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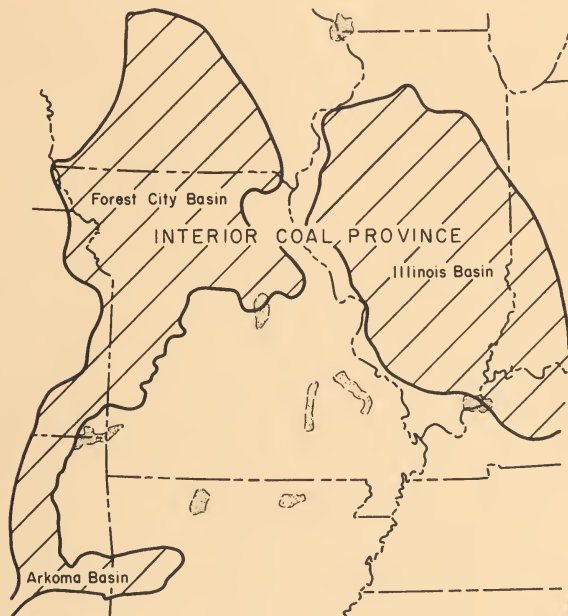
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FINAL REPORT

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GEOLOGY AND GEOCHEMISTRY OF SPHALERITE IN COAL

James Collins Cobb

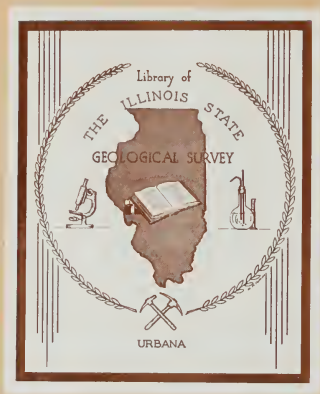


Prepared for

United States Geological Survey
Branch of Eastern Mineral Resources
United States Department of the Interior

Illinois State Geological Survey
Champaign, IL

Grant No. 14-08-0001-G-496
May 1981



ILLINOIS STATE GEOLOGICAL SURVEY



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BY

JAMES COLLINS COBB

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ABSTRACT

Middle Pennsylvanian (Desmoinesian) coals of certain areas of the Illinois and Forest City Basins contain epigenetic sphalerite and associated minerals in veins, clastic dikes, collapse structures, and other small-scale structural features. The mineral assemblage in the sphalerite veins consists of silicates, sulfides, and carbonates. The paragenesis is kaolinite-(quartz?)-pyrite-sphalerite-pyrite-calcite.

The morphology of sphalerite vein walls indicates that banding in the coal had achieved nearly its present stage of development at the time of sphalerite deposition. Sphalerite veins postdate cleats and are often developed in cleats. Some sphalerite deposition was contemporaneous with subsidence of coal into sinkholes. Compactional features in the coal show that from 8 to 14 percent of the compaction in the coal occurred after sphalerite deposition commenced. A relationship between porosity, inherent moisture, and compaction of the host coals suggests that the sub-bituminous (B) rank had been achieved at the time of sphalerite deposition.

Homogenization temperatures for the sphalerite fluid inclusions are nearly identical for the sphalerite from the Illinois and Forest City Basins and range from 75° to 113°C. There is a moderately high correlation coefficient ($r=.75$) between the vitrinite reflectance of the host coals and homogenization temperatures. This data may eliminate the possibility of fluid flow initiated by thermally-produced convection and raises the possibility of convection by compaction and

loading of basin sediments. This data and a paleogeothermal gradient of 2.35°C per 100m suggest a maximum depth of sphalerite deposition of 3.9 kilometers and a minimum depth of 2.2 kilometers.

The chemical and isotopic composition of the fluid inclusions are nearly the same for the six coal beds and two coal basins represented suggesting a similar fluid depositing the sphalerites. They are also similar to fluids observed in inclusions from nearby Mississippi Valley-type ore deposits, and bear close resemblance to basinal brines.

The occurrence of sphalerite in coal may record basinal processes that contribute to the genesis of Mississippi Valley-type ore deposits.

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CHAPTER 1

INTRODUCTION

Scope

The discovery of zinc-rich coals in the Interior Coal Province (Hatch et al., 1976 and Zubovic, 1960) has focused attention upon the origin of epigenetic sphalerite in these coals. This is a study of the geology, geochemistry, and origin of sphalerite and associated minerals in coals of the major Midcontinent coal basins. The occurrence of these minerals is helpful in interpreting conditions that existed in coals during mineral deposition. It is the purpose of this study to determine conditions under which minerals were deposited and to relate their deposition to coalification and other events in the history of the coal basins.

The approach used in this study was three-fold. First, field investigations of sphalerite to determine its modes of occurrence, structural controls on its occurrence, and regional distribution were carried out in coal beds of the eastern and western regions of the Interior Coal Province. Second, the mineral assemblages and textural aspects of sphalerite-bearing veins were studied in the laboratory. The purpose of this study was to compare the veins of each area and to determine paragenesis and timing of sphalerite deposition. Third, the geochemistry of sphalerite was investigated by chemical and isotopic analyses. The temperature of sphalerite formation was measured by the homogenization temperature of two-phase fluid inclusions.

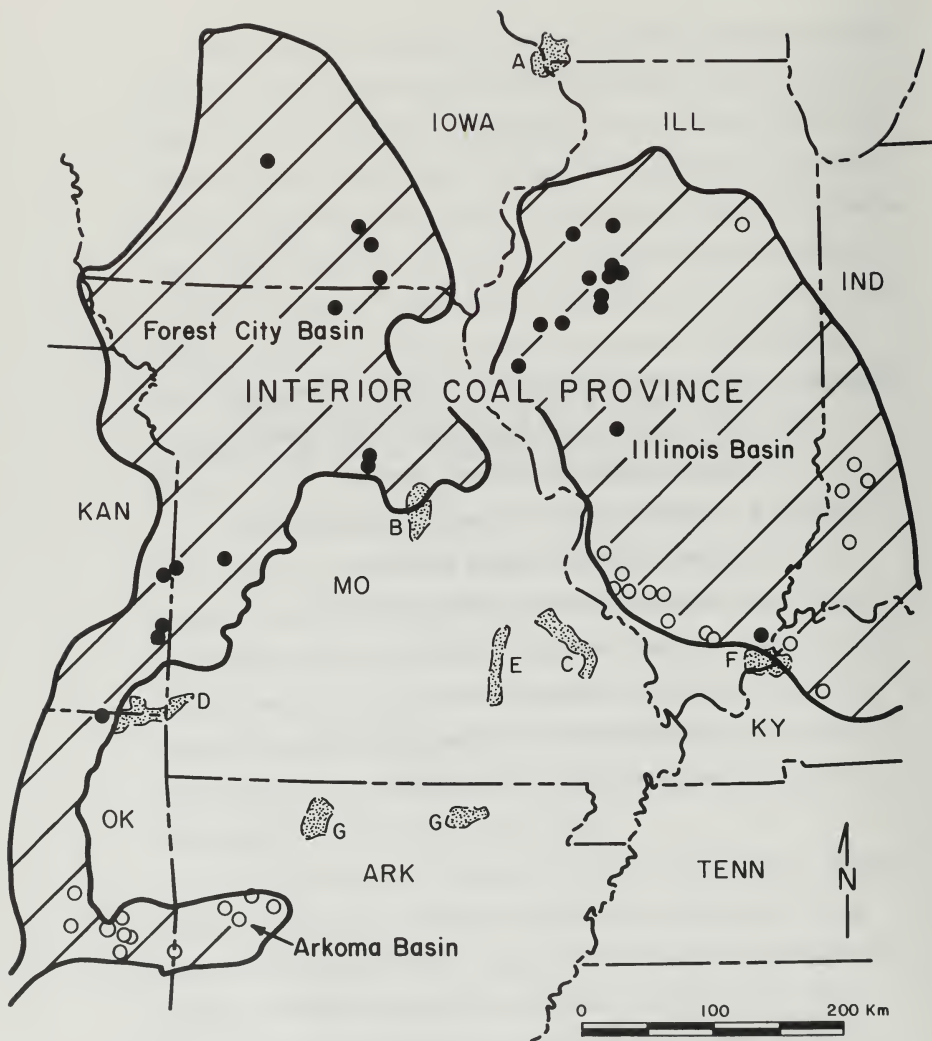
This study also considers the broader geological question of the origin of solutions which deposited the Mississippi Valley-type ores. There is general support at the present time for the hypothesis that brines from sedimentary basins were a major contributor to the solutions that deposited these ores. The occurrence of sphalerite-bearing coals in shelf areas of the major Midcontinent sedimentary basins, and thus in proximity to several of the major Mississippi Valley ore deposits, suggests a possible genetic relationship between basin brines, sphalerite in coal, and Mississippi Valley-type ore deposits. The study of the geology and geochemistry of sphalerite in coal affords insights into this geologically perplexing problem.

A wide assortment of sphalerite samples from coal was sought so that inter- and intra- basin comparisons could be made of fluid-inclusion homogenization temperature, fluid-inclusion composition, vein fillings, and paragenesis. Sixteen of the major producing coal seams in the eastern and western regions of the Interior Coal Province were examined. The location of the areas of study and sites where sphalerite was collected are shown in figure 1-1. Appendix I gives specific locations of field studies.

The zinc industry is the world's fourth largest metal producing industry. The U.S. is currently importing over 50 percent of its annual consumption of zinc. There has been an exponential increase in zinc consumption during the past several decades. This rapid increase in zinc consumption, coupled with diminishing reserves, has created an interest in unconventional sources of zinc. Sphalerite as a by-product of coal may be such a resource.

Figure 1-1. Eastern and Western Regions of the Interior Coal Province, showing Mississippi Valley-type base-metal mining districts and locations of field studies. (Black dots indicate sphalerite in coal, open circles indicate sphalerite not found in coal.)

- A. Upper Mississippi Valley lead-zinc district.
- B. Central Missouri barite district.
- C. Southeast Missouri lead-zinc district.
- D. Tri-State lead-zinc district.
- E. Viburnum Trend district.
- F. Kentucky-Illinois fluorspar district.
- G. Northern Arkansas zinc district.



The use of by-product zinc from sphalerite in coal is a new idea and one that is not likely to be followed by the coal industry unless some indication of its potential can be shown. The basic geologic information about sphalerite in coal provided by this study should be useful in that respect.

Glossary of Terms

This report utilizes terminology particular to both ore-deposits and coal literature. In order to inform the reader in advance of meanings of some of the more particular terms as used here, a glossary of important terms follows:

Butt cleat--the minor cleat or joint in a coal seam.

Clarain--a coal lithotype characterized by semi-bright luster, sheet-like fabric, and irregular fractures.

Clastic dike--a sedimentary dike (also referred to as a clay dike, clay vein, or horseback) of a variety of material derived from overlying strata, usually clay rich, and fills irregular crevices in coal beds.

Cleat--a joint or system of joints usually nearly vertical in a coal seam.

Coal banding--macroscopic layers of variable luster in coal whose constituents are vitrain, clarain, fusain, and durain.

Coal rank--a coal classification based on degree of metamorphism.

Coalification--the alteration or metamorphism of plant material into coal.

Epigenetic--refers to post-lithification changes or alterations in rocks.

Face cleat--the major cleat or joint system in a coal seam.

Fluid inclusion--a small cavity containing liquid and or gas which is formed by the entrapment of the fluid during growth of a crystal.

Fusain--a coal lithotype characterized by a charcoal-like appearance, dirty, and friable nature.

Gash vein--a mineral vein that is wide at the top and narrow at the bottom.

Gob--the coarse-grained refuse produced by coal cleaning operations.

Growth banding--the banded structure of sphalerite consisting of nearly parallel bands having different colors and textures produced by the addition of new material during the growth of crystals.

Homogenization temperature--the temperature at which a fluid inclusion attains equilibrium at atmospheric pressure and consists of only one phase, typically liquid. This temperature is measured as a means of determining the temperature of formation of certain minerals.

Inherent moisture--the moisture content of a coal seam that can not be removed by natural drying.

Median suture--a plane of demarcation at the center of a vein to which minerals growing from opposite walls meet.

Paragenesis--the sequence of mineral formation in a vein or ore deposit.

Primary fluid inclusion--a fluid-filled inclusion that forms simultaneously with the growth of the host crystal and therefore represents a sample of the depositing fluid.

Pseudosecondary fluid inclusion--a fluid-filled inclusion trapped after the formation of the surrounding mineral but prior to completion of crystal growth. It sometimes refers to an inclusion that results from "necking down" in a primary inclusion.

Secondary inclusion--an inclusion that forms after growth of the host crystal. Fluid from secondary inclusions does not represent the depositing solution. Secondary inclusions commonly form along cleavage fractures.

Slurry--the fine-grained refuse produced by coal cleaning operations.

Sphalerite-bearing coals--coals containing macroscopic deposits of sphalerite usually in vertical veins, cleats, and other fractures.

Sphalerite stratigraphy--the chronologic succession, classification, correlation, and mutual relationships of growth bands in sphalerite and because of its small scale sometimes referred to as microstratigraphy.

Vitrain--a coal lithotype characterized by brilliant, vitreous luster and conchoidal fracture.

Vitrinite--a coal maceral group also referred to as a microlithotype.

Vitrinite reflectance--a measurement of the reflectivity of vitrinite used in paleothermal and coal rank studies.

CHAPTER 2

SPHALERITE IN COALS OF THE INTERIOR COAL PROVINCE

Previous Investigations

Occurrences of sphalerite in coals have been known for many years. Stutzer (1940) discussed sphalerite in cleats of European coals. Research on minor elements in coal by Zubovic (1960) and Zubovic and others (1964) revealed anomalously high concentrations of zinc in coals of the Interior Coal Province. This research led to the speculation that zinc probably existed in the coal as sphalerite.

Earlier workers such as Roe (1934) reported sphalerite in clastic dikes in the Springfield (No. 5) Coal of west-central Illinois. Early reports by the Missouri Geological Survey gave accounts of min-able quantities of sphalerite in coals that filled sinkholes of Pennsylvanian age in central Missouri (Marbut, 1908; Van Horn, 1905). There are similar accounts of sphalerite production from sinkhole coal in the Kansas Geological Survey literature (Schoewe, 1959).

More recent studies of trace elements found significant concentrations of zinc in coals of Oklahoma, Kansas, Missouri, Iowa, and Illinois (Gluskoter et al., 1973; Ruch et al., 1974; Hatch et al., 1976a and 1976b; Wedge et al., 1976; and Gluskoter et al., 1977; and Hatch, 1979). Other investigations showed that the sphalerite is epigenetic in the coal, occurs in coal cleats, and is associated with pyrite, kaolinite, and calcite (Hatch et al., 1976).

The resource potential of sphalerite in coal was investigated by Cobb et al., (1979, 1980). These studies showed that the coal cleaning process concentrates sphalerite in slurry and gob refuse from the coal preparation plants and that the sphalerite is recoverable from refuse by density separation techniques. The zinc content of some coal seams was shown to be erratically distributed and to follow a lognormal frequency distribution. The average zinc concentration for three coal seams in west-central Illinois was calculated to be 1,050 $\mu\text{g/g}$.

Thus, although some work has been done in demonstrating the occurrence of zinc in coal, little has been done on the geology of sphalerite in coal. The geologic factors that control the regional distribution of sphalerite in coals of sedimentary basins were investigated in the field.

Field Investigations by the Author

Field investigations were conducted in Arkansas, Kansas, Kentucky, Illinois, Indiana, Iowa, Missouri, and Oklahoma to determine the regional distribution of sphalerite in coal and the structural relationships of sphalerite in coal beds. The coal-bearing strata examined lie within the Illinois, Forest City, and Arkoma Basins. Surface mines were utilized for the most part because of ease of accessibility and quality of exposures. In some cases, diamond drill core was examined for sphalerite; at other localities, outcrop exposures and underground mines were visited. Nearly 60 mines, producing coal from 22 coal beds

which represent the major producing coals of the eastern and western regions of the Interior Coal Province, were studied in the field.

Illinois Basin

Extensive field studies were carried out in three principal parts of the Illinois Basin; the northwestern, southwestern, and southeastern. Forty-five surface mines and six underground mines were examined for occurrences of sphalerite. These sites are shown in figure 2-1.

The Illinois Basin is a large structural depression bounded on the west by the Ozark Uplift and the Mississippi Arch, on the south by the Mississippi Embayment, and on the east by the Cincinnati Arch. The line of outcrop of coal-bearing strata in the Illinois Basin passes close to three major Mississippi Valley-type ore deposits: The Upper Mississippi Valley District, the Illinois-Kentucky Fluorspar District, and the Southeast Missouri Lead-Zinc District.

The coals of the Illinois Basin are generally of high-volatile B and C, bituminous rank and high in sulfur and ash. In certain areas, the sulfur content is low, and there is no evidence from either trace-element analyses or field investigations of sphalerite in these coals.

Western Shelf

The Western Shelf lies in the northwestern part of the Illinois Basin, separated from the central part of the basin by a subtle structure known as the Sangamon Arch (Clegg, 1970). Rocks of the Pennsylvanian System in the Western Shelf area range in thickness from 0 to 180 m and are overlain by Pleistocene glacial deposits. The total

Figure 2-1. Principal structural features of the Illinois Basin and locations of field studies. Solid dots represent occurrences of sphalerite in coal. Open circles represent localities where no sphalerite was found.

- A. Upper Mississippian Valley lead-zinc district.
- B. Central Missouri barite district.
- C. Southeast Missouri lead-zinc district.
- D. Tri-State lead-zinc district.
- E. Viburnum Trend district.
- F. Kentucky-Illinois fluorspar district.
- G. Northern Arkansas zinc district.



thickness of sedimentary strata overlying the Precambrian basement here ranges from 1,100 to 1,500 m. A generalized stratigraphic column is shown in figure 2-2 together with a detailed section for that portion of the Pennsylvanian that was examined for sphalerite. The strata in which the sphalerite occurs are shown by an asterisk.

The coal-bearing strata of the Western Shelf dip toward the center of the basin at less than 3.7 m per kilometer. There is no evidence in this area of major faulting, but local disturbances in the coals are common. The most frequent features are clastic dikes, fractures, faults with small displacement, and local warping of the beds.

The Rock Island (No. 1) Coal was not mined in the Western Shelf during the course of this study and, therefore, could not be examined in the field. Trace-element analyses on coal ash from the Rock Island (No. 1) Coal by Zubovic et al., (1964), however, strongly suggest the occurrence of sphalerite in this coal. Some bench samples from Henry County, Illinois, of the Rock Island (No. 1) Coal contained up to 2.1 percent zinc on a whole coal basis (Zubovic et al., 1964).

Sphalerite was found within a variety of structures in the Colchester (No. 2) Coal, in four counties of the Western Shelf (Brown, Fulton, McDonough, and Peoria). Single crystals and nodules of sphalerite occur in the clay-rich filling of clastic dikes (plate 1-a). Sphalerite is present in cleats (plate 1-b), and replaces part of a pyrite concretion (plate 1-c).

Figure 2-2. Generalized stratigraphic column and detailed sections of the middle Pennsylvanian for the Western Shelf and for southeastern Illinois (after Willman et al., 1975). (The beds in which sphalerite was found at one or more localities are shown by asterisks.)

SYSTEM	DOMINANT LITHOLOGY THICKNESS (m)	
Quaternary	Glacial drift	0-60
Pennsylvanian	Sst, slst, sh, lmst, & coal	0-180
Mississippian	Limestone	0-152
Devonian	Dol, lmst, sh	0-83
Silurian	Dolomite	0-120
Ordovician	Dolomite and limestone	350-450
Cambrian	Sandstone	60-822
Precambrian	Granite	

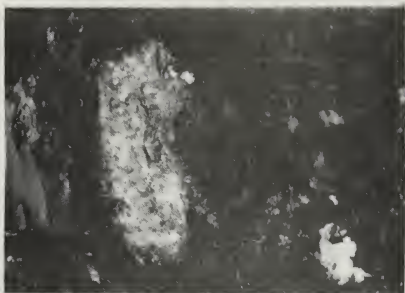
System	Series	Group	Lithology	Formations & Coal Members
Pennsylvanian	Alokta	Mc Cormick	—	Carbondale Fm Danville (No. 7) Coal*
	Desmoinesian	Keweenaw	—	Anno Shale* Herrin (No. 6) Coal unnamed black shale* Springfield (No. 5) Coal Summun (No. 4) Coal Lowell Coal Colchester (No. 2) Coal*
			—	Spoon Fm Greenbush Coal Wiley Coal De Long Coal
			—	Brush Coal Herron Coal Rock Island (No. 1) Coal*
			—	Abbott Fm gray shale siderite concretions

System	Series	Group	Lithology	Formations & Coal Members
Pennsylvanian	Desmoinesian	Keweenaw	—	Briar Hill (No. 5A) Coal Harrisburg (No. 5) Coal Summun (No. 4) Coal Shawneetown Coal Colchester (No. 2) Coal
			—	Carbondale Fm Danville (No. 7) Coal*
			—	Jamesstown Coal Anno Shale* Herrin (No. 6) Coal

Northwestern Illinois
Western Shelf

Southeastern Illinois
Eagle Valley Syncline

Plate 2-1. Sphalerite-bearing structures in the Colchester (No. 2) and Springfield (No. 5) Coals of the Western Shelf, Illinois Basin: ((a) sphalerite crystal 1.75 centimeters in length in clayey filling of a clastic dike in the Colchester (No. 2) Coal of Brown County, Illinois; (b) sphalerite in cleat (pencil for scale) in the Colchester (No. 2) Coal of Fulton County, Illinois; (c) sphalerite replacing pyrite in a concretion 15.0 centimeters across in the Colchester (No. 2) Coal of Fulton County, Illinois; (d) clastic dike (pencil for scale is 20 centimeters), containing sphalerite crystals, in the Springfield (No. 5) Coal of Fulton County, Illinois; and (e) sphalerite veins (pen for scale is 15 centimeters in length) in the Springfield (No. 5) Coal of Peoria County, Illinois.)



c



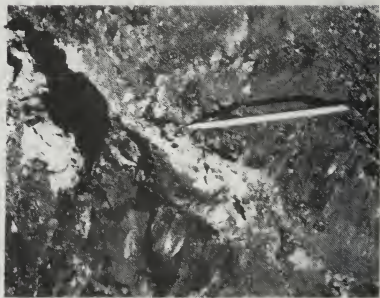
b



a



b



a

The Springfield (No. 5) Coal was studied in four surface mines having nine active pits in Fulton and Peoria counties. Sphalerite was found at all nine pits in clastic dikes (plate 1-d), and vertical veins (plate 1-e).

The Herrin (No. 6) Coal was examined at ten surface mines in Knox, Peoria, and Stark Counties. Sphalerite was found at all locations. It was observed in vertical veins up to 1 cm wide (plate 2-a), on fault surfaces (plate 2-b), and in gash veins (plate 2-c). Sphalerite crystals and nodules up to 4 cm in long dimension occur in clastic dikes (plate 2-d).

Occurrences of sphalerite in the Danville (No. 7) Coal are similar to those for the other coals, i.e., in cleats and vertical veins (plate 2-e), and in clastic dikes.

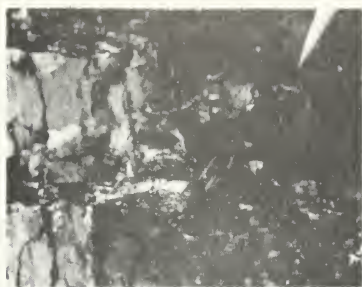
Sparta Shelf

The Sparta Shelf occupies the southwestern part of the Illinois Basin. In this area, numerous surface and underground mines yield a large percentage of the total coal production from the Springfield (No. 5) and Herrin (No. 6) Coals of Illinois. Ten mines were examined in this area and no sphalerite was found.

The Sparta Shelf is separated from the Western Shelf by the Sangamon Arch and from the central part of the Illinois Basin by the Du Quoin Monocline, along which the coal-bearing strata dip eastward toward the Fairfield Basin at about 4 m per kilometer.

No clastic dikes were seen in this area. Although no sphalerite was found, pyrite, barite, and calcite veins are common.

Plate 2-2. Sphalerite in the Herrin (No. 6) and Danville (No. 7) Coals of the Western Shelf, Illinois Basin: ((a) sphalerite vein (with pencil for scale) in the Herrin (No. 6) Coal of Peoria County, Illinois; (b) sphalerite on fault surface (with pencil for scale) in the Herrin (No. 6) Coal of Knox County, Illinois; (c) sphalerite gash veins (with pencil for scale) in the Herrin (No. 6) Coal of Knox County, Illinois; (d) sphalerite in clayey matrix of a clastic dike in the Herrin (No. 6) Coal of Peoria County, Illinois; and (e) sphalerite vein in the Danville (No. 7) Coal of Peoria County, Illinois.)



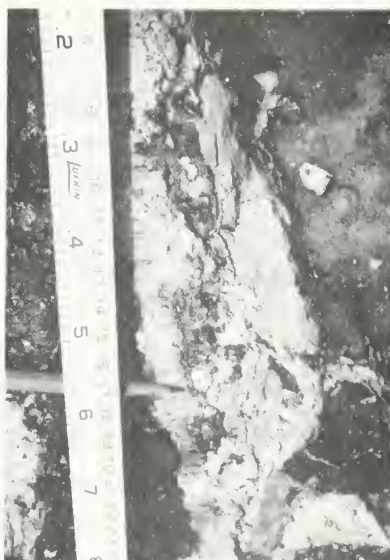
c



e



d



p



p

Eagle Valley Syncline

The Eagle Valley Syncline occurs in a structurally complex part of the Illinois Basin. The coal beds were examined at one surface mine and one underground mine in the area.

The Herrin (No. 6) Coal was found to contain sphalerite in vertical and inclined veins. Several large faults with normal fault displacement cut the coal at this location. Although the Wabash Valley fault cuts the Springfield (No. 5) Coal in an underground mine there is no sphalerite in this mine.

Eastern Shelf

The Eastern Shelf occupies the eastern part of the Illinois Basin and comprises mostly the Indiana and Kentucky portions of the basin. Coals at eighteen surface mines were examined in this area but no sphalerite was found. Clastic dikes, pyrite, and calcite-filled veins are abundant, however.

Forest City Basin

Visits were made to a number of mines in the platform areas of the Forest City Basin (figure 2-3) in order to study sphalerite in coals of the western region of the Interior Coal Province.

The Forest City Basin is a large structural depression bounded on the west by the Nemaha Structural Belt, on the south by the Arkoma Basin, and on the east by the Ozark Uplift and the Mississippi Arch. The line of outcrops of coal-bearing strata in the Forest City Basin passes close to two major Mississippi Valley-type ore deposits, the


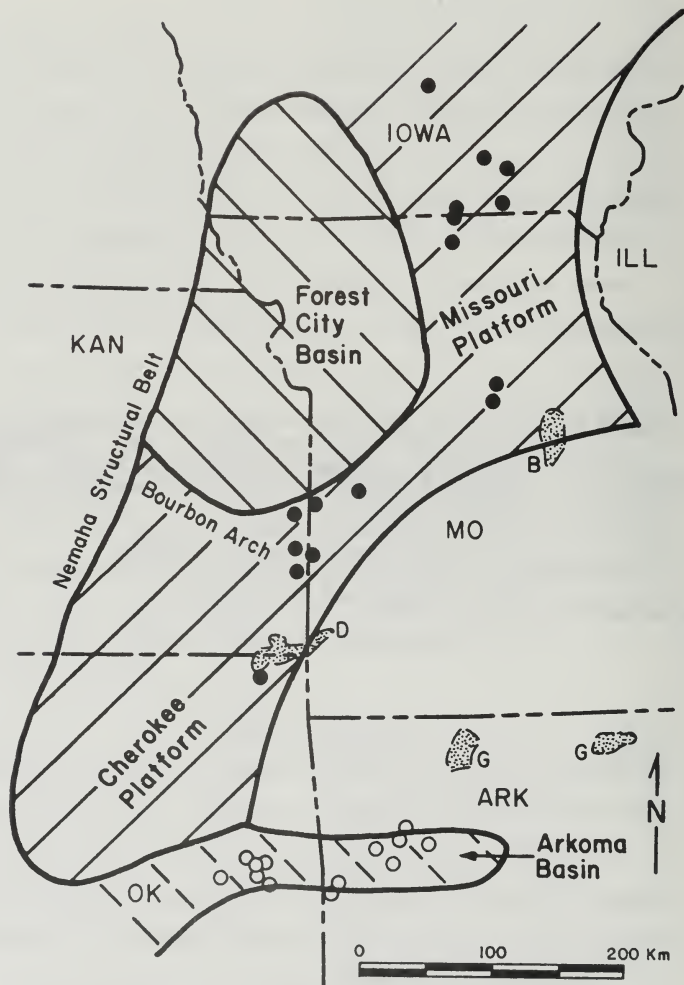


Figure 2-3. Principal structural features of the Forest City Basin and Arkoma Basin (after Branson, 1962). (Solid dots represent occurrences of sphalerite in coal. Open circles represent sites where coals were inspected and no sphalerite was found.)

- B. Central Missouri barite district.
- D. Tri-State lead-zinc district.
- G. Northern Arkansas zinc district.



Tri-State lead-zinc district and the Central Missouri barite district. The principal coal-producing areas of the Forest City Basin are its contiguous self areas--the Missouri and Cherokee Platforms.

Missouri Platform

The Missouri Platform (Branson, 1962) is a broad, saddle-shaped depression between the Illinois Basin on the east, the Ozark Uplift on the south, and the central part of the Forest City Basin on the west.

In Iowa there is approximately 1,225 m of sedimentary cover above the Precambrian basement, and the Pennsylvanian section is about 200 m thick. The coals are generally discontinuous and correlations are often uncertain. A generalized stratigraphic column is shown in figure 2-4, together with a detailed section for that part of the Pennsylvanian examined in this study. The Iowa Geological Survey informally divides the Cherokee Group into the Upper and Lower Cherokee (Avcin, personal communication, 1979).

The Iowa coals studied were the Mystic coal of the Marmaton Group and three uncorrelated beds of the Cherokee Group. In Monroe County, sphalerite was found in the Mystic coal and in both Upper and Lower Cherokee coals in Polk, Davies, and Wapello Counties.

The Lexington coal was examined in surface mines in Putnam County, Missouri, and across the state line in Appanoose County, Iowa, in vertical veins (plate 3-a) and cleat fillings (plate 3-b). Sphalerite was found in much the same structures in the Lexington coal as

Figure 2-4. Generalized stratigraphic column for the Missouri Platform, together with detailed middle Pennsylvanian sections for southeastern Iowa; Putnam County, Missouri; and Howard County, Missouri. (The beds in which sphalerite was found at one or more localities are shown by an asterisk.)

SYSTEM	DOMINANT LITHOLOGY	THICKNESS (m)
Tertiary	Shale, sst, gravel	0-600
Cretaceous	Sst, lmst, siltst	0-150
Permian	Sandstone	0-15
Pennsylvanian	Lmst, sh, sst, siltst, coal	0-520
Mississippian	Lmst, sh, sst	0-300
Devonian	Dolomite and limestone	0-300
Silurian	Limestone and chert	0-50
Ordovician	Dol, lmst, sst, chert	0-275
Cambrian	Dol, lmst, sst	0-550

System	Series	Group	Lithology	Formations & Coal Members
Pennsylvanian	Desmoinesian	Maraton		Lenapah Fm
				Nowata Fm
Pennsylvanian	Desmoinesian	Maraton		Altamont Fm
				Bandera Fm
Pennsylvanian	Desmoinesian	Maraton		Pawnee Fm
				Labette Fm Mystic Coal *
Pennsylvanian	Desmoinesian	Maraton		Marshall Coal Fort Scott Fm
				Summit Coal
Pennsylvanian	Desmoinesian	Maraton		Mulky Coal *
				Bever Coal *
Pennsylvanian	Desmoinesian	Cherokee		Wheeler Coal
				Whitebreast Coal
Pennsylvanian	Desmoinesian	Cherokee		Wiley Coal
				Meaterville Coal *

Southeast Iowa
Missouri Platform

System	Series	Group	Lithology	Formations & Coal Members
Pennsylvanian	Desmoinesian	Maraton		Pawnee Fm
				Anna Shale
Pennsylvanian	Desmoinesian	Maraton		Lexington Coal *
				Labette Fm
Pennsylvanian	Desmoinesian	Maraton		Higginsville Fm

Puñnam Co., Missouri
Missouri Platform

System	Series	Group	Lithology	Formations & Coal Members
Pennsylvanian	Desmoinesian	Cherokee		Mulky Fm
				Loganda Fm
Pennsylvanian	Desmoinesian	Cherokee		Bever Fm *
				Wheeler Coal
Pennsylvanian	Desmoinesian	Cherokee		Verdigris Fm
				Croweburg Fm
Pennsylvanian	Desmoinesian	Cherokee		Fleming Fm

Howard Co., Missouri
Missouri Platform

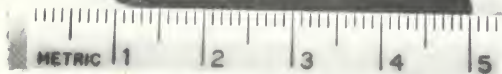
Plate 2-3. Sphalerite in coals of the Missouri Platform: ((a) sphalerite vein in the Lexington Coal of Putnam County, Missouri; (b) sphalerite veins offset along fusain band in Lexington Coal, Putnam County, Missouri; (c) sphalerite crystals from clastic dike in Bevier Coal, Howard County, Missouri; and (d) sphalerite vein in Bevier Coal, Howard County, Missouri.)



a



b



c



d

in the Herrin (No. 6) Coal, its probable stratigraphic equivalent in the Illinois Basin.

In central Missouri, the Bevier coal is the principal coal mined from surface mines in Randolph and Howard Counties. It is high-volatile bituminous in rank and has high sulfur and ash contents (Robertson, 1980). Examples are given of sphalerite from Howard County, Missouri, occurring as nodules in a clay-rich matrix (plate 3-c) and in vertical veins (plate 3-d).

Cherokee Platform

The Cherokee Platform covers parts of Kansas, Missouri, and Oklahoma. It is a coal-bearing structural depression that extends from the Forest City Basin on the north to the Nemaha Anticline on the west, the Arkoma Basin on the south, and the Ozark Uplift on the east (see figure 2-3). The high-volatile, mostly high-sulfur bituminous coals in this area are in a geographically restricted area that includes parts of eastern Kansas, southwestern Missouri, and north-eastern Oklahoma. The thickness of the sedimentary cover in this region is approximately 700 m and the thickness of the Pennsylvanian System is about 275 m. A generalized stratigraphic column together with a detailed section of that part of the Pennsylvanian System containing sphalerite-bearing coals is shown in figure 2-5. The Tri-State Mining district of Mississippi Valley-type ore deposits is adjacent to the southeastern margin of the Cherokee Platform.

The Mulberry coal is the youngest sphalerite-bearing coal mined in this area. Sphalerite is found for the most part in vertical veins

Figure 2-5. Generalized stratigraphic column, together with detailed sections of the middle Pennsylvanian for eastern Kansas and southwestern Missouri. (The beds in which sphalerite was found at one or more localities are shown by asterisks.)

SYSTEM DOMINANT LITHOLOGY THICKNESS (m)

Pennsylvanian	Sh, lmsl, ssf, coal	0-500
Mississippian	Dolomite and limestone	250-550
Devonian	Shale	10-25
Ordovician	Dolomite and chert	425-500
Cambrian	Dolomite and sandstone	300-350

System	Series	Group	Lithology	Formations & Coal Members
Pennsylvanian	Desmoinesian	Cherokee		Holdenville Shale
				Lanopoh Limestone
				Niwadjo Shale
				Alton Limestone
				Bandera Shale
				Mulberry Coal *
				Pawnee Limestone
				Loblette Shale
				Fort Scott Limestone
				Mulky Coal *
Pennsylvanian	Cherokee	Cherokee		Cabaniss Fm
				Bevier Coal *
				Croweburg Coal *
				Fleming Coal
				Mineral Coal *
				Scammon Coal
				Tobo Coal
				Weir-Pittsburg Coal
				Dry Wood Coal
				Rowe Coal
Neutral Coal				

Eastern Kansas
Cherokee Platform

System	Series	Group	Lithology	Formations & Coal Members
Pennsylvanian	Desmoinesian	Marmaton		Altamont Fm
				Bandera Fm
				Mulberry Coal *
				Pawnee Fm
				Labette Fm
				Alvis Coal
				Higginsville Fm
				Little Osage Fm
				St. Louis Coal
				Blackjack Cr Fm
Pennsylvanian	Cherokee	Cherokee		Excellio Fm
				Mulky Fm
				Lagonda Fm
				Bevier Fm
				Verdigris Fm
				Croweburg Fm
				Fleming Coal *
				Robinson Br Fm
				Mineral Fm
				Scammon Fm

Southwestern Missouri
Cherokee Platform

(plate 4-a and b), but where the coal bed dips steeply, sphalerite occurs in inclined veins. The steep dips are believed to result from local slumping into Pennsylvanian age sinkholes in the underlying Mississippian carbonates.

Sphalerite was found in vertical veins in the Mulky (plate 4-c), Croweburg, Fleming (plate 4-d), and Mineral Coals of eastern Kansas, western Missouri, and northeastern Oklahoma.

Arkoma Basin

The Arkoma Basin, which covers part of eastern Oklahoma and western Arkansas, is at the southern end of the western region of the Interior Coal Province (see figure 2-3). The basin is an elongated structural depression lying between the Ozark Uplift on the north and the Ouachita Uplift on the south.

The coals of the Arkoma Basin were subjected to higher temperatures and are, therefore, of low-volatile bituminous to semi-anthracite rank. The line of outcrop of the coal-bearing strata passes close to the Mississippi Valley-type ore deposits of the Northern Arkansas zinc district.

There are as yet no reports available on the trace element contents of Arkoma Basin coals from which to infer the presence or absence of sphalerite. It was, therefore, necessary to visit producing mines throughout the basin.

In eastern Oklahoma, the Secor, Upper McAlester, Sigler, and Upper and Lower Hartshorne Coals were examined in surface mines. These coals

Plate 2-4. Sphalerite veins in coals of the Cherokee Platform: ((a) Mulberry Coal, Linn County, Kansas; (b) Mulberry Coal, Linn County, Kansas; (c) Mulky Coal, Bourbon County, Kansas; and (d) Fleming Coal, Bates County, Missouri.)



a



b



c



d

have, in general, little mineralization of any kind. Calcite occurs in veins but was not abundant. There are rare occurrences of pyrite in discontinuous layers or lenses along the upper surfaces of some beds, but no sphalerite. These beds are intensively cleated and, where folding was intense, the coal was sometimes greatly fractured. Clastic dikes, clay-filled faults, and shear zones, which serve as sites for sphalerite deposition in other coals, do not occur.

In Arkansas, the Paris, Charleston, and Upper and Lower Hartshorne Coals were examined in surface mines and outcrops. As in eastern Oklahoma, no sphalerite was observed and only small amounts of calcite, pyrite, and kaolinite are present; consequently, these coals are low in sulfur and ash. They have been severely fractured by regional folding and faulting. There are no clastic dikes or clay-filled faults in these coals.

Other Sphalerite Occurrences

During the course of this study, other occurrences of sphalerite were found that have not been mentioned so far. Under reflected light, microscope studies of particulate pellets of the Herrin (No. 6) Coal from southern Illinois, sphalerite was found within cell lumens of fusinite (plate 5-a). In polished sections of the Anvil Rock Sandstone of western Illinois which overlies the Herrin (No. 6) Coal, sphalerite was observed in pore spaces between detrital grains and in fractures in black shale clasts (plate 5-b). Finally, black shales such as the Anna Shale that overlies the Herrin (No. 6) Coal of

Illinois and the Lexington coal of Missouri and an un-named black shale above the Springfield (No. 5) Coal of Illinois, were found to contain sphalerite in phosphate nodules and layers (plate 5-c). The occurrences of sphalerite in black shales are very widespread and have been described by Covney (1979).

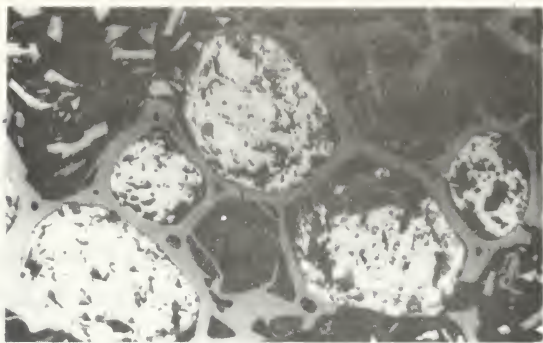
Structural Control of Sphalerite Deposition

Sphalerite occurs principally as an open-space filling in the coals of this study. Because coal is not susceptible to dissolution by most natural waters, sites of sphalerite deposition in coal were supplied by compaction generated features such as fractures, faults, cleat, and clastic dikes. The features closely related to the presence of sphalerite are described in some detail below, because the pattern of void distribution is one important criterion determining the origin of sphalerite in coal and for predicting which portions of coal seams may contain by-product zinc.

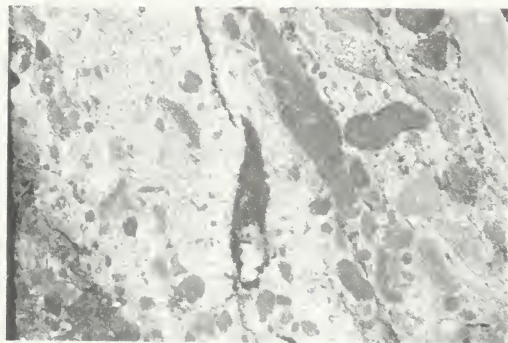
Dikes and Disturbed Coal

Chemical analyses for zinc in samples of sphalerite-bearing coals have shown that the zinc content in coals is highly variable (Ruch et al., 1974). In this study the distribution of zinc and, therefore, of sphalerite with respect to structural conditions in coal beds has been mapped in the Herrin (No. 6) Coal and the Springfield (No. 5) Coal of Illinois by making chemical analyses of samples obtained by drilling.

Plate 2-5. Additional occurrences of sphalerite in coal-bearing strata: ((a) sphalerite filling cell lumens in fusinite (the distance across the lumen in the upper-center of field is 0.1 millimeter); (b) sphalerite in black shale clast in Anvil Rock sandstone (the scale along left margin is in centimeters); and (c) sphalerite in phosphate nodules in black shale above a sphalerite-bearing coal (the scale is 2.5 centimeters in length).)



a



b



c

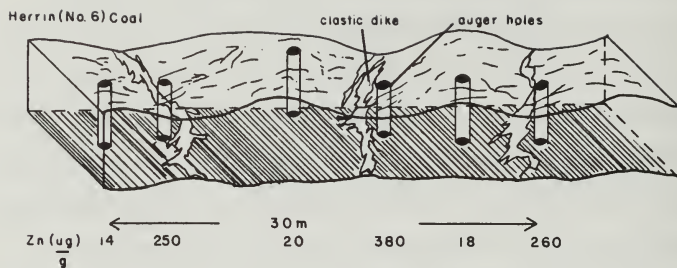
A group of six holes was drilled through only the thickness of the coal seam in an area where sphalerite had been observed in clastic dikes, cleats, fractures, and faults. Drill holes were placed in disturbed coal, near clastic dikes, and in relatively undisturbed coal, midway between clastic dikes. The chemical analyses show much higher zinc concentrations in disturbed coal than in undisturbed (figure 2-6a).

In another test of the role of disturbed coal as a host for sphalerite at this locality, a series of ten holes spaced 0.7 m apart was drilled along a traverse which intersected one clastic dike in the Springfield (No. 5) Coal. The chemical analyses clearly demonstrate that higher concentrations of zinc occur where the coal has been disturbed by clastic dikes (figure 2-6b).

Finally, a series of auger samples was collected from a site where the Herrin (No. 6) Coal appears to be unaffected by any disturbance of the coal, as indicated by its uniform thickness and the absence of features such as faults or dikes. The latter features are, however, present elsewhere along the total 0.4 km length of mine face as are veins containing sphalerite. Chemical analyses of the auger cuttings from these holes indicate an absence of sphalerite (figure 2-6c).

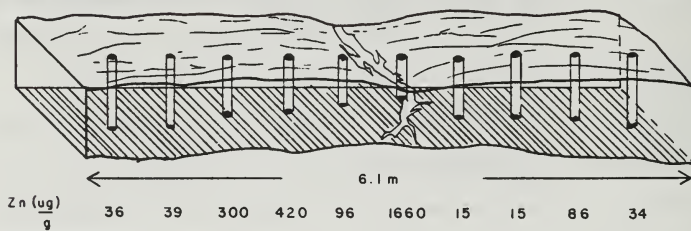
Clastic dikes, which are observed most frequently in the Western Shelf, Eastern Shelf, and Missouri Platform coals, are complex structures that characteristically have irregular walls and are filled with a light-grey clay or silty clay that contains fragments of coal (figure 2-7a and b). The clastic dikes rarely penetrate the entire thickness of the coal seam but where such penetration has occurred,

Figure 2-6. Sphalerite distribution in disturbed and undisturbed coal as indicated by zinc content: (a) Herrin (No. 6) Coal, Peoria County, Illinois; (b) Springfield (No. 5) Coal, Peoria County, Illinois; and (c) Herrin (No. 6) Coal, Knox County, Illinois.



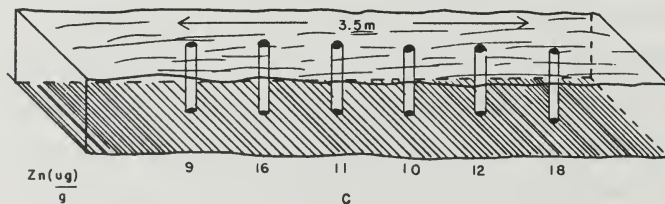
a

Springfield (No. 5) Coal



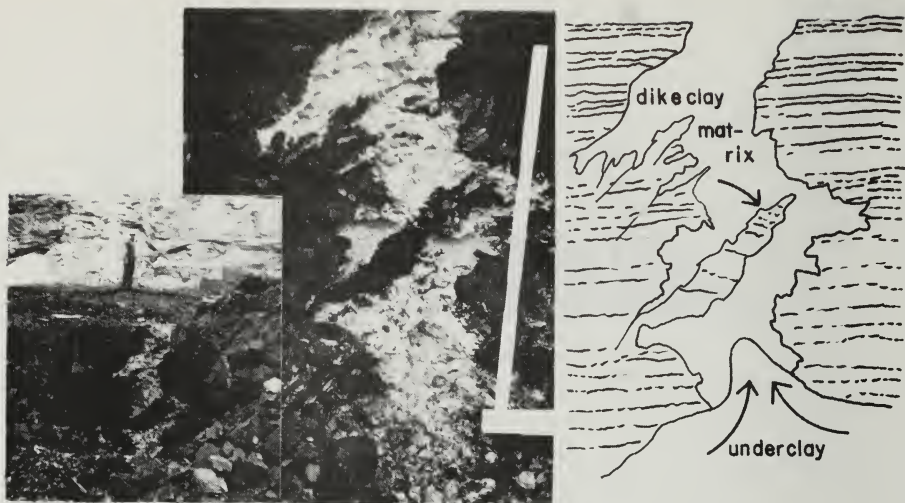
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Herrin (No.) Coal

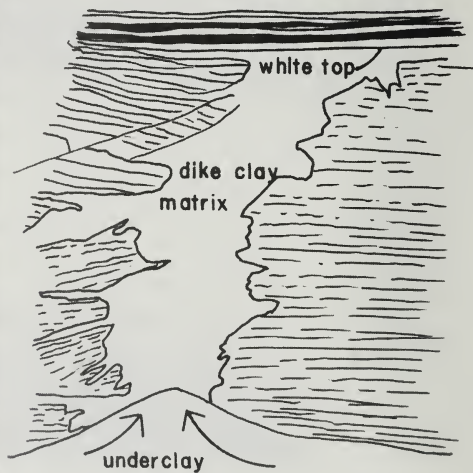


c

Figure 2-7. Clastic dikes in coal: (a) Colchester (No. 2) Coal, Fulton County, Illinois; (b) Herrin (No. 6) Coal, Peoria County, Illinois.



a



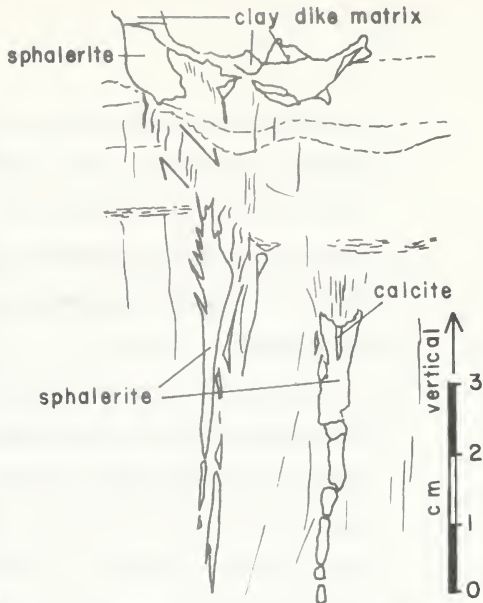
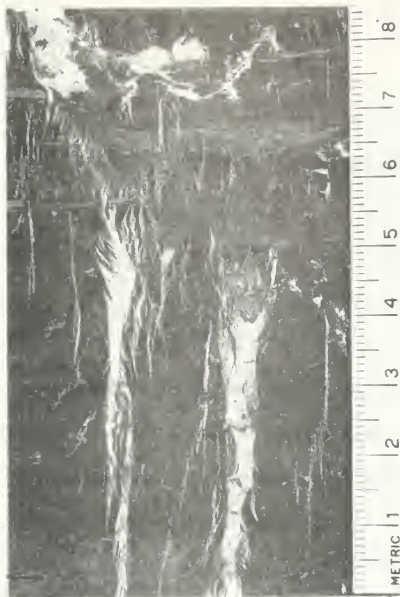
b

there is a sharp contact between the dike matrix and the underclay. Although the underclay may bulge upward slightly below a clastic dike, there is no evidence that any of the dike material was contributed by the underclay. In a mineralogical analysis primarily by powder X-ray techniques of the clay content of clastic dikes, overlying shales, and underclays, it was found that the clay minerals in clastic dikes more closely resembles that of roof shale than of underclay (Stepusin, personal communication, 1978). At several localities, clastic dikes were observed to penetrate upwards for as much as 7 m through black shale, narrowing to roughly a centimeter in width but still containing millimeter-sized sphalerite crystals. One clastic dike extended from the Herrin (No. 6) Coal 10 m up through grey shale to the Danville (No. 7) Coal.

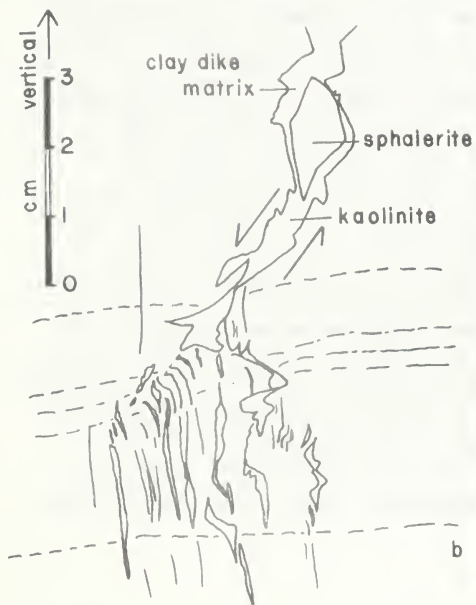
The irregular configuration of the clastic dikes suggests that they may originally have been nearly vertical, with relatively straight sides, but that they have been subsequently compacted. An attempt was made to estimate the amount of compaction by measuring the thickness of coal and the length of the perimeter of a dike wall. This method proved not to be quantitative, because the pre-compaction configuration cannot be assessed, but qualitatively it supports the idea that compaction of the dikes has taken place.

The close spatial relationship between clastic dikes and sphalerite is shown in figures 2-8a and b. In figure 2-8a, clastic dike material (clay matrix) terminates at a shear zone with normal fault displacement of about one centimeter. This fracture dies out into a

Figure 2-8. Relationships between clastic dikes and sphalerite deposition: (a) clastic dike with sphalerite crystal, shear fracture, and en echelon sphalerite-bearing veins in the Herrin (No. 6) Coal, Peoria County, Illinois; and (b) clastic dike with sphalerite crystal and shear fracture terminating in en echelon veins in Herrin (No. 6) Coal, Knox County, Illinois.



a



b



set of en echelon veins that contain sphalerite. The clay matrix also contains sphalerite. Figure 2-8b shows the termination of another clastic dike which also dies out into a shear zone. The clay matrix contains a subhedral sphalerite crystal. Numerous en echelon tension fractures containing sphalerite and kaolinite have opened along the shear zone.

The origin of clastic dikes in coal seams has been debated for many decades (Udden, 1912; Savage, 1927; Roe, 1934; Wanless, 1957; and Damberger, 1970 and 1973). Damberger (1973) described the physical characteristics of clastic dikes in the Springfield (No. 5) and Herrin (No. 6) Coals of Illinois. He also discussed their possible origin from earth-quake induced disturbances. One conclusion from his observations is that the Herrin (No. 6) Coal had been buried by only a few meters of sediment at the time of dike formation. This conclusion eliminates the possibility of differential compaction causing dike emplacement for lack of sufficient overburden needed to generate the necessary pressures. It was later found however that a clastic dike intruding the Herrin (No. 6) Coal continued vertically for 10 meters and intruded the Danville (No. 7) Coal. It is apparent that the Danville (No. 7) Coal plus enough strata overlying it to have caused its consolidation had also been deposited before dike emplacement.

In regards to the earthquake origin of clastic dikes (Damberger, 1970 and 1973), it can be said that to the extent that shock waves set off by earthquakes can bring about sudden large increases in hydraulic pressures in the subsurface, clastic dikes may be related

to earthquakes. Rapid sedimentation and differential compaction can also bring about localized increases in hydraulic pressure capable of rupturing coal seams.

Noting Hubbert's (1957) observation that vertical fracturing and dike emplacement is very similar to artificial hydraulic fracturing, it seems possible that clastic dikes may have been produced or enhanced by hydraulic pressure. The origin of the hydraulic pressure remains debatable. It is probable that dehydration, devolatilization, and differential compaction in the coal seams aided in producing the clastic dikes.

Sinkholes

The coals that have collapsed into sinkholes after dissolution of underlying carbonate rocks are unusual in that some of them are rich enough in sphalerite that they were mined in the last century. Deposits of this sort in central Missouri have been described by Van Horn (1905), Marbut (1908), and Mather (1946).

Sphalerite was produced as early as 1840 from a collapse structure or slump pipe in Linn County, Kansas, which appeared to be about 50 m across, with 10 to 15 m of relief (Schoewe, 1959). A more recent gravity survey indicated that the collapse structure is about 25 m across and extends downward for about 200 m (Yarger and Jarjur, 1972). Sphalerite has also been produced from slump structures in the nearby Tri-State district (McKnight and Fischer, 1970), where slumps extend downward into the St. Joe Limestone, the oldest Mississippian member

(McKnight and Fischer, 1970).

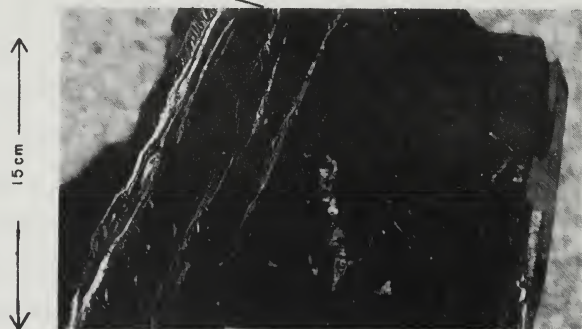
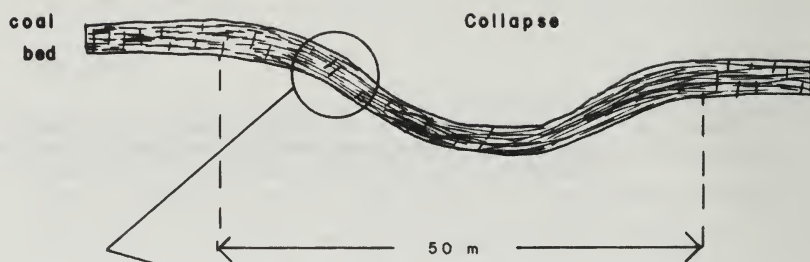
A collapse structure in the Mulberry Coal of Linn County, Kansas, was investigated for sphalerite (figure 2-9a). This structure is a bowl-shaped depression with a diameter of about 75 m and a relief of about 5 m. Sphalerite occurs in vertical veins where the coal is flat lying. Where the coal is inclined, the sphalerite veins are inclined (figure 2-9b) suggesting that fracture opening was in response to tensional stress brought about by the subsidence.

Coal Cleat

Cleat is the naturally occurring joint system in bituminous coal. It is characterized as a vertical, right-angled fracture system composed of a dominant fracture (face cleat) and a subordinate fracture (butt cleat). The cleats frequently contain mineral fillings of which kaolinite, pyrite, and calcite are the most common. Sphalerite, however, was one of the minerals reported by Stutzer (1940, p. 287) from cleats of European coals. Hatch et al. (1976) described sphalerite in cleat of coals in the Illinois Basin.

Many theories have been presented for the origin of cleat. Several authors have stressed the role of tectonic forces (e.g., Stutzer, 1940; and McCulloch et al., 1974). Many authors have considered cleats to result from a volume shrinkage of the coal either by dehydration or devolatilization (Spenser, 1969). Cleat increases in frequency with increases in rank, from lignite to bituminous. It appears that its formation does not commence until the lignite stage, where its

Figure 2-9. Collapse structure in the Mulberry Coal of Linn County, Kansas: (a) sketch shows subsided coal bed; (b) inclined sphalerite veins related to subsidence of coal bed.



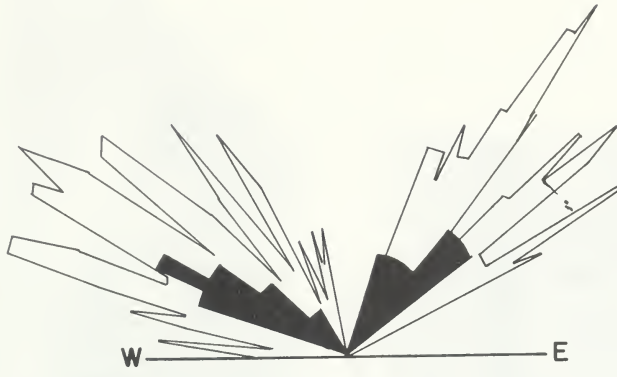
formation is directly related to moisture losses. Ting (1977) advocates a combination of several mechanisms for the origin of cleats including tectonic stress, dehydration, and devolatilization.

An important aspect of cleat is its effect on fluid flow through a coal bed. In dewatering and degasification studies of coal beds, the direction of maximum hydraulic conductivity was found by Stone and Snoeberger (1978) to correspond to the trend of the face cleat, and the direction of minimum hydraulic conductivity, to the butt cleat. Cleat has probably played a significant role in the migration of mineralizing solutions through coal beds.

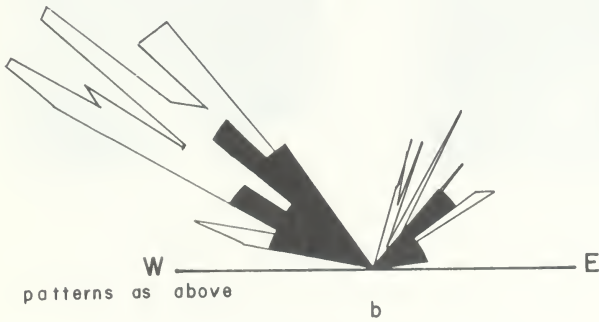
In order to investigate the structural relationship among these sphalerite-bearing structures, the strikes of cleats and sphalerite veins from the same coal beds were measured and recorded on rose diagrams (figure 2-10a and b). The strikes of sphalerite veins are parallel to principal cleat directions in coals of the Western Shelf that were examined.

A horizontal section through a sphalerite vein in the Fleming Coal of the Cherokee Platform (figure 2-11a) shows the veins intersecting at right angles in a cleat-like pattern. Also, in a horizontal section through an analogous specimen of a sphalerite vein in the Springfield (No. 5) Coal from the Western Shelf, the vein is parallel to the butt cleats and perpendicular to the face cleats (figure 2-11b). There is an obvious correspondence between the cleats on both sides of the vein, suggesting they were once continuous before they were cut through by the vein. Therefore, cleats must have formed before the veins.

Figure 2-10. Rose diagrams showing correspondence between the strike of cleats and the strike of sphalerite veins: (a) Herrin (No. 6) Coal in Knox, Peoria, and Stark Counties, Illinois; and (b) Springfield (No. 5) Coal in Fulton and Peoria Counties, Illinois.



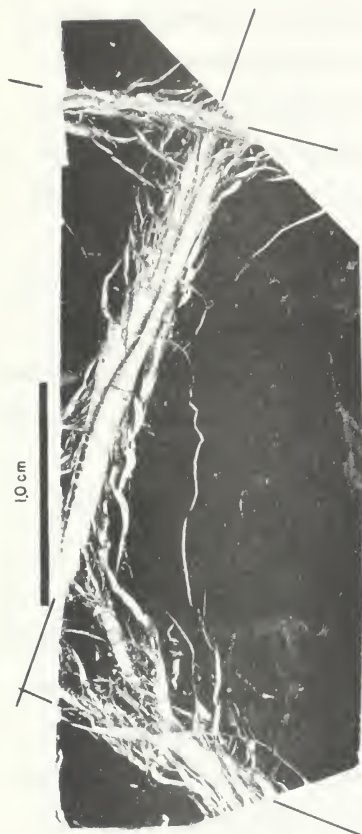
open patten - strike of cleats
black - strike of sphalerite veins a



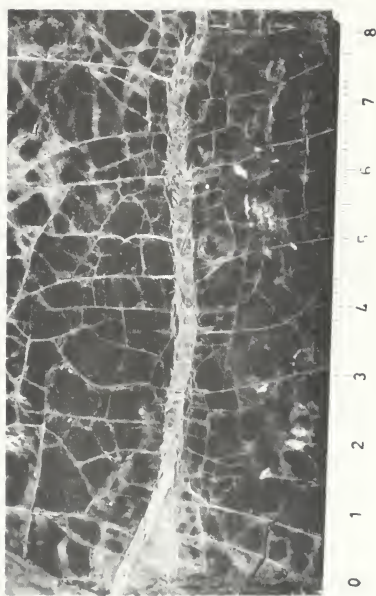
patterns as above

b

Figure 2-11. Sphalerite veins and coal cleats: (a) three sphalerite veins intersecting at right angles in the Fleming Coal, Bates County, Missouri; and (b) sphalerite-pyrite vein following the direction of the butt cleat in the Springfield (No. 5) Coal, Fulton County, Illinois (note the deflection of the cleats where they intersect the vein and the correlation of cleats across the vein).



a



b

(scale in cm)

Discussion

Sphalerite occurs in restricted geographical areas of nearly all the producing coal beds of the eastern and western regions of the Interior Coal Province. Where there are several coals in the same stratigraphic sequence, the areas of sphalerite deposition in the several coals are generally coincident. The localization of sphalerite within limited areas of a particular coal bed results from epigenetic filling of voids such as fractures, faults, clastic dikes, disturbed zones resulting from slumping, and cleat. The first four of these presumably result from structural disturbance, and cleat may, at least in part, be a response to structural disturbance but also to chemical processes in the coal.

The deposition of sphalerite does not appear to require large faults for movement of mineralizing solutions into the coals. The Anvil Rock sandstone-conglomerate, an aquifer above the Herrin (No. 6) Coal of the Illinois Basin, contains sphalerite in black shale clasts and in pore spaces. It is probable that highly permeable units such as this carried the solutions which deposited sphalerite and other minerals. There are no large faults in the sphalerite-bearing coals of the Western Shelf. On the other hand, there are large faults in the sphalerite-bearing coals in the southern and southeastern parts of Illinois, but only minor amounts of sphalerite in the coals of that area. It is apparent that structures restricted to coal beds play a more critical role in controlling the presence of sphalerite than do large structures involving many units.

In some areas, cleats in the coal have enhanced its permeability in the direction of a possible source of mineralizing solutions. On the Western Shelf, Missouri Platform, and Cherokee Platform the face cleat points in the direction of the deepest part of the adjacent basin, from which metal-bearing solutions might have ascended.

Most of the sphalerite-bearing coals are:

1. Middle Pennsylvanian (Desmoinesian) in age;
2. High-volatile bituminous in rank;
3. High in sulfur;
4. High in ash;
5. Associated with a characteristic set of minor features;
6. On shelf areas of major, midcontinent, sedimentary basins;
7. In proximity to major Mississippi Valley-type ore deposits.

In contrast, sphalerite was not found in deep mines near the center of major sedimentary basins nor in low sulfur coals of these basins. Sphalerite was not found in coals of the Arkoma Basin. These coals are low-volatile bituminous to semi-anthracite in rank, low in sulfur and ash, brecciated and disrupted by major folding and faulting.

The structures that contain sphalerite are roughly vertical in orientation and extensional in origin. The shear fractures are normal faults which cut the coal at approximately 45°. The clastic dikes exhibit large-scale extension and evidence of compaction. The gash veins are characteristically wedge-shaped in vertical profile. These structures indicate the absence of compressional forces. Because these types of structures tend to remain open and enhance permeability,

they are commonly sites of mineral deposition. It is probable that cleat formation, dehydration, devolatilization, and differential compaction aided in producing open space for mineralization and fluid flow.

CHAPTER 3

MINERALOGY AND PARAGENESIS

The mineral assemblage in sphalerite-bearing veins, defined as those minerals in direct contact with one another, consists of kaolinite, pyrite, sphalerite, and calcite. Barite is a vein-filling mineral in coal but was not found in any sphalerite-bearing veins. This section presents information about the mineral assemblage and discusses textures, structures, and paragenesis of the mineral assemblage, which provides information about changes in the physical and chemical environment during vein filling.

Techniques

Hand specimens of sphalerite-bearing veins were collected from coals of the Illinois Basin, Missouri Platform, and Cherokee Platform; in all, hand specimens were collected from 12 different coal beds at 50 locations from four states (see Appendix I).

Polished sections, as well as uncovered, doubly-polished thin sections, were prepared using a procedure recommended by Barton (personal communication, 1976) and were viewed with a petrographic microscope capable of simultaneous reflected and transmitted illumination. This procedure allows one to view the textural relationships of the opaque materials such as pyrite and coal that are revealed by reflected light, while also profiting from the improved visibility of detail in nonopaque minerals such as sphalerite and calcite. If

normal, unpolished thin sections are used (e.g., Hatch et al., 1976), internal textures and details of the sphalerite are lost because of severe scattering of light caused by its high index of refraction.

X-ray diffraction techniques and scanning electron microscopy was used whenever necessary to verify the microscopic identification of minerals.

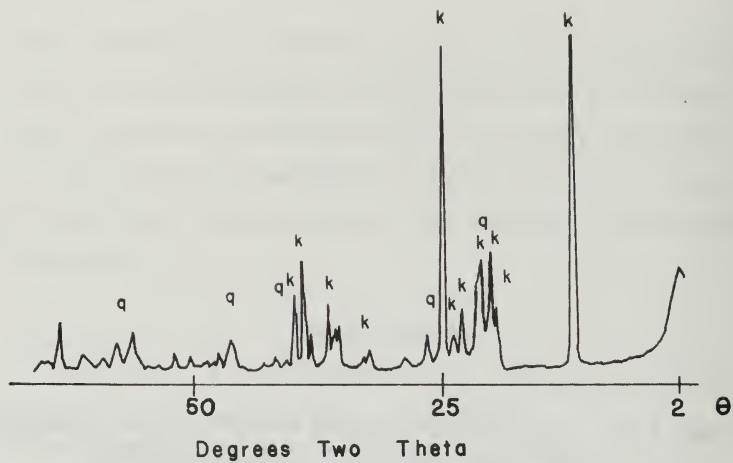
Kaolinite-Quartz

Kaolinite is a common constituent of sphalerite-bearing veins, and is the most abundant mineral in coal cleats.

A diffraction pattern for kaolinite from a sphalerite vein is shown in figure 3-1a. The diffraction pattern also shows the presence of quartz. Quartz in sphalerite veins has also been reported by Hatch et al., (1976). As indicated by the sharpness of the kaolinite diffraction peaks, the kaolinite is well-crystallized, and presumably authigenic (Gluskoter, 1967). It is very much the kaolinite described from coal cleats by Rao and Gluskoter (1973). The orderly stacking of kaolinite crystallites, and the perfection and size of the crystals shown in the scanning electron photomicrograph (figure 3-1b) also indicates an authigenic origin rather than a detrital origin for the kaolinite. Quartz was not seen in microscopic examinations of thin sections or polished sections. Quartz may be a minor co-precipitate with kaolinite although there is no direct evidence for this or it may be a contamination from the coal.

Figure 3-1a. X-ray diffraction pattern of kaolinite hand picked from a sphalerite vein (k-kaolinite peak, q-quartz peak, Cu $K\alpha$ radiation, 40kv, 20ma, Norelco instrument).

- b. Scanning electron photomicrograph of kaolinite from a sphalerite vein (bar for scale is 0.01 mm).



a



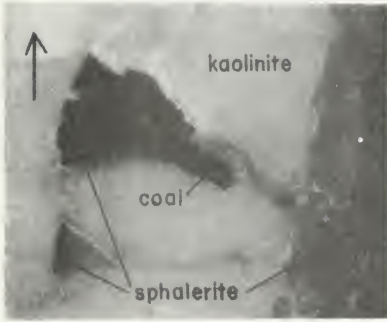
b

The kaolinite of sphalerite veins has coal particles and sphalerite crystals included within it (figure 3-2a). The sphalerite seen here penetrates into the kaolinite along tiny fractures, but there is also penetration into the kaolinite by euhedral crystals of sphalerite (figure 3-2b). Kaolinite is in the center of veins as narrow, straight-sided fragments, elongated in the vertical direction (figure 3-2c). The kaolinite in such cases is often surrounded by pyrite, sphalerite, or calcite. These segments appear to be fragments of former cleats that were broken and incorporated into the mineral filling.

Pyrite

Pyrite commonly fills cleat and other structures in coal and is a common constituent of sphalerite veins. There is no marcassite in any of the samples examined. The pyrite in sphalerite veins contains rafted coal particles which are aligned parallel to the vein walls, indicating that the fissure underwent dilation with rafting of coal from vein walls during pyrite deposition. In many cases pyrite occupies the center portion of sphalerite veins and is extensively replaced by sphalerite along preferred orientations at the vein walls (figure 3-3a). The preferred orientations are parallel to the coal banding. This particular case illustrates that new sphalerite, was added along the vein walls which are mechanically the weakest part of the vein.

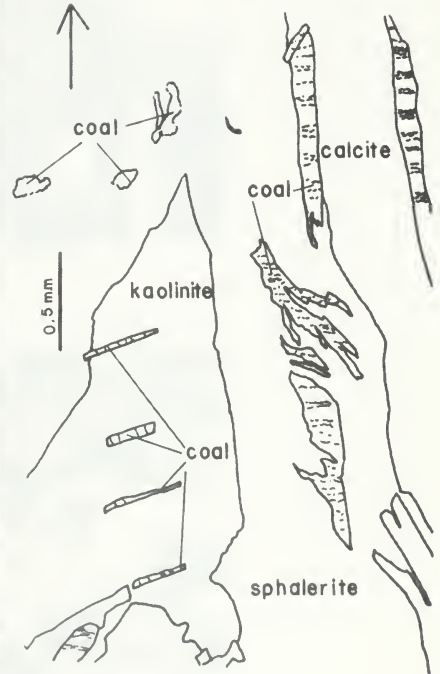
Figure 3-2. Paragenetic relations of kaolinite in sphalerite-bearing veins; (a) kaolinite with "floating" particles of coal and sphalerite (arrow for scale is 0.1 mm and indicates up direction); (b) euhedral sphalerite penetrating kaolinite (arrow for scale is 0.1 mm and indicates up direction); (c) kaolinite enclosed by sphalerite itself containing coal particles (identifications and scale given in the schematic).



a

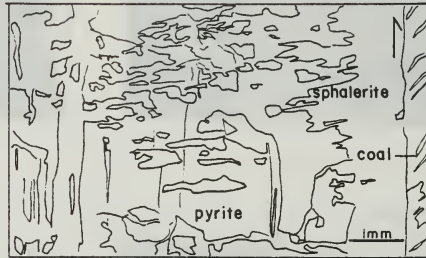


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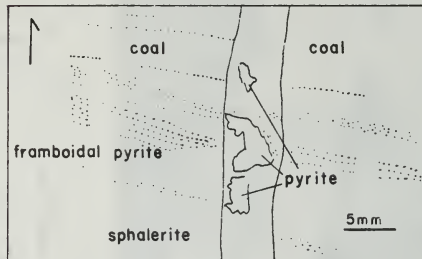


c

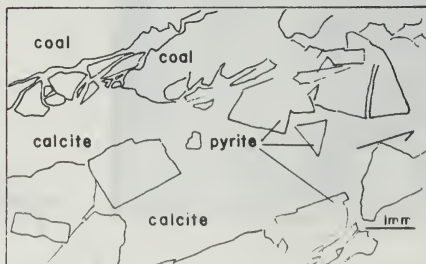
Figure 3-3. Paragenetic relations of pyrite in sphalerite-bearing veins: (a) photomicrograph in color in reflected-light illumination and sketch with identifications and scale showing sphalerite selectively replacing pyrite; (b) photomicrograph in reflected and transmitted-light illumination and sketch with identifications and scale showing mobilization and recrystallization of pyrite from the coal into the sphalerite vein; (c) photomicrograph in reflected and transmitted-light illumination and sketch with identification and scale showing euhedral pyrite within calcite.



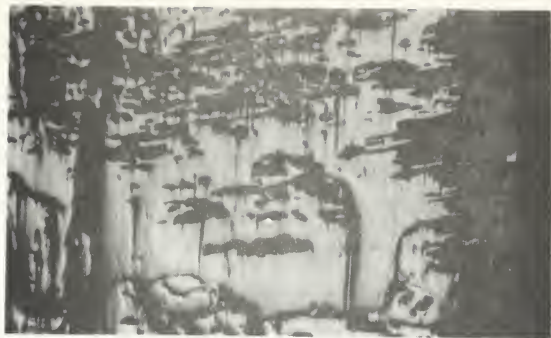
a



b



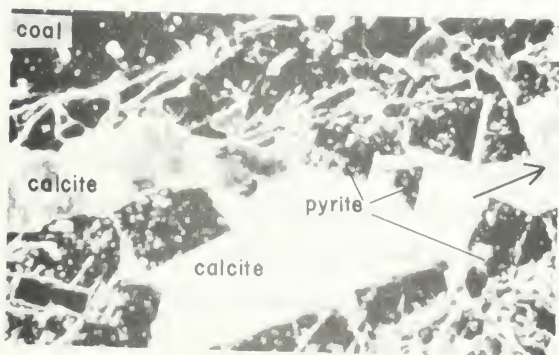
c



a



b



c

Concentrations of pyrite are found in sphalerite veins where concentrations of disseminated pyrite are adjacent to them in the coal walls (figure 3-3b). It appears that pyrite in veins is sometimes related to the occurrence of pyrite in the coal.

Euhedral pyrite crystals occur in calcite (figure 3-3c), although calcite veins more commonly cross-cut pyrite veins. Some of the pyrite may be younger than some of the calcite.

Sphalerite

In most cases, single sphalerite crystals fill voids in coal from wall to wall, but elsewhere several episodes of sphalerite deposition are evident, and there are also euhedral sphalerite crystals that appear to have grown into open space.

The sphalerite in coal contains regions of densely-packed purple rods (figure 3-4a). The rods of purple color maintain an orientation generally perpendicular to the walls of veins, and therefore, parallel to the direction of crystal growth. The rods are numerous, appearing in at least one band of sphalerite growth. They are parallel, often bent or curved, and have a maximum diameter of 0.01 mm. Their rod-like shape was verified by cutting a pair of thin sections perpendicular to the vein wall and to each other.

Wurtzite, another ZnS polymorph, is sometimes found in low temperature ore deposits associated with sphalerite and it was suspected that the purple rods could be wurtzite. The wurtzite must be distinguished by X-ray diffraction analysis. The sphalerite samples were

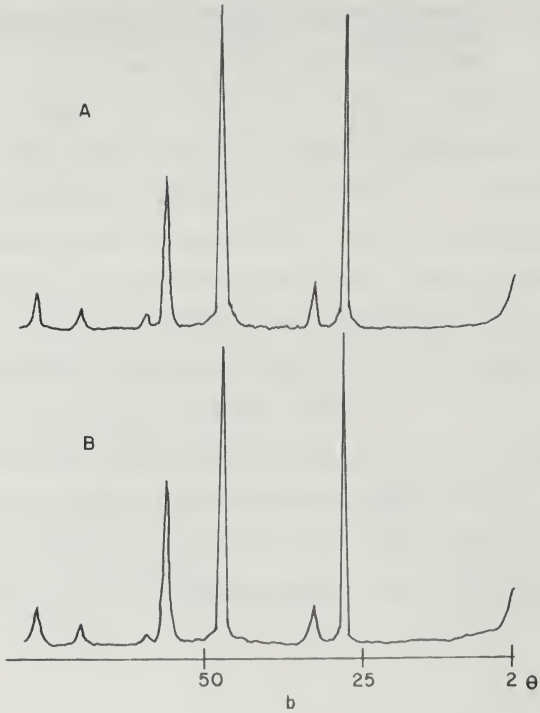


Figure 3-4a. Photomicrograph of sphalerite from a vein in coal containing abundant, parallel, and closely-spaced purple rods (bar for scale is 0.1 mm).

- b. X-ray diffraction patterns of sphalerite containing no purple rods (A) and sphalerite containing abundant purple rods (B).



a



hand picked under a microscope for visual purity and, as a precaution, were pulverized in alcohol in a mortar and pestle to avoid mineralogical changes due to the temperature and pressure of grinding. The X-ray pattern of sphalerite from coal (B) of figure 3-4b that contained purple rods has no wurtzite reflections. No positive identification of the purple rods was made.

The sphalerite also contains color banding parallel to vein walls. These color bands are growth features because of their orientation and the presence of aligned particles of coal at contacts between color bands.

Nodules of sphalerite that occur in the clay-rich matrix of clastic dikes in coal beds are usually oblate in shape and many of the larger ones are about the same size--approximately 5 cm by 3 cm (see previous section). The surface of a nodule consists of subhedral to euhedral terminations. In thin sections cut parallel to the long axis of nodules, the sphalerite is seen to consist of growth bands distinguishable by color and texture (figure 3-5a). The bands are concentric around the particle which acted as nucleus, e.g., a coal particle.

Several workers have discussed growth banding in sphalerite (Bastin, 1950; Barton, 1963; and McLimans, 1977). McLimans (1977) correlated sphalerite banding sequences from one ore body to the next across the Upper Mississippi Valley district. The growth bands in sphalerite nodules in coals constitute a microstratigraphy of sphalerite deposition.

Figure 3-5a. Concentric banding in sphalerite from a nodule from a clastic dike shown twice-natural size.

- b. Photomicrograph in color in transmitted-light showing color and textural details of the bands and the microstratigraphy from 1 to 5.



b

5

4

3

2

1



a

In the nodules from the Western Shelf of the Illinois Basin, five distinct color bands are recognizable (figure 3-5b): (1) yellow-brown (first-formed); (2) intermediate-purple; (3) light-purple; (4) dark-purple; and (5) pale yellow (last-formed). The banding sequence for those vertical veins from this region (figure 3-6a and b), in which a single crystal spans the full vein width, is 1-2-3-4-5. Other variations of color sequence in vertical veins spanned by single sphalerite crystals are shown in plate 3-1. The vein from the Lexington Coal of the Missouri Platform illustrated in plate 3-1a has the sequence 1-2-4-5, with 5 present as euhedral crystals, and correlates well with the veins in the Western Shelf. The microstratigraphies of sphalerite from veins at localities throughout the total area of this study are illustrated in plate 3-1. Detailed correlation is no longer possible, but there are no additional colors represented and the number of bands varies within narrow limits. Correlations among the five-color bands are shown in figure 3-7 for nodules from three coal beds on the Western Shelf of the Illinois Basin, one of which was sampled at two locations 100 km apart.

Calcite

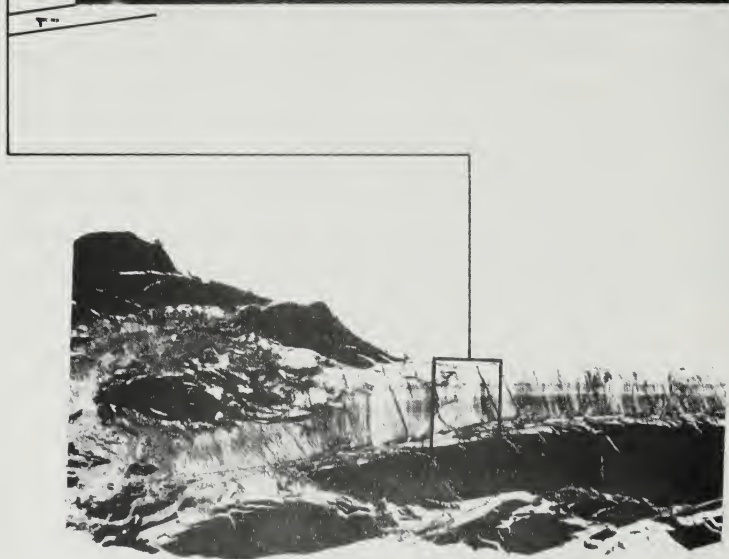
Calcite is one of the most common vein minerals in the coals studied. It very commonly occurs as cleat filling either by itself or with pyrite or kaolinite. Calcite is a common constituent in sphalerite-bearing veins but is not always present. Calcite veinlets cross-cut kaolinite, pyrite, and sphalerite. Calcite associated with

Figure 3-6a. Sphalerite banding in a vein shown twice-natural size.

- b. Photomicrograph in color in transmitted-light showing color and textural details of the bands and the microstratigraphy from 1 to 5.



b



a

Plate 3-1. Color banding of sphalerite that occurs in single crystals spanning full vein width; (a) are shown in color, in transmitted-light, and at the same magnification (bar for scale is 0.1 mm): (a) Herrin (No. 6) Coal (Illinois Basin); (b) Springfield (No. 5) Coal (Illinois Basin); (c) Colchester (No. 2) Coal (Illinois Basin); (d) Mystic Coal (Missouri Platform); (e) Lexington Coal (Missouri Platform); (f) Mulberry Coal (Cherokee Platform); and (g) Fleming Coal (Cherokee Platform).

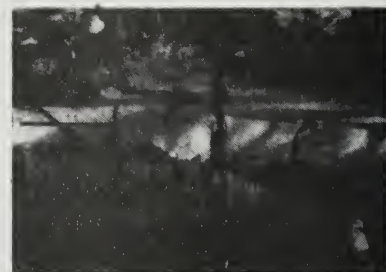
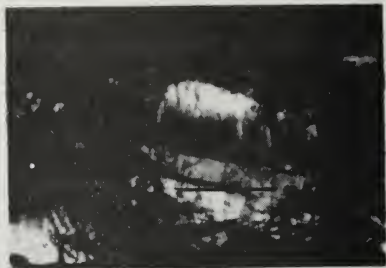
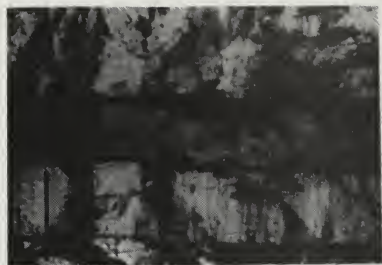


Figure 3-7. Color band correlation in sphalerite nodules from clastic dikes of the Illinois Basin (the microstratigraphy is indicated by numbers 1 to 5 showing the correlation of the sphalerite microstratigraphy from one area to another) (all specimens are shown twice-natural size): (A - Colchester (No. 2) Coal, Brown County; B - Herrin (No. 6) Coal, Peoria County; C - Springfield (No. 5) Coal, Fulton County; D - Colchester (No. 2) Coal, Fulton County.)



sphalerite has two distinct varieties. The calcite is commonly a colorless, inclusion-free spar. The other variety of calcite is characterized by the abundance of inclusions, usually coal, but also sphalerite and pyrite.

The "clean," inclusion-free calcite occurs between the sphalerite and the vein wall (figure 3-8a). This calcite is also characterized by a median suture (figure 3-8b), and is often displacive, wedging apart coal (figure 3-8c).

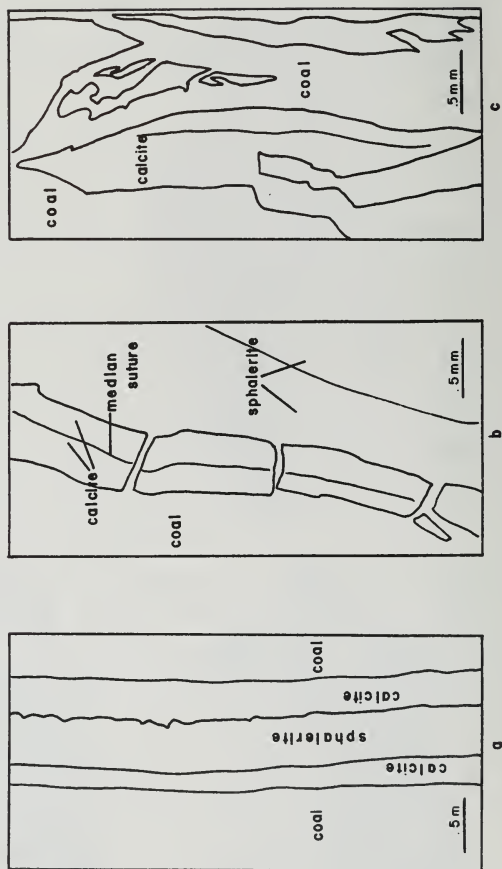
The growth of "clean" calcite is made evident by examination under cathode luminescence (figure 3-9a). Large scalenohedrons (yellow) can be seen to grow from the walls, in this case both coal and sphalerite, toward the center of the vein. Calcite of a different luminescent color (purple) later filled in the center of this vein.

"Dirty" calcite is also coarsely crystalline and has distinct bands distinguishable by alignments of inclusions and has no median suture (figure 3-9b). In this figure, the calcite-sphalerite contact is erosional and small particles of the yellow sphalerite have been rafted into the calcite filling.

Discussion

The vein filling nature of the minerals studied seems to preclude their deposition during the peat stage of coalification or earlier. Rather, the lignite stage had probably been achieved as required for the opening and dilation of fractures.

Figure 3-8. Paragenetic relations of calcite in sphalerite veins: (a) photomicrograph in color in transmitted-light and sketch with identifications and scale showing calcite enclosing sphalerite; (b) photomicrograph in color in transmitted-light and sketch showing details of calcite in sphalerite vein; and (c) photomicrograph in color in transmitted-light and sketch with identifications and scale showing displacive calcite in vein in coal.





c

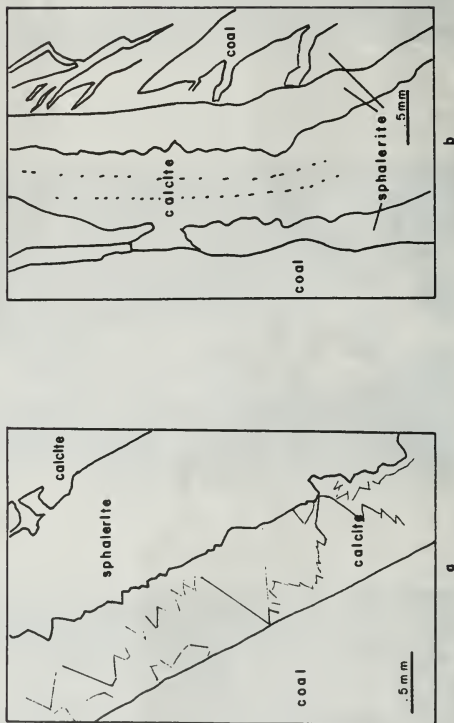


b



a

Figure 3-9a. Photomicrograph in color of cathodoluminescence and sketch with identifications of calcite enclosing sphalerite.
b. Photomicrograph in color in transmitted-light and sketch with identifications showing "dirty" calcite in sphalerite vein.





b



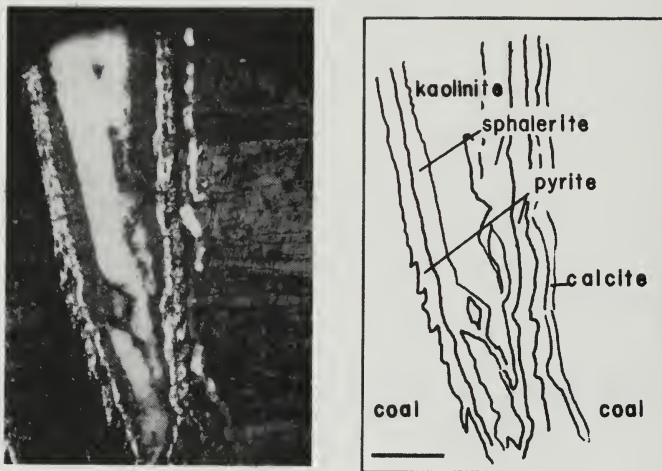
b

Hatch et al. (1976) discussed the paragenesis of sphalerite veins in coal and divided the mineralization into three principal stages: a sulfide (pyrite-sphalerite) stage, a silicate (quartz-kaolinite) stage, and a carbonate (calcite) stage. They determined the paragenesis to be pyrite-sphalerite-pyrite-quartz-kaolinite-calcite. The examination of thin sections in this study found no indication that silicates followed sulfides but rather found strong evidence that the silicates preceded pyrite and sphalerite. Calcite is the final mineral deposited but the occurrence of euhedral pyrite crystals "floating" within calcite indicates that sulfide deposition may have continued later than previously thought. Likewise, the occurrence of pyrite within sphalerite bands shows that pyrite co-precipitated with sphalerite. Figure 3-10a shows a rather complete sphalerite-bearing vein depositional sequence in which kaolinite, in the center of the vein, is followed and cut by sphalerite which is encrusted by pyrite. Finally, the pyrite is encrusted by calcite. The sequence of vein filling in figure 3-10a does not follow the classic crustification of veins where successively younger minerals are deposited toward the center of the vein, rather, in this case the younger minerals are deposited at the vein wall enclosing the previously deposited ones. The paragenesis, as determined from this study and revised from Hatch et al. (1976), is shown in figure 3-10b.

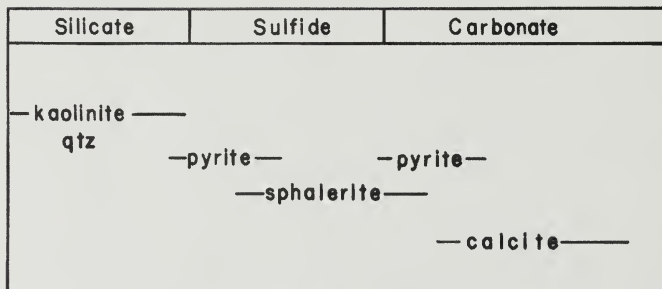
Sphalerite veins in the Interior Province coals have the same mineral assemblage and paragenesis; the sphalerites display the same assortment of colors and textures. The Pennsylvanian-age sections in

Figure 3-10a. Nearly complete paragenetic relations in a sphalerite-bearing vein in coal shown in photomicrograph in color in reflected-light and sketch with identifications and scale.

b. Paragenesis of sphalerite veins in coal.



a



Time →

b

which the coals occur contain the same group of lithologies, formed in the same cyclothemetic set of related environments. It may be assumed that sphalerite-bearing veins formed as part of an essentially common sequence of diagenetic events over the geographical area studied.

Correlation of the sphalerite microstratigraphy in veins and nodules shows that sphalerite deposition was occurring contemporaneously in some veins and clastic dikes. The fractures and clastic dikes must have acted as conduits for the substantial flow of solution required to supply the zinc. In the Western Shelf area of the Illinois Basin, the correlation of sphalerite microstratigraphy across several tens of kilometers suggests that the chemical character of the depositing fluid was mostly uniform over the area and pervasive throughout the portion of the stratigraphy from the Colchester (No. 2) Coal to the Danville (No. 7) Coal. The extent of the sphalerite deposition both geographically and stratigraphically as indicated by the sphalerite microstratigraphy identifies the existence of a large-scale hydrogeological system responsible for deposition of the sphalerite in coal.

Well-crystallized kaolinite is the earliest mineral to form in the paragenesis. It is also the dominant clay mineral in many coals including the ones in this study (Gluskoter, 1967). Speculations on the origin of kaolinite in coal range from precipitation in the peat swamp (Ward, 1977) and positionally controlled accumulation during the time of the peat swamp (Rao and Gluskoter, 1973) to precipitation

from modern groundwater following coalification and uplift (Shieh and Suter, 1979). None of these hypotheses are entirely satisfactory for explaining the kaolinite in veins. The length of time and the depth of burial required to produce coal, lithified enough to maintain fractures, is not known; however, it is well demonstrated that the kaolinite is authigenic and fills fractures in coal. The relatively slow advance of the coalification process just to the brown coal stage (lignite), which is the earliest stage in which kaolinite-filled cleats are observed, suggests that conditions within the peat swamp had little direct effect on the kaolinite discussed here.

There could well be several origins for the kaolinite in coal; those which require conditions found in the peat swamp and those related to deposition from circulating groundwaters. Ward (1977) and Rao and Gluskoter (1973) have speculated on several modes of origin. Following burial of the peat to an adequate depth for the formation of brown coal (lignite), groundwater flow systems would become established. If the movement of groundwater was capable of removing alkalis and alkaline earths while carrying SiO_2 and Al^{3+} , then kaolinite could precipitate.

Pyrite is the second mineral to form in the paragenesis. It is the principal sulfur-bearing mineral in the high-sulfur coals in which sphalerite is found. Gluskoter and Simon (1968) discuss to some extent the origin and distribution of pyrite in some coals. Pyrite occurs in several ways in coal such as framboids, disseminated crystals, layers, lenses, and concretions. Isotopic analysis of sulfur in pyrite shows

that it is bacterially-reduced sulfur (Price, 1979). Boctor et al. (1976), believe that iron sulfides form principally during the accumulation and compaction of peat--the biochemical stage of coalification. Casagrande (1977) found that all the sulfur in coal can be incorporated during the peat-forming stage. It again seems unlikely, however, that pyrite in the veins in this study form that early. The accumulation of pyrite in veins adjacent to coal layers containing abundant disseminated pyrite and marcasite suggests that dissolution and recrystallization of disseminated iron sulfide contributed to pyrite in veins. It is frequently observed that numerous pyrite veins extend from large pyrite concretions in coal. It is not difficult to imagine mobilization and recrystallization of pyrite in coal. Boctor et al. (1976) also recognized that mobilization and recrystallization of pyrite occurs during the metamorphic stage of coalification.

No marcasite was found in any of the veins. Experimental work indicates that marcasite forms under acidic conditions, but that pyrite forms under neutral to alkaline conditions. Therefore, the acidic conditions of the peat swamp played no direct role in the precipitation of pyrite in veins. The occurrence of pyrite later in the paragenesis with calcite is probably the result of mobilization and recrystallization of pre-existing iron sulfides in the coal under neutral to alkaline conditions.

Sphalerite, the third mineral formed, precipitated as coarse, banded crystals. The growth banding suggests that minor fluctuations in geochemical conditions occurred during deposition. The absence of

obvious solution leaching at contacts between sphalerite bands indicates that supersaturation was maintained during deposition. Sphalerite is a common replacement after pyrite; therefore, it is unlikely that the ZnS-FeS phases ever achieved equilibrium. Hatch et al. (1976) found the iron content of sphalerite in coal to vary from 0.17 to 2.45 percent.

Calcite is the last mineral to form in the paragenesis of sphalerite veins. Theories on the origin of calcite in coals range from influences due to marine conditions (Rao and Gluskoter, 1973) to precipitation from groundwater at or near the surface, perhaps in recent geologic time (Shieh and Suter, 1979). Kemezy and Taylor (1964) also recognized that calcite forms in some coals at a later stage than most other minerals in coal and is probably deposited relatively late from groundwater. Evidence from this study agrees with this assessment.

CHAPTER 4

VEIN MORPHOLOGY, DEVELOPMENT, AND TIMING

It is possible from the observed morphology and texture of sphalerite-bearing veins in coal to infer a good deal about the history and timing of vein development. This section describes some of the morphological and textural characteristics of veins. Because mineral veins in coal have distinctive three-dimensional orientations, their study requires examination of oriented sections. Textural aspects of opaque constituents and of transparent minerals are equally important in determining vein development; therefore, oriented, doubly-polished thin sections, as well as oriented polished sections, were used.

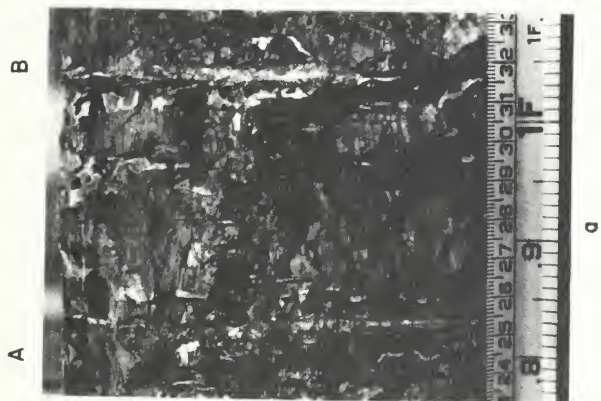
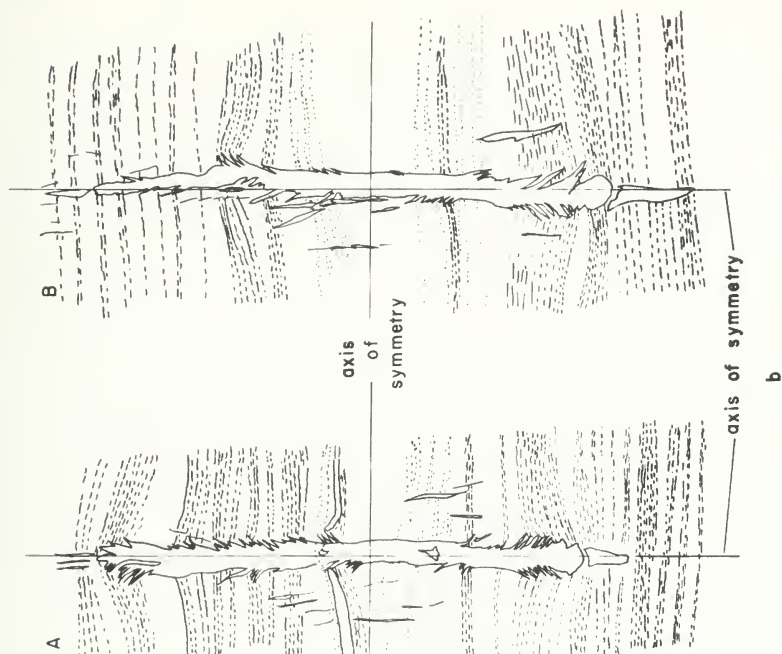
Vein Morphology

Two sphalerite-bearing veins in outcrops are shown in figure 4-1a. They strike N 35°W, parallel to the principal cleat direction, and are typical of numerous other veins both at this exposure and in other coal beds at other locations. These veins are cognate (i.e., they have parallel strike) and are presumed to have formed at about the same time.

The physical characteristics of the two veins are strikingly similar. The similarities arise from the morphology of the vein walls, which have distinctive fanning, feathering, and straight boundaries depending on the coal lithotype through which the vein is passing (figure 4-1b). Vitrain layers in the coal tend to break with smooth-sided

Figure 4-1a. Typical sphalerite veins in the Springfield (No. 5) Coal of Fulton County, Illinois.

- b. Veins shown in 4-1a from photographs of polished sections enlarged 110 percent showing the morphological similarities between the veins, axes of symmetry, and relationships between vein walls and coal lithotypes.

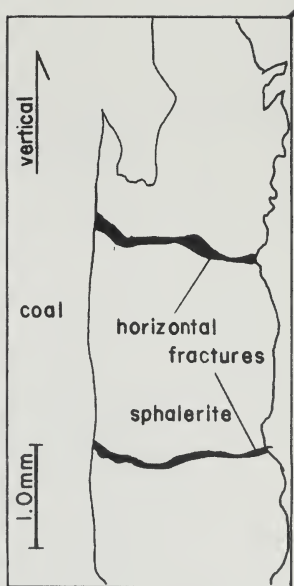


fractures so that vein walls are generally smooth in vitrain. Clarain layers, being finely-laminated, fracture with irregular walls and have a feathered pattern. Veins are commonly interrupted by fusain layers which are soft and friable. Veins have not been observed to pass into shale partings.

The veins also have similar, if crude, symmetry about both horizontal and vertical axes (see figure 4-1b). The symmetries are imparted by mirror-image similarities in irregularities in the vein walls with respect to these axes. The symmetries are enhanced by the orientation of the fanning and feathering veinlets and by the deflection of coal layers around the ends of the veins. The feathered veinlets point upward above the horizontal axis and downward below this axis. Similarly, the deflection of bands is convex upward above the horizontal axis and downward below this axis.

Horizontal fractures, which extend from wall to wall and are spaced a few millimeters apart vertically, are common in sphalerite and give the veins a segmented appearance (figure 4-2). Such fractures are not observed in any horizontal sections, which shows that they are restricted in orientation. In cases where substantial compressive stress is removed from samples of sphalerite in laboratory experiments (Clark and Kelly, 1973), the fracture pattern thus produced is very similar to the one in sphalerite veins in coal. This concordance is a strong indication that vein formation took place under large overburden pressure which was later removed by erosion of the overlying strata.

Figure 4-2. Photomicrograph in transmitted-light and sketch of a sphalerite vein showing horizontal fractures (vertical arrow points up).



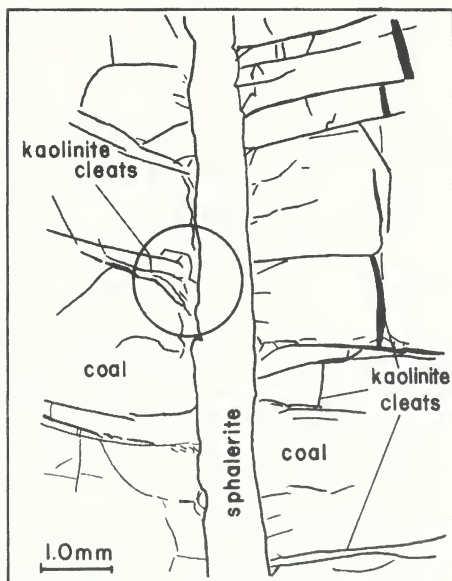
In sections viewed on the horizontal plane (figure 4-3), the morphology of the vein appears much different from that in vertical sections. The most apparent difference is the absence of fanning and feathering along vein walls. This absence indicates that without the laminations in the coal bands and the alternations of different lithotypes, the development of those features is impossible. Therefore, the various types of coal bands must have been developed before the mineral veins were formed.

Horizontal sections also show intersections of kaolinite-filled cleats with the sphalerite vein (see figure 4-3). There is an obvious correspondence between the cleats on both sides of the vein, although in places there are offsets by only tenths of a millimeter, indicating that they might have been continuous before being cut through by the vein. Of equal significance is the deflection of the ends of the cleats at the vein walls. These deflections may have been caused by retreat of the vein walls causing the ends of cleats to be deformed. Cleats were therefore most likely formed before the vein was formed. The orthogonal relationship of the cleats and the vein suggests that the vein may have developed in plane of weakness created by a cleat which formed at right angles to the ones now cut by the vein.

Internal Textures of Veins

A distinction in vein texture is made in this study according to whether there is a median suture or a central color band. A median

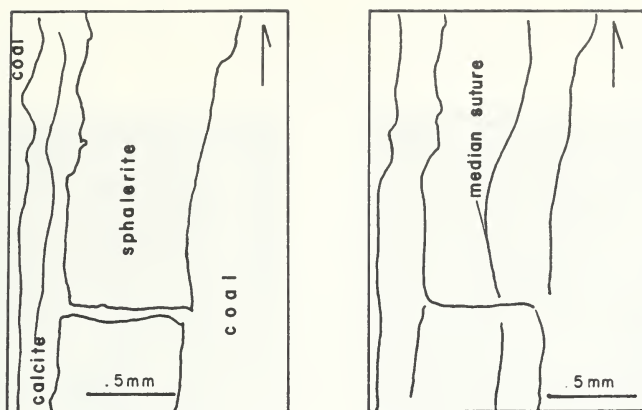
Figure 4-3. Photomicrograph taken under combined transmitted- and reflected-light and an interpretive sketch of a sphalerite vein shown parallel to the layering in the coal. (The circle is drawn around an intersection of a cleat and the vein where deflection of part of the cleat can be seen.)



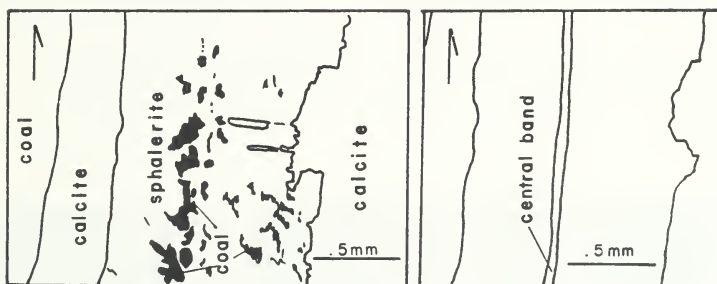
suture is a surface at the center of a vein which marks a break in continuity between crystals growing from opposite walls. In cases where no median suture is observed, there occurs at the center of the vein a distinct band delineated by the alignment of coal particles along its boundaries.

Figure 4-4a shows a sphalerite vein that contains a median suture. In reflected-light illumination, the sphalerite is relatively "clean" being free of included particles of coal. Under transmitted-light illumination, the median suture is distinct as the discontinuity dividing the yellow and purple sphalerite. Veins characterized by a median suture develop by progressive growth of new material at the center of the vein. Because new material is added at the median suture, particles from the vein walls are not rafted into the mineral filling.

Figure 4-4b shows a sphalerite vein that contains no median suture but does contain a color band that runs down the center of the vein. Under reflected-light an alignment of rafted coal particles parallel to the vein walls can be seen at the center of the vein. In transmitted-light illumination a distinctive color band of sphalerite occurs in the center of the alignment of rafted coal. The displacement of coal particles from vein walls seen in this figure, and their alignment and vertical orientation, and the absence of a median suture indicate that development of the vein was by addition of new material along vein walls. The process of vein growth occurring at the vein walls is illustrated in figure 4-5a, where coal from the vein wall can be seen progressively rafted toward the center of the vein. Figure 4-5b shows



a



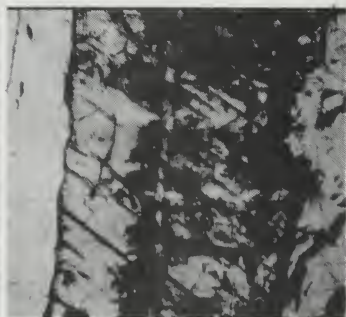
b

Figure 4-4a. Photomicrographs in color in reflected-light (left) and transmitted-light (right) and sketches of a sphalerite vein containing a median suture (bar for scale equals 0.5 mm; arrow indicates up).

b. Photomicrographs in color in reflected-light (left) and transmitted-light (right) and sketches of a sphalerite vein containing a central band (bar for scale equals 0.5 mm; arrow indicates up).

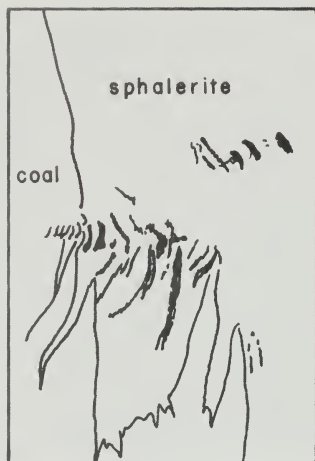
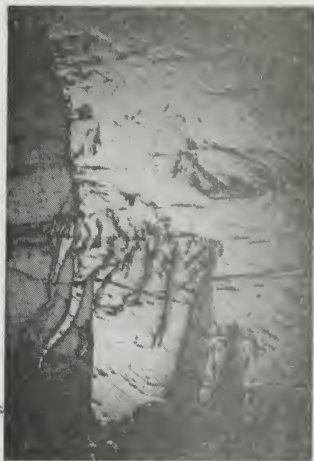


a

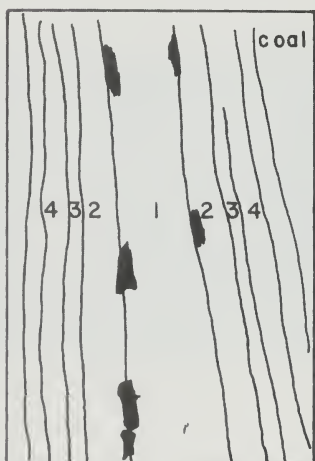


b

- Figure 4-5a. Photomicrograph in color in reflected-light and sketch of sphalerite rafting coal from the vein wall into the mineral filling (bar for scale is 0.5 mm; arrow indicates up).
- b. Photomicrograph in color in transmitted-light and sketch of a sphalerite vein showing symmetrical filling (bar for scale is 0.5 mm; arrow indicates up).



a



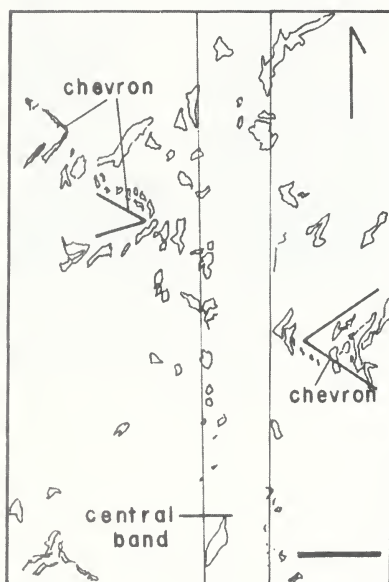
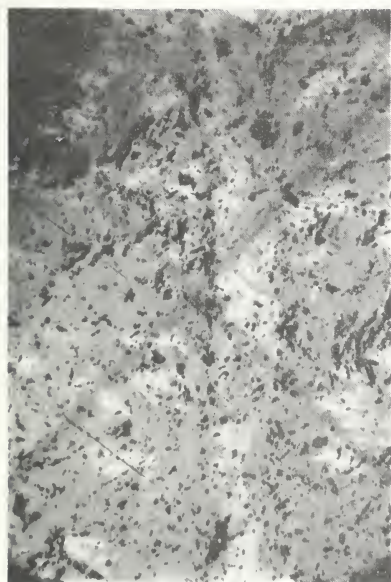
b

a sphalerite vein that contains a symmetrical array of sphalerite bands that were progressively added onto the vein at the vein walls.

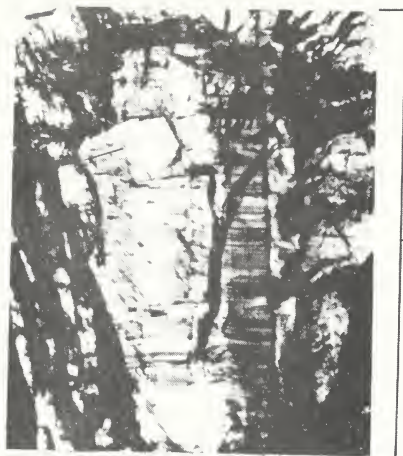
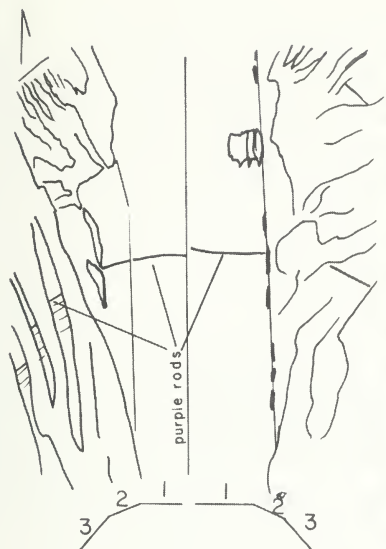
An element of the internal fabric of veins containing the central band is the symmetry and orientation of the alignment of rafted coal particles. It has already been shown how coal is plucked and moved into the vein by addition of new material at the vein walls. The continuation of this process produces lineaments and oriented patterns of coal particles. Some of these resemble a chevron pattern that has been inverted and points toward the center of the vein (figure 4-6). The symmetry exhibited by the chevron patterns on both sides of a vein and pointing toward the center of the vein is strong evidence that the veins opened by equal retreat of vein walls from an imaginary plane through the center of the vein.

Another textural feature of sphalerite veins is the tiny purple rods that were described in the previous chapter. These rods are always aligned in the direction of crystal growth, whether in veins or nodules. The orientation of purple rods is not always constant within a single vein, indicating that the direction of crystal growth may have changed during the formation of some veins. Figure 4-7a shows the texture of a sphalerite vein composed of numerous, parallel purple rods. The rods are nearly perpendicular to the central band but they progressively change their orientation toward the vein walls. Within the branching veinlets, the purple rods are at an angle of nearly 20° to the central band. Figure 4-7a shows the entire vein, including the enlarged portion shown in the previous figure. The coal layers

Figure 4-6. Photomicrograph in reflected-light and sketch showing the central band in a sphalerite vein and the chevron-like pattern of the rafted particles on both sides of it (bar for scale is 0.1 mm; arrow indicates up).



- Figure 4-7a. Photomicrograph in transmitted-light and sketch showing sphalerite texture demonstrating progressive deformation recorded by the purple rods (bar for scale is 5 mm; arrow indicates up).
- b. Photomicrograph in combined reflected- and transmitted-light and sketch of a sphalerite vein demonstrating progressive deformation recorded by the deflected layers in the coal (bar for scale is 5 mm; arrow indicates up).



a

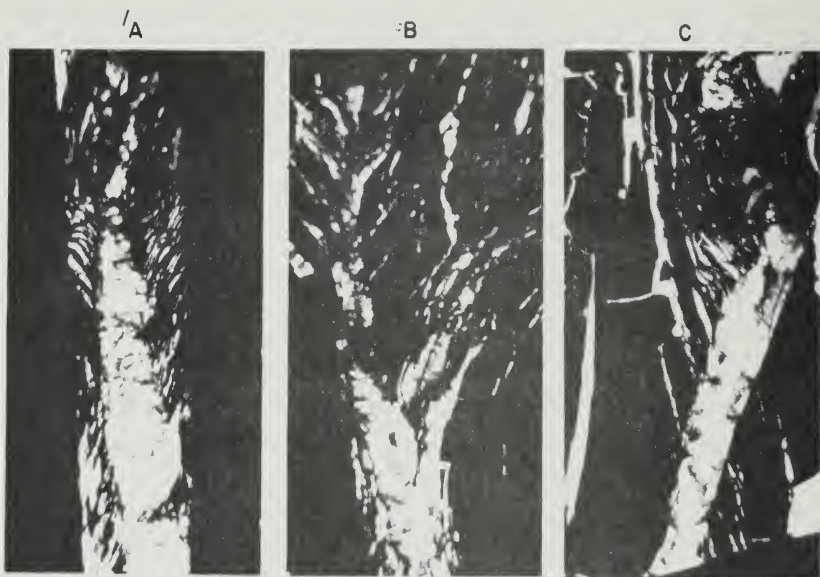
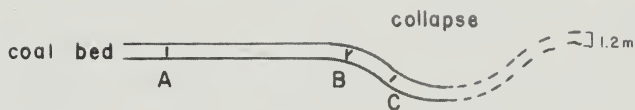


b

are deflected where they pass between the branching veinlets; this deflection is upward in the upper part of the vein and downward in the lower part of the vein. It appears that the orientation of purple rods, and thus the direction of crystal growth, parallels the orientation of the coal layers. The purple rods then record the increments of progressive deformation of the coal during vein formation.

An excellent example of sphalerite veins that record progressive deformation in the coal bed is shown in figure 4-8. In this case, the veins have a characteristic morphology and orientation which can be explained by their position relative to the subsidence of the coal into a sinkhole. The vein at A is vertical and perpendicular to the layering in the coal which is horizontal. The branching in this vein is symmetrical on both vein walls. This vein is representative of most veins not involved with exceptional structures in the coal and is not in the immediate area influenced by collapse. The vein at B, in part, is vertical, perpendicular to coal layers, and has normal branching veinlets. It also has a second part which is oblique to coal layers, not branching, and inclined in the direction of the collapse. It appears that because of its position on the hinge of the collapse, this vein underwent normal dilation until the effect of the subsidence opened fractures oblique to the layers in the coal. The vein at C is inclined from vertical, oblique to the layers in the coal, and does not have typical branching veinlets. The orientation of this vein, with respect to the coal and its position in the collapse, suggests that vein opening was controlled by subsidence into

Figure 4-8. Photomicrographs in transmitted-light of sphalerite veins and the location of the veins in a collapsed coal bed.



20 mm

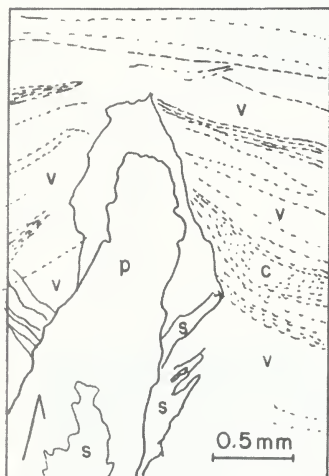
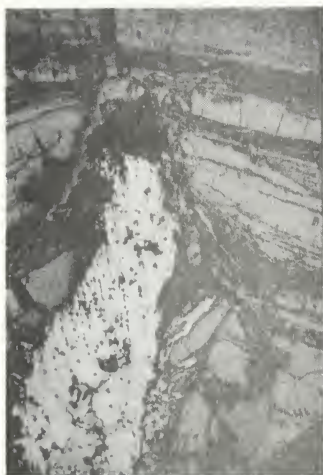
the sinkhole. The vertical orientation of the subsidiary veinlets indicates that normal dilation may have resumed after the subsidence had ceased.

A characteristic of many veins in coal is the presence of veinlets that branch outward from the ends. Cross (1952) described such veinlets and showed an example from the Pittsburgh Coal. He described the radiating veinlets as minute ramifications which had penetrated the coal. Figure 4-9 shows the end of a vein and the veinlets branching from it. Of particular interest is the bending of the coal layers around the end of this vein. The radiating veinlets might have originated from fractures that developed in the coal as it was deformed around the vein. The veins themselves are presumed to have acted as vertical supports and, during compaction, they did not compact equally with the surrounding coal. As a result, coal layers immediately above and below a vein are deflected upward above and downward below in equal amounts.

Timing of Vein Formation

Figures 4-10a, b, c, and d illustrate how the compaction ratio is measured and the relative timing of veins with respect to the compaction of coal is determined. Points A and B are on recognizable bands that pass around the ends of the vein and are used as index bands. Points A' and B' are along the index bands some distance away from the vein, where no further convergence of the index bands can be detected. The line segment AB is presumed to be the distance between

Figure 4-9. Photomicrograph in color in reflected-light and sketch of deformed coal layers around a vein (bar for scale is 0.5 mm; arrow indicates up).



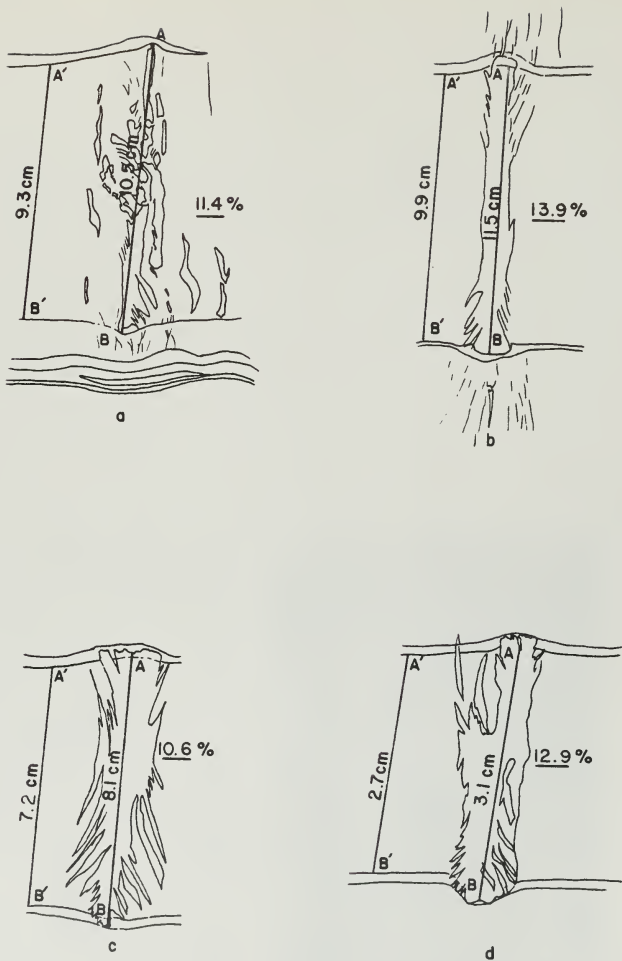
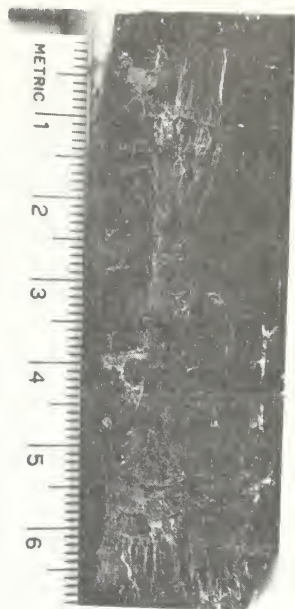


Figure 4-10. Sphalerite veins from the four principal geographic areas of sphalerite-bearing coals and sketches showing measurements of post-vein compaction.

- Herrin (No. 6) Coal, Gallatin County, Illinois.
- Springfield (No. 5) Coal, Fulton County, Illinois.
- Unnamed coal, Monroe County, Iowa.
- Mulberry Coal, Putnam County, Kansas.



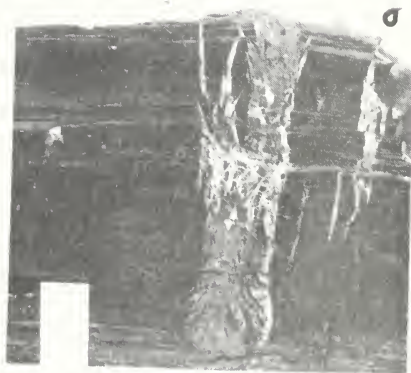
a



b



c



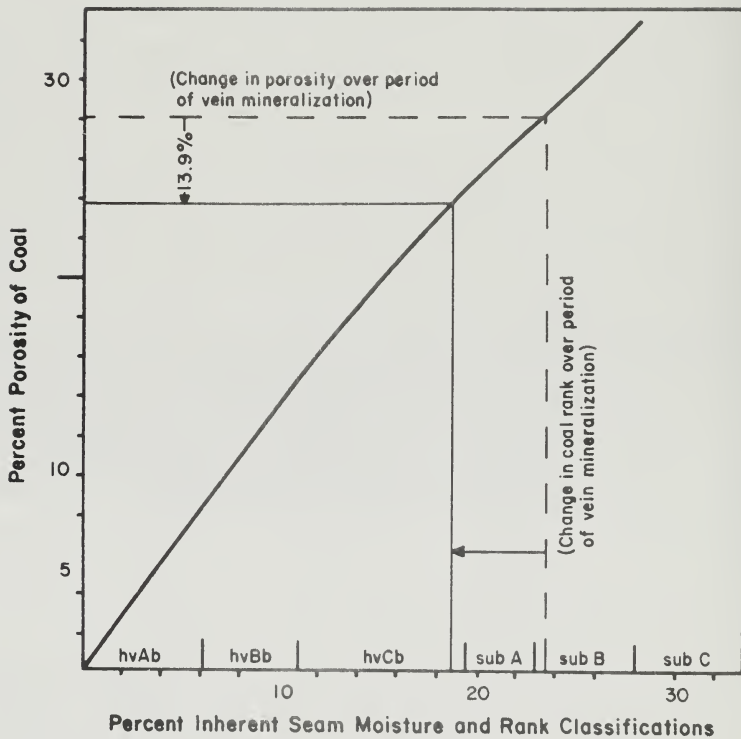
d

the index bands at the time of vein filling. Line segment A'B' is the distance between these bands away from the influence of the vein. The difference between lengths AB and A'B' is the compaction; the percentage of compaction (compaction ratio) being $[(AB - A'B') \div AB] \times 100$.

In figures 4-10a, b, c, and d the measurements of post vein compaction in veins from the four principal geographic locations of sphalerite in coal--the Western Shelf of the Illinois Basin (figure 4-10a), the southern part of the Illinois Basin (figure 4-10b), the Missouri Platform (figure 4-10c), and the Cherokee Platform (figure 4-10d)--are shown. The compaction ratios are 13.9, 11.4, 10.6, and 12.9 percent respectively. It is deduced from this that similar amounts of compaction occurred after the formation of sphalerite veins in these different areas suggesting that the timing of vein formation was nearly the same in each coal and in each coal basin.

A linear relationship exists between coal rank and inherent moisture content of coals (Stach, 1975). The regular change in inherent moisture for low-rank coals from sub-bituminous C (sub C) to high-volatile bituminous A (hvAb) is a principal criterion for assigning rank to coals and, therefore, is a routine coal analysis. The inherent moisture content of coals also gives an approximate measure of coal porosity (Thomas and Damberger, 1976). This is shown in figure 4-11. If the two-dimensional compaction, as measured in the convergence of layers around veins, can be ascribed mainly to a decrease in porosity, then the moisture-porosity-rank relationship

Figure 4-11. Relation between inherent moisture, rank and porosity (modified from Thomas and Damberger, 1976) showing the reduction in porosity and change in rank during compaction around sphalerite veins in the Springfield (No. 5) Coal of the Western Shelf. (The dashed line represents the porosity-moisture-rank condition in the Springfield (No. 5) Coal for example when the compaction around sphalerite veins began.)



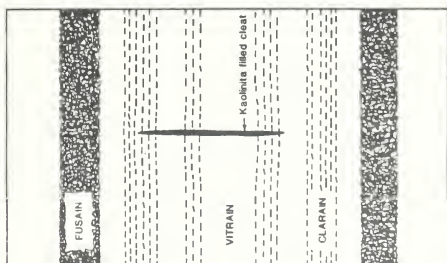
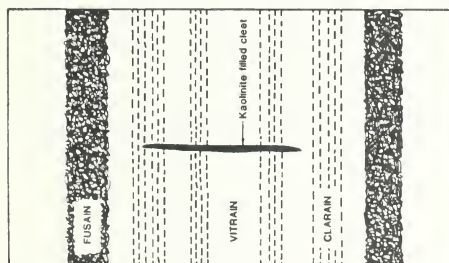
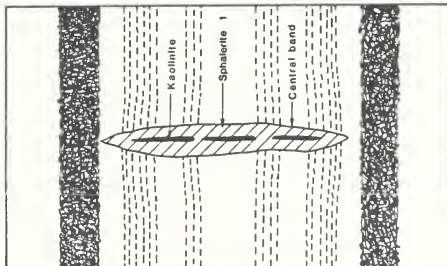
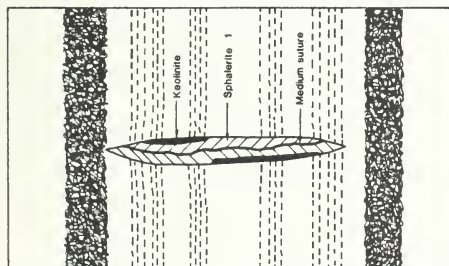
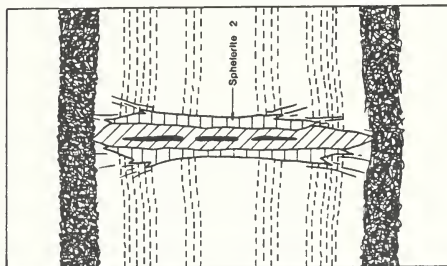
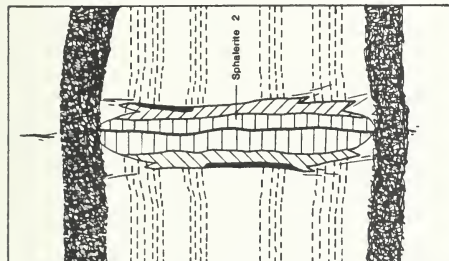
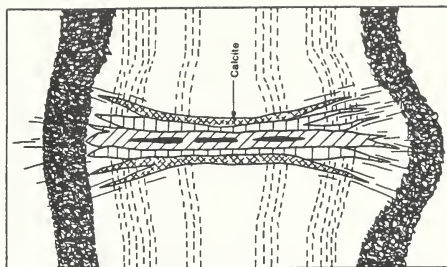
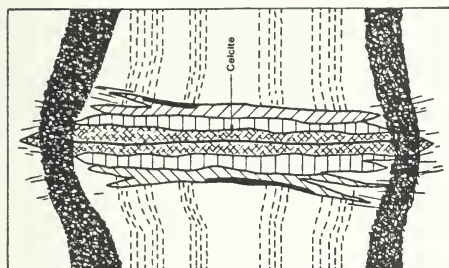
can be used to estimate the coal rank at the time compaction began. In figure 4-11, the inherent moisture and porosity of the Springfield (No. 5) Coal is plotted on the graph. The compaction around a vein in this coal, shown in figure 4-10b, is 13.9 percent. The dashed line on the graph in figure 4-11 shows what the porosity, moisture, and rank of this coal was when compaction around the vein began. This value is a maximum because some devolatilization and volume shrinkage of the coal, not due to decrease in porosity, probably accompanies the reduction in porosity.

General Vein Development

A generalized development of veins is illustrated in figures 4-11a and b. The first stage in the development of a vein containing a median suture (figure 4-12a) is the opening of a fracture. The second stage is the deposition of sphalerite on the vein walls. The third stage is the addition of sphalerite at the median suture. The fourth stage is the deposition of calcite at the center of the vein.

The typical development of veins containing a central band rather than a median suture is illustrated in figure 4-12b. The first stage is the development of a fracture along a plane of weakness commonly caused by a pre-existing cleat and the filling of the fracture with kaolinite. The second stage is the deposition of sphalerite (sphalerite 1) in the fracture which sometimes encases and cross-cuts the kaolinite. The third stage is continued dilation, which tends to create new open space at the mechanically weak vein walls, and into

- Figure 4-12a. Generalized development of veins containing a median suture.
- b. Generalized development of veins containing a central band.



which new sphalerite (sphalerite 2) is added. Some coal particles that become attached to the earlier-deposited sphalerite are rafted into the mineral filling by the continuation of this process. The fourth stage includes the opening of fractures due to compaction and the deposition of calcite at the vein walls.

The generalized vein development shown in figure 4-12a and b is oversimplified. Many of the veins observed show characteristics of both types of development.

Discussion

The morphology of sphalerite veins encountered in this study indicates that coal layering (lithotype bands) had probably developed to nearly its present condition by the time sphalerite veins formed. If this were not the case and lithotypes had undergone considerable development following sphalerite vein formation, then one would expect that the very close correspondence between layers in the coal and parts of these same layers "frozen" in the sphalerite would have been drastically changed. The indications that release fracturing had occurred in the sphalerite and the conclusion that sphalerite was deposited under substantially greater overburden than now exists is consistent with other interpretations of the geologic history of the coal basins. Several sources suggest that the Midcontinent coal basins were once buried under several thousand feet of sediment now eroded (Bushbach, 1971 and Damberger, 1971).

The relationship between sphalerite veins and cleats shows that veins formed after cleats. This supports the contention in Chapter 2 that the preferred orientation of sphalerite veins parallels the prominent cleat direction suggesting that sphalerite veins developed from existing cleats. It also supports the conclusion in Chapter 3 that the kaolinite in sphalerite veins represents remnants of former cleat fillings.

The symmetry in the internal fabric of veins that is imparted by rafted coal and the median suture or central band clearly shows that vein opening was by equal retreat of the walls from an imaginary vertical plane through the center of the vein. The symmetry exhibited by gross morphology, which includes orientation of the veinlets and convergence of coal layers around the ends of veins, supports the argument that compaction of the coal continued for a period of time during and after formation of the veins.

Vein textures observed in this study do not always exhibit the typical crustification so common to many ore deposits, a fact also recognized by Hatch et al. (1976). Neither does a single mechanism explain the textures and development of sphalerite veins examined in this study. The crustification of veins in typical ore deposits is by deposition of successive mineral layers toward the center of a fissure which produces symmetrical crusts on opposing walls. This type of filling requires rather static conditions and a fissure enlarged by dissolution. Such conditions were not present during vein filling in coal. Only rarely is open-cavity crystal growth of sphalerite observed

in coal. This study presents evidence that sphalerite veins were being filled synchronously with fissure dilation, progressive deformation caused by compaction, and in some cases with subsidence into sinkholes. These observations are certainly consistent with an absence of compressional forces where the vertical stress is the maximum principal stress, the horizontal stresses are nearly equal, and volume shrinkage of the coal caused by devolatilization is the driving force in vein dilation.

The fact that all of these observations hold for the entire study area shows that with the exception of subsidence into sinkholes none of the sphalerite-bearing coals underwent any exceptional deformation or development during the course of sphalerite deposition.

The average of 10 percent for the amount of post-vein compaction is a modest value considering the tremendous amount of compaction from the peat stage (95% moisture) to the brown coal stage (75% moisture). The 10 percent compaction is, however, a good indication that no large jump in rank was experienced by any of the coals from the time sphalerite was deposited to the present. An exact assessment of the organic maturity (rank) that the coal had achieved when the sphalerite was deposited is probably not possible, but the facts collected here suggest that the bright, hard-brown coal rank (25% moisture) had been attained. A subsequent decrease to the 18-20 percent moisture now in the coals can be accounted for, in part, by the post-vein compaction that was measured.

CHAPTER 5

PALEOTHERMAL STUDIES

The variations with time of temperature and geothermal gradient are important factors in the diagenesis of sedimentary piles. They influence chemical reactions involving minerals, pore fluids, and organic matter. Knowledge of the paleotemperatures at a number of points defined in space and time allows calculations to be made about paleothermal gradient, maximum depths of burial, and maximum temperature and pressure attained.

Two techniques that have been used in this study for the quantitative determination of paleotemperatures are: (1) homogenization temperatures of gas-liquid inclusions in sphalerite, and (2) reflectance of vitrinite in coal. Methods by other workers that have been attempted for determining paleotemperatures in coal are carbon and oxygen isotope abundances in kaolinite and calcite (Shieh and Suter, 1979) and authigenic mineral stability fields (Castaño and Sparks, 1974).

Homogenization Temperatures

The temperature at which some minerals were deposited can be determined by measuring the temperature at which a gas bubble in a primary fluid inclusion disappears on heating. In particular, the use of sphalerite homogenization temperatures has become a common tool in determining the temperature of formation of ore deposits.

Primary, two-phase inclusions could be identified in doubly-polished thin sections of sphalerite from most of the localities sampled in this study. Inclusions in sphalerite from six different coals of the Illinois Basin, Missouri Platform, and Cherokee Platform are shown in plate 5-1a, b, c, d, e, and f.

Previous Investigations

Leach (1973) was the first to report measurements of homogenization temperatures for sphalerite from coal. He reported a range of values from 76° to 110°C for sphalerite from coals in Pennsylvanian sinkholes in central Missouri.

Roedder (1979) obtained values from 90° to 102°C for 25 inclusions in sphalerite from veins and from 82° to 96°C for 19 inclusions in sphalerite from clastic dikes, all from the Herrin (No. 6) Coal of the Illinois Basin. Samples from the material used by Roedder (1979) were remeasured in this study for comparison. The techniques utilized in fluid inclusion geothermometry have been discussed by Roedder (1967, 1972).

Technique

A specially-constructed coring device was used to cut 3/16-inch-diameter discs, containing the fluid inclusions of interest, from thin sections. Discs of this size fit exactly into the specimen holder of the heating stage, so that all samples were positioned in the same manner.

Plate 5-1. Fluid inclusions in sphalerite from coal, ((a) primary inclusion in Danville (No. 7) Coal, Illinois, (b) pseudosecondary inclusion in Herrin (No. 6) Coal, Illinois (c) primary inclusion in Springfield (No. 5) Coal, Illinois, (d) primary inclusion in Colchester (No. 2) Coal, Illinois, (e) primary inclusion in Lexington Coal, Missouri, (f) primary inclusion in Bevier Coal, Missouri.)



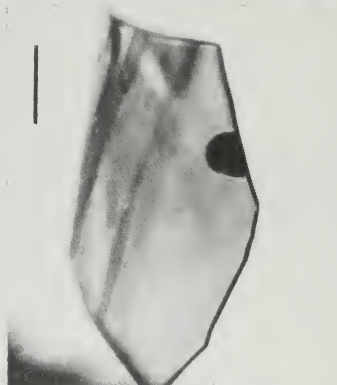
c



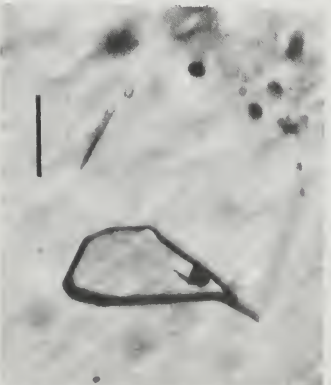
f



b



e



d



d

The heating stage was a Leitz^R model 350, and temperatures were measured by platinum vs. platinum -10% rhodium thermocouple connected to a Leeds and Northrup potentiometer sensitive to 0.001 volt. The thermocouple was calibrated against thermometric standards, naphthalene (triple point $80.25^{\circ}\text{C} \pm 0.05^{\circ}\text{C}$), and adipic acid (triple point $151.46^{\circ}\text{C} \pm 0.05^{\circ}\text{C}$), that bracketed the expected range of homogenization temperatures.

The most recent homogenization-temperature determinations have utilized heating stages modified to lessen the thermal gradient between specimen and thermocouple. Some have a continuously circulating liquid that maintains specimen and thermocouple at the same constant temperature. Because the heating stage used in this study was not so equipped, a correction had to be applied for the temperature difference between specimen and thermocouple.

The correction, which compensates not only for this thermal gradient but also for errors resulting from such things as thermocouple deterioration and inexact potentiometer zeroing, was determined by measuring the melting point of a thermometric standard before and after each series of homogenization-temperature determinations. The measured values were averaged, and the difference between this average and the known melting temperature was applied as a correction to the homogenization temperature. Calibration data of this sort are given in table 5-1 for the 33 sessions in which the heating stage was used.

Table 5-1. Heating stage temperature calibration.

Session	Thermocouple Measurement °C		Standard ¹ °C	Adjustment °C
	before	after		
1	76.3	75.7	80.25	+ 4.25
2	75.9	77.1	80.25	+ 3.75
3	77.0	77.3	80.25	+ 3.10
4	134.5	135.0	151.46	+ 15.71 ²
5	76.4	76.9	80.25	+ 3.60
6	77.3	77.6	80.25	+ 2.80
7	77.2	77.9	80.25	+ 2.70
8	77.1	77.6	80.25	+ 2.90
9	76.9	76.9	80.25	+ 0.00
10	77.4	77.7	80.25	+ 2.70
11	77.0	77.2	80.15	+ 3.15
12	77.5	77.5	80.25	+ 0.00
13	77.1	77.2	80.25	+ 3.10
14	77.2	77.2	80.25	+ 3.40
15	76.8	76.9	80.25	+ 3.45
16	76.7	76.9	80.25	+ 3.00
17	77.0	77.5	80.25	+ 2.55
18	77.5	77.9	80.25	+ 2.55
19	77.1	77.7	80.25	+ 2.85
20	77.3	77.9	80.25	+ 2.65
21	77.0	77.5	80.25	+ 3.00
22	76.2	77.0	80.25	+ 3.65
23	76.4	77.5	80.25	+ 3.30

¹Naphalene thermometric standard ($80.25 \pm 0.05^\circ\text{C}$).

²Adipic acid thermometric standard ($151.46 \pm 0.05^\circ\text{C}$) was rarely used in adjustments because homogenization temperatures rarely exceed even 100°C .

The temperature of the heating stage was increased in small increments, with several minutes allowed after each increase for temperature stabilization before recording the thermocouple reading. This procedure, which was repeated until the homogenization temperature was reached, is believed to have reduced the size of thermal-gradient effects and assisted in obtaining more accurate homogenization temperatures.

Experimental Results

The sphalerite samples used in this study were mainly from coal beds from Illinois, Iowa, Missouri, and Kansas. Homogenization temperatures, each of which is an average of several determinations made on one or more sample discs from a particular coal seam at a particular locality, are given in table 5-2. The overall range is 75° to 113°C, and the ranges for sample subsets from different stratigraphic positions within one area of sphalerite-bearing coals are not obviously different from the overall range. The ranges for sphalerite from different areas are likewise very similar, except that the temperatures from the Cherokee Platform are slightly higher on the average.

The values of table 5-2 have not been corrected for pressure. Assuming no more than 1,000 meters of overburden and an ore fluid under hydrostatic pressure, because most of the sphalerite was deposited in open spaces, the homogenization temperatures would be corrected downward by a maximum of 10°C (Klevtsov and Lemmlein, 1959).

Table 5-2. Homogenization temperatures for fluid inclusions in sphalerite.

		Range	Average
<u>Illinois Basin (Western Shelf)</u>			
Danville (No. 7) Coal	(21) [*]	75 to 96	88
Herrin (No. 6) Coal	(17)	81 to 99	94
Springfield (No. 5) Coal	(13)	85 to 99	93
Colchester (No. 2) Coal	(34)	83 to 105	96
Concretions			
Miss./Penn. boundary	(16)	98 to 113	107
<u>Southeastern Illinois</u>			
Herrin (No. 6) Coal	(5)	96 to 111	104
<u>Forest City Basin (Missouri Platform)</u>			
Lexington Coal	(11)	82 to 97	86
Bevier Coal	(19)	89 to 99	98
<u>Forest City Basin (Cherokee Platform)</u>			
Mulberry Coal	(21)	88 to 103	95
Mulky Coal	(10)	86 to 105	99
Croweburg Coal	(17)	91 to 99	96
Fleming Coal	(18)	93 to 108	101
Mineral Coal	(9)	92 to 106	97

* Number indicates the individual measurements.

Homogenization temperatures were measured at different points in a banded crystal to find out if temperature varied during mineral deposition. The homogenization temperatures were the same for early-formed sphalerite and for late-formed sphalerite and for bands of different color.

For comparison, temperatures of homogenization of inclusions in sphalerite from Mississippi Valley-type ore deposits, compiled from the literature, are given in table 5-3. These temperatures range from 70° to 220°C, with most in the 85° to 115°C range. The homogenization temperatures measured in this study lie in the lower portion of the range for Mississippi Valley-type ore deposits.

Coalification Studies

Coalification and rank of the sphalerite-bearing coals were investigated as a means of establishing burial metamorphic history in which to fix the deposition of sphalerite. It is also of interest to determine if the sphalerite depositing solutions were or were not significantly out of thermal equilibrium with the host coals.

Previous Investigations

The general increase in coal rank with depth is known as Hilt's rule (Hilt, 1873). Studies from various coal basins have shown that this regularity is a consequence of the geothermal gradient (Kuyf and Patijn, 1961; Teichmüller and Teichmüller, 1967; and Hacquebard and Donaldson, 1974). Temperatures of the order of 100° to 150°C are generally assumed necessary for bituminous-coal formation, if geological

Table 5-3. Homogenization temperatures for Mississippi Valley-type ore deposits.

Mineral	Temperature Range	Reference
Upper Mississippi Valley District		
Sphalerite	75° - 220°C	McLimans (1977)
Spahlerite	75° - 120°C	Bailey and Cameron (1951)
Spahlerite	80° - 105°C	Newhouse (1933)
Tri-State District		
L. Sphalerite	83° - 105°C	Schmidt (1962)
E. Sphalerite	85° - 120°C	Schmidt (1962)
Sphalerite	90° - 135°C	Newhouse (1933)
Southeastern Missouri District		
Sphalerite	105° - 125°C	Newhouse (1933)
Southern IL-KY District		
Sphalerite - 2	81° - 92°C	Freas (1961)
Sphalerite - 1	84° - 103°C	Freas (1961)
Sphalerite	70° - 90°C	Newhouse (1933)

observations are interpreted in terms of maximum burial and normal geothermal gradient (Stach et al., 1975). This temperature range, however, is greatly influenced by the duration of effective heating. Other variables that affect the rate of coalification to a lesser extent have been described by Stach et al. (1975). The particularly difficult problem of the time dependence of coalification has been discussed by Huch and Karweil (1955), Karweil (1956), Bostick (1973), and Hacquebard and Donaldson (1974).

The correlation established between coalification gradients and geothermal gradients has made it possible to estimate the paleotemperature and paleogeothermal gradient that affected a coal bed during coalification. Thus, Kuyl and Patijn (1961) determined the paleogeothermal gradient for Carboniferous coals of the Peel area, Netherlands, by comparing changes in their volatile-matter content with depth, a measure of coalification rank, with analogous values from an area of known geothermal gradient. Hacquebard and Donaldson (1974), using vitrinite-reflectance gradients of Pennsylvanian coals in the Canadian Rockies, determined the paleogeothermal gradients for ten stratigraphic sequences as an exploration tool for high-quality coal. They demonstrated a relationship between vitrinite reflectance (VR) and volatile-matter content which allows the use of vitrinite reflectance in estimates of burial depth and paleogeothermal gradient. Castaño and Sparks (1974) combined vitrinite-reflectance gradients and authigenic mineral data to arrive at burial histories and paleogeothermal gradients for Mesozoic and Tertiary sedimentary sequences in California.

Studies of this type have also come into routine use in evaluating reservoir rocks for their petroleum potential.

Technique

Vitrinite reflectance (VR) was measured for all coals for which homogenization temperatures were available from this study. The vitrinite reflectance (VR) was measured in samples of coal adjacent to sphalerite and then in samples of coal from a few centimeters away to determine if reflectance had been increased by the heat of the sphalerite-depositing solutions. Cores were obtained from sphalerite-bearing areas but did not have sufficient depth with which to adequately evaluate geothermal gradients. The material was prepared for analysis following the procedures described by ASTM 02797-72(76). Two particulate pellets were prepared from each sample and the VR of 50 vitrinite grains was measured using a Leitz MPV II microscope equipped with a voltage stabilizer and a photometer. There was good agreement between mean VR values of matched pairs.

Experimental Results

There is a moderately high correlation coefficient ($r = 0.748$) between sphalerite homogenization temperatures and vitrinite reflectance of the host coals (table 5-4). No enhancement of VR values at the vein wall compared with that several centimeters away could be detected.

Table 5-4. Average homogenization temperatures from sphalerite fluid inclusions and vitrinite reflectance of host coals.

Coal Seam	Mean Homogenization Temperature C	Mean %R _{max}
<u>Western Shelf</u>		
No. 7 Coal	88	.48
No. 6 Coal	94	.51
No. 5 Coal	93	.54
<u>Southeastern Illinois</u>		
No. 6 Coal	104	.82
<u>Northern Missouri</u>		
Lexington Coal	86	.54
<u>Central Missouri</u>		
Bevier Coal	98	.63
<u>Eastern Kansas--western Missouri</u>		
Mulberry Coal	95	.56
Mulky Coal	99	.76
Croweburg Coal	96	.75
Fleming Coal	101	.71
Mineral Coal	97	.69

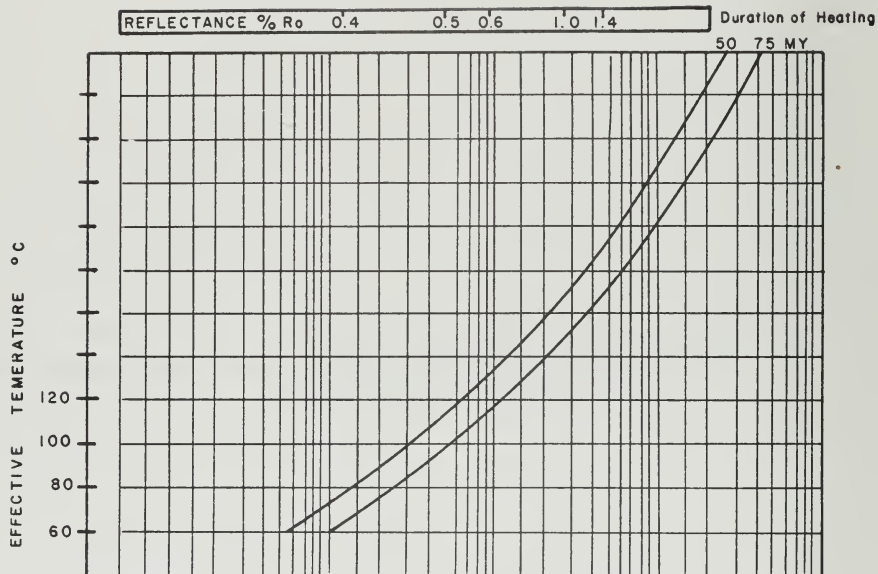
Estimates of Paleoparameters

Kaegi (1976) studied coalification in the Illinois Basin and used vitrinite reflectance of coals collected from seven deep cores in the deepest part of the basin where the average core penetrated 460 m and the maximum depth penetrated was 610 m. From vitrinite reflectance gradients which he converted to paleogeothermal gradients following a method by Hacquebard and Donaldson (1974), he obtained an average gradient of 2.35°C per 100 m. For comparison, a measurement of the geothermal gradient for the Illinois Basin was made by McGinnis (1968) who found about 2°C per 100 m.

Karweil (1956) used simple reaction-kinetic theory to construct a diagram, shown here in modified form as figure 5-1, that relates coal rank, temperature, and time. Using this diagram, one can estimate the effective temperature which brought the coal to its present rank if the duration of effective heating can be specified.

Duration of heating estimates will, in general, be quite inexact because they involve subjective judgments about geologic history. In the Interior Coal Province, in particular the Illinois Basin, the gap in the stratigraphic record between Permian and Gulfian rocks of Cretaceous age corresponds to a time gap of approximately 100 million years. If one assumes that the immediately underlying Pennsylvanian rocks were being buried under a progressively thicker overburden during the first 50 million years, and that there was uplift and erosion of this cover during the remaining 50 million years, the time period during which there was enough cover for these immediately underlying

Figure 5-1. Karweil's diagram relating coal rank, effective temperature, and duration of heating.



rocks to be heated significantly might then be arbitrarily estimated as from 50 to 75 million years.

For purposes of comparison of effective temperatures of coalification of sphalerite-bearing coals, the vitrinite reflectances of the Herrin (No. 6) Coal of the Illinois Basin (Western Shelf and Gallatin County), the Lexington Coal of the Missouri Platform, and the Mulberry Coal of the Cherokee Platform can be used (see table 5-3). Using the vitrinite reflectances and the duration-of-heating time of 50 to 75 million years, the effective temperatures of coalification taken from figure 5-1 are:

Herrin (No. 6) Coal, Western Shelf: 70° - 80°C
 Herrin (No. 6) Coal, Gallatin County: 90° - 110°C
 Lexington Coal, Missouri Platform: 70° - 80°C
 Mulberry Coal, Cherokee Platform: 75° - 85°C

Burial depths can be calculated for these coals using the paleogeothermal gradient of Kaegi (1976) and the effective temperatures of coalification. By subtracting an estimate for the average surface temperature from the effective temperatures of coalification and dividing by the paleogeothermal gradient of 2.35 C per 100 m (Kaegi, 1976), the following burial depths are attained:

Herrin (No. 6) Coal, Western Shelf: 2,213 to 2,638 m
 Herrin (No. 6) Coal, Gallatin County: 3,063 to 3,915 m
 Lexington Coal, Missouri Platform: 2,213 to 2,638 m
 Mulberry Coal, Cherokee Platform: 2,426 to 2,851 m

Other workers have estimated depths of burial for coals of the Carbondale Formation. The total depth of burial for the Colchester (No. 2) Coal in northern Illinois was estimated to be 1,213 m to 1,524 m, and for southern Illinois, approximately 3,048 m (Altschaeffe

and Harrison, 1959). These previous estimates are in general agreement with those from the present study.

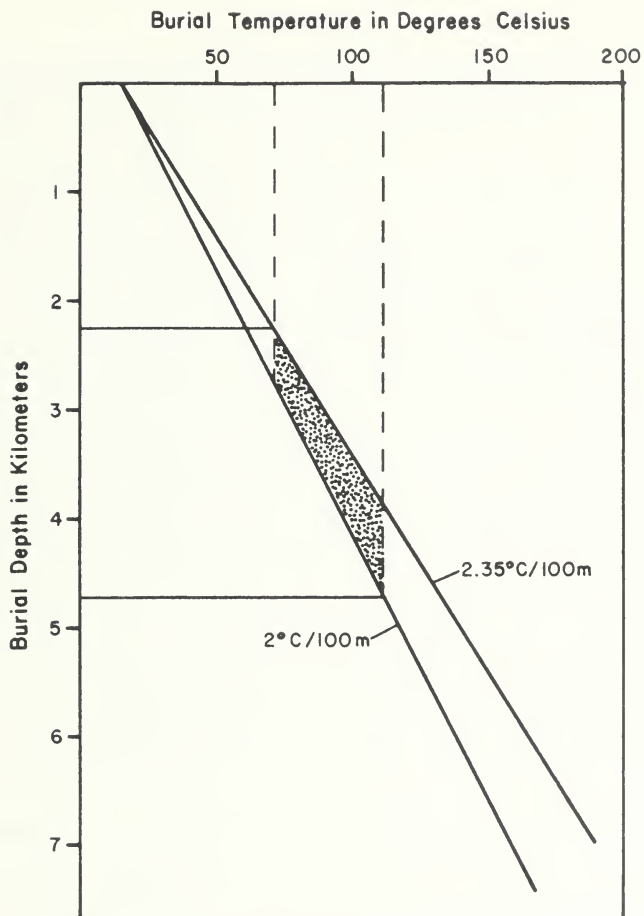
Until recently, no evidence had been found to show that late Pennsylvanian and Permian rocks were deposited in the Illinois Basin. In western Kentucky, a graben contains 640 m of strata that lie above the Shoal Creek Limestone Member. The uppermost 460 m of these strata, which have not been found in Illinois, have been tentatively assigned to the new Mauzy Formation of proposed Permian age, based on fusulinid studies (Kehn, Beard, and Williamson, 1979).

Discussion

The homogenization temperatures for sphalerite in this study range from 75° to 113°C, whereas the estimated coalification temperatures for the host coals using Karweil's diagram are in the range 70° to 110°C. Although the coalification temperatures are subject to considerable variation depending on rather arbitrarily selected parameters, a comparison of these independent sets of data is valuable. The failure of vitrinite reflectance to increase at the walls of sphalerite veins shows that the temperature difference between the mineralizing fluid and the host coal was not large enough, nor was the fluid present long enough, for the reflectance in the coal at the vein walls to increase. The high correlation coefficient ($r = .75$) between homogenization temperature and vitrinite reflectance indicates attainment of thermal equilibrium between the depositing solutions and the host coals.

During sphalerite deposition in coal, the depositing solutions and the host coals were exposed to the same maximum paleotemperatures. The heat source, therefore, must have been normal geothermal heating. This eliminates the possibility of fluid flow initiated by thermally-produced convection. The implication for this case is that sphalerite mineralization must have taken place under an appreciable sedimentary load during the time the host coal also reached its maximum temperature. This reasoning is expressed in figure 5-2. Figure 5-2 combines the present geothermal gradient and the paleogeothermal gradient for coalification in the Illinois Basin (Kaegi, 1976) with sphalerite homogenization temperatures to obtain a temperature-depth plot for sphalerite in coals of the Illinois Basin. The lack of paleogeothermal gradients for the Missouri and Cherokee Platforms prevents similar plots from being constructed for those areas. It could be assumed, however, based on the close agreement between sphalerite temperatures, vitrinite reflectances, and general geology of the coal basins, that the plots for each of these areas would be essentially the same. From figure 5-2 then, the minimum depth of sphalerite deposition is 2.2 kilometers and the maximum is 4.75 kilometers.

Figure 5-2. Temperature - depth plot for sphalerite deposition in coal host rocks of the Illinois Basin. (The stippled pattern indicates the temperature and depth conditions under which sphalerite was deposited. Bracketing the range are the sphalerite homogenization temperatures and estimates of geothermal gradient. In this model, depth and temperature are a consequence of normal geothermal heat and burial history.)



CHAPTER 6

FLUID INCLUSION CHEMISTRY AND STABLE ISOTOPE GEOLOGY
OF SPHALERITE IN COAL

Mineralizing solutions are sometimes trapped as fluid inclusions during the growth of minerals from aqueous solutions. These trapped fluids are particularly valuable as samples of original mineral depositing solutions. Present-day, room-temperature values of salinity, density, ionic strength, ionic concentration, stable isotopic composition, and gaseous constituents of these inclusions can be measured, and the temperature (see Chapter 5) and other parameters of the original environment of formation can be determined or inferred. This information restricts the possible choices of source and previous history of the mineralizing solution. Roedder (1972) has discussed techniques and limitations of fluid inclusion studies. There are also thousands of analyses of saline pore fluids from sedimentary basins (Meents et al., 1952; White, 1957, 1968; White et al., 1963; Hitchon, 1964; Taylor, 1964; Collins, 1975; Billings et al., 1969; Carpenter et al., 1974), which are useful in discussions of the source of mineralizing solutions. There is by now a respectable body of published measurements on fluid inclusions from Mississippi Valley-type ore deposits (Hall and Friedman, 1963; Roedder, 1967, 1972; McLimans, 1977) available for comparison with similar measurements made during the present study.

Technique

Hand specimens were collected from veins and clastic dikes in coal seams of the study area. The coals sampled, and the inclusion-bearing minerals extracted, follow.

(1) Illinois Basin--Western Shelf

Danville (No. 7) Coal--3 samples (sphalerite)
Herrin (No. 6) Coal--2 samples (sphalerite)
Herrin (No. 6) Coal--1 sample (pyrite)
Herrin (No. 6) Coal--1 sample (calcite)
Springfield (No. 5) Coal --2 samples (sphalerite)
Colchester (No. 2) Coal--3 samples (sphalerite)

(2) Forest City Basin--Missouri Platform

Lexington Coal--2 samples (sphalerite)
Bevier Coal--2 samples (sphalerite)

Doubly-polished thin sections were prepared and examined to verify that a crystal contained satisfactory inclusions and had as few included impurities as possible. After removing as many of the impurities as possible by hand picking, the sample was broken into fragments in a mortar and pestle and examined under a microscope. Small, visually-pure fragments were selected until approximately 20 grams had been collected.

The fragments were immersed in acetone for up to 24 hours to remove organic contamination, then in 5 percent nitric acid for up to 24 hours to remove carbonates, and finally washed in deionized water.

Next, an electrolytic cleaning apparatus similar to that of Pinckney (1972) was used to remove charged particles from the mineral surfaces. A 200-volt DC potential was applied across platinum electrodes inserted in the ends of the U-tubes, and deionized water (the

fluid used to carry off dislodged ions) was changed every 90 minutes. Current flow through the solution was plotted against time and cleaning was continued with successive changes of the deionized water until the declining current flow leveled out to a constant value, usually after about ten changes of deionized water.

The cleaned samples were oven dried at a temperature of $55^{\circ}\text{C} \pm 5^{\circ}\text{C}$ and loaded into a stainless steel extraction tube that had also been subjected to rigorous cleaning procedures. The stainless steel extraction tube, once loaded with a sample, was wrapped with a heating tape, heated to 60°C , and evacuated under high vacuum for 72 hours to degas the sample. The vacuum connection was then closed off, and if the tube maintained a vacuum of less than 0.1 microtorr for four hours, the extraction tube was considered to be leak free.

A Tinius and Olson^R hydraulic ram was then used to apply a uniaxial load of 300,000 pounds to each extraction tube, a procedure that reliably crushes all crystals to less than 100-mesh size. The crushed tubes were then connected to a high vacuum system, and the condensable and noncondensable fractions of the gases at the temperature of liquid nitrogen released by the crushing were collected and measured manometrically. The non-condensable gases were collected in an activated charcoal trap at the temperature of liquid nitrogen. Contamination effects from the activated charcoal were minimized by a preliminary baking-out at 400°C under vacuum until a vacuum of less than 0.1 microtorr could be maintained for one hour.

The inclusion water was vacuum distilled into a collection tube of known weight and the weight of water was measured by difference. For storage each collection tube was encapsulated in epoxy.

The crushed minerals were poured into filter paper and leached with known volumes of deionized water (50 ml). The insides of extraction tubes were also leached.

An ionization suppressant (cesium chloride) was added to the leachates and the leachates were analyzed by atomic absorption spectrophotometry. As a test of the effectiveness of the leaching technique, leachates were analyzed after each of five cycles. It was determined that three cycles of leaching were most effective and minimized sources of contamination. Blanks were run as a check on possible contamination from water and the extraction tubes. None was encountered

Material from the sphalerite and pyrite inclusion extraction runs was collected for sulfur isotope analysis. No attempt was made to segregate sphalerite from the different growth stages; rather the materials collected represent an average sphalerite from veins or nodules in coal. The materials were weighed, mixed with excess CuO , and heated to 1000°C . The gases produced, SO_2 , CO_2 , and H_2O , were separated by cold traps. The evolved SO_2 was measured manometrically. Sample purity was checked by calculation and any sample not achieving 99 percent yield was rejected. The SO_2 gas was introduced into a mass spectrometer for isotopic analysis (Joseph F. Whelan, U.S. Geological Survey, Branch of Isotope Geology, analyst).

H₂O from the extraction runs was allowed to react with hot uranium in order to produce hydrogen gas for isotopic analysis. The relative deuterium was then determined on a mass spectrometer (Joseph F. Whelan, U.S. Geological Survey, Branch of Isotope Geology, analyst).

Experimental Results

The salinity and elemental composition of the aqueous liquid from the fluid inclusions of epigenetic sphalerite, pyrite, and calcite in coal are given in tables 6-1, 2, 3, 4, and 5. Stable isotope data are given in table 6-6. The samples from the Illinois and the Forest City Basins are listed in stratigraphic order of the host coal. The lab number of each sample is listed in all tables so that the sample identity can be followed through the different analyses.

Results from three analyses were discarded as unreliable. For the two in which extracted H₂O was low, an ice block may have formed in the needle through which the H₂O was being collected, thereby preventing complete extraction. The extremely large amount of H₂O extracted from the other sample suggests contaminant H₂O from an unknown source.

The salinity of the inclusion fluid was calculated by dividing the sum of soluble salts (in milligrams) by the sum of the salts plus the extracted H₂O (in milligrams). This calculation gives minimum values because only the major cations were analyzed. If one assumes that Cl⁻ is the dominant anion, the Cl content of the fluid inclusions is then calculated from $m\text{Cl}^- = m\text{Na}^+ + m\text{K}^+ + \frac{1}{2}(m\text{Ca}^{+2} + m\text{Mg}^{+2})$.

Table 6-1. Composition of fluid inclusions in some minerals in various coals obtained by atomic absorption spectrophotometry (Ca, Calcite; Py, Pyrite; all others, Sphalerite).

Lab No.	Coal	H ₂ O Mg	Salinity Wt. %	Element Composition (molar)										
				Cl	Na	Ca	K	Mg	Zn	Fe	Cu	Pb		
5	No. 7	17.19	17.2	3.67	2.11	0.19	0.04	0.05	0.30	0.055	<0.002	<0.004		
9	No. 7	16.05	17.4	3.16	2.81	0.20	0.03	0.04	0.35	0.010	<0.002	<0.002		
0	No. 6	8.77	21.3	3.97	2.94	0.29	0.06	0.05	0.74	0.042	<0.003	<0.022		
19	No. 5	15.40	11.3	1.83	1.63	0.18	0.04	0.04	0.14	0.101	<0.002	<0.002		
8	No. 2	10.19	11.1	1.28	1.36	0.40	0.09	0.05	0.40	0.027	<0.003	<0.003		
18	No. 2	8.35	13.2	1.62	1.47	1.08	0.21	0.08	0.11	0.012	<0.004	<0.004		
4	No. 6 Py	12.82	36.1	3.28	2.06	9.76	0.15	0.31	1.11	8.6	0.004	0.062		
20	No. 6 Ca	6.65	9.9	-----	1.47	-----	0.06	0.19	-----	-----	-----	-----		
11	Lexington	9.26	19.3	3.38	2.46	0.05	0.02	0.04	0.60	0.025	<0.003	<0.004		
16	Lexington	6.18	26.1	3.66	3.53	3.50	0.02	0.07	0.004	<0.016	<0.005	<0.006		
12	Bevier	13.13	14.5	1.78	1.53	1.72	0.02	0.03	0.001	<0.008	<0.002	<0.003		
13	Bevier	6.40	27.2	4.02	3.50	3.66	0.09	0.08	0.005	<0.016	<0.005	<0.005		

Table 6.2 Comparison of major cations in fluid inclusions from minerals in coal; minerals in Mississippi Valley-type ores, and sea water (Py, Pyrite; Ca, Calcite; Sp, Sphalerite; and \bar{x} , grand mean).

Lab No.	Coal	Cation Ratios (Atomic)		
		K/Na	Ca/Na	Mg/Na
Illinois Basin				
5	No. 7 - Sp	.02	.09	.02
9	No. 7 - Sp	.04	.25	.05
0	No. 6 - Sp	.02	.29	.02
19	No. 5 - Sp	.02	.11	.02
8	No. 2 - Sp	.07	.29	.04
18	No. 2 - Sp	.14	.73	.05
	(\bar{x} Sp)	.05	.29	.03
4	No. 6 - Py	.07	4.74	.15
20	No. 6 - Ca	.04	2.09	.13
Forest City Basin				
11	Lexington - Sp	.01	.02	.02
16	Lexington - Sp	.01	.99	.02
12	Bevier - Sp	.01	1.72	.02
13	Bevier - Sp	.03	1.05	.02
	(\bar{x} Sp)	.02	.95	.02
Upper Mississippi Valley ^a				
	(\bar{x} Sp)	.03	.22	.04
	(\bar{x} Ca)	.03	.02	.09
Upper Mississippi Valley ^b				
	(\bar{x} Sp)	.03	.21	.03
	(\bar{x} Ca)	.07	n.a.	.46
Il-Ky Fluorspar District ^c				
	(\bar{x} Sp)	.03	.40	.10
Illinois Basin Brine ^d				
		.009	.17	.07
Michigan Basin Brine ^e				
		.058	1.29	.36
Sea Water ^f				
		.02	.02	.11

^aHall and Friedman, 1963

^dGraf et al., 1966

^bMcLimans, 1977

^eGraf et al., 1966

^cHall and Friedman, 1963

^fRiley and Chester, 1971

Table 6-3. Comparison of metals in natural solutions including a basin brine and fluid inclusions (concentrations in parts per million).

Salton Sea Brine ^a	Fluid Inclusions		Fluid Inclusions		Fluid Inclusions	
	Fluorite ^b	Sphalerite ^c	Sphalerite ^d	Sphalerite ^e	Sphalerite ^f	Sphalerite ^g
Zn	10,900	1,330	56,800	79,400	18,400	8,000
Fe	n.a.*	n.a.	64,700	27,900	1,960	731
Cu	9,100	140	12	150	145	193
Pb	n.a.	n.a.	130	55	1,059	674

^aSalton Sea Geothermal brine, after Muffler, & White, 1969.

^bFluid inclusion from fluorite, Kentucky-Illinois district, after Czamanske et al., 1963.

^cFluid inclusion from sphalerite, Creede Colorado, after Czamanske et al., 1963.

^dFluid inclusion from sphalerite, U.M.V. district, after McLimans, 1977.

^eFluid inclusion from sphalerite, U.M.V. district, after McLimans, 1977.

^fFluid inclusion from sphalerite in coal, Illinois Basin, present study.

^gFluid inclusion from sphalerite in coal, Forest City Basin, present study.

* n.a. = not available.

Table 6-4. Volumetric measurements of gases extracted from fluid inclusions.

Coal	μ moles	H ₂ O mole %	Gas Fractions				Noncondensable mole %	Noncondensable Condensable
			μ mole	Condensable mole %	μ mole	Noncondensable mole %		
Illinois Basin								
No. 7	891.1	96.0	8.40	0.9	30.00	3.2	3.6	
No. 6	330.6	99.0	0.21	0.06	1.78	0.5	8.5	
No. 5	855.6	94.2	39.88	4.4	12.92	1.4	0.3	
No. 2	157.8	97.9	0.23	0.1	3.10	1.9	13.0	
No. 2	565.6	98.0	2.80	0.5	8.80	1.5	3.1	
No. 2	463.8	95.9	14.78	3.1	5.09	1.0	0.3	
No. 6-y	711.7	94.3	20.00	2.6	23.10	3.1	1.2	
Forest City Basin								
Lexington	513.9	96.0	8.04	1.6	11.21	2.1	1.3	
Lexington	343.3	78.0	36.55	8.3	58.73	13.4	1.6	
Bevier	718.9	93.4	39.66	5.0	11.67	1.5	0.3	
Bevier	355.0	96.0	10.93	3.0	3.85	1.0	0.4	

Table 6-5. Molecular constituents of the noncondensable and condensable gas fractions of fluid inclusions in sphalerite from coal by gas chromatograph-mass spectrometry^a.

Constituent	Lab No.	Noncondensable				Condensable				Air
		3	9	16	19	3	9	16	19	Lab
N ₂		74	60	86	78	66	56	60	53	77.8
O ₂		6	24	nd ^b	21	23	31	19	25	20.9
Ar		10	10	9	12	3	6	10	5	0.9
CH ₄		nd	1	nd	1	nd	nd	nd	nd	0
CO ₂		8	4	3	.2	2	7	8	17	.2
H ₂ O		3	1	2	nd	6	nd	3	nd	nd

^aSemi-quantitative analysis based on total ionization reported in percent.

^bNot detected.

Table 6-6. Isotopic ratios for deuterium in fluid from sphalerite inclusions and for sulfur in sphalerite from coal*.

Lab No.	Coal-type	Isotopic Ratios	
		δD (‰ SMOW)	δS (‰ Canyon Diablo Std.)
5	No. 7-vein	-23.1	-7.57
9	No. 7-vein	-51.0	-7.58
6	No. 7-vein	n.t. ^a	-7.89
0	No. 6-vein	-54.6	-6.11
7	No. 5-vein	n.t.	-1.92
19	No. 5-vein	-37.4	-6.60, -6.54
18	No. 2-vein	n.t.	-4.29
4	No. 6-pyrite	-10.1	-2.04
8	No. 2-nodule	-22.5	2.55
2	No. 2-nodule	n.t.	4.90, 4.76
11	Lexington-vein	-2.5	-9.84
16	Lexington-vein	n.t.	-7.64
12	Bevier-vein	-15.6	- .45
13	Bevier-vein	n.t.	- .31

^an.t.--not tested.

* The reference deuterium material is standard mean ocean water; the reference sulfur material is the Canyon Diablo troilite. The equipment used is a Nier-type, 15 cm, 60° sector, double-collecting mass spectrometer. These analyses were made in R. O. Rey's laboratory, U.S. Geological Survey, Denver, Colorado.

Many of the salinity values of table 6-1 are in good agreement with those calculated by other workers from freezing-point-depression measurements made on fluid inclusions in sphalerite from coal. Roedder (1979) reported a range of salinity values from 17 to 25 weight percent NaCl equivalent, with an average of 21 weight percent NaCl equivalent, for 44 freezing-point-depression determinations for samples from the Herrin (No. 6) Coal of Illinois. The value from the present study for sphalerite inclusions from the Herrin (No. 6) Coal is 21.3 weight percent soluble salts. Leach (1973) made freezing-point-depression measurements on inclusions from sphalerite in the coals of central Missouri, and found salinities greater than 22 weight percent, NaCl equivalent. The values from the present study from central Missouri range from 14.5 to 27.2 weight percent soluble salts.

Those leaching values that do not agree well with the determinations made from depression of freezing temperature are low by as much as 50 percent. The difference stems, at least in part, from incomplete leaching.

Dissolved Solids

The salinities of inclusion fluids in sphalerite, pyrite, and calcite reported in table 6-1 range from 11.1 to 36.1 weight percent dissolved solids. The inclusion fluids from sphalerite range from 11.1 to 27.2 weight percent dissolved solids with a median value of 17.4 weight percent. These salinities are considered to be within the range of brines which is defined as any solution containing more

than 100,000 mg per liter total dissolved solids, equivalent to about 10 weight percent total dissolved solids (Davis, 1964). These concentrations are similar to those of many natural waters, basin brines, and inclusions in sphalerite and other sulfides from Mississippi Valley-type ore deposits. The relative abundances of constituents in sphalerite fluid inclusions are $Cl > Na > Ca > K > Mg$, the ionic proportions corresponding to a mixture of chloride salts dominated by $NaCl$ and $CaCl_2$. The single pyrite fluid measured is more saline than sphalerite with 36.1 weight percent salts. The single calcite inclusion fluid measured has a lower salinity of 9.9 weight percent salts with cation proportions in the same order as the pyrite: $Ca > Cl > Na > Mg > K$.

A comparison of salinity and major cations between the sphalerite in coals of the Illinois Basin and Forest City Basin shows, on the average, similar salinities and similar concentrations of the major cations. Neither do there appear to be any trends in salinity with respect to stratigraphic position. With respect to paragenesis, three samples from the same mine and coal bed--of pyrite, sphalerite, and calcite--represent early to late minerals, and suggest a decrease in salinity during the paragenesis.

For comparison of the major cations, the K/Na , Ca/Na , and Mg/Na ratios (atomic) are given in table 6-2 for the data from the present study together with data from various other groups including sea water, basin brines, and inclusion fluids from Mississippi Valley ore minerals. No apparent trends exist for the cation ratios with respect to

stratigraphy and there is little difference in the cation ratios between sphalerite inclusions in coals of the Illinois and Forest City Basins. The only exception is that, relative to sodium, calcium is somewhat higher in sphalerite inclusions from the Forest City Basin. Insufficient data prohibits statistical significance tests. There is a closer similarity between cation ratios for calcite and pyrite, each having much higher proportions of Ca and Mg than between these ratios in sphalerite inclusions.

A comparison among major cation ratios from various other types of brines shows that the closest similarity to those in sphalerite inclusions from coals are those in sphalerite inclusions from the Upper Mississippi Valley and Kentucky-Illinois Fluorspar districts. Major differences in major cation ratios exist between sphalerite inclusions from coals and sea water and between sphalerite inclusions from coals and basin brines. The major difference between the cation ratios in sphalerite inclusions from coals and Illinois Basin brine is the K/Na ratio which is less for Illinois Basin brine. Relatively speaking, sea water contains less calcium and more magnesium with respect to sodium than do sphalerite inclusions from coals.

Metals

The Zn, Fe, Pb, Cu values obtained from analyses of leachates from sphalerite and pyrite for fluid inclusion studies are shown in table 6-1. The ranges of metals in sphalerite inclusion fluids are 0.001 to 0.74 molal Zn (median value 0.14 molal Zn); 0.008 to 0.101

mo1al Fe (median value 0.016 mo1al Fe); 0.002 to 0.005 molar Cu (median value 0.003 mo1al Cu); and 0.002 to 0.022 mo1al Pb (median value 0.004 mo1al Pb). Their order of abundance is $Zn > Fe > Pb > Cu$. In pyrite, these metal concentrations in inclusion fluid are 1.11 mo1al Zn, 8.7 mo1al Fe, 0.004 Mo1al Cu, and 0.062 mo1al Pb. This is an order of abundance of $Fe > Zn > Pb > Cu$. The solubilities of these sulfides in distilled water at room temperature and atmospheric pressure are very small and not of concern here.

Table 6-3 shows the concentrations of selected metals from the present study together with similar data from other natural brines. Most of the zinc concentrations in sphalerite inclusions from coals are very similar to those from Upper Mississippi Valley sphalerite and Kentucky-Illinois Fluorspar district sphalerite. The Salton Sea sample contains less zinc but more iron than the sphalerite from coal. Copper and lead, from the most part, are represented by "less than" values, which cannot be compared.

Vaporizable Components

The portion of the fluid-inclusion content that can be extracted by applying a vacuum was subsequently separated into three fractions. Water was collected in a dry ice--alcohol trap, the noncondensable gases were collected on activated charcoal at liquid nitrogen temperature, and the condensable gases were collected in a liquid-nitrogen trap.

The water was measured by the difference between the weight of an evacuated vial and the weight of the vial after the water sample

was introduced into the vial through a needle penetrating the rubber stopper. The quantities of condensable and noncondensable gases were measured at constant temperature on a mercury manometer that had been calibrated with known volumes of gas.

Quantities of fluid components of the fluid inclusions are shown in table 6-4. It can be seen that water is the dominant gas phase in all samples, which is hardly surprising, as these are aqueous inclusions. Water makes up from 78 to 99 mole percent (median value, 96 mole percent) of the vaporizable material. The noncondensable gas fraction and the condensable gas fraction are nearly equal in mole percentage of the total vaporizable components. The noncondensable gas ranges from 0.5 to 13.4 mole percent (median value, 1.5 mole percent), and the condensable gas from 0.06 to 8.3 mole percent (median value, 2.6 mole percent). The percentages do not differ in an obvious way with stratigraphic position or from one basin to the other.

An attempt was made to determine the specific gas phases in the condensable and noncondensable gas fractions. Samples were analyzed for molecular constituents by a gas chromatograph-mass spectrometer (David King, Oil and Gas Branch, U.S. Geological Survey, analyst). The results of semi-quantitative analyses of molecular species in the inclusion gases are shown in table 6-5. The interpretation of these results is uncertain because of the presence of condensable fractions and water in the noncondensable gases and vice versa. The large percentage of atmospheric constituents N, O, and Ar indicates potential contamination from air. The presence of CH₄ and CO₂ far above what

could be attributed to contamination shows that these components are present in sphalerite fluid inclusions.

Deuterium

Deuterium concentrations in the H_2O extracted from eight sphalerite samples and one pyrite sample are given in table 6-6. The deuterium values are reported as per mil concentrations relative to standard mean ocean water ($^0/_{oo}$ SMOW). The range for deuterium in sphalerite and pyrite from coal is -2.5 $^0/_{oo}$ δD to -84.0 $^0/_{oo}$ δD (median -23.1 $^0/_{oo}$ δD). δD for the pyrite is -10.1 $^0/_{oo}$. The δD values of sphalerite of Illinois Basin samples range from -22.5 $^0/_{oo}$ to -84.0 $^0/_{oo}$ and the range of δD values from the Forest City Basin which is only two samples is -2.5 $^0/_{oo}$ to $-.50$ $^0/_{oo}$ δD . Although the Forest City Basin samples are isotopically heavier, no trend with respect to the two basins is made because of the scarcity of data. There is also no apparent trend of δD values with respect to stratigraphic position.

The δD values for nine sphalerite and one galena sample from the Upper Mississippi Valley district range from $+2$ $^0/_{oo}$ to -47 $^0/_{oo}$ δD (McLimans, 1977). Local, present-day meteoric water is -30 to -50 δD and Pleistocene water is -80 to -90 $^0/_{oo}$ δD (Craig, 1961). Also for comparison, Illinois Basin brines are $+1$ to -90 $^0/_{oo}$ δD , Michigan Basin brines are -30 to -110 $^0/_{oo}$ δD , Alberta Basin brines are -70 to -120 $^0/_{oo}$ δD , and Gulf Coast brines are $+20$ to -20 $^0/_{oo}$ δD (Clayton et al., 1966). The δD values from the present study, with one exception, do not resemble Pleistocene waters and only two of ten δD values

fall within the meteoric range. The range is within the range for Illinois Basin brines and for Upper Mississippi Valley ore fluids.

Sulfur Isotopes

The sulfur isotopic composition was examined in sphalerite and pyrite from six difference coal beds from the Illinois and Forest City Basins. The sulfur isotopic ratios, expressed as per mil values relative to the Canyon Diablo standard, are presented in table 6-6. The range in sulfur isotopic composition in sphalerite from veins in coal is -0.31 to -9.84 ‰ $\delta^{34}\text{S}$ and the value from a single pyrite sample from a sphalerite vein is -2.04 ‰ $\delta^{34}\text{S}$. The $\delta^{34}\text{S}$ values for sphalerite from nodules in clastic dikes are anomalous, being heavier and ranging from $+4.90$ to 2.55 ‰ $\delta^{34}\text{S}$. There is no apparent difference in $\delta^{34}\text{S}$ values for sphalerite in coals of the Illinois or Forest City Basins. Of special interest is an obvious trend in $\delta^{34}\text{S}$ with respect to stratigraphic position. This trend is an increase in $\delta^{34}\text{S}$ with a corresponding increase in depth. This trend is best defined by the data from the Illinois Basin where approximately 80 m of section are represented, and less well defined by data from the Forest City Basin.

The range of sulfur isotopic compositions of sulfides of the main Mississippi Valley deposits are: $+35$ to -10 ‰ $\delta^{34}\text{S}$, Southeast Missouri district; $+5$ to -10 ‰ $\delta^{34}\text{S}$, Tri-State district; and $+8$ to $+29.9$ ‰ $\delta^{34}\text{S}$, Upper Mississippi Valley district (Hall and Friedman, 1963; and McLimans, 1977). These values are much heavier and wider ranging than those in sphalerite in coal.

Price and Shieh (1979) made a systematic study of the distribution and isotopic composition of sulfur in coals from the Illinois Basin. In their study of massive pyrite in coal, they found a wide overall range of +24.2 to -13.7 ‰ $\delta^{34}\text{S}$. Within a single coal bed, however, range was narrow within a maximum variation of ± 4.4 ‰ $\delta^{34}\text{S}$. Nearly half of their $\delta^{34}\text{S}$ values cluster between -5 and -14 ‰ $\delta^{34}\text{S}$. Eight massive pyrites from a single column sample showed a range of -7 to -10.1 ‰ $\delta^{34}\text{S}$. This range corresponds closely to the range of $\delta^{34}\text{S}$ in sphalerite from veins in coal. The column sample was collected from the Indiana Coal V by Price and Shieh (1979). This coal correlates to the Springfield (No. 5) Coal of Illinois. The average $\delta^{34}\text{S}$ value for sphalerite in the Springfield (No. 5) Coal from the present study is -4.33 ‰ $\delta^{34}\text{S}$ and the average of the $\delta^{34}\text{S}$ for the massive pyrite in the Coal V of Indiana reported by Price and Shieh (1970) is -8.48 ‰ $\delta^{34}\text{S}$. It seems likely that the source of sulfur for massive pyrite in coals is similar to that for sphalerite in veins in coals.

The $\delta^{34}\text{S}$ values appear to be related to stratigraphy; that is, the sulfur isotopic ratio tends to be uniform for veins within a coal bed and to vary from one coal bed to another. Furthermore, there is a systematic increase in the $\delta^{34}\text{S}$ value with depth. Other workers such as Anger *et al.* (1966) and Lusk and Crockett (1969) have found systematic variations in $\delta^{34}\text{S}$ with stratigraphic position but these studies were performed on sulfide ore deposits. Price and Shieh (1979) thought that $\delta^{34}\text{S}$ values in coal might prove to be stratigraphic markers, so that they may have been biased toward recognizing

uniformity of sulfur isotopic ratios within coal beds, and variations between different coal beds. Price and Shieh (1979, table 3) presented $\delta^{34}\text{S}$ values for massive pyrite that show an increase with depth.

It is unlikely that sulfur was contributed from solutions circulating through the coals. If this had been the case, high-zinc coals would be expected to contain higher total sulfur than low-zinc coals. An arbitrary value of 250 ppm Zn was selected to distinguish high- and low-zinc coals. The average total sulfur content of high-zinc coals in the Illinois Basin was 2.7% while the average total sulfur for all other coal samples was 3.2% (unpublished data, Illinois Geological Survey).

Discussion

The chemical and isotopic composition of the fluid inclusions in sphalerite are nearly the same for the six coal beds and the two coal basins represented, suggesting a similar fluid depositing the sphalerites. These fluids are similar to those in inclusions from nearby Mississippi Valley-type ore deposits and bear resemblance to subsurface pore-fluids (oil-field brines) from sedimentary basins.

The Na-Ca-Cl subsurface brines found in sedimentary basins have been variously attributed to (1) dissolution of evaporite minerals (Carpenter et al., 1974); and (2) diagenetic reactions operating concurrently with concentration of the dissolved solids of sea water and fresh water by membrane filtration through shales (Graf et al., 1966).

The bromine content of many Na-Ca-Cl basin brines led Carpenter (1978) to conclude that these solutions originated as residual fluids in evaporite deposits. There are no significant evaporite deposits in the explored portion of the Illinois Basin. However, the deeper part of the basin has been penetrated by only a limited number of exploratory drill holes, and the nearly 3,000 m of Pennsylvanian and Permian strata that were eroded from the basin could have included evaporites.

The process of salt filtration of a shale membrane has been demonstrated experimentally (e.g., McKelvey and Milne, 1962; Hanshaw and Coplen, 1973; Kharaka and Smalley, 1976). For this mechanism to operate in nature, several conditions must be met. There must be a clay-rich shale that is not fractured and that covers a substantial part of the area of the sedimentary basin. Hydraulic pressure gradients large enough to drive the system must exist, and finally, there must be a moderately saline solution such as sea water filling the aquifers involved in the filtration system and, depending on the model, a means for replenishing this pore fluid with time. Graf et al. (1966) calculated that sea water equal to between three and ten times the present-day pore volume would be needed to derive the brine compositions in table 6-1.

In the Illinois Basin, the shales of the New Albany Group, Upper Devonian, attain a maximum thickness of 100 m and cover virtually all of the basin defined by the line of outcrop of the Pennsylvanian strata (William et al., 1975). For a 25 percent saline solution at

100°C, the osmotic pressure differential across a membrane is about 400 bars (Manheim and Horn, 1968). Reverse chemical osmosis, which increases salinity on the more saline side of a membrane, must be driven by a pressure opposite to and greater than the osmotic pressure. In nature, this means a pore-fluid pressure greater than that of a continuous liquid column to the surface ("overpressuring"). The principal causes of overpressuring are aquifer recharge at points sufficiently higher topographically, compaction of rapidly-deposited fine-grained sediments, the existence of an abnormally high thermal gradient in sediments lying under a shale cap, and lateral tectonic compression in a stratigraphic section containing fine-grained sediments (e.g., see Gretener, 1976). Of these, compaction is a particularly attractive mechanism during early diagenesis if the right mixture of lithologies is present. During maximum burial of the Illinois Basin there was more than 3,000 m of stratigraphic section, probably rich in shales, above the coals (see Chapter 5), so that there could have been a substantial increase in pore-fluid salinity high in the basin during compaction of this material, in addition to that which took place earlier under the New Albany Shales, for example.

The origin of the principal dissolved solids in subsurface brines and fluid inclusions remains in question; but, the compositional similarity between fluid inclusions in sphalerite from coal and basin brines is clear.

The range in deuterium values of inclusion fluids in sphalerite from coal is comparable to the ranges shown by Illinois Basin brines

and by Mississippi Valley-type ore fluids (McLimans, 1977; Hall and Friedman, 1963), and can be explained by the mixing of sea water and local meteoric water (Clayton et al., 1966).

Stanton (1972) attributed the isotopically-light sulfur in sphalerite in veins in coal to isotopic fractionation during bacterial sulfate reduction, so that the sphalerite would have to be a sedimentary precipitate. This interpretation is oversimplified, in view of the paragenetic relations between sphalerite and pyrite and between disseminated pyrite and pyrite in veins described in Chapter 3. Price and Shieh (1979) postulated that bacterial reduction of the sulfate of Pennsylvanian sea-water (+14 to +18 ‰ $\delta^{34}\text{S}$, Thode and Monster, 1965) would give a significant fractionation for pyrite in coal. However, the relatively narrow range of $\delta^{34}\text{S}$ values for both massive pyrite and sphalerite in coal indicates a homogenous sulfur source, not an expectable consequence of bacterial fractionation. $\delta^{34}\text{S}$ values produced by fractionation during bacterial reduction can vary due to temperature, pH, and Eh (Stanton, 1972). Framboidal pyrite, which comprises much of the disseminated pyrite in coal, forms very early during the peat stage (Scheihing et al., 1978), and as such, is subject to major changes in environmental conditions that give rise to a wide range of $\delta^{34}\text{S}$ values. The disseminated pyrite of early bacterial origin that occurs in coals of the Illinois Basin has a range of +15 to -23 ‰ in $\delta^{34}\text{S}$ (Price and Shieh, 1979).

The narrow range of sulfur isotopic composition in these sphalerites may result from their having obtained sulfur by dissolution of

massive pyrite that had previously been homogenized isotopically by remobilization and recrystallization of disseminated pyrite.

The fractionation factor for sulfur isotopes decreases with increase in temperature (Stanton, 1972), so that normal geothermal heating should have a measurable effect on the sulfur isotopic composition of sphalerites formed in various parts of a sedimentary basin, if isotopic equilibrium is achieved. Sphalerite from deeper coals should be heavier isotopically than that from shallower coals. The maximum temperature differential between the Danville (No. 7) Coal, stratigraphically the highest, and the Colchester (No. 2) Coal, the lowest, is only 8°C based on sphalerite homogenization studies. This temperature difference is inadequate to produce the 3.4 ‰ difference in $\delta^{34}\text{S}$ seen between samples from these two coals. It would be of interest to obtain sphalerite samples from a greater depth range.

Considerable quantities of gas are released during the coalification reaction, which extends from the beginning of the lignite stage (53 percent volatile matter) to high-volatile bituminous coal (40 percent volatile matter and similar to the host coals of this study). According to Jüntgen and Karweil (1962), nearly 100 m³ of CO₂ and about 200 m³ of CH₄ are produced per ton of bituminous coal. Nitrogen, H₂O, and H₂ are also expelled during the devolatilization associated with coalification. Coalification reactions probably supplied the condensable and noncondensable gases reported in table 6-5.

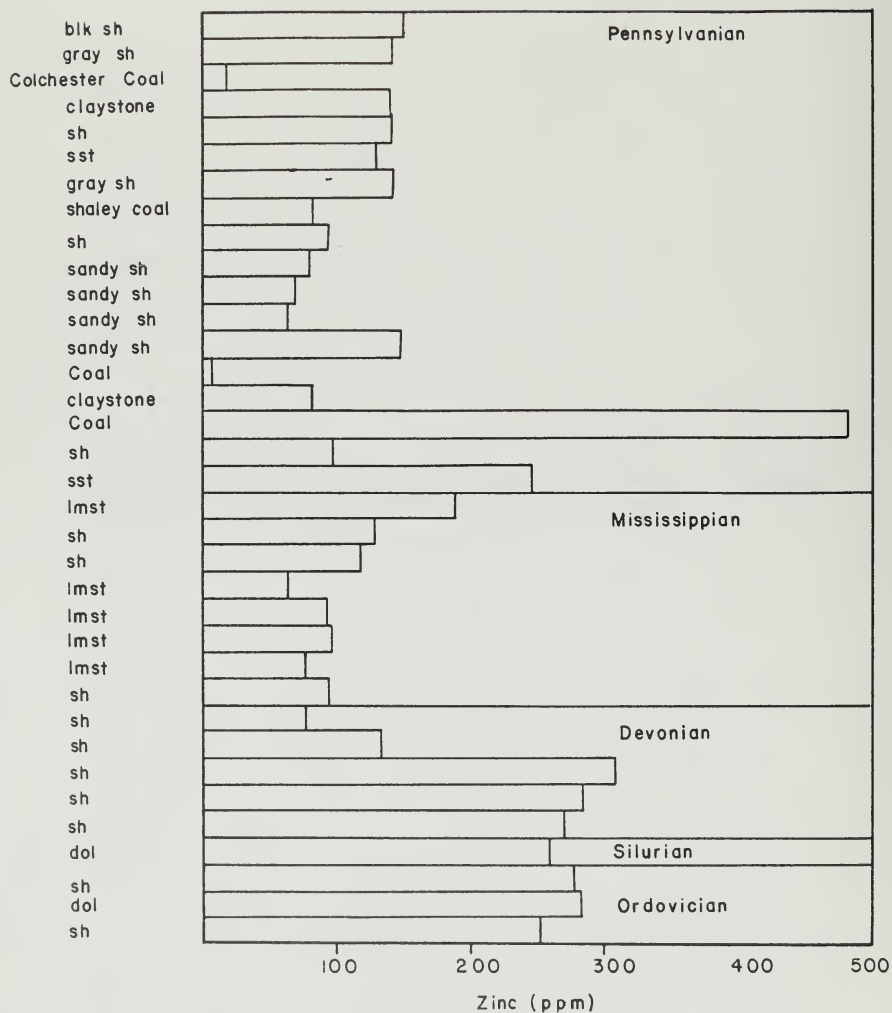
Coals are deficient in zinc, usually having less than the Clarke value of 70 ppm (Gluskoter *et al.*, 1977). On the other hand, when

epigenetic sphalerite is present, the zinc content of the whole coal can be as much as 0.1 percent (Cobb *et al.*, 1980). If this concentration of zinc is attributed to the billions of tons of coal in the sphalerite-enriched coal beds, the total amount of zinc that must have been transported into the coals is extremely large. There is a problem of zinc transport comparable to that for typical Mississippi Valley-type ore deposits except that for sphalerite in coal beds the deposits are within a basin and not adjacent to it.

A diamond drill core was obtained from an area of sphalerite-bearing coal in Fulton County, Illinois. The analyses of successive lithologic units, summarized in figure 6-1, show that the rocks of the Pennsylvanian and Mississippian Systems have a zinc content of 70 to 150 $\mu\text{g/g}$, whereas the section from the Devonian downward into the Silurian contains 260 to 310 $\mu\text{g/g}$ zinc. There is also a higher concentration of zinc at the Mississippian-Pennsylvanian boundary than within either of these systems. Of the three coals in this core, two have extremely low values for zinc, indicating the absence of epigenetic enrichment, but the stratigraphically lowest coal, with the highest zinc content of the entire core, must contain epigenetic sphalerite.

It is tempting in such cases to suppose that zinc was leached from underlying strata by circulating waters. If the thick shales of the underlying New Albany Group had earlier acted as a membrane filter, then zinc could have been preconcentrated to some extent, and then released upward by later changes in groundwater flow patterns or

Figure 6-1. Stratigraphic distribution of zinc in a core from the Western Shelf (Fulton County, Illinois) of the Illinois Basin.



by mild deformation that opened macroscopic flow channels. Recent trace element analyses of New Albany shales for the Eastern Gas Shales Project have shown zinc concentrations of up to 1,160 $\mu\text{g/g}$, with a mean value of about 250 $\mu\text{g/g}$ (J. Frost, Illinois State Geological Survey, personal communication, 1980).

CHAPTER 7

CONCLUSIONS

Origin of Sphalerite in Coal

The origin of sphalerite in coal suggested by this study involves deposition from zinc-bearing Na-Ca-Cl brines upon contact with sulfide sources in the immediate depositional environment, e.g., pyrite, H_2S , and organic sulfur. These brines were essentially at the temperature of the host coals, so that thermal density differences were probably not the major mechanism for driving the brines from deeper parts of the basin. Compaction under the loading of continuing sedimentation is a more likely explanation. Indeed, this study has demonstrated that compaction of the host coals was contemporaneous with sphalerite vein filling. Zones of high permeability such as sandstones and cleated coals presumably acted as conduits for the movement of the brines. The zinc was probably derived from underlying sedimentary units such as the Devonian-age New Albany shale. The open spaces where sphalerite was deposited resulted from minor deformation associated with differential compaction and cleat formation occasioned by volume shrinkage during coalification.

Of the possible precipitation mechanisms (Skinner, 1967 and MacQueen, 1979), pH change is thought to be of minor importance. There is no evidence of dissolution of the carbonate rocks within the stratigraphic section that includes the sphalerite-bearing coals. Cooling, dilution, and increase in the activity of reduced sulfur

species are more likely precipitation mechanisms. Reduced sulfur must have been available at both the coals that carry sphalerite today and those that do not. The restriction of sphalerite-bearing coals to shallow shelf areas suggests that cooling and/or dilution were important.

Basin Development and Diagenesis

The structural and paragenetic relationships of sphalerite to the host coals and to other minerals in the vein assemblage suggest a common sequence of events in the geologic histories of the several basins. The principal events in this sequence are summarized in table 7-1. The deposition of sphalerite probably occurred at maximum burial depth and highest temperature of the coal beds and may coincide with the "late stage" diagenesis in sedimentary basins linked to ore genesis by Jackson and Beales (1967). The maturation of host coals to sub-bituminous (B) rank at the time of sphalerite deposition called for in table 7-1 is in agreement with MacQueen's (1979) assertion that the point of thermal and structural evolution of a sedimentary basin necessary to generate Mississippi Valley-type ore deposits will also yield mature organic matter.

Relationship between Sphalerite in Coal and Mississippi Valley-type Ore Deposits

A considerable amount of attention is paid to the geologic history of sedimentary basins because of the oil and gas generated during this history, their highly saline brines from which a number of

Table 7-1. Correlation of events in coalification, basin subsidence, and inorganic mineral formation.

Coal Rank	Basin Subsidence	Compactional Condition of Coal	Mineral Formation	Temperature and depth
Peat	Organic Accumulation	Compaction	Disseminated pyrite	Near surface values
Lignite	Subsidence	Compaction and dilation; dikes and cleats form	Kaolinite	24° to 30°C; ^a 300 to 500 m
Sub-Bituminous	C Subsidence		Pyrite	
	B Maximum subsidence	Compaction and dilation	Sphalerite-Pyrite	75° to 113°C; 2.2 to 4 km
	A Erosion	Dilation		
High-volatile Bituminous	C Erosion	Release fracturing (inferred from sphalerite)	Calcite	13° to 28°C; ^a 150 to 300 m

^aTemperatures from Shieh and Suter (1979).

chemical substances can be extracted commercially, and their proximity to Mississippi Valley-type ore deposits. As a result, the origin of Mississippi Valley-type ores has been attributed to late-stage diagenesis during the evolution of sedimentary basins (Jackson and Beales, 1967; Dozy, 1970). What has come to be known as the basinal-brine origin of Mississippi Valley-type ore deposits has gained wide acceptance in geologic literature over the past twenty years since White (1958) first suggested it. More recently, Ohle (1980) has raised questions concerning this theory because of apparent inconsistencies. Sphalerite in coal offers a new body of evidence about the same basinal processes involved in the basinal-brine hypothesis for Mississippi Valley-type ore deposits.

The fluid inclusion compositions and temperatures of formation for sphalerite from coals of the Illinois and Forest City Basins are indistinguishable. This fact suggests that the sphalerites were deposited from quite similar fluids and that such similar fluids were produced independently in separate basins. The further coincidence of these measurements with those for inclusions in sphalerite from Mississippi-Valley ores suggests that the latter deposits were also formed from these fluids. Although there are mineralogical differences between the veins in coal and the Mississippi Valley-type ores, the common paragenesis silicate-sulfide-carbonate, the fluid inclusion chemistry, and the geographic proximity strongly suggest a genetic relationship.

The geographic proximity of Mississippi Valley-type ore deposits to sedimentary basins is used as a genetic link by Dozy (1970). Using similar reasoning, the geographic locations of sphalerite-bearing coals are such that basinal brines moving along shortest-path migration routes would pass from the deepest parts of basins through the sphalerite-bearing coals enroute to sites of Mississippi Valley-type ore deposits. At deposition and through the lignite stage, the coals were among the more continuous and permeable units within these sedimentary basins. The enclosing shales and underclays associated with coals enhance their hydraulic conductivity by maintaining hydraulic potential for long distances. These conditions make coals candidates for a Mississippi-Valley-ore plumbing system. Such a plumbing system is capable of connecting the deepest parts of sedimentary basins to carbonate rocks that host the Mississippi Valley-type ore deposits.

Sphalerite-bearing coals contain very large quantities of zinc metal. Cobb et al. (1980) estimated that there is as much as 6.35×10^9 kilograms of zinc in just three coal beds within a four-county area in the Illinois Basin. The volume of solution required to transport this amount of metal, assuming a reasonable concentration of zinc in solution, is large enough so that a basin-wide process would be needed. The requirement for making a significant contribution to a Mississippi-Valley-type deposit is comparable.

Timing is important for this implied genetic relationship between sphalerite in coal and in base metal deposits. Unfortunately, the time of deposition of Mississippi-Valley-type ores at various

localities can be dated only within very broad limits, although the host rocks in these districts range in age from Cambrian to Carboniferous. Ohle (1980) states that "a model calling for a fully developed Illinois basin would not be credible if the ore deposit was Mississippian or older; there was no deep Illinois basin until late Paleozoic time." The timing of sphalerite deposition in coals of typical Midcontinent basins is established in the present study as late Paleozoic.

Table 7-2 summarizes a number of characteristics of sphalerite in coal and of Mississippi-Valley-ore deposits. Many of the salient features are identical; in fact, enough similarities exist to support the idea that the sphalerite and associated minerals in coal are a coal-hosted Mississippi-Valley-type ore. On the other hand, the conspicuous absence of galena from the paragenesis in coal clearly shows that not all of the processes contributing to a Mississippi-Valley-type ore are involved for the coals. Conversely, an additional source appears to be required for the Pb of the latter deposits.

Summary

The principal conclusion of this study is that plumbing systems, basin-wide in extent, were in place during late Paleozoic time in both the Forest City and Illinois Basins and that these systems were capable of transporting large quantities of Zn-rich brine. A recapitulation of the detailed conclusions of the several parts of the study follows:

Table 7-2. Comparison of various characteristics of sphalerite in coal and of Mississippi-Valley-type ore deposits.

	Sphalerite in Coal	Mississippi-Valley-Type Ores
Occurrence	Vertical veins, gash veins, and clastic dikes	Vugs, pitch and flat, breccia, joints, veins, replacement
Distribution	Shelf areas of sedimentary basins, coal host rocks	Near edges of sedimentary basins, carbonate host rocks
Timing	Late Paleozoic	None younger than Late Paleozoic
Transport	Na-Ca-Cl brines of about 20 wt. %	Same
Precipitation	Increase in reduced S activity Cooling Dilution	pH change Cooling Dilution Increase in reduced S activity
Temperature	75° to 113°C	80° to 212°C
Paragenesis	silicates-sulfides-carbonates Kao-Py-Sph-Py-Calcite	silicates-sulfides-sulfates-carbonates Similar to coal veins but additional minerals
Associated Organics	Galena absent Mature	Galena present Mature

1. Sphalerite occurs in Desmoinesian age coal of four principal areas in the Interior Coal Province--the Western Shelf of the Illinois Basin, the Eagle Valley Syncline of the Illinois Basin, the Missouri Platform of the Forest City Basin, and the Cherokee Platform of the Forest City Basin.
2. The host coals are high-volatile bituminous B and C, high in sulfur and ash, and occur in proximity to Mississippi-Valley-type ore deposits.
3. The sphalerite is associated with particular minor structural features, namely, cleats, clastic dikes, and faults with small displacement. These structures are generally vertical in orientation and extensional in origin.
4. The paragenesis kaolinite-pyrite-sphalerite-pyrite-calcite is found in all coals studied.
5. A sphalerite microstratigraphy, based on the color and texture of growth bands, demonstrates simultaneous deposition of sphalerite in different coals in the stratigraphic column and in the same coal over distances of tens of miles.
6. Development of coal banding had probably reached its present state by the time sphalerite veins formed.
7. Many sphalerite veins formed in pre-existing cleats.
8. From about 8 to 14 percent compaction of the host coal occurred after emplacement of sphalerite veins.
9. Fluid-inclusion homogenization temperatures for sphalerite range from 75° to 113°C.
10. Depths of burial estimates for sphalerite deposition range from 2.2 to 4.75 km.
11. The chemical compositions of fluid inclusions are nearly identical for the different coals, as well as for sphalerite from Mississippi-Valley-type ores.
12. Deuterium concentrations suggest that although some inclusion waters may be unflushed sea water, most are a mixture of meteoric and sea water.
13. The narrow range of sulfur isotopic composition in these sphalerites (-.31 to -9.84 ‰^{34S}) may result from their having obtained sulfur by dissolution of massive pyrite that had previously been homogenized isotopically by remobilization and recrystallization of disseminated pyrite.

REFERENCES

- Alschaeffe, A. G., and Harrison, W., 1959, Estimation of the minimum depth of burial for a Pennsylvanian underclay: *Journal of Sedimentary Petrology*, v. 29, p. 178-185.
- Anger, G., Nielson, H., Puchelt, H., and Ricke, W., 1966, Sulfur isotopes in the Rammelsberg ore deposit (Germany): *Economic Geology*, v. 61, p. 511-536.
- ASTM Annual Book of Standards, 1974, Gaseous fuels; coal and coke; atmospheric analysis: Part 26, American Society for Testing and Materials, Philadelphia, 828 p.
- Bailey, S. W., and Cameron, E. N., 1951, Temperatures of mineral formation in bottom-run lead-zinc deposits of the Upper Mississippi Valley, as indicated by liquid inclusions: *Economic Geology*, v. 48, p. 626-651.
- Barton, P. B., Jr., Bethke, P. M., and Toulmin, P., 1963, Equilibrium in ore deposits: *Mineralogical Society of American, Special Paper 1*, p. 171-185.
- Bastin, E. S., 1950, Interpretation of ore textures: *Geological Society of America, Memoir 45*, 100 p.
- Billings, G. K., Hitchon, B., and Shaw, B. D., 1969, Geochemistry and origin of formational waters in the Western Canada Sedimentary Basin; 2, Alkali metals in geochemistry of subsurface brines: *Chemical Geology*, v. 4, p. 211-223.
- Boctor, N. A., Kullerud, G., and Sweany, J. L., 1976, Sulfide minerals in Seelyville coal III, Chinook Mines, Indiana: *Mineralium Deposita*, v. 11, p. 249-266.
- Bostick, N. H., 1973, Time as a factor in thermal metamorphism of phytoclasts (coaly particles): *7th Congrès International de Stratigraphie et de Géologie du Carbonifère, Compte Rendu*, v. 2, p. 183-193.
- Branson, C. C., 1962, Pennsylvanian system of the mid-continent: *in* Branson, C. C. (ed.), *Pennsylvanian system in the United States*, a symposium: *American Association of Petroleum Geologists, Tulsa*, p. 431-460.

- Bushbach, T. C., 1971, Stratigraphic setting of the Eastern Interior Region of the United States, in Bond, D. D., chairman, Background materials for symposium on future petroleum potential of NPC Region 9: Illinois Geological Survey, Illinois Petroleum 96, p. 3-20.
- Carpenter, A. B., 1978, Origin and chemical evolution of brines in sedimentary basins: Oklahoma Geological Survey Circular 79, p. 60-77.
- Carpenter, A. B., Trout, M. L., and Pickett, E. E., 1974, Preliminary report on the origin and chemical evolution of lead- and zinc-rich oil field brines in central Mississippi: Economic Geology, v. 69, p. 1191-1206.
- Casagrande, D. J., Siefert, K., Berschinski, C., and Sutton, N., 1977, Sulfur in peat-forming systems of the Okefenokee Swamp and Florida Everglades: origins of sulfur in coal: Geochimica et Cosmochimica Acta, v. 41, p. 161-167.
- Castaño, J. R., and Sparks, D. M., 1974, Interpretation of vitrinite reflectance measurements in sedimentary rocks and determination of burial history using vitrinite reflectance and authigenic minerals: in Dutcher, et al (ed.); Carbonaceous materials as indicators of metamorphism: Geological Society of America, Special Paper 153, p. 31-52.
- Clark, B. R., and Kelly, W. C., 1973, Sulfide deformation studies: I. Experimental deformation of pyrrhotite and sphalerite to 2,000 bars and 500°C: Economic Geology, v 68, p. 332-352.
- Clayton, R. N., Friedman, I., Graf, D. L., Mayeda, T. K., Meents, W. F., and Shimp, N. F., 1966, The origin of saline formation waters, I: Isotopic composition: Jour. Geophys. Res., v. 71, p. 3869-3882.
- Clegg, K. E., 1970, The La Salle Anticlinal Belt in Illinois: Illinois State Geological Survey Guidebook Series 8, p. 106-110.
- Craig, H., 1961, Isotopic variations in meteoric waters: Science, v. 133, p. 1702-1703.
- Cobb, J. C., Masters, J. M., Treworgy, C. G., and Helfinstine, R. J., 1979, Abundance and distribution of sphalerite and fine coal from mine waste in Illinois: Illinois Geological Survey Industrial Minerals Note 71, 11 p.
- Cobb, J. C., Steele, J. D., Treworgy, C. G., and Ashby, J. F., 1980, The abundance of zinc and cadmium in sphalerite-bearing coals in Illinois: Illinois Geological Survey Minerals Note 74, 28 p.

- Collins, A. G., 1975, Geochemistry of Oilfield Brines: Elsevier Scientific Publishing Company, Amsterdam, 496 p.
- Coveney, R. M., Jr., 1979, Sphalerite concentrations in Mid-Continent Pennsylvanian black shales of Missouri and Kansas: *Economic Geology*, v. 74, p. 131-140.
- Cross, A. T., 1952, *Geology of the Pittsburgh Coal: Stratigraphy, petrology, origin, composition, and geologic interpretation of mining problems*: Nova Scotia Department of Mines, 2nd Conference on Origin and Composition of Coal, Crystal Cliffs, Nova Scotia, p. 32-111.
- Czamanske, G. K., Roedder, E., Burns, F. C., 1963, Neutron activation analysis of fluid inclusions for copper, manganese, and zinc: *Science*, v. 140, p. 401-403.
- Damberger, H. H., 1970, Clastic dikes and related impurities in Herrin (No. 6) and Springfield (No. 5) Coals of the Illinois Basin: *Illinois Geological Survey Guidebook 8*, p. 111-119.
- Damberger, H. H., 1973, Physical properties of the Illinois Herrin (No. 6) Coal before burial, as inferred from earthquake-induced disturbances: *Proceeding, Seventh International Congress of Carboniferous Stratigraphy and Geology*, v. 2, p. 341-350.
- Davis, S. N., 1964, The chemistry of saline waters by R. A. Krieger-- Discussion: *Ground Water*, v. 2, no. 1, p. 51.
- Dozy, J. J., 1970, A geological model for the genesis of the lead-zinc ores of the Mississippi Valley, U.S.A.: *Institute of Mining and Metallurgy*, v. 79, p. B163-B170.
- Freas, P. H., 1961, Temperatures of mineralization by liquid inclusions, Cave-in-Rock fluorspar district, Illinois: *Economic Geology*, v. 56, p. 542-556.
- Gluskoter, H. J., 1967, Clay minerals in Illinois coals: *Journal of Sedimentary Petrology*, v. 37, p. 205-214.
- Gluskoter, H. J., Hatch, J. R., and Lindahl, P. C., 1973, Zinc in coals of the Illinois Basin: *Geological Society of America, Abstracts with Programs*, v. 5, p. 637.
- Gluskoter, H. J., Ruch, R. R., Miller, W. G., Cahill, R. A., Dreher, G. B., and Kuhn, J. K., 1977, Trace elements in coal: occurrence and distribution: *Illinois Geological Survey Circular 499*, 154 p.

- Gluskoter, J. H., and Simon, J. A., 1968, Sulfur in Illinois Coals: Illinois Geological Survey Circular 432, 28 p.
- Graf, D. L., Meents, W. F., Friedman, I., and Shimp, N. F., 1966, The origin of salin formation waters, III: calcium chloride waters: Illinois Geological Survey Circular 397, 60 p.
- Gretener, P. E., 1976, Pore pressure: fundamentals, general ramifications, and implications for structural geology: AAPG Continuing Education Course Note Series No. 4, 87 p.
- Hacquebard, P. A., and Donaldson, J. R., 1974, Rank studies of coals in the Rocky Mountains and Inner Foothills Belt Canada: in Dutcher et al (ed.): Carbonaceous materials as indicators of metamorphism: Geological Society of America, Special Paper 153, p. 75-94.
- Hall, W., and Friedman, I., 1963, Composition of fluid inclusions, Cave-in-Rock fluorite district, Illinois, and Upper Mississippi Valley zinc-lead district: Economic Geology, v. 58, p. 886-911.
- Hanshaw, B. B., and Coplen, T. B., 1973, Ultrafiltration by a compacted clay membrane--II. Sodium ion exclusion at various ionic strengths: Geochim. et Cosmochim. Acta, v. 37, p. 2311-2327.
- Hatch, J. R., 1979, Distribution of zinc and cadmium in coals from the eastern and western regions, Interior Coal Province: Ninth International Congress of Carboniferous Stratigraphy and Geology, Abstracts of Papers, p. 86.
- Hatch, J. R., Avein, M. J., Wedge, W. K., and Brady, L. L., 1976a, Sphalerite in coals from southeastern Iowa, Missouri, and south-eastern Kansas: U.S. Geological Survey, open-file report 76-796, 26 p.
- Hatch, J. R., Gluskoter, H. J., Lindahl, P. C., 1976b, Sphalerite in coals of the Illinois Basin: Economic Geology, v. 71, p. 613-614.
- Hilt, C., 1873, Die Beziehungen zwischender Zusammen-setzung und den techischen Eigenschaften der Steinkohlen: Zeitschrift des Vereins deutscher Ingenieure, v. 17, p. 195-202.
- Hitchon, B., 1964, Formation fluids: in McCrossan and Glaister (eds.); Geological history of western Canada: Alberta Society of Petroleum Geologists, Calgary, Alberta, p. 201-217.
- Hubbert, M. K., 1951, Mechanical basis for certain familiar geologic structures: Geological Society of American Bulletin, v. 62, p. 255-372.

- Huck, G., and Karweil, J., 1955, Physikalisch-chemische Probleme der Inkohlung: Brennstoff-Chem., v. 36, p. 1-11.
- Jackson, S. A., and Beales, F. W., 1967, An aspect of sedimentary basin evolution: The concentration of Mississippi-Valley-type ores during late stages of diagenesis: Canadian Petroleum Geology Bulletin, v. 15, p. 383-433.
- Jüntgen, H. and Karweil, J., 1962, Künstliche Inkohlung von Steinkohlen, Freiburger Forschungsh., v. 29, p. 27-36.
- Kaegi, D. D., 1976, A coal rank profile of southeastern Illinois as determined by vitrinite reflectance: Unpub. M.S. thesis, Southern Illinois University, Carbondale, 98 p.
- Karweil, J., 1956, Die metamorphose der Kolen vom standpunkt der physikalischen Chemie. Z. Deut. Geol. Ges. 107, pp. 132-139.
- Kehn, T. M., Beard, J. G., and Williamson, A. D., 1979, The Mauzy Formation, a new stratigraphic unit of Permian age in western Kentucky: U.S. Geological Survey Open-file Report.
- Kemezys, M. and Taylor, G. H., 1964, Occurrence and distribution of minerals in some Australian coals: Journal of Institute of Fuel, v. 37, p. 389-397.
- Kharaka, Y. K. and Smalley, W. C., 1976, Flow of water and salutes through compacted clays: American Association of Petroleum Geologists.
- Klevtsov, P. V. and Lemlein, G. G., 1959, Pressure correlations for the homogenization of aqueous NaCl solutions: Akad. Nauk. SSSR, Doklady, v. 128, p. 1250-1253, in Russian; translated in American Geological Institute, Doklady of the Academy of Sciences of the U.S.S.R., v. 128, p. 995-997, 1960.
- Kuyl, O. S. and Patijn, R. J. H., 1961, Coalification in relation to depth of burial and geothermic gradient: Congrès International de Stratigraphie et de Géologie du Carbonifère, C. R. 4, Heerlen, 1958, p. 357-365.
- Leach, D. L., 1973, A study of the barite-lead-zinc deposits of central Missouri and related mineral deposits in the Ozark region: Unpub. Ph.D. thesis, University of Missouri, Columbia, Missouri, 196 p.
- Lusk, J. and Crockett, J. H., 1969, Sulfur isotope fractionation in coexisting sulfides from the Heath Steele B-1 orebody, New Brunswick, Canada: Economic Geology, v. 64, p. 147-155.

- MacQueen, R. W., 1979, Base metal deposits in sedimentary rocks: some approaches: Presidential address to the Geological Association of Canada, *Geoscience Canada*, v. 6, p. 3-9.
- Manheim, F. T. and Horn, M. K., 1968, Composition of deeper subsurface waters along the Atlantic continental margin: *Southeastern Geology* v. 9, p. 215-236.
- Marbut, C. F., 1908, The geology of Morgan County: Missouri Bureau of Geology and Mines, 2nd Series, v. 7, p. 79-80.
- Mather, W. B., 1946, The mineral deposits of Morgan County: Missouri Bureau of Geology and Mines, v. 7, 2nd Series, p. 123-137.
- McCulloch, C. M., Deul, M., and Jeran, P. W., 1974, Cleat in bituminous coal-beds: U.S. Bureau of Mines, R. I. 7910, 25 p.
- McGinnis, L. D., 1968, Glaciation as a possible cause of mineral deposition: *Economic Geology*, v. 63, p. 390-400.
- McKelvey, J. G. and Milne, I. H., 1962, The flow of salt solutions through compacted clays: *Clays and Clay minerals*, v. 9, p. 248-259.
- McKnight, E. T., and Fischer, R. P., 1970, Geology and ore deposits of the Picher Field, Oklahoma and Kansas: U.S. Geological Survey Professional Paper 588, p. 165.
- McLimans, R. K., 1977, Geological, fluid inclusion, and stable isotope studies of the Upper Mississippi Valley Zinc-Lead District, Southwest Wisconsin: Unpub. Ph.D. thesis, The Pennsylvania State University, College Station, Pennsylvania, 175 p.
- Meents, W. F., Bell, A. H., Rees, O. W., and Tilbury, W. G., 1952, Illinois oil-field brines: *Illinois Geological Survey Petroleum Bulletin* 66, 38 p.
- Muffler, L. J. P. and White, D. E., 1969, Active metamorphism of Upper Cenozoic sediments in the Salton Sea geothermal field and the Salton Trough, southeastern California: *Geological Society of America, Bulletin* 80, p. 157-182.
- Newhouse, W. H., 1933, The temperature of formation of the Mississippi Valley lead-zinc deposits: *Economic Geology*, v. 28, p. 744-750.
- Ohle, E. L., 1980, Some considerations in determining the origin of ore deposits of the Mississippi Valley-type-Part II: *Economic Geology*, v. 75, p. 161-172.

- Pinckney, D. M., 1972, Electrolytic cells for cleaning crystals before fluid inclusion analysis: U.S. Geological Survey Professional Paper 800-B, p. B141-B145.
- Price, F. T. and Shieh, Y. N., 1979, The distribution and isotopic composition of sulfur in coals from the Illinois Basin: *Economic Geology*, v. 74, p. 1445-1461.
- Rao, C. P. and Gluskoter, J. H., 1973, Occurrence and distribution of minerals in Illinois coals: Illinois State Geological Survey Circular 476, 56 p.
- Riley, J. P. and Chester, R., 1971, Introduction to Marine Chemistry: Academic Press, New York, 465 p.
- Robertson, C. E., 1980, Missouri; description of coal seams; in Nielson, G. F. (ed.): 1980 Keystone Coal Industry Manual: McGraw Hill Mining Publications, New York, p. 533-535.
- Roe, W., 1934, Clay-veins in Illinois Springfield (No. 5) Coal: unpublished M.S. thesis, Northwestern University, Evanston, 105 p.
- Roedder, E., 1967, Fluid inclusions as samples of ore fluids: in Barnes, H. L. (ed.); Geochemistry of Hydrothermal Ore Deposits: Holt, Rinehart, and Winston, p. 515-567.
- Roedder, E., 1972, Composition of fluid inclusions: Chapter JJ, Data of Geochemistry: U.S. Geological Survey Professional Paper 440-JJ.
- Roedder, E., 1979, Fluid inclusion evidence on the environment of sedimentary diagenesis, a review: *Society of Economic Mineralogists and Paleontologists Special Publication No. 26*, p. 89-107.
- Roedder, E., Ingram, B., and Hall, W., 1963, Studies of fluid inclusions III--Extraction and quantitative analysis of inclusions in the milligram range: *Economic Geology*, v. 58, p. 353-374.
- Ruch, R. R., Gluskoter, H. J., and Shimp, N. F., 1974, Occurrence and distribution of potentially volatile trace elements in coal: Illinois Geological Survey Environmental Geology Note 72, 96 p.
- Savage, T. E., 1927, Significant breaks and overlaps in the Pennsylvanian rocks of Illinois: *American Journal of Science*, 5th Series, v. 14, p. 307-316.
- Scheiing, M. H., Gluskoter, H. J., and Finkelman, R. B., 1978, Interstitial networks of kaolinite within pyrite framboids in the Meigs Creek Coal of Ohio: *Journal of Sedimentary Petrology*, v. 48, p. 723-732.

- Schoewe, W. H., 1959, The first Kansas lead mines: The Kansas Historical Quarterly, Winter 1959, p. 391-401.
- Schmidt, R. A., 1962, Temperatures of mineral formation in the Miami-Picher district as indicated by liquid inclusions: Economic Geology, v. 57, p. 1-20.
- Shieh, Y. N. and Suter, T. G., 1979, Formation conditions of authigenic kaolinite and calcite in coals by stable isotope determination: Clays and Clay Minerals, v. 27, p. 154-156.
- Skinner, B. J., 1967, Precipitation of Mississippi Valley-type ores: A possible mechanism, *in* Brown, J. B. (ed.); Symposium on the Genesis of Stratiform Lead-Zinc-Barite-Fluorite Deposits: Economic Geology Monograph 3, p. 363-369.
- Spenser, E. W., 1969, Introduction to the structure of the earth: McGraw-Hill, Inc., New York, 597 p.
- Stach, E., Taylor, G. H., Mackowsky, M. -Th., Chandra, D., Teichmüller, M., and Teichmüller, R., 1975, Stach's textbook of coal petrology: Berlin, Gebrüder Borntraeger, 428 p.
- Stanton, R. L., 1972, Ore Petrology, McGraw-Hill, Inc., New York, 713 p.
- Stone, R., and Snoeberger, D. F., 1978, Cleat orientation and areal hydraulic anisotropy of a Wyoming coal aquifer: Groundwater, v. 15, p. 434-438.
- Stutzer, O., 1940, Geology of Coal: Translated and revised by A. C. Noe, Chicago, Illinois, The University of Chicago Press, 461 p.
- Taylor, S. R., 1964, Abundance of chemical elements in the continental crust: A new table: Geochimica et Cosmochimica Acta, v. 28, p. 1273-1285.
- Ting, F. T. C., 1977, Origin and spacing of cleats in coal beds: ASME preprint paper no. 77-Pet-24, 3 p.
- Teichmüller, M. and Teichmüller, R., 1967, Diagenesis of coal (coalification): *in* Larsen, G. and Chilingar, G. V. (ed.); Diagenesis of sediments, Developments in Sedimentology 8: Elsevier Publishing Company, Amsterdam-London-New York, p. 391-415.
- Thode, H. G. and Monster, J., 1965, Sulfur isotope geochemistry of petroleum, evaporites, and ancient seas; *in* A. Young and Galley, J. E., (eds.): Fluids in subsurface environments: American Association of Petroleum Geologists Memoir, v. 4, p. 367-377.

- Thomas, J. Jr. and Damberger, H. H., 1976, Internal surface area, moisture content, and porosity of Illinois coals: variations with rank: Illinois Geological Survey Circular 493, 38 p.
- Udden, A. O., 1912, On the earthquake of January 2, 1912, in the Upper Mississippi Valley: Illinois Academy of Science Transactions, v. 27, p. 111-115.
- Van Horn, F. B., 1905, The Geology of Moniteau County: Missouri Bureau of Geology and Mines, 2nd Series, v. 3, p. 63-68.
- Wanles, H. R., 1957, Geology and Mineral resources of the Beardstown, Glasford, Havana, and Vermont quadrangles, Illinois Geological Survey Bulletin 82, p. 83-113.
- Ward, C. R., 1977, Mineral matter in the Springfield-Harrisburg (No. 5) Coal Member in the Illinois Basin: Illinois State Geological Survey Circular 498, 35 p.
- Wedge, W. K., Bhatia, D. M. S., and Rueff, A. W., 1976, Chemical analyses of Missouri Division of Geology, Report of Investigations No. 60, 36 p.
- White, D. E., 1957, Magmatic, connate, and metamorphic waters: Geological Society of America Bulletin, v. 68, p. 1659-1682.
- White, D. E., 1968, Environments of generation of some base-metal ore deposits: Economic Geology, v. 63, p. 301-335.
- White, D. E., Hem, J. D., and Waring, G. A., 1963, Chemical composition of subsurface waters, Ch. F. in Data of Geochemistry, U.S. Geological Survey Professional Paper 440-F, Washington, p. F1-F68.
- Willman, H. B., Atherton, Elwood, Bushback, T. C., Callison, Charles, Frye, John C., Hopkins, M. E., Lineback, Jerry A., and Simon, Jack A., 1975, Handbook of Illinois Stratigraphy: Illinois State Geological Survey Bulletin 95, 261 p.
- Yarger, H. L., and Jarjur, S. Z., 1972, Gravity and magnetic survey of an abandoned lead and zinc mine in Linn County, Kansas: Kansas Geological Survey Bulletin 204, part 2, 13 p.
- Zubovic, P., Stadnichenko, T., and Sheffey, 1964, Distribution of minor elements in coal beds of the Eastern Interior region: U.S. Geological Survey Bulletin 117-A, 58 p.
- Zubovic, P., 1960, Minor element content of coal from Illinois Beds 5 and 6 and their correlations in Indiana and western Kentucky: U.S. Geological Survey open-file report, 79 p.

APPENDIX: LOCATIONS OF FIELD

This is a listing of sites visited during field investigations. Sphalerite was not found at all of these locations. If sphalerite was collected from a coal seam at these sites it is noted.

Arkansas

Sebastian County
SE $\frac{1}{4}$, Sec. 3, T4N, R32W
C and E Coal Company (no sphalerite)

Sebastian County
NE $\frac{1}{2}$, Sec. 17, T6N, R30W
Outcrop (no sphalerite)

Franklin County
Sec 32, T9N, R27W
Wilco Energy Company
Turkey Run Mine (no sphalerite)

Logan County
NE $\frac{1}{2}$, Sec. 35, T8N, R26W
Taten Mine (no sphalerite)

Johnson County
SW $\frac{1}{2}$, Sec. 17, T10N, R25W
Peabody Coal Company
Ozark Mine (no sphalerite)

Johnson County
Sec. 36, T10N, R23W
Outcrop (no sphalerite)

Johnson County
SE $\frac{1}{2}$, NE $\frac{1}{2}$, Sec. 3, T10N, R25W
Horsehead Lake Spillway (no sphalerite)

Illinois

Stark County
SE, NW, NW, Sec. 11, T13N, R6E
Midland Coal Company
Allendale Mine (sphalerite)

Illinois (continued)

Knox County

NW, NE, NE, Sec 10, T12N, R3E

Midland Coal Company

Mecco Mine (western pit) (sphalerite)

Knox County

NW $\frac{1}{4}$, Sec. 12, T12N, R3E

Midland Coal Company

Mecco Mine (eastern pit) (sphalerite)

Peoria County

NW, SW, NE, Sec. 28, T9N, R5E

Midland Coal Company (western pit) (sphalerite)

Peoria County

Sec. 24, T9N, R6E

Midland Coal Company

Edwards Mine (sphalerite)

Fulton County

NE $\frac{1}{4}$, Sec. 13, T7N, R3E

Consolidation Coal Company

Norris Mine (sphalerite)

Fulton County

NW, SW, NW, Sec. 6, T6W, R5E

Freeman United Coal Mining Company

Buckheart Mine (northern pit) (sphalerite)

Fulton County

NW $\frac{1}{4}$, Sec. 6, T5N, R4E

Freeman United Coal Mining Company

Buckheart Mine (southern pit) (sphalerite)

Fulton County

SW $\frac{1}{4}$, Sec. 15, T4N, R1E

AMAX Coal Company

Sun Spot Mine (sphalerite)

Macoupin County

NW $\frac{1}{4}$, Sec. 23, T12N, R6W

Freeman United Coal Mining Company

Crown No. 2 Mine (sphalerite)

St. Clair County

NE, SE, Sec. 29, T3S, R6W

Peabody Coal Company

River King Surface Mine No. 3 (no sphalerite)

Illinois (continued)

Randolph County
Sec. 28, T5S, R6W
Consolidation Coal Company
Burning Star No. 3 Mine (no sphalerite)

Perry County
Sec. 2, T6S, R4W
Consolidation Coal Company
Burning Star No. 4 Mine (no sphalerite)

Perry County
Sec. 12, T5S, R3W
Consolidation Coal Company
Buring Star No. 2 Mine (no sphalerite)

Perry County
Sec. 8, T6S, R4W
Southwestern Illinois Coal Corporation
Captain Mine (no sphalerite)

Williamson County
Sec. 17, T9S, R4E
AMAX Coal Company
Delta Mine (no sphalerite)

Williamson County
Sec. 16, T10S, R5E
Peabody Coal Company
Will Scarlet Mine (no sphalerite)

Gallatin County
Sec. 9, T10S, R8E
Peabody Coal Company
Eagle No. 2 Surface Mine (sphalerite)

Brown County
Sec. 13, T1N, R4W
Great American Energy Corporation
Big Eagle No. 1 Mine (sphalerite)

Indiana

Green County
Sec. 19, T8N, R7W
Peabody Coal Company
Latta Mine (no sphalerite)

Indiana (continued)

Dike County
 SE $\frac{1}{4}$, Sec. 6, T1S, R7W
 Old Ben Coal Company
 Old Ben No. 2 Mine (no sphalerite)

Iowa

Polk County
 SE, NE, NE, Sec. 4, T79N, R25W
 Core CP 47-9

Wapello County
 NW, SE, NE, Sec. 36, T72N, R15W
 Core CP 28-15 (sphalerite)

Davis County
 NE, SE, Sec. 1, T67N, R14W
 Core CP 24-17 (sphalerite)

Monroe County
 Lovillia Coal Company
 Underground mine--refuse pile (sphalerite)

Kansas

Linn County
 P and M Coal Company
 Midway Mine (sphalerite)

Bourbon County
 SW $\frac{1}{4}$, Sec. 28, T26S, R25W
 Bradbury Brother's Mine No. 1 (sphalerite)

Bourbon County
 Sec. 25, T26S, R25W
 Bill's Coal Company (sphalerite)

Missouri

Putnam County
 Sec. 8, T35N, R19W
 Missouri Mining Company (sphalerite)

Missouri (continued)

Howard County
NW $\frac{1}{4}$, Sec. 8, T51N, R14W
Howard County Coal Company (sphalerite)

Howard County
NE $\frac{1}{4}$, Sec. 28, T51N, R14W (sphalerite)

Henry County
Sec. 24, T40N, R28W
Peabody Coal Company
Power Mine (sphalerite)

Bates County
NW, SE, Sec. 33, T41N, R33W
P and M Coal Mining Company
Midway Mine (sphalerite)

Vernon County
Sec. 31, T35N, R33W
Bill's Coal Company
Ft. Scott Mine (sphalerite)

Oklahoma

McIntosh County
NW, SE, Sec. 22, T12N, R17E
Alpine Coal Company
Mine No. 2 (no sphalerite)

Muskogee County
SW $\frac{1}{4}$, Sec. 31, T11N, R20E
Carboner Coal Company
Porum Mine (no sphalerite)

Haskell County
Sec. 5, T9N, R21E
Garland Coal and Mining Company
Stigler #9 Mine (no sphalerite)

Haskell County
Sec. 31, T9N, R21E
Producers Energy Corporation
Quail Creek Mine No. 11 (no sphalerite)

Oklahoma (continued)

Haskell County

NW, SW, Sec. 13, T8N, R22E

Great National Coal Corporation

McCurtain Mine No. 2 (no sphalerite)

Le Flore County

NW, SW, Sec. 13, T8N, R23E

Dahlgren Contracting Company

Milton Mine (no sphalerite)

Latimer County

SE, NW, Sec. 2, T6N, R22E

Farrell-Cooper Mining Company (no sphalerite)

Pittsburg County

SE $\frac{1}{4}$, Sec. 1, T8N, R17E

Westhoff Brothers Mine (no sphalerite)

VITA

James Collins Cobb was born in Urbana, Illinois. He received his Bachelor of Science degree with a major in geology from the University of Illinois in 1971. As an undergraduate he was employed as a technical assistant at the Illinois State Geological Survey. He obtained his Master of Science degree from Eastern Kentucky University in 1974. In 1974 he joined Foster and Associates of Beirut, Lebanon, as a senior geologist in charge of field operations and basin analysis at Kufra and Sarir, Libyan Arab Republic. He carried out geophysical and geological investigations in the Sahara Desert, Lebanon, and Syria. Foster and Associates operations were suspended because of civil war in Lebanon. In October, 1975, he joined the Coal Section of the Illinois State Geological Survey as a research associate. He obtained a U.S. Geological Survey grant from the Branch of Eastern Mineral Resources to support his thesis research on the geology and geochemistry of epigenetic minerals in coal. In 1980 he joined the Coal Section of the Kentucky Geological Survey as a senior geologist.

The following is a list of his publications:

- Cobb, J. C., J. D. Steele, C. G. Treworgy, and Jim F. Ashby, 1980, The abundance of zinc and cadmium in sphalerite-bearing coals in Illinois: Illinois Geological Survey Industrial Minerals Note 74, 28p.
- Cobb, J. C., J. D. Steele, and J. F. Ashby, 1979, Sphalerite-bearing coals in the central region of the United States (abs.): Ninth International Congress of Carboniferous Stratigraphy and Geology Abstracts of Papers, Urbana, IL, p. 40.

- Cobb, J. C. and H. F. Krausse, 1979, Opening and mineralization of gash veins in coal, (abs.): Ninth International Congress of Carboniferous Stratigraphy and Geology Abstracts of Papers, Urbana, IL, p. 40.
- Cobb, J. C., J. M. Masters, C. G. Treworgy, and R. J. Helfinstine, 1978, Abundance and recovery of sphalerite and fine coal from mine waste in Illinois: 6th Mineral Waste Utilization Symposium, Illinois Institute of Technology and U.S. Bureau of Mines, 22p.
- Cobb, James C. and Gordon S. Fraser, Application of sedimentology to development of sand and gravel resources in McHenry and Kane Counties, Northwestern Illinois: Illinois Geological Survey Industrial Mineral Notes (in preparation).
- Cobb, James C., John D. Steele, Colin G. Treworgy, James F. Ashby, and S. J. Russell, 1978, The geology of zinc in coals of the Illinois Basin: Final Report to the U.S. Geological Survey, U.S. Department of the Interior Grant 14-08-0001-6-249, 69p.
- Cobb, James C. and Suzanne J. Russell, 1976, Sphalerite mineralization in coal seams of the Illinois Basin: Geological Society of American 1976 Annual Meetings abstracts with programs, vol. 8, no. 6, p. 816.
- Cobb, James C., 1975, Scientific findings on the geology and groundwater reservoir of the Sarir Basin: in Final Report of Activities of Foster and Associates for Kufra and Sarir Projects, Libyan Arab Republic, J. W. Foster (ed.), Foster and Associates, Beirut, Lebanon.
- Fraser, Gordon W. and James C. Cobb, 1975, Sedimentation along the margin of a late Wisconsinan moraine; Application to the origin of pebbly mudstones: Geological Society of America 1975 Annual Meetings, abstracts with programs, vol. 7, no. 7, p. 1078.
- Cobb, James C., and Norman C. Hester, 1974, The physical and chemical properties of Pike County chert gravel: Illinois Geological Survey Industrial Mineral Note 59, 21p.
- Cobb, James C., 1974, Sedimentary structures and textures in a Pleistocene outwash plain of northeastern Illinois: Geological Society of America 1974 North-Central Section Meetings, abstracts with programs, vol. 6, no. 6, p. 500.
- Fraser, Gordon S. and James C. Cobb, 1974, Deformed sediments associated with outwash deposits in the Woodfordian (Pleistocene) of Northeastern Illinois: Geological Society of America 1974 North-Central Section Meetings, abstracts with programs, vol. 6, no. 6, p. 508.

