

STATE OF OHIO
DEPARTMENT OF NATURAL RESOURCES
DIVISION OF GEOLOGICAL SURVEY
Horace R. Collins, Chief

Report of Investigations No. 104

**THE OCCURRENCE OF SULFIDE
AND ASSOCIATED MINERALS IN OHIO**

by

George Botoman
and
Ronald D. Stieglitz

Columbus

1978



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THE OCCURRENCE OF SULFIDE AND ASSOCIATED MINERALS IN OHIO

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and
Ronald D. Stieglitz**

ABSTRACT

This report provides information about the location and occurrence of sulfide minerals in Ohio. The data have been obtained through surface field work and subsurface studies by the Ohio Division of Geological Survey and from reports in the literature.

The sulfide and associated minerals were classified on the basis of geographic and stratigraphic locations and were described with special emphasis on mineral-bearing structure and petrographic characteristics of the host rocks. Sulfide minerals are particularly abundant in Ordovician, Silurian, and Devonian bioclastic carbonate rocks in the areas along the Cincinnati and Findlay arches. The mineralogy of sulfide minerals is relatively simple—pyrite-marcasite-sphalerite, and in some places galena; this resembles the Mississippi Valley type of mineralization.

INTRODUCTION

The central part of the United States is a relatively stable area characterized by basins and arches (fig. 1). The rocks of this area are nearly flat-lying Paleozoic sedimentary rocks that in places have been gently warped. Ohio forms a portion of the northeastern part of this stable platform of North America. Structure contours on the Precambrian basement show that the Cincinnati and Findlay arches and the Indiana-Ohio platform are about 3,000 to 14,000 feet higher than the Appalachian, Illinois, and Michigan Basins. Within Ohio, rocks representing all of the Paleozoic periods are present (fig. 2); however, in most places, Paleozoic rocks are covered by Pleistocene or younger material.

Presently very little is known about sulfide mineralization in Ohio. No systematic search has been conducted, and only scattered mineral accumulations have been encountered at the surface or in wells drilled for oil and gas exploration. In nearby states there are several major mining districts in which rocks of age and type similar to those in Ohio produce zinc, lead, barite, and fluorite (fig. 2). South of Ohio, in Kentucky and Tennessee, significant mineralization occurs in the Paleozoic formations (Oder and Ricketts, 1961; Jolly and Heyl, 1964). North of Ohio, in Ontario, Canada, important ore deposits are located in the basement rocks near the Grenville front, which in Ohio may be represented by the trend of the Cincinnati and Findlay arches.

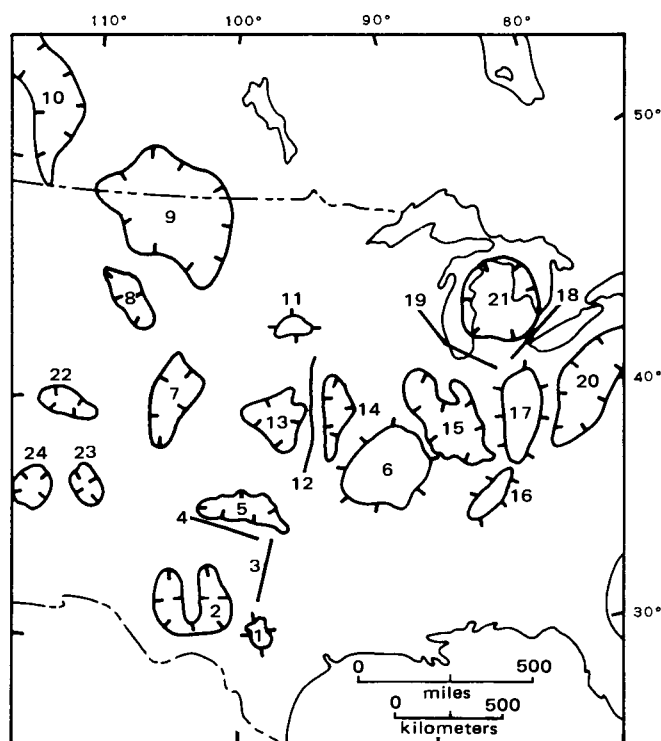
Possibly the first mention of unusual minerals in the

state was in several reports pointing out the occurrence of celestite, a strontium sulfate mineral, in the rocks along the Lake Erie shoreline (Bigsby, 1822; Delafield, 1822; Troost, 1822). Much of the interest in sulfide minerals has centered around the collection of specimens for display; little regard has been given to regional distribution patterns or geologic factors. Hayes (1969) cataloged, in a general way, the locations of many types of minerals in Ohio. Botoman (1975) discussed the regional geologic relationships and the potential for mineralization along the Cincinnati Arch in Ohio.

This report is an introduction to the sulfide minerals and a guide to the known occurrences within the state. It is hoped the report will help professional geologists, engineers, and others who are seeking information concerning Ohio's sulfide minerals. Information has been obtained through field work and subsurface studies conducted by Ohio Division of Geological Survey personnel, and an effort has been made to include all available literature data relating to the occurrence of sulfide minerals in Ohio.

AREAS OF OCCURRENCE OF SULFIDE MINERALS IN OHIO

Sulfide minerals are found in various generally small amounts in the carbonate rocks of western Ohio and in a few localities in eastern Ohio (fig. 3). Sulfides are widely distributed throughout the Paleozoic sedimentary rocks of



- | | |
|-----------------------|-----------------------|
| 1. Llano uplift | 13. Salina basin |
| 2. Permian basin | 14. Forest City basin |
| 3. Bend arch | 15. Illinois basin |
| 4. Wichita uplift | 16. Nashville dome |
| 5. Anadarko basin | 17. Cincinnati arch |
| 6. Ozark uplift | 18. Findlay arch |
| 7. Denver basin | 19. Kankakee arch |
| 8. Powder River basin | 20. Appalachian basin |
| 9. Williston basin | 21. Michigan basin |
| 10. Alberta basin | 22. Uinta basin |
| 11. Sioux uplift | 23. San Juan basin |
| 12. Nemaha uplift | 24. Black Mesa basin |

FIGURE 1.—Major basins and highs of central United States (after Matthews, 1974, fig. 5.2).

the state. The most common sulfide minerals are pyrite (FeS_2) and marcasite (FeS_2), which probably occur to some extent in every sedimentary formation in Ohio. The occurrences reported here are included for completeness and because their mode of formation or association with other minerals indicates an unusual situation. Sphalerite (ZnS), galena (PbS), and wurtzite (ZnS) also occur and are the main interest of this report. Associated minerals include the carbonates calcite (CaCO_3) and dolomite [$\text{CaMg}(\text{CO}_3)_2$], the sulfates celestite (SrSO_4), anhydrite (CaSO_4), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), barite (BaSO_4), and melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), and the halide fluorite (CaF_2). Small amounts of smithsonite (ZnCO_3) and hydrozincite [$2\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2$] have been noted as replacements of sphalerite. Wells drilled into the metamorphic and igneous basement rocks have encountered, in addition to pyrite, small amounts of pyrrhotite (Fe_7S_8), chalcopyrite (CuFeS_2), arsenopyrite (FeAsS), and scheelite (CaWO_4).

Little has been published about the occurrence of sulfide minerals in Ohio. Most occurrences have been reported from southwestern Ohio in the region of the Serpent Mound cryptoexplosion structure. There is similar sulfide mineralization in the area of the Findlay arch in northwestern Ohio.

Age, distribution, and manner of occurrence of sulfide mineralization in the Paleozoic formations of Ohio have important implications—metal source, occurrence, and mode of emplacement—for Mississippi Valley-type ore deposits.

The metamorphic, volcanic and metasedimentary rocks of Ohio appear to be as favorable for accumulation of sulfide minerals as those which contain known economic deposits in Ontario and Quebec, Canada.

Sulfide mineralization is found principally in northwestern, southwestern, and eastern Ohio. Knowledge of local geology and structure is essential for an understanding of the distribution of mineralized localities.

NORTHWESTERN OHIO

The most prominent geologic features in western Ohio are the Cincinnati and Findlay arches, which trend north-northeast to south-southwest through the length of the state. The Findlay arch is crossed in Lucas, Wood, Hancock, and Hardin Counties by a faulted monocline known as the Bowling Green structure, which trends almost north-south (fig. 2).

Morrison (1935) and Howard (1959) described the fluorite and celestite at Clay Center, Ottawa County, and also mentioned the occurrence of pyrite, marcasite, sphalerite, and galena. Stieglitz (1974) noted the occurrence of sparry white dolomite associated with sulfide mineralization (sphalerite and pyrite) in some of the wells which penetrated the Trenton Formation in northwestern Ohio. Botoman (1975) discussed a variety of structural, stratigraphic, and other traps favorable for sulfide accumulation. Botoman and Faure (1976) made the first investigation into the composition of the sulfur isotopes of the sulfides and sulfates of northwestern Ohio; the study concluded that sphalerite and galena were probably formed at temperatures between 43° and 63°C .

Sulfide minerals have been identified in numerous quarries in the Silurian and Devonian carbonate rocks and in the subsurface in Ordovician limestones and dolomites. The mineral composition is simple, and amounts are relatively small. Pyrite and marcasite, followed by sphalerite and galena, are the most common minerals. Calcite, celestite, and fluorite are the principal associated minerals. The minerals fill or line open spaces, vugs, fissures, or joints, or in some places replace fossils.

The Precambrian basement rocks penetrated by the Ketring well, Hardin Township, Lucas County, yielded pyrite, chalcopyrite, and traces of arsenopyrite (Gonterman, 1973).

SOUTHWESTERN OHIO

Sulfide mineralization in this area is centered on the Serpent Mound cryptoexplosion structure, which is located approximately 50 miles east of the junction of the Kankakee and Cincinnati arches. The sulfide minerals occur primarily in the Ordovician, Silurian, and Devonian limestones and dolomites (Heyl and Brock, 1962; Heyl, 1968; Reidel, 1972, 1975; Jacobs, 1971; Stryker, 1971). In general the units are bedded, and have many mud cracks, ripple marks, and reeflike structures which change laterally into biohermal and biostromal beds.

Heyl and Brock (1962) described the occurrence of sphalerite, hydrozincite, and smithsonite in the Greenfield-Peebles dolomite. Sphalerite was emplaced in gray dolomite

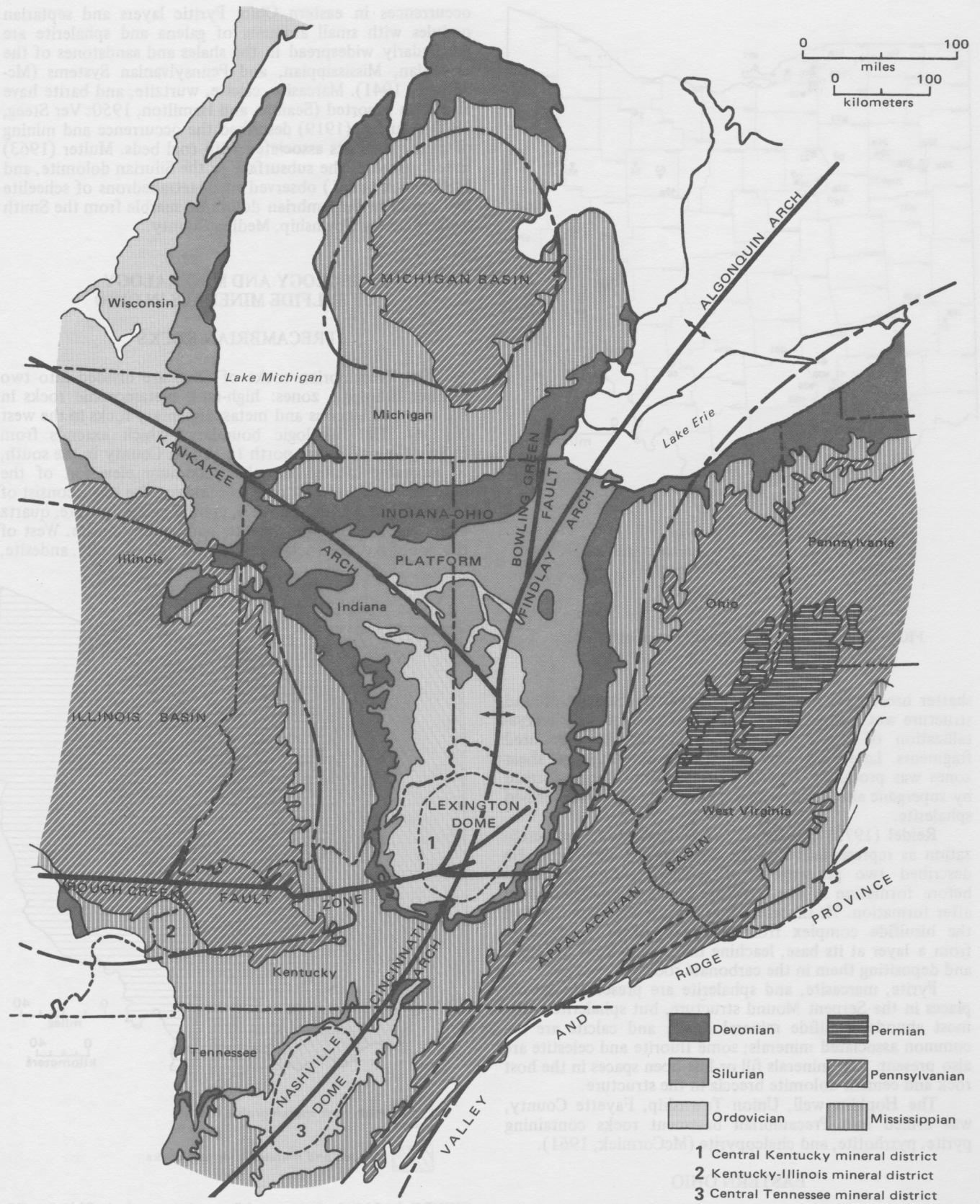


FIGURE 2.—Sketch map showing regional structural features and areal distribution of Ordovician through Permian rocks in Ohio and vicinity.

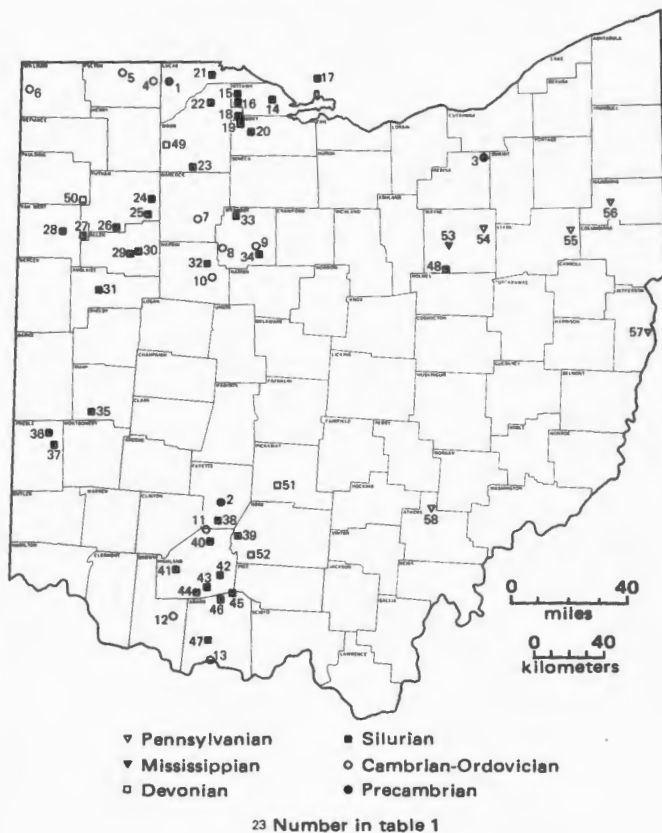


FIGURE 3.—Locations of the sulfide minerals in Ohio.

shatter breccia formed at the time that the Serpent Mound structure was formed. The breccia was cemented by recrystallization of the dolomite grains along the brecciated fragments. Later, a second set of fractures and small shear zones was produced. Hydrozincite and smithsonite formed by supergene alteration, whereas hypogene processes formed sphalerite.

Reidel (1972) considered the Serpent Mound mineralization as representative of the Mississippi Valley type. He described two generations of sphalerite, one deposited before formation of the structure and a second deposited after formation. He theorized that surface water transported the bisulfide complex from the Ohio Shale, particularly from a layer at its base, leaching the metals from the shale and depositing them in the carbonate rocks.

Pyrite, marcasite, and sphalerite are present in several places in the Serpent Mound structure, but sphalerite is the most abundant sulfide mineral. Chert and calcite are the common associated minerals; some fluorite and celestite are also present. The minerals fill or line open spaces in the host rock and cement dolomite breccia in the structure.

The Hopkins well, Union Township, Fayette County, was drilled into Precambrian basement rocks containing pyrite, pyrrhotite, and chalcopyrite (McCormick, 1961).

EASTERN OHIO

There are few publications dealing with sulfide mineral

occurrences in eastern Ohio. Pyritic layers and septarian nodules with small amounts of galena and sphalerite are particularly widespread in the shales and sandstones of the Devonian, Mississippian, and Pennsylvanian Systems (McAllister, 1941). Marcasite, calcite, wurtzite, and barite have also been reported (Seaman and Hamilton, 1950; Ver Steeg, 1940). Tucker (1919) described the occurrence and mining of pyrite deposits associated with coal beds. Multer (1963) noted galena in the subsurface in the Silurian dolomite, and McCormick (1961) observed small tetrahedrons of scheelite and pyrite in Precambrian dolomitic marble from the Smith well, Hinckley Township, Medina County.

GEOLOGY AND MINERALOGY OF SULFIDE MINERALS IN OHIO

PRECAMBRIAN ROCKS

The Precambrian rocks of Ohio are divided into two distinct lithologic zones: high-rank metamorphic rocks in the east and igneous and metasedimentary rocks in the west (fig. 4). The lithologic boundary, which extends from Fulton County in the north to Brown County in the south, is generally located on the maximum elevation of the basement surface. East of the boundary, the rocks consist of amphibolite, marble, hornfels, granite-gneiss, granite, quartz monzonite, monzonite, syenite, and gabbro-diorite. West of the boundary, the rock types are rhyolite-trachyte, andesite,

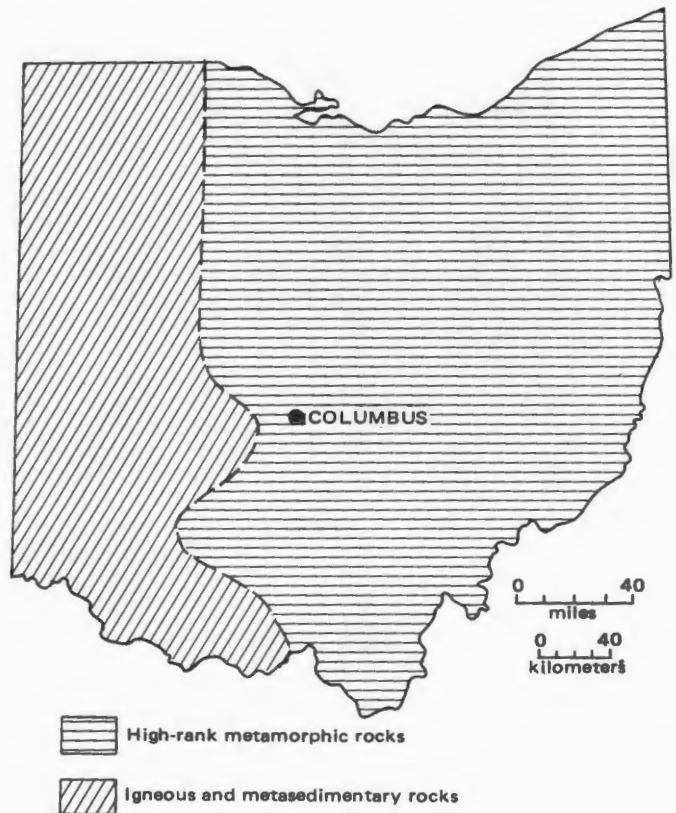


FIGURE 4.—Lithologic zones of Precambrian rocks in Ohio (modified from Hofmann, Faure, and Janssens, 1972).

TABLE 1.—Locations used in sulfide mineralization study

Age	Map number	County	Township(s)	Identification ¹	Group or formation(s)	Minerals
Precambrian	2	Fayette	Union	Kewanee #1 Hopkins (P-1, S-750)	Metamorphic rocks group	Pyrite, chalcopyrite, pyrrhotite
	1	Lucas	Harding	Liberty #1 Ketring (P-60, S-2811)	Metamorphic rocks group	Chalcopyrite, arsenopyrite, pyrite
	3	Medina	Hinckley	Wiser #1 Smith (P-1143, S-819)	Metamorphic rocks group	Pyrite, scheelite, quartz
Cambrian(?)—Ordovician	13	Monroe	Adams	Cominco American #1 Hughes (P-7, S-2405)	Knox	Sphalerite, barite, calcite, chalcopyrite?
	12	Brown	Jackson	Cominco American #1 Rockey (P-5, S-2507)	Knox	Sphalerite, barite
	5	Fulton	Chesterfield	Lorex #1 Reckner (P-39, S-2237)	Trenton	Sphalerite
	4		Fulton	Liberty #1 Slahunek (P-26, S-1811)	Knox	Sphalerite
	7	Hancock	Jackson	Ashland #1 Cotner (P-151, S-1649)	Wells Creek (Glenwood)	Sphalerite, pyrite
	10	Hardin	Dudley	McMahon-Bullington #1 Wolf (P-79, S-1231)	Knox	Sphalerite
	11	Highland	Fairfield	Cominco American CA-54 Swingley (P-6, S-2499)	Knox	Sphalerite
	6	Williams	Florence	Sohio #1 Lautzenheiser (P-47, S-2822)	Trenton	Sphalerite, dolomite, gypsum, calcite
	8	Wyandot	Jackson	Brinkerhoff #1 Fox (P-204, S-1511)	Knox	Sphalerite, pyrite
9		Pitt	White #1 Stubb (P-95, S-520)	Trenton	Pyrite, sphalerite, dolomite	
Silurian	45	Adams	Bratton, Franklin (also Brush Creek, Highland Co., Mifflin, Pike Co.)	Serpent Mound cryptoexplosion structure	Greenfield, Lilley-Peebles, Bisher, Brassfield	Pyrite, marcasite, sphalerite, calcite, fluorite
	46		Bratton	Measured section-OGS 14350	Brassfield	Sphalerite, calcite
	47		Tiffin	Measured section-OGS 12667	Brassfield	Sphalerite, calcite, barite
	29	Allen	Bath	National Lime & Stone Co. quarry	Tymochtee	Pyrite, sphalerite, fluorite, calcite
	30		Bath	Western Ohio Stone Co. quarry	Tymochtee	Pyrite, sphalerite, calcite
	31	Auglaize	Moulton	National Lime & Stone Co. quarry	Greenfield, Lockport	Sphalerite, calcite
	38	Fayette	Green	American Aggregates Corp., Blue Rock quarry	Greenfield	Sphalerite, pyrite, calcite
	32	Hardin	Pleasant	Hardin Quarry Co. quarry	Tymochtee	Sphalerite, fluorite
	44	Highland	Concord	Measured section-OGS 9732	Brassfield	Sphalerite, calcite
	40		Fairfield	G. E. Havens Limestone Co. quarry	Greenfield	Sphalerite, quartz, calcite
	41		Hamer	Davon, Inc., Highland Plant quarry; measured section-OGS 13610	Brassfield	Sphalerite, barite, pyrite, calcite
	43		Jackson	Measured section-OGS 13609	Brassfield	Sphalerite, calcite
	42		Marshall	Marshall quarry	Lilley-Peebles	Sphalerite, calcite
	21	Lucas	Waynesfield	Maumee Stone Co. quarry	Greenfield, Lockport	Sphalerite, pyrite, celestite, calcite, fluorite
35	Miami	Union	Measured section-OGS 12771	Brassfield	Sphalerite, calcite	
15	Ottawa	Allen	Kraemer Stone Co., White Rock quarry	Lockport	Pyrite, marcasite, sphalerite, galena, fluorite, calcite, celestite, gypsum	

TABLE 1.—Locations used in sulfide mineralization study—Continued

Age	Map number	County	Township(s)	Identification ¹	Group or formation(s)	Minerals
Silurian	14	Ottawa (cont.)	Benton	Maumee Stone Co. quarry	Lockport	Sphalerite, fluorite, calcite, celestite
	16		Clay	Old Genoa quarry	Lockport	Sphalerite, fluorite, calcite, gypsum
	17		Put-in-Bay (South Bass Island)	Crystal Cave	Tymochtee	Celestite, calcite
	36	Preble	Harrison	Old Marble Cliff; Lewisburg quarry; measured section-OGS 15756	Brassfield	Sphalerite, pyrite
	37		Twin	Measured section-OGS 15772	Brassfield	Sphalerite, calcite
	24	Putnam	Blanchard	Ottawa Stone Co., Inc., quarry	Raisin River, Tymochtee	Pyrite, sphalerite, fluorite, calcite
	25		Riley, Pleasant	Putnam Stone Co., Inc., quarry	Raisin River, Tymochtee	Pyrite, marcasite, sphalerite, fluorite, calcite
	26		Sugar Creek	National Lime & Stone Co. quarry	Raisin River, Tymochtee	Sphalerite, calcite
	39	Ross	Buckskin	Old Rucker quarry (Napper, 1917)	Greenfield	Sphalerite, quartz
	20	Sandusky	Madison	Charles Pfizer & Co. quarry	Lockport	Galena, fluorite, celestite
	19		Woodville	Martin Marietta Chemicals, Refractories Div. quarry	Lockport	Sphalerite, fluorite, calcite
	18		Woodville	Ohio Lime Co. quarry	Lockport	Galena, fluorite, celestite
	28	Van Wert	Ridge	Ridge Township Stone quarry	Tymochtee	Pyrite, sphalerite, fluorite
	27		Washington	Delphos Quarries Co. quarry	Tymochtee	Sphalerite, fluorite, calcite
	48	Wayne	Franklin	Blood #1 Schlabach (P-656); Blood #2 Schmidt (P-636); (Multer, 1963)	Lockport	Pyrite, galena, anhydrite
	23	Wood	Henry	France Stone Co. quarry	Tymochtee	Pyrite, marcasite, sphalerite, fluorite, calcite, gypsum
	22		Perrysburg	Maumee Stone Co. quarry	Greenfield, Lockport	Galena, sphalerite, fluorite, calcite, celestite
	33	Wyandot	Crawford	National Lime & Stone Co. quarry	Greenfield, Lockport	Sphalerite, celestite
34	Pitt		C. M. McCarthy quarry	Raisin River, Tymochtee	Sphalerite, gypsum, calcite	
Devonian	50	Paulding	Crane	Maumee Stone Co., Junction quarry	Dundee, Detroit River	Sphalerite, fluorite, calcite
	51	Pickaway	Perry	F. H. Brewer Co. quarry (formerly Hal-Mar Stone Co. quarry)	Columbus Limestone	Pyrite, marcasite, sparry dolomite
	52	Ross	Paxton	Outcrop near Bainbridge (Knille and Gibbs, 1940)	Ohio Shale	Marcasite, melanterite
	49	Wood	Milton	Pugh Quarry Co. quarry	Dundee, Detroit River	Pyrite, marcasite, sphalerite, fluorite, calcite, celestite
Mississippian-Pennsylvanian-Permian	58	Athens	Trimble	Old Glouster brick quarry (Seaman and Hamilton, 1950)	Conemaugh	Wurtzite in clay-ironstone concretions
	56	Jefferson	Cross Creek	Outcrop near Steubenville (Seaman and Hamilton, 1950)	Conemaugh	Wurtzite in clay-ironstone concretions
	57	Mahoning	Ellsworth	Outcrop near Ellsworth (Greene, 1935)		Pyrite, sphalerite, calcite, barite
	55	Stark	Washington	R. Immel coal mine (Rice, 1948)	Allegheny	Wurtzite in coal
	54	Wayne	Baughman	Outcrop near Marshallville (Ver Steeg, 1942)	Pottsville	Pyrite, galena, sphalerite, calcite
	53		Wooster	Outcrop near Wooster (Ver Steeg, 1940)	Cuyahoga	Pyrite, galena, sphalerite, calcite

¹ Quarries identified by operator name and/or name of quarry; oil and gas wells identified by operator, land owner, permit number (P), and sample number (S); measured sections identified by Ohio Division of Geological Survey (OGS) stratigraphic section file number; outcrop occurrences identified by nearest city and reference.

TABLE 2.—*Basement rock types*

Kind of parent rock	Grade of metamorphism	Rock types
Igneous	None	Rhyolite-trachyte, andesite, granite
Sedimentary	Low-rank	Argillite, dolomitic marble, green slate, quartzite
Metamorphic	Plutonic	Gabbro-diorite, monzonite, quartz monzonite, syenite, granite, granite gneiss
	High-rank	Hornfels, marble, amphibolite

granite, and metasedimentary rocks in a series consisting of argillite, green slate, dolomitic marble, and quartzite (table 2).

From the high-rank metamorphic rock group, Gonterman (1973) described an occurrence of sulfide mineralization in amphibolite rocks in the Ketring well. The sulfide minerals are pyrite and chalcopyrite; traces of arsenopyrite occur as subhedral monomineralic chips and very rarely as small thin veins. Gonterman attributed the presence of sulfide to postdepositional hydrothermal activity. McCormick (1961) described the occurrence of sulfide minerals in rocks of the amphibolite facies from the Hopkins well. Pyrite and the iron oxide minerals magnetite and ilmenite are concentrated at intervals, especially near the amphibolite-marble boundary. From the same well, McCormick described vuggy dolomite marble containing inclusions of apatite and zircon; there are also inclusions of pyrite and pyrrhotite occurring as anhedral grains ranging from 0.03 to 0.59 mm in diameter and associated with diopside and garnet. As much as 9 percent of the samples is pyrrhotite. Pyrrhotite and chalcopyrite, filling interstices between diopside grains, also appear in hornfels rocks from the Hopkins well. Pyrrhotite may constitute as much as 5 percent of these rocks. These sulfides were deposited from hydrothermal emanations rich in sulfur and iron (McCormick, 1961).

McCormick (1961) also described quartz which contained small tetrahedrons of scheelite from the Smith well. Trace amounts of pyrite in grains ranging from 0.02 to 0.003 mm in diameter were disseminated through the rock.

Sulfide minerals are rare in igneous-group rocks of western Ohio, although occurrences of pyrite associated with chalcopyrite have been described in some wells. No important sulfide mineral zones have been reported from the metasedimentary or volcanic rock groups. That sulfide minerals may exist in the metasedimentary rock sequence is evidenced by the presence of limonite-after-pyrite pseudomorphs near the veins of crystalline silica in the recrystallized limestone and dolomite. No well has penetrated deeply into the igneous and metasedimentary rocks, and no important sulfide accumulations have been discovered at this time.

CAMBRIAN AND ORDOVICIAN ROCKS

In Ohio the Mt. Simon Sandstone unconformably

overlies Precambrian rocks and is composed of fine- to coarse-grained sandstone which is conglomeratic in places. In western Ohio the Mt. Simon is overlain by fine-grained glauconitic sandstone, containing some shale and dolomite and belonging to the Eau Claire Formation. In central and eastern Ohio, lateral equivalents of the Eau Claire are placed in the Rome and Conasauga Formations. The Rome is primarily sandstone and dolomite, whereas the Conasauga sediments are mostly fine clastics with some sandstones and carbonates. In a large area of the state these formations are overlain by sandstone of the Kerbel Formation. Above these predominantly clastic sediments is a thick sequence of dolomite, containing some sandstone beds and termed the Knox Dolomite. The Cambrian-Ordovician boundary apparently lies within the Knox, but cannot be placed consistently and with certainty in the subsurface. Janssens (1973) has studied these rocks in detail, and the information in the preceding discussion has been generalized from his report.

A major unconformity, which marks the upper limit of the Knox Dolomite in Ohio, is found within the Ordovician rocks of the Midcontinent. The Glenwood Formation of Middle Ordovician age overlies the Knox and is composed of siltstone, green shale, sandstone, and some dolomite. The gray to brown lithographic limestones of the Black River Limestone are found above the Glenwood and are in turn succeeded by the bioclastic limestone and dolomite of the Trenton Limestone. The Upper Ordovician rocks consist of a thick sequence of thin limestones and dark shales which become red at the top in the eastern part of the state.

Indications of sulfide mineralization in Ordovician rocks are relatively few and are confined to the Knox Dolomite and the Trenton Limestone. For the most part, these formations do not outcrop within the state except along the Ohio River in Hamilton, Clermont, and Brown Counties, where rocks at least partially equivalent to the Trenton Limestone are exposed. No occurrences of sulfide mineralization have been reported from the Cambrian rocks, although it is possible that some of the occurrences attributed to the Knox Dolomite may be below the Cambrian-Ordovician boundary.

The Knox Dolomite is, for the most part, a microcrystalline to medium-crystalline light-gray to very light-brown dolomite. Recorded sulfide minerals within the formation include sphalerite and questionable chalcopyrite associated with the sulfate mineral barite. The most common occurrences of the minerals are as vug fillings or, in association with crystalline calcite, as linings or fillings of fractures.

The Trenton Limestone is primarily microcrystalline to medium-crystalline fossiliferous brown limestone, although in places in northwestern Ohio all or part of the formation has been altered to porous medium-crystalline to coarsely crystalline light-brown dolomite (Stieglitz, in press). Pyrite is common as disseminated crystals or masses filling vugs. Occurrences of dark-brown to lemon-yellow sphalerite are few and are from restricted stratigraphic intervals. Associated minerals include calcite, gypsum, and particularly sparry white dolomite that in some places, along with massive pyrite, fills vugs and cements breccias.

SILURIAN ROCKS

In Ohio, Silurian rocks crop out along both sides of the Cincinnati and Findlay arches and continue to form the bedrock along the western border of the state. To the east,

Silurian rocks dip under younger rocks in the Appalachian Basin.

The oldest Silurian rocks in Ohio belong to the Cataract Group. In eastern Ohio the group is divided into the Cabot Head Formation and the underlying "Clinton"; "Clinton" is an informal term used by drillers. Westward, the predominantly sandstone and shale sequence thins, and the "Clinton" gives way to limestone and dolomite of the Brassfield Formation.

Some uncertainty exists in the classification of the rocks immediately above the Cataract Group; however, it appears that the sequence of shale, limestone, and dolomite can be placed in the Clinton Group. The carbonates of this group generally lack chert and hematite and so can be distinguished from carbonates of the Brassfield Formation. The Clinton Group ranges in thickness from about 30 feet in the west to 375 feet in the southeast.

In southwestern Ohio, rocks of the Niagaran Series are divided, in ascending order, into the Dayton, Rochester, Bisher, Lilley, and Peebles formations. The Dayton Formation is hard crystalline-appearing blue-gray limestone and dolomite ranging in thickness from 7 to 13 feet. The Rochester Shale is a soft calcareous and ferruginous red and blue-gray to light-green shale with a thickness ranging from 40 to 90 feet. The Bisher Formation is a silty argillaceous irregularly bedded dolomite that ranges in thickness from 25 to 85 feet. The Lilley Formation is a bedded argillaceous gray dolomite and dolomitic limestone ranging from 40 to 80 feet thick. The Peebles Formation is a thickly bedded crystalline buff to light-blue-gray dolomite with numerous fossil molds. The thickness ranges from 50 to 120 feet.

In northwestern Ohio the Niagaran Series rocks are included in the Lockport Group. For the most part, the group is composed of porous and vuggy light-gray to dark-blue-gray dolomite, which outcrops along an approximately north-south line from Clay Center, Ottawa County, to Carey, Wyandot County. Thickness ranges from 150 to 300 feet. Breccia, solution collapse cavities, and karst features are not uncommon.

Cayugan rocks in Ohio are placed in the Salina Group and the overlying Bass Islands Dolomite. In eastern Ohio the Salina Group contains thick evaporites and is subdivided into units A through G. In the northwestern part of the state the lower part of the Salina Group is divided into the Greenfield Formation and the Tymochtee Formation. The upper part of the group is generally undifferentiated. To the south and southeast, only the Greenfield and Tymochtee are present. The Greenfield is vuggy finely crystalline brown and dark-gray dolomite with some brown carbonaceous partings. Locally it contains breccia composed of fragments of stromatolites related to solution within stromatolitic reefs. Thickness of the Greenfield ranges from 3 to 100 feet. The Tymochtee Formation is composed of argillaceous dark-gray dolomite with brown shale and evaporites. The average thickness of the unit is 100 feet.

The uppermost Silurian Bass Islands Dolomite is buff-gray and brown dolomite. Locally it may have pelletal, oolitic, or brecciated texture. Thickness ranges from 60 to 150 feet, with an approximate average of 70 feet. This unit outcrops probably only in Ottawa County.

In north-central Ohio, occurrences of pyrite, marcasite, sphalerite, and galena in the upper part of the Lockport Dolomite and the lower part of the Greenfield Dolomite in and around the famous Clay Center, Ottawa County,

locality have long been known to mineral collectors (Morrisson, 1935; McAllister, 1943; Zodac, 1947; Montage, 1948; Howard, 1959). Galena has also been reported from the upper part of the Lockport Dolomite in the Moreland oil pool in Wayne County (Multer, 1963).

From summary field and hand-specimen observations and from binocular microscope study, three types of sulfide occurrences can be recognized: (1) vug and fissure fillings, (2) breccia cementation, and (3), of least importance, replacements of fossils. None of these occurrences has proved to be of economic importance.

Pyrite and marcasite are minor minerals in Silurian rocks in northwestern Ohio. They are most abundant in the Tymochtee Dolomite as disseminated crystals and/or in small lenticular bodies associated with fossils or silicified algal material. Pyrite and marcasite are also found lining cavities or associated with organic material in dolomites of the Lockport Group, Greenfield Dolomite, and Bass Islands Dolomite. Generally pyrite and marcasite can be observed only in fresh samples because these minerals alter rapidly to limonite.

Sphalerite is most commonly found in quarries in Sandusky, Ottawa, Wood, Putnam, Paulding, Wyandot, Hardin, and Auglaize Counties, in northwestern Ohio. The sphalerite is concentrated in the upper part of the Lockport Group and the lower part of the Greenfield Dolomite. The contact between these two units seems to be an erosional surface with evidence of karst development, breccias, vugs, and molds of fossils and evaporite minerals, all sites of mineral deposition. The sulfide-bearing rock is commonly vuggy and stromatolitic light-gray to dark-brown dolomite. A characteristic of the dolomitic country rock is abundant organic matter that may be disseminated throughout the rock or may be concentrated as void fillings. Sphalerite most commonly occurs with brown fluorite as fissure or open-space fillings; examples are the Charles Pfizer & Co. quarry in Sandusky County and the Kraemer Stone Co. quarry at Clay Center. Sphalerite crystals are also common adjacent to stylolites in the dolomite and were found along with filled vugs in the Old Genoa quarry in Ottawa County. Replacement phenomena are especially common in the more brecciated zones in the Maumee Stone Company quarries at Maumee, Lucas County, and Lime City, Ottawa County. Calcite, fluorite, celestite, and some barite are the common associated minerals.

In the upper Tymochtee Dolomite and in the Bass Islands Dolomite, sphalerite occurs as small isolated crystals or as groups of crystals, with fluorite and calcite filling vugs in the reef rocks.

Black, brown, and reddish-brown sphalerite was observed in hand specimens from northwestern Ohio. Black sphalerite, termed "black jack," is the most common.

Galena was found in four quarries in northwestern Ohio: Charles Pfizer & Co., Kraemer Stone Co., Maumee Stone Co., Wood County, and Ohio Lime Co., Sandusky County. The mineral appears as 1- to 5-mm cubic crystals in veins of brown fluorite and/or celestite, in dolomite sand which fills cavities, or in dark-green material lining vugs. Galena was found only in the highly mineralized zones of the upper Lockport dolomite.

The most comprehensive descriptions of sulfide mineralization in southwestern Ohio are of the area of the Serpent Mound cryptoexplosion structure (Heyl and Brock, 1962; Reidel, 1972). Mineralization is present from the Brassfield

Formation to the Greenfield Formation, but is particularly concentrated in the Peebles and Greenfield Formations. The country rock is commonly dense gray to dark-brown dolomite derived from reef material and thin-bedded dolomite containing much organic matter. Sulfide minerals, particularly sphalerite, fill open spaces in fault breccia and replace some of the fine matrix (Reidel, 1972). Reidel found two colors of sphalerite, yellow and black, in hand specimens. In thin sections, several combinations of colors occur. It is important to note that the sphalerite is almost always associated with limonite, calcite, and quartz. Napper (1917) reported disseminated sphalerite associated with quartz-lined or quartz-filled cavities within the Greenfield dolomite in the abandoned Rucker quarry in Ross County.

Numerous minor occurrences of sulfide minerals have been reported from the Brassfield Formation in southwestern Ohio. Rogers (1936, p. 93) described crystals of sphalerite and calcite within the formation near Belfast, Highland County. Other occurrences shown on the map are recorded in measured sections or in field and sampling notes in the open files of the Division of Geological Survey. The sphalerite is generally found as disseminated crystals or in a few places, as veins within a fossiliferous fine- to medium-grained light-gray to gray limestone. Coarsely crystalline calcite and pyrite are the commonly associated minerals; barite and chert are important locally.

In the Lilley and Peebles rocks, sphalerite has been found in the Marshall quarry, Highland County, in open-textured vuggy black dolomite with asphaltic impregnation. Sphalerite in this dolomite has been observed filling fissures or as small lenticular masses up to several inches long and an inch thick. The sphalerite ranges from brown to black and is intimately associated with asphalt.

Sphalerite has been observed in the Greenfield Dolomite in two other quarries outside the Serpent Mound area. In the Blue Rock quarry in Fayette County, sphalerite occurs in a bed of dark-gray dolomite which is overlain by finely crystalline blue to brown dolomite. The sphalerite is yellow brown, is associated with chert and quartz, and commonly fills or lines open spaces in a zone of brecciation. In the Havens quarry in Highland County, the mineral is also present in a bed of gray-yellow dolomite located in the upper part of the quarry. A comparatively fresh exposure was found near a small patch of isolated muck as a lens 1 foot wide and 9½ inches thick; here the sphalerite is associated with chert. The sphalerite is honey yellow, and the chert is white, in contrast to the black organic material and asphalt. Rogers (1936, p. 114) reported aggregates of crystalline sphalerite from a quarry near Samantha, Highland County.

DEVONIAN ROCKS

During Early and Middle Devonian time, the Cincinnati arch was a positive feature separating the Appalachian, Illinois, and Michigan Basins. Erosion and/or lack of deposition resulted in the absence of Lower and some Middle Devonian rocks along the crest of the arch. Deeper in the Appalachian Basin in eastern Ohio, the Lower Devonian Helderberg Limestone is present in the subsurface and is overlain by the Oriskany Sandstone, which is in turn overlain by the Bois Blanc Formation. In north-central Ohio the Devonian is represented along the east flank of the Cincinnati and Findlay arches by the Middle Devonian

Columbus Limestone, which overlies the Bois Blanc. These rocks are succeeded, in stratigraphic order, by the Delaware Limestone, the Olentangy Shale, and the Ohio Shale. On the opposite side of the arch, in northwestern Ohio, the Devonian section is composed of the Detroit River Group, the Dundee Limestone, the Traverse Group, and the Ohio Shale.

The Detroit River Group can be divided into the Sylvania Sandstone, a basal unit of medium-grained white sandstone, and undifferentiated carbonates, which make up the bulk of the group. The limestones and dolomites are brown, finely to coarsely crystalline, and contain some sand, chert, and silicified fossil debris. The thickness of the group is approximately 120 feet (Janssens, 1970).

The Dundee Limestone is divided into lower and upper units by Janssens (1970). The lower unit consists of sucrosic sandy finely crystalline and medium-crystalline light-grayish-brown limestone and dolomite containing white and light-brown chert. The upper unit consists of fossiliferous medium- to coarse-grained light-yellowish-gray to medium-brown limestone, grading westward into lithographic limestone.

In northwestern Ohio the Traverse Group is divided into the Silica Formation and the Tenmile Creek Dolomite (Janssens, 1970). The Silica Formation, which ranges in thickness from 10 to 55 feet, is composed of dark-brown shale and dark-gray shaly limestone. The Tenmile Creek Dolomite consists of very finely crystalline to medium-crystalline dense yellowish-gray to grayish-brown dolomite with abundant chert nodules. The thickness of the group ranges from less than 20 to about 55 feet. In north-central Ohio the rocks of this sequence are primarily shales and are assigned to the Olentangy Shale.

The upper part of the Devonian Series is composed of dark-colored Ohio Shale. In northwestern Ohio this unit is over 300 feet thick. It is absent over much of the western and central parts of the state, but thickens to about 4,000 feet in eastern Ohio.

Pyrite, marcasite, and some sphalerite, associated with calcite, celestite, fluorite, anhydrite, and gypsum, are found in the Pugh Quarry in Wood County and in the Maumee Stone Company quarry at Junction, Ohio. Breccia cement and open-space fillings are most common. Pyrite and marcasite occur mainly in roughly lenticular masses up to several inches thick, as breccia cements, or as small drusy crystals in dolomite. Calcite is found as irregular bodies, as white or yellowish scalenohedral crystals filling vugs and small cavities, or as breccia cement. Small crystals or small aggregations of such crystals of sphalerite have been found in the Pugh quarry in a very few places. A small pocket of dark-reddish-brown sphalerite has been recorded from the Maumee Stone Company quarry at Junction, Paulding County. Celestite and fluorite are locally common as irregular bodies or crystals in large vugs and pockets in the upper beds of brecciated dolomite.

Pyrite and marcasite occur also in the Columbus Limestone in the Hal-Mar Stone Company quarry in Pickaway County. These minerals are much more common in the upper beds and are particularly concentrated in the southwestern wall of the quarry. Locally these minerals may comprise 50 percent of the freshly quarried rock; however, both minerals alter rapidly to limonite. A characteristic of the sulfide in this quarry is the presence of white and pink sparry dolomite as lenticular masses and as small crystals

associated with the pyrite.

Reidel (1972) mentioned the presence of sphalerite at the base of the Ohio Shale in the Serpent Mound area. Knille and Gibbs (1942) found many marcasite nodules and melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) interbedded in the Ohio Shale from the Copperas Mountain area near Bainbridge in south-central Ohio. Nodular beds containing pyrite and marcasite are particularly common in the Ohio Shale and probably formed as a result of the presence of abundant organic material.

MISSISSIPPIAN, PENNSYLVANIAN, AND PERMIAN ROCKS

During the Mississippian Period, arenaceous and fine clastics and limestones were deposited in the seas of the Appalachian region. In Ohio the clastics belong to the Bedford, Berea, Sunbury, Cuyahoga, and Logan formations. The Bedford Shale is a blue and red shale with interbedded siltstones. The Berea is a subangular fine-grained gray sandstone. The Sunbury is a gray-black shale. The Cuyahoga and Logan Formations consist of shale with interbedded sandstones. The total thickness of this clastic sequence is 600 to 700 feet. The Maxville Limestone is the uppermost Mississippian unit and lies unconformably upon the clastic rocks. The unit has a maximum thickness of 200 feet, but is irregular in occurrence because it is truncated by erosion.

Sphalerite and galena have been described by Ver Steeg (1940) in the Cuyahoga Formation near Wooster, Ohio. These minerals, along with pyrite and calcite, occur as fillings of cracks in nodules, or as fillings or replacements of fossils. Sphalerite is more common than the other minerals and is generally found in fossiliferous zones.

An extensive unconformity separates the Mississippian and Pennsylvanian Systems in the Appalachian Basin. In eastern Ohio the Pennsylvanian System consists of alternating clastics, thin limestones, and coals deposited in swamp and floodplain environments. The system is divided into the Pottsville, Allegheny, Conemaugh, and Monongahela Groups.

Sphalerite, galena, and pyrite associated with calcite and barite have been described by Ver Steeg (1942) in the Pottsville Group near Marshallville, Ohio. Seaman and Hamilton (1950) reported the occurrence of polymorphous wurtzite in shrinkage cracks in clay-ironstone concretions from above the Brush Creek limestone of the Conemaugh Group near Steubenville, Jefferson County. They also noted the occurrence of the mineral in the Old Glouster Brick quarry south of Glouster in Athens County. Rice (1948) described a similar occurrence of wurtzite in concretions from the underclay of the Middle Kittanning coal in the Richard Immel mine located southwest of Alliance in Stark County.

Pyrite and marcasite of syngenetic or diagenetic origin are widespread in some coals and shales of Pennsylvanian and Mississippian ages. In the coals of Ohio, pyrite and marcasite occur as balls, lenses, layers, nodules, thin sheets, and flakes scattered throughout the coal or within adjoining shale and sandstone (Tucker, 1919). Tucker estimated that

the total possible production of pyrite in Ohio coals was about 250,000 tons yearly, mostly from the Middle Kittanning (No. 6) and the Pittsburgh (No. 8) coals and to a lesser extent from the Pomeroy (No. 8A), the Upper Freeport (No. 7), and the Lower Kittanning (No. 5) coals.

In the shales of Ohio, layers and nodules of pyrite occur along some bedding planes, particularly filling low depressions in zones of local black organic beds.

In eastern Ohio the Permian System represents exclusively nonmarine environments. The Dunkard Group was deposited by streams flowing westward from the Appalachian Plateau into the continental interior. Many of the units are lenticular, composed of shale, sandstone, limestone, and thin coal. No sulfide minerals have been reported from these rocks in Ohio. No Mesozoic or Tertiary rocks are present in Ohio.

SUMMARY AND CONCLUSIONS

Summarizing the available data, it appears that most of the sulfide mineralization in the Ordovician through Devonian carbonate rocks of Ohio can be characterized as being of the Mississippi Valley type. Sulfide and associated minerals in the Mississippian and Pennsylvanian rocks appear to be of syngenetic and/or diagenetic origin. Several important features of the known occurrences can be pointed out:

(1) In western Ohio sulfide mineralization of the Paleozoic rocks is associated with the Cincinnati and Findlay arches. In northwestern Ohio the occurrences are centered on the Findlay arch, where the strata rise to their maximum elevation west of Sandusky and Seneca Counties. In southwestern Ohio the mineralization is centered on the Serpent Mound structure and is located along the eastern side of the Cincinnati arch. Similar mineralization is present along the Cincinnati arch south of Ohio in Kentucky and Tennessee.

(2) The sulfide minerals are present in Ordovician, Silurian, and Devonian bioclastic carbonate rocks. In northwestern Ohio the mineralization, although found throughout the formations, is concentrated at or just below surfaces of erosion and/or solution.

(3) The mineralogy of the sulfides is relatively simple; pyrite, marcasite, sphalerite, and, in some places, galena, are the most common minerals. The principal associated minerals are calcite, chert, fluorite, celestite, and white sparry dolomite. The minerals occur as fillings in pores, vugs, fissures, and joints. In some places fossils are replaced.

(4) The isotopic composition of sulfur in sphalerite and galena indicates, but does not prove, that the sulfur, and metals as well, were derived from a rather deep magmatic source (Botoman and Faure, 1976).

(5) In eastern Ohio the mineral zones associated with septarian nodules, shales, and coals appear to be the result of localized syngenetic and/or diagenetic conditions.

(6) Occurrences of sulfide minerals in the metamorphic and igneous basement rocks may provide helpful clues to the location of metallic deposits such as those known in Ontario and Quebec. Rocks present in Ohio are as favorable for sulfide accumulation as similar rocks in Canada.

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