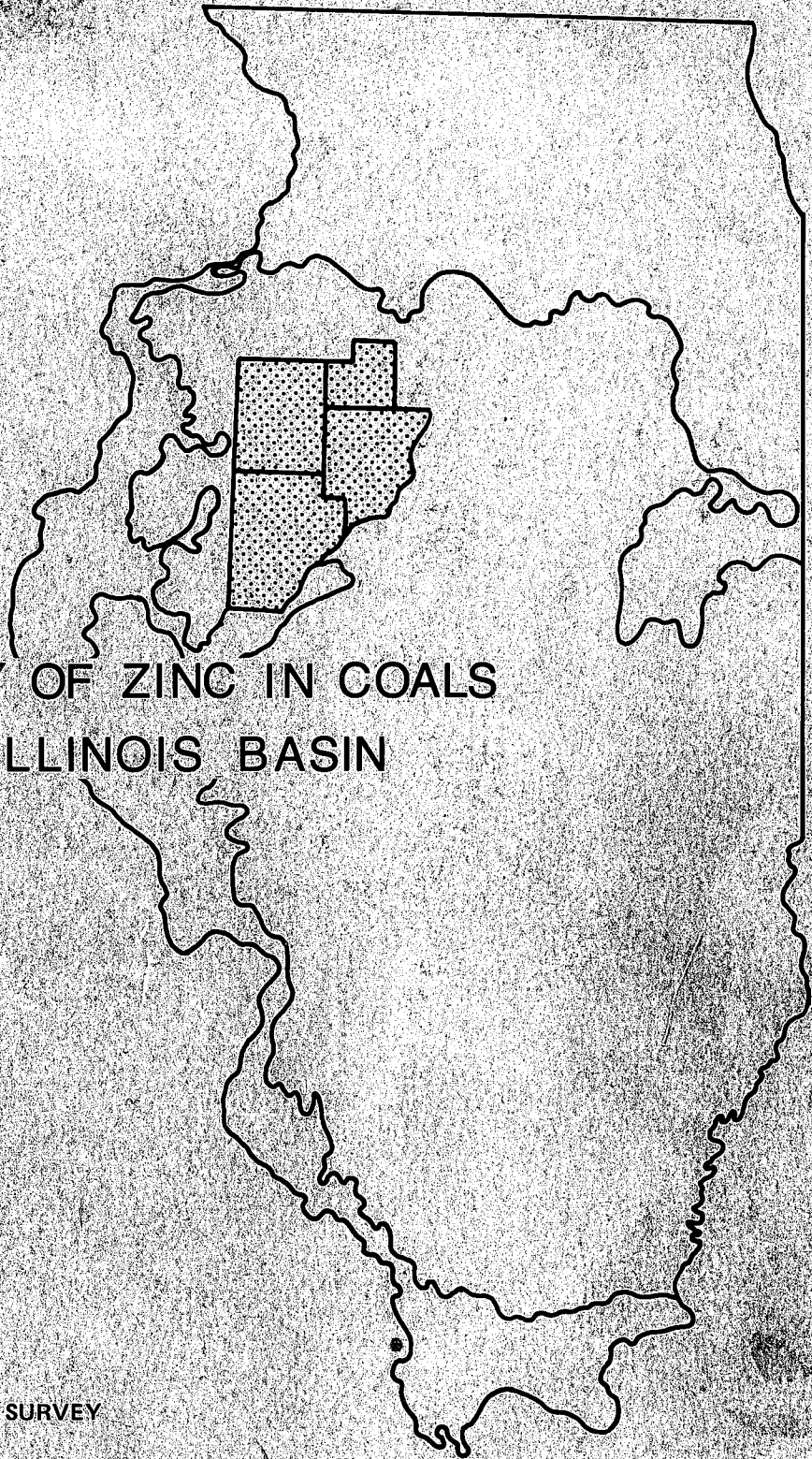


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THE GEOLOGY OF ZINC IN COALS
OF THE ILLINOIS BASIN

ILLINOIS STATE GEOLOGICAL SURVEY

Final Report to the U.S. Geological Survey
Branch of Eastern Mineral Resources
U.S. Department of Interior
August 1978
Grant No. 14-08-0001-G-249

THE GEOLOGY OF ZINC IN COALS
OF THE ILLINOIS BASIN

J. C. Cobb, J. D. Steele, C. G. Treworgy,
J. F. Ashby, and S. J. Russell

Illinois State Geological Survey
Urbana, Illinois

U.S. Department of Interior Grant 14-08-0001-G-249
June 1975 to September 1977

Branch of Eastern Mineral Resources
U.S. Geological Survey
Reston, Virginia

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ABSTRACT

Sphalerite occurs as an epigenetic mineral filling in fractures and other structures in coals of four Illinois counties: Fulton, Knox, Peoria, and Stark. The amount of sphalerite in the coals of these four counties has been investigated because of its potential as an economic resource of zinc and cadmium.

The arithmetic and geometric means for zinc and cadmium as determined by analyses of a large set of coal samples collected in the three producing coals of the district are, for zinc 750 $\mu\text{g/g}$ and 340 $\mu\text{g/g}$ respectively and for cadmium, 7.4 $\mu\text{g/g}$ and 3.5 $\mu\text{g/g}$ respectively. The confidence intervals at the 90 percent significance level for zinc and cadmium are $490 \leq \bar{x} \leq 1010 \mu\text{g/g}$ and $4.6 \leq \bar{x} \leq 10.2 \mu\text{g/g}$ respectively.

The data of zinc and cadmium in coal approximate a lognormal distribution; therefore the sample arithmetic means do not accurately represent the population arithmetic means or geochemical abundance. Sichel's t statistic is a derived estimate of geochemical abundance and is used to estimate the abundance of zinc and cadmium in coal.

The estimate of zinc and cadmium abundance in the coals studied is 1026 $\mu\text{g/g}$ and 8.1 $\mu\text{g/g}$ respectively. Using these estimates and the estimate of coal resources in the study area, 7 billion tons, we estimate the zinc resource to be about 7 million tons and the cadmium resource to be about 60,000 tons.

An in-place coal sampling program which included composite auger, composite face channel, composite face grid, channel, bench, and grab sampling was assessed. Findings were that assays of zinc and cadmium in sphalerite-bearing coals must be determined from samples which include disturbed and undisturbed portions of the coal beds. The composite auger and composite face grid samples are recommended.

Sphalerite occurs in the coals with pyrite, kaolinite, and calcite. The pyrite is heavily replaced by sphalerite. Small broken fragments of sphalerite are enclosed in kaolinite, demonstrating the later deposition of kaolinite. Calcite occurs in several bands, usually between the sphalerite filling and the coal.

Banding in the sphalerite is color distinct and compositionally distinct. Color bands are numerous and complex. Color banding is both gradational and abrupt, with some bands separated by irregular contacts where earlier sphalerite was partially removed. Similar color bands and color band sequences are found in sphalerite fracture filling in the Colchester (No. 2), Springfield (No. 5), Herrin (No. 6), and Danville (No. 7) Coals, strongly suggesting that the same episodes of sphalerite deposition were contemporaneous in all of these coals.

The color bands are compositionally distinct; the darker, reddish-brown bands contain up to 2 percent iron and only .2 percent cadmium. Lighter color bands contain up to 1.5 percent cadmium and only .15 percent iron.

Sphalerite fluid inclusion geothermometry and geochemistry indicate that the fluids of mineralization were saline waters with temperatures from 82 to 102°C. It is hypothesized that these brines originated in the Illinois Basin during compaction and consolidation of Pennsylvanian sediments and migrated through permeable strata which in part included fractured and cleated coal beds. The limiting factor in the amount of sphalerite deposited is the amount of available space for mineral deposition.

Introduction

This report on sphalerite in coals in a four county area (Fulton, Knox, Peoria, and Stark Counties) in west central Illinois and on the abundance and distribution of zinc and cadmium in these coals was undertaken to determine the economic potential of sphalerite as a by-product of coal production. The principal objectives of this investigation are:

1. To provide information on the occurrence of sphalerite in coals.
2. To outline methods of sampling, sample preparation and analytical procedures for determining zinc and cadmium in coals.
3. To evaluate which methods of sampling coal provide the best estimate of zinc and cadmium in coal.
4. To report data of the analyses of zinc and cadmium in coal samples.

The four counties, which are located in the northwestern portion of the Illinois Basin Coal Field, were selected for study because of the high zinc and cadmium values reported for the area in other reports (Zubovic et al., 1964; Ruch et al., 1974; Hatch et al., 1976; Gluskoter et al., 1977). Also the exposures of the coal afforded by the operating surface mines in these counties are numerous and accessible (fig. 1). Coal samples for zinc and cadmium analyses were collected for this study from only active surface mines in the four-county area. The sample locations, mines and coal companies, coals sampled, and sample types are listed in the appendix. Six mines in this district are currently producing from the Colchester (No. 2), Springfield (No. 5), and Herrin (No. 6) Coals. The Danville (No. 7) Coal, though exposed during mining, is not being mined and was not included in the sampling program. Where the Danville (No. 7) Coal was observed in highwalls, it contained sphalerite both as cleat and

fracture filling. Analyses of zinc and cadmium are fewest in the Colchester (No. 2) Coal because it is produced in only one mine. Analytical results are most numerous for the Springfield (No. 5) and Herrin (No. 6) Coals because each is produced by three mines in the district. One mine currently produces two coals from a single pit in which both the Springfield and Herrin Coals are mined.

Although zinc consumption has increased exponentially in this century, domestic reserves of primary zinc have not kept pace (Wedow and Gluskoter, 1977). Currently the U.S. imports approximately 60 percent of its zinc supply. Wedow and Gluskoter (1977) speculated that the zinc recovered as a by-product in coal production may greatly increase the amount of domestic zinc produced during the next 25 years, when huge quantities of sphalerite-bearing Interior Province coals will be mined.

The potential of northwestern Illinois coals for recovery of zinc was first studied by Hatch et al. (1976), who found high concentrations of zinc and cadmium in coals from both the northwestern and southeastern portions of the Illinois Basin Coal Field and identified sphalerite (ZnS that contains up to 1.2 percent by weight in cadmium) in fractures (cleat) in the coal. In washability tests, 99 percent of the zinc and cadmium were found in the heavier specific gravity fractions. These results indicate that sphalerite can be recovered from raw coal by specific gravity techniques.

ACKNOWLEDGMENTS

We wish to thank Helmuth Wedow, Jr., and Joseph R. Hatch for their continued assistance during the work on this report. Both gave valuable suggestions in field work and provided critical review of the manuscript. Joseph R. Hatch also provided samples of sphalerite in coal outside of Illinois.

The study was supported in part by the U.S. Geological Survey, Branch of Eastern Mineral Resources, under U.S. Department of Interior Grant 14-08-0001-G-249 to Dr. Harold J. Gluskoter, Illinois State Geological Survey.

GEOLOGY OF THE STUDY AREA

The four-county study area lies in the northwestern part of the Illinois Basin (fig. 1) in a stable tectonic area known as the Western Shelf. Regionally, the strata in this area dip gently southeast towards the center of the basin at less than 20 feet per mile. Minor structural features, such as small faults, clay dikes, and warping of strata are common. Total thickness of sedimentary strata overlying the Precambrian basement ranges from 3,600 to 5,100 feet. Figure 2 is a general stratigraphic section of the study area showing Precambrian to Quaternary principal lithologies.

Pennsylvanian strata ranging in thickness from 0 to 600 feet, and overlain by Pleistocene glacial deposits, cover nearly all of the study area. The Pennsylvanian strata are made up largely of sandstones and shales with thin limestones and coals scattered throughout (fig. 3). The coal resources of this area which were mapped by Cady (1952) and Smith and Berggren (1963) are currently estimated to be about 7 billion tons in place as defined in these studies. Only four coal seams in this area are considered minable: the Danville (No. 7), Herrin (No. 6), Springfield (No. 5), and Colchester (No. 2). Of these four coals, all but the Danville (No. 7) are actively mined at this time, although the Danville (No. 7) is frequently exposed during mining. In 1976, 5.4 million tons, or 9 percent of Illinois' total coal production, came from this area.

OCCURRENCE OF SPHALERITE IN COAL

General

Sphalerite occurs in coal as epigenetic mineral fillings in fractures, cleat, cavities, faults, and clay dike disturbances. Figures 4 a-d show examples of sphalerite in cleats of the Colchester, Springfield, and

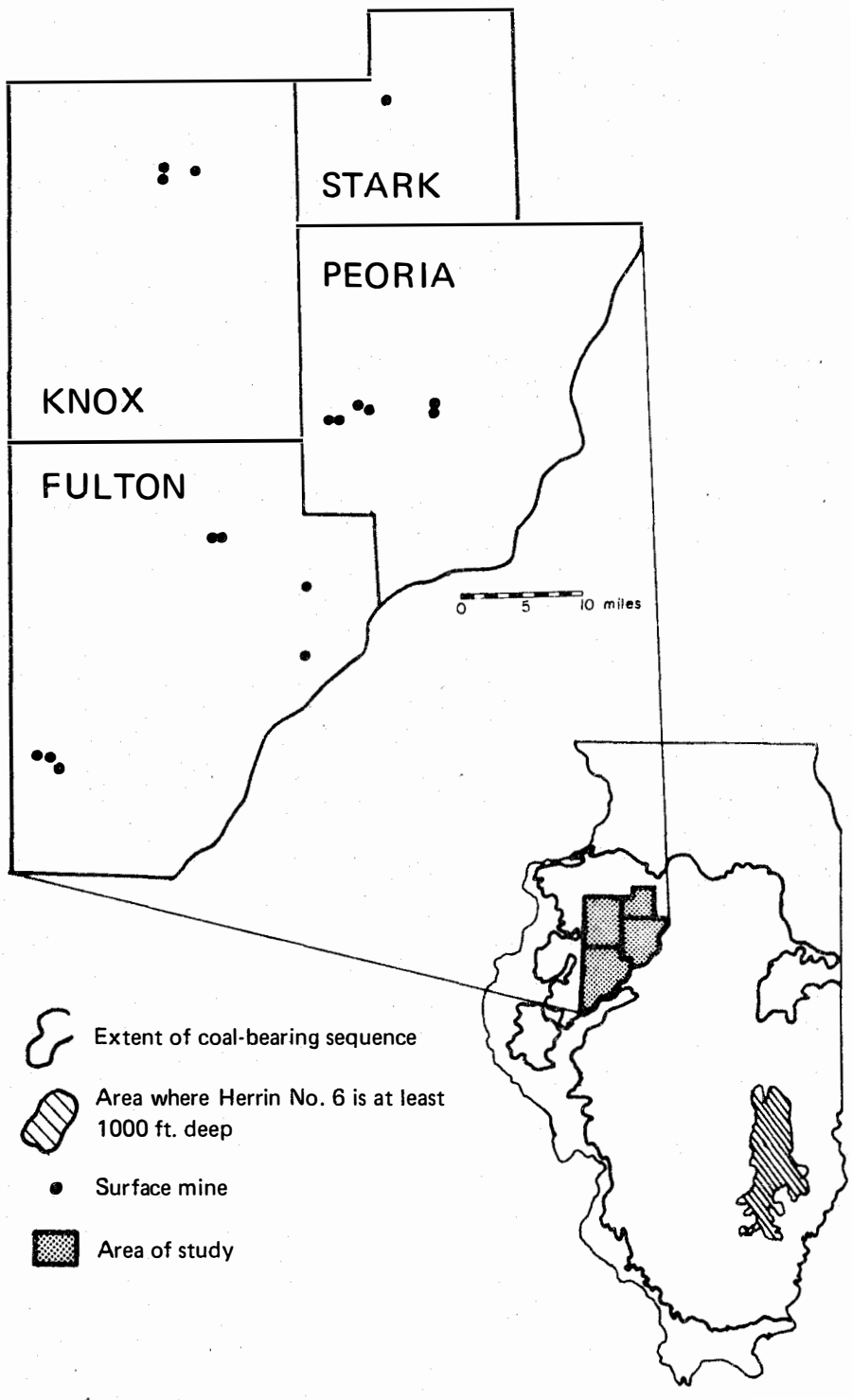
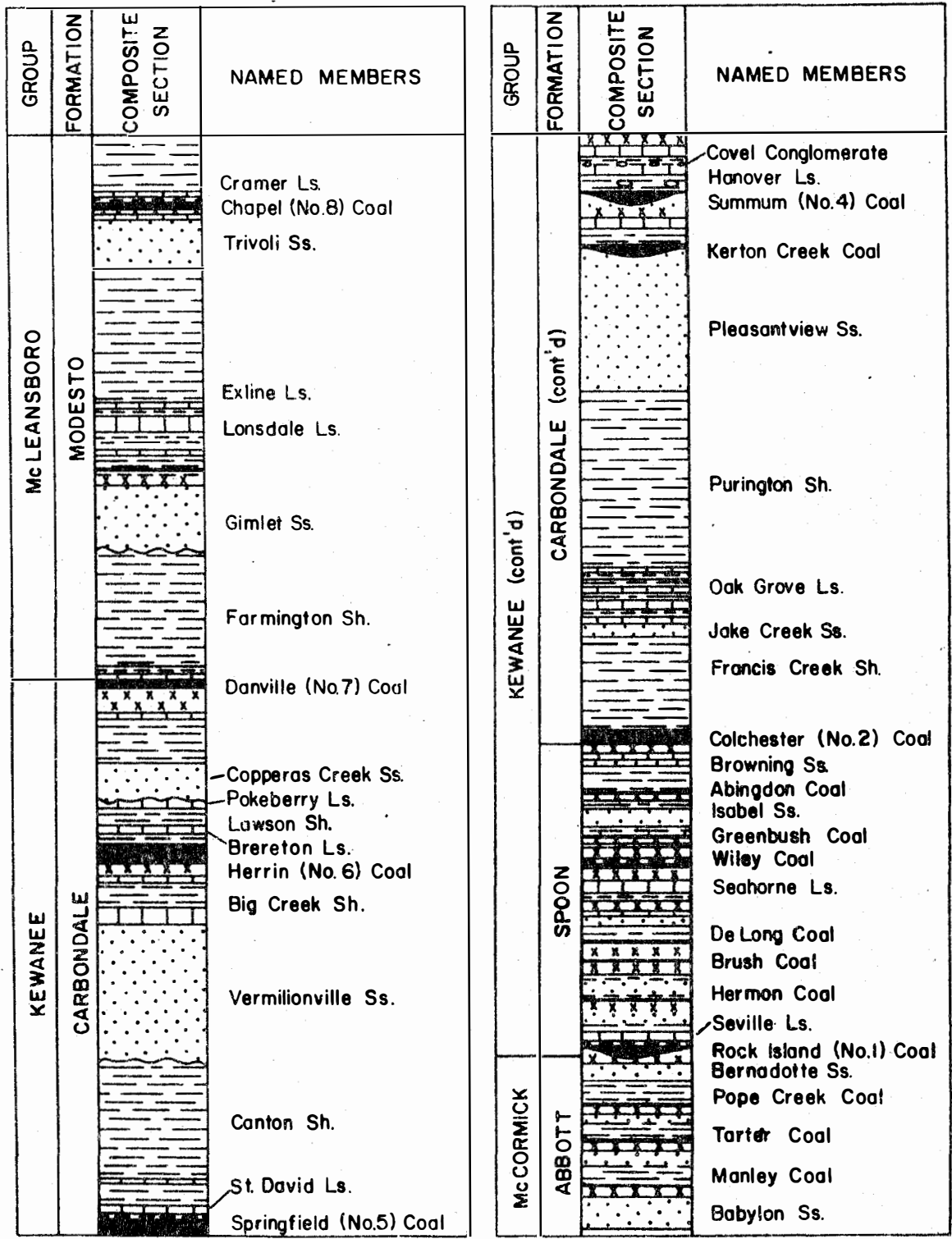


Fig. 1. Location of study area within the Illinois Basin Coal Field and distribution of sampling locations

SYSTEM	DOMINANT LITHOLOGY	THICKNESS (ft)
Quaternary	Glacial drift	0-200
Pennsylvanian	Sst, sltst, sh, lmst, & coal	0-600
Mississippian	Limestone	0-500
Devonian	Dol, lmst, sh	0-275
Silurian	Dolomite	0-400
Ordovician	Dolomite and limestone	1150-1500
Cambrian	Sandstone	200-2700
Precambrian	Granite	

Fig. 2. Generalized stratigraphic section of the study area



Approximate Scale in Feet

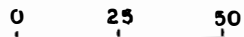


Fig. 3. Composite section of Pennsylvanian strata in western Illinois (from Smith & Berggren, 1963).

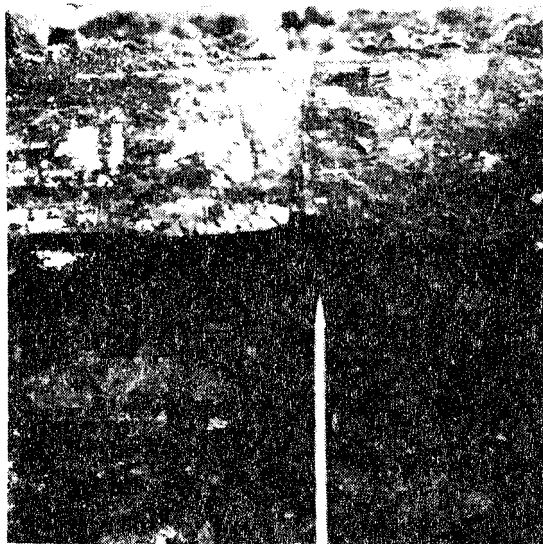
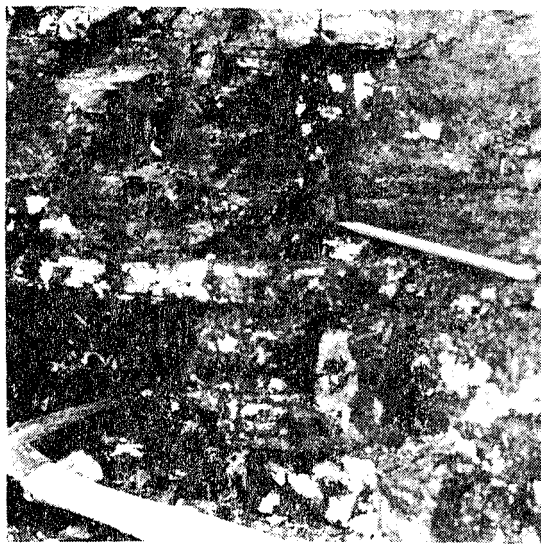
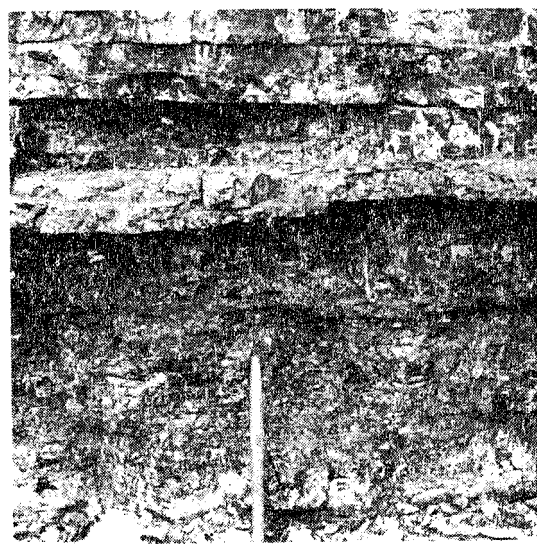
*a**b**c**d*

Fig. 4. *a*—The pencil is pointing to a sphalerite-filled cleat in the Colchester (No. 2 Coal) (area of coverage is 18 x 18 in.). *b*—Sphalerite-filled cleats in the upper part of the Springfield (No. 5) Coal (pen is 6 in. long). *c*—The pencil is pointing to an exposed sheet of sphalerite filling in the Herrin (No. 6) Coal (pencil is 6 in. long). *d*—Sphalerite-filled cleats in the lower part of the Springfield (No. 5) Coal (pen is 6 in. long).

Herrin Coals. Cleats are the vertical joint-like structures in the coals. The sphalerite in cleats and fractures is of the vein filling type; sphalerite in faults and slips is of the vein filling type along slickensided surfaces; and sphalerite in clay dikes occurs as crystalline aggregates and discrete crystals in the clastic matrix of the dikes. Euhedral sphalerite crystals are found in cavities which were produced in the coal as a result of structural disturbances of the coal bed such as clay dikes. Figures 5a and b show a vertical and horizontal section through a sphalerite vein filling. Figures 5c and d show two sphalerite crystalline aggregates.

Previous Investigations

Hatch et al. (1976) first described sphalerite in coal after speculating that samples of coal from the northwestern part of the Illinois Basin Coal Field had sufficient concentrations of zinc to be present as a separate zinc sulfide phase. Hatch et al. described sphalerite vein fillings in coal cleat and also described the mineralization of the veins. They recognized the complex history of vein filling and accompanying cleat opening. They also divided the mineralization into three stages: a sulfide stage with sphalerite and pyrite, a silicate stage with kaolinite and quartz, and a carbonate stage with calcite. The sequence of sphalerite deposition was described by Hatch et al. (1976) in five steps defined on the basis of sphalerite band color: (1) gray-white sphalerite with some irregular pale purple patches; (2) purple laminated sphalerite with more intense coloration toward end of the stage; (3) intense, almost opaque, purple sphalerite; (4) pale yellow to yellow-brown sphalerite; (5) gray-white sphalerite with irregular purple patches. Steps 1 through 4 were given as the most important quantitatively, and not all steps were present in all veins observed.

For the present study, sphalerite vein fillings and crystalline aggregates were prepared in doubly polished thin plates of about 250 micron

*a**b**c**d*

Fig. 5. *a* and *b*—Vertical and horizontal thin sections of sphalerite filling in cleats of the No. 5 Coal. Areas of view are 1.8 x .6 in. *c* and *d*—Thin sections of sphalerite crystal aggregates from the Herrin (No. 6) Coal (*c*) and the Colchester (No. 2) Coal (*d*). Areas of view are 1.6 x 1.0 in.

thickness (P. B. Barton, personal communication). The description of sphalerite in the present study may vary from descriptions given by Hatch et al. (1976) because those thin sections were prepared by conventional thin section procedures and were not doubly polished.

Sphalerite Vein Filling

Sphalerite vein fillings in coal are in cleat or fractures which measure from 0.124 in. to 0.75 in. wide and from 1 in. to the entire seam thickness (about 60 in.) long. Figures 5a and b are examples of sphalerite vein fillings in cleats of various coals. The vein fillings have a complex history of mineralization, cleat and fracture opening, dissolution and replacement, and cross-cutting bands. The vein fillings exhibit symmetrical and asymmetrical crustification which was in part controlled by the behavior of coal microlithotypes during cleat or fracture opening (dilatation). After the initial opening in the coal was filled with sphalerite, further dilation caused splitting down the sphalerite filling if the sphalerite-to-coal bond was strong, producing symmetrical vein filling having the oldest deposition on the outside and youngest in the middle. Clarite, a coal microlithotype, appears to bond to sphalerite with enough strength to produce symmetrical vein filling. Frequently, however, asymmetrical filling occurred because the bonding of sphalerite to inertite (a coal microlithotype with 95 percent inertinite, mostly fusinite) was weak, and subsequent dilation produced splitting between the coal and the sphalerite. In this case the older sphalerite band is in the middle and the younger is outside.

Symmetrical and asymmetrical vein fillings occur in a single cleat. This complex type of vein development is further complicated by later cross-cutting bands of sphalerite and by dissolution of sphalerite and replacement by kaolinite.

Pyrite does not occur in all vein fillings containing sphalerite, and there are a large number of pyrite filled veins in which sphalerite is quite scarce. Pyrite in some vein fillings occupies the central portion. This central pyrite "core" is flanked on both sides by sphalerite. While the pyrite "core" is often continuous over many inches, in some instances where replacement is extreme the pyrite is reduced to disconnected small blebs between two larger sphalerite bands.

Kaolinite occurs along the coal wall between coal and sphalerite and within sphalerite bands where cracks occurred, allowing dissolution of sphalerite and precipitation of kaolinite. Corroded fragments of sphalerite are embedded in kaolinite. In thin section the kaolinite appears to have a horizontal remnant layering which appears to be in response to sorting of the kaolinite crystallites as they precipitated out of solution.

The sequence of sphalerite color bands in vein fillings from recent studies is similar to the one described by Hatch et al. (1976): (1) pale yellow to colorless with variable intensities of purple laminations; (2) varieties of yellow to dark yellow, including some greenish yellow (some of the color variation may be due to thickness of the polished plates) with scattered patches of purple; (3) dark yellow with some lamellae, both purple and brown; and (4) reddish-brown to orange. Figures 6a-c show photomicrographs of sphalerite banding in the Herrin and Springfield Coals of Illinois and the Fleming Coal of Missouri. All of these photomicrographs have an orange band of sphalerite between a purple laminated band on one side and a yellow band on the other.

Sphalerite Crystalline Aggregates

Sphalerite crystalline aggregates overall are oblate in shape and measure 7 in. by 3 in. in long and short dimensions. They occur in the clastic matrix of clay dikes. Damberger (1970, 1973) discusses the origin

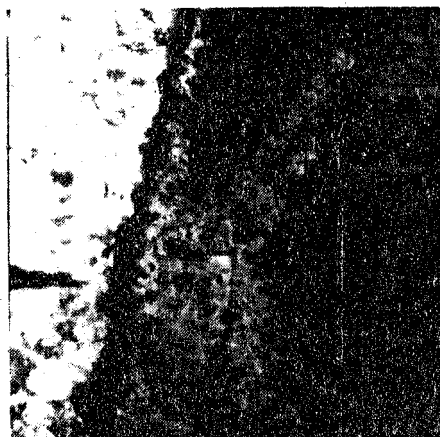
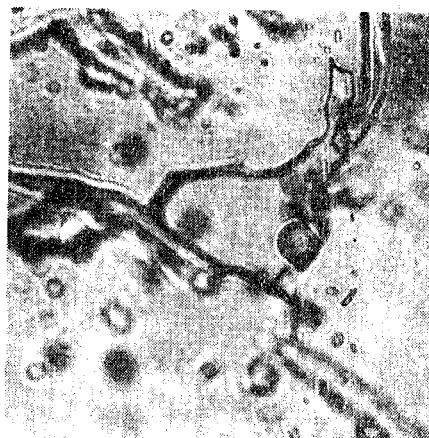
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Fig. 6. Photomicrographs of banding in sphalerite vein fillings and a fluid-filled inclusion in sphalerite from a clay dike. *a*—Vein filling in Herrin (No. 6) Coal, Peoria County, Illinois, with left band light yellow, center band orange, and right band intense purple lamellae. Center band width is 3mm and vertical orientation is parallel to center band. *b*—Vein filling in Springfield (No. 5) Coal, Fulton County, Illinois, with left band light yellow, center band orange, and right band yellow with purple lamellae. Center band width is 2mm and vertical orientation is parallel to center band. *c*—Vein filling in Fleming Coal, Vernon County, Missouri, with left band light yellow, center band orange, and right band light yellow with purple lamellae. Center band width is 2mm and vertical orientation is parallel to center band. *d*—Crystal aggregate from clay dike in Colchester (No. 2) Coal, Fulton County, Illinois, with fluid-filled inclusion in yellow sphalerite. Diameter of gas bubble at right center is 10 microns.

of clay dikes in coal beds. Figure 7a is an example of a sphalerite crystal aggregate in a clay dike. Figures 7b-d are examples of sphalerite in other structures in the coal bed. The crystalline aggregates usually envelop coal particles. The boundaries between growth stages are concentric to the coal/sphalerite interface, indicating that sphalerite nucleation commenced at the coal particle and growth continued outward. Kaolinite and calcite occur at crystal junctions in the aggregates.

The sequence of sphalerite bands in crystalline aggregates is divided into eight steps based on color. These steps are: (1) light brownish-yellow, (2) dark yellow with brown patches, (3) light yellow with light purple lamellae, (4) colorless to pale yellow, (5) yellow with intense purple lamellae, (6) colorless to pale yellow, (7) yellow with purple lamellae, and (8) yellow.

The relationship between sphalerite bands in crystal aggregates to vein fillings is not clear. The sequences of yellow with purple lamellae in the later steps of aggregates is very similar to the first steps in the vein fillings. The clay dikes in which the crystalline aggregates are found have an early history in the formation of the coal bed. It is merely speculation that the clay dike aggregates began forming shortly before cleats and fractures had opened sufficiently to begin mineral filling. However, by the end of the growth of aggregates, the vein filling had commenced.

Origin of Sphalerite in Coal

The origin of sphalerite in coal is an important consideration in estimating the extent of sphalerite-bearing coals and the ultimate amount of zinc and cadmium in coals of the Interior Province. A localized process of sphalerite deposition in coal, similar to the scattered occurrences of sphalerite-filled concretions, would preclude a widespread

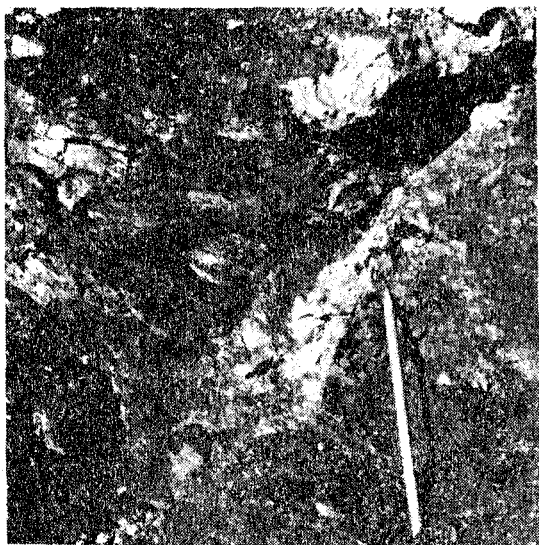
*a**b**c**d*

Fig. 7. *a*—The pencil is pointing to sphaerulite crystal in the clayey matrix of a dike in the Colchester (No. 2) Coal (pencil is 6 in. long). *b*—The pencil is pointing to a sphaerulite crystal on a slickensided surface in the Herrin (No. 6) Coal (pencil is 6 in. long). *c*—The pencil is pointing to sphaerulite filling in a fracture in the Herrin (No. 6) Coal (pencil is 6 in. long). *d*—The ruler is lying along two slickensided surfaces which contain sphaerulite in the Herrin (No. 6) Coal.

occurrence of sphalerite in coals. However, a mechanism of sphalerite deposition in coals on the scale of basins provides an optimistic picture of large quantities of sphalerite spread throughout much of the Pennsylvanian coals of the Midcontinent. Much of the evidence supporting a large-scale, basinal mechanism for sphalerite deposition in coal is problematic; however, there is a strong indication of a basinal source for the ore fluid.

Filling temperatures of fluid inclusions indicate a range of temperatures from 80°C to 102°C (E. Roedder, personal communication, and this study). Figure 6d shows a fluid-filled inclusion with a gas bubble measuring 10 microns in diameter. Composition of the inclusion fluids are sodium- and potassium-rich brines. The salt concentrations approach 100,000 µg/g total dissolved salts, similar in composition to inclusion fluids in Mississippi Valley type ores and present day Illinois Basin oil field brines.

No evaporite deposits are known in the stratigraphic section of the study area. The salinity of the inclusion fluids and therefore of the ore fluids is probably of marine origin, derived from waters trapped during sedimentation in the Illinois Basin sediments and concentrated by sediment consolidation processes. The metal content of the ore fluid was probably scavenged from shales, sandstones, and other sediments during residence of the ore fluid in the deeper parts of the basin. It is possible that the geothermal gradient for the basin was higher and that the basin was buried much deeper than at present. This would account for the slightly elevated temperatures of the ore fluid.

A change in the basin hydrology caused by changes in the tectonic regime affecting sedimentation, erosion, or compaction of the basin and its deep circulation cells provided the hydraulic potential to displace the ore fluid up through the coal beds. After the coal beds had become brittle

enough to fracture and cleat, they could behave as aquifers sandwiched between relatively impermeable shales and clays. Under such conditions the ore fluid could migrate many miles.

Although the paragenesis of vein-filling in coal is limited in comparison to Mississippi Valley type ores and the mineralogy is much simpler, nevertheless the temperature of formation, trace element suites, and inclusion fluid composition are all similar. The sphalerite in coal is multibanded as is the sphalerite in Mississippi Valley type ores, and the areal extent over which the banding is traceable is large (about 500 square miles).

COLLECTION, PREPARATION, AND ANALYSIS OF COAL FOR ZINC AND CADMIUM

Sample Collection

To determine the average content of zinc and cadmium in the coals, each producing coal bed was sampled carefully and uniformly. Varying conditions of mine exposures prevented standardizing the sampling program. Sampling procedures followed methods typically used in sampling coal for bulk composition and in sampling ore bodies for ore grade. Only unweathered, fresh coal samples were collected.

The types of samples used were composite auger, bench, channel, composite face channel, grab, and a variation of "chip sampling," here called composite face grid. These types are described as follows:

Bench sample--A sample of the coal taken in vertical segment 6 to 10 in. high, called benches. Each bench yields a separate sample. A series of bench samples of the entire coal thickness constitutes the bench set. Both the roof and floor of the coal bed are occasionally included in the bench set.

Channel sample—A sample of the entire coal thickness obtained by cutting a 6-inch-wide vertical channel down the coal face. For this study, all mineral partings were included in the sample.

Composite auger sample—A sample of cuttings collected from each auger hole in a series of ten holes, each 8 in. in diameter, spaced 1.5 ft apart, drilled through the entire coal thickness, and composited into a single sample.

Composite face channel—A standard sampling technique used to obtain coal samples for bulk compositional analysis. Three coal channel samples spaced randomly along a mine exposure are combined into a single composite sample.

Composite face grid (or chip sample)—A method used to evaluate the ore grade in disseminated ore deposits at a mine face. For this study, coal was sampled from fresh mine faces by measuring a 20-ft length of the coal face and placing a grid with intersections at 1-ft intervals on the coal face. A hand-sized sample was removed from each intersection of the grid lines and all the samples were then combined into a single large sample.

Grab sample—A sample of coal taken where exceptionally high concentrations of zinc and cadmium were suspected.

Rock materials associated with the coals were sampled to determine their zinc and cadmium content. Such materials included shales above the

coal beds, underclays, shaley partings, and clay dikes. These samples are described as follows:

Roof shale—A grab sample of the roof material immediately above the coal. Roof shale was also sampled as a part of the bench samples.

Underclay sample—A grab sample of underclay immediately below the coal. Underclay was often sampled as a separate bench in some bench samples.

Mineral or shale partings—A grab sample of prominent partings in a coal or a separate sample taken with bench sets. These samples include grab samples of clay dike material.

Slurry refuse—A bulk shovel sample taken from a slurry settling pond. Slurry is the fine-grained refuse of coal mine washer wastes.

Gob refuse—A bulk sample collected from preparation plants or mine dumps. Gob is coarse-grained refuse of coal mine washer wastes.

Sample Preparation

All samples were immediately processed according to the following procedures:

1. The coal sample was crushed in a small jaw crusher with jaws set open.
2. The sample was split in a one-inch riffler.
3. The sample was subjected to a second crushing in jaw crusher with jaws set tight.
4. The sample was split in an enclosed quarter-inch riffler.
5. The sample was weighed and placed in an air-dry pan and dried overnight.
6. Dry weight was recorded.

7. The sample was crushed with a small roll crusher.
8. The sample was split in the riffler to obtain about 1 kilogram for reserve.
9. A second sample was split from the remainder (in riffler) to obtain about .5 kg.
10. The .5-kg sample was pulverized in a Holmes Mill to <60 mesh.
11. The pulverized sample was split on a small riffler to obtain a 150-g sample.
12. The sample was bottled and agitated for 30 minutes to ensure thorough mixing.

Chemical Preparation and Analysis

Cadmium and zinc in the coal samples were determined by using a Perkin-Elmer Model 306 atomic absorption spectrophotometer equipped with a Perkin-Elmer Model 056 recorder. A 4-inch long, single-slot, flathead burner with an air-acetylene flame was used for sample atomization. A Perkin-Elmer electrodeless discharge lamp and hollow cathode lamp were used in the determination of Cd and Zn, respectively. Corrections for nonatomic background absorption were made simultaneously using a Perkin-Elmer deuterium arc background corrector.

All reagents used were ACS-certified reagent-grade chemicals; standard stock solutions were prepared from high-purity metals or compounds. Calibration standards prepared from diluted stock solutions contained the following matrix components: 1.4 percent v/v aqua regia (1:3:1, HNO_3 : HCl : H_2O), 1 percent v/v 48 percent HF, and 1 percent w/v H_3BO_3 .

About 2 grams of crushed and ground coal samples of approximately <60 mesh were placed in a 30-ml Vycor crucible and ashed in a muffle furnace at 500°C for 5 hours. The ash was then ground with a mullite mortar and pestle to approximately <200 mesh and stored in acid-washed glass vials.

Approximately 0.1 g of ash, dried at 110°C for several hours, was transferred to an acid-washed 60-ml linear polyethylene bottle. The sample was treated with 1 ml of distilled HCl and heated to dryness on a steam bath. The sample was then wetted with 0.7 ml aqua regia followed with the addition of 0.5 ml of 48 percent HF. The bottle was capped tightly and placed on a steam bath for approximately 2 hours. The digested sample was treated with 10 ml of a 50-g/liter solution of H_3BO_3 to complex the fluorine. The digested sample was transferred to a 50-ml Pyrex volumetric flask, diluted to volume with deionized water, and returned to the decomposition bottle for storage. (See Bernas, 1968; French and Adams, 1973; and Ruch et al., 1974 for a more detailed discussion of the dissolution procedure.)

The analytical wavelengths used for the analyses were 228.8 nm for Cd and 213.9 nm for Zn. Calibration standards were in the range of 0.01 to 1.0 $\mu\text{g/g}$ for Cd and 0.1 to 10.0 $\mu\text{g/g}$ for Zn. Where sample concentrations were greater than the upper limit of linear response, either the samples were diluted or the burner was rotated from its parallel orientation to bring all absorbance values within the range of linearity. The metal concentrations were calculated by solving for concentrations in a calibration curve constructed from least squares, where absorbance was a function of concentration. A new calibration curve was calculated for each set of analyses.

It has been demonstrated (Ruch et al., 1974) that Cd and Zn are retained during ashing; none is lost by volatilization. A comparison of our laboratory procedures performed on the National Bureau of Standards coal sample SRM 1632 with the certified results of the National Bureau of Standards procedures on SRM 1632 shows the accuracy of our atomic absorption procedures. The NBS values for Cd and Zn are 0.19 and 37 $\mu\text{g/g}$ respectively,

and the values determined in this study were $<0.23 \mu\text{g/g}$ for Cd and $36.7 \mu\text{g/g}$ for Zn. The average relative standard deviation for both Cd and Zn determinations by atomic absorption spectrometry in this study was 6 percent or less.

TRACE ELEMENTS IN SPHALERITE FROM COAL

Trace elements and trace element trends were investigated in vein filling and crystalline aggregates using neutron activation, atomic absorption spectrophotometry, and electron microprobe analytical techniques. Table 1 shows trace element concentrations as determined from crushed samples of sphalerite hand picked to visual purity. The samples labeled "purple" and "yellow" were hand picked particles of predominantly purple sphalerite and yellow sphalerite from the same sphalerite crystalline aggregate sample.

In general the samples contain iron (0.15-0.93 weight percent), cadmium (0.30-0.56 weight percent), copper (360-470 $\mu\text{g/g}$), nickel (<10 -440 $\mu\text{g/g}$), gallium (33-110 $\mu\text{g/g}$), and lesser amounts of other elements (see table 1). No significant difference is found between the "purple" and "yellow" sphalerite.

Table 2 shows concentrations of zinc and cadmium in sphalerite samples from coals. The sphalerite samples were crushed and hand picked to visual purity under a microscope. The analyses were performed with atomic absorption spectrophotometry.

Sphalerite color bands corresponding to growth stages in vein fillings and crystalline aggregates were distinguished by cross-cutting relationships, concentric growth development, and other relationships as previously described. The electron microprobe was employed to characterize the iron and cadmium content of the color bands. These studies indicate that the iron content in vein filling sphalerite increases while the

Table 1. Minor and Trace Elements in Sphalerite from Coal Cleat, Cavities, and Clay Dikes by Neutron Activation Analysis^a

Element	Cleat filling Herrin Coal	Clay Dike Colchester Coal	Clay Dike Colchester Coal	Clay Dike Colchester Coal	Cavity filling Herrin Coal	Clay Dike Colchester Coal— Purple	Clay Dike Colchester Coal— Yellow
Na	31	48	56	34	37	60	98
K	19	75	14	79	<14	107	104
Rb	23	n.d. ^b	41	n.d.	n.d.	110	n.d.
Ga	82±6	89±8	110±7	97±11	65±6	92	33
In	0.7	0.9	0.7	2.7	9.0	n.t. ^c	n.t.
As	6.9±.9	n.d.	0.6	n.d.	n.d.	0.2	0.4
Sb	n.d.	0.2	0.3	0.3	0.8	n.d.	<0.1
Mn	11	2.7	11	3.7	1.9	7.3	n.d.
Co	1.7	<0.4	<0.6	n.d.	0.4	n.d.	<0.5
Ni	n.d.	n.d.	n.d.	300	440	n.d.	n.d.
La	2.3	2.3	3.0	2.7	2.0	<2	<2
Sm	<0.1	n.d.	0.1	.08	n.d.	0.2	n.d.
Eu	0.02	0.02	0.04	0.02	0.02	n.d.	<0.03
Dy	n.d.	n.d.	0.2	<0.1	0.3	n.t.	n.t.
Cd	.56% ^d	n.t.	n.t.	n.t.	n.t.	.34%	.30%
Cu	400	380	360	420	390	470	420
Fe	.93% ^e	.26%	.28%	.20%	.24%	.20%	.15%

NOTE: Except where percentages are indicated, all values are in parts per million.

^aSphalerite hand-picked to visual purity.

^bNot detected.

^cNot tested.

^dQuantitative electron microprobe analysis.

^eAtomic absorption spectrophotometry.

Table 2. Zinc and Cadmium Concentrations in Sphalerite Associated with Coal

Sample number	Coal Association	Zinc (%)	Cadmium (µg/g)
C-19051	6	63.1	3870
C-19052	2	66.4	6900
C-19053	2	64.6	4160
C-19058	2	66.7	3700
C-19059	6	65.6	6120

cadmium content decreases from the initial growth to the final growth. Conversely, the iron content in sphalerite crystalline aggregates decreases while the cadmium content increases from the initial growth to the final growth (Cobb and Russell, 1976).

The quantitative electron microprobe determinations were made by taking probe traverses along color bands and taking counts from points about 10 microns apart. The representative concentrations given are arithmetic means of at least 60 point determinations in a single band. The iron and cadmium content in vein filling sphalerite is characterized by the following representative samples:

- (1) Initial stage: band color is light yellow with purple lamellae, iron content is 0.1 weight percent and cadmium content, 0.9.
- (2) Second stage: band color is yellow with scattered purple patches, iron content is 0.4 weight percent and cadmium content, 0.4.
- (3) Third stage: band color is medium dark yellow, iron content is 0.51 weight percent and cadmium content, 0.3.
- (4) Final stage: band color is reddish brown (orange in some cases), iron content is 1.1 weight percent and cadmium content, 0.3.

The iron and cadmium content in crystalline aggregates is characterized as follows:

- (1) Initial stage: band color is light brownish yellow iron content is 0.7 weight percent and cadmium content, 0.2.

- (2) Second stage: band color is dark yellow with brown patches, iron content is 0.7 weight percent and cadmium content 2.0.
- (3) Third stage: band color is light yellow with purple lamellae, iron content is 0.4 weight percent and cadmium, 0.2.
- (4) Fourth stage: band color is pale yellow to colorless, iron content is 0.2 weight percent and cadmium content, 0.3.
- (5) Fifth stage: band color is intense purple lamellae, iron content is 0.4 weight percent and cadmium content, 0.3.
- (6) Sixth stage: band color is yellow with purple lamellae, iron content is 0.4 weight percent and cadmium content, 0.3.
- (7) Seventh stage: band color is light yellow, iron content is 0.3 weight percent and cadmium content, 0.4.

For purposes of comparing sphalerite in coals of the study area with similar vein filling sphalerite in coals of Missouri, iron and cadmium determinations were made on corresponding color bands. The three most distinctive color bands common to all vein fillings were analyzed. These results are summarized below.

Coal—Location	Color Band					
	Reddish brown		Yellow		Purple lamallae	
	Cd	Fe	Cd	Fe	Cd	Fe
Fleming Coal—Missouri	0.5	0.7	0.3	0.4	0.2	0.3
Mineral Coal—Missouri	0.7	1.8	0.3	0.5	0.2	0.5
Springfield Coal—Fulton County	0.3	1.1	0.3	0.5	0.4	0.4
Springfield Coal—Fulton County	0.5	1.3	0.5	0.7	0.4	0.5
Herrin Coal—Peoria County	0.3	1.5	1.2	0.4	0.3	0.6

The iron and cadmium content in the same color bands in these different vein fillings is similar. Because these preliminary studies show similar color and trace element content in sphalerite vein fillings from coals in widely separated sample locations, continued work is necessary to better understand the processes which control deposition of sphalerite in coal.

RESULTS AND DISCUSSION OF COAL SAMPLING FOR ZINC AND CADMIUM

General

Tables 3 through 7 present the atomic absorption spectrophotometry data for zinc and cadmium content in coal for the five different coal sampling methods evaluated in this study. The locations of these samples, mine and coal company names, coal seam mined, sampling method, and sample numbers are given in the appendix. The data are most complete for the Herrin (No. 6) and Springfield (No. 5) coals, while limited exposures prevented more comprehensive sampling of the Colchester (No. 2) coal. From the standpoint of the different sampling methods, the data are most numerous for the bench, channel, composite face channel, and composite face grid, while least numerous for the composite auger samples.

A general survey of all the data is necessary before an evaluation of the various sampling methods is begun. The frequency distribution of zinc and cadmium content in coal for all samples shows a bimodal tendency (fig. 8). Field observations made during sample collection indicate that the lower mode (0 to 200 $\mu\text{g/g}$ zinc and 0 to 3 $\mu\text{g/g}$ cadmium) is composed of samples collected from flat or undisturbed parts of the coal beds and is attributed to sphalerite filling small fractures and cleats. Figures 9a and b show undisturbed portions of coal beds which were sampled and found to contain smaller concentrations of zinc and cadmium. The

Table 3. Zinc and Cadmium
Concentrations in Bench Sets

Sample number	Coal	Sample Type ^a	Ash %	Zinc (µg/g)	Cadmium (µg/g)
C-19060	2	RK1	95.37	79	<3.1
C-19062	2	B1	6.52	5	<0.2
C-19063	2	B2	6.74	5	<0.2
C-19064	2	B3	5.87	6	<0.2
C-19065	2	B4	5.02	18	<0.2
C-19061	2	RK2	92.96	67	<2.8
C-19079	5	B1	11.37	1770	19.4
C-19080	5	B2	10.77	7660	80.9
C-19081	5	B3	14.65	46	<0.3
C-19082	5	B4	16.92	14	<0.3
C-19083	5	B5	15.86	290	2.9
C-19084	5	B6	16.97	17	<0.3
C-19227	5	B1	14.14	370	3.4
C-19228	5	B2	10.07	160	2.1
C-19229	5	B3	11.20	420	4.7
C-19230	5	B4	10.22	330	3.3
C-19231	5	B5	14.02	10	<0.3
C-19232	5	RK2	95.61	24	<2.2
C-18982	6	RK1	91.34	32	<2.8
C-18983	6	B1	7.95	230	1.8
C-18984	6	B2		16	<1.0
C-18985	6	B3	10.08	14	<0.3
C-18986	6	B4	6.30	6	<0.2
C-18987	6	B5	10.77	9	0.6
C-18988	6	B6	17.90	14	<0.5
C-18989	6	RK2	87.85	34	<2.7
C-19066	6	B1	11.73	6	<0.4
C-19067	6	B2	8.12	8	<0.3
C-19068	6	B3	7.09	9	<0.1
C-19069	6	B4P	62.11	14	<1.9
C-19070	6	B5	24.10	45	<0.4
C-19071	6	B6	22.42	12	<0.7
C-19093	6	RK1	97.59	91	<2.5
C-19105	6	B1	9.95	950	11.1
C-19085	6	B2	10.35	11500	84.0
C-19086	6	B3	14.45	14900	117
C-19087	6	B4	7.74	420	3.4
C-19088	6	B5P	90.88	57	<1.6
C-19089	6	B6	11.83	48	0.3
C-19090	6	B7	13.41	20	<0.3
C-19091	6	B8	22.57	33	<0.5
C-19092	6	RK2	93.25	71	<2.4

Table 3. Continued

Sample number	Coal	Sample Type ^a	Ash %	Zinc (µg/g)	Cadmium (µg/g)
C-19094	6	RK1	90.90	42	<2.1
C-19095	6	B1	20.43	11	<0.5
C-19096	6	B2	11.94	122	0.5
C-19097	6	B3	15.18	186	0.5
C-19098	6	B4	9.21	13	<0.2
C-19099	6	B5	6.49	6	<0.2
C-19100	6	B6P	84.42	20	<1.9
C-19101	6	B7	15.03	10	<0.4
C-19102	6	B8	13.44	2210	17.6
C-19103	6	RK2	90.56	43	<2.1
C-19211	6	RK1	96.60	71	<2.2
C-19212	6	B1	17.92	15	<0.4
C-19213	6	B2	11.03	34	<0.3
C-19214	6	B3	13.08	6180	55.7
C-19215	6	B4P	93.04	13	<2.2
C-19216	6	B5	27.12	11	<0.6
C-19217	6	B6	18.86	103	0.9
C-19218	6	RK2	97.36	40	<2.3
C-19220	5	B1	11.29	8	<0.3
C-19221	5	B2	12.59	11	<0.3
C-19222	5	B3	13.76	28	<0.3
C-19223	5	B4	18.50	2390	23.6
C-19224	5	B5	12.49	470	4.6
C-19225	5	RK2	94.26	30	<2.2
C-19234	6	B1	28.98	2590	6.1
C-19235	6	B2	10.42	33	<0.2
C-19236	6	B3	8.50	61	0.8
C-19237	6	B4P	86.41	20	<2.0
C-19238	6	B5	10.80	7	<0.3
C-19239	6	B6	32.30	320	3.7
C-19240	6	RK2	86.63	15	<2.0
C-19246	6	RK1	86.84	31	<2.0
C-19241	6	B1	34.95	21	<0.8
C-19242	6	B2	14.05	18	<0.3
C-19243	6	B3	12.15	8	<0.3
C-19244	6	B4	18.76	14	<0.4
C-19245	6	RK2	94.17	34	<2.2

Table 3. Continued

Sample number	Coal	Sample Type ^a	Ash %	Zinc (µg/g)	Cadmium (µg/g)
C-19248	6	RK1	88.96	59	<2.1
C-19249	6	B1	14.55	8	<0.3
C-19250	6	B2	18.62	13	<0.4
C-19251	6	B3P	90.65	19	<2.1
C-19252	6	B4	8.79	14	<0.2
C-19253	6	B5	10.39	13	<0.2
C-19254	6	RK2	89.49	40	<2.1

NOTE: Some shale and underclay samples are included.

^aRK1 Overlying shale (roof)

RK2 Underclay

B1-B8 = Coal benches

B4P Shale parting in seam

Table 4. Zinc and Cadmium Concentrations in Channel Samples

Sample number	Coal	Ash %	Zinc (µg/g)	Cadmium (µg/g)
C-19210	6	18.66	1360	17.0
C-19219	5	22.70	610	4.3
C-19226	5	13.72	62	0.5
C-19233	6	26.59	1100	16.0
C-19256	6	15.88	690	5.3
C-19257	6	19.20	109	<0.4
C-19258	5	17.74	630	8.1
C-19418	2	7.56	1540	10.4
C-19421	5	13.50	410	2.7
C-19424	5	24.53	790	7.7
C-19426	6	26.93	270	2.3

Table 5. Zinc and Cadmium
Concentrations in Composite Face Channel Samples

Sample number	Coal	Ash %	Zinc ($\mu\text{g/g}$)	Cadmium ($\mu\text{g/g}$)
C-14650	2	9.46	930	8.7
C-14774	5	12.82	960	7.2
C-15079	6	15.31	46	<0.2
C-15117	6	13.60	117	1.2
C-15125	6	13.07	620	7.8
C-15872	6	14.44	310	2.2
C-16264	5	12.53	159	2.7
C-16265	6	9.50	13	<0.4
C-16317	6	12.00	2670	28.0
C-16543	6	11.94	5350	65.0
C-16741	6	12.89	290	1.8

Table 6. Zinc and Cadmium
Concentrations in Composite Face Grid Samples

Sample number	Coal	Ash %	Zinc ($\mu\text{g/g}$)	Cadmium ($\mu\text{g/g}$)
C-18979	6	10.98	1050	8.0
C-18980	6	9.08	810	7.0
C-18981	6	16.32	760	6.3
C-19072	6	15.15	980	15.6
C-19398	5	12.14	360	4.4
C-19399	5	16.19	540	5.9
C-19400	2	10.33	400	4.1
C-19401	2	7.92	400	2.8
C-19404	5	11.49	180	2.5
C-19415	6	16.18	380	3.2
C-19419	2	12.70	850	6.3
C-19422	5	13.48	250	1.8
C-19425	5	13.90	1570	11.7
C-19427	6	21.84	310	3.6

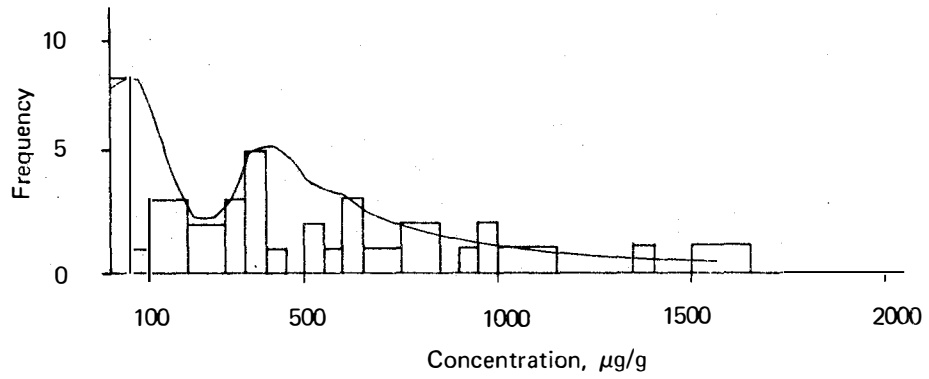
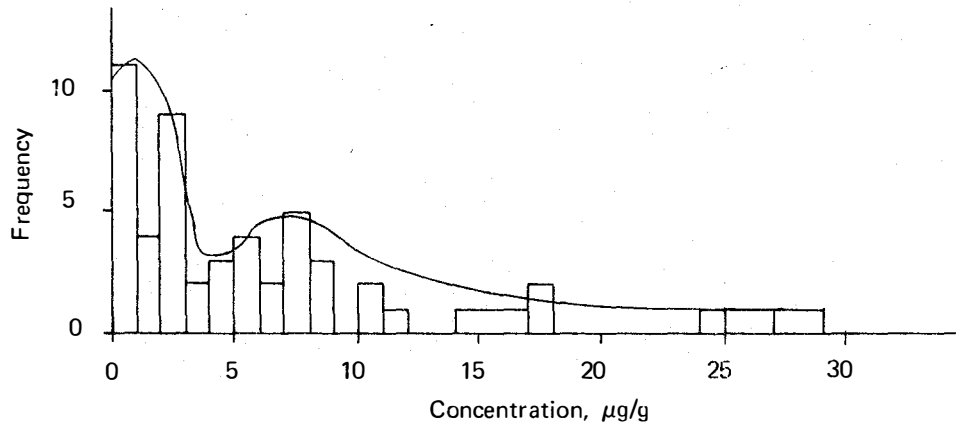
*a**b*

Fig. 8. *a*—Histogram showing distribution of zinc for all coal sample data. *b*—Histogram showing distribution of cadmium for all coal sample data.

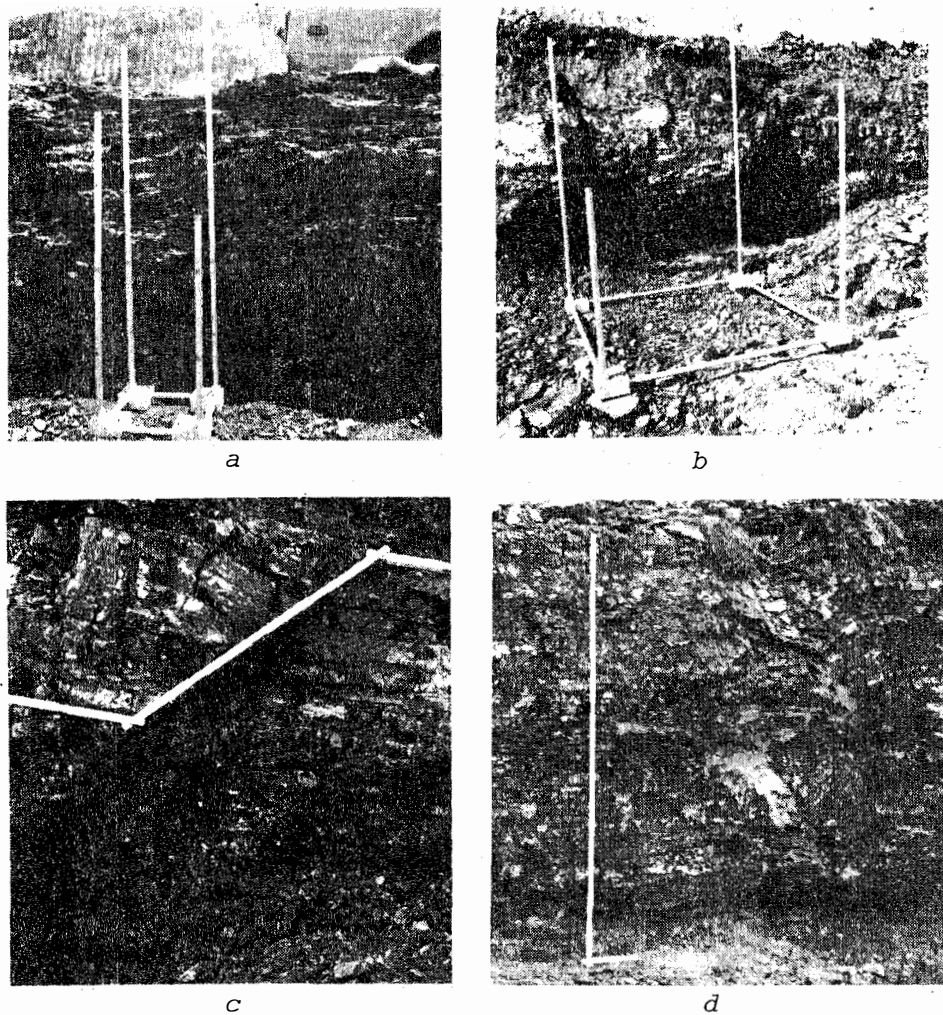


Fig. 9. a—Undisturbed portion of the Springfield (No. 5) Coal at site of composite face grid sample. Site contains 183 $\mu\text{g/g}$ zinc. b—Undisturbed portion of the Herrin (No. 6) Coal at site of composite face grid sample. Site contains 13 $\mu\text{g/g}$ zinc. c—Disturbed portion of the Herrin (No. 6) Coal at site of composite face grid sample. Site contains 1,048 $\mu\text{g/g}$ zinc. d—Disturbed portion of the Herrin (No. 6) Coal at site of composite face grid sample (rule shows 4 ft vertical). Site contains 807 $\mu\text{g/g}$ zinc.

higher mode (300 to 1100 $\mu\text{g/g}$ zinc and 4 to 15 $\mu\text{g/g}$ cadmium) is composed of samples collected primarily from disturbed sections of the coal beds. The disturbed areas found in the coals in this study are characterized by clay dikes, faults, cavities, slips, and large fractures. Figures 9c and d show faulted and clay dike disturbed coal, which was sampled and found to contain higher amounts of zinc and cadmium. Beyond the higher modes, there are a number of samples which range in zinc and cadmium as high as 5,400 $\mu\text{g/g}$ and 65 $\mu\text{g/g}$ respectively. These scattered samples represent the high tailing end of the upper mode.

These arithmetic distributions (fig. 8) exhibit significant skewness toward higher values. This skewness is such that two-thirds of the values for both zinc and cadmium are less than the arithmetic mean. These high values which account for only one-third of the total samples exert influence on the mean equal to the remaining two-thirds of the samples with lower values. This suggests that fewer very high values overly influence the mean, resulting in a higher value for the arithmetic mean.

It has been suggested by Ahrens (1954a and b) that in a natural population, the distribution of trace elements in many types of rock materials most often approximates a lognormal distribution. One indication of a lognormal distribution is a positive (or negative) skewness as is exhibited in the arithmetic distributions for all of the samples. The lognormal frequency distributions for the present data are shown in figures 10a and b.

An additional test for lognormality is to plot a cumulative frequency curve using probability paper. A lognormal distribution will plot on probability paper as a straight line. Figures 11 and 12 show the zinc and cadmium data plotted. These two plots consist of at least two line segments with differing slopes. These plots are interpreted as representing a mixture of populations of zinc and cadmium in the coal or more likely the two populations as already indicated as undisturbed and disturbed

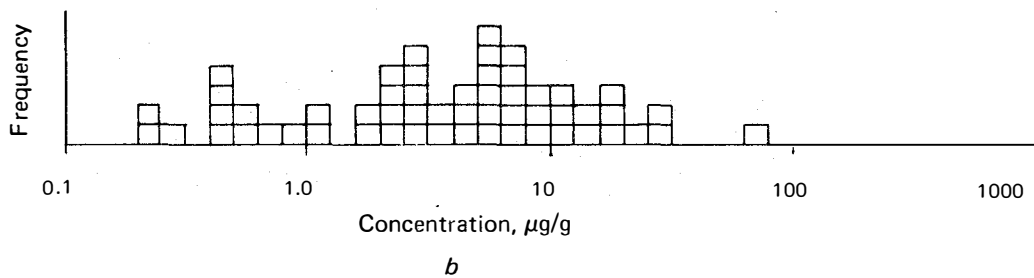
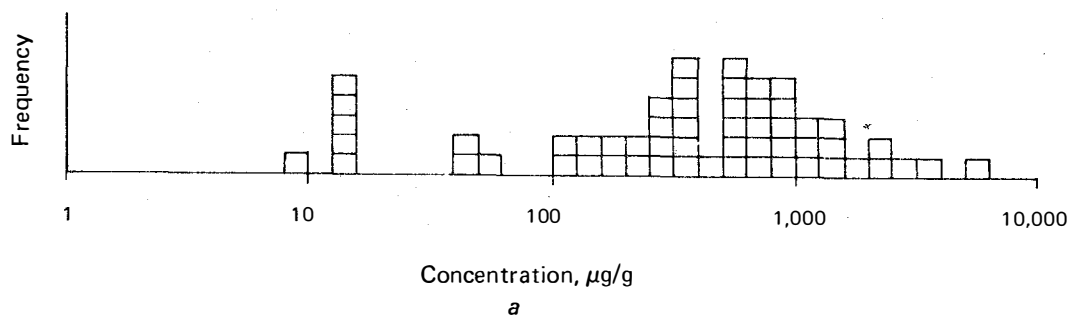


Fig. 10. *a*—Semilogarithmic histogram showing lognormal frequency distribution of zinc in all coal samples. *b*—Semilogarithmic histogram showing lognormal frequency distribution of cadmium in all coal samples.

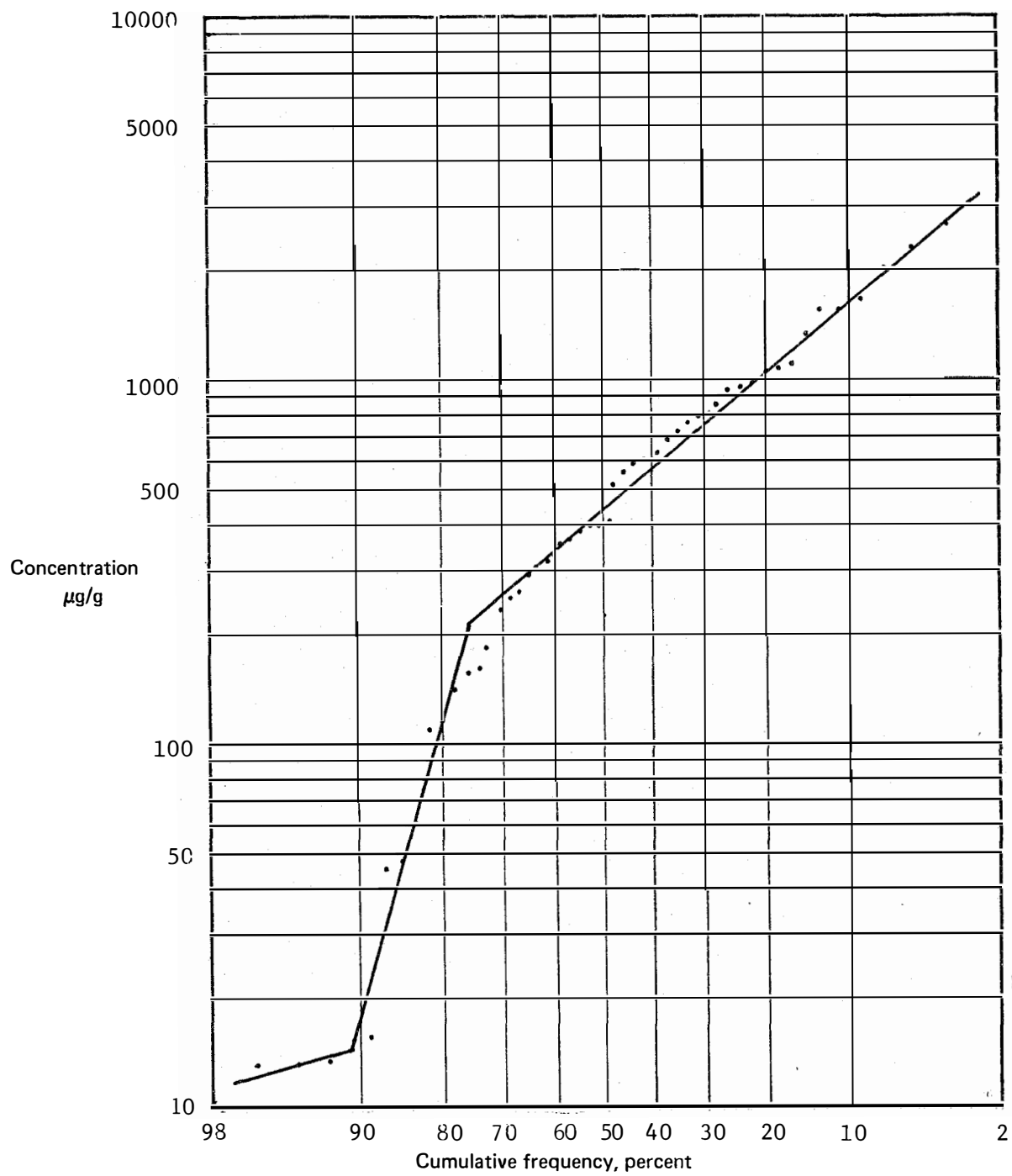


Fig. 11. Cumulative frequency plot of zinc in coal sampling data.

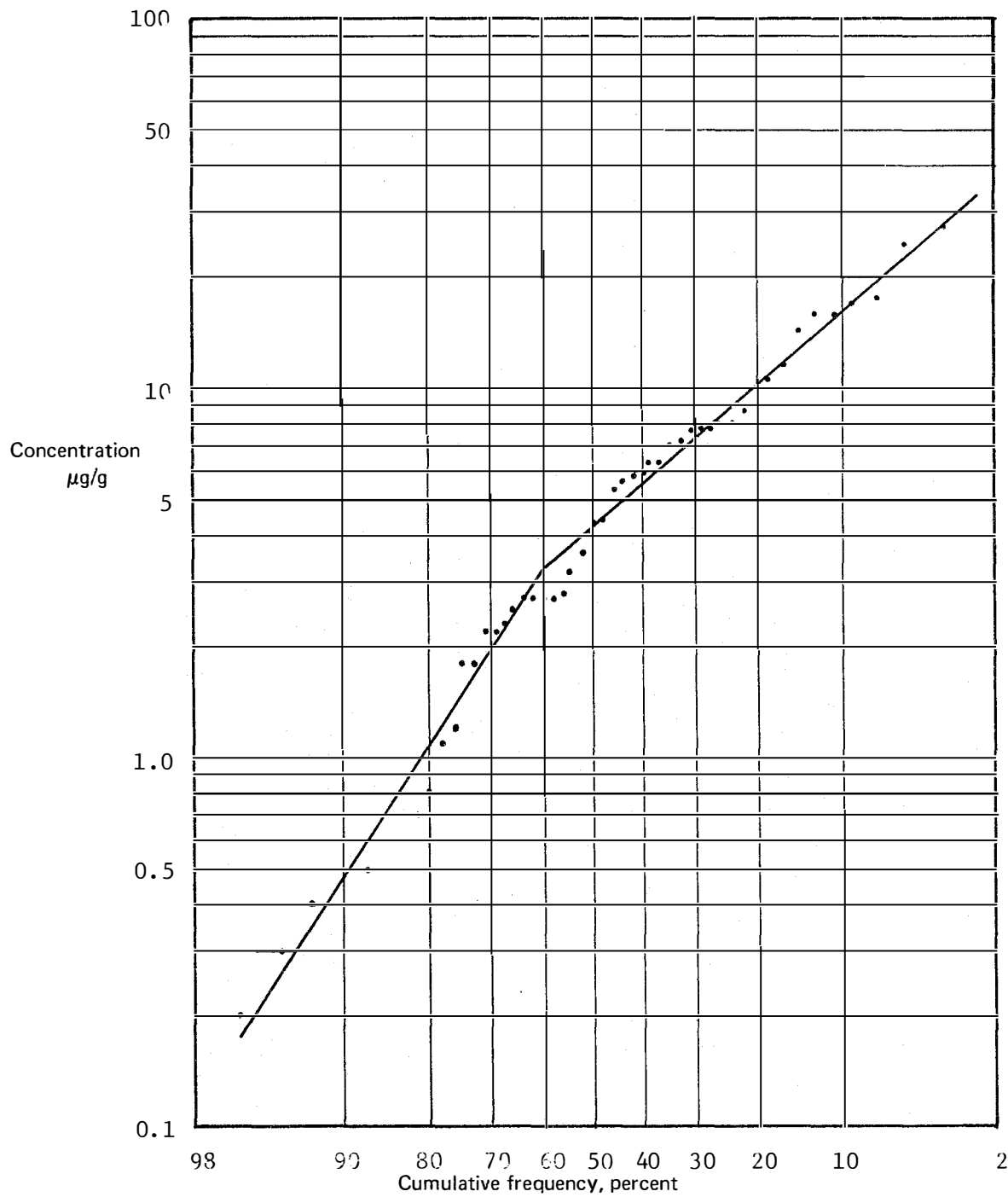


Fig. 12. Cumulative frequency plot of cadmium in coal sampling data.

portions of the coal beds. In the plot for zinc (fig. 11), the two major line segments intersect in the region between 200 and 300 $\mu\text{g/g}$, which matches exactly the interval between the high and low modes of the arithmetic distribution. In the plot for cadmium (fig. 12), the same relationship occurs. That is, the two principal line segments from the probability plot intersect in the region between 3 and 4 $\mu\text{g/g}$, again matching the division between the modes of the arithmetic distribution. Therefore, two separate populations of zinc and cadmium have been sampled in these coals.

Subjective Evaluation of Sampling Methods

The standard coal sampling methods (channel, composite face channel, and bench) were originally devised to ascertain the bulk properties of the coal such as proximate and ultimate analyses, calorific value, and ash content. On the other hand, the zinc and cadmium contents of coal are controlled primarily by their occurrence in sphalerite. The occurrence of sphalerite in coal is controlled by a somewhat erratic pattern of mineralization which has no apparent relationship to the bulk properties of the coal but rather to the structures in coal beds. This variation is demonstrated by a series of consecutive auger holes showing highly variable zinc and cadmium (table 8). Therefore, the geologist sampling coal for its zinc and cadmium contents must make a transition from viewing the coal for its bulk, fuel-related properties, to considering the coal as a two-phase system with the coal acting primarily as a host for sphalerite mineralization. In making this transition, an evaluation should be made of the adequacy of present and proposed coal sampling methods used to estimate zinc and cadmium resources in coal. This evaluation is a subjective one based on the following criteria:

1. Numbers of samples collected and analyzed.
2. Sampling pattern.

Table 7. Zinc and Cadmium
Concentrations in Composite Auger Samples

Sample number	Coal	Ash %	Zinc ($\mu\text{g/g}$)	Cadmium ($\mu\text{g/g}$)
C-18861-66	6	35.93	157	0.8
C-19436-43	5	20.86	290	4.6
C-19452-59	6	28.87	14	<0.4
C-19523	5	18.62	141	1.1
C-19524	5	19.67	710	7.8
C-19525	6	30.19	2320	14.7
C-19526	6	31.36	2020	24.7

Table 8. Zinc and Cadmium
Concentrations in Consecutive Auger Samples

Sample number	Coal	Ash %	Zinc ($\mu\text{g/g}$)	Cadmium ($\mu\text{g/g}$)
C-18861	6	35.99	14	<0.6
C-18862	6	30.21	250	0.7
C-18863	6	53.51	380	0.9
C-18864	6	29.25	18	<0.5
C-18865	6	27.84	260	1.3
C-18866	6	38.96	20	<0.6
C-19434	5	17.54	36	<0.3
C-19435	5	24.33	39	<0.4
C-19436	5	21.13	500	5.3
C-19437	5	20.04	420	5.1
C-19438	5	18.38	48	0.3
C-19439	5	27.85	96	1.1
C-19440	5	20.80	1660	31.6
C-19441	5	17.73	15	<0.3
C-19442	5	23.26	15	<0.4
C-19443	5	17.55	86	0.9
C-19452	6	32.13	9	<0.5
C-19453	6	22.40	16	<0.4
C-19454	6	21.03	11	<0.3
C-19455	6	15.30	10	<0.2
C-19456	6	18.04	12	<0.3
C-19458	6	36.61	18	<0.4
C-19459	6	56.59	19	<0.9

3. Area covered by sampling pattern.
4. Scale of sample variation which can be detected.
5. Sources of bias.
6. Relative cost of sample collection and analysis.

The data for each of the three coal seams, the Colchester, Springfield, and Herrin will be combined in the discussion for each of the different sampling methods. The Student's t test shows that at the 0.1 level of significance, there is no reason to reject the hypothesis that the mean zinc and cadmium concentrations for each of the three coal seams has been taken from the same population. Therefore, the large range in the data makes it impossible to differentiate with any confidence between the three coals on the basis of the zinc and cadmium content. The summary data for the different sampling methods and the different coals and will be discussed later (tables 9 and 10).

Statistical Evaluation of Sampling Methods

The bench samples (table 3) show arithmetic means for zinc and cadmium of 662 and 5.9 $\mu\text{g/g}$ respectively. The range in the data is quite large, as reflected by the standard deviations. The geometric means for zinc and cadmium in these samples are 155 and 2.2 $\mu\text{g/g}$ respectively. The large differences between the geometric and arithmetic means for the bench sets are not surprising considering the large ranges and standard deviations for the data. The confidence intervals at the 90 percent significance level for zinc and cadmium are $133 \leq \bar{x} \leq 1192$ and $1.5 \leq \bar{x} \leq 10.3$ respectively (where \bar{x} is the arithmetic mean).

A single bench set consists of several benches, the number of which is a function of the coal seam thickness. Each bench set shows vertical variations in a coal face but in only one location. The detection of district-wide variations in the zinc and cadmium contents in the coals

of this area would require the collection of great numbers of bench sets and the analysis of much greater numbers of individual benches. This method would be relatively inexpensive from a collection standpoint, but the analytical costs would be high due to the relatively great number of separate determinations required. The location of bench sets will, on a mine scale, be determined by the availability of exposed seam faces and, on a smaller scale, by the sampling bias of the collector. This method is an unrigorous random sampling scheme with no established criteria for determining the location of each bench set. Thus the sample locality is determined by the biases of the collector, by the geology exposed in the mine, and by the seam face appearance.

The channel samples (table 4) show arithmetic means for zinc and cadmium of 684 and 6.8 $\mu\text{g/g}$ respectively. These results are quite similar to the bench sample means, but the ranges and standard deviations of the data for the channel samples are much less than for the benches. This lower range and standard deviation is also reflected in the closer agreement of the geometric mean with the arithmetic means. The geometric means for zinc and cadmium are 480 and 4.1 $\mu\text{g/g}$ respectively. The confidence intervals at the 90 percent significance level for zinc and cadmium are $418 \leq x \leq 950$ and $3.7 \leq x \leq 9.9$, respectively.

Channel samples can generally be considered a composite bench set and therefore will reflect an "average" zinc and cadmium content for the total thickness of the coal seam, but again at only one location. The number of channel samples necessary to detect district-wide variations in zinc and cadmium would be the same as the number necessary for bench sets, but the number of determinations will be fewer than for the bench samples by a factor equal to the average number of benches per bench set. Aside from the advantage of needing fewer numbers of determinations, all of the limitations of bench sampling apply to channel sampling.

Not only do the composite face channel samples (table 5) exhibit the largest arithmetic means for zinc and cadmium of 1042 and 11.4 $\mu\text{g/g}$ respectively, but the standard deviations and ranges are also the largest of all of the sampling methods. The geometric means for zinc and cadmium of 344 and 3.5 $\mu\text{g/g}$ respectively result in the greatest differential between the two types of means. The confidence intervals at the 90 percent significance level for zinc and cadmium are $157 \leq \bar{x} \leq 1926$ and $0.7 \leq \bar{x} \leq 22.0$ respectively.

Composite face channel sampling covers larger areas of the coal face and partially accounts for the variability in sphalerite mineralization. A single composite face channel sample will most likely be insufficient for an adequate evaluation of sphalerite distribution. The number of samples necessary for an evaluation is less than the number of channel samples needed by factor of three. The limitations associated with bench and channel sampling apply to composite face channel sampling. Without established criteria for locating sampling sites, there is always a potential for collection bias.

As mentioned previously, the three standard coal sampling methods were not designed to take into account the extreme variability in sphalerite mineralization and seam face appearance. The sampling density and pattern must be such that both disturbed and undisturbed areas are sampled and that the weighting of samples from these two areas reflects the proportion of disturbed to undisturbed areas for the region being evaluated. A sampling pattern based on some type of grid appears to be the most promising method to provide the proper weighting. The scale of the grid will determine how well the grid system will include both types of areas.

The composite face grid samples (table 6) show the closest agreement between the arithmetic and geometric means with values for zinc of 629 and 529 $\mu\text{g/g}$ respectively and for cadmium of 5.9 and 5.0 $\mu\text{g/g}$ respectively.

The standard deviations and ranges for the zinc and cadmium data in the composite face grid samples is the least of any of the sampling methods. This method, more than any of the others, due to its composite nature, smooths out both the high and low values of the subsamples to yield a more tightly grouped set of data. The confidence intervals at the 90 percent significance level for zinc and cadmium are $445 \leq \bar{x} \leq 814$ and $4.1 \leq \bar{x} \leq 7.8$, respectively.

A composite face grid sample consists of $21 \times Y$ subsamples, where Y equals the thickness, in feet, of the coal face. The grid is 20 feet long, a length which, if a disturbed area is encountered, will be sufficient to include both disturbed and undisturbed areas. The limitation of this method lies in locating a sufficient number of separate grids so as to provide the proper weighting of the two areas. This sampling method may provide one of the better opportunities to obtain good zinc and cadmium data with the fewest number of samples; the composite nature of the method also allows for the analysis of few samples, thus keeping analytical costs low. The setting up and collecting from a grid may be tedious and time consuming, but the costs should be minimized because fewer analyses are required. Seam face availability still remains a potential source of bias as does choosing the location of the grid.

Since there are so few composite auger samples (table 7), it is difficult to statistically evaluate them. The arithmetic means for zinc and cadmium are 817 and 7.9 $\mu\text{g/g}$ respectively. The range and standard deviation of the data are intermediate relative to face grid and channel samples on the low side and face channel and bench samples on the high side. The geometric means for zinc and cadmium are 320 and 3.3 $\mu\text{g/g}$ respectively. The confidence intervals at the 90 percent significance level for zinc and cadmium are $117 \leq \bar{x} \leq 1517$ and $1.2 \leq \bar{x} \leq 14.5$, respectively.

Of all the sampling methods considered in this study, the composite auger method appears to have the lowest potential for bias. Auger sampling, unlike the other sampling methods, has the advantage of not being subject to the availability of an exposed seam face, as are all of the other sampling methods. Thus one of the potential sources of bias is removed. Except for the high cost of auger sampling, which is the major drawback of this method, most of the other factors concerning composite auger sampling are the same as for composite face grid sampling.

Summary of Zinc and Cadmium Data

The zinc and cadmium contents of the coal represented by the arithmetic means for the different sampling methods range from a low value of 629 and 5.9 $\mu\text{g/g}$ respectively for the composite face grid sampling procedure, to a high value of 1042 and 11.4 $\mu\text{g/g}$ respectively for the composite face channel sampling procedure. The question still remaining is which sampling method yields the truest approximation of the zinc and cadmium in the population.

The five methods were paired for all possible combinations and subjected to the t-test. It was found that at the 0.1 level of significance, there is no reason to reject the hypothesis that the arithmetic mean zinc and cadmium concentrations in coal for all of the sampling methods under consideration have been taken from the same population. This fact means that because of the large variability in the data, the five sampling methods produce results which cannot, with any certainty, be distinguished from one another.

In making a final evaluation of the sampling methods and attempting to estimate the zinc and cadmium resources of the coals under study, the limitations in the present data must be kept in mind. Based on simple significance tests, it has been shown that the different sampling methods

yielded similar results, primarily because the data have large standard deviations. At the 95 percent level of significance, the confidence intervals for zinc and cadmium for all the samples are $498 \mu\text{g/g} \leq \bar{x} \leq 1010$ and $4.6 \mu\text{g/g} \leq \bar{x} \leq 10.2$ respectively.

The central tendency of the zinc and cadmium in coal data is indicated by the arithmetic and geometric means. Trace element concentrations in rocks commonly approximate lognormal distributions, as is the case with zinc and cadmium in coal. The best estimate of central tendency (mode or most probable concentration) is frequently the geometric mean. The arithmetic mean, on the other hand, is the correct and unbiased estimate of abundance, the population arithmetic mean (Miesch, 1967). The geometric mean is always less than the arithmetic mean except when the variance is zero.

A problem arises in estimating geochemical abundance because of the lognormal distributions exhibited by the trace element data. The sample arithmetic mean in this lognormal case does not approximate the population arithmetic mean. Another statistical parameter, Sichel's *t* statistic, has been derived as a function of the geometric mean to estimate the population arithmetic mean (Miesch, 1967). The purpose of this statistic is therefore to estimate geochemical abundance.

The summary data in tables 9 and 10 include three measures of central tendency and four measures of variation. Measures of central tendency are the arithmetic mean, geometric mean (GM), and Sichel's *t*. The measures of variation are standard deviation, geometric deviation (GD), the 90 percent confidence interval, and an estimated range of the central 95 percent of the observed distribution. This 95 percent range has a lower limit equal to $\text{GM}/(\text{GD})^2$ and an upper limit equal to $\text{GM} \times (\text{GD})^2$ (Connor et al., 1976).

Resource Evaluation of Zinc and Cadmium in Coal

Sichel's t statistic is used in this resource evaluation to estimate the population arithmetic means for zinc and cadmium abundance in coal. The sample data are too scattered to rely on the sample arithmetic means for resource estimates. Sichel's t is a derived estimate and will not be construed as the actual geochemical abundance of zinc and cadmium. However, as an estimate of abundance, Sichel's t gives the concentration of zinc in the coals sampled at 1026 $\mu\text{g/g}$ and for cadmium 8.1 $\mu\text{g/g}$. The coal resources in the study area have been estimated at 7 billion tons (Smith and Berggren, 1963). Therefore, the estimated zinc resource is about 7 million tons and the estimated cadmium resource is 60,000 tons.

RESULTS OF SAMPLING SHALE, UNDERCLAY, PARTINGS, AND MINE REFUSE FOR ZINC AND CADMIUM

General

Tables 11, 12, and 13 show the analyses for zinc and cadmium in shales, underclays, and associated rock materials. The data show unimodal arithmetic frequency distributions for zinc that center about mean values of 58 $\mu\text{g/g}$ for shale and 44 $\mu\text{g/g}$ for underclay. The average concentration of zinc in shales is reported to be 95 $\mu\text{g/g}$ (Turekian and Wedepohl, 1961). Clay partings differ little in zinc content from underclays. Results of these analyses give no indication of zinc enrichment in shales, clay partings, or underclays associated with sphalerite-bearing coals.

Correlation between Zinc and Cadmium

Consistently high correlations of zinc and cadmium data for all samples demonstrate the mineralogical tie between zinc and cadmium and a uniform ratio of zinc to cadmium. The correlation coefficients for the different coal sampling methods range from 0.76 to 0.99.

Results of Analyzing Coal Mine Refuse

Table 14 contains the results of analyses of mine refuse samples for zinc and cadmium. Slurry, the fine-grained material piped to settling ponds, and gob, the coarse-grained material trucked to refuse dumps, are produced in the preparation plant during the washing of raw coal. Crushing and heavy media separators remove the waste material, which is denser than the coal. Analysis of these refuse samples indicated that sphalerite is effectively concentrated by a factor of 5 to 10 times over in situ values in both slurry and gob. Figure 13a shows a mine slurry deposit and figure 13b shows the surface of the deposit with a sphalerite fragment highlighted.

The feasibility of producing a sphalerite-enriched product from coal mine slurry is being investigated with a Humphreys spiral concentrator. Analyses of slurry show that it is composed of up to 50 percent coal fragments, 42 percent rock fragments (including shale, sandstone, limestone, calcite, siderite, and clay), 7 percent pyrite and pyritized shale, and 1 percent sphalerite. The preliminary tests with the Humphreys spiral concentrator showed that the sphalerite can be increased by 700 percent in the high-density product. Conversely, with rejection of the middlings (rock fragments), a coal-enriched low-density fraction is also produced.

Recovery of sphalerite and coal from coal mine slurry appears to be feasible; however, recovery will depend on the availability of sphalerite-rich slurry and the distributions of sphalerite and coal in the various types of slurry deposits.

Table 9. Summary of Zinc Data

Sample	Coal	No. of Samples	Arith. Mean	Geom. Mean	Estimated Abundance Sichel's t	Std. Dev.	Geom. Dev.	90% Conf. Interval	Observed Range	Expected 95% Range	Zn/Cd Atomic Ratio
Bench	2	1	8	—	—	—	—	—	—	—	—
	5	3	820	630	—	720	2.51	—	258-1630	99-3944	166
	6	8	680	132	—	1190	8.84	—	13.4-3490	2-10315	223
	All	12	660	155	1040	1020	8.27	133-1192	9.5-3490	2-10669	202
Channel	2	1	1540	—	—	—	—	—	—	—	253
	5	5	500	378	—	280	2.82	—	62-790	48-3006	204
	6	5	700	497	—	540	2.86	—	109-1360	61-4065	164
	All	11	680	486	768	490	2.77	418-950	62-1540	63-3729	193
Composite Face	2	1	930	—	—	—	—	—	—	—	183
	5	2	560	391	—	—	—	—	159-960	—	165
Channel	6	8	1180	294	—	1900	7.35	—	13-5350	5-15883	188
	All	11	1040	344	1345	1690	5.77	117-1517	13-5350	10-11453	182
Composite Face	2	3	550	514	—	260	1.55	—	400-850	214-1235	213
	5	5	580	424	—	570	2.31	—	180-1570	79-2263	177
Grid	6	6	710	649	—	310	1.67	—	310-1050	233-1810	181
	All	14	630	530	615	390	1.86	445-814	180-1570	153-1834	187
Composite Auger	2	0	—	—	—	—	—	—	—	—	—
	5	3	380	307	—	300	2.25	—	141-710	61-1554	162
	6	4	1130	319	—	1210	11.28	—	14-2320	3-40589	249
	All	7	810	314	1241	960	5.91	117-1517	14-2320	9-10967	206
All	2	6	690	347	1440	540	6.54	263-1113	8.5-1540	8-14436	217
	5	18	560	412	556	450	2.36	379-747	62-1630	74-2295	180
	6	31	880	306	1285	1190	5.91	513-1242	13-5350	9-10688	202
	All	55	750	342	1026	950	4.60	498-1010	8.5-5350	16-7237	192

Table 10. Summary of Cadmium Data

Sample	Coal	No. of Samples	Arith. Mean	Geom. Mean	Estimated Abundance Sichel's t	Std. Dev.	Geom. Dev.	90% Conf. Interval	Observed Range	Expected 95% Range	Zn/Cd Atomic Ratio
Bench	2	1	<0.2	—	—	—	—	—	—	—	—
	5	3	8.6	6.5	—	7.7	2.47	—	2.7-17.4	1.1-39.7	166
	6	8	5.6	1.9	—	9.3	4.42	—	<0.5-27.3	0.1-37.1	223
	All	12	5.9	2.2	6.2	8.5	4.72	1.5-10.3	<0.2-27.3	0.1-49.3	202
Channel	2	1	10.4	—	—	—	—	—	—	—	253
	5	5	4.7	3.2	—	3.3	3.13	—	0.5-8.1	0.3-31.4	204
	6	5	8.2	4.2	—	7.8	4.74	—	<0.4-17.0	0.2-94.4	164
	All	11	6.8	4.1	8.6	5.7	3.55	3.7-9.9	<0.4-17.0	0.3-51.7	193
Composite Face Channel	2	1	8.7	—	—	—	—	—	—	—	183
	5	2	5.0	4.4	—	—	—	—	2.7-7.2	—	165
	6	8	13.3	2.9	—	22.9	7.38	—	<0.2-65.0	0.1-157.9	188
	All	11	11.4	3.5	13.3	19.5	5.59	1.2-14.5	<0.2-65.0	0.1-109.4	182
Composite Face Grid	2	3	4.4	4.2	—	1.8	1.50	—	2.8-6.3	1.9-9.5	213
	5	5	5.3	4.2	—	3.9	2.08	—	1.8-11.7	1.0-18.2	177
	6	6	7.3	6.3	—	4.5	1.78	—	3.2-15.6	2.0-20.0	181
	All	14	5.9	5.0	5.8	3.8	1.83	4.1-7.8	1.8-15.6	1.5-16.7	187
Composite Auger	2	0	—	—	—	—	—	—	—	—	—
	5	3	4.5	3.4	—	3.4	2.76	—	1.1-7.8	0.4-25.9	162
	6	4	10.2	3.3	—	11.8	7.85	—	<0.4-24.7	0.1-203.4	249
	All	7	7.7	3.3	9.6	9.1	4.81	1.2-14.5	<0.4-24.7	0.1-76.3	206
All	2	6	5.4	3.3	8.1	3.8	4.29	2.4-8.4	<0.2-10.4	0.2-60.7	217
	5	18	5.5	4.1	5.6	4.2	2.36	3.8-7.2	0.5-17.4	0.7-22.8	180
	6	31	8.9	3.3	10.2	13.3	4.74	4.9-13.0	<0.2-65.0	0.1-74.1	202
	All	55	7.4	3.5	8.1	10.4	3.80	4.6-10.2	<0.2-65.0	0.2-50.5	192

Table 11. Zinc and Cadmium
Concentrations in Shales of Selected Coals

Sample number	Coal	Zinc ($\mu\text{g/g}$)	Cadmium ($\mu\text{g/g}$)
C-18982	6	32	<2.8
C-19060	2	79	<3.1
C-19093	6	91	<2.5
C-19094	6	42	<2.1
C-19211	6	71	<2.2
C-19246	6	31	<2.0
C-19248	6	59	<2.1

Table 12. Zinc and Cadmium
Concentrations in Underclays Below Selected Coals

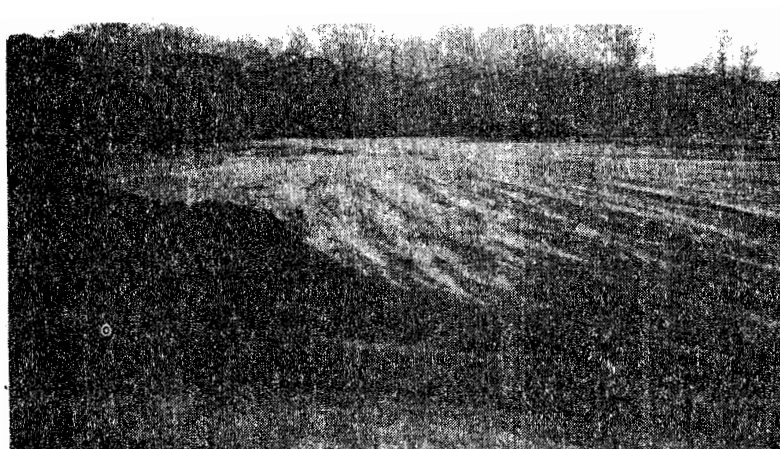
Sample number	Coal	Zinc ($\mu\text{g/g}$)	Cadmium ($\mu\text{g/g}$)
C-18989	6	34	<2.7
C-19057	2	84	<4.8
C-19061	2	67	<2.8
C-19092	6	71	<2.4
C-19103	6	43	<2.1
C-19218	6	40	<2.3
C-19225	6	30	<2.2
C-19232	5	24	<2.2
C-19240	6	15	<2.0
C-19245	6	34	<2.2
C-19254	6	40	<2.1

Table 13. Zinc and Cadmium
Concentrations in Materials Associated with Selected Coals

Sample number	Coal	Zinc ($\mu\text{g/g}$)	Cadmium ($\mu\text{g/g}$)
C-19073 parting	6	30	<1.5
C-19074 parting	6	41	<1.4
C-19078 clay dike	5	80	<1.2
C-19056 clay dike	2	75	<4.8
C-19054 shale	2	264	<4.8
C-19055 shale	2	118	<4.8

Table 14. Zinc and Cadmium
Concentrations in Mine Refuse

Sample number	Sample Type	Ash %	Zinc ($\mu\text{g/g}$)	Cadmium ($\mu\text{g/g}$)
C-19260	Slurry	82.67	6530	70.8
C-19402	Gob	81.05	4380	2.3
C-19403	Gob	86.82	6440	7.0
C-19429	Gob	76.52	2290	21.2
C-19520	Slurry	81.98	3200	37.9
C-19521	Slurry	79.04	4110	48.0
C-19528	Slurry	79.45	17500	191



a



b

Fig. 13. *a*—Slurry pond and slurry discharge pipe. *b*—Surface of slurry deposit with pen pointing to sphalerite fragment. Numerous fragments containing sphalerite in field of view.

CLEAT ORIENTATION

A program of measuring coal cleat directions was undertaken. This investigation was based on the assumption that cleat orientation was a function of regional stresses, as has been suggested by a number of studies in the Appalachian coal fields (Nickelsen and Hough, 1967; McCulloch et al., 1976). Consequently, little note was made of the distribution and orientation of cleats in relation to local anomalies or different levels of the coal seam. About 1000 cleats were measured using photogrammetric techniques (Brandow et al., 1975) and over 600 were measured by hand using a Brunton compass. The photogrammetric measurements were made at 8 different locations, five in the Herrin (No. 6) Coal and three in the Springfield (No. 5) Coal. The number of cleats measured at each location ranged from 63 to 239. A total of 408 measurements were collected from the Springfield Coal and 587 measurements from the Herrin Coal. The hand measurements were collected at scattered locations over the period of the entire study. These consisted of 102 measurements from the Colchester Coal, 154 measurements from the Springfield Coal, and 362 measurements from the Herrin Coal.

Conflicting results were obtained from the two methods of cleat measurement. Data from hand-measured cleats indicated conjugate sets of cleats trending $N30^{\circ}E$ to $N40^{\circ}E$ and $N50^{\circ}W$ to $N60^{\circ}W$ in all three coals. The photogrammetric measurements did not show a consistent trend between locations and, in some cases, showed no significant trend at all. This discrepancy is probably caused by the biases inherent in the hand measurements and the total lack of discretion in the photogrammetric technique. Hand measurements were made only on large, well developed cleats, whereas photogrammetric measurements were made on all plane surfaces regardless of size, development, or accessibility.

Although further investigation is necessary, it appears that cleat orientation is not solely a function of regional stress. The trend observed by hand measurements, which probably represents the orientation of the most prominent cleats, may be due to regional stress. The other trends shown by the composite of large and small cleats at a particular location may be due to dewatering or local structural anomalies.

VERTICAL MAGNETIC INTENSITY SURVEY

A ground magnetic survey of Knox, Fulton, Stark, and Peoria Counties, Illinois, was made to identify the existence of deep structures or intrusive bodies which could have contributed fluids or heat to the mineralization of sphalerite in coal.

The instrument used in the survey was a Scintrex MF2-100 vertical component fluxgate magnetometer accurate to ± 1 gamma. Stations were occupied at 2-mile intervals except where regular spacing would have made the station inaccessible or too close to man-made structures. Field observations were corrected for diurnal variations in the magnetic field by reoccupying specified stations at regular intervals throughout the field day. Latitude corrections were made by subtracting 9 gammas per mile in the direction of the average magnetic declination in the study area, which was 2.5°E 1975 (Fabiano, 1975).

The map of residual vertical magnetic intensity theoretically includes anomalies whose sources are lateral magnetic susceptibility contrasts in the rocks of the upper crust from the earth's surface down to the Curie Point Geotherm. The station spacing used in this survey was chosen to eliminate small localized anomalies so that the resulting map would show regional magnetic anomalies (fig. 14).

Analyses of these larger anomalies using simple geometrical anomalous mass models of appropriate magnetic susceptibilities (Heiland,

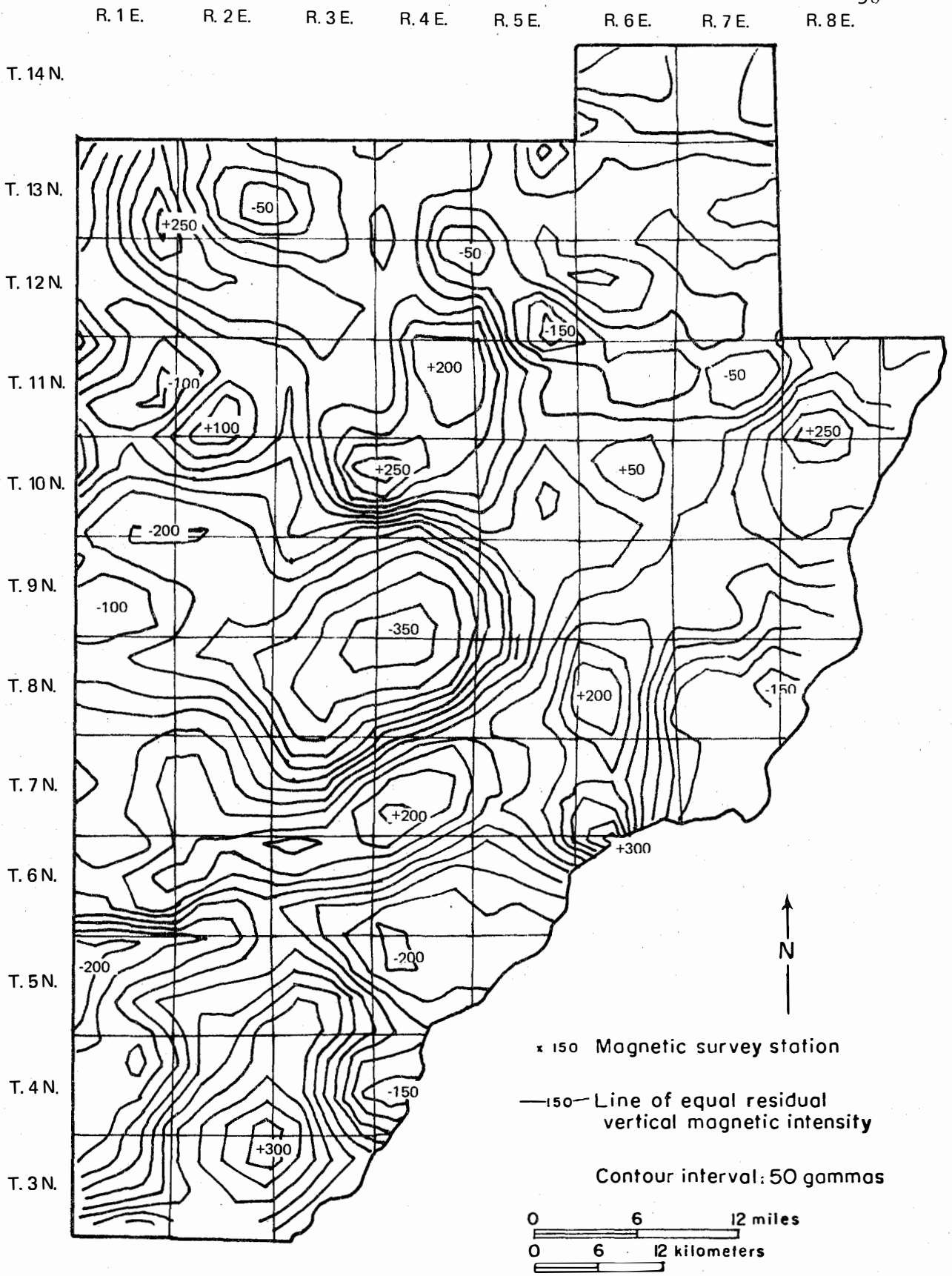


Fig. 14. Residual vertical magnetic intensity survey of study area.

1940) indicate that the sources of these anomalies are lithologic changes in the basement rocks well below the basement surface. In the surveyed area, the approximate elevation of the basement surface is 4,000 feet below mean sea level. There is no evidence that any large intrusive body extends upward to or beyond the basement surface.

OCCURRENCES OF ZINC IN SEDIMENTARY ROCKS AND SURFACE WATERS

Occurrences of sphalerite filling cavities and joints in rocks of Mississippian and Pennsylvanian age in western Illinois have been reported (Harvey, 1964). A brief field investigation was conducted of lower Pennsylvanian rocks in McDonough County, which is adjacent to and west of the four county area of this study. Sphalerite was found in several localities as cavity and vein fillings in siderite concretions. These concretions were abundant in a silty, gray shale estimated to be within 50 feet stratigraphically of the base of the Pennsylvanian. The sphalerite in the concretions was observed in polished sections to be yellow with purple patches.

A core obtained from Fulton County penetrated rocks of Pennsylvanian to Ordovician age. Samples were taken of each lithologic unit and analyzed for zinc. The results are shown in figure 15. The results indicate that rocks of Pennsylvanian, Mississippian, and late Devonian age have a base level zinc content ranging from 70 to 150 $\mu\text{g/g}$ whereas those of middle Devonian age or older have a base zinc content ranging from 260 to 310 $\mu\text{g/g}$. Zinc appears to be concentrated in rocks immediately above and below the base of the Pennsylvanian. Of the four coal samples in this core, two have a very low zinc content ($<20 \mu\text{g/g}$), one has a very high content (480 $\mu\text{g/g}$), and another has a zinc content within base-level range for the Pennsylvanian rocks (83 $\mu\text{g/g}$).

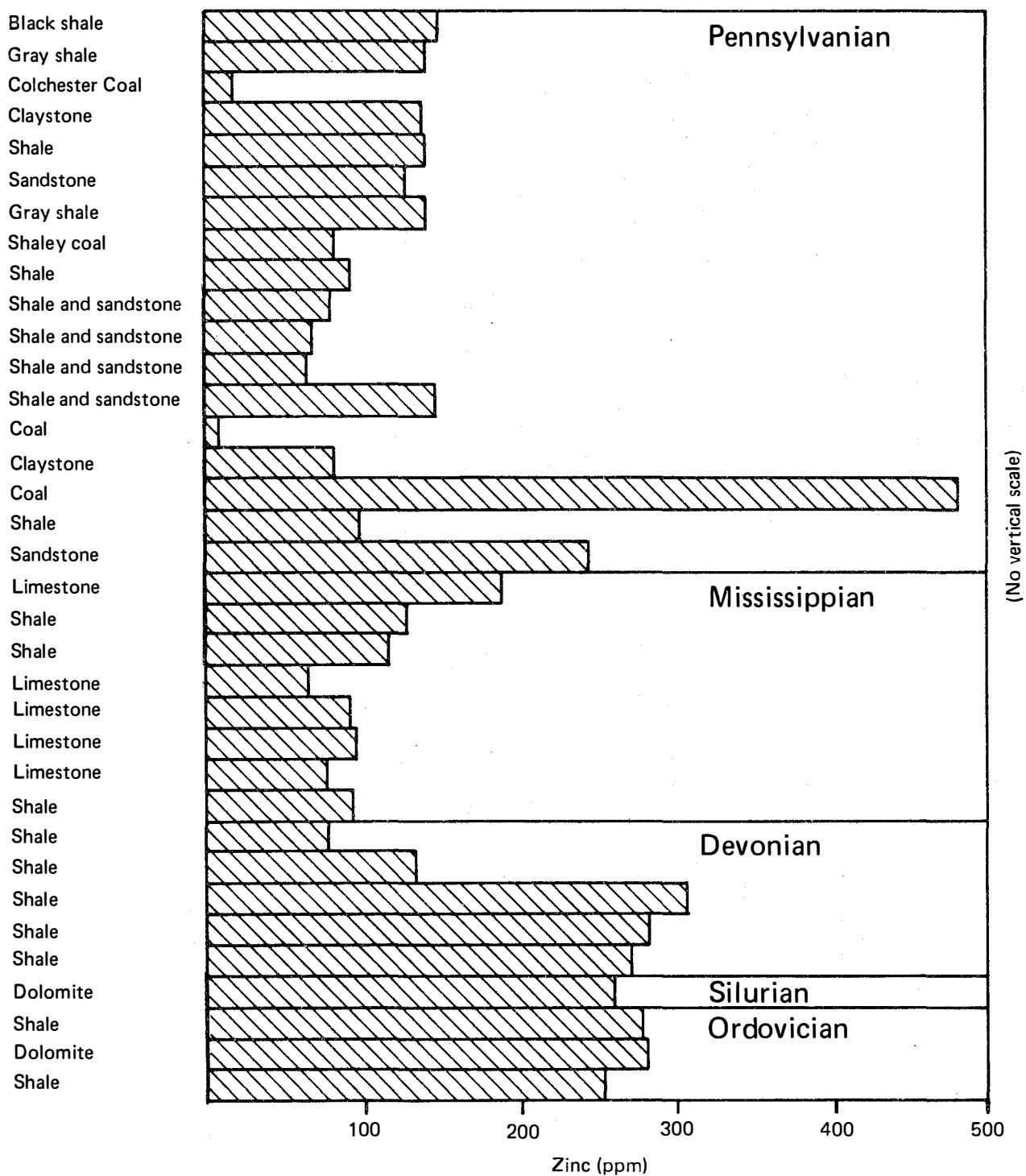


Fig. 15. Stratigraphic distribution of zinc in a core from Fulton County, Illinois.

Stream sediment and surface waters have been analyzed for zinc and cadmium by the Illinois State Geological Survey staff and other workers. Natural waters in Illinois contain from about 30 to 60 $\mu\text{g/g}$ Zn and less than .2 $\mu\text{g/g}$ Cd. In industrial areas where pollution is suspected, zinc content in surface water has been found to be approximately 400 $\mu\text{g/g}$. In these industrial areas, the stream sediment contains from 200 to 700 $\mu\text{g/g}$ Zn. In nonindustrial areas, the stream sediment contains from 20 to 40 $\mu\text{g/g}$ Zn. The maximum observed zinc content in waters of the study area from slurry pipes, overflow, and plant effluents is 6 $\mu\text{g/g}$. In southern Illinois, where little zinc has been reported from the coal, analyses of water from refuse runoff showed 80 $\mu\text{g/g}$ Zn and 0.6 $\mu\text{g/g}$ Cd, and analyses of water from shallow wells in slurry deposits showed 123 $\mu\text{g/g}$ Zn and 3.0 $\mu\text{g/g}$ Cd.

CONCLUSIONS

1. Sphalerite occurs in coal as epigenetic mineral fillings in fractures, cleats, cavities, faults, and clay dikes.
2. The sphalerite is multibanded. Bands are color distinct and compositionally distinct. Sequences of bands are recognizable in the four coals investigated, the Colchester (No. 2), Springfield (No. 5), Herrin (No. 6), and Danville (No. 7) Coals.
3. Sphalerite vein fillings exhibit symmetrical and asymmetrical crustification controlled by cleat or fracture dilation and coal microlithotypes.
4. Growth of sphalerite crystal aggregates nucleated around coal particles and continued outward. The color banding in crystal aggregates is concentric to the coal-sphalerite interface. These aggregates are found in the clay-rich matrices.
5. The arithmetic frequency distributions of zinc and cadmium data exhibit bimodal tendencies. These distributions also have a positive skewness.
6. The zinc and cadmium data closely approximate lognormal distributions.

7. Frequency plotted on probability paper for the zinc and cadmium data distinguishes two line segments of differing slopes. These line segments represent two possible populations from which the samples were collected and are in agreement with the mode divisions of the arithmetic frequency distributions. The two separate populations are identified as the higher zinc, disturbed portions of coal beds, and the lower zinc, undisturbed portions of coal beds.

8. No significant differences exist in the concentration of zinc and cadmium in the Colchester (No. 2), Springfield (No. 5), Herrin (No. 6), and Danville (No. 7) Coals in the study area.

9. A test of the different coal sampling methods based on statistical significance tests shows that the results of these methods could be considered similar due to the large standard deviations in the data.

10. The composite face grid sample is one of two recommended methods of assaying coal for zinc and cadmium because it has the closest agreement between its arithmetic mean and Sichel's t abundance estimate, covers disturbed and undisturbed portions of coal beds, and requires few analyses.

11. The composite auger sample is also recommended for assaying coal for zinc and cadmium because it is a composite sample requiring few analyses, can cover disturbed and undisturbed portions of the coal bed, and has the lowest potential for sampling bias.

12. The values for the concentration of zinc and cadmium in the coals sampled are Sichel's t statistic. These values are 1026 $\mu\text{g/g}$ for zinc and 8.1 $\mu\text{g/g}$ for cadmium.

13. Zinc and cadmium resources in the coals of Fulton, Knox, Peoria, and Stark Counties can be estimated to be 7 million tons zinc and 60,000 tons cadmium.

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Appendix 1. Location of Samples

Sample No.	Coal Bed	Sample type	County	Location	Mine Name and Company
C-19523	5 ^a	CA	Fulton	SE SE NW Sec. 6 T. 5N., R. 5E	Buckheart Mine Freeman United Coal Co.
C-19524	5	CA	Fulton	SE NW NW Sec. 13 T. 7N., R. 3E	Norris Mine Consolidation Coal Co.
C-19525	6 ^b	CA	Peoria	NE NE SE Sec. 20 T. 9N., R. 6E.	Elm Mine Midland Coal Co.
C-19526	6	CA	Knox	NE SW SW Sec. 12 T. 12N., R. 3E.	Mecco Mine Midland Coal Co.
C-14650	2 ^c	CFC	Fulton	T. 4N., R. 1E	Buckheart Mine Freeman United Coal Co.
C-14774	5	CFC	Fulton	T. 5N., R. 5E	Buckheart Mine Freeman United Coal Co.
C-15079	6	CFC	Peoria	T. 9N., R. 6E.	Elm Mine Midland Coal Co.
C-15117	6	CFC	Peoria	T. 9N., R. 6E.	Elm Mine Midland Coal Co.
C-15125	6	CFC	Fulton	T. 13N., R. 3E.	Norris Mine Consolidation Coal Co.
C-15872	6	CFC	Fulton	T. 13N., R. 6E.	Allendale Mine Midland Coal Co.
C-16264	5	CFC	Fulton	T. 7N., R. 3E.	Norris Mine Consolidation Coal Co.
C-16265	6	CFC	Fulton	T. 7N., R. 3E	Norris Mine Consolidation Coal Co.
C-16317	6	CFC	Peoria	T. 9N., R. 6E.	Elm Mine Midland Coal Co.
C-16543	6	CFC	Knox	T. 12N., R. 3E.	Mecco Mine Midland Coal Co.
C-16741	6	CFC	Fulton	T. 12N., R. 3E	Norris Mine Consolidation Coal Co.
C-18979	6	Gd	Peoria	NW SE NE Sec. 28 T. 9N., R. 5E.	Elm Mine Midland Coal Co.
C-18980	6	Gd	Peoria	NE SE NE Sec. 28 T. 9N., R. 5E.	Elm Mine Midland Coal Co.
C-18981	6	Gd	Peoria	NW SW NE Sec. 28 T. 9N., R. 5E.	Elm Mine Midland Coal Co.
C-18982	6	RK1	Peoria	NW SW NE Sec. 28 T. 9N., R. 5E.	Elm Mine Midland Coal Co.
C-18983	6	B1	Peoria	NW SW NE Sec. 28 T. 9N., R. 5E.	Elm Mine Midland Coal Co.

^aRefers to Springfield (No. 5) Coal

^bRefers to Herrin (No. 6) Coal

^cRefers to Colchester (No. 2) Coal

Sample No.	Coal bed	Sample type	County	Location	Mine Name and Comapny
C-18984	6	B2	Peoria	NW SW NE Sec. 28 T. 9N., R. 5E.	Elm Mine Midland Coal Co.
C-18995	6	B3	Peoria	NW SW NE Sec. 28 T. 9N., R. 5E.	Elm Mine Midland Coal Co.
C-18986	6	B4	Peoria	NW SW NE Sec. 28 T. 9N., R. 5E.	Elm Mine Midland Coal Co.
C-18987	6	B5	Peoria	NW SW NE Sec. 28 T. 9N., R. 5E.	Elm Mine Midland Coal Co.
C-18988	6	B6	Peoria	NW SW NE Sec. 28 T. 9N., R. 5E.	Elm Mine Midland Coal Co.
C-18989	6	RK2	Peoria	NW SW NE Sec. 28 T. 9N., R. 5E.	Elm Mine Midland Coal Co.
C-19054	2	RK	Fulton	SE NE SW Sec. 15 T. 4N., R. 1E.	Sunspot Mine Amax Coal Co.
C-19055	2	RK	Fulton	SE NE SW Sec. 15 T. 4N., R. 1E.	Sunspot Mine Amax Coal Co.
C-19056	2	RK	Fulton	SE NE SW Sec. 15 T. 4N., R. 1E.	Sunspot Mine Amax Coal Co.
C-19057	2	RK2	Fulton	SE NE SW Sec. 15 T. 4N., R. 1E.	Sunspot Mine Amax Coal Co.
C-19060	2	RK1	Fulton	NW NE SW Sec. 15 T. 4N., R. 1E.	Sunspot Mine Amax Coal Co.
C-19061	2	RK2	Fulton	NW NE SW Sec. 15 T. 4N., R. 1E.	Sunspot Mine Amax Coal Co.
C-19062	2	B1	Fulton	NW NE SW Sec. 15 T. 4N., R. 1E.	Sunspot Mine Amax Coal Co.
C-19063	2	B2	Fulton	NW NE SW Sec. 15 T. 4N., R. 1E.	Sunspot Mine Amax Coal Co.
C-19064	2	B3	Fulton	NW NE SW Sec. 15 T. 4N., R. 1E.	Sunspot Mine Amax Coal Co.
C-19065	2	B4	Fulton	NW NE SW Sec. 15 T. 4N., R. 1E.	Sunspot Mine Amax Coal Co.
C-19066	6	B1	Knox	SW SE NW Sec. 12 T. 12N., R. 3E.	Mecco Mine Midland Coal Co.
C-19067	6	B2	Knox	SW SE NW Sec. 12 T. 12N., R. 3E.	Mecco Mine Midland Coal Co.
C-19068	6	B3	Knox	SW SE NW Sec. 12 T. 12N., R. 3E.	Mecco Mine Midland Coal Co.
C-19069	6	B4P	Knox	SW SE NW Sec. 12 T. 12N., R. 3E.	Mecco Mine Midland Coal Co.
C-19070	6	B5	Knox	SW SE NW Sec. 12 T. 12N., R. 3E.	Mecco Mine Midland Coal Co.
C-19071	6	B6	Knox	SW SE NW Sec. 12 T. 12N., R. 3E.	Mecco Mine Midland Coal Co.
C-19072	6	Gd	Knox	SW NE NW Sec. 12 T. 12N., R. 3E.	Mecco Mine Midland Coal Co.
C-19073	6	RKP	Knox	SW SE NW Sec. 12 T. 12N., R. 3E.	Mecco Mine Midland Coal Co.
C-19074	6	RKP	Knox	SW SE NW Sec. 12 T. 12N., R. 3E.	Mecco Mine Midland Coal Co.

Sample No.	Coal Bed	Sample type	County	Location	Mine Name and Company
C-19075	2	B1	Fulton	NE NE SW Sec. 15 T. 4N., R. 1E.	Sunspot Mine Amax Coal Co.
C-19076	2	B2	Fulton	NE NE SW Sec. 15 T. 4N., R. 1E.	Sunspot Mine Amax Coal Co.
C-19077	2	B3	Fulton	NE NE SW Sec. 15 T. 4N., R. 1E.	Sunspot Mine Amax Coal Co.
C-19078	5	RKC	Fulton	SW SE NW Sec. 6 T. 5N., R. 4E.	Buckheart Mine Freeman United Coal Co.
C-19079	5	B1	Fulton	SW SE NW Sec. 6 T. 5N., R. 4E.	Buckheart Mine Freeman United Coal Co.
C-19080	5	B2	Fulton	SW SE NW Sec. 6 T. 5N., R. 4E.	Buckheart Mine Freeman United Coal Co.
C-19081	5	B3	Fulton	SW SE NW Sec. 6 T. 5N., R. 4E.	Buckheart Mine Freeman United Coal Co.
C-19082	5	B4	Fulton	SW SE NW Sec. 6 T. 5N., R. 4E.	Buckheart Mine Freeman United Coal Co.
C-19083	5	B5	Fulton	SW SE NW Sec. 6 T. 5N., R. 4E.	Buckheart Mine Freeman United Coal Co.
C-19084	5	B6	Fulton	SW SE NW Sec. 6 T. 5N., R. 4E.	Buckheart Mine Freeman United Coal Co.
C-19105	6	B1	Peoria	NE SW NW Sec. 28 T. 9N., R. 5E.	Elm Mine Midland Coal Co.
C-19085	6	B2	Peoria	NE SW NW Sec. 28 T. 9N., R. 5E.	Elm Mine Midland Coal Co.
C-19086	6	B3	Peoria	NE SW NW Sec. 28 T. 9N., R. 5E.	Elm Mine Midland Coal Co.
C-19087	6	B4	Peoria	NE SW NW Sec. 28 T. 9N., R. 5E.	Elm Mine Midland Coal Co.
C-19088	6	B5P	Peoria	NE SW NW Sec. 28 T. 9N., R. 5E.	Elm Mine Midland Coal Co.
C-19089	6	B6	Peoria	NE SW NW Sec. 28 T. 9N., R. 5E.	Elm Mine Midland Coal Co.
C-19090	6	B7	Peoria	NE SW NW Sec. 28 T. 9N., R. 5E.	Elm Mine Midland Coal Co.
C-19091	6	B8	Peoria	NE SW NW Sec. 28 T. 9N., R. 5E.	Elm Mine Midland Coal Co.
C-19092	6	RK2	Peoria	NE SW NW Sec. 28 T. 9N., R. 5E.	Elm Mine Midland Coal Co.
C-19093	6	RK1	Peoria	NE SW NW Sec. 28 T. 9N., R. 5E.	Elm Mine Midland Coal Co.
C-19094	6	RK1	Peoria	SE SW NE Sec. 20 T. 9N., R. 6E.	Elm Mine Midland Coal Co.
C-19095	6	B1	Peoria	SE SW NE Sec. 20 T. 9N., R. 6E.	Elm Mine Midland Coal Co.
C-19096	6	B2	Peoria	SE SW NE Sec. 20 T. 9N., R. 6E.	Elm Mine Midland Coal Co.
C-19097	6	B3	Peoria	SE SW NE Sec. 20 T. 9N., R. 6E.	Elm Mine Midland Coal Co.
C-19098	6	B4	Peoria	SE SW NE Sec. 20 T. 9N., R. 6E.	Elm Mine Midland Coal Co.

Sample No.	Coal bed	Sample type	County	Location	Mine Name and Company
C-19099	6	B5	Peoria	SE SW NE Sec. 20 T. 9N., R. 6E.	Elm Mine Midland Coal Co.
C-19100	6	B6P	Peoria	SE SW NE Sec. 20 T. 9N., R. 6E.	Elm Mine Midland Coal Co.
C-19101	6	B7	Peoria	SE SW NE Sec. 20 T. 9N., R. 6E.	Elm Mine Midland Coal Co.
C-19102	6	R8	Peoria	SE SW NE Sec. 20 T. 9N., R. 6E.	Elm Mine Midland Coal Co.
C-19103	6	RK2	Peoria	SE SW NE Sec. 20 T. 9N., R. 6E.	Elm Mine Midland Coal Co.
C-19104	6	RK	Peoria	SE SW NE Sec. 20 T. 9N., R. 6E.	Elm Mine Midland Coal Co.
C-19210	6	C	Stark	SE NW NW Sec. 11 T. 13N., R. 6E.	Allendale Mine Midland Coal Co.
C-19211	6	RK1	Stark	SE NW NW Sec. 11 T. 13N., R. 6E.	Allendale Mine Midland Coal Co.
C-19212	6	B1	Stark	SE NW NW Sec. 11 T. 13N., R. 6E.	Allendale Mine Midland Coal Co.
C-19213	6	B2	Stark	SE NW NW Sec. 11 T. 13N., R. 6E.	Allendale Mine Midland Coal Co.
C-19214	6	B3	Stark	SE NW NW Sec. 11 T. 13N., R. 6E.	Allendale Mine Midland Coal Co.
C-19215	6	B4P	Stark	SE NW NW Sec. 11 T. 13N., R. 6E.	Allendale Mine Midland Coal Co.
C-19216	6	B5	Stark	SE NW NW Sec. 11 T. 13N., R. 6E.	Allendale Mine Midland Coal Co.
C-19217	6	B6	Stark	SE NW NW Sec. 11 T. 13N., R. 6E.	Allendale Mine Midland Coal Co.
C-19218	6	RK2	Stark	SE NW NW Sec. 11 T. 13N., R. 6E.	Allendale Midland Coal Co.
C-19219	5	C	Fulton	SE SW NW Sec. 13 T. 7N., R. 3E.	Norris Mine Consolidation Coal Co.
C-19220	5	B1	Fulton	SE SW NW Sec. 13 T. 7N., R. 3E.	Norris Mine Consolidation Coal Co.
C-19221	5	B2	Fulton	SE SW NW Sec. 13 T. 7N., R. 3E.	Norris Mine Consolidation Coal Co.
C-19222	5	B3	Fulton	SE SW NW Sec. 13 T. 7N., R. 3E.	Norris Mine Consolidation Coal Co.
C-19223	5	B4	Fulton	SE SW NW Sec. 13 T. 7N., R. 3E.	Norris Mine Consolidation Coal Co.
C-19224	5	B5	Fulton	SE SW NW Sec. 13 T. 7N., R. 3E.	Norris Mine Consolidation Coal Co.
C-19225	5	RK2	Fulton	SE SW NW Sec. 13 T. 7N., R. 3E.	Norris Mine Consolidation Coal Co.
C-19226	5	C	Fulton	SE SW NW Sec. 13 T. 7N., R. 3E.	Norris Mine Consolidation Coal Co.
C-19227	5	B1	Fulton	SW NE NE Sec. 13 T. 7N., R. 3E.	Norris Mine Consolidation Coal Co.
C-19228	5	B2	Fulton	SW NE NE Sec. 13 T. 7N., R. 3E.	Norris Mine Consolidation Coal Co.