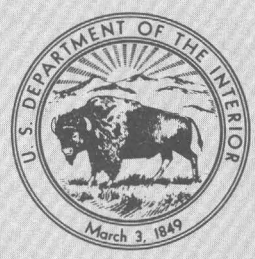
Geochemistry of Loess and Carbonate Residuum

GEOLOGICAL SURVEY PROFESSIONAL PAPER 954-G



Geochemistry of Loess and Carbonate Residuum

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

GEOCHEMICAL SURVEY OF MISSOURI

GEOLOGICAL SURVEY PROFESSIONAL PAPER 954-G

An examination of geochemical variability of two surficial geologic units in Missouri

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON: 1980

UNITED STATES DEPARTMENT OF THE INTERIOR

CECIL D. ANDRUS, *Secretary*

GEOLOGICAL SURVEY

H. William Menard, *Director*

Library of Congress Cataloging in Publication Data
Ebens, Richard J.
Geochemistry of loess and carbonate residuum.
(Geochemical survey of Missouri)
(Geological Survey Professional Paper 954-G)
Bibliography: p. 29
Supt. of Docs. no.: I 19.16:954-G
1. Loess—Missouri—Analysis. 2. Sediments (Geology)—Missouri—Analysis. I. Connor, Jon J., joint author.
II. Title. III. Series IV. Series: United States Geological Survey Professional Paper 954-G.
QE499.E23 553.6 80-607796

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

CONTENTS

	Page
Abstract	G1
Introduction	1
Acknowledgments	2
Geologic setting	2
Sampling designs	3
Loess	3
Residuum	5
Analytical methods and data evaluation	9
Geochemical variability	11
Loess	11
Bluff study	12
Geochemical variability—Continued	
Loess —Continued	
Transect study	G13
Residuum	15
Highway study	17
Final study	20
Barite ore	23
The relation of residuum to bedrock	24
Discussion	27
References cited	29

ILLUSTRATIONS

	Page
FIGURE 1. Map showing distribution of surficial geologic units in Missouri and sampling localities of loess and residuum	G4
2–13. Graphs showing:	
2. Variation of SiO_2 and Al_2O_3 in loess samples and distribution of Fe_2O_3 and CaO in loess samples	11
3. Variation of CaO and MgO in loess	12
4. Variation of Al_2O_3 and K_2O in loess	13
5. Chemical concentrations in loess that decrease as a function of distance east of the Missouri River floodplain	16
6. Chemical concentrations in loess that increase as a function of distance east of the Missouri River floodplain	17
7. Variation of SiO_2 and Al_2O_3 and the distribution of Fe_2O_3 in residuum	19
8. Variation of Al_2O_3 and K_2O in residuum	19
9. Variation of CaO and MgO in residuum	20
10. Barium, copper, lead, and zinc content in residuum	24
11. Concentrations of barium, manganese, titanium, copper, and zinc in residuum and underlying carbonate bedrock	27
12. Concentrations of silicon and aluminum in residuum and underlying carbonate bedrock	28
13. Trace element concentrations in loess and residuum in Missouri	30

TABLES

	Page
TABLE 1. Sampling localities of loess in Missouri	G6
2. Sampling localities of residuum in Missouri and Arkansas	7
3. Analytical methods for elements determined in loess and residuum	10
4. Comparison of variance components for loess in bluffs along the Mississippi and Missouri Rivers	14
5. Regression of loess chemistry with distance east of the Missouri River floodplain	15
6. Geochemical summary of loess in Missouri	18
7. Comparison of variance components for residuum of the highway study	21
8. Parameters used to assess sampling requirements in residuum	22
9. Comparison of variance components for residuum of the final study	23
10. Parameters used to assess stability in averages based on the final study	25
11. Geochemical summaries of carbonate residuum, undifferentiated by bedrock area, Missouri and northern Arkansas	25
12. Geochemical summaries of carbonate residuum, by bedrock area, in Missouri and northern Arkansas	26
13. Chemical analyses of barite ore from Missouri	26

GEOCHEMICAL SURVEY OF MISSOURI

GEOCHEMISTRY OF LOESS AND CARBONATE RESIDUUM

By RICHARD J. EBENS and JON J. CONNOR

ABSTRACT

Alluvium, loess, glacial till, and carbonate residuum are the four most prominent surficial geologic materials in the landscape of Missouri. Of these, loess and residuum are the most widespread and constitute the "parent" upon which most of the State's soils are developed. Geochemically, loess is one of the most uniform geologic materials in the State, and residuum one of the most heterogeneous.

Regional geochemical variation of loess consists principally of weak, but statistically significant, changes in concentration with distance away from the Missouri River drainage, which is the presumed source of much of the loess in the northern half of the State. Elements observed to increase away from the source are aluminum, arsenic, cobalt, copper, fluorine, gallium, iron, lithium, scandium, strontium, vanadium, and ytterbium; elements observed to decrease are barium, calcium, carbon, magnesium, manganese, silicon, sodium, phosphorus, potassium, and zirconium. The first element suite reflects an increasing clay content away from source, and the second indicates a decreasing dolomite, feldspar, zircon, apatite, and quartz content away from source. The concentration trends increase or decrease exponentially with distance.

Regional geochemical variation of residuum reflects concentration changes from one major area of bedrock to another. This variation is statistically significant for aluminum, beryllium, chromium, copper, iron, gallium, lithium, manganese, scandium, selenium, silicon, vanadium, yttrium, ytterbium, and zinc and to a large extent reflects a greater clay content in residuum over areas of Mississippian bedrock (rocks of Osagean and Meramecian age) than in residuum over areas of pre-Mississippian bedrock (including the Bonneterre, Potosi, Gasconade, Roubidoux, and Jefferson City Formations). The more aluminous residuum also appears to be higher in the rare-earth elements cerium, dysprosium, gadolinium, holmium, praseodymium, and samarium. This bedrock-related variability suggests that the residuum is at least in part truly residual, although the predictive power of residuum geochemistry as a guide to the immediately underlying rock geochemistry is low. On average, it appears that six thicknesses of parent carbonate are required to produce a unit thickness of residuum.

Samples of residuum collected in the State's lead districts were not unusually high in base metals, but many samples from the Washington County barite district were anomalously high in copper, lead, mercury, neodymium, and zinc, as well as barium; some appeared to be anomalously low in cadmium. The barite ore mined from residuum in the district is generally low in accessory elements except for a percent or so of aluminum and about half a percent of strontium.

The geochemical differences between loess and residuum and the differences among residua overlying areas of different bedrock in southern Missouri impart a complex regional geochemical pattern to the surficial geologic deposits of the State. These patterns are difficult to show on maps, however, because of insufficient knowledge of the detailed distributions of the geologic deposits themselves. Nevertheless, the geochemical summaries in this report constitute "first-order" estimates of the local geochemical background in these materials, which should prove useful in judging unusual or "anomalous" samples.

INTRODUCTION

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 data concerning the expected ranges of element concentration in ordinary near-surface environmental materials under natural conditions. A reconnaissance geochemical survey of the State of Missouri was undertaken during the years 1969–73; the object of the survey was to examine the geochemical variability of the major components of the State's landscape. The survey was undertaken in cooperation with personnel of the Environmental Health Surveillance Unit at the University of Missouri in support of their studies on the role of the geochemical environment in health and disease.

This report is one of a series describing the results of that survey and focuses on the geochemical variation observed in two widespread surficial geologic units. Previous reports have described the geochemistry of selected soils, plants, waters, and rocks (Tidball, 1976; Erdman and others, 1976a, 1976b; Feder, 1979; Connor and Ebens, 1980). Miesch (1976) gave a general statement of goals and methods of the survey. Much of the work on which the present report is based appeared in seven progress reports issued at six-month intervals during the life of the survey (U.S. Geological Survey, 1972a–f, 1973).

ACKNOWLEDGMENTS

We express our appreciation to many U.S. Geological Survey colleagues for their assistance in this study. A. T. Miesch conceived, initiated, and gave direction to the Missouri geochemical investigations as a whole. Josephine G. Boerngen assisted in computer processing of the geochemical data. Hundreds of samples of loess and residuum were analyzed in laboratories of the U.S. Geological Survey for nearly 60 elements. The analysts who performed this work are A. J. Bartel, L. A. Bradley, F. W. Brown, Mike Brown, J. W. Budinsky, C. L. Burton, J. P. Cahill, J. I. Dinnin, E. J. Fennely, W. H. Ficklin, L. D. Forshey, I. C. Frost, Johnnie Gardner, Herbert Kirschenbaum, L. M. Lee, V. 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, Jr.

We acknowledge with thanks the services and facilities provided by Dr. Carl J. Marienfeld and his associates of the Environmental Health Surveillance Unit at the University of Missouri. Personnel of the Missouri Division of Geology and Land Survey assisted us in many ways; specifically, we wish to thank W. B. Howe, State Geologist, and Larry Fellows, Assistant State Geologist.[1] Particular thanks are due Tom Boyer of National Lead Co., Steve Sitkich of Dresser Industries, Joe Rosier of Milchem, Inc., and Robert Griffey of Pfizer, Inc., for aid in sampling the barite ores of Washington County.

GEOLOGIC SETTING

Extensive deposits of unconsolidated sand, silt, and clay overlie the geologic bedrock units and underlie the soil units nearly everywhere in Missouri. In northern Missouri these deposits are heterogeneous accumulations of glacially derived sand, silt, and clay. Glaciation and deposition associated with glaciation in this region were both complex (Wickham and Lineback, 1978; Aber, 1977; Bayne and others, 1971), and temporal and spatial relations among the constituent deposits, particularly the older ones, are only poorly understood (Boellstorff, 1978; Dreeszen, 1970). Even so, these deposits are of enormous importance to the general economy of the region, because they influence the character of the agricultural soils and host a plentiful supply of potable ground water in some areas (Bayne and others, 1971).

In southern Missouri the surficial deposits consist largely of locally thick accumulations of red, cherty clay called carbonate residuum. This material is generally viewed as the residue of prolonged weathering of the carbonate bedrock. Soils developed on these clays are generally acid and of low fertility; as a consequence, they are commonly used for pasturage (Wisconsin University, 1960, p. 101–102). Also, extensive deposits of alluvial sand, silt, and clay lie along floodplains of the major rivers. The most prominent of these deposits occurs in the Mississippi River floodplain of southeasternmost Missouri, where the alluvium locally thickens to as much as 70 m (Fuller, 1977). Soils developed on these materials tend to be young with little profile development (Wisconsin University, 1960, p. 22–23). Minor areas in southeastern Missouri and a major area in western Missouri are underlain by noncarbonate bedrock. Weathering of bedrock in these areas gives rise to a silt-clay residuum which tends to be geochemically similar to the underlying bedrock.

A highly generalized map showing the distribution of these surficial geologic materials is given in figure 1. Of these materials, loess and residuum form the most visible part of the Missouri landscape. Thick accumulations of loess along the Missouri and Mississippi Rivers weather to vertical cliffs, and residuum colors roadcuts and excavations a deep red or red-brown throughout southern Missouri.

Loess in Missouri consists of wind-laid deposits of silt and clay accumulated during the latter half of the Pleistocene Epoch. It is thickest on bluffs above the Missouri and Mississippi Rivers, whose floodplains constitute the sources of the loess, but it occurs in lesser thicknesses over large parts of the State. The loess deposits have been assigned to the Bignell and Peoria Loesses and the Roxana(?) Silt of Wisconsin age and to the Loveland Loess of Illinoian age. The thickest accumulations, in northwesternmost Missouri (fig. 1), consist largely of the Peoria Loess (Bayne and others, 1971, p. 7–8). In Iowa, Wisconsin loess has been dated at 29,000 to 14,000 years old with the older deposits being closer to the source (Ruhe, 1969, p. 29). In contrast, residuum tends to be much older, as it occurs in areas that have been subjected to subaerial weathering for tens of millions of years.

In sampling loess and residuum in this study, a conscious effort was made to exclude the *A* and *B* soil horizons, if recognizable, of the present-day soil profile. In general, loess in deposits less than a meter or so thick tended to be severely weathered. Where more than a few meters thick, residuum commonly displayed in its upper parts the color mottling and clay accumulation typical of soil development. Below this weathered cap, however, it tended to be uniformly red

[1]Now State Geologist at Arizona Bureau of Geology and Mineral Technology.

or red-brown and, in places, distinctly stratified, which likely reflects relict bedding. Neither alluvium nor till were sampled in this work. Alluvium is a quantitatively minor part of the surficial geologic cover in the State, and till is in general poorly exposed.

SAMPLING DESIGNS

Geochemical variability in loess and residuum was examined in part through the use of hierarchical sampling plans designed to estimate the proportions of the total geochemical variance occurring over selected ranges of scale (Miesch, 1976). Such designs are exploratory and are based on a system of hierachically arranged sampling units such that each 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 (Miesch, 1976)

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

where X_{ijklmn} represents an analytical value for a given element reported on a sample of some landscape material by the laboratory; μ represents the grand average logarithmic concentration for that material; α, β, γ, and η (with subscripts) are deviations reflecting geochemical variation arising at decreasing geographic scales; and ϵ_{ijklmn} represents the difference between the logarithm of the reported concentration and the true logarithmic concentration in the analyzed sample. Logarithms of concentration are commonly employed in trace-element work to help meet some of the assumptions underlying the statistical procedures used in data analysis (Miesch, 1976, p. 27). The model in equation (1) is discussed in mathematical detail in the context of a geochemical field problem by Krumbein and Slack (1956).

The target population in this study is the aggregate of all potential samples of loess and residuum in the study area. A sample is defined as a few kilograms of material cut or dug from a homogeneous part (generally a single stratum) of the unit. Because the only collecting tools used were geologic pick or shovel, the sampled population was confined to areas of natural or artificial exposure, largely roadcuts. In order to minimize personal bias in estimating the statistical properties of the units, an attempt was made to collect samples for the hierarchical designs at randomly selected locations in outcrop. This selection depended on outcrop distribution, but was considered effectively random because the outcrop distribution is controlled by a large number of geologic and human factors. In order to minimize analytical bias, all samples and analytical splits were submitted to the laboratory in a randomized sequence.

LOESS

Two independent studies of loess geochemistry were undertaken. Samples for the first study (termed the bluff study) were collected in the fall of 1970 from thick loess deposits cropping out in the bluffs above the Missouri and Mississippi Rivers. Sampling localities for this study are shown in figure 1 and specific locations are listed in table 1.

For this study, the bluffs along the two rivers were divided into six segments (areas), each approximately 150 km long. Within each of these segments, two subsegments, each a few kilometers long, were selected randomly, and two samples were taken randomly from the best exposed section in the subsegment. The statistical model used in this study was modified from equation (1), as follows

$$\log X_{ijkl} = \mu + \beta_i + \gamma_{ij} + \delta_{ijk} + \epsilon_{ijkl}, \quad (2)$$

where β_i represents the difference between μ and the average logarithmic concentration of the ith bluff segment; γ_{ij} represents the difference between the average of the jth stratigraphic section and the average of the ith segment; and δ_{ijk} represents the difference between the averages of the kth sample and the jth section.

Four components of variance were estimated:

$$S^2_{\log X} = S^2_\beta + S^2_\gamma + S^2_\delta + S^2_\epsilon. \quad (3)$$

These components reflect variation among segments (S^2_β, representing geochemical variation at scales greater than about 150 km), variation between stratigraphic sections within segments (S^2_γ, representing geochemical variability at scales less than about 150 km), variation between samples within sections (S^2_δ), and analytical variation (S^2_ϵ). The analytical variance was estimated in a very approximate way from replicate analyses of three samples of loess.

The sample design used in the bluff study was a Stage 2a design, as described by Connor and others (1972), and was designed to examine scale-related variation in the thick (better developed) parts of the loess blanket of Missouri. A second study, undertaken in 1972, was aimed at examination of the geochemistry of the thinner (less well-developed) deposits blanketing regions away from the major drainage as well. Because the Missouri River valley is the apparent source for much of the loess deposited in northern Missouri, three

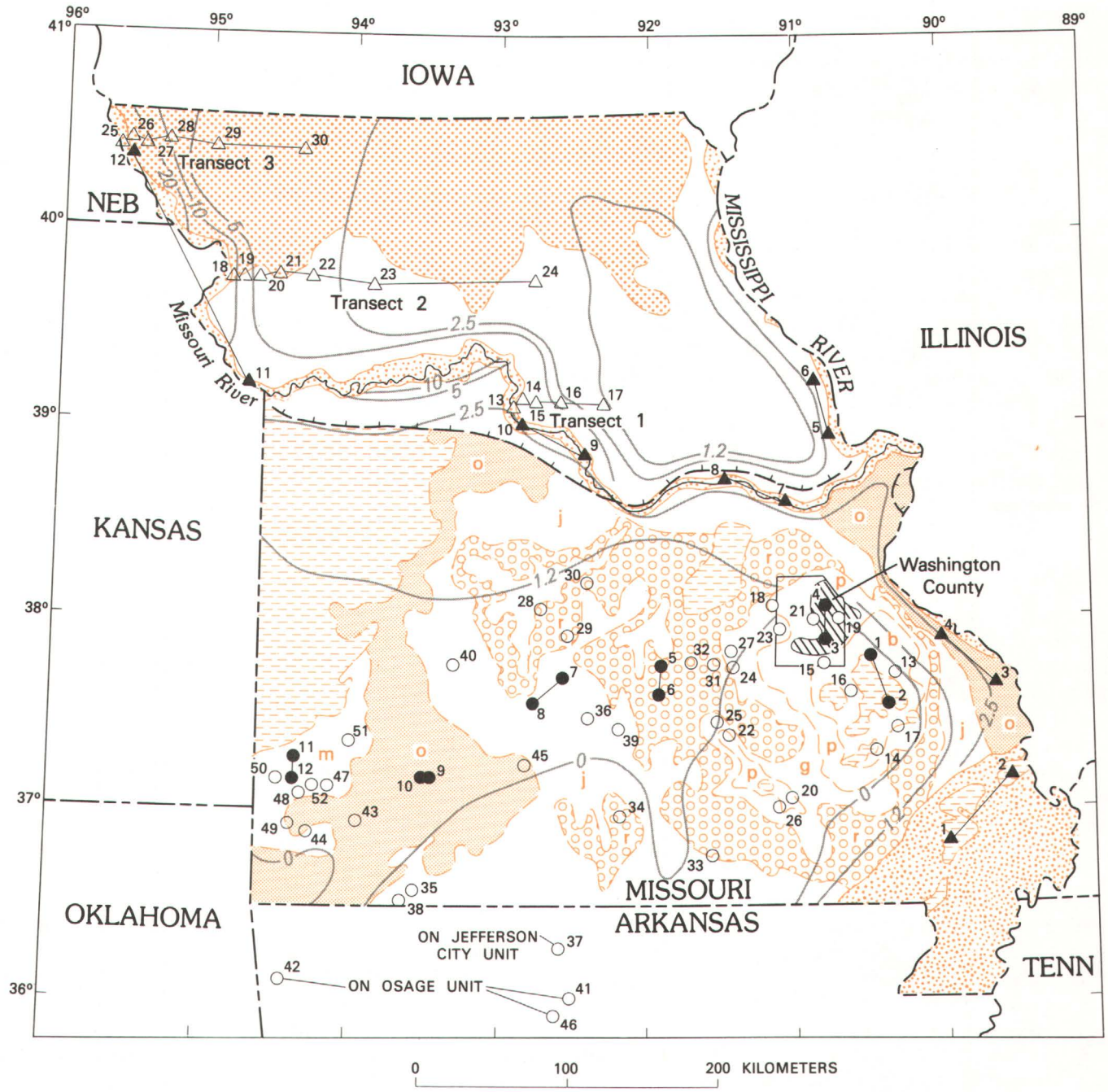


FIGURE 1.—Distribution of surficial geologic units in Missouri and sampling localities of loess and residuum. The four sampling localities within the Washington County barite district are all on the Potosi bedrock unit. (Adapted from Oetking and others, 1966; McCracken, 1961; and Stout and Hoffman, 1973.)

east-west transects were sampled east of this river to measure downwind changes in composition (fig. 2).

The longest transect was the middle one (transect 2), which followed U.S. Route 36 eastward from St. Joseph, Mo. The southernmost transect (transect 1) followed State Route 124 east of Lisbon, Mo., and the northernmost (transect 3) followed U.S. Route 136 east of Rockport. Along each transect, sampling localities were spaced at approximate geometric intervals of 0.75, 1.5, 3, 6 . . . km from the edge of the Missouri River floodplain as far eastward as recognizable loess could be found. In each locality, three samples of loess were collected randomly from the best exposed vertical section of loess.

These samples were tested for the presence of downwind geochemical trends by regression analysis:

EXPLANATION

ALLUVIUM

GLACIAL DEPOSITS (Present north of limit of glaciation; dotted area contains deposits locally greater than 30 m thick)

CARBONATE RESIDUUM
(Distributions approximate; shown only south of limit of glaciation)

m — On the Meramec bedrock unit

o — On the Osage bedrock unit

j — On the Jefferson City bedrock unit

r — On the Roubidoux bedrock unit

g — On the Gasconade bedrock unit

p — On the Potosi bedrock unit

b — On the Bonneterre bedrock unit

SILT-CLAY RESIDUUM

WASHINGTON COUNTY BARITE DISTRICT

SOUTHERN LIMIT OF GLACIATION

—5— APPROXIMATE MAXIMUM THICKNESS OF LOESS IN METERS

SAMPLING LOCALITIES

▲ Loess-Bluff study

△ Loess-Highway study

● Residuum-Highway study

○ Residuum-Final study

$$\log X = a + b \cdot \log(\text{km}) + r. \quad (4)$$

Here, X is the concentration of an element in a sample as reported by the laboratory, a is the estimated logarithmic concentration at a distance of 1 km (estimated from the regression), and b is the slope of the geochemical trend away from presumed source. The last term, r, represents the difference between the estimated logarithmic concentration in the sample and the actual logarithmic concentration.

The total variation ($S^2_{\log X}$) observed along a transect may be subdivided into two components:

$$S^2_{\log X} = S^2_\tau + S^2_\rho, \quad (5)$$

where S^2_τ is that part of the total observed variance accounted for by the trend and S^2_ρ is the remainder. The first component (S^2_τ) is similar in meaning to S^2_β and S^2_γ combined of equation (3); S^2_ρ is not equal to S^2_ϵ in equation (3), because it contains variation attributable to more than just analytical error. S^2_ρ, however, does contain S^2_ϵ within it. Although neither S^2_τ nor S^2_ρ have been computed here, S^2_τ may be computed from

$$S^2_\tau = cb^2, \quad (6)$$

where b is as defined in equation (4) and c is equal to 0.2719 for transect 1, 0.4833 for transect 2, and 0.3700 for transect 3. The values of S^2_ρ can be computed from

$$S^2_\rho = S^2_{\log X} - S^2_\tau. \quad (7)$$

RESIDUUM

Two studies of residuum were undertaken also: a preliminary (highway) study in 1970 and a final study in 1972. Sampling localities for both studies are shown in figure 1; specific sample localities are listed in table 2. In both studies, residuum was classified according to the major bedrock unit over which it lay. The bedrock units were those appearing on the State geologic map published by the State of Missouri (McCracken, 1961). The residuum units used in the highway study were areas overlying (1) the Bonneterre Formation and the Elvins Group; (2) the Potosi and Eminence Formations; (3) the Roubidoux Formation; (4) the Jefferson City, Cotter, Powell, and Smithville Formations; (5) the rocks of the Osage Series; and (6) the rocks of the Meramec Series. A seventh residuum unit, the area overlying the Gasconade Formation, was added to the final study (1972). For convenience, these residuum units will be referred to in this report as the Bonneterre, Potosi, Roubidoux, Jefferson City, Osage, Meramec, and Gasconade residuum units, respectively (fig. 1).

In the highway study, six samples each were collected from the Bonneterre, Potosi, Roubidoux, Jefferson City, Osage, and Meramec residuum units. Because one object of this particular study was to examine the geochemical relation of residuum to the underlying bedrock (in addition to estimating scale-related components of variance), sampling localities were restricted to exposures where bedrock could be sampled along with the overlying residuum. As a consequence, all sampling was done along a few major highways where the probability of finding such exposures seemed greatest; thus, the use of the term "highway study" in this report.

TABLE 1.—*Sampling localities of loess in Missouri*

[Localities shown in figure 1]

Locality No.	Field No.	County	Site description[1]	Thickness (m)	Comments
1	REOL-01, 02	Stoddard-------	In quarry 2.3 km NE. jct. U.S. 60 State--Rt. 25.	1.8	Rootlets.
2	03, 04	Scott----------	On U.S. 61, 3.2 km S. of Kelso----------	4.6	
3	05, 06	Perry----------	On County Rt. A, E. edge of Altenburg----	7.6	
4	07, 08	Ste. Genevieve-	On U.S. 61, 0.8 km S. of Aux Vase R------	9.1	
5	09, 10	Lincoln--------	At jct. of State Rts. 79 and 47----------	1.8	Weathered.
6	11, 12	Pike-----------	On County Rt. W. 3.2 km S. of Paynesville	.9	B-horizon?
7	13, 14	Warren---------	In quarry 2.3 km NE. of Marthasville-----	4.6	
8	15, 16	----do---------	On State Rt. 94, 6.4 km E. of McKittrick-	3.1	
9	17, 18	Boone----------	On County Rt. K, 1.6 km E. of McBaine----	4.6	
10	19, 20	Howard---------	On County Rt. J, 1.6 km E. of Petersburg-	6.1	
11	21, 22	Platte---------	On State Rt. 45, 3.2 km W. of State Rt. 9	4.6	
12	23, 24	Atchison-------	On U.S. 136, 3.2 km E. of Rock Port------	9.1	
13	E2L-111, 112, 113	Howard---------	On County Rt. K, 0.7 km E. of Lisbon-----	6.1	
	121, 122, 123	---do----------	On County Rt. K, 1.5 km E. of Lisbon-----	3.1	Soil(?).
	131, 132, 133	---do----------	On County Rt. K, 3 km E. of Lisbon-------	1.8	Do.
14	141, 142, 143	---do----------	On State Rt. 87, 6 km NE. of Lisbon------	3.7	
15	151, 152, 153	---do----------	On County Rt. J, 5 km W. of Fayette------	1.5	Soil(?).
16	161, 162, 163	---do----------	On State Rt. 124, 6.5 km E. of Fayette---	1.8	Do.
17	171, 172, 173	Boone----------	At jct. of U.S. 63 and State Rt. 124-----	1.8	Do.
18	211, 212, 213	Buchanan-------	On U.S. 36, 1 km E. of Missouri R--------	7.6	
	221, 222, 223	---do----------	On U.S. 36, 1.5 km E. of Missouri R------	4.6	
	231, 232, 233	---do----------	On U.S. 36, 3 km E. of Missouri R--------	6.1	
19	241, 242, 243	---do----------	On U.S. 36, 0.5 km E. of I-29----------	3.1	
20	251, 252, 253	---do----------	At jct. of U.S. 36 and County Rt. C------	1.8	
21	261, 262, 263	DeKalb---------	On U.S. 36, 4 km W. of Stewartsville-----	1.2	Soil(?).
22	271, 272, 273	---do----------	On U.S. 36, 4 km E. of Osburn----------	.2	
23	281, 282, 283	Caldwell-------	On U.S. 36, 3 km S. of Breckenridge------	.9	Soil(?).
24	291, 292, 293	Macon----------	On U.S. 36, 2 km SE. of New Cambria------	.9	Do.
25	311, 312, 313	Atchison-------	On U.S. 136, 0.5 km E. of Missouri R----- floodplain.	6.1	
	321, 322, 323	---do----------	On U.S. 136, 1.5 km E. of Missouri R----- floodplain.	9.1	
	331, 332, 333	---do----------	On U.S. 136, W. edge of Rock Port--------	4.6	
26	341, 342, 343	---do----------	On U.S. 136, at jct. with County Rt. Y---	6.7	
27	351, 352, 353	---do----------	On U.S. 136, 4 km SW. of Tarkio----------	4.6	
28	361, 362, 363	---do----------	On County Rt. M, 1 km N. of U.S. 136-----	1.5	Weathered.
29	371, 372, 373	Nodaway--------	2.5 km NE. of Wilcox----------	1.5	Do.
30	381, 382, 383	Worth----------	3.5 km NW. of Denver----------	.9	Do.

[1]Abbreviations: jct., junction; Rt., Route; R., River.

In this study, two localities of the required kind were selected, randomly if possible, from each residuum unit along the chosen highway. Within each locality, two sections of residuum were selected randomly; in one of these sections, two random samples were collected; in the other, one sample was taken randomly, for a total of 36 samples.

The pairing of sampled sections in each locality required that in S^2_γ in equation (3) be redefined as two components, so the statistical model used in this study was modified from equation (1) as follows:

$$\log X_{ijklm} = \mu + \beta_i + \theta_{ij} + \kappa_{ijk} + \delta_{ijkl} + \epsilon_{ijklm}, \quad (8)$$

where β_i represents the difference between μ and the average logarithmic concentration in the ith residuum unit (area of bedrock); θ_{ij} represents the difference between the average (in logs) of the jth locality and the average of the ith unit; κ_{ijk} represents the difference between the average (in logs) of the kth stratigraphic section and the average of the jth locality; and δ_{ijkl} represents the difference between the average (in logs) of the lth sample and the average of the kth section. The term γ_{ij} in equation (2) is here represented by $(\theta_{ij} + \kappa_{ijk})$.

The five components of variance were estimated as

$$S^2_{\log X} = S^2_\beta + S^2_\theta + S^2_\kappa + S^2_\delta + S^2_\epsilon. \quad (9)$$

where S^2_β reflects variation among the six residuum units, S^2_θ represents variation between localities within units, S^2_κ represents variation between sections within localities, S^2_δ represents variation between samples

TABLE 2.—*Sampling localities of residuum in Missouri and Arkansas*

[All localities in Missouri except 37, 41, 42, and 46; localities shown in fig. 1. A sample of bedrock was collected at both residuum sites in each of the first 12 localities]

Locality No.	Field No.	County	Site description[1]	Thickness (m)	Underlying bedrock unit[2]
1	REOR-R01	St. Francois----	On U.S. 67, 5.6 km S. of Flat R. exit-----	3.1	Bonneterre.
	R02, R02D	----do----------	On U.S. 67, 1 km S. of Flat R. exit-------	1.2	Do.
2	R03	Madison---------	On U.S. 67, 1.1 km S. of Fredericktown---- exit.	1.5	Do.
	R04, R04D	----do----------	On U.S. 67 at Fredericktown exit----------	4.6	Do.
3	R05, R05D	Washington------	On State Rt. 21, 1.1 km S. of County Rt. E	4.6	Potosi.
	R06	----do----------	On State Rt. 21, 3.7 km S. of State Rt. 8-	.6	Do.
4	R07	----do----------	On State Rt. 47, 2.4 km N. of State Rt. 21	1.5	Do.
	R08, R08D	----do----------	On State Rt. 47, 0.3 km N. of State Rt. 21	1.2	Do.
5	R09	Phelps----------	On U.S. 63, 4.7 km S. of Yancy Mills------	23	Roubidoux.
	R10, R10D	----do----------	On U.S. 63, 1.8 km S. of Yancy Mills------	6.1	Do.
6	R11, R11D	Texas-----------	On U.S. 63, 0.2 km N. of County Rt. CC----	3.1	Do.
	R12	Phelps----------	On U.S. 63 at Phelps-Texas County line----	3.1	Do.
7	R13	Laclede---------	On U.S. 66, 6 km W. of County Rt. T-------	3.1	Jefferson City
	R14, R14D	----do----------	On U.S. 66, 6.6 km W. of County Rt. T-----	3.1	Do.
8	R15, R15D	----do----------	On U.S. 66, 1.8 km NE. of County Rt. A----	1.5	Do.
	R16	----do----------	On U.S. 66, 0.5 km NE. of County Rt. A----	6.1	Do.
9	R17	Greene----------	On I-44, 2.4 km E. of County Rt. N--------	1.5	Osage.
	R18, R18D	----do----------	On I-44 at County Rt. MM exit------------	3.1	Do.
10	R19	----do----------	On I-44, 3.1 km E. of County Rt. PP-------	3.2	Do.
	R20, R20D	----do----------	On I-44, 3.7 km E. of County Rt. PP-------	4.6	Do.
11	R29, R29D, R30.	Jasper----------	On U.S. 71, 2.4 km S. of County Rt. M-----	3.1	Meramec.
12	R31	----do----------	On U.S. 66, 0.4 km E. of State Rt. 96-----	1.5	Do.
	R32, R32D	----do----------	In quarry 1.5 km NW. of Spring R. and----- U.S. 71.	3.1	Do.
13	E2R-B011, B012	St. Francois----	On U.S. 67, 0.5 km S. of County Rt. DD----	2.1	Bonneterre.
	B013, B014	----do----------	On U.S. 67, 2 km S. of County Rt. T-------	1.5	Do.
14	B021, B022	Wayne-----------	On U.S. 67, 1 km S. of Coldwater----------	7.6	Do.
	B023, B024	----do----------	On U.S. 67, 3 km S. of Coldwater----------	3.1	Do.
15	B032	Washington------	On County Rt. M, 3.5 km E. of State Rt. 21	1.8	Do.
	B033, B034	----do----------	On County Rt. M, 2 km E. of State Rt. 21--	1.5	Do.
	B041, B042	----do----------	On County Rt. JJ, 0.2 km S. of Belgrade---	3.1	Do.
	B043, B044	----do----------	On County Rt. JJ, 2.1 km S. of Belgrade---	.9	Do.
16	B051, B052	Iron------------	On County Rt. JJ. 0.5 km S. of State Rt. 72	1.5	Do.
	B053, B054	----do----------	On County Rt. JJ, 4 km S. of State Rt. 72-	2.1	Do.
17	B071, B072	Madison---------	On U.S. 67, 1.8 km N. of County Rt. JJ----	9.1	Do.
	B073, B074	----do----------	On U.S, 67, 3.5 km N. of County Rt. JJ----	6.1	Do.
18	P011, P012	Crawford--------	On County Rt. N, 1.8 km E. of Meramac R---	.9	Potosi.
	P013, P014	----do----------	On County Rt. N at Washington County line-	2.4	Do.
19	P021, P022	Washington------	On road 7.5 km NW. of Old Mines----------	1.2	Do.
	P023, P024	----do----------	On road 7.3 km NW. of Old Mines----------	.6	Do.
	P031, P032	----do----------	On County Rt. E, 0.6 km S. of State Rt. 47	.6	Do.
	P033, P034	----do----------	On County Rt. E, 1.2 km S. of State Rt. 47	.6	Do.
20	P041, P042	Carter----------	On County Rt. D, 11 km N. of Van Buren----	9.1	Do.
	P043, P044	----do----------	On County Rt. D, 9 km N. of Van Buren-----	3.1	Do.
21	P051, P052, P053, P054.	Washington------	On County Rt. F, 5.5 km NW. of Potosi-----	3.1	Do.
22	P061, P062	Shannon---------	On County Rt. A, 5.5 km E. of State Rt. 19	6.1	Do.
	P063, P064	----do----------	On County Rt. A, 5.3 km E. of State Rt. 19	.9	Do.
23	G011, G012	Washington------	On road 1.2 km S. of State Rt. 8, about--- 4 km E. of county line.	3.7	Gasconade.
	G013, G014	----do----------	On State Rt. 8, 3 km E. of county line----	1.2	Do.
24	G021, G022	Dent------------	On State Rt. 19, 1.8 km SW. of Meramac R--	2.4	Do.
	G023, G024	----do----------	On State Rt. 19, 1.6 km SW. of Meramac R--	7.6	Do.
25	G041, G042	----do----------	On road 3 km E. of jct. of State Rt. 19--- and County Rt. WW.	1.2	Do.
	G043, G044	----do----------	On road 3.7 km NE. of jct. of State Rt. 19 and County Rt. WW.	.9	Do.

TABLE 2.—*Sampling localities of residuum in Missouri and Arkansas*—Continued

Locality No.	Field No.	County	Site description[1]	Thickness (m)	Underlying bedrock unit[2]
26	G051, G052	Carter----------	On County Rt. M, 2.5 km NW. of Van Buren--	1.5	Do.
	G053, G054	----do----------	On County Rt. M, 5 km NE. of Van Buren----	1.8	Do.
27	G061	Crawford--------	On County Rt. M, 2.5 km N. of Cook Station	.9	Do.
	G063, G064	----do----------	On County Rt. YY, 1.5 km NW. of Cook------ Station.	.6	Do.
28	G071, G072	Camden----------	On U.S. 54, 3 km NE. of Camdenton---------	1.5	Do.
	G073, G074	----do----------	On County Rt. V, 1 km S. of Linn Creek----	1.5	Do.
29	E2R-R011, R012, R013, R014.	Camden----------	On State Rt. 7, 2 km E. of jct. with------ County Rt. T.	.9	Roubidoux.
30	R022	Miller----------	On State Rt. 17, 2.5 km SE. of State R. 52	1.8	Do.
	R023, R024	----do----------	On State Rt. 17, 3 km SE. of State Rt. 52-	1.5	Do.
31	R041, R042	Dent------------	On County Rt. JJ, 5 km N. of State Rt. 19-	.9	Do.
	R043, R044	----do----------	On County Rt. JJ, 3.5 km NE. of State Rt.- 19.	1.2	
32	R051, R052	----do----------	On State Rt. 72, 0.8 km N. of Lake Spring-	.9	Do.
	R053, R054	Phelps----------	On State Rt. 72, 2.1 km N. of Lake Spring-	.9	Do.
33	R061, R062	Oregon----------	On U.S. 160, 2.1 km S. of State Rt. 99----	1.5	Do.
	R063, R064	----do----------	On U.S. 160, 1.9 km S. of State Rt. 99----	3.1	Do.
34	R071, R072	Douglas---------	On State Rt. 76, 4 km W. of State Rt. 181-	1.5	Do.
	R073, R074	----do----------	On State Rt. 76, 1.2 km W. of State Rt. 181	4.6	Do.
35	J011, J012	Stone-----------	On County Rt. H, 2 km E. of State Rt. 39--	1.5	Jefferson City.
	J013, J014	----do----------	On County Rt. H, 0.8 km E. of State Rt. 39	1.2	Do.
36	J021, J022	Laclede----------	On County Rt. O, 0.8 km W. of County Rt. AD	1.2	Do.
	J023, J024	Wright----------	On County Rt. AF, 0.6 km S. of county line	.9	Do.
37	J041, J042	Marion (Ark.)---	On State Rt. 101, 3 km SE. of U.S. 62-----	1.8	Do.
	J043, J044	----do----------	On State Rt. 101, 0.9 km SE. of U.S. 62---	3.1	Do.
38	J051, J052, J053, J054.	Barry-----------	On State Rt. 86, 2 km W. of State Rt. 39--	1.2	Do.
39	J061, J062, J063, J064.	Texas-----------	On County Rt. M, 2.3 km W. of State Rt. 17	1.2	Do.
40	J071, J072	Polk------------	On State Rt. 64, 2.2 km E. of County Rt. D	1.5	Do.
	J073, J074	----do----------	On State Rt. 64, 1.3 km E. of County Rt. D	.9	Do.
41	0011, 0012	Searcy (Ark.)---	On State Rt. 14, 4 km N. of Harriet-------	3.1	Osage.
	0013, 0014	----do----------	On State Rt. 14, 1.5 km N. of Harriet-----	.6	Do.
42	0021, 0022	Washington (Ark)	On State Rt. 16, 1 km E. of Benton County- line.	.9	Do.
	0023, 0024	Benton (Ark.)---	On State Rt. 16, 1.2 km SE. of Osage Creek	.9	Do.
43	0031, 0032	Lawrence--------	On U.S. 60, 2 km S. of Verona-------------	4.6	Do.
	0033, 0034	----do----------	On U.S. 60 at Barry County line-----------	7.6	Do.
44	0041, 0042	Newton----------	On County Rt. D, 2.5 km W. of Boulder City	7.6	Do.
	0043, 0044	----do----------	On County Rt. D, 1.5 km W. of Boulder City	3.1	Do.
45	0051, 0052	Webster---------	On road 3.5 km SW. of jct. of County Rt. C and County Rt. P.	.9	Do.
	0053, 0054	----do----------	On road 3 km NW. of jct. of County Rt. C-- and County Rt. V.	.6	Do.
46	0061, 0062	Searcy (Ark.)---	On State Rt. 74, 2.9 km W. of Dongola-----	2.4	Do.
	0063, 0064	----do----------	On State Rt. 74, 2.1 km W. of Dongola-----	2.1	Do.
47	M011, M012	Jasper----------	On State Rt. 37, 2.5 km N. of County Rt. F	4.6	Meramec.
	M013, M014	----do----------	On State Rt. 37, 1.2 km N. of County Rt. F	4.6	Do.
48	M021, M022	----do----------	On U.S. Alt. 71, 2 km N. of I-44----------	6.1	Do.
	M023, M024	----do----------	On U.S. Alt. 71, 3.8 km N. of I-44--------	3.7	Do.
49	M031, M032	Newton----------	On U.S. 60, 5.5 km W. of U.S. 71----------	1.5	Do.
	M033, M034	----do----------	On U.S. 60, 3.5 km W. of U.S. 71----------	.6	Do.
50	M061, M062	Jasper----------	On U.S. 66, 2.5 km NE. of Carterville-----	1.8	Do.
	M063, M064	----do----------	On road 3.2 km E. of Carterville----------	1.2	Do.
51	M071, M072	Dade------------	On U.S. 160, 0.4 km E. of Lockwood--------	1.5	Do.
	M073, M074	----do----------	On U.S. 160, 1.2 km E. of Lockwood--------	1.2	Do.
52	M081, M082	Jasper----------	On County Rt. F, 3.8 km W. of State Rt. 37	.9	Do.
	M083, M084	----do----------	On County Rt. F, 6.9 km W. of State Rt. 37	1.2	Do.

[1]Abbreviations: jct., junction; Rt., Route; R, River; Alt., Alternate.

[2]McCracken (1961).

within sections, and S_ϵ^2 represents analytical variation. Geographic scales represented by these components are similar to the distances represented in the study of loess, except that S_θ^2 reflects variation arising at scales of about 3–150 km, and S_κ^2 reflects variation arising at scales less than about 3 km (the approximate dimension of a sampling locality).

The highway study was employed (not wholly successfully) as a Stage 2a sampling scheme to design the final study (a Stage 2b scheme, Connor and others, 1972). The final study was then used to estimate averages for each residuum unit. In the final study, 24 samples of residuum were collected from each of seven units—the six units of the highway study plus the Gasconade residuum unit. In addition, the study areas for the Jefferson City and Osage residuum units were expanded to include areas of occurrence in northern Arkansas. The 24 samples in each unit were collected from six localities (each about 3 km across). These localities were located randomly in each unit, two sampling sites were randomly located in a section of exposed residuum at each locality, and two samples were taken randomly from each section. The same statistical model was used in the final study as was used in the highway study (equation 8). Of the total of 168 samples collected in the final study, 25 were split prior to analysis for estimation of analytical error. After chemical analysis, three samples—one each from localities 15, 27, and 30 (fig. 1)—were discarded because they contained too much carbonate for estimation of a proper geochemical background for residuum. Thus, the final study was based on the geochemistry of 165 samples.

The only important chemical resource in the surficial materials of Missouri is barite. Commercial quantities are mined from residuum in Washington County in southeastern Missouri (fig. 1). Accordingly, eight samples of barite ore that had been prepared for grinding were collected for trace element analysis from four milling sites and analyzed. No formal sampling design was used in this part of the study.

ANALYTICAL METHODS AND DATA EVALUATION

All analyses were performed in laboratories of the U.S. Geological Survey. The analytical data on which this report is based are given in Boerngen, VanTrump, and Ebens (1975), except for the data on barite, which are given below (table 13). The samples collected during the course of this work were analyzed for a variety of elements (table 3). Much of the trace element analysis was based on a semiquantitative emission spectrographic technique that was slightly revised from that described in Myers, Havens, and Dunton (1961). This technique was supplemented by methods based on X-ray fluorescence, atomic absorption, neutron activation analysis, and specialized techniques for determining fluorine and arsenic concentrations. Details of the analytical procedures are given in Miesch (1976).

In the laboratory, each sample was ground in a ceramic mill to 150-μm (minus-100-mesh) particle size. Before being ground, a randomly selected subset of each material was divided into two parts with a splitter, so that analytical variance could be estimated. The samples of each material in each study were analyzed in a randomized batch. Each sample was routinely analyzed for 55 elements, one of these being carbon, which was measured in both its organic and inorganic (carbonate) forms. Then, depending on composition, some samples were checked for 15 additional elements, most of them rare-earth elements. Of this total, about 30 elements were consistently detected.

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 may substantially exceed 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 than the arithmetic mean. 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 range GM/GD to $GM \times GD$. About 95 percent should fall within the range $GM/(GD)^2$ to $GM \times (GD)^2$, and more than 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 cases 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) which 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.

Analysis of variance procedures, however, require

TABLE 3.—*Analytical methods, with approximate lower limits of determination, for elements determined in the geochemical study of loess and residuum*

Element	Analytical method	Lower limit of determination (ppm)
Ag	Spectrographic	0.5
Al	X-ray fluorescence	5300
As	Colorimetric	1
B	Spectrographic	20
Ba	----do	1.5
Be	----do	1
C (Tot)	Gasometric	400
C (CO_3)	----do	500
C (Org)	Calculated	1000
Ca	Spectrographic	20
Ca	X-ray fluorescence	710
Cd	Atomic absorption	1
Ce	Spectrographic	150
Co	----do	2
Cr	----do	1
Cu	----do	1
Dy	----do	50
F	F-selective ion electrode	10
Fe	Spectrographic	10
Fe	X-ray fluorescence	700
Ga	Spectrographic	5
Gd	----do	70
Hg	Flameless atomic absorption	.01
Ho	Spectrographic	70
I	Neutron activation	.2
K	X-ray fluorescence	830
La	Spectrographic	30
Li	Atomic absorption	5
Mg	----do	60
Mn	Spectrographic	1
Mo	----do	3
Na	Atomic absorption	74
Nb	Spectrographic	10
Nd	----do	70
Ni	----do	5
P	X-ray fluorescence	130
Pb	Spectrographic	10
Pr	----do	150
Sc	----do	5
Se	X-ray fluorescence	.1
Si	Spectrographic	20
Si	X-ray fluorescence	4700
Sm	Spectrographic	100
Sr	----do	5
Ti	----do	2
V	----do	7
Y	----do	10
Yb	----do	1
Zn	Atomic absorption	10
Zr	Spectrographic	10

completely uncensored data, and the following arbitrary practice was used where necessary to circumvent problems of censoring. If less than a third of the frequency distribution of any element subjected to analysis of variance 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 (represented by one or more pairs of sampled stratigraphic sections of surficial material) 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 by repetition of the field sampling and laboratory analysis. Thus, it is useful to identify those situations where the area means are 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 tables and graphs summarizing the geochemical data.

A basic criterion for the sufficiency of differences among area 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 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_s, be smaller than a critical value, E_r. E_r is the maximum permissible variance (at a given probability level) for an area mean where the F-statistic is defined as

$$F = 1 + n_r v, \tag{10}$$

where v for loess is defined as

$$v = S_\beta^2/(S_\gamma^2 + S_\delta^2 + S_\epsilon^2), \tag{11}$$

and where v for residuum is defined as

$$v = S_\beta^2/(S_\theta^2 + S_\kappa^2 + S_\delta^2 + S_\epsilon^2). \tag{12}$$

In equation (10), F uses 1 and $2n_r - 2$ degrees of freedom for a test of significance 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). E_s for loess is computed as

$$E_s = \frac{S_\gamma^2}{n_\gamma} + \frac{S_\delta^2}{n_\gamma n_\delta} + \frac{S_\epsilon^2}{n_\gamma n_\delta n_\epsilon}, \quad (13)$$

and E_s for residuum is computed as

$$E_s = \frac{S_\theta^2}{n_\theta} + \frac{S_\kappa^2}{n_\theta n_\kappa} + \frac{S_\delta^2}{n_\theta n_\kappa n_\delta} + \frac{S_\epsilon^2}{n_\theta n_\kappa n_\delta n_\epsilon}. \quad (14)$$

The subscripted n's in equations (13) and (14) represent the number of sampling units at each level of the hierarchical design. In practice, n_ϵ in both equations is set to 1 because of incomplete duplication of sample splits. Further, in the highway study (residuum, equation 14), n_δ was also set to 1 because of incomplete duplication of samples within each stratigraphic section. Finally, E_r for loess is computed as

$$E_r = (S_\gamma^2 + S_\delta^2 + S_\epsilon^2)/n_r, \quad (15)$$

and E_r for residuum is computed as

$$E_r + (S_\theta^2 + S_\kappa^2 + S_\delta^2 + S_\epsilon^2)/n_r. \quad (16)$$

Where E_r is larger than E_s, 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 (equations 11 and 12).

GEOCHEMICAL VARIABILITY

LOESS

Loess consists principally of quartz and clay and contains minor amounts of dolomite, potassium-feldspar and plagioclase. X-ray diffraction traces of many samples show distinct peaks at the three common clay wavelengths (14, 10 and 7 angstroms), which likely represent mostly illitic and mixed-layer clay. The normative mineralogy is consistent with a composition of about 45–60 percent quartz (fig. 2), as much as 20 percent dolomite (fig. 3), and perhaps 25–40 percent illite (fig. 4).

Samples with less than 90 percent normative quartz and illite combined tend to be rich in calcium or iron, but not both (fig. 2). The distribution of calcium in loess is distinctly bimodal; figure 3 demonstrates that the peak at about 3.5 percent CaO represents dolomite. The quartz-rich samples (L252, L143, L11, L12, L01, L113, and L13) and the dolomite-rich samples (L321, L09, L322, and L08) were all collected from within a few kilometers of the Missouri or Mississippi floodplains, whereas many of the iron-rich (and clay-rich) samples (L381, L171, L292, and L291) were collected more than 50 km from floodplains.

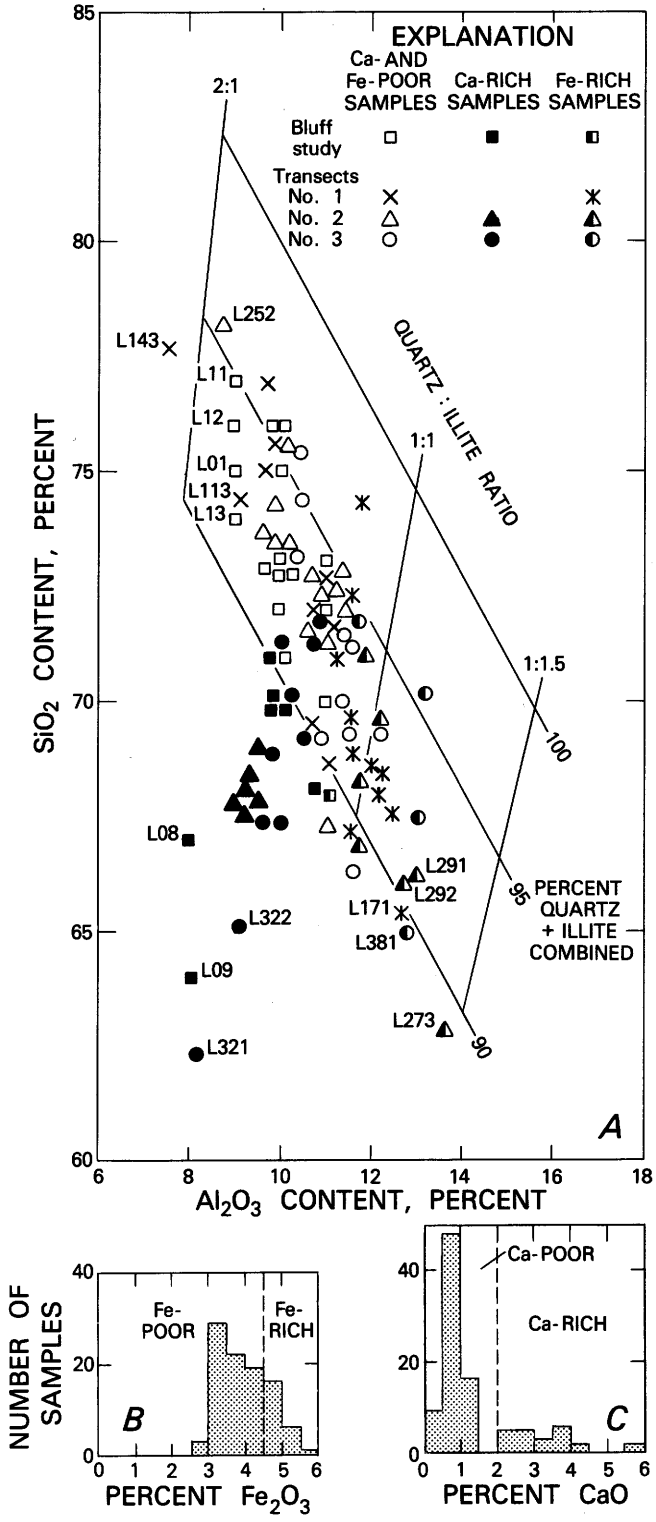


FIGURE 2.—Variation of SiO_2 and Al_2O_3 in loess samples having various contents of Fe_2O_3 and CaO (*A*), and the distributions of Fe_2O_3 (*B*) and CaO (*C*) in loess samples. Iron-rich samples have $Fe_2O_3 \geq 4.5$ percent; calcium-rich samples have CaO ≥ 2 percent; calcium- and iron-poor samples have lesser amounts of both contituents. Compositions of normative quartz and illite shown. The illite composition is that of Weaver and Pollard (1973, p. 9) and contains 26 percent Al_2O_3 and 50 percent SiO_2.

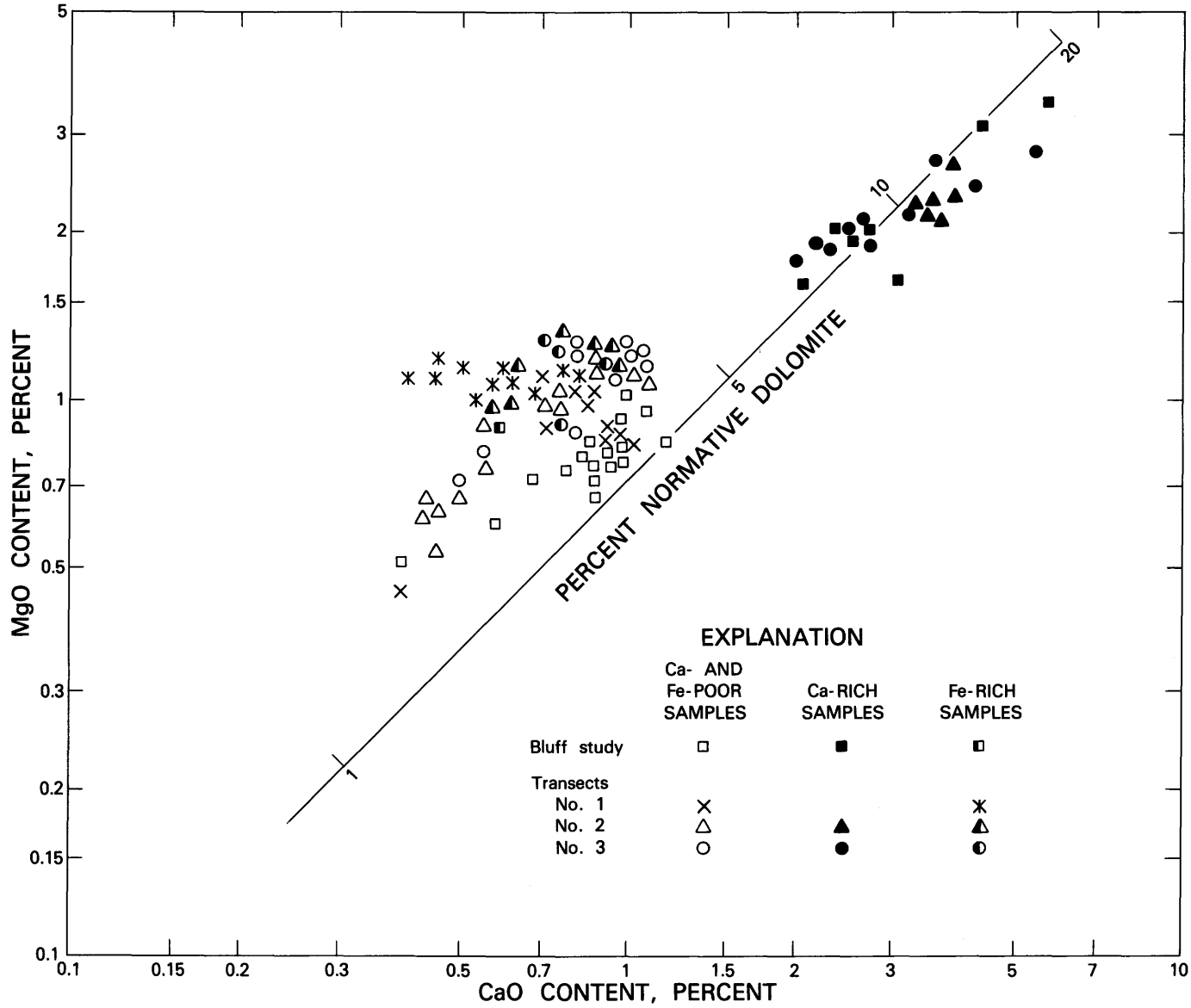


FIGURE 3.—Variation of CaO and MgO in loess. Samples grouped as iron-rich, calcium-rich, and iron- and calcium-poor, as defined in figure 2. Composition of normative dolomite shown.

X-ray work suggested the presence of potassium-poor clay phases (such as kaolinite and montmorillonite), and the relation of potassium to aluminum (fig. 4) supports this suggestion in that the clay appears to be poorer in potassium than common illite (Weaver and Pollard, 1973, p. 9). Because the feldspar in the loess also requires potassium in its composition, the aluminum-potassium ratios in figure 4 reflect a complex of potassium- and aluminum-bearing minerals. The dashed line represents a mixture of illite, kaolinite, and potassium feldspar that appears to be reasonable for average loess, particularly if the loess is dolomitic (high CaO). Permissible percentages of these three normative minerals are shown in boxes around the boundaries of the plotted points.

BLUFF STUDY

The loess capping the bluffs along the Mississippi and Missouri Rivers was sampled to assess the magnitude of geochemical change occurring in these deposits along the river. The analysis of variance (table 4) suggests that in the main there is little such variation. Only barium, phosphorus and strontium exhibit statistically significant components of regional geochemical variance (S^2_β). Area (segment) averages for these elements were examined for stability as described above. E_s was computed by

$$E_s = \frac{S^2_\gamma}{2} + \frac{S^2_\delta + S^2_\epsilon}{4}. \quad (17)$$

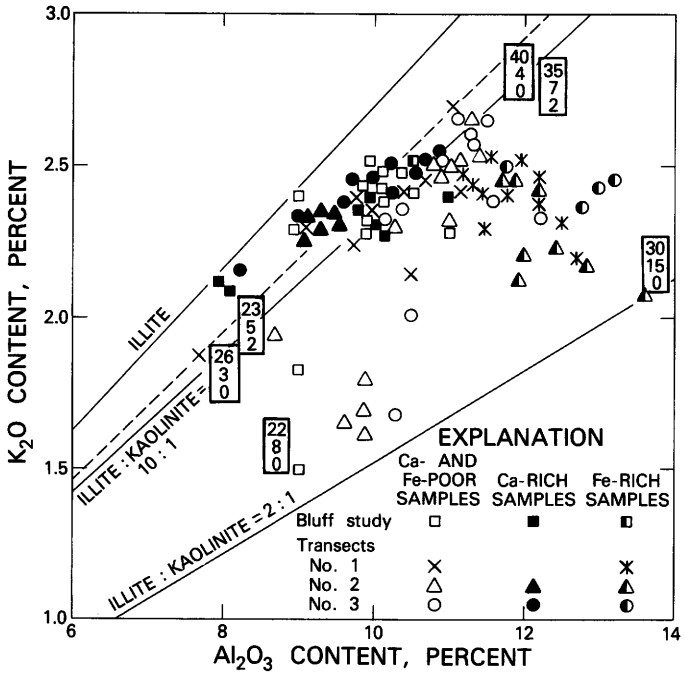


FIGURE 4.—Variation of Al_2O_3 and K_2O in loess. Samples grouped as iron-rich, calcium-rich, and iron- and calcium-poor as defined in figure 2. The boxed numbers are permissible percentages of normative illite (top), kaolinite (middle), and potassium feldspar (bottom). The dashed line represents a ratio of illite:kaolinite:feldspar of 10:2:1.

The pertinent parameters for this estimation are listed below:

Element	v	n_r	E_r	E_s
Ba	1.21	5	0.0012	0.0015
P	.57	7	.0033	.0071
Sr	.84	6	.0011	.0016

Area averages based on the data collected from the river bluffs are not sufficiently stable according to the criterion used ($E_s > E_r$), and additional data are required if area averages are to be computed for these three elements.

Between-locality variance (S^2_γ) is significant for calcium and magnesium, which reflects variation of dolomite, and for chromium, potassium, lithium, sodium, nickel, titanium, and zirconium. Variation in potassium and sodium may reflect variation of feldspar, and variation of nickel, chromium, titanium, and zirconium could reflect variation of clay or heavy mineral content or both. Overall, however, loess in the river bluffs in Missouri is rather uniform in chemical composition. Only 11 of the 35 constituents listed in table 4 exhibit more than half of their total variation as variation between localities ($S^2_\beta + S^2_\gamma$). They are barium, calcium, chromium, potassium, lithium, magnesium, sodium, nickel, phosphorus, titanium, and zirconium.

TRANSECT STUDY

Geochemical variation transverse to major drainage was examined by regression analysis of data collected along three transects (fig. 1). The parameters for each fitted trend (equation 4) are given in table 5 along with the correlation of geochemical variation with distance. Each equation predicts the concentration for that constituent in loess at various distances from the Missouri River drainage. Most of the statistically significant trends are plotted in figures 5 and 6.

As noted above, calcium decreases (fig. 5) and iron increases (fig. 6) away from the source (the floodplain). Trends in magnesium and carbon (not shown) parallel those in calcium (fig. 5) because all three are major components of dolomite, whose occurrence largely controls their distributions. Concentrations of phosphorus, barium, manganese, and strontium (fig. 5) also decrease with distance in one or more of the transects. The trend in manganese is so weak that suppression of either the first or the last sampling locality would result in a nonsignificant trend. Variation in phosphorus may reflect variation of apatite. The trends in barium and strontium are similar to those in potassium and sodium (fig. 5), and all four elements largely reflect a decrease in feldspar with distance. These trends, along with decreases in silicon (quartz) and zirconium (zircon), indicate that small but apparently real decreases in the common rock-forming minerals dolomite, apatite, feldspar, quartz, and zircon occur downwind of the source.

In contrast, a number of clay-related elements increase downwind of the source (fig. 6). These trends are about as weak as most of the decreasing trends and many (specifically copper, selenium, aluminum, and iron along transect 1; arsenic and vanadium along transect 2; and arsenic along transect 3) would be nonsignificant if the first or the last sampling locality were suppressed. Nevertheless, the overall pattern in figure 6 seems real and is antithetic to the pattern in figure 5. The pattern in figure 6 reflects an increase in clay content with distance, probably at the expense of quartz (mostly) and dolomite.

Two obvious causes of the geochemical change with distance seen here are (1) more thorough weathering of the thinner loess deposits, and (2) elutriation of the original windborne material by wind fractionation. Hall (1977) found in southwest Indiana that soil development in Wisconsin loess tended to increase as the loess thinned away from source, and Rieger and Juve (1961) in Alaska found soil development during

TABLE 4.—*Comparison of estimated logarithmic variance components for loess in bluffs along the Mississippi and Missouri Rivers in Missouri*

[Asterisk (*), significantly different from zero at the 0.05 probability level]

Element	Total $\log_{10}$ variance ($S^2_{\log X}$)	Between segments		Between localities		Between samples		Between replicates	
		Component S^2_β	Percent of total	Component S^2_γ	Percent of total	Component S^2_ϕ	Percent of total	Component S^2_ε	Percent of total
Al-------	0.0019	0.0004	21	<0.0001	<1	0.0011	58	0.0004	21
As-------	.0193	.0030	15	<.0001	<1	.0015	8	.0148	77
B--------	.0273	.0028	10	<.0001	<1	.0081	30	.0164	60
Ba-------	.0128	.0070*	55	<.0001	<1	<.0001	<1	.0058	60
Be-------	.0074	<.0001	<1	.0001	1	<.0001	<1	.0073	99
C (CO_3)--	.5826	<.0001	<1	.0942	16	.4104	70	.0780	13
C (Org)--	.0443	.0045	10	<.0001	<1	<.0001	<1	.0398	90
Ca-------	.1203	<.0001	<1	.0804*	67	.0383	32	.0016	1
Co-------	.0123	<.0001	<1	.0009	7	.0022	18	.0092	75
Cr-------	.0041	.0003	7	.0020*	49	.0018	44	<.0001	<1
Cu--------	.0136	<.0001	<1	.0040	29	.0044	32	.0052	38
F---------	.0276	<.0001	<1	.0113	41	<.0001	<1	.0163	59
Fe--------	.0020	<.0001	<1	.0007	35	.0013	65	<.0001	<1
Ga--------	.0039	<.0001	<1	.0007	18	.0006	15	.0026	67
Hg--------	.0635	.0133	21	<.0001	<1	<.0001	<1	.0502	79
I---------	.0174	.0123	17	.0190	27	.0387	54	.0014	2
K---------	.0028	.0008	29	.0013*	46	.0006	21	.0001	4
La--------	.0152	<.0001	<1	.0055	36	<.0001	<1	.0097	64
Li--------	.0088	<.0001	<1	.0060*	68	.0023	26	.0005	6
Mg--------	.0693	<.0001	<1	.0467*	67	.0220	32	.0006	1
Mn--------	.0518	.0015	3	<.0001	<1	.0432	83	.0071	14
Na--------	.0068	.0001	1	.0041*	60	.0013	19	.0013	19
Ni--------	.0149	<.0001	<1	.0079*	53	.0070	47	<.0001	<1
P---------	.0360	.0130*	36	.0055	15	.0001	<1	.0174	48
Pb--------	.0128	.0019	15	<.0001	<1	<.0001	<1	.0109	85
Se--------	.0935	<.0001	<1	<.0001	<1	<.0001	<1	.0935	100
Sc--------	.0052	.0002	4	<.0001	<1	.0010	19	.0040	77
[1]Si-------	13.13	<.01	<1	4.92	37	7.21	55	1.0	8
Sr--------	.0118	.0054*	46	<.0001	<1	.0012	10	.0052	44
Ti--------	.0187	.0017	9	.0087*	47	.0083	44	<.0001	<1
V---------	.0074	<.0001	<1	.0001	1	.0073	99	<.0001	<1
Y---------	.0223	<.0001	<1	.0042	19	.0047	21	.0134	60
Yb--------	.0192	<.0001	<1	<.0001	<1	.0110	57	.0082	43
Zn--------	.0110	<.0001	<1	.0039	35	.0062	56	.0009	8
Zr--------	.0143	<.0001	<1	.0085*	59	<.0001	<1	.0058	41

[1]Variance calculated on nontransformed data rather than log data.

active loess deposition to be fastest in those places where deposition was slowest. Similar processes almost certainly operated in northwest Missouri during loess deposition there. However, the prevalence of element concentrations that follow conventional exponential decay-type curves (fig. 5) strongly suggests elutriation by wind as the major cause. The apparent decrease with distance in quartz, dolomite, apatite, feldspar, and zircon indicates mineral sorting. The mineral sorting in loess noted by Ruhe (1969) underscores the importance of this mechanism.

The patterns in figures 5 and 6 demonstrate that the geochemical character of loess is different in deposits far from the source than it is in deposits near the source (bluff loess). In order to take such differences into account in defining the geochemical background for loess in Missouri, a selected subset of the transect samples was used to geochemically characterize the deposits away from the bluffs (table 6). The samples selected for this subset were from deposits that appeared to be thin (commonly less than 6 m), heavy textured (clay-rich), and locally mottled red, yellow, or white. Some of this loess may contain weathered till.

Finally, for purposes of comparison, summary data

TABLE 5.—*Regression of loess chemistry with distance east of the Missouri River floodplain*

[*a*, *b*, defined in equation (4); *r*, correlation of geochemical property and distance; asterisk (*), *r* significantly different from zero at the 0.05 probability level; Ratio, number of samples in which constituent was detected to total number of samples analyzed; data in parts per million except where noted as percent (pct). Leaders (—) indicate insufficient data for computation]

Geochemical Property	Transect 1				Transect 2				Transect 3			
	a	b	r	Ratio	a	b	r	Ratio	a	b	r	Ratio
Log Al_2O_3, pct---	1.01	0.035	0.41*	21:21	0.99	0.035	0.53*	27:27	0.99	0.054	0.78*	24:24
As----------	1.07	.028	.15	21:21	1.05	.024	.36*	27:27	.93	.054	.35*	24:24
B----------	1.41	-.007	-.05	21:21	1.38	-.020	-.17	26:27	1.35	.023	.18	24:24
Ba----------	3.01	-.020	-.20	21:21	3.02	-.083	-.53*	27:27	3.01	-.025	-.40*	24:24
Total C, pct-	-.57	.049	.17	21:21	-.17	-.196	-.54*	27:27	-.13	-.217	-.48*	24:24
CaO, pct-----	-.08	-.109	-.53*	21:21	.36	-.332	-.80*	27:27	.46	-.326	-.77*	24:24
Co----------	.89	.076	.34	21:21	.86	.056	.37*	27:27	.90	.032	.21	24:24
Cr----------	1.78	.017	.15	21:21	1.73	.030	.32	27:27	1.77	.019	.18	24:24
Cu----------	1.20	.062	.39*	21:21	1.21	.004	.03	27:27	1.19	.048	.53*	24:24
F----------	2.62	.019	.12	21:21	2.65	.002	.01	27:27	2.66	.047	.38*	24:24
Fe_2O_3, pct---	.58	.056	.44*	21:21	.56	.050	.56*	27:27	.53	.070	.79*	24:24
Ga----------	1.10	.028	.20	21:21	1.11	-.003	-.03	27:27	1.07	.070	.63*	24:24
Hg----------	-1.60	.049	.13	20:21	-1.50	-.014	-.04	26:27	-1.67	.099	.29	22:24
K_2O, pct-----	.39	-.017	-.33	21:21	.39	-.038	-.51*	27:27	.39	-.013	-.21	24:24
La----------	1.60	.044	.26	15:21	---	---	---	12:27	---	---	---	8:24
Li----------	1.35	.053	.72*	21:21	1.33	.079	.82*	27:27	1.34	.075	.82*	24:24
MgO, pct-----	-.02	.030	.20	21:21	.24	-.164	-.68*	27:27	.30	-.160	-.68*	24:24
Mn----------	2.72	-.083	-.21	21:21	2.68	-.156	-.50*	27:27	2.50	.016	.05	24:24
Na_2O, pct----	.09	-.048	-.42*	21:21	.12	-.073	-.57*	27:27	.14	-.051	-.57*	24:24
Ni----------	1.32	-.011	-.04	21:21	1.30	-.026	-.15	27:27	1.25	.038	.25	24:24
P_2O_5---------	3.23	-.108	-.46*	21:21	3.28	-.248	-.64*	22:27	3.19	-.110	-.28	21:24
Pb----------	1.19	-.010	-.22	21:21	1.18	.009	.18	27:27	1.17	.005	.07	24:24
Sc----------	.90	.064	.43*	21:21	.86	.063	.63*	27:27	.84	.088	.79*	24:24
Se----------	-.99	.258	.50*	14:21	-.93	.163	.47*	21:27	---	---	---	16:24
SiO_2, pct--------	73.1	-2.4	-.43*	21:21	70.1	.3	.06	27:27	69.4	.2	.05	24:24
Log Sr----------	2.28	-.035	-.34	21:21	2.30	-.073	.58*	27:27	2.30	-.016	-.24	24:24
V----------	1.95	.032	.20	21:21	1.90	.041	.36*	27:27	1.88	.100	.74*	24:24
Y----------	1.42	-.021	-.14	21:21	1.29	.029	.24	27:27	1.30	.034	.22	24:24
Yb----------	.47	-.007	-.11	21:21	.36	.045	.42*	27:27	.35	.056	.44*	24:24
Zn----------	1.84	.015	.12	21:21	1.85	-.011	-.09	27:27	1.82	.033	.30	24:24
Zr----------	2.24	-.064	-.40*	21:21	2.14	.077	.05	27:24	2.12	.002	.01	24:24

for dolomite-bearing loess are given in the middle column of table 6. Most of the dolomite-bearing samples were collected from the region in northwesternmost Missouri where the maximum thickness of capping loess is 10 m or more (fig. 1). Thus, these data should prove most useful in that particular area of the State, although carbonate-bearing loess locally occurs in bluffs all along the Missouri River in the State. Ray (1967, p. D224) suggested that loess in western Kentucky originally had a uniform carbonate content, and that the present variation in the carbonate of those deposits reflects a variable degree of leaching during deposition (the slower the deposition, the greater the leaching). In general, calcite is leached before dolomite, and the smaller carbonate grains are leached before the larger. A similar history of carbonate in loess along the Missouri River would account for the erratic distribution of dolomite noted in those deposits.

In spite of these geochemical distinctions, differences between bluff loess, non-bluff loess, and dolomite-bearing loess are minimal, the exception being that carbon, calcium, and magnesium occur in the dolomite-bearing loess in concentrations twice as high as in the other types. Other observed differences are very minor and may not be significant; these include higher boron, iodine, and yttrium and lower fluorine in bluff loess; lower selenium and ytterbium in dolomite-bearing loess; and higher arsenic and selenium and lower phosphorus in loess away from the river bluffs.

RESIDUUM

Like loess, residuum is composed principally of quartz and clay. However, the residuum is everywhere much more iron rich than loess, and the quartz in

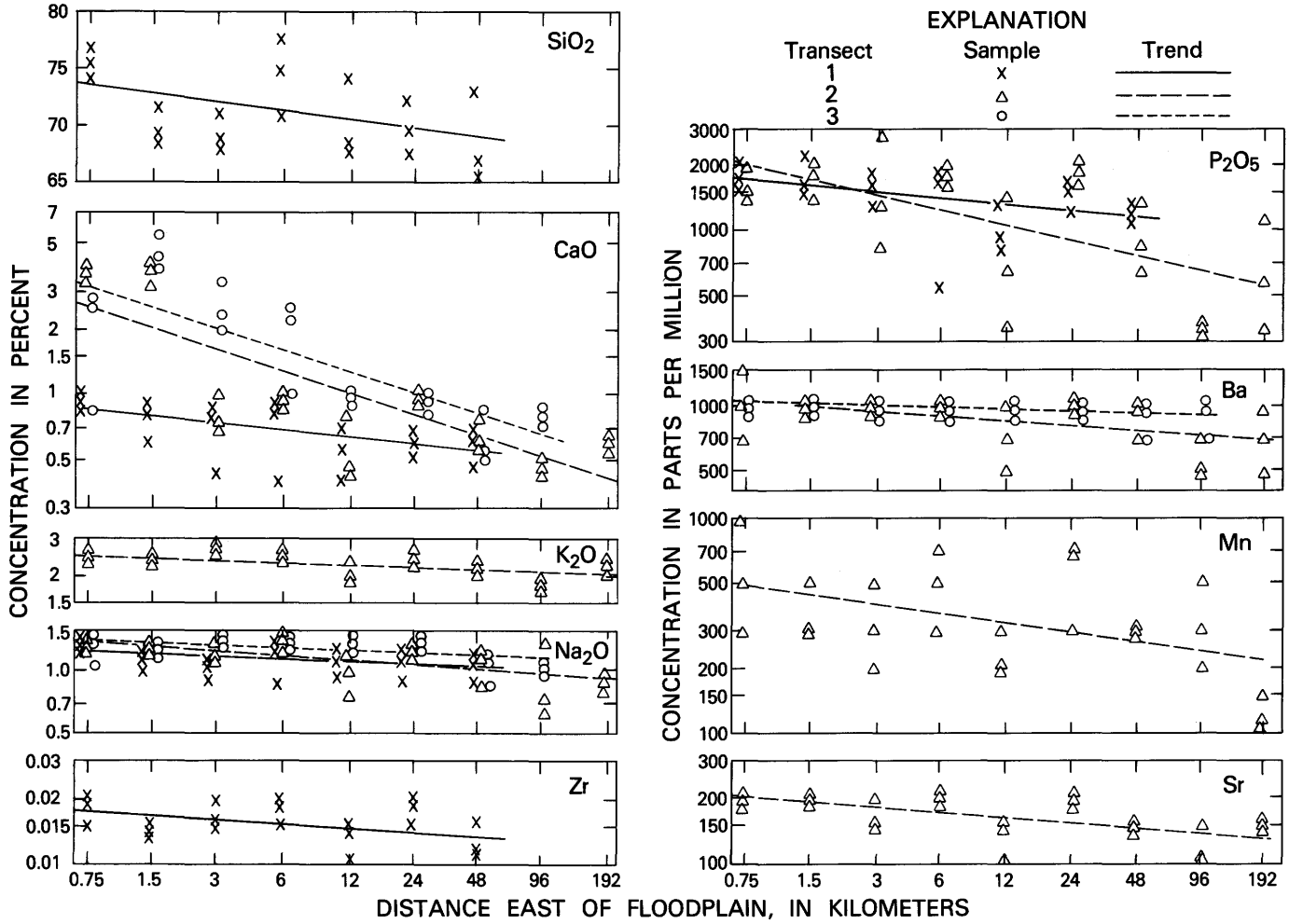


FIGURE 5.—Chemical concentrations in loess that decrease as a function of distance east of the Missouri River floodplain.

residuum occurs mostly as large fragments rather than as sand or silt. Compositions of residuum samples are plotted in figure 7, in the same type of plot used for the loess samples (fig. 2). The approximate outline of variation of loess is noted, showing clearly that residuum is much more variable than loess. The iron-rich nature of residuum is indicated by the fact that 28 samples contain more than 10 percent Fe_2O_3. Sample R01 (from the Bonneterre residuum unit) contained more than 20 percent Fe_2O_3, and samples P023 and P024R (from the Potosi unit) each contained more than 30 percent Fe_2O_3.

Most samples lie within a normative composition based on a simple mixture of quartz and common illite. The samples richest in aluminum have compositions equivalent to mixtures of normative quartz and kaolinite or of quartz, illite, and kaolinite. (See dashed line, fig. 7.) Samples poorest in aluminum (including R10, R052, R10D and R11D, all from the arenaceous Roubidoux unit) consisted of more than 90 percent normative quartz.

Residuum is distinctly poorer in potassium than loess (fig. 8), although a few samples from the Bonneterre, Roubidoux, and Jefferson City units (R062, R02D, J042, J054R, B052, B054, R01, and R02) are so potassium-rich as to suggest the presence of minor amounts of muscovite or potassium feldspar. The boxed numbers in figure 8 show permissible percentages of normative illite and kaolinite in residuum. On average, residuum consists of about 50 percent total clay, slightly more than that estimated for loess.

Although three samples containing visible dolomite were excluded from the geochemical evaluation of residuum, more than 10 percent normative carbonate appeared in the norms of 11 other samples (fig. 9). Sample R07 (from the Potosi unit in the highway study) contained nearly 30 percent normative dolomite. Samples R17, R18D, and R31 (from the Osage and Meramec units) contained more than 10 percent normative calcite. The carbonate in these samples is probably interspersed through chert fragments. CaO and MgO concentrations in the calcium-poor samples from

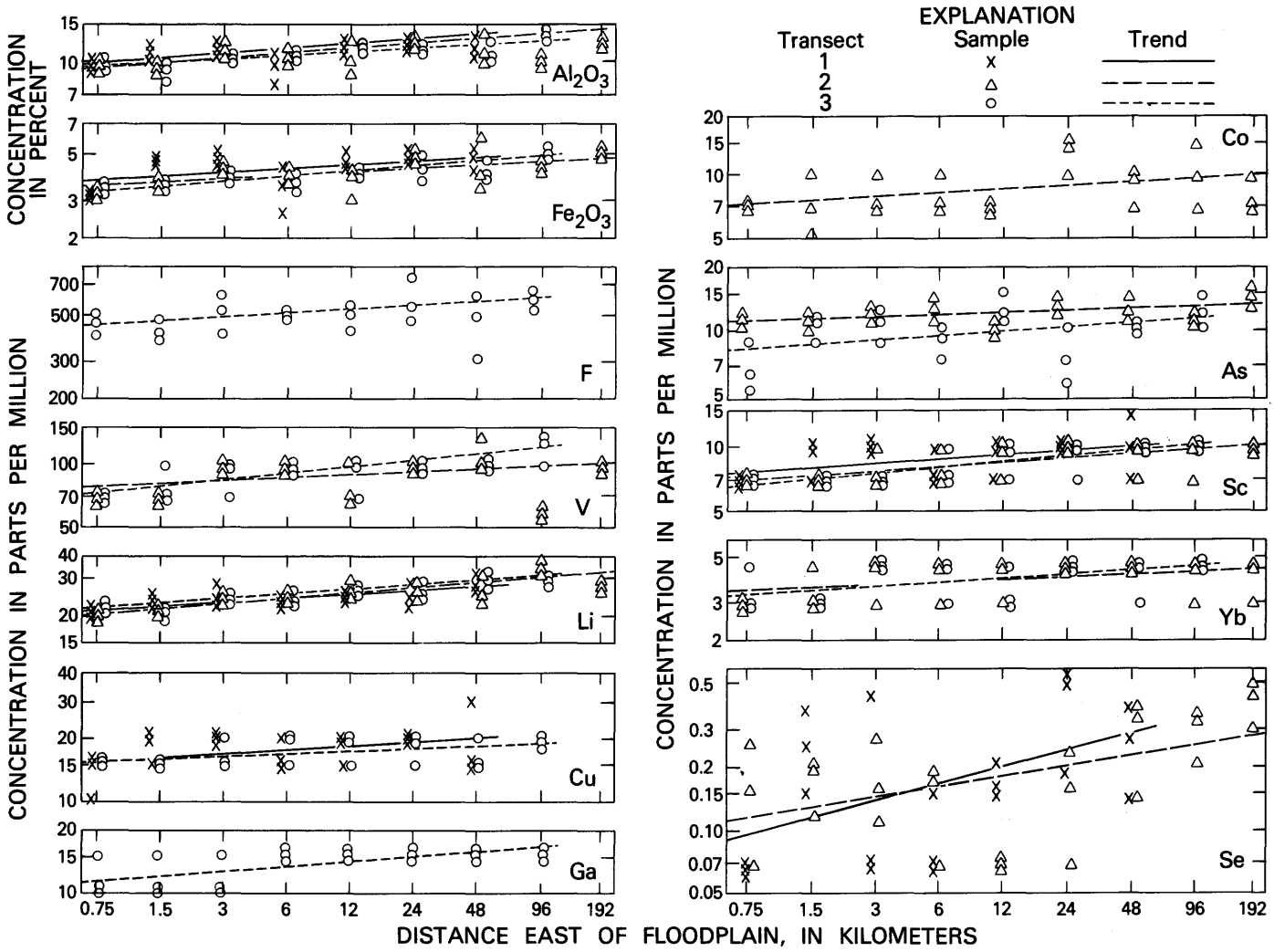


FIGURE 6.—Chemical concentrations in loess that increase as a function of distance east of the Missouri River floodplain.

the Bonneterre, Potosi, Gasconade, Roubidoux, and Jefferson City units (circles) are positively correlated (in logarithms, $r = 0.64$), suggesting that these samples may contain small amounts of dolomite (1–5 percent). The regression line fitted to these points demonstrates that the excess of MgO over that needed for the dolomite is about 0.7–1 percent, which could occur in 30–50 percent illitic or montmorillonitic clay.

HIGHWAY STUDY

Statistical tests of scale-related geochemical variation in residuum of the highway study are summarized in table 7. All but five elements (carbon, mercury, phosphorus, selenium, and zirconium) exhibit statistically significant variation (S_β^2) among the six residuum units. In particular, three elements of economic interest—lead, copper, and zinc—exhibit approximately half or more of their total observed variation at this scale of the design. This high percentage reflects the fact that six samples of the Potosi unit, collected in or near the Washington County barite district, an area of known anomalous lead, copper, and zinc in residuum (Ebens and Connor, 1977), were unusually high in these elements. Maximum concentrations measured in these six samples were 0.27 percent zinc (in sample R08D), 0.3 percent lead (sample R05), and 10 percent barium (sample R08).

The general lack of variability between sampling localities within units (S_θ^2) is more apparent than real and, as will be seen below in the section describing results of the final study, residuum within each unit does in fact vary in a geochemically significant fashion. The failure of the highway study to show that variation is due to the sampling bias arising from the restriction of sampling to a few major highways.

Variation at local scales is large for many elements.

TABLE 6.—*Geochemical summary of loess in Missouri*

[GM, geometric mean; GD, geometric deviation; GE, geometric error; Ratio, number of samples in which element was determined to total number of samples analyzed. Leaders (---) indicate insufficient data for computation. Geometric means are in parts per million except where noted as percent (pct) or parts per billion (ppb)]

Element	Loess in bluffs				Dolomite-bearing loess[1]			Loess away from bluffs[2]			
	GM	GD	GE	Ratio	GM	GD	Ratio	GM	GD	GE	Ratio
Al_2O_3, pct---	9.8	1.09	1.05	24:24	9.6	1.09	23:23	11.3	1.12	<1.03	39:39
As----------	8.3	1.33	1.32	24:24	9.2	1.37	23:23	12	1.28	1.14	39:39
B----------	39	1.36	1.34	24:24	26	1.37	23:23	24	1.24	1.23	38:39
Ba----------	840	1.26	1.19	24:24	940	1.23	23:23	900	1.26	1.14	39:39
Be----------	.95	1.17	1.22	18:24	<1	---	5:23	1.2	1.27	---	15:39
C, pct:											
Total------	.30	2.43	---	24:24	.97	1.50	23:23	.32	1.52	1.19	39:39
Carbonate--	[3] .05	---	1.90	22:24	.59	3.20	22:23	<.01	---	---	1:7
Organic----	.13	1.53	1.58	24:24	.18	1.99	23:23	---	---	---	7:7
CaO, pct-----	1.2	1.96	1.10	24:24	3.1	1.34	23:23	.67	1.31	<1.03	39:39
Cd----------	<1	---	---	0:24	<1	---	4:23	<1	---	---	5:39
Ce----------	<100	---	---	2:24	<100	---	0:23	<100	---	---	0:39
Co----------	9.8	1.28	1.25	24:24	8.1	1.27	23:23	9.4	1.34	1.29	39:39
Cr----------	70	1.16	<1.03	24:24	61	1.22	23:23	63	1.17	1.20	39:39
Cu----------	18	1.30	1.18	24:24	17	1.24	23:23	18	1.23	1.27	39:39
F----------	290	1.42	1.34	24:24	420	1.28	23:23	470	1.27	1.18	39:39
Fe_2O_3, pct---	3.4	1.10	<1.03	24:24	3.4	1.07	23:23	4.4	1.17	<1.03	39:39
Ga----------	16	1.14	1.12	24:24	13	1.22	23:23	14	1.19	1.16	39:39
Hg, ppb------	35	1.62	1.68	23:24	28	1.48	23:23	29	1.80	1.40	36:39
I----------	1.2	1.83	1.09	24:24	.76	1.84	7:7	---	---	---	0:0
K_2O, pct-----	2.3	1.13	<1.03	24:24	2.4	1.05	23:23	2.3	1.13	<1.03	39:39
La----------	42	1.31	1.25	24:24	34	1.37	10:23	45	1.19	1.26	27:39
Li----------	23	1.20	1.05	24:24	21	1.10	23:23	27	1.14	<1.03	39:39
MgO, pct-----	1.1	1.66	1.06	24:24	2.2	1.21	23:23	.99	1.26	<1.03	39:39
Mn----------	510	1.54	1.21	24:24	380	1.65	23:23	370	1.88	1.30	39:39
Mo----------	<3	---	---	0:24	<3	---	2:23	<3	---	---	1:39
Na_2O, pct----	1.3	1.21	1.09	24:24	1.3	1.06	23:23	1.1	1.22	1.05	39:39
Nb----------	<10	---	---	4:24	<10	---	0:23	7.1	1.29	---	10:39
Ni----------	22	1.29	<1.03	24:24	19	1.28	23:23	20	1.42	1.34	39:39
P_2O_5, pct----	.14	1.53	1.35	24:24	.15	1.52	22:23	.11	1.74	1.25	33:39
Pb----------	15	1.27	1.27	24:24	15	1.16	23:23	15	1.12	1.08	39:39
Sc----------	9.0	1.18	1.16	24:24	7.4	1.15	23:23	9.4	1.18	1.16	39:39
Se----------	.18	2.00	2.02	19:24	.14	1.80	18:23	.21	1.88	1.52	33:39
[4]SiO_2, pct----	73	3.2	1.0	24:24	68	2.4	23:23	71	3.2	.83	83:83
Sr----------	220	1.26	1.18	24:24	210	1.12	23:23	170	1.21	1.08	39:39
V----------	93	1.21	<1.03	24:24	83	1.24	23:23	100	1.23	<1.03	39:39
Y----------	32	1.36	1.31	24:24	22	1.31	23:23	23	1.27	1.16	39:39
Yb----------	3.5	1.34	1.23	24:24	2.5	1.29	23:23	2.8	1.15	1.16	39:39
Zn----------	61	1.25	1.07	24:24	68	1.16	23:23	72	1.23	1.11	39:39
Zr----------	230	1.29	1.19	24:24	140	1.28	23:23	140	1.31	1.28	39:39

[1]Twenty-three samples of loess were used in computing these statistics. Bluff loess samples were REOL-07, 08, 09, 15, 17, 23, and 24. Transect loess samples were E2L-211, 212, 213, 221, 222, 223, 311, 312, 321, 322, 323, 331, 332, 333, 342, and 343.

[2]Only samples from localities 13 (excepting samples E2L-111, 112, and 113), 21, 22, 23, 24, 28, 29, and 30 were used in computing these statistics.

[3]This average is a median.

[4]Summary statistics given as arithmetic means, standard deviations, and standard errors.

Fourteen elements differ in a significant way between sections (S_K^2) spaced as much as 3 km apart. The presence of a clay-related suite of elements (aluminum, lithium, scandium, vanadium, yttrium, and ytterbium) and a carbonate-related suite (calcium, magnesium, and strontium) suggests that differences among these closely spaced sections reflect simple variation in carbonate content and perhaps also in chert content, in-

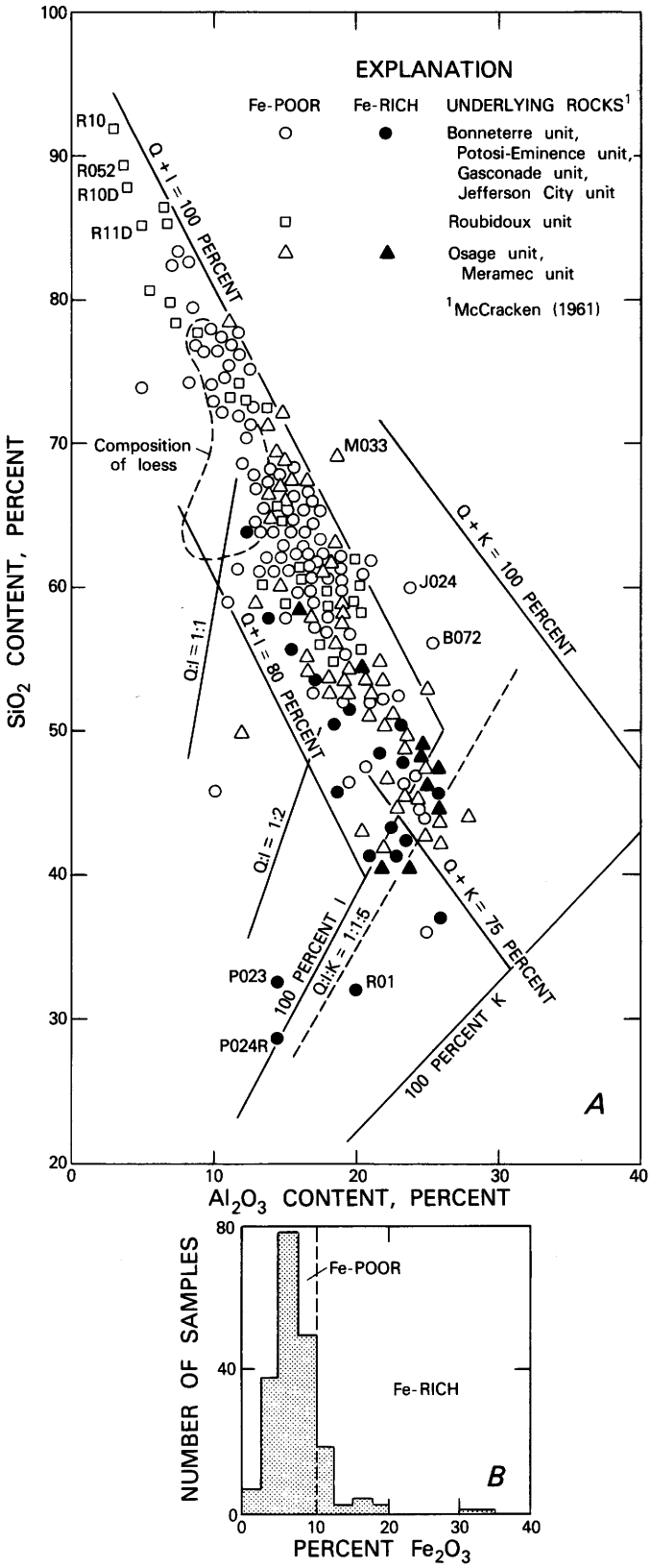


FIGURE 7.—Variation of SiO_2 and Al_2O_3 (*A*) and the distribution of Fe_2O_3 (*B*) in residuum. Samples grouped as iron-rich ($\geq$10 percent Fe_2O_3) and iron-poor ($\geq$10 percent Fe_2O_3). Compositions of normative quartz (Q), illite (I), and kaolinite (K) shown.

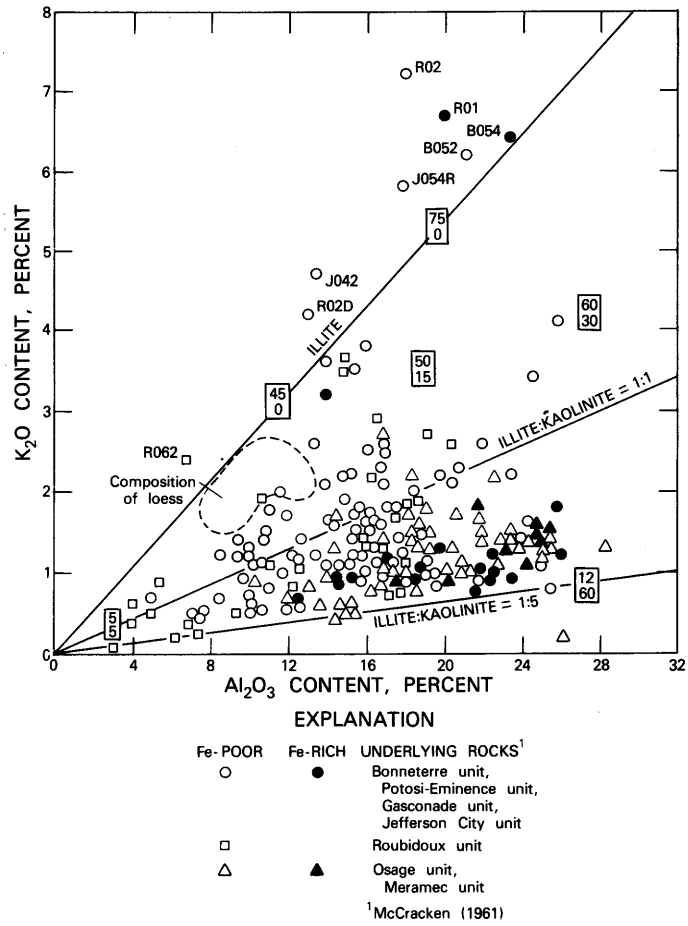


FIGURE 8.—Variation of Al_2O_3 and K_2O in residuum. Samples grouped as iron-rich and iron-poor, as defined in figure 7. The boxed numbers are permissible percentages of normative illite (top) and kaolinite (bottom).

asmuch as silicon shows significant variation also. Variation between sections and between samples combined ($S_\kappa^2 + S_\delta^2$) exceeds 50 percent of the total observed variation for 19 elements and indicates a high degree of geochemical heterogeneity in residuum at local scales.

The strong geochemical differences among the residuum units prompted a second sampling effort aimed at quantifying these differences. An attempt was made to collect enough samples from each unit to produce realistic geochemical averages. Based on the variance components in table 7, a final sampling design was set up using six localities within each unit, two sections in each locality, and two samples from each section. Thus, the final sampling involved 24 samples from each unit (in contrast to the six samples per unit of the highway design). Table 8 gives the parameters used to assess sampling requirements in residuum. E_s is the basic criterion used in this assessment; $E_s(1)$ is computed for the highway sampling and $E_s(2)$ is estimated for the final sampling.

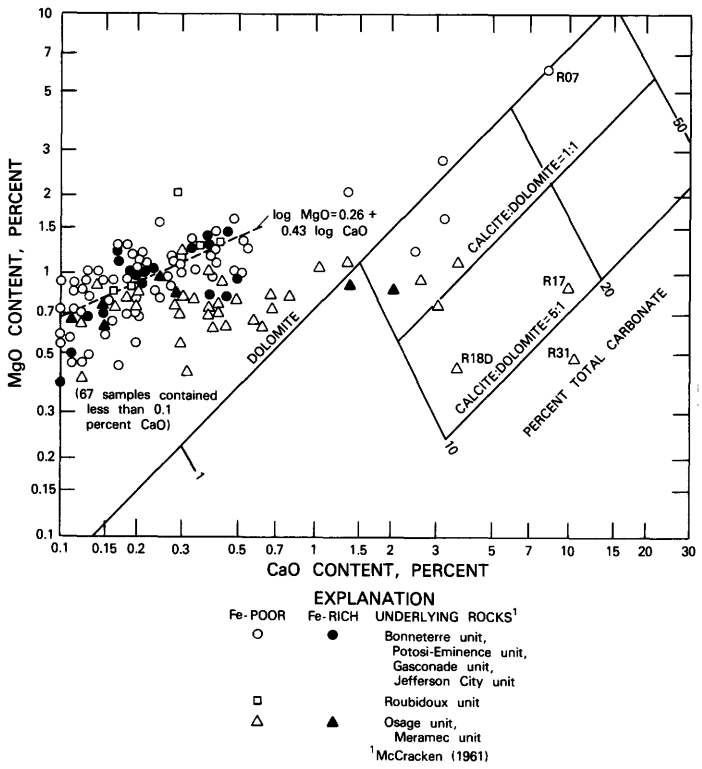


FIGURE 9.—Variation of CaO and MgO in residuum. Samples grouped as iron-rich and iron-poor, as defined in figure 7. Compositions of normative calcite and dolomite shown. The dashed line is the regression of CaO on MgO for low-CaO residuum samples collected over pre-Mississippian bedrock.

$$E_s(1) = \frac{S_\theta^2}{2} + \frac{S_\kappa^2 + S_\delta^2 + S_\epsilon^2}{4} ; \quad (18)$$

$$E_s(2) = \frac{S_\theta^2}{6} + \frac{S_\kappa^2}{12} + \frac{S_\delta^2 + S_\epsilon^2}{24} . \quad (19)$$

Even though the geochemical differences among the six units (as indicated by the analysis of variance, table 7) are large, the data of the highway study are judged to be too few for computation of satisfactory averages for each residuum unit ($E_s(1) > E_r$). The sampling load of the final design, however, should be sufficiently large ($E_s(2) \leq E_r$). In fact, for some geochemical constituents, the sampling bias in the highway study (noted above) resulted in an underestimation of the required sampling load.

FINAL STUDY

The analysis of variance of residuum collected in the final study is given in table 9. The results of this analysis differ from those of the highway study (table 7) in that the variance estimated between units (S_β^2) is much less in this study and the variance estimated between localities (S_θ^2) is correspondingly enhanced. These changes reflect the fact that the localities used within each unit of the highway study were spaced less than 50 km apart on the average (fig. 1), but the localities in the final study were spaced 150 km apart on the average. Thus, the between-unit component (S_β^2) in the highway study includes variance at scales which in the final study are part of the between-localities component (S_θ^2).

For many elements, the total observed variance in the highway study (table 7) is nearly 2–3 times that estimated in the final study (table 9). Part of this contrast reflects the fact that 23 samples from Washington County were excluded from the analysis of variance in table 9 because they were anomalously high in barium, lead, copper, and zinc (fig. 10). Thus, the inflated variances seen in these metals in the highway study (table 7) have been reduced in the final study to values more commensurate with the other trace elements listed in table 8. Overall, though, the inflated estimates of total variance in the highway study may be related to the bias in the selection of localities.

Nevertheless, the analysis of variance in the final study (table 9) confirmed that a number of geochemical differences in fact exist among the seven residuum units studied. A clay-related suite of elements (aluminum, beryllium, chromium, gallium, lithium, scandium, vanadium, yttrium, and ytterbium) exhibits significant between-unit variance, as do two ore metals (copper and zinc) and iron and manganese. The lower percentages attributed to the between-areas component (S_β^2) in the final study resulted in $E_s(2)$ values much greater than those estimated from the highway study. Consequently the sampling load of the final study turned out to be inadequate for computing unit averages of some elements. The parameters used to assess stability in averages based on the final study are given in table 10.

Six elements (aluminum, chromium, iron, scandium, yttrium, and ytterbium) display a sufficiently low $E_s(2)$ to permit computation of realistic averages of the data from each unit. The remaining elements require still further sampling if useful averages are to be computed, although averages for copper, gallium, silicon, vanadium and zinc would require only a little more sampling.

Geochemical summaries based on residuum from the final study are given in tables 11 and 12. Grand averages for residuum regardless of unit are given in table 11. Table 12 lists averages of 16 selected constituents for each bedrock area: the first six constituents have $E_s(2) \leq E_r$; the 10 remaining constituents have $E_s(2) > E_r$ but also have between-unit components (S_β^2)

TABLE 7.—*Comparison of estimated logarithmic variance components for residuum of the highway study in Missouri*

[Asterisk (*), significantly different from zero at the 0.05 probability level]

Elements	Total $\log_{10}$ variance (s^2_{logX})	Between units		Between localities		Between sections		Between samples		Between replicates	
		Component s^2_β	Percent of total	Component s^2_θ	Percent of total	Component s^2_κ	Percent of total	Component s^2_δ	Percent of total	Component s^2_ϵ	Percent of total
Al---------	0.0803	0.0257*	32	<0.0001	<1	0.0385*	48	0.0157	20	0.0005	1
As---------	.1147	.0614*	54	<.0001	<1	.0180	16	<.0001	<1	.0350	31
B----------	.0653	.0172*	26	<.0001	<1	.0255	39	<.0001	<1	.0226	34
Ba---------	.4778	.3063*	64	.0026	1	.1325*	28	.0265	6	.0099	2
Be---------	.0664	.0261*	40	<.0001	<1	.0065	10	.0284	35	.0104	16
Total C----	.2274	<.0001	<1	.0879*	39	<.0001	<1	.1277	56	.0117	5
Carbonate C	.3952	<.0001	<1	.0382	10	.1490	38	.1857	47	.0224	6
Organic C--	.1540	<.0001	<1	.0450	29	<.0001	<1	.0548	36	.0544	35
Ca---------	.4133	.1677*	41	.0824	20	.1005*	24	.0602	15	.0005	<1
Co---------	.0887	.0447*	50	<.0001	<1	.0146	16	.0182	21	.0102	11
C----------	.0716	.0288*	40	<.0001	<1	.0183	25	.0197	28	.0049	7
Cu---------	.1551	.0752*	48	<.0001	<1	.0570*	37	.0148	10	.0082	5
F----------	.1638	.0306*	19	<.0001	<1	.0571	35	.0597	36	.0164	10
Fe---------	.0957	.0397*	41	<.0001	<1	.0349*	36	.0211	22	.0001	<1
Ga---------	.0717	.0142*	20	<.0001	<1	.0269	37	.0275	38	.0032	4
Hg---------	.1468	.0162	11	.0084	6	.0196	13	.0777	53	.0250	17
I----------	.2257	.1043*	46	<.0001	<1	.0982	21	.0720	32	.0011	<1
K----------	.1403	.0661*	47	.0019	1	.0205	15	.0518	37	.0001	<1
Li---------	.0781	.0287*	37	<.0001	<1	.0384*	49	.0108	14	.0002	<1
Mg---------	.1118	.0375*	34	<.0001	<1	.0557*	50	.0113	10	.0074	7
Mn---------	.4346	.2290*	53	<.0001	<1	.0805	19	.1210	28	.0051	1
Na---------	.0569	.0145*	26	.0051	9	<.0001	<1	.0022	4	.0350	62
Ni---------	.1037	.0337*	33	<.0001	<1	.0313	30	.0315	30	.0072	7
P----------	.0855	.0062	7	.0100	12	<.0001	<1	.0507	59	.0187	22
Pb---------	.4388	.2956*	67	<.0001	<1	.0228	5	.1026	24	.0158	4
[1]Si--------	248.8	103.2*	41	<.1	<1	114.9*	46	29.7	12	1.0	<1
Se---------	.0908	.0051	6	<.0001	<1	.0179	20	.0108	12	.0569	63
Sc---------	.0669	.0216*	32	<.0001	<1	.0455*	51	.0084	13	.0069	10
Sr---------	.1896	.0671*	35	<.0001	<1	.0826*	44	.0350	18	.0049	3
Ti---------	.0412	.0141*	34	.0021	5	.0133	32	.0070	17	.0048	12
V----------	.0728	.0236*	32	<.0001	<1	.0318*	44	.0143	20	.0032	4
Y----------	.2298	.1154*	50	<.0001	<1	.0953*	40	.0267	12	.0059	2
Z----------	.1316	.0503*	32	<.0001	<1	.0452*	47	.0136	10	.0140	11
Zn---------	.3187	.2433*	76	<.0001	<1	.0452*	14	.0290	9	.0012	<1
Zr---------	.0381	.0052	14	.0095*	25	.0109	29	<.0001	<1	.0125	33

[1]Variance calculated on nontransformed data rather than log data.

that were found to be significant (table 9). For these last 10 constituents, only those two units showing the highest and lowest averages are tabulated. (The analysis of variance results in table 9 indicate that the highest and lowest averages are distinct even if $E_s(2)$ indicates that any two randomly selected averages are not necessarily distinct.)

The data collected in Washington County were averaged independently of the rest (table 11). A comparison of these averages with those for undifferentiated residuum suggests that not only is Washington County residuum anomalous in the ore metals—barium, copper, lead, and zinc (see Ebens and Connor, 1977)—but it also tends to be high in arsenic, mercury, and neodymium and low in cadmium. In addition, the only sample in which silver was detected (sample P031R, 0.5 ppm silver) was taken from the Potosi unit in Washington County.

Among the seven residuum units (table 12) there is a tendency for the Osage and Meramec units (over Mississippian bedrock) to be distinctly high in aluminum, chromium, iron, scandium, yttrium, and ytterbium. These same two units are also higher in zinc and lower in copper and silicon than residuum of the Bonneterre, Potosi, Gasconade, Roubidoux, and Jefferson City units. Other comparisons suggest that residuum of the Bonneterre unit is high in manganese and zirconium and low in lithium; residuum of the Potosi unit tends to be high in beryllium and silicon and low in zirconium; residuum of the Gasconade unit tends to be high in copper and low in selenium; residuum of the Roubidoux unit tends to be low in beryllium, gallium, manganese, and vanadium; residuum of the Jefferson City unit tends to be high in lithium and low in zinc; residuum of the Osage unit tends to be high in gallium and vanadium; and residuum of the Meramec unit tends to be high in gallium, selenium, and vanadium.

TABLE 8.—*Parameters used to assess sampling requirements in residuum*

[v, variance ratio (defined in equation 12); n_r, minimum number of randomly collected samples needed to represent each area; E_r, maximum permissible variance; $E_s(1)$, variance computed for the highway sampling (by equation 18); $E_s(2)$, variance estimated for the final study (by equation 19)]

Element	v	n_r	E_r	$E_s(1)$	$E_s(2)$
Al-----	0.47	8	0.007	0.014	0.004
As-----	1.15	5	.011	.013	.003
B------	.36	10	.005	.012	.003
Ba-----	1.79	4	.043	.044	.013
Be-----	.65	7	.006	.010	.002
Ca-----	.69	6	.041	.082	.025
Co-----	.98	5	.009	.011	.002
Cr-----	.67	6	.007	.011	.003
Cu-----	.94	5	.016	.020	.006
F------	.23	14	.010	.033	.008
Fe-----	.71	6	.009	.014	.004
Ga-----	.25	13	.004	.014	.004
I------	.86	6	.020	.030	.007
K------	.89	5	.015	.019	.004
Li-----	.58	7	.007	.012	.004
Mg-----	.50	8	.009	.019	.005
Mn-----	1.11	5	.041	.051	.012
Na-----	.34	11	.004	.012	.002
Ni-----	.48	8	.009	.018	.004
Pb-----	2.06	4	.036	.036	.007
Si-----	.71	6	24.3	36.4	10.9
Sc-----	.48	8	.008	.015	.004
Sr-----	.55	7	.018	.031	.009
Ti-----	.52	8	.003	.007	.002
V------	.48	8	.006	.012	.003
Y-------	1.01	5	.026	.032	.009
Yb------	.62	7	.010	.018	.005
Zn------	3.23	3	.025	.019	.005

Other elements, determined in too few samples to permit a quantitative test of regional variation, also appear to differ between residuum overlying the Mississippian and pre-Mississippian bedrock areas. Boron, for example, was determined in a substantially lower percentage of samples in residuum over Mississippian bedrock (7 of 48; 15 percent) than in samples of residuum over pre-Mississippian bedrock (57 of 94; 61 percent). Cadmium, cerium, and lanthanum, on the other hand, were determined in a higher percentage of residuum samples collected over Mississippian bedrock (21 percent for cadmium, 13 percent for cerium, and 57 percent for lanthanum) compared to residuum samples over pre-Mississippian bedrock (5 percent for cadmium and cerium and 15 percent for lanthanum).

These comparisons suggest that residuum over bedrock of Mississippian age is relatively rich in rare-earth elements compared to residuum over bedrock of pre-Mississippian age. In addition to cerium and lanthanum, praseodymium and samarium were detected in two samples of the final study collected over Mississippian bedrock and in none taken over pre-Mississippian bedrock. Sample O063 (Searcy County, Ark.) contained 200 ppm cerium, 150 ppm praseodymium, 700 ppm neodymium, 150 ppm samarium, and 100 ppm dysprosium; sample M022 (Jasper County, Mo.) contained 200, 150, 700, 150, and 70 ppm of these same elements, respectively; and sample R17 in the highway study (from the Osage unit, Greene County, Mo.) contained 300 ppm each of lanthanum and neodymium, 100 ppm each of samarium and gadolinium, and 70 ppm each of dysprosium and holmium. Residuum over Mississippian bedrock is relatively rich in aluminum (table 12), and the distribution of rare-earth elements probably reflects the fact that this residuum is simply more clay-rich than residuum over pre-Mississippian bedrock.

In general, those elements for which the regional component of variance in the final study (S_β^2) was nonsignificant displayed significant components between localities within units (S_θ^2). These include two alkali elements (potassium and sodium), a carbonate-related suite (carbon, calcium, magnesium, and strontium), an ore-element suite (barium, copper, lead, and zinc), and a miscellaneous trace-element suite of arsenic, cobalt, chromium, fluorine, nickel, yttrium, and zirconium. The differences in the carbonate suite result from minor variations of calcite or dolomite in the samples. Potassium is high in localities 16, 37, and 38 (as high as 6.4 percent K_2O in sample B052), and sodium is high in locality 19 (as high as 0.28 percent Na_2O in sample P011). These high values may reflect in part an arkosic heritage for the residuum in those localities.

The greatest concentrations of ore elements outside of Washington County were reported for the following localities: Barium (as high as 500 ppm) in localities 16, 17, and 18; copper (as high as 150 ppm) in 25, 27, and 34; lead (as high as 150 ppm) in 16, 28, 30, and 43; and zinc (as high as 1040 ppm) in 30, 44, and 51. Other trace elements were highest at these localities (still excluding Washington County): Arsenic (as high as 61 ppm) in locality 37; cobalt (as high as 100 ppm) in 18; chromium (as high as 200 ppm) in 42; fluorine (as high as 5900 ppm) in 28; nickel (as high as 100 ppm) in 48 and 51; yttrium (as high as 500 ppm) in 46; and zirconium (as high as 200 ppm) in 14 and 17. In addition to these elements, boron appears to be high in locality 16 (as much as 70 ppm), molybdenum appears to be high in locality 37 (as much as 7 ppm), cadmium appears to be high in locality 51 (as much as 6 ppm), and

TABLE 9.—*Comparison of estimated logarithmic variance components for residuum of the final study in Missouri*

[Asterisk (*), significantly different from zero at the 0.05 probability level. Note: 23 samples collected from Washington County were excluded from this analysis because they were judged to be geochemically anomalous]

Element	Total $\log_{10}$ variance (s^2_{logX})	Between units		Between localities		Between sections		Between samples		Between replicates	
		Component s^2_β	Percent of total	Component s^2_θ	Percent of total	Component s^2_κ	Percent of total	Component s^2_δ	Percent of total	Component s^2_ε	Percent of total
Al-----	0.0253	0.0051*	20	0.0017	7	0.0118*	47	0.0065	26	0.0002	<1
As-----	.0503	<.0001	<1	.0202*	40	.0197*	39	.0050	10	.0054	11
Ba-----	.0243	<.0001	<1	.0098*	40	.0047*	19	.0058	24	.0040	16
Be-----	.0222	.0018*	8	.0035	16	.0094*	42	.0044	20	.0031	14
C (Tot)	.0665	.0071	11	.0154*	23	.0111*	17	.0235	35	.0094	14
[1]Ca-----	.2673	.0185	7	.0999*	37	.0530*	20	.0707	27	.0252	9
Co-----	.0886	<.0001	<1	.0292*	33	.0280*	32	.0286	32	.0028	3
Cr-----	.0407	.0148*	36	.0067*	16	.0102*	25	.0045	11	.0045	11
Cu-----	.0596	.0117*	20	.0128*	21	.0194*	33	.0118	20	.0039	7
F------	.0660	.0003	<1	.0195*	30	.0246*	37	.0075	11	.0141	21
Fe-----	.0312	.0065*	21	<.0001	<1	.0173*	55	.0073	23	.0001	<1
Ga-----	.0397	.0074*	19	.0020	5	.0185*	47	.0087	22	.0031	8
Hg-----	.1241	.0024	2	.0155	12	.0546*	44	.0394	32	.0122	10
K------	.0696	<.0001	<1	.0405*	58	.0189*	27	.0101	15	.0001	<1
Li-----	.0347	.0031*	9	.0072	21	.0161*	46	.0075	22	.0008	2
Mg-----	.0427	.0027	6	.0165*	39	.0152*	36	.0080	19	.0003	<1
Mn-----	.1498	.0200*	13	.0239	16	.0532*	36	.0444	30	.0083	6
Na-----	.0419	<.0001	<1	.0139*	33	.0130*	31	.0126	30	.0024	6
Ni-----	.0556	.0020	4	.0186*	33	.0137*	25	.0099	18	.0114	21
Pb-----	.0636	<.0001	<1	.0365*	57	.0127*	20	.0045	7	.0099	16
Sc-----	.0328	.0093*	28	.0031	9	.0106*	32	.0086	26	.0012	4
Se-----	.1482	.0167*	11	<.0001	<1	.0596*	40	<.0001	<1	.0719	49
[2]Si-----	124.4	22.9*	18	15.9	13	44.2*	36	38.8	31	2.6	2
Sr-----	.0635	.0019	3	.0208*	33	.0237*	37	.0119	19	.0052	8
Ti-----	.0087	<.0001	<2	.0008	9	.0036*	41	.0027	31	.0016	18
V------	.0301	.0050*	17	.0022	7	.0130*	43	.0050	17	.0049	16
Y------	.1249	.0350*	28	.0237*	19	.0261*	21	.0385	31	.0016	1
Yb-----	.0790	.0168*	21	.0013	2	.0271*	34	.0287	36	.0051	6
Zn-----	.0738	.0142*	19	.0150*	20	.0296*	40	.0146	20	.0004	<1
Zr-----	.0178	.0002	<2	.0059*	33	.0014	8	.0074	42	.0029	16

[1]Determined by semiquantitative emission spectrography.
[2]Variance calculated on nontransformed data rather than log data.

lanthanum appears to be high in locality 46 (as much as 1000 ppm).

The geochemical heterogeneity noted at local scales in the highway study ($S^2_\kappa + S^2_\delta$, table 7) is confirmed in the final study. In table 9, 21 of 30 entries exhibit half or more of their total observed variances at scales less than a few kilometers. If the laboratory variance (S^2_ε) is added to this, 27 of the 30 listed elements exhibit over half of the total variance at these three levels of design, and 16 exhibit over two-thirds. For the most part, these three combined variances estimate the basic geochemical imprecision which would be encountered in representing a residuum locality by a single sample, if that sample were analyzed by the methods listed in table 3 or by methods with similar precision.

BARITE ORE

The State of Missouri is a leading producer of barite, which is mined from residuum in the Washington County barite district. It is used principally as a component of oil-well drilling fluids and secondarily in paint, rubber, and glass manufacturing (Stout and Hoffman, 1973, p. 22; Wharton and others, 1969, p. 227). Minor amounts of lead are recovered from the barite operations (Kisvarsanyi and Searight, 1965).

Results of chemical analyses of eight samples of washed but unground barite ore are given in table 13. Two samples were collected in 1971 from each of four operating companies in the barite district. The trace-element content in barite is one of the lowest among geologic materials in the State. Apart from about 2 percent alumina and about 0.5 percent strontium, few elements occur in amounts much above a tenth of a percent. Of the constituents listed in table 13, only lead occurs in barite ore in quantities substantially greater than in the host residuum (compare table 11). Calcium, copper, and mercury occur in the barite in about the same amount that they occur in residuum; all other elements tend to occur in very low amounts in barite. Many elements commonly determined in more typical geologic materials at low levels (see table 3) were not detected in barite.

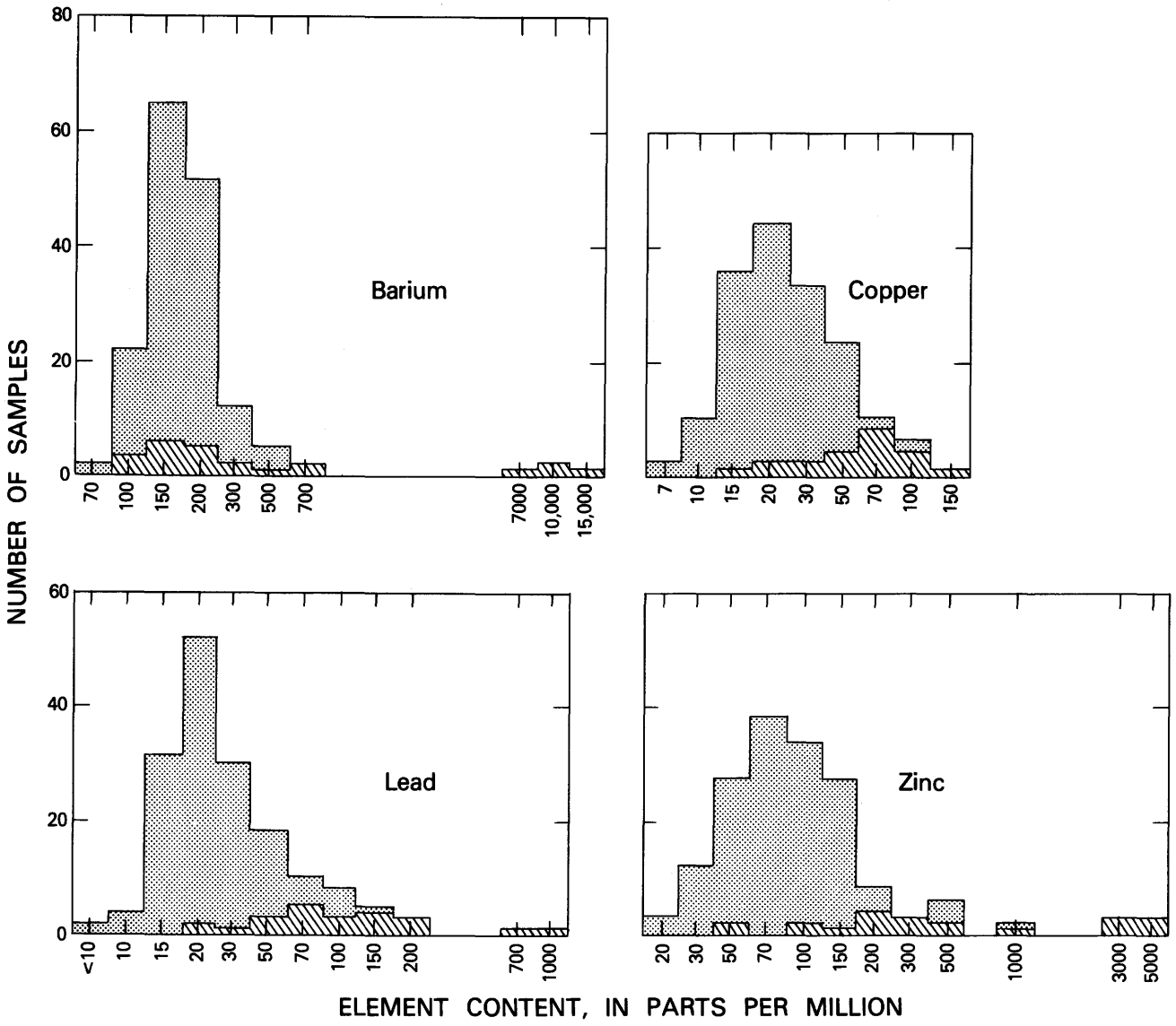


FIGURE 10.—Barium, copper, lead, and zinc content in residuum. Diagonal line pattern represents samples from Washington County, Missouri.

The aluminum-silicon ratio in the barite ore is about 10 times too high to account for these two elements in any common clay. It is probable that the alumina occurs instead as a hydrated oxide. The strontium probably substitutes for the barium in barite.

THE RELATION OF RESIDUUM TO BEDROCK

In the highway study, a sample of bedrock, assumed to be the parent material, was collected underneath each sampled section of residuum. Correlations between logarithms of element concentration in these two materials are given here for those elements that were represented by sufficient data from both materials. (Many trace elements occur in carbonate rock in concentrations too low to be determined.) Data for the Roubidoux unit and overlying residuum have been excluded from these calculations because the bedrock sampled was quartzite, the distinguishing component of the Roubidoux unit. The correlations are:

Element	Correlation	Element	Correlation
Al	−0.19	Mn	0.51
Ba	.52	Na	−.16
Cr	.32	Si	.61
Cu	.67	Sr	−.17
F	.37	Ti	.55
Fe	.29	Zn	.79
Hg	−.48		

TABLE 10.—*Parameters used to assess stability in averages based on the final study*

[v, variance ratio (defined in equation 12); n_r, minimum number of randomly collected samples needed to represent each area; E_r, maximum permissible variance; $E_s(2)$, actual variance computed in the final study]

Element-----	v	n_r	E_r	$E_s(2)$
Al----------	0.25	13	0.0016	0.0016
Be----------	.09	<50	<.0004	.0017
Cr----------	.57	7	.0037	.0023
Cu----------	.24	14	.0034	.0044
Fe----------	.26	13	.0019	.0018
Ga----------	.23	14	.0023	.0024
Li----------	.10	30	.0011	.0029
Mn----------	.15	20	.0065	.0106
Sc----------	.40	9	.0026	.0018
Se----------	.13	23	.0057	.0080
Si----------	.23	14	7.3	8.1
V-----------	.20	16	.0016	.0019
Y-----------	.39	9	.0100	.0082
Yb----------	.27	13	.0048	.0039
Zn----------	.24	14	.0043	.0056

Those elements having a correlation greater than 0.5 are shown on the graph in figure 11, except for silicon and aluminum, which are shown in figure 12. A correlation of 0.5 indicates that 25 percent of the variance in one of the materials can be related to variation in the other material. Clearly, the positive relation seen in barium is controlled by a single point, sample R08 (which was collected from the Potosi unit in the Washington County barite district). The relations in copper, manganese, silicon, titanium, and zinc seem to be real, although the strength of some of these relations depends on the presence of subpopulations. The positive relations in manganese and zinc are greatly enhanced by the presence of samples from the Bonneterre (R01, R03, R04) and Potosi (R05, R06, R07, R08) units, respectively. The high zinc samples, like the high barium sample, come from the Washington County barite district.

These relations indicate that the concentrations of at least some elements in residuum appear to directly reflect the geochemistry of the immediately underlying bedrock. Olsen and Ruhe (1978) concluded that terra rosa (residuum) in southern Indiana is probably more of a transported deposit than a residual one, and it's likely that major parts of the residuum in southern Missouri are also exotic, reflecting deposition of alluvial, colluvial, or eolian materials. However, because the carbonate bedrock underlying the residuum is everywhere highly soluble, at least part of the residuum represents the insoluble residue of the bedrock.

Residuum is rich in aluminum and silicon and, if it is assumed that only negligible amounts of these elements were removed during weathering, the relative amount of parent carbonate required to produce a unit amount of daughter residuum may be estimated (fig. 12). These estimates, given as concentration factors by weight, range from about 5 (sample R04, collected from the Bonneterre unit) to about 500 (sample R17, collected from the Osage unit). A comparison of the average abundance in residuum (from the final

TABLE 11.—*Geochemical summaries of carbonate residuum, undifferentiated by bedrock area, Missouri and northern Arkansas*

[GM, geometric mean; GD, geometric deviation; GE, geometric error; Ratio, number of samples in which element was determined to total number of samples analyzed. Leaders (—) indicate insufficient data for computation. Geometric means are in parts per million except where noted as percent (pct) or parts per billion (ppb)]

Element	All residuum				Washington County, Missouri		
	GM	GD	Ratio	GE	GM	GD	Ratio
Ag--------	<0.5	----	0:142	----	<0.5	----	1:23
Al_2O_3, pct	16	1.40	142:142	1.03	17	1.36	23:23
As--------	19	1.63	142:142	1.18	30	1.76	23:23
B---------	16	1.36	54:142	1.05	12	1.52	4:23
Ba--------	170	1.41	142:142	1.16	400	4.99	23:23
Be--------	1.3	1.72	103:142	1.14	1.4	1.85	17:23
Total C, pct-----	.20	1.81	142:142	1.25	.34	1.70	23:23
CaO, pct--	.82	4.18	77:142	1.07	.34	2.34	22:23
Cd--------	1.5	1.75	15:142	1.15	.92	2.10	11:23
Ce--------	26	2.96	11:142	----	<150	----	0:23
Co--------	5.8	2.44	110:142	1.13	7.9	1.50	23:23
Cr--------	69	1.54	142:142	1.17	65	1.29	23:23
Cu--------	23	1.72	142:142	1.15	50	1.80	23:23
Dy--------	31	2.03	4:11	----	<50	----	1:2
F---------	790	1.74	142:142	1.31	750	1.55	23:23
Fe_2O_3, pct	6.5	1.46	142:142	1.02	9.7	1.76	23:23
Ga--------	21	1.54	141:142	1.14	21	1.40	23:23
Gd--------	<70	----	0:11	----	<70	----	1:2
Hg, ppb---	57	2.90	139:142	1.29	85	3.39	22:23
K_2O, pct--	1.4	1.78	142:142	1.02	1.0	1.38	23:23
La--------	26	2.73	50:142	1.11	30	1.96	8:23
Li--------	39	1.50	142:142	1.07	50	1.36	23:23
MgO, pct--	.73	1.57	142:142	1.04	.96	1.49	23:23
Mn--------	110	2.43	142:142	1.23	120	2.66	23:23
Mo--------	.78	2.73	16:142	----	<3	----	0:23
Na_2O, pct-	500	1.57	142:142	1.12	570	1.55	23:23
Nb--------	3.8	1.54	5:142	----	5.1	1.43	2:23
Nd--------	23	3.62	16:62	----	45	2.31	4:10
Ni--------	22	1.71	142:142	1.28	27	1.60	23:23
Pb--------	24	1.78	140:142	1.26	99	2.59	23:23
P_2O_5, pct-	.97	1.23	64:142	1.43	.78	1.24	11:23
Pr--------	49	1.63	2:62	----	<150	----	0:10
Sc--------	10	1.50	140:142	1.08	9.4	1.35	23:23
Se--------	.39	2.04	126:142	1.85	.46	2.05	21:23
[1]SiO_2, pct-	62	12	142:142	1.6	53	13	23:23
Sm--------	49	1.63	2:62	----	<150	----	0:10
Sr--------	46	1.77	142:142	1.18	51	1.55	23:23
Ti, pct---	.15	1.24	142:142	1.09	.14	1.40	23:23
V---------	100	1.46	142:142	1.18	130	1.45	23:23
Y---------	13	2.76	112:142	1.09	12	3.14	17:23
Yb--------	1.7	2.11	126:142	1.18	2.0	2.00	20:21
Zn--------	80	1.83	142:142	1.54	470	4.08	23:23
Zr--------	69	1.36	142:142	1.13	57	1.63	23:23

[1]Summary statistics given as arithmetic means, standard deviations, and standard error.

TABLE 12.—*Geochemical summaries of carbonate residuum, by bedrock area, in Missouri and northern Arkansas*

[GM, geometric mean; GD, geometric deviation; Ratio, number of samples in which element was determined to total number of samples analyzed. Leaders (---) indicate insufficient data for computation. Geometric means are in parts per million except where noted as percent (pct). Bedrock units from McCracken (1961)]

Element	Bonneterre			Potosi			Gasconade			Roubidoux			Jefferson City			Osage			Meramac		
	GM	GD	Ratio	GM	GD	Ratio	GM	GD	Ratio	GM	GD	Ratio	GM	GD	Ratio	GM	GD	Ratio	GM	GD	Ratio
Al_2O_3, pct	16.0	1.52	16:16	13.0	1.32	12:12	16.0	1.29	19:19	12.0	1.57	23:23	15.0	1.24	24:24	19.0	1.21	24:24	20.0	1.26	24:24
Be	----	----	----	2.0	2.04	11:12	----	----	----	.95	1.84	12:23	----	----	----	----	----	----	----	----	----
Cr	55	1.47	16:16	47	1.65	12:12	59	1.33	19:19	52	1.52	23:23	71	1.27	24:24	100	1.44	24:24	93	1.30	24:24
Cu	----	----	----	----	----	----	39	1.84	19:19	----	----	----	----	----	----	----	----	----	17	1.36	24:24
Fe_2O_3, pct	7.6	1.64	16:16	5.3	1.30	12:12	6.4	1.28	19:19	5.0	1.60	23:23	5.6	1.25	24:24	7.6	1.31	24:24	8.2	1.33	24:24
Ga	----	----	----	----	----	----	----	----	----	15	1.79	22:23	----	----	----	26	1.33	24:24	26	1.39	24:24
Li	28	1.37	16:16	----	----	----	----	----	----	----	----	----	45	1.39	24:24	----	----	----	----	----	----
Mn	280	2.89	16:16	----	----	----	----	----	----	73	1.98	23:23	----	----	----	----	----	----	----	----	----
Sc	10	1.57	16:16	9.5	1.31	12:12	9.3	1.27	19:19	7.6	1.64	21:23	9.2	1.34	24:24	15	1.29	24:24	12	1.40	24:24
Se	----	----	----	----	----	----	.31	1.62	19:19	----	----	----	----	----	----	.54	1.96	22:24	----	----	----
[1]SiO_2, pct	----	----	----	69	8.5	12:12	----	----	----	----	----	----	----	----	----	----	----	----	54	10	24:24
V	----	----	----	----	----	----	----	----	----	83	1.67	23:23	----	----	----	130	1.30	24:24	130	1.33	24:24
Y	13	1.59	14:16	15	2.22	11:12	9.0	1.61	14:19	7.2	2.25	13:23	6.4	2.48	13:24	28	2.58	24:24	27	2.64	23:24
Yb	1.8	1.66	15:16	1.9	2.25	11:12	1.4	1.65	17:19	1.1	2.04	17:23	1.1	2.02	18:24	2.6	2.01	24:24	2.6	1.89	24:24
Zn	----	----	----	----	----	----	----	----	----	----	----	----	50	1.35	24:24	----	----	----	120	1.97	24:24
Zr	87	1.43	16:16	64	1.44	12:12	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----

[1]Summary statistics given as arithmetic means, standard deviations, and standard error.

TABLE 13.—*Chemical analyses of barite ore from Missouri*

[Field samples B01, B02 from Baroid Division, National Lead Co.; B03, B04 from Dresser Minerals Division of Dresser Industries, Inc.; B05, B06 from Pfizer, Inc.; and B07, B08 from Milchem, Inc. All data in parts per million except where noted as percent (pct); GM, geometric mean; GD, geometric deviation. Leaders (---) indicate insufficient data for computation. Analysts: Violet Merritt, I. C. Frost, R. L. Rahill, J. A. Thomas, R. L.Turner, Mike Brown, J. W. Budinsky, Leung Mei, and L. C. Bradley]

Sample No.		Al_2O_3	As	Total C	Ca[1]	Cr	Cu	Fe[1]	Hg	Mg	Mn	Na_2O	Pb	P_2O_5	Se	Si[1]	Sr	Ti	Zn[2]
Lab D153-	Field RE1-	(pct)		(pct)				(pct)				(pct)		(pct)					
788W	B01	1.1	<1	<0.05	200	<1	50	0.2	0.08	50	7	0.01	70	<0.05	<0.1	500	5000	2	18
794W	B02	1.8	1.2	<.05	200	<1	70	.15	.02	<50	7	<.01	200	<.05	<.1	700	2000	2	27
792W	B03	2.0	<1	<.05	200	1	20	.3	<.01	<50	5	.03	100	<.05	<.1	2000	3000	7	28
793W	B04	2.3	2.5	<.05	200	3	20	.2	.06	<50	7	.01	200	.06	<.1	2000	3000	15	77
790W	B05	2.2	1.4	<.05	300	<1	15	.15	.03	150	5	<.01	70	<.05	<.1	700	7000	2	15
787W	B06	2.8	<1	<.05	200	3	150	.1	.08	50	7	<.01	150	<.05	<.1	700	3000	<2	33
786	B07	1.9	<1	<.06	500	2	70	.5	<.01	150	15	<.01	200	<.05	.2	500	3000	10	155
789W	B08	.3	1	.20	1000	<1	30	.15	.03	50	15	<.01	150	<.05	.1	800	3000	10	17
Summary																			
GM		1.9	<1	<.05	290	<1	40	.19	.03	<50	7.8	<.01	130	<.05	<.1	840	3600	4.1	33
GD		1.36	---	---	1.82	--	2.82	1.64	2.77	---	1.53	---	1.57	---	---	1.75	1.39	2.74	2.25

[1]Determined by semiquantitative emission spectrography.

[2]Analyses of acid-soluble fractions.

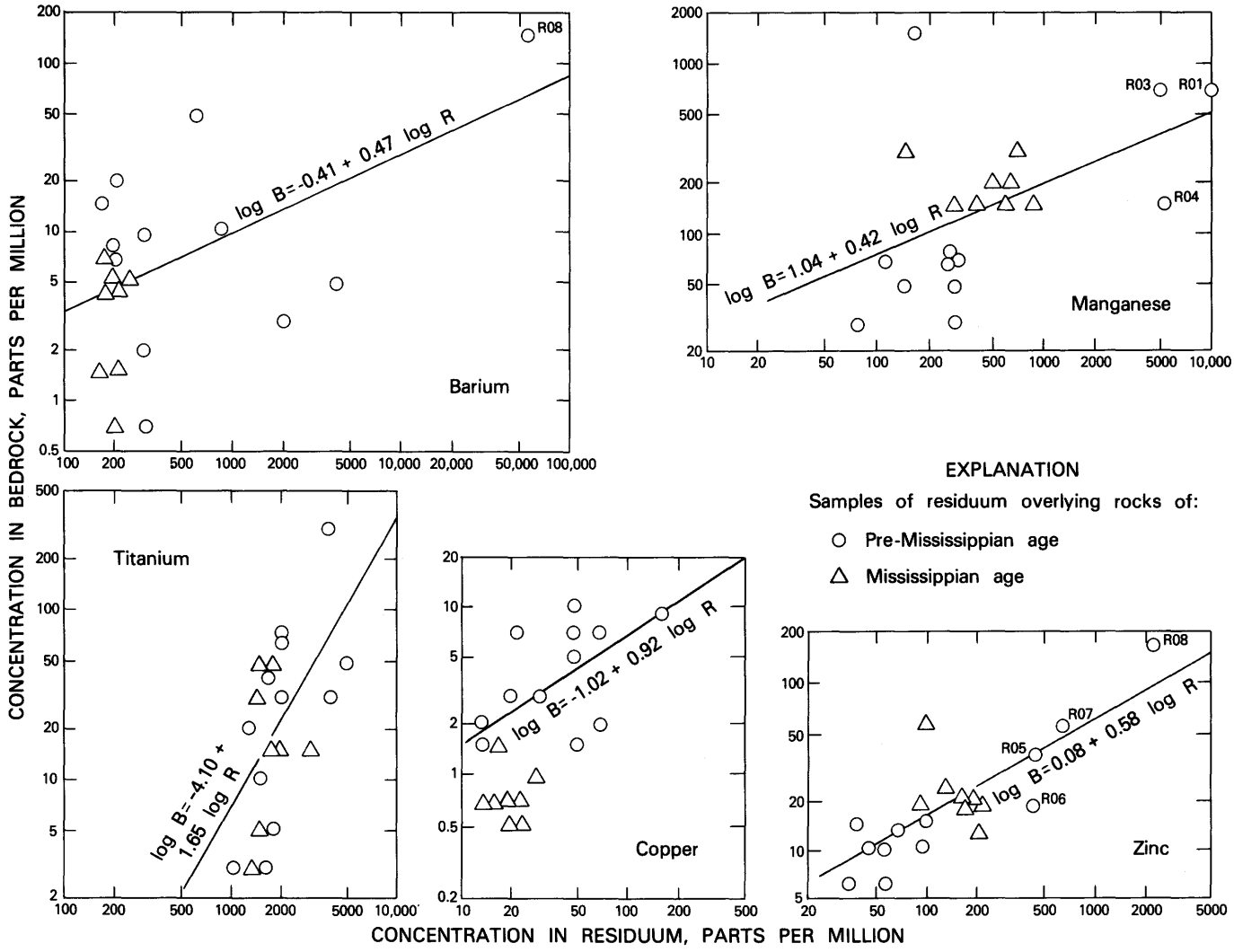


FIGURE 11.—Concentrations of barium, manganese, titanium, copper, and zinc in residuum (R) and underlying carbonate bedrock (B).

study, table 11) to the average abundance in bedrock of both Mississippian and pre-Mississippian age (from Connor and Ebens, 1980) indicates that the average concentration factor is probably in the range of 10–20.

Because the specific gravity of residuum is substantially less than that of carbonate rock, concentration factors on a volume basis are less than those shown in figure 12. If the specific gravity of residuum is taken as 1.5 and the specific gravity of rock is taken as 2.5, the factors in figure 12 would be reduced by about 40 percent. Under this assumption, the concentration factors then range from about 3 to 300 for the individual samples and from about 6 to 12 for the averages. Residuum as sampled in the final study ranged in thickness from <1 to 23 m and averaged perhaps 3 m. Concentration factors of a 100 or more (suggesting that 3 m of residuum is equivalent to 300 m of parent rock) seem unrealistic. A factor of 6 (3 m of residuum equivalent to 18 m of parent rock) may be more realistic.

DISCUSSION

The data of this work were collected for the specific purpose of defining the regional geochemical character of two of the most widespread surficial deposits in the State of Missouri. The data summaries in tables 5, 11, and 12 constitute this geochemical definition. The primary use of the data or the data summaries is expected to be in evaluation of geochemical anomalies in the local landscape of Missouri, although any assessment of geochemically related disease in plants, animals, or humans would likely make use of these summaries also.

The strongest geochemical contrast in the surficial deposits is that between the two units themselves.

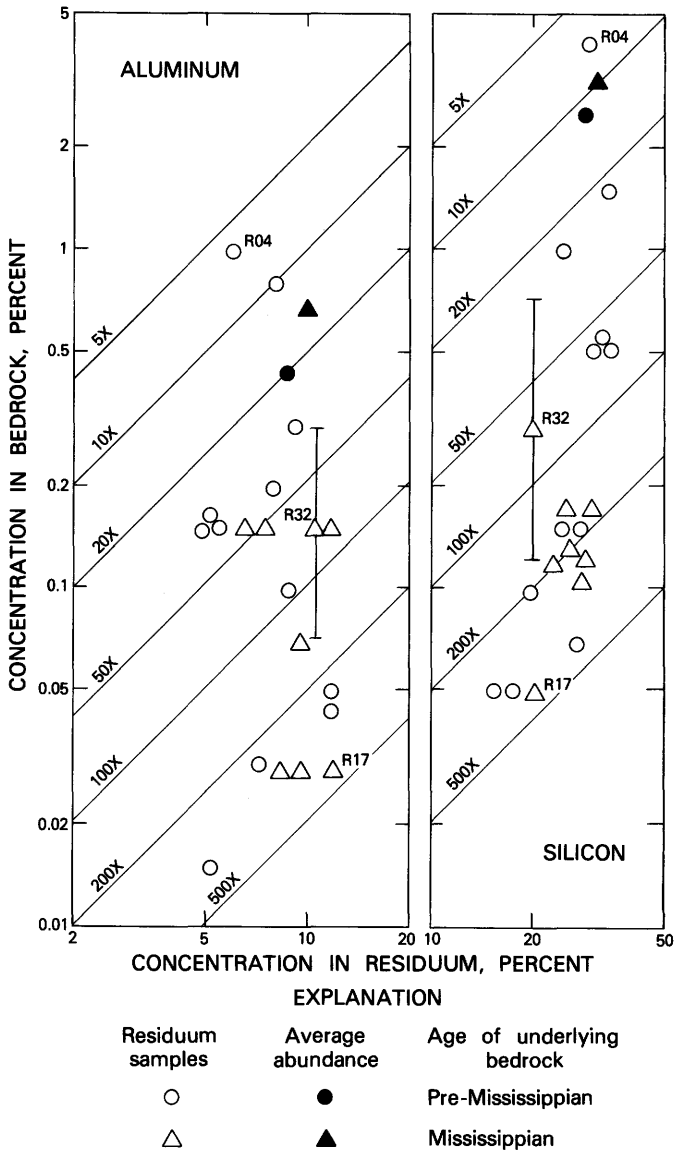


FIGURE 12.—Concentrations of silicon and aluminum in residuum and underlying carbonate bedrock. Diagonal lines show concentration factors of the elements in residuum. Average abundances are based on table 11 for residuum and on Connor and Ebens (1980) for bedrock. The standard deviation (vertical bar) on sample R32 represents the imprecision in the bedrock sample due to sampling and analytical errors.

Although the residuum is only slightly more clay-rich than loess, it contains as much as twice the aluminum, because the clay in residuum is more kaolinitic than that in loess. Fluorine and lithium are also about twice as high in residuum as in loess, but a variety of other clay-related elements, including boron, gallium, scandium, yttrium, ytterbium, and zirconium, occur in about the same concentration in both units or are even higher in loess. The illitic clay (more common in loess) probably offers a greater opportunity for trace-element substitution or surface adsorption than does the kaolinitic clay (more common in residuum). Boron, the alkali elements sodium and potassium, and the alkaline earth elements calcium, magnesium, strontium, and barium are all at least twice as high in loess as in residuum, reflecting in part the geologically prolonged leaching of these more soluble elements from residuum. Iron and manganese are about twice as high in residuum as in loess, as are two ore elements (lead and zinc) and three trace elements of particular environmental interest (arsenic, mercury, and selenium). The iron and manganese occur in residuum as hydrated oxides, which are capable of "scavenging" base metals from percolating waters.

The geochemical summaries in tables 5, 11, and 12 are best used in conjunction with maps showing the distribution of the surficial geologic deposits in the State. Unfortunately, few such maps are available, in part because of the complexities of origin of these deposits. (See Dean and Davis, 1973, for a detailed map showing the distribution of loess in a small area.) The map in figure 1 indicates something of the distribution of these materials, but it is only grossly approximate and must be used with caution. The surficial geologic deposits are almost everywhere separated by gradational boundaries.

The development of soil profiles in these materials commonly poses problems of differentiating soil from unconsolidated geologic material. For residuum, particularly, the distinction between soil and geologic material is difficult. The distributions in figure 1 are means to portray the kind of geologic material that might be expected immediately underneath a conventional soil profile; that is, the material at a depth of 1–2 m. In large parts of the State, such material would likely be recognizable as alluvium, loess, till, carbonate residuum, or perhaps some mixture of these.

Bar graphs for 28 trace elements are shown in figure 13. These graphs compare the ranges of element concentration in loess and residuum over the State. The expected concentrations and the expected 68- and 95-percent ranges in concentration are shown for those units that have sufficient data in tables 5 and 12 to permit computation. Where such data were judged to be insufficient for computation, only the observed range in concentration is given. In general, the comparisons shown in these graphs have not been tested statistically, except for the individual residuum units. They do, however, provide the opportunity to visually compare both average properties and the degree of variability of the two materials. For example, the range of element concentrations in loess rarely exceeds threefold, but in residuum it commonly exceeds tenfold. In bedrock, variation in element concentrations

commonly exceeded a hundredfold (Connor and Ebens, 1980, fig. 14).

The purpose of these graphs is to aid the user in judging the ranges of element concentration to be expected in the two surficial materials in different parts of the State. Thus a sample of such material may be judged as ordinary or unusual by comparing its composition with the ranges given for the appropriate surficial unit. Use of the graphs requires that the sample or samples being judged be assigned to the correct surficial unit, as the units have been classified for this study. To this end, the user may need geological advice, readily available from the Division of Geology and Land Survey of the State of Missouri or from local offices of the U.S. Geological Survey.

In examining a local field area of interest, the user first determines what surficial unit (or units) may be present. In localities far from a geologic boundary, the unit underlying the area of interest can probably be determined from figure 1. Localities near to or straddling boundaries will likely require geological consultation. In particular, the distinction between bluff and nonbluff loess or the determination of a specific bedrock area of residuum may prove difficult in the field, especially to the inexperienced eye. Field differentiation among soil, till, and loess is difficult where the till or loess is thin or weathered. Once the unit is identified, however, the expected range in concentration for a number of trace elements can be read from figure 13. Also, if samples are collected and analyzed, the results can be compared to the graphs (fig. 13) or summaries (tables 5, 11, and 12) to determine whether the samples in question should be viewed as geochemically unusual.

REFERENCES CITED

Aber, J. S., 1977, Multiple advances of the Kansan glacier south of the Kansas River valley [abs.]: Geological Society of America Abstracts with Programs, v. 9, no. 5, p. 569.

Bayne, C. K., Davis, S. N., Howe, W. B., and O'Connor, H. G., 1971, Regional Pleistocene stratigraphy, *in* Pleistocene stratigraphy of Missouri River valley along the Kansas-Missouri border: Kansas Geological Survey Special Distribution Publication 53, p. 5–8.

Boellstorff, John, 1978, Proposed abandonment of pre-Illinoian Pleistocene stage terms [abs.]: Geological Society of America Abstracts with Programs, v. 10, no. 6, p. 247.

Boerngen, J. G., VanTrump, George, Jr., and Ebens, R. J., 1975, Analytical data for geologic units in Missouri and parts of Kansas, Oklahoma and Arkansas: U.S. Geological Survey Open-File Report 75–137, 276 p.

Cohen, A. C., Jr., 1959, Simplified estimators for the normal distribution when samples are singly censored or truncated: Technometrics, v. 1, no. 3, p. 217–237.

Connor, J. J., and Ebens, R. J., 1980, Geochemical survey of Missouri—Geochemistry of bedrock units in Missouri and parts of adjacent States: U.S. Geological Survey Professional Paper 954–F, 55 p.

Connor, J. J., Feder, G. L., Erdman, J. A., and Tidball, R. R., 1972, Environmental geochemistry in Missouri—A multidisciplinary study: International Geological Congress, 24th, Montreal, 1972, Symposium 1, Proceedings, no. 24, p. 7–14.

Dean, T. J., and Davis, S. N., 1973, Geology of the Platte City quadrangle, Platte County, Missouri, and Leavenworth County, Kansas: Missouri Division of Geological Survey and Water Resources, Geologic Quadrangle Map Series, no. 6.

Dreeszen, V. H., 1970, The stratigraphic framework of Pleistocene glacial and periglacial deposits in the central plains, *in* Pleistocene and Recent environments of the central Great Plains: Kansas University Department of Geology, Special Publication 3, p. 9–22.

Ebens, R. J., and Connor, J. J., 1977, Cu, Pb, Zn, and Ba in carbonate residuum of southern Missouri: American Institute of Mining, Metallurgical, and Petroleum Engineers, Society of Mining Engineers, Preprint no. 77–L–325, 4 p.

Erdman, J. A., Shacklette, H. T., and Keith, J. R., 1976a, Geochemical survey of Missouri—Elemental composition of selected native plants and associated soils from major vegetation-type areas in Missouri: U.S. Geological Survey Professional Paper 954–C, 87 p.

_____1976b, Geochemical survey of Missouri—Elemental composition of corn grains, soybean seeds, pasture grasses and associated soils from selected areas in Missouri: U.S. Geological Survey Professional Paper 954–D, 23 p.

Feder, G. L., 1979, Geochemical survey of Missouri—Geochemical survey of waters of Missouri: U.S. Geological Survey Professional Paper 954–E, 78 p.

Fuller, D. L., 1977, Groundwater resources along Interstate-55, *in* Guidebook to the geology along Interstate-55 in Missouri: Missouri Geological Survey Report of Investigations no. 62, p. 91–98.

Hall, R. D., 1977, Weathering of Wisconsinan loess and related surficial materials in southwestern Indiana [abs.]: Geological Society of America Abstracts with Programs, v. 9, no. 5, p. 602.

Kisvarsanyi, E. B., and Searight, W. V., compilers, 1965, Mineral resources and industry map of Missouri: Rolla, Mo., Missouri Division of Geological Survey and Water Resources.

Krumbein, W. C., and Slack, H. A., 1956, Statistical analysis of low-level radioactivity of Pennsylvanian black fissile shale in Illinois: Geological Society of America Bulletin, v. 67, p. 739–762.

McCracken, M. H., compiler, 1961, Geologic map of Missouri: Rolla, Mo., Missouri Division of Geological Survey and Water Resources.

Miesch, A. T., 1967, Methods of computation for estimating geochemical abundance: U.S. Geological Survey Professional Paper 574–B, 15 p.

_____1976, Geochemical survey of Missouri—Methods of sampling, laboratory analysis, and statistical reduction of data, *with sections on* Laboratory methods by 11 others: U.S. Geological Survey Professional Paper 954–A, 39 p.

Myers, A. T., Havens, R. G., and Dunton, P. J., 1961, A spectrochemical method for the semiquantitative analysis of rocks, minerals, and ores: U.S. Geological Survey Bulletin 1084–I, p. 207–220.

Oetking, Philip, Feray, D. E., and Renfro, H. B., compilers, 1966, Geological highway map of the mid-continent region—Kansas, Oklahoma, Missouri, Arkansas: American Association of Petroleum Geologists, U.S. Geological Highway Map Series, no. 1.

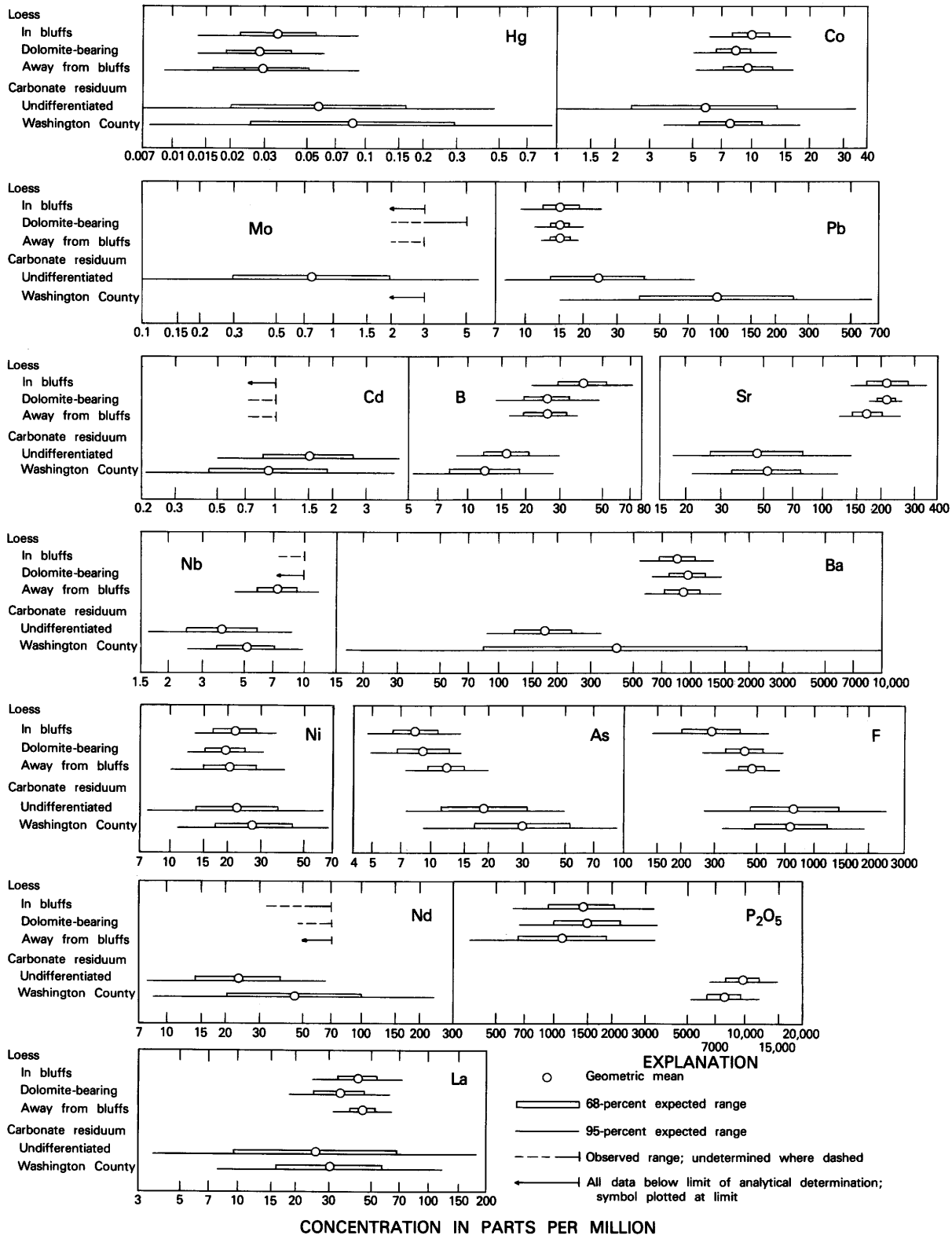
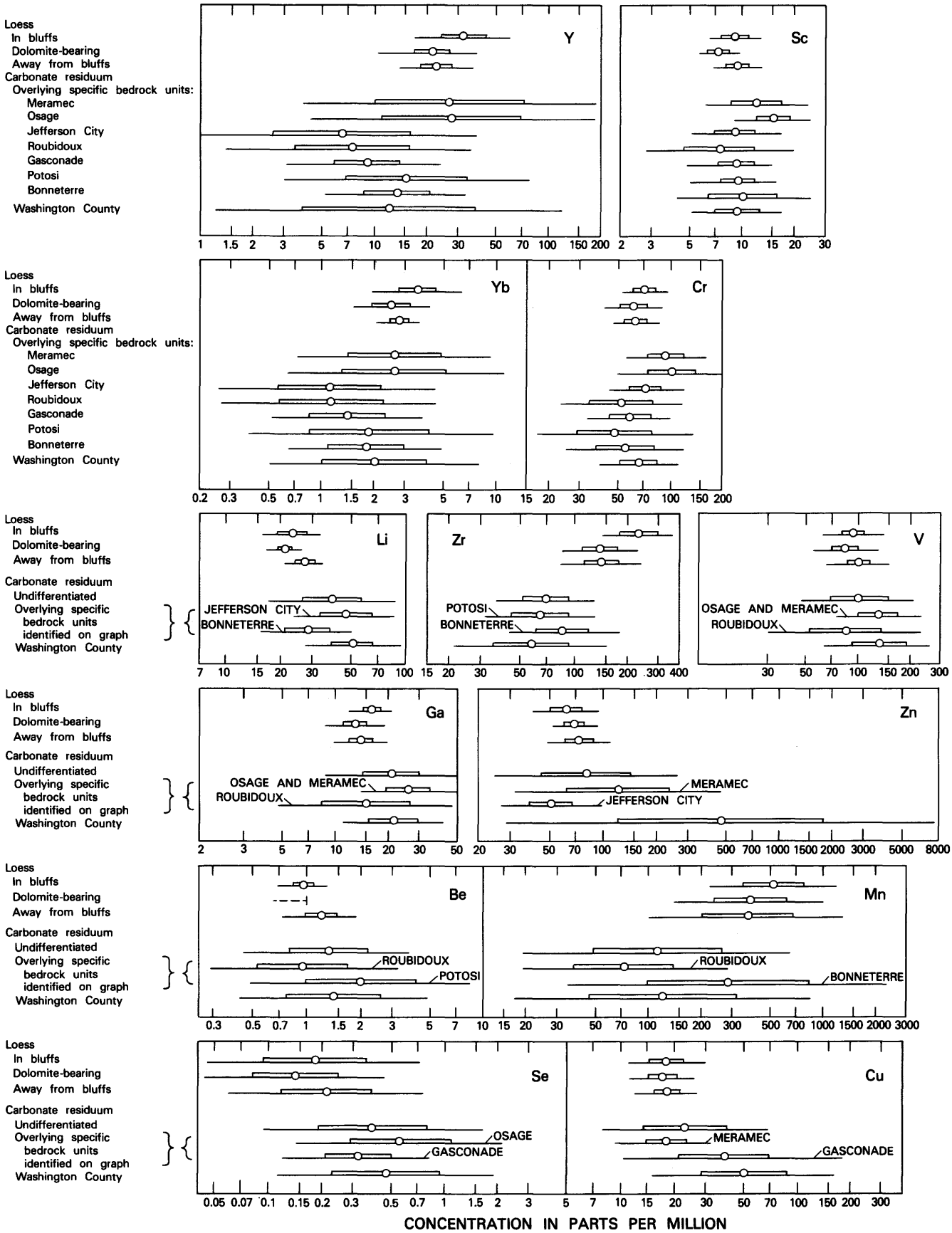


FIGURE 13.—Trace element concentrations in loess and residuum in Missouri. Bedrock units are from McCracken (1961).


Loess
In bluffs
Dolomite-bearing
Away from bluffs
Carbonate residuum
Overlying specific bedrock units:
Meramec
Osage
Jefferson City
Roubidoux
Gasconade
Potosi
Bonneterre
Washington County
Y
Sc
1 1.5 2 3 5 7 10 15 20 30 50 70 100 150 200
2 3 5 7 10 15 20 30
Yb
Cr
0.2 0.3 0.5 0.7 1 1.5 2 3 5 7 10 15 20 30 50 70 100 150 200
Carbonate residuum
Undifferentiated
Overlying specific bedrock units identified on graph
Li
Zr
V
JEFFERSON CITY
BONNETERRE
POTOSI
BONNETERRE
OSAGE AND MERAMEC
ROUBIDOUX
7 10 15 20 30 50 70 100
15 20 30 50 70 100 150 200 300 400
30 50 70 100 150 200 300
Ga
Zn
OSAGE AND MERAMEC
ROUBIDOUX
MERAMEC
JEFFERSON CITY
2 3 5 7 10 15 20 30 50
20 30 50 70 100 150 200 300 500 700 1000 1500 2000 3000 5000 8000
Be
Mn
ROUBIDOUX
POTOSI
ROUBIDOUX
BONNETERRE
0.3 0.5 0.7 1 1.5 2 3 5 7 10 15 20 30 50 70 100 150 200 300 500 700 1000 1500 2000 3000
Se
Cu
OSAGE
GASCONADE
MERAMEC
GASCONADE
0.05 0.07 0.1 0.15 0.2 0.3 0.5 0.7 1 1.5 2 3
5 7 10 15 20 30 50 70 100 150 200 300
CONCENTRATION IN PARTS PER MILLION

Olsen, C. G., and Ruhe, R. V., 1978, A mechanism for the origin of terra rosa in humid karst, southern Indiana, U.S.A. [abs.]: Geological Society of America Abstracts with Programs, v. 10, no. 6, p. 280.

Ray, L. L., 1967, An interpretation of profiles of weathering of the Peorian Loess of western Kentucky, *in* Geological Survey research 1967: U.S. Geological Survey Professional Paper 575-D, p. D221-D227.

Rieger, Samuel, and Juve, R. L., 1961, Soil development in Recent loess in the Matanuska Valley, Alaska: Soil Science Society of America Proceedings, v. 25, p. 243-248.

Ruhe, R. V., 1969, Quaternary landscapes in Iowa: Ames, Iowa, Iowa State University Press, 255 p.

Stout, L. N., and Hoffman, David, 1973, An introduction to Missouri's geologic environment: Missouri Geological Survey Educational Series, no. 3, 44 p.

U.S. Geological Survey, 1972a, Geochemical survey of Missouri—Plans and progress for first six-month period (July-December, 1969): U.S. Geological Survey open-file report, 49 p.

_____1972b, Geochemical survey of Missouri—Plans and progress for second six-month period (January-June, 1970): U.S. Geological Survey open-file report, 60 p.

_____1972c, Geochemical survey of Missouri—Plans and progress for third six-month period (July-December, 1970): U.S. Geological Survey open-file report, 33 p.

_____1972d, Geochemical survey of Missouri—Plans and progress for fourth six-month period (January-June, 1971): U.S. Geological Survey open-file report, 63 p.

_____1972e, Geochemical survey of Missouri—Plans and progress for fifth six-month period (July-December, 1971): U.S. Geological Survey open-file report, 145 p.

_____1972f, Geochemical survey of Missouri—Plans and progress for sixth six-month period (January-June, 1972): U.S. Geological Survey open-file report, 86 p.

_____1973, Geochemical survey of Missouri—Plans and progress for seventh six-month period (July-December, 1972): U.S. Geological Survey open-file report, 86 p.

Weaver, C. E., and Pollard, L. D., 1973, The chemistry of clay minerals: Amsterdam, Elsevier Scientific Publishing Company, Developments in Sedimentology, no. 15, 213 p.

Wharton, H. M., Martin, J. A., Rueff, A. W., Robertson, C. E., Wells, J. S., and Kisvarsanyi, E. B., 1969, Missouri minerals—Resources, production and forecasts: Missouri Division of Geological Survey and Water Resources Special Publication, no. 1, 303 p.

Wickham, J. T., and Lineback, J. A., 1978, Multiple glacial advances of western Illinois [abs.]: Geological Society of America Abstracts with Programs, v. 10, no. 6, p. 287.

Wisconsin University, Agricultural Experiment Station, 1960, Soils of the north central region of the United States—Their characteristics, classification: Wisconsin University Agricultural Experiment Station Bulletin 544, 192 p.

☆ U.S. GOVERNMENT PRINTING OFFICE: 1980—777-034/17