5	3.8	3.3
Mg.....	9	1	1.5	2	3	5	2.6	2.3
MgO.....	10	.30	1.24	2.06	3.78	5.74	2.6	2.0
(Mg).....		(.18)	(.75)	(1.2)	(2.3)	(3.5)	(1.6)	(1.2)



# ELEMENT DISTRIBUTION IN SOME TYPES OF BLACK SHALE H13

TABLE 2.—*Element concentration in four sets of Paleozoic black shale samples—Con.*

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>		
Mg.....	11	0.5	0.7	0.7	1	1.5	0.80	0.77
Mg.....	12	.2	.7	.7	1	1.5	.78	.69
Ca.....	9	.3	.7	1.5	7	>10	4.8	3.5
CaO.....	10	.64	2.19	5.04	9.79	30.2	7.4	4.6
(Ca).....	11	(.46)	(1.6)	(3.6)	(7.0)	(22)	(5.3)	(3.3)
Ca.....	11	.15	.2	.3	5	7	2.0	.76
Ca.....	12	.007	.03	.07	.15	.3	.22	.067
Na.....	9	.1	.7	1	1	2	.90	.75
Na <sub>2</sub> O.....	10	.11	.22	.27	.36	.48	.29	.27
(Na).....	11	(.08)	(.16)	(.20)	(.27)	(.36)	(.21)	(.20)
Na.....	11	1	1	1.5	1.5	1.5	1.3	1.3
Na.....	12	<.05	.3	1	1.5	2	1.0	.65
K.....	9	2	3	5	5	7	4.0	3.7
K <sub>2</sub> O.....	10	.32	1.06	1.62	2.04	3.12	1.6	1.4
(K).....	11	(.27)	(.88)	(1.3)	(1.7)	(2.6)	(1.3)	(1.2)
K.....	11	2	3	3	3	3	2.9	2.9
K.....	12	1	3	3	3	3	2.8	2.7
Tl.....	9	.07	.2	.2	.3	.3	.24	.22
	10	.03	.07	.1	.15	.2	.12	.10
	11	.1	.2	.2	.3	.3	.24	.23
	12	.15	.3	.3	.3	.5	.31	.29
Mn.....	9	.007	.015	.03	.1	.15	.10	.04
	10	.005	.01	.03	.07	.1	.039	.030
	11	.015	.03	.05	.07	.1	.046	.040
	12	.0015	.015	.03	.05	.1	.044	.027
C <sub>total</sub> .....	9	.25	.88	2.3	5.0	7.7	3.2	2.2
	10	1.44	3.65	7.06	8.83	14.21	7.1	5.8
	11	.67	1.86	3.60	11.00	14.80	6.2	4.1
	12	.16	.42	.91	1.43	2.70	1.3	.83
C <sub>mineral</sub> .....	9	<.01	.02	.72	3.2	5.8	1.8	.35
	10	.25	.52	1.63	2.60	6.99	2.9	1.3
	11	.03	.24	.55	.83	1.15	.60	.43
	12	<.01	.03	.05	.09	.69	.16	.062
C <sub>organic</sub> .....	9	.02	.05	1.3	2	2.7	1.3	1.0
	10	<.01	1.3	5.0	7.1	12.5	5.1	2.6
	11	.6	1.4	3.2	10.2	14.1	5.6	3.4
	12	.2	.4	.6	1.0	1.8	1.1	.72
Ag.....	10	<.0001	<.0001	.0001	.0002	.0002	.00012	.00009
	11	.0002	.0003	.0004	.0005	.0006	.00037	.00034
B.....	9	.003	.007	.015	.02	.03	.013	.011
	10	<.001	<.001	.001	.002	.007	.0022	.001
	11	.003	.005	.005	.005	.007	.0054	.0053
	12	<.002	.003	.003	.007	.01	.0039	.0033
Ba.....	9	.01	.02	.03	.05	.07	.033	.029
	10	.005	.007	.015	.02	.03	.015	.010
	11	.015	.02	.03	.03	.05	.027	.026
	12	.02	.03	.05	.07	.15	.071	.054
Be.....	9	<.0001	.0002	.0003	.0005	.0007	.00034	.00031
	10	<.0001	<.0001	<.0001	<.0001	.0003	.00017	.00016
	11	<.0002	<.0002	.0002	.0002	.0003	.00017	.00017
	12	<.00015	.0002	.0002	.0002	.0003	.00018	.00017
Co.....	9	.0005	.001	.001	.0015	.002	.0011	.0010
	10	.0007	.003	.01	.02	.03	.014	.0080
	11	.001	.0015	.002	.002	.003	.0019	.0018
	12	<.001	.001	.0015	.0015	.002	.0014	.0013
Cr.....	9	.005	.01	.01	.01	.015	.0099	.0096
	10	.0005	.002	.003	.005	.015	.0055	.0030
	11	.01	.01	.015	.03	.07	.026	.020
	12	.007	.01	.01	.015	.02	.012	.011

TABLE 2.—*Element concentration in four sets of Paleozoic black shale samples—Con.*

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>		
Cu.....	9	0.0007	0.002	0.003	0.005	0.01	0.0040	0.0031
	10	.005	.015	.02	.03	.05	.021	.020
	11	.003	.007	.01	.015	.02	.013	.0098
	12	.002	.003	.005	.005	.01	.0047	.0042
Ga.....	9	.001	.002	.003	.005	.005	.0031	.0028
	10	<.0005	.0005	.0007	.001	.0015	.00074	.00070
	11	.002	.003	.003	.005	.005	.0035	.0033
	12	<.001	.003	.003	.005	.005	.0037	.0032
La.....	9	<.003	.005	.007	.01	.015	.0073	.0064
	10	.001	.001	.003	.007	.01	.0048	.0033
	11	<.003	.003	.003	.005	.005	.0036	.0034
	12	<.002	.002	.003	.003	.005	.0030	.0027
Mo.....	10	<.0005	.0005	.007	.015	.015	.0076	.0040
	11	<.0005	<.0005	<.0005	.0015	.003	.00089	.00048
Ni.....	9	.002	.003	.003	.005	.007	.0039	.0035
	10	.005	.02	.05	.07	.1	.049	.030
	11	.002	.005	.005	.015	.02	.010	.0079
	12	.002	.005	.005	.005	.007	.0048	.0045
Pb.....	9	.0007	.0007	.0015	.003	.01	.0026	.0015
	10	.0005	.003	.005	.007	.015	.0052	.0040
	11	.001	.002	.002	.007	.01	.0046	.0033
	12	.001	.0015	.002	.002	.005	.0021	.0019
Sc.....	9	.001	.002	.002	.003	.003	.0023	.0022
	10	<.0003	<.0003	<.0003	.0007	.001	-----	-----
	11	.0007	.001	.001	.0015	.0015	.0012	.0011
	12	.0005	.001	.0015	.0015	.0015	.0012	.0012
Sr.....	9	.005	.015	.015	.02	.07	.021	.016
	10	.0015	.007	.02	.03	.05	.023	.020
	11	.02	.02	.03	.05	.05	.033	.030
	12	.003	.007	.01	.015	.02	.016	.011
V.....	9	.005	.01	.01	.015	.015	.011	.011
	10	.005	.01	.015	.02	.05	.021	.020
	11	.007	.01	.015	.03	.05	.022	.017
	12	.015	.02	.02	.02	.03	.021	.020
Y.....	9	.002	.003	.005	.005	.005	.0040	.0037
	10	.001	.002	.003	.007	.01	.0049	.0040
	11	.002	.002	.003	.003	.005	.0028	.0026
	12	.0015	.002	.003	.003	.005	.0024	.0023
Yb.....	9	<.00015	.0003	.0003	.0005	.0005	-----	-----
	10	<.0003	<.0003	.0003	.0005	.001	.00041	.00020
	11	<.0002	<.0002	<.0002	.0003	.0003	-----	-----
	12	<.0003	.0003	.0003	.0003	.0003	.00030	.00029
Zn.....	10	.012	.037	.090	.12	.24	.092	.070
	11	.0063	.083	.014	.076	.23	.050	.024
Zr.....	9	.003	.005	.007	.01	.02	.0077	.0068
	10	.003	.005	.007	.01	.02	.0094	.0080
	11	.003	.005	.005	.007	.015	.0063	.0058
	12	.003	.007	.01	.01	.015	.0087	.0079
Tl.....	10	<.003	<.003	<.003	.005	.007	.0031	.0030
S.....	10	.20	2.65	6.73	9.78	13.89	6.7	4.5
Nb.....	12	<.001	.001	.001	.0015	.0015	.0013	.0012

## BELDEN SHALE FROM COLORADO

*Major elements.*—The major elements in the Belden Shale (set 9), in order of decreasing abundance, are silicon, aluminum, potassium, iron, magnesium, calcium, sodium, and titanium. Of the 43 samples studied, 40 contained 10 percent or more of silicon, and more than half contained 10 percent or more of aluminum. Although many of the samples are dark gray to black, the total carbon content is low in comparison with that in many black shales. The range of mineral carbon content is greater than that of organic carbon, but the total carbon content is rather evenly divided between the two types in many samples.

*Minor elements.*—The median concentrations of most of the minor elements are not unusual, but at the 95th percentile, boron, beryllium, gallium, and lead contents are high in comparison with those in the other black shales that have been studied. Moreover, lithium was reported to occur in 36 of the 43 samples in set 9, although no attempt was made to determine the amount quantitatively. This suite of minor elements may reflect the nature of the granitic terrain from which the sediments were derived, for Precambrian rocks with similar trace-element suites have been reported from a nearby area of the ancestral Rocky Mountains (Hawley and others, 1966).

*Element associations.*—The correlations and associations shown in tables 3 and 4 for the Belden Shale can be used to divide the elements into four groups, as shown on the vector diagram (fig. 2). Organic carbon and mineral carbon occur in the same segment of the diagram, but only mineral carbon is well represented. Lead and copper may be partly associated with the organic carbon, but they are also poorly represented. Calcium, magnesium, and manganese seem to be chiefly associated with carbonate minerals, whereas strontium seems to correlate with both carbonate minerals and organic carbon. The second group, which consists of aluminum, titanium, vanadium, lanthanum, scandium, gallium, chromium, barium, and cobalt, is probably detrital in origin and mode of occurrence, and it seems to be inversely related

TABLE 3.—Coefficients of correlation for element pairs in

Al	Fe	Mg	Ca	Na	K	Tl	Mn	B	Ba	Be	Co	Cr	Cu
Al	-0.01	-0.10	-0.52	0.35	0.33	0.64	0.54	0.27	0.46	0.42	0.44	0.62	0.12
	Fe	-.13	-.14	-.31	-.26	.05	.20	-.29	.14	-.27	.38	-.19	-.27
		Mg	.57	.17	.36	-.32	.59	.41	-.11	.36	.09	-.09	.23
			Ca	-.02	.02	-.71	.79	.01	-.26	.14	-.33	-.38	.22
				Na	.42	.38	-.26	.42	.35	.41	.09	.41	.08
					K	.06	-.05	.80	.11	.52	.34	.21	.27
						Tl	-.67	.07	.52	.23	.28	.56	-.10
							Mn	-.02	-.26	-.01	-.09	-.52	.24
								B	.03	.60	.34	.31	.23
									Ba	.31	.22	.37	-.12
										Be	.16	.38	.19
											Co	.24	.25
												Cr	.15
													Cu

Significance level, 41 degrees of freedom

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>org</sub>, organic carbon.  
<sup>3</sup> C<sub>min</sub>, carbonate carbon.



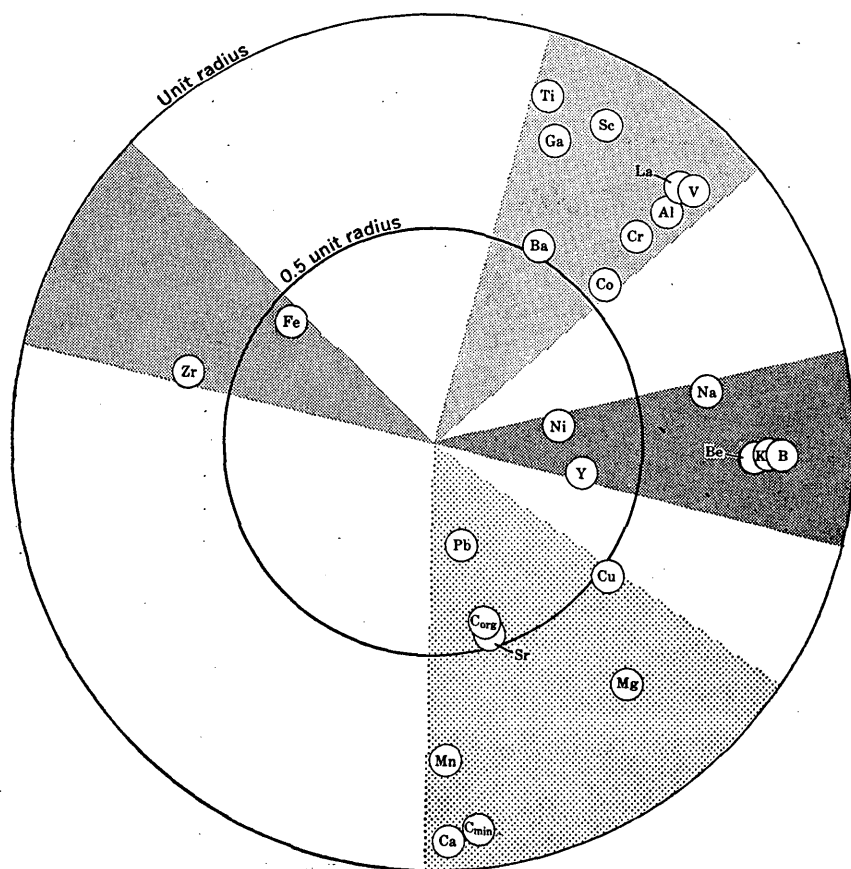


FIGURE 2.—Rotated two-dimensional vector diagram of the principal-component analysis of the correlation matrix for set 9, 43 samples of Belden Shale from Colorado. Patterned areas suggest geochemical groupings of elements.

to the mineral carbon and organic carbon group. Zirconium and iron, which make up the third group, show a fairly strong association with each other but not with any of the other elements. They may represent a heavy detrital mineral group. The fourth group, which consists of potassium, sodium, beryllium, and boron, has a negative correlation with the iron and zirconium group, but its origin and mineral composition are uncertain. It may represent a light detrital fraction that would include feldspars.

TABLE 4.—*Element associations in set 9, 43 samples of Belden Shale from Colorado*

[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
Ti, Sc, Ga, Al, V, La, Cr, Ba	C <sub>min</sub>	Sr, Mg, Mn, Ca
Ti, Sc, Ga, La, V, Al, Cr, Co	Ca	C <sub>org</sub> , Sr, Mg, Mn, C <sub>min</sub>
Ti, Al, Sc, Cr, Ga, V, La	Mn	Y, Pb, Mg, C <sub>min</sub> , Ca
Sc, Ti	Mg	Y, Ni, Be, K, B, Ca, Mn, C <sub>min</sub>
Ni	Sr	Na, C <sub>org</sub> , C <sub>min</sub> , Ca
	C <sub>org</sub>	Ca, Sr, Pb, Cu
	Cu	Pb, C <sub>org</sub>
	Pb	Mn, C <sub>org</sub> , Cu
	Fe	Co, Zr
B, K, Na, V, Be	Zr	Fe
Sr	Ni	Co, Mg, Y
	Y	La, Mn, Mg, Sc, K, Ni, B, Be
Zr	B	Cr, Co, Sc, Mg, Y, V, Na, La, Be, K
Ca	Co	B, K, Ni, Fe, Sc, Al, Ga, V, La
Zr	Be	La, Ba, Sc, Mg, Cr, Na, Al, V, Y, K, B
Zr	K	Y, Ga, Al, Co, Mg, V, Na, La, Be, B
C <sub>min</sub>	Ba	V, Be, La, Na, Ga, Cr, Sc, Al, Ti
Zr, Fe	Na	Ba, La, Al, Ti, Sr, B, Be, Cr, Sc, V, K
Ca, Mn, C <sub>min</sub> , Zr	V	Ba, K, B, Na, Be, Co, Ga, Cr, La, Ti, Sc, Al
Ca, C <sub>min</sub> , Mn, Mg	Sc	Y, Be, B, Ba, Co, Na, Cr, Al, V, Ga, La, Ti
Ca, C <sub>min</sub> , Mn, Mg	Ti	Na, Ba, Cr, La, V, Al, Ga, Sc
Ca, C <sub>min</sub> , Mn	Ga	K, Cr, Ba, Co, V, Al, La, Ti, Sc
Ca, C <sub>min</sub> , Mn	La	Y, Be, Ba, Na, Cr, K, B, Ti, Ga, V, Co, Al, Sc
Mn, C <sub>min</sub> , Ca	Cr	B, Ga, Ba, La, Be, Na, Sc, Ti, V, Al
Mn, Ca, C <sub>min</sub>	Al	K, Na, Be, Co, Ba, Ga, Sc, La, Cr, Ti, V

#### HOUY FORMATION FROM TEXAS

*Major elements.*—The most abundant constituent in samples of the Houy Formation (set 10) is SiO<sub>2</sub>, which has a median value of 45.6 percent and a 95th percentile of 93.0 percent. About a quarter of the samples are siliceous enough to be classified as black chert. The next most abundant constituents are Fe<sub>2</sub>O<sub>3</sub> and sulfur, which together reflect the abundance of pyrite nodules and disseminations in the Houy. The amount of pyrite in these samples greatly exceeds that of any other set of black shale samples that have been studied. If most of the iron and sulfur are combined in the form of pyrite, at the median level more than 12 percent pyrite may be present. Five percent of the samples contain more than 25 percent pyrite. Carbon is also abundant and has a median value of 7 percent. Of this, organic carbon is more abundant and more widely dispersed than mineral carbon.

The next most abundant constituent is  $\text{CaO}$ , which has a median value of 5 percent, followed by  $\text{MgO}$ , which has a median value of 2 percent, reflecting the fact that some of the samples contain abundant calcite and dolomite. The contents of  $\text{Al}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ , and titanium are relatively low because of the abundance of chert, carbonate, and organic matter. As much as 3 percent phosphorus was also detected in a few samples.

*Minor elements.*—Many minor elements are unusually abundant in the core samples of the Houy Formation. Previous analyses of rocks from the Houy Formation, reported by Tourtelot (1956, p. 76) and Swanson (1960, p. 38), suggested this possibility. The median concentrations of cobalt, copper, molybdenum, nickel, lead, and zinc are several times the average concentrations for shale as estimated by Turekian and Wedepohl (1961, table 2), and at the 95th percentile concentrations of most of these elements are remarkably high. Thallium was also reported in 21 of the 51 samples and is about 50 times as abundant at the 95th percentile as in the average shale. All these elements are sulfophile, and, therefore, their enrichment in these rocks may be related to the unusually high pyrite content. Thallium and zinc, in particular, show a greater concentration in a pyrite-rich heavy-mineral separation prepared from one of the black shale samples. The median contents of detrital elements like boron, gallium, and scandium are less than those in most of the other black shale sets previously studied. Other minor elements are present in nearly normal amounts.

*Element associations.*—The diluting effect of  $\text{SiO}_2$ , contained in both detrital quartz and chert, has a pronounced effect on the correlations between other elements in the samples of the Houy Formation (tables 5 and 6; fig. 3). The strong negative correlation between  $\text{SiO}_2$ , and most other elements increases the tendency of the other elements to correlate positively with each other. However, it is possible to divide most of the elements into several major groups. Mineral carbon correlates best with  $\text{CaO}$ , manganese, strontium, and  $\text{MgO}$ , but these constituents overlap the segment of the vector diagram (fig. 3) that is occupied by the detrital elements. Organic carbon shows its strongest correlation with molybdenum; it also shows strong positive correlations with silver, nickel, zinc, cobalt, copper, and thallium. These elements correlate about equally well with sulfur, as indicated by their position in figure 3 intermediate between organic carbon and



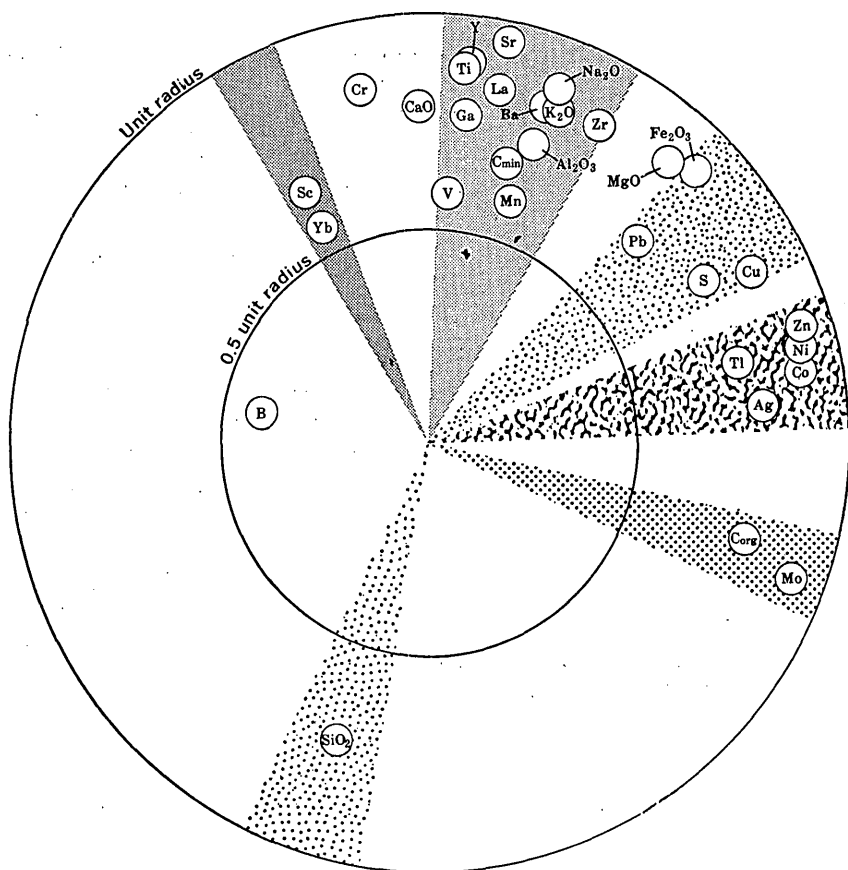


FIGURE 3.—Rotated two-dimensional vector diagram of the principal-component analysis of the correlation matrix for set 10, 51 core samples of the Houy Formation from Texas. Patterned areas suggest geochemical groupings of elements.

sulfur. Sulfur also shows a very strong correlation with  $\text{Fe}_2\text{O}_3$  and lead. The sulfur and organic carbon groups are probably very closely associated. The detrital group includes most of the remaining elements and oxides:  $\text{Al}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ , titanium, gallium, zirconium, chromium, lanthanum, yttrium, barium, and vanadium. Scandium and ytterbium seem to be weakly associated with the detrital group of elements (fig. 3). Boron seems to vary almost independently of all other elements, although the correlation estimates may not be entirely reliable because of the large number of substitutions for indeterminate values.

TABLE 5.—Coefficients of correlation for element pairs in

Ti	Mn	Ag	B	Ba	Co	Cr	Cu	Ga	La	Mo	Ni	Pb	Sc	Sr	Tl
Ti	0.22	0.08	0.34	0.69	0.19	0.86	0.43	0.70	0.68	−0.11	0.28	0.29	0.63	0.80	0.27
	Mn	.25	−.57	.47	.27	.19	.40	.34	.51	−.16	.23	.47	−.03	.58	.26
		Ag	−.36	.39	.68	−.06	.51	.24	.26	.64	.65	.33	−.27	.24	.68
			B	−.09	−.34	.43	−.29	.17	−.08	−.14	−.23	−.43	.57	−.05	−.22
				Ba	.32	.50	.42	.62	.82	.04	.39	.39	.22	.75	.44
					Co	−.04	.70	.14	.32	.65	.87	.61	−.09	.37	.67
						Cr	.17	.72	.52	−.29	.04	.11	.72	.72	.04
							Cu	.38	.36	.48	.74	.70	−.08	.44	.47
								Ga	.55	−.04	.20	.23	.45	.62	.19
									La	−.13	.38	.44	.40	.83	.39
										Mo	.69	.09	−.31	−.16	.60
											Ni	.55	−.02	.39	.61
												Pb	.05	.56	.27
													Sc	.49	.01
														Sr	.32
															Tl

Significance level, 49 degrees of freedom

95 percent	99 percent	99.9 percent
0.28	0.36	0.45

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

set 10, 51 core samples of the Houy Formation from Texas

[illegible]

TABLE 6.—*Element associations in set 10, 51 core samples of the Houy Formation from Texas*

[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
SiO <sub>2</sub> , B	C <sub>min</sub>	Co, Zn, S, K <sub>2</sub> O, Ti, Cr, Yb, Fe <sub>2</sub> O <sub>3</sub> , Cu, Pb, Ga, <b>La</b> , Ba, Na <sub>2</sub> O, Y, Zr, Sr, MgO, CaO, Mn
SiO <sub>2</sub> , Cor <sub>g</sub> , Mo, B	CaO	Sc, S, K <sub>2</sub> O, Fe <sub>2</sub> O <sub>3</sub> , Yb, Ga, Ti, Zr, Pb, Ba, Cr, Na <sub>2</sub> O, <b>La</b> , MgO, Y, Mn, Sr, C <sub>min</sub>
SiO <sub>2</sub> , B, Cor <sub>g</sub>	Mn	Ga, S, Yb, Fe <sub>2</sub> O <sub>3</sub> , Cu, Ba, Pb, Na <sub>2</sub> O, <b>La</b> , Y, Zr, Sr, MgO, CaO, C <sub>min</sub>
SiO <sub>2</sub>	Ti	Sr, Na <sub>2</sub> O, <b>La</b> , Al <sub>2</sub> O <sub>3</sub> , Ba, K <sub>2</sub> O, S, Cu, MgO, Zr, Fe <sub>2</sub> O <sub>3</sub> , Cor <sub>g</sub> , Zn, Mo, Ni, Co, Ag
B	Ag	Al <sub>2</sub> O <sub>3</sub> , Pb, Na <sub>2</sub> O, K <sub>2</sub> O, Ba, Zr, S, Fe <sub>2</sub> O <sub>3</sub> , Cu, MgO, Cor <sub>g</sub> , Mo, Ni, Zn, Co, Ti
Yb, CaO, Sc, Cr	Mo	Fe <sub>2</sub> O <sub>3</sub> , S, Cu, Ti, Ag, Co, Ni, Zn, Cor <sub>g</sub>
Yb, CaO, Mn	Cor <sub>g</sub>	K <sub>2</sub> O, Fe <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> , S, Cu, Co, Ti, Ag, Ni, Zn, Mo
SiO <sub>2</sub>	Ni	Ti, Y, Al <sub>2</sub> O <sub>3</sub> , <b>La</b> , Ba, Sr, K <sub>2</sub> O, Na <sub>2</sub> O, Zr, Pb, MgO, Cor <sub>g</sub> , Ti, Ag, Mo, Fe <sub>2</sub> O <sub>3</sub> , Cu, S, Zn, Co
	Zn	C <sub>min</sub> , <b>La</b> , Y, Ti, V, Ga, Sr, Ba, Al <sub>2</sub> O <sub>3</sub> , K <sub>2</sub> O, Na <sub>2</sub> O, Pb, Zr, Ti, S, Cor <sub>g</sub> , MgO, Ag, Mo, Fe <sub>2</sub> O <sub>3</sub> , Co, Ni, Cu
SiO <sub>2</sub> , B	Cu	<b>La</b> , Ga, Al <sub>2</sub> O <sub>3</sub> , C <sub>min</sub> , Y, Mn, Ba, Ti, Cor <sub>g</sub> , Sr, K <sub>2</sub> O, V, Ti, Mo, Ag, Na <sub>2</sub> O, Zr, S, Co, Pb, Ni, Fe <sub>2</sub> O <sub>3</sub> , Zn
SiO <sub>2</sub> , B	Pb	Ti, Ag, Na <sub>2</sub> O, Ba, K <sub>2</sub> O, Zr, <b>La</b> , C <sub>min</sub> , V, Mn, CaO, Y, Ni, Sr, Zn, MgO, Co, Cu, S, Fe <sub>2</sub> O <sub>3</sub>
SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Cor <sub>g</sub> , Mo, Mn, Cr, C <sub>min</sub> , CaO, Ag, Ga, Ti, Ba, V, Al <sub>2</sub> O <sub>3</sub> , <b>La</b> , Na <sub>2</sub> O, Y, Ti, Zr, K <sub>2</sub> O, Ni, Co, Sr, MgO, Zn, Pb, Cu, S
SiO <sub>2</sub> , B	Co	C <sub>min</sub> , Na <sub>2</sub> O, Al <sub>2</sub> O <sub>3</sub> , Ba, <b>La</b> , K <sub>2</sub> O, Sr, Zr, MgO, Cor <sub>g</sub> , Pb, Mo, S, Ti, Ag, Co, Fe <sub>2</sub> O <sub>3</sub> , Zn, Ni
SiO <sub>2</sub>	S	Al <sub>2</sub> O <sub>3</sub> , C <sub>min</sub> , Cor <sub>g</sub> , CaO, Mo, Ti, Mn, Ba, Na <sub>2</sub> O, V, K <sub>2</sub> O, Zr, Ag, Y, Ti, <b>La</b> , Sr, MgO, Zn, Co, Cu, Pb, Ni, Fe <sub>2</sub> O <sub>3</sub>
Sr, CaO, C <sub>min</sub> , Mn, <b>La</b> , Fe <sub>2</sub> O <sub>3</sub> , Y, Pb, MgO, S, Zr, Ti, Co, Sc, K <sub>2</sub> O, Ba, Cr, Cu, Ti, Ni, Na <sub>2</sub> O, V, Ga, Mn, C <sub>min</sub> , Pb, MgO, Ag, Co, CaO, Cu	SiO <sub>2</sub>	
	B	Ti, V, Al <sub>2</sub> O <sub>3</sub> , Cr, Sc
SiO <sub>2</sub> , Mo	Sc	CaO, <b>La</b> , Y, Ga, Sr, K <sub>2</sub> O, Al <sub>2</sub> O <sub>3</sub> , B, V, Ti, Cr
SiO <sub>2</sub>	V	<b>La</b> , MgO, B, Zn, S, Y, Cu, Na <sub>2</sub> O, Ga, Pb, Sr, Fe <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> , K <sub>2</sub> O, Sc, Cr, Ti
Mo, Cor <sub>g</sub>	Yb	Cr, MgO, Ti, <b>La</b> , Ga, Sr, Zr, Mn, Y, C <sub>min</sub> , Ba, CaO, Na <sub>2</sub> O
SiO <sub>2</sub>	Y	Ni, Zn, Yb, Cu, V, Sc, S, Pb, Mn, C <sub>min</sub> , Al <sub>2</sub> O <sub>3</sub> , Ga, Cr, MgO, Fe <sub>2</sub> O <sub>3</sub> , K <sub>2</sub> O, CaO, Zr, Ti, Na <sub>2</sub> O, Ba, <b>La</b>
SiO <sub>2</sub>	La	V, Zn, Co, Yb, Cu, Ni, Ti, Sc, Pb, S, C <sub>min</sub> , Mn, Cr, Ga, MgO, Al <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> , CaO, K <sub>2</sub> O, Ti, Na <sub>2</sub> O, Zr, Ba, Y
SiO <sub>2</sub>	Ba	Co, S, Ag, Ni, Pb, Yb, Zn, Cu, Ti, Mn, Cr, C <sub>min</sub> , CaO, Fe <sub>2</sub> O <sub>3</sub> , Ga, Ti, Al <sub>2</sub> O <sub>3</sub> , MgO, Sr, K <sub>2</sub> O, Y, Na <sub>2</sub> O, <b>La</b> , Zr
SiO <sub>2</sub> , B	MgO	V, Yb, Cr, Al <sub>2</sub> O <sub>3</sub> , Ti, Ti, Co, Ag, Ni, S, Ga, <b>La</b> , Pb, K <sub>2</sub> O, CaO, Y, Zn, Ba, Sr, Mn, Fe <sub>2</sub> O <sub>3</sub> , Cu, Na <sub>2</sub> O, Zr, C <sub>min</sub>

TABLE 6.—*Element associations in set 10, 51 core samples of the Houy Formation from Texas—Continued*

Negative Correlation—	Element	→Positive Correlation
SiO <sub>2</sub>	Sr	Tl, Yb, Co, Zn, Ni, Cu, Sc, V, S, Pb, Mn, Ga, Al <sub>2</sub> O <sub>3</sub> , C <sub>min</sub> , MgO, Fe <sub>2</sub> O <sub>3</sub> , Zr, Cr, Ba, Na <sub>2</sub> O, K <sub>2</sub> O, Ti, CaO, Y
SiO <sub>2</sub>	Ti	Ni, Pb, Yb, B, Zn, S, C <sub>min</sub> , Cu, CaO, MgO, Sc, Fe <sub>2</sub> O <sub>3</sub> , V, La, Ba, Ga, Zr, Y, Na <sub>2</sub> O, Sr, Al <sub>2</sub> O <sub>3</sub> , K <sub>2</sub> O, Cr
SiO <sub>2</sub> , Mo	Cr	Yb, MgO, C <sub>min</sub> , Fe <sub>2</sub> O <sub>3</sub> , B, Zr, Ba, La, CaO, Y, V, Na <sub>2</sub> O, Ga, Sc, Sr, K <sub>2</sub> O, Al <sub>2</sub> O <sub>3</sub> , Ti
SiO <sub>2</sub>	K <sub>2</sub> O	C <sub>org</sub> , C <sub>min</sub> , Ag, Co, S, Ni, Pb, CaO, Cu, Ti, Zn, Sc, V, MgO, Y, La, Fe <sub>2</sub> O <sub>3</sub> , Zr, Cr, Ga, Ba, Na <sub>2</sub> O, Sr, Ti, Al <sub>2</sub> O <sub>3</sub>
SiO <sub>2</sub>	Na <sub>2</sub> O	Co, Ti, Ag, S, Pb, Yb, Ni, V, Mn, C <sub>min</sub> , CaO, Zn, Cu, Fe <sub>2</sub> O <sub>3</sub> , Cr, La, Ga, Al <sub>2</sub> O <sub>3</sub> , MgO, Y, Sr, K <sub>2</sub> O, Ti, Ba, Zr
SiO <sub>2</sub>	Zr	Yb, S, Ag, Pb, Co, Cr, CaO, Ti, Ni, Mn, C <sub>min</sub> , Zn, Cu, Ga, Al <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> , K <sub>2</sub> O, Ti, Sr, Y, La, MgO, Na <sub>2</sub> O, Ba
SiO <sub>2</sub>	Ga	Mn, Yb, Zn, Cu, Sc, Fe <sub>2</sub> O <sub>3</sub> , CaO, C <sub>min</sub> , V, La, MgO, Y, Zr, Ba, Sr, Ti, Cr, Na <sub>2</sub> O, K <sub>2</sub> O, Al <sub>2</sub> O <sub>3</sub>
	Al <sub>2</sub> O <sub>3</sub>	S, Co, Ag, Ni, C <sub>org</sub> , Cu, B, Ti, MgO, Zn, Sc, Y, V, Fe <sub>2</sub> O <sub>3</sub> , La, Sr, Zr, Ba, Cr, Na <sub>2</sub> O, Ga, Ti, K <sub>2</sub> O

## CHEROKEE GROUP FROM KANSAS AND OKLAHOMA

*Major elements.*—More than 10 percent silicon was reported in all the samples from the Cherokee Group (set 11). Aluminum, which has a median concentration of 7 percent, is next in abundance, followed by total carbon, which has a median of 3.6 percent. Most of this carbon is organic. Some of the samples are slightly phosphatic, but phosphorus, in amounts of 2 percent or less, was detected in only 14 samples, and its median value could not be determined. The other major elements, in approximate order of abundance, are potassium, iron, sodium, magnesium, calcium, and titanium.

*Minor elements.*—The abundance of minor elements in these black shale samples is similar to that in other black shale samples associated with coal beds in the Interior coal province (for example, Vine, 1969, set 5). In general, the samples from the Cherokee Group are characterized by high content of silver, chromium, gallium, lead, vanadium, and zinc at the 95th percentile. The median content of chromium and molybdenum is lower in set 11 than in set 5 and the median content of cobalt and gallium is higher. The content of strontium, lead, and zinc is higher in both sets 5 and 11 at the 95th percentile than in similar shales from the western Kentucky coal field (Vine, 1966, sets 1 and 2).

*Element associations.*—Correlations for the elements in set 11 (tables 7, 8) can be divided into three major groups, as shown in

TABLE 7.—Coefficients of correlation for element pairs in set 11,

Al	Fe	Mg	Ca	Na	K	Ti	Mn	B	Ba	Be	Co	Cr	Cu	Ga	La
Al	0.40	0.01	-0.28	0.29	0.44	0.45	0.16	0.06	0.42	0.13	-0.02	-0.24	-0.34	0.29	0.27
	Fe	-0.21	-0.42	.31	.47	.58	.44	.04	.52	.08	.09	-.48	-.56	.53	.33
		Mg	.63	-.07	-.11	-.32	-.29	-.13	-.33	.15	-.29	.56	.43	-.57	.12
			Ca	-.31	-.34	-.68	-.32	-.12	-.45	.16	-.10	.86	.72	-.69	.22
				Na	.45	.30	.38	.45	.32	.03	.20	-.46	-.38	.29	.09
					K	.45	.23	.25	.42	.23	.18	-.39	-.55	.36	.27
						Ti	.47	.02	.51	.21	.30	-.63	-.63	.40	.26
							Mn	.06	.33	-.01	.45	-.49	-.39	.34	.08
								B	-.06	.21	.22	-.15	.05	.17	-.01
									Ba	-.10	.24	-.50	-.56	.49	.36
										Be	-.08	.11	.03	-.12	.25
											Co	-.23	-.07	-.04	.14
												Cr	.70	-.67	.28
													Cu	-.64	.01
														Ga	-.06
															La

Significance level, 45 degrees of freedom		
95 percent	99 percent	99.9 percent
0.29	0.37	0.47

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

## H27

47 core samples of the Cherokee Group from Kansas and Oklahoma

[illegible]

figure 4: (1) the detrital group, which shows a strong negative correlation with the organic carbon and mineral carbon groups and which consists of aluminum, zirconium, potassium, scandium, manganese, iron, titanium, barium, and gallium; (2) the organic-carbon group, which consists of nickel, silver, vanadium, molybdenum, copper, chromium, and zinc; and (3) the mineral carbon group, which consists of calcium, magnesium, strontium, and lead. Lanthanum and yttrium seem to fall between the major groups, whereas boron shows no particular correlation with any other element but possibly sodium. The proximity of the mineral carbon and organic carbon groups shown in figure 4 is probably due to the dilution effect of the dominant detrital group.

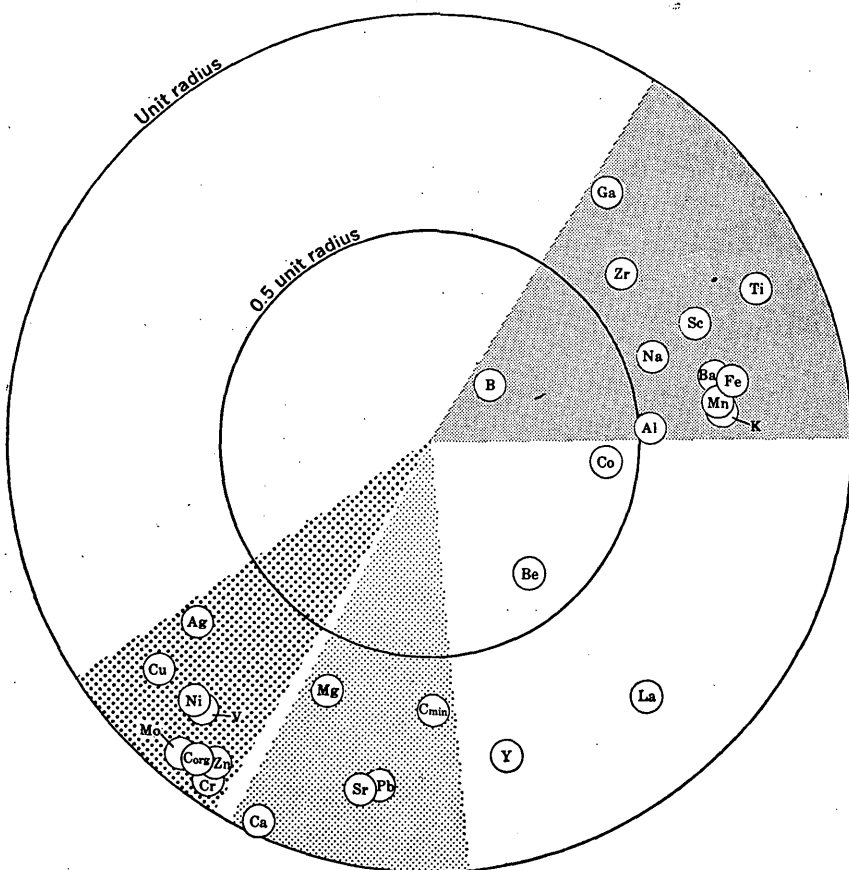


FIGURE 4.—Rotated two-dimensional vector diagram of the principal-component analysis of the correlation matrix for set 11, 47 core samples of the Cherokee Group from Kansas and Oklahoma. Patterned areas suggest geochemical groupings of elements.



TABLE 8.—*Element associations in set 11, 47 core samples of the Cherokee Group from Kansas and Oklahoma*

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

Negative correlation←	Element	→Positive correlation
Ti, Ga, Zr, Sc, Ba, Fe, K, Mn, Na	C <sub>org</sub>	C <sub>min</sub> Y, Mg, Ag, Sr, V, Pb, Ni, Cu, Cr, Zn, Ca, Mo
Ti, Ga, Sc, Fe, Mn, Zr, K, Na, Ba	Mo	C <sub>min</sub> Y, Mg, Pb, Ag, Sr, Ni, Cu, V, Ca, C <sub>org</sub> , Zn, Cr
Ti, Ga, Mn, Zr, Sc, K, Fe, Co, Ba, Na	V	Ag, Pb, Sr, Cu, Mg, C <sub>org</sub> , Ni, Ca, Zn, Mo, Cr
Ti, Zr, Na, Ga, Mn, Ba, Fe, Co, Sc, K	Ni	C <sub>min</sub> Y, Mg, Pb, Sr, Ag, Cu, Zn, V, C <sub>org</sub> , Mo, Ca, Cr
Ga, Sc, Ti, Fe, Ba, K, Mn, Na, Zr, Al	Cu	C <sub>min</sub> Y, Mg, Pb, Sr, Ag, V, Ni, Zn, Cr, Ca, C <sub>org</sub> , Mo
Zr, Ti, Mn, Sc, Na, K, Ga, Fe	Ag	Sr, Y, Pb, Mg, V, Ca, Cu, Ni, Zn, Cr, C <sub>org</sub> , Mo
Zr, Ti, Ga, Na	Pb	Ag, C <sub>min</sub> , La, Cu, Mg, Ni, Y, V, Mo, Zn, Sr, C <sub>org</sub> , Cr, Ca
	La	Sr, Fe, Ba, Pb, Y
Ga, Ba, Ti, Zr, Co, Mn	Mg	C <sub>min</sub> , Ag, Cu, Ni, C <sub>org</sub> , Sr, Pb, Mo, Zn, Cr, Ca, V
Ti, Ga, Sc, Zr, Ba, Mn, Fe, Na, K	Cr	C <sub>min</sub> Y, Mg, Ag, Sr, Pb, Cu, Ni, C <sub>org</sub> , Zn, V, Ca, Mo
Ti, Ga, Sc, Fe, K, Zr, Mn, Na, Ba, B, Al	Zn	C <sub>min</sub> Y, Mg, Ag, Ni, Pb, Sr, Cu, V, Cr, C <sub>org</sub> , Ca, Mo
Ti, Ga, Zr, Sc, Ba, Fe, K, Mn, Na	Ca	Ag, C <sub>min</sub> Y, Mg, V, Cu, Pb, Ni, Sr, Zn, Mo, Cr, C <sub>org</sub>
Ga, Ti, Zr, Sc, Fe	Sr	La, Ag, Mg, Y, C <sub>min</sub> , Cu, V, Ni, C <sub>org</sub> , Mo, Zn, Pb, Cr, Ca
Ga	Y	Cu, Ag, Mo, C <sub>org</sub> , Ni, C <sub>min</sub> , La, Pb, Zn, Cr, Sr, Ca
Ga, Ti	C <sub>min</sub>	Cu, Ni, Mg, Mo, Pb, Cr, C <sub>org</sub> , Zn, Y, Sr, Ca
	Be	
Zn	B	Na
Ni, Cr, Mo, Zn, Ag, Cu, V, C <sub>org</sub> , Ca, Pb	Na	Ga, Al, Ti, Fe, Ba, Zr, Sc, Mn, B, K
Cu, Mo, Zn, C <sub>org</sub> , V, Cr, Ni, Ag, Ca	K	Ga, Ba, Al, Na, Fe, Sc, Ti
Cu, Zn, C <sub>org</sub> , Mo, Cr, Ag, Ca, V, Ni, Sr	Sc	Al, Na, Mn, Ba, K, Fe, Ti, Ga
V, Mo, Cr, Ag, Ni, Zn, Cu, C <sub>org</sub> , Ca, Mg	Mn	Ba, Ga, Sc, Na, Zr, Co, Fe, Ti
V, Ni, Mg	Co	Ti, Zr, Mn
Ag, Ni, C <sub>org</sub> , Ca, Cr, Mo, Pb, V, Zn, Sr, Cu, Mg	Zr	Ba, Fe, Na, Mn, Co, Ti
C <sub>org</sub> , Mo, Ca, Ni, Cr, Cu, Zn, V, Ag, Sr, Pb, Mg, C <sub>min</sub>	Ti	Na, Co, Ga, Al, Mn, K, Ba, Sc, Fe, Zr
Cu, Mo, C <sub>org</sub> , Cr, Zn, Ca, V, Ni, Ag, Sr, Cu, Zn	Fe	Zr, Na, La, Al, Mn, K, Sc, Ba, Ga, Ti
Cu, C <sub>org</sub> , Cr, Ca, Mo, Ni, Zn, V, Mg	Al	Ga, Na, Sc, Fe, Ba, K, Ti
Zn, Ca, Mo, Cr, Cu, C <sub>org</sub> , Mg, V, Sr, C <sub>min</sub> , Ni, Pb, Y, Ag	Ba	Zr, Na, Mn, La, K, Al, Sc, Ga, Ti, Fe
	Ga	Al, Na, Mn, K, Ti, Ba, Fe, Sc

It is of particular interest to compare this set with set 5, described in another report (Vine, 1969), in view of their similar stratigraphic setting. The samples in set 5 were collected from outcrops and shallow artificial exposures in the same strata represented by core samples in set 11. In both sets the organic carbon fraction includes nickel, vanadium, molybdenum, silver, chromium, and copper, and the detrital fraction includes titanium, zirconium, gallium, and scandium. The chief differences are among elements that may be mobile in the zone of weathering. These are sodium, potassium, iron, and manganese.

UPPER PALEOZOIC BLACK SHALE FROM ARKANSAS  
AND OKLAHOMA

*Major elements.*—In set 12 the major elements, in decreasing order of abundance, are silicon, aluminum, iron, potassium, sodium, carbon, magnesium, titanium, and calcium. Silicon content exceeded 10 percent in each of the 30 samples, and aluminum exceeded 10 percent in 26 of the samples. The median value for total carbon is only 0.91 percent, and at the 95th percentile total carbon content is only 2.7 percent. Most of this carbon is organic; only a minor part is mineral.

*Minor elements.*—The gross minor-element content of the samples in set 12 is similar to that in set 9. This distribution may be typical of fine-grained marine sedimentary rocks that contain only a small amount of organic material. Barium, gallium, and zirconium contents are relatively high at the 95th percentile. Gallium and zirconium are most likely to be contained in minerals of detrital origin, whereas barium is probably in minerals of authigenic or diagenetic origin, and its distribution is probably related to the barite deposits at the base of the Stanley Shale.

*Element associations.*—The correlations among element groups computed for set 12 (tables 9, 10) show that most of the elements fall in the detrital-mineral group, as shown on the vector diagram (fig. 5). These elements are iron, potassium, gallium, lead, manganese, cobalt, magnesium, scandium, sodium, titanium, zirconium, yttrium, niobium, and possibly lanthanum. Nickel and chromium seem to form a separate group, but they are probably of detrital origin also. Organic carbon has a negative correlation with the principal detrital elements. Vanadium has no significant positive correlations, but it seems to be more closely associated with organic carbon than with any other element. Copper, barium, and boron all seem to be independent of other elements although copper and barium show a positive correlation with each other. Mineral carbon and calcium fall in the same segment of the vector diagram as strontium, yttrium, and beryllium; but the correlations are poor, and therefore they may not all be associated geochemically.

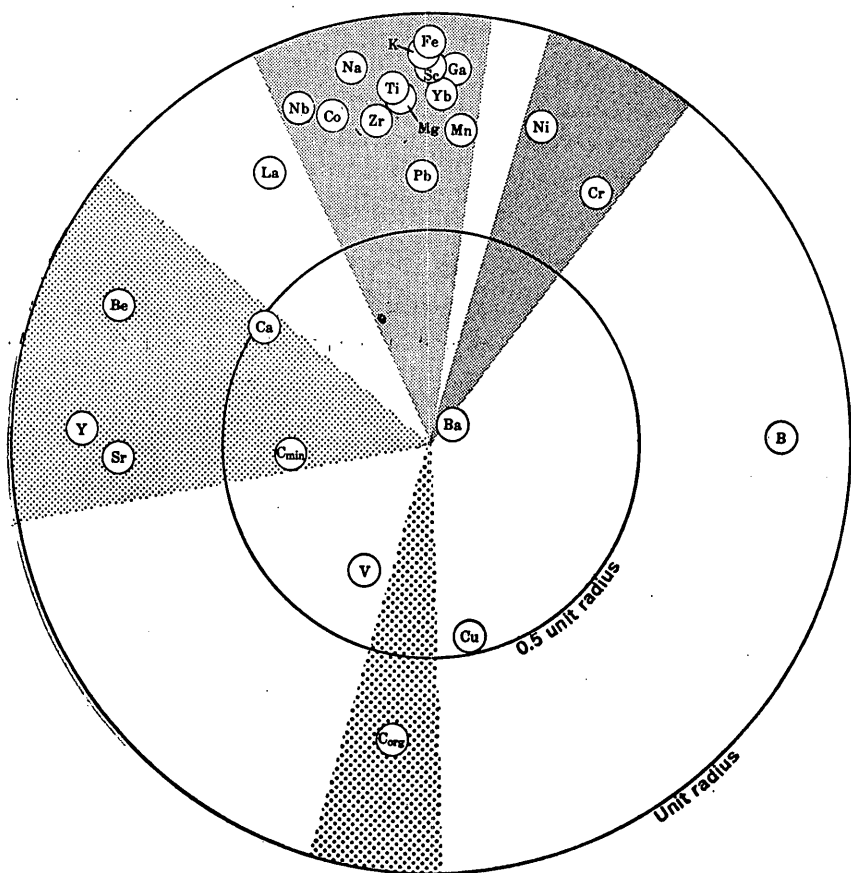


FIGURE 5.—Rotated two-dimensional vector diagram of the principal-component analysis of the correlation matrix for set 12, 30 samples of upper Paleozoic black shale from Arkansas and Oklahoma. Patterned areas suggest geochemical groupings of elements.

TABLE 9.—*Coefficients of correlation for element pairs in set 12, 30*

Fe	Mg	Ca	Na	K	Ti	Mn	B	Ba	Be	Co	Cr	Cu	Ga
Fe	0.74	0.30	0.81	0.86	0.69	0.79	-0.08	0.02	0.28	0.78	0.41	-0.46	0.83
	Mg	.36	.71	.64	.69	.66	-.07	-.21	.25	.68	.32	-.47	.68
		Ca	.43	.19	.35	.37	-.31	-.47	.14	.40	.00	-.39	.20
			Na	.79	.82	.57	-.11	-.05	.46	.68	.59	-.55	.85
				K	.68	.62	.05	.26	.37	.62	.54	-.35	.85
					Ti	.49	.10	-.03	.36	.56	.64	-.45	.75
						Mn	-.08	-.06	.08	.58	.24	-.47	.59
							B	.08	-.49	-.35	.49	-.02	.11
								Ba	.13	-.23	.05	.37	.00
									Be	.33	.03	-.21	.35
										Co	.30	-.29	.63
											Cr	-.31	.70
												Cu	-.35
													Ga

Significance level, 28 degrees of freedom

95 percent	99 percent	99.9 percent
0.36	0.46	0.57

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

*samples of upper Paleozoic black shale from Arkansas and Oklahoma*

[illegible]

TABLE 10.—*Element associations in set 12, 30 samples of upper Paleozoic black shale from Arkansas and Oklahoma*

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

Negative Correlation←	Element	→Positive Correlation
<b>C<sub>org</sub></b>	La	Y, Zr, Fe, Yb, Co, Na, K, Sc, Pb, Ga, Nb, Ti, Mg, Be
<b>B</b>	Be	Ti, K, Na, Sr, Nb, La, Y
<b>B</b>	Y	La, Sr, Be
<b>B</b>	Sr	Be, Y, Ca
<b>Ba, Cu</b>	Ca	Mg, Mn, Co, Na, Sr
	<b>C<sub>min</sub></b>	<b>C<sub>org</sub></b>
<b>Y, Sr, Be</b>	<b>B</b>	<b>Cr</b>
	<b>Cr</b>	Fe, Zr, Ni, B, Sc, K, Yb, Na, Ti, Ga
<b>Cu, C<sub>org</sub></b>	<b>Ti</b>	Be, Pb, Mn, Ni, Co, La, Cr, K, Zr, Nb, Mg, Fe, Sc, Yb, Ga, Na
<b>Cu, C<sub>org</sub></b>	<b>Na</b>	Ca, Be, Pb, Ni, La, Mn, Cr, Zr, Co, Yb, Nb, Mg, Sc, K, Fe, Ti, Ga
<b>C<sub>org</sub>, Cu</b>	<b>Nb</b>	Pb, Ni, Be, Mn, Ga, Co, La, Mg, Sc, Zr, Fe, Ti, Na, K, Yb
<b>C<sub>org</sub></b>	<b>Yb</b>	Mn, La, Pb, Ni, Mg, Co, Cr, Zr, Ga, Sc, Fe, Na, Ti, K, Nb
<b>C<sub>org</sub>, Cu</b>	<b>Zr</b>	Co, Ni, La, Mn, Cr, Ga, Mg, K, Fe, Yb, Na, Nb, Ti, Sc
<b>C<sub>org</sub>, Cu</b>	<b>Sc</b>	Pb, Cr, Mn, Co, La, Ni, Yb, Nb, Mg, Zr, Ti, Na, Ga, Fe, K
<b>C<sub>org</sub></b>	<b>Ga</b>	Zr, Nb, La, Pb, Mn, Yb, Co, Ni, Mg, Cr, Ti, Sc, Fe, Na, K
<b>C<sub>org</sub>, Cu</b>	<b>Mg</b>	Ca, Pb, Ni, Zr, Yb, Nb, La, K, Sc, Mn, Ga, Co, Ti, Na, Fe
<b>C<sub>org</sub></b>	<b>Co</b>	Zr, Ca, La, Nb, Ti, Yb, Sc, Mn, Pb, K, Ga, Na, Mg, Ni, Fe
<b>C<sub>org</sub></b>	<b>Ni</b>	Zr, Nb, Mg, Cr, Na, Yb, Ti, Sc, Pb, Mn, Ga, K, Co, Fe
<b>V, C<sub>org</sub>, Cu</b>	<b>Mn</b>	Ca, Yb, Zr, Ti, Nb, Sc, Na, Co, Ga, K, Ni, Mg, Fe
<b>C<sub>org</sub></b>	<b>Pb</b>	Nb, Ti, Mg, Na, Sc, Yb, Fe, Ga, La, Ni, Co, K
<b>C<sub>org</sub></b>	<b>K</b>	Be, Cr, Zr, La, Co, Mn, Pb, Mg, Ni, Ti, Nb, Yb, Na, Sc, Ga, Fe
<b>C<sub>org</sub>, Cu, V</b>	<b>Fe</b>	Cr, La, Pb, Zr, Yb, Nb, Ti, Ni, Mg, Co, Mn, Na, Sc, Ga, K
<b>Fe, Yb, Mg, Mn, Nb, K, Co, Sc, Ni, Zr, Pb, La, Ti, Na, Ga</b>	<b>C<sub>org</sub></b>	<b>C<sub>min</sub></b>
<b>Mn, Fe</b>	<b>V</b>	
<b>Ca</b>	<b>Ba</b>	<b>Cu</b>
<b>Na, Nb, Mn, Mg, Fe, Ti, Sc, Ca, Zr</b>	<b>Cu</b>	<b>Ba</b>

## SUMMARY AND CONCLUSIONS

Black shale is the name given to a wide variety of dark-colored fine-grained marine sedimentary rocks composed of a mixture of detrital minerals, chemically or biologically precipitated minerals, and organic matter. Each of the three major components of these rocks may contain a characteristic suite of major and minor elements. Rocks from different environments may be characterized by different suites of elements that are assignable to each of the major rock-forming components. In this study, coefficients of correlation were used to suggest the suite of elements associated with the major rock-forming components in four different sets of samples. Marked differences were found in the four sets of samples studied, each set representing a

different environment of black shale deposition. Most of the sample sets included other rock types associated with black shale and transitional with black shale.

Samples of the Belden Shale and associated rocks from a deep trough of Pennsylvanian rocks in central Colorado were found to be chiefly detrital in origin. These rocks are dark gray but do not contain much organic matter. Only lead and copper show any tendency to be associated with the organic matter. Chemically or biologically precipitated minerals are also a minor constituent of these rocks, and only calcium, magnesium, and manganese are associated with the carbonate fraction of the rocks. The only unusual concentrations of minor elements are associated with the inorganic mineral component of the Belden Shale samples. High boron, beryllium, gallium, and possibly lithium are associated with the authigenic and detrital mineral fractions and may reflect a similar concentration of the same elements along with lead in the source area terrane in Precambrian rocks of the ancestral Rocky Mountains. Deposition and burial in this trough probably proceeded so rapidly that there was little opportunity for the chemically or biologically precipitated minerals to accumulate or for the thinly disseminated organic matter to adsorb minor elements from the sea water.

The samples of upper Paleozoic black shale and associated rocks from the Ouachita geosyncline in Arkansas and Oklahoma are similar in many respects to the Belden Shale samples from Colorado. Like the Belden Shale, these rocks are chiefly detrital, and, although they contain sufficient organic matter to impart a dark-gray color, they show little association between any of the minor elements and the organic matter or the sparse carbonate minerals present. Most of the major and minor elements occur in the detrital-mineral fraction. Barium, gallium, and zirconium are present locally in relatively high concentration. Gallium and zirconium are associated with the detrital-mineral fraction and are probably of detrital origin. Barium, which probably occurs as the authigenic mineral barite, is not associated with anything else that was determined in the rocks, except possibly copper. Minable deposits of barite occur locally at the base of the Stanley Shale. The apparent localization of the barite along the axes of folds indicates secondary redistribution after deposition of the enclosing rocks. A similarly high concentration of barium was found in the western-facies eugeosynclinal rocks of Nevada (Vine, 1966).

The distribution of elements in samples of the Cherokee Group from Kansas and Oklahoma is significantly different from that of the other sample sets discussed here. Because of the similarity with other

sets of samples from the Pennsylvanian strata in the Interior coal province, these samples from the Cherokee Group may be considered a good example of shallow-water transgressive marine sediments deposited on the continental platform. Elements showing local enrichment in these rocks include silver, zinc, chromium, and vanadium in association with organic matter, lead in association with carbonate mineral matter, and gallium and zirconium in association with the detrital-mineral fraction. Samples from the Kansas and Oklahoma area have more lead and zinc and less molybdenum than similar rocks in western Kentucky. Some of the elements associated with organic matter were probably extracted from sea water by adsorption or by complexing with the decaying organic matter at the time of deposition. To what extent minor elements were added later to the rock by adsorption from connate waters after deposition and burial cannot be evaluated from the present data.

Samples of black shale and associated rocks, including cherty and dolomitic siltstone from the Houy Formation in Texas, are the most interesting and unusual of the rocks included in this study. Four rock constituents in addition to silica can be distinguished: a carbonate-mineral fraction, organic matter, a sulfide-mineral fraction, and a detrital-mineral fraction. Many minor elements including cobalt, copper, molybdenum, nickel, lead, thallium, zinc, and vanadium are unusually abundant. Except for vanadium, all are associated with organic-matter and the sulfide-mineral fractions of the rock. Other investigators have suggested that these rocks were probably deposited very slowly from quiet shallow marine waters on the continental platform. The black shale facies is only about 12 feet thick and may represent a restricted lagoonal setting contemporaneous with the more widely distributed black shales of the Chattanooga Shale equivalents in the midcontinent area. A slow rate of deposition may be one important factor in the concentration of minor elements with organic matter and sulfide minerals. The elements now concentrated in the black shale may have been adsorbed by decaying organic matter from the sea water at the time of deposition. If so, the sea water could not have been greatly enriched in these elements, for many are highly toxic and could not have coexisted with the abundance of organisms required to produce the amount of organic matter in the rocks. One other alternative that cannot be proved with the present data is that the organic matter could also have adsorbed the minor elements from connate water after deposition and burial of the sediment.



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