Geol Survey

T/GRANT REPORT: 1983-4

# Mineral matter and trace elements in the Herrin and Springfield Coals, Illinois Basin Coal Field

R. D. Harvey, R. A. Cahill, C.-L. Chou, and J. D. Steele

April 1983

Illinois Department of Energy and Natural Resources
STATE GEOLOGICAL SURVEY DIVISION
Champaign, Illinois

Prepared for the
U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, D.C. 20460
Grant R806654

Harvey, R. D. (Richard)
Mineral matter and trace elements in the Herrin and Springfield Coals, Illinois Basin Coal Field / R. D. Harvey and others. — Champaign, Ill. : Illinois State Geological Survey, April 1983.

161 p. ; 28 cm. — (Illinois—Geological Survey. Contract/Grant report ; 1983-4)
Prepared for the U.S. Environmental Protection Agency.

1. Coal—Illinois Basin. 2. Trace elements in coal. 3. Coal—Mineral matter. I. Title. II. Series.

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FINAL REPORT

Prepared for:

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, D.C. 20460

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# ACKNOWLEDGMENTS

This research program was supported by the U.S. Environmental Protection Agency Grant Agreement R806654 through the University of Illinois. This support is gratefully acknowledged.

Mining and exploration companies that provided or assisted greatly in collection of samples for this study include: AMAX Coal Company, ARCO Coal Company, Consolidation Coal Company, Freeman United Coal Mining Company, Inland Steel Company, Midland Coal Company, NICOR, Old Ben Coal Company, Peabody Coal Company, Sahara Coal Company, and Southwestern Illinois Coal Corporation.

Several members and former members of the ISGS scientific staff contributed significantly to the project: S. J. Russell initiated the project and was the principal investigator during the first year of the project. F. L. Fiene supervised the mineralogical work, and T. F. Tsui the geochemical mapping during the first year. W. J. Nelson, P. J. DeMaris, and S. K. Danner collected many of the samples studied from underground and strip mines; J. D. Cooper crushed and prepared the samples. L. D. Applequist and E. I. Fruth assisted in the analytical chemistry phases. L. P. Leahey and M. D. Boyd typed the manuscript.

Other technical staff working on the project were: P. Bowden and I. Demir, mineralogical work; D. J. Lowry, operation of low-temperature ashers; and P. M. Jarrell, computer programming. The electron microscope and other facilities of the University of Illinois Center for Electron Microscopy were used extensively for this study. We greatly appreciate the cooperation of the entire staff of the Center.

*Drafting: Sandra Stecyk*

# ABSTRACT

Analytical data are given for 67 chemical elements and related parameters and 8 mineralogical components in 102 newly collected samples of coal from the Springfield and Herrin Coals, the two principal coal seams mined throughout the Illinois Basin Coal Field. (This field extends from Illinois into southwestern Indiana and western Kentucky.) These data were combined with equivalent data for 128 other samples studied previously (Gluskoter et al., 1977, Rao and Gluskoter, 1973, and Ward, 1977) to evaluate the statistical variation and areal distribution of impurities of potential environmental concern. The two seams studied account for more than 90 percent of the coal produced in the Illinois Basin Coal Field and about 75 percent of the identified coal reserves in this coal field. The samples analyzed represent the coal as it occurs in the ground, exclusive of major shale interbeds and large mineral nodules encountered in the seam at collection sites.

The sulfur content of these two seams is generally too high to meet current environmental requirements. Analytical data on sulfur and the other elements of greatest and moderate potential environmental concern and their regional distribution are summarized in this report.

Two samples from each seam were subjected to washability tests, which involve float-sink separations of the samples into various specific gravities in the range of less than 1.3 to greater than 1.6. Analyses of these fractions combined with similar data for two other samples from the Herrin provide elemental compositions corresponding to that of washed coal, such as 80 percent recovery of coal material. This recovery is believed to approximate the coal product from many existing coal preparation (washing) plants. These results make it possible to estimate the average expected elemental composition of washed coal products for all of the samples studied. The expected values for the elements of concern are given in table i.

None of the elements except sulfur is thought to be present in sufficient quantities in washed coals to cause environmental problems associated with combustion; however, trace element analyses of waste materials from preparation plants processing coals from the Springfield and Herrin Coals need to be made.

Maps included in this report show areal distributions of the concentrations of sodium, chlorine, and other deleterious elements in the two coal seams.

TABLE i. Summary: Concentration of chemical elements and mineral matter of environmental concern in samples of the Herrin (H) and Springfield (S) Coals and trends in the regional distribution of these constituents.

| | Whole-coal samples | | | | Estimated average for washed coals | Regional distribution within the Illinois Basin Coal Field † |
|---|---|---|---|---|---|---|
| | Units | Mean | Common range | Maximum | | |
| CHEMICAL ELEMENTS | | | | | | |
| *Arsenic | ppm | 11 | 2-20 | 61 | 4 | H: ≥6 clustered in NW and SO Ill.<br>S: >10 mostly along Galatia channel |
| Beryllium | ppm | 1.5 | 1.1-1.9 | 3.9 | 1.4 | H & S: no apparent trends |
| *Boron | ppm | 118 | 40-200 | 225 | 113 | H: somewhat higher values in W Ill.<br>S: somewhat lower values along the Galatia channel |
| *Cadmium | ppm | 1.5 | <5. | 65 | <1.5 | H: >5(?) clustered in NW and SE Ill.<br>S: >5(?) clustered in NW and SE Ill. |
| Chromium | ppm | 18 | 14-22 | 60 | 15 | H & S: no apparent trends |
| Copper | ppm | 12.5 | 7-17 | 67 | 9 | H: higher values in NW Ill.<br>S: no apparent trend |
| Fluorine | | 68 | 10-125 | 262 | 50 | H & S: no apparent trends |
| *Lead | ppm | 28 | 11-45 | 206 | 17 | H: >50 mostly in NW, EC and SE Ill.<br>S: >30 mostly in SE Ill. |
| *Mercury | ppm | 0.16 | 0.1-0.2 | 0.71 | 0.13 | H: >0.2 mostly in NW Ill.<br>S: >0.3 (few), scattered |
| *Molybdenum | ppm | 9.2 | 6-12 | 29 | 5 | H & S: no apparent trends |
| Nickel | ppm | 18 | 14-22 | 46 | 17 | H: higher values in NW Ill.<br>S: no apparent trends |
| *Selenium | ppm | 2.4 | 2-3 | 8.5 | 2 | H & S: no apparent trends |
| Silver | ppm | 0.06 | 0.04-0.08 | 0.18 | 0.04 | insufficient data |
| *Sulfur | % | 3.5 | 2.8-4.2 | 8.4 | 2.6 | H: lower values in certain areas near Walshville channel<br>S: lower values in certain areas near Galatia channel |
| Thallium | ppm | 1.0 | 0.3-2.2 | 7.2 | 0.5 | H & S: no apparent trends |
| Thorium | ppm | 2.2 | 1.7-2.7 | 7.6 | 1.7 | H: >3 scattered<br>S: >2 scattered |
| Uranium | ppm | 1.5 | 0.5-2.9 | 9.3 | 1.5 | H & S: no apparent trends |
| MINERAL MATTER | | | | | | |
| Calcite ($CaCO_3$) | % | 1.3 | 0.8-1.8 | 5.2 | - | H & S: no apparent trends |
| Clays (Al-Silicates) | % | 8.5 | 7.2-9.8 | 19.1 | - | H & S: no apparent trends |
| Pyrite ($FeS_2$) | % | 3.4 | 2.4-4.4 | 11.6 | - | H & S: same as sulfur above |
| Quartz ($SiO_2$) | % | 2.3 | 1.8-2.8 | 5.4 | - | H & S: no apparent trends |
| Ash (750°) | % | 12.1 | 9-15 | 22.9 | - | H: lower values in areas near Walshville channel and in KY<br>S: lower values in certain areas near Galatia channel and in KY |
| LTA | % | 15.5 | 12-19 | 28.1 | - | H & S: same as Ash above |

†H=Herrin Coal; S=Springfield Coal; NW=northwestern; EC=east central; SE=southeastern; SO=southern; W=western.

*Elements of greatest potential environmental concern; all other chemical elements listed are of moderate potential concern (U.S. National Committee for Geochemistry, 1980).

# I. INTRODUCTION

## ISSUES

In recent years coal has provided about 20 percent of the energy consumed in the United States (DOE, 1981). About 50 percent of all the electric power consumed in the country is generated by combustion of coal (NERC, 1980)—this usage accounted for 72 percent of the coal produced in 1979 (DOE, 1980). In 1980, 830 million tons of coal was produced in the country (National Coal Association); thus, about 600 million tons was used to generate the electricity consumed in 1980.

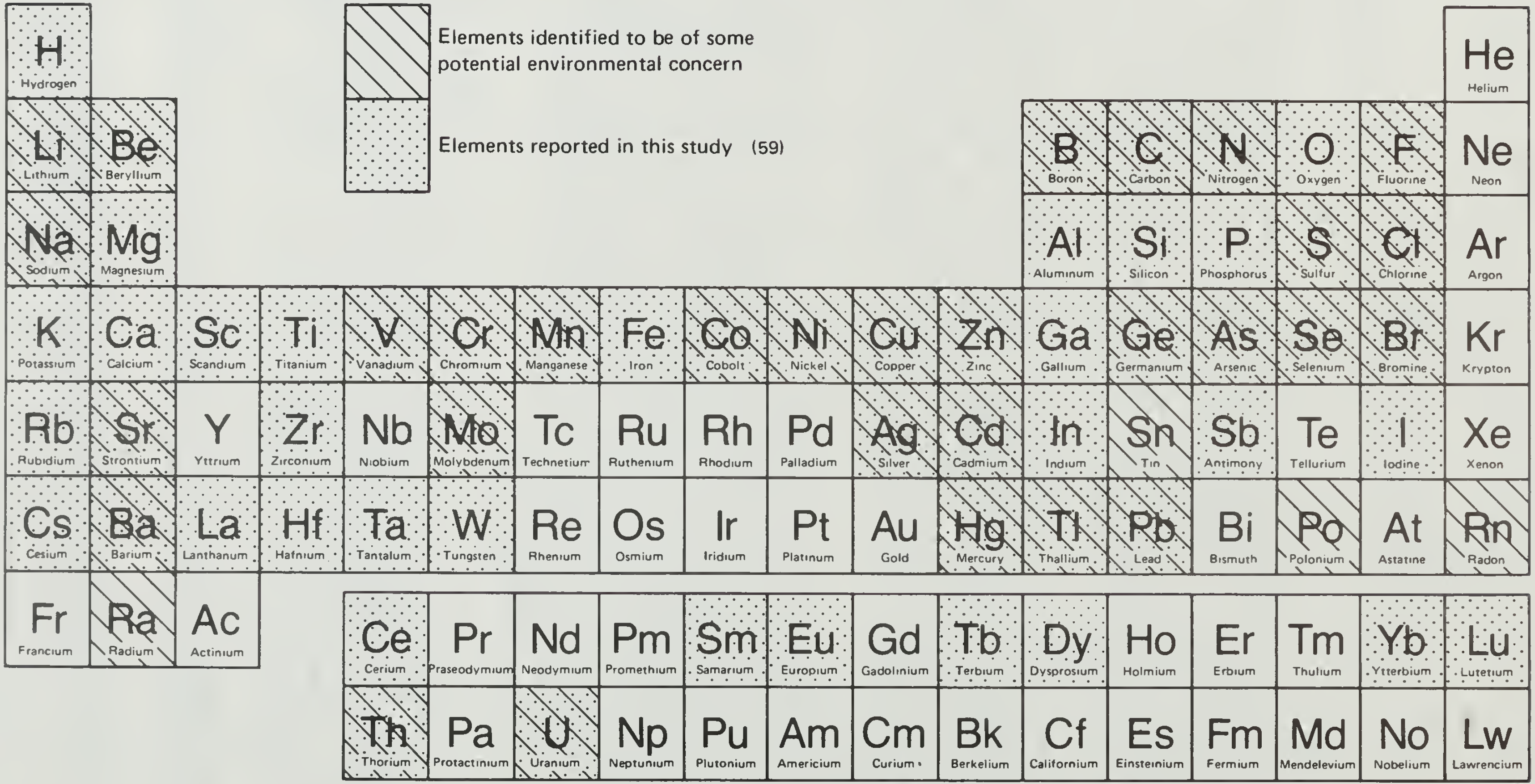
Sulfur is the element of major environmental concern in coal, primarily because of its adverse effects on air quality. Other gaseous compounds of concern are the oxides of carbon and nitrogen released into the air during combustion of coal. These and other elements of concern are indicated on the periodic table of elements (fig. I-1), as adapted from the report of the National Research Council Panel on Trace Element Geochemistry of Coal Resource Development Related to Health (U.S. National Committee for Geochemistry, 1980).

In addition to the gaseous elements, the NRCP report lists trace elements of varying degrees of concern, depending on a wide range of conditions. Trace elements considered of greatest concern are arsenic, boron, cadmium, lead, mercury, molybdenum, and selenium. These elements occur in coal, and in residues from coal cleaning and combustion, in amounts generally greater than their average amount in the earth's crust. Arsenic, cadmium, mercury, and lead are thought to be highly toxic to most biological systems. If coal-derived fly ash were disposed of on crop soils, molybdenum and selenium might find their way to forage crops, making the crop unsafe for animal consumption. Boron contamination is only a remote possibility, but might lead to some poisoning of plants.

Elements of moderate concern to the Panel included chromium, copper, fluorine, nickel, vanadium, and zinc. These elements are potentially toxic and occur in slightly enriched concentrations in some residues produced during coal combustion. Elements classified as of minor concern include barium, strontium, sodium, manganese, cobalt, antimony, lithium, chlorine, and bromine. These elements frequently occur in fly ash in concentrations greater than in the average crustal rock material. Specific adverse impact of these elements is considered remote.

Although tin, beryllium, thallium, silver, and tellurium have some adverse effects upon health, these elements usually have negligible concentrations in coal.

The radioactive elements (uranium and thorium and their daughters) are found in coal in amounts comparable to those found elsewhere in nature.



ISGS 1981

Figure 1-1. Elements determined for this study and those identified to be of some potential environmental concern—including elements of minor concern but with negligible concentrations in coal and coal residues (U.S. National Committee for Geochemistry, 1980).

The Panel considered their effects on health to be negligible; however, at the time of the Panel's study, little information was available on these elements.

In addition to health considerations, trace and minor elements in coal can cause a range of technical problems associated with the utilization of coal. Sodium and chlorine are known to be corrosive in combustion processes. Sodium and vanadium may poison the catalysts used for coal liquefaction (Alpert and Wolk, 1981); calcium is thought to be somewhat beneficial because it partly catalyzes the combustion processes (Essenhigh, 1981). It is thus imperative to analyze chemical and mineral impurities and their variability in coals so that these properties can be accurately evaluated.

## OBJECTIVES

The primary objective of our study was to compile a data base on the characteristics and distribution of elements of environmental concern in the two principal coal seams throughout the Illinois Basin Coal Field. Because of the expected association of many of these elements with mineral matter in the coals, another major objective was to investigate the mineralogical composition of the coals, and evaluate the results in terms of the elemental composition.

Other study objectives were: (1) to determine local and regional variations of chemical and mineral components in the two most important commercial seams in the Illinois Basin; (2) to assess the abundance and variation of the trace elements of environmental concern; and (3) to investigate the spatial distribution of the trace elements and mineral components throughout the coals in order to facilitate prediction of the properties of the two coals in unexplored areas of the basin.

## SCOPE

This project is a continuation of a major research effort to characterize the mineral and chemical constituents in Illinois coals, initiated some 18 years ago at the Illinois State Geological Survey (ISGS). The previous work culminated in a report by Gluskoter et al. (1977): ISGS Circular 499 (C 499); in this report, analytical data were given for 172 samples, including 128 samples collected from the two coal seams under investigation in the present study. Analytical data are presented here for 102 new samples. Thirty five of these samples were collected from mines and drill cores in the Springfield Coal, and 67 from mines and drill cores in the Herrin Coal. The statistical and geological evaluations of the chemical and mineral compositions are based on the data from this report identified as MMC-80 and on the data in C 499. Analytical determinations reported here include 76 chemical and mineralogical properties of each of the samples collected for this project. Many of the C 499 samples had also been previously analyzed for their mineral matter contents; some of these data were reported by Rao and Gluskoter (1973) and others by Ward (1977). In these reports the areal distribution of the mineral compositions were reported in terms of the percentage of the ash fraction. We have compiled those data together with our new data and converted them to a more useful basis--percentage of the whole coal. The trace element data on C 499 samples are included in the statistical treatments only.

Additional trace element and mineralogical data on the Springfield and Herrin Coals are available at the Institute for Mining and Minerals Research, and at the Kentucy and Indiana Geological Surveys.

The abbreviations used throughout this report are listed in table I-1, the chemical elements and their symbols in figure I-1. Elements analyzed for this study also are indicated on this figure.

**TABLE I-1.** Abbreviations used in text and tables.

| | |
|---|---|
| A | angstrom unit of length |
| AA | atomic absorption method of analytical chemistry |
| B | purpose code for bench set |
| Bi | bench sample, *i*th bench (layer) of seam; top bench *i* = 1 |
| Btu | British thermal unit of energy |
| CFC | composite sample of 2 or more channels of an impure* seam (FC) from the same mine; the sample excludes the thick mineral layers |
| DC | drill core sample |
| DL | detection limit for the indicated element |
| EDX | energy dispersive x-ray method of analysis |
| F | float sample of the indicated gravity |
| FC | channel (face) of an impure* seam, the sample excludes the thick (>3/8") mineral layers |
| FIXC | fixed carbon (C) in the indicated sample |
| FS | float-sink sample: the float of the indicated gravity and the sink of the gravity indicated for the preceeding sample |
| INAA | instrumental neutron activation analysis (analytical method) |
| ISE | ion selective electrode method of analysis |
| L | local area purpose (or use) code for the indicated sample. followed by the numerical designation of the particular local area |
| LTA | low temperature asher or residue from the asher |
| M | mesh designation (Tyler) of particle size, or mineral purpose code |
| MOIS | moisture, as received |
| OE | optical emission method of analysis |
| ORS | organic sulfur, a variety of sulfur (S) in coal |
| PC | channel sample of a pure* seam |
| ppb | parts per billion ($10^9$) |
| ppm | parts per million |
| PYS | pytitic sulfur, a variety of sulfur (S) in coal |
| R | regional purpose (or use) code |
| RM | run of mine sample |
| RNAA | radiochemical neutron activation method of analysis |
| S | sink sample of the indicated gravity; or size fraction purpose code |
| SD | standard deviation |
| SP | special sample of vitrain or of a mineral |
| SUS | sulfate sulfur, a variety of sulfur (S) in coal |
| TOS | total sulfur |
| μm | a millionth ($10^{-6}$) of a meter |
| VOL | volatile matter content in the indicated sample |
| V | purpose code for hand picked vitrain samples |
| W | washed sample of sample set for which washability (float-sink) tests were made |
| WC | whole-coal sample types; include FC, CFC, PC, CPC, DC, or RM |
| $\bar{X}$ | arithmetic mean or average |
| XRF | x-ray fluorescence method of analysis |
| # | number or pounds |

*pure and impure seam or bench refers to the absence or presence of layers of mineral matter that are thicker than 3/8 inch that occur in some places within coal seams.

# II. MINERALS AND CHEMICALS IN ILLINOIS COAL

## MINERALS AND THEIR CHEMICAL COMPOSITION

Coal consists mostly of organic matter that burns, but it also contains a variety of inorganic impurities (mineral matter) that form ash during combustion of the coal. The mineral matter comprises a large variety of distinct mineral phases and elements. Most of the trace and minor elements in coals occur within the structure or on the external surfaces of the mineral grains. However, some trace elements are associated with the organic matter, chemically bound within C-H-O-N structures of the organic macerals (see table II-2) or chemically adsorbed to their internal and external surfaces. Some of these elements were part of the original plant materials retained during the coalification process; others were added later by a variety of other geological processes.

It is important to distinguish between the two modes of occurrence of trace elements because of the critical role each type plays in terms of environmental and engineering processes.

The minerals occurring in Illinois coals and their chemical compositions are listed in table II-1. Each mineral listed can, and probably often does, contain some trace elements substituted for the main cations cited in the table.

Mineral matter in coals can be classified on the basis of the physical occurrences of the minerals within the coal and coal seam. Discrete mineral grains occur in coals in one of five modes of occurrences: *disseminated* (tiny granular inclusions within macerals); *layers* (or partings and lenses in which fine-grained minerals are concentrated in layers of variable thickness); *nodules* (including concretions); *fissures* (joint or fracture fillings, especially in cleat-type joints); and *rock fragments* (megascopic masses of rock occurring in place of coal because of faulting, slumping, or related features). The main occurrences of the minerals in Illinois coals are indicated in Table II-1. The mode of the occurrence of the minerals affects mining operations and coal preparation. Thick layers and abundant nodules or rock fragments hamper mining. Disseminated minerals and the thinner (microscopic) layers are inefficiently removed from run-of-mine coal by existing coal preparation methods; however, minerals occurring in other modes are efficiently removed because of the greater density of minerals and rock fragments in comparison to that of the organic matter. Future developments in the fine grinding and cleaning of fine coal will undoubtedly facilitate removal of disseminated and microlayered mineral matter. These types of mineral matter are chiefly mixtures of clay minerals, quartz, pyrite and traces of accessory minerals (table II-1). Except for disseminated pyrite (mainly framboidal), the disseminated minerals may be derived from the inorganic matter inherited from the original plant materials (Sprunk and O'Donnell, 1942; Cecil et al., 1979).

**TABLE II-1.** Minerals occurring in Illinois coals, their stochiometric composition, and their modes of occurrence in the coals.

| Mineral | Composition | Main physical Occurrences* | Relative Abundance |
|---|---|---|---|
| SILICATES | | | |
| Clay minerals | | | |
| illite | $KAl_2(AlSi_3O_{10})(OH)_2$ | D,L,N | common |
| kaolinite | $Al_4Si_4O_{10}\,(OH)$ | F,L,N,D(?) | common |
| mixed-layer | $Al_2Si_4O_{10}\,(OH)_2\ XH_2O$ | L,D(?) | common |
| (illite smectite = with adsorbed cations and variable water content) | | | |
| chlorite | $Mg_5Al(AlSi_3O_{10})(OH)_8$ | L | rare |
| Quartz | $SiO_2$ | D,L,N | common |
| Feldspar group | $K(Na)AlSi_3O_8$ | L,D(?) | rare |
| Zircon | $ZrSiO_4$ | L,D(?) | very rare |
| SULFIDES | | | |
| Pyrite | $FeS_2$(isometric) | D,F,N | common |
| Marcasite | $FeS_2$(orthorhombic) | D(?) | rare |
| Sphalerite | ZnS | F | rare |
| CARBONATES | | | |
| Calcite | $CaCO_3$ | F,N | common |
| Dolomite (ankerite) | $Ca(Mg,Fe)(CO_3)_2$ | N | rare |
| Siderite | $FeCO_3$ | N | rare |
| SULFATES | | | |
| Barite | $BaSO_4$ | F | rare |
| Anhydrite | $CaSO_4$ | F | rare |
| Gypsum | $CaSO_4 \cdot 2H_2O$ | F | rare |
| Rozenite | $FeSO_4 \cdot 4H_2O$ | O | rare |
| Melanterite | $FeSO_4 \cdot 7H_2O$ | O | rare |
| Coquimbite | $Fe_2(SO_4)_3 \cdot 9H_2O$ | O | rare |
| Jarosite | $(Na,K)Fe_3(SO_4)_2(OH)_6$ | O | rare |
| OTHERS | | | |
| Hematite | $Fe_2O_3$ | D,L,N | rare |
| Rutile | $TiO_2$ | D,L(?) | rare |
| Apatite | $Ca_5(PO_4)_3(F,Cl,OH)$ | D,L,N | rare |

*D = disseminated; L - layered (in partings); N = nodules; F = fissures (cleat); O = Oxidation product of pyrite. Each mineral may also occur in rock fragments within coals. See text for details.

## ORGANIC MATTER

### Rank of coals tested

Rank is a measure of the degree of metamorphism the coal has undergone during its formation within the earth's crust. Metamorphism causes compositional changes, primarily in response to increased temperature and pressure that accompany increased depth of burial in the crust.

Several chemical and physical properties of the organic matter are progressively altered in response to metamorphism: moisture, carbon, and, in part, heating (Btu) values. Illinois Basin coals are high volatile bituminous in rank, subclassified as high volatile A, B, and C as defined by their heating value (ASTM, 1980).

## Coal type and maceral constituents of organic matter

The physical constituents comprising the organic matter are classified as megascopic (observable by eye) or as microscopic (observable with the aid of a microscope). The terms used for these two systems of classification are outlined in table II-2.

Megascopically, each of the channel samples tested for this study consisted of mixtures of at least three different coal types (table II-2) interlayered on a scale of 1/8 inch or so. Rarely do layers of vitrain, fusain, and dull coal exceed 3/8 inch in Illinois coals. The dominant type of coal in the samples studied is referred to as bright-banded coal.

Microscopically, the organic matter in coals is classified as one of several macerals; the classification of macerals used for this study is shown at the bottom of table II-2. A discussion of the maceral constituents of the samples studied is beyond the scope of this study, but it is important to add that the two coal seams studied are characterized as high vitrinite (generally 80 to 85% by volume), low liptinite (ca. 5 to 8% by volume), and intermediate inertinite (ca. 8 to 10% by volume). These figures were calculated on a mineral-free basis.

**TABLE II-2.** Megascopic and microscopic constituents of organic matter in Illinois coals.

Megascopic classification of Illinois coals
(adapted from ASTM—D2797, 1980) (Minimum thickness of layer for separate description is 3/8 inch)

| Coal type | Description |
|---|---|
| vitrain | splendent layers (the brightest) |
| bright banded coal | bright and thinly banded layers |
| dull banded coal | relatively dull layers |
| fusain | charcoal-like and dusty layers |
| canneloid coal | nonbanded, dense, greasy layers |

Microscopic classification of macerals for Illinois coals
(adapted from ASTM—D2797, 1980 and Teichmüller, 1975)

| Group maceral: | Vitrinite | Liptinite | Inertinites |
|---|---|---|---|
| Maceral: | Vitrinite | Sporinite | Fusinite |
| | | Cutinite | Semifusinite |
| | | Resinite | Macrinite (>10μm) |
| | | Alginite* | Micrinite (<10μm) |
| | | Fluorinite* | Sclerotinite |
| | | Bituminite* | |

*Trace constituent in some Illinois coals

# III. PROCEDURES

## SAMPLE TYPES AND PREPARATION

Samples for this study include channel and block materials taken from mines and drill cores (fig. III-1). Block samples consist of 1- to 5-inch blocks taken from particular layers in the coal seam that have a unique lithologic aspect. Only a few such samples were taken for microscopic study. Channel samples were obtained by cutting a channel of coal material from the top to the bottom of the coal seam normal to its bedding. Channel samples are representative of the whole coal, exclusive of major mineral partings (>3/8 in. [1 cm.]) if present within the seam at the sample site. Bench samples are taken as a channel but the several layers or benches of the seam are taken separately. The various types of samples tested for this project are outlined in table III-1. These designations conform to the sampling and sample type codes described by Gluskoter et al. (1977). In the present report we use the term *whole coal* to include all the sample types that represent the entire coal at the sampling site (table III-1). In this project a purpose code was established for the samples; this code is also described in table III-1.

Preparations of the samples in the laboratory for analytical tests followed the procedures given in figure III-1.

**TABLE III-1.** Sample type and purpose codes.

| | Sample code | | Purpose code | |
|---|---|---|---|---|
| I. | WHOLE COAL SAMPLES | | | |
| | FC (or PC) | channel | variability in | |
| | CFC | composite of 3-FC samples | regional | (R) |
| | DC | drill core | and | |
| | RM | run of mine from operations in a single seam mine | local | (L) |
| | | | areas | |
| II. | BENCH SAMPLES | | | |
| | B*1* | subdivions of whole coal (bench set) | variability | |
| | B*2* | | within the | (B) |
| | ↓ | | coal (seam) | |
| | B*i* | | | |
| III. | WASHED COALS | | | |
| | density fraction of the whole coal sample | | washability and organic affinity | (W) |
| IV. | SIZED COALS | | | |
| | particle size fraction of the whole coal sample | | variability of particle size | (S) |
| V. | SPECIAL SAMPLES | | | |
| | SP (hand picked) | | impurities in: | |
| | | | vitrain | (V) |
| | | | minerals | (M) |
| VI. | BLOCK SAMPLES | | microscopic studies | |

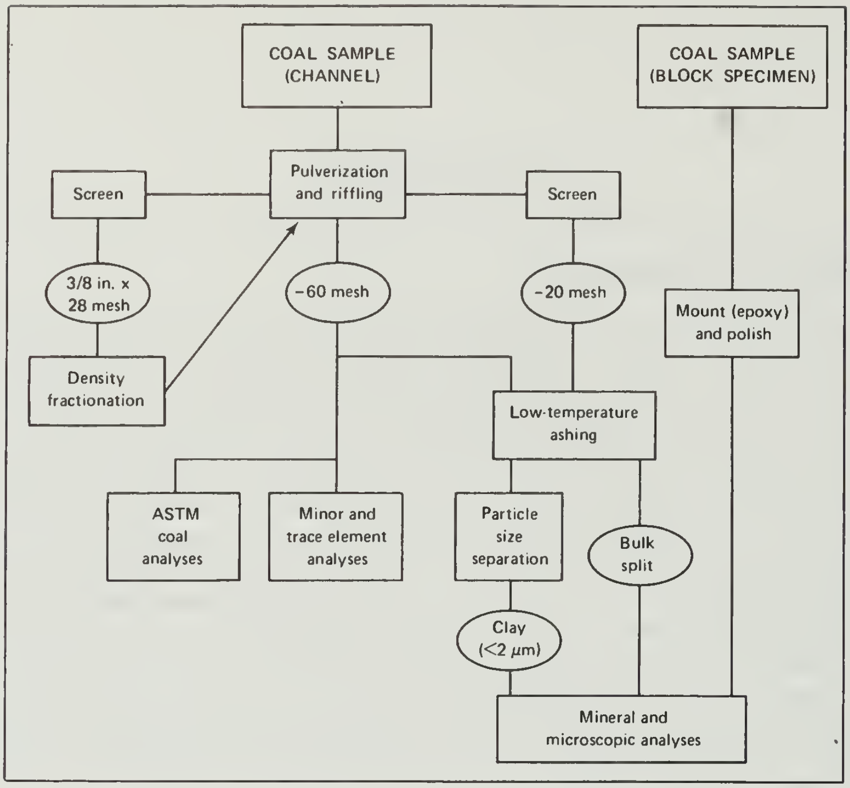
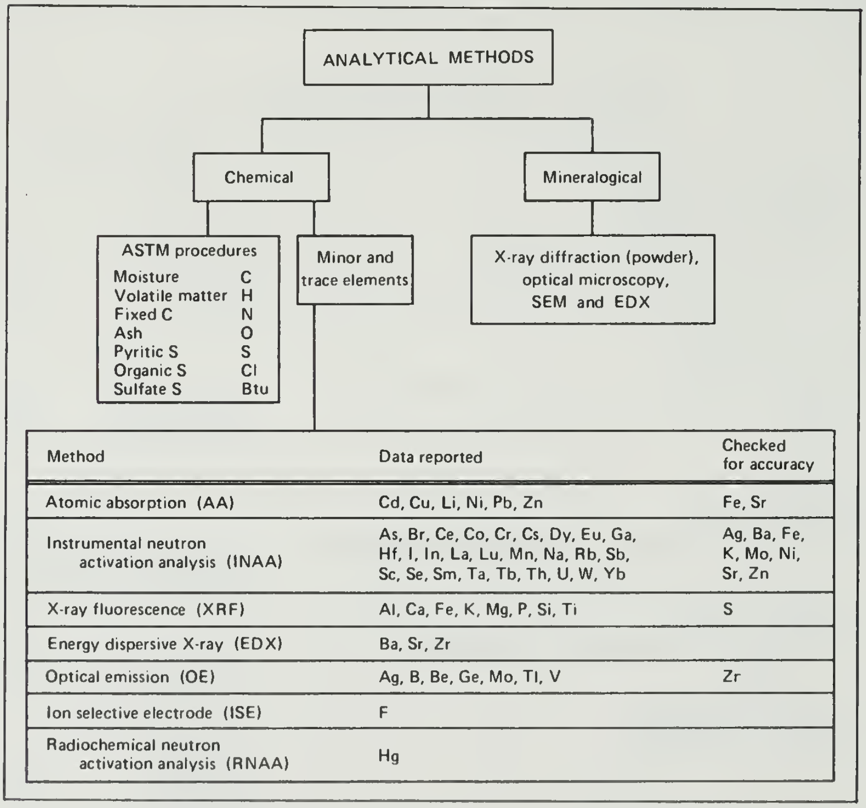


FIGURE III-1. Sample preparations used for coal analyses.



| Method | Data reported | Checked for accuracy |
|---|---|---|
| Atomic absorption (AA) | Cd, Cu, Li, Ni, Pb, Zn | Fe, Sr |
| Instrumental neutron activation analysis (INAA) | As, Br, Ce, Co, Cr, Cs, Dy, Eu, Ga, Hf, I, In, La, Lu, Mn, Na, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, U, W, Yb | Ag, Ba, Fe, K, Mo, Ni, Sr, Zn |
| X-ray fluorescence (XRF) | Al, Ca, Fe, K, Mg, P, Si, Ti | S |
| Energy dispersive X-ray (EDX) | Ba, Sr, Zr | |
| Optical emission (OE) | Ag, B, Be, Ge, Mo, Tl, V | Zr |
| Ion selective electrode (ISE) | F | |
| Radiochemical neutron activation analysis (RNAA) | Hg | |

FIGURE III-2. Methods used for analyses of coal samples.

## CHEMICAL METHODS AND PRECISION

Methods used for the analyses are outlined in figure III-2; detection limits and relative precision of the analytical values are given in table III-2.

### Standard coal determinations

Methods and procedures used for the standard analyses of coal were those described in the standard test methods of the American Society for Testing and Materials (ASTM) Committee D-5 on Coal and Coke (ASTM, 1980) or the International Standards Organization (ISO) Technical Committee 27, Solid Mineral Fuels. The standard number and a brief outline of the procedure used for this study are given in appendix A.

### Minor and trace element determinations

Methods used for analyses of coal samples in this study are indicated in figure II-2 and described in detail in appendix A. Each method provides the highest accuracy and reliability for the determination of the elements listed as "data reported." Because of the wide range of methods available, several elements could be determined by two different methods, as noted in figure III-2; this provided a valuable check on the accuracy of the reported values.

**TABLE III-2.** Detection limits (DL)* and average relative standard deviation (SD)* of the five analytical methods used.

| | INAA | | AA | | XRF | | EDX | | OE | |
|---|---|---|---|---|---|---|---|---|---|---|
| Element | DL (ppm) | ±SD (%) | DL (ppm) | ±SD (%) | DL (%) | ±SD (%) | DL (ppm) | ±SD (%) | DL (ppm) | ±SD (%) |
| Ag | 0.3 | 30 | | | | | | | 0.24 | 6.2 |
| Al | | | | | 0.1 | 3.1 | | | | |
| As | 0.1 | 10 | | | | | | | | |
| B | | | | | | | | | 11. | 6.9 |
| Ba | 30. | 20 | | | | | 5. | 20 | | |
| Be | | | | | | | | | 0.45 | 7.5 |
| Br | 0.1 | 10 | | | | | | | | |
| Ca | | | | | 0.05 | 1.6 | | | | |
| Cd | | | 1.5 | 10 | | | | | | |
| Ce | 1.0 | 15 | | | | | | | | |
| Cl | 20. | 15 | (ASTM method: DL = .05 %, SD = 10 %) | | | | | | | |
| Co | 0.01 | 5 | | | | | | | | |
| Cr | 0.5 | 10 | | | | | | | | |
| Cs | 0.05 | 15 | | | | | | | | |
| Cu | | | 2.5 | 6 | | | | | | |
| Dy | 0.05 | 10 | | | | | | | | |
| Eu | 0.01 | 5 | | | | | | | | |
| F | Method by ion selective electrode: DL = 1. ppm, SD = 5% | | | | | | | | | |
| Fe | 50. | 10 | 5. | 5 | 0.01 | 1.9 | | | | |
| Ga | 0.2 | 15 | | | | | | | | |
| Ge | | | | | | | | | 7.5 | 17.3 |
| Hf | 0.1 | 20 | | | | | | | | |
| Hg | Method by RNAA: DL = 0.005 ppm, SD = 20% | | | | | | | | | |
| I | 0.2 | 20 | | | | | | | | |
| In | 0.005 | 20 | | | | | | | | |
| K | 10. | 10 | | | 0.01 | 4.5 | | | | |
| La | 0.1 | 5 | | | | | | | | |
| Li | | | 5.5 | 12 | | | | | | |
| Lu | 0.05 | 15 | | | | | | | | |
| Mg | | | | | 0.1 | 4.4 | | | | |
| Mn | 0.1 | 5 | | | | | | | | |
| Mo | 5. | 30 | | | | | | | 20. | 6.2 |
| Na | 1.0 | 5 | | | | | | | | |
| Ni | 10. | 30 | 3.5 | 7 | | | | | | |
| P | | | | | 0.01 | 25 | | | | |
| Pb | | | 15. | 15 | | | | | | |
| Rb | 5. | 20 | | | | | | | | |
| S | (ASTM methods for reported data: DL = 0.1%, SD = 10%) | | | | | | | | | |
| Sb | 0.1 | 10 | | | | | | | | |
| Sc | 0.01 | 10 | | | | | | | | |
| Se | 0.1 | 15 | | | | | | | | |
| Si | | | | | 0.1 | 2.0 | | | | |
| Sm | 0.01 | 5 | | | | | | | | |
| Sr | 10. | 20 | 5. | 5 | | | 5. | 20 | | |
| Ta | 0.01 | 10 | | | | | | | | |
| Tb | 0.1 | 10 | | | | | | | | |
| Th | 0.1 | 10 | | | | | | | | |
| Ti | | | | | 0.01 | 3.2 | | | | |
| Tl | | | | | | | | | 1.0 | 10.2 |
| U | 0.1 | 20 | | | | | | | | |
| V | | | | | | | | | 3.0 | 9.3 |
| W | 0.2 | 30 | | | | | | | | |
| Yb | 0.05 | 10 | | | | | | | | |
| Zn | 5. | 20 | 2.0 | 5 | | | | | | |
| Zr | | | | | | | 5. | 20 | 10. | 10.3 |

* SD values apply to results in this report on whole coal basis. DL values for elements analyzed by AA, XRF, EDX, and OE methods are based on element concentration in ash fraction.

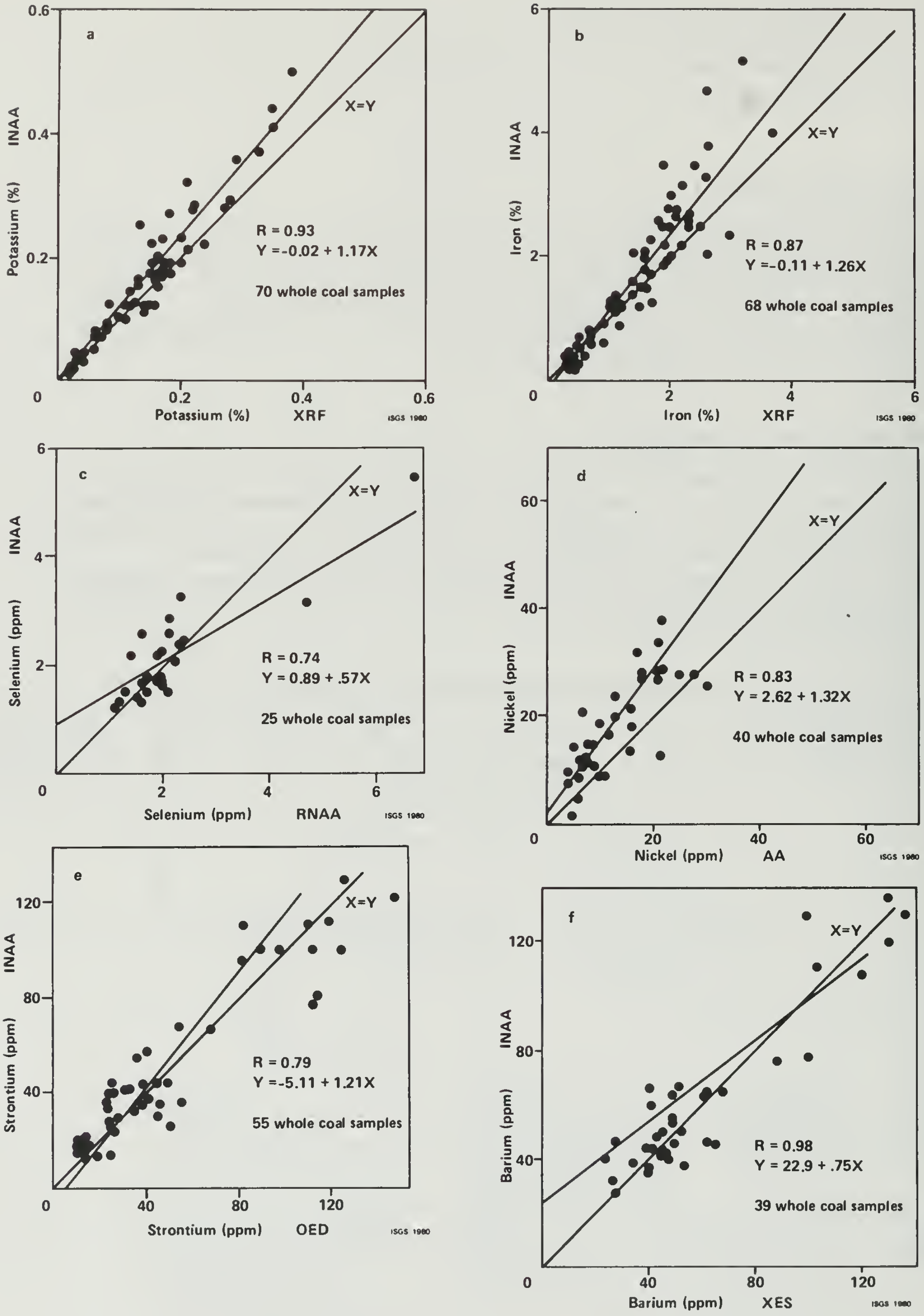


FIGURE III-3. Determinations of six elements in whole coals by two methods.

The raw coal sample was tested to obtain the analytical values by instrumental neutron activation analysis (INAA), ion selective electrode (ISE), and by radiochemical neutron activation analysis (RNAA) methods; the high temperature (500°C) ash was tested by atomic absorption (AA), x-ray fluorescence (XRF), energy dispersive x-ray (EDX) and optical emission (OE) methods. All analytical values reported herein are reported on the moisture-free whole coal basis.

### Analytical significance of minor and trace element results

During the course of this and other investigations at ISGS, data have been compiled for several hundred coal and coal-related materials. Two or more analytical techniques were often used for the determination of an element.

Comparison of results from different analytical techniques is useful to identify errors that might have occurred in the processing of large amounts of data. For example, if results for a single element determined by two independent techniques were in large disagreement, that particular element would be redetermined; however, if only one method was available, the errors might go unnoticed. In many cases, the choice of the better method of analysis was easily made; in other cases in which the choice was unclear several years ago, the recommended values reported were the average of results by two or more methods (Gluskoter et al., 1977). The criteria used to make these decisions were based on a method's demonstrated precision and accuracy relative to available reference standards and the frequency of erroneous or biased results. Examples of the results of comparisons of methods are shown in figures III-3a-f. The comparison is shown graphically in scatter plots that include the calculated regression line and correlation coefficient. Comparison of analytical results is especially important in this study, in which regional trends are being evaluated and results have been collected over a number of years.

Figure III-3a compares results obtained by x-ray fluorescence spectroscopy (XRF) with those obtained by instrumental neutron activation analysis (INAA) for potassium in 70 whole coals. The results generally fall near the X = Y line and the coefficient of the regression (0.93) is good.

Figure III-3b compares XRF and INAA results for the determination of iron in 68 whole coals. The results show more scatter than that observed for potassium in figure III-3a. The correlation coefficient of the regression line is also lower (0.87), and the INAA results are systematically higher relative to the XRF data. The scatter becomes significant at iron concentrations greater than 2 percent; this indicates that sample homogeneity could be a problem, or that a systematic error exists between the methods.

In figure III-3c, INAA results for the determination of selenium in 25 whole coals are compared with those obtained by neutron activation with a radiochemical separation (RNAA) procedure. The results between the two methods is in most cases within ±25 percent, which indicates good agreement.

Nickel results, determined by INAA and by atomic absorption spectroscopy (AA), are compared in figure III-3d. In this case, the scatter is probably due to rather poor counting statistics, which resulted in imprecise INAA results.

Determinations of strontium in 55 coal samples, by INAA and by optical emission spectroscopy (OED), are compared in figure III-3e. This figure shows a high degree of scatter. In this study, strontium results obtained by AA and XES were consistent with INAA results; correlation coefficients of 0.98 and 0.97, respectively, were obtained.

Figure III-3f shows results for barium determined by INAA and by energy-dispersive x-ray fluorescence spectroscopy (EDX). The agreement of the data on the 39 whole coals is within ±25 percent for 30 of the 39 plotted values. A factor that might have affected these results is the presence in the coal samples of discrete particles of the mineral barite ($BaSO_4$); these may not be completely homogenized by grinding.

A means of determining the accuracy and precision of the results of coal analysis is to perform repeated analyses of standard reference materials during the course of an investigation. Replicated INAA results for the standard reference material NBS 1632 obtained from the National Bureau of Standards (NBS) were published in Gluskoter et al. (1977) and Ruch et al. (1979). These data were generally consistent with the NBS certified values and results from Ondov et al. (1975). However, NBS 1632 has not been available for some time.

Table III-3 compares our results of NBS 1632A with those reported by Germani et al. (1980) and with the certified values. The results are generally quite similar; however, values for Cl, I, Na, and W, obtained by the INAA method, are not as precise (higher standard deviation) in this study as are those in Germani et al. (1980). In addition, results in this study for Mg, Ni, Pb, and S are not in as good agreement as desired with those listed from the literature. However, S values reported for the samples in this study were obtained by the ASTM method rather than by XRF.

## MINERALOGICAL METHODS AND PRECISION

The mineral matter was separated from the organic matter in the coal samples by use of a low-temperature asher (LTA), which oxidizes and vaporizes the organic matter and leaves a residue of minerals essentially unaltered from their original state in the coal. The minerals in the residue were quantitatively analyzed by x-ray diffraction methods for their quartz, pyrite, calcite, and clay content. The clay content was determined by difference, assuming the entire mineral assemblage consisted of these four types. (This is quite a reasonable assumption given the relative imprecision of the x-ray diffraction method.) However, the presence of trace and minor amounts of other minerals detected in the samples was noted. The determined amount of the quartz, calcite, and pyrite is the average of three separate x-ray analyses of each sample. The amount is based on the ratio of peak intensities of the mineral to that of an internal standard (alumina). The results of the samples were compared to calibrated mixtures of the individual minerals within a

**TABLE III-3.** Results of analyses of standard reference material (coal) 1632 from National Bureau of Standards (NBS) in this study, and in Germani et al. (1980), and certified values for the NBS coal.

| Element | Unit | This work | Method | Germani | NBS[†] |
|---|---|---|---|---|---|
| Ag | ppm | <0.3 | INAA | | |
| Al | % | 2.95 ± .04 | XRF | 2.94 ± .13 | (3.07) |
| As | ppm | 9.1 ± 1.0 | INAA | 10.2 ± .5 | 9.3 ± 1 |
| B | ppm | * | OE | 53 ± 2 | |
| Ba | ppm | 132 | EDX | 122 ± 11 | |
| Be | ppm | * | OE | | |
| Br | ppm | 40 ± 8 | INAA | 41 ± 4 | |
| Ca | % | 0.23 ± .01 | XRF | 0.23 ± .02 | |
| Cd | ppm | <.3 | AA | 0.21 ± .03 | 0.17 ± .02 |
| Ce | ppm | 29 ± 3 | INAA | 32 ± 4 | (30) |
| Cl | ppm | 720 ± 100 | INAA | 790 ± 20 | |
| Co | ppm | 7.8 ± .8 | INAA | 6.5 ± .2 | (6.8) |
| Cr | ppm | 37 ± 4 | INAA | 34 ± 2 | 34.4 ± 1.5 |
| Cs | ppm | 2.3 ± .4 | INAA | 2.0 ± .3 | (2.4) |
| Cu | ppm | 14.7 ± .4 | AA | | 16.5 ± 1.0 |
| Dy | ppm | 2.2 ± .1 | INAA | 2.2 ± .3 | |
| Eu | ppm | 0.53 ± .02 | INAA | 0.55 ± .03 | (0.54) |
| F | ppm | 113 ± 5 | ISE | | |
| Fe | % | 1.07 ± .03 | XRF | 1.16 ± .03 | 1.11 ± .02 |
| Ga | ppm | 8.5 ± .5 | INAA | 8.0 ± .8 | (8.5) |
| Ge | ppm | * | OE | | |
| Hf | ppm | 1.6 ± .2 | INAA | 1.55 ± .08 | (1.6) |
| Hg | ppm | 0.17 ± .05 | RNAA | | 0.13 ± .03 |
| I | ppm | 1.6 ± .4 | INAA | 1.8 ± .2 | |
| In | ppb | 41 ± 7 | INAA | 36 ± 4 | |
| K | % | 0.37 ± .01 | XRF | 0.42 ± .02 | |
| La | ppm | 16 ± 1 | INAA | 18 ± 2 | |
| Li | ppm | 37 ± .4 | AA | | |
| Lu | ppm | 0.21 ± .05 | INAA | 0.18 ± .03 | |
| Mg | % | 0.06 ± .03 | XRF | 0.13 ± .03 | |
| Mn | ppm | 29 ± 2 | INAA | 32 ± 3 | 28 ± 2 |
| Mo | ppm | ≤5 | INAA | | |
| Na | ppm | 730 ± 90 | INAA | 850 ± 40 | |
| Ni | ppm | 16 ± 1 | AA | 26 ± 4 | 19.4 ± 1 |
| P | ppm | 280 ± 8 | XRF | | |
| Pb | ppm | 18 ± 1 | AA | 15 ± 4 | 12.4 ± .6 |
| Rb | ppm | 30 ± 4 | INAA | 29 ± 1 | (31) |
| S | % | 1.2 ± .04 | XRF | 1.59 ± .02 | (1.64) |
| Sb | ppm | 0.7 ± .1 | INAA | 0.60 ± .09 | (0.58) |
| Sc | ppm | 6.4 ± .5 | INAA | 6.8 ± .6 | (6.3) |
| Se | ppm | 3.0 ± .4 | INAA | 2.6 ± .3 | 2.6 ± .7 |
| Si | % | 5.92 ± .01 | XRF | 5.8 ± .1 | |
| Sm | ppm | 2.7 ± 1 | INAA | 2.10 ± .07 | |
| Sr | ppm | 79 | EDX | 84 ± 9 | |
| Ta | ppm | 0.35 ± .05 | INAA | 0.40 ± .03 | |
| Tb | ppm | 0.34 ± .05 | INAA | 0.36 ± .12 | |
| Th | ppm | 4.7 ± .5 | INAA | 4.8 ± .2 | 4.5 ± .1 |
| Ti | % | 0.18 ± .01 | XRF | .161 ± .004 | (0.175) |
| Tl | ppm | * | OE | | |
| U | ppm | 1.2 ± .2 | INAA | 1.2 ± .1 | 1.28 ± .02 |
| V | ppm | * | OE | 44 ± 3 | 44 ± 3 |
| W | ppm | 0.8 ± .2 | INAA | 0.6 ± .02 | |
| Yb | ppm | 1.1 ± .1 | INAA | 0.98 ± .08 | |
| Zn | ppm | 27 ± 2 | AA | 31 ± 6 | 28 ± 2 |
| Zr | ppm | 36 | EDX | 53 ± 5 | |

[†] Values bracketed are informative, others are certified.
*Not available, sample used for calibration.

matrix composed of clay varieties comparable to those found in Illinois coals (Ward, 1977). The details of these procedures are given in appendix B.

The precision of the determined values is indicated by the relative standard deviations (SD) computed from the three separate runs on 45 samples: yielding average SD of 7 percent for quartz, 16 percent for calcite, and 6 percent for pyrite. The distribution of the SD for these minerals is shown in table III-4. These data indicate that results for pyrite are the most precise, and results for calcite the least precise. This is expected for calcite because of its perfect cleavage, which makes it most difficult to prepare a truly random packing of powdered sample for the x-ray analysis. An error of ±5 to 7 percent in the determinations is recognized

**TABLE III-4.** Frequency distribution of the relative standard deviation (SD)* of mineral compositions in 45 samples.

| | Frequency (%) | | |
|---|---|---|---|
| Relative %SD* | Quartz | Calcite | Pyrite |
| <10 | 84 | 43 | 93 |
| 10-20 | 16 | 32 | 5 |
| 20-30 | | | 2 |
| 20-50 | | 23 | |
| >50 | | 2 | |

* SD converted to a percentage of the main value.

as inherent in the method (Russell and Rimmer, 1979). The results of the quantitative determinations of the minerals in the LTA residue were converted to the whole coal basis according to the measured LTA value.

Despite the relative consistency of the pyrite values obtained by the diffraction method, their comparison with values calculated from the pyritic sulfur determined by chemical methods revealed undesirable scatter of results. We therefore concluded that the most reliable and consistent values for pyrite were obtained chemically, and for this reason only chemical data for pyrite are referred to subsequently.

The varieties of clay minerals were determined by x-ray diffraction analyses of clay separations (-2μm particles) deposited under vacuum onto ceramic slides. The procedures used are described in appendix 2.

The precision of the semiquantitative analyses of the varieties of clay minerals in the samples is recognized to be relatively low. Reliability of the analysis data depends very much upon the consistency of the sample preparation. Although considerable effort was made to be consistent in preparing the clay slides and to provide the same amount of clay, the relatively small amount of clay available from several samples made it difficult to obtain slides with the needed consistency of clay material. Nevertheless, the results are useful guides to the relative changes in the clay mineral compositions between the samples. In contrast to other reported results in this study, those of the clay mineral analyses are reported as a percentage value of the clay fraction.

# IV. EXTENT OF COAL SEAMS AND SOURCE LOCATIONS OF SAMPLES

In Illinois the two coal seams studied are formally known as the Herrin (No. 6) Coal Member and the Springfield (No. 5) Coal Member of the Carbondale Formation—the middle formation of the seven that are included in the Pennsylvanian System in Illinois. Both coals extend into Indiana and Kentucky. The name Herrin is used in the entire tri-state area; this name will be used throughout this report without reference to the numbers (No. 6 in Illinois and No. 11 in Kentucky). The name Springfield is used in Indiana and Illinois, but in Kentucky this coal is known as the Number 9 Coal. In this report we will use hereafter the name Springfield for this coal in all three states.

## HERRIN COAL

The extent of the Herrin is shown in figure IV-1. In Indiana the Herrin is quite thin or absent in many places, and in others its recognition is somewhat in doubt. The boundary line shown is where the coal would crop out if it were present. This coal is of high commercial interest in the areas where its thickness is greater than 28 inches (fig. IV-1).

The Walshville channel (fig. IV-1) marks the course of an ancient river that flowed through the extensive Herrin peat swamp (Johnson, 1972; Smith and Stall, 1975; and Palmer, Jacobson, and Trask, 1979). Within the channel area the coal is absent and in adjacent areas the coal is commonly split by sandstone and shale partings; however, the coal usually attains its maximum thickness on the far sides of these major partings. Near the end of the peat-forming period the river overflowed its banks with relatively fresh waters at several places along its course, depositing mud and silt over the peat. These sediments formed thick deposits of nonmarine types of shale and siltstone known as the Energy Shale. The coal that developed under the Energy Shale, especially where the Energy is 20 feet or more thick, usually has a relatively low sulfur content of 0.5 to 2.5 percent (Gluskoter and Simon, 1968; Gluskoter and Hopkins, 1970; Hopkins, Nance, and Treworgy, 1979). In most other areas the Herrin underlies the Anna Shale, a black marine shale that was deposited from a subsequent flooding of the region by marine waters. The sulfur content of the underlying coal in these areas is usually greater than 2.5 percent.

In Kentucky the large east-west indentations of the boundary line of the Herrin are due to structural and erosional features along the Rough Creek Fault System, which caused the coal to be absent in these areas. The large "V" configuration of the boundary of the coal along its northern border in eastern Illinois is also a structural-erosional feature. The Herrin and associated strata are covered by pebbly clay and other glacial deposits in most of the northern and central areas of Illinois.

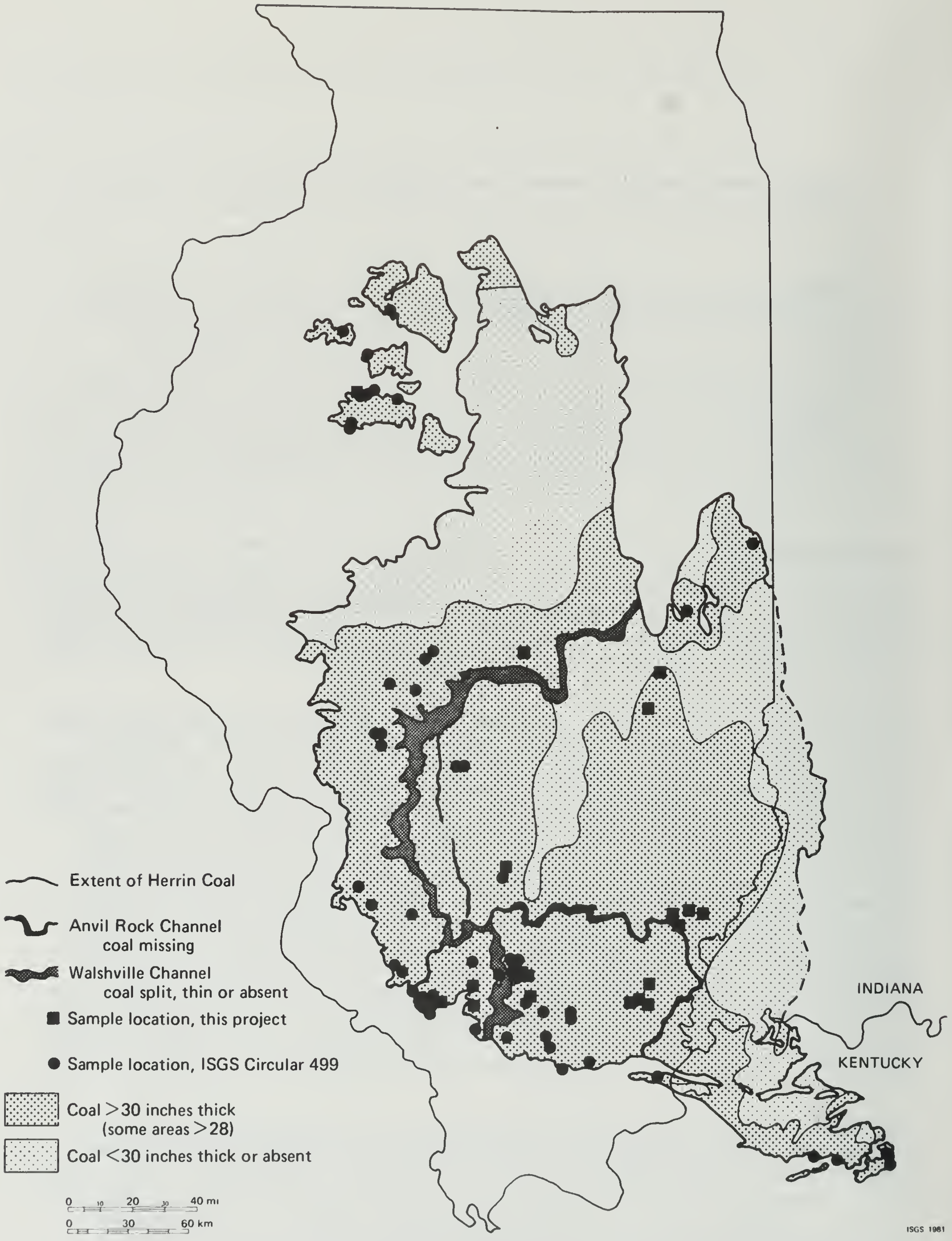


FIGURE IV-1. Locations of samples from the Herrin Coal. Kentucky boundary of the coal is from Smith and Brant (1978), Indiana boundary from Indiana Geological Survey (1971).

The separation of the coal deposits in the northwestern region from the main deposits to the southeast is mostly due to erosion, but there is some uncertainty as to whether or not the Herrin peat swamp extended from this northwestern area interruption into the more extensive swamp to the southeast.

The locations of samples collected from the Herrin and analyzed for this project are shown as squares in figure IV-1. The source locations of samples reported in Circular 499 (Gluskoter et al., 1977) also are shown. The sample numbers, types, the mine index of the source (if a mine in Illinois), and the purpose code of the samples are given in table IV-1. The samples for this project (MMC-80) are listed in the table after those of Circular 499.

## Geologic setting of the bench set study area

An analysis of the composition of various beds or benches constituting the Herrin Coal was done on samples from an underground mine in southern Illinois (fig. IV-2). The mine is located approximately 8 miles east of the Walshville

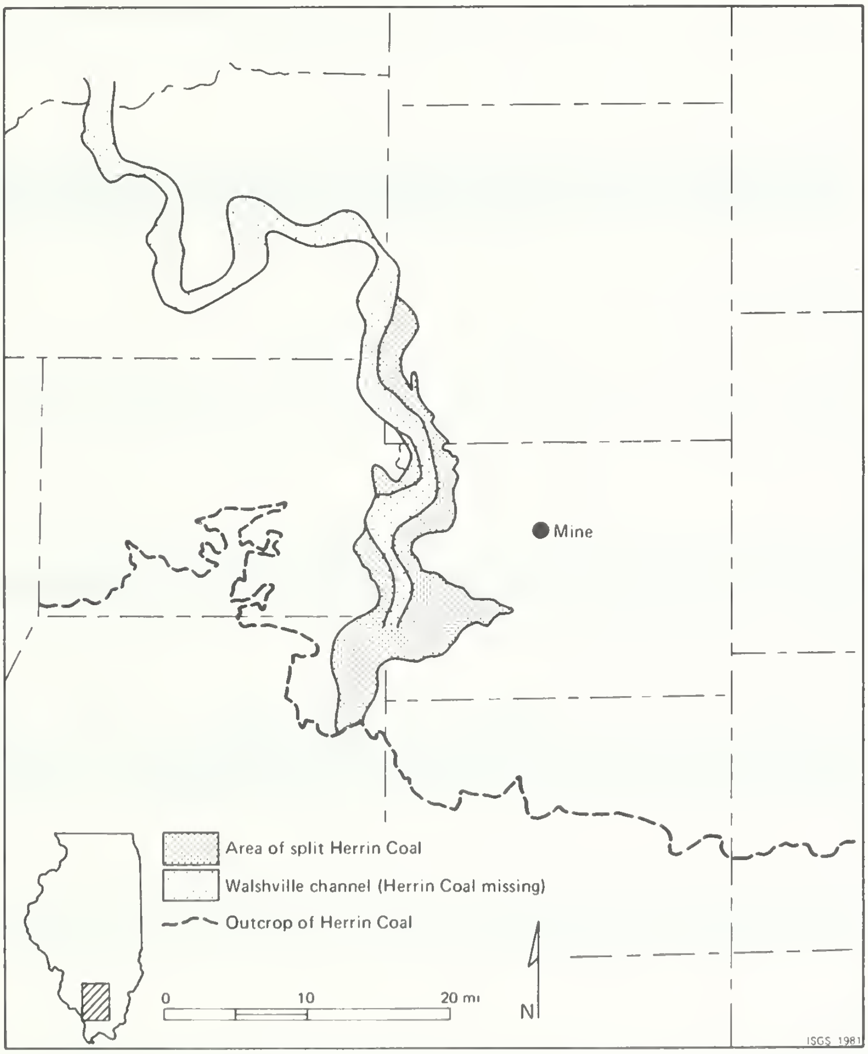


FIGURE IV-2. Location of mine sampled for bench study (after Smith and Stall, 1975).

TABLE IV-1. Sample identification, Herrin Coal.

C499 SAMPLES: DATA ON THESE ARE GIVEN IN GLUKOSTER ET AL., 1977.

| SAMPLE | STATE | S.TYPE | MINE I# | PURPOSE-CODE |
|---|---|---|---|---|
| C12059 | IL | CFC | 850 | RL 1 |
| C12831 | IL | CFC | 448 | R |
| C12942 | IL | FC | 858 | R |
| C13324 | IL | DC | - | R |
| C13433 | IL | DC | - | R |
| C13464 | IL | CFC | 207 | R |
| C13895 | IL | CFC | 857 | R |
| C13975 | IL | CFC | 684 | R |
| C14574 | IL | CFC | 668 | R |
| C14613 | IL | CFC | 690 | L 5 |
| C14630 | IL | CFC | 863 | L 5 |
| C14684 | IL | CFC | 847 | R |
| C14721 | IL | CFC | 622 | R |
| C14838 | IL | CFC | 693 | RL 2 |
| C14970 | IL | CFC | 871 | R |
| C14982 | IL | CFC | 701 | R |
| C15038 | IL | CFC | 688 | R |
| C15079 | IL | CFC | 881 | RL 1 |
| C15117 | IL | CFC | 880 | RL 1 |
| C15231 | IL | CFC | 699 | R |
| C15432 | IL | CFC | 694 | R |
| C15436 | IL | CFC | 843 | L 3 |
| C15456 | IL | CFC | 873 | RL 4 |
| C15717 | IL | CFC | 929 | R |
| C15791 | IL | CFC | 885 | RL 5 |
| C15868 | IL | CFC | 877 | R |
| C15872 | IL | CFC | 859 | RL 1 |
| C15999 | IL | CFC | 638 | R |
| C16030 | IL | CFC | 883 | R |
| C16139 | IL | CFC | 707 | RL 2 |
| C16265 | IL | CFC | 890 | L 1 |
| C16317 | IL | CFC | 887 | L 1 |
| C16501 | IL | CFC | 866 | R |
| C16543 | IL | CFC | 862 | RL 1 |
| C16993 | IL | C | 702 | R |
| C17016 | IL | C | 693 | L 2 |
| C17278 | IL | FC | 886 | L 3 |
| C17279 | IL | CFC | 886 | RL 3 |
| C18044 | IL | CFC | 928 | L 4 |
| C18121 | IL | 3/8X28M | 887 | S |
| C18122 | IL | -28M | 887 | S |
| C18123 | IL | 1.25F | 887 | W 1 |
| C18124 | IL | 1.29FS | 887 | W 1 |
| C18125 | IL | 1.33FS | 887 | W 1 |
| C18126 | IL | 1.40FS | 887 | W 1 |
| C18127 | IL | 1.60FS | 887 | W 1 |
| C18128 | IL | 1.60S | 887 | W 1 |
| C18320 | IL | CFC | 932 | R |
| C18368 | IL | CFC | 872 | L 4 |
| C18389 | KY | CFC | - | R |
| C18398 | KY | CFC | - | R |
| C18407 | KY | CFC | - | R |
| C18415 | KY | CFC | - | R |
| C18552 | IL | B1 | 934 | B 1 |
| C18553 | IL | B2 | 934 | B 1 |
| C18554 | IL | B3 | 934 | B 1 |
| C18555 | IL | B4 | 934 | B 1 |
| C18556 | IL | B5 | 934 | B 1 |
| C18557 | IL | B6 | 934 | B 1 |
| C18558 | IL | B7 | 934 | B 1 |
| C18559 | IL | B8 | 934 | B 1 |
| C18560 | IL | C | 934 | RL 4 |
| C18562 | IL | -28M | 934 | S |
| C18563 | IL | 1.29 | 934 | W 2 |
| C18564 | IL | 1.33FS | 934 | W 2 |
| C18565 | IL | 1.40FS | 934 | W 2 |
| C18566 | IL | 1.60FS | 934 | W 2 |
| C18567 | IL | 1.60S | 934 | W 2 |
| C18704 | IL | B1 | 871 | B 2 |
| C18705 | IL | B2 | 871 | B 2 |
| C18706 | IL | B3 | 871 | B 2 |
| C18707 | IL | B4 | 871 | B 2 |
| C18708 | IL | B5 | 871 | B 2 |
| C18709 | IL | B6 | 871 | B 2 |
| C18710 | IL | B7 | 871 | B 2 |
| C18711 | IL | B8 | 871 | B 2 |
| C18728 | IL | B1 | 877 | B 3 |
| C18729 | IL | B2 | 877 | B 3 |
| C18730 | IL | B3 | 877 | B 3 |
| C18731 | IL | B4 | 877 | B 3 |
| C18732 | IL | B5 | 877 | B 3 |
| C18733 | IL | B7 | 877 | B 3 |
| C18807 | IL | B1 | 873 | B 4 |
| C18808 | IL | B2 | 873 | B 4 |
| C18809 | IL | B3 | 873 | B 4 |
| C18810 | IL | B4 | 873 | B 4 |
| C18811 | IL | B5 | 873 | B 4 |
| C18812 | IL | B6 | 873 | B 4 |
| C18813 | IL | B7 | 873 | B 4 |
| C18814 | IL | B8 | 873 | B 4 |
| C18857 | IL | FC | 933 | RL 4 |
| C18983 | IL | B1 | 887 | B 5 |
| C18984 | IL | B2 | 887 | B 5 |
| C18985 | IL | B3 | 887 | B 5 |
| C18986 | IL | B4 | 887 | B 5 |
| C18987 | IL | B6 | 887 | B 5 |
| C18988 | IL | B7 | 887 | B 5 |

TABLE IV-1. Sample identification, Herrin Coal. *(continued)*

| SAMPLE | STATE | S.TYPE | MINE I# | PURPOSE-CODE |
|---|---|---|---|---|
| MMC-80 SAMPLES: | | | | |
| C20154 | IL | DC | - | R |
| C20242 | IL | DC | - | R |
| C20323 | IL | DC | - | L 8 |
| C20613 | IL | DC | - | R |
| C20620 | IL | CFC | 887 | RL 1 |
| C20628 | IL | CFC | 873 | L 4 |
| C20635 | IL | CFC | 622 | R |
| C20636 | IL | RM | 928 | L 4 |
| C20641 | IL | CFC | 877 | L 5 |
| C20642 | IL | RM | 877 | L 5 |
| C20654 | IL | CFC | 864 | R |
| C20658 | IL | CFC | 967 | R |
| C20659 | IL | 3/8X28M | 928 | S |
| C20660 | IL | -28M | 928 | S |
| C20661 | IL | 1.29F | 928 | W 3 |
| C20662 | IL | 1.31FS | 928 | W 3 |
| C20663 | IL | 1.33FS | 928 | W 3 |
| C20664 | IL | 1.40FS | 928 | W 3 |
| C20665 | IL | 1.60FS | 928 | W 3 |
| C20666 | IL | 1.60FS | 928 | W 3 |
| C20678 | IL | DC | - | R |
| C20683 | IL | 3/8X28M | 877 | S |
| C20684 | IL | -28M | 877 | S |
| C20685 | IL | 1.28F | 877 | W 4 |
| C20686 | IL | 1.30FS | 877 | W 4 |
| C20687 | IL | 1.32FS | 877 | W 4 |
| C20688 | IL | 1.42FS | 877 | W 4 |
| C20689 | IL | 1.60FS | 877 | W 4 |
| C20690 | IL | 1.60S | 877 | W 4 |
| C20759 | IL | DC | - | R |
| C20965 | IL | B 1 | 886 | B 6 |
| C20966 | IL | B 2 | 886 | B 6 |
| C20967 | IL | B 3 | 886 | B 6 |
| C20968 | IL | B 4 | 886 | B 6 |
| C20969 | IL | B 5 | 886 | B 6 |
| C20970 | IL | B 6 | 886 | B 6 |
| C20971 | IL | B 1 | 886 | B 7 |
| C20972 | IL | B 2 | 886 | B 7 |
| C20973 | IL | B 3 | 886 | B 7 |
| C20974 | IL | B 4 | 886 | B 7 |
| C20975 | IL | B 5 | 886 | B 7 |
| C20976 | IL | B 6 | 886 | B 7 |
| C20977 | IL | B 1 | 886 | B 8 |
| C20978 | IL | B 2 | 886 | B 8 |
| C20979 | IL | B 3 | 886 | B 8 |
| C20980 | IL | B 4 | 886 | B 8 |
| C20981 | IL | B 5 | 886 | B 8 |
| C20982 | IL | B 6 | 886 | B 8 |
| C20983 | IL | B 1 | 886 | B 9 |
| C20984 | IL | B 2 | 886 | B 9 |
| C20985 | IL | B 3 | 886 | B 9 |
| C20986 | IL | B 4 | 886 | B 9 |
| C20987 | IL | B 5 | 886 | B 9 |
| C21164 | IL | DC | - | RL 7 |
| C21166 | IL | DC | - | L 7 |
| C21168 | IL | DC | - | L 7 |
| C21170 | IL | DC | - | L 7 |
| C21172 | IL | DC | - | L 8 |
| C21174 | IL | DC | - | RL 8 |
| C21176 | IL | DC | - | L 8 |
| HAND PICKED VITRAIN AND MINERALS (MMC 80) | | | | |
| C20368 | IL | SP | 859 | V (VITRAIN) |
| C20369 | IL | SP | 881 | V (VITRAIN) |
| C20370 | IL | SP | 638 | V (VITRAIN) |
| C20371 | IL | SP | 883 | V (VITRAIN) |
| R14532 | IL | SP | 940 | M (CALCITE) |
| R14533 | IL | SP | 940 | M (FE-SULFATE MIXED) |
| R14534 | IL | SP | 940 | M (BARITE) |

channel and adjacent sandstone and siltstone lenses that split the adjacent Herrin Coal. This site was selected for this study because it had been the site of previous geologic and petrologic studies (Bauer and DeMaris, 1977; DeMaris and Bauer, 1978; and Johnson, 1979). The samples collected by Johnson were available for mineral and chemical analyses for the project. The samples consisted of blocks of coal taken sequentially from the top to the bottom of the seam at four columns (B6–B9) along a traverse in the mine. The traverse underlies both nonmarine gray shales and marine black shales, and the samples enable the differentiation of coals flooded mostly by fresh (low sulfur) waters from those flooded by marine (high sulfur) waters. The distribution of the two shales in the study area is shown in figure IV-3. The gray shale extends 18.6 feet above the coal at B6 and only 7.5 feet at B7. The overlying black shales are commonly about 3 feet thick in the region (Bauer, personal communication).

Johnson (1979) delineated six layers or units within the seam; we used these to guide the selection of the bench samples. Using Johnson's crushed samples we made composite bench samples proportional to their thickness so as to be representative of each of the coal units from the four columns, two columns (bench sites) under the gray shale and two under the black shale.

Figure IV-4 shows the correlations of Johnson's units along the traverse with the sample type code (bench number) and the bench set number (at the top of the figure). Note that the top bench at B8 does not contain a complete section of the original peat material of unit I because the upper part of the unit was eroded; furthermore, this unit and the upper beds of unit II in bench set B9 were entirely eroded.

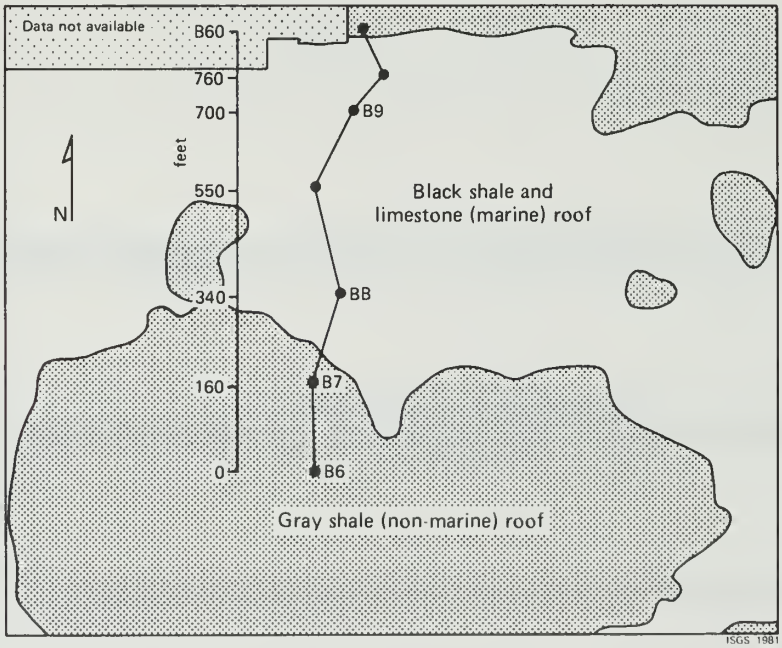


FIGURE IV-3. Lithology of strata immediately overlying the Herrin Coal in bench set study area of mine 866, showing locations of bench sets (after Bauer and DeMaris, 1977).

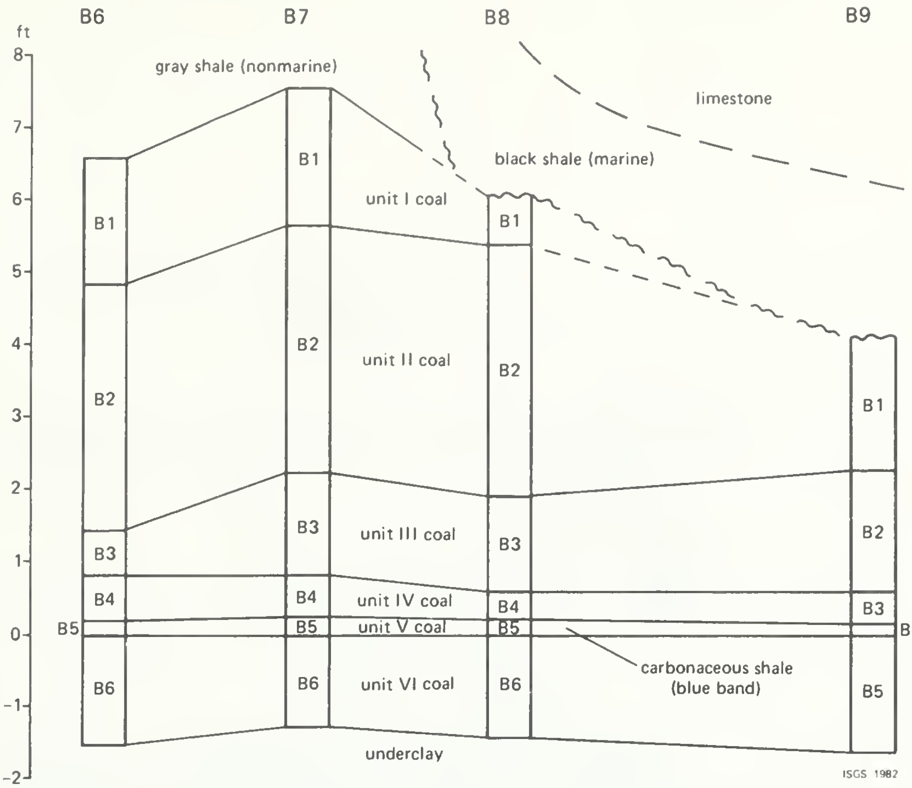


FIGURE IV-4. Geologic cross section of the Herrin Coal and roof strata along north-south traverse, looking west in mine 866, showing correlation of units and erosional surface (∿) (after Johnson, 1979), and bench numbers (B#) for bench sets B6-9.

## SPRINGFIELD COAL

The extent of the Springfield Coal (fig. IV-5) is similar to that of the Herrin, but in Indiana, the Springfield--in contrast to the Herrin--is a principal commercial coal. The two coals are separated in Illinois by shales, sandstones, and some limestones ranging between 40 and 120 feet thick (Smith and Stall, 1975).

The Galatia channel (fig. IV-5), located in southeastern Illinois (Hopkins, Nance, and Treworgy, 1979) and adjacent Indiana (Ault et al., 1979; Eggert and Adams, 1982), was the course of an ancient stream that flowed through the Springfield peat swamp. The channel contains deposits of sandstone and siltstone that split the coal on either side of the channel in the same manner described above for the Walshville channel. The other major boundary configurations of the Springfield Coal are controlled by structural-erosional features identical to those of the Herrin discussed previously.

The Springfield samples analyzed for this project are shown in figure IV-5, sample numbers and other identifying items and purpose codes in table IV-2.

## LOCAL STUDIES OF WHOLE-COAL SAMPLES

Certain areas were identified as locations for evaluation of the variability of composition of whole coal samples of the Herrin and Springfield Coals.

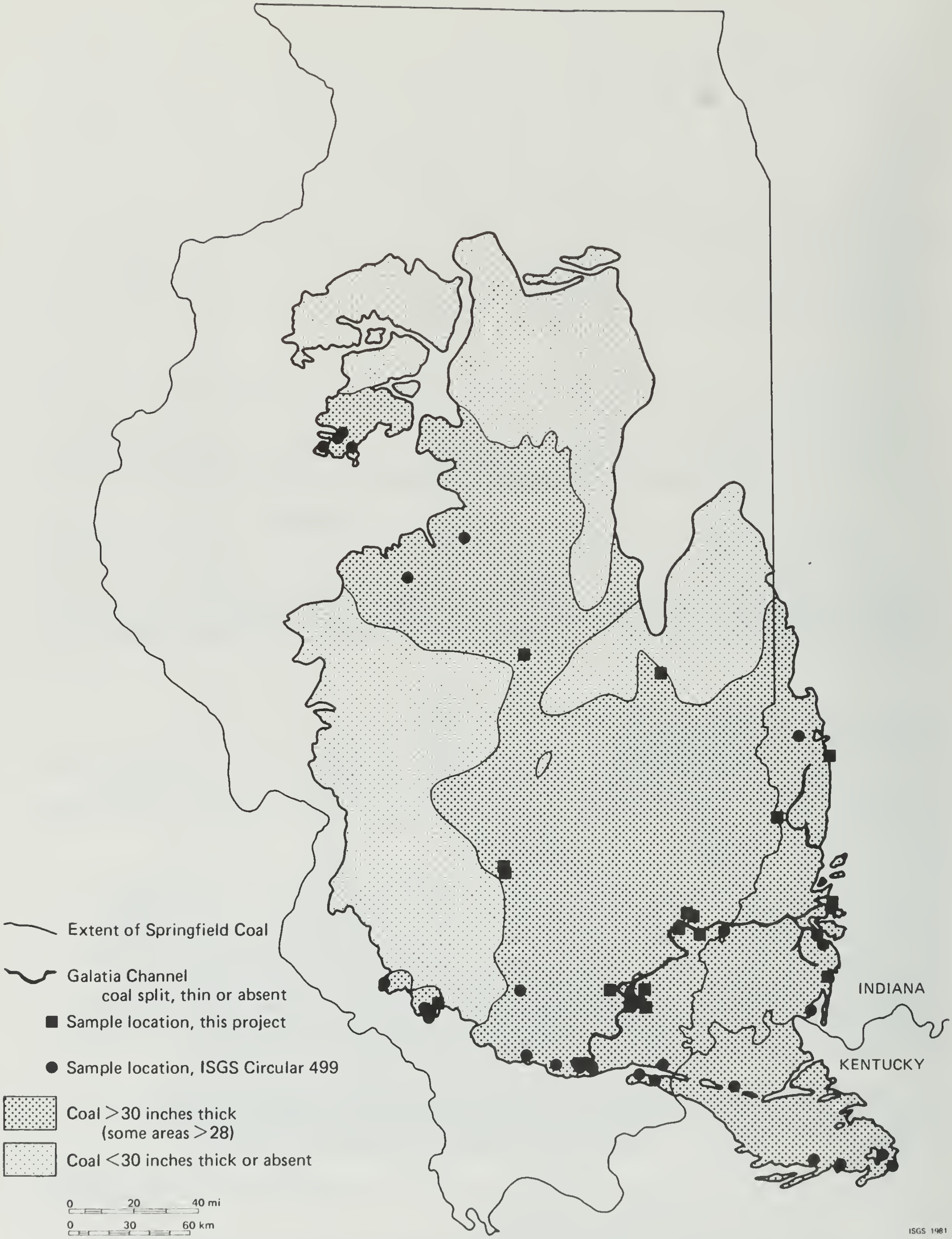


**FIGURE IV-5.** Location of samples from the Springfield Coal. Kentucky boundary of coal is from Smith and Brant (1978), Indiana boundary from Indiana Geological Survey (1971).

TABLE IV-2. Sample identification, Springfield Coal.

| SAMPLE | STATE | S.TYPE | MINE I# | PURPOSE-CODE |
|---|---|---|---|---|
| MMC-80 SAMPLES | | | | |
| C15140 | IL | DC | - | R |
| C20314 | IN | FC | - | R |
| C20324 | IL | DC | - | RL 6 |
| C20615 | IL | DC | - | R |
| C20616 | IL | DC | - | R |
| C20631 | IL | CFC | 873 | L 3 |
| C20637 | IL | PC | 928 | L 3 |
| C20669 | IL | 3/8X28 | 928 | S |
| C20670 | IL | -28M | 928 | S |
| C20671 | IL | 1.29F | 928 | W 1 |
| C20672 | IL | 1.31FS | 928 | W 1 |
| C20673 | IL | 1.35FS | 928 | W 1 |
| C20674 | IL | 1.40FS | 928 | W 1 |
| C20675 | IL | 1.60FS | 928 | W 1 |
| C20676 | IL | 1.60S | 928 | W 1 |
| C20679 | IL | DC | - | R |
| C20705 | IN | CFC | - | R |
| C20709 | IN | CFC | - | L 7 |
| C20760 | IL | DC | - | R |
| C21067 | IL | CFC | 938 | L 5 |
| C21076 | IL | 3/8X28 | 938 | S |
| C21077 | IL | -28M | 938 | S |
| C21096 | IL | 1.27F | 938 | W 2 |
| C21097 | IL | 1.30FS | 938 | W 2 |
| C21098 | IL | 1.32FS | 938 | W 2 |
| C21099 | IL | 1.4FS | 938 | W 2 |
| C21100 | IL | 1.6FS | 938 | W 2 |
| C21101 | IL | 1.6S | 938 | W 2 |
| C21165 | IL | DC | - | RL 5 |
| C21167 | IL | DC | - | L 5 |
| C21169 | IL | DC | - | L 5 |
| C21171 | IL | DC | - | L 5 |
| C21173 | IL | DC | - | L 6 |
| C21175 | IL | DC | - | L 6 |
| C21177 | IL | DC | - | L 6 |

| SAMPLE | STATE | S.TYPE | MINE I# | PURPOSE-CODE |
|---|---|---|---|---|
| C499 SAMPLES: DATA ON THESE ARE GIVEN IN GLUKOSTER ET AL.,1977. | | | | |
| C12495 | IL | CFC | 861 | R |
| C13046 | IN | CFC | - | R |
| C13983 | IL | CFC | 873 | L 3 |
| C14194 | IL | CFC | 876 | R |
| C14609 | IL | CFC | 664 | L 4 |
| C14735 | IL | CFC | 879 | R |
| C14774 | IL | CFC | 705 | L 1 |
| C14796 | IL | CFC | 801 | L 4 |
| C15012 | IL | CFC | 882 | R |
| C15125 | IL | CFC | 704 | RL 1 |
| C15208 | IL | CFC | 639 | R |
| C15384 | IL | CFC | 884 | R |
| C15448 | IL | CFC | 930 | R |
| C16264 | IL | CFC | 890 | L 1 |
| C16729 | IL | CFC | 912 | L 4 |
| C16741 | IL | CFC | 738 | L 1 |
| C17001 | IL | CFC | 898 | R |
| C17721 | IL | CFC | 921 | L 6 |
| C17984 | IL | CFC | 909 | L 4 |
| C17988 | IL | CFC | 911 | RL 4 |
| C18040 | IL | CFC | 928 | RL 3 |
| C18392 | KY | CFC | - | R |
| C18395 | KY | CFC | - | R |
| C18404 | KY | CFC | - | R |
| C18411 | KY | CFC | - | R |
| C18590 | KY | RM | - | R |
| C18594 | KY | CFC | - | R |
| C18689 | IN | CFC | - | R |
| C18693 | IN | CFC | - | L 7 |
| C18697 | IN | CFC | - | L 7 |
| C18701 | IN | CFC | - | RL 7 |

Data on samples from both Circular 499 and this study (MMC-80) were included in these evaluations. These areas are:

| Herrin Coal | | Springfield Coal | |
|---|---|---|---|
| L1 | Northwestern Illinois | L1 | Northwestern Illinois |
| L2 | Central Illinois | L3 | Southwestern Illinois |
| L3 | South central Illinois | L4 | Southern Illinois |
| L4 | Southwestern Illinois | L5 | Southeastern Illinois |
| L5 | South central Illinois | L6 | Eastern part of southern Illinois |
| L7 | Southeastern Illinois | L7 | Central part of southwestern Indiana |
| L8 | Eastern part of southern Illinois | | |

Samples used for local area evaluations are identified by their L numbers (purpose codes) in tables IV-1 and IV-2.

# V. MINERAL COMPOSITION OF THE COALS

## MINERAL VARIATION OF BENCH SAMPLES OF THE HERRIN COAL

The bench set study was undertaken to evaluate the variation of impurities in coals within one seam exposed in a small area of a mine. Twenty-three samples at four sites along a traverse were analyzed. Results of the mineralogical analyses of the four bench sets are given in table V-1. Each of the bench sets (B6-B9) consists of a sequential set of samples from the top to the bottom of the Herrin Coal along the 700-foot traverse in mine 866 (figs. IV-3 and IV-4).

The correlation of the LTA and the pyrite contents along the traverse are shown in figure V-1. The prominence of the shale bench (parting) about a foot above the base of the coal seam is quite evident from the LTA data shown in this figure. This shale parting, known as the "blue band," occurs within the lower part of the Herrin Coal throughout much of the extent of this coal. It is a useful stratum within the Herrin for correlation purposes (the footage scale on the left of figure IV-4 is based on the position of the base of this shale). The LTA content of the benches varies considerably between benches and along the traverse, and the pyrite content is somewhat less variable (fig. V-1). Both components are generally highest in the lower two benches of the seam, except in bench set B6. The pyrite is highest in the lowest bench in sets B7-B9 where the coal is overlain by marine shales or relatively thin nonmarine shales. The coals in bench set B6 contain lower amounts of pyrite than do the other sets because the roof shale at this site is a relatively thick nonmarine type. The distribution of the relative amounts of pyrite along this traverse conforms to the geological model discussed in section IV, p. 19 (Herrin Coal).

The calcite content of the bench sets ranges from less than 1 to more than 13 percent. The high assay sample (C10983) was taken from the uppermost unit, under the marine shale, at site B9 (table V-1 and fig. V-1). The calcite in this sample occurred in a small coalball in the sample. Calcite assays in the other bench samples (0.3 to 7.3%) are more typical of those determined in the whole coal samples discussed below.

In order to compare the bench set data with that of the channel samples, composite assays of the benches were computed from the bench data, proportioned to the thickness of the benches. The shales were excluded from these computations to provide an analysis equivalent to that of face channel samples. The results of the computation are listed under the respective bench set data in table V-1. Comparisons of these "channel" samples along the traverse indicate the local variability of channel (whole-coal) samples. The ranges and means of these data for the four composites are as follows:

|  | LTA | QTZ | CAL | PYR | TCLAY |
|---|---|---|---|---|---|
| Minimum | 11.1 | 1.7 | 0.8 | 1.8 | 6.8 |
| Maximum | 19.9 | 3.0 | >5.0 | 5.8 | 8.0 |
| Mean | 16.3 | 2.5 | >2.9 | 3.5 | 7.5 |

The clay content of the benches correlates directly with the LTA contents because clay constitutes the most abundant mineral impurity in the coals. The results of the composite calculations (table V-1) show that Bench set B8 is notably lower in kaolinite (K + C) and higher in expandable clays than are the other sets. Aside from this variation, the clay minerals show rather consistent assays among the bench sets.

TABLE V-1. Mineral composition of bench samples of Herrin Coal (MMC80 samples only).*

| SAMPLE | BENCH UNIT | THKN (FT.) | LTA ( % ) | QTZ ( % ) | CAL ( % ) | PYR ( % ) | TCLAY ( % ) | K+C | ILL | EXP | OTHER MNRLS PRESENT (MINOR-1, TRACE-2) |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  | (% OF | TCLAY | FRACTION) |  |
| BENCH SET B 6 |  |  |  |  |  |  |  |  |  |  |  |
| C20965 | I | 1.53 | 10.30 | 1.1 | 1.1 | 4.0 | 4.1 | 33. | 42. | 25. | ANH2, |
| C20966 | II | 3.54 | 7.88 | 1.1 | .4 | .6 | 5.8 | 49. | 30. | 21. | SID1 |
| C20967 | III | .60 | 19.38 | 3.7 | 1.2 | 1.4 | 13.1 | 38. | 41. | 22. | ANH2,MARC1,PLAG2,HEM2 |
| C20968 | IV | .62 | 17.80 | 3.4 | .9 | 3.0 | 10.5 | 42. | 38. | 20. |  |
| C20969 | V(SH) | .15 | 54.89 | 10.4 | 1.1 | .6 | 42.8 | 51. | 28. | 21. |  |
| C20970 | VI | 1.39 | 13.35 | 2.4 | 1.2 | 2.1 | 7.7 | 43. | 45. | 12. | ANH2,MARC1 |
|  |  | ---- |  |  |  |  |  |  |  |  |  |
| COMPOSITE+ |  | 7.68+ | 11.05 | 1.7 | 0.8 | 1.8 | 6.8 | 43. | 37. | 20. |  |
| BENCH SET B 7 |  |  |  |  |  |  |  |  |  |  |  |
| C20971 | I | 1.82 | 9.47 | .9 | .5 | 2.7 | 5.4 | 34. | 41. | 25. | PLAG1,ORTH1 |
| C20972 | II | 3.40 | 14.84 | 1.5 | 7.3 | 2.2 | 3.8 | 50. | 33. | 17. | BASS2 |
| C20973 | III | 1.53 | 25.00 | 4.5 | 4.5 | 4.8 | 11.2 | 22. | 37. | 41. | ANH2 |
| C20974 | IV | .47 | 12.41 | 2.1 | 2.5 | 4.2 | 3.6 | 45. | 40. | 15. | MARC1,PLAG2 |
| C20975 | V(SH) | .36 | 50.71 | 6.6 | 1.5 | 23.3 | 19.3 | 38. | 28. | 34. | HEM1 |
| C20976 | VI | 1.17 | 47.33 | 6.6 | .9 | 22.7 | 17.1 | 39. | 31. | 30. | MARC1,HEM1,COQ2 |
|  |  | ---- |  |  |  |  |  |  |  |  |  |
| COMPOSITE+ |  | 8.39+ | 19.92 | 2.7 | 4.2 | 5.8 | 7.3 | 40. | 36. | 25. |  |
| BENCH SET B 8 |  |  |  |  |  |  |  |  |  |  |  |
| C20977 | I | .64 | 12.20 | 2.3 | 1.2 | 1.2 | 7.5 | 21. | 36. | 43. | MARC2 |
| C20978 | II | 3.50 | 11.47 | 1.6 | 2.0 | 1.5 | 6.4 | 31. | 35. | 34. | COQ2 |
| C20979 | III | 1.31 | 18.91 | 4.2 | .6 | .9 | 13.2 | 21. | 38. | 41. |  |
| C20980 | IV | .48 | 14.47 | 2.7 | .3 | 1.7 | 9.8 | 34. | 32. | 35. | MARC1,PLAG2 |
| C20981 | V(SH) | .23 | 59.09 | 13.6 | .6 | 1.8 | 43.1 | 26. | 31. | 43. | HEM2 |
| C20982 | VI | 1.28 | 20.39 | 2.9 | 2.2 | 8.4 | 6.9 | 31. | 30. | 39. | PLAG2 |
|  |  | ---- |  |  |  |  |  |  |  |  |  |
| COMPOSITE+ |  | 7.21+ | 14.67 | 2.4 | 1.6 | 2.6 | 8.0 | 28. | 35. | 37. |  |
| BENCH SET B 9 |  |  |  |  |  |  |  |  |  |  |  |
| C20983 | II | 1.82 | 21.72 | 2.0 | >13.0 | 1.7 | <5.0 | 63. | 26. | 11. |  |
| C20984 | III | 1.70 | 18.72 | 3.2 | .7 | 2.2 | 12.6 | 30. | 33. | 37. | ANH2 |
| C20985 | IV | .58 | 11.58 | 2.1 | .5 | 1.3 | 7.7 | 40. | 22. | 38. | MARC2,PLAG2 |
| C20986 | V(SH) | .08 | 81.10 | 20.3 | 0.0 | .8 | 60.0 | 24. | 38. | 39. | ANH2 |
| C20987 | VI | 1.57 | 21.35 | 4.3 | 2.1 | 8.3 | 6.7 | 35. | 38. | 28. | ANH2,BASS1,MARC1,PLAG |
|  |  | ---- |  |  |  |  |  |  |  |  |  |
| COMPOSITE+ |  | 5.67+ | 19.68 | 3.0 | >5.0 | 3.6 | 8.0 | 43. | 31. | 26. |  |

* Mineral abbreviations:

ANH - anhydrite
BASS- bassanite
CAL - calcite
COQ - coquimbite & other Fe-sulfates
EXP - expandable mixed layered clay
GYP - gypsum
HEM - hematite
ILL - illite
K + C - kaolinite + chlorite
LTA - low temp. ash
MARC- marcasite
ORTH- orthoclase
PLAG- plagioclase
PYR - pyrite
QTZ - quartz
SID - siderite
SPH - sphalerite
TCLAY- total clay

\+ Calculated from the bench set exclusive of the shale (sh) bench. Equivalent to a face channel type of whole coal sample

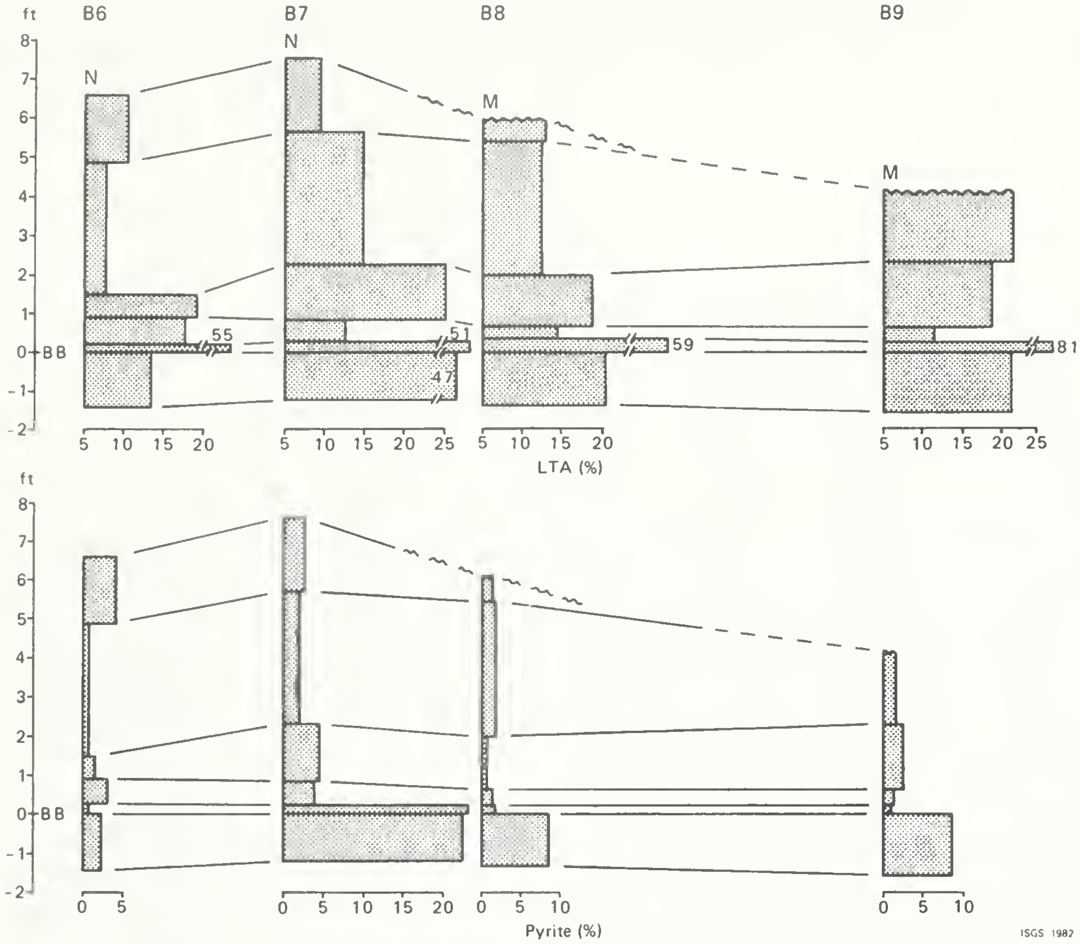


FIGURE V-1. LTA and pyrite contents of benches within the Herrin along a traverse in mine 866. Nonmarine (N) shales extend 18.6 ft above coal at B6 and 7.5 at B7; marine (M) shales overlie coal at B8 and B9.

The variation of the non-clay minerals is significant and is probably due to the complexities of the geology along this particular traverse.

## MINERAL VARIATION OF WHOLE-COAL SAMPLES FROM THE HERRIN

The variation of the mineral composition of the Herrin Coal was determined from analyses of 61 whole-coal samples from widely scattered localities where the coal is more than 28 inches thick (IV-1). Results of the mineral analyses are listed in table V-2. The mineral data for 26 of the samples were compiled from Rao and Gluskoter (1973). The mineral data on the remaining 35 samples (C15999 and all below C16543) were completed for this work. The data are listed in table V-2 in the same format as in table V-1.

### Mineral variation of the Herrin Coal in local areas

An analysis was made of variations in mineral composition within certain local areas. The samples included in these local areas are indicated in table V-2 by their purpose codes (L1-L5 and L7-L9). Unfortunately there are only a few samples from each local area—too few for good statistical analyses.

**TABLE V-2.** Mineral composition of whole coal samples of the Herrin Coal.*

| SAMPLE | PURPOSE-CODE | LTA | QTZ | CAL | PYR | TCLAY | K+C | ILL | EXP | OTHER MNRLS PRESENT |
|---|---|---|---|---|---|---|---|---|---|---|
| | | ( % ) | ( % ) | ( % ) | ( % ) | ( % ) | (% OF TCLAY FRACTION) | | | (MINOR-1, TRACE-2) |
| | (C499 SAMPLES) | | | | | | | | | |
| C12059 | RL | - | - | - | - | - | - | - | - | - |
| C12831 | R | - | - | - | - | - | - | - | - | - |
| C12942 | R | - | - | - | - | - | - | - | - | - |
| C13324 | R | - | - | - | - | - | 35. | 30. | 35. | - |
| C13433 | R | 11.07 | .8 | .2 | 1.9 | 8.2 | 33. | 37. | 30. | - |
| C13464 | R | 17.91 | 2.5 | 1.4 | 1.6 | 12.4 | 27. | 31. | 42. | - |
| C13895 | R | - | - | - | - | - | - | - | - | - |
| C13975 | R | 15.73 | 3.8 | 1.4 | 3.1 | 7.4 | - | - | - | - |
| C14574 | R | 9.29 | 2.2 | .5 | 1.5 | 5.1 | 45. | 32. | 23. | - |
| C14613 | L 5 | 10.84 | 2.0 | .8 | 1.0 | 7.0 | - | - | - | - |
| C14630 | L 5 | 11.11 | 2.2 | 1.0 | 1.1 | 6.8 | - | - | - | - |
| C14684 | R | 12.91 | 2.2 | .9 | 2.5 | 7.3 | - | - | - | - |
| C14721 | R | 14.76 | 2.4 | 1.8 | 2.8 | 7.8 | 29. | 29. | 42. | - |
| C14838 | RL2 | 15.81 | 1.7 | 1.1 | 2.5 | 10.5 | - | - | - | - |
| C14970 | R | - | - | - | - | - | - | - | - | - |
| C14982 | R | 15.68 | 2.2 | 1.4 | 2.2 | 9.9 | - | - | - | - |
| C15038 | R | 11.43 | 2.1 | 1.9 | 1.8 | 5.6 | - | - | - | - |
| C15079 | R | 20.90 | 3.3 | 1.0 | 3.1 | 13.5 | - | - | - | - |
| C15117 | R | 15.85 | 1.0 | 1.4 | 2.2 | 11.3 | 34. | 32. | 34. | - |
| C15231 | R | 16.26 | 3.3 | 1.3 | 3.1 | 8.6 | 29. | 34. | 37. | COQ1,MARC2 |
| C15432 | R | 14.56 | 3.2 | 1.9 | 2.3 | 7.2 | - | - | - | COQ1,SPHL2 |
| C15436 | L 3 | 12.40 | 3.1 | 1.4 | 2.9 | 5.0 | 40. | 32. | 28. | COQ1,SPHL2 |
| C15456 | RL 4 | 15.37 | 2.8 | 2.0 | 2.9 | 7.7 | - | - | - | - |
| C15717 | R | 17.71 | 2.3 | 1.9 | 3.0 | 10.5 | - | - | - | COQ1 |
| C15791 | RL 5 | 12.94 | 2.2 | 1.3 | 2.7 | 6.7 | - | - | - | GYP1,COQ1,PLAG1 |
| C15868 | R | 10.80 | 2.2 | 1.0 | .8 | 6.8 | - | - | - | COQ1,SPHL2 |
| C15872 | R | 15.56 | 1.4 | 3.3 | 3.3 | 7.6 | 26. | 38. | 36. | GYP1,COQ1 |
| C15999 | R | 15.09 | 2.4 | .5 | 3.3 | 8.9 | 31. | 39. | 30. | COQ1,PLAG1 |
| C16030 | R | 14.26 | 2.7 | .3 | 3.4 | 7.9 | 26. | 43. | 32. | ANH1,COQ1,SPHL1 |
| C16139 | R | 18.89 | 3.6 | 1.7 | 4.3 | 9.3 | 27. | 33. | 40. | COQ1,MARC1 |
| C16265 | L | 16.55 | 2.8 | 1.3 | 2.3 | 10.2 | - | - | - | GYP1,COQ1 |
| C16317 | L 1 | 17.89 | 3.8 | 2.1 | 2.7 | 9.3 | - | - | - | COQ2,SPHL1 |
| C16501 | R | 15.51 | 3.7 | 1.4 | 2.5 | 7.9 | - | - | - | COQ1 |
| C16543 | R | 16.83 | 3.2 | 5.2 | 2.7 | 5.7 | 44. | 30. | 26. | COQ1,SPHL1 |
| C16993 | R | 20.65 | 5.4 | 1.3 | 3.5 | 10.5 | - | - | - | COQ1,PLAG1 |
| C17016 | L 2 | 19.49 | 2.5 | 1.2 | 5.5 | 10.3 | 30. | 28. | 42. | COQ1,PLAG1 |
| C17278 | L 3 | - | - | - | - | - | - | - | - | - |
| C17279 | RL 3 | 14.05 | 2.1 | .8 | 3.0 | 8.2 | - | - | - | COQ1 |
| C18044 | L 4 | 17.00 | 2.7 | .9 | 3.4 | 1 - | - | - | - | COQ1 |
| C18320 | R | 17.77 | 2.5 | 1.8 | 2.8 | 10.7 | - | - | - | COQ1,PLAG1 |
| C18368 | L 4 | 16.45 | 2.3 | 1.3 | 3.8 | 9.1 | 30. | 32. | 38. | COQ1 |
| C18389 | R | 13.82 | 1.2 | - | 5.0 | 7.6 | 27. | 43. | 30. | GYP1,COQ1 |
| C18398 | R | 12.89 | 1.2 | 1.9 | 3.7 | 6.1 | 39. | 33. | 28. | COQ1 |
| C18407 | R | 9.82 | .7 | .5 | 2.1 | 6.5 | 37. | 37. | 26. | MARC1,PLAG1,COQ1 |
| C18415 | R | 11.16 | 1.7 | 1.0 | 2.0 | 6.5 | 39. | 33. | 28. | GYP1,COQ1 |
| C18560 | R | 20.37 | 3.1 | 1.2 | 6.7 | 9.4 | - | - | - | COQ1,MARC1,PLAG1 |
| C18857 | R | 17.44 | 4.2 | 1.2 | 6.6 | 5.4 | - | - | - | GYP1,COQ1,MARC1 |
| | (MMC80 SAMPLES) | | | | | | | | | |
| C20154 | R | 17.04 | 1.7 | 1.9 | .5 | 12.9 | 37. | 35. | 28. | PLAG1,COQ1 |
| C20242 | R | 14.27 | .9 | .3 | 2.0 | 11.1 | 32. | 39. | 29. | MARC1,PLAG1 |
| C20323 | L 8 | 21.04 | 2.5 | .6 | 4.6 | 13.3 | 24. | 38. | 38. | COQ1,MARC1 |
| C20613 | R | 14.51 | 2.0 | 2.3 | 3.8 | 6.4 | 28. | 45. | 27. | GYP1,MARC1,PLAG2 |
| C20620 | RL 1 | 17.34 | 1.9 | 1.6 | 2.6 | 11.2 | 32. | 39. | 29. | MARC1,PLAG2,SPHL1 |
| C20628 | L 4 | 16.58 | 2.3 | 1.0 | 4.0 | 9.3 | 29. | 38. | 33. | MARC1 |
| C20635 | R | 15.66 | 1.6 | 1.4 | 3.6 | 9.1 | 26. | 37. | 37. | MARC1,PLAG2,SPHL1 |
| C20636 | L 4 | 17.15 | 2.1 | 1.7 | 4.5 | 8.9 | 28. | 34. | 38. | MARC1,PLAG1 |
| C20641 | L 5 | 11.94 | 1.3 | 1.0 | 1.0 | 8.6 | 34. | 39. | 27. | COQ1,PLAG2 |
| C20642 | L 5 | 10.68 | 1.0 | 1.0 | 1.6 | 7.1 | 40. | 35. | 25. | GYP1,MARC1,PLAG1 |
| C20654 | R | 17.26 | 2.2 | 1.7 | 3.5 | 9.9 | 32. | 30. | 38. | ANH1,MARC1 |
| C20658 | R | 14.90 | 1.8 | .1 | .3 | 12.7 | 26. | 36. | 38. | COQ1,PLAG1 |
| C20678 | R | 25.64 | 3.1 | 1.8 | 4.4 | 16.3 | 43. | 32. | 25. | - |
| C20759 | R | 17.29 | 2.4 | .7 | 3.6 | 10.6 | 34. | 28. | 38. | MARC1 |
| C21164 | RL 7 | 18.51 | 2.4 | 1.3 | 5.0 | 9.8 | 37. | 38. | 25. | MARC2 |
| C21166 | L 7 | 17.52 | 3.0 | 1.6 | 2.1 | 10.8 | 30. | 33. | 37. | ANH2 |
| C21168 | L 7 | 17.46 | 2.4 | 1.2 | 1.6 | 12.3 | 31. | 37. | 32. | M77 |
| C21170 | L 7 | 19.05 | 2.1 | .6 | 4.4 | 12.0 | 29. | 37. | 34. | SID2,ANH2,COQ2,MARC1, |
| C21172 | L 8 | 17.17 | 2.4 | 1.4 | 3.8 | 9.6 | 35. | 32. | 33. | - |
| C21174 | RL 8 | 17.05 | 2.2 | .3 | 3.6 | 11.0 | 32. | 37. | 31. | ANH2,COQ2,MARC1,HEM2 |
| C21176 | L 8 | 22.67 | 3.4 | .9 | 11.6 | 6.8 | 37. | 35. | 28. | MARC1,ORTH2,HEM1 |

* SEE FOOTNOTE TO TABLE 5.1 FOR ABBREVIATONS OF MINERALS
- NOT DETERMINED

The variation of the mineral composition within these local areas is shown in figure V-2. The means and standard deviations vary for each mineral in different areas.

| Mineral matter | Range of means(%) | Areas | Differences(%) |
|---|---|---|---|
| QTZ | 1.7 - 3.0 | L5, L2 | 1.3 |
| CAL | 1.0 - 2.3 | L5, L1 | 1.3 |
| TCLAY | 7.2 - 11.2 | L5, L7 | 4.0 |
| PYR | 1.5 - 5.9 | L5, L8 | 4.4 |
| LTA | 11.5 - 19.5 | L5, L8 | 8.0 |

Most notable is the high range of the mean results of LTA (11.5 to 19.5%). In terms of the differences, the mean assays--quartz and calcite--show the least variability between local areas; total clay and pyrite show intermediate variability. Area L5 is identified as an area of low mineral matter content.

The variability of the mineral matter within the separate areas is indicated by the standard deviation (SD), the length of the vertical line in figure V-2. The range of SD of the minerals, excluding area L3, is as follows:

| Mineral matter | Mimimum SD | Area | Maximum SD | Area |
|---|---|---|---|---|
| QTZ | 0.3 | L4 | 1.1 | L2 |
| CAL | 0.3 | L5 | 1.4 | L1 |
| TCLAY | 0.8 | L5 | 2.7 | L8 |
| LTA | 0.7 | L4 | 2.8 | L8 |
| PYR | 0.3 | L1 | 3.8 | L8 |

These results show that the mineral composition of the Herrin varies considerably from one area to another.

Comparisons of the results within the local areas and those collected elsewhere (regional samples, purpose code R) can be made from the data given in figure V-2. The comparable statistical data for the regional samples (shown on the right side of the figure) reflect the variability of the

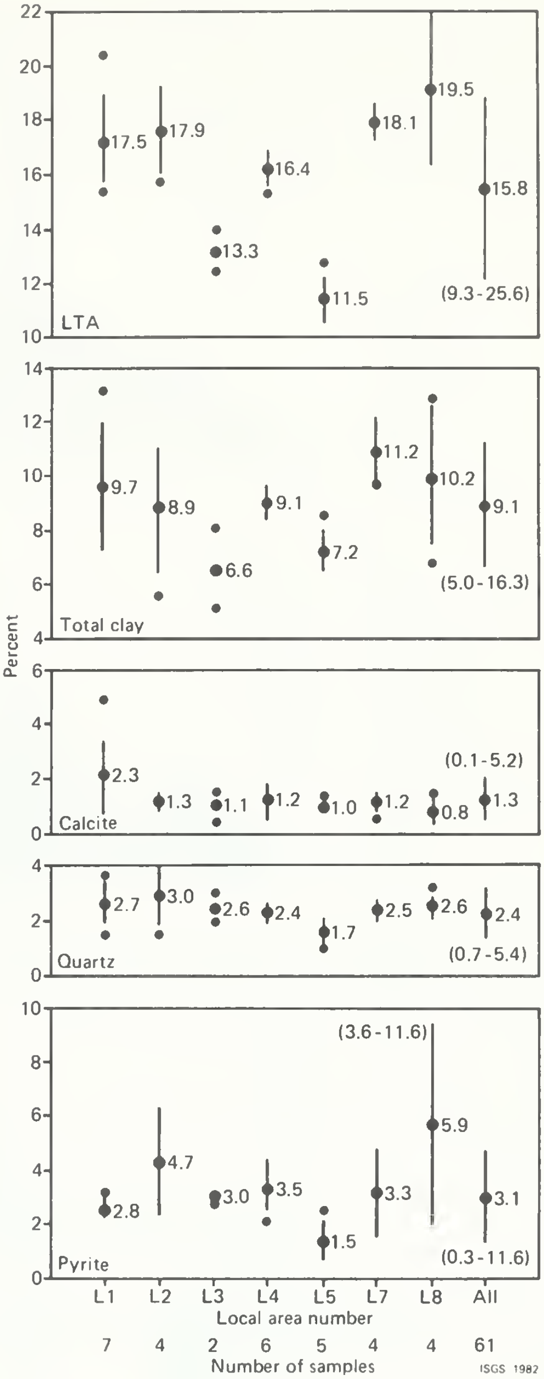


FIGURE V-2. Mineral variations in local areas and in all whole-coal samples (L and R) from the Herrin. Mean, standard deviations (length of solid line), and range (dots off ends of line) are shown. Some ranges are in parentheses.

means and standard deviation over the entire Illinois Basin as well as the variation within the local areas. The mean and standard deviation of each of the mineral components fall within the ranges observed in the local area. These statistical results confirm that the local areas of the Herrin studied contain mineral variations typical of those found in other places in the Herrin where it is of minable thickness.

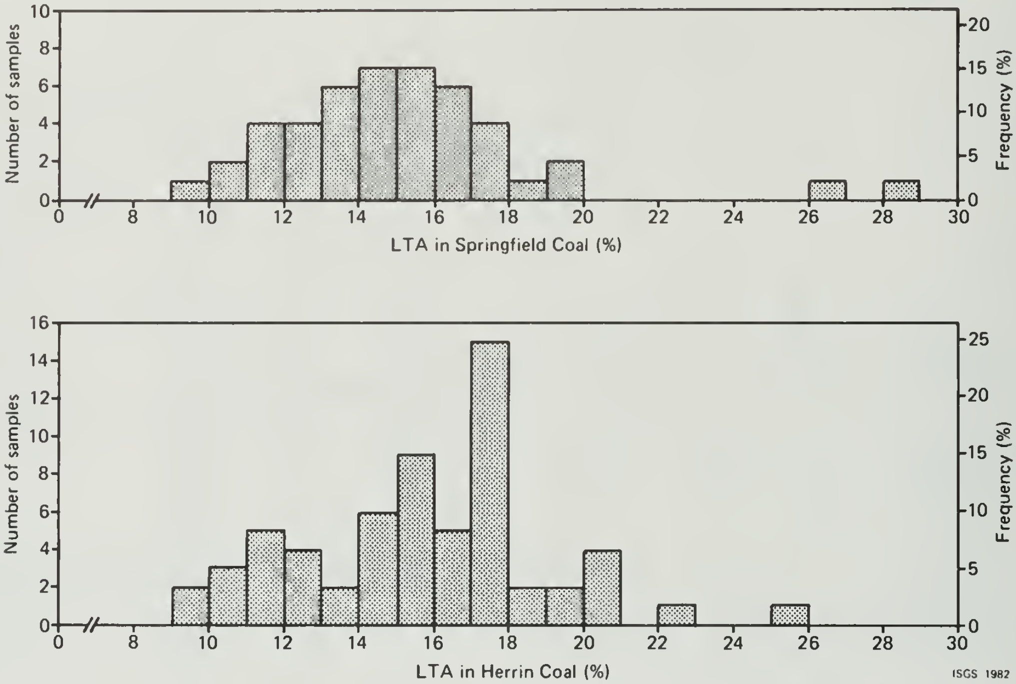


**FIGURE V-3.** Frequency distribution of LTA in whole-coal samples from the Springfield and Herrin Coals.

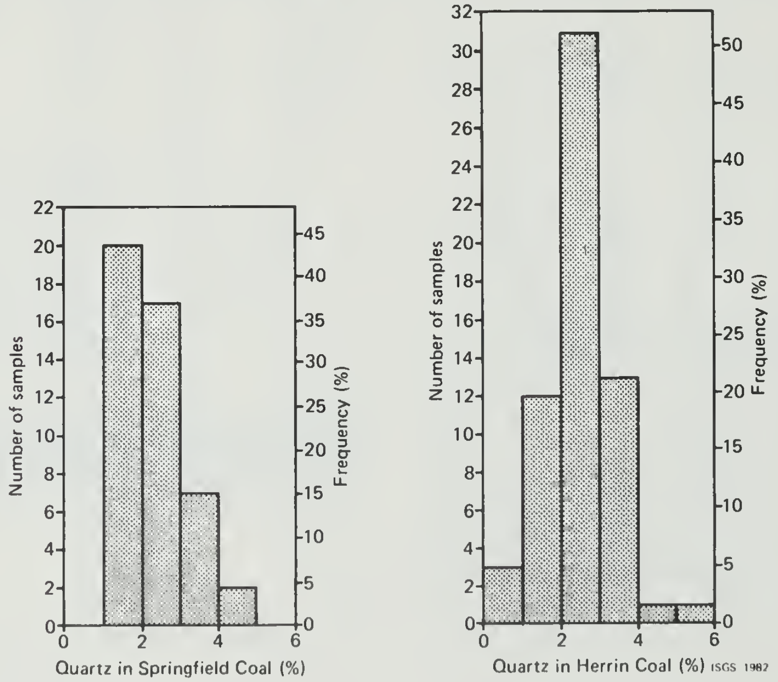


**FIGURE V-4.** Frequency distribution of quartz in whole-coal samples from the Herrin and Springfield Coals.

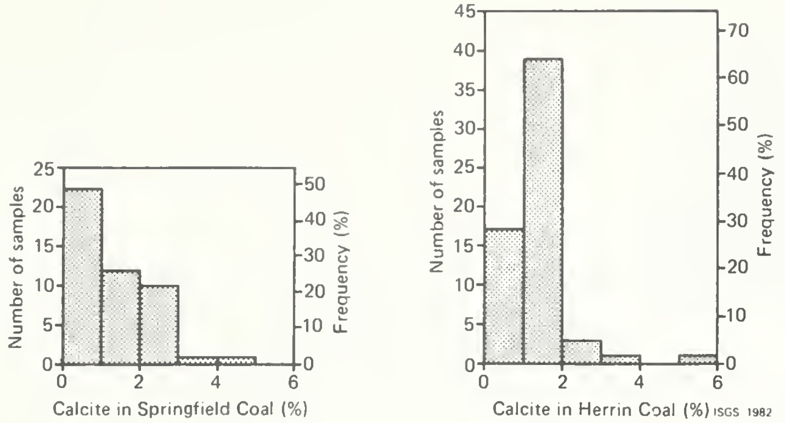


FIGURE V-5. Frequency distribution of calcite in whole-coal samples from the Herrin and Springfield Coals.

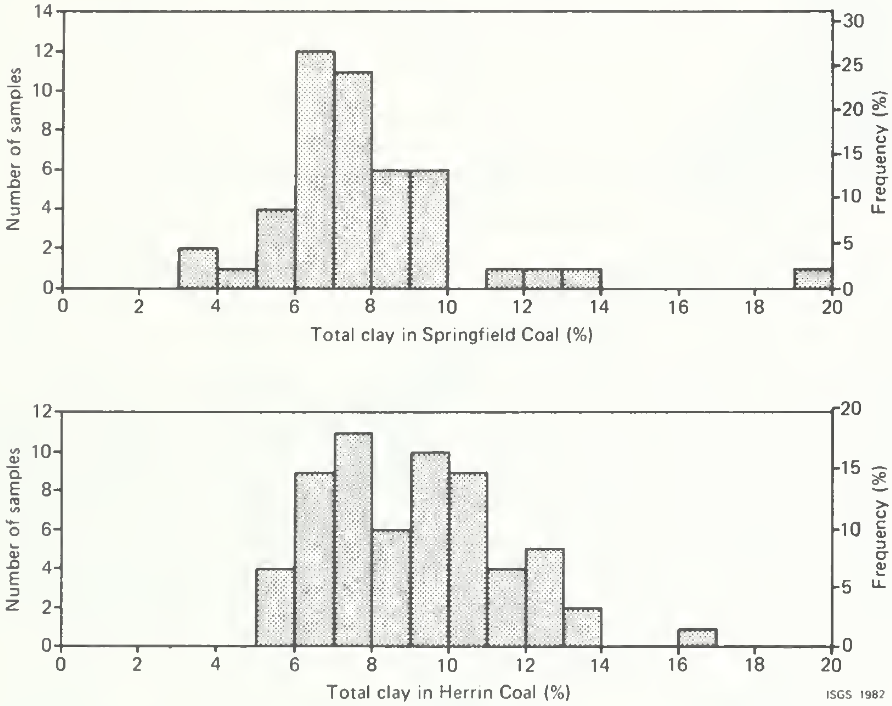


FIGURE V-6. Frequency distribution of total clay in whole-coal samples from the Herrin and Springfield Coals.

In order of increasing standard deviation, the variability of mineral components for all 61 samples is as follows: calcite 0.8; quartz, 0.9; pyrite, 1.7; TClay, 2.4; and LTA, 3.2.

The variation of mineral matter assays from the Herrin Coal is illustrated by histograms V-3 to V-7. No single mode dominates the distributions of LTA and total clay in the Herrin (figs. V-3 and V-6), but the distributions of quartz (fig. V-4), calcite (fig. V-5), and pyrite in this coal are each centered mainly around a single mode. Comparisons of these results with those of the Springfield Coal will be discussed later.

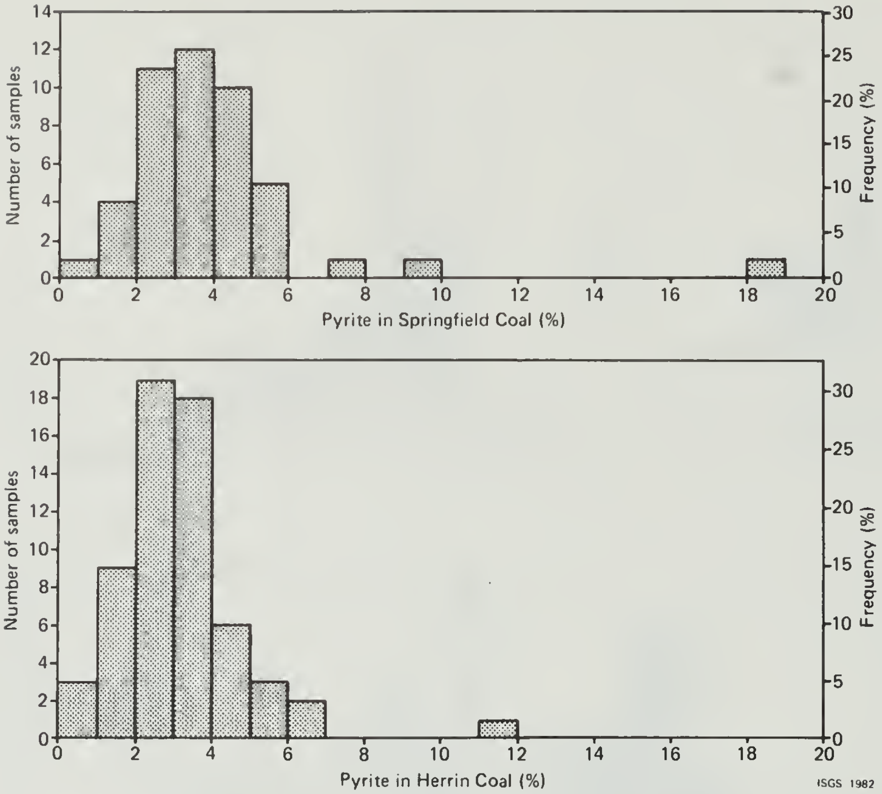


FIGURE V-7. Frequency distribution of pyrite in whole-coal samples from the Herrin and Springfield Coals.

### Regional distribution of mineral matter in the Herrin Coal

The spatial variability of mineral matter within the Herrin is best evaluated from maps showing assays plotted according to the sample location. Such maps provide a means by which regional geological factors can be evaluated and possible predictions made for areas between sample sites or nearby areas not yet explored. The frequency distribution (e.g. fig. V-7) of each mineral component was used to identify low-, medium-, and high-assay groups for each mineral component and the results were plotted on maps for each mineral to aid in the evaluation of the regional distribution of the minerals.

*LTA in the Herrin*—The spatial distribution of the LTA data is shown in figure V-8. The low-assay group occurs mainly in areas on either side of the split coal zone along the Walshville channel. The samples from Kentucky also belong to the low-assay group.

*Total clay in the Herrin*—Results show an increase in clay content (trending from the northwest to the southeast) in the northwestern area of the basin. Values ranging from a low of 5.7 percent, through 7.6 to 11.3, to a high of 13.5 percent, are recorded for this southeastward traverse in this area. Additional samples are needed to confirm this trend. Of the remaining 54 samples tested, the 7 high-assay and the 4 low-assay sample groups are widely scattered among the 43 middle-assay group throughout the central and southern areas of the basin.

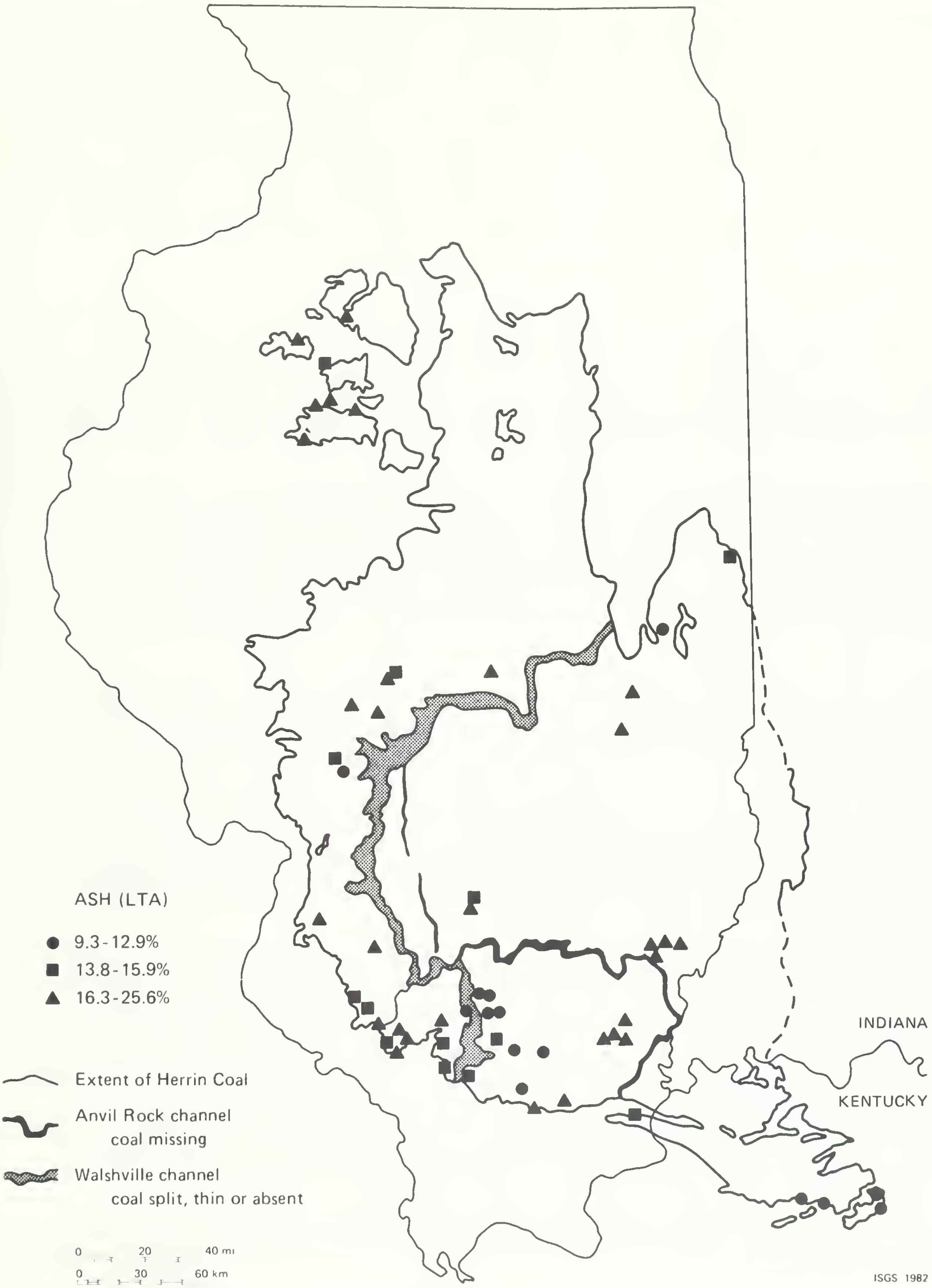


FIGURE V-8. Distribution of LTA in whole-coal samples from the Herrin.

*Pyrite in the Herrin.* Figure V-9 shows the distribution of pyrite in whole coal samples from the Herrin. With one exception the low-assay group of pyrite samples occurs on both sides of the split-coal adjacent to the Walshville channel in the lower reaches of the channel. The three high-assay samples of pyrite occur widely scattered among the remaining 52 samples from the middle-assay group. The location of low-assay pyrite near the Walshville channel is consistent with the spatial pattern of Rao and Gluskoter (1973), and with the depositional model for low-sulfur occurrences in coals that underlie relatively thick, nonmarine shales associated with this channel (described in section IV).

*Calcite in the Herrin.* The spatial pattern for calcite is a mixed one. Assays suggest that in the northwest area (fig. IV-1) calcite content decreases from the north to the southeast. In this area, two high assays lie in the northernmost part, one low assay in the southeastern part, and the remaining four middle assays lie in the intermediate area. Additional samples are needed from this area to confirm the significance of this trend.

The remaining samples from other areas of the basin fall in the low- and middle-assay groups. Many of the low-group assays occur near the Walshville channel, but because there are too many exceptions, no conclusions can be drawn. The pattern of increased amount of calcite from east to west across the southern half of Illinois, based on the percentage assay of the LTA (fig. 21 of Rao and Gluskoter, 1973), is not confirmed by the new data in this work.

*Quartz in the Herrin.* The spatial distribution pattern for quartz appears to be random. The 14 high-assay samples and the 11 low-assay ones are scattered among the 36 middle-assay samples throughout the basin.

*Other minerals in the Herrin.* No significant trends could be identified in the spatial distribution of the varieties of clay (illite, kaolinite-chlorite, and expandable mixed-layer clay minerals). The low- and high-assay samples were scattered among the medium-assay group in what appears to be a random pattern.

It is of some environmental interest that many samples from both Herrin and Springfield Coals contain minor or trace amounts of marcasite, a sulfide material. The chemical composition of marcasite and pyrite is the same ($FeS_2$) but marcasite's structure is orthorhombic while pyrite's is isometric. Marcasite is thought to oxidize more readily than pyrite. Until this study, no marcasite had been positively identified in Illinois coals (Gluskoter and Simon, 1968); however, we obtained diagnostic x-ray diffraction data to substantiate the presence of marcasite in the samples reported (tables V-2 and V-3). Traces of marcasite are observed in 40 percent of the Herrin samples and 55 percent of the Springfield samples.

No spatial pattern was observed in the distribution of marcasite in the Herrin. Further remarks on the spatial occurrences of marcasite appear at the end of this section.

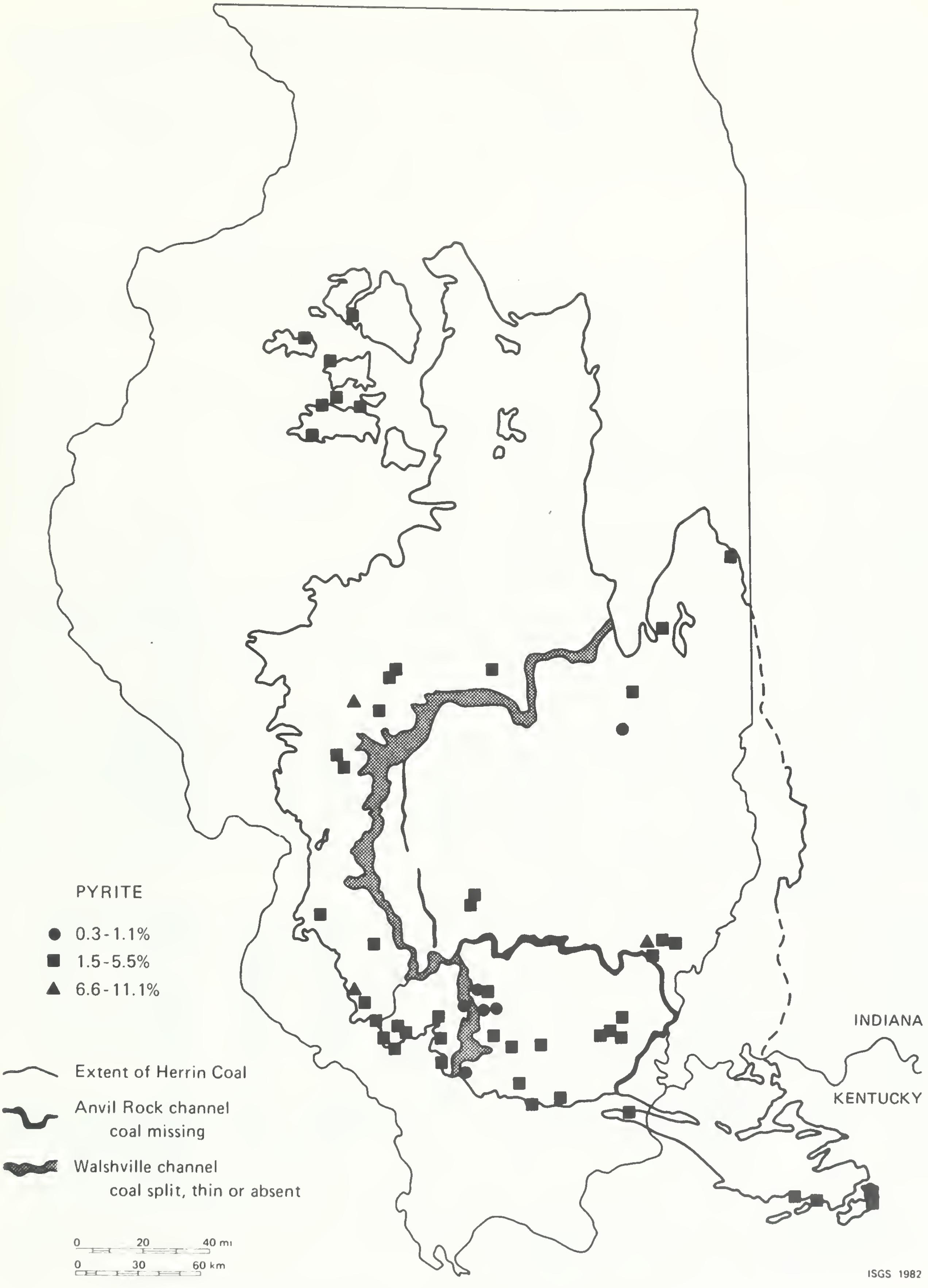


FIGURE V-9. Distribution of pyrite in whole-coal samples from the Herrin.

## MINERAL VARIATION OF WHOLE-COAL SAMPLES FROM THE SPRINGFIELD

The variation of the mineral composition of the Springfield Coal is evaluated on the basis of data assembled on 26 whole coal samples studied previously by Ward (1977) and on 20 new samples collected for this study (purpose codes R and L) from widely scattered localities throughout the basin (fig. IV-5). Results of the mineralogical compilations and analyses are given in table V-3.

**TABLE V-3.** Mineral composition of whole coal samples of the Springfield Coal.*

| SAMPLE | PURPOSE-CODE | LTA | QTZ | CAL | PYR | TCLAY | K+C | ILL | EXP | OTHER MNRLS PRESENT |
|---|---|---|---|---|---|---|---|---|---|---|
| | | ( % ) | ( % ) | ( % ) | ( % ) | ( % ) | (% OF | TCLAY | FRACTION) | (MINOR-1, TRACE-2) |
| | (C499 SAMPLES) | | | | | | | | | |
| C12495 | R | - | - | - | - | - | - | - | - | - |
| C13046 | R | - | - | - | - | - | - | - | - | - |
| C13983 | L 3 | 16.37 | 2.1 | .8 | 2.1 | 11.4 | 37. | 34. | 29. | - |
| C14194 | R | 17.30 | 2.4 | 2.9 | 2.8 | 9.2 | - | - | - | - |
| C14609 | L 4 | 13.85 | 1.5 | 1.0 | 2.9 | 8.5 | - | - | - | - |
| C14735 | R | 18.57 | 4.5 | 1.9 | 5.7 | 6.5 | - | - | - | - |
| C14774 | L 1 | 17.19 | 3.8 | 1.9 | 2.6 | 8.9 | 29. | 45. | 26. | - |
| C14796 | L 4 | 13.00 | 1.4 | .8 | 1.6 | 9.2 | - | - | - | - |
| C15012 | R | - | - | - | - | - | - | - | - | - |
| C15125 | RL 1 | 14.45 | 3.0 | 2.0 | 2.6 | 6.9 | - | - | - | GYP1,COQ1,PLAG1 |
| C15208 | R | 19.00 | 3.6 | 2.3 | 4.0 | 9.1 | - | - | - | ANH1,GYP2,COQ1 |
| C15384 | R | 15.20 | 2.7 | 1.4 | 4.0 | 7.1 | - | - | - | COQ1 |
| C15448 | R | 16.50 | 2.8 | 1.0 | 5.0 | 7.7 | - | - | - | COQ1 |
| C16264 | L 1 | 15.87 | 2.1 | 2.4 | 4.3 | 7.1 | - | - | - | COQ1,SPHL2 |
| C16729 | L 4 | 14.01 | 2.0 | 2.9 | 4.3 | 4.8 | - | - | - | COQ1,MARC1,PLAG1 |
| C16741 | L 1 | 15.73 | 3.5 | 3.0 | 2.8 | 6.4 | 29. | 37. | 34. | COQ1,PLAG1,SPHL2 |
| C17001 | R | 16.01 | 2.4 | 2.4 | 5.0 | 6.2 | - | - | - | COQ1 |
| C17721 | L 6 | 10.99 | 1.4 | .3 | 2.5 | 6.8 | - | - | - | COQ1 |
| C17984 | L 4 | 10.66 | 1.2 | .6 | 2.8 | 6.1 | - | - | - | - |
| C17988 | RL 4 | 14.24 | 2.8 | 2.8 | 2.6 | 6.0 | - | - | - | COQ1 |
| C18040 | L 3 | 15.40 | 4.3 | 4.9 | 3.2 | 3.0 | - | - | - | COQ1 |
| C18392 | R | 12.39 | 1.9 | .6 | 3.3 | 6.6 | - | - | - | CYP1,COQ1,MARC1,PLAG1 |
| C18395 | R | 12.64 | 1.2 | .6 | 3.3 | 7.5 | - | - | - | COQ1,MARC1 |
| C18404 | R | 12.31 | 1.2 | .9 | 3.2 | 7.0 | - | - | - | MARC1,COQ1 |
| C18411 | R | 16.49 | 1.5 | 1.3 | 5.3 | 8.4 | - | - | - | MARC1,COQ1 |
| C18590 | | 17.17 | 2.7 | .7 | 4.5 | 9.3 | - | - | - | CYP1,COQ1,MARC1,PLAG2 |
| C18594 | R | 14.03 | 1.7 | 1.3 | 4.6 | 6.4 | - | - | - | COQ1,MARC1 |
| C18689 | R | 11.42 | 1.1 | 1.6 | 3.0 | 5.7 | - | - | - | COQ1,MARC1 |
| C18693 | L 7 | 15.88 | 1.7 | 2.4 | 7.9 | 3.9 | - | - | - | MARC1,COQ1 |
| C18697 | L 7 | 14.08 | 2.0 | .7 | 4.1 | 7.3 | - | - | - | - |
| C18701 | RL 7 | 12.77 | 1.3 | .9 | 3.6 | 7.0 | - | - | - | MARC1,PLAG1 |
| | (MMC80 SAMPLES) | | | | | | | | | |
| C15140 | R | 13.12 | 1.8 | .7 | 1.2 | 9.4 | 37. | 33. | 30. | COQ1,PLAG1,SPHL1 |
| C20314 | R | 17.73 | 1.1 | .2 | 3.5 | 12.9 | 38. | 35. | 27. | PLAG1 |
| C20324 | RL 6 | 11.29 | 1.2 | .4 | 2.5 | 7.2 | 26. | 42. | 32. | COQ1,MARC1,PLAG2 |
| C20615 | R | 16.26 | 2.3 | .8 | 4.6 | 8.6 | 31. | 35. | 34. | MARC1,SPHL1 |
| C20616 | | - | - | - | - | - | 28. | 35. | 37. | - |
| C20631 | L 3 | 15.30 | 2.0 | 1.4 | 5.0 | 6.9 | 27. | 41. | 32. | ANH1,GYP1,MARC1,PLAG2 |
| C20637 | L 3 | 13.00 | 1.8 | .5 | 3.8 | 6.9 | 33. | 40. | 27. | COQ1,MARC1 |
| C20679 | R | 13.42 | 2.1 | 1.7 | 3.9 | 5.7 | 22. | 45. | 33. | COQ1 |
| C20705 | | 26.30 | 3.7 | .3 | 3.2 | 19.1 | 24. | 41. | 35. | COQ1,MARC1,PLAG1 |
| C20709 | R | 11.35 | 1.0 | .3 | 1.7 | 8.4 | 36. | 40. | 24. | MARC1,PLAG1 |
| C20760 | R | 14.86 | 2.4 | .3 | 3.3 | 8.9 | 26. | 36. | 38. | MARC1 |
| C21067 | L 5 | 9.82 | 1.3 | 1.1 | 1.7 | 5.7 | - | - | - | - |
| C21165 | RL 5 | 13.08 | 2.7 | .8 | 4.6 | 5.0 | 31. | 42. | 27. | MARC1 |
| C21167 | L 5 | 16.17 | 2.1 | .5 | .5 | 13.1 | 29. | 52. | 19. | SID1,ANH1,PLAG1 |
| C21169 | L 5 | 28.13 | 3.4 | 2.3 | 18.0 | 9.8 | 26. | 39. | 35. | MARC1,PLAG1,ORTH1,HEM |
| C21171 | L 5 | 11.78 | 1.9 | .9 | 2.0 | 7.0 | 44. | 35. | 21. | SID2,ANH2,COQ1,MARC1, |
| C21173 | L 6 | 19.01 | 1.9 | 1.7 | 9.3 | 6.1 | 30. | 42. | 29. | SID2,ANH2,COQ2 |
| C21175 | L 6 | 15.64 | 3.6 | .9 | 3.8 | 7.3 | 31. | 45. | 24. | COQ2,MARC1,PLAG2 |
| C21177 | L 6 | 14.32 | 2.1 | 2.0 | 4.7 | 5.5 | 36. | 41. | 23. | COQ1,MARC1,PLAG2 |

* SEE FOOTMOTE TO TABLE 5.1 FOR ABBREVIATIONS OF MINERALS
- NOT DETERMINED

## Mineral variation of the Springfield Coal in local areas

An analysis was made of the variation of minerals within certain local areas. The samples included in the local areas are indicated in table V-3 by their purpose codes (L#).

The variation of the minerals within the local areas is shown in figure V-10. As in the case of the Herrin, the Springfield data show similar variation of means in different areas. The means range between the limits and their difference are as follows:

| Mineral matter | Range of means(%) | Areas | Differ-ences(%) |
|---|---|---|---|
| TCLAY | 6.6 - 7.3 | L6, L1 | 0.7 |
| CAL | 1.1 - 2.3 | L7, L1 | 1.2 |
| QTZ | 1.5 - 3.1 | L7, L1 | 1.6 |
| PYR | 2.8 - 5.4 | L4, L5 | 2.6 |
| LTA | 13.2 - 15.8 | L4, L5 | 2.6 |

The total clay has the smallest range of mean assays by local area, followed by calcite, quartz, pyrite, and finally LTA, with the largest range.

The variability of the minerals within the separate areas is indicated by the standard deviation, the length of the vertical line in figure V-10. The range of standard deviation of the mineral is as follows:

| Mineral matter | Minimum SD | Area | Maximum SD | Area |
|---|---|---|---|---|
| QTZ | 0.4 | L7 | 1.2 | L3 |
| CAL | 0.5 | L1 | 3.0 | L3 |
| TCLAY | 0.8 | L6 | 3.5 | L5 |
| PYR | 0.8 | L1 | 7.2 | L5 |
| LTA | 1.0 | L1 | 7.3 | L5 |

The highest variability is found in areas L3 and L5, the lowest (for three components) in area L5.

The statistical data for the mineralogical results for all the whole-coal samples (L and R purpose codes) are shown in figure V-10.

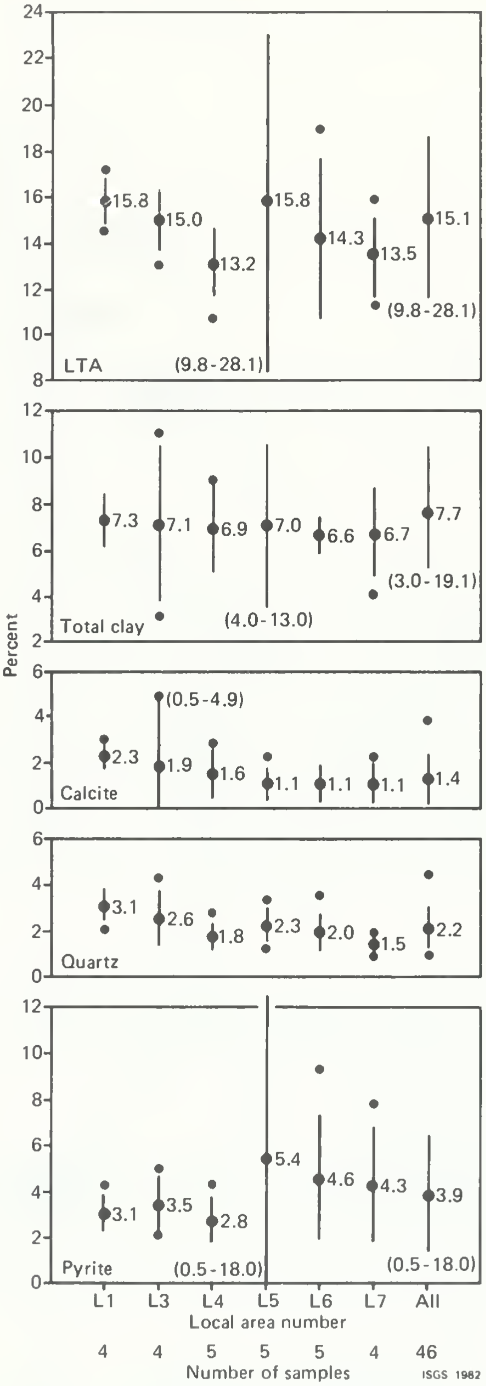


FIGURE V-10. Mineral variation in local areas in all whole-coal samples (L and R) from the Springfield Coal. Mean, standard deviations (length of line), and range (dots off ends of line) are shown. Some ranges are in parentheses.

FIGURE V-11. Distribution of LTA in whole-coal samples from the Springfield.

The variability of the mineral matter for all 46 samples--expressed in order of increasing standard deviation--is as follows: quartz, 0.9; calcite, 1.0; pyrite, 2.5; total clay, 2.6; and LTA, 3.5.

The variation of mineral matter assays of the Springfield Coal is shown in figures V-2 to V-6. Comparisons of the mineral data for the Springfield and Herrin Coals indicate the following general tendencies:

| | |
|---|---|
| LTA: | Herrin > Springfield |
| QTZ: | Herrin > Springfield |
| CAL: | Herrin > Springfield |
| TCLAY: | Herrin > Springfield |
| PYR: | Springfield > Herrin |

## Regional distribution of mineral matter in the Springfield Coal

The regional variability of the minerals in the Springfield Coal was evaluated from maps showing the assays plotted according to sample locations. In the following discussion of regional trends, the distribution and the number of samples constituting the data base should be kept in mind.

*LTA in the Springfield.* The spatial distribution of LTA assays of whole-coal (channel) samples from the Springfield is shown in figure V-11. The low-assay group tends to be located along the Galatia channel that runs from southwestern Indiana into Illinois. In Indiana, samples from the low-assay group are also found in areas bordering the tributaries to the main channel. However, in Illinois, two samples located along this channel belong to the middle assay group and two to the high-assay group. Five other high-assay samples and the rest of the middle-assay samples occur well outside the channel area. However, not all low-assay samples occur along this channel. One occurs in southwestern Illinois, one in east central Illinois; four of the five samples from Kentucky also belong to this low-assay group.

*Total clay in the Springfield.* The spatial distribution of total clay from the Springfield is essentially random. Samples from the low-, medium-, and high-assay groups are scattered throughout the same areas and no pattern is apparent.

*Pyrite in the Springfield.* Six whole-coal samples fall into the low-assay group for pyrite; five of these lie along the Galatia channel and the other is located in southwestern Illinois. However, two of the four from the high-assay group also occur along this channel, as do eight that are classified as middle-assay pyrites. All other sampling sites yielded pyrite assays in the middle assay group.

While pyrite represents only a part of the sulfur component of these coals, it is known to correlate proportionally with the total sulfur in samples from the Springfield in southeastern Illinois (Hopkins, 1968). The locations of the low-assay pyrite samples along the Galatia channel are thought to be places where relatively thick nonmarine shale overlies the coal (see section IV, p. 25).

*Calcite in the Springfield.* Most of the calcite assays in the Springfield range from 0.2 to 3.0 percent, although one assay is 4.9 percent. The spatial pattern for calcite distribution is essentially random, and no trends can be recognized.

*Quartz in the Springfield.* No spatial trends or patterns for quartz distribution can be distinguished in the Springfield Coal.

*Other minerals in the Springfield.* The distribution of the other minerals in the Springfield was evaluated. In contrast to the findings of Ward (1977), the kaolinite and chlorite fraction tend to be higher ($\geq$36%) near the Galatia channel in southern Indiana and southwestern Illinois. Elsewhere, these clays accounted for 22 to 33 percent of the clay mineral fraction.

No pattern could be recognized in the distribution of illite and expandable clay minerals.

Marcasite was detected in all samples from Kentucky, all samples but one from Indiana, and half the samples from southern Illinois. Marcasite was not detected in five of the six samples from central and northern Illinois. This pattern suggests a regional geological process, operating primarily in the southeastern region of the Illinois Basin, that promoted the growth of marcasite. Further study is needed to determine fully the significance of the marcasite occurrences.

# VI. CHEMICAL COMPOSITION OF COALS

## CHEMICAL VARIATION OF BENCH SAMPLES OF THE HERRIN COAL

The geologic setting of the bench set study area has been described in Section IV. Two main types of variability in the chemical composition of samples are observed in the bench sets: (1) vertical variability between the benches at a site and (2) lateral variability along a bench or in composite benches at different sites. Both types result from geochemical changes in the environment of the coal either at the time of deposition of the benches or site, or later, when infiltration of aqueous solutions, erosion, or other postdepositional processes occurred.

Chemical data for the four bench sets studied are reported in tables VI-1 and VI-2. An examination of the data by several statistical procedures indicated that the variability in chemical composition between the benches at a given site is greater than the compositional variability of the bench at different sites (bench sets). Analysis of variance tests indicate that significant differences between the bench sets exist for only a few elements, whereas chemical variability among the benches in a set is significant for many elements; therefore, the data from the four bench sets are averaged for each bench unit (table VI-3). Included in this table are the results of the analysis of variance tests for each element (see footnote * in table).

The analytical data on the 19 bench samples of coal were used as criteria for forming clusters by 2-cluster analysis routine; the resulting cluster dendrogram is shown in figure VI-1A. Description of the cluster analysis is given by Davis (1973). The dendrogram provides the cross section correlation of the four bench sets shown in figure VI-1B, in which chemically similar benches are identified by the same symbol. This correlation is consistent with the stratigraphic correlation shown in figure IV-4. The resulting groupings are generally lateral rather than vertical, because of lateral similarities in the chemistry of the bench units. It is possible that this differentiation of the coal beds would be more apparent if fewer elements were used to define clusters.

Whether the basic groupings are examined from a stratigraphic or paleogeographic viewpoint, the chemical behavior of the groups is to a large extent due to the mineral-chemical associations. Lithophile elements (those having an affinity with rock) are usually closely associated with the quartz or clay components; likewise, many of the chalcophile elements (those having an affinity with sulfur) are closely associated with pyrite, and many of the elements having an affinity with calcite are commonly associated with carbonates. Chemical differences observed among groups appear to be at least partly due to differing proportions or amounts of the minerals.

TABLE VI-1. Standard coal analyses of bench samples, Herrin Coal (MMC80), dry basis.*

| SAMPLE | BENCH-UNIT | THKN (FT.) | MOIS ( % ) | VOL ( % ) | FIXC ( % ) | ASH ( % ) | TOTS ( % ) | ORGS ( % ) | SUS ( % ) | PYRS ( % ) |
|---|---|---|---|---|---|---|---|---|---|---|
| | BENCH SET B 6 | | | | | | | | | |
| C20965 | I | 1.53 | 2.59 | 38.39 | 53.74 | 7.85 | 3.19 | .99 | .34 | 1.85 |
| C20966 | II | 3.54 | 2.70 | 37.10 | 56.17 | 6.72 | 1.81 | 1.39 | .05 | .36 |
| C20967 | III | .60 | 2.40 | 34.01 | 48.56 | 17.41 | 1.89 | 1.30 | .03 | .55 |
| C20968 | IV | .62 | 2.50 | 34.15 | 50.41 | 15.43 | 2.75 | 1.28 | .10 | 1.37 |
| C20969 | V (SH) | .15 | 1.79 | 21.89 | 27.25 | 50.85 | .99 | .60 | .08 | .30 |
| C20970 | VI | 1.39 | 2.50 | 36.82 | 51.78 | 11.39 | 2.59 | 1.48 | .01 | 1.09 |
| | COMPOSITE+ | (7.83) | 2.59 | 36.54 | 53.32 | 10.12 | 2.28 | 1.30 | .103 | .87 |
| | BENCH SET B 7 | | | | | | | | | |
| C20971 | I | 1.82 | 2.59 | 43.83 | 49.14 | 7.01 | 3.28 | 1.41 | .33 | 1.54 |
| C20972 | II | 3.40 | 2.20 | 38.75 | 47.88 | 13.36 | 2.67 | 1.57 | .12 | .98 |
| C20973 | III | 1.53 | 2.09 | 36.05 | 41.83 | 22.10 | 3.75 | 1.32 | .19 | 2.23 |
| C20974 | IV | .47 | 2.40 | 40.77 | 49.17 | 10.05 | 3.42 | 1.67 | .05 | 1.69 |
| C20975 | V (SH) | .36 | 1.60 | 26.42 | 32.90 | 40.67 | 12.78 | .71 | .38 | 11.68 |
| C20976 | VI | 1.17 | 1.89 | 28.64 | 32.97 | 38.37 | 10.58 | .57 | .31 | 9.68 |
| | COMPOSITE+ | (8.75) | 2.21 | 37.58 | 44.54 | 21.72 | 4.50 | 1.33 | .21 | 2.96 |
| | BENCH SET B 8 | | | | | | | | | |
| C20977 | I | .64 | 2.29 | 37.66 | 51.85 | 10.48 | 2.33 | 1.77 | .06 | .49 |
| C20978 | II | 3.50 | 2.20 | 37.32 | 53.00 | 9.67 | 2.73 | 1.88 | .06 | .77 |
| C20979 | III | 1.31 | 2.20 | 34.35 | 48.44 | 17.19 | 2.11 | 1.64 | .01 | .46 |
| C20980 | VI | .48 | 2.29 | 38.58 | 49.50 | 11.90 | 3.25 | 2.08 | .26 | .91 |
| C20981 | V (SH) | .23 | 2.00 | 20.30 | 24.77 | 54.91 | 1.72 | .83 | .14 | .74 |
| C20982 | VI | 1.28 | 2.50 | 36.10 | 47.91 | 15.97 | 5.84 | 1.41 | .65 | 3.77 |
| | COMPOSITE+ | (7.44) | 2.26 | 36.17 | 50.12 | 13.69 | 3.12 | 1.73 | .17 | 1.22 |
| | BENCH SET B 9 | | | | | | | | | |
| C20983 | II | 1.82 | 2.00 | 42.04 | 39.76 | 18.19 | 2.35 | 1.77 | .04 | .53 |
| C20984 | III | 1.70 | 2.40 | 35.45 | 48.86 | 15.68 | 3.15 | 1.74 | .08 | 1.33 |
| C20985 | IV | .58 | 2.40 | 39.95 | 50.35 | 9.68 | 2.71 | 2.02 | .05 | .63 |
| C20986 | V (SH) | .08 | 1.89 | 13.25 | 10.96 | 75.77 | .96 | .41 | .21 | .33 |
| C20987 | VI | 1.57 | 2.50 | 35.89 | 47.98 | 16.11 | 5.84 | 1.41 | .99 | 3.43 |
| | COMPOSITE+ | (5.75) | 2.94 | 37.8 | 45.4 | 16.82 | 3.56 | 1.67 | 3.15 | 1.57 |

* SEE TABLE I-1 AND FIG I-1 FOR ABBREVIATIONS AND SYMBOLS

\+ CALCULATED FROM THE BENCH SET EXCLUSIVE OF THE SHALE (SH) BENCHES, EQUIVALENT TO A FACE CHANNEL TYPE OF WHOLE COAL SAMPLE

## Bench set B6

The composite values for most of the elements in bench set B6 are the lowest (or lower than average) of the four bench sets (see figure IV-3 for details). These low composite values generally reflect the low mineral matter content of this bench set as indicated by the low LTA, HTA, and pyrite values (table VI-3). The trace element/mineral associations thus are not especially influenced by any one mineral. The few elements that have higher composite values in this set (Be, Br, Hg, and Sb) generally occur in association with the organic matter; elements occurring mainly in association with the minerals tend to be fairly low in concentration.

TABLE VI-2. Minor and trace element compositions of bench samples, Herrin Coal (MMC80), dry basis.*

| SAMPLE | BENCH UNIT | THKN (FT.) | AG (PPB) | AL ( % ) | AS (PPM) | B (PPM) | BA (PPM) | BE (PPM) | BR (PPM) | CA ( % ) | CD (PPM) | CE (PPM) | CO (PPM) | CR (PPM) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BENCH SET B 6 | | | | | | | | | | | | | | |
| C20965 | I | 1.53 | 52. | .64 | 3.6 | 120. | 20. | 1.3 | 16. | .46 | <.3 | 3. | 1.9 | 7. |
| C20966 | II | 3.54 | 45. | .88 | .8 | 86. | 23. | 0.28 | 20. | .24 | <.2 | 7. | 2.1 | 10. |
| C20967 | III | .60 | 68. | 2.12 | 1.7 | 70. | 65. | 0.58 | 18. | .37 | <.6 | 18. | 3.5 | 19. |
| C20968 | IV | .62 | 70. | 1.66 | 7.4 | 94. | 49. | 0.7 | 21. | .45 | <.5 | 14. | 5.5 | 18. |
| C20969 | V(SH) | .15 | 270. | 7.40 | 2.9 | 85. | 180. | 0.93 | 13. | .13 | <1.7 | 97. | 10. | 71. |
| C20970 | VI | 1.39 | 51. | 1.09 | 6.2 | 106. | 73. | 1.17 | 16. | .64 | <.4 | 13. | 7.9 | 15. |
| | COMPOSITE+ | (7.83) | 51. | 1.03 | 2.9 | 96. | 37. | 0.70 | 18. | .38 | <.3 | 9. | 3.5 | 12. |
| BENCH SET B 7 | | | | | | | | | | | | | | |
| C20971 | I | 1.82 | 37. | .60 | 1.5 | 110. | 21. | 1.14 | 15. | .29 | <.3 | 4. | 2.1 | 7. |
| C20972 | II | 3.40 | 48. | .81 | 1.0 | 76. | 25. | 0.29 | 16. | 2.57 | <.5 | 8. | 2.3 | 10. |
| C20973 | III | 1.53 | 96. | 1.86 | 3.4 | 88. | 590. | 0.56 | 16. | 1.94 | <.8 | 19. | 5.9 | 19. |
| C20974 | IV | .47 | 48. | .94 | 2.1 | 95. | 32. | 0.84 | 15. | .64 | <.4 | 6. | 3.7 | 17. |
| C20975 | V(SH) | .36 | 160. | 3.35 | 20.3 | 68. | 223. | 0.72 | 10. | .88 | <1.4 | 24. | 15. | 40. |
| C20976 | VI | 1.17 | 140. | 3.60 | 17. | 58. | 163. | 0.67 | 10. | .55 | <1.3 | 25. | 14. | 51. |
| | COMPOSITE+ | (8.75) | 67. | 1.35 | 3.9 | 84. | 147. | 0.61 | 15. | 1.57 | <.6 | 11. | 4.6 | 17. |
| BENCH SET B 8 | | | | | | | | | | | | | | |
| C20977 | I | .64 | 81. | 1.17 | 1.6 | 86. | 1160. | 0.39 | 14. | .61 | <.4 | 8. | 2.2 | 30. |
| C20978 | II | 3.50 | 41. | .98 | 1.2 | 82. | 39. | 0.22 | 14. | .90 | <.3 | 9. | 2.5 | 11. |
| C20979 | III | 1.31 | 57. | 2.06 | .7 | 95. | 61. | 0.45 | 14. | .22 | <.6 | 19. | 3.4 | 23. |
| C20980 | IV | .48 | 58. | 1.41 | 3.3 | 116. | 34. | 0.82 | 14. | .11 | <.4 | 9. | 6.7 | 16. |
| C20981 | V(SH) | .23 | 340. | 7.27 | 5.4 | 97. | 182. | 0.82 | 7. | .19 | <1.9 | 103. | 9.0 | 64. |
| C20982 | VI | 1.28 | 76. | 1.11 | 6.5 | 96. | 723. | 0.71 | 15. | .84 | <.6 | 103. | 9.9 | 15. |
| | COMPOSITE+ | (7.44) | 55. | 1.24 | 2.2 | 90. | 265. | 0.40 | 14. | .69 | <.4 | 27. | 4.2 | 16. |
| BENCH SET B 9 | | | | | | | | | | | | | | |
| C20983 | II | 1.82 | 117. | .58 | .7 | 113. | 288. | 0.28 | 13. | 6.61 | <.7 | 5. | 1.7 | 7. |
| C20984 | III | 1.70 | 71. | 1.67 | 2.4 | 105. | 184. | 0.41 | 15. | .51 | <.5 | 16. | 3.7 | 18. |
| C20985 | IV | .58 | 57. | 1.18 | 2.2 | 101. | 31. | 0.77 | 15. | .25 | <.3 | 7. | 4.7 | 17. |
| C20986 | V(SH) | .08 | 380. | 10.75 | 6.4 | 150. | 330. | 0.98 | 5. | .06 | <2.6 | 90. | 18. | 71. |
| C20987 | VI | 1.57 | 70. | 1.00 | 7.0 | 102. | 88. | 0.62 | 17. | .83 | <.6 | 9. | 8.7 | 16. |
| | COMPOSITE+ | (5.75) | 84. | 1.08 | 3.1 | 106. | 175. | 0.46 | 15. | 2.52 | <.6 | 10. | 4.6 | 14. |

+CALCULATED FROM THE BENCH SET EXCLUSIVE OF THE SHALE (SH) BENCH, EQUIVALENT TO FACE CHANNEL TYPE OF WHOLE COAL SAMPLE.

TABLE VI-2. Minor and trace element compositions of bench samples, Herrin Coal (MMC80).* (*continued*)

| SAMPLE | CS (PPM) | CU (PPM) | DY (PPM) | EU (PPM) | F (PPM) | FE ( % ) | GA (PPM) | GE (PPM) | HF (PPM) | HG (PPM) | I (PPM) | IN (PPB) | K ( % ) | LA (PPM) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BENCH SET B 6 | | | | | | | | | | | | | | |
| C20965 | .6 | 5.6 | .6 | .13 | 31. | 2.09 | 1.9 | <0.63 | .2 | .54 | - | 8. | .08 | 2.4 |
| C20966 | .6 | 5.5 | .6 | .19 | 42. | .44 | 2.1 | <0.53 | .3 | .20 | - | 24. | .10 | 5.8 |
| C20967 | 2.1 | 10.2 | 1.1 | .35 | 156. | .80 | 3.5 | <1.4 | .7 | .13 | - | 14. | .37 | 11. |
| C20968 | 1.3 | 13.8 | 1.2 | .32 | 90. | 1.61 | 5.5 | <1.2 | .6 | 1.18 | - | <103. | .27 | 7.7 |
| C20969 | 5.7 | 30.1 | 3.6 | 1.4 | 231. | .82 | 10. | <3.8 | 2.8 | .16 | - | <204. | .63 | 57. |
| C20970 | .6 | 11.9 | .9 | .27 | 53. | 1.28 | 7.9 | 3.4 | .4 | .19 | - | <205. | .15 | 7.5 |
| COMPOSITE | .8 | 7.7 | .7 | .22 | 55. | 1.04 | 2.9 | <1.2 | .4 | .35 | - | <59. | .14 | 6.0 |
| BENCH SET B 7 | | | | | | | | | | | | | | |
| C20971 | .7 | 5.0 | .6 | .16 | 30. | 1.82 | 2.1 | 1.16 | .2 | .14 | - | <82. | .08 | 2.8 |
| C20972 | .6 | 7.8 | .8 | .27 | 39. | 1.07 | 2.3 | <1. | .3 | .13 | - | <51. | .09 | 4.7 |
| C20973 | 2.3 | 11.6 | 1.4 | .37 | 100. | 2.49 | 5.9 | <1.7 | .7 | .16 | - | <31. | .32 | 10. |
| C20974 | .8 | 9.3 | .9 | .19 | 40. | 1.75 | 3.7 | 1.8 | .6 | .07 | - | <31. | .12 | 4.2 |
| C20975 | 2.0 | 20.1 | 1.5 | .41 | - | 11.43 | 15. | <3.1 | 1.2 | .14 | - | 20. | .30 | 17. |
| C20976 | 3.1 | 19.0 | 1.5 | .41 | - | 9.59 | 14. | <2.9 | 1.6 | .26 | - | 20. | .30 | 17. |
| COMPOSITE | 1.3 | 9.5 | 1.0 | .28 | 50. | 2.72 | 3.8 | 1.5 | .6 | .15 | - | <49. | .16 | 7.0 |
| BENCH SET B 8 | | | | | | | | | | | | | | |
| C20977 | 1.9 | 7.3 | .3 | .14 | 103. | .58 | 2.2 | 1.3 | .6 | .13 | - | 31. | .21 | 4. |
| C20978 | 1.0 | 7.0 | .6 | .18 | 95. | .82 | 2.5 | <0.76 | .5 | .08 | - | 17. | .14 | 5. |
| C20979 | 3.2 | 10.6 | 1.3 | .38 | 126. | .64 | 3.4 | <1.3 | 1.1 | .12 | - | 19. | .42 | 11. |
| C20980 | 1.7 | 10.6 | 1.0 | .25 | 59. | 1.24 | 6.7 | <0.91 | .7 | .14 | - | <102. | .24 | 5. |
| C20981 | 6.4 | 51.6 | 3.7 | 1.9 | 291. | 1.29 | 9.0 | <4.1 | 3.5 | .15 | - | <102. | .86 | 64. |
| C20982 | .8 | 12.3 | 1.6 | .21 | 52. | 4.06 | 9.9 | 1.5 | .5 | .12 | - | <103. | .15 | 62. |
| COMPOSITE | 1.5 | 8.9 | .9 | .22 | 91. | 1.37 | 3.3 | <1.1 | .6 | .10 | - | <40. | .21 | 16.0 |
| BENCH SET B 9 | | | | | | | | | | | | | | |
| C20983 | .3 | 9.4 | .3 | .11 | - | .61 | 1.7 | <1.6 | .3 | .10 | - | <153. | .05 | 2.5 |
| C20984 | 2.6 | 11.2 | 1.0 | .29 | - | 1.50 | 3.7 | <1.2 | 1.0 | .11 | - | <51. | .32 | 9. |
| C20985 | 1.2 | 12.5 | 1.0 | .22 | 67. | .78 | 4.7 | 0.78 | .6 | .08 | - | 41. | .16 | 4.2 |
| C20986 | 1.2 | 38.7 | 3.2 | .82 | 515. | 1.14 | 18. | <5.8 | 4.8 | .17 | - | 19. | 1.23 | 62. |
| C20987 | .8 | 13.5 | .7 | .19 | - | 4.19 | 8.7 | 5.4 | .6 | .13 | - | 33. | .15 | 5.4 |
| COMPOSITE | 1.2 | 11.4 | .7 | .20 | 67. | 1.89 | 3.4 | <2.5 | .6 | .11 | - | <78. | .17 | 5.4 |

TABLE VI-2. Minor and trace element compositions of bench samples, Herrin Coal (MMC80).* *(continued)*

| SAMPLE | LI (PPM) | LU (PPM) | MG ( % ) | MN (PPM) | MO (PPM) | NA (PPM) | NI (PPM) | P (PPM) | PB (PPM) | RB (PPM) | SB (PPM) | SC (PPM) | SE (PPM) | SI ( % ) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BENCH SET B 6 | | | | | | | | | | | | | | |
| C20965 | 8.4 | .08 | .03 | 42. | 8.5 | 832. | 4. | <100. | 42. | 10. | 1.3 | 2. | 1.9 | 1.07 |
| C20966 | 13.1 | .09 | .03 | 21. | <1.4 | 1470. | 4. | <100. | 22. | 11. | 2.7 | 1.8 | 1.9 | 1.52 |
| C20967 | 41.4 | .12 | .09 | 26. | <3.6 | 2889. | 8. | <100. | 18. | 29. | .9 | 4.0 | 1.8 | 4.58 |
| C20968 | 32.3 | .13 | .10 | 28. | 4.1 | 2841. | 8. | <100. | 33. | 22. | 1.9 | 4.0 | 3.6 | 3.68 |
| C20969 | 294. | .32 | .11 | 27. | <10. | 4043. | 25. | 100. | 33. | 42. | .3 | 9.5 | 6.5 | 15.78 |
| C20970 | 15.3 | .12 | .03 | 39. | 6.2 | 1733. | 26. | <100. | 30. | 11. | .5 | 3.1 | 2.5 | 2.48 |
| COMPOSITE | 16.3 | .10 | .04 | 29.0 | <4.1 | 1161. | 9.0 | <100. | 28. | 13. | 1.8 | 2.4 | 2.1 | 2.02 |
| BENCH SET B 7 | | | | | | | | | | | | | | |
| C20971 | 8.1 | .09 | .03 | 20. | 5.2 | 909. | 3. | <100. | 17. | 10. | 1.9 | 2.5 | 2.2 | 1.08 |
| C20972 | 9.0 | .10 | .06 | 172. | <2.8 | 1851. | 5. | <100. | 13. | 7. | .4 | 1.8 | 2.2 | 1.45 |
| C20973 | 29.2 | .19 | .10 | 130. | 5.2 | 2349. | 8. | <100. | 40. | 28. | .2 | 4.2 | 1.3 | 4.18 |
| C20974 | 10.4 | .13 | .04 | 36. | 4.6 | 1199. | 9. | <100. | 23. | 10. | .5 | 3.3 | 3.3 | 1.81 |
| C20975 | 110. | .25 | .23 | 106. | 33. | 2104. | 34. | <100. | 154. | 35. | .7 | 5.5 | 9.5 | 6.41 |
| C20976 | 117. | .17 | .22 | 69. | 19. | 1998. | 30. | <100. | 132. | 25. | .5 | 5.7 | 9.6 | 6.72 |
| COMPOSITE | 27.7 | .13 | .08 | 109.0 | 6.1 | 1722. | 9.0 | <100. | 36. | 14. | .7 | 3.0 | 3.1 | 2.63 |
| BENCH SET B 8 | | | | | | | | | | | | | | |
| C20977 | 9.6 | .07 | .05 | 20. | 16. | 1208. | 8. | <100. | 9. | 20. | .3 | 2.1 | 2.1 | 2.55 |
| C20978 | 8.3 | .05 | .04 | 29. | 4.5 | 1411. | 4. | <100. | 10. | 11. | .2 | 1.9 | 1.4 | 1.86 |
| C20979 | 15.9 | .14 | .10 | 23. | <3.5 | 1810. | 8. | <100. | 14. | 36. | .2 | 4.5 | 1.4 | 5.08 |
| C20980 | 11.8 | .12 | .04 | 16. | 4.4 | 1310. | 8. | <100. | 23. | 20. | .2 | 4.0 | 5.1 | 3.18 |
| C20981 | 83.4 | .26 | .14 | 51. | <11. | 3571. | 27. | <100. | 40. | 48. | .5 | 7.8 | 7.5 | 17.58 |
| C20982 | 9.2 | .12 | .05 | 49. | 14. | 1313. | 18. | <100. | 47. | 12. | .2 | 3.0 | 2.8 | 2.45 |
| COMPOSITE | 10.2 | .09 | .05 | 30.0 | <7.0 | 1441. | 8.0 | <100. | 18. | 17. | .2 | 2.7 | 2.0 | 2.70 |
| BENCH SET B 9 | | | | | | | | | | | | | | |
| C20983 | 5.9 | .06 | .16 | 178. | 8. | 1041. | 4. | <100. | 24. | 3. | .6 | 1.0 | 1.2 | 1.14 |
| C20984 | 13.6 | .12 | .07 | 34. | 5.2 | 1834. | 7. | <100. | 14. | 26. | .4 | 3.4 | 1.0 | 3.76 |
| C20985 | 10.9 | .11 | .03 | 22. | 3.2 | 1240 | 12. | <100. | 14. | 13. | .6 | 3.6 | 2.1 | 2.44 |
| C20986 | 101. | .34 | .13 | 45. | <15. | 4975. | 50. | <100. | 48. | 70. | .9 | 10. | 4.7 | 25.05 |
| C20987 | 8.8 | .11 | .03 | 59. | 15. | 1590. | 26. | <100. | 55. | 15. | .6 | 2.8 | 2.9 | 2.40 |
| COMPOSITE | 9.5 | .10 | .08 | 86.0 | 8.6 | 1451. | 12. | <100. | 29. | 14. | .5 | 2.5 | 1.7 | 2.41 |

TABLE VI-2. Minor and trace element compositions of bench samples, Herrin Coal (MMC80).* *(continued)*

| SAMPLE | SM (PPM) | SR (PPM) | TA (PPM) | TB (PPM) | TH (PPM) | TI ( % ) | TL (PPM) | U (PPM) | V (PPM) | W (PPM) | YB (PPM) | ZN (PPM) | ZR (PPM) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BENCH SET B 6 | | | | | | | | | | | | | |
| C20965 | .5 | 28. | .10 | .07 | .7 | .03 | 0.76 | <.5 | 4.9 | .3 | .3 | 25.0 | 5. |
| C20966 | .8 | 35. | .09 | .12 | 1.2 | .04 | 0.13 | <1. | 7.3 | .5 | .3 | 16.1 | 7. |
| C20967 | 1.8 | 32. | .25 | .17 | 2.7 | .11 | 0.3 | <1. | 20. | <.5 | .7 | 37.3 | 22. |
| C20968 | 1.4 | 30. | .18 | .15 | 2.4 | .08 | 0.51 | <1. | 15. | <1. | .7 | 45.4 | 16. |
| C20969 | 7.6 | 73. | .79 | .62 | 13. | .47 | <0.51 | 2.9 | 46. | .9 | 2.2 | 19.7 | 67. |
| C20970 | 1.1 | 23. | .15 | .16 | 1.9 | .06 | 0.36 | <1. | 16. | .3 | .5 | 86.6 | 12. |
| COMPOSITE | .9 | 31. | .12 | .12 | 1.4 | .05 | .34 | <.9 | 10.0 | <0.5 | 0.4 | 34.7 | 9.0 |
| BENCH SET B 7 | | | | | | | | | | | | | |
| C20971 | .5 | 28. | .06 | .10 | .7 | .03 | 1.8 | <.5 | 5.1 | .5 | .7 | 17.4 | 6. |
| C20972 | .9 | 33. | .09 | .13 | 1.1 | .04 | 0.22 | <.5 | 5.2 | <.4 | 1.1 | 64.9 | 6. |
| C20973 | 1.6 | 36. | .27 | .24 | 2.8 | .09 | 0.29 | <.7 | 10.2 | <.5 | 2.8 | 16.3 | 16. |
| C20974 | .7 | 27. | .09 | .13 | .06 | .04 | 0.11 | <.5 | 15. | <.5 | .06 | 14.9 | 10. |
| C20975 | 2.1 | 51. | .41 | .31 | 6. | .19 | 0.81 | <1. | 20. | .7 | 6.1 | 20.5 | 31. |
| C20976 | 2.1 | 43. | .47 | .24 | 7.2 | .21 | 0.75 | <1. | 18. | .4 | 7.2 | 88.8 | 35. |
| COMPOSITE | 1.1 | 34.0 | .17 | .16 | 2.1 | .07 | .64 | <0.6 | 8.4 | <0.5 | 2.1 | 46.3 | 12.0 |
| BENCH SET B 8 | | | | | | | | | | | | | |
| C20977 | .9 | 41. | .15 | .08 | 1.7 | .06 | 0.27 | 8. | 13. | <.5 | .2 | 19.3 | 10. |
| C20978 | .8 | 33. | .12 | .09 | 1.4 | .05 | 0.35 | <1. | 4. | <.5 | .2 | 64.5 | 7. |
| C20979 | 1.7 | 31. | .26 | .17 | 3.4 | .11 | <0.18 | <1. | 10.3 | <.5 | .7 | 306. | 22. |
| C20980 | 1.0 | 22. | .16 | .16 | 2.2 | .06 | 1.04 | <.5 | 15. | <.5 | .6 | 34.7 | 12. |
| C20981 | 11. | 50. | 1.0 | .82 | 13. | .46 | 0.79 | <2. | 48. | .9 | 1.8 | 18.5 | 76. |
| C20982 | .9 | 25. | .12 | .31 | 2.1 | .05 | 1.05 | .4 | 9.3 | <.5 | .5 | 22.0 | 10. |
| COMPOSITE | 1.0 | 31. | .15 | .15 | 2.0 | .06 | <.48 | <1.5 | 7.6 | <0.5 | .4 | 94.6 | 11. |
| BENCH SET B 9 | | | | | | | | | | | | | |
| C20983 | .4 | 88. | .08 | .07 | .9 | .02 | 0.28 | <.5 | 6.5 | <.5 | .2 | 18.5 | <1. |
| C20984 | 1.3 | 27. | .26 | .3 | 2.8 | .09 | 0.55 | 1. | 15. | .4 | .5 | 19.3 | 18. |
| C20985 | .8 | 25. | .12 | .5 | 2.4 | .05 | 0.46 | <.7 | 17. | <.5 | .4 | 301. | 13. |
| C20986 | 11. | 98. | 1.8 | .5 | 14. | .70 | <0.77 | <1. | 44. | 3. | 2.3 | 33.2 | 97. |
| C20987 | .9 | 25. | .16 | .14 | 2. | .05 | 1.19 | <1. | 10.8 | <.5 | .5 | 203. | 14. |
| COMPOSITE | 0.9 | 46. | .16 | .20 | 1.9 | .05 | <.62 | <0.8 | 11.3 | <0.5 | 0.4 | 99.5 | 11. |

TABLE VI-3. Average and composite concentrations† of bench sets coded* for significant differences based on analysis of variance between coal benches (shale excluded).

| Bench Unit | Qtz,% | Cal,% | Pyr,% | Clay,% | LTA,% | Moist,% | Volit,% | Fix C,% | HTA,% | Tot S,% |
|---|---|---|---|---|---|---|---|---|---|---|
| I | 1.4a | 0.9a | 2.6a | 5.7a | 10.66a | 2.49a | 39.96 b | 51.58a | 8.45a | 2.93a |
| II | 1.6a | 5.7a | 1.5a | 5.3a | 13.98ab | 2.28a | 38.80ab | 49.20a | 11.99ab | 2.39a |
| III | 3.9 b | 1.8a | 2.3a | 12.5 b | 20.50ab | 2.27a | 35.12ab | 46.92a | 18.10ab | 2.73a |
| IV | 2.6ab | 1.1a | 2.6a | 7.9ab | 14.07ab | 2.40a | 38.36ab | 49.86a | 11.77ab | 3.03a |
| Shale | 12.7 | 1.1 | 6.6 | 41.3 | 61.45 | 1.82 | 20.47 | 23.97 | 55.55 | 4.11 |
| VI | 4.1 b | 1.6a | 10.4 b | 9.6ab | 25.61 b | 2.35a | 34.36a | 45.16a | 20.46 b | 6.21 b |
| Average | 2.5 | 2.9 | 3.5 | 7.8 | 16.34 | 2.35 | 37.43 | 48.91 | 12.92 | 3.31 |

| Bench Unit | Org S,% | Sul S,% | Pyr S,% | Si,% | Al,% | Fe,% | Mg,% | Ca,% | Na,ppm | K,% |
|---|---|---|---|---|---|---|---|---|---|---|
| I | 1.39ab | 0.24ab | 1.29a | 1.57a | 0.80a | 1.50a | 0.04a | 0.45a | 983a | 0.12a |
| II | 1.65 b | 0.07a | 0.66a | 1.49a | 0.81a | 0.74a | 0.07a | 2.58a | 1443ab | 0.10a |
| III | 1.50ab | 0.08a | 1.14a | 4.40 b | 1.93a | 1.36a | 0.09a | 0.76a | 2221 b | 0.36 b |
| IV | 1.76 b | 0.12ab | 1.15a | 2.78ab | 1.30a | 1.35a | 0.05a | 0.36a | 1648ab | 0.20a |
| Shale | 0.64 | 0.20 | 3.26 | 16.2 | 7.19 | 3.67 | 0.15 | 0.31 | 3673 | 0.76 |
| VI | 1.22a | 0.49 b | 4.49 b | 3.51ab | 1.70a | 4.78 b | 0.08a | 0.72a | 1659ab | 0.19a |
| Average | 1.53 | 0.20 | 1.58 | 2.44 | 1.18 | 1.76 | 0.06 | 1.29 | 1556 | 0.17 |

| Bench Unit | Ti,% | Mn,ppm | Ag,ppb | As,ppm | B,ppm | Ba,ppm | Be,ppm | Br,ppm | Ce,ppm | Co,ppm |
|---|---|---|---|---|---|---|---|---|---|---|
| I | 0.04a | 27a | 57a | 2.2a | 105a | 400a | 0.94 c | 15a | 5a | 2.1a |
| II | 0.04a | 100 b | 63a | 0.9a | 89a | 94a | 0.27a | 16a | 7a | 2.2a |
| III | 0.10a | 53ab | 73a | 2.1a | 90a | 225a | 0.50ab | 16a | 18a | 4.1a |
| IV | 0.06a | 26a | 58a | 3.8a | 102a | 37a | 0.78 bc | 16a | 9a | 5.2 b |
| Shale | 0.46 | 57 | 288 | 8.8 | 100 | 229 | 0.86 | 9 | 79 | 13 |
| VI | 0.09a | 54ab | 84a | 9.2 b | 91a | 262a | 0.79 bc | 15a | 38a | 10.1 c |
| Average | 0.06 | 64 | 64 | 3.0 | 94 | 156 | 0.54 | 16 | 14 | 4.23 |

| Bench Unit | Cr,ppm | Cs,ppm | Cu,ppm | Dy,ppm | Eu,ppm | Ga,ppm | Hf,ppm | Hg,ppm | La,ppm | Li,ppm |
|---|---|---|---|---|---|---|---|---|---|---|
| I | 15a | 1.1a | 6.0a | 0.5a | 0.14a | 2.1a | 0.3a | 0.27a | 3.1a | 8.7a |
| II | 10a | 0.6a | 7.4a | 0.6a | 0.19ab | 2.4ab | 0.4a | 0.13a | 4.5a | 9.1a |
| III | 20a | 2.6 b | 10.9 b | 1.2 b | 0.35 c | 4.9 c | 0.9 b | 0.13a | 10.3a | 25.0a |
| IV | 17a | 1.3a | 11.6 b | 1.0 b | 0.25abc | 5.1 c | 0.6ab | 0.38a | 5.3a | 16.4a |
| Shale | 62 | 3.8 | 35.1 | 3.0 | 1.13 | 13.1 | 3.1 | 0.16 | 50 | 147. |
| VI | 24a | 1.3a | 14.2 b | 1.2 b | 0.27 bc | 4.4 bc | 0.8ab | 0.18a | 23.0a | 37.6a |
| Average | 15 | 1.2 | 9.4 | 0.8 | 0.23 | 3.4 | 0.5 | 0.18 | 8.6 | 15.9 |

| Bench Unit | Lu,ppm | Mo,ppm | Ni,ppm | Pb,ppm | Rb,ppm | Sb,ppm | Sc,ppm | Se,ppm | Sm,ppm | Sr,ppm |
|---|---|---|---|---|---|---|---|---|---|---|
| I | 0.08a | 9.9ab | 5ab | 23a | 13a | 1.2a | 2.2a | 2.1ab | 0.6a | 32a |
| II | 0.08a | 4.2a | 4a | 17a | 8a | 1.0a | 1.6a | 1.7ab | 0.7a | 47a |
| III | 0.14 b | 4.4a | 8ab | 22a | 30 b | 0.4a | 4.0 b | 1.4a | 1.6 b | 32a |
| IV | 0.12 b | 4.1a | 9 b | 23a | 16a | 0.8a | 3.7 b | 3.5ab | 1.0a | 29a |
| Shale | 0.29 | 17.3 | 34 | 69 | 49 | 0.6 | 8.2 | 7.1 | 7.9 | 68 |
| VI | 0.13 b | 13.6 b | 25 c | 66 b | 16a | 0.5a | 3.7 b | 4.5 b | 1.3ab | 25a |
| Average | 0.11 | 6.5 | 9 | 28 | 15 | 0.8 | 2.7 | 2.2 | 1.0 | 35 |

| Bench Unit | Ta,ppm | Tb,ppm | Th,ppm | Tl,ppm | V,ppm | Yb,ppm | Zn,ppm | Zr,ppm |
|---|---|---|---|---|---|---|---|---|
| I | 0.10a | 0.08a | 1.0a | 0.94a | 7.7ab | 0.4a | 20.6a | 7ab |
| II | 0.10a | 0.10a | 1.2a | 0.25a | 5.8a | 0.5a | 41.0a | 5a |
| III | 0.26 b | 0.22a | 2.9a | 0.33a | 13.9 c | 1.2a | 94.7a | 20 c |
| IV | 0.14ab | 0.23a | 1.8a | 0.53a | 15.5 c | 0.4a | 99.0a | 13abc |
| Shale | 1.00 | 0.56 | 11.5 | 0.72 | 39.5 | 3.1 | 23.0 | 68 |
| VI | 0.23ab | 0.21a | 3.3a | 0.84a | 13.5 bc | 2.2a | 100 a | 18 bc |
| Average | 0.15 | 0.16 | 1.9 | 0.52 | 9.4 | 0.8 | 68.8 | 11 |

†The values reported are weighted with respect to bench thickness and exclude shales.

*Concentrations for a particular element or mineral coded with the same letter as other benches are not significantly different from one another at the five percent level using Duncan's Multiple Range Test.

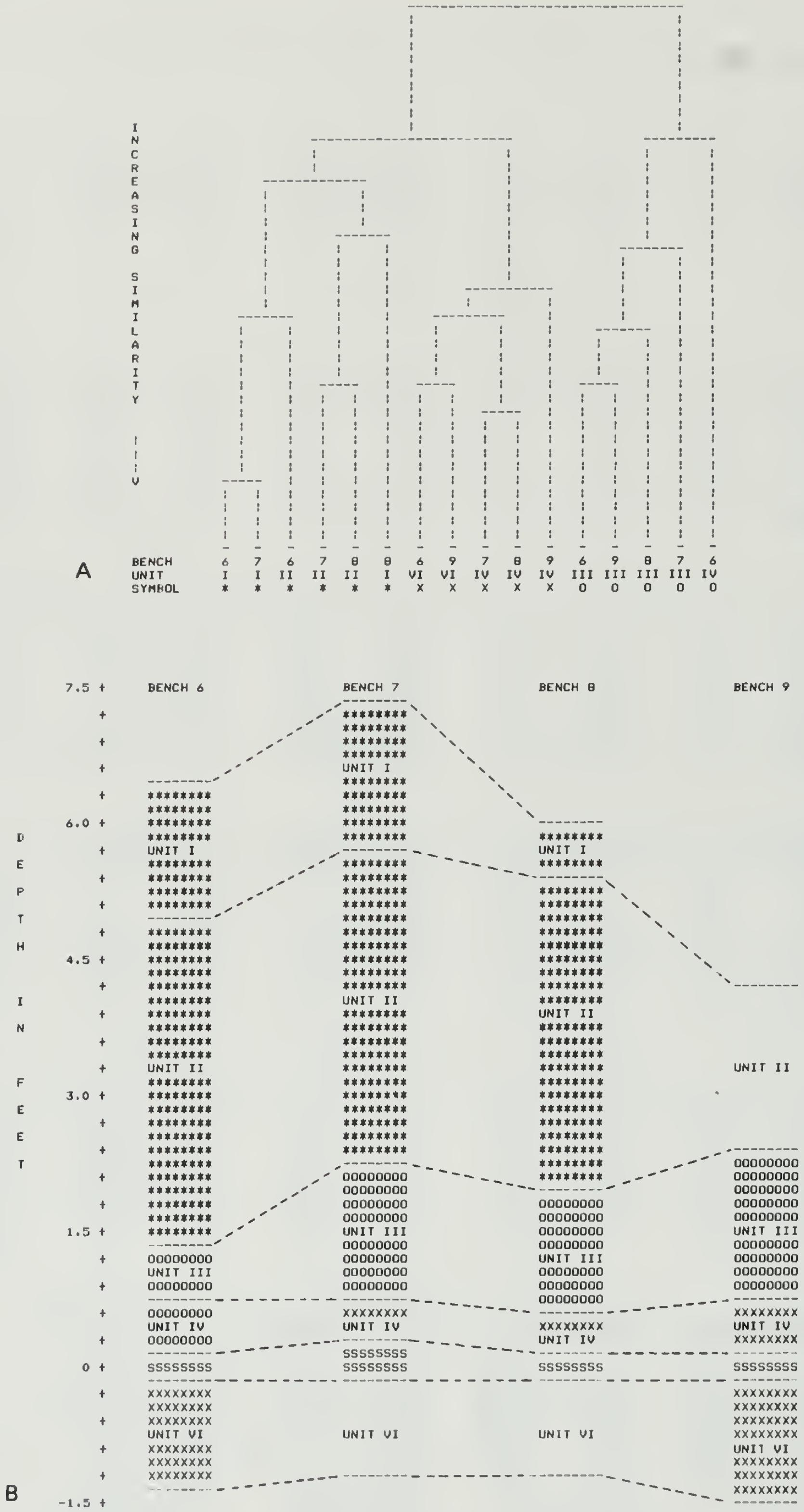


FIGURE VI-1. (A) Cluster dendogram of chemical constituents by bench number and unit designation; (B) resulting correlation of units that cluster in upper three levels of A, shown with shared symbols.

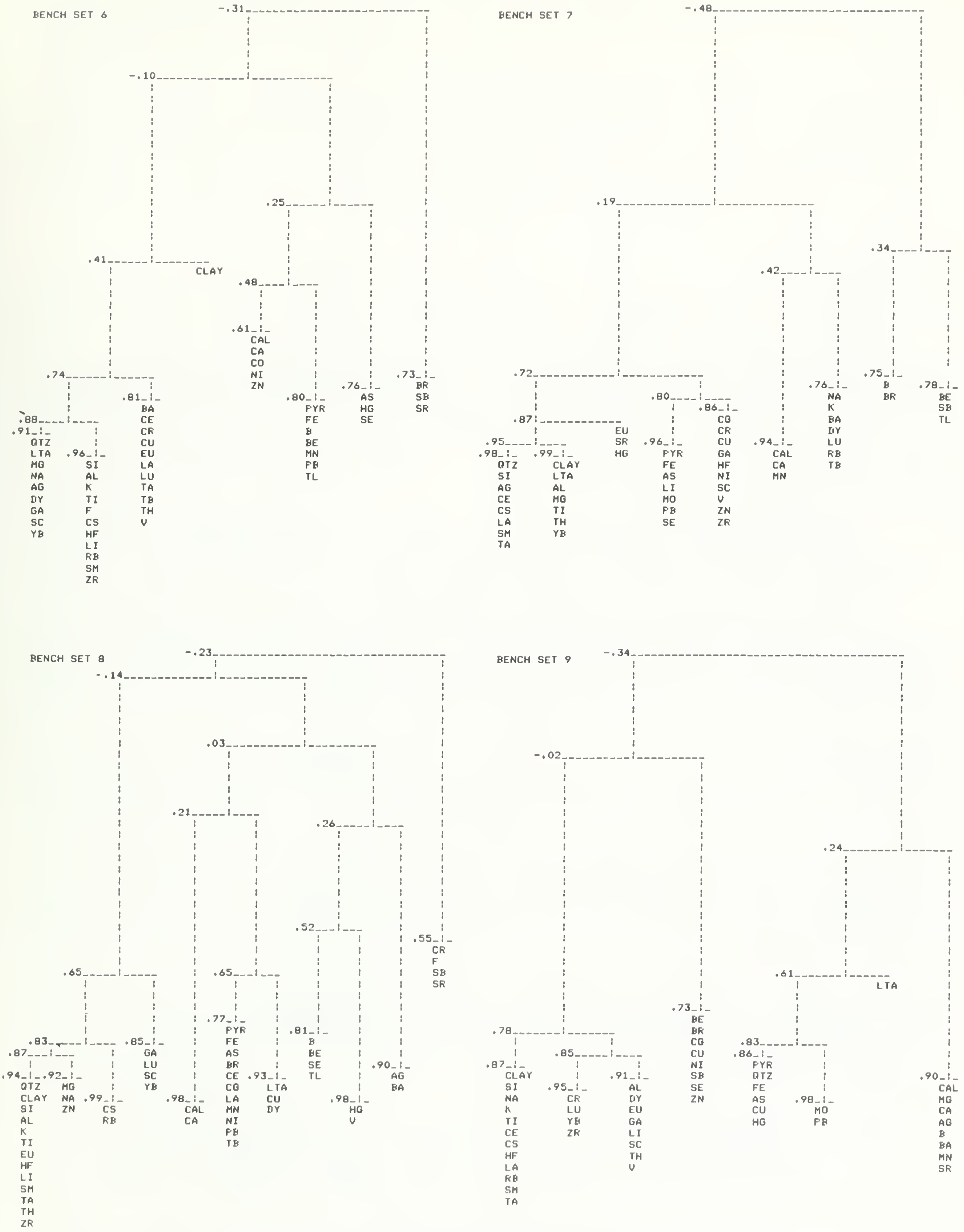
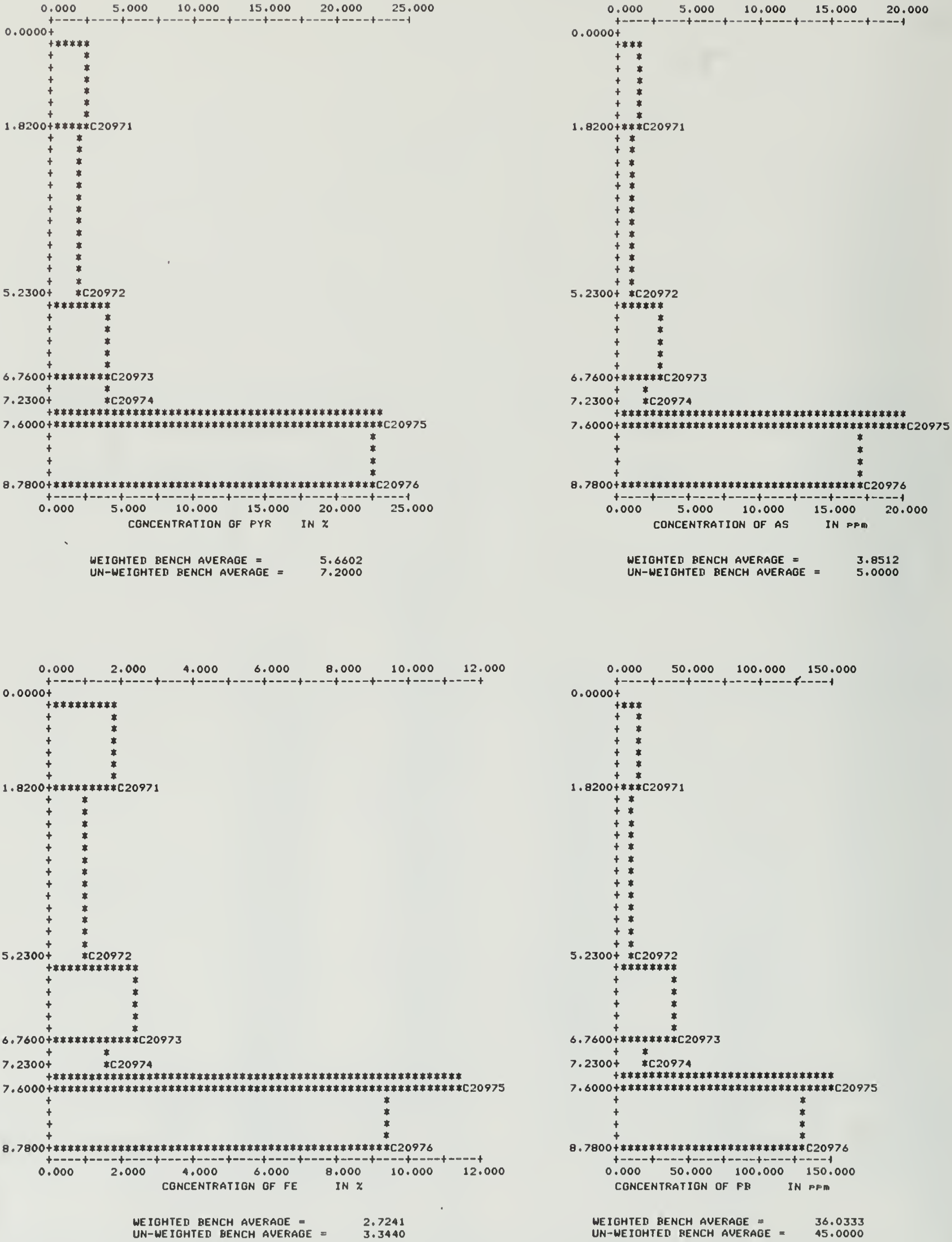


**FIGURE VI-2.** Chemical clusters for each bench set.



```
WEIGHTED BENCH AVERAGE =        5.6602
UN-WEIGHTED BENCH AVERAGE =     7.2000
```

```
WEIGHTED BENCH AVERAGE =        3.8512
UN-WEIGHTED BENCH AVERAGE =     5.0000
```

```
WEIGHTED BENCH AVERAGE =        2.7241
UN-WEIGHTED BENCH AVERAGE =     3.3440
```

```
WEIGHTED BENCH AVERAGE =        36.0333
UN-WEIGHTED BENCH AVERAGE =     45.0000
```

**FIGURE VI-3.** Bench set profiles for pyrite, Fe, As, and Pb from bench set B7.

### Bench set B7

This bench set is relatively high in calcite (particularly benches 2, 3, and 4) and especially high in pyrite. All but the top bed are high in pyrite, and the bottom bed has the highest observed pyrite value of all the bench sets (22.3%). Cluster analysis showed that this bench set had the greatest number of pyrite/element associations of the four bench sets. Bench set profiles for pyrite, Fe, As, and Pb are shown in figure VI-3.

### Bench set B8

This bench is similar to bench set B6 in that it is fairly low in overall mineral matter, but it does have the highest clay content of the four bench sets. Elements found in high concentrations in this set include: Al*, Ba, Ce, Cs*, Dy, F, K*, La, Mo, Rb*, Sc, Si*, Sm*, Th*, Zn, Zr*, most of which are lithophile in nature. (Elements with an asterisk, along with quartz and clay, show a similar pattern of behavior.) Bench set profiles for clay, Si, Al, and Th are shown in figure VI-4.

### Bench set B9

Many of the common mineral element associations can be found in this set because of its high mineral matter content. Of special interest in this set is the exceptionally high calcite content of the top bed (unit VI). The clustering procedure groups calcite with the elements Ca, Mg, Sr, Ba, Ag, and B. The high concentration of Ca and Sr, along with the slightly higher concentration of B in this set (table IV-2) offer supportive evidence that these beds had been exposed to percolating sea water. Bench set profiles for calcite, Ca, Mn, and Sr are shown in figure VI-5.

### Stratigraphic vs chemical correlation

The important trends of the chemical and mineral data related to the bench units are as follows:

Unit I (fig. VI-1) is generally low in mineral components and high in volatile matter and moisture. The only constituents found in high concentrations in this unit are B, Ba, Be, Sb, and Tl; even these elements are variable among the three bench sets containing this unit.

Unit II (fig. VI-1) is characterized by a high calcite content. The concentrations of Ca, Mn, and Sr are also high, especially in bench sets B7 and B9. Although the concentrations of As, B, Ba, Ce, and Mg are not especially high in this unit, they tend to correlate well with the calcite/Ca/Mn/Sr concentrations.

Unit III is characterized by a high clay content and correspondingly high concentrations of Al, Cs, Dy, Eu, Hf, K, Lu, Mg, Na, Rb, Sc, Si, Sm, Ta, Ti, and Zr; these elements are all lithophile in nature.

Unit IV, which overlies the shale bench (unit V—not discussed here), is undistinguished with respect to mineral/chemical associations, being neither high nor low in most constituents. Of the elements with relatively high

```
     0.000     20.000    40.000
      +----+----+----+----+----+
0.0000+
      +***
      +  *
 .6500+***C20977
      +  *
      +  *
      +  *
      +  *
      +  *
      +  *
      +  *
      +  *
      +  *
      +  *
      +  *
      +  *
      +  *
      +  *
4.1500+  *C20978
      +******
      +     *
      +     *
      +     *
      +     *
5.4600+******C20979
      +   *
5.9400+   *C20980
6.1700+*********************C20981
      +  *
      +  *
      +  *
      +  *
      +  *
7.4600+***C20982
      +----+----+----+----+----+
     0.000     20.000    40.000
     CONCENTRATION OF CLAY   IN %

WEIGHTED BENCH AVERAGE =        8.0459
UN-WEIGHTED BENCH AVERAGE =     8.7600
```

```
     0.000     5.000    10.000    15.000    20.000
      +----+----+----+----+----+----+----+----+
0.0000+
      +*****
      +    *
 .6500+*****C20977
      +  *
      +  *
      +  *
      +  *
      +  *
      +  *
      +  *
      +  *
      +  *
      +  *
      +  *
      +  *
      +  *
      +  *
4.1500+  *C20978
      +**********
      +         *
      +         *
      +         *
      +         *
5.4600+**********C20979
      +     *
5.9400+     *C20980
6.1700+***********************************C20981
      +   *
      +   *
      +   *
      +   *
      +   *
7.4600+****C20982
      +----+----+----+----+----+----+----+----+
     0.000     5.000    10.000    15.000    20.000
             CONCENTRATION OF SI      IN %

        WEIGHTED BENCH AVERAGE =        2.6984
        UN-WEIGHTED BENCH AVERAGE =     3.0240
```

```
     0.000     2.000     4.000     6.000     8.000
      +----+----+----+----+----+----+----+----+
0.0000+
      +*****
      +    *
 .6500+*****C20977
      +   *
      +   *
      +   *
      +   *
      +   *
      +   *
      +   *
      +   *
      +   *
      +   *
      +   *
      +   *
      +   *
      +   *
4.1500+   *C20978
      +**********
      +         *
      +         *
      +         *
      +         *
5.4600+**********C20979
      +      *
5.9400+      *C20980
6.1700+************************************C20981
      +    *
      +    *
      +    *
      +    *
      +    *
7.4600+*****C20982
      +----+----+----+----+----+----+----+----+
     0.000     2.000     4.000     6.000     8.000
            CONCENTRATION OF AL     IN %

       WEIGHTED BENCH AVERAGE =        1.2445
       UN-WEIGHTED BENCH AVERAGE =     1.3460
```

```
     0.000     5.000    10.000    15.000
      +----+----+----+----+----+----+
0.0000+
      +***
      +  *
 .6500+***C20977
      + *
      + *
      + *
      + *
      + *
      + *
      + *
      + *
      + *
      + *
      + *
      + *
      + *
      + *
4.1500+ *C20978
      +******
      +     *
      +     *
      +     *
      +     *
5.4600+******C20979
      +   *
5.9400+   *C20980
6.1700+**************************C20981
      +   *
      +   *
      +   *
      +   *
      +   *
7.4600+****C20982
      +----+----+----+----+----+----+
     0.000     5.000    10.000    15.000
      CONCENTRATION OF TH     IN ppm

   WEIGHTED BENCH AVERAGE =        1.9674
   UN-WEIGHTED BENCH AVERAGE =     2.1600
```

**FIGURE VI-4.** Bench set profiles for clay, Si, Al, and Th from bench set B8.

concentrations (Br, Ga, Hg, Tb, and V), all but Tb are commonly associated with the organic matter.

Unit VI (except for bench set 6) is high in quartz, pyrite, and ash; the pyrite content appears to have the greatest influence on the chemistry. The highest concentrations (in all the bench sets) of Ag, As, Ce, Co, Cr, Cu, Fe, La, Li, Mo, Ni, Pb, Se, Th, Yb, and Zn are found in this unit. Of these elements, most are chalcophile with the exception of Ce, Cr, La, Li, and Yb, which are lithophile in character and reflect the above average clay content of this unit.

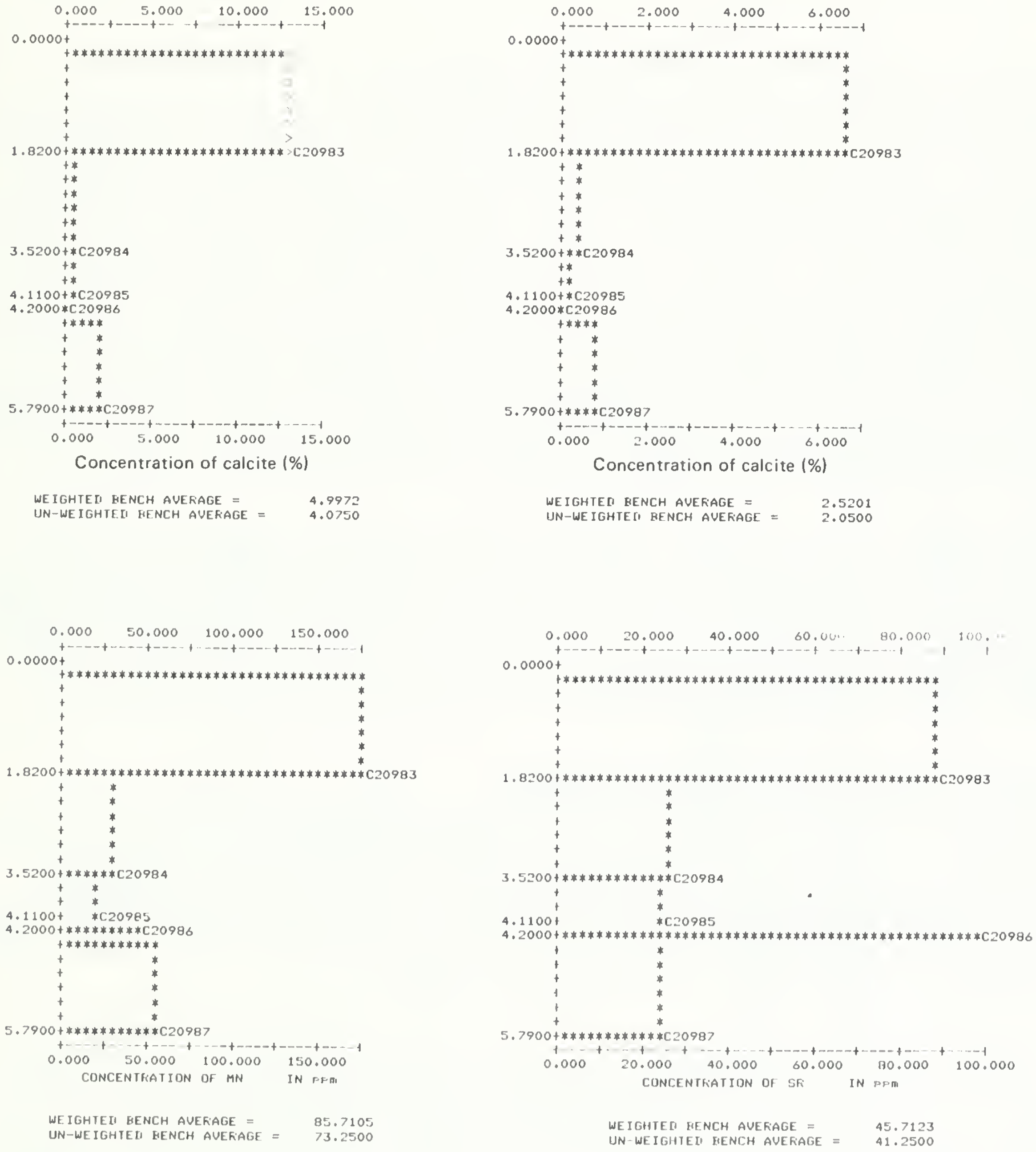


FIGURE VI-5. Bench set profiles for calcite, Ca, Mn, and Sr in bench set B9.

Although the trends we have noted here generally hold for the four bench sets considered collectively, there are usually exceptions within any one coal unit. Since the mineral content in each of the four bench sets differs somewhat, and since the mineral content appears to be the controlling factor in the chemical content of the benches, then chemical similarity among the bench sets should not occur frequently. Strong chemical correlations among individual benches based on chemical similarities in composition cannot be found. In contrast, there is good stratigraphic correlation of individual benches across the four bench sets on the basis of physical characteristics (figure IV-4). The exceptions to this are Co, Cu, Lu, and Ni, in which the chemical pattern is similar for the four bench sets (e.g., fig. VI-6 for Ni). These four elements are often not strongly associated with inorganic minerals.

## CHEMICAL VARIATION OF WHOLE-COAL SAMPLES OF THE HERRIN COAL

Chemical analyses data on whole-coal samples (MMC80) taken for this study from widely scattered localities within the Herrin are given in tables VI-4 and VI-5. The chemical variation of these results is evaluated in terms of the arithmetic mean, standard deviation, and the maximum of the analytical results of the various elements found in the samples. However, statistical evaluation for ten elements is somewhat indefinite because part of the results on these elements are upper-limit values (table VI-5). Three alternative methods can be used to compute the mean (and standard deviation): (1) ignore the samples when the element has a less-than value; (2) set the less-than values equal to the given value; (3) set the less-than values equal to zero. Method 1 yields a high mean for elements with many less-than values. Method 2 yields a value that is somewhat *high* although close to the true mean. Method 3 yields a value that is probably too *low*. The true mean lies between the results of methods 2 (*high*) and 3 (*low*).

The statistics for the trace elements in all whole-coal samples from the Herrin Coal (C499 and MMC80 sample sets) were computed using methods 2 and 3; the results are given in table VI-6. The low and high statistical values are the same for elements having no less-than values (or an insignificantly few number of samples), and only one is reported (table VI-6). The differences between the high and low means are important only for iodine (I), indium (In), and phosphorous (P).

### Chemical variation of the Herrin Coal in local areas

Six local areas in the Herrin Coal have been delineated (section IV) for the purpose of studying the variation of chemical properties in a small area. Six elements (S, As, Hg, Pb, Th, and U) have been selected for comparing mean concentrations and standard deviations in local areas (fig. VI-~~7~~ 19, p 81 RAH). The first four of these elements, classified as chalcophile elements, were among 13 metals on the EPA list of priority pollutents.

The sulfur content is lower in L5 than in other local areas. The area L5 is within the low-sulfur coal region close to the south part of the Walshville channel. The mercury content is somewhat higher in L1 than in other areas. The L1 area is located in the northwest part of the basin where the coal has been strongly affected by mineralizing solutions. The variation of arsenic among local areas is similar to that of mercury, but the average As content

FIGURE VI-6. Bench set profiles for nickel (all bench sets).

**TABLE VI-4.** Standard coal analyses of local area and regional whole coal samples, dry basis.

| SAMPLE | PURPOSE-CODE | THKN (FT.) | MOIS ( % ) | VOL ( % ) | FIXC ( % ) | ASH ( % ) | H ( % ) | C ( % ) | N ( % ) | O ( % ) | TOTS ( % ) | ORGS ( % ) | SUS ( % ) | PYRS ( % ) | TCL ( % ) | BTU (BTU/LB) | LB SO2/ MBTU |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HERRIN COAL | | | | | | | | | | | | | | | | | |
| C20154 | R | 4.30 | 2.50 | 35.70 | 49.30 | 15.00 | 4.98 | 69.45 | 1.40 | 8.28 | .85 | .56 | .01 | .29 | .77 | 12350 | 1.37 |
| C20242 | R | 6.00 | 10.30 | 38.50 | 49.70 | 11.80 | 5.26 | 71.40 | 1.33 | 8.52 | 1.68 | .60 | .01 | 1.07 | .46 | 12820 | 2.61 |
| C20323 | L 8 | 5.00 | 5.70 | 36.50 | 46.30 | 17.20 | 4.25 | 64.74 | 1.27 | 7.75 | 4.76 | 1.75 | .23 | 2.78 | .18 | 11737 | 8.06 |
| C20613 | R | 5.90 | 8.53 | 40.71 | 46.98 | 12.29 | - | - | - | - | 3.34 | 1.48 | .01 | 1.84 | .40 | 12803 | 5.19 |
| C20620 | RL 1 | 4.46 | 15.00 | - | - | 14.40 | - | - | - | - | 3.13 | 1.57 | .11 | 1.45 | .04 | 12148 | 5.12 |
| C20628 | L 4 | 5.00 | 10.36 | 36.76 | 49.84 | 13.39 | 4.73 | 67.12 | 1.31 | 9.56 | 3.86 | 1.60 | .08 | 2.17 | .04 | 12057 | 6.36 |
| C20635 | R | 6.33 | 8.13 | 38.57 | 48.78 | 12.63 | 4.85 | 68.11 | 1.34 | 9.11 | 3.94 | 1.84 | .07 | 2.01 | .04 | 12309 | 6.36 |
| C20636 | L 4 | 6.06 | 9.56 | 38.12 | 48.68 | 13.18 | 4.88 | 67.93 | 1.24 | 8.99 | 3.75 | 1.50 | .01 | 2.23 | .03 | 12275 | 6.07 |
| C20641 | L 5 | 7.43 | 7.98 | 35.47 | 54.25 | 10.27 | 5.02 | 73.21 | 1.70 | 8.73 | 1.04 | .50 | - | .53 | .47 | 12955 | 1.60 |
| C20642 | L 5 | 7.41 | 8.01 | 36.46 | 54.90 | 8.62 | 5.03 | 74.02 | 1.69 | 9.20 | 1.41 | .57 | - | .83 | .45 | 13220 | 2.12 |
| C20654 | R | 5.30 | 9.02 | 37.12 | 48.30 | 14.56 | 4.80 | 67.02 | 1.31 | 8.56 | 3.72 | 1.72 | .08 | 1.91 | .14 | 11944 | 6.19 |
| C20658 | R | 6.45 | 9.43 | 32.35 | 54.18 | 13.45 | 4.60 | 70.60 | 1.59 | 8.97 | .76 | .57 | .01 | .17 | .02 | 12468 | 1.21 |
| C20678 | R | 2.50 | 7.02 | 29.98 | 47.85 | 22.15 | - | - | - | - | 3.14 | .73 | .05 | 2.35 | - | - | - |
| C20759 | R | 5.46 | 11.04 | 38.12 | 47.87 | 14.00 | 4.72 | 67.52 | 1.24 | 8.37 | 4.11 | 2.12 | .07 | 1.91 | .71 | 12128 | 6.74 |
| C21164 | RL 7 | 5.59 | 4.90 | 36.69 | 48.59 | 14.71 | 4.73 | 66.09 | 1.14 | 9.41 | 3.90 | .95 | .39 | 2.54 | .17 | - | - |
| C21166 | L 7 | 4.50 | 5.09 | 37.30 | 47.75 | 14.94 | 4.76 | 66.86 | 1.27 | 9.38 | 2.78 | 1.21 | .41 | 1.14 | .17 | - | - |
| C21168 | L 7 | 5.80 | 5.90 | 34.75 | 50.04 | 15.20 | 4.60 | 67.43 | 1.18 | 9.14 | 2.42 | 1.18 | .27 | .95 | .26 | - | - |
| C21170 | L 7 | 5.00 | 5.19 | 36.49 | 48.57 | 14.92 | 4.72 | 65.50 | 1.24 | 9.62 | 3.96 | 1.09 | .56 | 2.31 | .21 | - | - |
| C21172 | L 8 | 5.58 | 6.09 | 36.31 | 49.08 | 14.60 | 4.65 | 67.33 | 1.26 | 8.85 | 3.29 | 1.06 | .26 | 1.95 | .29 | - | - |
| C21174 | RL 8 | 4.58 | 5.90 | 36.98 | 49.57 | 13.44 | 4.66 | 65.85 | 1.30 | 10.98 | 3.74 | 1.25 | .59 | 1.89 | .26 | - | - |
| C21176 | L 8 | 4.55 | 5.90 | 37.08 | 46.40 | 16.50 | 4.59 | 62.61 | 1.19 | 8.37 | 6.70 | 1.16 | .95 | 4.59 | .28 | - | - |
| SPRINGFIELD COAL | | | | | | | | | | | | | | | | | |
| C15140 | R | 5.48 | 9.10 | 43.60 | 46.00 | 10.40 | 5.47 | 71.84 | 1.79 | 7.25 | 3.25 | 2.08 | .01 | 1.16 | .10 | 13049 | 4.95 |
| C20314 | R | 2.55 | 13.10 | 38.70 | 47.50 | 13.80 | 5.13 | 68.48 | 1.34 | 7.10 | 4.18 | 1.17 | .47 | 2.55 | .04 | - | - |
| C20324 | RL 6 | 6.80 | 6.60 | 37.20 | 53.90 | 8.90 | 4.94 | 72.56 | 1.67 | 9.49 | 2.45 | .76 | .15 | 1.54 | .25 | 13119 | 3.71 |
| C20615 | R | 4.94 | 9.34 | 39.36 | 47.91 | 12.71 | - | - | - | - | 4.49 | 2.09 | .03 | 2.36 | .38 | 12491 | 7.15 |
| C20616 | R | 4.30 | 9.37 | 39.79 | 50.28 | 9.91 | - | - | - | - | 3.00 | 1.63 | .01 | 1.35 | .36 | 13033 | 4.58 |
| C20631 | L 3 | 3.19 | 8.95 | 37.18 | 50.71 | 12.09 | 4.73 | 68.51 | 1.30 | 8.81 | 4.53 | 1.91 | .10 | 2.51 | .01 | 12325 | 7.31 |
| C20637 | L 3 | 4.46 | 9.80 | 38.92 | 51.07 | 9.99 | 4.91 | 70.25 | 1.21 | 9.66 | 3.94 | 1.78 | .04 | 2.11 | .02 | 12719 | 6.16 |
| C20679 | R | 4.40 | 7.82 | 39.57 | 49.60 | 10.81 | 5.03 | 71.93 | 1.39 | 6.84 | 3.96 | 1.92 | .03 | 2.01 | .56 | 13077 | 6.02 |
| C20705 | R | 5.10 | 10.24 | 37.01 | 40.07 | 22.91 | 4.62 | 60.91 | 1.12 | 6.86 | 3.55 | 1.87 | .04 | 1.64 | .01 | 11021 | 6.40 |
| C20709 | L 7 | 7.41 | 13.15 | 40.08 | 50.31 | 9.59 | 5.11 | 73.43 | 1.62 | 8.53 | 1.68 | .67 | .01 | .99 | - | 13170 | 2.54 |
| C20760 | R | 4.75 | 10.98 | 40.51 | 47.32 | 12.16 | 4.92 | 69.37 | 1.31 | 8.64 | 3.58 | 1.81 | .06 | 1.69 | .61 | 12559 | 5.67 |
| C21067 | L 5 | 6.50 | 10.30 | 34.70 | 56.40 | 8.90 | 4.92 | 74.87 | 1.51 | 8.84 | 1.21 | .38 | .03 | .81 | .56 | 13103 | 1.84 |
| C21165 | RL 5 | 6.53 | 4.00 | 39.06 | 50.62 | 10.31 | 5.05 | 70.43 | 1.24 | 9.31 | 3.63 | 1.14 | .29 | 2.18 | .17 | - | - |
| C21167 | L 5 | 7.00 | 6.30 | 32.23 | 53.05 | 14.71 | 4.74 | 68.91 | 1.41 | 9.23 | .97 | .58 | .11 | .26 | .30 | - | - |
| C21169 | L 5 | 4.09 | 3.09 | 36.01 | 42.88 | 21.09 | 4.25 | 59.11 | 1.02 | 6.09 | 8.42 | .81 | .89 | 6.70 | .22 | - | - |
| C21171 | L 5 | 4.50 | 6.50 | 36.36 | 54.16 | 9.47 | 4.86 | 72.52 | 1.58 | 9.42 | 2.12 | .82 | .35 | .95 | .28 | - | - |
| C21173 | L 6 | 8.64 | 4.30 | 38.55 | 46.91 | 14.52 | 4.77 | 65.45 | 1.19 | 7.99 | 6.06 | 1.59 | .47 | 3.99 | .24 | - | - |
| C21175 | L 6 | 6.03 | 5.30 | 38.75 | 48.55 | 12.69 | 4.83 | 67.94 | 1.34 | 9.64 | 3.53 | 1.28 | .54 | 1.71 | .25 | - | - |
| C21177 | L 6 | 5.15 | 5.50 | 37.98 | 50.52 | 11.48 | 4.65 | 70.10 | 1.42 | 8.28 | 4.04 | 1.42 | .54 | 2.07 | .32 | - | - |

- NOT DETERMINED

TABLE VI-5. Minor and trace element analyses of local area and regional whole coal samples, dry basis.

| SAMPLE | PURPOSE-CODE | AG (PPB) | AL ( % ) | AS (PPM) | B (PPM) | BA (PPM) | BE (PPM) | BR (PPM) | CA ( % ) | CD (PPM) | CE (PPM) | CO (PPM) | CR (PPM) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HERRIN COAL | | | | | | | | | | | | | |
| C20154 | R | 102. | 2.37 | <2. | 94. | 56. | 1.7 | 33. | 1.71 | .3 | 22. | 10. | 26. |
| C20242 | R | 67. | 1.51 | 12. | 120. | 61. | 1.9 | 14. | .15 | <.1 | 30. | 6.2 | 26. |
| C20323 | L 8 | 102. | 1.92 | 4. | 109. | 52. | .94 | 10. | .61 | <1.1 | 25. | 7.6 | 33. |
| C20613 | R | 90. | .77 | 3.5 | 114. | 73. | .81 | 13. | 1.11 | <.2 | 10. | 4.9 | 15. |
| C20620 | RL 1 | 87. | 1.40 | 9. | 118. | 45. | 1.4 | 4. | .86 | 2.5 | 13. | 6.0 | 25. |
| C20628 | L 4 | 67. | 1.08 | 3.0 | 160. | 45. | 1.5 | 1. | .76 | .9 | 17. | 6. | 21. |
| C20635 | R | 69. | 1.02 | 4.0 | 160. | 39. | 1.4 | 2. | .55 | 1.2 | 12. | 3.8 | 17. |
| C20636 | L 4 | 79. | .98 | 3.5 | 170. | 32. | 1.16 | 9.5 | .40 | <.2 | 13. | 4.0 | 27. |
| C20641 | L 5 | 75. | .91 | 15. | 108. | 27. | 1.4 | 18. | .48 | <.2 | 17. | 7.1 | 15. |
| C20642 | L 5 | 103. | .83 | 48. | 111. | 30. | 1.4 | 18. | .27 | <.2 | 14. | 7. | 12. |
| C20654 | R | 79. | 1.24 | 5.3 | 150. | 49. | 1.2 | 6.0 | .77 | <.3 | 14. | 3.9 | 19. |
| C20658 | R | 63. | 1.82 | 1.7 | 89. | 64. | 1.3 | 1.8 | .05 | .7 | 22. | 6.5 | 23. |
| C20678 | R | 180. | 2.41 | 151. | 76. | 113. | 1.7 | 19. | .65 | <.3 | 57. | 18. | 29. |
| C20759 | R | 89. | 1.32 | 3.2 | 140. | 41. | 1.7 | 24. | .27 | <.2 | 22. | 5.2 | 22. |
| C21164 | RL 7 | <36. | 1.47 | 3.4 | 111. | 104. | 1.18 | 189. | .62 | .8 | 15. | 3.4 | 23. |
| C21166 | L 7 | 71. | 1.57 | 3.4 | 111. | 102. | 2.4 | 232. | .78 | <.2 | 19. | 4. | 18. |
| C21168 | L 7 | 89. | 1.70 | 2. | 102. | 50. | 1.18 | 319. | .76 | <.2 | 17. | 4.5 | 21. |
| C21170 | L 7 | 77. | 1.60 | 3.6 | 87. | 50. | .9 | 185. | .41 | <.2 | 18. | 5.6 | 19. |
| C21172 | L 8 | 75. | 1.50 | 3.8 | 100. | 44. | .87 | 288. | .55 | <.2 | 17. | 4.4 | 19. |
| C21174 | RL 8 | 77. | 1.48 | 5.0 | 83. | 47. | 2.8 | 244. | .07 | <.2 | 17. | 5.6 | 19. |
| C21176 | L 8 | 79. | 1.22 | 5.4 | 103. | 52. | 1.08 | 159. | .26 | <.2 | 16. | 7.9 | 15. |
| SPRINGFIELD COAL | | | | | | | | | | | | | |
| C15140 | R | 58. | .98 | 4.0 | 120. | 35. | 1.9 | <.2 | .33 | <.1 | 14. | 4.8 | 13. |
| C20314 | R | 68. | 1.42 | 7.1 | 120. | 49. | 2.8 | 1.5 | .23 | <.2 | 40. | 7.1 | 22. |
| C20324 | RL 6 | 63. | 1.17 | 15. | 104. | 39. | 1.04 | 16. | .20 | <.8 | 12. | 5.5 | 15. |
| C20615 | R | 130. | 1.00 | 6.0 | 109. | 47. | 1.17 | 13. | .36 | <.2 | 13. | 4.6 | 28. |
| C20616 | R | - | .91 | 3. | - | 42. | - | 13. | .38 | - | 12. | 3.0 | 10.4 |
| C20631 | L 3 | 84. | 1.04 | 9.1 | 160. | 40. | .91 | 1.9 | .55 | .3 | 16. | 5.7 | 13. |
| C20637 | L 3 | 58. | .84 | 1.7 | 150. | 28. | 1.8 | 1.6 | .28 | 1.8 | 8. | 2.7 | 12. |
| C20679 | R | 58. | .64 | 6.5 | 81. | 24. | 1.2 | 16. | .74 | <.1 | 7. | 1.8 | 9. |
| C20705 | R | 160. | 2.69 | 6. | 140. | 136. | 3.2 | 1.8 | .10 | .9 | 51. | 6.0 | 41. |
| C20709 | L 7 | 68. | 1.21 | 29. | 117. | 65. | 2.4 | 1.8 | .26 | <.1 | 35. | 5.3 | 17. |
| C20760 | R | 120. | 1.04 | 3.6 | 140. | 1671. | 2.5 | 22. | .09 | 30.5 | 11. | 3.2 | 20. |
| C21067 | L 5 | - | .87 | 43. | - | 46. | - | 32. | .50 | - | 15. | 4.1 | 9.4 |
| C21165 | RL 5 | 49. | .77 | 18. | 95. | 86. | 0.6 | 326. | .36 | <.2 | 7. | 2.3 | 8. |
| C21167 | L 5 | 98. | 2.21 | 12. | 88. | 91. | 1.01 | 336. | .24 | <.2 | 21. | 5.1 | 19. |
| C21169 | L 5 | 130. | 1.15 | 24. | 63. | 94. | .75 | 341. | .85 | 2.0 | 19. | 9. | 20. |
| C21171 | L 5 | 56. | .97 | 21. | 82. | 200. | 1.2 | 231. | .35 | 3.0 | 13. | 4.9 | 11. |
| C21173 | L 6 | 64. | 1.08 | 13. | 85. | 79. | 1.3 | 209. | .59 | <.2 | 22. | 3. | 13. |
| C21175 | L 6 | 45. | .98 | 8.2 | 81. | 712. | .93 | 180. | .47 | <.2 | 13. | 3.5 | 11. |
| C21177 | L 6 | 73. | .87 | 37. | 85. | 2666. | .89 | 116. | .73 | <.2 | 10. | 5.0 | 11. |

262.2
19
=14.06

TABLE VI-5. Minor and trace element analyses of local area and regional whole coal samples. *(continued)*

| SAMPLE | CS (PPM) | CU (PPM) | DY (PPM) | EU (PPM) | F (PPM) | FE ( % ) | GA (PPM) | GE (PPM) | HF (PPM) | HG (PPM) | I (PPM) | IN (PPB) | K ( % ) | LA (PPM) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HERRIN COAL | | | | | | | | | | | | | | |
| C20154 | 1.5 | 12.3 | 1.4 | .33 | 55. | .66 | 5.5 | 6.5 | .5 | .08 | 1.2 | <72. | .32 | 12. |
| C20242 | 1.8 | 22.4 | 2.0 | .6 | 80. | 1.15 | 4.9 | 7.1 | .8 | .11 | 1.9 | <111. | .29 | 11. |
| C20323 | 1.5 | 12.0 | 1.5 | .40 | 262. | 2.05 | 5.3 | 3.1 | 1.0 | .22 | <.9 | <42. | .21 | 11. |
| C20613 | 1.0 | 6.7 | .9 | .18 | 60. | 1.77 | 2.6 | 3.8 | .4 | .21 | 1.2 | 22. | .13 | 4.9 |
| C20620 | 1.3 | 12.8 | .9 | .2 | 52. | 1.66 | 5.2 | 8. | .8 | .23 | 2.7 | <6. | .22 | 6.8 |
| C20628 | 1.7 | 10.2 | 1.2 | .36 | 68. | 2.13 | 4.0 | 2.1 | .8 | .07 | <.6 | 33. | .18 | 8.4 |
| C20635 | 1.4 | 8.5 | 1.3 | .27 | 83. | 2.09 | 3.5 | 3.3 | .4 | .09 | 1.3 | 26. | .18 | 6.0 |
| C20636 | 1.3 | 9.1 | 1.2 | .29 | 75. | 1.74 | 3.4 | 2. | .4 | .09 | <.6 | <77. | .18 | 7. |
| C20641 | 1.2 | 8.9 | 1.3 | .32 | 82. | .86 | 3.8 | 5.9 | .7 | .07 | 2. | 54. | .12 | 10.1 |
| C20642 | .9 | 10.1 | 1.0 | .26 | 53. | .70 | 3.4 | 9.6 | .4 | .06 | 2.0 | 22. | .12 | 7.3 |
| C20654 | 1.4 | 10.8 | 1.3 | .32 | 53. | 1.91 | 4.5 | 3.1 | .6 | .07 | 2.1 | 11. | .20 | 7.1 |
| C20658 | 2. | 18.3 | 1.6 | .47 | 77. | .35 | 5.9 | 1.8 | .8 | .03 | 1.8 | 22. | .36 | 3.8 |
| C20678 | 2. | 31.6 | 2.9 | .83 | 90. | 2.37 | 6.9 | 9.6 | 1.4 | .13 | <1.6 | <65. | .27 | 30. |
| C20759 | 1.5 | 14.8 | 1.5 | .5 | 64. | 1.84 | 3.8 | 3.7 | .8 | .71 | 1.4 | <22. | .20 | 10. |
| C21164 | 1.5 | 9.6 | 1.0 | .25 | 57. | 2.82 | 3.8 | 1.9 | .6 | .08 | - | 8. | .17 | 6. |
| C21166 | 1.9 | 10.5 | 1. | .33 | 130. | 1.55 | 5. | 3.5 | .7 | .08 | - | <11. | .23 | 11. |
| C21168 | 1.4 | 10.9 | 1.0 | .37 | 110. | 1.28 | 4.5 | 3.2 | .7 | .09 | - | <11. | .23 | 7. |
| C21170 | 1.6 | 10.6 | 1.3 | .3 | 134. | 2.82 | 5.7 | 2.2 | .7 | .07 | - | <105. | .24 | 9. |
| C21172 | 1.5 | 10.6 | .5 | .2 | 60. | 2.14 | 3.7 | 2.2 | .6 | .09 | - | <107. | .19 | 7. |
| C21174 | 1.6 | 12.0 | 1.2 | .3 | 71. | 2.52 | 3.8 | 3.8 | .7 | .06 | - | <106. | .22 | 10. |
| C21176 | 1.4 | 12.5 | 1. | .3 | 36. | 5.24 | 3.1 | 3.1 | .5 | .17 | - | <21. | .16 | 10. |
| SPRINGFIELD COAL | | | | | | | | | | | | | | |
| C15140 | 1.0 | 6.6 | 1. | .32 | 56. | 1.12 | 1.8 | 5.9 | .5 | .08 | <1. | <22. | .17 | 5. |
| C20314 | 2.0 | 24.9 | 4.1 | 1. | 73. | 2.70 | 5.2 | 12. | .8 | .49 | 2. | 23. | .24 | 20. |
| C20324 | .8 | 8.0 | .8 | .20 | 61. | 1.84 | 3.8 | 5.7 | .6 | .16 | 1.6 | <64. | .21 | 6. |
| C20615 | 1.3 | 11.4 | 1.3 | .31 | 80. | 2.35 | 3.5 | 2.9 | .6 | .11 | 1.4 | 66. | .15 | 7.0 |
| C20616 | .9 | - | .8 | .20 | - | 1.26 | 2.7 | - | .4 | - | - | <132. | .15 | 6. |
| C20631 | 1. | 8.5 | 1.7 | .37 | 49. | 1.95 | 4.1 | 2.3 | .4 | .10 | 2.0 | <22. | .06 | 9. |
| C20637 | 1.0 | 6.7 | 1.0 | .22 | 52. | 1.96 | 3.0 | 2.3 | .4 | .06 | 1.0 | 33. | .14 | 4.1 |
| C20679 | .9 | 5.0 | .8 | .16 | 40. | 1.81 | 2.0 | 7.9 | .3 | .09 | <1.6 | <22. | .09 | 4. |
| C20705 | 3.8 | 66.5 | 3.6 | 1.00 | 114. | 1.79 | 8.5 | 5. | 1.3 | .13 | .7 | <33. | .64 | 23. |
| C20709 | 1. | 38.8 | 2.9 | .96 | 112. | .97 | 3.7 | 3.2 | .6 | .07 | 3.2 | <23. | .20 | 16. |
| C20760 | 1. | 7.7 | .9 | .22 | 54. | 1.60 | 5.2 | 12. | .7 | .42 | 1.9 | 79. | .19 | 5.5 |
| C21067 | 1.1 | - | - | .26 | - | .72 | 2.9 | - | .3 | - | - | - | .15 | 8. |
| C21165 | .7 | 7.1 | .6 | .16 | 40. | 2.27 | 2.3 | 2.2 | .3 | .07 | - | 4. | .13 | 4. |
| C21167 | 1.7 | 19.5 | 1.2 | .35 | 103. | .69 | 5.6 | 2.8 | .8 | .05 | - | <21. | .49 | 12. |
| C21169 | 1.2 | 11.7 | 1. | .29 | 102. | 6.83 | 4.0 | 2.1 | .6 | .42 | - | <52. | .22 | 8. |
| C21171 | .9 | 6.2 | 1.2 | .23 | 38. | 1.32 | 2.9 | 7.6 | .4 | .10 | - | <214. | .15 | 9. |
| C21173 | 1. | 16.7 | 1.8 | .49 | 77. | 4.06 | 3.7 | 1.3 | .4 | .12 | - | <209. | .21 | 9. |
| C21175 | 1.2 | 7.5 | .5 | .2 | 15. | 2.19 | 2.8 | 5.6 | .5 | .06 | - | <32. | .18 | 5. |
| C21177 | .7 | 6.5 | .7 | .21 | 41. | 2.42 | 2.8 | 5.8 | .5 | .15 | - | 12. | .12 | 5. |

TABLE VI-5. Minor and trace element analyses of local area and regional whole coal samples. (*continued*)

| SAMPLE | LI (PPM) | LU (PPM) | MG ( % ) | MN (PPM) | MO (PPM) | NA (PPM) | NI (PPM) | P (PPM) | PB (PPM) | RB (PPM) | SB (PPM) | SC (PPM) | SE (PPM) | SI ( % ) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HERRIN COAL | | | | | | | | | | | | | | |
| C20154 | 32.8 | .12 | .10 | 195. | <3.1 | 4082. | 28. | 250. | 154. | 22. | 3. | 4.2 | 2.2 | 4.97 |
| C20242 | 39.7 | .2 | .07 | 36. | 4.9 | 2007. | 13. | <100. | 31. | 25. | 1.2 | 5.2 | 4.7 | 2.56 |
| C20323 | 12.0 | .16 | .05 | 35. | 14. | 880. | 18. | 1400. | 44. | 29. | .4 | 3.9 | 5.6 | 4.02 |
| C20613 | 4.5 | .1 | .04 | 153. | 7. | 1967. | 9. | <100. | 16. | 17. | 1.4 | 2.1 | 2.4 | 2.03 |
| C20620 | 19.7 | .12 | .06 | 118. | 8.9 | 541. | 16. | <100. | 67. | 18. | 1.5 | 4.7 | 3.3 | 2.71 |
| C20628 | 14.7 | .09 | .06 | 33. | 9.0 | 424. | 12. | <100. | 18. | 20. | .2 | 3.6 | 2.5 | 2.45 |
| C20635 | 8.2 | .1 | .06 | 65. | 10. | 174. | 9. | <100. | 38. | 15. | 1.3 | 2.6 | 3.5 | 2.37 |
| C20636 | 10.3 | .14 | .04 | 53. | 15. | 509. | 9. | <100. | 13. | 15. | 1.6 | 2.9 | 4.5 | 2.29 |
| C20641 | 19.7 | .12 | .03 | 53. | 2.7 | 1489. | 18. | <100. | 25. | 16. | 1.6 | 3.0 | 2. | 1.67 |
| C20642 | 15.7 | .10 | .03 | 24. | 3.6 | 978. | 18. | <100. | 35. | 12. | 2.9 | 2.8 | 1.9 | 1.59 |
| C20654 | 16.4 | .17 | .07 | 88. | 7.7 | 802. | 10. | <100. | 32. | 15. | 1.0 | 2.9 | 2.4 | 2.88 |
| C20658 | 39.7 | .16 | .07 | 12. | 3.7 | 199. | 22. | <100. | 15. | 28. | 1.0 | 4.8 | 2.0 | 3.68 |
| C20678 | 85.6 | .4 | .11 | 97. | 13. | 2721. | 46. | 800. | 77. | 24. | 3.8 | 6.2 | 4.1 | 4.63 |
| C20759 | 16.1 | .13 | .07 | 47. | 9.5 | 3865. | 36. | <100. | 16. | 16. | .7 | 3.6 | 4.8 | 3.04 |
| C21164 | 17.4 | .11 | .03 | 57. | 12. | 568. | 9. | <100. | 33. | 15. | .4 | 2.8 | 1.9 | 2.81 |
| C21166 | 13.6 | .14 | .03 | 42. | 4.7 | 653. | 12. | <100. | 25. | 19. | .7 | 3.3 | 1.6 | 3.32 |
| C21168 | 16.3 | .14 | <.01 | 78. | 10.6 | 691. | 11. | <100. | 16. | 18. | .4 | 3.4 | 2.3 | 3.46 |
| C21170 | 13.6 | .14 | .04 | 31. | 18. | 696. | 16. | 400. | 58. | 17. | .2 | 3.0 | 2.2 | 3.00 |
| C21172 | 17.0 | .15 | .03 | 52. | 11.1 | 809. | 10. | <100. | 15. | 19. | .2 | 2.9 | 1.6 | 2.80 |
| C21174 | 14.2 | .13 | .04 | 16. | 11.4 | 818. | 12. | <100. | 15. | 18. | .2 | 3.1 | 2.4 | 2.82 |
| C21176 | 14.9 | .15 | <.01 | 36. | 20. | 818. | 21. | <100. | 36. | 15. | .4 | 2.6 | 2.1 | 2.53 |
| SPRINGFIELD COAL | | | | | | | | | | | | | | |
| C15140 | 7.3 | .1 | .03 | 44. | 6.5 | 737. | 5. | <100. | 7. | 18. | 1.4 | 2.8 | 2.1 | 2.21 |
| C20314 | 33.8 | .4 | .06 | 33. | 13. | 621. | 21. | 100. | 13. | 24. | .5 | 6.3 | 2.4 | 2.28 |
| C20324 | 8.7 | .08 | .05 | 25. | 6.8 | 664. | 21. | 200. | 47. | 14. | 1.3 | 2.9 | 2. | 2.35 |
| C20615 | 10.3 | .1 | .03 | 66. | 9.6 | 2172. | 8. | <100. | 15. | 11. | 1.8 | 2.9 | 6.1 | 2.49 |
| C20616 | - | .08 | .01 | 38. | - | 1634. | - | <100. | - | 9. | .9 | 1.7 | 3.3 | 2.13 |
| C20631 | 9.8 | .15 | .05 | 76. | 9.4 | 407. | 7. | <100. | 21. | 15. | .2 | 2.3 | 2. | 2.33 |
| C20637 | 7.0 | .08 | .04 | 24. | 10.4 | 211. | 6. | <100. | 14. | 16. | .1 | 2.0 | 1.8 | 1.85 |
| C20679 | 5.0 | .07 | .04 | 100. | 6.2 | 2180. | 2. | <100. | 13. | 12. | .3 | 1.6 | 2. | 1.90 |
| C20705 | 17.0 | .37 | .08 | 33. | 18. | 523. | 25. | 100. | 20. | 49. | 2. | 8. | 8.5 | 5.78 |
| C20709 | 15.5 | .20 | .03 | 17. | 6.2 | 161. | 17. | 500. | 21. | 20. | 1.3 | 4.0 | 3.0 | 2.01 |
| C20760 | 5.7 | .15 | .05 | 29. | 6.4 | 3303. | 13. | <100. | 14. | 13. | 1.6 | 3. | 5.2 | 2.83 |
| C21067 | - | .08 | .02 | 38. | - | 1071. | - | 200. | - | 9. | 2.0 | 2.0 | 1.4 | 1.65 |
| C21165 | 5.8 | .05 | .02 | 24. | 8.4 | 427. | 4. | <100. | 18. | 9. | .6 | 1.6 | 1.9 | 2.08 |
| C21167 | 29.2 | .15 | .05 | 41. | <3. | 928. | 16. | <100. | 30. | 25. | 1.2 | 3.6 | 1.8 | 3.84 |
| C21169 | 7.1 | .16 | .01 | 70. | 23. | 578. | 19. | <100. | 138. | 14. | 1.9 | 2.3 | 3.7 | 2.71 |
| C21171 | 11.3 | .14 | .01 | 30. | 4.6 | 599. | 15. | <100. | 31. | 12. | 1.3 | 2.6 | 1.7 | 1.94 |
| C21173 | 10.1 | .16 | .03 | 32. | 16. | 606. | 11. | <100. | 10. | 13. | 1.4 | 2.9 | 2.3 | 1.96 |
| C21175 | 6.0 | .14 | .03 | 40. | 8. | 739. | 5. | <100. | 18. | 17. | 1.0 | 2. | 2.6 | 2.63 |
| C21177 | 6.0 | .20 | <.01 | 52. | 7.2 | 677. | 17. | <100. | 32. | 11. | 1. | 2. | 2. | 1.74 |

TABLE VI-5. Minor and trace element analyses of local area and regional whole coal samples. *(continued)*

| SAMPLE | SM (PPM) | SR (PPM) | TA (PPM) | TB (PPM) | TH (PPM) | TI ( % ) | TL (PPM) | U (PPM) | V (PPM) | W (PPM) | YB (PPM) | ZN (PPM) | ZR (PPM) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HERRIN COAL | | | | | | | | | | | | | |
| C20154 | 1.9 | 85. | .27 | .3 | 2.9 | .13 | <.16 | <2. | 21. | .8 | .7 | 96.0 | 14. |
| C20242 | 2.1 | 74. | .18 | .3 | 3.2 | .08 | .43 | 1. | 24. | .5 | 1.0 | 37.0 | 15. |
| C20323 | 2.7 | 23. | .26 | .2 | 2.8 | .11 | 2.1 | 9.3 | 45. | .6 | .9 | 17.0 | 19. |
| C20613 | 1.6 | 26. | .1 | .2 | 1.5 | .04 | 1.05 | <1. | 24. | <.6 | .4 | 105. | 13. |
| C20620 | 1.1 | 19. | .15 | .4 | 3.3 | .08 | .35 | 1.5 | 18. | .4 | .6 | 527. | 18. |
| C20628 | 1.7 | 26. | .15 | .2 | 2.9 | .06 | 1.4 | .8 | 18. | .3 | .7 | 347. | 12. |
| C20635 | 1.3 | 18. | .08 | .2 | 2.1 | .06 | .92 | 2. | 19. | .3 | .5 | 467. | 12. |
| C20636 | 1.4 | 22. | .13 | .3 | 2. | .06 | 1.09 | 2.4 | 27. | .4 | .6 | 48.5 | 12. |
| C20641 | 1.7 | 35. | .12 | .2 | 2.3 | .05 | .43 | <.5 | 17. | .2 | .5 | 35.7 | 15. |
| C20642 | 1.5 | 35. | .09 | .1 | 1.7 | .05 | .93 | .8 | 16. | .3 | .5 | 26.4 | 14. |
| C20654 | 1.5 | 22. | .1 | .15 | 2.5 | .07 | 1.8 | 1.0 | 17. | .3 | .4 | 101. | 14. |
| C20658 | .9 | 31. | .19 | .2 | 4.0 | .09 | .33 | 1.6 | 29. | .3 | .7 | 354. | 20. |
| C20678 | 4.4 | 236. | .26 | .4 | 6.1 | .14 | <.23 | <1. | 44. | .3 | 1.5 | 151. | 11. |
| C20759 | 2.0 | 42. | .14 | .2 | 2.7 | .08 | .72 | 1. | 14. | <.6 | .8 | 38.1 | 15. |
| C21164 | 1.3 | 20. | .2 | .16 | 2.4 | .09 | .61 | 1.2 | 36. | .5 | .5 | 378. | 19. |
| C21166 | 1.7 | 19. | .2 | .14 | 2.5 | .09 | .9 | 1.2 | 20. | .4 | .7 | 17.4 | 19. |
| C21168 | 1.9 | 19. | .2 | .15 | 2.6 | .09 | .5 | 2.8 | 31. | 1.0 | .7 | 138. | 23. |
| C21170 | 2.0 | 21. | .1 | .16 | 2.4 | .09 | 1.8 | 4.0 | 17. | .6 | .5 | 23.9 | 19. |
| C21172 | 1.2 | 16. | .2 | .19 | 2.3 | .09 | .7 | <1. | 19. | <.8 | .5 | 19.5 | 19. |
| C21174 | 1.7 | 15. | .1 | .19 | 1.8 | .09 | 2.2 | .9 | 21. | <.7 | .6 | 15.2 | 19. |
| C21176 | 1.6 | 14. | .1 | .19 | 1.8 | .07 | 5.5 | .9 | 14. | <.7 | .6 | 34.1 | 14. |
| SPRINGFIELD COAL | | | | | | | | | | | | | |
| C15140 | <2. | 15. | .1 | .14 | 2.1 | .06 | 0.73 | 1. | 17. | <.5 | .5 | 17.4 | 13. |
| C20314 | 6.7 | 24. | .17 | .78 | 5.1 | .07 | 2.7 | <1. | 37. | <.4 | 1.7 | 27.4 | 21. |
| C20324 | 1.0 | 39. | .15 | .15 | 1.5 | .10 | 0.49 | .9 | 1.4 | .4 | .4 | 89.0 | 15. |
| C20615 | 1.5 | 21. | .13 | .3 | 2.1 | .06 | 0.86 | 1.5 | 33. | .4 | .6 | 300. | 15. |
| C20616 | 1.0 | 20. | .13 | .14 | 1.7 | .05 | - | 1.8 | - | .2 | .4 | - | 11. |
| C20631 | 1.8 | 17. | .1 | .2 | 1.8 | .06 | 2.0 | <.6 | 19. | .3 | .7 | 81.0 | 11. |
| C20637 | 1.0 | 16. | .08 | .1 | 1.6 | .05 | .72 | 1.6 | 13. | .3 | .4 | 399. | 12. |
| C20679 | .7 | 24. | .4 | .1 | 1.2 | .03 | 0.36 | <1. | 7.6 | .3 | .4 | 16.6 | 7. |
| C20705 | 5.4 | 39. | .2 | .5 | 7.6 | .13 | 1.4 | .5 | 140. | .5 | 1.9 | 109. | 30. |
| C20709 | 4.0 | 154. | .8 | .5 | 3.9 | .05 | 0.43 | 2.5 | 32. | .2 | 1. | 30.4 | 1. |
| C20760 | .9 | 48. | .15 | .2 | 2.0 | .07 | 0.67 | 1.0 | 39. | <.6 | .5 | 805. | 15. |
| C21067 | 1.2 | 40. | .18 | .16 | 1.7 | .05 | - | <.7 | - | .3 | .3 | - | 11. |
| C21165 | .7 | 14. | .1 | .07 | 1.2 | .05 | 1.3 | <1. | 13. | .3 | .2 | 40.4 | 12. |
| C21167 | 1.9 | 63. | .2 | .18 | 3.1 | .10 | .25 | .8 | 28. | .6 | .5 | 146. | 18. |
| C21169 | 1.7 | 19. | .2 | .16 | 2. | .07 | 7.2 | 1.1 | 60. | 1.2 | .4 | 471. | 17. |
| C21171 | 1. | 25. | .1 | .12 | 1.5 | .06 | .51 | <1. | 14. | <1. | .4 | 547. | 16. |
| C21173 | 2.4 | 23. | .1 | .3 | 2.3 | .05 | 2.2 | <2. | 19. | .7 | .6 | 62.6 | 17. |
| C21175 | 1. | 24. | .1 | .15 | 1.3 | .05 | 1.06 | 1.6 | 30. | <1. | .5 | 14.0 | 15. |
| C21177 | 1.0 | 23. | .1 | .14 | 1.2 | .05 | 1.6 | <1. | 10.4 | <1. | .4 | 43.0 | 17. |

TABLE VI-6. Statistical evaluation of chemical elements in whole-coal samples (C499 and MMC80, R and L purpose codes) from the Herrin Coal.

| Element | # Samples | Units | Arithmetic mean* |  | Standard deviation* |  | Maximum | Element | # Samples | Units | Arithmetic mean* |  | Standard deviation* |  | Maximum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | Low | High | Low | High |  |  |  |  | Low | High | Low | High |  |
| Ag | 35 | ppb | 59.7 | 60.7 | 36 | 37. | 180. | Mn | 68 | ppm | 54.4 | - | 39. | - | 195. |
| Al | 68 | % | 1.37 | - | 0.3 | - | 3.04 | Mo | 68 | ppm | 9.3 | - | 5.5 | - | 29. |
| As | 68 | ppm |  | - | 19.0 | - | 151. | Na | 68 | ppm | 828. | - | 770. | - | 4082. |
| B | 59 | ppm | 127.0 | - | 39.3 | - | 225. | Ni | 68 | ppm | 19.8 | - | 8.7 | - | 46. |
| Ba | 52 | ppm | 86. | - | 105. | - | 750. | P | 68 | ppm | 74.8 | 99.1 | 194. | 199. | 1400. |
| Be | 68 | ppm | 1.5 | - | 0.7 | - | 3.9 | Pb | 68 | ppm | 28.1 | - | 35.2 | - | 206. |
| Br | 61 | ppm | 12.8 | - | 7.2 | - | 31. | Rb | 57 | ppm | 17.6 | - | 6.4 | - | 42. |
| Ca | 68 | % | 0.7 | - | 0.4 | - | 2.67 | S | 68 | % | 3.46 | - | 1.26 | - | 6.70 |
| Cd | 15 | ppm | 2.1 | 2.2 | 9.5 | - | 65. | OrgS | 67 | % | 1.57 | - | 0.66 | - | 3.20 |
| Ce | 57 | ppm | 15.4 | - | 7.8 | - | 57. | PyrS | 67 | % | 1.76 | - | 0.80 | - | 4.59 |
| Cl | 63 | % | 0.18 | - | 0.17 | - | 0.77 | Sb | 68 | ppm | 0.91 | - | 0.91 | - | 4.2 |
| Co | 68 | ppm | 6.0 | - | 2.9 | - | 18. | Sc | 57 | ppm | 2.96 | - | 0.88 | - | 6.2 |
| Cr | 68 | ppm | 20.2 | - | 8.6 | - | 60. | Se | 68 | ppm | 2.35 | - | 1.16 | - | 7.7 |
| Cs | 57 | ppm | 1.3 | - | 0.5 | - | 3.6 | Si | 68 | % | 2.72 | - | 0.67 | - | 4.97 |
| Cu | 68 | ppm | 12.8 | - | 4.4 | - | 31.6 | Sm | 57 | ppm | 1.38 | - | 0.67 | - | 4.4 |
| Dy | 57 | ppm | 1.1 | - | 0.37 | - | 2.9 | Sr | 52 | ppm | 36.3 | 36.7 | 35.8 | 36.2 | 236. |
| Eu | 57 | ppm | 0.28 | - | 0.12 | - | 0.83 | Ta | 57 | ppm | 0.16 | - | 0.06 | - | 0.30 |
| F | 68 | ppm | 70.9 | - | 31.8 | - | 262. | Tb | 49 | ppm | 0.19 | - | 0.09 | - | 0.45 |
| Fe | 68 | % | 1.87 | - | 0.74 | - | 5.24 | Th | 57 | ppm | 2.33 | - | 0.79 | - | 6.10 |
| Ga | 68 | ppm | 4.2 | - | 2.3 | - | 18. | Ti | 68 | % | 0.07 | - | 0.02 | - | 0.15 |
| Ge | 68 | ppm | 5.0 | 5.1 | 4.5 | 4.6 | 26. | Tl | 44 | ppm | 0.89 | 0.90 | 0.86 | 0.87 | 5.50 |
| Hf | 57 | ppm | 0.57 | - | 0.2 | - | 1.4 | U | 57 | ppm | 1.50 | 1.62 | 1.37 | 1.45 | 9.3 |
| Hg | 68 | ppm | 0.16 | - | 0.11 | - | 0.71 | V | 68 | ppm | 29.3 | - | 10.1 | - | 55.0 |
| I | 45 | ppm | 1.35 | 1.54 | 0.84 | 1.04 | 3.5 | W | 57 | ppm | 0.53 | 0.59 | 0.41 | 0.44 | 2.1 |
| In | 57 | ppb | 67. | 107. | 76. | 89. | 230. | Yb | 57 | ppm | 0.58 | - | 0.20 | - | 1.5 |
| K | 68 | % | 0.184 | - | 0.04 | - | 0.36 | Zn | 68 | ppm | 310. | - | 809. | - | 5300. |
| La | 57 | ppm | 7.64 | - | 3.7 | - | 30. | Zr | 58 | ppm | 38.9 | - | 27.9 | - | 115. |
| Li | 21 | ppm | 21.1 | - | 17.3 | - | 85.6 |  |  |  |  |  |  |  |  |
| Lu | 57 | ppm | 0.11 | - | 0.05 | - | 0.40 |  |  |  |  |  |  |  |  |
| Mg | 68 | % | 0.05 | - | 0.02 | - | 0.11 |  |  |  |  |  |  |  |  |

*Low and high statistics result from the two methods of computing assays that were < the detection limits; see text for details. The dash (-) indicates the low and high values were equal; the assays for these elements were above the detection limit.

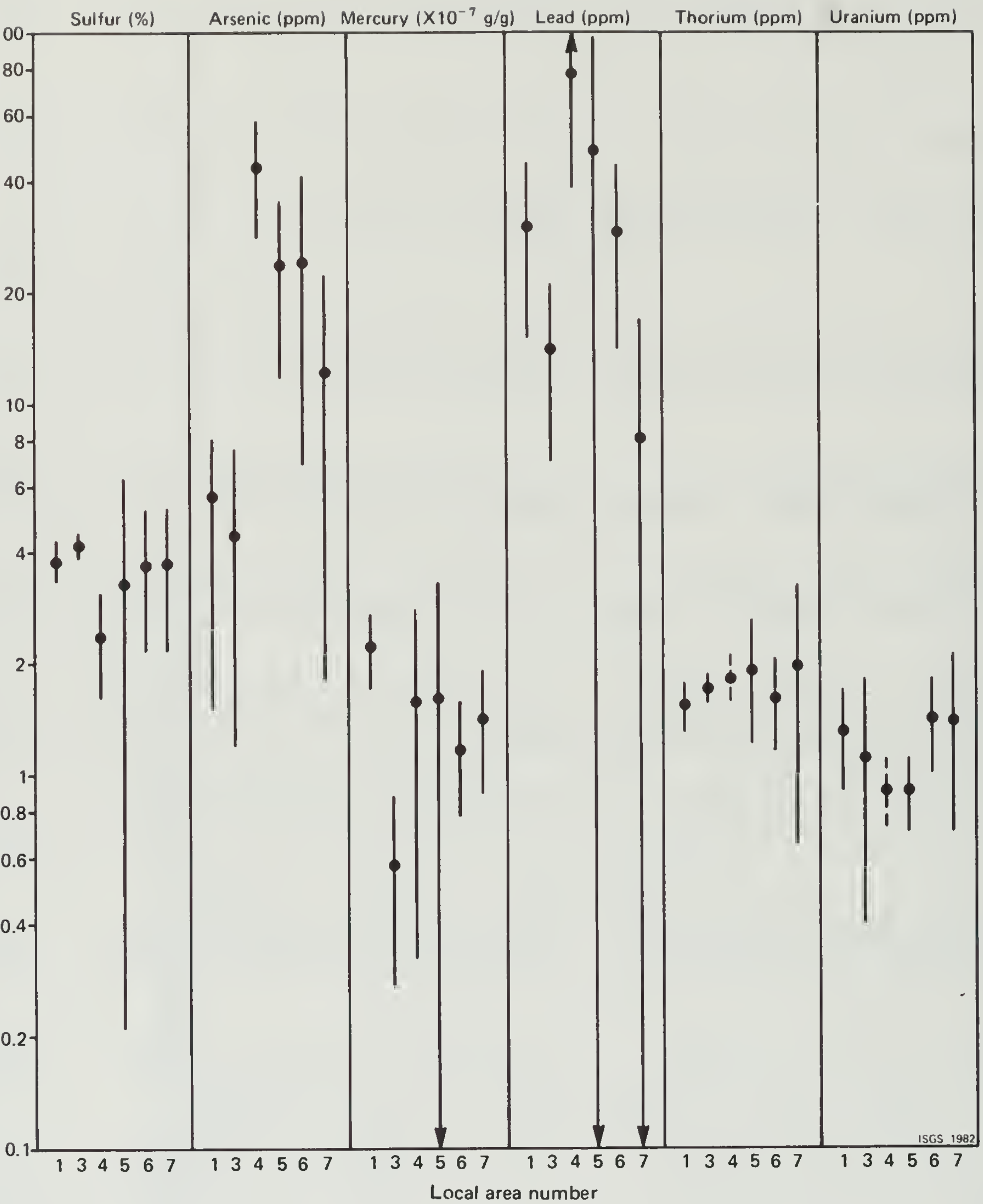


FIGURE VI-7. Arithmetic mean and standard deviation of elemental concentrations of greatest environmental concern from within local areas of the Springfield Coal.

(20 ppm) is high in area L5 and has a large range (1-48 ppm). Samples C20641 and C20642, collected from a single mine in L5, have the highest As contents (15 and 48 ppm respectively). It should be noted that C20641 is a face-channel composite sample and C20642 is a run-of-mine sample (table IV-1). The lower As content in C20641 may result from the homogenization in the preparation of a composite sample or may be due to the fact that shale bands were excluded from analysis. Lead is variable among local areas with the highest concentrations in L1, lower concentrations in L5, L7, and L8, and the lowest concentration in L2 and L4. This variation reflects various degrees of mineralization caused by hydrothermal solutions. Thorium is fairly uniformly distributed in local areas. Uranium is similar to thorium, but its concentration varies widely in L8.

## Regional distribution of elements in Herrin Coal

Data in tables VI-4 and VI-5 and data from Circular 499 samples (Gluskoter et al., 1977) have been plotted on maps to discover trends of areal distribution. These maps (VI-8 to VI-30) show that many elements are rather uniformly distributed and that a number of other elements show characteristic distribution patterns. These patterns are discussed below.

*Sodium, chlorine, bromine.* Figures VI-8 and VI-9 are contour maps indicating chlorine and sodium contents in the Herrin Coal. The sources of data used in the preparation of these two maps include Gluskoter and Rees (1964), this report, and some unpublished data. The most significant difference in the maps shown in figure VI-8 and in figure 2 of Gluskoter and Rees (1964) is in an area in southeastern Illinois around Edwards, Wabash, and White Counties. Gluskoter and Rees (1964) found that the Cl content of this coal is correlated with that in groundwater, so that increasing Cl content with depth is due to the fact that the salinity of groundwater increases with depth.

Figure VI-9 shows that the Na content also increases toward the deeper part of the basin, suggesting a relationship between Na in coal and in groundwater. Figure VI-10 shows Br distribution in the Herrin Coal. In the main swamp area the samples with low Br contents (<10 ppm) lie almost entirely (with one exception) to the west of the Walshville channel, suggesting a tendency of increasing Br content with increasing depth of the coal. But there is not enough data for the east part of the basin to suggest a similar trend there.

*Zinc and cadmium.* Hatch et al. (1976) found that Zn and Cd are more concentrated in the northwest and southeast parts of the basin, and suggested that sphalerite was deposited in the cleats of coal. Our version of Zn distribution (fig. VI-11) is quite similar to that of Hatch et al.; cadmium and zinc have similar patterns reflecting that cadmium is associated with zinc in sphalerite.

*Boron.* The distribution of B in the Herrin Coal is shown in figure VI-12. Areas with high B content (≥150 ppm) are indicated. In the main swamp of the basin the high-B areas are located to the west of the Walshville channel; since the B content in seawater is much higher than in surface waters, this suggests that the peat in the west margin of the basin had been subjected to more intense marine influence than other areas.

*Sulfur.* The total S content in the Herrin Coal ranges from 0.77 to 6.45 percent. The samples with lower than average sulfur contents (<2.5 percent) are located mostly in the southern part of the basin close to the Walshville channel (fig. VI-13); a few samples are located in the east-central part of the basin (Vermilion, Douglas and Cumberland Counties). The occurrence of low-sulfur coal (<2.5 percent S) may be related to splay deposits of contemporaneous rivers.

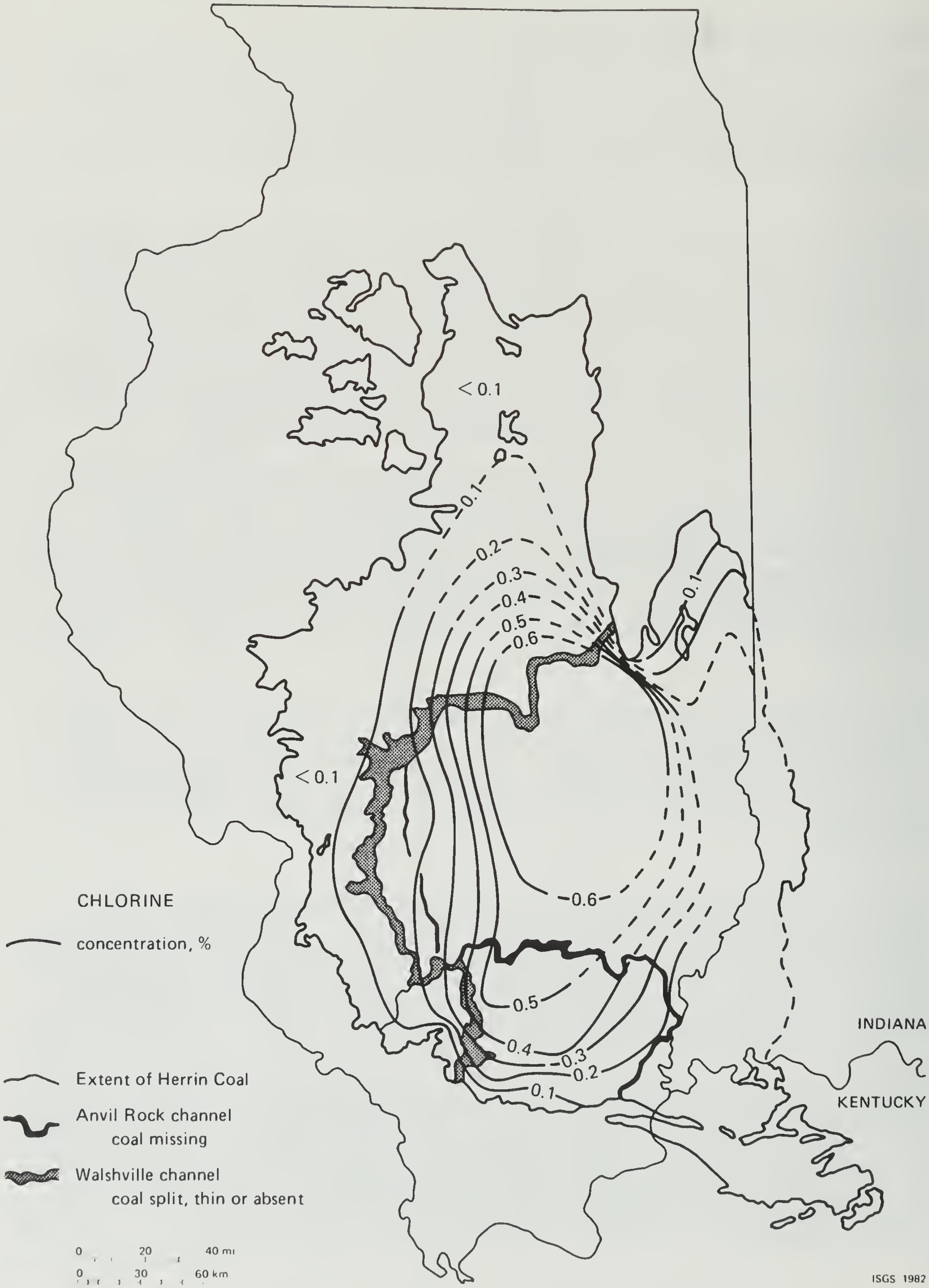


FIGURE VI-8. Areal distribution of chlorine in the Herrin Coal.

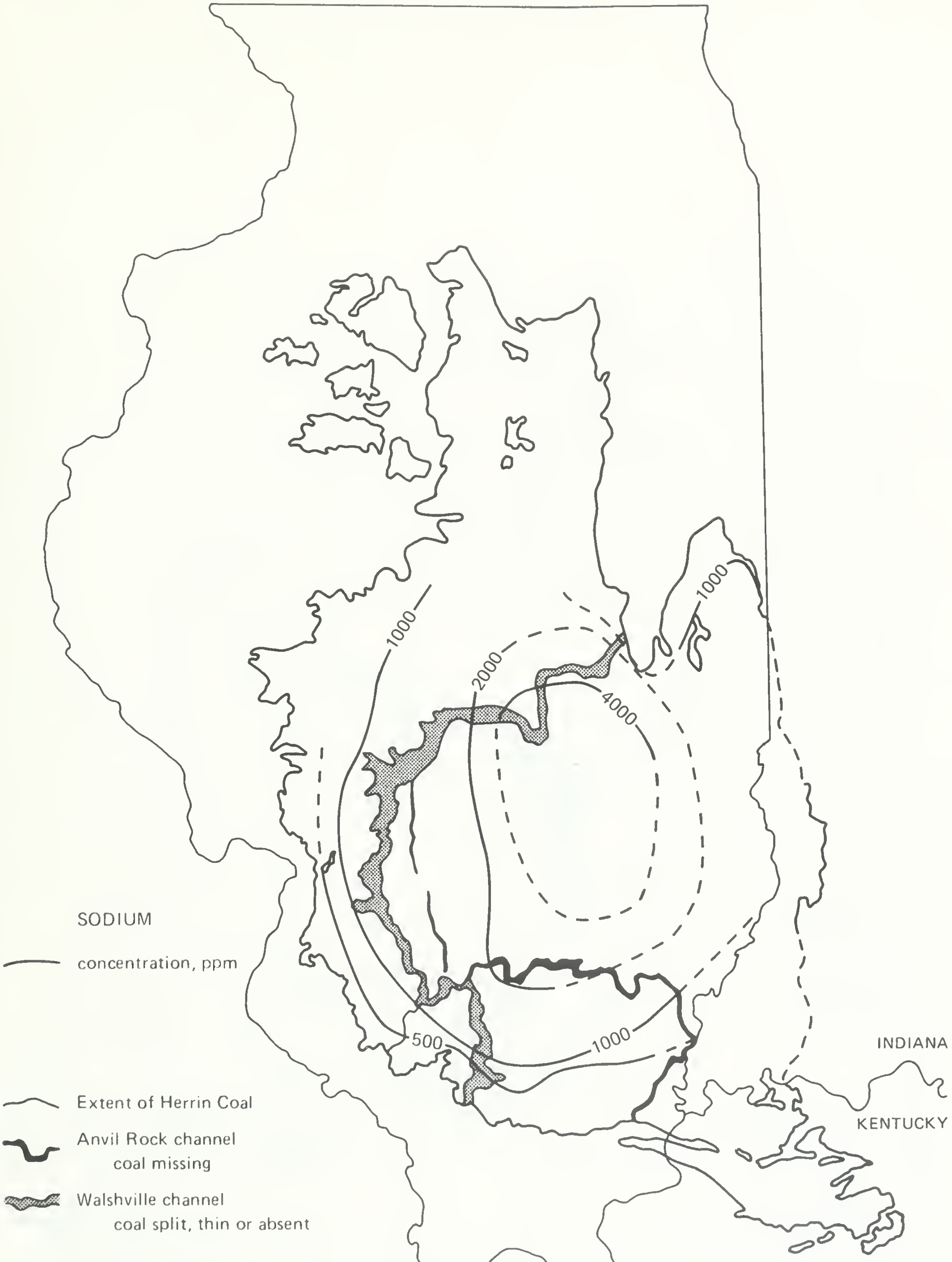


FIGURE VI-9. Areal distribution of sodium in the Herrin Coal.

FIGURE VI-10. Areal distribution of bromine in the Herrin Coal.

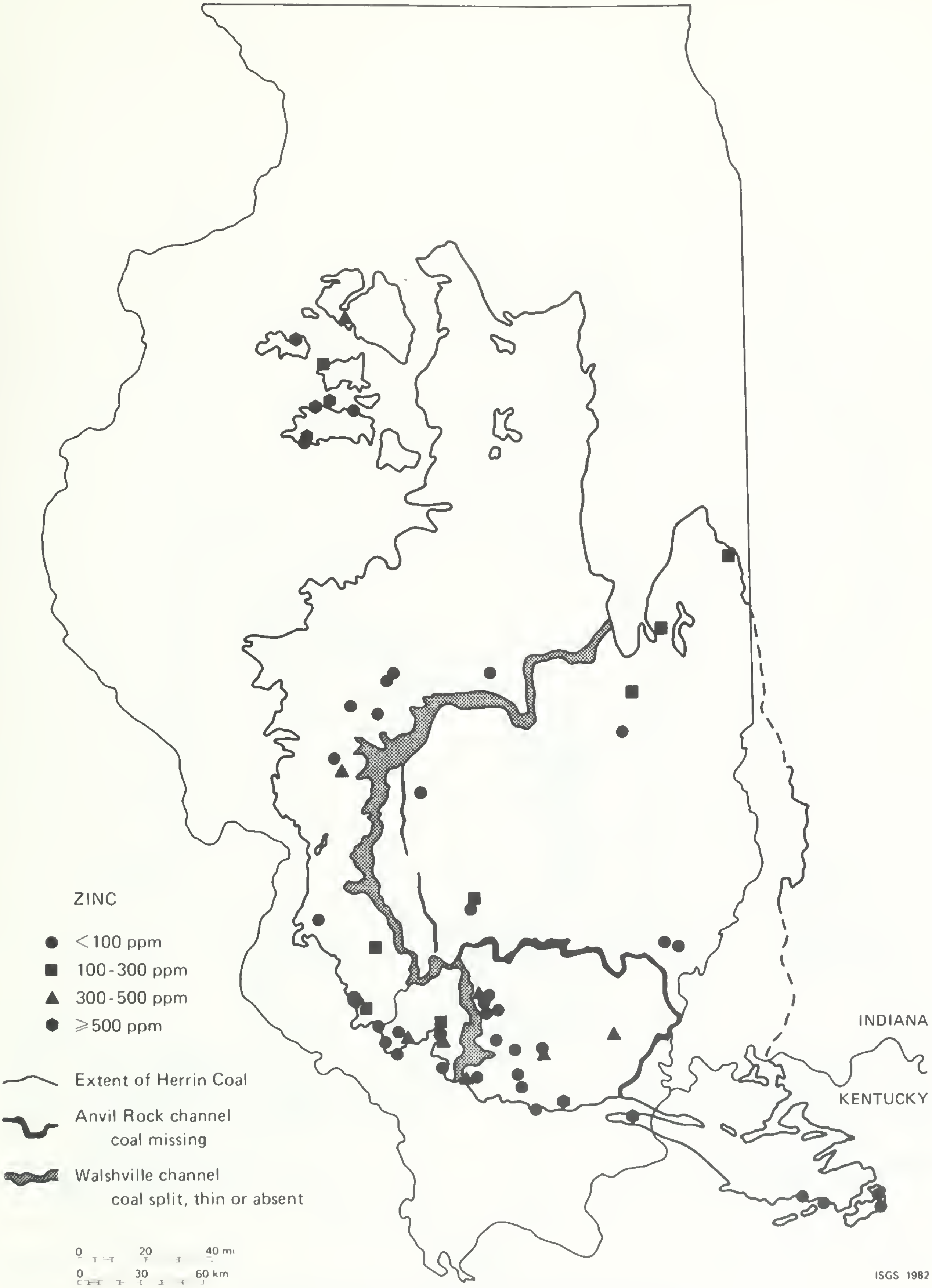


FIGURE VI-11. Areal distribution of zinc in the Herrin Coal.

**FIGURE VI-12.** Areal distribution of boron in the Herrin Coal.

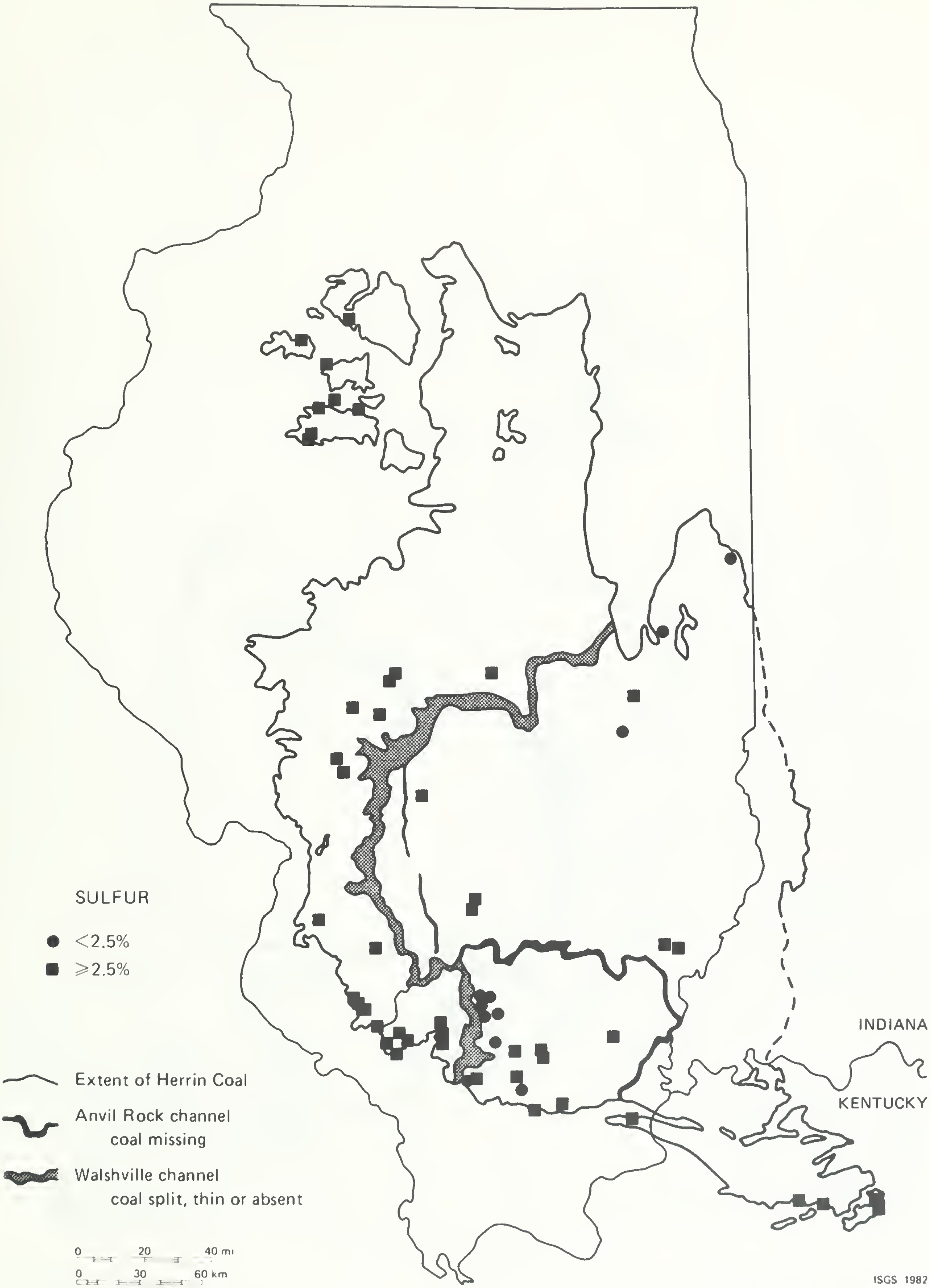


FIGURE VI-13. Areal distribution of sulfur in the Herrin Coal.

FIGURE VI-14. Areal distribution of arsenic in the Herrin Coal.

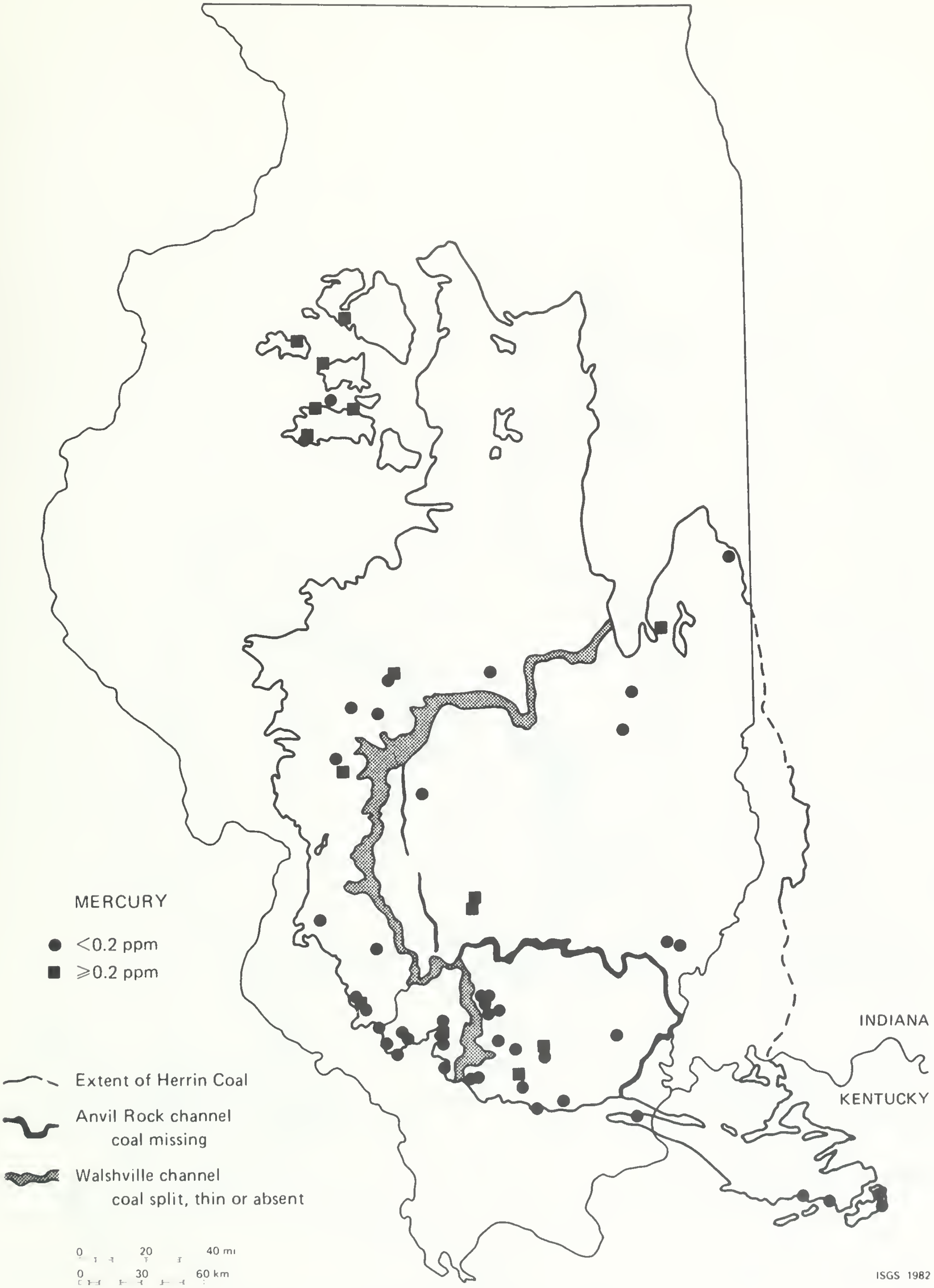


**FIGURE VI-15.** Areal distribution of mercury in the Herrin Coal.

FIGURE VI-16. Areal distribution of lead in the Herrin Coal.

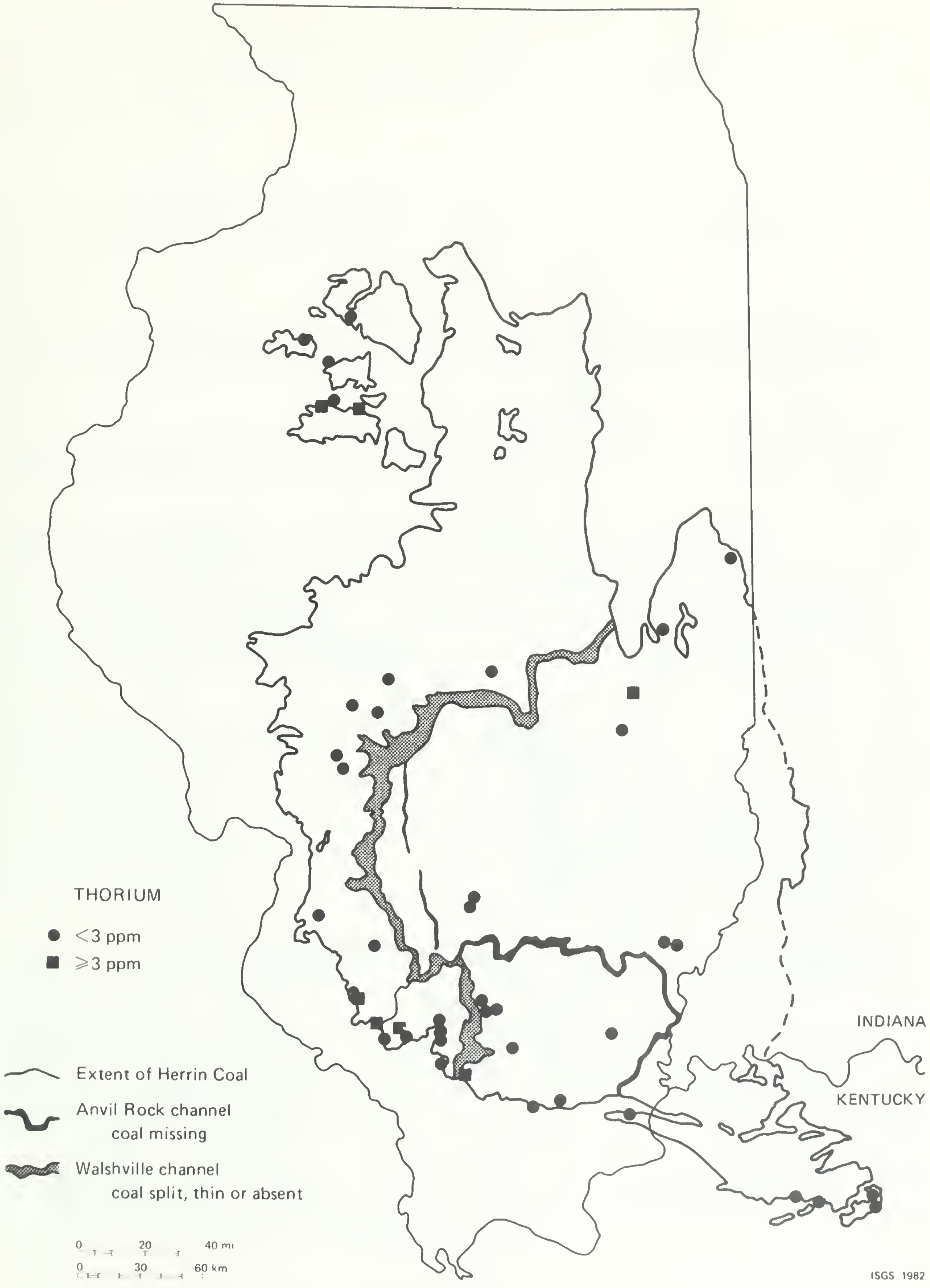


**FIGURE VI-17.** Areal distribution of thorium in the Herrin Coal.

FIGURE VI-18. Areal distribution of uranium in the Herrin Coal.

*Mercury.* The areal distribution of mercury in the Herrin Coal is shown in figure VI-15. Samples with greater than 0.22 ppm Hg are distributed partly as a cluster in the northwest part of the basin and partly randomly throughout the basin.

*Lead.* The lead content in the Herrin Coal varies from 1 to 206 ppm. Some of the samples with high Pb contents (>50 ppm) are located as a cluster in the northwest part; others are partly scattered in the east-central and southeast parts of the basin (fig. VI-16).

*Thorium.* Seven samples have higher Th content (≥3 ppm) than others (<3 ppm), and these higher values are scattered in the northwest, southern, and east-central parts of the basin (fig. VI-17).

*Uranium.* Four samples have >3 ppm uranium content and are randomly distributed throughout the basin (fig. VI-18).

## CHEMICAL VARIATION OF WHOLE-COAL SAMPLES OF THE SPRINGFIELD

The variations of trace and minor elements in whole-coal samples of the Springfield Coal are expressed in terms of the arithmetic mean, the standard deviation, and the maximum of the analytical assays. These statistical results, based on all whole coals from Circular 499 and MMC80 samples, are given in table VI-7.

### Chemical variation of the Springfield Coal in local areas

Six local areas within the Springfield Coal have been defined (section IV-3) for purposes of examining the variations of chemical properties of coal samples in each restricted area. The analytical data for MMC80 samples are given in tables VI-4 and VI-5. Since each local area consists of only four to five samples the variations in local areas are smaller than those for the whole basin.

7, P.66 RWH

Figure VI-~~19~~ shows the mean abundances and standard deviations of sulfur and five selected trace elements (As, Hg, Pb, Th, U) in each local area. Sulfur, Th, and U have more-or-less similar mean concentrations in six local areas and overlapping ranges. Mercury content in local area 3 (L3) is somewhat lower than other areas, but the limits of one standard deviation overlap with those of L4 and L5. The larger standard deviation of Hg in L5 is due to the presence of a high-Hg sample (0.43 ppm) along with other samples of lower Hg contents (0.05-0.11 ppm).

Arsenic contents in L1 and L3 appear to be lower than in L4-L7, which may warrant further investigation. Lead contents in L5 and L7 show large standard deviations. Anomalous high Pb contents indicate that some restricted areas have been affected by hydrothermal solutions.

TABLE VI-7. Statistical evaluation of chemical elements in whole-coal samples (C499 and MMC80, R and L purpose codes) from the Springfield Coal.

| Element | # Samples | Units | Arithmetic mean* |  | Standard deviation* |  | Maximum | Element | # Samples | Units | Arithmetic mean* |  | Standard deviation* |  | Maximum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | Low | High | Low | High |  |  |  |  | Low | High | Low | High |  |
| Ag | 29 | ppb | 60. | - | 39. | - | 160. | Mn | 50 | ppm | 56.1 | - | 39.4 | - | 206. |
| Al | 50 | % | 1.12 | - | 0.41 | - | 2.77 | Mo | 50 | ppm | 9.1 | - | 5.1 | 5.2 | 24. |
| As | 50 | ppm | 14.5 | - | 14.6 | - | 61. | Na | 49 | ppm | 596. | - | 613. | - | 3303. |
| B | 50 | ppm | 108. | - | 39. | - | 216. | Ni | 50 | ppm | 15.1 | - | 7.0 | - | 33. |
| Ba | 31 | ppm | 230. | - | 547. | - | 2666. | P | 50 | ppm | 67.1 | 95.5 | 90 | 99.7 | 500. |
| Be | 50 | ppm | 1.5 | - | 0.7 | - | 3.7 | Pb | 50 | ppm | 27.5 | 27.6 | 30.7 | - | 138. |
| Br |  | ppm | 11.9 | - | 8.5 | - | 32. | Rb | 40 | ppm | 15.3 | - | 7.6 | - | 49. |
| Ca | 50 | % | 0.66 | - | 0.48 | - | 2.18 | S | 50 | % | 3.66 | - | 1.24 | - | 8.42 |
| Cd | 48 | ppm | 1.3 | 1.4 | 4.4 | 4.5 | 30.5 | OrgS | 50 | % | 1.49 | - | 0.52 | - | 2.26 |
| Ce | 40 | ppm | 13.8 | - | 9.2 | - | 51. | PyrS | 50 | % | 2.04 | - | 0.96 | - | 6.70 |
| Cl | 47 | % | 0.16 | - | 0.16 | - | 0.61 | Sb | 50 | ppm | 1.15 | - | 0.7 | - | 3.3 |
| Co | 50 | ppm | 4.4 | - | 2.2 | - | 10. | Sc | 40 | ppm | 2.38 | - | 1.27 | - | 8.0 |
| Cr | 50 | ppm | 15.9 | - | 6.4 | - | 41. | Se | 50 | ppm | 2.56 | - | 1.50 | - | 8.5 |
| Cs | 40 | ppm | 1.1 | - | 0.5 | - | 3.8 | Si | 50 | % | 2.34 | - | 0.65 | - | 5.78 |
| Cu | 50 | ppm | 12.2 | - | 10.2 | - | 66.5 | Sm | 40 | ppm | 1.40 | 1.45 | 1.24 | 1.26 | 6.7 |
| Dy | 40 | ppm | 1.1 | - | 0.8 | - | 4.1 | Sr | 31 | ppm | 28.8 | - | 26.0 | - | 154. |
| Eu | 40 | ppm | 0.3 | - | 0.2 | - | 1.0 | Ta | 40 | ppm | 0.16 | - | 0.12 | - | 0.80 |
| F | 50 | ppm | 62.9 | - | 26.7 | - | 143. | Tb | 36 | ppm | 0.19 | - | 0.14 | - | 0.78 |
| Fe | 50 | % | 2.04 | - | 0.92 | - | 6.83 | Th | 40 | ppm | 1.95 | - | 1.19 | - | 7.6 |
| Ga | 50 | ppm | 3.4 | - | 1.6 | - | 9.0 | Ti | 50 | % | 0.06 | - | 0.02 | - | 0.13 |
| Ge | 50 | ppm | 6.1 | - | 3.5 | - | 18.0 | Tl | 21 | ppm | 1.31 | - | 1.51 | - | 7.2 |
| Hf | 40 | ppm | 0.51 | - | 0.19 | - | 1.3 | U | 40 | ppm | 1.23 | 1.44 | 0.85 | 1.02 | 4.6 |
| Hg | 48 | ppm | 0.17 | - | 0.11 | - | 0.50 | V | 50 | ppm | 32.3 | - | 23.8 | - | 140. |
| I | 22 | ppm | 1.23 | 1.49 | 1.17 | 1.33 | 5.80 | W | 40 | ppm | 0.54 | 0.66 | 0.64 | 0.68 | 4.2 |
| In | 40 | ppb | 55. ** | 120.** | ** | 146.** | 630.** | Yb | 40 | ppm | 0.51 | - | 0.33 | - | 1.9 |
| K | 50 | % | 0.18 | - | 0.09 | - | 0.64 | Zn | 50 | ppm | 16 | - | 214. | - | 958. |
| La | 40 | ppm | 7.13 | - | 4.20 | - | 23.0 | Zr | 43 | ppm | 30.7 | - | 26. | - | 133. |
| Li | 19 | ppm | 10.9 | - | 8.0 | - | 33.8 |  |  |  |  |  |  |  |  |
| Lu | 40 | ppm | .12 | - | 0.09 | - | 0.44 |  |  |  |  |  |  |  |  |
| Mg | 50 | % | .04 | - | 0.03 | - | 0.17 |  |  |  |  |  |  |  |  |

* Low and high statistics result from the two methods of computing assays that were < the detection limits; see text for details. The dash (-) indicates the low and high values were equal.

**Useful only as a guide because several of the high values were also < values; the listed maximum is the maximum analysis above the detection limit.

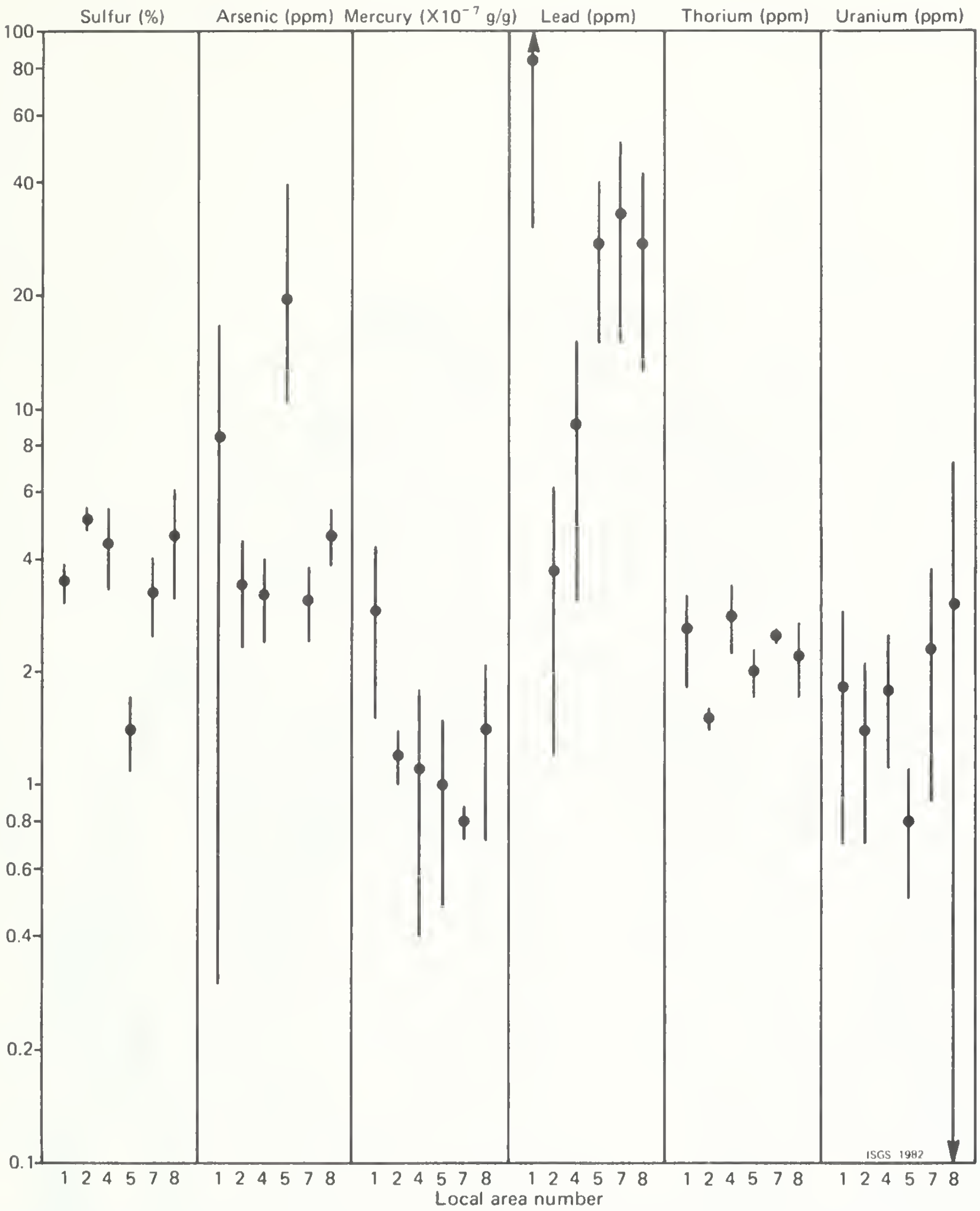


**FIGURE VI-19.** Arithmetic mean and standard deviation of elemental concentrations of greatest environmental concern from within local areas of the Herrin Coal.

## Regional distribution of elements in the Springfield Coal

The data in tables VI-4 and VI-5 and in Circular 499 for the Springfield Coal have been plotted on maps to show areal distribution of elemental abundances in the Springfield Coal. The elements that show characteristic patterns in the Herrin Coal also have similar patterns in the Springfield Coal. Apparently the geologic processes that caused trace element variations had affected both coal seams.

*Sodium, chlorine, and bromine.* Areal distributions of Cl and Na in the Springfield Coal are shown in figures VI-20 and VI-21. The sources of data include Gluskoter and Rees (1964), this report, and some unpublished data.

FIGURE VI-20. Areal distribution of chlorine in the Springfield Coal.

**FIGURE VI-21.** Areal distribution of sodium in the Springfield Coal.

FIGURE VI-22. Areal distribution of bromine in the Springfield Coal.

The distribution patterns of these elements in the Springfield are quite similar to those found in the Herrin; however, the 0.4 and 0.6 percent chlorine lines are rather hypothetical because of the scarcity of samples in the deeper part of the basin. These high-concentration lines are likely to be significantly changed when more samples become available.
The Bromine distribution in the Springfield Coal is shown in figure VI-22. Samples located along the southeastern basin margin have <10 ppm Br, and samples located to the west have >10 ppm Br, suggesting a possible relationship between Br and the depth. But most samples from the southern basin margin in the state of Illinois have higher Br contents, and there appears to be no relation to depth.

*Zinc and cadmium.* The regional distribution of zinc in the Springfield Coal is shown in figure VI-23. Most samples with high Zn contents (>100 ppm) are located in the northwest and southeastern parts of the basin. Three exceptions are one sample each from Shelby and Marion Counties, and one from Indiana. As in the Herrin Coal, the Zn enrichment resulted from sphalerite mineralization. The distribution pattern of Cd is similar to that of Zn, since Cd occurs in sphalerite.

*Boron.* Regional distribution of B in the Springfield Coal is shown in figure VI-24. Samples with high B contents (≥120 ppm) are distributed in the northwest, and in the east and southwest margins of the basin. Samples located close to the Galatia channel have significantly lower B contents (48-105 ppm), probably because of the influence of low-B freshwater from the river.

*Sulfur.* Eight samples have <2.5 percent sulfur (fig. VI-25); the low-sulfur samples are distributed along the Galatia channel.

*Arsenic.* Figure VI-26 shows the areal distribution of As in the Springfield Coal. Most of the samples with high As contents are located in the southeastern part of the basin.

*Mercury.* A few samples have ≥0.3 ppm Hg and are scattered in the basin (fig. VI-27).

*Lead.* Areal distribution of lead in the Springfield Coal is shown in figure VI-28. Most samples with ≥30 ppm Pb are from the southeastern part; one sample comes from the northwestern part of the basin.

*Thorium.* Samples with somewhat high Th contents (≥2 ppm) are scattered throughout the basin (fig. VI-29).

*Uranium.* Samples with relatively high U contents (≥1.5 ppm) are scattered in the basin (fig. VI-30).

FIGURE VI-23. Areal distribution of zinc in the Springfield Coal.

FIGURE VI-24. Areal distribution of boron in the Springfield Coal.

FIGURE VI-25. Areal distribution of sulfur in the Springfield Coal.

**FIGURE VI-26.** Areal distribution of arsenic in the Springfield Coal.

FIGURE VI-27. Areal distribution of mercury in the Springfield Coal.

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FIGURE VI-28. Areal distribution of lead in the Springfield Coal.

FIGURE VI-29. Areal distribution of thorium in the Springfield Coal.

FIGURE VI-30. Areal distribution of uranium in the Springfield Coal.

## CHEMICAL COMPOSITION OF WASHED COALS

The washability characteristics of the coals were evaluated by specific-gravity separations. Results of the chemical analysis for two sets from the Herrin Coal and two from the Springfield Coal are given in tables VI-8 and VI-9.

### Analytical considerations

Errors associated with the analysis of density fractions are more significant than those associated with the analysis of the whole coal samples.

TABLE VI-8. Standard coal analyses of washed (sink-float) samples, dry basis.*

| SAMPLE | PURPOSE-CODE | SPEC GRAV | RECOVERY ( % ) | ASH ( % ) | PYRS ( % ) | ORGS ( % ) | TOTS ( % ) |
|---|---|---|---|---|---|---|---|
| | HERRIN COAL | | | | | | |
| C20659 | S | 3/8X28 | 90.2 | 11.22 | 1.65 | 1.53 | 3.31 |
| C20661 | W 3 | 1.29F | 33.6 | 3.50 | .48 | 1.74 | 2.23 |
| C20662 | W 3 | 1.31FS | 19.8 | 5.58 | .67 | 2.03 | 2.73 |
| C20663 | W 3 | 1.33FS | 10.3 | 7.66 | .79 | 1.91 | 2.73 |
| C20664 | W 3 | 1.40FS | 19.1 | 11.91 | .84 | 1.89 | 2.77 |
| C20665 | W 3 | 1.60FS | 10.5 | 22.05 | 1.43 | 1.45 | 2.93 |
| C20666 | W 3 | 1.60S | 6.7 | 50.39 | 16.31 | 1.08 | 17.58 |
| C20683 | S | 3/8X28 | 90.6 | 7.28 | .64 | .56 | 1.27 |
| C20685 | W 4 | 1.28F | 43.7 | 2.29 | .37 | .69 | 1.08 |
| C20686 | W 4 | 1.30FS | 20.5 | 3.77 | .47 | .67 | 1.16 |
| C20687 | W 4 | 1.32FS | 11.6 | 6.34 | .49 | .64 | 1.15 |
| C20688 | W 4 | 1.40FS | 15.4 | 11.20 | .49 | .50 | 1.00 |
| C20689 | W 4 | 1.60FS | 5.2 | 21.41 | .78 | .35 | 1.13 |
| C20690 | W 4 | 1.60S | 3.6 | 43.75 | 7.32 | .02 | 7.41 |
| | SPRINGFIELD COAL | | | | | | |
| C20669 | S | 3/8X28 | 91.0 | 9.30 | 1.46 | 2.09 | 3.88 |
| C20671 | W 1 | 1.29F | 28.5 | 3.03 | .32 | 2.22 | 2.57 |
| C20672 | W 1 | 1.31FS | 19.5 | 4.99 | .46 | 2.32 | 2.83 |
| C20673 | W 1 | 1.35FS | 25.4 | 8.20 | .72 | 2.13 | 2.96 |
| C20675 | W 1 | 1.60FS | 9.3 | 19.79 | 3.74 | 1.43 | 5.68 |
| C20676 | W 1 | 1.60S | 4.2 | 43.27 | 18.25 | .91 | 19.83 |
| C21076 | S | 3/8X28 | 93.0 | 9.50 | .80 | .45 | 1.26 |
| C21096 | W 2 | 1.27F | 20.6 | 2.91 | .28 | .54 | .83 |
| C21097 | W 2 | 1.30FS | 21.1 | 3.10 | .33 | .52 | .86 |
| C21098 | W 2 | 1.32FS | 23.1 | 5.29 | .51 | .47 | .98 |
| C21099 | W 2 | 1.40FS | 26.1 | 9.94 | .85 | .42 | 1.30 |
| C21100 | W 2 | 1.60FS | 5.4 | 22.27 | 2.38 | .26 | 2.69 |
| C21101 | W 2 | 1.60S | 3.7 | 54.72 | 5.90 | .12 | 6.11 |

* S,THE SIZE FRACTION (3/8X28M) WAS THE RAW MATERIAL FOR THE FLOAT-SINK SEPARATIONS

TABLE VI-9. Minor and trace element analyses of washed (sink-float) samples, dry basis.*

| SAMPLE | PURPOSE-CODE | SPEC GRAV | AG (PPB) | AL ( % ) | AS (PPM) | B (PPM) | BA (PPM) | BE (PPM) | BR (PPM) | CA ( % ) | CD (PPM) | CE (PPM) | CO (PPM) | CR (PPM) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HERRIN COAL | | | | | | | | | | | | | | |
| C20659 | S | 3/8X28 | 65. | 1.27 | 2.5 | 160. | 106. | 1.01 | 1. | 2.19 | <.2 | 12. | 3.6 | 28. |
| C20661 | W 3 | 1.29F | 53.0 | .36 | 1.6 | 120.0 | 13. | 0.69 | 2.5 | .07 | <.1 | 7. | 2.2 | 34. |
| C20662 | W 3 | 1.31FS | 58.0 | .60 | 1.4 | 150.0 | 16. | 0.86 | 1.9 | .06 | <.1 | 6. | 2.7 | 23. |
| C20663 | W 3 | 1.33FS | 52.0 | .85 | 1.6 | 150.0 | 23. | 0.99 | 1.9 | .06 | <.2 | 6. | 3.2 | 19. |
| C20664 | W 3 | 1.40FS | 62.0 | 1.32 | 1.7 | 170.0 | 31. | 1.3 | 2.4 | .10 | <.2 | 12. | 3.9 | 19. |
| C20665 | W 3 | 1.60FS | 78.0 | 2.30 | 1.6 | 140.0 | 59. | 1.3 | 3.7 | .51 | <.4 | 22. | 4.5 | 20. |
| C20666 | W 3 | 1.60S | 240.0 | 2.52 | 1.7 | 91.0 | 89. | 0.6 | 1.6 | 3.20 | <1. | 40. | 7.4 | 33. |
| | | | | | | | | | | | | | | |
| C20683 | S | 3/8X28 | | 1.31 | 31. | - | 53. | - | 18. | .38 | <.2 | 15. | 6.7 | 12. |
| C20685 | W 4 | 1.28F | 45.0 | .22 | 13. | 66.0 | 10. | 0.91 | 22. | .06 | <.1 | 6. | 3.6 | 8. |
| C20686 | W 4 | 1.30FS | 48.0 | .42 | 15. | 77.0 | 18. | 1.07 | 20. | .06 | <.1 | 12. | 5.4 | 10. |
| C20687 | W 4 | 1.32FS | 64.0 | .78 | 12. | 76.0 | 28. | 1.19 | 19. | .06 | <.1 | 18. | 10. | 15. |
| C20688 | W 4 | 1.40FS | 76.0 | 1.44 | 11. | 81.0 | 47. | 1.3 | 19. | .05 | <.2 | 27. | 12. | 20. |
| C20689 | W 4 | 1.60FS | 114.0 | 2.75 | 24. | 73.0 | 87. | 1.5 | 19. | .14 | <.3 | 41. | 9. | 29. |
| C20690 | W 4 | 1.60S | 570.0 | 5.95 | 511. | 74.0 | 162. | 1.08 | 6. | 4.73 | <.8 | 70. | 10. | 34. |
| SPRINGFIELD COAL | | | | | | | | | | | | | | |
| C20669 | S | 3/8X28 | 39. | .79 | 1.3 | 140. | 27. | 1.8 | 1.3 | .20 | 1.8 | 8.2 | 2.8 | 12. |
| C20671 | W 1 | 1.29F | 20.0 | .36 | .3 | 102.0 | 11. | 1.1 | 2.6 | .04 | <.1 | 4. | 1.8 | 9. |
| C20672 | W 1 | 1.31FS | 28.0 | .57 | .4 | 111.0 | 18. | 1.3 | 2.3 | .04 | <.1 | 8. | 2.3 | 11. |
| C20673 | W 1 | 1.35FS | 37.0 | .87 | .7 | 130.0 | 29. | 1.6 | 2.5 | .04 | <.1 | 11. | 2.8 | 13. |
| C20675 | W 1 | 1.60S | <50.0 | 1.58 | 2.7 | 140.0 | 52. | 2.3 | 2.3 | .07 | <.2 | 15. | 4.4 | 18. |
| C20676 | W 1 | 1.60S | <110.0 | 1.15 | 15. | 39.0 | 40. | 0.91 | 1.6 | 3.21 | 34.4 | 11. | 7.2 | 14. |
| | | | | | | | | | | | | | | |
| C21076 | S | 3/8X28 | 119. | .97 | 47. | 78. | 47. | 1.3 | 28. | .72 | .2 | 12. | 8. | 11. |
| C21096 | W 2 | 1.27F | 39.0 | .35 | 7. | 54.0 | 14. | 0.99 | 31. | .07 | .2 | 4. | 3. | 7. |
| C21097 | W 2 | 1.30FS | 47.0 | .37 | 8. | 55.0 | 16. | 1.14 | 28. | .06 | <.05 | 5. | 3. | 7. |
| C21098 | W 2 | 1.32FS | 75.0 | .65 | 15. | 67.0 | 25. | 1.2 | 29. | .09 | <.08 | 10. | 7. | 9. |
| C21099 | W 2 | 1.40FS | 150.0 | 1.21 | 38. | 70.0 | 48. | 1.4 | 28. | .28 | <.1 | 15. | 10. | 13. |
| C21100 | W 2 | 1.60FS | 330.0 | 2.20 | 186. | 160.0 | 156. | 1.5 | 22. | 1.57 | .4 | 21. | 19. | 22. |
| C21101 | W 2 | 1.60S | 510.0 | 4.35 | 519. | 40.0 | 501. | 0.66 | 9. | 11.07 | 9.6 | 29. | 24. | 32. |

* S, THE SIZE FRACTION (3/8X28M) WAS THE RAW MATERIAL FOR THE FLOAT-SINK SEPARATIONS

TABLE VI-9. Minor and trace element analyses of washed (sink-float) samples.* (*continued*)

| SAMPLE | CS (PPM) | CU (PPM) | DY (PPM) | EU (PPM) | F (PPM) | FE ( % ) | GA (PPM) | GE (PPM) | HF (PPM) | HG (PPM) | I (PPM) | IN (PPB) | K ( % ) | LA (PPM) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HERRIN COAL | | | | | | | | | | | | | | |
| C20659 | 1.4 | 7.8 | 1.0 | .26 | 59. | 1.64 | 3.5 | 1.5 | .4 | .31 | - | <11. | .17 | 5.2 |
| C20661 | .7 | 4.6 | .8 | .14 | 39. | .52 | 2.3 | 3.3 | .2 | .16 | - | 11. | .07 | 1.8 |
| C20662 | 1.0 | 5.7 | .8 | .16 | 40. | .70 | 2.8 | 2.1 | .2 | .07 | - | 11. | .12 | 3.1 |
| C20663 | 1.1 | 7.0 | 1.0 | .20 | 55. | .83 | 3.8 | 1.4 | .3 | .08 | - | <21. | .15 | 3.9 |
| C20664 | 1.7 | 8.4 | 1.3 | .26 | 81. | .94 | 4.2 | <0.92 | .4 | .08 | - | <43. | .24 | 6.3 |
| C20665 | 3.1 | 10.4 | 1.7 | .43 | 114. | 1.52 | 5.2 | <1.7 | .8 | .09 | - | <84. | .39 | 13. |
| C20666 | 4.3 | 19.0 | 2.8 | .85 | 287. | 14.07 | 6.0 | <3.8 | 1.3 | .37 | - | <102. | .41 | 24. |
| | | | | | | | | | | | | | | |
| C20683 | 1.0 | 8.4 | 1.0 | .2 | 59. | 2.15 | 4.5 | | .4 | .09 | - | 22. | .21 | 8. |
| C20685 | .4 | 4.7 | .7 | .15 | 19. | .36 | 4.1 | 12.0 | .3 | .09 | - | 15. | .04 | 3. |
| C20686 | .6 | 5.6 | 1.0 | .24 | 32. | .45 | 3.4 | 10.1 | .4 | .12 | - | 15. | .07 | 5. |
| C20687 | .9 | 7.5 | 1.2 | .34 | 44. | .53 | 3.5 | 23. | .5 | .06 | - | 16. | .13 | 9. |
| C20688 | 1.7 | 9.8 | 1.5 | .40 | 63. | .59 | 3.7 | 2.8 | 1.0 | .06 | - | 5. | .24 | 12. |
| C20689 | 3.5 | 15.2 | 2.2 | .63 | 110. | .97 | 7.1 | 2.0 | 1.6 | .08 | - | <31. | .46 | 18. |
| C20690 | 3.9 | 49.1 | 3.6 | 1.1 | 89. | 6.80 | 12. | 5.0 | 2.5 | .43 | - | <41. | .53 | 31. |
| SPRINGFIELD COAL | | | | | | | | | | | | | | |
| C20669 | 1. | 5.8 | .9 | .19 | 45. | 1.79 | 3.0 | 2.8 | .3 | .10 | - | <44. | .14 | 3.9 |
| C20671 | .3 | 3.1 | .7 | .15 | 29. | .35 | 2.0 | 3.5 | .2 | .05 | - | 9. | .05 | 1.8 |
| C20672 | .8 | 4.3 | .8 | .18 | 38. | .52 | 2.6 | 3.6 | .3 | .06 | - | 13. | .10 | 3. |
| C20673 | 1.1 | 5.0 | 1.2 | .24 | 54. | .85 | 3.3 | 3.6 | .5 | .07 | - | 16. | .16 | 4. |
| C20675 | 2.5 | 8.3 | 1.2 | .26 | 86. | 4.06 | 3.8 | 2.5 | .8 | .15 | - | 21. | .31 | 7.4 |
| C20676 | 1.1 | 21.8 | .9 | .31 | 140. | 15.73 | 4.1 | <3.4 | .3 | .19 | - | <52. | .17 | 5.5 |
| | | | | | | | | | | | | | | |
| C21076 | .8 | 8.3 | .9 | .27 | 55. | .86 | 4.3 | 9.7 | .6 | .61 | - | 9. | .18 | 7. |
| C21096 | .3 | 3.6 | .3 | .09 | 32. | .31 | 1.9 | 10.8 | .2 | .10 | - | <11. | .06 | 3. |
| C21097 | .3 | 3.4 | .3 | .10 | 20. | .34 | 2.2 | 7.1 | .2 | .17 | - | <11. | .06 | 3. |
| C21098 | .6 | 5.4 | .6 | .17 | 34. | .53 | 2.4 | 8.7 | .3 | .15 | - | <22. | .11 | 7. |
| C21099 | 1.1 | 9.7 | .9 | .30 | 63. | .93 | 3.0 | 8.8 | .7 | .27 | - | <76. | .22 | 11. |
| C21100 | 1.7 | 22.6 | 2.3 | .86 | 100. | 2.43 | 6.0 | 9.3 | 1.0 | .68 | - | <212. | .47 | 14. |
| C21101 | 2.6 | 50.5 | 2.9 | .9 | 170. | 5.89 | 8.0 | <4.8 | 1.8 | .74 | - | <611. | .72 | 16. |

## TABLE VI-9. Minor and trace element analyses of washed (sink-float) samples.* (*continued*)

| SAMPLE | LI (PPM) | LU (PPM) | MG ( % ) | MN (PPM) | MO (PPM) | NA (PPM) | NI (PPM) | P (PPM) | PB (PPM) | RB (PPM) | SB (PPM) | SC (PPM) | SE (PPM) | SI ( % ) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HERRIN COAL | | | | | | | | | | | | | | |
| C20659 | 8.7 | .08 | .05 | 36. | 10.6 | 305. | 8. | <100. | 11. | 17. | 1.7 | 2.6 | 5.0 | 2.70 |
| C20661 | 2.6 | .08 | .02 | 16. | 10.6 | 217. | 8. | <100. | 5. | 10. | 2.9 | 1.6 | 4.3 | .76 |
| C20662 | 5.1 | .06 | .03 | 15. | 40.0 | 237. | 10. | <100. | 7. | 11. | 1.6 | 1.9 | 4.6 | 1.32 |
| C20663 | 7.3 | .13 | .03 | 18. | 7.6 | 279. | 11. | <100. | 9. | 15. | 1.0 | 2.1 | 4.4 | 1.87 |
| C20664 | 12.1 | .10 | .04 | 26. | 7.6 | 375. | 9. | <100. | 9. | 18. | .4 | 2.8 | 2.9 | 3.18 |
| C20665 | 21.4 | .16 | .10 | 58. | 8.5 | 549. | 9. | <100. | 13. | 32. | .3 | 3.9 | 2.4 | 5.79 |
| C20666 | 24.1 | .24 | .06 | 215. | 59.0 | 727. | <8. | 300. | 48. | 32. | 1.8 | 4.7 | 8.5 | 6.16 |
| C20683 | 15.0 | .09 | .05 | 22. | | 1025. | 18. | <100. | 28. | 12. | 2.9 | 2.9 | 2.3 | 2.74 |
| C20685 | 1.9 | .06 | .01 | 4. | 1.5 | 757. | 16. | <100. | 22. | 4. | 3.4 | 2.2 | 2.1 | .38 |
| C20686 | 4.5 | .11 | .01 | 5. | 1.8 | 900. | 18. | <100. | 21. | 5. | 3.0 | 2.5 | 2.1 | .77 |
| C20687 | 10.1 | .12 | .02 | 9. | 2.1 | 1166. | 23. | <100. | 17. | 11. | 2.3 | 2.9 | 2.3 | 1.51 |
| C20688 | 24.5 | .12 | .05 | 15. | 2.8 | 1596. | 22. | 100. | 18. | 22. | 1.5 | 3.5 | 2.3 | 2.90 |
| C20689 | 65.2 | .25 | .08 | 27. | <4.3 | 2092. | 17. | 200. | 32. | 48. | 1.3 | 5.4 | 3.8 | 5.71 |
| C20690 | 169. | .36 | .11 | 347. | 24. | 1941. | 11. | 200. | 178. | 56. | 6.0 | 8.0 | 7.7 | 11.26 |
| SPRINGFIELD COAL | | | | | | | | | | | | | | |
| C20669 | 6.9 | .10 | .04 | 17. | 7.9 | 197. | 4. | <100. | 15. | 17. | .2 | 2.1 | 2.1 | 1.85 |
| C20671 | 2.7 | .08 | .01 | 7. | 2.9 | 126. | 5. | <100. | 3. | 4. | .17 | 1.4 | 1.6 | .70 |
| C20672 | 4.4 | .10 | .03 | 9. | 2.9 | 163. | 6. | <100. | 5. | 10. | .07 | 1.9 | 1.7 | 1.23 |
| C20673 | 7.2 | .11 | .03 | 14. | 4.3 | 228. | 5. | <100. | 7. | 17. | .05 | 2.2 | 2.0 | 2.04 |
| C20675 | 15.4 | .15 | .06 | 20. | 16.0 | 321. | 5. | <100. | 36. | 30. | .17 | 3.3 | 3.2 | 4.06 |
| C20676 | 13.3 | .05 | .14 | 146. | 46.0 | 218. | <8. | <100. | 112. | 22. | .21 | 2.6 | 6.6 | 2.59 |
| C21076 | 9.5 | .07 | .06 | 55. | 3.7 | 1521. | 21. | 135. | 23. | 13. | 2.6 | 2.4 | 1.9 | 1.87 |
| C21096 | 2.6 | .04 | .01 | 5. | 1.3 | 1057. | 13. | 100. | 10. | 3. | 1.4 | 1.2 | 1.2 | .61 |
| C21097 | 2.7 | .04 | .02 | 4. | 1.4 | 1053. | 15. | 100. | 11. | 5. | 1.6 | 1.2 | 1.1 | .65 |
| C21098 | 5.6 | .05 | .02 | 9. | 2.2 | 1131. | 21. | 100. | 15. | 9. | 2.1 | 1.7 | 1.3 | 1.23 |
| C21099 | 12.7 | .09 | .04 | 25. | 3.7 | 1328. | 29. | 200. | 24. | 15. | 3.2 | 2.6 | 1.9 | 2.37 |
| C21100 | 27.9 | .22 | .13 | 127. | 10.6 | 1873. | 53. | 400. | 63. | 32. | 8.3 | 5.2 | 3.9 | 4.30 |
| C21101 | 37.0 | .36 | .12 | 631. | 22.0 | 2138. | 36. | 300. | 174. | 48. | 15.3 | 9.5 | 9.2 | 8.17 |

TABLE VI-9. Minor and trace element analyses of washed (sink-float) samples.* (*continued*)

| SAMPLE | SM (PPM) | SR (PPM) | TA (PPM) | TB (PPM) | TH (PPM) | TI ( % ) | TL (PPM) | U (PPM) | V (PPM) | W (PPM) | YB (PPM) | ZN (PPM) | ZR (PPM) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HERRIN COAL | | | | | | | | | | | | | |
| C20659 | 1.2 | 51. | .11 | .14 | 2.1 | .06 | .96 | 2.3 | 22. | .3 | .8 | 28.0 | 10. |
| C20661 | .8 | 16. | .09 | .11 | 1.1 | .03 | 0.36 | 5.3 | 34.0 | .5 | .3 | 8.8 | 7. |
| C20662 | .8 | 14. | .16 | .11 | 1.4 | .04 | 0.48 | 2.8 | 22.0 | .4 | .3 | 8.7 | 7. |
| C20663 | .9 | 15. | .07 | .12 | 1.7 | .05 | 0.45 | 1.7 | 20.0 | .3 | .4 | 9.4 | 10. |
| C20664 | 1.2 | 19. | .11 | .20 | 2.4 | .08 | 0.48 | 1.6 | 21.0 | .3 | .4 | 11.9 | 14. |
| C20665 | 2.1 | 31. | .13 | .45 | 3.7 | .12 | 0.7 | 1.3 | 20.0 | .3 | .8 | 30.4 | 24. |
| C20666 | 4.1 | 53. | .14 | .57 | 3.5 | .13 | 6.8 | 2.1 | 23.0 | .7 | .8 | 246. | 26. |
| C20683 | 1.3 | 27. | .08 | .17 | 1.9 | .08 | - | <2. | - | <.5 | .4 | 33.4 | 17. |
| C20685 | .5 | 26. | .06 | .12 | 1.0 | .02 | 0.25 | <3. | 10.7 | <.2 | .2 | 16.3 | 7. |
| C20686 | 1.1 | 38. | .11 | .14 | 1.3 | .03 | 0.28 | <2. | 12.0 | <.3 | .3 | 11.6 | 11. |
| C20687 | 1.4 | 37. | .09 | .22 | 2.1 | .06 | 0.27 | <1. | 18.0 | <1. | .5 | 16.4 | 15. |
| C20688 | 1.8 | 35. | .19 | .27 | 3.5 | .09 | 0.34 | <2. | 19.0 | <1. | .7 | 25.9 | 22. |
| C20689 | 2.9 | 43. | .29 | .32 | 6.1 | .16 | 0.89 | <3. | 25.0 | <1. | 1.2 | 40.8 | 34. |
| C20690 | 5.3 | 65. | .50 | .71 | 9.0 | .22 | 9.5 | <1. | 16.0 | <1. | 2.3 | 315. | 53. |
| SPRINGFIELD COAL | | | | | | | | | | | | | |
| C20669 | .9 | 15. | .1 | .16 | 1.8 | .05 | .59 | 1.4 | 13. | .3 | .4 | 407. | 12. |
| C20671 | .7 | 11. | .06 | .11 | 1.1 | .03 | 0.09 | 1.0 | 8.5 | .7 | .3 | 8.3 | 6. |
| C20672 | .8 | 12. | .09 | .16 | 1.5 | .04 | 0.13 | 1.1 | 9.1 | .4 | .4 | 8.9 | 9. |
| C20673 | 1.0 | 13. | .11 | .10 | 2.0 | .06 | 0.33 | 1.6 | 10.3 | .4 | .7 | 9.9 | 13. |
| C20675 | 1.3 | 19. | .15 | .19 | 2.8 | .10 | 1.3 | 1.8 | 15.0 | .3 | .6 | 26.7 | 23. |
| C20676 | 1.4 | 44. | .09 | .21 | 1.7 | .04 | 4.6 | .9 | 8.8 | .2 | .4 | 6450. | 13. |
| C21076 | 1.2 | 43. | .14 | .16 | 1.3 | .05 | 1.4 | 1. | 11. | <1. | .4 | 76.6 | 12. |
| C21096 | .4 | 26. | .07 | .07 | .7 | .03 | 0.27 | <2. | 8.6 | <1. | .2 | 16.6 | 5. |
| C21097 | .4 | 29. | .05 | .07 | .8 | .03 | 0.72 | <1. | 9.4 | <1. | .2 | 13.0 | 6. |
| C21098 | .9 | 43. | .06 | .10 | 1.1 | .04 | 1.1 | <1. | 10.1 | <1. | .2 | 14.6 | 8. |
| C21099 | 1.4 | 53. | .12 | .15 | 1.6 | .07 | 1.8 | <1. | 11.8 | <1. | .5 | 33.1 | 17. |
| C21100 | 3.8 | 65. | .17 | .60 | 2.5 | .11 | 7.8 | 1.4 | 27.0 | <1. | 1.2 | 164. | 38. |
| C21101 | 3.5 | 85. | 2.8 | .63 | 3.9 | .11 | 7.3 | 3. | 25.0 | <2. | 1.7 | 1750. | 37. |

The INAA procedure, which uses coal powders (as opposed to ash), will have significant errors attributable to poor counting statistics. Errors are particularly likely to occur in determinations for Ce, Cs, Dy, Eu, Ga, Hf, In, Lu, Rb, Sb, Se, Sm, Tb, Th, U, W, and Yb because of the low levels of these elements in the mineral-deficient float fraction.

Other methods used in this study (section III) require a high-temperature ash sample for analysis and have a different set of problems. There is a good possibility that the small amounts of ash produced in the lighter fraction could become contaminated. The loss of elements during ashing could be enhanced in these lighter fractions because of the use of perchloroethylyene, which would add chlorine; the formation of volatile metal halides could therefore result in the loss of an element.

One check of the analysis is provided by comparing the results of the starting coal used (3/8" x 28 mesh) with cumulative summation of the specific gravity fractions adjusted for each individual yield. Table VI-10 gives these results as a ratio of the calculated 100 percent recovery with that of the starting coal. In general, results with both procedures are very similar when the associated analytical errors are considered. Significant errors in one or more of the four washed samples are found only for Mg, Ba, Br, Eu, Hf, Hg, Lu, Mo, Sb, Sr, Ta, Tb, U, W, and Yb (only 25 results in more than 200). In most cases the errors can be attributed to the low levels of these elements, particularly in the lighter specific gravity fractions.

**TABLE VI-10.** Mass balance: ratio of the elemental composition of the washed coal data (extrapolated to 100% recovery) to that of direct analysis of starting sample, the 3/8 x 28M coal.

| ELEMENT | W1 | W2 | W3 | W4 |
|---|---|---|---|---|
| Si | 0.85 | 0.91 | 1.02 | 1.04 |
| Al | 0.87 | 0.93 | 1.01 | 1.02 |
| Fe | 1.33 | 0.99 | 0.97 | 1.00 |
| Mg | 3.00 | 0.50 | 1.00 | 1.00 |
| Ca | 0.47 | 0.86 | 0.83 | 0.85 |
| Na | 1.02 | 0.81 | 1.07 | 1.05 |
| K | 0.93 | 0.89 | 0.94 | 1.08 |
| Ti | 1.00 | 1.00 | 1.00 | 1.00 |
| P | **** | 1.11 | >1.13 | >1.09 |
| Mn | 1.00 | 0.75 | 1.00 | 0.91 |
| Sul S | 0.44 | 2.67 | 0.28 | 0.80 |
| Pyr S | 1.15 | 1.03 | 1.07 | 1.08 |
| Org S | 0.97 | 1.04 | 1.15 | 1.11 |
| Tot S | 0.99 | 1.02 | 1.08 | 1.05 |
| F | 1.16 | 0.85 | 1.24 | 0.66 |
| Ag | 0.95 | 0.93 | 1.09 | **** |
| As | 1.08 | 0.98 | 1.12 | 1.00 |
| B | 0.81 | 0.85 | 0.87 | **** |
| Ba | 0.62 | 1.11 | 0.88 | 0.97 |
| Be | 0.78 | 0.92 | 0.92 | **** |
| Br | 1.85 | 1.00 | 2.0 | 1.11 |
| Cd | **** | **** | **** | **** |
| Ce | 1.10 | 0.83 | 0.92 | 1.07 |
| Co | 1.00 | 0.88 | 0.92 | 0.97 |
| Cr | 1.00 | 1.00 | 0.93 | 1.08 |
| Cs | 1.00 | 0.88 | 1.07 | 1.00 |
| Cu | 0.95 | 1.00 | 0.95 | 0.96 |
| Dy | 1.11 | 0.78 | 1.1 | 1.1 |
| Eu | 1.11 | 0.89 | 0.96 | 1.45 |
| Ga | 1.00 | 0.93 | 1.10 | 0.96 |
| Ge | 1.18 | 0.90 | 1.53 | **** |

| ELEMENT | W1 | W2 | W3 | W4 |
|---|---|---|---|---|
| Hf | 1.33 | 0.67 | 1.00 | 1.5 |
| Hg | 0.80 | 0.38 | 0.42 | 1.11 |
| In | **** | **** | **** | 0.68 |
| La | 0.97 | 1.00 | 1.12 | 0.88 |
| Li | 0.99 | 0.91 | 1.01 | 1.08 |
| Lu | 1.00 | 1.14 | 1.25 | 1.22 |
| Mo | 0.87 | 0.92 | 1.75 | **** |
| Ni | 1.25 | 1.05 | 1.13 | 1.00 |
| Pb | 0.87 | 1.04 | 0.91 | 0.96 |
| Rb | 0.82 | 0.85 | 0.94 | 1.00 |
| Sb | 0.65 | 1.15 | 0.94 | 1.00 |
| Sc | 1.00 | 0.92 | 0.92 | 1.00 |
| Se | 1.05 | 0.95 | 0.84 | 1.04 |
| Sm | 1.00 | 0.92 | 1.00 | 0.92 |
| Sr | 0.32 | 0.98 | 0.91 | 0.94 |
| Ta | 1.00 | 0.90 | 1.00 | 1.5 |
| Tb | 0.81 | 0.94 | 1.14 | 1.12 |
| Th | 0.94 | 1.00 | 0.90 | 1.11 |
| Tl | 0.95 | 1.14 | 0.92 | **** |
| U | 1.00 | 1.30 | 1.35 | >1.15 |
| V | 0.78 | 1.05 | 1.14 | **** |
| W | 1.67 | 1.00 | 1.33 | >1.00 |
| Yb | 1.00 | 1.00 | 0.80 | 1.25 |
| Zn | 0.69 | 1.20 | 0.99 | 0.87 |
| Zr | 1.00 | 1.00 | 1.00 | 1.00 |
| Qtz | 1.07 | 1.00 | 0.82 | 0.83 |
| Cal | 1.00 | 1.23 | 0.82 | 0.83 |
| Pyr | 1.19 | 1.27 | 1.00 | 1.00 |
| Clay | 0.83 | 0.81 | 1.00 | 1.05 |
| LTA | 0.94 | 0.92 | 0.97 | 1.00 |

## Construction of washability curves

Washability tests produce data in the form of measured concentrations for each of a series of specific gravity fractions of known yield or percentage of fraction of the raw sample. The data by itself or displayed graphically in the form of histograms provide only limited information on washability behavior.

A more useful method of displaying washability data is in the form of a washability curve, a cumulative curve based on the data for each specific gravity fraction weighted according to the yield. The cumulative weighted concentrations are plotted versus cumulative yield (recovery). The calculated concentration of 100 percent recovery should then represent the elemental concentration in raw coals; the low recovery end of the curve represents the cleanest and most mineral matter free part of the coal.

The actual calculations used to construct the washability curve can be summarized by the following equation:

$$\mathrm{CUMCON(I)} = \frac{[\mathrm{CUMCON(I-1)}\cdot\mathrm{CUMYLD(I-1)}] + [\mathrm{CON(I)}\cdot\mathrm{YLD(I)}]}{\mathrm{CUMYLD(I)}} \qquad \text{eq. 1}$$

where, CON = measured elemental concentration for each specific gravity fraction

CUMCON = cumulative elemental concentration

YLD = weight fraction of each specific gravity fraction (yield of recovery)

CUMYLD = cumulative weight fractions

## Chemical and mineral relationships in washability tests

Washability tests are used to determine whether the elements are associated with the organic or inorganic fractions of the coal. The more closely an element is associated with the mineral matter in coal the greater chance there is that it can be removed (washed) from the coal by the proper choice of specific gravity medium. Washability curves with positive slopes represent situations in which the washing procedures tend to remove mineral constituents. The chalcophile elements, for instance, are closely associated with mineral matter in coal and thus can be efficiently removed from the coal by these procedures. The series of curves shown in figure VI-31 demonstrates the intimate association of pyrite with Fe, pyritic S, As, Mo, and Tl. All the illustrated curves (except for Mo) are nearly identical in shape, indicating at least 50 percent reduction in these elements between 100 percent recovery and 80 percent recovery.

In contrast, elements or mineral which have small grain size or lower specific gravity are not so efficiently removed and give less positive or flattened washability curves. The slope can become negative for a few elements: Br, Ge, Sb, U, and V.

The example in figure VI-32 demonstrates the effect of a mixed phase association on washability behavior. Sulfur is known to occur in coal in association with sulfate minerals, with sulfide minerals (primarily pyrite), and

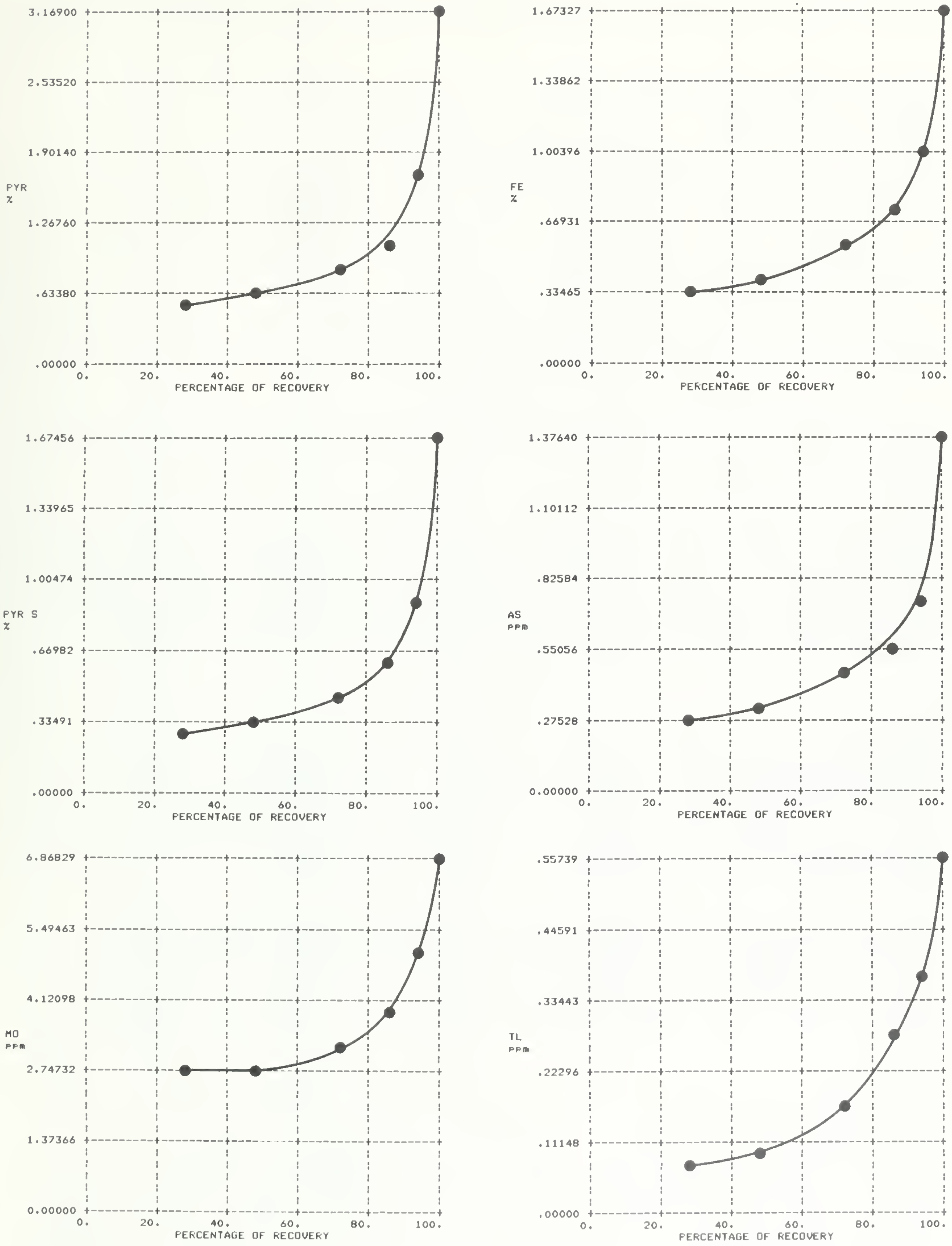


**FIGURE VI-31.** Washability curves for pyrite, Fe, As, pyritic S, As, Mo, and Tl in washed samples (W1) of the Springfield Coal.

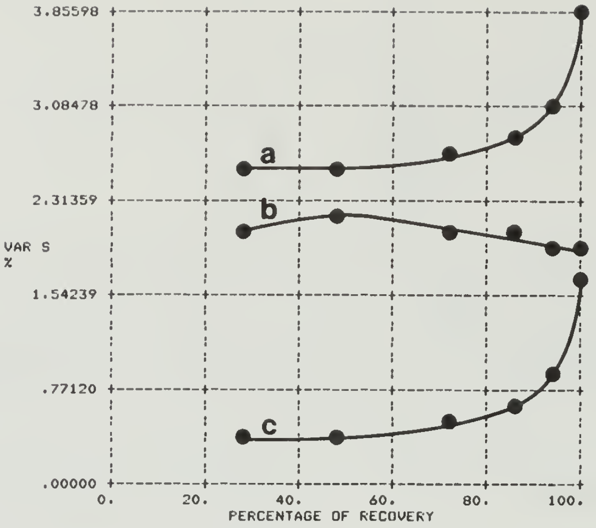


FIGURE VI-32. Washability curves for total S (curve A), organic S (curve B), and pyritic S (curve C) in washed samples (W1) of the Springfield Coal.

with organic matter. In this example the total sulfur comes from two major sources—pyritic sulfur and organic sulfur. It can be seen that the initial reduction in total sulfur is due entirely to the reduction in pyritic sulfur. Below 80 percent recovery, the washability behavior of total sulfur is controlled by the organic sulfur, which is not removed by specific gravity cleaning and actually shows a slight increase.

## Coal cleaning

Washability curves indicate how effectively an element might be removed at a coal cleaning plant by washing procedures. Coal cleaning operations in Illinois normally operate at about an 80 percent weight recovery rate of the feed coal. Table VI-11 compares the 80 percent recovery concentration with the values at 100 percent recovery. Included in the table are data adapted from Cavallaro et al. (1978).

Data in this table indicate that those elements that can be most completely removed from the coal are those commonly associated with mineral matter—pyrite and other sulfides (Fe, Zn, Cd, As, Tl, and pyritic S) and calcite (Ca and Mn). Elements that consistently cannot be effectively removed (B, Be, Br, Ge, Ni, U, V, and W) are interpreted to be associated with organic matter.

## Calculation of organic affinity

In order to quantify washability behavior and to evaluate the extent of mineral matter association an organic affinity index was devised by Gluskoter et al. (1977) and expanded by Kuhn et al (1980). This index represents the degree of association that an element from a particular coal has with organic phases, as determined from washability data. The lower the index, the greater

TABLE VI-11. Washability results for two recovery points (100% and 80%) for washed coal sets (purpose codes W1-W4), and two other sets computed from data in Cavallaro et al., 1978.

| | Springfield Coal | | Herrin Coal | | Cavallaro et al., 1978 | |
|---|---|---|---|---|---|---|
| | W1 | W2 | W3 | W4 | | |
| | C20637 | C21067 | C20636 | C20642 | Springfield | Herrin |
| ELEMENT | 100%-80%* | 100%-80%* | 100%-80%* | 100%-80%* | 100%-80%* | 100%-80%* |
| Si,% | 1.82-1.43 | 1.70-1.02 | 2.34-1.50 | 1.65-0.71 | | |
| Al,% | 0.79-0.64 | 0.90-0.54 | 0.99-0.67 | 0.85-0.41 | | |
| Fe,% | 1.67-0.66 | 0.85-0.48 | 1.68-0.68 | 0.70-0.40 | | |
| Mg,% | 0.03-0.02 | 0.03-0.02 | 0.04-0.03 | 0.03-0.01 | | |
| Ca,% | 0.18-0.04 | 0.62-0.09 | 0.33-0.07 | 0.23-0.05 | | |
| Na | 200-175 | 1228-1105 | 327-257 | 1075-873 | | |
| K,% | 0.14-0.11 | 0.16-0.10 | 0.17-0.13 | 0.13-0.07 | | |
| Ti,% | 0.05-0.05 | 0.05-0.04 | 0.06-0.04 | 0.05-0.03 | | |
| P | *** | <150-<<111 | <113-<<98 | <109-<<97 | | |
| Mn | 17-10 | 41-8 | 36-18 | 20-5 | 89.9-9 | 40-11 |
| SuS,% | 0.145-0.065 | 0.032-0.005 | 0.033-0.019 | 0.051-0.056 | | |
| PyS,% | 1.68-0.51 | 0.82-0.45 | 1.78-0.58 | 0.70-0.40 | | |
| OrS,% | 2.04-2.16 | 0.47-0.49 | 1.77-1.85 | 0.62-0.68 | | |
| ToS,% | 3.86-2.75 | 1.29-0.91 | 3.59-2.47 | 1.33-1.08 | | |
| F | 52-42 | 47-34 | 73-48 | 39-28 | 34-25 | 75-56 |
| Ag,ppb | 37-29 | 111-67 | 71-54 | 75-49 | | |
| As | 1.4-0.5 | 46-13 | 2.8-1.5 | 31-13 | | |
| B | 114-114 | 66-59 | 139-138 | 72-69 | | |
| Ba | 26-20 | 52-21 | 28-18 | 29-16 | | |
| Be | 1.4-1.3 | 1.19-1.13 | 0.93-0.87 | 1.07-0.99 | | |
| Br | 2.4-2.4 | 28-29 | 2.4-2.2 | 20-21 | | |
| Cd | *** | *** | *** | *** | 0.34-0.03 | 0.65-0.01 |
| Ce | 9-8 | 10-8 | 11-8 | 16-10 | | |
| Co | 2.8-2.3 | 7-5 | 3.3-2.7 | 6.5-5.6 | 10.6-10.3 | 15.7-13.0 |
| Cr | 12-11 | 11-8 | 26-25 | 13-10 | | |
| Cs | 1.0-0.8 | 0.7-0.5 | 1.5-1.0 | 1.0-0.4 | | |
| Cu | 5.5-4.2 | 8.3-4.9 | 7.4-5.8 | 8.1-5.4 | 7.0-5.4 | 7.6-4.4 |
| Dy | 1.0-0.9 | 0.7-0.5 | 1.1-0.9 | 1.1-0.9 | | |
| Eu | 0.21-0.19 | 0.24-0.14 | 0.25-0.17 | 0.29-0.22 | | |
| Ga | 3.0-2.7 | 2.8-2.2 | 3.4-3.0 | 4.3-3.7 | | |
| Ge | 3.3-3.4 | 8.7-8.6 | 2.3-2.2 | 10.7-11 | | |
| Hf | 0.4-0.4 | 0.4-0.3 | 0.4-0.3 | 0.6-0.4 | | |
| Hg | 0.08-0.06 | 0.23-0.15 | 0.13-0.11 | 0.10-0.09 | 0.05-0.05 | 0.09-0.07 |
| In | *** | *** | *** | *** | | |
| La | 3.8-3.1 | 7-6 | 5.8-3.2 | 7-4 | | |
| Li | 6.8-5.0 | 8.6-4.8 | 8.8-5.8 | 16.2-4.8 | | |
| Lu | 0.10-0.09 | 0.08-0.05 | 0.10-0.08 | 0.11-0.08 | | |
| Mo | 6.9-3.6 | 3.4-1.9 | 18.6-**** | 2.8-1.7 | | |
| Ni | 5-5 | 22-18 | 9-9 | 18-18 | 7.1-6.9 | 16-14 |
| Pb | 13-5 | 24-14 | 10-7 | 27-20 | 3.1-2.6 | 10-5 |
| Rb | 14-11 | 11-7 | 16-12 | 12-6 | | |
| Sb | 0.1-0.1 | 3.0-1.8 | 1.6-1.8 | 2.9-3.0 | | |
| Sc | 2.1-1.8 | 2.2-1.5 | 2.4-2.0 | 2.9-2.4 | | |
| Se | 2.1-1.8 | 1.8-1.3 | 4.2-4.0 | 2.4-2.1 | | |
| Sm | 0.9-0.8 | 1.1-0.7 | 1.2-0.9 | 1.2-0.8 | | |
| Sr | 14-12 | 42-35 | 20-15 | 33-31 | | |
| Ta | 0.10-0.09 | 0.09-0.07 | 0.11-0.11 | 0.12-0.08 | | |
| Tb | 0.13-0.12 | 0.15-0.09 | 0.16-0.12 | 0.19-0.15 | | |
| Th | 1.7-1.6 | 1.3-1.0 | 1.9-1.5 | 2.1-1.4 | | |
| Tl | 0.56-0.22 | 1.6-0.9 | 0.88-0.40 | 0.64-0.24 | | |
| U | 1.4-1.3 | *** | 3.1-3.4 | *** | | |
| V | 10.1-9.4 | 11.6-9.6 | 25-26 | 14-12 | | |
| W | 0.5-0.5 | *** | 0.4-0.4 | *** | | |
| Yb | 0.4-0.5 | 0.4-0.2 | 0.4-0.2 | 0.5-0.3 | | |
| Zn | 282-2 | 92-14 | 27.6-9.1 | 28.9-14.8 | | |
| Zr | 12-10 | 12-8 | 12-9 | 14-10 | | |
| Qtz,% | 1.6-1.1 | 1.4-0.8 | 1.8-1.1 | 1.0-0.5 | | |
| Cal,% | 0.5-0.1 | 1.6-0.1 | 0.9-0.1 | 0.5-0.1 | | |
| Pyr,% | 3.2-0.9 | 1.9-0.8 | 3.3-1.1 | 1.1-0.6 | | |
| Clay,% | 6.4-5.0 | 5.2-3.5 | 7.5-5.4 | 6.2-3.2 | | |
| LTA,% | 11.65-7.36 | 9.59-5.27 | 13.54-7.78 | 8.96-4.42 | | |

* Concentrations are in ppm unless otherwise indicated.

the inorganic mineral matter association; the higher the index, the higher the organic assocation.

The derivation and procedures for calculating the organic affinity index are provided by Kuhn et al. (1980). Briefly, the organic affinity is defined as the area under a normalized and adjusted washability curve, adjusted (corrected) for what is called inseparable mineral matter. The correction factor F is based on the assumption that part of the mineral matter in coal cannot be separated from the coal during the washing procedure. It is also assumed that the amount of this inseparable mineral matter is approximated by the low temperature ash value of the lightest specific gravity fraction. The final assumption is that the concentration of the constituent of interest in this inseparable mineral matter fraction is the same as the concentration in the heaviest specific gravity fraction.

The correction factor is thus obtained from the expression:

$$F = \frac{\mathrm{LTA(lightest)}}{\mathrm{LTA(heaviest)}} \cdot \mathrm{CON}_{\mathrm{heaviest}} \qquad \text{eq. 2}$$

This value is then substracted from the individual concentrations of each of the specific gravity fractions before that value is used in eq. 1 for the construction of the washability curve.

The adjusted washability curve is normalized to fit a constant grid size, the area of which is defined as being equal to 1.00 to 100 percent recovery. The area that falls below the curve then represents some fractional portion of 1.00.

The area under the curve may be determined in a number of ways. For this study, the adjusted washability data were plotted on a line printer with the background grid systematically filled with characters. The curve was then sketched in and the number of characters falling below the curve was counted. This method was found to be quite satisfactory.

### Results of calculated organic affinities

The calculated organic affinities of the washability sets—two from the Herrin Coal (purpose codes W3 and W4) and two from the Springfield Coal (W1 and W2)—are shown in table VI-12. Included in the table are the organic affinities for two Herrin washed coal sets (W1 and W2) reported in Kuhn et al. (1980) and also in Gluskoter et al. (1977).

Wide ranges in the calculated organic affinity sometimes occur; this must be kept in mind as the results are interpreted. The particle size as well as the density of a mineral will control its washability characteristics. Quartz and clay minerals, which had organic affinities ranging from .14-.52, could be classified as inorganic to intermediate-organic on the basis of the criteria of Gluskoter et al. (1977). Elements associated with these minerals will also often reflect the behavior of the mineral.

TABLE VI-12. Organic affinities of elements and minerals in washed coal sets (W#).

| | Springfield | | Herrin | | | |
|---|---|---|---|---|---|---|
| | W1<br>C20637 | W2<br>C21067 | W3<br>C20636 | W4<br>C20642 | W2<br>C18560* | W1<br>C18121* |
| Si | .51 | .34 | .32 | .15 | .45 | .09 |
| Al | .56 | .37 | .39 | .14 | .30 | .10 |
| Fe | .07 | .21 | .04 | .17 | .06 | .16 |
| Mg | .34 | .37 | .58 | .34 | .27 | .32 |
| Ca | .02 | .03 | .05 | .02 | .06 | .04 |
| Na | .72 | .85 | .65 | .73 | .64 | 43. |
| K | .49 | .36 | .41 | .26 | .56 | .13 |
| Ti | .63 | .63 | .53 | .35 | .29 | .16 |
| P | *** | .66 | *** | *** | .03 | .16 |
| Mn | .10 | .04 | .09 | .03 | .06 | .04 |
| SuS | .16 | .07 | .22 | 1.72 | *** | *** |
| PyS | .06 | .18 | .03 | .15 | *** | *** |
| OrS | 1.03 | 1.13 | 1.00 | 1.12 | 1.11 | 1.15 |
| ToS | .53 | .60 | .43 | .76 | .45 | .54 |
| F | .58 | .62 | .41 | .50 | *** | *** |
| Ag | *** | .34 | .67 | .42 | *** | *** |
| As | .05 | .06 | .04 | .02 | .04 | .05 |
| B | .91 | .84 | .92 | .92 | .77 | .94 |
| Ba | .54 | .07 | .41 | .23 | .15 | *** |
| Be | .82 | .88 | .79 | .86 | .87 | .88 |
| Br | .95 | 1.05 | .94 | .97 | .92 | *** |
| Cd | *** | <.02 | *** | *** | .07 | .04 |
| Ce | .56 | .49 | .48 | .33 | .07 | *** |
| Co | .66 | .45 | .66 | .60 | .74 | .35 |
| Cr | .76 | .66 | 1.19 | .61 | .77 | .37 |
| Cs | .47 | .44 | .44 | .37 | .44 | *** |
| Cu | .53 | .29 | .58 | .47 | .66 | .26 |
| Dy | .81 | .41 | .67 | .59 | .89 | *** |
| Eu | .80 | .39 | .48 | .50 | .67 | *** |
| Ga | .74 | .70 | .70 | .92 | .15 | .41 |
| Ge | >1.07 | >1.07 | *** | 1.2 | *** | *** |
| Hf | .59 | .44 | .44 | .45 | .48 | *** |
| Hg | .66 | .51 | 1.14 | .83 | *** | *** |
| In | *** | *** | *** | *** | *** | *** |
| La | .58 | .53 | .20 | .38 | .04 | *** |
| Li | .49 | .27 | .30 | .08 | *** | *** |
| Lu | .85 | .46 | .7 | .54 | .59 | *** |
| Mo | .12 | .23 | *** | <.30 | *** | .52 |
| Ni | >.91 | .66 | >.95 | .93 | .75 | .36 |
| Pb | .07 | .24 | .33 | .71 | .32 | .05 |
| Rb | .45 | .32 | .63 | .24 | .45 | *** |
| Sb | 1.1 | .41 | 1.54 | 1.17 | .90 | .67 |
| Sc | .74 | .51 | .68 | .74 | .57 | *** |
| Se | .70 | .57 | 1.1 | .84 | .28 | .39 |
| Sm | .79 | .42 | .57 | .35 | .39 | *** |
| Sr | .75 | .69 | .74 | .76 | .07 | *** |
| Ta | .72 | .02 | .80 | .47 | .44 | *** |
| Tb | .8 | .43 | .51 | .60 | *** | *** |
| Th | .73 | .60 | .62 | .55 | .55 | *** |
| Tl | .09 | .26 | .03 | .04 | *** | *** |
| U | .77 | *** | 1.43 | *** | 1.29 | *** |
| V | .85 | .76 | 1.18 | .78 | .97 | .58 |
| W | 1.29 | *** | 1.17 | *** | *** | *** |
| Yb | .74 | .45 | .72 | .39 | .52 | *** |
| Zn | .02 | .04 | .04 | .12 | .04 | .04 |
| Zr | .62 | .45 | .59 | .44 | *** | *** |
| Qtz | .41 | .33 | .23 | .14 | *** | *** |
| Cal | <.02 | <.02 | .03 | .02 | *** | *** |
| Pyr | .05 | .06 | .02 | .10 | *** | *** |
| Clay | .52 | .46 | .48 | .20 | *** | *** |
| LTA | .23 | .18 | .18 | .14 | *** | *** |

* Data from Gluskoter et al., 1977

**TABLE VI-13.** Summary of organic affinity results.

| Average organic affinity index | Association and coal component |
|---|---|
| <0.3 | STRONG INORGANIC ASSOCIATIONS (10 elements and 2 epigenetic minerals) |
| | As, Ba, Ca, Cd, Fe, Mn, Mo, Pb, Tl, Zn, pyrite, calcite |
| 0.3-0.8 | MIXED ASSOCIATIONS (33 elements and syngenetic minerals) |
| | Ag, Al, Ce, Co, Cr, Cs, Cu, Dy, Eu, F, Ga, Hf, Hg, In*, K, La, Li, Lu, Mg, Na, Rb, Sc, Se, Si, Sm, Sr, Ta, Tb, Th, Ti, Yb, Zr, clay minerals, quartz |
| >0.8 | HIGH ORGANIC ASSOCIATIONS (10 elements) |
| | B, Be, Br, Ge, Ni, P*, Sb, U, V, W* |

*Analytical values highly uncertain, especially in the lighter fractions analyzed.

Despite the stated drawbacks several general trends are apparent in the data summarized in table VI-13. Elements and minerals were assigned to three general classifications (strong inorganic association, strong organic association, or a mixed association) if they were consistently included in one of the three groups. Se and Cr had high organic association in two of the six sets but mixed associations in the other four sets.

Arsenic, Ba, Ca, Cd, Fe, Mn, Mo, Pb, Tl and Zn all showed consistent high inorganic association. Calcite (dolomite) and pyrite and trace(s) of other sulfur minerals (sphalerite, barite, galena) undoubtedly control distribution of these elements. These minerals have higher specific gravities and occur more often in cleat fractures in the coals than do other mineral phases such as the clays; therefore, they are more efficiently removed by specific gravity methods.

Boron, Be, Br, Ge, Ni, Sb, U, and V are strongly associated with organic matter in these coals. Germanium, Be, Br, B, U, and V were consistently classified as organic in previous work (Gluskoter, 1977). The high organic affinity for antimony (1.54 in the Herrin set W3) is consistent with previous results (Kuhn et al., 1980) in which antimony often showed high retention in coal demineralized with various acids. Although nickel showed mixed association in previous studies (Gluskoter et al., 1977), three of the four samples in this study were reported to yield affinities greater than 0.9.

The majority of the elements (33 of 54 measured) are of mixed association; their affinities fall somewhere between a clear organic or inorganic association. The elements in this group are normally associated with clay minerals or are lithophile in nature. This includes the rare-earth elements (the Ce through Lu line of fig. I-1), Ag, Al, Cs, F, Ga, Hf, K, Li, Mg, Na, Rb, Sc, Si, Sr, Ta, Th, Ti, and Zr. Some of the fluorine (F) probably occurs in the apatite mineral grains (see section VII, and plate VII-f. Anomalously, the clay minerals fall in this mixed group because of their ultra small grain size and their frequent occurrence as tiny inclusions in the coal macerals. This characteristic occurrence of the clays probably accounts for the mixed association of many of the forenamed elements. Cobalt, Cr, Cu, and Se had moderately high organic affinites but also were quite variable. Chromium, for example, ranged from 0.37-1.19 and selenium from 0.28-1.40. This indicates that for these elements there may be two forms present that will vary depending on the location of coal samples. Selenium could be present in organic form as well in sulfide minerals. The general relationship between organic sulfur and the organic affinity of selenium, however, is not consistent, as shown in figure VI-33.

### Relationship of chemical analyses to organic affinity results

Direct analysis of mineral grains in coal via a scanning electron microscope equipped with an energy-dispersive x-ray analyzer has resulted in the in situ identification of minerals in coal (see section VII of this report). Specific elements often can be assigned to particular trace minerals such as zinc to sphalerite or barium to barite. However, it is difficult to obtain information on the minor and trace components of mineral grains by this technique. Analysis of sufficient quantities of hand-picked mineral grains and coal macerals, although tedious, provides information on the minor components of specific minerals.

Four hand-picked vitrain and three hand-picked minerals were included in this study. The chemical results are tabulated in table VI-14. Because of the limited amount of sample available, results were obtained only by INAA, XRF, and AA on the four vitrain samples.

If the assumption is made that vitrain samples contain very little finely dispersed mineral matter, results for the four vitrain samples can be considered as representing the lighter specific gravity fractions or a

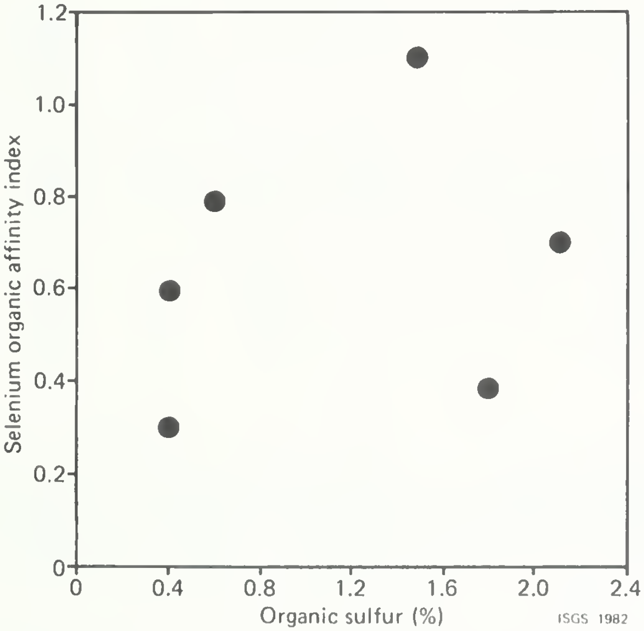


FIGURE VI-33. Organic affinity index for Se vs concentration of organic S in whole-coal samples.

TABLE VI-14. Hand-picked vitrain and minerals.

| SAMPLE | DESCRIPTION | AG (PPM) | AL (%) | AS (PPM) | B (PPM) | BA (%) | BE (PPM) | BR (PPM) | CA (%) | CD (PPM) | CE (PPM) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C20368 | VITRAIN | | .14 | 1.9 | | | | 6.7 | .12 | <.06 | 1.6 |
| C20369 | VITRAIN | | | 3.0 | | | | 3.3 | | <.06 | 1.4 |
| C20370 | VITRAIN | | .49 | .3 | | | | 10 | .28 | <.16 | 1.0 |
| C20371 | VITRAIN | | | .6 | | | | 23 | | <.32 | 2.1 |
| R14532 | CLEAT CAL* | <.24 | 2.00 | 20 | <11 | 1.22 | <.45 | <2 | 34.34 | 3.8 | 1.5 |
| R14533 | SULFATE EFFL* | <.24 | 1.85 | 17 | <11 | 360 PPM | <.45 | <2 | .43 | <2.0 | 23 |
| R14534 | CLEAT BARITE | <.24 | | <5 | <11 | >50. | <.45 | <2 | .68 | <2.0 | <2 |

| SAMPLE | DESCRIPTION | CO (PPM) | CR (PPM) | CS (PPM) | CU (PPM) | DY (PPM) | EU (PPM) | F (PPM) | FE (%) | GA (PPM) | HF (PPM) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C20368 | VITRAIN | 2.0 | 8 | .1 | 4.2 | | .09 | | .26 | 3.6 | .1 |
| C20369 | VITRAIN | 2.1 | 5 | .09 | 4.5 | | .07 | | .32 | 3.7 | .1 |
| C20370 | VITRAIN | .9 | 4 | .3 | 1.7 | | .08 | | .29 | 1.5 | .06 |
| C20371 | VITRAIN | .8 | 6 | .2 | 2.5 | | .08 | | .70 | 1.8 | .1 |
| R14532 | CLEAT CAL | 1.7 | 3.6 | <.2 | 7.8 | <2 | .6 | 8 | 1.64 | 2 | <.5 |
| R14533 | SULFATE EFFL | 50 | 26 | 1.8 | 27.1 | <1 | .4 | 131 | 17.44 | <6 | 1.1 |
| R14534 | CLEAT BARITE | <1 | <4 | <.2 | 2.0 | <1 | <.1 | 4 | .05 | <5 | <1 |

| SAMPLE | DESCRIPTION | HG (PPM) | K (PPM) | LA (PPM) | LI (PPM) | LU (PPM) | MG (%) | MN (PPM) | MO (PPM) | NA (PPM) | NI (PPM) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C20368 | VITRAIN | | 80 | .8 | 1.1 | .07 | .01 | | | 31 | 3.3 |
| C20369 | VITRAIN | | 40 | .4 | .49 | .07 | | | | 62 | 21 |
| C20370 | VITRAIN | | 150 | .7 | 1.7 | .07 | .01 | | | 83 | 2.4 |
| C20371 | VITRAIN | | 230 | .9 | 4.0 | .06 | | | | 64 | 2.5 |
| R14532 | CLEAT CAL | .02 | 200 | 1.5 | 5.8 | .4 | .20 | 1980 | <20 | 160 | <4 |
| R14533 | SULFATE EFFL | .07 | 5100 | 12 | 40 | .2 | .67 | 400 | 54 | 2200 | 100 |
| R14533 | CLEAT BARITE | .01 | 100 | <5 | 18 | <.2 | <.01 | 50 | <20 | 30 | <4 |

| SAMPLE | DESCRIPTION | P (PPM) | PB (PPM) | RB (PPM) | SB (PPM) | SC (PPM) | SE (PPM) | SI (%) | SM (PPM) | SR (PPM) | TA (PPM) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C20368 | VITRAIN | 39 | 14 | <1 | .2 | 1.6 | .7 | .18 | .3 | | .04 |
| C20369 | VITRAIN | | 18 | <5 | 4.0 | 2.3 | .7 | | .3 | | <.03 |
| C20370 | VITRAIN | 44 | 5 | <2 | .2 | 1.3 | .7 | .41 | .3 | | .04 |
| C20371 | VITRAIN | | 39 | 2 | <.1 | 1.1 | .7 | | .3 | | .05 |
| R14532 | CLEAT CAL | <100 | 36 | 4 | <.3 | 13 | <1 | 1.52 | 2.4 | 1870 | <.1 |
| R14533 | SULFATE EFFL | 200 | 55 | 32 | .2 | 4 | <2 | 5.34 | 2.1 | 60 | .2 |
| R14534 | CLEAT BARITE | <100 | 24 | <5 | <.5 | .02 | <1 | .31 | <5 | 12300 | <.1 |

| SAMPLE | DESCRIPTION | TB (PPM) | TH (PPM) | TI (%) | TL (PPM) | U (PPM) | V (PPM) | W (PPM) | YB (PPM) | ZN (PPM) | ZR (PPM) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C20368 | VITRAIN | .06 | .3 | .01 | | .5 | | <.3 | .3 | 3.4 | |
| C20369 | VIRTAIN | .09 | .3 | | | 1.0 | | .2 | .3 | 2.6 | |
| C20370 | VITRAIN | .08 | .3 | .01 | | .5 | | .5 | .2 | 22 | |
| C20371 | VITRAIN | .11 | .4 | | | <.5 | | .6 | .2 | 71 | |
| R14532 | CLEAT CAL | .6 | <.1 | <.01 | <1.0 | <2 | 3.9 | <1 | 1.6 | 1420 | 17 |
| R14533 | SULFATE EFFL | .2 | 5 | .09 | 1.2 | <1 | 15 | <2 | .5 | 68.9 | 40 |
| R14534 | CLEAT BARITE | <.1 | <1 | .27 | <1.0 | <2 | <3 | <1 | <.5 | 5.0 | 96 |

*CAL=calcite; EEFL=Fe

direct measure of what elements are organically associated. The samples of vitrain analyzed unfortunately do not come from coal samples for which calculated organic affinities are available. They do, however, come from four different areas of the Illinois Basin and hence should be a good approximation of the range of concentrations expected in vitrain samples.

Arsenic, Br, Co, Cu, Fe, Ni, Pb, Se, U and Zn occur at concentrations in the vitrains comparable to the levels found in the light specific gravity fractions; this implies that these elements are incorporated in coal macerals early in the coalification process as included mineral grains or associated with original plant materials. The levels of the other elements present in the vitrain samples are lower than their concentrations in the light specific gravity fractions. This group includes the rare-earth elements, as well as Al, K, Si, Na, Rb, and Cs. These elements may be in association with clay minerals that remain in the light specific gravity fractions, but portions of these may also be dispersed through the coal macerals in an organic association (section VII of this report).

The chemical results for the hand-picked minerals indicate a number of expected associations. The cleat calcite sample contained expected high levels of Mn, Sr and Ba. Also included in the calcite sample were traces of other minerals, kaolinite type clay and pyrite. The presence of these minerals in the calcite explains the presence of As, Zn, and Fe. The second sample was a mixture of two hydrated phases of iron sulfate, formed in the coal by oxidation of pyrite coal. Iron, Co, Cu, Ni, As, Mn and Na were at elevated concentrations in this sample. The third sample was a relatively pure barite which also contained 1.23 percent strontium.

The elements B, Be, Ge, and U, which generally show strong organic associations, were not detected in the three mineral samples; however, Sb, V, and P, which also often show organic association, were present in the mixed iron-sulfate sample.

# VII. PETROGRAPHIC (SEM-EDX) CHARACTERIZATION

## INTRODUCTION

Elements occur in coal in organic (maceral) association and in inorganic minerals. Bulk chemical techniques are used to identify elements in coal; however, these techniques do not allow the determination of the distribution of elements (either organically bound or as minerals) at the level of specific grain locations. Associations which may exist among various elements in macerals and minerals can be studied by means of a scanning electron microscope equipped with an energy dispersive x-ray analyzer.

## METHODS AND MATERIALS

In this study the scanning electron microscope (SEM) was combined with an energy dispersive x-ray (EDX) analyzer to determine the distribution of detected elements. SEM images of microsurfaces show mineral and maceral morphologies and associations. EDX peak presence and the relative peak intensities provide a qualitative composition of the microsurfaces imaged by the SEM. The combined SEM-EDX analyses yield information that is not otherwise available.

Two types of coal specimens were studied (table VII-1): blocks and granular pellets. The blocks were cut to have a surface area about 1 cm$^2$ normal to the bedding of the coal. The blocks had been previously studied with an optical microscope and characterized as typical of the bright banded mineral-rich lithotype of coal (unit IIIB) by Johnson (1979). They were from coal beds which are stratigraphically encompassed by sample C20983, which is included in the bench sets discussed in sections V and VI of this report. The granular pellets were epoxy mounts made of the 1.6 gravity sink fraction after the fraction had been crushed to pass a 60M screen. These high gravity samples were splits of those chemically analyzed in the washability tests (W3 and W4) of the Herrin Coal, and they were expected to be enriched in trace elements possibly concentrated in some trace mineral grains.

In petrographic studies of coals using an optical microscope, the organic constituents are classified into three major maceral groups (vitrinite, liptinite, and inertinite, table II-2). Stanton and Finkelman (1979) were able to distinguish these groups on polished coal pellets in SEM back-scattered mode; however, in a previous study (unpublished) we had found it difficult to evaluate polished specimens of coaly materials in this mode as well as in the secondary emission mode. To improve the image quality we etched our specimens in the low temperature asher (LTA). A period of 30 minutes in the LTA effectively etched the most reactive organic constituents and produced a much improved quality of image in the SEM. The etched specimens were carbon coated prior to the SEM studies.

**TABLE VII-1.** SEM specimens studied for mineral, maceral and trace element associations.

| Specimen No | Specimen Type | Sample No | Source |
|---|---|---|---|
| 814 | Block | CP1931-1E* | Upper, unit IIIB, Column 6, Mine 866 |
| 815 | Block | CP1931-3H-1* | Middle, Unit IIIB, Column 6, Mine 866 |
| 816 | Block | CP1931-3H-2* | Middle, Unit IIIB, Column 6, Mine 866 |
| 817 | Block | CP1931-3H-3* | Middle, Unit IIIB, Column 6, Mine 866 |
| 818 | Granular Pellet | C20666 | 1.6 Sink, Mine 928 |
| 819 | Granular Pellet | C20690 | 1.6 Sink, Mine 877 |

*Stratigraphically equivalent to nearby sample C20983, also from unit IIIB. Specimens described by optical microscopy; units defined by Johnson (1979).

Each specimen was first optically studied with a petrographic microscope, by using a 10x dry or a 50x oil objective lens. Maceral particles and some mineral grains were thereby identified and mapped. When oil was used it was subsequently removed with a quick xylene rinse, followed by soapy hot water, photoflo wash, and hot water rinse. After air drying, the specimen was made ready for SEM study by the LTA etching operation followed by carbon coating under vacuum.

A Cambridge SEM equipped with a Nuclear Diodes EDX analyzing system (located at the University of Illinois Center for Electron Microscopy) was used for this study. Maximum x-ray signal was achieved by operating the electron gun at 20 KV and adjusting the specimen orientation and condenser potentials in the secondary emission mode. Microphotography required slightly different orientations and condenser settings.

## DATA GENERATION AND ANALYSES

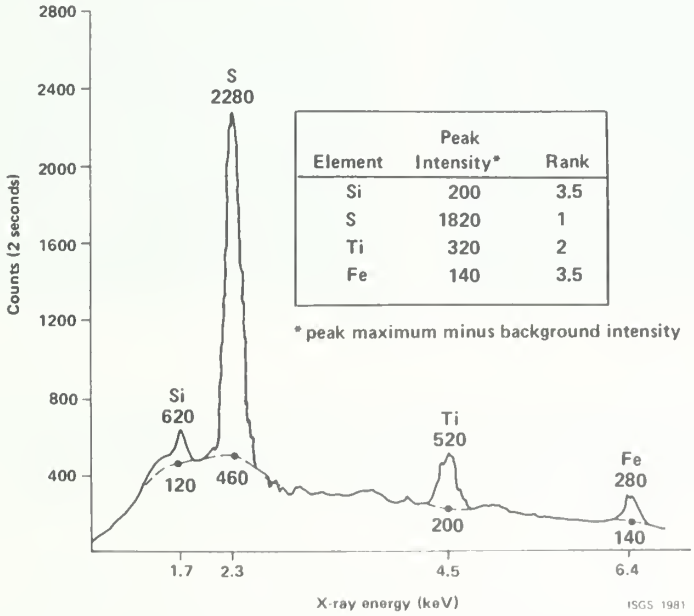
Carbon coating does not interfere with the EDX analysis, but in our study it limited the useful magnification to about 5,000X. With the equipment used, only a few of the trace elements known to occur in the samples were sufficiently excited by the operating voltage of the SEM. Given the composition of the coals it was possible to detect only the elements with atomic numbers from 11 (Na) to about 30 (Zn) plus Ba. For the elements detectable by the EDX system, the system generally detects them at concentrations as little as a few percentage points or less within the area excited by the electron beam of the SEM (Finkelman, 1978). However, if the element is not widely dispersed within the specimen it may go undetected, given the time constraints on the analyst to study the specimen at ultra-high magnification.

The SEM-EDX system allowed only qualitative x-ray analysis. The relative composition of the elements detected was determined from observed peak heights in counts per second, corrected only for the background signal. The analyses were restricted to relative measures, such as ranking of peak size, and frequency of peak occurrence. However, for sulfur distribution studies, the absolute counts of sulfur and the ratio of iron and sulfur peak heights were also considered.

The duration of signal collection varied among particles. Observed mineral grains always gave strong signals, and compositional presence or absence as well as relative peak size could be quickly determined; 0.8 minute was usually more than sufficient to obtain absolute counts in the range of 10,000. The small amounts of elements detectable in macerals by the EDX system meant that the spectra of macerals had to be collected for longer times. Up to four minutes was needed to obtain absolute counts in the range of 1,000 from most maceral particles. EDX spectra for macerals were taken only from homogeneous areas within the analyzed particles.

The frequency of each element detected in each of the group macerals was computed from the raw data. In addition, a scheme was used to determine a peak intensity ranking value of each element in the spectrum taken of an identified maceral particle (the procedure is illustrated in figure VII-1). An average ranking was determined for each of the maceral groups in each specimen by dividing the sum of the individually determined rank values by the number of spectra within each group. An overall elemental ranking value by maceral group was similarly determined from spectra taken from all of the specimens studied. Note that from the procedures for determining the ranking values (fig. VII-1) the more intense peaks have a lower numerical ranking value; likewise, a large numerical ranking value is determined from low peak intensities.

Assignment of peaks to either barium or titanium was difficult unless they were quite abundant, because of peak overlap. In our studies inseparable



| Element | Peak Intensity* | Rank |
|---|---|---|
| Si | 200 | 3.5 |
| S | 1820 | 1 |
| Ti | 320 | 2 |
| Fe | 140 | 3.5 |

* peak maximum minus background intensity

FIGURE VII-1. Procedure for assignment of ranking values: S, with highest peak intensity, is assigned a rank of 1; Ti, the second most intense peak, a rank of 2; Si and Fe, both with low peak intensity, are both assigned a rank of 3.5.

barium/ titanium peaks were treated as one "element"; however, identifiable peaks of either element were separately recorded.

## RESULTS AND DISCUSSION

LTA-etched block samples were easier to study than were the etched granular pellets, because particles in the surface of these pellets were too small for bedding and other natural alignment features of the coal components to be observed. On granular pellets, relocation of areas previously (optically) mapped was very difficult. It is suggested that larger grains such as the 20 mesh particles be used for future work.

### Mineral matter characterization

Minerals identified by the SEM-EDS method were illite and kaolinite, pyrite, calcite, quartz, feldspar, and apatite; clays are the most common. In block specimens most of the clays are draped about other mineral and maceral grains or occur between vitrinite microlaminae (pl. VII-a and j). Clay flakes tend to be oriented parallel to the bedding of the coal and similar microlaminar planes within macerals. Kaolinite (pl. VII-e) is distinguishable by its EDX spectra of about equal intensities of Al and Si peaks; illite by its Al and Si together with a relatively intense K peak. Identification of the expandable mixed-layer clay minerals and of chlorite by the SEM-EDX method would require a considerable research effort beyond the scope of this project.

Pyrite occurs in several forms, as large, irregular masses (pl. VII-a), framboids (pl. VII-b) and as single octahedral grains. Single calcite crystals also occur (pl. VII-c). Pyrite (in its several forms), calcite, or occasionally kaolinite and/or illite types of clay minerals are distributed as isolated grains or as massive filling in cleat fractures, plant cell lumens, and other cracks and voids.

Quartz grains in the coals studied are silt-sized (4-20 μm dia.), semi-angular and oblong-rectangular grains, with occasional marginal indentations (pl. VII-d).. Our observations indicate that these grains have not experienced marked fluvial rounding, but most of the grains occur in aggregated partings oriented more or less parallel to the bedding which suggests fluvial deposition. Finkelman and Stanton (1978) found only authigenic quartz in samples of the lower part of the Pittsburgh No. 8 seam, Washington County, Pennsylvania. Quartz occurred there as doubly terminated euhedral crystals, as intergrowths with pyrite, and as filling in semifusinite pores.

Other silt-sized particles are abundant (except for apatite, which occurs only rarely) as isolated grains in our specimens from heavy fractions of washed coals. Apatite is the rarest mineral, identified by its phosphorus content. Plate VII-f shows one such occurrence, an elongate apatite grain, free of organic matter, in a 1.60 gravity sink fraction specimen. In contrast, our other observed phosphorus occurrence, illustrated in plate VII-g is that of abundant 1-2 μm grains scattered in a vitrinite particle. These grains yield spectra with strong phosphorus peaks and traces of potassium and sulfur. The latter element is

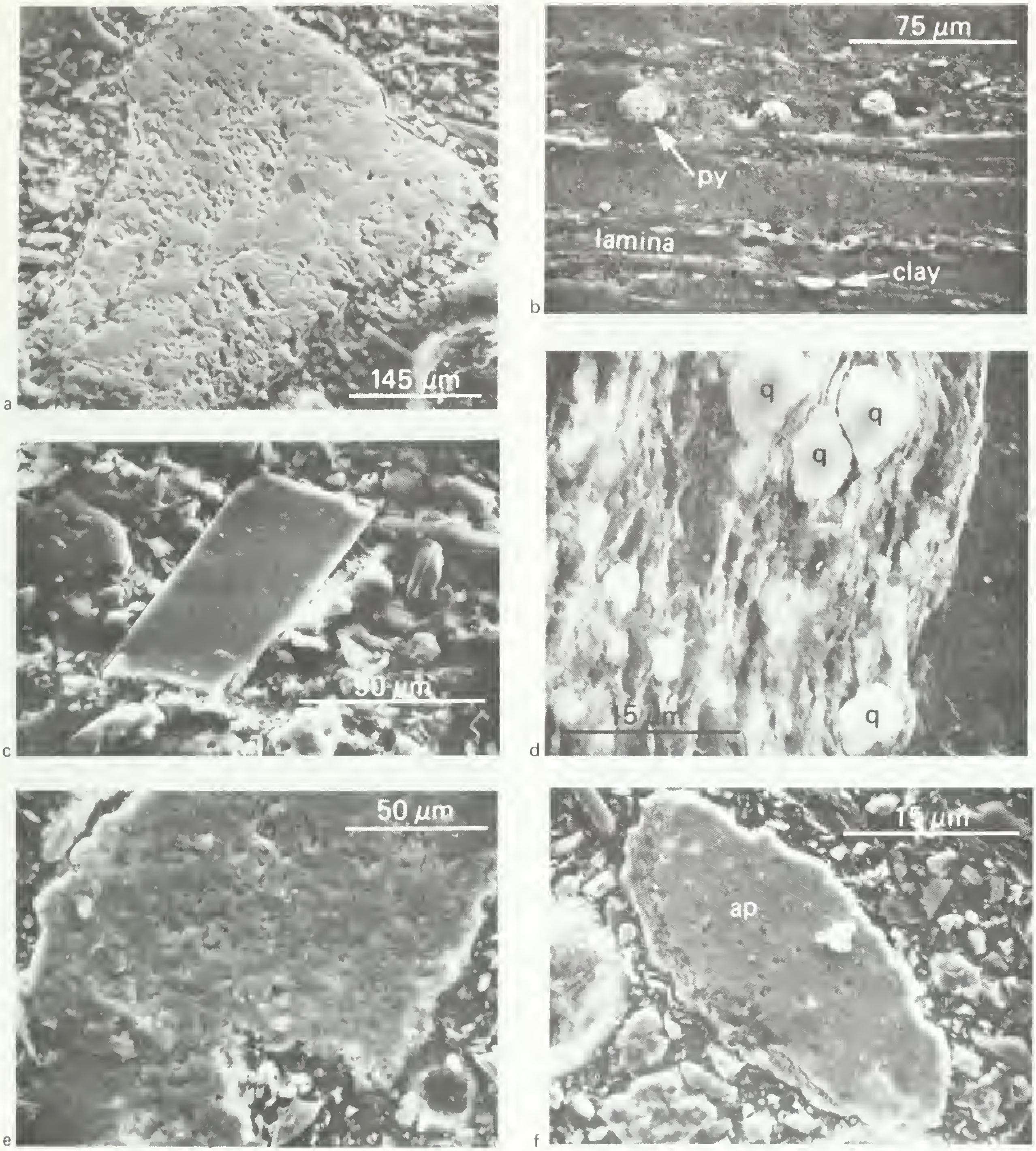


**PLATE VII.** SEM micrographs of polished and LTA-etched surfaces of minerals and macerals in coals. The very dark gray matrix on granular specimens is epoxy.

(a) Massive, porous, pyrite grain in granular specimen 818, with smaller particles of various composition; (b) framboids of pyrite (py) and flakes of clay inclusions in and associated with various macerals (block specimen 816); (c) cleavage rhomb of calcite in specimen 818; (d) subhedral quartz grain (q) and enclosing clay matrix associated with vitrinite (dark area on right) in specimen 818; (e) large particle of kaolinite in specimen 818; (f) apatite (ap) with smaller particles of various composition in specimen 818.

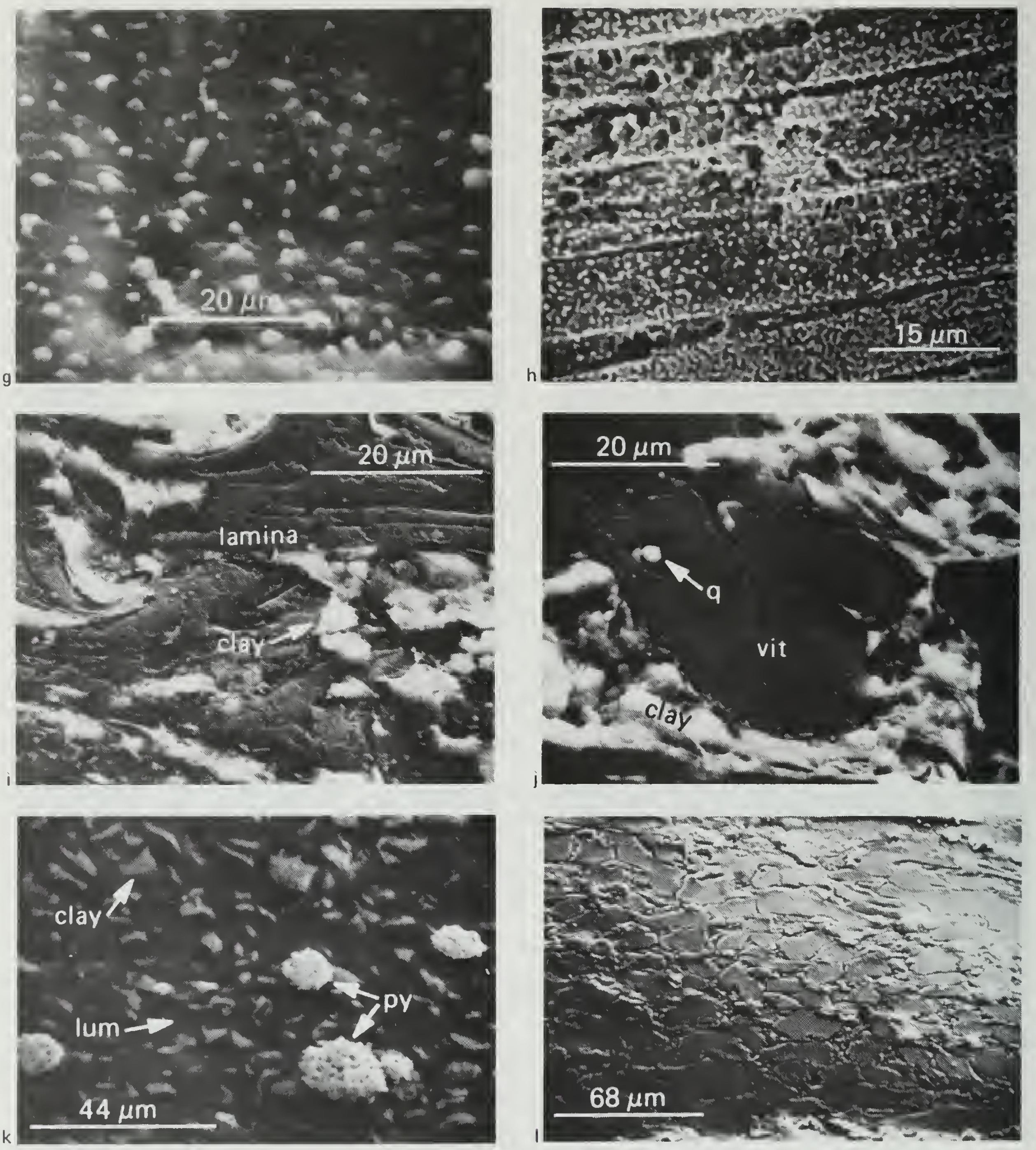


**PLATE VII.** *(continued)*

(g) Appatite inclusions in vitirinite in block specimen 816; the large square is an artifact of the SEM operation; (h) detail of typical etched surface of vitrinite showing its laminated structure in block specimen 814; (i) swirled microlamina in vitrinite with associated clay inclusions in block specimen 815; (j) vitrinite (vit), in rounded particles with quartz (q) inclusion, enclosed by clay materials, in specimen 815; (k) vitrinite with collapsed cell lumens (lum, barely resolved) and abundant clay and pyrite (py) mineral inclusions, in specimen 815; (l) vitrinite with cell-like structures in block specimen 814.

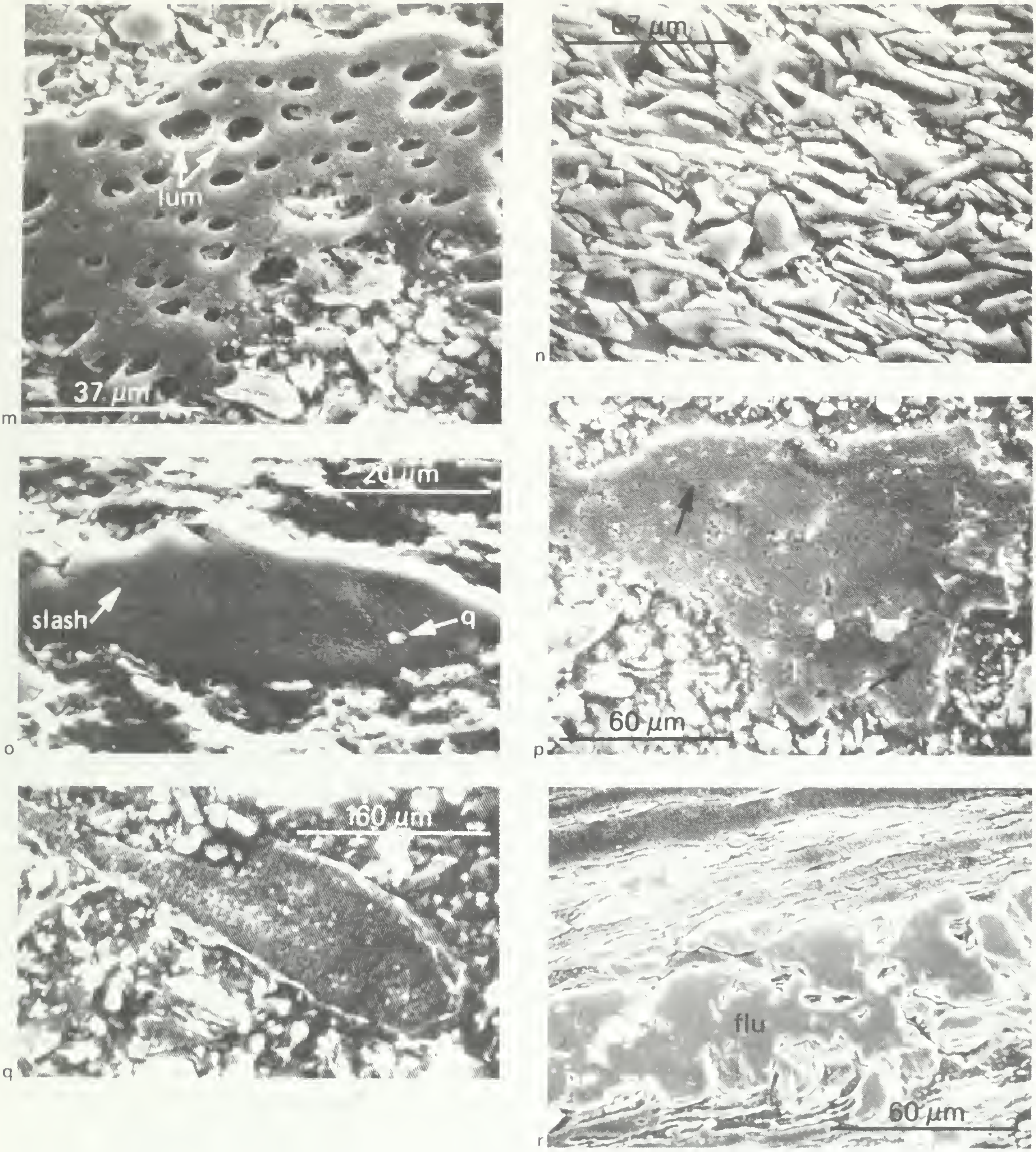


PLATE VII. *(continued)*

(m) Fusinite showing cell lumens (lum) in specimen 818; (n) crushed fusinite in block specimen 817; (o) macrinite type of inertinite particle with inclusion of quartz (q) set in a clay-quartz matrix, in specimen 815; (p) mixed vitrinite and liptinite (perhaps microsporinite) particle in specimen 818; (q) part of a sporinite type of liptinite particle in granular specimen 819; (r) fluorinite (flu) type of liptinite interlayered with clay minerals and laminated vitrinite (?) in specimen 814.

interpreted as part of the vitrinite matrix. Thus, each of the minerals identified in this study may occur as inclusions within various maceral particles (pl VII-k and o).

## Maceral characterization

*Vitrinite.* Vitrinite most commonly shows a uniformly pocked or etched surface produced during the LTA etching process. The extent and degree of pocking varies. Plate VII-h shows a pocked area of laminated vitrinite, which, prior to LTA etching, appeared homogeneous at 500X through an oil immersion lens. Vitrinite layers vary in thickness and outline, sometimes swirling (pl. VII-i ), occasionally forming ovoid shaped particles (pl. VII-j ). This latter type of vitrinite is not as pocked as other vitrinite forms.

Several unusual vitrinite structures were seen. Plate VII-k shows collapsed cell structure, with the cell lumina outlines lighter in color than the cell walls. Clay minerals are associated with these structures as are framboids of pyrite. Plate VII-l shows distorted remnants of cell structure; optically, under oil, this area showed mottled vitrinite. At magnifications higher than that shown, each "cell" has a pocked surface.

*Inertinite.* In the SEM, the common macerals of the inertinite group, semifusinite, fusinite, and macrinite all have a smoother texture and a distinct positive relief relative to vitrinite, because of the greater hardness of inertinites, noted previously by Stanton and Finkelman (1979). Semifusinite and fusinite were not always distinguishable from one another, but both are distinguishable by their characteristic shape and relief from macrinite on the LTA-etched specimens. Fusinite, as in plate VII-m, always displays some cell structure. The open areas representing cell lumina are commonly filled with pyrite or calcite. Plate VII-n shows masses of broken cellular material which form the bulk of the observed fusinite and/or semifusinite. In the SEM the LTA etched surfaces of macrinite particles range from smooth to slightly pocked (pl. VII-o). Slashes in the surface are frequent, and inclusions of quartz (pl. VII-o) and kaolinite occur.

*Liptinite.* Liptinites were rarely distinguishable from one another in our specimens and from vitrinite on LTA-etched surfaces in the SEM secondary electron emission mode. Their texture, spectral composition, or gray tone are all nearly identical in the SEM to that of vitrinite. Elongate particles with rounded ends and somewhat higher relief distinguish certain sporinite macerals. Such high liptinite relief relative to vitrinite has been previously seen by Stanton and Finkelman (1979). Plate VII-p includes vitrinite and resinites, swirled about one another. Plate VII-o shows heavy etching on a spore surface. Plate VII-r shows fluorinite occurring in an irregular bedding surface in a block specimen; this is the only occurrence of fluorinite that we observed. This one is characterized by having a relatively high positive relief, an irregular and somewhat globular structure, and a smooth texture on LTA-etched specimens.

### Elemental frequency and ranking in macerals

At the start, we wish to restate that the elements we observed by SEM-EDX and discussed below were noted from areas within maceral particles that were free of observed inclusions of mineral grains. We thus provisionally attribute the results as indicative of the organically associated elements. However, we acknowledge that some of the EDX signals observed may be derived from ultra-small mineral inclusions, too small to be resolved at 5,000X (less than ca. 0.05 μm). The findings of Strehlow et al. (1978) and of Harris and Yust (1979) do confirm that mineral grains as small as 0.004 μm might be present as mineral grains undetected by our methods. In particular, in the size range 0.004 μm-0.100 μm (1) Strehlow et al. (1978) found principally illite, kaolinite, quartz, and calcium carbonate, but *little* pyrite; (2) Harris and Yust in a limited number of samples found the presence of elements of atomic number, 11 (Na) or greater, *except* for sulfur, always correlated with presence of ultrafine mineral grains. Thus, it is possible that some of our results could be derived from minute mineral inclusions on and just under the surface, which contributed to the x-ray signal (Goldstein and Yakowitz, 1975). However, our SEM-EDX system as operated generates x-rays from within the macerals, and as the maceral particles are always much larger, these inclusions should be of secondary importance.

*Heterogeneity among specimens.* Heterogeneity characterizes the elemental composition of the macerals analyzed in both the granular specimens (high density samples) and the block specimens of in-situ coal layers. The variability suggests major differences in microenvironmental chemistries of the coal formation conditions.

Chlorine in vitrinite varies considerably as indicated below.

Chlorine EDX signal from vitrinites

| Specimen | Total # Spectra | Frequency | Average peak intensity |
|---|---|---|---|
| 814 | 11 | In more than half the spectra | 4th largest peak |
| 815 | 5 | In fewer than half the spectra | Very small peak (7th) |
| 816 | 6 | Not detected | Not detected |
| 817 | 9 | In fewer than half the spectra | 2nd largest peak |
| 818 | 15 | Not detected | Not detected |
| 819 | 3 | In all spectra | 2nd largest peak (S also) |

Iron is a small but persistent peak in vitrinite spectra on specimens 816 through 819, but is absent from 814 and 815.

No major differences were observed in elemental compositions between the inertinites; semifusinite and fusinite could not be routinely distinguished from each other. Nevertheless, compositional variation of inertinites in different specimens is deemed important: silica is more abundant relative to sulfur in the inertinites of two of the three block specimens (815 and 816), than in all the others.

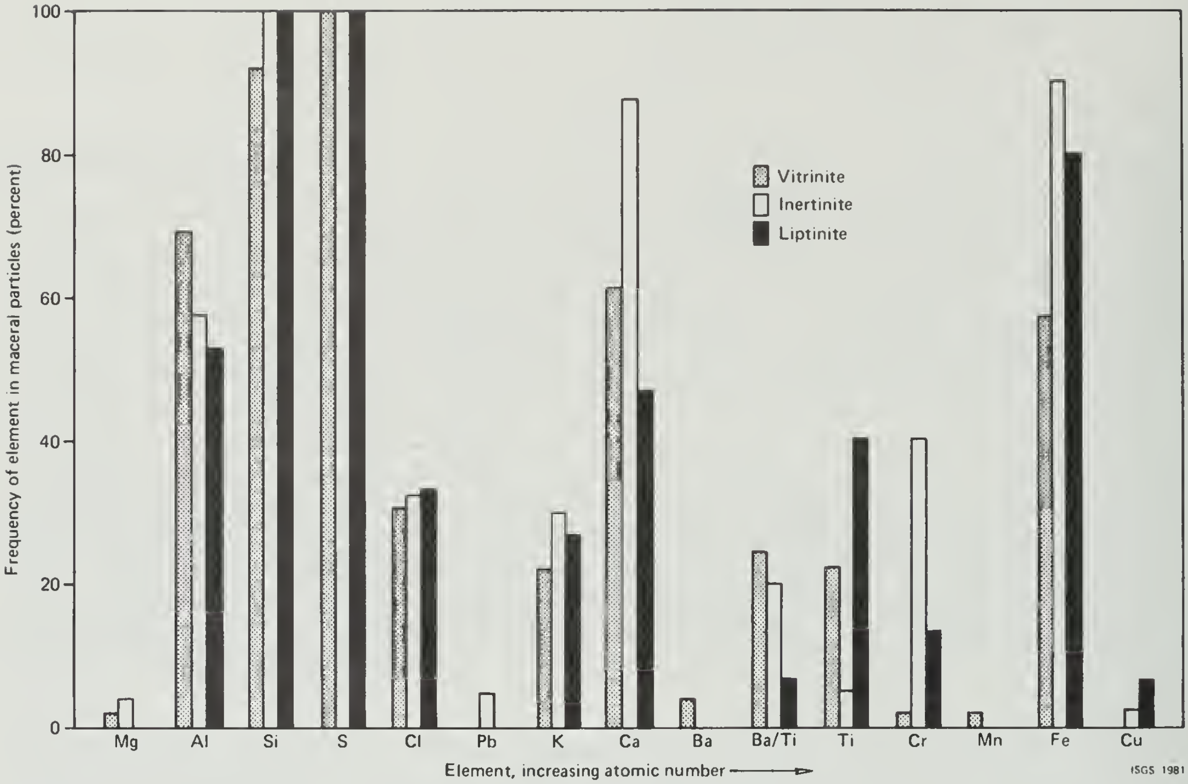


FIGURE VII-2. Frequency of elements detected in maceral groups (all specimens).

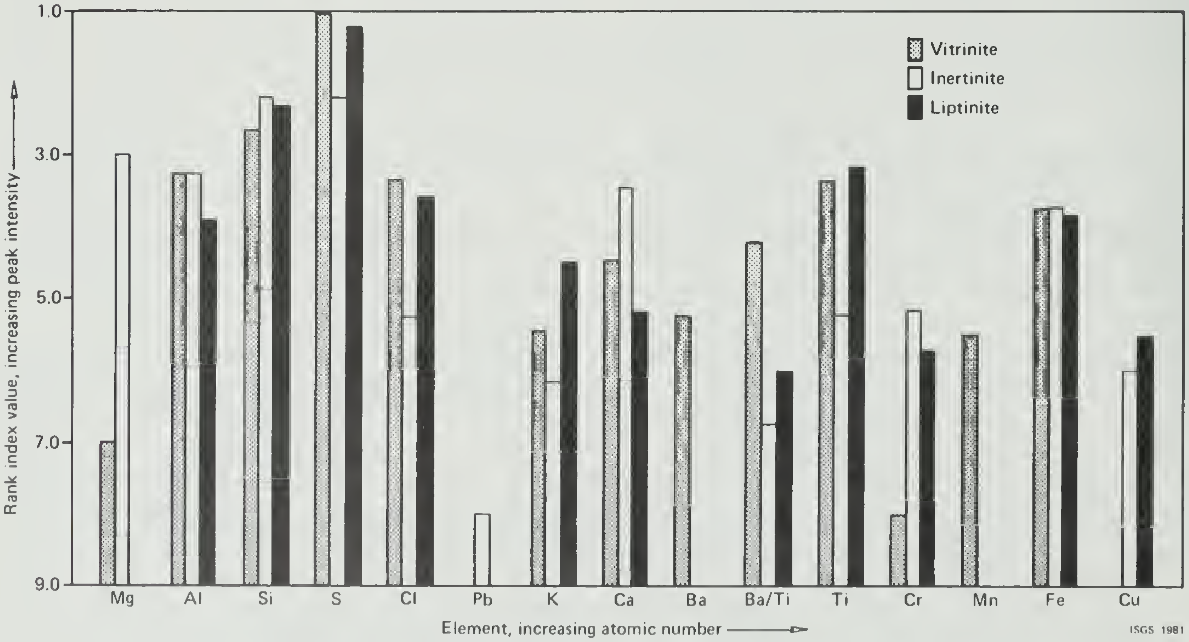


FIGURE VII-3. Ranking values of elements detected in maceral groups (all specimens).

Liptinites were identified in only three specimens, 814, 818, and 819. Of the more important elements in the liptinites, iron appears to be less uniformly distributed than silicon and sulfur but more so than the other elements in the specimens.

*Frequency and ranking of elements by maceral group.* The SEM-EDX spectra from all the specimens were evaluated and the frequency of the elemental peaks was determined for the three maceral groups. These results are shown in figure VII-2. Magnesium was detected in only about 2 percent of the vitrinite and the inertinite particles tested, and it was not detected in any liptinites; furthermore, lead, barium, manganese and copper were observed in only certain macerals. In contrast, aluminum, silicon, sulfur, and iron were observed in more than half of all the spectra in all three maceral groups. Calcium was very frequently observed in both vitrinites and inertinites but less so in the liptinites studied. Chromium appears unique in that it is enriched in inertinite particles; the data suggest that potassium, calcium, and iron are also enriched in inertinites, but to lesser degrees.

The relative abundance of the elements is indicated by the ranking values (fig. VII-1). The ranking values of elements in the three maceral groups are shown in figure VII-3. Here again, silicon and sulfur head the list with the lower ranking values (the largest average peak heights); aluminum, chlorine, calcium, titanium and iron are also very important peaks on the spectra. Of special interest is the relative difference in ranking of magnesium: low abundance in vitrinite and high abundance in inertinites. Manganese, observed only in vitrinites, averaged a lowly 5th in ranking of peak intensity on the spectra. Barium occurrences were quite similar in frequency and ranking to that of manganese.

Comparison of the frequency and ranking values of the elements between the block specimens and the high-gravity specimens revealed much the same results for all of the elements except the following: aluminum was enriched in the maceral components of the blocks relative to the macerals in the high gravity specimens, barium (not including Ba/Ti peaks) was detected only in the blocks, and titanium and iron were distinctly more abundant in the high-gravity fractions.

These results can be compared with those of Raymond (1979), who used an electron microprobe to make quantitative analyses of several elements in identified macerals particles. His specimens represented 18 different locations of coal in the United States, ranging in rank from low-volatile bituminous to subbituminous C, and in age from Pennsylvanian to Paleocene. Raymond separated specimens into four levels of increasing weight percent of element in the coal (0.02, 0.05, 0.10, and 1.0 wt %). The qualitative nature of our data and the fact that it was not possible to convert them accurately to a weight percent basis, enable comparisons to be made only in a limited way. Furthermore, Raymond's study included more maceral types than our study. His vitrinite and pseudovitrinite are equated with our vitrinite, his fusinite and semifusinite with our inertinite, and his sporinite and resinite with our liptinite. Raymond's macrinite and micrinite have no counterparts in the current study and are excluded from the comparison of the two studies' results. The comparisons are summarized as follows:

| | Raymond (1979) | This study | |
|---|---|---|---|
| Element | % of element | Frequency | Peak intensity (Inverse of rank value) |
| Mg | I > L > V | I ≥ V | I > V |
| Al | I ≃ L ≥ V | (V > I ≥ L)* | (V ≃ I > L)* |
| Si | I > L ≥ V | I ≃ L ≥ V | I ≃ L ≥ V |
| S | V ≃ L > I | (V ≃ I ≃ L)* | V ≃ L ≥ I |
| K | L > I > V | I ≥ L ≥ V | (L > V > I)* |
| Ca | I > V ≥ L | I > V > L | I > V > L |
| Ti | V > I   L | (L > V > I)* | (L ≃ V > I)* |
| Fe | I ≃ L > V | I > L > V | (V ≃ L > I)* |

*indicates poor pattern match.

About half of the trends we observed were also apparent in Raymond's data. For aluminum, however, the trend changes substantially with Raymond's weight percent concentration. At 0.1 and 1.0 percent, his data indicate Al has I ≃ L ≥ V (this is the sequence listed above); but at 0.05 percent, his data indicate Al has V ≥ I ≃ L, which is the same pattern our work shows.

### Iron-sulfur ratios

The EDS spectra were evaluated for the Fe/S ratios obtained from macerals and from identified grains of pyrite. The results are shown as smoothed histograms in figure VII-4, where the ratios are multiplied by 100. The results from the three maceral groups overlap considerably; however, vitrinite and liptinite tend to have lower ratios—higher relative amounts of sulfur—than do the inertinites. Furthermore, some of the data from inertinite particles overlap that of a few grains thought to have been pyrite. This suggests that tiny grains of pyrite were associated with these inertinite particles, but they were not observed in our studies. A very high percentage of the pyrite grains gave Fe/S (100) values of 38. Given a stochiometric composition for these pyrites ($FeS_2$), the factor 50/38 could be used to adjust observed ratios of pyrites in subsequent studies to obtain quantitative analyses.

### Apparent organic sulfur in macerals

An analysis of the SEM-EDX data for sulfur was based on the EDX peak intensity in the spectra, corrected only for background and normalized to counts per minute. The results of the analysis in terms of the three maceral groups in the specimens are shown in table VII-2. The liptinites showed a wide spread of sulfur data, but on the three specimens identified,

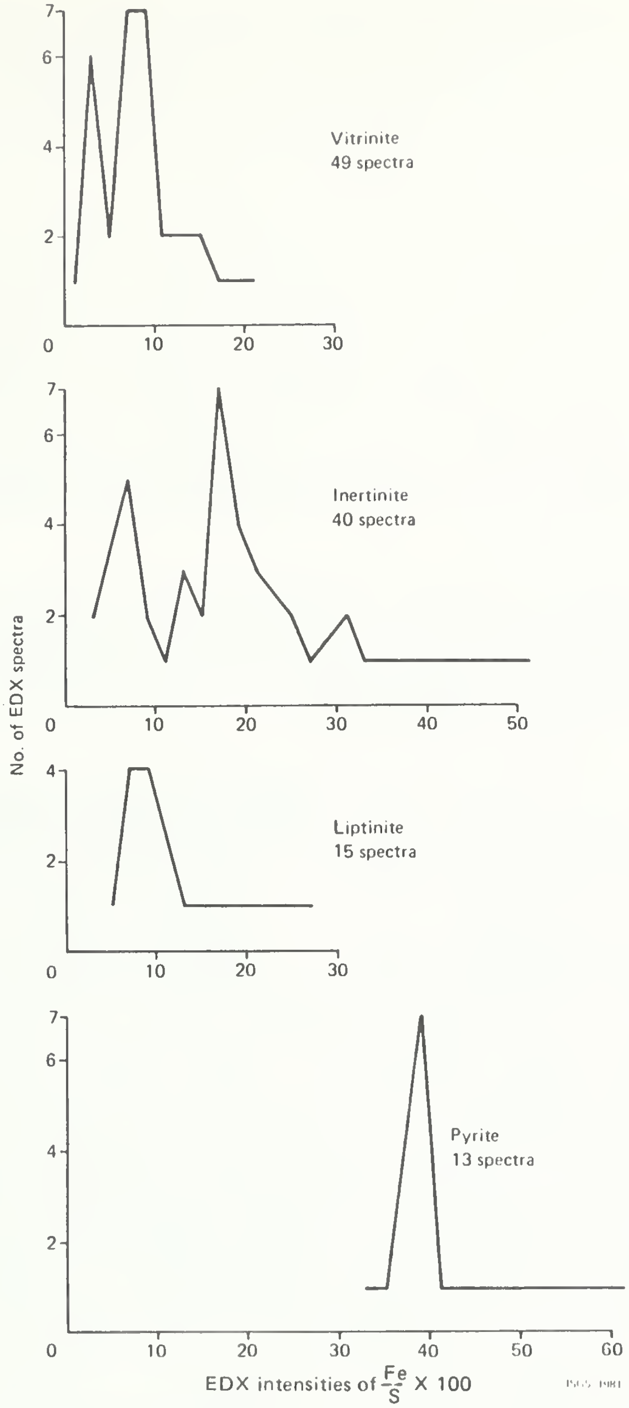


FIGURE VII-4. Observed intensity ratio (Fe/S) in macerals and in pyrite grains. Curves shown are smoothed-frequency histograms (class interval 2%) with zero frequency points deleted.

they contained higher amounts of sulfur (in this case apparent organic sulfur) than did the associated vitrinites. The inertinite macerals appear to have generally the least amount of apparent organic sulfur. This is the same trend found by Harris, Yust, and Crouse (1977) and Raymond and Gooley (1979), in their surveys, but Minkin et al. (1979) found that the amount of sulfur in liptinite was more similar to that in vitrinite; in their specimens, inertinite organic sulfur was about half that found in vitrinite.

**TABLE VII-2.** Apparent organic sulfur (sulfur not associated with pyrite) in macerals.

| | Apparent organic sulfur in counts per minute mean (number of particles tested) and standard deviation | | |
|---|---|---|---|
| Specimen | Liptinite | Vitrinite | Inertinite |
| 814 | 2040 (3) 1660 | 1150 (11) 750 | — |
| 815 | — | 1020 (5) 610 | 690 (15) 960 |
| 816 | — | 2550 (6) 740 | 510 (2) 90 |
| 817 | — | 8900 (9) 7250 | 1670 (7) 1650 |
| 818 | 1110 (8) 830 | 720 (15) 450 | 270 (15) 220 |
| 819 | 300 (4) 150 | 150 (3) 30 | 600 (1) — |

## Organic association of certain elements

The qualitative and semiquantitative elemental data on macerals given in this section can be summarily stated as listed in table VII-3. For this table we have grouped our observed frequency of occurrence and ranking values into descriptive groups as follows:

| Frequency of detection | | Ranking value (inverse of relative peak intensity) | |
|---|---|---|---|
| Rare | 1- 24% | Trace | 8.0-5.2 |
| Common | 27- 61% | Minor | 4.6-3.0 |
| Persistent | 69-100% | Major | 2.7-1.1 |

The gaps between these ranges were breaks in the observed distribution.

In our study, the high frequency of occurrence of certain elements detected by SEM-EDX methods within maceral particles that appear free of minerals is significant. Silicon, for instance, occurred in more than 90 percent of all macerals tested, aluminum in more than 50 percent, calcium in 45 to 90 percent (depending on the maceral), iron in more than 60 percent, chlorine in 30 percent, potassium in 25 percent, and titanium in 5 to 40 percent (depending on the maceral group). Additionally, if we consider the same elements detected by our SEM-EDX system and look at their average weight percent (or ppm values) remaining after acid leaching of raw Herrin Coal (Kuhn et al., 1980), we can divide these remnant values by their appropriate atomic numbers and rank the dividends. This produces a ranking of importance by number of organically associated atoms. The ranking so produced is very similar to that generated by our data when spectra of all three maceral groups are combined to make a grand total elemental importance ranking.

It is well known that about half the sulfur in Illinois coals is organic sulfur, in that this type is bound in some way to the carbon of the macerals. However, uncertainty remains as to whether or not the other elements frequently detected are so bound. The SEM data of Strehlow et al. (1978) and of Harris and Yust (1979) suggest that the presence of all elements greater than 11 in atomic weight (Na and higher), except for sulfur, can be accounted for by presence of ultrafine mineral grains. Data from Kuhn et al. (1980) similarly support mineral association, as shown by removability with acid leaching, of the bulk of elements in raw coal.

Kuhn et al. (1980) did state, however, that "minerals and exchangeable ions, or perhaps, chelated elements on the surfaces of the coal particles are the materials thought to be removed by acid leaching," and that other material is in the coal matrix. Although our data are not quantitative and although there may have been some ultra small—and therefore unobserved—mineral inclusions in some of the macerals tested, our data support the proposition that significant amounts of Si, Al, Ca, Fe, Cl, and Ti, in addition to the well known component of sulfur (organic S), do occur dispersed within maceral particles of the Herrin Coal and should be considered as organically associated.

**TABLE VII-3.** Summary: elemental frequency and relative abundance in coal macerals.*

| Element | Frequency of occurrence | Relative abundance |
|---|---|---|
| Mg | Rare in v + i (not noted in l) | Minor amounts in v + i (not noted in l) |
| Al | Persistent in v, common in others | Minor amounts in all macerals |
| Si | Persistent in all macerals | Major amounts in all macerals |
| S | Persistent in all macerals | Major amounts in all macerals |
| Cl | Common in all macerals | Trace amounts in i, minor in others |
| K | Rare in v, common in others | Minor amounts in l, trace in others |
| Ca | Persistent in i, common in others | Trace amounts in l, minor in others |
| Ti | Common in l, rare in others | Trace amounts in i, minor in others |
| Cr | Common in i, rare in others | Trace amounts in all macerals |
| Mn | Rare in v (not noted in others) | Trace amounts in v (not noted in others) |
| Fe | Common in v, persistent in others | Minor amounts in all macerals |
| Cu | Rare in i + l (not noted in v) | Trace amounts in i + l (not noted in v) |
| Pb | Rare in i (not noted in others) | Trace amounts in i (not noted in others) |

*Abbreviations: v = vitrinite; i = inertinite, l - liptinite.

# VIII. SUMMARY: FINDINGS RELATED TO ENVIRONMENTAL CONCERNS

More study will be required to evaluate all aspects of the significance of the large amount of data generated during the course of this 2-year project. The environmental importance of the analytical data is discussed in this section. The data base assembled consists of 67 chemical elements and compounds and 8 mineral components analyzed in 230 samples (164 samples representing the Herrin Coal at 88 locations and 66 samples representing the Springfield Coal at 56 locations.

## VARIATION OF ELEMENTAL CONCENTRATIONS

The elemental compositions of layers (benches) within the Herrin seam differed considerably from top to bottom as shown by the data reported in Section VI. These variations are based on data from 23 bench samples obtained from 4 locations within a single mine. The variations, represented by the ratio of the maximum/minimum compositional values exclusive of the shale partings, differ from element to element. Of those elements of potential environmental concern, barium varied most—up to 34 times its minimum value. Other elements follow in decreasing order of maximum/minimum (ratio): arsenic (17), zinc (17), thallium (16), lithium (15), antimony (10), thorium (10), and lead (10). All other elements of environmental concern have smaller compositional variations. However, nearly all samples in the bench study sets were too low in uranium and cadmium (<1 and <1.3 ppm, respectively, in the coal benches) to determine their variations. Nevertheless, it is important to note that while the elemental as well as the mineralogical variations between layers of the Herrin at one site tend to be much greater than the variations of whole seams samples from widely spaced locations, the variations between layers are without engineering significance because mining operations invariably take the whole seam.

Elemental composition of whole seams is measured by the mean of analytical results on individual whole-coal (channel equivalent) samples that represent the entire thickness of the seam at each collection site. The average elemental compositions of the Herrin and Springfield seams are listed separately in table VIII-1, in decreasing order of abundance. These results indicate that the two seams are similar in composition, but that the concentration of some elements differs significantly in some areas within the coal field (see sections V and VI for details). The tabulated averages show that sulfur (S) content is only slightly higher in the Springfield than in the Herrin. Of the elements of greatest environmental concern other than sulfur, boron (B) is next highest in abundance, followed by lead (Pb), arsenic (As) or molybdenum (Mo), etc. However, several of these elements show wide departures in individual samples from these mean values. The indicated differences in the average for zinc (Zn), barium (Ba), and phosphorus (P), are not significant, considering the large differences in assays observed for each of these elements.

The variation among whole-coal samples is indicated by the standard deviation (SD) of the elemental assays (tables VI-6 and VI-7), and also by the ratio of SD to the mean ($\bar{x}$) as listed for the two seams in table VIII-2. The element that has the highest variability relative to its mean value is cadmium (Cd). The standard deviation of the cadmium assays in the

**TABLE VIII-1.** Average concentrations of elements in the Herrin and Springfield Coals.

| Springfield | Minor Elements Average (%) | Herrin |
|---|---|---|
| * S | 3.7 | |
| | 3.5 | S * |
| | 2.7 | Si |
| Si | 2.3 | |
| Fe | 2.0 | |
| | 1.9 | Fe |
| | 1.4 | Al |
| Al | 1.2 | |
| | 0.7 | Ca |
| Ca | 0.66 | |
| K | 0.18 | K,Cl |
| Cl | 0.16 | |
| | 0.08 | Na |
| | 0.07 | Ti |
| Na,Ti | 0.06 | |
| | 0.05 | Mg |
| Mg | 0.04 | |

| Springfield | Trace Elements Average (ppm) | Herrin |
|---|---|---|
| | 310 | Zn |
| Ba | 230 | |
| Zn | 164 | |
| | 127 | B * |
| * B | 108 | |
| | 86 | Ba |
| | 75 | P |
| | 71 | F |
| P | 67 | |
| F | 63 | |
| Mn | 56 | |
| | 54 | Mn |
| | 39 | Zr |
| | 36 | Sr |
| V | 32 | |
| Zr | 31 | |
| Sr | 29 | V |
| * Pb | 28 | Pb * |
| | 21 | Li |
| | 20 | Cr |
| | 18 | Rb |
| Cr | 16 | |
| * As,Ni,Rb | 15 | Ce |
| Ce | 14 | |
| | 13 | Cu,Br |
| Cu,Br | 12 | |
| Li | 11 | |
| * Mo | 9 | Mo * |
| | 8 | La,As * |
| La | 7 | |
| Ge | 6 | Co |
| | 5 | Ge |
| Co | 4 | Ga |
| Ga | 3 | Sc |
| * Se | 2.6 | |
| Sc | 2.4 | Se * |
| | 2.3 | Th |
| | 2.1 | Cd * |
| Th | 2.0 | |
| Be | 1.5 | Be,U |
| Sm | 1.4 | I,Sm |
| * Cd,Tl | 1.3 | Cs |
| Sb,U,I | 1.2 | |
| Cs,Dy | 1.1 | Dy |
| | 0.9 | Tl,Sb |
| | 0.6 | Hf,Yb |
| Hf,W,Yb | 0.5 | W |
| Eu | 0.3 | Eu |
| * Hg,Tb,Ta | 0.2 | Tb,Ta,Hg * |
| Ag,In,Lu | 0.1 | Ag,In,Lu |

* Elements of greatest environmental concern.

Springfield Coal is 4.5 times their mean value of 2.1 ppm. Other metals of concern that have high variability are arsenic (As), zinc (Zn), barium (Ba), and lead (Pb). Those elements with significantly less variation are uranium (U), mercury (Hg), molybdenum (Mo), and selenium (Se). The high variability of these metals is shown to be related to local areas where sulfide mineralization has been observed (Section VI).

Comparisons of the average amount of the elements of environmental concern in all whole-coal samples tested (Springfield and Herrin) with those of other coals in the United States can be seen from the data compiled in table VIII-3. Lead (Pb) and boron (B) appear to be slightly higher in the Herrin and Springfield Coals than in the coals of other regions. Mercury (Hg) and antimony (Sb) are about the same in all the coals. Arsenic (As), beryllium (Be), and copper (Cu) tend to be slightly lower in the Herrin

**TABLE VIII-2.** Relative variation of elemental compositions of the Springfield and Herrin Coals, expressed as the ratio of the standard deviation to the mean.

| Herrin | $SD/\bar{x}$ (rounded) | Springfield |
|---|---|---|
| Cd | 4.50 | |
| | 3.40 | Cd |
| P,Zn | 2.60 | In |
| As | 2.40 | |
| | 2.30 | Ba |
| | 1.40 | Be |
| | 1.35 | P |
| | 1.30 | Zn |
| Pb | 1.25 | |
| Ba | 1.20 | W |
| In | 1.15 | Pb,Tl |
| Sb,Sr | 1.00 | As,Cl,Na |
| Cl,Na,Tl | 0.95 | I |
| Ge,U | 0.90 | Sm,Sr |
| | 0.85 | Cu,Zr |
| Li | 0.80 | Lu |
| W | 0.75 | Dy,Li,Mg,Ta,Tb,V |
| Hg,Mn,Zr | 0.70 | Br,Ca,Mn,U |
| | 0.65 | Ag,Ce,Eu,Hg,Yb |
| Ag,I,Mo | 0.60 | La,Sb,Se,Th |
| Br,Ca,Ga | 0.55 | Ge,Mo,Sc |
| Be,Ce,Co,La,Se,Sm | 0.50 | Co,K,Rb |
| Cr,Eu,F,Lu,Ni,Tb | 0.45 | Cs,Fe,Ga,Ni |
| Cs,Fe,Mg,Ta | 0.40 | Cr,F |
| Cu,Dy,Hf,Rb,S,Th,V,Yb | 0.35 | Al,B,Hf,S,Ti |
| B,Sc,Ti | 0.30 | Si |
| Al,Si | 0.25 | |
| K | 0.20 | |

TABLE VIII-3. Average amounts of elements of environmental concern in Herrin and Springfield Coals as compared with amounts in other U.S. coals.

| | Units | Herrin & Sprngfld | U.S. bituminous | Applachian region coals | Northern Great Plains coals | Rocky Mountain coals |
|---|---|---|---|---|---|---|
| Ag | ppm | 0.06 | -- | -- | -- | -- |
| As | " | 11. | 25. | 27. | 3. | 2. |
| B | " | 118. | 50. | 30. | 70. | 70. |
| Ba | " | 140. | 100. | 100. | 500. | 200. |
| Be | " | 1.5 | 2. | 2. | 0.5 | 0.7 |
| Br | " | 12. | -- | -- | -- | -- |
| C | % | 69.7 | -- | -- | -- | -- |
| Cd | ppm | 1.5 | 1.6 | 0.7 | 0.2 | <0.1 |
| Cl | % | .17 | -- | -- | -- | -- |
| Co | ppm | 5. | 7. | 7. | 2. | 2. |
| Cr | " | 18. | 15. | 20. | 5. | 5. |
| Cu | " | 12.5 | 22. | 24. | 8.3 | 9.1 |
| F | " | 68. | 77. | 80. | 45. | 70. |
| Ge | " | 5.5 | -- | -- | -- | -- |
| Hg | " | .16 | 0.20 | 0.24 | 0.09 | 0.06 |
| Li | " | 16. | 23. | 27.6 | 6.0 | 9.2 |
| Mn | " | 55. | 100. | 620. | 51. | 36. |
| Mo | " | 9.2 | 3. | 3. | 2.0 | 1.5 |
| N | % | 1.3 | -- | 1.3 | 0.9 | 1.2 |
| Na | ppm | 731. | 400. | 320. | 1820. | 1020. |
| Ni | " | 18. | 20. | 15. | 3. | 30. |
| Pb | " | 28. | 22. | 15.3 | 5.3 | 5.5 |
| S | % | 3.5 | 2.7 | 2.3 | 1.2 | 0.6 |
| Sb | ppm | 1.0 | 1.4 | 1.2 | 0.6 | 0.4 |
| Se | " | 2.4 | 4.6 | 4.7 | 1.0 | 1.6 |
| Sr | " | 33. | 100. | 100. | 150. | 100. |
| Th | " | 2.2 | -- | -- | -- | -- |
| Tl | " | 1.0 | -- | 4.9 | 2.7 | 3.6 |
| U | " | 1.4 | 1.9 | 1.4 | 0.9 | 1.6 |
| V | " | 31.6 | 20. | 20. | 10. | 15. |
| Zn | " | 250. | 53. | 20. | 25.6 | 9.9 |

and Springfield than in other U.S. bituminous coals; these three elements tend to be the least abundant in the coals of the northern Great Plains and Rocky Mountain regions.

## APPLICATION OF WASHABILITY RESULTS TO WASHED COAL PRODUCTS

For many years, a high proportion of raw coals produced from mines in the Illinois Basin has been cleaned to some degree by physical methods. The actual degree of removal of the dense mineral impurities and associated trace elements is not known. However, the four washability sample sets from the two seams studied here provide a way to estimate the amount of metals that will remain in cleaned coal products. Extensive studies of the sulfur removal in washability tests of Illinois coals (Helfinstine et al., 1971, 1974) showed that an optimum removal of sulfur was achieved for most samples tested when the cleaned product had a composition represented at the 80 percent recovery on the washability curves. The weight recovery of cleaned (washed) coal from existing preparation plants is known to vary; however, the fraction marketed to that mined is reported generally to vary from 70 to 85 percent. By use of the recovery level of

80 percent for the four washability sets tested for their trace elements (see table VI-4), the average reductions of elements from the 100 percent to 80 percent recovery levels were determined for the elements of interest. These results are listed in table VIII-4. The calculated reduction of 27 percent for S using this procedure is consistent with the 25 percent reduction that Helfinstine et al. (1974) found typical for the 65 samples they tested.

**TABLE VIII-4.** Estimated average concentration of elements of environmental concern in washed coals.

| | Average in Whole-coal (ppm) | †Average reduction in washed coals (%) | Estimated average in washed coals (ppm) |
|---|---|---|---|
| INORGANIC ASSOCIATED ELEMENTS | | | |
| *As | 11. | 60 | 4. |
| Ba | 140. | 41 | 83. |
| *Cd | 1.5 | ? | <1.5 |
| Li | 16. | 44 | 9. |
| Mn | 55. | 62 | 21. |
| *Mo | 9.2 | 44 | 5. |
| *Pb | 28. | 40 | 17. |
| Tl | 1.0 | 55 | 0.5 |
| Zn | 250. | 75 | 63. |
| MIXED ASSOCIATED ELEMENTS | | | |
| Ag | 0.06 | 30 | 0.04 |
| Co | 5. | 20 | 4. |
| Cr | 18. | 16 | 15. |
| Cu | 12.5 | 30 | 9. |
| F | 68. | 27 | 50. |
| *Hg | 0.16 | 21 | 0.13 |
| Na | 731. | 16 | 614. |
| *S(%) | 3.5 | 27 | 2.6 |
| *Se | 2.4 | 15 | 2. |
| Sr | 33. | 16 | 28. |
| Th | 2.2 | 21 | 1.7 |
| ORGANIC ASSOCIATED ELEMENTS | | | |
| *B | 118.0 | 3.9 | 113. |
| Be | 1.5 | 6.5 | 1.4 |
| Br | 12.0 | 0 | 12. |
| Ge | 5.5 | 0 | 5.5 |
| Ni | 18. | 4.5 | 17. |
| Sb | 1.0 | 6.0 | 0.9 |
| U | 1.4 | 0 | 1.4 |
| V | 31.6 | 8.6 | 29. |

†Calculated at the 80% recovery of coal from washability results, table 6.11.

*Metals of greatest environmental concern.

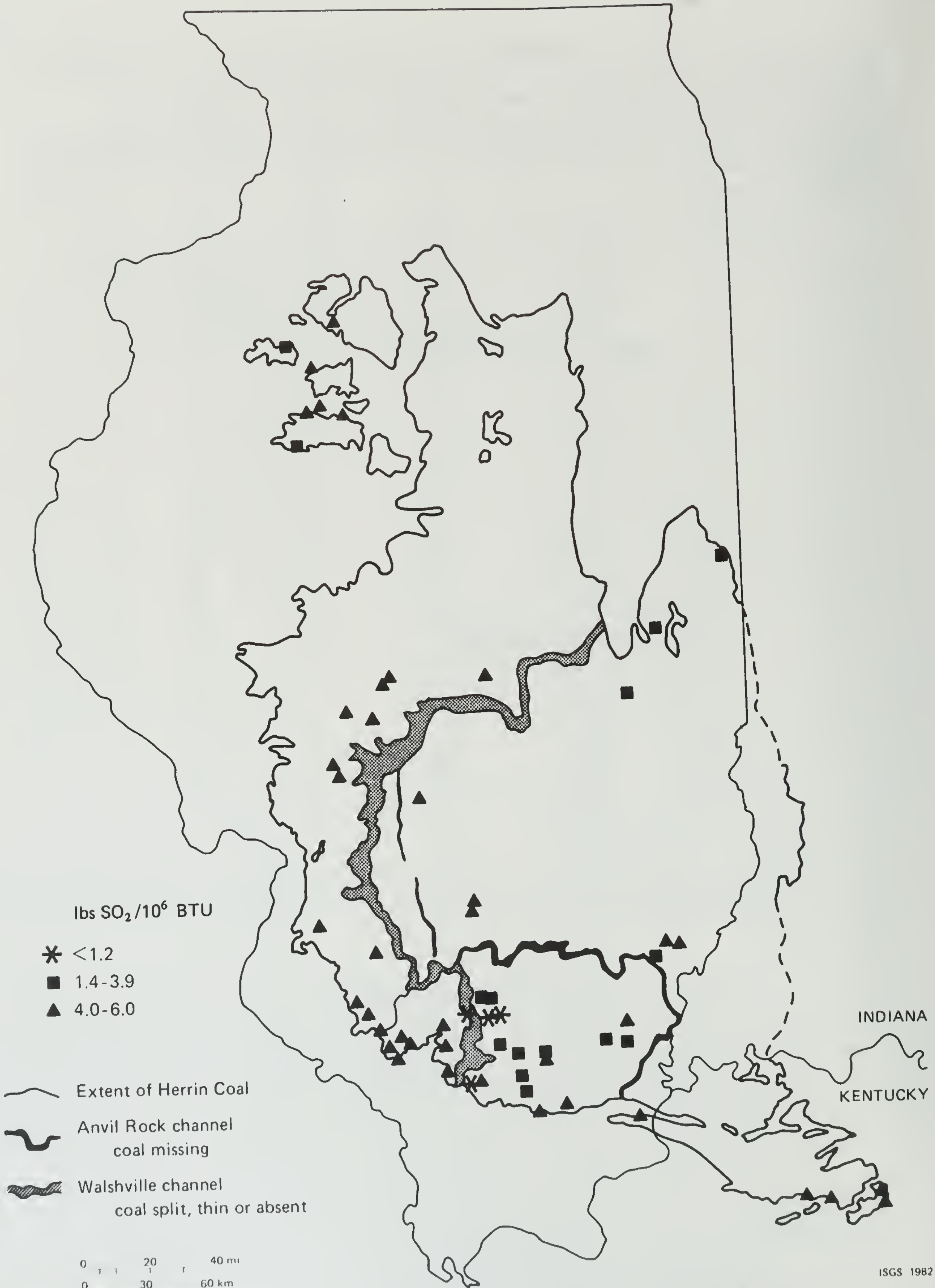


FIGURE VIII-1. Distribution of sulfur in the Herrin Coal expressed in pounds $SO_2$ per million Btu adjusted to a washed (estimated, laboratory) coal basis.

The mean abundance of the elements whose occurrence in coals is associated with the inorganic (mineral) constituents is reduced 40 percent or more of their mean abundance in the washed (float-sink) sample sets (table VIII-4). The organically associated elements have reductions less than 8.6 percent.

The middle group of mixed association have reductions between 15 and 30 percent. By multiplying these reductions by the average concentration of the various elements in the Illinois coals an estimate is obtained for the average metal content in washed coals (table VIII-4). Naturally, departures from these estimated values are to be expected for commercially washed coals; the variations are probably of the same order of magnitude as the standard deviations of the respective elements (tables VI-6 and VI-7). These ranges are expected particularly for those elements in the mixed and organic associated groups (table VIII-4); however, the variability of the inorganic (mineral) associated elements, particularly As, Ba, Cd, Pb, and Zn, probably do not vary as much in washed coals as they do in whole coals. It is also important to note that the percentage reduction of the elements in the washability tests differed quite a lot for many elements. For example, selenium ranged from 4.8 to 27.8 percent reduction between the 100 to 80 percent recovery points on the washability curves; arsenic, 46 to 72 percent; lead, 30 to 62 percent.

With exception of sulfur, the estimated amount of the elements of potential environmental concern in washed coals is indeed low (table VIII-4). If washed coal is used in combustion, none of these elements, except sulfur, is thought by the writers to cause serious environmental problems. These metals, however, will be concentrated in the waste materials from coal preparation plants, and present different problems of disposal depending on the degree of their concentrations (Wewerka et al., 1978). Further investigations as to the extent of these concentrations and their environmental impacts should be undertaken in Illinois.

High sulfur levels present a serious problem to the coal industry in the Illinois Basin. Except for a few of the Herrin samples, the coal contains too much sulfur to meet existing emission requirements for use in newly constructed electric power plants not having desulfurization facilities. To illustrate this problem, the total sulfur value "expected" for washed coal (27% reduction) was calculated, then converted to pounds $SO_2$ per million Btu. The results for the samples from the Herrin are plotted in figure VIII-1 and from the Springfield in figure VIII-2. These maps show that, for washed coals from the Herrin, only 4 samples, from locations adjacent to the southern end of the Walshville channel, could be considered in compliance with a 1.2-lb $SO_2/10^6$ Btu (516 ng $SO_2$/J)emission limit. These calculations illustrate the condition of total combustion for which no $SO_2$ is removed at the power plant and all of the sulfur in the washed coal is converted to $SO_2$. None of the samples tested from the Springfield Coal, when calculated to the washed coal basis, yield less than 1.2 lbs $SO_2/10^6$ Btu. Research and development of new processes for removal of sulfur from Illinois is urgently needed.

FIGURE VIII-2. Distribution of sulfur in the Springfield Coal expressed in pounds $SO_2$ per million Btu adjusted to a washed (estimated, laboratory) coal basis.

# APPENDIXES

## APPENDIX A. ANALYTICAL PROCEDURES FOR CHEMICAL ANALYSES

Discussions of the precision of the analytical results are included in Section III of the main text; the procedures are as follows:

### Proximate analyses

1. Moisture—ASTM D 3173. Weighed samples are dried in an electric oven ($104^{o}$-$110^{o}$C) with a dry air flow, cooled, and reweighed to determine moisture loss.

2. Ash—ASTM D 3174. Weighed samples are ashed in an electric muffle furnace ($750^{o}$C), cooled, and reweighed to determine the percentage of ash.

3. Volatile Matter—ASTM D 3175. Weighed samples in capped, platinum crucibles are heated in an electric furnace ($950^{o}$C) for 7 minutes, cooled, and reweighed to determine volatile matter plus moisture loss.

4. Fixed Carbon—Calculated as 100 percent minus the sum of the percentages of moisture, ash, and volatile matter.

### Ultimate analyses

1. Carbon and Hydrogen—ISO 609. Weighed samples are placed in combustion boats, covered with a layer of finely divided alumina, and slowly pushed into an electric furnace ($1350^{o}$C). Pure oxygen is passed over the sample through a roll of silver gauze at $700^{o}$C (to trap oxides of sulfur and halides), and finally through a pair of weighed Nesbitt bulbs, the first containing magnesium perchlorate to trap $H_2O$, the second containing ascarite to trap $CO_2$. The Nesbitt bulbs are reweighed and C and H are calculated from the weights of $CO_2$ and $H_2O$, respectively.

2. Nitrogen-Semi-micro Kjeldahl-ISO-333. Weighed samples are digested in concentrated sulfuric acid, using cupric selenite as a catalyst. The nitrogen compounds are converted to ammonium salts. The acid is neutralized with NaOH and the resulting ammonia is steam distilled into a saturated boric acid solution, forming $NH_4OH$. An acidimetric titration with standardized $H_2SO_4$, using a methylene blue/methyl red mixed indicator, is used to determine the nitrogen content.

3. Total sulfur—ASTM D 3177A. Weighed samples are mixed with Eschka's mixture (2 parts MgO, 1 part $Na_2CO_3$), placed in porcelain crucibles, and ignited in an electric muffle furnace at $800^{o}$C for at least 90 minutes. Samples are cooled, leached with boiling water, and

filtered. The filtrate is acidified, barium chloride is added, and resulting barium sulfate is eventually recovered by filtration. Filter papers are placed in porcelain crucibles and burned away in an 800°C muffle furnace, crucibles are cooled, weighed, and the percentage of total sulfur is calculated.

4. Oxygen—Calculated as 100 percent minus the sum of the percentages of carbon, hydrogen, nitrogen, total sulfur, and ash.

### Forms of sulfur—ASTM D 2492

1. Sulfate sulfur—Weighed samples are boiled with 2:3 hydrochloric acid for 30 minutes and filtered. Filtrate is made basic with $NH_4OH$, precipitate is filtered and discarded, filtrate is acidified, barium chloride solution is added, and resulting barium sulfate is eventually recovered by filtration. Filter papers are placed in porcelain crucibles and burned away in an 800°C muffle furnace, crucibles are cooled, weighed, and the percentage of sulfate sulfur is calculated.

2. Pyritic sulfur—Filter paper and sample from the HCl extraction of part 1 are washed, boiled with 1:7 nitric acid for 30 minutes, and filtered. Filtrate is made basic with $NH_4OH$, precipitate is filtered and recovered, filtrate is discarded. Precipitate is washed, redissolved in HCl, and all $Fe^{+3}$ is reduced to $Fe^{+2}$ with $SnCl_2$ solution. $Fe^{+2}$ is titrated with standard potassium dichromate solution using barium diphenylamine sulfonate indicator. The percentage of pyritic sulfur is calculated from measured percentage of Fe, assuming all iron extracted by nitric acid was in the form of iron pyrite.

3. Organic sulfur—Calculated as percentage of total sulfur minus the sum of the percentages of sulfate sulfur and pyritic sulfur.

### Calorific value—ASTM D 3286

A weighed sample in a stainless steel capsule is placed in a Parr bomb, which is then pressurized to $\sim$30 atmospheres with pure oxygen. The bomb is immersed in a known quantity of water in a bucket, which is placed inside an isothermal-jacket calorimeter. The sample is electrically ignited and allowed to burn while the jacket is at all times maintained at precisely the same temperature as the bucket. After 8 minutes, the increase in the bucket temperature is measured to the nearest .001°C, and the calorific value is calculated.

## METHODS FOR DETERMINING THE MINOR AND TRACE ELEMENTS

### Preparation of 500 C temperature ash (HTA)

Approximately 2 grams of whole coal, as received, was placed in an acid-washed 30 ml Vycor brand crucible that had been previously dried at 100°C for several hours, cooled to room temperature, and accurately weighed. The crucible and sample were placed in a moisture oven at 100°C to 110°C for 2 hours. The dried sample was removed from the moisture oven and placed in a desiccator to cool. The sample was then carefully weighed, covered with a Vycor brand crucible cover, and placed in a room-temperature, muffle furnace that had been adjusted to obtain a maximum temperature of 500°C for 20 to 24 hours, or until no carbonaceous material remained. The sample was then placed in a desiccator to cool. After it had cooled, the sample was weighed and then ground in a mullite mortar with pestle. The ground sample was placed in a 3 dram glass vial, dried at 110°C for several hours, and stored in a desiccator until used.

## Atomic absorption spectrometry (AA)

Atomic absorption (AA) methods were used for the determination of Cd, Cu, Li, Ni, Pb, and Zn (also Fe and Sr for accuracy check) in a 500°C ash of the coal samples in this study. Measurements were made using a Perkin-Elmer Model 306 Atomic Absorption Spectrophotometer. Absorbance signals were recorded on a strip chart recorder. Standard single element hollow cathode lamps were used except for Cd where an electrodeless discharge lamp was used. Corrections for non-atomic background absorption were made simultaneously using a deuterium arc background corrector.

All reagents used were ACS certified reagent grade chemicals. Standard stock solutions were prepared from high purity metals or compounds. The calibration standards were prepared from diluted stock solutions and contained the following matrix: 3 percent V/V aqua regia (1;3:1; $HNO_3$-$HCl$-$H_2O$), 5 percent V/V concentrated HF reagent (48% W/W), 2.5 percent W/V $H_3BO_3$, and 2000 ppm Cs as CsCl.

Approximately 0.1 g of 500°C ash was weighed into a 60 ml linear polyethylene screw cap bottle. The sample was wetted with 1.5 ml of aqua regia, and 2.5 ml of 48 percent HF was then added. The bottle was capped tightly and placed on a steam bath for approximately two hours. The cap was then removed carefully and 25 ml of a 50 g/l $H_3BO_3$ solution was added. If a residue or precipitate persisted, the bottle was returned to the steam bath for approximately half an hour. The sample was then allowed to cool and 200 μl of a 0.500 g/ml Cs solution was added to make the final solution 2000 ppm Cs. The solution was diluted to 50 ml with deionized water, and returned to the sample bottle for storage.

Standard recommended operating conditions for AA were used and are summarized in table A-1. Calibration curves were constructed by least squares method and new calibration curves were calculated for each set of analyses.

## Optical emission spectrographic analyses (OE)

Optical emission spectrographic (OE) methods developed for this work employ a high-temperature ashed sample and d.c. arc/powder techniques with photographic recording of spectra, with data reduction by computer programs. Standardization and calibration of the determined elements are based on NBS standard reference materials, round-robin analyses of reference samples, and synthetic standards.

The elements of interest are treated in two separate groups: relatively volatile elemental elements, including thallium and silver; and relatively

**TABLE A-1.** Operating parameters for atomic absorption spectroscopy.

| Element | Current | Wave-length (nm) | Slit (nm) | Flame oxidant/fuel | Typical Sensitivity (ppm/0.0044 Abs) |
|---|---|---|---|---|---|
| Cd | 8ma | 228.8 | 0.7 | Air/$C_2H_2$ | 0.023 |
| Cu | 10ma | 324.7 | 0.7 | Air/$C_2H_2$ | 0.07 |
| Fe | 30ma | 302.1 | 0.2 | Air/$C_2H_2$ | 1.4 |
| Li | 15ma | 670.8 | 1.4 | Air/$C_2H_2$ | 0.04 |
| Ni | 18ma | 232.0 | 0.2 | Air/$C_2H_2$ | 0.1 |
| Pb | 10ma | 283.3 | 0.7 | Air/$C_2H_2$ | 0.5 |
| Sr | 25ma | 460.7 | 1.4 | $N_2O$/$C_2H_2$ | 0.09 |
| Zn | 15ma | 213.9 | 0.7 | Air/$C_2H_2$ | 0.14 |

**TABLE A-2.** Instrumental parameters for optical emission spectrography.

| | |
|---|---|
| Spectrographic | |
| Spectrograph | Jarrell-Ash 3.4-M Ebert |
| Grating angle | 6.02 degrees off normal |
| Slit width | 25 µM |
| Step sector | 1:2 |
| External optics | Intermediate aperture and crossed cylindrical relay lenses |
| Arc current | 13.0 A (short circuit) |
| Arc gap | 4 mm |
| Arc atmosphere | 80% Ar, 20% $O_2$ @ 14 SCFH |
| Photographic | |
| Pre-arc | None |
| Exposure | Thallium 10 sec.;silver 35 sec. (volatile element group)<br>80 sec. (refractory element group) ıp) |
| Emulsion type | Eastman SA-1 |
| Developer | D-19; 2 min @ 20°C |

**TABLE A-3.** Wavelengths used for trace elements in coal by optical emission spectrography.

| Element | Wavelength (nm) | Element | Wavelength (nm) |
|---|---|---|---|
| Ag | 338.3 | Mo | 317.0 |
| B | 249.68 | Tl | 276.8 |
| Be | 313.1 | V | 311.0 |
| Ge | 265.1 | Zr | 339.1 |

refractory elements, including boron, beryllium, germanium, molybdenum, vanadium and zirconium. The analytical method for the volatile element group employs a carrier-distillation technique using a barium fluoride carrier. A novel electromechanical optical shutter system provides, in a single spectrogram, exposures of different integration-time periods for thallium and silver during the same excitation cycle to maximize analytical sensitivity for each element. A total volatilization procedure is employed for the refractory element group to minimize the effects of preferential volatilization. A controlled-atmosphere semi-automated accessory device provides reproducible plasma geometry and attenuation of cyanogen spectral interference.

Emission spectra are recorded in duplicate. A reference sample (plate standard) is exposed on each plate to provide the necessary standardization corrections. Instrumental parameters are listed in table A-2. Wavelengths used for determining elements by OE are summarized in table A-3.

Data processing of analytical results is done with a CYBER computer system (University of Illinois). Computer programs for automation of the conventional H & D curve emulsion calibration use a Gaussian transformation of the densitometric data and a smoothing cubic spline. The transformation removes an inflection point in the emulsion calibration curve and allows the cubic spline to operate more efficiently. The computer programs for computation of element concentrations accomodate log-log coordinate analytical curves that are linear, quadratic or cubic, or any combination of these.

### Instrumental neutron activation analysis (INAA)

INAA depends on the production of radioactive isotopes, normally in a research nuclear reactor, and the detection and resolution of the resulting gamma-ray spectrum by high resolution semiconductor detectors such as lithium-drifted germanium detectors [Ge(Li)]. The amount of activity produced for an element in a sample can be controlled by varying the quantity of the sample irradiated, the irradiation time, and the length of the decay interval. Coal represents a nearly ideal matrix for INAA. A relatively large quantity of whole coal can be activated because the major constituents (carbon, hydrogen and oxygen) do not form radioactive species under normal thermal neutron irradiation conditions. In addition, because coal is heterogenous, a finely ground sample is essential, and the sample size of approximately 1.0 g in a 1.5 ml polyethylene vial ensures a representative sample.

Details of the isotopes produced, half-lives, cross sections, decay intervals gamma-rays utilized for analysis, and limits of detection are shown in table A-4. The irradiation and counting times chosen were a compromise for the determination of the majority of elements. The particular gamma-ray wavelengths used were chosen because they were free of significant spectral interferences and had sufficient intensities to give adequate statistics. Gamma-ray activities of the samples were compared with those of multi-elemental standards that consisted of Whatman 41 filter papers onto which aliquots of solutions containing the several elements had been spotted and evaporated. The mixed standard solutions were prepared from reagent grade elements or compounds. All samples and standards were weighed into

**TABLE A-4.** Nuclear properties of isotopes used for analysis of coal.

| | Isotope Produced | Half Life | Cross Section (Barns) | Counting Period | Major Gamma-Ray Utilized (keV) |
|---|---|---|---|---|---|
| Na | $^{24}$Na | 15 hr | 0.53 | B, C | 1368 |
| Cl | $^{38}$Cl | 37 min | 0.40 | A | 1642 |
| K | $^{42}$K | 12.4 hr | 1.2 | B, C | 1525 |
| Sc | $^{46}$Sc | 83.8 day | 13 | D | 889, 1120 |
| Cr | $^{51}$Cr | 27.8 day | 17 | D | 320 |
| Mn | $^{56}$Mn | 2.58 hr | 13.3 | B, C | 847, 1811 |
| Fe | $^{59}$Fe | 44.6 day | 1.1 | D | 1099, 1292 |
| Co | $^{60}$Co | 5.26 yr | 37 | D | 1173, 1333 |
| Ni | $^{58}$Co | 71 day | 0.2 | D | 811 |
| Zn | $^{65}$Zn | 244 day | 0.5 | D | 1115 |
| Zn | $^{69}$Zn | 13.9 hr | 0.1 | B, C | 439 |
| Ga | $^{72}$Ga | 14.2 hr | 5.0 | B, C | 834 |
| As | $^{76}$As | 26.3 hr | 4.5 | C | 559, 657 |
| Se | $^{75}$Se | 120 day | 30 | D | 136, 265 |
| Br | $^{82}$Br | 35.4 hr | 3.0 | B, C | 554, 777 |
| Rb | $^{86}$Rb | 18.7 day | 0.7 | D | 1077 |
| Sr | $^{87m}$Sr | 2.8 hr | 1.3 | B | 388 |
| Sr | $^{85}$Sr | 64.5 day | 1.0 | D | 514 |
| Mo | $^{99}$Mo | 66.2 hr | 0.15 | C, | 141 |
| Ag | $^{110m}$Ag | 252.4 day | 3.5 | D | 658 |
| In | $^{116m}$In | 54 min | 160 | A, B | 417, 1097 |
| Sb | $^{122}$Sb | 2.7 day | 6.5 | C | 564 |
| Sb | $^{124}$Sb | 60.2 day | 2.5 | D | 1691 |
| I | $^{128}$I | 25 min | 6.2 | A | 443 |
| Cs | $^{134}$Cs | 2.06 yr | 31 | D | 796, 569 |
| Ba | $^{131}$Ba | 11.5 day | 8.8 | C, D | 496, 216 |
| Ba | $^{139}$Ba | 83 min | 0.35 | B | 166 |
| La | $^{140}$La | 40.3 hr | 8.9 | C | 1596, 487 |
| Ce | $^{141}$Ce | 32.4 day | 0.6 | D | 145 |
| Sm | $^{153}$Sm | 46.5 hr | 210 | C | 103 |
| Eu | $^{152m}$Eu | 9.3 hr | 2800 | B, C | 122, 344 |
| Eu | $^{152}$Eu | 12 yr | 5900 | D | 1408 |
| Tb | $^{160}$Tb | 72.3 day | 46 | D | 879 |
| Dy | $^{165}$Dy | 2.36 hr | 700 | B | 95, 362 |
| Yb | $^{175}$Yb | 4.2 day | 55 | C | 396, 282 |
| Yb | $^{169}$Yb | 32 day | 5500 | D | 198, 177 |
| Lu | $^{177}$Lu | 6.7 day | 2100 | D | 208 |
| Hf | $^{181}$Hf | 43 day | 10 | D | 482, 133 |
| Ta | $^{182}$Ta | 111 day | 21 | D | 156, 222 |
| W | $^{187}$W | 23.9 hr | 38 | B, C | 480, 686 |
| Au | $^{198}$Au | 65 hr | 99 | C, | 412 |
| Th | $^{233}$Pa | 27 day | 7.4 | D | 312 |
| U | $^{239}$Np | 56 hr | 2.7 | C, | 277, 228 |

| Counting Period | Irradiation | Flux $(n \cdot cm^{-2} \cdot s^{-2})$ | Decay Interval | Count Interval |
|---|---|---|---|---|
| A | 15 min | $2 \times 10^{12}$ | 30 min | 500 s |
| B | 15 min | $2 \times 10^{12}$ | 3 hr | 3000-4000 s |
| C | 2 hr | $2 \times 10^{12}$ | 24 hr | 6000-8000 s |
| D | 2 hr | $2 \times 10^{12}$ | 30 day | 8-11 hr |

1.5 mL washed polyethylene vials, heat sealed, and activated in the Advanced TRIGA MARK II reactor at the University of Illinois in the rotary specimen assembly (lazy susan) which rotates continuously during the irradiation to ensure that all receive the same neutron flux distribution. The Cd ratio (RCd) at this location was about 5.0, indicating that the neutron flux is thermal.

The gamma counting system used in this study is shown in block diagram form in figure A-1. The samples were counted using a pneumatic sample changer (Massoni et al., 1973) which ensured reproducible geometry and

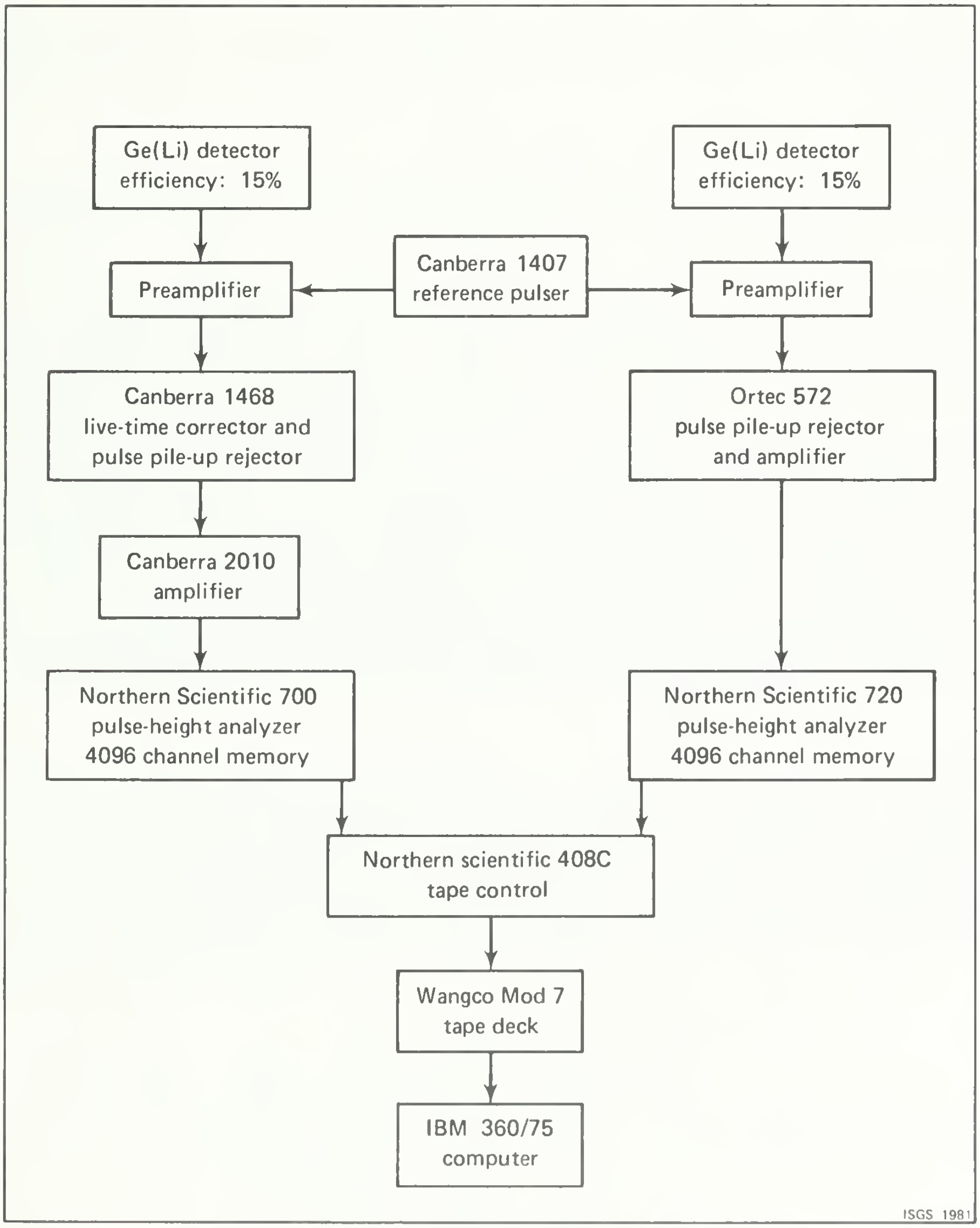


Figure A-1. Block diagram of INAA system.

permitted optimum counting times. Data reduction was accomplished with the computer facilities at the University of Illinois using programs (Manley et al., 1977) adapted to be compatible with the counting equipment.

### Wavelength-dispersive x-ray fluorescence analysis (XRF)

The XRF equipment consists of a Phillips vacuum spectrometer equipped with a Mark I electronics panel and a chromium target X-ray tube. X-ray fluorescence analyses were done on the 500°C ashes of coal for P, Mg, K, Ca, Fe, Ti, Al, and Si.

Because the matrix interference problems presented by coal ash are similar to those of rocks, the dilution technique of Rose, Adler, and Flanagan (1962), developed primarily for silicate rock samples, was used to analyze coal ash samples.

A 125 mg aliquot of dried 500°C ash sample was weighed into a graphite crucible containing 1.000 gm of lithium tetraborate. A depression made in the lithium tetraborate prior to addition of the ash sample prevented contact of the sample with the crucible wall. Next, 125 mg of lanthanum oxide was added as a heavy-element absorber, and the contents of the crucible were mixed as thoroughly as possible with a glass stirring rod, without scraping the crucible bottom or wall. The mixture was fused in a furnace for 15 minutes at 1000°C, removed, covered with a second crucible, and allowed to cool to room temperature. The resulting pellet was weighed to determine loss of weight on fusion and was placed in the tungsten carbide grinding vial of a No. 6 Wig-L-Bug with 2 percent by weight of Somar mix (a commercial grinding and plasticizing agent). The sample was ground for 3 minutes, transferred to a die, and pressed into a disk at 40,000 psi. When backed with a layer of pressed Somar mix, the pressed disk was semi-permanent and was used for the quantitative determination of major and minor elements by X-ray analysis. Table A-5 demonstrates the accuracy of this method for the determination of Si, Ti, Al, Fe, Mg, Ca, K, and P in coal ash samples.

**TABLE A-5.** ISGS x-ray fluorescence analyses and BCURA* analyses of coal ash (percent).

| | BCURA No. 4 | | BCURA No. 5 | | BCURA No. 7 | | BCURA No. 10 | | BCURA Slag | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Oxide | XRF | Reported* | XRF | Reported* | XRF | Reported* | XRF | Reported* | XRF | Reported* | Ave. Diff. |
| $SiO_2$ | 53.28 | 53.41 | 29.27 | 29.43 | 20.01 | 20.37 | 44.03 | 44.49 | 51.45 | 51.58 | 0.25 |
| $TiO_2$ | 1.65 | 1.70 | 0.65 | 0.70 | 0.26 | 0.34 | 1.18 | 1.19 | 0.96 | 0.96 | 0.04 |
| $Al_2O_3$ | 34.11 | 33.88 | 19.73 | 19.82 | 10.03 | 10.33 | 29.93 | 30.02 | 28.20 | 28.45 | 0.19 |
| $Fe_2O_3$ | 5.83 | 5.76 | 39.02 | 39.24 | 62.16 | 62.31 | 13.56 | 13.82 | 6.27 | 5.99 | 0.17 |
| MgO | 0.66 | 0.71 | 1.18 | 1.29 | 0.58 | 0.63 | 2.05 | 2.00 | 2.33 | 2.26 | 0.06 |
| CaO | 0.73 | 0.77 | 2.47 | 2.54 | 2.31 | 2.30 | 1.24 | 1.29 | 7.89 | 7.91 | 0.04 |
| $K_2O$ | 2.45 | 2.38 | 1.94 | 1.95 | 1.38 | 1.39 | 3.68 | 3.71 | 2.84 | 2.81 | 0.03 |
| $P_2O_5$ | 0.48 | 0.41 | 0.14 | 0.14 | 0.17 | 0.15 | 0.77 | 0.77 | 0.09 | 0.05 | 0.03 |

*British Coal Utilization Research Association (Dixon et al., 1964).

TABLE A-6. X-ray fluorescence settings for analysis of coal ash.

| Element | X-ray | $2\theta$ angle | Background $2\theta$ | Crystal | Vacuum | Base | Window |
|---|---|---|---|---|---|---|---|
| Si | KL$_3$ & KL$_2$ | 108.01 | 111.01 | EDDT | yes | 7 | 17 |
| Al | KL$_3$ & KL$_2$ | 142.44 | 145.95 | EDDT | yes | 5 | 12 |
| Ti | KL$_3$ & KL$_2$ | 87.12 | 89.12 | LiF | no | 5 | 18 |
| Fe | KL$_3$ & KL$_2$ | 57.51 | 60.51 | LiF | no | 5 | 25 |
| Ca | KL$_3$ | 44.85 | 47.95 | EDDT | yes | 14 | 30 |
| K | KL$_3$ & KL$_2$ | 50.32 | 53.90 | EDDT | yes | 14 | 21 |
| Mg | KL$_{23}$ | 136.69 | 139.69 | ADP | yes | 4 | 8 |
| F | KL$_3$ & KL$_2$ | 110.99 | 113.99 | Ge | yes | 9 | 15 |

Operating parameters of the X-ray fluorescence spectrometer for the analysis of coal and coal ash samples are listed in table A-6.

## Energy-dispersive x-ray fluorescence analysis (EDX)

The instrumentation consists of a Kevex Si (Li) detector with a resolution of 155 eV (FWHM) at 5.9 KeV, a 300 MCi $^{241}$Am excitation source, and a Tracor Northern 1700 multichannel analyzer.

Determinations of Ba, Sr, and Zr were made by EDX on the $500^{\circ}$C ash. The ash was ground to pass a -200 mesh sieve and 0.500 gm (1.000 gm when unashed coal was used) was placed in a polyethylene cup. The mouth of the cup was sealed with a piece of Mylar film (0.00015 inch thick). The cup was inverted and tapped so that the sample settled as a uniform layer on the Mylar. The sample was then placed in an aluminum sample holder and exposed to monochromatic radiation generated from a secondary target of Dy for Ba and a secondary target of Sn for Sr and Zr.

Standards were coal ashes that were previously analyzed by other methods. The standards were analyzed in the same manner as the sample. Count rates obtained on samples and standards were corrected for background and a blank. For each element, a plot was made of concentration versus net count rate for standards over a range of concentrations. The concentration of an element in a sample was then calculated as the product of net count rate for the sample and the slope of the curve of concentration versus count rate for the standards.

## Determination of fluorine: fluoride ion-selective electrode (ISE)

This ISE method has been previously published (Thomas and Gluskoter, 1974) and is presently accepted as the ASTM D3761-79 method for the analysis of F in coal. A resume of the method is as follows.

One gram of feed coal or liquefaction residue, weighed to the nearest 0.5 mg and contained in a fused quartz sample holder, is placed in a combustion bomb containing 5 mL of a 1M sodium hydroxide solution. The bomb is pressurized to about 28 atmospheres with oxygen and is fired. At least 15 minutes are allowed to elapse before the bomb is depressurized slowly over a period of about 1 minute. Three 5 mL aliquots of demineralized water are used to rinse the bomb contents into a 50 mL plastic beaker. The beaker contents are stirred while the pH is adjusted to 5.0 and 5.2 with 0.25M $H_2SO_4$. (This reduces the initially high bicarbonate content sufficiently to minimize its possible interference in the fluoride determination.) Five mL of a 1M citrate ionic-strength-adjustment buffer are added to the beaker contents to buffer the solution at a pH of about 6.0, and to release most of the fluoride from complexes with iron, aluminum, and hydrogen ions. The total volume is adjusted to 50 mL with deionized water in a plastic volumetric flask, and the contents returned to the plastic beaker for a measurement. The potential is determined with the fluoride ion-selective electrode. One mL of a solution 0.01M in fluoride (190 ppm) is added to the beaker contents and the potential is determined again. The fluoride content in the coal is calculated from the $\Delta E$ resulting from the known fluoride addition. With care, the reproducibility of the method is about ±5 percent, relative, in the concentration range of 5 ppm to 1000 ppm.

The error is not large in the above method when the ash content is as great as 20 percent. However, when the ash content surpasses 20 percent, the residue that remains in the bomb after the soluble material has been washed out following combustion is fused in a nickel crucible with 3 gm of powdered sodium hydroxide, and the fusion mixture is taken up in deionized water. The pH is adjusted to 5.0 to 5.2 (the solution volume is much larger in this case—200 mL total solution); then 20 mL of the 1M citrate ionic-strength-adjustment buffer solution is added. The volume is adjusted to 200 mL and the potential is determined. After addition of 5 mL of 0.01M fluoride solution $\Delta E$ is again determined and the fluoride concentration of the combustion bomb residue is determined. The result of this determination is added to that obtained for the combustion bomb washings. Because of the small sample size and the high dilution factor, the detection limit of fluoride in the fusion method is 10 ppm.

## Determination of Hg: Radiochemical neutron activation analysis (RNAA)

From 0.6 to 1.0 gm of coal is accurately weighed into a two-fifths dram polyethylene snap-cap vial. A 1 mL aliquot of a 10.0 mg/mL standard solution of $Hg^{+2}$ (as nitrate) is sealed in a similar polyethylene vial. Samples and standard are simultaneously irradiated for 2 hours in the University of Illinois Advanced TRIGA reactor at the flux of $1.4 \times 10^{12} n \cdot cm^{-2} sec^{-1}$. One day is allowed for radiation levels to decrease by the preferential decay of shorter-lived radioisotopes such as $^{24}Na$, $^{31}Si$, and $^{56}Mn$, to permit safe handling of the samples.

A method modified from that of Rook, Gills, and LaFleur (1971) is used to determine mercury. Each sample is mixed 1:1 with 60-mesh Norton Alundum RR ($Al_2O_3$), transferred to a 4-inch porcelain boat (Fisher Combax, size A), and covered with Alundum. The boat, previously impregnated with 2 mg $Hg^{+2}$ carrier, is placed in a 1-inch diameter Vycor tube and the contents then combusted slowly in a tube furnace at 900° to 1000°C. An oxygen or air flow of about 50 to 75 mL per minute is maintained through the tube. The gaseous and volatilized products are collected in a cold trap that is cooled by dry ice-acetone mixture. The combustion process requires several hours to ensure controlled burning and efficient transfer of volatile products to the trap. After combustion of the sample is complete, the cold trap is warmed to room temperature and the mercury is washed out with dilute $HNO_3$. The solution is heated to $80^{\circ}C$, and the $^{82}Br$ interference is removed by precipitation of AgBr while the more soluble $HgBr_2$ remains in solution. The $Hg^{++}$ solution is decanted, and the 77 keV $\gamma$-ray activity that is due to Hg is counted with a NaI(Tl) detector. The mercury standard is treated identically to the samples. Radiochemical yields are determined by re-irradiation and range from 50 to 90 percent. The average relative standard deviation is 15 percent, and the detection limit is 0.005 ppm for a 1 gram sample and 2 hour irradiation. Analyses of NBS SRM-1632 standard coal using this method gave a Hg value of 0.13±03 and is in excellent agreement with the certified value (0.13±02 ppm).

Supervising analysts for the procedures described were:

Standard coal analyses: L. B. Kohlenberger
Atomic absorption (AA): J. D. Steele
Optical emission (OE): R. S. Vogel
Instrumental neutron activation (INAA): R. A. Cahill
X-ray fluorescence (XRF): L. R. Henderson
Energy dispersive X-ray (EDX): L. R. Henderson
Ion selective electrode (ISE): J. Thomas, Jr.
Radiochemical neutron activation (RNAA): L. R. Camp

# APPENDIX B. PROCEDURES FOR MINERALOGICAL ANALYSES

## PREPARATION OF LOW TEMPERATURE ASH (LTA)

Whole coal samples were low-temperature ashed in a L.F.E. Corp. Model LTA-504 radio-frequency asher in which oxygen was introduced into a radio-frequency field producing an "activated" oxygen-plasma atmosphere. A 10- to 20-g subsample was spread evenly over the bottoms of 3 pyrex boats, to a depth of about 3 mm. The boats were either 9 cm in diameter or about 12 x 4 cm in size. The samples were then dried in a vacuum desiccator for a minimum of 24 hours.

The samples were placed in the asher and the pressure brought down to approximately 1 torr. The radio frequency was then introduced at 37.5 watts per chamber (a total of 150 watts distributed between four chambers). An oxygen flow rate of 20 $cm^3$ per minute was then introduced to produce the plasma. The ashing temperature was monitored occasionally with a Raynar infrared remote thermometer and with Wahl temp-plate tabs. Neither of these methods is very accurate, yet they are the best available. None of the readings obtained was above 137°C.

The samples were stirred twice and weighed once each day. The samples were always weighed in the same sequence to facilitate accurate measurement of their changes in weight. The placement of the three boats within the ashing chambers was alternated every 24 hours to expose each boat to approximately the same amount of exhaust gases. About 10 days were required to achieve complete oxidation of the organic matter. Four samples (12 boats) were simultaneously ashed in one ashing machine and three machines were commonly operated continuously.

The percentage of mineral matter (% LTA) was determined from the ratio of the lowest measured weight to the initial (dry) weight; the percentage of weight loss (100 - % LTA) is the percentage of organic matter in the sample. The mineral matter determined by this procedure is not corrected for: (1) possible minute amounts of sulfur that might be fixed in the LTA residue derived from the organic sulfur in the coal; (2) possible minute amounts of unburned carbon; and (3) possible absorption of moisture by the minerals during the weighing operations. Each of these sources of error tends to increase the measured amount of mineral matter, and we have not determined their actual proportional amounts. Previous results of Gluskoter et al., 1977; Ruch et al., 1979; O'Gorman and Walker, 1972; and Miller and Given, 1978, based on substantially the same procedures as used in this study, indicate that these sources of error are negligibly small for Illinois and similar coals.

## QUANTITATIVE ANALYSIS OF NONCLAY MINERALS

Quantitative analysis of nonclay minerals was obtained by using standard graphs (fig. B-1). These graphs were prepared from x-ray results of various mixtures of pure minerals found in Illinois coal mixed with a fixed amount of alumina as an internal standard. Twenty percent by weight of 0.3µm Linde A alumina ($Al_2O_3$) was used as the internal standard. A clay matrix was added to these mixtures to insure that the matrix materials would be essentially the same as that in the coal derived samples. The procedures, based on those described by Ward (1977) and Russell and Rimmer (1979), are as follows:

Precisely 0.04 g of $Al_2O_3$ is added to 0.20 g of LTA (or to standard mixture if standard curves are to be constructed). This mixture is ground by hand in 99 percent ethanol in a mullite mortar with pestle for about 15 to 20 minutes until the individual grains become invisible to naked eye (free of grit, feel between the fingers). After the sample is ground it is oven dried at about $35^{\circ}$C to avoid moisture in open air.

The dry sample is slightly reground and three subsamples are prepared, each mounted in a cavity powder mount consisting of a rectangular aluminum plate of 2 mm thickness with a rectangular opening and a glass slide backing. The aluminum plate is placed on the glass slide and the powdered sample is placed in the opening with a minimum of packing. A second glass slide is lowered onto the powder filled cavity. The mount is then inverted and the first glass slide lifted directly off the aluminum plate without sliding it across the sample surface. A mount properly prepared will have a smooth and densely packed surface. The subsamples are then run by x-ray diffraction, one run from $2^{\circ}2\theta$ to $60^{\circ}2\theta$ and two from $19^{\circ}2\theta$ to about $40^{\circ}2\theta$. The

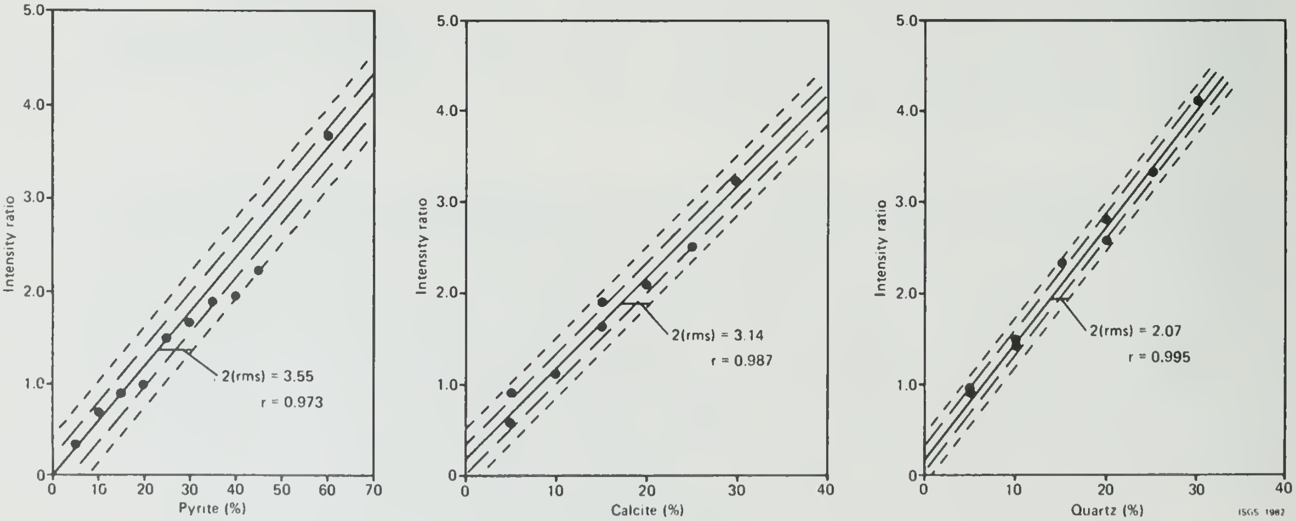


FIGURE B-1. X-ray diffraction calibration graphs used to convert the observed intensity ratio, the intensity of the mineral/intensity of internal standard, to the percentage of the mineral in the sample. The dashed lines indicate the uncertainty of the determined percent. The root mean square (rms) error times 2, and the correlation coefficient (r) are indicated.

diffractogram generated from the first run is used for complete qualitative analysis of minerals present in the sample. All three diffractograms are used for the quantitative analysis of quartz, calcite, and pyrite. A scanning speed of 2°/min was used for each run in this study. Range and time constant were kept at 500 counts and 5 seconds, respectively, except for those samples whose high intensities necessitated the use of higher ranges and small time constants.

The following peaks are used for construction of standard curves and measurement of unknowns: (101) quartz at 3.34 A; (104) calcite at 3.04 A; (200) pyrite at 2.71 A; and (104) $Al_2O_3$ at 2.56 A. Areas of these peaks are determined for each standard and unknown. Peak areas are obtained by multiplying the height of the peak above the base line times the width of the peak at half the height. In order to construct standard curves the average peak areas of three runs for each mineral are divided by that of internal standard ($Al_2O_3$). These ratios and their corresponding percentage mineral weights are then plotted on an Intensity (I = the peak area of mineral/the peak area of the internal standard) versus % mineral graph (fig. B-1).

The peak area ratios of unknowns are determined in the same way as those of standards. These calculated peak area ratios for the samples analyzed are then located on the y axis of the proper standard curve and corresponding percentages of minerals are read from the x axis.

## SEMIQUANTITATIVE ANALYSES OF CLAY MINERALS

The method used for quantitative x-ray diffraction (XRD) analysis of clay minerals is similar to that of Russell and Rimmer (1979) with some minor changes. The procedure used for this study is outlined here and then described in more detail.

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1. Wash 0.2 to 1.5 g sample in ~80 ml distilled $H_2O$
   Centrifuge and decant liquid *(to remove soluble ions)*

2. Warm in ~50 ml 5% acetic acid for 2 hrs
   Centrifuge→decant liquid *(to remove carbonates and acid soluble Fe compounds)*

3. Heat to 70° to 80°C in a solution of
   40 ml 0.3M Na-citrate and 5 ml 1M Na-bicarbonate
   Add 1 g $NaHSO_3$ 3 times at 15-min intervals *(to reduce $Fe^{3+}$ to $Fe^{2+}$)*
   Centrifuge→decant liquid *(to remove $Fe^{2+}$ and excess $Na^+$)*

4. Wash in 50 to 60 ml distilled water two or three times
   *(to disperse the clays and agitate)*

5. Let the suspensions settle for 21 minutes
   Remove the top 0.5 cm of suspension with pipette and deposit on to a ceramic slide under vacuum
   Air dry the slides

6. Solvate the slide over liquid glycol in a closed jar for 48 hours

7. Run XRD of the slide from 2 to $35^{\circ}2\theta$

8. Heat the slide at 375°C for 1 hr in an oven

9. Run XRD of the slide from 2 to $35^{\circ}2\theta$

---

## Preparation of slides

*Step 1:* A small amount of LTA (0.2-1.5 g) is added to 80 ml distilled water and thoroughly agitated in a 100 ml beaker. The suspensions are centrifuged and the supernatant is decanted to remove water soluble ions.

*Step 2:* The sample is placed in approximately 50 ml of 5 percent acetic acid and warmed (at about 35-45°C) for two hours. After the sample cools it is centrifuged again and the clear liquid on top is decanted to remove carbonates and acid soluble iron compounds.

*Step 3:* A solution containing 40 ml 0.3M sodium citrate ($Na_3C_6H_5O_7H_2O$) and 5 ml 1M sodium bicarbonate ($NaHCO_3$) is added to each sample. This mixture of solution and sample is heated to 70 to 80°C after which 1 g of sodium dithonite ($Na_2S_2O_4$) is added to it three times at 15-minute intervals and stirred with a glass rod after each addition. The samples are kept heated while sodium dithonite is added. Sodium dithonite reduces ferric iron ($Fe^{3+}$) to ferrous iron ($Fe^{2+}$) in a basic or neutral system (not in acid system), which is maintained by the addition of a buffer, sodium bicarbonate in this case. The role of sodium citrate is to hold reduced iron in suspension by forming an organo-metallic complex with it and thus to prevent the precipitation of iron sulfide (Jackson, 1975). After cooling and centrifuging the samples the supernatant is decanted to remove reduced iron ($Fe^{+2}$) and excess $Na^{+}$.

*Step 4:* The samples are washed twice or three times in distilled water to disperse the clays. At the final washing, the samples are thoroughly agitated in about 50 to 60 ml distilled water in a 100 ml beaker. This suspension is allowed to settle for 21 minutes, the time needed for 2μm clay particles to settle from the top 0.5 cm of the suspension.

*Step 5:* Finally, the <2μm fraction is removed with a pipet and sedimented onto a ceramic slide which is placed horizontally on top of a bottle that is under a slight vacuum so as to deposit the clay on the slide within one minute. Slides are then allowed to air dry completely over night. The ceramic slides provide fairly good orientation and good reproducibility.

## X-ray diffraction and computations

The clay slides are solvated with ethylene glycol for 48 hours after which time they are scanned by x-ray diffraction at $2^{\circ}2\theta$/min scanning speed over the region $2^{\circ}2\theta$-$35^{\circ}2\theta$. Range and time constants were kept at 1000 counts and 2 seconds, respectively, except for those samples whose high intensities required the use of higher ranges and smaller time constants. After this ethylene glycol run, the slides are allowed to air dry over night Dry slides are then heated to 375°C in an oven for 1 to 2 hours, after which time they are scanned again in the same manner.

A method developed by Griffin (1971), and modified by Ward (1977) was used for the computations. Assumptions made in this method are: (1) clay minerals comprise 100 percent of the sample; (2) refracting ability of clay minerals is constant, although it is known that refracting ability varies somewhat according to the clay mineral composition, grain size, and degree of crystallinity. Since grain size effect is largely eliminated, peak heights instead of peak areas are used for clay mineral analysis. Another reason for using peak heights rather than peak areas is that the broad diffraction band of the x-ray patterns of ethylene glycol solvated slides between 10 and 17 A (angstroms) creates difficulty in estimating the peak widths. The formulas used to calculate the relative amounts of clay minerals (kaolinite, chlorite, illite, and expandables) are derived as follows:

All expandables collapse to a d-spacing of 10 A, equal to that of illite after heating to 375°C for 1 to 2 hours. Therefore, the peak intensities after heating will reflect the presence of only illite, chlorite, and kaolinite (i.e., % kaolinite + % chlorite + "% illite" = 100%). The peaks used to compute percent (kaolinite + chlorite) in total clay are the (001) reflection of kaolinite and (002) reflection of chlorite, both at 7.15 A. To compute the percentage of "illite" its (001) reflection on the heated slide at 10 A is used. Griffin (1971) indicates that a structure factor of 2.5 can be used to convert 7 A peak intensities of kaolinite and chlorite to an equivalent 10 A intensity of illite; and he proposed the following relation between the proportions of kaolinite and chlorite and illite:

$$\%\ (K+C) = \frac{7\ Ah/2.5}{7\ Ah/2.5 + 10\ Ah} \times 100, \text{ where h refers to heated slides}$$

In this and the following equations, the numeric value preceding the A (angstrom) stands for the peak intensity on the diffractogram corresponding to that peak (e.g., 7A stands for the intensity of the 7-angstrom peak).

If both chlorite and kaolinite are present the (002) reflection of kaolinite at 3.59 A and (004) reflection of chlorite at 3.54 A are used to determine their relative amounts. The intensities of these two peaks are taken to be proportional to the relative abundance of these two clay minerals.

The percentage of kaolinite (%K) and the percentage of chlorite (%C) are thus calculated by the equations

$$\%K = \frac{3.59\ Ah}{3.59\ Ah + 3.54\ Ah} \times \%\ (K+C)$$

$$\%C = \%\ (K+C) - \%K$$

Since both illite and expandables add to the 10 A peak in heated slides their total percentage, % (I+Exp), is given by

$$\% (I + Exp) = 100 - \% (K+C)$$

When the slides are solvated with ethylene glycol the 10 A peak is representative of only illite, i.e., 10 Ah = (I+Exp) while 10 Ag = I, where g refers to glycol solvated slide. Percentage illite (%I) and percentage expandables (%Exp) are then given by the equations

$$\%I = \frac{10\ Ag}{10\ Ah} \times (I+Exp) \times \frac{7\ Ah}{7\ Ag}$$

$$\%\ Exp = \%\ (I+Exp) - \%I$$

The term $\frac{7\ Ah}{7\ Ag}$ in the above equation is ideally equal to unity since the intensity of 7 A peak is not altered by either the heat or glycol treatment. It is included here to check fluctuations caused by operating conditions.

# APPENDIX 3. PUBLICATIONS

The following publications were prepared during the course of this investigation:

## Abstracts of papers presented at meetings

Fiene, F. L., S. J. Russell, R.-F. Tsui, 1980, Mineral matter and trace elements in the Herrin (No. 6) Coal in the Illinois Basin: presented at the annual meeting Geol. Soc. Amer., November, Atlanta, Georgia.

Fiene, F. L., 1980, Mineralogy and trace elements in coals of the Illinois Basin: Kentucky Acad. Science, Nov. 8, Lexington, KY.

Harvey, R. D., C.-L. Chou, R. J. Helfinstine, and R. R. Ruch, 1981, Mineral and elemental occurrences in Illinois coals: presented at the annual meeting, AIME, Feb., Chicago, IL.

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Cahill, R. A., J. K. Frost, L. R. Camp, and R. R. Ruch, 1980, Application and comparison of neutron activation analysis with other analytical methods for the analysis of coal: Proc. Atomic Nuclear Methods in Fossil Energy Research, Dec., Mayaguez, Puerto Rico, 17 p.

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## Papers in press

Cahill, R. A. and J. C. Mills, Trace elements of low abundance in Australian bituminous coals. A survey by instrumental neutron activation analysis: Proc. 6th Australian Symposium on Analytical Chemistry.

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