

# GEOCHEMICAL SURVEY OF MISSOURI

Geochemistry of Bedrock Units in Missouri  
and Parts of Adjacent States



GEOLOGICAL SURVEY PROFESSIONAL PAPER 954-F



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By JON J. CONNOR *and* RICHARD J. EBENS

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*An examination of geochemical  
variability in rocks of  
Paleozoic and Precambrian ages*



UNITED STATES DEPARTMENT OF THE INTERIOR

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## GEOCHEMICAL SURVEY OF MISSOURI

# GEOCHEMISTRY OF BEDROCK UNITS IN MISSOURI AND PARTS OF ADJACENT STATES

By JON J. CONNOR and RICHARD J. EBENS

### ABSTRACT

Distributions of elements were studied in 12 bedrock units of Precambrian and Paleozoic age in Missouri and adjacent parts of Kansas, Oklahoma, and Arkansas. This work constituted one part of a larger study aimed at characterizing the broad-scaled features of the geochemical landscape of Missouri. Rock units sampled were granite and rhyolite of Precambrian age; shale, dolomite, sandstone, and sulfide ore of the Sauk sequence (Cambrian to Early Ordovician in age); shale, carbonate, and sandstone of the Tippecanoe sequence (Middle Ordovician to Middle Devonian); shale, limestone, sandstone, and chert of the Kaskaskia sequence (Late Devonian to Late Mississippian); and shale, carbonate, sandstone, and coal of Pennsylvanian age. Eleven of these units were sampled according to hierarchical sampling schemes explicitly designed to estimate proportions of geochemical variation occurring at various geographic scales.

The most important scale of geochemical variation is a local one that reflects a common tendency in sedimentary rocks for closely spaced samples to vary rather widely in their proportions of the common rock-forming minerals calcite, dolomite, quartz, and "clay." In fact, for many trace elements in many of the units studied, samples collected as much as 100 km apart are expected to vary in their geochemical properties little more than samples collected within a kilometer or two of each other. Regional geochemical variation reflects the contrasting lithology of the largely argillaceous units of Pennsylvanian age in the northern and western parts of the study area, and the largely calcareous units of the Kaskaskia, Tippecanoe, and Sauk sequences in the southern and eastern parts.

Weaker geochemical distinctions that occur over intermediate geographic scales reflect correspondingly weak mineralogic variations within some of the lithic units. Limestone and sandstone samples from outcrops of Pennsylvanian age in northeastern Oklahoma generally have higher concentrations of trace elements than similar samples from northern Kansas and Missouri. Samples of carbonate rock from outcrops of the Kaskaskia sequence are more dolomitic in Missouri than in Arkansas, and dolomite samples from outcrops of the upper Sauk sequence tend to be slightly more argillic (and slightly higher in many trace elements) than dolomite samples from the lower Sauk (pre-Jefferson City rocks).

The general control of rock geochemistry by lithology in the study area results in regional geochemical patterns largely indistinguishable from regional geologic patterns. This work has quantified such patterns in terms of the expected element concentrations to be found in the lithic units of the various regions of the study area. Therefore, geologic maps may be used in conjunction

with the geochemical summaries given in this report to define "first-order" estimates of the local geochemical background or of threshold values useful in characterizing unusual or "anomalous" samples.

### INTRODUCTION

This report describes the results of a geochemical study of Precambrian and Paleozoic bedrock units of Missouri and adjacent States that was undertaken as part of a general survey of the geochemical environment in Missouri (Miesch, 1976; Tidball, 1976; Erdman and others, 1976a, b; Feder, 1979). The survey was conducted in cooperation with personnel of the Environmental Health Surveillance and Research Center of the University of Missouri in support of studies being made on the role of environmental geochemistry in health and disease. A preliminary description of the survey and its implications for epidemiological research was published by Connor and others (1972), and a general statement of goals and methods was given by Miesch (1976). Much of the work on which this paper is based has appeared in a series of progress reports (U.S. Geological Survey, 1972a-f, 1973) issued at intervals of 6 months during the life of the survey. Also, provisional geochemical summaries for most of the rock units discussed in this report have appeared in a geochemical compilation of landscape units of the United States (Connor, Shacklette, and others, 1975).

The role of trace elements in health and disease has been of interest to medical researchers for a long time, and an increasing public awareness of trace-element hazards in the environment has focused attention on the need for reliable data on the probable concentrations and ranges of many of these elements in ordinary environmental materials under natural conditions. Most such studies have concentrated on the presence of trace elements in air, potable water supplies, foodstuffs, and soils. Nevertheless, rocks constitute

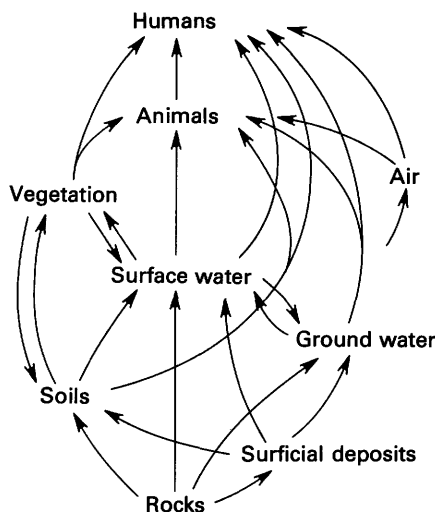


FIGURE 1.—Diagram of major paths traveled in the natural migration of trace elements from rocks to humans (from Miesch, 1972).

the ultimate source of elements in the human environment (fig. 1), and their chemical character commonly plays an important role in the local geochemical setting. Rock geochemistry may be especially important in areas where mining or related activity has disturbed the surface of the Earth (Connor and others, 1971; Ebens and others, 1973).

We express our appreciation to many U.S. Geological Survey colleagues for their assistance in this study. A. T. Miesch conceived, initiated, and directed the geochemical survey as a whole. Josephine G. Boerngen assisted in computer processing of the resulting data. About 450 rock and mineral samples were analyzed in laboratories of the U.S. Geological Survey for nearly 60 chemical elements. The analysts who performed this work follow: A. J. Bartel, L. A. Bradley, Floyd W. Brown, Mike Brown, J. W. Budinsky, C. L. Burton, J. P. Cahill, J. I. Dinnin, E. J. Fennelly, W. H. Ficklin, L. D. Forshey, I. C. Frost, Johnnie Gardner, H. Kirschenbaum, Lorraine M. Lee, Violet M. Merritt, Leung Mei, H. T. Millard, Jr., Roosevelt Moore, Wayne Mountjoy, H. G. Neiman, D. R. Norton, R. L. Rahill, V. E. Shaw, G. D. Shipley, M. W. Solt, J. A. Thomas, J. H. Turner, R. L. Turner, J. S. Wahlberg, and T. L. Yager. Samples were prepared for analysis by John Moreland.

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## GEOLOGIC SETTING

The study area is situated near the south-central edge of the cratonic interior of the North American continent and is dominated structurally by the Ozark Uplift (fig. 2), a site of mild but repeated uplift since late Precambrian time (Snyder, 1968, p. 73). The area is underlain largely by stratified rocks of Paleozoic age whose deposition, for the most part, reflects the slow epeirogenic transgressions and regressions of continental seas. The highest area, both topographically and structurally, is the St. Francois Mountains area of southeastern Missouri, away from which the enclosing Paleozoic sediments dip rather gently. The area is bordered on the east by the Illinois Basin, on the southeast by the Mississippi Embayment, on the south by the Ouachita Mountains, on the southwest by the Anadarko Basin, on the west by the Nemaha Uplift, and on the northwest by the Forest City Basin.

The general distribution of major stratigraphic units examined in this work is shown in figure 2. In general, these units are readily distinguished in outcrop as they are stratigraphically bounded by major unconformities easily recognized in the field. More detailed distributions of map units are shown on the State geologic maps of Missouri (McCracken, 1961); Iowa (Iowa Geological Survey, 1969); Nebraska (Nebraska Geological Survey, 1950); Kansas (University of Kansas, 1964); Oklahoma (Miser, 1954), and Arkansas (Banner, 1929). A recent synthesis of the geological environment of Missouri can be found in Stout and Hoffman (1973).

The succession of geologic formations in Missouri is described by Koenig (1961); the succession in Kansas is described by Merriam (1963). Except for a few distinctive formations (the St. Peter Sandstone, for example), individual units in general cannot be traced very far across the area of outcrop. Detailed Paleozoic nomenclature in the Illinois Basin bears little resemblance to Paleozoic nomenclature in eastern Kansas (Adkison, 1966). In addition, stratified rocks are

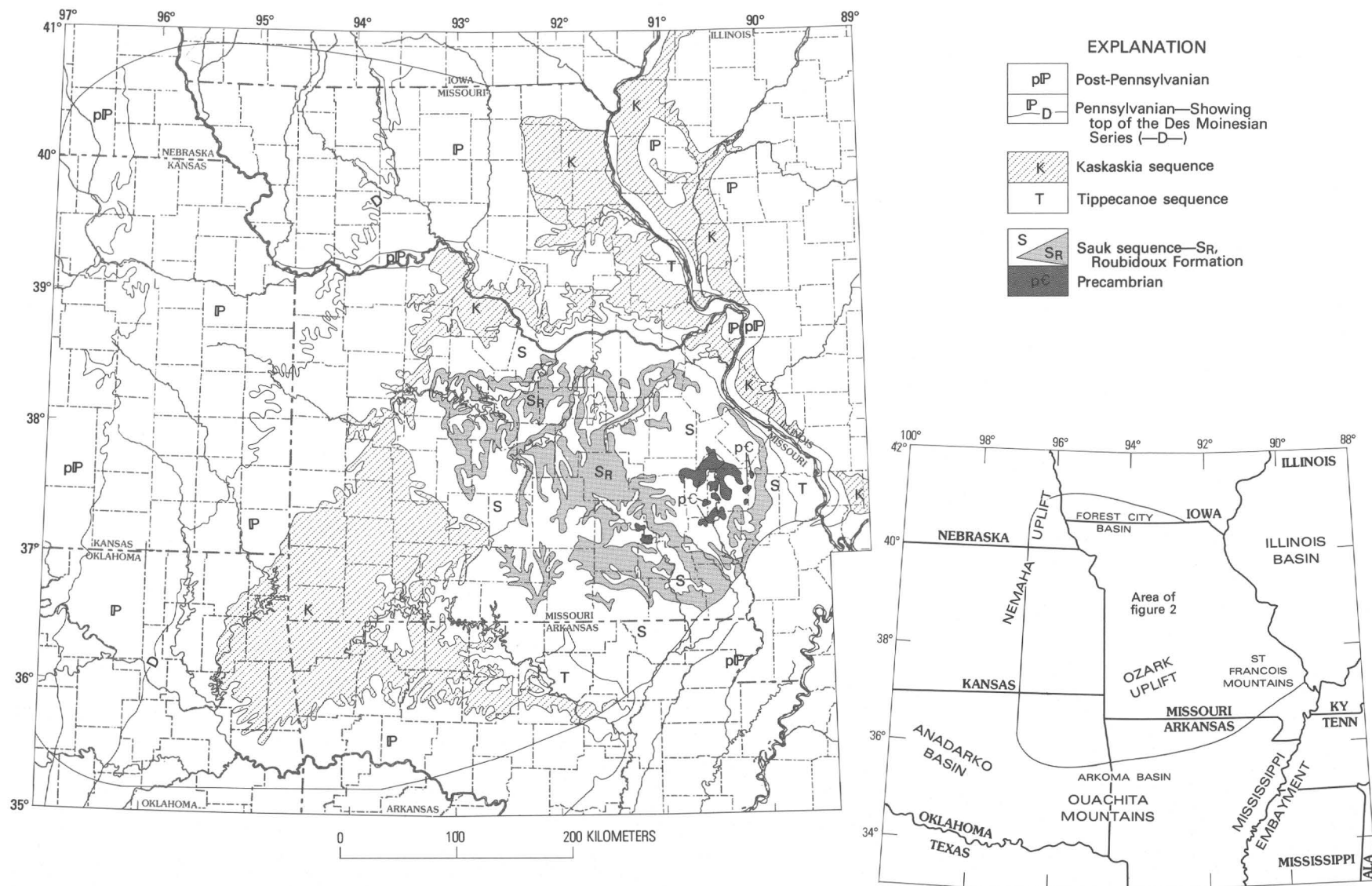


FIGURE 2.—Generalized geology of Missouri and parts of adjacent States. Modified from King and Beikman (1974) and American Association of Petroleum Geologists (1966).

conventionally correlated on the basis of geologic age; and, commonly, where the age of a lithic interval changes laterally, its name changes also. Because the geochemical survey was broad in scale, a broad-scale classification of the Paleozoic rocks, based largely on the sequences of Sloss (1963), was used.

Outcrops of igneous rocks are generally restricted to southeast Missouri, where they consist of a thick sequence of felsitic flows and welded tuffs intruded by a granitic batholith (fig. 3). The age of these rocks is about 1500 m.y. (Bickford, 1976, p. 152; Bickford and Mose, 1975). Diabasic and basaltic dikes and sills have been locally intruded into both the felsites and granites, but they are of limited extent in outcrop and were not sampled in this work.

The felsites are believed to have been extruded onto an eroded terrane of metamorphic and igneous rocks of early to middle Precambrian age similar to those presently exposed on the Canadian Shield (Hayes, 1961, p. 15). Tolman and Robertson (1969) divided the felsites into two major groups—the Middlebrook Group and the younger Van East Group. Both groups are dominantly composed of rhyolite, although the Middlebrook Group has a higher potash-to-soda ratio than the Van East Group, which appears to be a more typical rhyolite (Hayes, 1961). Pratt (1978) noted the probable identification of a latitic assemblage in the lower part of the volcanic pile. Stratigraphic nomenclature of the volcanic rocks continues to evolve (Berry, 1976), but the system used in this study is that of Tolman and Robertson (1969).

The intrusive granitic rocks, which range in texture from fine grained and slightly porphyritic to coarse grained, are divided into two groups which are believed to represent two distinct stages of emplacement. Rocks of the earlier stage, designated the Musco Group, are generally fine grained or porphyritic. Rocks of the later stage, designated the Bevos Group, consist of fine- to coarse-grained granite (Tolman and Robertson, 1969, p. 32).

The Paleozoic rocks in the study area and adjoining parts of nearby States are included in four of Sloss' (1963) cratonwide lithic sequences. In ascending order, they are the Sauk, Tippecanoe, Kaskaskia, and Absaroka. These sequences are bounded by unconformities of continental proportions, each representing an important interval of geologic time. The Sauk strata are nearly pure dolomite in composition and are of Late Cambrian to Early Ordovician age. The overlying Tippecanoe sequence is composed largely of limestone and ranges in age from Middle Ordovician to Early Devonian. Strata in the Kaskaskia and Ab-

saroka sequences contrast with the underlying Sauk and Tippecanoe in that shale generally forms a more prominent part of the local section. Also, sandstones in the Kaskaskia and Absaroka tend to be much less quartzose and carbonates tend to be much more argillaceous. These petrologic features reflect a fundamental change in depositional style during the mid-Paleozoic and, in the Illinois Basin at least, a change in location of source material as well (Potter and Pryor, 1961). Kaskaskia strata range in age from Middle Devonian to Late Mississippian and the Absaroka in the study area is of Pennsylvanian age.

Rocks of the Sauk sequence in the study area consist of a relatively thin, basal sandstone (the Lamotte Sandstone), the initial deposit of a transgressive sea, overlain by a thick sequence of dolomitized carbonates. Minor amounts of interbedded shale and siltstone occur in the lower part of the sequence (Elvins Group), and minor amounts of interbedded sandstone are scattered throughout the upper part of the sequence (Roubidoux through Powell Formations). These sandstones represent the regressive phase of late Sauk deposition (Sloss, 1963, p. 97) and are most prominent in the Roubidoux Formation. In central Missouri, the Roubidoux Formation is predominantly a quartzose sandstone whereas, in other parts of the State, as little as 10 percent of the formation contains sandstone and most of the rock is cherty dolomite, generally indistinguishable from dolomite in underlying formations (Koenig, 1961, p. 22). The sandstone is composed predominantly of fine- to medium-grained quartz sand. As a general rule, dolomites in the upper part of the sequence, consisting mostly of the Jefferson City Formation, tend to be fine grained and thin bedded, whereas dolomites in the lower part tend to be more coarsely crystalline and thicker bedded. Chert is locally abundant in the dolomites and, in the St. Francois Mountains area, large deposits of lead, zinc, and copper sulfide occur in rocks of the lower Sauk, mostly in the Bonnetterre Formation (Kisvarsanyi, 1977, p. 436; Vineyard, 1977, p. 337).

The Tippecanoe sequence in Missouri is relatively thin and contains numerous local unconformities. The St. Peter Sandstone or sandstone of the Everton Formation, representing the initial transgressive phase of Tippecanoe deposition, occurs at the base of the sequence. Most of the overlying formations are composed of clean, thin- to medium-bedded, fine- to medium-grained limestones or cherty limestones that in part have been dolomitized. Beds of shale (Decorah and Maquoketa Formations) occur in the middle of the sequence, and thin, interbedded sandstones occur

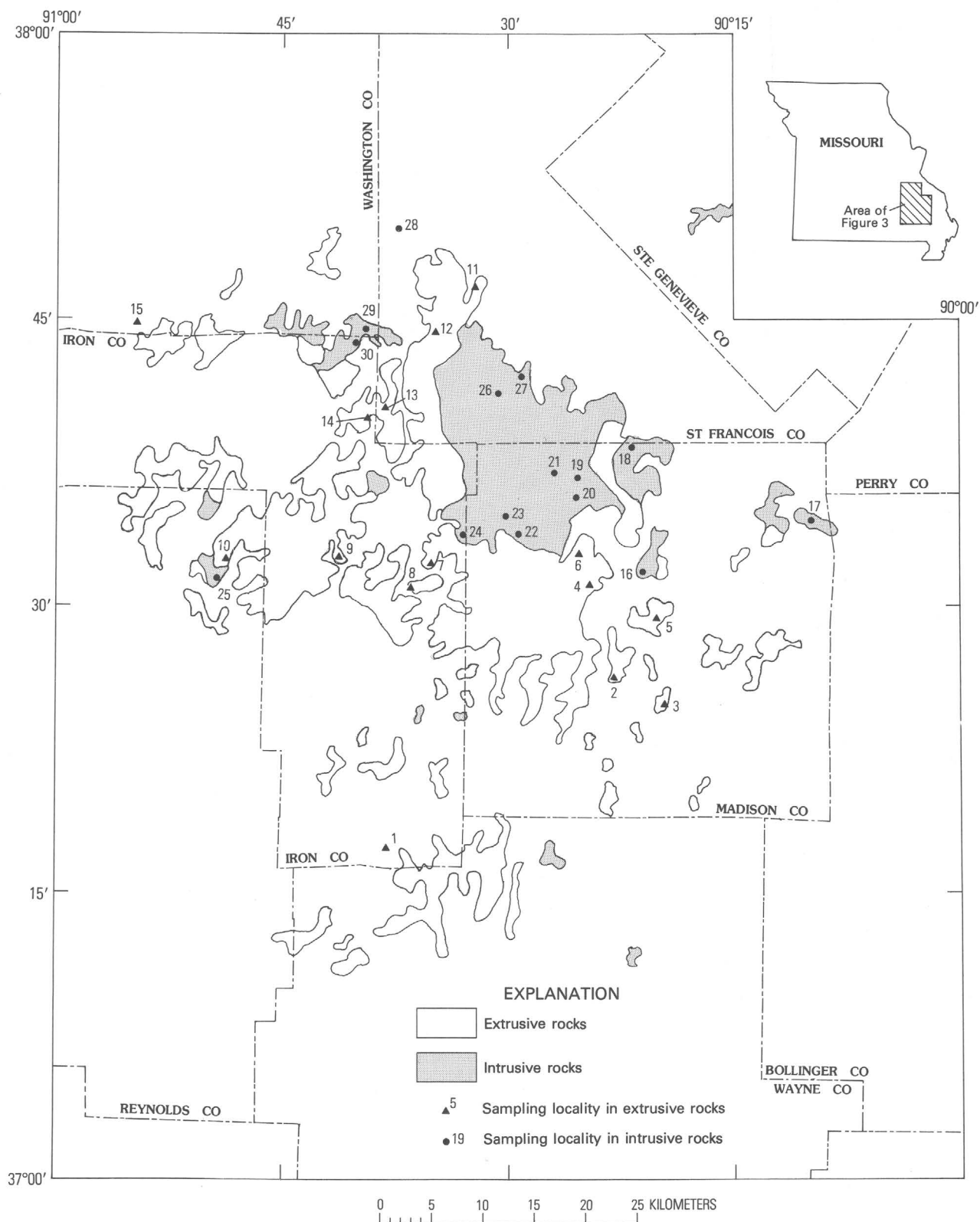


FIGURE 3.—Generalized distribution of igneous rocks of Precambrian age in southeastern Missouri and distribution of sampling localities (modified from Tolman and Robertson, 1969).



locally. Outcrops of Tippecanoe strata are restricted to the southeastern and eastern borders of the study area. Widespread uplift at the end of Early Devonian time, followed by extensive erosion, resulted in removal of many of the younger beds of the Tippecanoe sequence.

Kaskaskia strata are extensively exposed in the northeastern, central, and southwestern parts of Missouri; in northeastern Oklahoma; and in northern Arkansas. The sequence is composed predominantly of cherty, coarse-grained, irregularly bedded limestone; but it also contains fine-grained limestone, tan dolomite, calcareous shale, and sandstone. Coarse-grained limestone, typified by the Burlington and Keokuk Limestones, is especially characteristic of the middle part of the section (upper Kinderhookian through lower Meramecian) in Missouri. Chert is widespread in these strata, particularly in Missouri, and generally occurs as discrete nodules, or layers interbedded with the carbonate layers. Shale is a minor component of the sequence in Missouri but forms a prominent part of the sequence in northeastern Oklahoma and northern Arkansas. In Missouri and Oklahoma this shale is generally silty and calcareous, and in northern Arkansas it is locally carbonaceous.

Lower Absaroka (Pennsylvanian) strata crop out throughout most of northern and western Missouri, southern Iowa, eastern Kansas, southeastern Nebraska, northeastern Oklahoma, and northern Arkansas; these strata consist of cyclic deposits of interstratified shale, limestone, and sandstone. Shale is the dominant rock type, although limestone is a prominent component in northwestern Missouri and eastern Kansas, and sandstone forms an important part of the sequence in northeastern Oklahoma and northern Arkansas. The limestone tends to be argillaceous and the sandstone contains varying amounts of feldspar, rock fragments, mica, and iron-stained clay matrix. Extensive beds of bituminous coal occur in the lower part of the section, principally in the Des Moines Series. All in all, strata of Pennsylvanian age are the most geochemically diverse of those examined in the study.

Numerous formations are recognized in the Pennsylvanian rocks. (See Koenig, 1961, p. 78-122; Merriam, 1963, p. 103-135.) The basal rocks (of Morrowan and Atokan age) are limited in outcrop to northern Arkansas, southeastern Oklahoma, and extreme southwestern Missouri. The overlying rocks (of Des Moinesian, Missourian, and Virgilian age) crop out in continuous bands over northern and western Missouri, eastern Kansas, and northeastern Oklahoma. Remnant outliers of Des Moinesian strata crop out on the north flank of the Ozark Uplift and contain economically important deposits of clay. Rocks of Des Moinesian age

are several times as thick in southeastern Oklahoma (Arkoma Basin) as in Kansas and Missouri (platform area). The basin facies is predominantly shale with massive sandstone tongues, whereas the platform strata consist of cyclic deposits of sandstone, coal, limestone, and shale. The Arkoma Basin was quiet during Missourian and Virgilian time, and rocks of these ages are fairly uniform in thickness throughout the study area (Branson, 1962). These strata consist predominantly of shale and sandstone in the basin area and shale and limestone in the platform area.

## SAMPLING DESIGN

Geochemical variability in this study was examined largely through the use of hierarchical sampling plans designed to estimate the proportions of the total geochemical variance at selected ranges of geographic scale within various bedrock geologic units (Miesch, 1976). Such designs are essentially exploratory and are based on a system of hierarchically arranged sampling units such that each level of the hierarchy includes paired sampling units separated by a given distance or a selected range of distances.

The general statistical model used in all phases of the geochemical survey of Missouri is as follows (Miesch, 1976):

$$\log X_{ijklmn} = \mu + \alpha_i + \beta_{ij} + \gamma_{ijk} + \delta_{ijkl} + \eta_{ijklm} + \epsilon_{ijklmn} \quad (1)$$

For the bedrock units,  $X_{ijklmn}$  represents an analytical value reported on a rock sample by the laboratory:  $\mu$  represents the grand average (in logs) for all units studied; and the subscripted terms are deviations, each reflecting a separate source of variation, most of which are geographic in nature. The first of these terms,  $\alpha_i$ , represents the difference between  $\mu$  and the average (in logs) for the  $i$ th bedrock unit; the second,  $\beta_{ij}$ , represents the difference between the average (in logs) of the  $j$ th area of the  $i$ th unit and the average for the  $i$ th unit; the third,  $\gamma_{ijk}$ , represents in most units the difference between the average (in logs) for the  $k$ th stratigraphic section in the  $j$ th area and the average of the  $j$ th area; the fourth,  $\delta_{ijkl}$ , represents in most units the difference between the average (in logs) for the  $l$ th portion of the  $k$ th section and the average of the  $k$ th section; and the fifth,  $\eta_{ijklm}$ , represents the difference between the logarithmic concentration of the  $m$ th sample in the  $l$ th stratigraphic portion and the average of the  $l$ th portion. The last term,  $\epsilon_{ijklmn}$ , represents the difference between the logarithm of the reported concentration and the true logarithmic concentration. Logarithms of concentration in trace-element work are commonly employed to help meet some of the assump-

tions underlying the statistical procedures used in data analysis (Miesch, 1976, p. 27).

The model in equation 1 is a specific case of the analysis of variance (the hierarchical or "nested" case), and was first applied to a problem in field geology by Potter and Olsen (1954). It is discussed in mathematical detail in the context of a geochemical field problem by Krumbein and Slack (1956). Based on equation 1, the total observed logarithmic variance,  $S^2_{\log x}$ , is viewed as the sum of six estimated components, one for each subscripted term on the right side of 1:

$$S^2_{\log x} = S^2_{\alpha} + S^2_{\beta} + S^2_{\gamma} + S^2_{\delta} + S^2_{\eta} + S^2_{\epsilon} \quad (2)$$

The variance components are, respectively, estimates of the variance among geologic units ( $S^2_{\alpha}$ ), variance at large scales over each unit ( $S^2_{\beta}$ ), variance between stratigraphic sections ( $S^2_{\gamma}$ ), variance within stratigraphic sections ( $S^2_{\delta}$ ), variance between samples at a sampling site ( $S^2_{\eta}$ ), and analytical variance ( $S^2_{\epsilon}$ ).

The model in equation 1 was modified for use in this study in order to overcome problems peculiar to sampling bedrock in the study area. Compositional variation among the bedrock units ( $S^2_{\alpha}$ ) was not formally estimated because the geochemical disparity among the calcareous, aluminous, and siliceous units was expected to be obvious. Rather, each bedrock unit was examined using an independent sampling plan designed to estimate  $S^2_{\beta}$ ,  $S^2_{\gamma}$ , and so forth. In all, 11 different sampling plans were established for the bedrock units, 4 of them in carbonate rocks (Sauk, Tippecanoe, and Kaskaskia carbonates, and carbonates of Pennsylvanian age); 4 in siliceous rocks (granitic rocks of Precambrian age, sandstones of the Roubidoux Formation, chert of the Kaskaskia sequence, and sandstones of Pennsylvanian age); 2 in shale (Kaskaskia shales and shales of Pennsylvanian age); and 1 in coal of Pennsylvanian age. A twelfth study was made of the lead-copper-zinc ores of the Southeast Missouri Lead Belt; and, throughout the study area, a few samples of minor intercalated, lithically distinct beds within the 11 bedrock units were collected. No formal sampling designs were employed in collecting the ore samples or samples of these minor lithic units.

Details of the sampling designs used are given below, and the 11 formal designs are summarized in table 1. In a general way, however, each component of variance defined in equation 2 reflects variation over a relatively specific range of geographic scales regardless of the bedrock unit studied. The second component,  $S^2_{\beta}$ , reflects geographic variation at distances generally greater than 100 km,  $S^2_{\gamma}$  reflects variation at distances generally ranging from a few tens of kilometers to 100 or more kilometers (for the most part

measured as differences between stratigraphic sections),  $S^2_{\delta}$  reflects variation from a few tens of meters to many tens of kilometers (for the most part measured as differences within stratigraphic sections), and  $S^2_{\eta}$  reflects variation among samples separated by as much as a few tens of meters in a sampling site. For most of the bedrock units,  $S^2_{\delta}$  was subdivided into two components, one ( $S^2_{\theta}$ ) reflecting stratigraphic variation over a few to many tens of kilometers and the other ( $S^2_{\kappa}$ ) representing stratigraphic variation from a few tens of meters to a few kilometers. The multiple sampling designs used in this study each constitute a stage 2a sampling scheme (Connor and others, 1972) in which each unit defined in the area of study is examined individually to determine the important scales of geochemical variation.

The target population in this study is the aggregate of all potential bedrock samples of Precambrian and Paleozoic age in the study area. A sample is defined in geologically familiar terms as a few kilograms of rock cut or chipped from a homogeneous part (generally a single stratum) of bedrock. Because the only collecting tools used were geologic pick or sledge and chisel, the sampled population was confined to areas containing rock exposure, either natural or artificial. In order to minimize personal bias in estimation of the variance components, the samples were collected at randomly selected locations in outcrop. Moreover, in order to minimize analytical bias, all samples (and analytical splits) were submitted to the laboratory in a randomized sequence. The selection of areas sampled and stratigraphic sections depended on the outcrop distributions, but was considered effectively random because the outcrop distributions are controlled by a large number of complicated factors.

## PRECAMBRIAN ROCKS

The distribution of sampling localities for the granitic and rhyolitic rocks of Precambrian age is shown in figure 3; specific locations and formations sampled are listed in table 2. Two randomly located samples were collected from surface exposures in each of 15 localities in each of the two general rock types: (1) granitic and associated intrusives, and (2) felsitic and associated extrusives. Each locality was about 1 km<sup>2</sup> in area, and each was located randomly in the area of outcrop. A total of 60 samples was collected. The two rock types are intermixed in outcrop, although the intrusive rocks are more prominent in the northern part of the St. Francois Mountains, and the extrusive rocks are more prominent in the southern part. Distances between sampling localities range from 1 to 50 km.

TABLE 1.—*Distribution of terms in the hierarchical statistical models used in sampling major bedrock units in Missouri and adjacent States*  
[Greek letters are subscripts indicating hierarchical levels; nd, terms not defined]

System or sequence and material sampled	Subdivisions of bedrock units ( $\alpha$ )				
	$\beta$	$\gamma$	$\delta$		
			$\theta$	$\kappa$	$\eta$
Precambrian System:					
Granite and rhyolite-----	nd-----	Major rock types	Localities within outcrop areas of types.	nd-----	Samples within localities.
Sauk sequence:					
Dolomite-----	Areas of outcrop.	Stratigraphic sections within areas.	Deciles of stratigraphic thickness within sections.	Percentiles of stratigraphic thickness within deciles.	Samples within percentiles.
Roubidoux Formation, sandstone only-----	---do---	-----do-----	nd-----	nd-----	Samples within sections.
Tippecanoe sequence:					
Limestone and dolomite-----	nd-----	Stratigraphic sections in area of outcrop.	nd-----	Deciles of stratigraphic thickness within sections.	Samples within deciles.
Kaskaskia sequence:					
Limestone and dolomite-----	Areas of outcrop.	Stratigraphic sections within areas.	nd-----	-----do-----	Do.
Shale-----	---do---	-----do-----	nd-----	nd-----	Samples within sections.
Chert-----	---do---	-----do-----	nd-----	nd-----	Do.
Pennsylvanian System:					
Shale-----	---do---	-----do-----	Deciles of stratigraphic thickness within sections.	Percentiles of stratigraphic thickness within deciles.	Samples within percentiles.
Sandstone-----	---do---	-----do-----	-----do-----	-----do-----	Do.
Limestone and dolomite-----	---do---	-----do-----	-----do-----	-----do-----	Do.
Coal-----	nd-----	Minable beds-----	nd-----	nd-----	Samples within beds.

TABLE 2.—*Sampling localities of rocks of Precambrian age in Missouri*

Loc. No. (fig. 3)	Field No. REIPC-	County	North latitude	West longitude	Stratigraphic Unit <sup>1</sup>
1	01, 02	Iron-----	37°17'35"	90°38'05"	Mudlick Dellenite.
2	03, 04	Madison-----	37°26'15"	90°22'55"	Felsite.
3	05, 06	-----do-----	37°24'55"	90°19'45"	Do.
4	07, 08	-----do-----	37°31'20"	90°24'30"	Middlebrook Group.
5	09, 10	-----do-----	37°29'35"	90°20'10"	Felsite.
6	11, 12	-----do-----	37°32'40"	90°25'05"	Middlebrook Group.
7	13, 14	Iron-----	37°32'20"	90°35'20"	Stouts Creek Rhyolite.
8	15, 16	-----do-----	37°31'05"	90°36'30"	Do.
9	17, 18	-----do-----	37°32'35"	90°41'00"	Royal Gorge Rhyolite.
10	19, 20	Reynolds-----	37°32'30"	90°48'55"	Hogan Mountain Rhyolite.
11	21, 22	St. Francois--	37°46'45"	90°32'15"	Stouts Creek Rhyolite.
12	23, 24	-----do-----	37°44'30"	90°34'40"	Hogan Mountain Rhyolite.
13	25, 26	-----do-----	37°40'30"	90°38'05"	Middlebrook Group.
14	27, 28	Iron-----	37°39'40"	90°39'10"	Do.
15	29, 30	Washington--	37°44'50"	90°54'35"	Felsite.
16	31, 32	Madison-----	37°31'50"	90°21'05"	Slabtown Granite.
17	33, 34	-----do-----	37°34'35"	90°09'55"	Granite.
18	35, 36	-----do-----	37°38'30"	90°21'45"	Slabtown Granite.
19	37, 38	-----do-----	37°36'45"	90°25'20"	Butler Hill Granite.
20	39, 40	-----do-----	37°35'45"	90°25'20"	Do.
21	41, 42	-----do-----	37°37'00"	90°27'00"	Do.
22	43, 44	-----do-----	37°33'40"	90°29'25"	Silvermine Granite.
23	45, 46	-----do-----	37°34'45"	90°30'20"	Do.
24	47, 48	Iron-----	37°33'50"	90°33'05"	Brown Mountain Rhyolite Porphyry.
25	49, 50	Reynolds	37°31'35"	90°49'35"	Munger Granite Porphyry.
26	51, 52	St. Francois--	37°41'10"	90°30'45"	Breadtray Granite.
27	53, 54	-----do-----	37°42'20"	90°28'45"	Butler Hill Granite.
28	55, 56	-----do-----	37°49'55"	90°37'20"	Granite.
29	57, 58	Washington--	37°44'35"	90°39'25"	Buford Granite Porphyry.
30	59, 60	Iron-----	37°43'40"	90°40'05"	Do.

<sup>1</sup>Modified from Tolman and Robertson, 1969.

The components of geochemical variance estimated for the Precambrian rocks are:

$$S^2_{\log x} = S^2_{\gamma} + S^2_{\theta} + S^2_{\eta} + S^2_{\epsilon} \quad (3)$$

These components reflect variation between the two rock types ( $S^2_{\gamma}$ ), variation among sampling localities within rock types ( $S^2_{\theta}$ ), variation between samples within localities ( $S^2_{\eta}$ ), and analytical variance ( $S^2_{\epsilon}$ ).

### SAUK SEQUENCE

The distribution of sampling localities used in the study of the Sauk sequence is shown in figure 4; specific locations and formations sampled are listed in table 3. The sampling plan for the Sauk is based on six composite stratigraphic sections radiating outward from the St. Francois Mountains. These six sections were paired so that each pair represents an area of the total Sauk outcrop. The sections within each pair lie some 40–80 km apart.

In the sampling plan for the carbonates (the dominant lithic type in the Sauk), each stratigraphic section was subdivided into 10 approximately equal parts

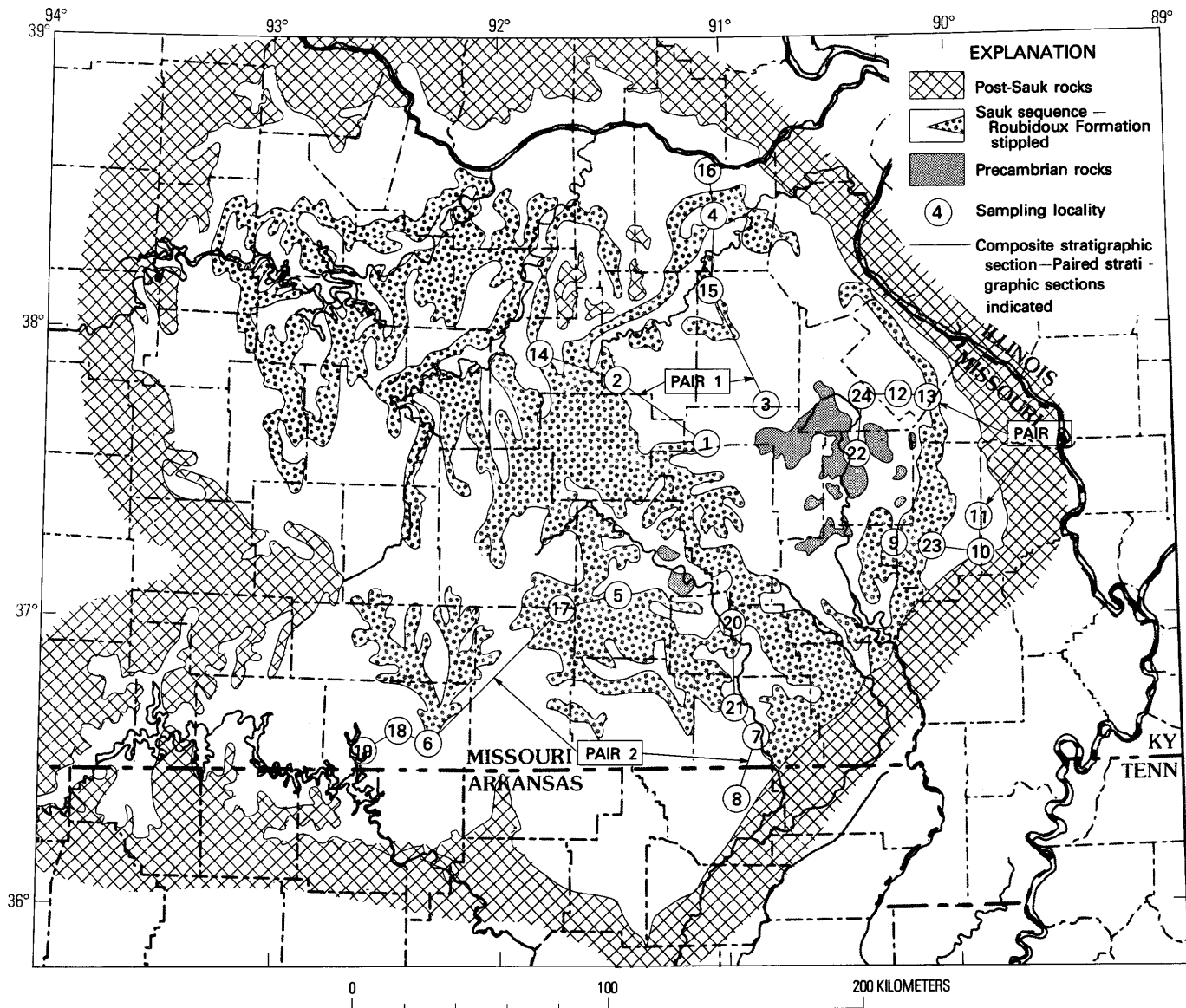


FIGURE 4.—Sampling localities in the Sauk sequence.

(deciles) from which 2 were randomly selected for sampling. Each of these 2 deciles was further subdivided into 10 approximately equal parts (percentiles), and 2 of the percentiles were selected randomly. From each percentile two samples of carbonate rock were collected at random, except at locality 7 (fig. 4), where only one sample was taken. Thus, a total of 47 carbonate samples was collected from this sequence. A stratigraphic decile in these rocks encompasses about 30 m of section in most of the State and as much as 60 m of section on the edge of the Illinois Basin in southeasternmost Missouri. For the most part, the 2

percentiles in each stratigraphic decile generally could be sampled in a single outcrop of carbonate.

Based on this plan, six components of geochemical variance were estimated for the carbonate rocks of the Sauk:

$$S^2_{\log X} = S^2_{\beta} + S^2_{\gamma} + S^2_{\theta} + S^2_{\kappa} + S^2_{\eta} + S^2_{\epsilon} \quad (4)$$

These components reflect variation among areas of outcrop ( $S^2_{\beta}$ , where each area is represented by a pair of sampled sections), variation between stratigraphic sections within areas ( $S^2_{\gamma}$ ), variation between strati-

## GEOCHEMICAL SURVEY OF MISSOURI

TABLE 3.—Sampling localities of stratified bedrock units in Missouri and adjacent States

Loc. No. (figs. 4, 6, 7, 8)	Field No. (REO-)	State	County	North latitude	West longitude	Stratigraphic Unit
Carbonate rocks of the Sauk sequence						
1	SD01, SD02-----	Missouri--	Iron-----	37°38'15"	91°02'00"	Bonneterre Formation.
	SD03, SD04-----	do-----	do-----	37°38'15"	91°02'00"	Potosi Dolomite.
2	SD05, SD06, SD07, SD08----	do-----	Crawford-----	37°50'50"	91°25'45"	Eminence Dolomite.
3	SD09, SD10-----	do-----	Washington-----	37°45'55"	90°46'10"	Bonneterre Formation.
	SD11, SD12-----	do-----	do-----	37°45'55"	90°47'15"	Do.
4	SD13, SD14-----	do-----	Franklin-----	38°27'30"	91°00'25"	Jefferson City Formation.
	SD15, SD16-----	do-----	do-----	38°29'00"	91°00'30"	Do.
5	SD17, SD18-----	do-----	Shannon-----	37°08'45"	91°26'40"	Gasconade Dolomite.
	SD19, SD20-----	do-----	do-----	37°08'40"	91°26'00"	Do.
6	SD21, SD22-----	do-----	Ozark-----	36°35'05"	92°17'55"	Roubidoux Formation.
	SD23, SD24-----	do-----	do-----	36°35'05"	92°18'15"	Jefferson City Formation.
7	SD25-----	do-----	Ripley-----	36°37'20"	90°50'00"	Roubidoux Formation.
	SD27, SD28-----	do-----	do-----	36°37'30"	90°49'50"	Jefferson City Formation.
8	SD29, SD30, SD31, SD32--	Arkansas--	Randolph-----	36°24'55"	90°55'15"	Cotter Formation.
9	SD33, SD34-----	Missouri--	Bollinger-----	37°17'40"	90°13'00"	Gasconade Dolomite.
	SD35, SD36-----	do-----	do-----	37°15'10"	90°12'15"	Do.
10	SD37, SD38-----	do-----	Cape Girardeau--	37°14'00"	89°48'15"	Jefferson City Formation.
11	SD39, SD40-----	do-----	do-----	37°21'40"	89°48'30"	Do.
12	SD41, SD42-----	do-----	Ste Genevieve--	37°47'20"	90°10'10"	Bonneterre Formation.
	SD43, SD44-----	do-----	do-----	37°47'20"	90°10'20"	Do.
13	SD45, SD46, SD47, SD48----	do-----	do-----	37°47'30"	90°04'00"	Gasconade Dolomite.
Sandstone of the Sauk sequence						
14	SS01, SS02-----	Missouri--	Phelps-----	37°56'25"	91°48'30"	Roubidoux Formation.
3	SS03, SS04-----	do-----	Washington-----	37°45'55"	90°45'10"	Lamotte Sandstone.
15	SS05, SS06-----	do-----	do-----	38°08'00"	91°00'30"	Gunter Sandstone Member of Gasconade Dolomite.
16	SS07, SS08-----	do-----	Franklin-----	38°36'00"	91°03'00"	Roubidoux Formation.
4	SS09-----	do-----	do-----	38°27'30"	91°00'25"	Jefferson City Formation.
16	SS10-----	do-----	Warren-----	38°37'00"	91°01'30"	Jefferson City Formation.
17	SS11, SS12-----	do-----	Texas-----	37°03'35"	91°39'55"	Roubidoux Formation.
18	SS13-----	do-----	Ozark-----	36°36'40"	92°25'05"	Jefferson City Formation.
19	SS14-----	do-----	do-----	36°35'10"	92°33'40"	Do.
20	SS15, SS16-----	do-----	Carter-----	37°00'40"	90°59'55"	Gunter Sandstone Member of Gasconade Dolomite.
21	SS17-----	do-----	Ripley-----	36°40'00"	90°52'20"	Roubidoux Formation.
	SS18-----	do-----	do-----	36°37'20"	90°50'00"	Do.
8	SS19, SS20-----	Arkansas--	Randolph-----	36°24'55"	90°55'00"	Cotter Formation.
22	SS21, SS22-----	Missouri--	Madison-----	37°34'20"	90°23'10"	Lamotte Sandstone.
23	SS23, SS24-----	do-----	Bollinger-----	37°18'50"	90°00'05"	Roubidoux Formation.
24	SS25-----	do-----	Ste Genevieve--	37°48'00"	90°15'55"	Lamotte Sandstone.
	SS26-----	do-----	do-----	37°47'40"	90°16'05"	Do.
13	SS27, SS28-----	do-----	do-----	37°47'40"	90°03'50"	Roubidoux Formation.
Shale of the Sauk sequence						
25	SH01, SH02-----	Missouri--	Washington-----	37°46'45"	90°53'40"	Davis Formation.
13	SH05, SH06-----	do-----	St Genevieve--	37°47'00"	90°08'30"	Do.
Carbonate rocks of the Tippecanoe sequence						
26	TL01, TL02-----	Missouri--	Cape Girardeau--	37°15'45"	89°35'00"	Joschim Dolomite.
27	TL03, TL04-----	do-----	do-----	37°18'00"	89°31'00"	Kimmswick Limestone.

TABLE 3.—*Sampling localities of stratified bedrock units in Missouri and adjacent States—Continued*

Loc. No. (figs. 4 6, 7, 8,)	Field No. (REO-)	State	County	North latitude	West longitude	Stratigraphic Unit
Carbonate rocks of the Tippecanoe sequence --Continued						
28	TL05, TL06-----do-----	Jefferson-----		38°15'15"---90°24'00"		Joachim Dolomite.
	TL07, TL08-----do-----	do-----		38°17'00"---90°23'30"		Plattin Limestone.
29	TL09, TL10-----do-----	Ralls-----		39°31'35"---91°21'00"		Decorah Formation.
	TL11, TL12-----do-----	do-----		39°31'45"---91°21'00"		Kimmswick Limestone.
Sandstone of the Tippecanoe sequence						
26	TS01, TS02-----Missouri--	Cape Girardeau---		37°15'30"---89°38'30"		St Peter Sandstone.
28	TS03, TS04-----do-----	Jefferson-----		38°14'30"---90°23'30"		Do.
Shale of the Tippecanoe sequence						
28	TH01, TH02-----Missouri--	Jefferson-----		38°15'15"---90°24'00"		Joschim Dolomite.
	TH04-----do-----	do-----		38°16'56"---90°23'15"		Decorah Formation.
30	TH03-----do-----	Pike-----		39°27'45"---91°24'45"		Maquokata Formation.
Carbonate rocks of the Kaskaskia sequence						
31	ML01, ML02-----Missouri--	St Charles-----		38°49'50"---90°44'55"		Keokuk Limestone.
	ML03, ML04-----do-----	do-----		38°48'20"---90°44'25"		Warsaw Formation.
30	ML05, ML06, ML07, ML08-----do-----	Pike-----		39°24'00"---91°21'55"		Burlington Limestone.
32	ML09, ML10, ML11, ML12-----do-----	Boone-----		38°55'35"---92°17'40"		Do.
33	ML13, ML14-----do-----	Pettis-----		38°49'05"---93°13'35"		Sedalia Limestone.
	ML15, ML16-----do-----	do-----		38°49'05"---93°13'35"		Burlington Limestone.
34	ML17, ML18-----do-----	Hickory-----		37°49'05"---93°35'00"		Northview Shale Sedalia Limestone.
	ML19, ML20-----do-----	do-----		37°49'20"---93°32'55"		Burlington Limestone.
35	ML21, ML22-----do-----	Lawrence-----		37°09'00"---93°42'10"		Compton Limestone.
36	ML23, ML24-----do-----	do-----		37°05'20"---93°51'40"		Keokuk Limestone.
37	ML25, ML26-----Oklahoma--	Mayes-----		36°26'15"---95°03'30"		Reeds Spring Member of Boone Formation.
38	ML27, ML28-----do-----	do-----		36°11'00"---95°15'00"		Fayetteville Shale.
39	ML29, ML30-----do-----	Sequoyah-----		35°36'00"---94°52'00"		Hindsville Limestone.
	ML31, ML32-----do-----	do-----		35°36'00"---94°52'00"		Fayetteville Shale.
40	ML33, ML34-----Arkansas--	Searcy-----		35°58'30"---92°53'00"		Boone Formation.
	ML35, ML36-----do-----	do-----		35°59'20"---92°53'40"		Do.
41	ML37, ML38-----do-----	Stone-----		35°56'00"---92°07'30"		Fayetteville Shale.
	ML39, ML40-----do-----	do-----		35°56'00"---92°07'30"		Pitkin Limestone.
Sandstone of the Kaskaskia sequence						
45	FL01, FL02-----Missouri--	Buchanan-----		39°48'20"---94°41'15"		Iaton Limestone.
46	FL03, FL04-----do-----	Andrew-----		39°54'30"---94°53'30"		Plattsouth Limestone
	FL05, FL06-----do-----	do-----		39°54'45"---94°53'10"		Member of Oread Limestone.
	FL07, FL08-----do-----	do-----		39°55'20"---94°54'45"		Lecompton Limestone.
						Ozawkie Limestone Member
						of Deer Creek Limestone.
47	FL09, FL10-----do-----	Johnson-----		38°33'45"---93°35'35"		Verdigris Limestone Member
						of Senora Formation.
48	FL11, FL12-----do-----	Cass-----		38°30'45"---94°06'45"		Marmaton Group
49	FL13-----Kansas--	Douglas-----		39°00'00"---95°22'50"		Rock Bluff Limestone Member
						of Deer Creek Limestone.
	FL14-----do-----	do-----		39°00'00"---95°22'50"		Ervine Creek Limestone Member
						of Deer Creek Limestone.
50	FL15, FL16-----do-----	Shawnee-----		39°02'05"---95°36'05"		Curzon Limestone Member of Topeka Limestone.

TABLE 3.—*Sampling localities of stratified bedrock units in Missouri and adjacent States—Continued*

Loc. No. (figs. 4 6, 7, 8)	Field No. (REQ-)	State	County	North latitude	West longitude	Stratigraphic Unit
Sandstone of the Kaskaskia sequence--Continued						
51	FL17, FL18-----	Oklahoma--	Nowata-----	36°44'00"	--95°48'00"	Hogshooter Limestone.
52	FL19, FL20-----	do-----	Washington-----	36°43'40"	--95°57'30"	Dewey Limestone.
53	FL21, FL22-----	do-----	Osage-----	36°40'15"	--96°24'45"	Deer Creek Limestone.
	FL23, FL24-----	do-----	do-----	36°40'15"	--96°24'45"	Topeka Limestone.
54	FL25, FL26-----	do-----	Tulsa-----	36°05'25"	--95°47'15"	Senora Formation.
55	FL27, FL28-----	do-----	do-----	35°54'40"	--95°47'55"	Fort Scott Limestone.
56	FL29, FL30-----	do-----	Lincoln-----	35°45'00"	--96°40'10"	Reading Limestone Member of Emporia Limestone.
57	FL31, FL32-----	do-----	do-----	35°43'50"	--96°44'00"	Brownville Limestone Member of Wood Siding Formation.
Shale of Pennsylvanian age						
58	PH01, PH02-----	Missouri--	Daviess-----	39°55'25"	--93°57'35"	Kansas City Group.
	PH03, PH04-----	do-----	do-----	39°55'20"	--93°57'50"	Do.
59	PH05, PH06, PH07, PH08--	Kansas--	Jackson-----	39°35'45"	--95°36'35"	Wabauunsee Group.
60	PH09, PH10-----	Missouri--	Cass-----	38°38'15"	--94°21'15"	Pleasanton Formation.
	PH11, PH12-----	do-----	do-----	38°40'30"	--94°22'35"	Do.
61	PH13, PH14-----	do-----	Clay-----	39°11'40"	--94°35'20"	Wyandotte Limestone.
62	PH15, PH16-----	Kansas--	Wyandotte-----	39°05'25"	--94°53'55"	Vilas Shale.
63	PH17, PH18-----	Oklahoma--	Osage-----	36°46'00"	--96°04'45"	Barnsdall.
	PH19, PH20-----	do-----	do-----	36°44'50"	--96°08'25"	Tallant Formation.
53	PH21, PH22-----	do-----	do-----	36°40'15"	--96°24'45"	Calhoun Shale.
	PH23, PH24-----	do-----	do-----	36°40'30"	--96°25'00"	Severy Shale.
64	PH25, PH26-----	do-----	Tulsa-----	35°58'25"	--95°55'30"	Nowata Shale.
65	PH27, PH28-----	do-----	do-----	36°04'45"	--95°53'10"	Holdenville Shale.
66	PH29, PH30-----	do-----	Creek-----	35°59'20"	--96°11'00"	Nellie Bly Formation.
	PH31, PH32-----	do-----	do-----	35°55'25"	--96°14'50"	Do.
Chert of Kaskaskia sequence						
31	MC01-----	Missouri--	St. Charles-----	38°49'50"	--90°44'55"	Keokuk Limestone.
	MC02-----	do-----	do-----	38°48'20"	--90°44'30"	Do.
30	MC03, MC04-----	do-----	Pike-----	39°24'00"	--91°21'55"	Burlington Limestone.
32	MC05, MC06-----	do-----	Boone-----	38°55'35"	--92°17'40"	Do.
33	MC07-----	do-----	Pettis-----	38°49'05"	--93°13'05"	Sedalia Limestone.
	MC08-----	do-----	do-----	38°49'05"	--93°13'05"	Burlington Limestone.
34	MC09-----	do-----	Hickory-----	37°49'05"	--93°35'00"	Northview Shale Sedalia Limestone.
	MC10-----	do-----	do-----	37°49'20"	--93°32'55"	Burlington Limestone.
35	MC11-----	do-----	Lawrence-----	37°09'00"	--93°42'10"	Reeds Spring Member of Boone Formation.
36	MC12-----	do-----	do-----	37°05'20"	--93°51'40"	Keokuk Limestone.
37	MC13-----	Oklahoma--	Meyes-----	36°26'15"	--95°03'30"	Reeds Spring Member of Boone Formation.
38	MC14-----	do-----	do-----	36°11'00"	--95°15'00"	Keokuk Limestone
39	MC15, MC16-----	do-----	Sequoyah-----	35°36'00"	--94°52'00"	Boone Formation
40	MC17-----	Arkansas--	Searcy-----	35°58'30"	--92°53'00"	Do.
	MC18-----	do-----	do-----	35°59'20"	--92°53'40"	Do.
41	MC19, MC20-----	do-----	Stone-----	36°55'30"	--92°06'45"	Do.



TABLE 3.—*Sampling localities of stratified bedrock units in Missouri and adjacent States—Continued*

Loc. No. (figs. 4, 6, 7, 8)	Field No. (REO-)	State	County	North latitude	West longitude	Stratigraphic Unit
Sandstone of Pennsylvanian age						
67	PS01, PS02-----	Missouri--	Carroll-----	39°34'05"	--93°16'45"	Cabaniss Group.
	PS03, PS04-----	do-----	do-----	39°35'15"	--93°18'10"	Do.
68	PS05, PS06-----	do-----	Livingston-----	39°45'00"	--93°40'00"	Pleasanton Formation.
69	PS07, PS08-----	do-----	do-----	39°55'35"	--93°57'00"	Do.
62	PS09, PS10-----	Kansas--	Wyandotte-----	39°05'30"	--94°53'40"	Lansing Group.
49	PS11, PS12-----	do-----	Douglas-----	38°59'55"	--95°18'40"	Lawrence Formation.
70	PS13, PS14-----	do-----	Wabaunsee-----	39°03'30"	--96°01'00"	Wabaunsee Group.
71	PS17, PS18-----	Oklahoma--	Craig-----	36°40'30"	--95°20'00"	Senora Formation.
72	PS19, PS20-----	do-----	Nowata-----	36°42'00"	--95°29'30"	Labette Shale.
53	PS21, PS22-----	do-----	Osage-----	36°41'00"	--96°27'30"	Silver Lake Shale Member of Seraton Shale.
73	PS23, PS24-----	do-----	do-----	36°41'15"	--96°32'30"	Wabaunsee Group.
74	PS25, PS26-----	do-----	Wagoner-----	35°57'05"	--95°34'30"	Blue jacket Sandstone Member of Boggy Formation.
	PS27, PS28-----	do-----	do-----	35°57'05"	--95°37'40"	Oolagah Limestone.
66	PS29, PS30-----	do-----	Creek-----	35°59'30"	--96°09'20"	Nellie Bly Formation.
	PS31, PS32-----	do-----	do-----	35°59'20"	--96°11'00"	Do.
Coal of Pennsylvanian age						
75	C01, C02-----	Missouri--	Barton-----	37°22'00"	--94°35'30"	Rowe Coal.
	C03, C04-----	do-----	do-----	37°22'00"	--94°35'30"	Drywood (Kniveton) Coal.
76	C05, C06-----	do-----	Vernon-----	37°42'25"	--94°28'30"	Mineral Coal.
77	C07, C08-----	do-----	do-----	38°01'20"	--94°22'00"	Do.
78	C09, C10-----	do-----	Henry-----	38°18'00"	--94°00'00"	Weir-Pittsburg Coal.
	C11, C12-----	do-----	do-----	38°18'00"	--94°00'00"	Tebo Coal.
79	C13, C14-----	do-----	do-----	38°21'00"	--93°52'45"	Do.
80	C15, C16-----	do-----	do-----	38°26'30"	--93°42'15"	Do.
81	C17, C18-----	do-----	Putnam-----	40°32'30"	--92°50'45"	Lexington Coal.
82	C19, C20-----	do-----	Macon-----	39°45'15"	--92°43'30"	Mulky Coal.
83	C21, C22-----	do-----	do-----	39°39'30"	--92°30'15"	Bevier Coal.
	C23, C24-----	do-----	do-----	39°39'30"	--92°30'15"	Mulky Coal.
84	C25, C26-----	do-----	Randolph-----	39°33'45"	--92°37'15"	Bevier Coal.
85	C27, C28-----	do-----	Boone-----	39°03'00"	--92°14'00"	Do.
	C29, C30-----	do-----	do-----	39°05'30"	--92°18'15"	Summit Coal.
Shale of Kaskaskia sequence						
31	MH01-----	Missouri--	St. Charles-----	38°48'20"	--90°44'30"	Warsaw Formation.
30	MH03, MH04-----	do-----	Pike-----	39°27'30"	--91°24'30"	Hannibal Shale.
33	MH05, MH06-----	do-----	Pettis-----	38°47'50"	--93°13'30"	Chouteau Limestone.
34	MH07, MH08-----	do-----	Hickory-----	37°49'05"	--93°35'00"	Northview Shale.
35	MH09, MH10-----	do-----	Lawrence-----	37°09'00"	--93°42'10"	Do.
42	MH11, MH12-----	Oklahoma--	Delaware-----	36°23'15"	--94°56'00"	Chattanooga Shale.
38	MH13, MH14-----	do-----	Mayes-----	36°11'15"	--95°14'30"	Fayetteville Shale.
39	MH15, MH16-----	do-----	Sequoyah-----	35°37'15"	--94°49'00"	Chattanooga Shale.
	MH17, MH18-----	do-----	do-----	35°35'00"	--94°52'00"	Fayetteville Shale.
43	MH19, MH20-----	Arkansas--	Searcy-----	35°54'00"	--92°37'00"	Fayetteville Shale.
41	MH21-----	do-----	Stone-----	35°52'45"	--92°06'15"	Ruddell Shale Member of Moorefield Formation.
	MH22-----	do-----	do-----	35°52'40"	--92°06'10"	Do.

graphic deciles within sections ( $S^2_\theta$ ), variation between percentiles within deciles ( $S^2_\kappa$ ), variation between samples within percentiles ( $S^2_\eta$ ), and analytical variance ( $S^2_\epsilon$ ).

In addition to the carbonate samples, 28 samples of sandstone and four samples of shale were also collected from the Sauk sections. Twelve of the sandstone samples were collected from the Roubidoux Formation (fig. 4, table 3), two from each of the same sections used in the study of the carbonates. These 12 samples were used to estimate four components of geochemical variance:

$$S^2_{\log X} = S^2_\beta + S^2_\gamma + S^2_\eta + S^2_\epsilon \quad (5)$$

These components reflect variation among the three areas of outcrop ( $S^2_\beta$ ), variation between stratigraphic sections within the areas ( $S^2_\gamma$ ), variation between samples within the sections ( $S^2_\eta$ ), and analytical variance ( $S^2_\epsilon$ ).

A suite of samples was collected of the sulfide ore that occurs in the lower Sauk strata in the Southeast Missouri Lead Belt. Twenty-seven samples of ore and concentrate, collected over a mill-operating period of at least 10 days, were obtained from seven mining and milling operations (fig. 5).

### TIPPECANOE SEQUENCE

The distribution of sampling localities used in the study of the Tippecanoe sequence is shown in figure 6; specific locations and formations sampled are listed in table 3. Samples of carbonate rocks were collected from three composite stratigraphic sections—one each in the southeastern, central, and northeastern parts of the outcrop area of eastern Missouri. Each section was subdivided into 10 approximately equal parts (deciles), and two randomly located samples were collected from each of two randomly selected deciles, for a total of 12 samples. A stratigraphic decile in these rocks encompasses about 4.5 m of section in the northeastern part

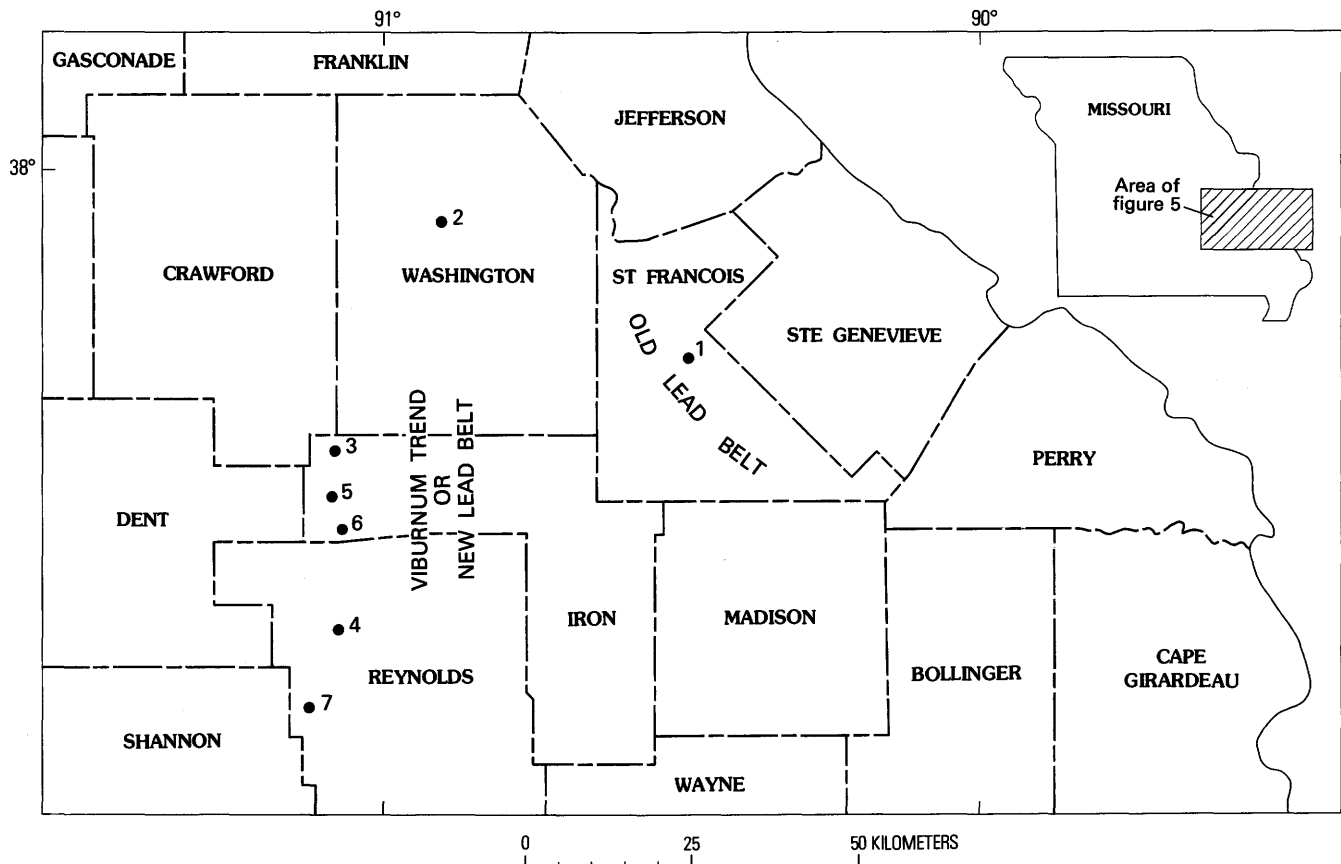


FIGURE 5.—Major lead mining and milling operations in southeastern Missouri showing sampling localities (numbered dot). Mine-Mill operations: 1, Federal Division, St. Joe Minerals Co.; 2, Indian Creek Division, St. Joe Minerals Co.; 3, Viburnum Division, St. Joe Minerals Co.; 4, Fletcher Division, St. Joe Minerals Co.; 5, Magmont, Cominco American Inc.; 6, Buick, Missouri Lead Operating Co.; 7, Sweetwater, Ozark Lead Co. (Modified from Wharton and others, 1969, p. 59.)

of the outcrop belt and about 12 m in the southeastern part.

The components of geochemical variance estimated for carbonate in the Tippecanoe are:

$$S^2_{\log X} = S^2_{\gamma} + S^2_{\kappa} + S^2_{\eta} + S^2_{\epsilon} \quad (6)$$

These components reflect variation among stratigraphic sections ( $S^2_{\gamma}$ ), variation between stratigraphic deciles within sections ( $S^2_{\kappa}$ ), variation between samples within deciles ( $S^2_{\eta}$ ), and analytical variance ( $S^2_{\epsilon}$ ). Concurrent with the carbonate sampling, four samples each of intercalated sandstone and shale were also collected from the Tippecanoe (fig. 6, table 3).

### KASKASKIA SEQUENCE

The distribution of sampling localities used for the Kaskaskia sequence are shown in figure 7; specific locations and formations sampled are listed in table 3. For the carbonates, five pairs of stratigraphic sections were sampled around the outcrop belt; thus, each pair represents an area of outcrop. The sections in each pair are spaced about 80 km apart. Each section was subdivided into 10 approximately equal stratigraphic parts (deciles), and two randomly selected samples were collected from each of 2 randomly selected deciles, for a total of 40 carbonate samples. A stratigraphic decile ranges from about 4.5 m of section

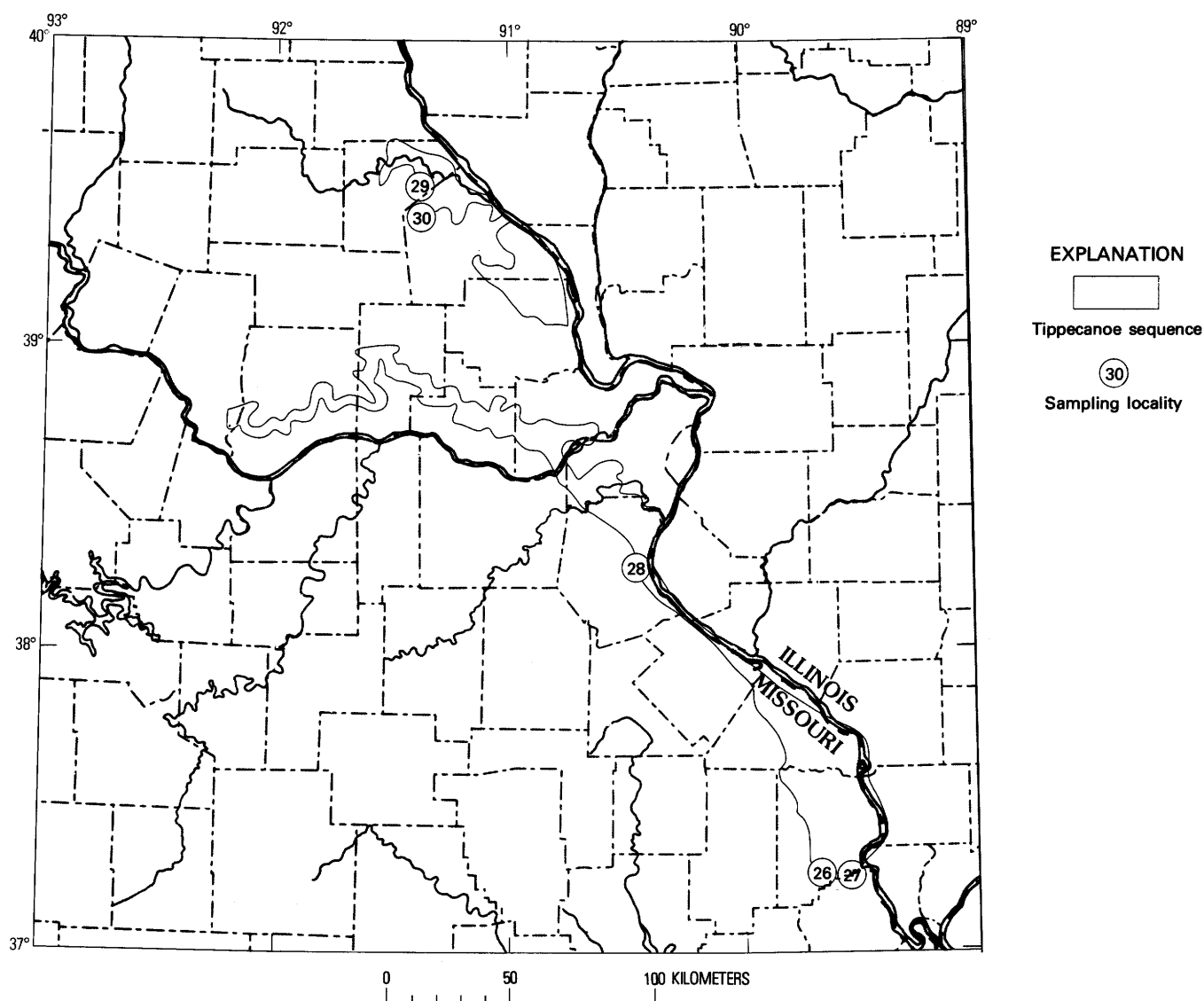


FIGURE 6.—Sampling localities in the Tippecanoe sequence.

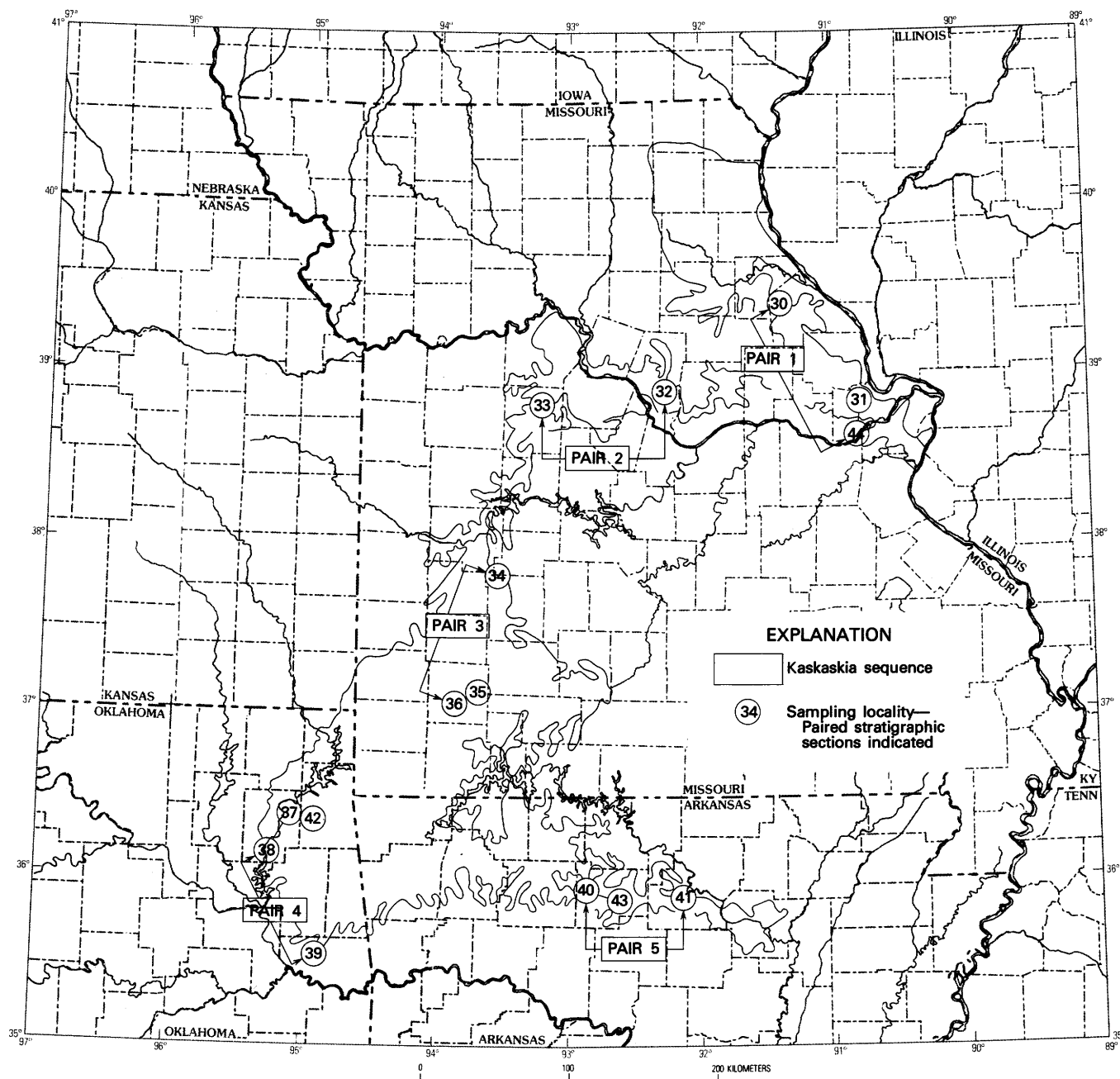


FIGURE 7.—Sampling localities in the Kaskaskia sequence.

in west-central Missouri to about 26 m in northern Arkansas.

The components of geochemical variance estimated for the carbonate rocks of the Kaskaskia sequence are:

$$S^2_{\log X} = S^2_{\beta} + S^2_{\gamma} + S^2_{\kappa} + S^2_{\eta} + S^2_{\epsilon} \quad (7)$$

These components reflect variation among the five areas of outcrop ( $S^2_{\beta}$ ), variation between stratigraphic sections within areas ( $S^2_{\gamma}$ ), variation between

stratigraphic deciles within sections ( $S^2_{\kappa}$ ), variation between samples within deciles ( $S^2_{\eta}$ ), and analytical variance ( $S^2_{\epsilon}$ ).

Because both shale and chert form locally prominent parts of the Kaskaskia sequence, the geochemical variation in each was examined using the same stratigraphic sections as those used in the study of the carbonate rocks. A single sample of chert was collected from each decile sampled in the carbonate study, resulting in 20 samples (fig. 7, table 3). For shale (ex-

cluding the organic-rich Chattanooga Shale at the base of the Kaskaskia), two randomly selected samples were taken from 8 of the 10 sections used in the carbonate study, and 1 sample was collected from a ninth section (locality 31) for a total of 17 shale samples (fig. 7, table 3). The components of geochemical variance for chert and shale in the Tippecanoe are the same as those estimated for sandstone in the Roubidoux Formation. (See equation 5.)

All but the basal few formations of the Kaskaskia in the study area are of Mississippian age, and the carbonate and chert samples collected from these strata are exclusively Mississippian in age. However, four samples of Chattanooga Shale of Devonian age (basal Kaskaskian) in northeastern Oklahoma and two of the Devonian Sylamore Sandstone in southeastern Missouri were collected. Finally, two samples of sandstone were collected from the Bushberg Sandstone (Mississippian) in southeastern Missouri (fig. 7, table 3).

#### PENNSYLVANIAN SYSTEM

The distribution of sampling localities used in the study of the Pennsylvanian System is shown in figure 8; specific locations and formations sampled are listed in table 3. Samples of shale, sandstone, and carbonate were collected from four composite stratigraphic sections, two located in the northern part of the outcrop belt, and two in the southern part. The sections in each pair are separated by about 80 km. Each section was subdivided into 10 approximately equal stratigraphic parts (deciles), and 2 deciles were selected randomly. Each selected decile was subdivided into 10 approximately equal stratigraphic parts (percentiles), and two randomly selected samples were taken from each of 2 randomly selected percentiles, making a total of 32 samples of each lithic type, except for sandstone for which the two required samples could not be located in one of the percentiles.

A decile in these rocks encompasses about 45 m of section in the northern pair of sections and about 110 m in the southern pair. The 2 percentiles in each selected decile could generally be sampled in a single outcrop, but the deciles in each section were located as much as 120 km apart. The components of geochemical variance estimated for the shale, sandstone, and carbonate of Pennsylvanian age are the same as those estimated for carbonate rocks in the Sauk sequence. (See equation 4.)

Independent of the shale, sandstone, and carbonate studies, 15 coal beds, ranging in thickness from 30 to 107 cm, were sampled from the working face in 11 operating strip pits in Missouri (fig. 8, table 3). The

total thickness of each bed was subdivided into 8-cm sections, two of these sections were selected randomly, and a composite sample was collected in each, for a total of 30 coal samples. The components of geochemical variance estimated for coal are:

$$S^2_{\log X} = S^2_{\gamma} + S^2_{\eta} + S^2_{\epsilon} \quad (8)$$

These components reflect variation among coal beds ( $S^2_{\gamma}$ ), variation between samples within coal beds ( $S^2_{\eta}$ ), and analytical variance ( $S^2_{\epsilon}$ ).

#### ANALYTICAL METHODS AND DATA EVALUATION

The rocks collected during the course of this study were analyzed by a variety of laboratory methods (table 4). Much of the trace element analysis is based on a semiquantitative emission spectrographic technique. This technique was supplemented by methods based on X-ray fluorescence, atomic absorption, and specialized techniques for determining fluorine and arsenic concentrations. Details of the analytical procedures are described in Miesch (1976, p. 10-17). All analyses were made in laboratories of the U.S. Geological Survey.

All rock samples were collected from outcrop and trimmed of obvious weathering rinds or other surface features. The lead-zinc-copper ore samples consisted of mined or milled material. Coal samples were collected from working faces at strip mines. Each sample was crushed in a jaw crusher and ground in a ceramic mill to minus-100-mesh particle size. Before grinding, randomly selected samples of each lithic type were divided into two parts using a Jones splitter, thus permitting an estimate of analytical variance (table 5).

The coal samples were not washed or subjected to flotation techniques, but were ground to pass through a 100-mesh sieve. A part of the ground material was weighed, then burned to ash in a muffle furnace in which the heat was increased 50° C each half hour to a temperature of 525° C and held at this temperature for about 24 hours. The resulting ash was then weighed to determine the ash yield of the coal. Analytical methods for most elements employed a weighed aliquot of the ash and are the same as those previously described for rock materials. For determining concentrations of arsenic, fluorine, mercury, and selenium, all of which may be volatilized and lost by burning the sample, weighed aliquots of raw coal were used for analysis. The methods of analysis used for these elements were, respectively, spectrophotometric, specific-ion electrode, flameless atomic absorption, and X-ray fluorescence.

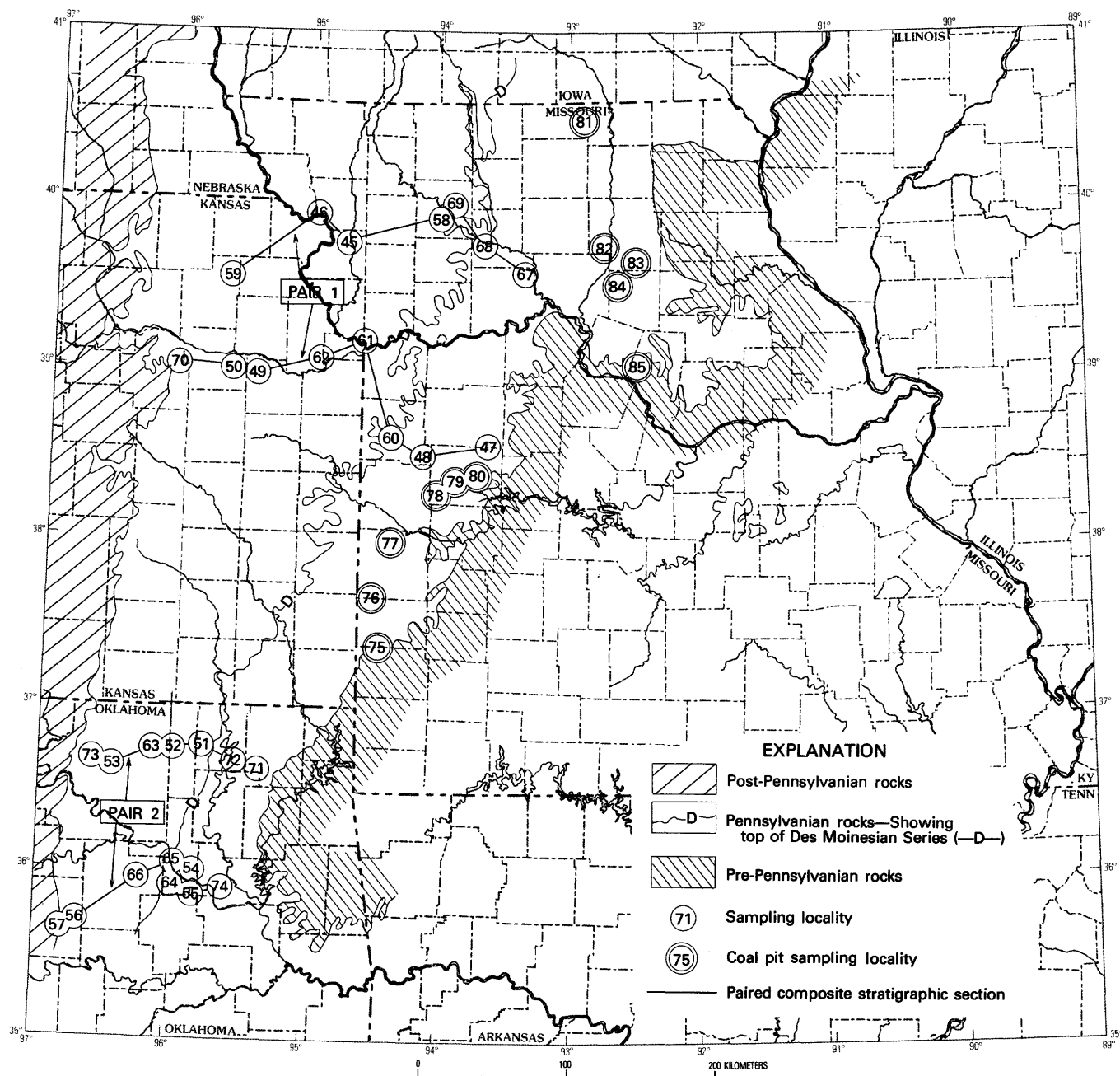


FIGURE 8.—Sampling localities in the Pennsylvanian System.

Elements determined on coal ash were converted to concentrations in the raw coal prior to data evaluation using the relation:

$$C = AP/(100) \quad (9)$$

where  $C$  estimates the concentration in raw coal,  $A$  is the concentration observed in ash, and  $P$  is the percent ash.

Because of the unusually high concentrations of copper and zinc in the lead-zinc-copper sulfide ores, these two elements were determined in ore by an atomic absorption method.

Insofar as possible, all samples of each lithic type were analyzed in a randomized sequence, thus converting any potential analytical drift into a random variation which cannot be mistakenly construed as geological in origin. Each sample was analyzed for 55

TABLE 4.—Analytical methods, with approximate lower limits of determination, for elements in this study

Element	Analytical method	Lower Limit of determination (parts per million)	Element	Analytical method	Lower limit of determination (parts per million)
Ag-----	Spectrographic-----	0.5	Li-----	Atomic absorption--	5
Al-----	X-ray fluorescence-----	10,000	Mg-----	-----do-----	300
As-----	Colorimetric-----	1	Mn-----	Spectrographic-----	1
B-----	Spectrographic-----	20	Mo-----	-----do-----	3
Ba-----	-----do-----	1.5	Na-----	Atomic Absorption	100
Be-----	-----do-----	1	Nb-----	Spectrographic	10
C, carbonate-	Gasometric-----	500	Nd-----	-----do-----	70
C, organic--	Calculated-----	1,000	Ni-----	-----do-----	5
Ca-----	X-ray fluorescence-----	1,000	P-----	X-ray fluorescence--	300
Cd-----	-----do-----	1	Pb-----	Spectrographic-----	10
Ce-----	Spectrographic-----	150	Sb-----	-----do-----	150
Co-----	-----do-----	2	Sc-----	-----do-----	5
Cr-----	-----do-----	1	Se-----	X-ray fluorescence--	.1
Cu-----	-----do-----	1	Si-----	-----do-----	10,000
F-----	F selective ion electrode--	10	Sn-----	Specteographic-----	10
Fe-----	X-ray fluorescence-----	1,000	Sr-----	-----do-----	5
Ga-----	Spectrographic-----	5	Ti-----	-----do-----	2
Ge-----	-----do-----	10	V-----	-----do-----	7
Hg-----	Flameless atomic absorption	.01	Y-----	-----do-----	10
In-----	Spectrographic-----	10	Yb-----	-----do-----	1
K-----	X-ray fluorescence-----	1,000	Zn-----	Atomic absorption--	10
La-----	Spectrographic-----	30	Zr-----	Spectrographic	10

elements. Depending on the sample composition, 15 additional elements, most of them rare earths, were on occasion looked for; and both organic carbon and inorganic (carbonate) carbon concentrations were determined. About 34 elements were consistently detected in most shale, coal, granite, and sulfide ore samples, and about 23 were routinely detected in most sandstone and carbonate samples. The analytical data on which this report is based are too voluminous for inclusion here, with the exception of data on the lead-zinc-copper ores. All other chemical data have been published in Boerngen, VanTrump, and Ebens (1975).

The frequency distributions of trace element determinations commonly exhibit a marked positive skewness, that is, low concentrations tend to be much more frequently observed than high concentrations. As a consequence, the average value in such a distribution will substantially overestimate the most common, or expected, value (the mode); and the standard deviation may give rise to an unrealistic range in probable concentration. In order to circumvent such difficulties, summary statistics of most of the distributions in this study are based on logarithms of the data. The geometric mean (GM), defined as the antilog of the average of the logarithmic concentrations, is generally

a less biased estimate of the median. The geometric deviation (GD), defined as the antilog of the standard deviation of the logarithmic concentrations, is a factor useful in computing probable expected ranges in concentration. For example, if a distribution is lognormal, about 68 percent of the determinations in a randomly selected suite should fall within the limits  $GM/GD$  and  $GM \times GD$ . About 95 percent should fall within the range  $GM/(GD)^2$  to  $GM \times (GD)^2$ , and over 99 percent should be within the range  $GM/(GD)^3$  to  $GM \times (GD)^3$ .

Commonly a suite of samples may contain one or more elements in concentrations too low to be measured by the analytical method used. In these circumstances the element distribution is said to be censored, and a problem arises as to how to estimate the mean and variance (or their logarithmic counterparts) in an unbiased manner. Miesch (1967, 1976) described procedures based on a method of Cohen (1959) that constitute an adjustment of the mean and variance computed for the uncensored part of the data. The same adjustment can be made if censoring occurs at the higher end of the distribution.

Many kinds of statistical analyses, however, require completely uncensored data, and the following arbitrary practice was used to circumvent problems of



TABLE 5.—*Estimated variance of the analytical procedures (including sample preparations) for five rock types sampled in Missouri and adjacent States*

[The variance estimates are based on duplicate analyses of 10 samples of granitic rocks; 15 samples of carbonate rocks; 15 samples of sandstone and chert; 15 samples of clay and silt; and 15 samples of coal. Leaders (—) indicate no data available]

Element or ash	Analytical log <sub>10</sub> variance (S <sub>r</sub> <sup>2</sup> )				
	Granitic rocks	Carbonate rocks	Sandstone and chert	Claystone, siltstone, and shale	Coal
Al-----	0.0003	0.0074	0.0031	0.0005	0.0074
As-----	0.0026	0.0102	0.0438	0.0067	0.0623
Ash-----	--	--	--	--	0.103
B-----	--	--	0.0215	0.0562	0.0099
Ba-----	0.0008	0.0128	0.0088	0.0099	0.0365
Be-----	0.0062	--	--	0.0104	0.0046
C, carbonate--	--	0.0705	0.0922	0.0223	--
C, organic----	--	0.1418	0.0815	0.0544	--
Ca-----	0.0001	0.2333	0.0150	0.0005	0.0261
Co-----	--	--	0.0107	0.0102	0.0130
Cr-----	--	0.0123	0.0155	0.0049	0.0122
Cu-----	0.0052	0.0130	0.0083	0.0082	0.0191
F-----	0.2931	0.0449	0.0164	0.1284	0.0091
Fe-----	0.0001	0.0003	0.0039	0.0001	0.0228
Ga-----	0.0309	--	0.0005	0.0032	--
Ge-----	--	--	--	--	0.0069
Hg-----	0.0281	0.0164	0.0171	0.0250	0.0288
K-----	<.0001	0.0022	<.0001	0.0001	0.0099
La-----	0.0054	--	0.0034	0.0059	--
Li-----	--	--	0.0105	0.0002	0.0184
Mg-----	0.0010	0.0008	0.0349	0.0074	0.0092
Mg(dolomite)	--	0.2030	--	--	--
Mn-----	0.0078	0.0124	0.1238	0.0051	0.0133
Mo-----	--	--	--	--	0.0071
Na-----	0.0001	0.0242	0.0260	0.0350	0.0060
Nb-----	0.0039	--	0.0099	--	--
Nd-----	0.0045	--	--	--	--
Ni-----	--	0.0014	0.0248	0.0072	0.0180
P-----	0.0359	0.0941	0.0277	0.0187	--
Pb-----	0.0315	0.0170	0.0075	0.0158	0.0173
Sc-----	0.0115	--	<.0001	0.0069	0.0170
Se-----	0.0573	0.0848	0.0498	0.0569	0.0304
Si-----	0.2700	0.0008	0.2333	0.0001	0.0091
Sr-----	0.0040	0.0082	0.0094	0.0049	0.0110
Ti-----	0.0018	0.0193	0.0121	0.0048	0.0103
V-----	--	0.0073	0.0007	0.0032	0.0069
Y-----	0.0036	0.0016	0.0007	0.0059	0.0081
Yb-----	0.0052	0.0021	0.0033	0.0140	--
Zn-----	0.0003	0.0560	0.0032	0.0012	0.0869
Zr-----	0.0201	0.0036	0.0148	0.0268	0.0213

<sup>1</sup>Variance calculated on nontransformed data.

censoring when necessary. If less than a third of the frequency distribution of any element in any unit of study was censored, a value equal to approximately seven-tenths of the lower limit of determination was used in place of the censored values. The only justification for such a replacement is that substitution of any reasonable value below the analytical limit would not substantially alter geochemical conclusions drawn from the statistical analysis.

Finally, the problem arises as to whether the area means (most areas being represented by a pair of sampled stratigraphic sections) are sufficiently different to form the basis of a geochemical map. If not sufficiently different, any resulting map may be unstable, that is, not generally reproducible on repetition of the field sampling and laboratory analysis. Too

few areas were sampled within each geologic unit in this study to warrant the construction of maps, but it still seems useful to identify those situations where the area means were sufficiently different to meet the criteria for geochemical mapping. Where these criteria are met, the means and associated statistics for the areas are given separately on the tables summarizing the geochemical data.

A basic criterion for the sufficiency of differences among means is the conventional *F*-statistic which is based on measures of variance between and within areas. If the *F*-statistic is found to be statistically significant, one can have a prescribed confidence that, at the least, one of the areas is different from some other. However, this does not seem to be an adequate criterion for predicting whether the general configuration of a geochemical map would be reproducible. Several more stringent empirical criteria were described by Miesch (1976, p. A9-A10). The one used here requires that the variance of the area means, *E<sub>s</sub>*, be smaller than a critical value, *E<sub>r</sub>*. *E<sub>r</sub>* is the maximum permissible variance for an area mean if the *F*-statistic, given by:

$$F=1+n_r v \quad (10)$$

$$v=S^2_{\beta}/(S^2_{\gamma}+S^2_{\theta}+S^2_{\kappa}+S^2_{\eta}+S^2_{\epsilon}) \quad (11)$$

and using only 1 and  $2n_r-2$  degrees of freedom, is significant at the 0.05 probability level. The term  $n_r$  is the minimum number of randomly collected samples needed from each area (if random sampling were employed) and can be read from a graph in Miesch (1976, p. A9).

In situations where all hierarchical sampling levels (listed in table 1) were used, *E<sub>s</sub>* is computed by:

$$E_s = \frac{S^2_{\gamma}}{n_{\gamma}} + \frac{S^2_{\theta}}{n_{\theta}n_{\gamma}} + \frac{S^2_{\kappa}}{n_{\kappa}n_{\theta}n_{\gamma}} + \frac{S^2_{\eta}}{n_{\eta}n_{\kappa}n_{\theta}n_{\gamma}} + \frac{S^2_{\epsilon}}{n_{\epsilon}n_{\eta}n_{\kappa}n_{\theta}n_{\gamma}} \quad (12)$$

and *E<sub>r</sub>* is computed by:

$$E_r = (S^2_{\gamma}+S^2_{\theta}+S^2_{\kappa}+S^2_{\eta}+S^2_{\epsilon})/n_r \quad (13)$$

The subscripted *n*'s in equation 12 are the number of sampling units at each level of the hierarchical design. Where *E<sub>s</sub>* is larger than *E<sub>r</sub>*, the number of samples collected within each area (based on the hierarchy) is effectively less than the critical number  $n_r$ , required by the variance ratio, *v* (equation 11).

## GEOCHEMICAL VARIABILITY

## LIMESTONE AND DOLOMITE

Limestone and dolomite are the most widespread rocks in the near-surface landscape of the study area. They compose most of the Sauk, Tippecanoe, and Kaskaskia strata, underlying much of eastern and southern Missouri and northern Arkansas (fig. 3); and they are scattered as tabular lenses through the Pennsylvanian strata in northwestern Missouri and eastern Kansas (fig. 3), where they tend to support broad interfluvies. Carbonate aquifers are the main source of drinking water supplies in southern Missouri and northern Arkansas.

The carbonate rocks are also important because of the large deposits of lead, zinc, and copper sulfide ore contained in them in the southeastern and southwestern parts of Missouri. In addition, limestone and dolomite are two of the major mineral commodities produced in the State. Major uses are as crushed and broken stone for concrete aggregate, roadstone, cement, lime manufacture, riprap, and agriculture. Throughout much of the southern part of the study

area, prolonged weathering of these rocks has resulted in a cherty, clay-rich, base-deficient soil of poor agricultural quality.

Normative mineral compositions of 131 samples of carbonate rock are compared in figure 9. In computation of these norms, all MgO was put into dolomite, and excess CaO into calcite. The normative clay component was assumed to contain 26 percent  $Al_2O_3$  and 50 percent  $SiO_2$ , proportions which approximate those found in illitic mica (Weaver and Pollard, 1973, p. 9). Excess  $SiO_2$  was computed as quartz, which occurs in these rocks as both sand and chert. Over half of the samples consist of more than 90 percent normative calcite and dolomite combined. Few contain more than 20 percent normative quartz and clay combined, and all but two of those are of Mississippian and Pennsylvanian age.

The distribution in figure 9 shows the following: (1) The Sauk carbonates consist of reasonably pure dolomite (sample SD09 from the Bonneterre Formation being the only exception), and carbonate in the lower Sauk (pre-Jefferson City strata) tends to be slightly purer dolomite than that in the upper Sauk. (2) The Tippecanoe carbonates consist largely of

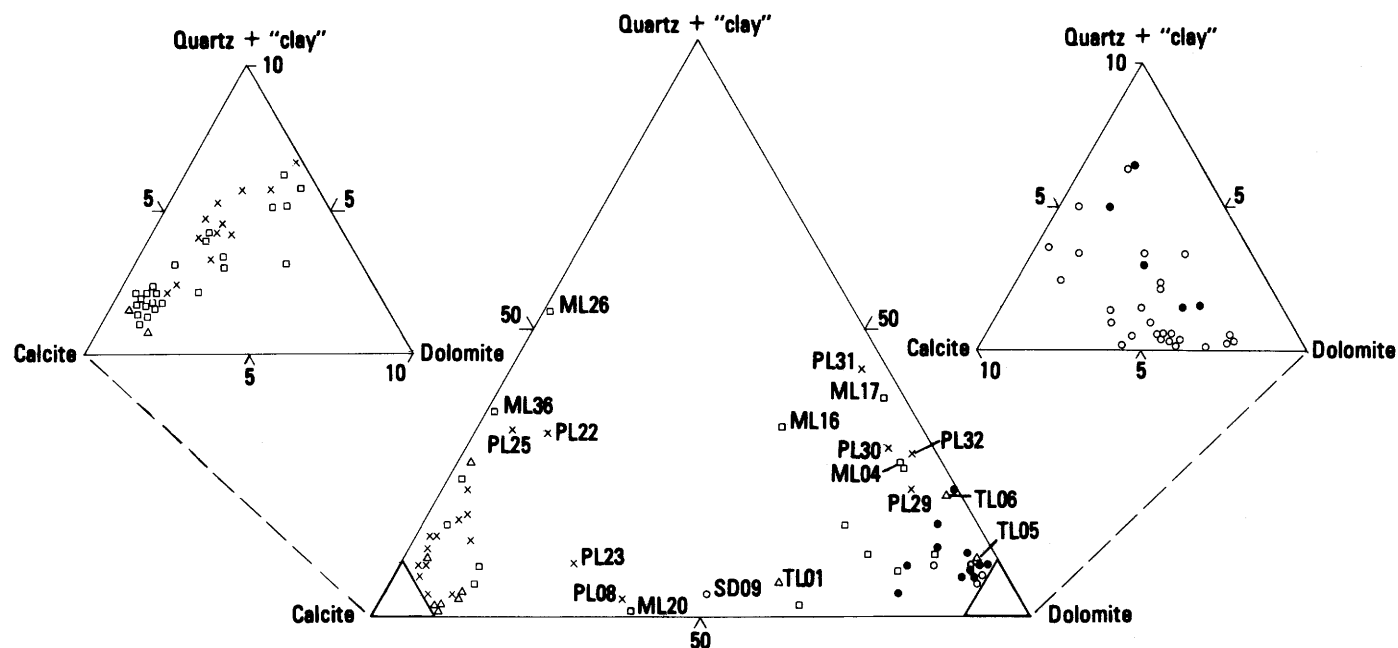


FIGURE 9.—Normative mineralogy of limestone and dolomite samples of the lower Sauk sequence (circle), the upper Sauk sequence (dot), the Tippecanoe sequence (triangle), the Kaskaskia sequence (square), and of Pennsylvanian age (X). Numbered samples are referred to in text.

relatively pure limestone, although three samples (TL01, TL05, and TL06, all from the Joachim Formation) are normative dolomites. (3) Carbonate of the Kaskaskia sequence contains both limestone and dolomite. Nine of forty samples consist of reasonably pure dolomite (two of these are fairly siliceous—ML16 and ML17), and a tenth (ML20) is distinctly dolomitic. These 10 samples were collected in Missouri, and 9 of them (all except ML04) are Early Mississippian in age (Kinderhookian or Osagean). Two of the limestones (ML26 and ML36) are distinctly siliceous. (4) Carbonate of Pennsylvanian age is largely limestone, some of it siliceous (PL22 and PL25) or dolomitic (PL08 and PL23). Four dolomite samples (PL29, PL30, PL31, and PL32), collected from the Brownville Limestone Member of the Wood Siding Formation and the Reading Limestone Member of the Emporia Limestone at the top of the Pennsylvanian section in Oklahoma (loc. Nos. 56 and 57, fig. 8), represent a localized carbonate variant. They were taken from red-colored, fine-grained, thin, poorly bedded strata which contrast strongly with the more ordinary gray, thinly bedded, fossiliferous limestones of Pennsylvanian age in Kansas and Missouri.

Results of the analysis of variance for these four carbonate units are given in tables 6–9, and summary statistics are given in tables 10–13. Carbonate rocks in the Sauk appear to be distinctly more uniform geochemically than carbonate rocks in the three other intervals studied. The total observed variation ( $S^2_{\log x}$ , table 6) of all elements except carbonate carbon, calcium, magnesium, and titanium is nearly as small as or smaller in the Sauk than that estimated for the other three carbonate units (figs. 7–9). Moreover, the total observed variance in barium, fluorine, iron, silicon, and titanium tends to be smaller in both the Sauk and the Pennsylvanian carbonates (figs. 6, 9) than in carbonates of the Tippecanoe and Kaskaskia (figs. 7, 8). Thus, the less widespread carbonate units appear to be more geochemically variable than the more widespread units.

The between-areas variance ( $S^2_{\beta}$ , between pairs of sections) is generally small in the carbonate rocks of this study, except for those of Pennsylvanian age (table 9). The Pennsylvanian rocks are the only ones to consistently exhibit elemental variation between areas of more than 10–15 percent of the total estimated variance. This variability is statistically significant for four elements (chromium, potassium, phosphorus, and titanium) and reflects in part the higher concentrations

found in the samples from Oklahoma. Copper in the Sauk (table 6) is the only other element in the carbonate rocks showing statistically significant variation at this scale. Five carbonate samples collected at loc. Nos. 2, 3, and 4 (fig. 4) are unusually high in copper (7–20 ppm) when compared to an expected level of 2 ppm (table 10). All of these samples were collected in or near the Washington County Barite District, an area of known anomalous near-surface copper. Although no visible indications of mineralization were noted at the points of collection, the rocks cropping out in the sampled areas may be weakly mineralized.

Area averages for copper in the Sauk and chromium, potassium, phosphorus, and titanium in the Pennsylvanian were examined for stability as described above.  $E_s$  was computed by:

$$E_s = \frac{S^2_y}{2} + \frac{S^2_{\theta}}{4} + \frac{S^2_{\kappa}}{8} + \frac{S^2_{\eta} + S^2_{\epsilon}}{16} \quad (14)$$

The pertinent parameters for this examination are listed below:

Element	$v$	$n_r$	$E_r$	$E_s$
Sauk sequence				
Copper .....	0.49	8	0.0110	0.0131
Pennsylvanian carbonates				
Chromium .....	.32	11	.0070	.0064
Potassium .....	.30	12	.0103	.0109
Phosphorus .....	.59	7	.0289	.0154
Titanium .....	.21	16	.0129	.0176

Area averages for only chromium and phosphorus in Pennsylvanian carbonate are sufficiently stable ( $E_s \leq E_r$ ) to be listed in the summary statistics (table 13). Additional data are required if stable averages for the remaining three elements are to be computed.

Between-section variance ( $S^2_{\eta}$ ) is most prominent in the carbonates of the Kaskaskia sequence. Nine elements in this unit, including magnesium, exhibit statistically significant variation between sections within areas of outcrop. The presence of magnesium in this element group suggests that this variation reflects

TABLE 6.—*Components of variance estimated for carbonate rocks of the Sauk sequence*

[Variance calculated on data transformed to logarithms, except as noted. Asterisk (\*), value significantly greater than zero at the 0.05 probability level]

Element	Total log <sub>10</sub> variance ( $S_{\text{Log } X}^2$ )	Variance									
		Between areas		Between sections		Between deciles		Between percentiles		Between samples	
		Component	Percent of total	Component	Percent of total	Component	Percent of total	Component	Percent of total	Component	Percent of total
		( $S_B^2$ )		( $S_Y^2$ )		( $S_\theta^2$ )		( $S_K^2$ )		( $S_\eta^2 + S_\epsilon^2$ )	
Ba-----	0.2856	0.0	<1	0.0453	16	*0.1654	58	0.0	<1	0.0758	27
C, carbonate <sup>1</sup>	.6383	.0215	3	.1234	19	*.1590	25	.1252	20	.2092	33
Ca <sup>1</sup> -----	3.7063	.1889	5	.1552	4	0	<1	*1.6687	45	1.6935	46
Cr-----	.1745	0	<1	.0725	42	*.0574	33	.0027	2	.0418	24
Cu-----	.1315	*.0432	33	.0158	12	0	<1	.0102	8	.0622	47
F-----	.1921	0	<1	.0154	8	.0207	11	0	<1	.1553	81
Fe-----	.1446	0	<1	.0536	37	*.0545	38	.0101	7	.0265	18
Hg-----	.0922	0	<1	.0264	29	*.0222	24	.0030	3	.0406	44
K-----	.2722	0	<1	.1023	38	*.1148	42	.0044	2	.0508	19
Mg-----	3.8368	0	<1	*1.2122	32	0	<1	.1287	3	2.4960	65
Mn-----	.2389	0	<1	.0625	26	*.0915	38	.0277	12	.0571	24
Na-----	.0289	0	<1	.0041	14	*.0105	37	0	<1	.0142	49
Se-----	.0824	0	<1	0	<1	0	<1	.0131	16	.0693	84
Si-----	.2304	.0193	8	.0148	6	*.0732	32	0	<1	.1230	53
Sr-----	.0267	0	<1	0	<1	*.0155	58	0	<1	.0112	42
Ti-----	.4754	0	<1	.0647	14	*.2588	54	.0028	1	.1491	31

<sup>1</sup>Variance calculated on nontransformed data.TABLE 7.—*Components of variance estimated for carbonate rocks of the Tippecanoe sequence*

[Variance calculated on data transformed to logarithms, except as noted. Asterisk (\*), value significantly greater than zero at the 0.05 probability level]

Element	Total log variance ( $S_{\text{Log } X}^2$ )	Variance					
		Between sections		Between deciles		Between samples	
		Component	Percent of total	Component	Percent of total	Component	Percent of total
		( $S_Y^2$ )		( $S_K^2$ )		( $S_\eta^2 + S_\epsilon^2$ )	
Ba-----	0.4942	0.0	<1	*0.4497	91	0.0444	9
C, carbonate <sup>1</sup>	1.3973	0	<1	*.9568	68	.4405	32
C, organic--	.1650	0	<1	*.1094	66	.0556	34
Ca <sup>1</sup> -----	99.6371	0	<1	*82.0679	82	17.5992	18
Cr-----	.1717	.0106	6	.0809	47	.0802	47
F-----	.5798	0	<1	.2307	40	.3491	60
Fe-----	.1986	0	<1	*.1315	66	.0671	34
Hg-----	.1676	0	<1	0	<1	.1676	100
K-----	.2842	0	<1	*.2047	72	.0795	28
Mg-----	.4916	0	<1	*.4194	85	.0721	15
Mn-----	.1753	.0300	17	*.1161	66	.0293	17
Na-----	.1343	0	<1	*.1203	90	.0140	10
Se-----	.0869	0	<1	.0480	55	.0389	45
Si-----	.4309	0	<1	*.3426	79	.0883	20
Sr-----	.1268	0	<1	*.1077	85	.0191	15
Ti-----	.8735	0	<1	.5632	64	.3103	36
Zn-----	.0341	*.0137	40	.0106	31	.0098	29

<sup>1</sup>Variance calculated on nontransformed data.

in part the uneven distribution of dolomite from section to section. Fluorine, iron, mercury, manganese, and sodium are distinctly higher in the dolomite than in the limestone samples from this sequence, whereas strontium is distinctly lower (table 12). Yttrium and zinc are slightly lower in the dolomite. Maximum yttrium levels of 50–70 ppm were detected in carbonate samples from loc. No. 32 (Missouri) and No. 40 (Arkansas). More than 100 ppm zinc were found in one sample from loc. No. 31 (fig. 7). In the other three carbonate units, only magnesium in the Sauk, zinc in the Tippecanoe, and silicon in the Pennsylvanian exhibit a statistically significant variance component at the between-section scale ( $S_Y^2$ ). Variation in the magnesium and silicon reflects variation in proportions of dolomite and quartz (chert), respectively, from section to section. The variation in zinc reflects slightly elevated levels (as much as 22 ppm) in Tippecanoe samples from loc. No. 28 (fig. 6).

Stratigraphic variation ( $S_B^2 + S_K^2$ ) is large in all units. More than half of the elements listed in tables 6–9 ex-

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TABLE 8.—Components of variance estimated for carbonate rocks of the Kaskaskia sequence

[Variance calculated on data transformed to logarithms, except as noted. Asterisk (\*), value significantly greater than zero at the 0.05 probability level]

Element	Total log <sub>10</sub> variance (S <sup>2</sup> <sub>Log X</sub> )	Variance							
		Between areas		Between sections		Between deciles		Between samples	
		Component (S <sup>2</sup> <sub>B</sub> )	Percent of total	Component (S <sup>2</sup> <sub>Y</sub> )	Percent of total	Component (S <sup>2</sup> <sub>K</sub> )	Percent of total	Component (S <sup>2</sup> <sub>n</sub> + S <sup>2</sup> <sub>e</sub> )	Percent of total
Ba-----	0.6919	0.0	<1	0.1960	28	*0.3700	53	0.1259	18
C, carbonate <sup>1</sup>	2.8499	0	<1	0	<1	.6977	24	2.1522	76
C, organic--	.1318	.0130	10	0	<1	.0058	4	.1129	86
Ca <sup>1</sup> -----	112.4386	0	<1	38.9863	35	26.2827	23	47.1695	42
Cr-----	.2641	0	<1	.0380	14	*.1625	62	.0636	24
F-----	.6071	0	<1	*.3013	50	*.1387	23	.1671	27
Fe-----	.3246	0	<1	*.1866	57	*.0987	30	.0393	12
Hg-----	.1398	0	<1	*.0844	60	.0208	15	.0346	25
Mg-----	.6030	0	<1	*.3628	60	*.2005	33	.0398	6
Mn-----	.0972	.0375	39	*.0216	22	.0017	2	.0365	38
Na-----	.1766	0	<1	*.1164	66	*.0252	14	.0350	20
Se-----	.1282	0	<1	.0141	11	.0043	3	.1098	86
Si-----	.4305	0	<1	0	<1	*.2620	61	.1684	39
Sr-----	.3124	0	<1	*.2692	86	.0114	4	.0318	11
Ti-----	1.2834	0	<1	.3456	27	*.7667	60	.1711	14
Y-----	.0869	0	<1	*.0214	25	.0234	27	.0422	49
Zn-----	.0506	.0001	<1	*.0089	18	.0164	32	.0252	50

<sup>1</sup>Variance calculated on nontransformed data.

TABLE 9.—Components of variance estimated for carbonate rocks of Pennsylvanian age

[Variance calculated on data transformed to logarithms, except as noted. Asterisk (\*), value significantly greater than zero at the 0.05 probability level]

Element	Total log <sub>10</sub> variance (S <sup>2</sup> <sub>Log X</sub> )	Variance									
		Between areas		Between sections		Between deciles		Between percentiles		Between samples	
		Component (S <sup>2</sup> <sub>B</sub> )	Percent of total	Component (S <sup>2</sup> <sub>Y</sub> )	Percent of total	Component (S <sup>2</sup> <sub>θ</sub> )	Percent of total	Component (S <sup>2</sup> <sub>K</sub> )	Percent of total	Component (S <sup>2</sup> <sub>n</sub> + S <sup>2</sup> <sub>e</sub> )	Percent of total
As-----	0.2214	0.0358	16	0.0118	5	*0.0636	29	0.0	<1	0.1102	50
Ba-----	.2294	.0116	5	.0248	11	0	<1	*.1297	57	.0633	28
C, carbonate <sup>1</sup>	1.8762	.1097	6	.4679	25	.0447	2	.3562	19	.8977	48
Ca-----	93.5272	10.3323	11	7.7837	8	*59.5987	64	0	<1	15.8125	17
Cr-----	.1025	*.0251	25	0	<1	0	<1	.0255	25	.0519	51
Cu-----	.1089	.0016	1	0	<1	0	<1	*.0556	51	.0518	48
F-----	.2906	0	<1	0	<1	.0359	12	.0607	21	.1940	67
Fe-----	.1573	.0129	8	0	<1	.0732	47	*.0358	23	.0355	23
Hg-----	.2224	0	<1	.0347	16	0	<1	*.0919	41	.0958	43
K-----	.1613	*.0374	23	0	<1	.0062	4	.0313	19	.0864	54
Mg-----	.3773	.0301	8	0	<1	*.2700	72	0	<1	.0772	20
Mn-----	.1400	.0172	12	.0183	13	*.0440	31	.0158	11	.0446	32
Na-----	.1485	.0035	2	0	<1	.0256	17	.0251	17	.0943	63
P-----	.3220	*.1198	37	.0062	2	0	<1	0	<1	.1961	61
Se-----	.1843	.0075	4	.0007	<1	0	<1	.0556	30	.1206	65
Si-----	.2253	.0174	8	*.0685	30	0	<1	.0533	24	.0860	38
Sr-----	.3437	0	<1	.1340	39	*.1582	46	.0095	3	.0420	12
Ti-----	.2497	*.0430	17	0	<1	0	<1	.0757	30	.1309	52
V-----	.1288	.0290	23	0	<1	*.0336	26	.0142	11	.0520	40
Zn-----	.1340	.0395	30	0	<1	*.0441	33	.0053	4	.0450	34
Zr-----	.1279	.0265	21	0	<1	.0432	34	*.0334	26	.0248	19

<sup>1</sup>Variance calculated on nontransformed data.

TABLE 10.—*Geochemical summary of rocks of the Sauk sequence in Missouri and adjacent States*

[GM, geometric mean, except as noted; GD, geometric deviation, except as noted; Ratio, number of samples in which element detected to total number of samples; ppm, parts per million; leaders (—) indicate no data available]

Element	Dolomite			Sandstone of the Roubidoux Formation			Sandstone (except Roubidoux)			Shale of the Davis Formation		
	GM	GD	Ratio	GM	GD	Ratio	GM	GD	Ratio	Observed range	Ratio	
Al, percent--	0.31	2.18	16:47	0.43	1.75	6:12	0.67	2.55	8:14	7.9 - 9.0	4:4	
As, ppm-----	1.1	2.51	27:47	1.1	1.57	7:12	1.0	2.08	6:14	---	---	
B, ppm-----	<20	---	0:47	18	1.78	6:12	20	2.11	7:14	100 - 150	4:4	
Ba, ppm-----	8.8	3.42	47:47	38	1.92	12:12	77	2.47	14:14	300 - 500	4:4	
Be, ppm-----	<1	---	0:47	<1	---	0:12	<1	---	0:14	1 - 1.5	4:4	
C, carbonate, percent---	<sup>1</sup> 12	<sup>2</sup> 2.80	47:47	<.01	---	6:12	<.01	---	6:14	.21 - 1.5	4:4	
C, organic, percent---	.11	3.04	27:47	.30	3.13	11:12	.31	1.43	14:14	.1 - 2.7	4:4	
Ca, percent--	<sup>1</sup> 21	<sup>2</sup> 2.28	47:47	<sup>3</sup> .017	---	6:12	<.07	---	4:14	3.9 - 4.6	4:4	
Co, ppm-----	<3	---	4:47	<3	---	1:12	<10	---	1:14	10 - 15	4:4	
Cr, ppm-----	3.6	2.62	47:47	2.0	2.47	10:12	2.8	2.84	13:14	100 - 150	4:4	
Cu, ppm-----	2.0	2.30	39:47	1.2	2.14	8:12	1.3	2.55	8:14	7 - 20	4:4	
F, ppm-----	91	2.74	44:47	9.8	4.83	6:12	26	6.41	9:14	---	---	
Fe, percent--	.17	2.40	45:47	.090	3.26	7:12	.11	3.38	9:14	2.0 - 3.4	4:4	
Ga, ppm-----	<5	---	2:47	<5	---	0:12	<5	---	4:14	30	4:4	
Hg, ppm-----	.028	2.01	46:47	.0079	2.82	6:12	<.01	---	8:14	.02 - .07	4:4	
K, percent---	.19	3.32	38:47	.083	2.99	7:12	.32	5.43	11:14	.83 - 9.1	4:4	
La, ppm-----	<30	---	0:47	<30	---	0:12	<30	---	0:14	50	4:4	
Li, ppm-----	1.1	2.66	5:47	2.1	2.47	3:12	<5	---	7:14	16 - 20	4:4	
Mg, percent--	<sup>1</sup> 11	<sup>2</sup> 2.52	47:47	<sup>3</sup> .22	---	12:12	.085	7.73	14:14	1.3 - 2.8	4:4	
Mn, ppm-----	83	3.08	47:47	29	3.42	12:12	40	4.39	14:14	70 - 150	4:4	
Mo, ppm-----	.81	2.97	7:47	<3	---	0:12	>7	---	1:14	---	---	
Na, percent--	.027	1.48	47:47	.013	2.53	12:12	.018	2.90	14:14	.052 - .096	4:4	
Nb, ppm-----	<10	---	0:47	<10	---	0:12	<10	---	0:14	<10	0:4	
Ni, ppm-----	<5	---	2:47	<5	---	1:12	<7	---	1:14	20 - 30	4:4	
P, ppm-----	94	2.51	12:47	100	2.22	5:12	210	1.38	12:14	130 - 440	4:4	
Pb, ppm-----	<10	---	7:47	<10	---	0:12	<10	---	5:14	<10 - 15	2:4	
Sc, ppm-----	<5	---	0:47	<5	---	0:12	<5	---	0:14	15	4:4	
Se, ppm-----	.18	1.94	35:47	.086	2.06	6:12	.13	1.69	10:14	<.1 - .4	3:4	
Si, ppm-----	1.5	3.02	39:47	<sup>1</sup> 40	<sup>2</sup> 8.06	12:12	<sup>1</sup> 43	7.78	14:14	20 - 22	4:4	
Sr, ppm-----	100	1.46	47:47	13	2.23	12:12	14	2.36	14:14	200 - 300	4:4	
Ti, ppm-----	33	4.89	46:47	83	5.63	12:12	130	2.39	14:14	2000 - 3000	4:4	
Y, ppm-----	<10	---	0:47	<10	---	0:12	<10	---	2:14	10 - 15	4:4	
Yb, ppm-----	<1	---	0:47	<1	---	0:12	<1.5	---	2:14	1 - 1.5	4:4	
V, ppm-----	6.4	2.04	28:47	5.3	1.43	5:12	<7	---	5:14	70 - 100	4:4	
Zn, ppm-----	6.4	2.04	17:47	5.2	1.61	2:12	<11	---	3:14	15 - 43	4:4	
Zr, ppm-----	7.1	1.88	20:47	22	1.63	12:12	41	2.26	14:14	70	4:4	

<sup>1</sup>Arithmetic mean.<sup>2</sup>Standard deviation.<sup>3</sup>Median.

hibit statistically significant variation at one or the other of these scales. Such variation is expected because compositional layering is a distinguishing feature of sedimentary rocks. The large-scale stratigraphic variation in the Sauk carbonates reflects mostly the slightly higher argillitic content of the upper

Sauk (fig. 9) compared to the lower Sauk. In general, the upper Sauk has slightly less total carbonate and slightly more barium, chromium, iron, potassium, sodium, silicon, and titanium. The large-scale stratigraphic variation ( $S^2_0$ ) in the carbonates of Pennsylvanian age reflects the presence of four dolomite

TABLE 11.—*Geochemical summary of rocks of the Tippecanoe sequence in Missouri and adjacent States*

[GM, geometric mean, except as noted; GD, geometric deviation, except as noted; Ratio, number of samples in which element detected to total number of samples; ppm, parts per million; leaders (—) indicate no data available]

Element	Combined data for limestone and dolomite			Limestone only			Dolomite only		Shale		St. Peter Sandstone	
	GM	GD	Ratio	GM	GD	Ratio	Observed range	Ratio	Observed range	Ratio	Observed range	Ratio
Al, percent--	<0.53	--	3:12	<0.53	--	1:9	<0.53 - 1.6	2:3	3.2 - 6.4	4:4	<0.53	0:4
As, ppm-----	.74	1.53	3:12	1	--	0:9	1.0 - 1.5	3:3	3.4 - 7.8	4:4	<1	0:4
B, ppm-----	<20	--	1:12	<20	--	0:9	<20 - 20	1:3	30 - 100	4:4	<20 - 30	2:4
Ba, ppm-----	5.6	5.04	10:12	3.0	3.75	7:9	20 - 70	3:3	150 - 700	4:4	10 - 20	4:4
Be, ppm-----	<1	--	0:12	<1	--	0:9	--	0:3	<1 - 2	2:4	<1	0:4
C, carbonate, percent----	<sup>1</sup> 11	<sup>2</sup> 1.18	12:12	<sup>1</sup> 11	<sup>2</sup> 1.16	9:9	10 - 12	3:3	.59 - 5.8	4:4	<.01 - .03	2:4
C, organic, percent----	.28	2.55	12:12	.28	2.50	9:9	.1 - .6	3:3	<.1 - .4	2:4	.1 - .4	4:4
Ca, percent--	<sup>1</sup> 32	<sup>2</sup> 8.44	12:12	<sup>1</sup> 36	<sup>2</sup> 3.19	9:9	17 - 27	3:3	.71 - 9.3	4:4	<.071	0:4
Co, ppm-----	<3	--	1:12	<3	--	0:9	<3 - 3	1:3	5 - 10	4:4	<3	0:4
Cr, ppm-----	2.7	2.60	11:12	1.8	1.94	8:9	7 - 15	3:3	50 - 100	4:4	1 - 2	4:4
Cu, ppm-----	.84	3.51	6:12	.60	1.99	3:9	3 - 5	3:3	15 - 20	4:4	<1	0:4
F, ppm-----	67	5.77	10:12	32	3.77	7:9	36 - 62	3:3	950 - 3300	4:4	<10 - 70	3:4
Fe, percent--	.11	2.79	10:12	.074	1.51	7:9	.28 - .56	3:3	1.2 - 3.4	4:4	<.070	0:4
Ga, ppm-----	<5	--	1:12	<5	--	0:9	<5 - 7	1:3	10 - 20	4:4	<5	0:4
Hg, ppm-----	.022	2.57	11:12	.018	2.40	8:9	.02 - .07	3:3	.01 - .11	4:4	<.01 - .01	2:4
K, Percent---	.12	3.41	8:12	.077	2.46	5:9	.5 - 1.4	3:3	3.0 - 5.9	4:4	<.083	0:4
La, ppm-----	<30	--	0:12	<30	--	0:9	--	0:3	<50 - 50	1:4	<30	0:4
Li, ppm-----	1.2	6.26	3:12	<5	--	0:9	9 - 18	3:3	33 - 90	4:4	<5	0:4
Mg, percent--	1.2	5.03	12:12	1.0	2.62	9:9	7.7 - 11	3:3	.98 - 5.5	4:4	.006- .018	4:4
Mn, ppm-----	110	2.62	12:12	110	2.82	9:9	70 - 150	3:3	50 - 2000	4:4	1.5 - 15	4:4
Mo, ppm-----	<5	--	0:12	<5	--	0:9	--	0:3	<5 - 5	1:4	<5	0:4
Na, percent--	.013	2.33	12:12	.0093	1.41	9:9	.030- .037	3:3	.052- .089	4:4	<.007- .007	1:4
Ni, ppm-----	<5	--	0:9	<5	--	0:9	<5 - 5	1:3	20 - 30	4:4	<5 - 7	1:4
P, ppm-----	<220	--	4:12	<220	--	3:9	<220 - 350	1:3	310 - 870	4:4	170 - 260	4:4
Pb, ppm-----	4.0	2.06	2:12	<10	--	0:9	<10 - 15	2:3	15 - 30	4:4	<10	0:4
Sc, ppm-----	<5	--	0:12	<5	--	0:9	--	0:3	5 - 15	4:4	<5	0:4
Se, ppm-----	.16	1.97	9:12	.18	1.83	7:9	<.1 - .3	2:3	.1 - .6	4:4	<.1 - .2	3:4
Si, percent--	1.0	4.53	9:12	<.47	--	6:9	1.9 - 7.0	3:3	19 - 30	4:4	44 - 47	4:4
Sr, ppm-----	360	2.27	12:12	440	2.11	9:9	150 - 300	3:3	100 - 200	4:4	<7 - 7	2:4
Ti, ppm-----	<sup>3</sup> 50	--	10:12	<sup>3</sup> 50	--	7:9	70 - 600	3:3	1500 - 300	4:4	70 - 150	4:4
V, ppm-----	3.9	2.42	4:12	<7	--	1:9	<7	0:3	30 - 70	4:4	<7	0:4
Y, ppm-----	<10	--	1:12	<10	--	1:9	--	0:3	10 - 15	4:4	<10	0:4
Yb, ppm-----	<1	--	0:12	<1	--	0:9	--	0:3	1.5	4:4	<1	0:4
Zn, ppm-----	12	1.53	9:12	12	1.54	7:9	<10 - 15	2:3	11 - 30	4:4	<10	0:4
Zr, ppm-----	<10	--	4:12	<10	--	1:9	10 - 50	3:3	50 - 200	4:4	20 - 150	4:4

<sup>1</sup>Arithmetic mean.

<sup>2</sup>Standard deviation.

<sup>3</sup>Median.

samples (loc. Nos. 56 and 57, fig. 8). Compared to the other Pennsylvanian carbonates (table 13), these samples are high in manganese and vanadium, as well as in magnesium, and are low in calcium and strontium. Variation in arsenic and zinc at this scale reflects the presence of three samples from loc. No. 53 (fig. 8), which contained as much as 39 ppm arsenic and 140 ppm zinc. The association of these two metals suggests that the rocks in this locality contained sphalerite.

Small-scale stratigraphic variation ( $S^2_x$ ) is large in the carbonate units, except in the Sauk, and reflects compositional layering within stratigraphic intervals of about 100 m or less. Together with the sampling and

analytical variance ( $S^2_n + S^2_e$ ), the three components collectively account for over one-half of the total observed variance in more than half of the elements listed in tables 6-9. However, only for organic carbon, sodium, selenium, strontium, and zinc in one or more sampled units did analytical variance ( $S^2_e$ , table 5) form more than half of the three variances combined. Thus, the largest part of the total geochemical variability in these rocks represents a small-scaled interstratification of rock layers composed of differing proportions of the major rock-forming constituents calcite, dolomite, quartz, and "clay." For the most part, the three combined variances estimate the basic geochemical im-



TABLE 12.—*Geochemical summary of rocks of the Kaskaskia sequence in Missouri and adjacent States*

[GM, geometric mean, except as noted; GD, geometric deviation, except as noted; Ratio, number of samples in which element detected to total number of samples; ppm, parts per million; leaders (—) indicate no data available]

Element	Combined data for Limestone and dolomite			Limestone only			Dolomite only			Shale			Chert			Chattanooga Shale		Bushburg Sandstone and Sylvania Sandstone Member of Chattanooga Shale	
	GM	GD	Ratio	GM	GD	Ratio	GM	GD	Ratio	GM	GD	Ratio	GM	GD	Ratio	Observed range	Ratio	Observed range	Ratio
Ag, ppm-----	<0.5	--	0:40	<510.5	--	0:30	<0.5	--	0:10	<0.5	--	3:18	<0.5	--	0:20	<0.5	--	0:4	0:4
Al, percent--	<.53	--	9:40	.83	1.72	4:30	.46	2.68	5:10	4.4	1.64	18:18	<.53	--	1:20	5.3	--	8.5	4:4
As, ppm-----	.83	2.58	17:40	.57	3.04	11:30	1.1	2.74	6:10	6.4	2.22	18:18	<1	--	7:20	--	--	--	--
B, ppm-----	<20	--	2:40	<20	--	1:30	<20	--	1:10	64	1.73	18:18	39	1.80	18:20	50	--	100	4:4
Ba, ppm-----	6.4	6.79	37:40	4.0	5.72	27:30	24	3.73	10:10	220	2.15	18:18	23	1.52	20:20	300	--	500	4:4
Be, ppm-----	1	--	0:40	<1	--	0:30	<1	--	0:10	<sup>4</sup> 1.1	1.64	12:18	<1	--	0:20	1.5	--	2.0	4:4
C, carbonate, percent--	<sup>1</sup> 11	<sup>2</sup> 1.69	40:40	<sup>1</sup> 11	<sup>2</sup> 1.42	30:30	<sup>1</sup> 11	<sup>2</sup> 1.69	10:10	1.2	7.77	18:18	<sup>3</sup> .06	--	13:20	.01	--	.08	4:4
C, organic, percent--	.22	2.31	34:40	.23	2.41	25:30	.21	1.85	9:10	.27	3.89	16:18	.44	2.26	20:20	1.0	--	4.3	4:4
Ca, percent--	<sup>1</sup> 32	<sup>2</sup> 8.96	40:40	<sup>1</sup> 36	<sup>2</sup> 6.7	30:30	<sup>1</sup> 21	<sup>2</sup> 5.17	10:10	3.4	6.59	17:18	<sup>3</sup> .86	--	15:20	<.071-	.21	2:4	4:4
Cd, ppm-----	<1	--	1:40	<1	--	0:30	<1	--	1:10	<1	--	2:18	<1	--	0:20	<1	--	0:4	0:4
Ce, ppm-----	<150	--	0:40	<150	--	0:30	<150	--	0:10	<150	--	2:18	<150	--	0:20	<150	--	0:4	4:4
Co, ppm-----	<3	--	2:40	<3	--	1:30	<3	--	1:10	4.8	1.91	18:18	<3	--	0:20	7	--	15	4:4
Cr, ppm-----	9.4	3.27	38:40	7.7	3.22	28:30	17	2.64	10:10	<sup>4</sup> 130	2.28	18:18	2.8	2.62	20:20	70	--	100	4:4
Cu, ppm-----	.85	2.04	20:40	.62	2.56	11:30	1.9	2.18	9:10	.3	2.83	18:18	1.1	2.02	12:20	50	--	70	4:4
F, ppm-----	38	6.01	27:40	<sup>3</sup> 60	--	17:30	120	3.49	10:10	1400	3.23	18:18	<10	--	6:20	--	--	--	--
Fe, percent--	.15	3.71	30:40	.10	3.24	20:30	.60	1.95	10:10	1.8	1.58	18:18	.081	1.96	10:20	2.2	--	3.3	4:4
Ga, ppm-----	<5	--	2:40	<5	--	1:30	<5	--	1:10	16	1.81	18:18	<5	--	0:20	20	--	30	4:4
Hg, ppm-----	.030	2.37	38:40	.029	2.36	28:30	.036	1.95	10:10	.39	3.09	17:18	.017	2.28	18:20	.02	--	.42	4:4
K, percent--	.077	2.83	21:40	.051	3.41	12:30	.34	3.19	9:10	2.2	1.56	18:18	<.083	--	2:20	3.1	--	4.3	4:4
La, ppm-----	<30	--	11:40	24	1.20	8:30	24	1.19	3:10	30	--	14:18	<30	--	1:20	30	--	70	4:4
Li, ppm-----	.78	3.87	5:40	<5	--	2:30	<5	--	3:10	25	1.84	18:18	2.8	2.01	6:20	25	--	38	4:4
Mg, percent--	.56	5.98	40:40	.23	2.19	30:30	<sup>1</sup> 8.1	<sup>2</sup> 1.62	10:10	1.6	2.62	18:18	<sup>3</sup> .012	--	17:20	.80	--	1.1	4:4
Mn, ppm-----	160	2.05	40:40	150	2.11	30:30	220	1.38	10:10	140	2.05	18:18	49	4.38	20:20	50	--	150	4:4
Mo, ppm-----	<3	--	3:40	.34	3.85	2:30	<3	--	1:10	<3	--	6:18	<3	--	0:20	3	--	30	4:4
Na, percent--	.017	2.63	38:40	.015	2.38	28:30	.026	1.69	10:10	.088	2.16	18:18	.013	1.71	19:20	.15	--	.24	4:4
Nb, ppm-----	<10	--	0:40	<10	--	0:30	<10	--	0:10	<10	--	3:18	<10	--	0:20	<10	--	10	1:4
Nd, ppm-----	--	--	--	--	--	--	--	--	--	<70	--	3:14	<70-	--	0:1	<70	--	70	2:4
Ni, ppm-----	2.3	2.43	11:40	2.0	2.24	6:30	3.9	2.30	5:10	21	2.23	18:18	<5	--	1:20	30	--	70	4:4
P, ppm-----	92	6.35	17:40	200	3.90	16:30	<220	--	1:10	<sup>4</sup> 300	2.95	13:18	<220	--	8:20	<130	--	310	3:4
Pb, ppm-----	<10	--	5:40	<10	--	1:30	6.5	2.34	4:10	11	1.58	13:18	<10	--	2:20	10	--	20	4:4
Sc, ppm-----	<5	--	3:40	.22	5.24	2:30	<5	--	1:10	8.2	1.60	17:18	<5	--	0:20	10	--	15	4:4
Se, ppm-----	.19	2.28	32:40	.19	2.53	24:30	.20	2.38	8:10	<sup>4</sup> .64	3.47	18:18	.11	1.76	12:20	.6	--	1.4	4:4
Si, percent--	1.1	4.53	28:40	.70	5.59	19:30	3.5	4.22	9:10	23	1.40	18:18	<sup>1</sup> 44	<sup>3</sup> 3.07	20:20	27	--	30	4:4
Sr, ppm-----	270	3.62	40:40	390	3.17	30:30	88	1.45	10:10	150	1.87	18:18	8.1	2.55	16:20	70	--	100	4:4
Ti, ppm-----	<sup>3</sup> 70	--	34:40	<sup>3</sup> 18	--	24:30	190	5.18	10:10	<sup>4</sup> 2300	<sup>4</sup> 1.76	18:18	209	5.15	20:20	3000	--	7000	4:4
V, ppm-----	7.5	2.11	25:40	6.1	2.53	16:30	12	2.24	9:10	120	1.87	18:18	<7	--	0:20	200	--	300	4:4
Y, ppm-----	17	1.97	34:40	17	1.84	26:30	6	1.84	8:10	25	1.87	18:18	<10	--	1:20	20	--	50	4:4
Yb, ppm-----	.85	1.69	18:40	.78	1.73	13:30	.86	2.23	5:10	<sup>4</sup> 2.3	1.93	18:18	<1	--	0:20	3	--	5	4:4
Zn, ppm-----	19	1.68	38:40	21	1.39	30:30	15	2.67	8:10	55	3.09	18:18	<10	--	5:20	87	--	120	4:4
Zr, ppm-----	6.7	4.79	18:40	5.2	3.69	11:30	20	4.45	7:10	95	2.00	18:18	<10	--	3:20	100	--	150	4:4

<sup>1</sup>Arithmetic mean<sup>2</sup>Standard deviation.<sup>3</sup>Median.<sup>4</sup>See table 16.

precision which would be encountered in representing a carbonate outcrop by one sample, if that sample were analyzed by the methods listed in table 4 or by methods of similar precision.

The element averages listed for carbonate rocks in tables 10-13 estimate the most probable concentration to be expected in a randomly selected carbonate sample from an outcrop in the study area. Because of the marked control on concentration of some elements by rock type (limestone versus dolomite), a summary for both types is given when appropriate. A summary of the combined rock types is also given for those elements whose variation is relatively independent of carbonate mineralogy. A number of elements—barium, cobalt, chromium, copper, iron, potassium, lithium, phosphorus, silicon, strontium, titanium, and zirconium—show levels of concentration of five times or

more in dolomite compared to limestone in the same unit. The presence of potassium, titanium, and zirconium in this list suggests that the dolomitic rocks tend to be more clay rich than the limestones.

The data in tables 10-13 show that, even in limestone or dolomite, element concentration may vary within rather wide limits depending upon what unit is being studied. Both the dolomite and the limestone of Pennsylvanian age tend to be more element rich than similar rocks in the underlying units. The Pennsylvanian dolomite is particularly rich in iron, manganese, and phosphorus; and the Pennsylvanian limestone is particularly rich in barium, chromium, copper, iron, manganese, and silicon. These differences reflect the fact that carbonate in the Pennsylvanian rocks is everywhere admixed with considerable noncarbonate detritus.

TABLE 13.—*Geochemical summary of rocks of Pennsylvanian age in Missouri and adjacent States*

[GM, geometric mean, except as noted; GD, geometric deviation, except as noted; Ratio, number of samples in which element detected to total number of samples; ppm, parts per million; leaders (—) indicate no data available]

Element or ash	Shale			Sandstone			Combined data for limestone and dolomite			Limestone only			Dolomite only		Coal		
	GM	GD	Ratio	GM	GD	Ratio	GM	GD	Ratio	GM	GD	Ratio	Observed range	Ratio	GM	GD	Ratio
Ag, ppm-----	<0.5	--	0:32	<0.5	--	0:30	<0.5	--	0:32	<0.5	--	0:28	--	0:4	<0.05	--	14:30
Al, percent---	8.5	1.24	32:32	3.1	2.46	30:30	.44	2.50	16:32	.36	2.58	12:28	0.53--	1.6	.75	1.85	30:30
As, ppm-----	9.0	2.11	32:32	4.0	2.31	27:30	2.5	2.95	27:32	2.2	3.01	23:28	2	8.3	4.2	2.87	30:30
Ash, percent---	--	--	--	--	--	--	--	--	--	--	--	--	--	--	10	1.84	30:30
B, ppm-----	72	1.34	32:32	38	1.78	26:30	<20	--	1:32	<20	--	0:28	<20	20	25	2.24	30:30
Ba, ppm-----	430	1.48	32:32	--	--	--	44	3.01	32:32	42	2.61	28:28	30	300	25	2.24	30:30
Northern area	--	--	--	240	1.48	14:14	--	--	--	--	--	--	--	--	--	--	--
Southern area	--	--	--	120	1.74	16:16	--	--	--	--	--	--	--	--	--	--	--
Be, ppm-----	1.7	1.44	31:32	1.0	1.46	14:30	<1	--	1:32	<1	--	1:28	--	0:4	1.6	1.40	30:30
C, carbonate, percent-----	.16	5.07	31:32	.010	--	22:30	.11	1.37	32:32	.11	1.03	28:28	6.6	10	--	--	--
C, organic, percent-----	.32	2.57	27:32	.34	1.97	30:30	.10	2.77	19:32	.10	3.18	17:28	<.1	.7	--	--	--
Ca, percent---	1.1	4.15	32:32	.22	5.09	24:30	.31	8.18	32:32	.34	3.77	28:28	11	16	<15	3.15	30:30
Cd, ppm-----	<1	--	0:32	<1	--	0:32	<1	--	2:32	<1	--	1:28	<1	1	<1	--	5:20
Ce, ppm-----	<150	--	9:32	<150	--	10:30	<150	--	0:32	<150	--	0:28	--	--	<15	--	1:30
Co, ppm-----	12	1.67	32:32	--	--	--	1.3	3.24	12:32	<3	--	8:28	3	7	3.4	3.04	30:30
Northern area	--	--	--	11	1.66	14:14	--	--	--	--	--	--	--	--	--	--	--
Southern area	--	--	--	4.4	2.59	13:16	--	--	--	--	--	--	--	--	--	--	--
Cr, ppm-----	95	1.26	32:32	33	2.35	30:30	--	--	--	--	--	--	--	--	9.1	1.81	30:30
Northern area	--	--	--	--	--	--	12	1.84	16:16	12	1.84	16:16	--	--	--	--	--
Southern area	--	--	--	--	--	--	20	1.77	16:16	19	1.90	12:12	20	30	--	--	--
Cu, ppm-----	23	2.61	32:32	8.1	2.57	30:30	3.5	2.14	32:32	3.3	1.79	28:28	2	15	22	2.21	30:30
F, ppm-----	700	1.66	32:32	--	--	--	100	3.46	29:32	83	3.85	25:28	240	290	72	1.63	30:30
Northern area	--	--	--	200	2.25	14:14	--	--	--	--	--	--	--	--	--	--	--
Southern area	--	--	--	56	4.39	13:16	--	--	--	--	--	--	--	--	--	--	--
Fe, percent---	3.8	1.50	32:32	--	--	--	.96	2.49	32:32	.82	1.97	28:28	2.2	3.7	1.9	2.65	30:30
Northern area	--	--	--	2.7	1.71	14:14	--	--	--	--	--	--	--	--	--	--	--
Southern area	--	--	--	1.4	1.86	16:16	--	--	--	--	--	--	--	--	--	--	--
Ga, ppm-----	30	1.45	32:32	11	1.94	27:30	2.2	2.34	8:32	1.5	2.80	5:28	<5	7	--	--	--
Ge, ppm-----	<10	--	0:32	<10	--	0:32	<10	--	0:32	<10	--	0:28	--	--	15	1.82	29:30
Hg, ppm-----	.045	2.60	30:32	.015	2.12	22:30	.030	2.96	30:32	.032	2.78	26:28	.01--	.04	.093	1.75	30:30
K, percent---	2.7	1.29	32:32	.49	3.47	29:30	.16	2.52	28:32	.14	2.42	24:28	.17--	.58	.15	2.78	30:30
La, ppm-----	49	1.37	32:32	34	1.65	24:30	24	1.20	5:32	14	1.93	5:28	--	--	<3	--	11:30
Li, ppm-----	79	1.48	32:32	17	2.38	29:30	2.6	2.93	11:32	<5	--	7:28	5	13	5.1	2.82	30:30
Mg, percent---	.95	1.45	32:32	.20	4.40	30:30	.67	4.11	32:32	.48	2.27	28:28	6.3	8.4	.036	1.96	30:30
Mn, ppm-----	170	1.97	32:32	260	4.54	30:30	830	2.37	32:32	680	1.86	28:28	2000	7000	22	2.31	30:30
Mo, ppm-----	<3	--	0:32	<3	--	4:30	<3	--	3:32	1.9	1.28	3:28	--	--	1.8	3.07	26:30
Na, percent---	.50	1.67	32:32	.33	7.05	30:30	.045	2.43	32:32	.041	2.24	28:28	.03--	.17	.013	1.81	30:30
Nb, ppm-----	7.7	1.25	11:32	9.0	1.22	18:30	<10	--	0:32	<10	--	0:28	--	--	<1	--	0:30
Nd, ppm-----	<70	--	11:32	<70	--	8:24	<70	--	0:4	<70	--	0:4	--	--	--	--	--
Ni, ppm-----	38	1.50	32:32	--	--	--	4.3	2.24	17:32	4.4	2.32	15:28	<5	7	20	2.99	30:30
Northern area	--	--	--	31	2.22	14:14	--	--	--	--	--	--	--	--	--	--	--
Southern area	--	--	--	11	2.69	13:16	--	--	--	--	--	--	--	--	--	--	--
P, ppm-----	610	1.89	32:32	570	2.11	28:30	--	--	--	--	--	--	--	--	<220	--	6:30
Northern area	--	--	--	--	--	--	180	3.68	8:16	380	3.68	8:16	--	--	--	--	--
Southern area	--	--	--	--	--	--	690	2.29	16:16	550	2.18	12:12	870	1700	--	--	--
Pb, ppm-----	17	1.92	30:32	15	1.81	27:30	4.2	3.13	9:32	3.5	3.57	7:28	<10	15	48	2.94	30:30
Sc, ppm-----	15	1.26	32:32	7.2	1.43	24:30	<5	--	4:32	.55	4.48	4:28	--	--	2.0	1.96	29:30
Se, ppm-----	.46	3.63	29:32	.12	3.15	17:30	<.31	2.69	29:32	.31	2.56	26:28	.3	.9	1.9	1.95	30:30
Si, percent---	27	1.15	32:32	.39	4.09	30:30	2.9	2.98	32:32	2.4	2.46	28:28	8.4	17	1.7	2.15	30:30
Sr, ppm-----	200	1.65	32:32	83	3.73	30:30	990	3.86	32:32	1400	2.13	28:28	70	150	22	1.51	30:30
Ti, ppm-----	4200	1.41	32:32	2400	2.84	30:30	180	3.16	32:32	160	2.73	28:28	300	700	320	2.44	30:30
V, ppm-----	140	1.36	32:32	39	1.45	30:30	15	2.29	29:32	13	2.05	25:28	30	50	13	1.97	30:30
Y, ppm-----	30	1.61	32:32	22	1.69	26:30	8.0	2.39	15:32	6.5	2.43	11:28	20	30	6.3	2.20	29:30
Northern area	--	--	--	3.3	1.48	14:14	--	--	--	--	--	--	--	--	--	--	--
Southern area	--	--	--	1.7	1.86	13:16	--	--	--	--	--	--	--	--	--	--	--
Zn, ppm-----	82	1.47	32:32	32	2.77	25:30	24	2.32	31:32	24	2.22	27:28	17	37	22	4.39	30:30
Zr, ppm-----	110	1.48	32:32	190	2.20	30:30	14	2.28	25:32	12	1.89	21:28	50	70	11	2.24	29:30

<sup>1</sup> Arithmetic mean.

<sup>2</sup> Standard deviation.

<sup>3</sup> Computed for raw.

In summary, the dominant control on geochemical variation in carbonate rocks of this study is the distribution of constituent calcite, dolomite, quartz, and "clay." The distribution of these constituents is highly variable at local scales and results in a very large geochemical heterogeneity within or among

closely spaced carbonate outcrops. This heterogeneity arises for the most part from local compositional interlayering in the rocks. Imprinted upon this local variability is a weak but discernible regional geochemical difference that reflects a tendency for carbonate of Pennsylvanian age to be richer in most trace

elements than the older carbonates. Variation at broad scales within the bedrock units is similarly weak and largely reflects variation in dolomite content. The upper Sauk is discernibly less dolomitic (slightly more argillic) than the lower Sauk; and scattered sections of Tippecanoe, Kaskaskia, and Pennsylvanian carbonate rocks are distinctly more dolomitic than others.

### SHALE

Shale is considered in this study to include all varieties of fine-grained detrital sedimentary rock containing large amounts of clay minerals, whether the rock is fissile or not. Shale underlies extensive parts of

western and northern Missouri and eastern Kansas as it forms a major part of the Pennsylvanian rocks and a minor part of the Kaskaskia rocks (fig. 3). Throughout most of this area it tends to be covered by glacial deposits; nevertheless, it is an environmentally important part of the landscape in west-central Missouri, eastern Kansas, and northeastern Oklahoma, where it forms a prominent parent material of soil. In addition, it is intimately associated with large deposits of stripable coal in Missouri, Kansas, and Oklahoma.

The normative mineral compositions of 62 samples of shale are compared in figure 10. The norms were computed as for the carbonate rocks, except that only MgO in excess of 2 percent was put into dolomite. The

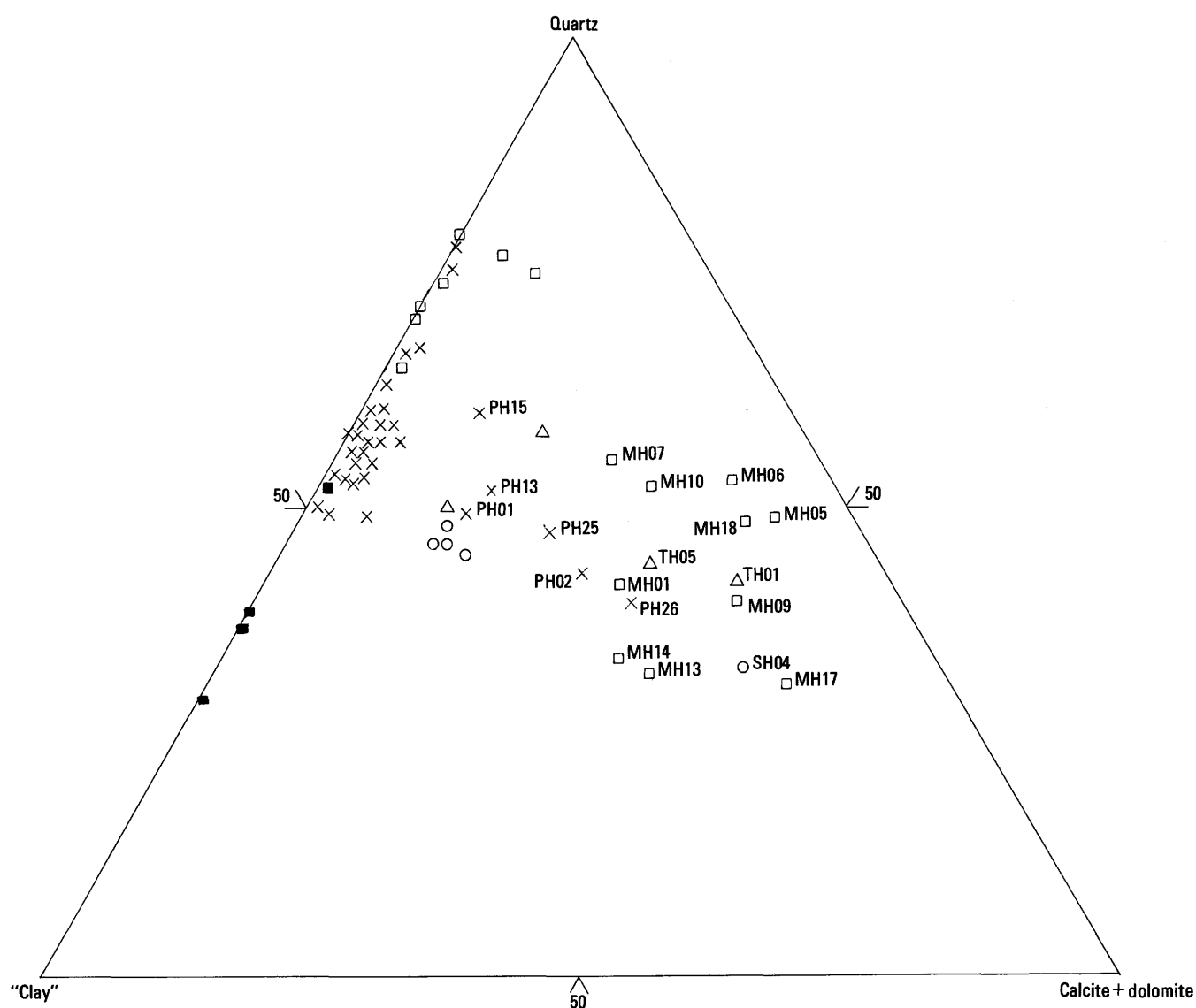


FIGURE 10.—Normative mineralogy of shale samples of the Sauk sequence (circle), the Tippecanoe sequence (triangle), the Chattanooga Formation (closed square), the Kaskaskia sequence (open square), and of Pennsylvanian age (X). Numbered samples are referred to in text.

pattern in figure 10 suggests the following: (1) shale in this study generally contains between 30 and 80 percent normative quartz, contains between 5 and 50 percent normative clay, and exhibits a quartz-clay ratio consistently greater than 1.0; (2) shale in the Pennsylvanian rocks is rarely calcareous (exceptions are PH01, PH02, PH13, PH15, PH25, and PH26); (3) shale in the Kaskaskia is distinctly calcareous, with 10 of 17 samples (MH01, MH05–MH07, MH09, MH10, MH13, MH14, MH17, and MH18) containing more than 25 percent normative calcite plus dolomite; all of the dolomitic shales of this sequence (MH01, MH06, MH07, MH09, and MH10) were collected in Missouri; and (4) shale in the Sauk and Tippecanoe is dolomitic (particularly SH04, TH01, and TH05).

Results of the analysis of variance for shale of the Kaskaskia sequence and of Pennsylvanian age are given in tables 14 and 15, and summary statistics are given in tables 12 and 13. The total geochemical variability ( $S^2_{\log X}$ ) in shale of the Kaskaskia sequence is notably larger than that in shale of Pennsylvanian age, except for lead. This parallels the situation found in the carbonate studies, in which units having the larger area of outcrop tended to be more geochemically uniform. In the carbonate study, this situation largely reflected a sample mix of nearly pure limestone and dolomite (in the units with the larger variability). Here the increase in variation reflects more a variable admixture of calcite and dolomite minerals in the samples of shale of the Kaskaskia sequence (fig. 10).

Statistically significant variation in the major rock-forming elements (aluminum, carbonate carbon, calcium, magnesium, and silicon), which reflects variation in the distributions of "clay," calcite, dolomite, and quartz, occurs largely within stratigraphic sections ( $S^2_{\theta} + S^2_{\epsilon}$ ) in shale of Pennsylvanian age, but occurs between sections ( $S^2_{\theta} + S^2_{\gamma}$ ) in shale of the Kaskaskia sequence. Between-area variation ( $S^2_{\theta}$ ) in shale of the Kaskaskia sequence is statistically significant for half of the elements in table 14 and reflects a tendency for shale units in the Kaskaskia, which occur as isolated lenses or formations, to be more or less geochemically distinct. In Missouri, these formations tend to be highly calcareous (low aluminum, high carbonate), whereas in Oklahoma and Arkansas, they tend to be more aluminous and less calcareous.

Area averages in shale of the Kaskaskia sequence were examined for stability by the criterion described previously.  $E_s$  was computed by:

$$E_s = \frac{S^2_{\gamma}}{2} + \frac{S^2_{\eta} + S^2_{\epsilon}}{4} \quad (15)$$

The pertinent parameters for this examination are listed below:

Element	$\nu$	$n_r$	$E_r$	$E_s$
Aluminum .....	0.93	5	0.0048	0.0091
Boron .....	.49	8	.0048	.0141
Barium .....	.67	6	.0111	.0167
Beryllium .....	1.32	4	.0050	.0050
Carbon, org. ....	.62	7	.0307	.0787
Chromium .....	3.90	3	.0087	.0087
Iron .....	1.83	4	.0035	.0040
Gallium .....	.66	6	.0067	.0151
Potassium .....	.49	8	.0031	.0061
Sodium .....	1.50	4	.0112	.0143
Nickel .....	.55	7	.0125	.0326
Phosphorus .....	1.57	4	.0476	.0476
Scandium .....	1.10	5	.0039	.0072
Selenium .....	6.78	3	.0125	.0109
Titanium .....	2.20	4	.0047	.0047
Vanadium .....	.87	5	.0079	.0144
Ytterbium .....	1.81	4	.0073	.0073

TABLE 14.—Components of logarithmic variance estimated for shale of the Kaskaskia sequence

[Asterisk (\*), value significantly greater than zero at the 0.05 probability level]

Element	Total $\log_{10}$ variance ( $S^2_{\log X}$ )	Variance					
		Between areas		Between sections		Between samples	
		Component ( $S^2_{\theta}$ )	Percent of total	Component ( $S^2_{\gamma}$ )	Percent of total	Component ( $S^2_{\eta} + S^2_{\epsilon}$ )	Percent of total
Al-----	0.0466	*0.0224	48	0.0123	27	0.0119	25
As-----	.1204	.0291	24	*.0762	63	.0151	13
B-----	.0569	*.0187	33	.0182	32	.0200	35
Ba-----	.1111	*.0445	40	0	<1	.0666	60
Be-----	.0460	*.0262	57	0	<1	.0198	43
C, carbonate	.7927	.4899	62	*.2273	29	.0755	9
C, organic--	.3485	*.1333	38	.0994	29	.1158	33
Ca-----	.6702	.2229	33	*.3313	49	.1160	17
Co-----	.0794	.0282	36	0	<1	.0512	64
Cr-----	.1278	*.1017	80	.0086	7	.0175	14
Cu-----	.2044	.1422	70	*.0387	19	.0235	11
F-----	.2595	0	<1	.0280	11	.2315	89
Fe-----	.0399	*.0258	65	.0019	5	.0122	31
Ga-----	.0669	*.0267	40	.0203	30	.0197	30
Hg-----	.2407	.0009	<1	*.1916	80	.0481	20
K-----	.0369	*.0121	33	.0123	33	.0124	34
La-----	.0452	.0067	15	.0204	45	.0180	40
Li-----	.0695	.0137	20	*.0323	46	.0235	34
Mg-----	.1745	.1026	59	*.0563	32	.0156	9
Mn-----	.0977	.0505	52	*.0276	28	.0196	20
Na-----	.1113	*.0667	60	.0124	11	.0322	29
Ni-----	.1358	*.0482	36	.0426	31	.0450	33
P-----	.4905	*.3000	61	0	<1	.1905	39
Pb-----	.0397	0	<1	*.0323	81	.0074	19
Sc-----	.0411	*.0215	52	.0090	22	.0107	26
Se-----	.2916	*.2541	87	.0059	2	.0316	11
Si-----	.0217	0	<1	*.0163	75	.0054	25
Sr-----	.0745	0	<1	*.0463	62	.0282	38
Ti-----	.0604	*.0415	69	0	<1	.0189	31
V-----	.0737	*.0342	46	.0180	24	.0215	29
Y-----	.0738	.0242	33	0	<1	.0496	67
Yb-----	.0815	*.0525	64	0	<1	.0290	36
Zn-----	.2401	.1530	64	*.0616	26	.0255	10
Zr-----	.0910	.0242	27	*.0444	49	.0224	25

TABLE 15.—Components of logarithmic variance estimated for shale of Pennsylvanian age

(Asterisk (\*), value significantly greater than zero at the 0.05 probability level)

Element	Total log <sub>10</sub> variance ( $S^2_{\log X}$ )	Variance									
		Between areas		Between sections		Between deciles		Between percentiles		Between samples	
		Component	Percent of	Component	Percent of	Component	Percent of	Component	Percent of	Component	Percent of
		( $S^2_{\beta}$ )	total	( $S^2_{\gamma}$ )	total	( $S^2_{\delta}$ )	total	( $S^2_{\kappa}$ )	total	( $S^2_{\eta} + S^2_{\epsilon}$ )	total
Al-----	0.0086	0.0	>1	0.0	<1	*0.0025	29	0.0017	20	0.0044	51
As-----	.1045	.0040	4	.0175	17	*.0363	35	0	<1	.0467	45
B-----	.0164	.0003	2	0	<1	0	<1	*.0088	53	.0074	45
Ba-----	.0293	.0008	3	0	<1	0	<1	*.0200	67	.0088	30
Be-----	.0250	0	<1	0	<1	*.0087	35	0	<1	.0163	65
C, carbonate	.6206	0	<1	0	<1	.2960	48	*.1732	28	.1513	24
C, organic--	.1679	0	<1	0	<1	0	<1	*.0825	49	.0854	51
Ca-----	.3821	0	<1	0	<1	.1964	51	*.1129	30	.0728	19
Co-----	.0499	.0003	1	0	<1	.0061	12	.0067	13	.0369	74
Cr-----	.0097	0	<1	0	<1	*.0048	49	.0012	12	.0037	38
Cu-----	.1733	.0266	15	0	<1	*.0349	20	.0351	20	.0766	44
F-----	.0490	.0085	17	0	<1	.0160	33	*.0157	32	.0087	18
Fe-----	.0306	.0022	7	0	<1	0	<1	.0093	30	.0192	63
Ga-----	.0258	0	<1	0	<1	.0044	17	.0061	24	.0154	60
Hg-----	.1727	0	<1	0	<1	.0466	27	*.0852	49	.0408	24
K-----	.0125	0	<1	0	<1	*.0041	33	.0028	23	.0056	45
La-----	.0183	0	<1	0	<1	0	<1	*.0126	69	.0057	31
Li-----	.0292	0	<1	0	<1	.0014	5	*.0167	57	.0111	38
Mg-----	.0259	.0006	2	0	<1	*.0057	22	.0075	29	.0121	47
Mn-----	.0865	.0325	38	*.0123	14	0	<1	.0133	15	.0284	33
Na-----	.0494	*.0210	43	0	<1	*.0203	41	.0049	10	.0032	6
Ni-----	.0312	0	<1	0	<1	0	<1	.0027	9	.0286	91
P-----	.0770	*.0275	36	.0131	17	0	<1	*.0202	26	.0163	21
Pb-----	.0806	0	<1	0	<1	*.0361	45	.0027	3	.0418	52
Sc-----	.0097	.0022	23	0	<1	0	<1	*.0046	47	.0029	30
Se-----	.3138	.0095	3	0	<1	*.1344	43	.0568	18	.1132	36
Si-----	.0037	0	<1	0	<1	.0002	7	*.0018	48	.0017	45
Sr-----	.0470	.0044	9	0	<1	.0053	11	.0147	31	.0025	48
Ti-----	.0225	0	<1	0	<1	0	<1	*.0154	68	.0071	32
V-----	.0178	0	<1	0	<1	0	<1	*.0102	57	.0076	43
Y-----	.0425	*.0112	26	.0015	4	0	<1	.0104	24	.0194	46
Yb-----	.0304	.0034	11	.0008	3	0	<1	*.0174	57	.0088	29
Zn-----	.0276	.0005	2	0	<1	0	<1	.0087	31	.0186	67
Zr-----	.0288	0	<1	.0004	1	.0045	16	*.0129	45	.0110	38

The area averages for beryllium, chromium, phosphorus, selenium, titanium, and ytterbium are sufficiently stable ( $E_s \leq E_r$ ) to be computed using the available data. These averages are given as medians in table 16. The tendency for shale in this sequence to be geochemically distinct by formation is apparent from these medians. Clearly, the differences in phosphorus and titanium are controlled almost entirely by exceptionally high phosphorus and exceptionally low titanium in shale of the Choteau Limestone. Just as clearly, differences in selenium are controlled by the

high concentrations in samples from Arkansas. Both the Fayetteville Shale (3.2, 9.0 ppm) and the Ruddell Shale Member (3.2, 4.8 ppm) of the Moorefield Formation are high in selenium here. Additional data are needed if the area averages for the remaining elements are to be computed.

Between-section variance ( $S^2_{\gamma}$ ) within the areas of the Kaskaskia also reflects at least in part the erratic distribution of geochemically distinct formations. For example, two organic-rich samples taken from the Fayetteville Shale at loc. No. 43 (fig. 7) contained 5 per-

TABLE 16.—*Geochemical medians for selected elements in areas of shale of the Kaskaskia sequence*  
[Data are in parts per million]

Area-----	1	2	3	4	5
Number of samples--	3	2	4	4	4
Localities (fig.7 )	30, 31	33	34, 35	38, 39	41, 43
Geologic formations	Warsaw and Hannibal	Choteau	Northview	Fayetteville(?)	Fayetteville and Ruddell Shale Member <sup>1</sup>
Element:					
Beryllium	1.5	<1	1	<1	2
Chromium	100	50	130	85	300
Phosphorus	220	5500	<220	410	370
Selenium	.3	.35	.45	.35	4.0
Titanium	3000	850	2500	2000	4000
Ytterbium	3	1	2.5	1.5	4

<sup>1</sup> Of Moorefield Formation.

cent or more organic carbon as well as some of the highest trace element concentrations measured in shale during this study. Sample MH20 contained 3 ppm silver, 5 ppm cadmium, 700 ppm chromium, 150 ppm lanthanum, 1.7 percent phosphorus, 500 ppm vanadium, and 150 ppm yttrium; and sample MH19 contained 3 ppm beryllium, 50 ppm gallium, and 250 ppm zinc. The relatively high phosphorus in MH20 suggests that this sample is probably high in apatite. Three elements in shale of Pennsylvanian age (sodium, phosphorus, and yttrium) exhibit statistically significant between-area variance ( $S^2_{\beta}$ ). Averages for these areas were examined for stability by the methods previously described.  $E_s$  was computed from equation 14. The pertinent parameters for this examination are as follows:

Element	$\nu$	$n_r$	$E_r$	$E_s$
Sodium .....	0.74	6	0.0047	0.0051
Phosphorus .....	.56	7	.0067	.0101
Yttrium .....	.36	10	.0031	.0033

Additional data are required if area averages for these elements are to be computed.

Stratigraphic variation ( $S^2_{\sigma} + S^2_{\kappa}$ ) is large in shale of Pennsylvanian age, with all but eight elements exhibiting statistically significant variation at these levels of the design. The larger scaled stratigraphic variance ( $S^2_{\sigma}$ ) in aluminum, arsenic, beryllium, chromium, copper, potassium, manganese, sodium, lead, and selenium reflects a tendency for shale samples taken low in the section (loc. Nos. 58, 60, 63,

64, and 65, fig. 8) to be slightly higher in these elements than samples taken higher in the section (loc. Nos. 59, 61, 62, 53, and 66). In fact, samples PH01 and PH04 (both from loc. No. 58) contained 200 ppm copper and 12 ppm selenium, respectively, the highest measured values in shale of the study, and well above the average concentrations in these rocks of 23 ppm copper and 0.46 ppm selenium (table 13). The presence of sodium in this suite of elements suggests that this variation could be reflecting, in part, a variation in feldspar content of the shales.

Variation between percentiles ( $S^2_{\kappa}$ ) is the dominant scale of geochemical variability in shales of Pennsylvanian age and reflects compositional interlayering within stratigraphic intervals of about 100 m or less. Together with sampling and analytical variance ( $S^2_{\eta} + S^2_{\epsilon}$ ), the three components collectively account for over half of the total observed variance in 27 of 34 entries listed in table 15, although for eight elements the analytical variance ( $S^2_{\epsilon}$ , table 5), forms more than half of the three components combined. (The eight elements are beryllium, chromium, fluorine, sodium, phosphorus, scandium, ytterbium, and zinc.) Still, like the carbonate rocks, the largest part of the total variation in Pennsylvanian shale is quite local and reflects differences among closely spaced beds. For the most part, the three combined variances estimate the basic geochemical imprecision which would be encountered in representing an outcrop of Pennsylvanian shale by a single sample, if that sample were analyzed by the methods listed in table 4.

The component of stratigraphic variability in shale of the Kaskaskia sequence is contained in the between-sample variance ( $S^2_{\eta}$ ), because each stratigraphic section is represented by two samples collected from throughout the section (table 1). In contrast to the carbonates and the Pennsylvanian shales, the combined sampling-stratigraphic and analytical variance ( $S^2_{\eta} + S^2_{\epsilon}$ ) in this unit is not the most prominent part of the total variance. Nevertheless, for many elements, the absolute value of these combined components is comparable to the combined geochemical imprecision ( $S^2_{\kappa} + S^2_{\eta} + S^2_{\epsilon}$ ) in the Pennsylvanian shale, so that the imprecision encountered in representing shale outcrops by one sample each is roughly equal for the two units. Nine elements in shale of the Kaskaskia sequence exhibit an analytical component ( $S^2_{\epsilon}$ , table 5) which forms more than half of this imprecision: boron, beryllium, fluorine, mercury, sodium, lead, scandium, selenium, and zirconium.

The element averages for shale (tables 12, 13, and 16) are estimates of the most probable concentration to be expected in a randomly collected shale sample from an

outcrop in the study area. Shales of the Kaskaskia contain at least twice the calcium and carbonate carbon of the shale of Pennsylvanian age, reflecting the relatively calcareous nature of the Kaskaskia. These shales also contain less than half of the aluminum found in shale of Pennsylvanian age, indicating considerably less clay material in the Kaskaskia. Shale of Pennsylvanian age is consistently higher in all other elements compared, except for chromium, fluorine, magnesium, and selenium.

In summary, geochemical variability is greater in shales of the Kaskaskia sequence than in shales of Pennsylvanian age and reflects a highly variable admixture of carbonate material. This variability manifests itself partly as differences among the numerous shale formations which tend to crop out in different areas, and partly as differences between closely spaced organic-rich and organic-poor beds. Although shale of Pennsylvanian age tends to be more geochemically uniform overall than shale in the Kaskaskia, it is distinctly richer in trace elements because it is a more clay rich unit.

### SANDSTONE AND CHERT

Sandstone is abundant only in the Pennsylvanian outcrops of northeastern Oklahoma and in a few local areas in southeastern Missouri where sandstone in the Roubidoux Formation is well developed (fig. 3). The general paucity of sandstone over large parts of the study area makes it of less environmental interest than carbonate or shale, although water supplies are locally drawn from sandstones of Pennsylvanian age and strip mining of coal in Missouri has brought sandstone to the surface where it may form a conspicuous part of the newly formed land surface. Chert is prominent in outcrop as both nodules and interlayers in strata of Mississippian age; but, being chemically inert, it is resistant to weathering and has little effect on the local geochemical environment.

The normative mineral compositions of 86 samples of sandstone and chert are compared in figure 11; the normative minerals were computed as for the shales. Sandstones of Pennsylvanian age are mostly mixtures of quartz and clay, except for four moderately

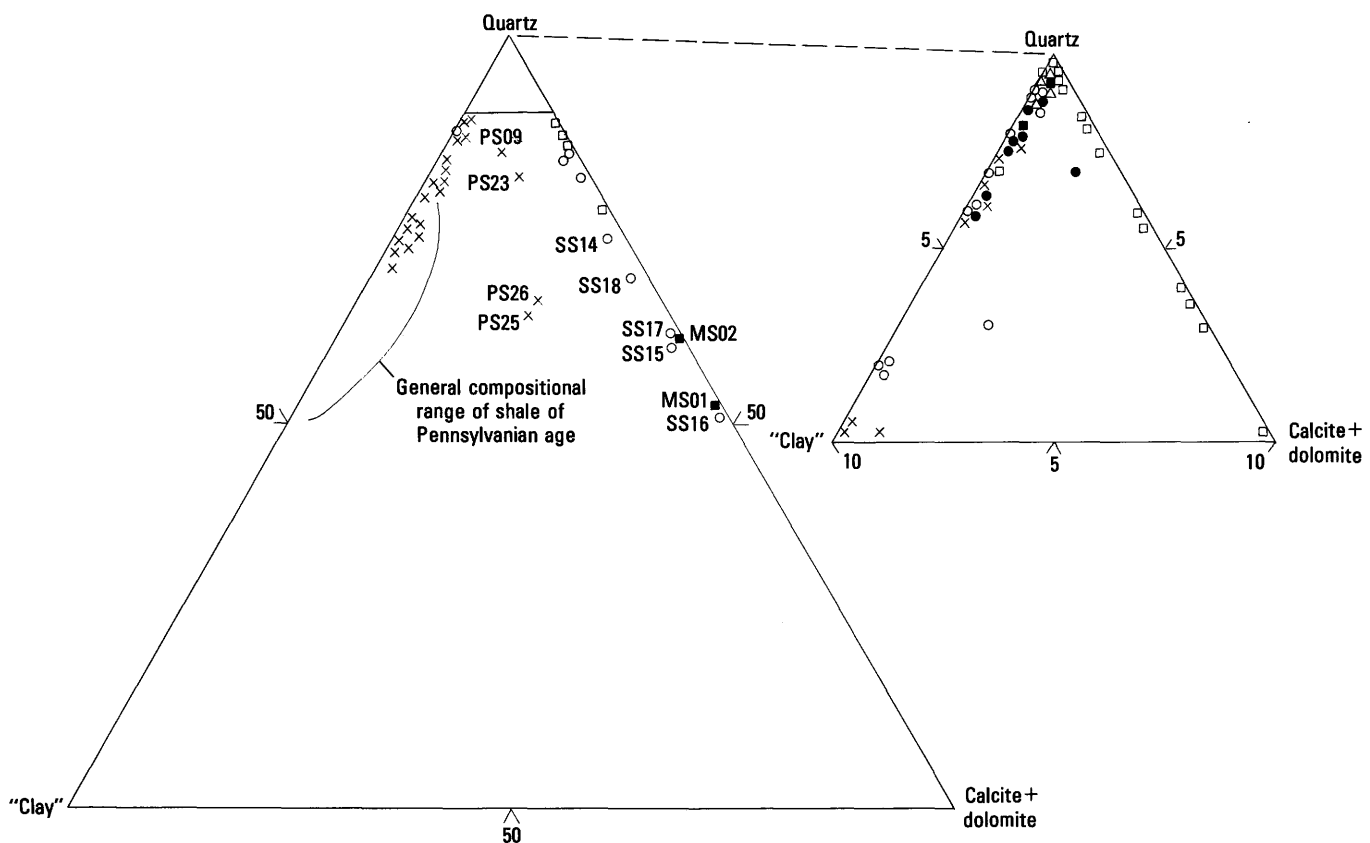


FIGURE 11.—Normative mineralogy of sandstone of the Sauk sequence exclusive of the Roubidoux Formation (circle), from the Roubidoux Formation (dot), the Tippecanoe sequence (triangle), and the Kaskaskia sequence (solid square), from Pennsylvanian rocks (X), and from chert of the Kaskaskia sequence (open square). Numbered samples are referred to in text.

calcareous sandstones (PS09, PS23, PS25, and PS26). Mineralogically, most of the sandstones can be viewed as quartz-rich shales, and Pennsylvanian sandstone and shale together tend to form a normative quartz-clay compositional continuum from near zero to about 50 percent clay (fig. 11). In contrast, lower Paleozoic sandstones tend to form a quartz-carbonate continuum. The most calcareous of these lower Paleozoic sandstones are five samples from the Sauk sequence (SS14-SS18), including two of the Roubidoux Formation (SS17, SS18), and two samples of the Mississippian Bushberg Sandstone (MS01, MS02). Chert of the Kaskaskia sequence is normatively similar to the lower Paleozoic sandstones because it is pervasively mixed with appreciable calcite.

Results of the analysis of variance for these units are given in tables 17-19, and summary statistics are given in tables 10, 12, and 13. Sandstones of the Roubidoux are much more variable in magnesium (mostly in dolomite) and silicon (mostly in quartz) than are the cherts in the Kaskaskia or the sandstones of Pennsylvanian age and reflect the spotty occurrence of admixed dolomite in the Roubidoux samples from loc. Nos. 20 and 21 (fig. 4). The chert samples are more variable in carbonate carbon and calcium (mostly in calcite) than are the sandstones of Pennsylvanian age, but overall (in contrast to the carbonates and shales), the total observed variance ( $S^2_{\log x}$ ) in the trace elements is not notably larger in any one unit.

Between-area variance ( $S^2_{\beta}$ ) is large in sandstone of Pennsylvanian age, compared with sandstone in the Roubidoux Formation and chert in the Kaskaskia sequence. Eleven elements in Pennsylvanian sandstone, nine of them trace elements and two elements in sandstones of the Roubidoux, exhibit statistically signifi-

TABLE 17.—Components of variance estimated for sandstone of the Roubidoux Formation

[Variance calculated on data transformed to logarithms, except as noted. Asterisk (\*), value significantly greater than zero at the 0.05 probability level]

Element	Variance					
	Total log variance ( $S^2_{\log x}$ )	Between areas		Between sections		Between samples
		Component ( $S^2_{\beta}$ )	Percent of total	Component ( $S^2_{\gamma}$ )	Percent of total	Component ( $S^2_{\eta} + S^2_{\epsilon}$ )
Ba-----	0.0803	0.0	<1	0.0095	12	0.0708
C, organic	.2462	0	<1	.0980	40	.1482
Cr-----	.1540	0	<1	*.1168	76	.0372
Cu-----	.1087	0	<1	.0283	26	.0804
Mg-----	1.2534	.4084	33	.3852	31	.4598
Mn-----	.2847	*.1187	42	.0336	12	.1323
Na-----	.1624	*.0500	31	0	<1	.1124
Si-----	139.0892	42.0284	30	72.8832	52	24.1776
Sr-----	.1210	.0212	18	0	<1	.0998
Ti-----	.5629	0	<1	.3204	57	.2425
Zr-----	.0450	.0008	2	0	<1	.0442

<sup>1</sup>Variance calculated on nontransformed data.

TABLE 18.—Components of variance estimated for chert of the Kaskaskia sequence

[Variance calculated on data transformed to logarithms, except as noted. Asterisk (\*), value significantly greater than zero at the 0.05 probability level]

Element	Variance					
	Total log variance ( $S^2_{\log x}$ )	Between areas		Between sections		Between samples
		Component ( $S^2_{\beta}$ )	Percent of total	Component ( $S^2_{\gamma}$ )	Percent of total	Component ( $S^2_{\eta} + S^2_{\epsilon}$ )
B-----	0.0650	0.0	<1	0.0287	44	0.0363
Ba-----	.0330	.0030	9	.0069	21	.0232
C, carbonate	1.1036	0	<1	*.6276	57	.4760
C, organic--	.1250	0	<1	.0608	49	.0642
Ca-----	.8685	0	<1	*.6032	69	.2653
Cr-----	.1747	0	<1	.0915	52	.0832
Hg-----	.1286	0	<1	*.0827	64	.0459
Mg-----	.7287	0	<1	.3876	53	.3411
Mn-----	.4115	0	<1	.1514	37	.2601
Na-----	.0541	.0103	19	0	<1	.0438
Si-----	20.1129	0	<1	9.7411	48	10.3718
Sr-----	.1653	0	<1	.0719	43	.0934
Ti-----	.5077	0	<1	.2674	53	.2403

<sup>1</sup>Variance calculated on nontransformed data.

cant variation at this level. Averages for the areas were examined for stability by the methods previously described.  $E_s$  for Pennsylvanian sandstone was computed from equation 14, and  $E_s$  for the Roubidoux was computed from equation 15. The pertinent parameters for this examination are as follows:

Element	$v$	$n_r$	$E_r$	$E_s$
Roubidoux Formation				
Manganese .....	0.72	6	0.0277	0.0499
Sodium .....	.44	9	.0125	.0281
Pennsylvanian Sandstones				
Boron .....	.15	20	.0028	.0071
Barium .....	.71	6	.0099	.0089
Cobalt .....	.63	7	.0078	.0053
Fluorine .....	.49	8	.0261	.0258
Iron .....	.51	8	.0089	.0085
Potassium .....	.79	6	.0203	.0212
Lithium .....	.45	9	.0111	.0148
Nickel .....	.46	8	.0152	.0133
Strontium .....	.59	7	.0293	.0356
Titanium .....	.31	11	.0143	.0182
Ytterbium .....	.58	7	.0067	.0052

Area averages for barium, cobalt, fluorine, iron, nickel, and ytterbium in Pennsylvanian sandstone are sufficiently stable ( $E_s \leq E_r$ ) when computed from the available data to be listed separately in table 13. Additional data are required if the area averages for the remaining elements are to be computed. This variation reflects compositional differences in sandstone from the northern (Kansas and Missouri) and southern areas of outcrop (fig. 8). The variation in potassium suggests that sandstone in the northern area is higher in clay material than sandstone in the southern area.



TABLE 19.—Components of variance estimated for sandstone of Pennsylvanian age

[Variance calculated on data transformed to logarithms, except as noted. Asterisk (\*), value significantly greater than zero at the 0.05 probability level]

Element	Total log <sub>10</sub> variance ( $S^2_{\log X}$ )	Variance									
		Between areas		Between sections		Between deciles		Between percentiles		Between samples	
		Component	Percent of	Component	Percent of	Component	Percent of	Component	Percent of	Component	Percent of
		( $S^2_B$ )	total	( $S^2_Y$ )	total	( $S^2_\theta$ )	total	( $S^2_\kappa$ )	total	( $S^2_\eta + S^2_\epsilon$ )	total
Al-----	0.1531	0.0390	26	0.0	<1	0.0577	38	*0.04371	29	0.0126	8
As-----	.1320	0	<1	.0278	21	.0042	3	.0058	4	.0942	71
B-----	.0630	*.0080	13	.0060	9	0	<1	.0159	25	.0332	53
Ba-----	.1025	*.0424	41	0	<1	.0189	18	.0272	27	.0131	14
C, carbonate	.6493	.0042	1	0	<1	0	<1	*.4724	73	.1728	27
C, organic--	.0870	0	<1	0	<1	.0168	19	0	<1	.0702	81
Ca-----	.0500	.0172	3	0	<1	0	<1	*.3367	67	.1457	29
Co-----	.0890	*.0343	39	0	<1	0	<1	*.0296	33	.0249	28
Cr-----	.1380	.0222	16	0	<1	0	<1	*.0994	72	.0164	12
Cu-----	.1676	.0273	16	.0340	20	0	<1	*.0787	47	.0275	16
F-----	.3107	*.1022	33	0	<1	0	<1	*.1209	39	.0876	28
Fe-----	.1077	*.0365	34	0	<1	.0054	5	*.0493	46	.0165	15
Ga-----	.0834	.0117	14	0	<1	.0282	34	*.0312	37	.0123	15
Hg-----	.1071	0	<1	.0183	17	0	<1	.0360	34	.0527	49
K-----	.2186	*.0968	44	0	<1	.0512	23	*.0641	29	.0064	3
La-----	.0470	.0123	26	0	<1	*.0242	51	0	<1	.0105	22
Li-----	.1451	*.0452	31	0	<1	.0316	22	*.0416	29	.0267	18
Mg-----	.4136	.1237	30	0	<1	*.1663	40	*.0687	16	.0587	14
Mn-----	.4313	0	<1	0	<1	.0445	10	*.2813	65	.1055	25
Na-----	.7190	.1683	23	0	<1	*.4102	56	.0210	3	.1286	18
Nb-----	.0072	.0012	17	0	<1	*.0039	54	0	<1	.0021	29
Ni-----	.1771	*.0555	31	0	<1	.0056	3	*.0743	42	.0418	24
P-----	.1049	.0130	12	0	<1	0	<1	.0241	23	.0678	65
Pb-----	.0658	0	<1	*.0176	27	0	<1	.0012	2	.0470	71
Sc-----	.0244	0	<1	.0005	2	0	<1	.0075	31	.0164	67
Si <sup>1</sup> -----	35.8132	6.4903	18	0	<1	12.0215	34	*9.0786	25	8.2227	23
Sr-----	.3266	*.1216	37	0	<1	.0967	30	*.0740	23	.0343	11
Ti-----	.2059	*.0483	23	0	<1	.0238	12	.0616	30	.0722	35
V-----	.1405	.0182	13	0	<1	.0445	32	*.0613	44	.0166	12
Y-----	.0522	.0109	21	0	<1	0	<1	*.0330	63	.0084	16
Yb-----	.0739	*.0272	37	.0005	1	0	<1	*.0324	44	.0137	19
Zn-----	.1958	0	<1	0	<1	*.0896	46	.0258	13	.0804	41
Zr-----	.1174	.0218	19	.0014	1	0	<1	*.0725	62	.0217	18

<sup>1</sup>Variance calculated on nontransformed data.

Between-section variation ( $S^2_Y$ ) in the siliceous rocks is relatively small. Statistically significant variation at this scale is exhibited only by chromium in sandstones of the Roubidoux; lead in the Pennsylvanian sandstones; and carbonate carbon, calcium, and mercury in the Kaskaskia chert. The variation in carbonate carbon and calcium in the Kaskaskia reflects the variation in admixed calcite in the chert. Mercury tends to be high in samples with low calcite. Lead was unusually high in two samples of Pennsylvanian sandstone collected from the southernmost traverse (fig. 8). Sample PS27 (loc. No. 74) contained 150 ppm lead and PS31 (loc. No.

66) contained 50 ppm, in contrast to an average concentration of 11 ppm in these rocks (table 13).

Large-scale stratigraphic variation ( $S^2_\theta$ ) in sandstones of Pennsylvanian age is moderate. Statistically significant variation is exhibited by lanthanum, magnesium, sodium, niobium, and zinc. The variation in sodium probably reflects mostly variation in feldspar, and the variation in magnesium might reflect variation in the type of clay material. Geochemical variation between percentiles ( $S^2_\kappa$ ) is marked in sandstone of Pennsylvanian age and reflects, to a large degree, the distribution of calcareous sandstone in-

terlayered through stratigraphic intervals of about 100 m or less. Calcium and carbonate carbon each exhibit over half of their total variance at this level, and the statistically significant variation in the remaining 18 entries of the table probably also reflects this variation in admixed calcite.

Variation at the lowest levels ( $S^2_{\text{r}} + S^2_{\text{e}} + S^2_{\text{c}}$ ) is large in all three units, accounting for over half of the total observed variation in more than half of the entries listed in tables 17–19. Only for boron, organic carbon, manganese, niobium, and sodium in one or more of the sampled units did analytical variance ( $S^2_{\text{a}}$ , table 5) form more than half of the total variation at these three levels. Thus, like the variability of the carbonate rocks and the Pennsylvanian shale, the largest part of the total geochemical variation in the sandstone and chert represents a small-scaled interstratification of compositionally differing beds. In the Pennsylvanian sandstones this difference appears to be due almost solely to variable amounts of contained calcite. As in the other stratified units of this study, the three combined variances estimate the basic geochemical imprecision which would be encountered in representing an outcrop of sandstone or chert by one sample, if that sample were analyzed by the methods listed in table 4.

The averages listed for sandstone in tables 10 and 13, and for chert in table 12, are estimates of the most probable concentration to be expected in a randomly collected sample from an outcrop in the study area. Sandstone in the Roubidoux Formation and chert in the Kaskaskia sequence both are highly siliceous and poor in trace elements. Sandstones of Pennsylvanian age are relatively rich in trace elements due to their argillic content, and those in the northern part of the outcrop area tend to be more argillic than those in the southern part. Practically every element listed for sandstone or chert is higher in sandstones of Pennsylvanian rocks than in the two older units. Most show average concentrations 5–10 times those in the Kaskaskia chert or the Roubidoux sandstones. As with the carbonates and shales, variability between closely spaced beds of sandstone is large and reflects the presence or absence of calcareous interbeds.

#### GRANITE AND RHYOLITE

The igneous rocks are of the least environmental significance of all the units studied owing to their restricted area of occurrence, their general resistance to weathering, and their limited supply of potable ground water. Locally, they contain a few large deposits of economic minerals including iron ore (Hayes and Guild, 1967).

All of the samples collected in this part of the study are granitic, and their gross compositional variation is largely controlled by feldspar variation. The 60 samples are compared in figure 12 on the basis of their normative feldspar composition. All calcium was put into anorthite, all sodium into albite, and all potassium into orthoclase. The rhyolite (extrusive) samples are much more variable in normative feldspar than are the granite (intrusive) samples, and include the most albite-rich (PC06) as well as the most orthoclase-rich (PC18) samples.

Normative anorthite is highest in samples from loc. Nos. 2 (PC03), 3 (PC06), 14 (PC28), 22 (PC43), and 23 (PC46), which are aligned in a northwest direction across the central part of the Precambrian outcrop area (fig. 3). Nine samples, all of them rhyolite, are distinctly high in normative orthoclase—PC09 and PC10 (loc. No. 5), PC16 (loc. No. 8), PC17 through PC20 (loc. Nos. 9 and 10), and PC25 and PC26 (loc. No. 13). Four of these five localities are aligned in a westerly direction across the outcrop (fig. 3). This alignment in both anorthite and orthoclase may reflect structural features of some sort. From imagery studies, Lowell, Osburn, and Roth (1977) noted the existence of both a pronounced N.45 W./N.45 E. structural pattern and a subordinate north-south/east-west lineament set in southeast Missouri.

Results of the analysis of variance for the Precambrian rocks are given in table 20, and summary statistics are given in table 21. Only beryllium and zirconium show statistically significant differences between the two rock types ( $S^2_{\text{r}}$ ). This difference in beryllium reflects the unusually low concentrations measured in the high-potassium rhyolites (table 21). The between-locality variance ( $S^2_{\text{a}}$ ) accounts for the largest part of the geochemical variation in these rocks; 23 of 28 elements exhibit statistically significant variation at this level of the sampling design, and 14 of the 28 exhibit 75 percent or more of the total observed variation at this level. Included in these 23 elements are most of the major rock-forming elements: aluminum, calcium, iron, potassium, magnesium, sodium, and titanium. Thus, variation at this scale reflects mostly simple variation in mineral composition. Some portion of this variance is apparently regionally controlled as Sides (1977) noted the presence of linear trends in these rocks for the oxides of silicon, aluminum, iron, potassium, calcium, and titanium. He speculated that these trends may reflect tilting of the igneous mass to the southwest, with subsequent deeper erosion to the northeast.

In contrast to the sedimentary rocks, the sampling and analytical variance ( $S^2_{\text{r}} + S^2_{\text{a}}$ ) tends to be relatively small in the igneous rocks. Only fluorine, mercury,

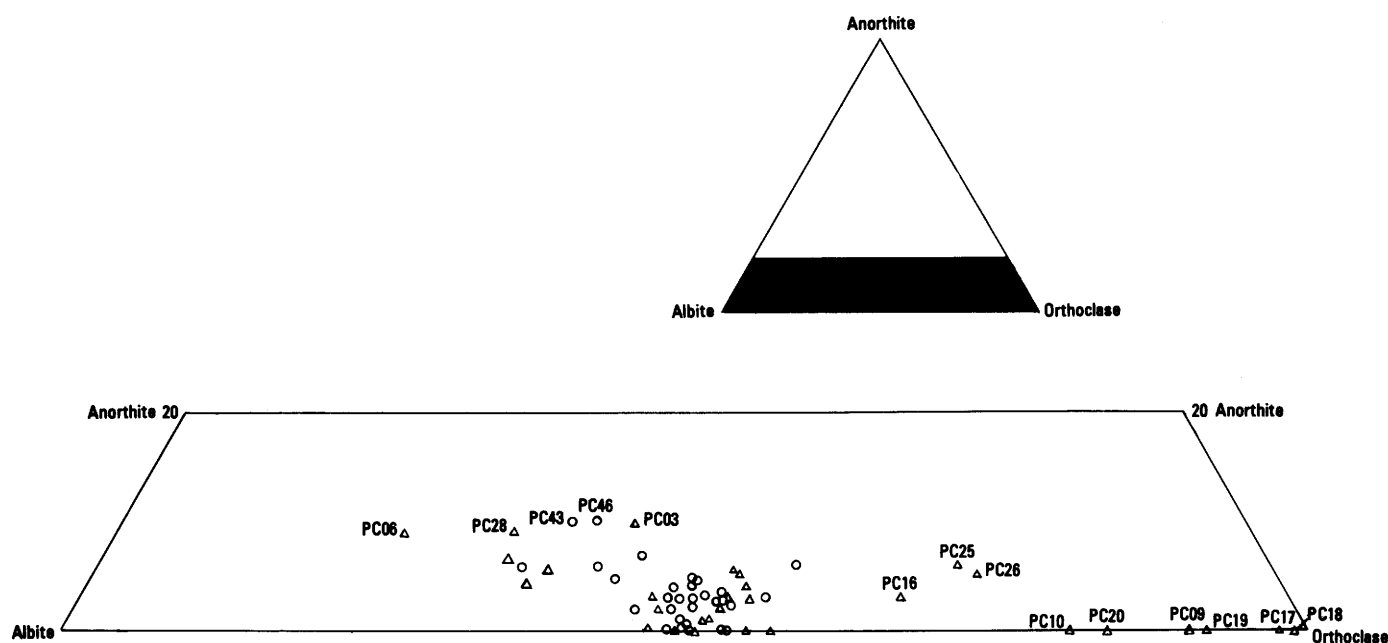


FIGURE 12.—Normative anorthite, albite, and orthoclase in samples of granite (circle) and rhyolite (triangle). Numbered samples are referred to in text.

TABLE 20.—Components of variance estimated for igneous rocks of Precambrian age

[Variance calculated on data transformed to logarithms, except as noted. Asterisk (\*), value significantly greater than zero at the 0.05 probability level]

Element	Total log variance ( $S^2_{\log x}$ )	Variance					
		Between granite and rhyolite		Between localities		Between samples	
		Component ( $S^2_y$ )	Percent of total	Component ( $S^2_\theta$ )	Percent of total	Component ( $S^2_n + S^2_e$ )	Percent of total
Al-----	0.0013	0.0	<1	*0.0010	78	0.0003	22
As-----	.2401	.0092	4	*.2193	91	.0115	5
Ba-----	.1317	0	<1	*.1079	82	.0239	18
Be-----	.0418	*.0084	20	*.0242	58	.0093	22
Ca-----	.2313	.0268	12	*.1801	78	.0243	10
Cu-----	.1082	.0038	4	*.0863	80	.0181	16
F-----	.2642	0	<1	.0134	5	.2508	95
Fe-----	.0272	0	<1	*.0261	96	.0011	4
Ga-----	.0042	<.0001	<1	*.0024	57	.0018	43
Hg-----	.0615	0	<1	.0181	29	.0434	71
K-----	.0106	.0008	7	*.0088	83	.0011	10
La-----	.0334	0	<1	*.0169	51	.0165	49
Mg-----	.2113	.0055	3	*.1870	88	.0188	9
Mn-----	.1369	0	<1	*.1033	75	.0336	25
Na-----	.1202	.0149	12	*.1027	85	.0026	2
Nb-----	.0140	.0004	3	0	<1	.0135	97
Nd-----	.0149	0	<1	*.0049	33	.0100	67
P-----	.1993	0	<1	*.1410	71	.0583	29
Pb-----	.0321	.0007	2	*.0137	43	.0177	55
Sc-----	.1197	0	<1	*.1047	87	.0150	13
Se-----	.0532	0	<1	.0033	6	.0499	94
Si <sup>1</sup> -----	3.7226	0	<1	*2.6402	71	1.0824	29
Sr-----	.1144	0	<1	*.1092	95	.0052	4
Ti-----	.0499	0	<1	*.0415	83	.0084	17
Y-----	.0194	0	<1	*.0087	45	.0107	55
Yb-----	.0117	.0006	5	*.0040	34	.0071	61
Zn-----	.1104	0	<1	*.0995	90	.0109	10
Zr-----	.0608	*.0118	19	.0061	10	.0428	70

<sup>1</sup>Variance calculated on nontransformed data.

niobium, neodymium, lead, selenium, yttrium, ytterbium, and zinc exhibit more than half their total observed variance at these two levels combined. For 12 of the 28 entries in table 20, the analytical variance ( $S^2_e$ , table 5) accounts for more than half of this sum. Thus, the geochemical imprecision which would be encountered in representing a granite or rhyolite outcrop by one sample (if that sample were analyzed by the methods listed in table 4) would be considerably less for most elements in these rocks than in the sedimentary rocks.

Overall, the igneous rocks are more similar in their trace element content to the shale and sandstone in the study area than they are to the limestone or dolomite (table 21 versus tables 10–13), although for copper, lithium, and vanadium, the reverse appears to be true. Sodium is consistently higher in the igneous rocks, regardless of which sedimentary lithology is used, and chromium is consistently lower.

## ECONOMIC MATERIALS

The economic geology of Missouri is briefly summarized in Stout and Hoffman (1973). Major products include limestone, dolomite, shale, granite, coal, iron, lead-zinc-copper sulfide ore, and oil and gas. Although coal and lead-zinc-copper ore constitute only a small fraction of the total mass of rocks studied, they are both materials of great environmental importance.

TABLE 21.—*Geochemical summary of igneous rocks of Precambrian age in Missouri*

[GM, geometric mean, except as noted; GD, geometric deviation, except as noted; Ratio, number of samples in which element detected to total number of samples; ppm, parts per million; leaders (---) indicate no data available]

Element	Combined data, except as indicated, for granite and rhyolite of typical composition			Potassium-rich rhyolite only		
	GM	GD	Ratio	GM	GD	Ratio
Al, percent	6.7	1.08	51:51	6.4	1.11	9:9
As, ppm----	2.9	2.20	48:51	14	5.82	9:9
B, ppm----	14	1.22	7:51	17	1.37	4:9
Ba, ppm----	560	2.37	51:51	830	1.51	9:9
Be, ppm						
Granite--	2.0	1.48	29:30	--	--	--
Rhyolite--	1.8	1.35	21:21	.80	1.73	4:9
Ca, percent	.35	2.59	50:51	<.071	--	3:9
Ce, ppm----	140	1.15	38:51	130	1.20	5:9
Co, ppm----	<3	--	13:51	<3	--	0:9
Cr, ppm----	.64	3.44	22:51	.67	4.21	4:9
Cu, ppm----	1.9	2.22	43:51	1.1	3.39	5:9
F, ppm----	380	3.54	48:51	290	2.99	9:9
Fe, percent	1.7	1.49	51:51	1.8	1.15	9:9
Ga, ppm----	29	1.10	51:51	24	1.31	9:9
Hg, ppm----	.015	1.84	43:51	.012	2.15	6:9
K, percent--	4.2	1.16	51:51	7.0	1.08	9:9
La, ppm----	60	1.45	50:51	42	1.66	8:9
Li, ppm----	3.1	3.48	26:51	1.5	4.94	3:9
Mg, percent	.080	2.92	51:51	.049	2.19	9:9
Mn, ppm----	310	2.39	51:51	280	1.88	9:9
Mo, ppm----	<3	--	17:51	<3	--	0:9
Na, percent--	2.8	1.15	51:51	.51	3.31	9:9
Nb, ppm----	11	1.32	45:51	11	1.22	9:9
Nd, ppm----	76	1.32	46:51	72	1.45	7:9
Ni, ppm----	<5	--	2:51	<5	--	0:9
P, ppm----	280	3.06	35:51	1220	--	6:9
Pb, ppm----	19	1.48	51:51	18	1.67	9:9
Sc, ppm----	5.7	2.55	36:51	4.4	2.05	6:9
Se, ppm----	.10	2.02	30:51	.051	3.14	3:9
Si, percent--	.35	1.31	51:51	.35	1.34	9:9
Sn, ppm----	<10	--	1:51	<10	--	0:9
Sr, ppm----	74	2.20	51:51	61	1.94	9:9
Ti, ppm----	1,300	1.70	51:51	1,100	1.37	9:9
V, ppm----	4.5	5.05	22:51	<10	--	2:9
Y, ppm----	69	1.34	51:51	63	1.56	9:9
Yb, ppm----	7.1	1.27	51:51	8.2	1.31	9:9
Zn, ppm----	50	2.12	51:51	31	1.93	9:9
Zr, ppm						
Granite--	140	1.56	30:30	150	--	--
Rhyolite--	220	1.47	21:21	170	2.32	9:9

<sup>1</sup>Median.

<sup>2</sup>Arithmetic mean.

<sup>3</sup>Standard deviation.

Both contain a large number of trace elements in extraordinarily high concentrations which are introduced into the near-surface environment upon mining, processing, and use.

#### COAL

Thirty samples of coal are compared in figure 13 on the basis of three normative minerals and percent combustible material (hydrocarbons) in the raw coal. Percent combustibles were calculated as 100 minus the percent ash, normative pyrite was calculated from percent total iron, and clay and quartz were calculated as for the sedimentary rocks. Four samples contained more than 1 percent calcium in the raw coal (C12, C16, C18, C24—two Tebo, one Mulky, and one Lexington sample), suggesting that a few samples may contain a

calcium-bearing mineral. The normative compositions provide no obvious basis for classification of Missouri coal, although samples from the Rowe, Drywood, Mineral(?), and Weir-Pittsburg coal beds are consistently higher in ash than samples from the Tebo, Lexington, and Mulky coals.

Results of the analysis of variance are given in table 22, and summary statistics are given in table 13. Between-bed variation ( $S^2_b$ ) is statistically significant for a number of environmentally important elements, particularly for two of the more volatile elements—arsenic and mercury. Eleven of twenty-one elements exhibit statistically significant variation between beds, although constituents of the detrital fraction (aluminum and silicon) do not. A major cause of bed-to-bed variation appears to be the spotty occurrence of pyrite (or marcasite). Normative pyrite ranges from 0.6 percent (C23, C24, the Mulky coal) to 14.9 percent (C11, Tebo coal).

Sphalerite was observed in one sample (C16, Tebo coal) which contained over 7000 ppm zinc and 37 ppm

TABLE 22.—*Components of logarithmic variance estimated for coal of Pennsylvanian age*

[Asterisk (\*), value significantly greater than zero at the 0.05 probability level]

Element or ash	Variance				
	Total log <sub>10</sub> variance ( $S^2_{\log X}$ )	Between coal beds <sup>1</sup>		Between samples	
		Component ( $S^2_b$ )	Percent of total	Component ( $S^2_n + S^2_e$ )	Percent of total
Al-----	0.0722	0.0230	32	0.0429	68
As-----	.2148	*.1294	60	.0854	40
Ash-----	.0708	.0261	37	.0447	63
B-----	.1025	*.0936	91	.0099	9
Ba-----	.1319	0	<1	.1319	100
Be-----	.0218	.0069	31	.0149	69
Ca-----	.2505	.0696	28	.1809	72
Co-----	.2393	*.1739	73	.0654	27
Cr-----	.0669	.0027	4	.0642	96
Cu-----	.1197	.0332	28	.0866	72
F-----	.0456	.0036	8	.0420	92
Fe-----	.1841	*.1499	81	.0341	19
Ge-----	.0716	*.0326	46	.0390	54
Hg-----	.0597	*.0295	49	.0302	51
K-----	.2166	0	<1	.2116	100
Li-----	.2052	.0644	31	.1407	69
Mg-----	.0916	0	<1	.0916	100
Mn-----	.1326	.0277	21	.1049	79
Mo-----	.2203	*.1784	81	.0419	19
Na-----	.0662	.0093	14	.0569	86
Ni-----	.2320	*.1832	79	.0487	21
Pb-----	.2232	*.1234	55	.0998	45
Sc-----	.0863	.0240	28	.0623	72
Se-----	.0843	.0135	16	.0708	84
Si-----	.1116	.0171	15	.0945	85
Sr-----	.0325	.0026	8	.0298	92
Ti-----	.1669	0	<1	.1669	100
V-----	.0881	.0255	29	.0625	71
Y-----	.1198	*.0937	78	.0262	22
Zn-----	.4234	*.2924	69	.1310	31
Zr-----	.1259	.0152	12	.1107	88

<sup>1</sup>See table 3 for names of coal beds.

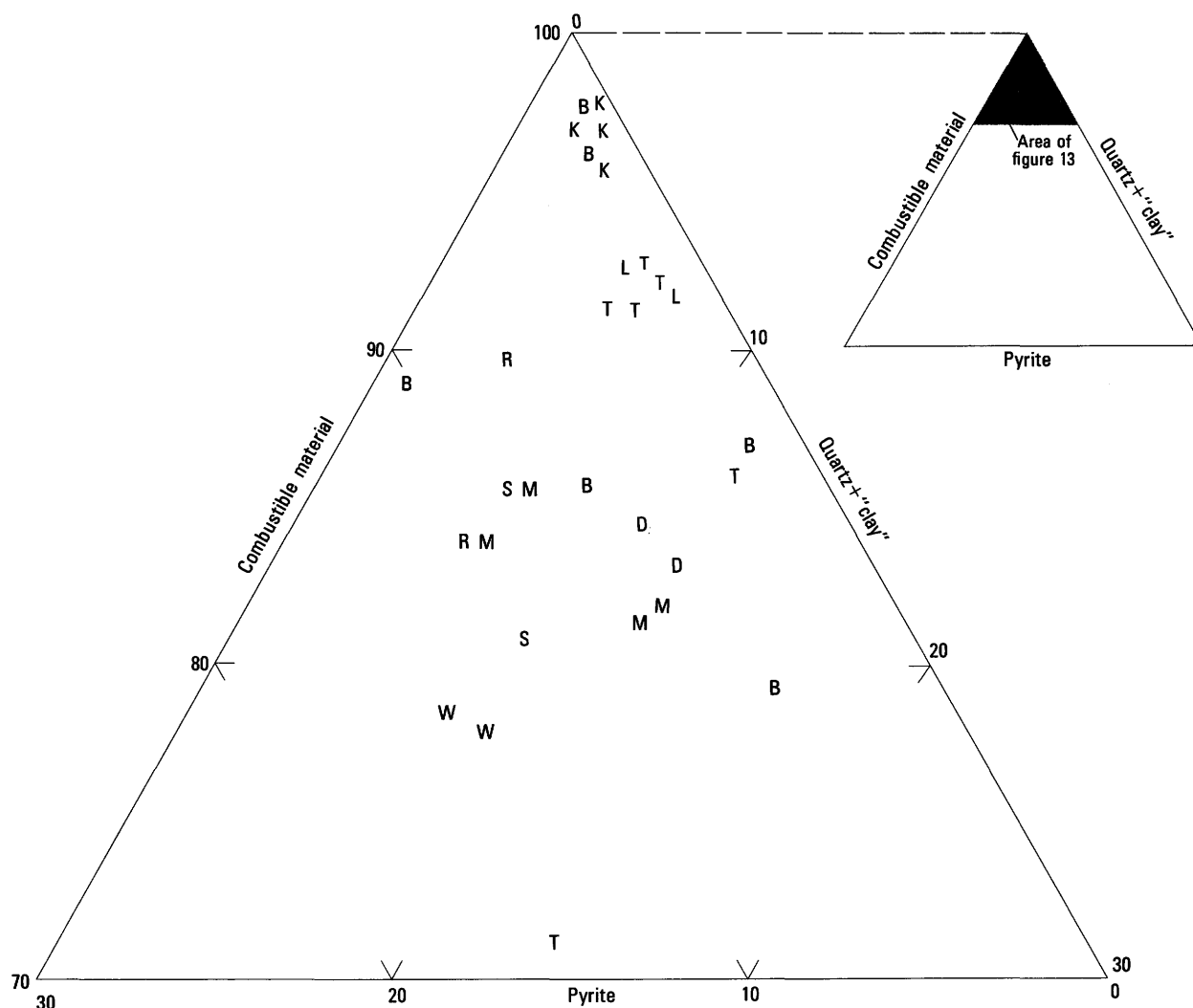


FIGURE 13.—Comparison of samples of coal on the basis of three normative minerals and percent of combustible material (computed as 100 minus percent ash). Coal beds are: B, Bevier; D, Drywood; L, Lexington; K, Mulky; M, Mineral(?); R, Rowe; S, Summit; T, Tebo; W, Weir-Pittsburg.

cadmium. Hatch and others (1976) noted the widespread, but erratic, distribution of sphalerite through coals of southeast Iowa, Missouri, and southeast Kansas (as much as 1.9 percent zinc and 175 ppm cadmium in raw coal). The sphalerite occurs in vertical cracks as much as 1.5 cm wide. Other elements exhibiting important bed-to-bed variation, such as arsenic, cobalt, mercury, nickel, lead, and perhaps germanium and molybdenum, may also reflect in part the distribution of sulfide minerals.

Average concentrations of many elements in raw Missouri coal are roughly similar to concentrations in the enclosing sedimentary rocks (table 13) or even to the underlying rocks (tables 10–12). Among the common rock-forming elements, aluminum, potassium, and silicon are present in coal in about the same

amounts as in carbonates, and calcium is present in about the same amount as in sandstone or chert. Magnesium and phosphorus are notably lower in coal than in the common sedimentary rock types; and only germanium, mercury, lead, and zinc appear to be consistently higher in raw coal (on the average) when compared to non-coal rocks in the study area. The highest individual trace-element concentrations observed were 50 ppm arsenic (C30, Summit coal), 48 ppm cobalt (C01, Rowe coal), 49 ppm germanium (C18, Lexington coal), 177 ppm nickel (C11, Tebo coal), and 318 ppm lead (C30).

Sampling and analytical variance ( $S^2_n + S^2_e$ ) are large for many elements, particularly barium, chromium, fluorine, potassium, magnesium, strontium, and titanium. The analytical component ( $S^2_e$ , table 5) ac-

## GEOCHEMICAL SURVEY OF MISSOURI

TABLE 23.—Concentrations of elements in samples of crushed and pulverized ore, lead concentrate, zinc concentrate and typical concentrations in District and typical concentrations in  
[Concentrations are in percent, parts per million (ppm),

Sample No., median or type of surficial material	Element														
	Ag (ppm)	Al (percent)	As (ppm)	Ba (ppm)	Ca (percent)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (percent)	F (ppm)	Fe (percent)	Ga (ppm)	Ge (ppm)	Hg (ppb)	In (ppm)
Crushed ore															
1	30	0.3	160	50	16	170	150	5	0.4	140	4.3	<5	<10	50	<10
1R	50	.5	240	30	15	190	200	2	.7	70	6.8	<5	15	80	<10
Pulverized ore															
2	2	0.5	12	30	20	16	70	10	0.04	120	3.9	<5	<10	20	<10
2R	1	.5	9.5	30	21	16	100	10	.05	130	3.9	<5	<10	50	<10
3	5	1.	21	70	17	35	150	7	.2	150	3.1	<5	<10	10	<10
3R	5	1.	22	70	17	36	100	7	.2	150	3.1	<5	<10	30	<10
4	15	.5	48	50	20	110	200	10	.3	130	1.7	--	<10	20	<10
4R	10	.5	52	70	20	110	70	20	.3	120	1.7	<5	<10	30	<10
5	10	.3	62	50	20	110	200	7	.3	90	1.8	<5	<10	<10	<10
5R	10	.3	54	70	20	110	100	7	.3	90	1.8	--	<10	10	<10
6	20	.3	100	20	18	130	150	3	.4	80	4.8	<5	<10	30	<10
6R	20	1.	100	15	17	130	100	3	.4	90	4.6	<5	10	60	<10
7	10	.5	35	30	20	140	100	7	.1	50	1.9	<5	<10	50	<10
7R	7	.3	42	30	20	140	70	3	.1	50	1.9	<5	<10	<10	<10
8	30	.5	99	50	18	350	200	10	.2	130	2.0	<5	<10	20	<10
8R	50	.3	88	20	19	330	150	7	.2	90	2.0	<5	<10	10	<10
Median	10	.5	50	40	19	110	100	7	.2	110	2.0	<5	<10	20	<10
Lead concentrate															
9	100	0.1	53	20	0.50	210	1,500	150	0.3	<10	3.3	<5	<10	240	<10
9R	100	.15	55	10	.50	200	2,000	150	.3	10	3.3	<5	<10	260	<10
10	70	.1	69	15	.53	250	1,000	20	1.8	10	3.2	<5	20	130	<10
10R	50	.15	65	15	.60	250	1,500	30	2.0	<10	3.5	<5	20	110	<10
11	200	.2	330	10	.52	330	1,000	20	1.7	<10	4.3	<5	20	80	<10
11R	200	.15	330	20	.52	310	1,000	20	1.7	<10	4.4	<5	20	90	<10
12	70	.1	190	15	.92	360	500	30	.6	<10	1.4	<5	<10	90	<10
12R	70	.15	180	15	.90	350	500	30	.6	<10	1.3	<5	<10	80	<10
13	100	.15	220	10	.86	160	700	2	.4	10	3.3	<5	10	100	<10
13R	100	.1	240	10	.86	240	500	3	.4	<10	3.4	<5	<10	80	<10
14	70	.07	140	10	.96	320	500	2	.9	<10	1.4	<5	15	140	<10
14R	100	.1	160	10	.90	290	700	2	1.	50	1.4	<5	15	60	<10
15	50	.1	260	10	.40	160	1,000	2	1.3	<10	2.7	<5	15	80	<10
15R	50	.1	250	5	.43	160	1,000	5	1.3	<10	2.9	<5	15	80	<10
Median	85	.13	190	10	.56	250	1,000	20	.95	<10	3.4	<5	15	90	<10
Zinc concentrate															
16	700	0.2	100	15	1.9	6,300	700	10	1.6	20	7.8	15	30	230	<10
16R	500	.2	100	50	2.0	6,400	1,000	15	1.8	70	7.7	--	30	140	<10
17	1,000	.2	140	70	1.5	7,800	500	7	.9	40	3.6	--	50	50	<10
17R	1,000	.2	150	15	1.5	8,200	500	7	.9	50	3.6	70	30	210	<10
18	300	.3	260	30	2.4	7,600	700	15	1.5	60	2.2	--	30	200	50
18R	700	.15	220	15	2.4	7,600	1,000	15	1.2	10	2.6	50	30	120	50
19	500	.1	170	7	1.1	7,100	1,000	1	.6	50	2.4	70	150	100	50
19R	700	.1	170	10	1.2	7,100	700	1	.6	20	2.4	70	150	110	50
20	500	.07	240	10	.70	9,000	1,000	5	.6	<10	1.9	70	20	150	<10
20R	500	.07	220	10	.68	8,600	700	5	.7	<10	1.8	100	20	160	20
21	700	.1	160	10	1.5	6,800	500	1	.4	<10	2.0	70	70	90	20
21R	500	.1	150	30	1.5	6,700	500	2	.4	50	1.9	--	70	240	50
Median	600	.13	170	13	1.5	7,100	700	6	.8	50	2.5	70	30	150	20
Copper concentrate															
22	50	0.2	480	30	.19	170	20,000	150	26	<10	15	<5	100	210	150
22R	70	.07	440	20	.19	180	20,000	200	27	50	17	<5	100	280	200
23	30	.05	330	10	.21	120	7,000	50	28	<10	19	<5	300	180	150
23R	20	.05	330	10	.25	110	5,000	70	27	<10	15	<5	200	210	70
24	70	.05	1,900	5	.21	92	7,000	300	29	<10	18	<5	200	200	70
24R	50	.03	2,000	5	.22	88	10,000	200	28	<10	17	<5	150	200	150
25	30	.15	>2,300	70	.47	230	7,000	100	27	30	19	--	200	100	100
25R	50	.05	2,200	5	.48	230	10,000	150	26	<10	15	<5	200	150	70
26	50	.2	>2,300	70	.26	94	5,000	5	28	20	18	--	200	120	150
26R	100	.05	2,500	7	.25	94	5,000	10	28	<10	18	<5	150	170	150
Median	50	.05	2,000	10	.24	120	7,000	130	29	<10	18	<5	200	190	150
Mill tailings															
27	10	0.3	59	30	20	30	70	5	0.1	160	4.5	<5	<10	30	<10
27R	10	.3	63	20	20	25	100	7	.1	110	4.8	<5	<10	30	<10
Typical concentrations in surficial materials in southeast Missouri															
Cultivated soils (Tidball, 1974)--	<1	3.8	8.4	510	0.20	<1	11	52	15 <sup>1</sup>	270	2.0	11	--	38	--
Uncultivated soils (Erdman and others, 1976a, table 6)-----	<1	2.1	6.7	340	.065	<1	9.5	30	12 <sup>1</sup>	160	1.5	5.9	--	45	--
Carbonate residuum (U.S. Geological Survey, 1973, p. 10)-----	<1	8.3	22	190	<.15	<1	<7.7	58	36 <sup>1</sup>	810	5.1	20	--	--	--

<sup>1</sup>In parts per million.

*trate, copper concentrate, and tailings from mining and milling operations in the Southeast Missouri Lead surficial materials of southeast Missouri*

or parts per billion (ppb); R, sample split; ---, no data]

Element															
K (percent)	Mg (percent)	Mn (ppm)	Mo (ppm)	Na (percent)	Ni (ppm)	P (percent)	Pb (percent)	Sb (ppm)	Se (ppm)	Si (percent)	Sr (ppm)	Ti (ppm)	V (ppm)	Zn (percent)	Zr (ppm)
Crushed ore															
0.35 .38	8.8 7.7	700 1,000	3 7	0.030 .022	300 500	0.033 .024	>10 >10	<150 <150	<0.10 .24	1.6 2.2	70 70	150 150	7 <5	1.2 1.5	15 <10
Pulverized ore															
0.73 .71 .99 .98 .58 .69 .25 .23 .41 .39 .48 .48 .36 .35 .48	9.8 9.5 8.4 8.3 11 11 11 9.2 9.4 9.9 10 10 9.5 10 9.7	3,000 3,000 2,000 3,000 1,000 1,000 1,500 1,500 1,000 1,000 2,000 2,000 1,500 1,000 1,500	<3 <3 <3 <3 3 3 3 3 3 7 3 3 3 3 3	0.030 .030 .030 .030 .030 .030 .022 .022 .022 .022 .015 .015 .022 .022 .030	70 70 100 100 300 100 200 150 300 500 100 100 300 200 200	0.067 .035 .072 .083 .029 .025 .033 .038 .052 .030 .026 .022 .020 .022 .036	3 2 5 5 7 7 10 10 7 >10 7 10 10 10 7	<150 <150 <150 <150 <150 <150 <150 <150 <150 <150 <150 <150 <150 <150	<0.10 .32 <1.0 <1.0 .14 .22 .10 <1.0 .14 2.2 <1.0 1.4 1.4 1.5 1.4 1.5	2.1 2.4 8.6 8.8 1.5 1.5 .57 .53 2.2 2.0 2.0 2.0 2.0 2.0	70 70 70 70 100 70 70 70 70 70 70 70 70 70	200 150 500 300 150 150 100 70 100 100 150 150 150 150	5 <5 10 10 7 7 15 15 15 15 5 5 7 7 7	.07 .07 .2 .2 .7 .7 .6 .7 .8 1. 1. 1. 2.5 2.6 .7	10 <10 20 20 30 30 15 15 15 15 15 10 10 15 13
Lead concentrate															
0.090 .098 .13 .18 .14 .13 .087 .12 .11 .15 .12 .15 <.083 <.083 .12	0.25 .27 .31 .31 .30 .30 .51 .48 .48 .55 .52 .55 .24 .25 .31	150 150 100 150 150 70 150 150 70 50 150 50 30 70	5 5 7 3 10 10 10 7 10 10 20 10 10 10 10	<0.0074 <0.0074 <0.0074 <0.0074 <0.0074 <0.0074 <0.0074 <0.0074 <0.0074 <0.0074 <0.0074 <0.0074 <0.0074	2,000 3,000 1,000 1,500 2,000 2,000 700 700 700 1,000 1,000 1,500 1,500 1,300	0.031 .030 .057 .052 .031 .036 .022 .022 .048 .022 .029 .022 .041 .036 .031	>10 >10 >10 >10 >10 >10 >10 >10 >10 >10 >10 >10 >10 >10	<150 <150 <150 <150 <150 <150 <150 <150 <150 <150 <150 <150 <150 <150	1.8 1.8 .93 1.0 .26 .52 .27 .24 .10 .29 .12 .58 .60 .40	<0.47 <0.47 .52 .62 .47 .47 .47 .47 .47 .47 .47 .47 .47 .47	10 10 7 10 5 7 5 5 5 5 5 5 5 5	200 200 700 700 200 200 100 100 150 150 150 150 150	7 5 7 7 5 7 5 5 5 5 5 5 5 5	1.2 1.2 1.4 1.4 2.2 2.1 2.1 2.1 1.3 1.8 2.1 1.2 1.2 1.6	20 20 30 20 20 15 15 15 30 30 20 20 20 20
Zinc concentrate															
0.21 .23 .16 .17 .20 .18 .084 .11 <.083 <.083 .084 .091 .14	0.97 .98 .80 .78 1.2 1.3 .44 .59 .36 .36 .53 .71 .69	500 300 150 150 300 300 100 150 150 100 100 150 150	-- <3 <3 7 3 10 7 5 5 7 7 3 3 5	0.015 .022 .015 .015 .015 .015 .015 .0074 .0074 .0074 .015 .015 .015 .015	500 700 700 700 700 1,000 700 700 700 500 300 300 300 700	0.030 .038 .026 .026 .046 .030 .022 .024 .22 .024 .033 .022 .028	6 5 1.5 1.5 2 3 5 10 2 3 2 1.5 3	<150 <150 <150 <150 <150 <150 <150 <150 <150 <150 <150 <150 <150	0.52 .61 .22 <.10 .18 .13 .64 .10 .67 .47 .49 .24 .11	0.63 .84 .47 .47 .50 .64 .61 .10 .67 .47 .49 .47 .51	10 15 10 7 10 10 5 5 5 5 7 7 7	500 300 200 150 150 150 50 50 70 100 50 70 130	<5 7 5 5 5 5 5 5 5 5 5 5 5	40 39 51 52 48 48 52 54 53 58 56 53 52	20 20 15 15 20 30 10 10 10 10 15 15 15
Copper concentrate															
<0.083 <.083 <.083 <.083 <.083 <.083 <.083 <.083 <.083 <.083 <.083 <.083 <.083	0.090 .084 .11 .11 .11 .11 .24 .25 .12 .11 .11	50 50 30 30 15 15 70 50 30 15 30	3 -- -- -- -- 3 3 3 3 3 3	0.0074 .0074 .0074 .0074 .0074 .0074 .0074 .0074 .0074 .0074 .0074	20,000 30,000 5,000 5,000 20,000 20,000 10,000 10,000 10,000 10,000 10,000	<0.022 .21 .17 .20 .19 .20 .15 .13 .17 .029 .17	7 >10 10 7 7 5 7 10 7 7 7	<150 150 <150 150 300 200 300 200 300 300 200	2.1 2.1 .35 .56 .50 .59 .87 .78 .10 .10 .10	<0.47 <.47 <.47 <.47 <.47 <.47 <.47 <.47 <.47 <.47 <.47	10 50 70 70 70 70 30 70 30 30 60	15 7 7 5 5 5 15 5 15 7 7	0.9 1. .6 .6 .5 .5 1.4 1.6 .7 .6 .7	70 70 15 10 20 10 30 20 30 15 20	
Mill tailings															
0.53 .48	10 10	1,000 1,000	3 <3	0.022 .030	150 200	0.032 .046	0.5 .05	<150 <150	0.27 .24	2.1 2.1	70 100	150 100	7 <5	0.2 .2	10 <10
Typical concentrations in surficial materials in southeast Missouri															
1.4 .86 1.0	0.23 .11 .50	1,100 660 120	-- <3 --	0.33 .19 .039	14 8.8 24	0.048 .030 .021	28 <sup>1</sup> 18 <sup>1</sup> 45 <sup>1</sup>	--- --- ---	0.22 .27 .23	36 41 27	89 42 40	3,300 3,300 1,400	63 37 110	54 <sup>1</sup> 30 <sup>1</sup> 110 <sup>1</sup>	300 260 61

counts for more than half of this combined variation in five elements (arsenic, boron, iron, mercury, and zinc) and most of the combined variation reflects within-bed variability. The combined variance represents the imprecision which would be encountered in representing a coal bed by a single sample if that sample were analyzed by the methods in table 4.

#### LEAD-ZINC-COPPER ORE

The lead-zinc-copper sulfide deposits occur as replacement orebodies predominantly in the Bonnetterre Formation of Cambrian age (Kiilsgaard and others, 1967, p. 45-47). The Southeast Missouri Lead District is one of the few mining districts in the United States that has produced over one and a half billion dollars worth of ore (Wharton and others, 1969, p. 63). Most of the past production of the district was from the Old Lead Belt. The New Lead Belt, or the Viburnum Trend (fig. 5), which was discovered in 1955, accounted for 85 percent of the total U.S. lead production in 1974, as well as for the production of significant amounts of zinc, copper, silver, and cadmium (Vineyard, 1977). Kiilsgaard and others (1967, p. 45-55) presented a succinct summary of the geology and origin of the southeast Missouri lead deposits. More recently, the May 1977 issue of *Economic Geology* (v. 72, no. 3) was devoted exclusively to papers on the Viburnum Trend.

Samples in this study include one sample of crushed ore (consisting of pieces approximately 2.5 cm in diameter), seven of pulverized ore, seven of lead concentrate, six of zinc concentrate, five of copper concentrate, and one of mill tailings. All samples were split, and the resulting 54 samples were analyzed in a randomized sequence. The analytical results are given in table 23. Differences among the various materials may be judged by comparing median concentrations. (The median is the value of the middle item, or the average of the middle two items, if the items are arranged in order of concentration.) The median estimates the typical or most common concentration. Differences among individual samples of ore (or ore concentrate) may be judged by comparing averages of the replicated analyses, and the degree of analytical error is indicated by differences between the replicated analyses.

Processing of ore to concentrate tends to increase levels of silver, arsenic, cobalt, nickel, and mercury (table 23). Antimony, chromium, selenium, and titanium also appear to be enriched in lead concentrate; and cadmium, molybdenum, gallium, indium, and selenium appear to be enriched in copper concentrate. A comparison of trace-metal levels in the different concentrates indicates that the zinc concentrate

has the highest levels of cadmium, fluorine, gallium, and silver, and that the copper concentrate has the highest levels of arsenic, chromium, cobalt, germanium, indium, nickel, and phosphorus. Cadmium and silver are recovered from the concentrates during smelting (Kiilsgaard, 1967, p. 72; Guild, 1967, p. 73).

Of greater environmental interest here, though, is a comparison of these materials to the ordinary surficial materials of the local landscape. Elemental concentrations most likely to be encountered in cultivated soil, uncultivated soil, and carbonate residuum in this part of southeastern Missouri are given at the bottom of table 23. Concentrations in cultivated soil are given as medians of the average concentrations measured in Iron, Reynolds, St. Francois, and Washington Counties (Tidball, 1974); concentrations in uncultivated soils are taken from Erdman and others (1976a, table 6); and concentrations in residuum are medians of average concentrations listed for residuum overlying the Bonnetterre Formation and Eminence, Potosi, and Gasconade Dolomites of southeastern Missouri (U.S. Geological Survey, 1973, p. 10).

The ores and concentrates are much higher than the surficial materials in the ore-related trace metals arsenic, cobalt, and nickel, and much lower than the surficial materials in the clay-related elements aluminum, barium, fluorine, potassium, titanium, vanadium, and zirconium. When compared to the surficial materials, the one sample of mill tailings is also distinctly high in arsenic, cobalt, and nickel as well as silver, cadmium, and the ore metals lead, zinc, and copper. The mill sample is low in aluminum, barium, chromium, gallium, silicon, titanium, vanadium, and zirconium.

The introduction of these or similar materials into the near-surface environment will produce marked effects in the landscape simply because of the strong geochemical contrasts between ore and surficial materials. More important, in an environmental context, is the potential for rapid and widespread dispersal of the elements in these materials into the local environment. For example, Proctor, Butz, and Sinha (1976) noted increased concentrations of copper, lead, zinc, and cadmium (but not nickel) in stream sediments draining the Viburnum region to the north since the start of mining there. A general study of the chemical impact of the New Lead Belt on the surrounding area is given in Boggess and Wixson (1978). A similar impact of the Old Lead Belt is even more marked, as witnessed by roadside accumulations of lead in cedar within the belt of as much as 70 times background (Connor and others 1971) and by alluvial soils in Big Creek draining the belt which contain about 100 times the expected amount of lead for such soils (U.S. Geological Survey, 1973, table 5).



## DISCUSSION

Geochemical variation in the bedrock units of the study area is dominated by the distribution of the major rock-forming minerals: calcite, dolomite, quartz, and clay. This distribution tends to manifest itself at very large or very small geographic scales. At the larger scales, rocks in the eastern and southern parts of the study area (Sauk, Tippecanoe and Kaskaskia sequences) are rich in calcite and dolomite; they contrast markedly with rocks in the northern and western parts (Pennsylvanian System) which are rich in quartz and clay. At the smaller scales (representing distances of a few kilometers or less), this variation arises as a result of interstratification of mineralogically dissimilar beds.

The largest scale of variation is evident in the differences among the means of the major geologic units, given in tables 10-13, 16, and 21. In general, the statistical data for the most widespread lithic type in each geologic unit are given in the left-most column of each table, and subordinate lithic types are summarized in columns to the right. The tabled summaries may be used in conjunction with conventional geologic maps to make first-order approximations showing the gross regional distributions of the elements over the study area. Unfortunately, geologic maps in the area of this report do not generally show detailed distributions of the different lithic types (see Gentile, 1976, for example); thus, the local interstratification of contrasting lithic types, which largely controls local geochemical patterns (particularly in the Pennsylvanian), cannot be shown over the area as a whole.

Bar graphs for 19 trace elements are shown in figure 14. The graphs compare the ranges in element concentration in bedrock units of the study area. The Pennsylvanian rocks have been subdivided into two parts where appropriate to represent the few geochemical differences noted between the northern and southern outcrops of Pennsylvanian age. Similarly, the Precambrian rocks have been subdivided into granite and rhyolite on the graphs of beryllium and zirconium.

In the graphs of figure 14, the expected concentration and the expected 68 and 95 percent ranges in concentration are shown for those units for which data in tables 10-13 and 21 permit computation. For many units, when the data are judged to be insufficient for such computation, only the observed range in concentration is given. The observed ranges given in figure 14 are probably more comparable to a 68 percent expected range than to a 95 percent expected range because they are based on relatively few samples. The graphs indicate just how variable the chemistry of rocks in outcrop of the study area are. Commonly, the total range in concentration over all units exceeds a

thousandfold, and for some elements (fluorine, for example), it exceeds ten-thousandfold. For most elements, the overlap of ranges tends to be large.

The purpose of these graphs is to aid the user in judging the ranges of element concentration to be expected in the various types of bedrock in different parts of the area. Thus, a sample of bedrock from any part of the study area may be judged as ordinary or unusual by comparing its composition with the ranges given for the appropriate lithic type in the appropriate part of the area. Use of the bar graphs requires that the sample or samples being judged be assigned to the correct geologic unit, as the units have been classified for this study. To this end, the user may need geological maps or geological advice, both available from the appropriate State geological survey, State university, or local office of the U.S. Geological Survey.

In examining a local field area of interest, the user first determines what major rock unit (or units) may be present. In localities far from the major geologic boundaries, the major unit underlying the area of interest can be determined from figure 2 or the appropriate State geologic map. Localities near to or straddling major boundaries may require detailed maps or geological consultation in order to determine which of the major units the bedrock belongs to. In particular, the Roubidoux-Sauk and Sauk-Kaskaskia contacts may prove difficult to locate in the field, especially for the inexperienced eye. All geologic boundaries display a more intricate pattern than that shown in figure 2. The Precambrian-Sauk contact in southeast Missouri is especially intricate, but because it consists of a carbonate-granite contrast, field examination should readily determine which unit is which in the field.

Once the major unit(s) in a locality is determined, the lithic type(s) needs to be identified. Some types are readily distinguished, such as coal or carbonate rock. Field differentiation between limestone and dolomite can be difficult, as can differentiation between granite and rhyolite. Differentiation between fine-grained, laminated sandstone and silty shale may be difficult in the Pennsylvanian rocks. Geologic maps are generally of only moderate help in differentiating rock types; commonly, rocks are classified on maps more by geologic time than by chemical composition or lithology. If necessary, aid should be requested from geologists familiar with the area of interest.

After the major rock unit and the rock type are identified, the expected ranges in composition of the rock types present can be read from figure 14. Also, if rock samples are collected and analyzed, the results can be compared against the graphs of figure 14 (or the summaries in tables 10-13, 16, and 21) to determine whether the samples in question are geochemically unusual. For example, copper, lead, and zinc in 14

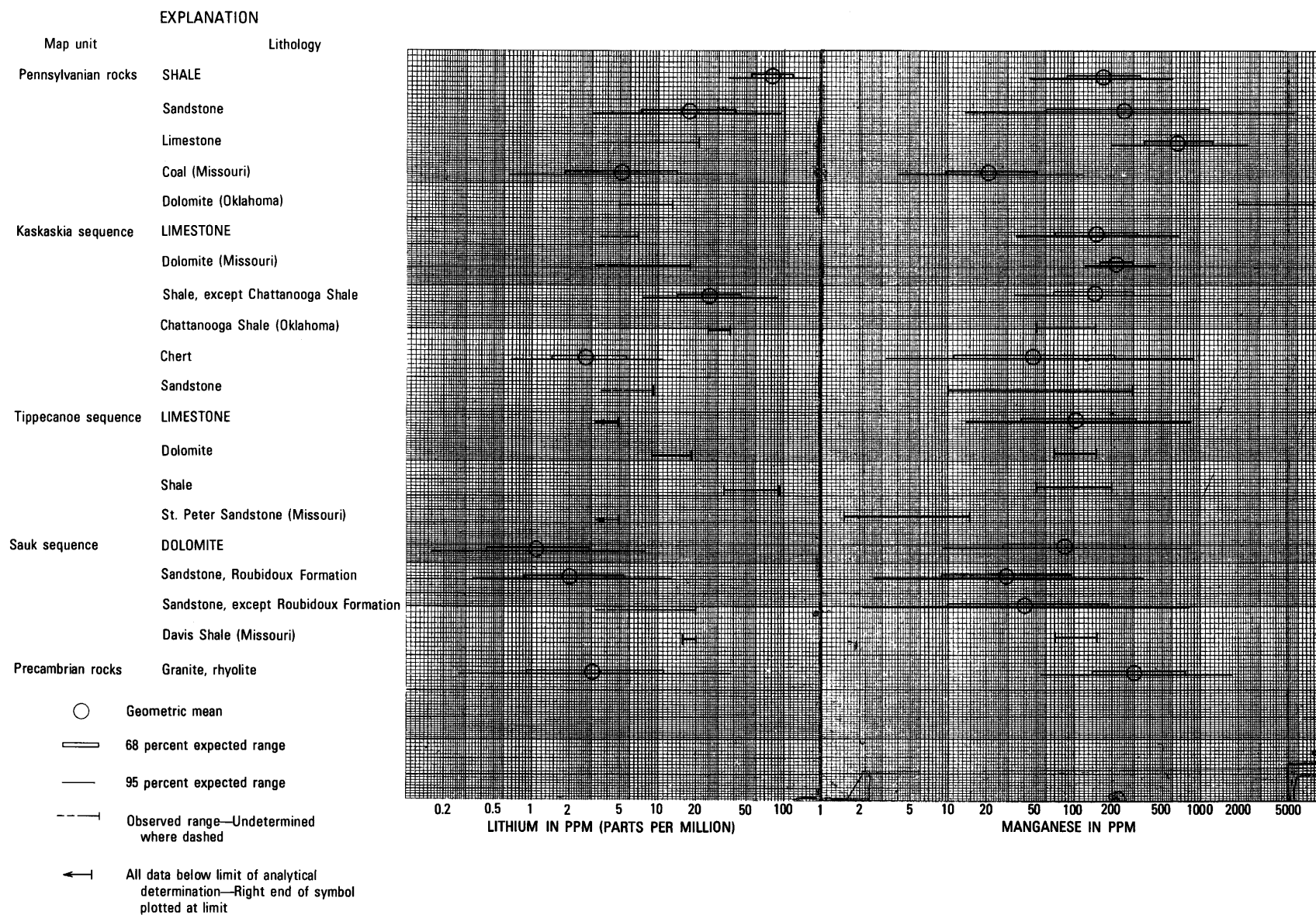


FIGURE 14.—Graphs showing trace-element concentrations in lithic bedrock units in Missouri and parts of adjacent States.

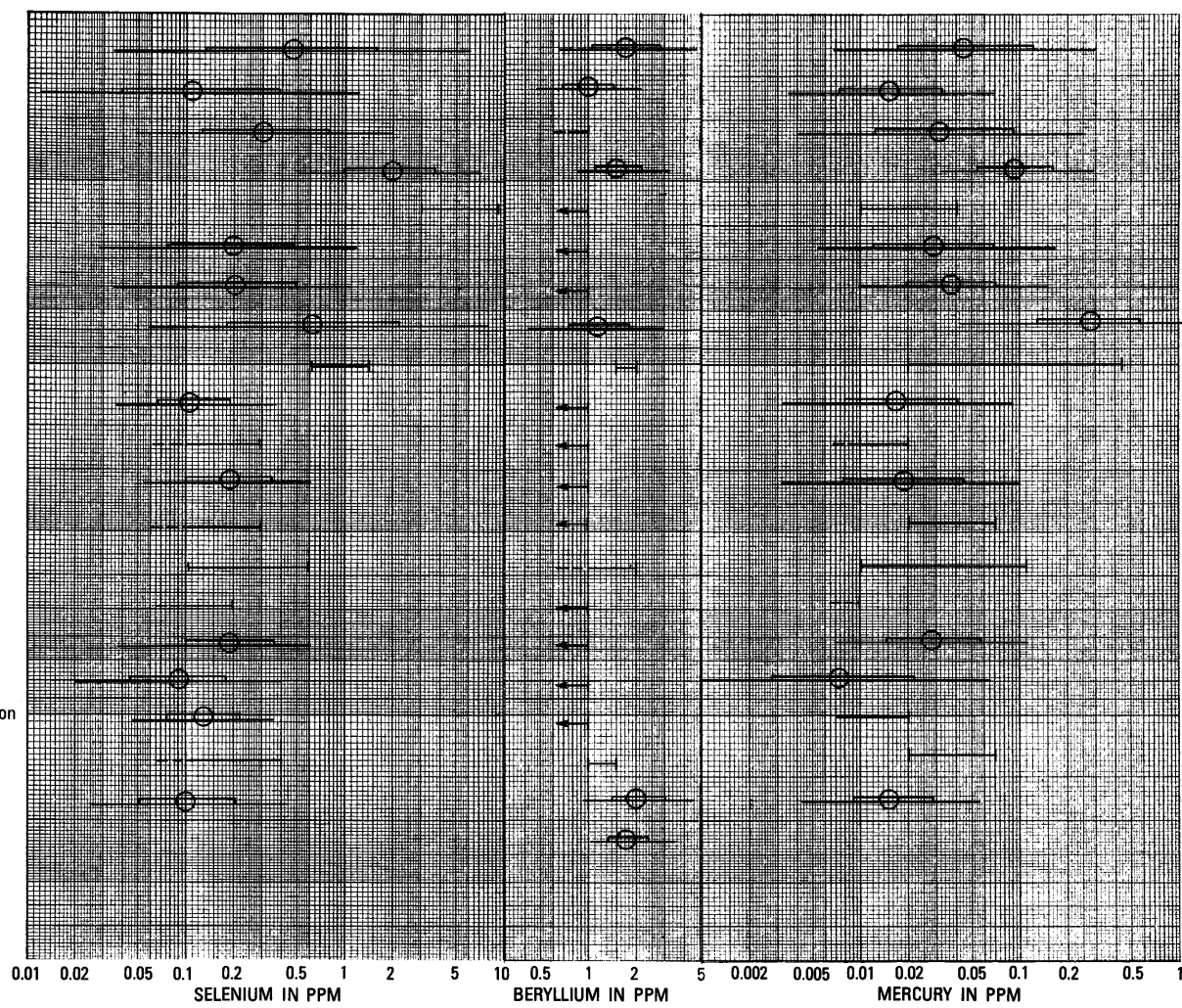
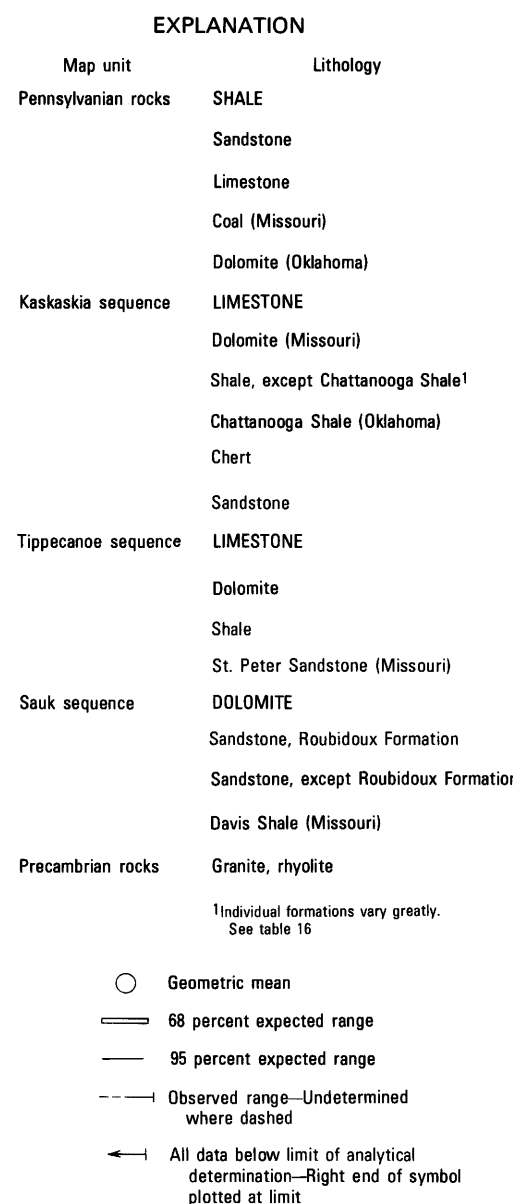


FIGURE 14.—Trace-element concentrations—Continued

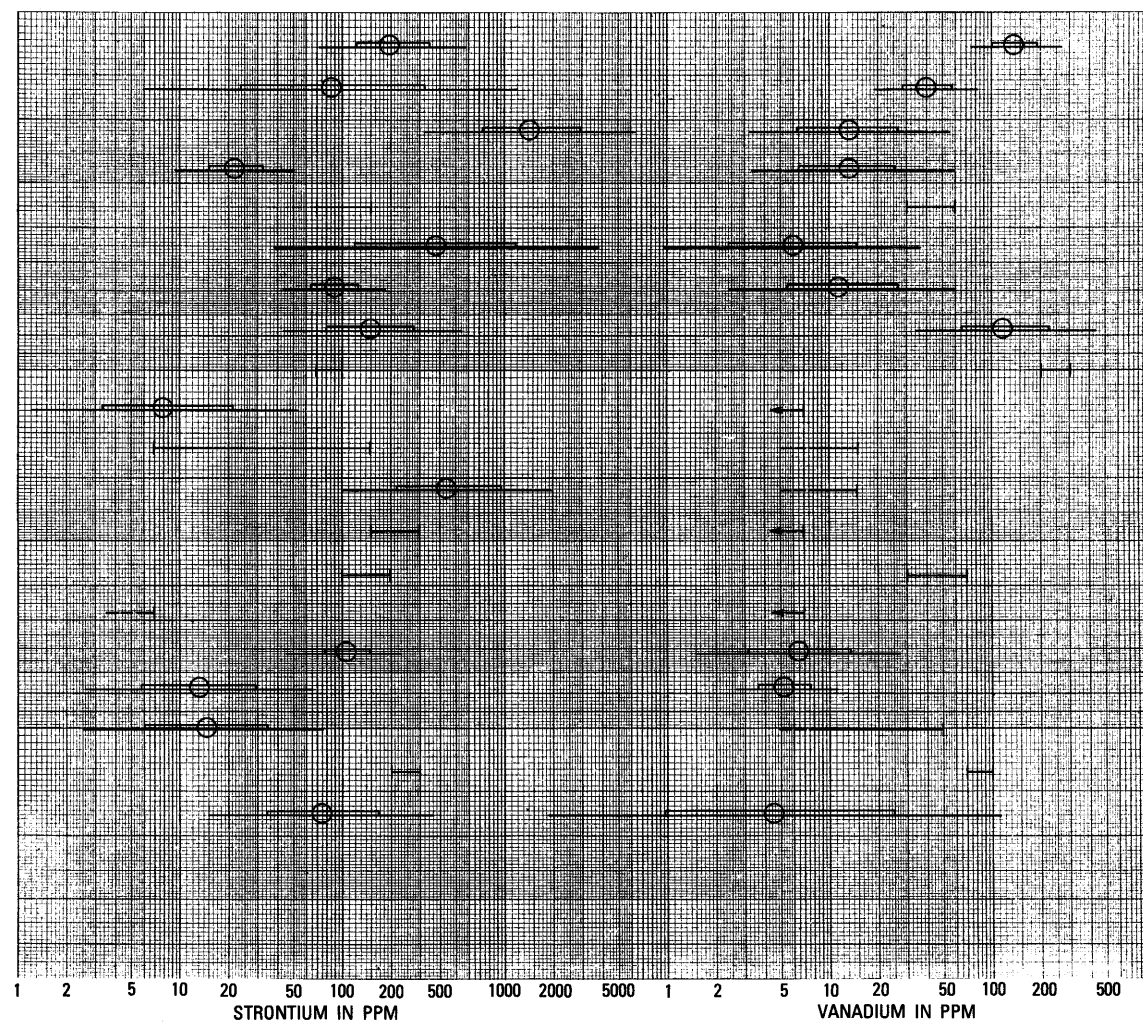
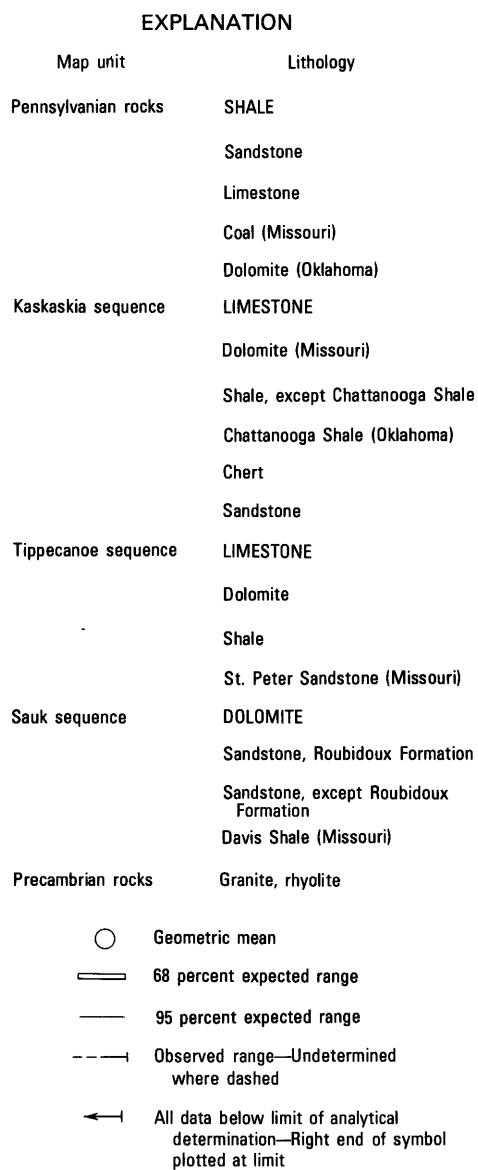


FIGURE 14.—Trace-element concentrations—Continued



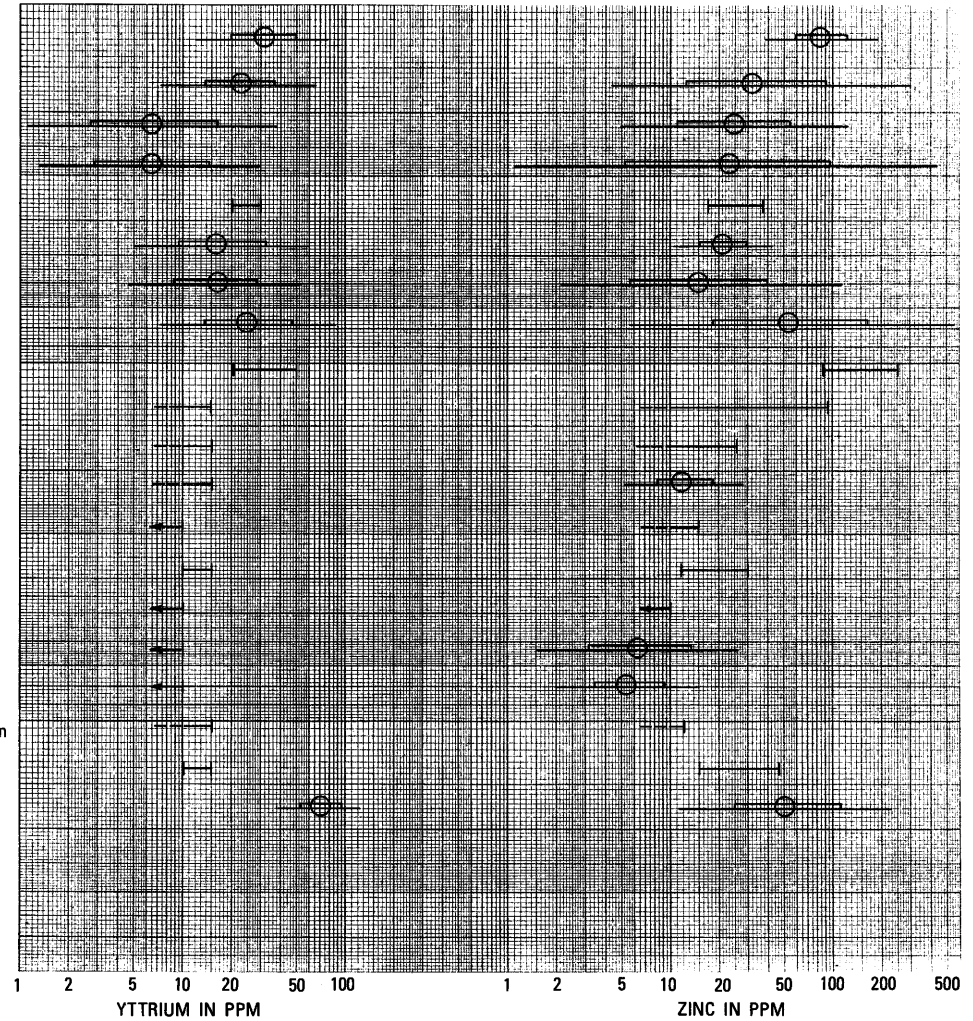
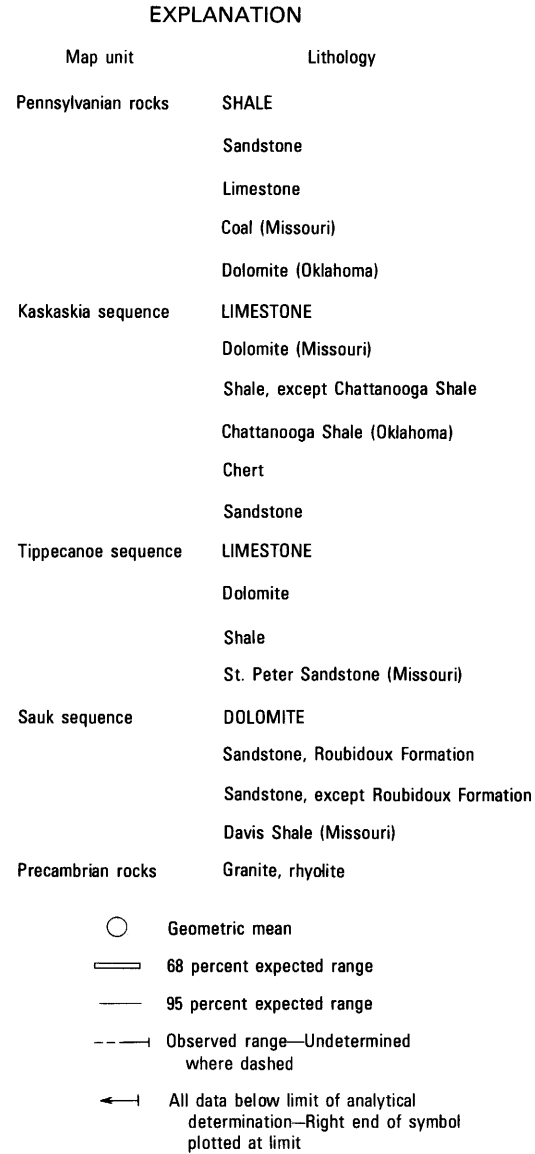


FIGURE 14.—Trace-element concentrations—Continued

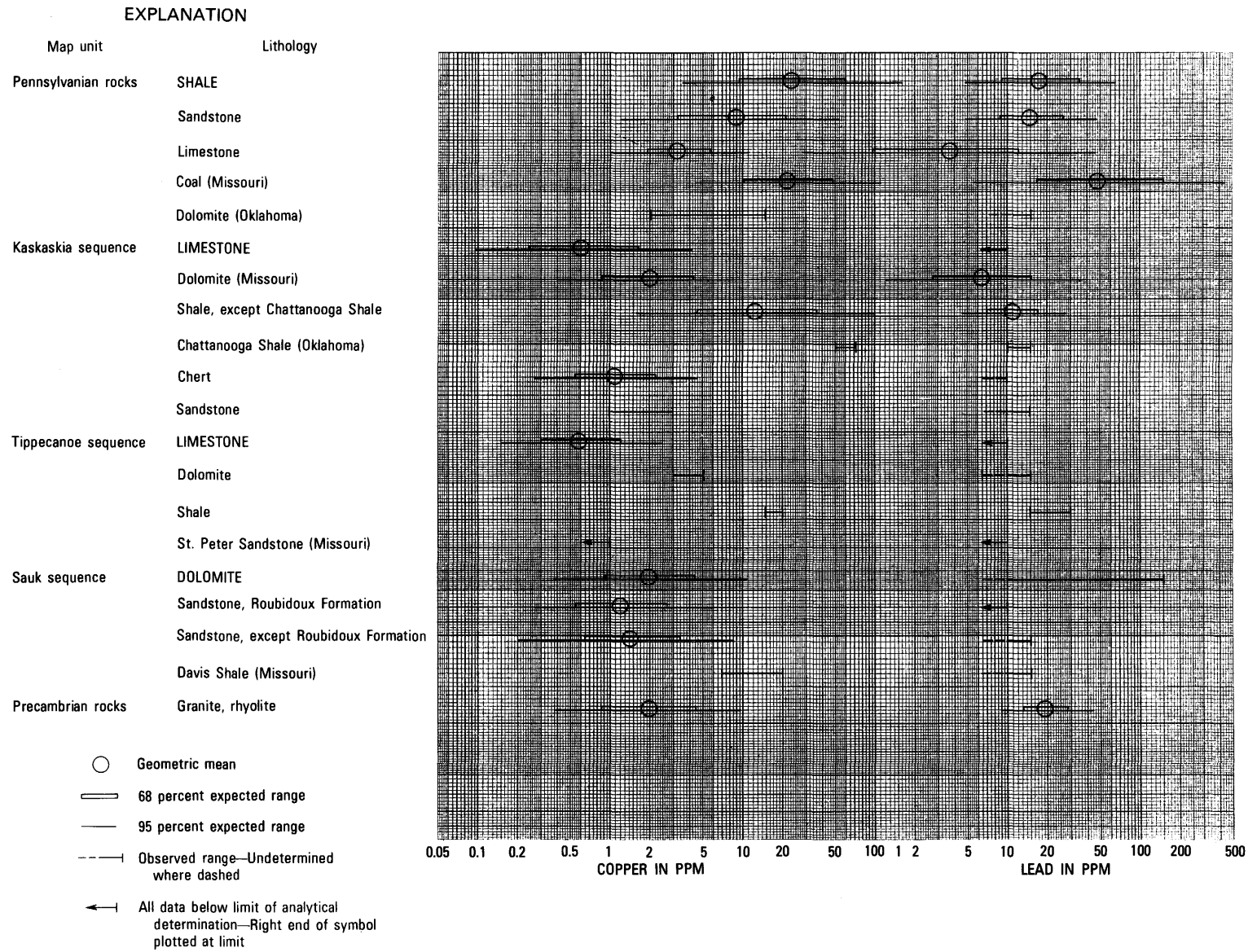


FIGURE 14.—Trace-element concentrations—Continued

# EXPLANATION

Map unit	Lithology
Pennsylvanian rocks	SHALE
	Sandstone
	Limestone
	Coal (Missouri)
	Dolomite (Oklahoma)
Kaskaskia sequence	LIMESTONE
	Dolomite (Missouri)
	Shale, except Chattanooga Shale
	Chattanooga Shale (Oklahoma)
	Chert
	Sandstone
Tippecanoe sequence	LIMESTONE
	Dolomite
	Shale
	St. Peter Sandstone (Missouri)
	DOLOMITE
Sauk sequence	Sandstone, Roubidoux Formation
	Sandstone, except Roubidoux Formation
	Davis Shale (Missouri)
Precambrian rocks	Granite, rhyolite

- Geometric mean
- ▬ 68 percent expected range
- 95 percent expected range
- Observed range—Undetermined where dashed
- ← All data below limit of analytical determination—Right end of symbol plotted at limit

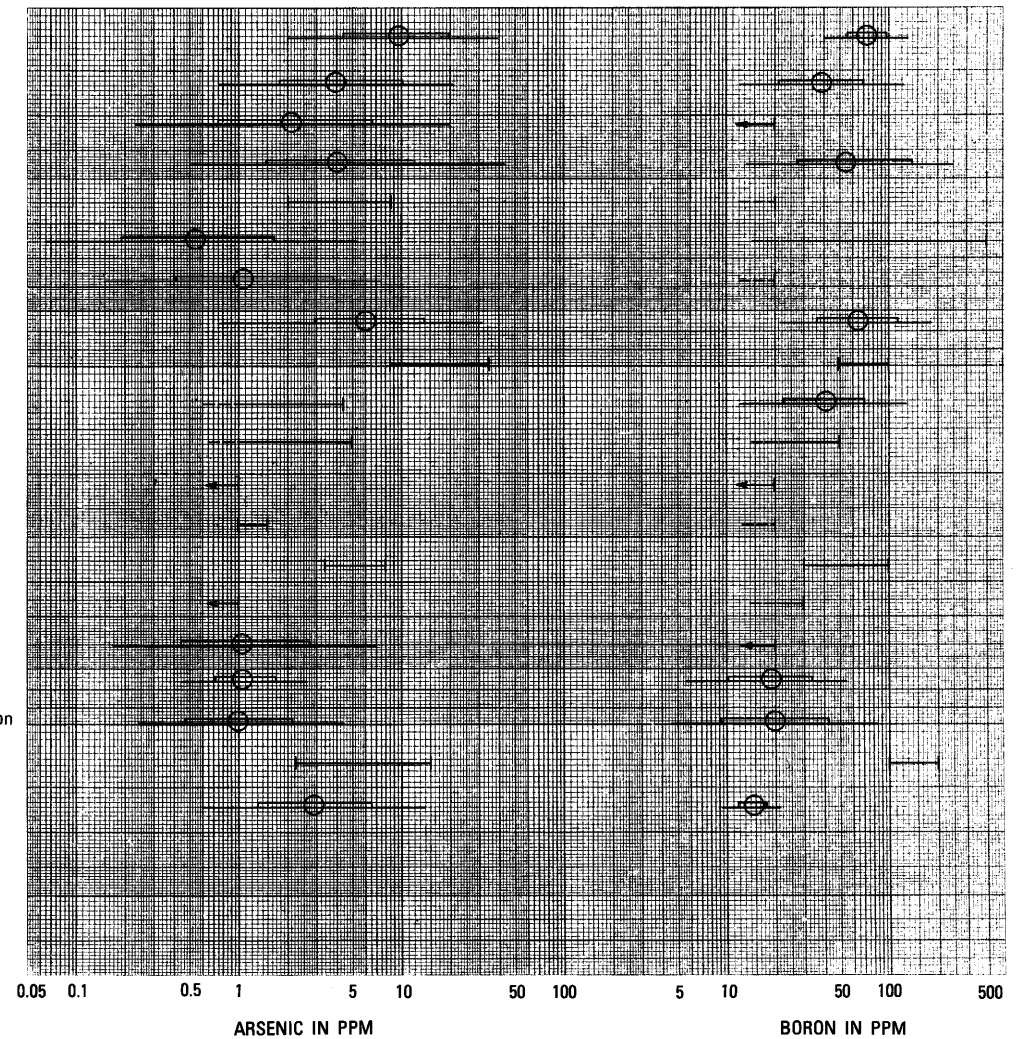


FIGURE 14.—Trace-element concentrations—Continued

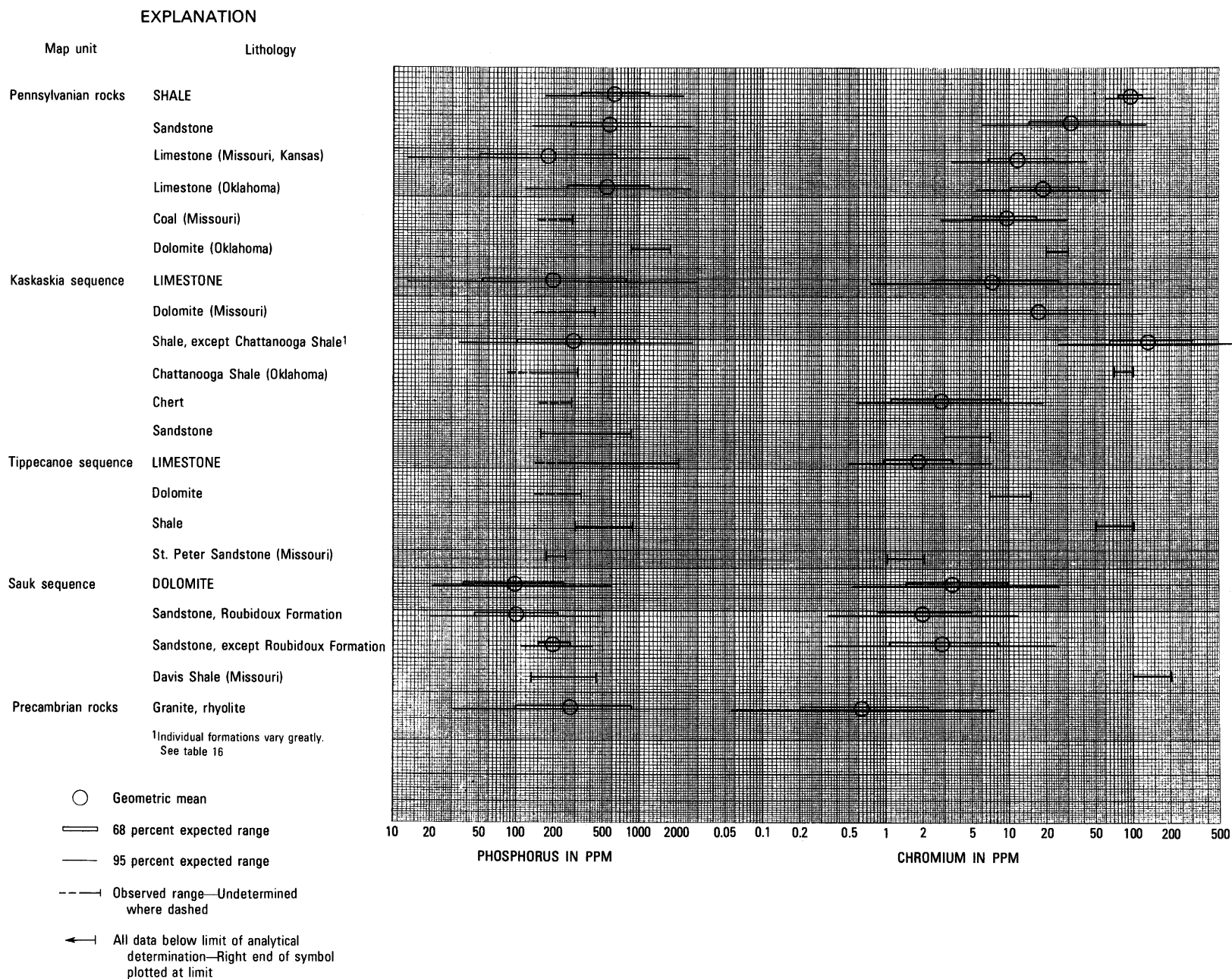
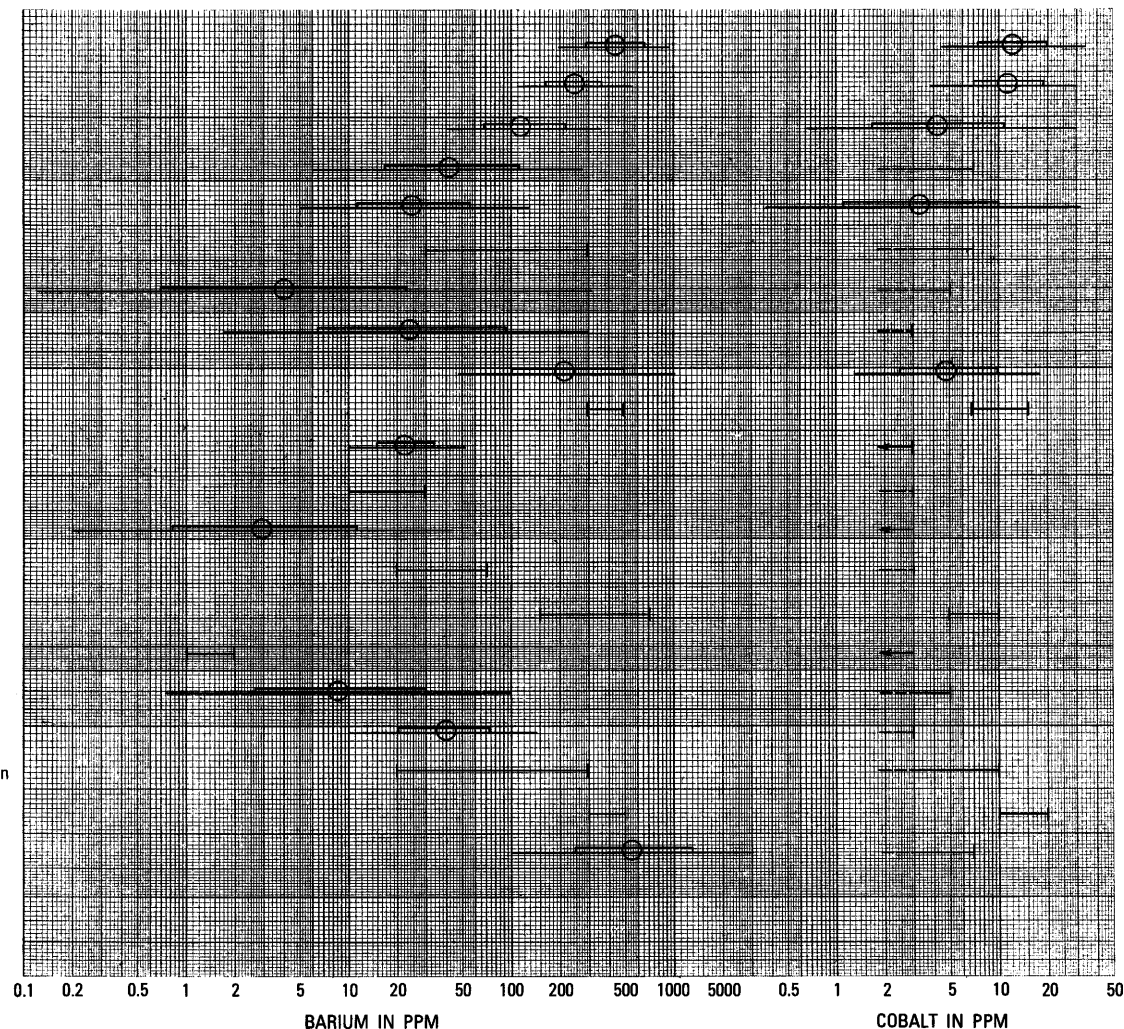
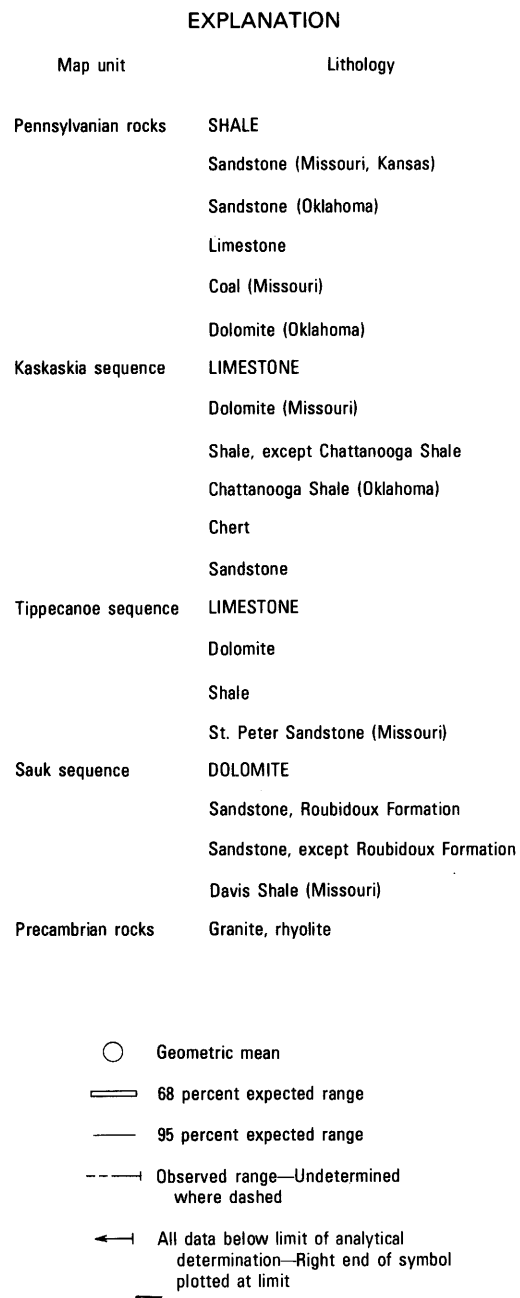


FIGURE 14.—Trace-element concentrations—Continued





BEDROCK UNITS IN MISSOURI AND PARTS OF ADJACENT STATES

FIGURE 14.—Trace-element concentrations—Continued

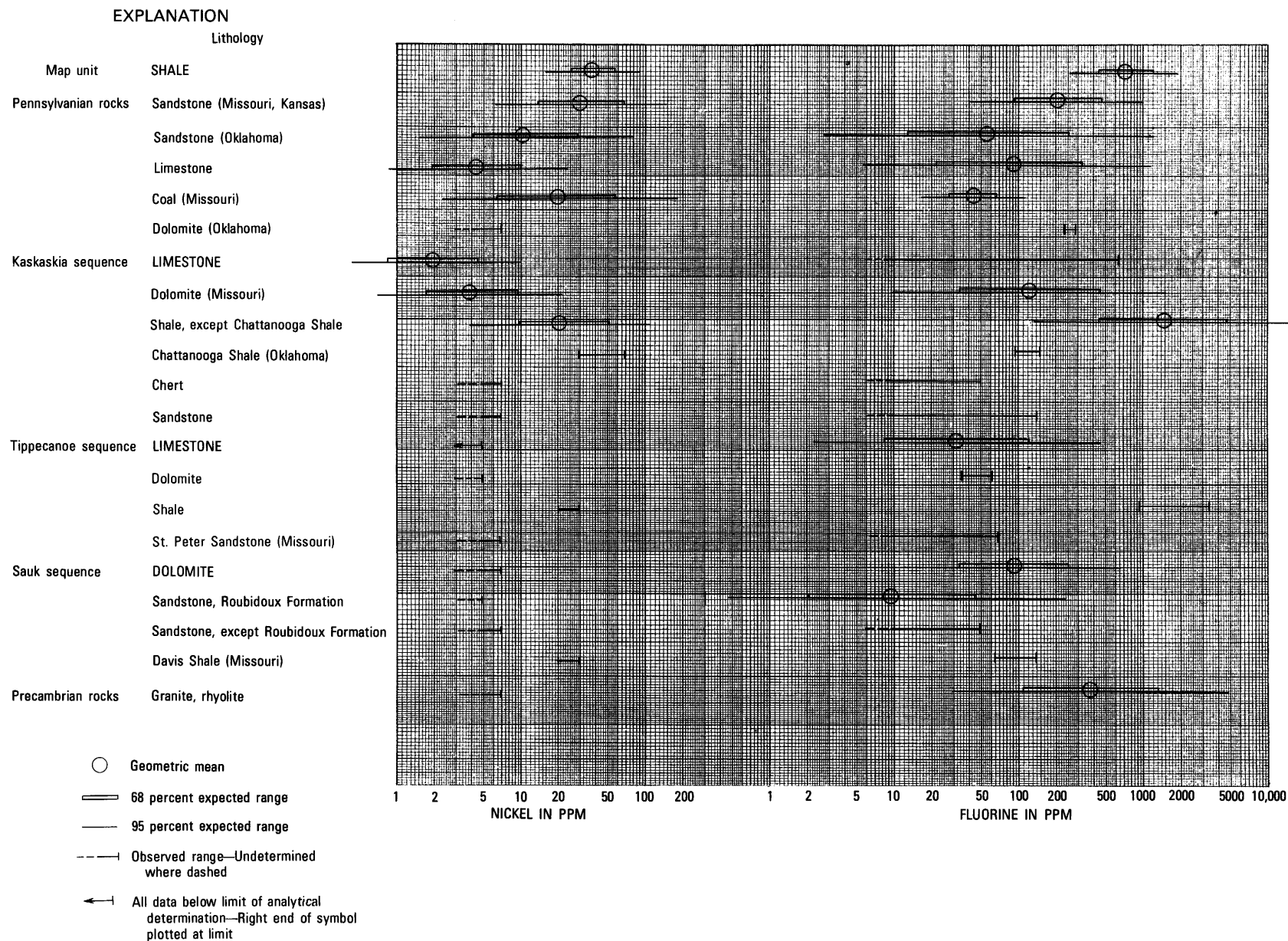


FIGURE 14.—Trace-element concentrations—Continued

samples of bedrock from a roadcut northeast of Centerville, Mo. (fig. 15), are listed below:

Sample No.	Rock type	Element (parts per million)		
		Lead	Zinc	Copper
D142203	Rhyolite(?) .....	30	105	3
D142214	Dolomite .....	<10	11	<1
D142217	do .....	<10	10	<1
D142220	do .....	<10	<10	<1
D142221	do .....	<10	14	1
D142223	do .....	<10	<10	2
D142224	do .....	<10	<10	<1
D142227	do .....	<10	<10	<1
D142228	do .....	<10	13	1
D142229	do .....	<10	<10	<1
D142230	do .....	<10	<10	2
D142232	do .....	<10	<10	2
D142234	do .....	<10	11	3
D142236	do .....	15	10	200

These samples were collected in 1969 during an investigation of an unusual field geochemical feature. A cedar tree (*Juniperus virginiana* L.) growing on the roadside in this locality was found to contain 20,000 ppm lead, 1,080 ppm zinc, and 300 ppm copper in ash (Connor and others, 1971). As these concentrations contrast greatly with typical concentrations in cedar ash (280 ppm lead, 380 ppm zinc, and 68 ppm copper), the roadside geochemical environment must be viewed as highly anomalous. This locality lies well within the Southeast Missouri Lead district, and the bedrock cropping out along the roadside, in which the cedar is rooted, was sampled to determine if the cedar

chemistry was reflecting in some way an unusual bedrock geochemistry.

Field examination showed the bedrock outcrop to be mostly dolomite, and the general location requires that it belong to the Sauk sequence. There was nothing visibly unusual about the dolomite in outcrop, and the trace-element chemistry of 12 samples taken from outcrop (D142214–D142234, above) fall wholly within ordinary limits as defined in figure 14. These data support the conclusion that the unusual cedar chemistry is probably not related to bedrock geochemistry.

Nevertheless, a small mass of geochemically unusual rock was found in the vicinity; a small pile of sulfide-bearing aggregate had been dumped by the roadside about 15 m from the cedar. The pile contained two kinds of rock: altered, mineralized rhyolite (D142203) and mineralized dolomite (D142236). Assignment of these rock types to the major units of this report is provisional, but on the assumption that both types were locally derived, the rhyolite chemistry may be judged against the Precambrian geochemical summaries and the dolomite against the Sauk geochemical summaries. The mineralized dolomite (D142236) is distinctly high in copper and could be viewed as a possible source for the high copper in the cedar, but neither rock type constitutes a realistic source for the high lead or zinc in the cedar. (In fact, it was finally concluded that the high lead, zinc, and copper reflected contamination from vehicular transport of lead-bearing ore.)

Finally, a few comments on possible future sampling are in order. The data generated in this study are exploratory and serve primarily as a guide to general ranges of geochemical variation. They are viewed as insufficient to construct a geochemical map. Sampling undertaken to produce a map always involves a judgment as to the number of samples and the sample spacing needed to insure adequate stability and resolution in the resulting pattern, and such judgments can only be based on a knowledge of the most important scales at which the natural variation occurs. Estimates of the distribution of the total geochemical variance among various ranges of scale in each of the major rock units have been given in tables 6–9, 14, 15, 17–20, and 22. These estimates are expected to be of use in planning efficient sampling programs for more detailed geochemical investigations by future workers. However, the major conclusion from the present study is that large-scale geochemical variability within any specific rock type in most of the geologic units is generally small (compared to other scales of variation), and the most useful information conveyed by the variance estimates is that sampling to define geochemical variation at large scales within units generally will not be fruitful. In fact, variation ob-

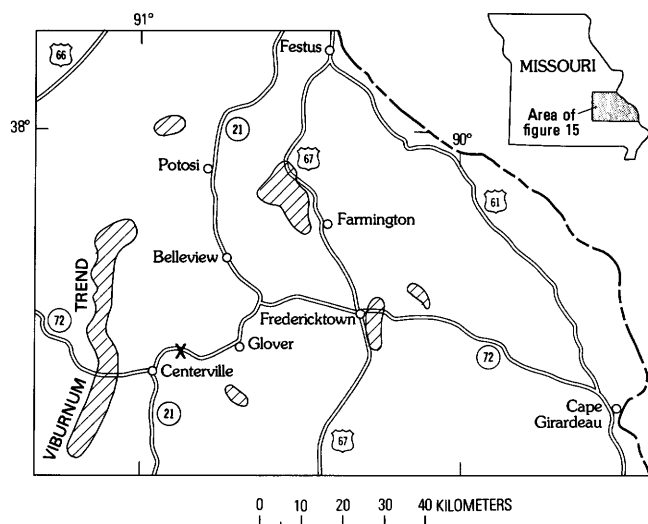


FIGURE 15.—Map showing location of cedar tree (X) with unusually high concentrations of lead, zinc, and copper. Major areas of lead mineralization are patterned. (From Connor, Shacklette, and Erdman, 1971.)

served at such scales is likely to be spurious, the result of high local variation and inadequate sampling. The major part of the total geochemical variability in the bedrock of Missouri occurs between rock types of geologic units, and the most efficient way to predict the geochemical character of the bedrock in any given locality is to use the geochemical summaries in tables 10-13, 16, 21, and 23 in conjunction with geologic maps and lithologic descriptions of the map units.

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