

STRONTIUM ISOTOPES AS A TRACER FOR THE
ORIGIN OF MISSISSIPPI VALLEY-TYPE SULFIDE
DEPOSITS FROM THE SOUTHEAST MISSOURI
AND TRI-STATE DISTRICT OF MISSOURI

by

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I N T R O D U C T I O N

The southeast Missouri lead deposits, the southeast Missouri barite deposits, and the Tri-State District lead-zinc deposits are well-known examples of the stratiform Mississippi Valley-type sulfide deposits (Fig. 1). The long productive history of these districts and continued interest in exploration for additional reserves in these areas have resulted in repeated structural, stratigraphic, geochemical, and geophysical studies of these sulfide deposits. Despite this nearly one hundred years of study, controversy continues over the origin of these deposits.

P R E S E N T S T U D Y

Scope

This investigation determined the Rb and Sr contents and the Sr isotopic composition of the sulfide minerals, gangue minerals, and their host rocks from the Tri-State, the southeast Missouri lead-barite, and the southeast Missouri Viburnum lead deposits. The purpose of this geochemical study was to obtain data that could be useful in determining the period of mineralization by the Rb-Sr method and characterizing the mineralizing fluid from the Rb-Sr isotopic composition of the several phases in the deposits.

Rationale

The only published data of the Rb-Sr isotopic composition in sulfide minerals are those of Reesman (1968). Although he was not successful in obtaining a reliable isochron date for ores from the

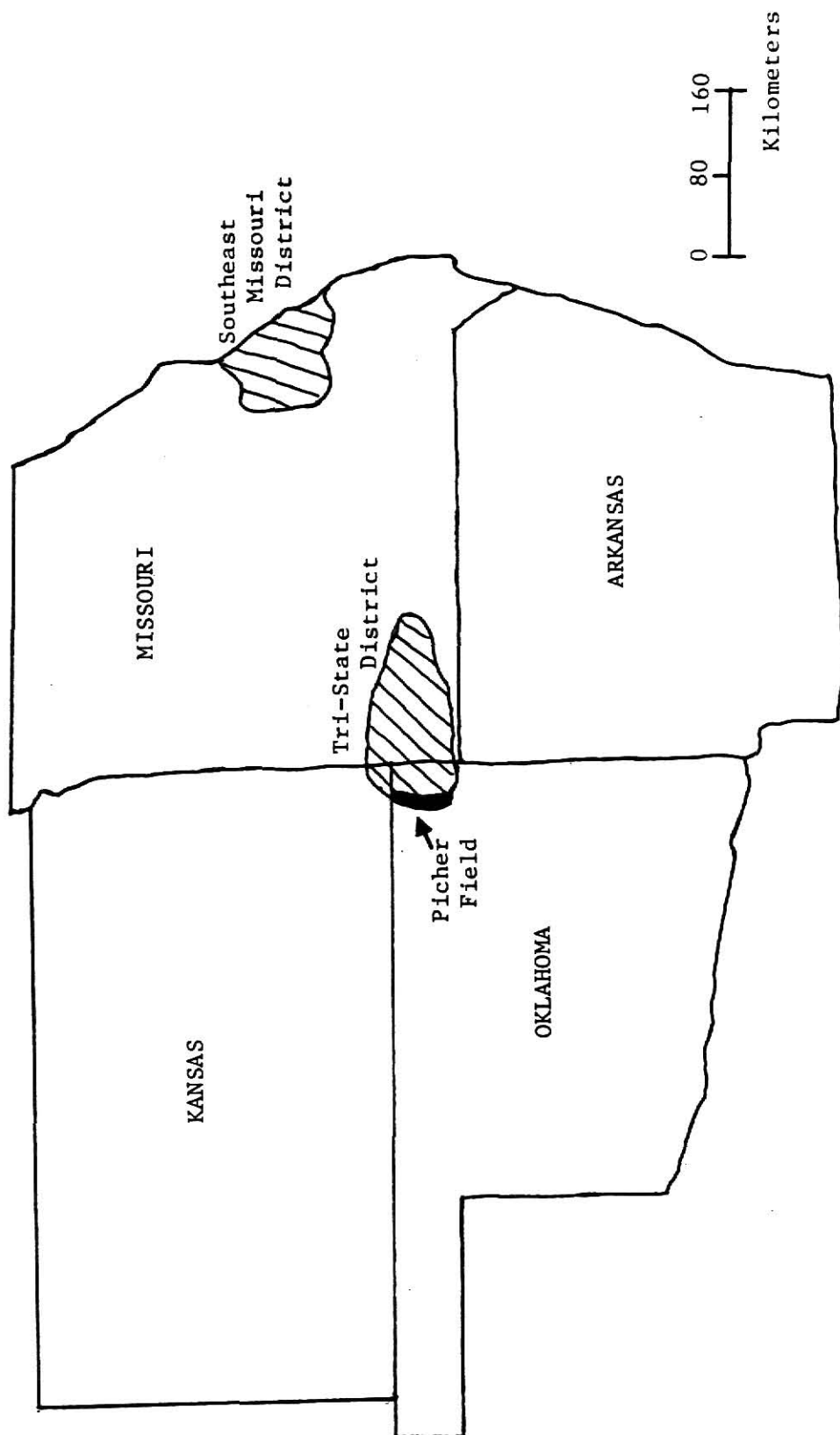


Figure 1. Location of the Tri-State and Southeast Missouri Districts (After Heyl, 1967)

Noranda district in Quebec, his study suggested that massive sulfide deposits contain small, but measurable amounts of Rb and Sr that are sufficient for isotopic investigation. Fleischer (1955), in his summary of trace elements in sulfides, noted Sr in carefully selected samples of galena and sphalerite. Fluid inclusion studies by Newhouse (1933) and Roedder et al. (1963) and Roedder (1967) indicated common alkali and alkaline earth elements in sulfide minerals from the Mississippi Valley-type deposits. These geochemical studies point to the feasibility of a Rb-Sr isotopic investigation of sulfide deposits from the Southeast Missouri and Tri-State districts. Any significant difference in Rb-Sr ratios of the phases having a common initial isotopic composition will allow the calculation of an age of mineralization, provided that the phases remained closed to both Rb and Sr since their formation.

The decay of ^{87}Rb in any phase generates ^{87}Sr with time. In addition, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio serves as a geochemical tracer in the study of the origin of the phase. Crustal materials are enriched in ^{87}Rb in comparison to mantle materials, and hence the former have a higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio than the latter. Faure and Powell (1972) summarized the Rb and Sr data and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from a wide variety of rocks and fluids. Recently, Chaudhuri (1978) reported Sr isotopic compositions of many oilfield brines. These brines were characterized by $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ranging from 0.711 to 0.734. Therefore, if metal-rich brines were responsible for transportation and deposition of these Mississippi Valley-type deposits, the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios will indicate a crustal source. Hedge (1974) discussed the possibility of using Rb-Sr isotopic studies in ore genesis investigations.

Selection of Study Area

Brown (1970, p. 117) in his review paper of the Mississippi Valley-type deposits, noted that "the distinguishing characteristic of a truly Mississippi Valley-type lead-zinc deposit is the presence of J-type anomalous lead" (lead which produces a negative age). This definition was used in determining which deposits could be considered as truly of the Mississippi Valley type (Fig. 1). Because no completely satisfactory *a priori* method for evaluating the suitability of a given area for study was available, three deposits were selected for study.

The Picher mining field, along the Oklahoma-Kansas state line, is part of the Tri-State mining region. The Picher area was chosen because it has been intensely studied by several other methods. The Picher field is unique in the predominance of sphalerite over galena and the intense silicification of the wall rocks.

The barite deposits of Washington County, Missouri, were chosen because the high concentration of strontium in the barite makes this area highly suitable for study by the Rb-Sr method. Small amounts of galena and sphalerite are also in these deposits. The lead in the galena crystals is of the J-type, and so these barite deposits meet the criteria for inclusion in this study.

In mid-1960, production began in the Viburnum Trend area of the Southeast Missouri Lead District. Galena is the primary ore mineral although lesser amounts of sphalerite and chalcopryrite are also present. Because this area is currently being actively explored and mined, the collection of controlled samples is greatly facilitated. Samples analyzed were collected from the Viburnum mine.

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MISSISSIPPI VALLEY - TYPE DEPOSITS

PREVIOUS ISOTOPIC STUDIES

The isotopic compositions of lead, sulfur, hydrogen, oxygen, and carbon have been studied by many investigators of the origin of Mississippi Valley-type deposits. Although such studies have not always been conclusive, they do place significant constraints on models for the origin of the deposits.

Lead Isotopes

Neir et al. (1941) showed that the variation of the isotopic composition of lead is the result of the addition of varied amounts of the radiogenic isotopes ^{206}Pb , ^{207}Pb , and ^{208}Pb , produced by the radioactive decay of uranium and thorium. Two distinct categories of lead, called ordinary and anomalous lead, have been recognized. Ordinary lead was proposed by Russel et al. (1954) for lead which has an isotopic composition that can be related to (1) the age of the earth, (2) proportions of uranium, thorium, and lead in the source rocks, and (3) time of mineral deposition. Anomalous leads were defined by Holmes (1947) as those having isotopic ratios which define an age either older than the age of the host rock or related to a future age. Houtermans (1953) designated those leads which produce a negative age as J-type. Like all true Mississippi Valley-type deposits, the lead in samples of galena from the Tri-State and Southeast Missouri lead and barite deposits is J-type (Table 1).

Cannon et al. (1961) concluded that the J-type lead might be the product of two distinct ore-forming processes: (1) evolution of lead by accumulating increments of radiogenic lead during a protracted span

Table 1

Lead Isotopic Composition of Galena from
Mississippi Valley-type Deposits (Doe, 1970)

District	Kind of ratio	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
Illinois-Kentucky fluorite (8 samples)	Minimum	19.91	15.80	39.92
	Maximum	21.01	15.98	40.64
	Average	20.36	15.90	40.27
Southeast Missouri galena (131 samples)	Minimum	19.96	15.65	39.10
	Maximum	21.46	16.19	41.02
	Average	20.81	15.97	40.08
Tri-State sphalerite (14 samples)	Minimum	21.31	16.00	41.07
	Maximum	22.66	16.28	41.92
	Average	22.11	16.15	41.46
Wisconsin- Illinois-Iowa sphalerite-galena (19 samples)	Minimum	20.83	15.96	40.45
	Maximum	24.44	16.33	43.95
	Average	22.54	16.15	42.31

of geologic time, or (2) instantaneous geochemical mixing of radiogenic lead with an ordinary lead. They also suggested that rock-lead in the Paleozoic sedimentary rocks and Precambrian basement rocks of the region should be studied to determine whether these rocks could have been the source of J-type lead. This suggestion was later followed by Kanasewich (1962), Brown (1967), McKnight (1967) Doe and Delevaux (1972) and Sverjensky et al. (1979). In general, the lead from the Tri-State district is the most radiogenic, whereas the lead from the Virburnum area is the least radiogenic.

Lead isotope data have generated considerable controversy as to the source of the metal. Kanasewich (1962) and Heyl et al. (1974) suggested that the lead originated in the Precambrian basement rocks which have Pb-Pb ages of 1300 ± 300 m.y. Cannon et al. (1963) postulated that the data indicated the carbonate host rocks were the source of the lead. Brown (1967) contended that the ore fluid was essentially connate water generated in the Paleozoic sediments, circulated through the Precambrian units, and then into the host carbonate units.

Doe (1970) summarized the lead isotope data for four of the main Mississippi Valley-type districts (Table 1). Doe further pointed out that these ores characteristically are highly radiogenic and that no igneous rock anywhere in the world has the appropriate initial lead isotopic composition.

Doe and Delevaux (1972) compared the isotopic composition of lead in galena with that of lead leached from the Lamotte Sandstone. They concluded that brines moving through the Lamotte Sandstone could have acquired the lead which formed the ore deposits. More recently, Sverjensky et al. (1979) documented the Lamotte Sandstone as the major

source of the lead. However, their data indicate the need for additional sources of lead for the galena ore bodies in southeast Missouri.

Sulfur Isotopes

Sulfur isotope studies (Ault and Kulp, 1959, 1960; Jensen and Dessau, 1967; Pinckney and Rafter, 1972) indicated that the bulk of the sulfur in Mississippi Valley-type deposits is of crustal origin and that each district exhibits a distinctive range in $\delta^{34}\text{S}$ of sulfide and sulfate phases (Fig. 2). Sulfide sulfur values are lighter than sulfate, and sulfur values from galena are generally lighter than those from sphalerite. The observed ranges in isotopic composition can be explained by fractionation as a function of mineral species, temperature, or chemical environment (Sakai, 1968; Ohmato, 1972; Rye and Ohmato, 1974) or mixing of different sources of sulfur. However, the wide range in $\delta^{34}\text{S}$ precludes the use of magmatic sulfur as a major source.

Though the major source of sulfur for the Mississippi Valley-type deposits is crustal, individual districts may exhibit a complex and unique mode of sulfur derivation. Ohmato (1972) and Sakai (1957, 1968) showed that sulfur isotope partitioning between sulfur-bearing species is strongly dependent on temperatures, $f\text{O}_2$, and pH values of the hydrothermal solutions. The process involving biogenic reduction of evaporite or sea water sulfate to derive the necessary sulfur is but one mechanism for producing the large range in $\delta^{34}\text{S}$ of Mississippi Valley-type deposits. The fluid chemistry, sulfate-sulfide isotope fractionation, and kinetic isotope effects are important parameters in determining the sulfur isotopic composition (Ohmato, 1972; Thode, 1964).

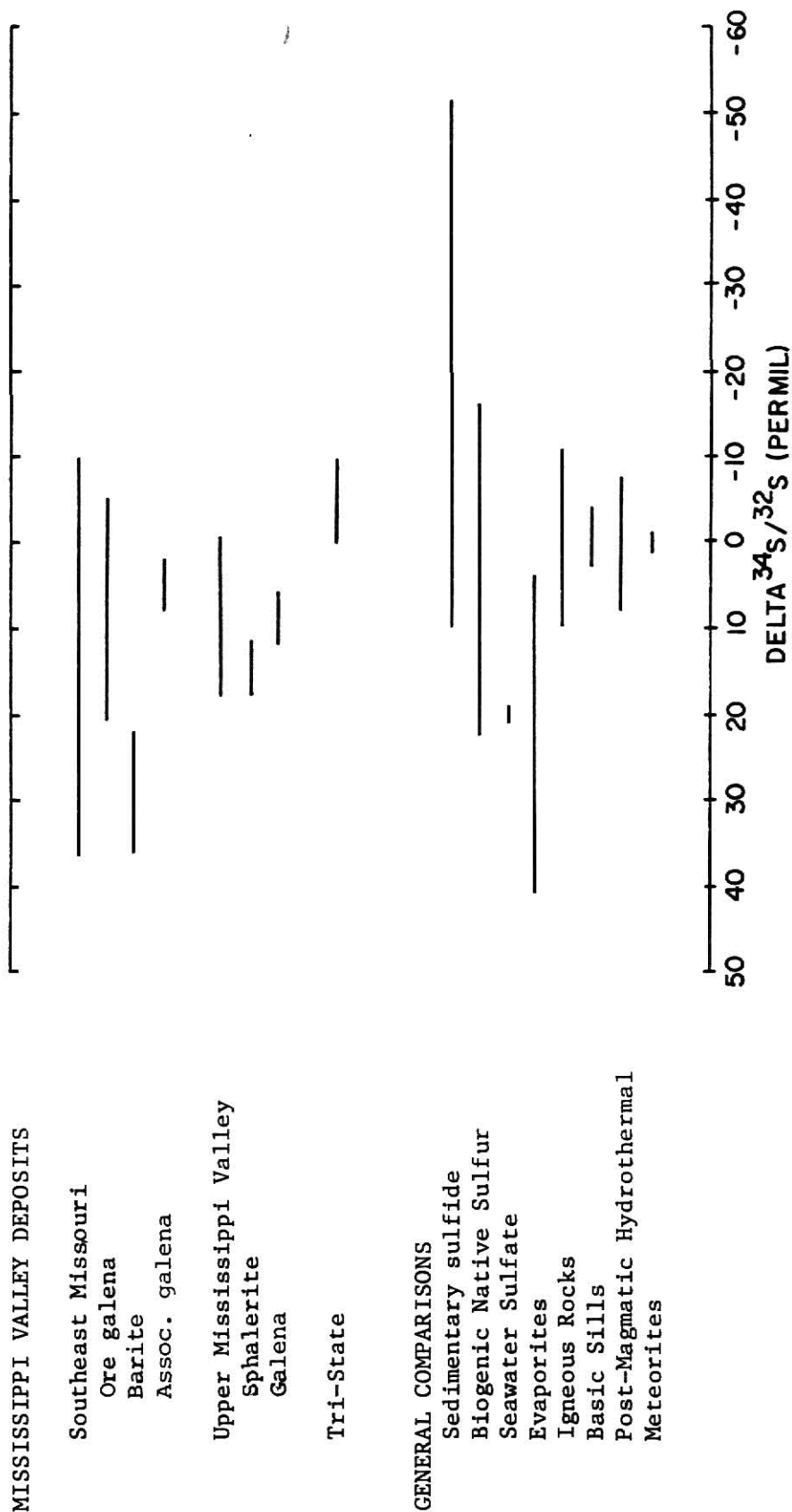


Figure 2. Comparison of Sulfur Isotopic Composition of a Number of Materials (After Heyl et al., 1974)

Brown (1967) noted two distinct patterns of sulfur isotope compositions in the Southeast Missouri Lead District. He found lighter sulfur associated with more radiogenic lead and heavier sulfur with less radiogenic lead. He concluded that the sulfur in the lead deposits of the Bonneterre Dolomite is either from sea water or perhaps a mixture of sea water and magmatic fluid. In a recent study, Sverjensky et al. (1979) reported the sulfur isotopic composition of several galena samples from the Southeast Missouri Lead District. The delta ^{34}S values of these samples ranged from + 3.5 to + 21.2 per mil. These authors contended that the sulfur isotopic compositions were generated by precipitation from many solutions, each of which was the result of mixing different proportions of at least two solutions.

Oxygen and Carbon Isotopes

Hall and Friedman (1969) investigated variations in oxygen and carbon isotopic compositions of ore and host rock of selected deposits in the Tri-State and Upper Mississippi Valley districts. They attributed these differences in isotopic composition to fractionation by a temperature gradient.

The calculated delta ^{18}O value of the ore solution that deposited the late calcite in the Tri-State district is -3 per mil. Hall and Friedman considered this value to be compatible with the deposition of these minerals from a solution formed by the mixing of meteoric and heated brine waters.

Hydrogen Isotopes

The deuterium content of fluid inclusions in minerals from Mississippi Valley-type deposits was studied by Hall and Friedman (1963) and Roedder et al. (1963). These studies indicated that hydrogen

isotopes are a useful indicator of the sources of water in a fluid and may be a guide to ore genesis. Although incomplete, the data suggest that a two-component mixing model is the most likely mechanism for deposition of the ore.

ORE DEPOSITS

THE PICHER FIELD

Location and Physiography

The Picher field is the westernmost of the deposits that make up the Tri-State mining region. It is on the Osage Plains, immediately adjacent to the west edge of the Ozark Upland. The Picher area is a flat prairie with a local relief of less than 27 m.

Stratigraphy

A generalized stratigraphic column of the Picher, Oklahoma, area is in Fig. 3. Because the economic ore deposits are in rocks of Mississippian age, the discussion of the stratigraphy is limited to these rocks. The following description is modified from McKnight and Fischer (1970), Howe and Koenig (1961), and Brockie et al. (1968).

Disconformably overlying the unassigned Devonian-Mississippian Chattanooga Shale is the "Boone Limestone", which consists of light to dark gray and brown, fine- to coarse-grained, fossiliferous limestone alternating with bedded cherts, which may be as thick as 18 m. The "Boone Limestone" is 106 to 121 m thick and is the host rock for the ore deposits in the Picher field. The rocks designated as "Boone Limestone" in the older literature of the district have been divided in ascending order into the Fern Glen Formation, Reeds Spring Formation, Keokuk Formation, and Warsaw Formation by Brockie et al. (1968) and McKnight and Fischer (1970).

The Fern Glen Formation consists of fine grained, soft, silty and shaly limestone with a few blue and gray chert nodules. It has an average thickness of 8 m.

PENNSYLVANIAN	SERIES	FORMATION	REMARKS	
	Des Moines	Cherokee Shale	Cherokee Shale is the surface formation in the Picher Field	
MISSISSIPPIAN	Chester	Fayetteville Shale Batesville Sandstone Hindsville Limestone	The Chester Series is referred to as the Mayes Formation in older literature. The Carterville Formation in the Joplin area is faunally related to the Fayetteville and the Batesville formations.	
	Meramec	Warsaw Formation	B-Jbed = Warsaw Formation J bed is equivalent to Cowley Formation of southeastern Kansas	All Meramec and Osage rocks are referred to in some literature as the Boone Limestone
	Osage	Keokuk Formation	K-Q beds (N,O,P&Q=Grand Falls Chert)	
		Reeds Spring Formation	R bed	
		Fern Glen Formation	Corresponds to Pierson Formation in recent literature	
	Kinderhook	Northview Shale	Thin to absent in Picher Field	
		Compton Limestone		
	MISSISSIPPIAN DEVONIAN		Chattanooga Shale	Absent except as local patches in Picher Field. Subcrop edge is located a few miles south of district

Figure 3. Generalized Stratigraphic Column of the Picher Field (after Brockie et al., 1968)

The Reeds Spring Formation, conformably overlying the Fern Glen Formation, contains bedded and irregular nodules of gray to black chert in dark gray to brown, fine-grained limestone. Thickness of the unit ranges from 15 to 30 m. An unconformity separates the Reeds Spring Formation from the Keokuk Formation.

The Keokuk Formation consists of a series of fine- to coarse-grained fossiliferous limestone and bedded chert. Maximum thickness of the unit is 65 m. The upper 45 m consists of gray and brown, medium- to coarse-grained limestone, containing chert beds with an aggregate thickness of about 12 m. The principal ore horizon, in the upper part of the unit, consists of pale brown crystalline and fossiliferous limestone and contains abundant light gray chert nodules. The persistent oolitic limestone, 1 to 3 m thick, occurs at the top of the ore-bearing bed. The lower part of the Keokuk Formation consists of white to light-brown and gray bedded chert and brown to gray fine-grained limestone. The chert members do not persist from place to place. Thin brown limestone beds alternating with thin gray chert beds near the middle of the Keokuk Formation, contain some ore bodies in the district.

The Warsaw Formation is primarily a light gray and light brown abundantly cherty fine- to coarse-grained limestone. Some beds consist almost entirely of chert 5 to 6 m thick. The Warsaw Formation is the second most important ore-producing horizon in the district. The ore horizon is in the lower part of the unit, which is about 45 m thick. The lowermost member of the Warsaw Formation consists of gray to dark gray, locally glauconite-speckled, cherty, fine-grained limestone with

phosphate nodules. This unit ranges from 1 m to nearly 12 m in thickness and is a good marker throughout most of the Picher field.

The Mississippian Chester Series, which unconformably overlies the Warsaw Formation, consists (in ascending order) of the Hindsville Limestone, the Batesville Sandstone, and the Fayetteville Shale. The Hindsville Formation consists of alternating limestone and shale. The beds of limestone are generally fossiliferous, partly oolitic and siliceous, but lack chert. The Batesville Formation is a yellow-brown, fine-grained, friable, calcareous sandstone. Near the ore deposits the Batesville Formation is intensely silicified because of replacement of calcite. The Fayetteville Formation consists of shale and interbedded limestone and sandstone. Some shale beds contain an abundance of bryozoans. Total thickness of the Chester Series is about 30 m.

Structure

The Picher mining field is on the northwestern edge of the Ozark Geanticline. The rocks of the area are nearly horizontal with a northwest regional dip of 6 m per mile. Folds and faults cause irregularities and, in places, reversals in the regional dip. The major structural features are shown in Fig. 4.

Faults. The Seneca Fault is a continuous structure that extends from near Tipton Fords in Newton County, Missouri, approximately S 40° W to near Pryor in Mayes County, Oklahoma. It is a combination of graben and synclinal sag, having a width of 3 to 792 m and a maximum displacement of 45 m.

The Miami Trough is a linear combination of syncline and graben which resembles the Seneca Graben except that synclinal sag predominates

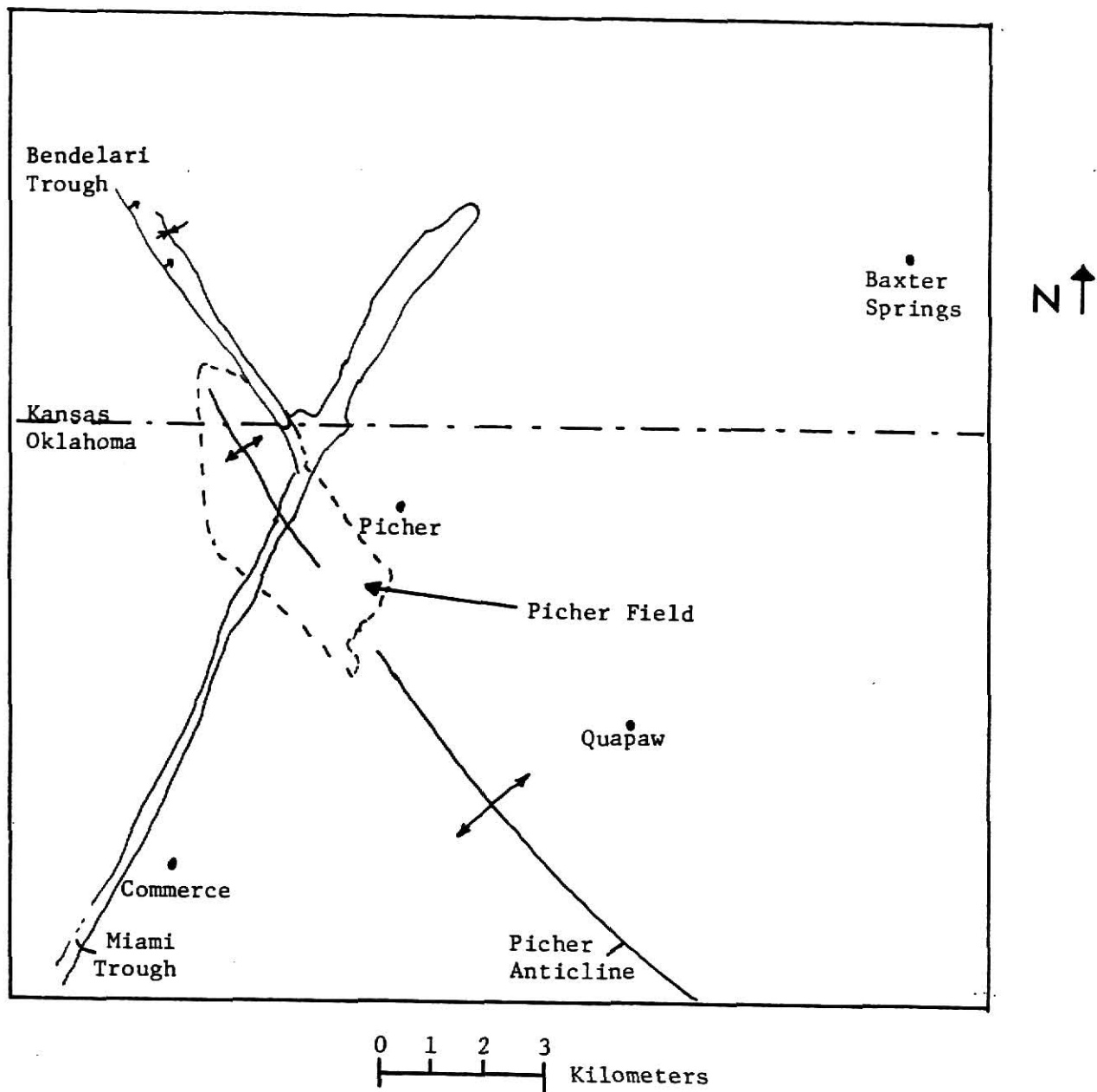


Figure 4. Structural Map of the Picher Field (After McKnight and Fisher, 1970)

over true graben. The trough crosses the western part of the Picher field with an average trend of N 26° E. Within the mining field the trough is 91 to 609 m wide with a maximum vertical displacement of 91 m.

Folds. The Bendelari Trough crosses the mining field with a northeast trend. The maximum dip is 20° northeast. This structure is not recognized in the overlying Pennsylvanian strata.

The Rialto Basin is an irregular east-trending synclinal sag a mile long and a quarter mile wide having a maximum structural depth of 24 m. Detailed contouring on the top of the Grand Falls Chert by McKnight (1967) shows many small, shallow basins with many flat, anticlinal ridges and domes all in random orientation. McKnight attributed these structures to depositional irregularities modified by diagenesis.

Pipes and Breccias. Underground workings show numerous slump pipes bounded by near-vertical circular faults, within which the rocks have been displaced downward from 3 to 6 m. The block of ground within a pipe is generally tilted, squeezed, and mashed with some shattering of enclosed chert but without extreme brecciation. These pipes probably formed during slow dissolution of underlying limestone. Although the development of the pipes predated the deposition of the ore, they are generally unmineralized.

Slump breccias have been produced in zones of solution, and, by inference, underlie every slump pipe. In the mineralized ground, tectonic breccias are abundant. These were formed by plastic deformation of incompetent limestone causing brecciation of the enclosed brittle chert. Later mineralization has replaced the limestone with little effect on the chert.

Joints. The mineral-bearing ground was fractured along curvilinear vertical zones by joint sets along which the mineralizing solutions were introduced. These joint systems appear to be contemporaneous with the tectonic breccias.

Economic Geology

The ore deposits of the Picher field are restricted primarily to the Mississippian strata, specifically the "Boone Limestone". The Pennsylvanian beds of shale have acted as an impermeable barrier to rising mineralizing solutions and have aided in the localization of the ore in Mississippian units (Siebenthal, 1916). The deposits consist of ore and gangue minerals that replace limestone in some stratigraphic horizons. Although many minerals have been identified, only galena and sphalerite are commercially significant.

Ore Deposition. The typical mineral deposit consists of a central dolomite core surrounded progressively outward by the main lead-zinc mineralized zone, then by a jasperoid zone which grades into undisturbed limestone. Also much greater amounts of chert are in the limestone nearer the mineralized areas. The sequence of mineral deposition is as described in Fig. 5.

Ore Minerals. Sphalerite and galena occur as massive replacement masses, as disseminated grains, and are also abundant in vugs and other openings as crystals. Sphalerite occurs mainly as yellowish-brown, modified tetrahedral crystals and grains; however, in dolomite the sphalerite crystals are ruby red or black. Galena generally occurs as cubic crystals and also as octahedral crystals. Commonly, the galena shows pronounced etching, resolution, and resurgent crystallization.

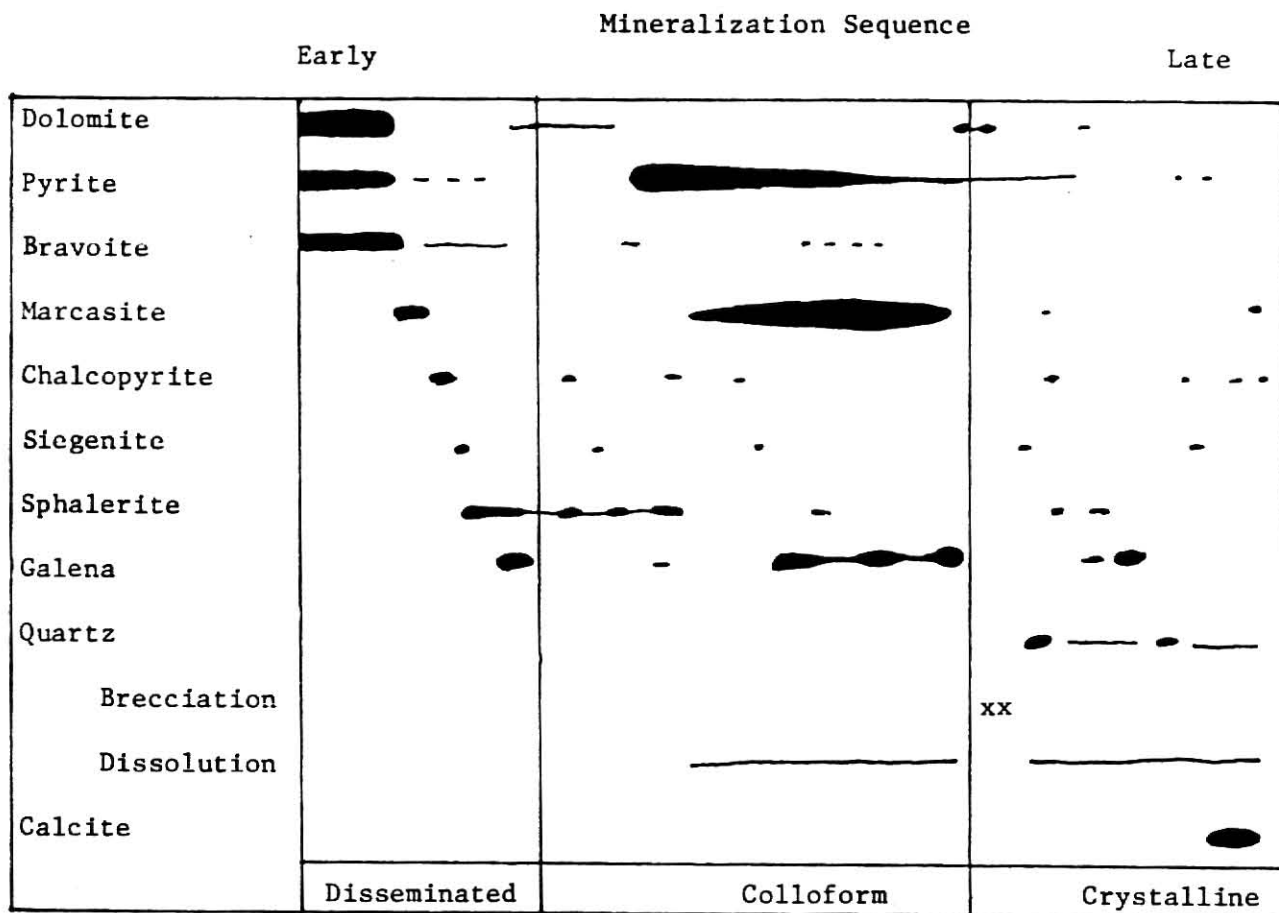


Figure 5. Paragenetic Sequence of Ore Minerals in the Picher Field (Brockie et al., 1968)

Although several copper sulfide minerals have been identified, they are not important commercially.

Gangue Minerals. Quartz is the most abundant gangue mineral associated with the ore deposits and occurs as chert, jasperoid, quartz druses, and well-formed quartz crystals. Calcite and dolomite also occur in significant amounts. Pyrite and marcasite only occur locally and in small amounts.

The chert occurs principally as (1) thick beds; (2) beds 1 to 2 cm thick with equal or slightly thicker limestone beds; (3) nodules and lenses in limestone parallel to the bedding; and (4) irregular masses in limestone. Evidence presented by Bastin (1933) and Giles (1935) indicates that most of the chert replaced limestone and appears to be diagenetic; however, a small amount of chert cuts across the bedding planes and may be related to ore deposition.

Jasperoid consists mostly of microcrystalline quartz crystals. Most jasperoid is brown to black, the coloring agent being a brown, opaque, organic material. Jasperoid is closely associated with the sulfide mineralization, occurring interbedded with chert and filling spaces in the breccias. The quartz druses and crystals sparingly line vugs and coat the sulfide minerals.

Dolomite occurs as (1) uncommon, fine-grained, gray sedimentary dolomite in beds; (2) coarse-grained gray gangue dolomite, generally in thick beds that commonly contain an abundance of brecciated chert fragments and nodules; and (3) pink dolomite, mostly as crystals in vugs and as fracture fillings that cut the gray gangue dolomite and the jasperoid. The sedimentary dolomite has no apparent relationship

to ore mineralization; however, the coarser gray gangue dolomite is closely associated with lead-zinc mineralization.

Calcite occurs as transparent, nearly colorless to amber crystals. The mineral is abundant along the fringes of the Picher field. Much of the calcite may be secondary and much later than the lead-zinc mineralization.

Pyrite and marcasite occur as small crystals, pellets, and grains disseminated in jasperoid, chert, dolomite, and limestone. The marcasite appears to be later than much of the pyrite (Brockie et al. 1968).

Origin. The occurrence of some zinc and lead mineralization in the Pennsylvanian Cherokee Shale suggests that at least part of the mineralization is post-Cherokee in age. Fluid inclusion studies by Newhouse (1933) and Schmidt (1962) indicated that the temperatures at which the ore minerals formed ranged from 83° to 120° C and that the fluids were essentially brines of sodium and calcium chlorides. From the lead isotopic data, Cannon et al. (1963) concluded that the source rocks for the metals were younger than Precambrian and were presumably Paleozoic sedimentary rocks in the Tri-State District. Brockie et al. (1968) contended that the warm, ore-bearing brines were derived from some distant source. These migrated through the Cambrian and Ordovician sedimentary rocks until a zone of structural weakness permitted concentration and access of the ascending solutions into the Mississippian formations. The minerals were in material that was already prepared by brecciation and dolomitization of the host rock.

THE SOUTHEAST MISSOURI LEAD AND BARITE DISTRICTS

Location and Regional Geology

The lead, zinc, and barite deposits of southeast Missouri are known in Madison, St. Francois, Washington, Crawford, Iron, Reynolds and Shannon counties, Missouri. Although the barite district and the lead district are within the same geographic area, the ore deposits are distinctly different. The lead district has no barite, whereas barite is the only significant economic mineral in the Barite District.

The Southeast Missouri Lead Districts are on the flanks of the St. Francois Mountains on the northeast margin of the Ozark Uplift. The St. Francois Mountains, consisting of Precambrian igneous rocks at the core, were highly dissected by erosion prior to being partly covered by Upper Cambrian sedimentary rocks. While some areas of the dissected Precambrian surface remained exposed during the Cambrian Period, others were covered by deposits of shelf sedimentation (Thacker and Anderson, 1977). Upper Cambrian rocks in the Southeast Missouri District consist primarily of several types of carbonate rock that overlie a basal Paleozoic sandstone. Because of complex facies changes of Upper Cambrian sedimentary rocks, correlation of these units even on a local scale has been extremely difficult (Howe, 1968). The carbonate rocks were deposited on a marine shelf. Lower Paleozoic rocks dip away from the St. Francois Mountains and have been overlapped by younger formations around the high-standing Precambrian knobs. Thacker and Anderson (1977) reported a total thickness of about 609 m of Cambrian strata in Missouri. Figure 6 depicts the general geologic features of southeastern Missouri.

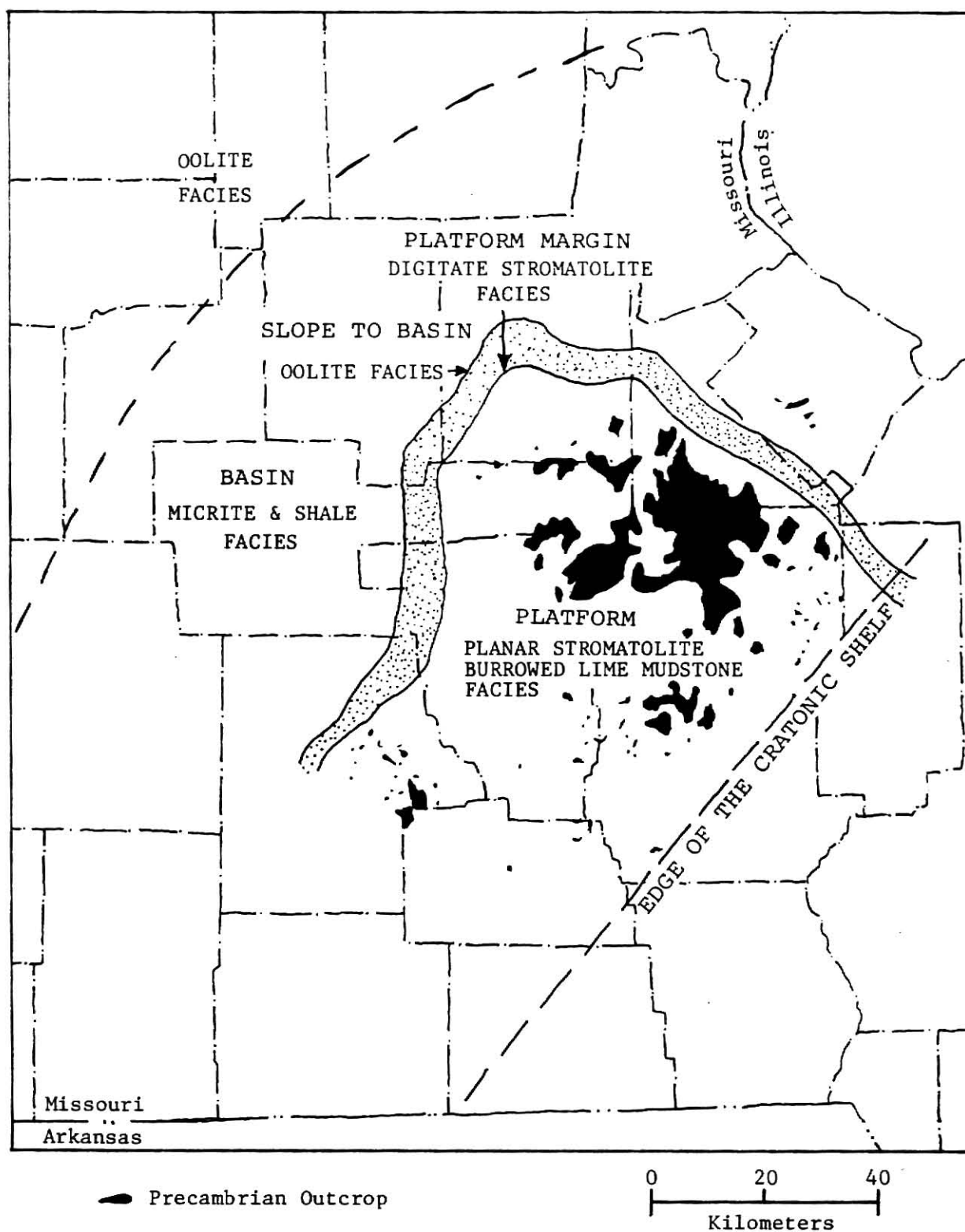


Figure 6. Geologic Map of the Southeast Missouri District (From Snyder and Gerdemann, 1968)

Stratigraphy

A generalized stratigraphic column of the rock units in this area is in Fig. 7. The ages of the rocks range from Precambrian to Ordovician; however, the discussion of stratigraphy is limited to Upper Cambrian because the economic lead and barite deposits occur in these strata. These ore-bearing Cambrian strata consist predominantly of carbonate rock and a few clastic rocks that represent essentially continuous deposition. The description of the stratigraphic units is adapted from Thacker and Anderson (1977), Snyder and Gerdemann (1968), Larsen (1977) and Howe (1966, 1968). The sedimentary formations in ascending order are: Lamotte Sandstone, Bonnetterre Dolomite, Davis Shale, Derby-Doerun Dolomite, Potosi Dolomite, and Eminence Dolomite.

Lamotte Sandstone. The Lamotte Sandstone is the basal Paleozoic formation in southeast Missouri. It rests unconformably on the Precambrian igneous rocks and has a maximum thickness of about 114 m. Thickness differs because it fills valleys on the eroded Precambrian surface and locally pinches out against Precambrian knobs. Most of the Lamotte Sandstone consists of fine- to medium-grained quartz sandstone with rounded and frosted grains. The lowest part of the Lamotte Sandstone, which contains quartz grains as large as 4 mm, is an arkose locally. Thin, wavy partings of shale occur in the upper part of the Lamotte Sandstone. Ojakangas (1963) considered the Lamotte Sandstone to be a time-transgressive marine orthoquartzite. Howe et al. (1972) stated that it may also be partly fluvial and aeolian. The boundary between the Lamotte Sandstone and the overlying Bonnetterre Dolomite is generally placed at the base of

ERA		ORDOVICIAN SYSTEM		LOWER CANADIAN SERIES		Lithologic Description		Mineral Commodities		Subdistricts of the SE Mo. Lead District	

a zone of gradation from a slightly calcareous sandstone to an overlying sandy dolomite. The transition zone consists of dolomite, quartz, small amounts of glauconite and fine-grained mud (Thacker and Anderson, 1977).

Bonneterre Dolomite. The Bonneterre Dolomite is the host for the lead deposits in the Viburnum and Old Lead Belt areas in southeast Missouri. This formation is composed almost exclusively of dolostone in the mining areas along the Viburnum Trend; it is mostly limestone outside of the mineralized areas. The formation has an average thickness of about 85 m. The Bonneterre Dolomite formed in response to different sedimentary and structural conditions near the Precambrian mountains, which influenced the environments of carbonate deposition during the Cambrian Period. Many investigators (Ohle and Brown, 1954; Snyder and Odell, 1958; Howe, 1966 and 1968; Gerdemann and Myers, 1972; and Larsen, 1977) recognized several facies of the Bonneterre Formation. Four carbonate facies and one mixed carbonate-quartz sand facies have been recognized (Larsen, 1977; Howe et al., 1972). The carbonate facies include: (1) the micrite and shale, (2) the oolitic calcarenite, (3) the digitate stromatolite, and (4) the planar stromatolite and burrowed carbonate mudstone. The mixed carbonate-quartz sand facies marks the contact between the Lamotte Sandstone and the Bonneterre Dolomite. Figure 8 shows the relationship among the several Bonneterre facies. Larsen (1977) divided the Bonneterre Dolomite into a fore reef facies (equivalent to the basal sandy zone facies), a reef complex facies (equivalent to the planar stromatolite and burrowed carbonate mudstone facies), and an offshore shelf facies (equivalent to the micrite and shale facies).

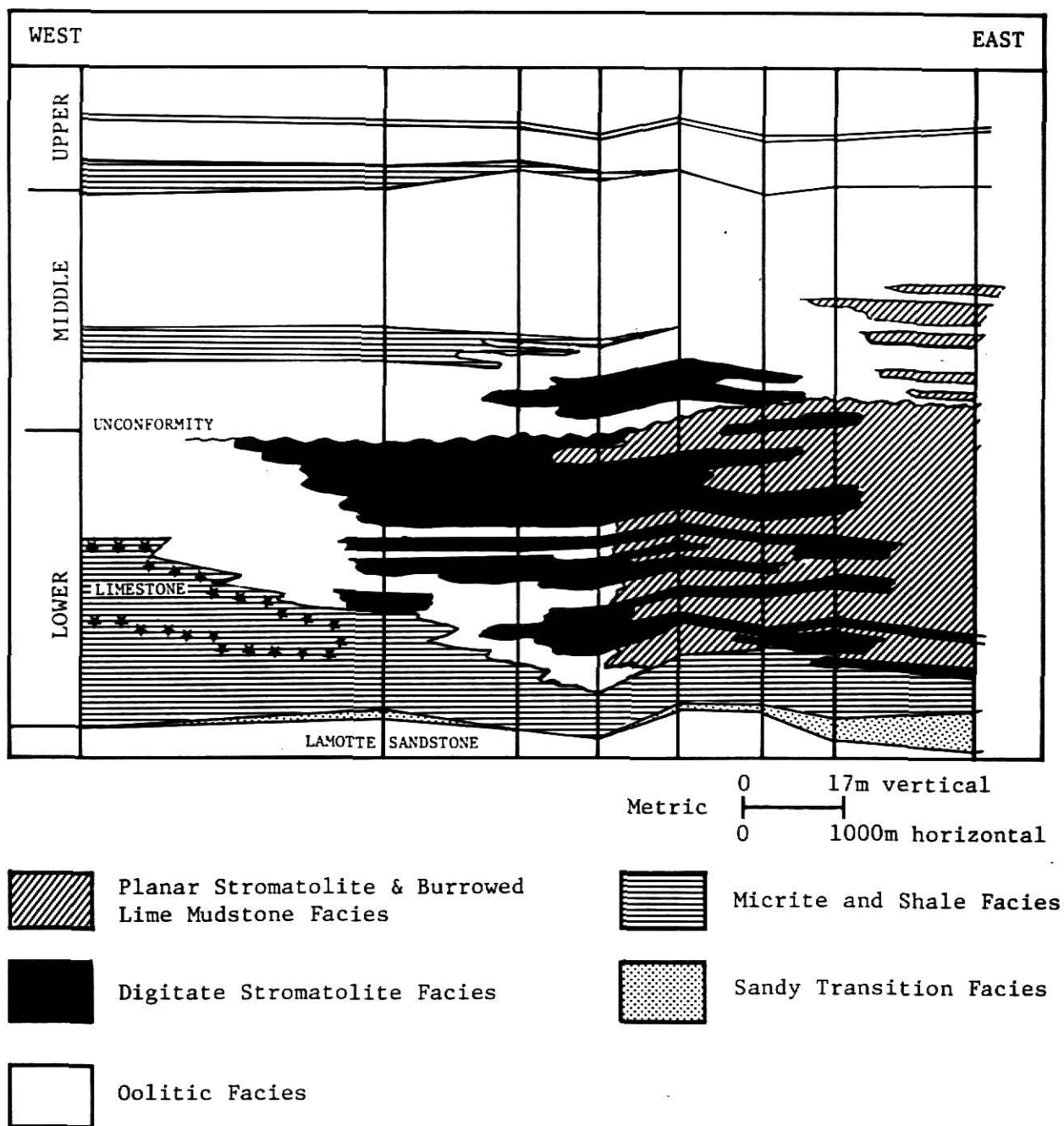


Figure 8. Facies of the Bonnetterre Dolomite in the Viburnum Trend (From Larsen, 1977)

The micrite and shale facies covered much of central and southern Missouri. An area of more than 5,200 sq km around the St. Francois Mountain Precambrian high was the area of deposition of the planar stromatolite and burrowed carbonate mudstone facies. Low-energy environments of deposition were typically associated with the two carbonate mudstone facies, whereas high- to moderate-energy environments were associated with the oolitic and digitate stromatolite facies (Howe, 1968; Gerdemann and Myers, 1972; Larsen, 1977). During the deposition of the Bonneterre Dolomite the shift in facies produced differences in the stratigraphic succession along the Viburnum Trend and this would explain a unique stratigraphic sequence for each mine (Larsen, 1977). A limestone-dolomite interface cuts across the facies pattern. In the fore reef facies, limestone is dominant. Parts of the reef complex, offshore shelf, and back reef are also composed of limestone; elsewhere the Bonneterre is predominantly dolomite.

Throughout much of southeastern Missouri, the Bonneterre is unconformably overlain by the Davis Shale. In places, it has been found that sedimentation continued without interruption into the Davis Shale (Thacker and Anderson, 1977).

Davis Shale. The Davis Shale consists of interbedded green shale, sandy and silty limestone and calcareous siltstone. Beds of flat pebble conglomerate are common within the Davis Shale. Small amounts (less than 5 percent) of glauconite grains occur throughout the formation.

The Davis Shale has an average thickness of about 51 m. The contact of the Davis Shale with the overlying Derby-Doerun Dolomite is placed where the green Davis Shale below grades into brown shale in

the Derby-Doerun Formation above. The conformable relationship between the two formations is marked by an intertonguing of their lithologic units.

Derby-Doerun Dolomite. The Derby-Doerun Dolomite, having an average thickness of 33 m, consists of a lower thin and irregularly bedded, fine- to medium-crystalline, burrowed, argillaceous dolomite. In places, beds of planar stromatolite dominate; in others digitate stromatolite is dominant. The contact between the two major units is marked by a decrease in silt-size quartz grains in the upper as compared to the lower unit. The contact with the Potosi Dolomite above is apparently transitional (Thacker and Anderson, 1977).

Potosi Dolomite. The Potosi Dolomite is a brown, thick-bedded, fine- to medium-crystalline, highly burrowed dolomite. It consists of 70 m of dolomitized oolitic calcarenite, digitate stromatolite and planar stromatolite in the St. Francois Mountains (Howe et al., 1972). The Potosi Dolomite seems to be conformable with the overlying Eminence Dolomite (Thacker and Anderson, 1977). The upper Potosi Dolomite is the host for the lead-barite deposits.

Eminence Dolomite. The Eminence Dolomite consists of more than 61 m of bedded, highly burrowed, coarsely crystalline dolomite. Silicification of the Eminence Dolomite is widespread as quartz druses that fill numerous vugs and cavities, as chert in massive fillings, and as floating quartz sand grains. Beds of stromatolite and calcarenite continue into the Eminence Dolomite from the lower Potosi Dolomite. The Eminence Dolomite marks the end of the Cambrian deposition in Missouri and is unconformably overlain by the Lower Ordovician Gasconade Dolomite (Thacker and Anderson, 1977).

Structure

The dominant structural feature of southern Missouri is the Ozark Geanticline, which has a core of Precambrian granite, volcanic rock, and a few mafic intrusive rocks. An erosion surface underlies these Paleozoic rocks. The sedimentary units dip radially outward from the dome where there are small reversals owing to faults.

Faults. A system of faults roughly brackets the Ozark Geanticline. Major faults are represented by the currently active New Madrid Fault Zone and by the northwestward-trending St. Genevieve Fault system. Although the subsurface geology is better known within the mining areas, the mineralized areas do appear to be more intensely faulted.

Pipes and Breccias. Many buried crypto-explosive features have been identified, such as the Furnace Creek, Dents Branch, Crooked Creek, Hazelgreen and Decaturville structures. These features plus the Avon dikes and diatremes are a distinctive group of structures in a 650 km east-west trending zone across southern Illinois, Missouri, and eastern Kansas. Additional structures of this type will undoubtedly be found by additional drilling.

Economic Geology

The Southeast Missouri Lead Belt is a classic example of a Mississippi Valley-type deposit. The important sub-districts are Mine La Motte, the Old Lead Belt, Indian Creek, and the recently discovered Viburnum Lead Belt. The Precambrian basement strongly influenced the pattern of sedimentation and the development and distribution of faults and fractures in the Paleozoic sedimentary rocks. The

interrelationship between the Precambrian basement rocks and the Paleozoic sedimentary rocks in this district strongly affected the movement of ore fluids and deposition of ore bodies. In the Southeast Missouri Lead District, the commercial mineralization occurs in the Bonneterre Dolomite. Minor mineralization occurs in the upper Lamotte Sandstone and at the contact between the two. Only trace amounts of sulfide minerals have been found in the Precambrian basement rocks near the contacts with Paleozoic sedimentary rocks. In the Southeast Missouri Barite District, the ore mineralization is primarily in the upper Potosi Dolomite and lower Eminence Dolomite.

The mineralization within the Bonneterre Dolomite ranges throughout the formation. At Mine La Motte the mineralization is restricted to the lower 15 m of the Bonneterre Dolomite. At Leadwood, it occurs within the lower 30 m of the host rock, whereas in parts of the Viburnum Trend, the mineralization is restricted to the upper part of the Bonneterre Dolomite below the Davis Shale.

More than 90 percent of the ore from the Viburnum mine is associated with the algal reef complex (Grundmann, 1977) of the Bonneterre Dolomite. Minor mineralization occurs within the back-reef and fore-reef deposits. Locally, they could be major ore horizons. For example, in the St. Joe Fletcher mine, the ore mineralization is associated with a porous, thick-bedded, oolitic, clastic carbonate unit above the algal reef zone (Paarlberg and Evans, 1977). In the Brushy Creek mine, the mineralization occurs both in the digitate stromatolite and the oolitic units (Evans, 1977). In the Ozark Lead Company mine near Sweetwater, the ore occurs throughout the vertical range of the Bonneterre Dolomite (Mouat and Clendenin, 1977).

Ore Minerals. In the Southeast Missouri Lead District, the primary ore minerals are galena, sphalerite, and chalcopyrite. Galena occurs as (1) bedded or sheet deposits along unconformities and bedding planes; (2) open space fillings, disseminated crystals, and crystalline aggregates in dolomite; (3) fracture fillings; and (4) intergranular pore fillings.

In most places sphalerite is a minor constituent of the ore in the district, but may be important locally. Most occurs either with or above the zone of highest galena mineralization in a given deposit. The chalcopyrite mineralization is restricted to the eastern part of the district and is commonly in the lower part of the Bonneterre Dolomite, either below or with the zone of the lowest galena mineralization.

In the Southeast Missouri Barite District, mineral deposits in the Potosi Dolomite and Eminence Dolomite contain barite as the major, or sole, economic mineral. Small amounts of galena and traces of sphalerite may occur as scattered veins or pockets. The barite occurs as veins and fracture fillings in a 30 m zone that includes the upper part of the Potosi Formation and the lower part of the Eminence Dolomite.

Gangue Minerals. The only gangue material of volumetric importance is the host dolomite. The introduced or recrystallized gangue minerals are pyrite, marcasite, calcite, dolomite, dickite, quartz, and jasperoid. They occur in small amounts and in limited areas.

The Lead Belt is unique among mid-continent base-metal districts because it lacks silicification. The Bonneterre Dolomite lacks chert,

and most mine workings show no silicification. Slight silicification, however, occurs in a few areas, the most notable example being jasperoid at the Magmont Mine in the Viburnum Trend (Hagni and Trancynger, 1977).

Marcasite and pyrite are locally abundant in the Viburnum Trend subdistrict, but are rare elsewhere. Well-formed crystals of calcite are common in the vugs and in masses almost 36 cm in diameter. Some calcite may be secondary and not related to ore deposition. A paragenetic sequence of ore minerals of this district is in Fig. 9.

The principal gangue minerals associated with the barite deposits are quartz, calcite, and chalcedony. The quartz and chalcedony druses are apparently groundwater-related and not associated with the primary mineralization. The clear, yellow calcite is in small veins and fissure-fillings and is related to the ore deposition.

Origin. Divergent views exist as to the source of the metals, the source of the heat, and the cause of fluid migration. The period of mineralization is still unresolved. Davis (1977) summarized different hypotheses that have been proposed for the origin of the Mississippi Valley-type deposits. Since the fluid inclusion studies by Newhouse (1932, 1933), and later by Roedder et al. (1963) and Roedder (1967), a unanimity of opinion exists concerning the chemical composition and range of temperature of the mineralizing fluids. These studies established that the fluid inclusions were concentrated Na-Ca-Cl brines devoid of sulfide and that the temperatures at the time of mineralization ranged from 80° to 150° C. Numerous models have been proposed to explain the source of metals and the mechanism of deposition of these Mississippi Valley-type sulfide deposits. Among these are --

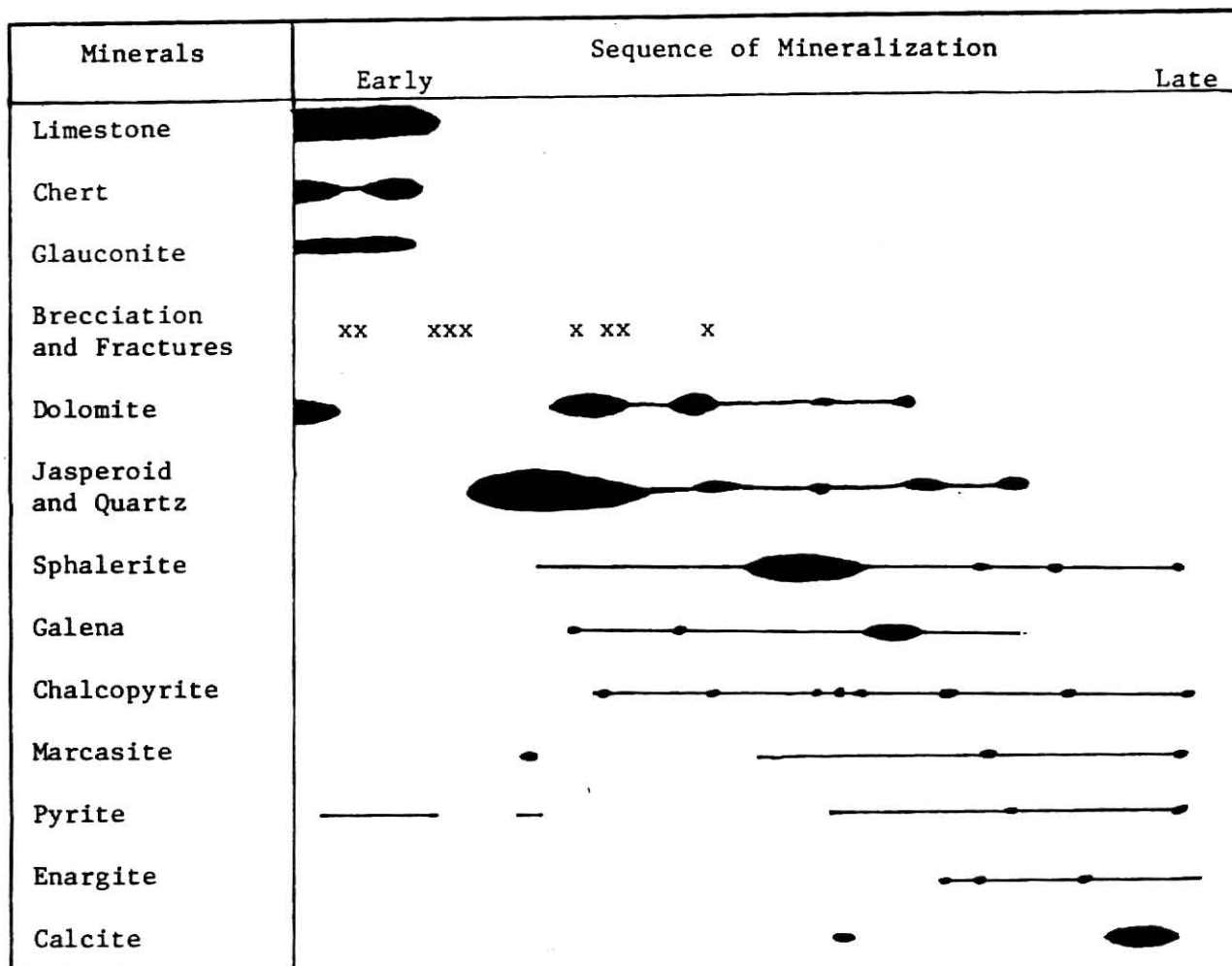


Figure 9. Paragenetic Sequence of Ore Minerals of the Viburnum Trend (From Hagni and Tranczynger, 1977)

- (1) the lead originated in magmatic ore solutions at depth, rose along fractures in the Precambrian basement rocks, and migrated through the Lamotte Sandstone and into the Bonneterre Dolomite (Ohle and Brown, 1954; Ohle, 1959, 1976);
- (2) hydrothermal solutions extracted lead from the Precambrian basement, moved through the Lamotte Sandstone and into the Bonneterre Dolomite (Kanasewich, 1962; Heyl et al., 1966; Kisvarsanyi, 1977);
- (3) connate waters in the Paleozoic section deposited the lead in the Bonneterre Dolomite (Brown, 1967);
- (4) the ore fluids were related to the few alkalic igneous rocks in the region (Heyl et al., 1966; McKnight, 1967);
- (5) one third of the lead was derived from the basement rocks and two thirds from the Paleozoic sedimentary rocks by the transporting fluids (Brown, 1967);
- (6) the lead was remobilized and concentrated within the host carbonate rocks (Cannon et al., 1963);
- (7) fluids leached the lead from the Lamotte Sandstone and deposited it in the Bonneterre Dolomite (Doe and Delevaux, 1972);
- (8) lead-bearing fluids, released from metal-rich algal limestones of the back reef zone of the Bonneterre, deposited the lead where sulfide ion-containing brines were encountered (Davis, 1977);
- (9) sulfur-deficient Na-Ca-Cl brines transported the lead to the Bonneterre Dolomite and deposited the lead where a reduced sulfur source was encountered (Brown, 1965; Skinner, 1967; Jackson and Beals, 1967; Gerdemann and Myers, 1972).

FIELD PROCEDURES

SELECTION OF SAMPLES

The sampling procedure for this study involved the collection of sample sets composed of host rock, ore minerals and gangue minerals from individual deposits within the major district. Only samples whose stratigraphic position could be determined were collected. Material from mine dumps or loose surface materials were avoided.

FIELD SAMPLING

Picher Field

Neither the ore deposits nor the host Keokuk Formation crop out in the Picher vicinity, therefore, the access to the ore bodies had to be through existing mines. The only suitable mine in this currently inactive mining area is the Van Pool Mine which is operated as a tourist mine.

Samples of chert, dolomite, sphalerite, and galena were collected from this mine. Because the sulfide minerals contain very little Sr and Rb, large samples (about 1 kg) were collected. Individual sets of samples were collected from areas of less than one square meter.

Southeast Missouri Barite District

The Eminence Dolomite and the Potosi Dolomite, hosts of the ore deposits, crop out within the district. Samples of barite and host dolomite were collected from four mines within this district. Samples of galena and sphalerite were collected from two mines. The samples of barite and host dolomite were collected as a single sample in the field, and separated into components later in the laboratory.

Viburnum Trend

The Viburnum Mine, which is operated by St. Joe Minerals, was selected for sampling of the ore deposits of the Viburnum Trend. Neither the ore deposits nor the host Bonneterre Dolomite crop out within the district. This mine was chosen because the mineralogy of this deposit is simpler than others of the district.

Samples of the Bonneterre Dolomite from both mineralized and unmineralized areas were obtained. The samples of cubic galena were collected from vugs exposed in the working areas of the mine. Two samples of calcite associated with the ore mineralization were also collected at this mine.

LABORATORY PROCEDURES AND ANALYSIS

PREPARATION OF SAMPLES

Crushing and X-ray Analysis

Field samples were catalogued and mineral separates prepared by hand sorting. All sulfides and sulfates were cleaned with 6N HCl to remove any carbonate residues. Carbonates were rinsed in demineralized water. All samples were then reduced to a powder utilizing a clean and precontaminated diamonite mortar and pestle. Powders were stored in sample bottles cleaned in hot 6N HCl and precontaminated.

A preliminary analysis of the carbonate and barite samples was made with a wavelength dispersive X-ray spectrograph to determine the rubidium and strontium concentrations. These analyses were made utilizing a Phillips X-ray Spectrograph with either a molybdenum or tungsten target. The peak intensities of the samples were compared with the U. S. Geological Survey standard granite G-1 and rock W-1 to determine Rb and Sr concentrations. These data were then used to calculate the optimum volume of spike solution to add for isotope dilution analysis.

Reagents and Apparatus

Reagent-grade hydrochloric and nitric acids used in the analytical procedures were triple-distilled in Vycor glass at constant-boiling concentrations. Hydrofluoric acid and perchloric acid were vacuum-distilled, and the lithium carbonate and methanol were a

spectroscopically-pure grade. All water was purified by passing distilled water through two demineralizing columns.

Laboratory ware and apparatus used in the dissolution and separation procedures were constructed of Teflon, Vycor glass, polypropylene or polycarbonate. All dissolution and collection vessels were washed in detergent, soaked in hot 6N HCl, and then rinsed in triple-distilled acid and demineralized water.

Dissolution of Samples

The weights of samples for dissolutions were calculated to provide a minimum of 15 micrograms of Rb or Sr in solution to insure a sufficient sample for repeat analysis. Samples were dissolved in cleaned Teflon dishes or beakers. Samples for unspiked runs were roughly weighed and wetted with a few milliliters of water prior to acid addition. For spiked runs, a few milliliters of water were added to the dish prior to adding the weighed sample and spike solution.

Carbonate Samples. The wetted samples of carbonate were dissolved in an approximate mixture of 20 ml hydrochloric acid and 2 ml perchloric acid per gram of sample. The dishes were heated on a hot plate to a perchlorate mush. The perchlorate residues for rubidium analysis were cooled and stored. The residues for strontium analysis were redissolved in 15 ml of 2N hydrochloric acid and filtered or centrifuged to remove undissolved residue.

Chert Samples. A mixture of 10 ml hydrofluoric acid and 3 ml of perchloric acid per gram of each chert sample was added to the Teflon dishes containing the powdered sample. The mixture was evaporated to a perchlorate mush. The residues for strontium analysis were redissolved in 15 ml of 2N HCl and filtered while the residues for rubidium analysis were stored.

Barite Samples. A lithium carbonate flux was added to the powdered samples of barite in the approximate ratio of 5 parts flux to 1 part sample. The mixture was fused in a crucible over a burner until red and well mixed. The samples were cooled and dissolved in 2N HCl. Any remaining residues were removed by filtering. After testing for complete dissolution, subsequent samples were processed by partial dissolution in warm water.

Sulfide Samples. Because of the large mass of sulfide samples (15-40 g) required to obtain the necessary strontium and rubidium, 250 ml Teflon beakers were used. The dissolution of the samples was accomplished by adding 10 ml 6N nitric acid per gram of sample. The samples were then heated on a hot plate until the sulfur mattee turned white. The samples were filtered and the filtrate evaporated to dryness. The samples for rubidium analyses were converted to perchlorates and stored. The samples were redissolved in 2N HCl and the residues filtered.

Ion-Exchange Separations

Strontium. The strontium ion-exchange columns contained 30 cm x 2 cm of Dowex 50W-X8 resin. The columns were first washed with 3 to 5 bed volumes of 2N HCl and the surface leveled. The solutions were then carefully poured into the columns and allowed to settle into the resin bed. The strontium in each column was monitored by following an identical column with a ^{85}Sr solution added.

The columns were eluted with 2N HCl and the strontium containing portion collected in 20 ml increments. These 20 ml portions were then evaporated to dryness. The residues were redissolved in a few drops

of 3N nitric acid and transferred to 2 ml Vycor glass beakers for fluid evaporation. The nitrates were then heated over a burner to oxidize organic residues, then cooled, sealed, and stored for analysis.

Rubidium. The perchlorates obtained from the dissolution procedure were washed with a few ml methanol and transferred to clean centrifuge tubes. The residues were washed with methanol, centrifuged, and the supernate discarded. After several repeat methanol washings, the perchlorates were dissolved in water, transferred to clean dishes and evaporated to dryness. The residues were then dissolved in 3-5 ml of 0.5 nitric acid.

Exchange columns of granular zirconium phosphate were prepared and cleaned with 50 ml of 6N nitric acid and then 100 ml of 2N nitric acid. The solutions were then added to the columns. The columns were first eluted with 0.5N nitric acid and the eluant discarded. The rubidium was then eluted with 50 ml of 6N nitric acid. The acid volumes were evaporated to 1 ml and transferred to 2 ml Vycor glass beakers for storage.

ANALYSIS OF SAMPLES

Spectrometry of Samples

Mass spectrometric runs were made on a 6-inch radius, 60° sector, Neir-type instrument (Nuclide Corporation, Model 6-60S), equipped with a solid source in single filament configuration. Ion collection used a Faraday cup, and ion currents were multiplied by a Cary vibrating reed electrometer. Ion intensities were recorded on a strip chart modified with expanded-scale circuitry.

Filaments were constructed of tantalum ribbon, and both rubidium and strontium nitrates were evaporated onto the filaments from solution. Filaments were cleaned in the instrument and checked for Sr or Rb contaminants.

Isotope Analysis

Rubidium Isotope Dilution. Rubidium concentrations were obtained using a ^{87}Rb enriched spike solution with characteristics as shown in Table 2. Samples were spiked to give sample-plus-spike mixture $^{87}\text{Rb}/^{85}\text{Rb}$ of about 1.0. Rubidium runs were conditioned for 30 - 60 minutes at a filament current of 0.5 amps, and analyses normally made in the low 10^{-6} torr range. Measured ^{85}Rb and ^{87}Rb peak heights were summed in sets of six and the isotope ratios calculated. A single analysis consists of the average of 4 - 7 such sets.

Strontium Isotope Dilution. A ^{84}Sr -enriched spike with the characteristics shown in Table 2 was used for the Sr concentration determinations. Samples were spiked to give $^{84}\text{Sr}/^{86}\text{Sr}$ ratio of about 1.0. Because strontium separates commonly contained Rb, it was necessary to condition the filaments until no ^{85}Rb was detected. Analyses were made in the 10^{-7} torr range. Isotope ratios were calculated for sets of six measurements with a single analysis consisting of the average of 6 - 10 such sets. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was also calculated from these data using the method of Van Schmus (1966).

Strontium Isotope Ratios. Although it is possible to calculate the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from ^{84}Sr spiked runs, it was desirable to measure the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio directly for many of the samples. The samples were analyzed under similar conditions and procedures as the isotope

Table 2

Rb and Sr Spike Solution Composition

Isotopic Composition of ^{84}Sr -Enriched Spike Solution

$$^{86}\text{Sr}/^{84}\text{Sr} = 0.04718$$

$$^{87}\text{Sr}/^{84}\text{Sr} = 0.01601$$

$$^{88}\text{Sr}/^{84}\text{Sr} = 0.14047$$

$$\text{Sr Concentration of the Spike Solution} = 2.397 \mu\text{g}/\text{ml } ^{84}\text{Sr}$$

Isotopic Composition of ^{87}Rb Spike Solution

$$^{87}\text{Rb}/^{85}\text{Rb} = 120.9512$$

$$\text{Rb Concentration of Spike Solution} = 9.323 \mu\text{g}/\text{ml Rb}$$

dilution analyses. All strontium analyses have been corrected for fractionation effects assuming linear mass-dependent fractionation. All $^{87}\text{Sr}/^{86}\text{Sr}$ ratios have been corrected to $^{86}\text{Sr}/^{88}\text{Sr}$ values of 0.1194 (Neir, 1938).

Rubidium and Strontium Blanks

Rubidium and strontium blanks were prepared from the solution reagents and treated in the same manner as solution of samples. The blanks for the sulfide dissolution averaged less than 0.006 $\mu\text{gm}/$ dissolution and less than 0.004 $\mu\text{gm}/$ dissolution for other sample types. Rubidium blanks were less than 0.0015 $\mu\text{gm}/$ dissolution for all samples. Blank corrections were negligible for sample weights used in this study.

Accuracy and Precision of Isotopic Data

Replicate analysis of spiked samples using separate dissolutions for Sr and Rb indicate a maximum error of ± 3 percent for $^{87}\text{Rb}/^{86}\text{Sr}$ ratios. Replicate analysis of samples of the Eimer and Amend strontium standard (lot. no. 492327) indicated that unspiked runs are reported to ± 0.3 percent. All strontium isotopic data are reported relative to an Eimer and Amend $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7081.

RESULTS AND DISCUSSION

PICHER FIELD

The Sr isotope composition and the Rb and Sr contents of six samples of chert and a sample each of galena, sphalerite, and dolomite from the Mississippi Keokuk Formation are in Table 3.

Chert

The Rb content ranged from 1.80 to 9.85 ppm, the Sr content ranged from 2.73 to 21.81 ppm and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ranged from 0.7180 to 0.7276. These data are plotted on a Sr isotopic evolution diagram (Fig. 10). Except for the sample Pc-4, the remaining data generally define a linear trend, whose slope, calculated from a least-squares analysis, gave an age of 530 m.y. $\pm$ 38 and an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.712. The cause of the deviation of the data for sample PC-4 remains unanswered. Because the Boone Limestone is of Mississippian age (310-345 m.y.), the calculated isotopic age of 530 m.y. is clearly fictitious.

A mixture of two or more components having different Sr isotopic compositions and Rb/Sr ratios could generate a "false" isochron. The prerequisite for the positive linear trend among the data points is that the high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios be associated with high Rb/Sr-bearing phases of the chert at the time of its deposition. A knowledge of the phase with which the Rb and Sr is associated could help explain the cause of the linear trend indicating an anomalous age. Although no attempt was made to search for specific evidence to resolve this problem, Rb and Sr can be associated with microcrystalline silicate

Table 3

Rb-Sr Isotopic Data of Samples from the
Keokuk Formation, Van Pool Mine, Picher, Oklahoma

Sample #	Material	Sr, ppm	Rb, ppm	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$
SL- 1-75	Sphalerite	N.A.	N.A.	N.A.	0.7135
SL- 4-75	Galena	N.A.	N.A.	N.A.	0.7117
SL- 8-75	Dolomite	N.A.	N.A.	N.A.	0.7095
SL- 9-75	Chert	19.52	5.36	0.797	0.7180
SL-13-75	Chert	21.81	6.70	0.890	0.7193
SL-15-75	Chert	21.47	7.42	1.00	0.7186
PC-1	Chert	17.26	9.85	1.65	0.7245
PC-2	Chert	2.73	1.80	1.91	0.7261
PC-4	Chert	6.23	2.16	1.01	0.7276

N.A. = Not available.

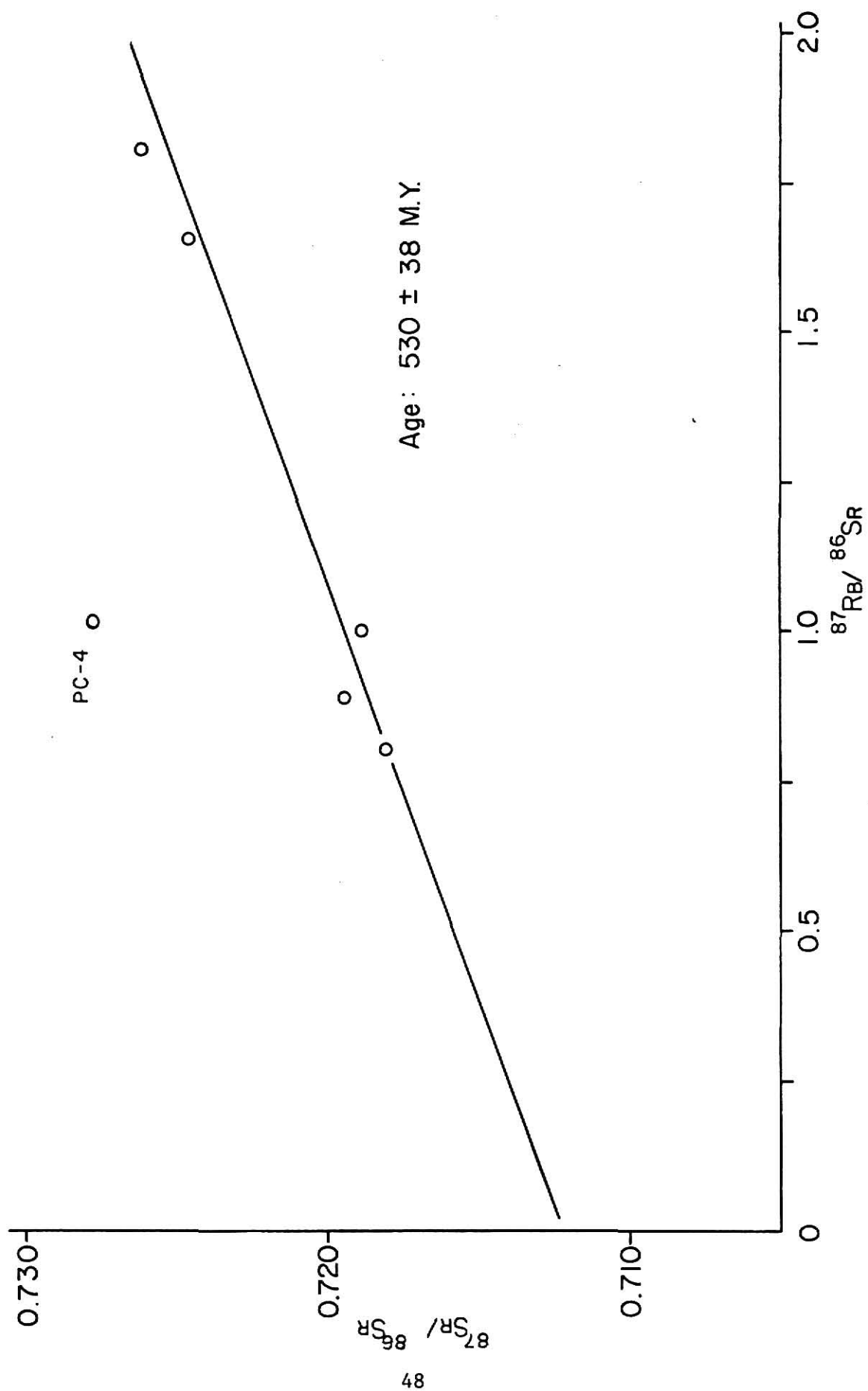


Figure 10. Isochron plot for the samples of chert from the Picher Area

phases of quartz and clay minerals. In dealing with the data of the cherts, the mixing line can be generated by mixing different proportions of two genetically distinct silicate phases differing in their isotopic and chemical compositions.

Sulfide Minerals and Dolomite

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of a galena is 0.7113, that of a sphalerite 0.7135, and the dolomite 0.7095. All the sulfide values are present-day isotopic composition. As the Rb and Sr contents were not measured for the sulfide samples, the initial isotopic composition cannot be determined. The Rb/Sr ratio of dolomite from the ore zone is 0.710 resulting in a calculated initial ratio of 0.7091. The initial value is identical to the isotopic composition of the Mississippian sea water given by Peterman et al. (1970). In the Tri-State District, the host rock in the ore horizon shows clear evidence of extensive reaction with the mineralizing fluid (Brockie et al., 1968; Beales, 1975), but the ore mineralization seems to have had no effect in changing the original composition of the host rock.

SOUTHEAST MISSOURI BARITE DISTRICT

The Sr isotopic composition and the Rb and Sr contents of barite, cubic galena, sphalerite and host rock from the Potosi Dolomite are in Table 4. These ore minerals were collected from vug deposits. Among the samples analyzed were two of barite (SL-23, SL-26b) and one of galena (SL-25), which came from the same stratigraphic horizon and were several centimeters from each other.

Table 4

Rb-Sr Isotopic Data for the
Southeast Missouri Barite Deposits

Sample #	Material	Sr, ppm	Rb, ppm	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	Location
SL-19 -75	Barite	1205	0	0	0.7107	1
SL-21 -75	Barite	1170	0	0	0.7117	1
SL-22 -75	Dolomite	87.58	N.A.	N.A.	0.7082	1
SL-23 -75	Barite	1310	0	0	0.7103	2
SL-25 -75	Galena	N.A.	N.A.	N.A.	0.7135	2
SL-26b-75	Barite	1437	0	0	0.7105	2
SL-26s-75	Sphalerite	N.A.	N.A.	N.A.	0.7125	2
SL-27 -75	Dolomite	62	N.A.	N.A.	0.7089	2
SL-29 -75	Galena	0.120	0.018	0.434	0.7127	2
SL-29 -75	Galena	N.A.	N.A.	N.A.	0.7125	2
SL-30 -75	Dolomite	113.5	N.A.	N.A.	0.7086	3
SL-32- 75	Barite	1450	0	0	0.7099	3
SL-33- 75	Barite	1361	0	0	0.7110	4
SL-34- 75	Dolomite	60.74	N.A.	N.A.	0.7084	4
SL-35- 75	Barite	1341	N.A.	N.A.	0.7109	4
SL-36- 75	Barite	1633	0	0	0.7099	4
SL-36- 75	Barite	N.A.	N.A.	N.A.	0.7098	4

¹SE $\frac{1}{4}$, Sec. 17, T36N, R1E

²SW $\frac{1}{4}$, Sec. 18, T37N, R3E

³W $\frac{1}{2}$, Sec. 1, T37N, R2E

⁴Unsurveyed Land Grant East of Racola.

N.A. = Not available.

Dolomite

Four samples of host rock dolomite were measured at $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.7082 and 0.7089. The Sr contents of these samples ranged from 60.7 ppm to 113.5 ppm. The Rb content was measured for only one sample (SL-30, Table 4) and the concentration was 2.1 ppm. The low Rb/Sr ratio of about 0.02 for this dolomite indicates that the isotopic composition of the rock has not changed since its formation. Hence the measured 0.7086 value should be considered the initial isotopic composition of the rock. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the other three samples of dolomite are very similar to that of sample SL-30. Even if there were any radiogenic growth of ^{87}Sr in these three samples, the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios cannot be higher than 0.7086. Assuming that the dolomite samples are very low in Rb/Sr and have an average value of 0.02, the mineralized horizon of the Potosi Dolomite has an average initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7085. The range of measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the Potosi Dolomite probably reflects the isotopic composition of Late Cambrian sea water, because Faure (1978) reported similar isotopic data for Upper Cambrian carbonate rocks from the Antarctic.

Barite

The Sr content of samples of barite ranged from 1170 ppm to 1633 ppm. No Rb was detected in these samples. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the barite ranged from 0.7099 to 0.7117. The measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the barite samples are presumably the values of their initial Sr isotopic composition because of their extremely low Rb/Sr ratios.

From the isotopic data of samples of barite and dolomite, two important observations can be made: (1) barite was not in isotopic equilibrium with the host Potosi Dolomite, and (2) the barite had a range of isotopic composition from 0.7099 to 0.7117. In the Southeast Missouri Lead Districts, the replacement of host rocks by the mineralizing fluids is minimal (Beales, 1975). The discordance in the Sr isotopic composition between barite and dolomite tends to suggest the lack of any extensive reaction between the ore-bearing fluids and the host rocks.

The different Sr isotopic compositions of barite are related to the differences in the isotopic compositions of the mineralizing fluids. Whether any variation in the isotopic composition exists within a single crystal of barite has not been established in this study. Leach (1973) reported a microprobe analysis of a single barite crystal which showed different Sr content across crystal plates. Such zoning can also explain the strontium isotopic variations among samples of barite. This indicates a time-dependent variation in the isotopic composition of the mineralizing fluids, a situation analogous to the one recognized by Ault and Kulp (1959) and Eckelmann and Kulp (1959) for the lead and sulfur isotopic zones within a single crystal of galena from the southeast Missouri area.

The strontium isotopic data suggest a lack of chemical reaction between the mineralizing fluid and the host rock. The precipitation of barium sulfate in numerous pockets and cavities within the host rock can be attributed to the presence of at least a second fluid at the site of deposition. To assess whether or not the mineralization

resulted from a mixing of two isotopically and chemically distinct fluids, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the samples of barite were compared with their Sr contents. Faure (1978) reported that for a simple mixing of two components having different Sr isotopic compositions and Sr contents, the resultant $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of different mixtures bear a linear relationship to $1/\text{Sr}$ content according to the following equation:

$$\begin{aligned} (^{87}\text{Sr}/^{86}\text{Sr})_{\text{mix}} = & \frac{\text{Sr}_A \text{Sr}_B ((^{87}\text{Sr}/^{86}\text{Sr})_B - (^{87}\text{Sr}/^{86}\text{Sr})_A)}{(\text{Sr}_A - \text{Sr}_B)} \times \frac{1}{\text{Sr}_{\text{mix}}} \\ & + \frac{\text{Sr}_A (^{87}\text{Sr}/^{86}\text{Sr})_A - \text{Sr}_B (^{87}\text{Sr}/^{86}\text{Sr})_B}{\text{Sr}_A - \text{Sr}_B} \end{aligned}$$

Where:

Sr_A = Sr content of phase A

Sr_B = Sr content of phase B

Sr_{mix} = Sr content of mixture of phase A and phase B

$(^{87}\text{Sr}/^{86}\text{Sr})_{A, B, \text{mix}}$ = the isotopic ratios of the indicated phase

As in Fig. 11, the plot of $^{87}\text{Sr}/^{86}\text{Sr}$ against $1/\text{Sr}$ has a linear trend suggesting that a two-component mixing model may explain the depositional history of the barite. The departure from a clear-cut linear relationship can be attributed to a variation in the distribution coefficient of Sr in different crystals of barite, caused by temperature

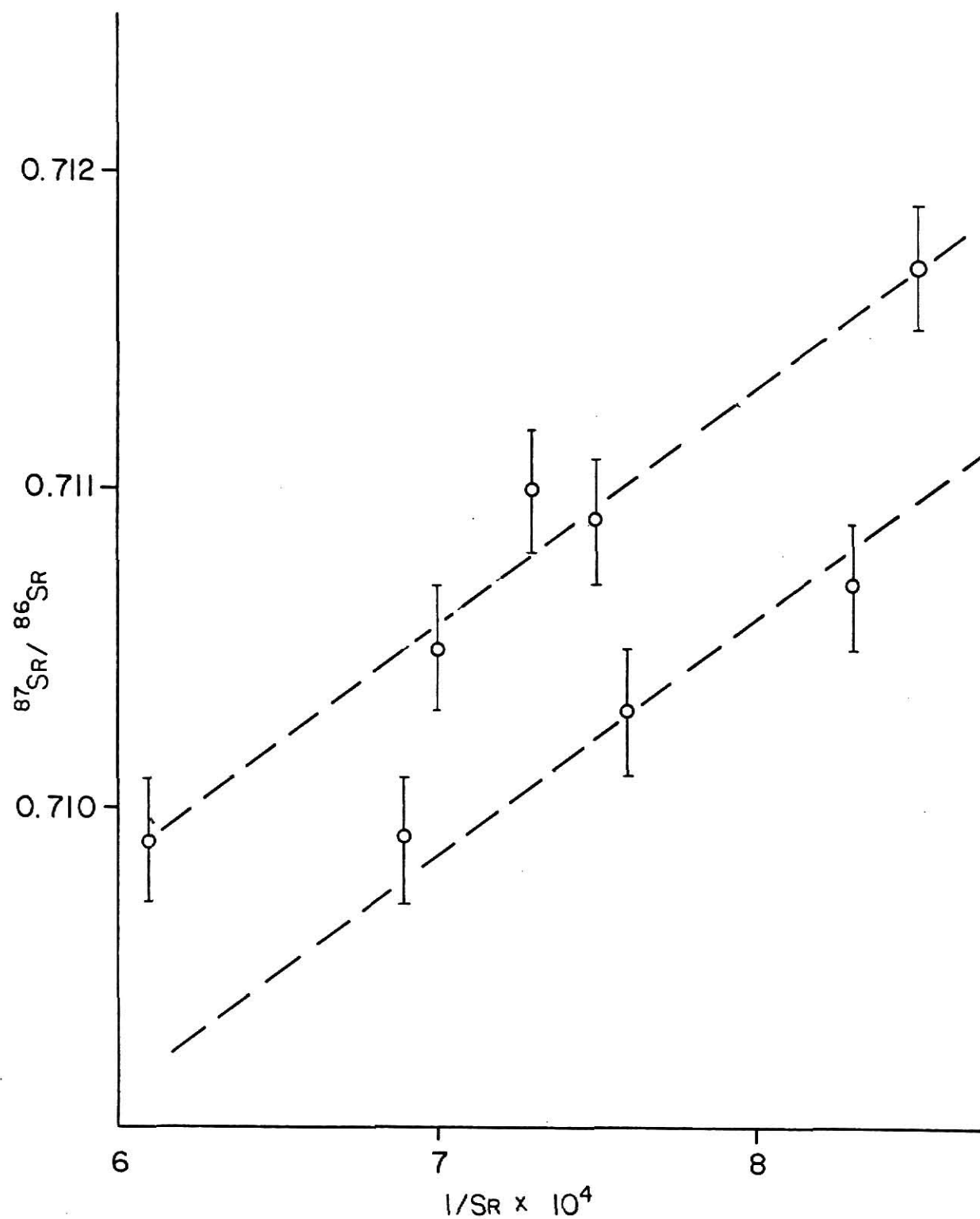


Figure 11. Strontium mixing trend for samples of barite from Southeast Missouri Barite District

differences of the mineralizing fluids (Roedder, 1967, 1977). Additionally, the scatter may have resulted from random variation in the strontium isotopic composition of the mineralizing fluids. Although it is highly suggestive, the trend of increasing $^{87}\text{Sr}/^{86}\text{Sr}$ ratio with decreasing Sr content for the samples of barite can be explained by having intermittent crystal growth from introduction into the depositional sites of the minerals of several pulses of mineralizing fluids with limited, but different, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

Sulfide Minerals

Only one galena sample was analyzed for both the Rb/Sr and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, and the data from it were considered for the calculation of a possible age by assuming an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. The choice of an initial ratio is critical to the calculation of a meaningful age from a single set of data. As barite and galena are intimately associated in this lead-barite district, the isotopic composition of the barite may be safely assumed to be the initial isotopic composition of the fluid forming the galena. Two barite samples (23 and 26b) analyzed in this study were adjacent to the galena. The ^{87}Sr and ^{86}Sr ratios of these two barite samples were 0.7103 and 0.7105; hence, a value of 0.7105 was assumed to be the initial isotopic composition of the galena. The calculated Rb-Sr age of 380 m.y. corresponds to the Devonian Period.

VIBURNUM TREND

The Rb and Sr contents and the Sr isotopic composition of four cubic galena samples, two calcite samples associated with vug-filling

sulfide deposits, and ten dolomite samples representative of rocks from both the mineralized and non-mineralized portions of the Bonnetterre Dolomite in the Viburnum mine were analyzed (Table 5). The four galena samples, with Sr contents ranging from 0.22 to 0.60 ppm and Rb contents ranging from 0.01 to 0.44 ppm, yielded $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ranging from 0.7110 to 0.7224. When the data are plotted on the strontium evolution diagram, a linear trend of increasing $^{87}\text{Sr}/^{86}\text{Sr}$ with increasing $^{87}\text{Rb}/^{86}\text{Sr}$ resulted (Fig. 12).

The Sr contents of dolomite ranged from 32.02 to 106.84 ppm, whereas the Rb contents ranged from 2.54 to 3.82 ppm. The measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the dolomite ranged from 0.7082 to 0.7089. No difference in the isotopic composition of the samples from the sulfide-mineralized zone and those from the non-mineralized zone was recognized. The two calcite samples associated with sulfide minerals yielded $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7128 and 0.7130.

Dolomite

The $^{87}\text{Rb}/^{86}\text{Sr}$ ratios of the samples of dolomite are generally less than 0.16. The high value of 0.33 for the sample SL-9 remains unexplained. By assuming a maximum age of about 500 m.y. for rocks of the Cambrian Period, the initial ratios of the samples are approximately 0.708. The initial ratios of these carbonate rocks are very similar to those of the Potosi Dolomite and Eminence Dolomite from the barite-galena district. As is pointed out in the following discussion, the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the samples of sulfide and calcite are significantly higher than either the samples of barite or dolomite.

Table 5

Rb-Sr Isotopic Data for the Viburnum Ore Deposits

Sample #	Material	Sr, ppm	Rb, ppm	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{87}\text{Sr}$
SL- 1 -76	Dolomite	68.24	3.82	0.162	0.7089
SL- 5 -76	Dolomite	68.24	3	0.126	0.7083
SL- 7 -76	Dolomite	31.02	3.5	0.326	0.7089
SL- 8 -76	Galena	0.59	0.44	2.160	0.7224
SL-10 -76	Dolomite	106.84	2.54	0.069	0.7087
SL-11 -76	Galena	0.22	0.011	0.145	0.7130
SL-13 -76	Dolomite	33.53	N.A.	N.A.	0.7084
SL-14 -76	Galena	0.60	0.028	0.134	0.7110
SL-15 -76	Galena	0.46	0.076	0.478	0.7128
SL-16 -76	Dolomite	40.80	N.A.	N.A.	0.7087
SL-19 -76*	Dolomite	79	N.A.	N.A.	0.7085
SL-22 -76	Dolomite	87.58	N.A.	N.A.	0.7082
SL-30a-76	Dolomite	N.A.	N.A.	N.A.	0.7089
SL-30c-76	Dolomite	N.A.	N.A.	N.A.	0.7083
SL-Ca -1	Calcite	N.A.	N.A.	N.A.	0.7128
SL-Ca -2	Calcite	N.A.	N.A.	N.A.	0.7130

* Non-mineralized stromatolitic dolomite from zone 7.

N.A. = Not available.

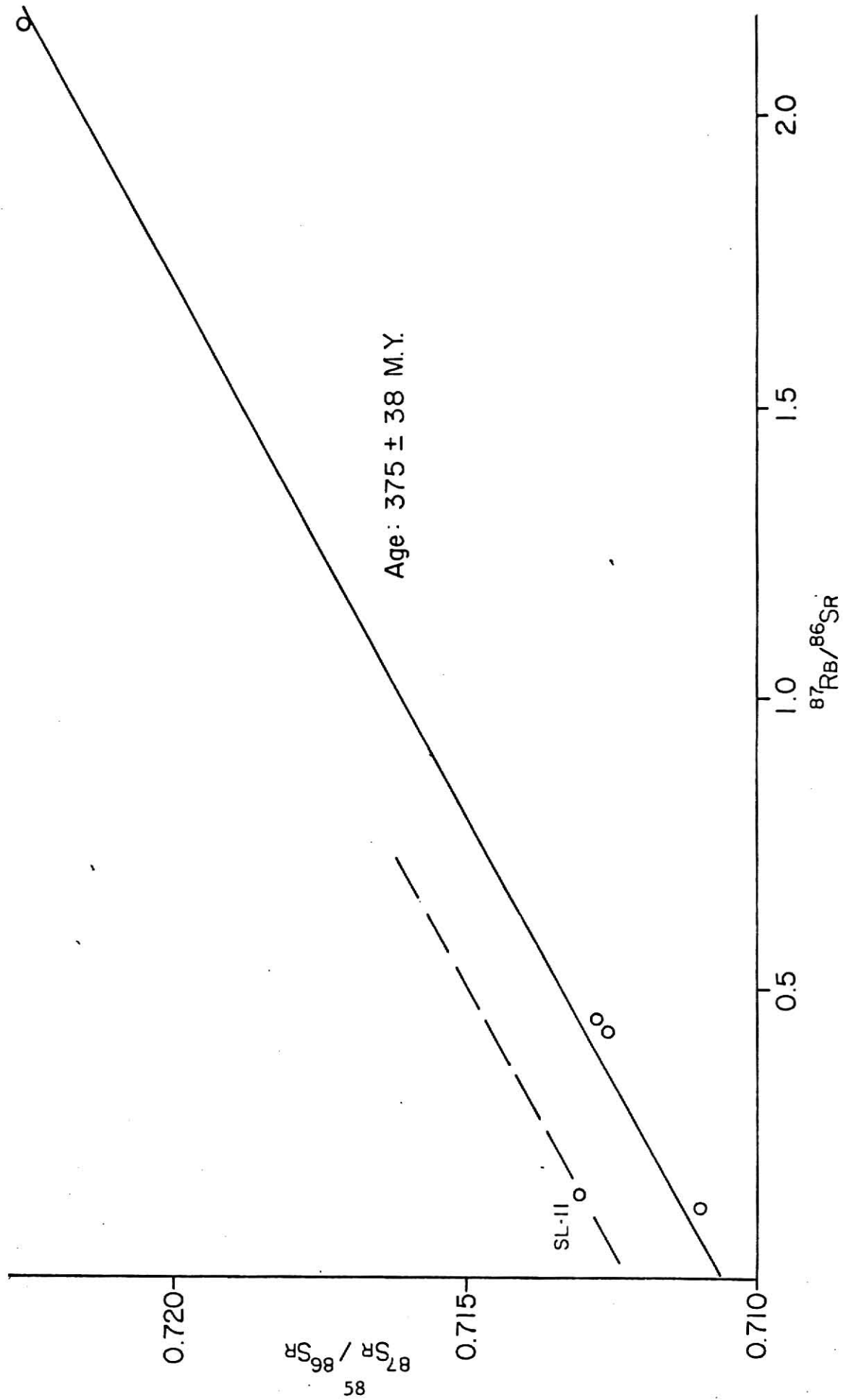


Figure 12. Isochron plot for sulfide minerals from southeast Missouri

Davis (1977) suggested that the dolomitizing-brine fluids transported the metals from the limestone of the back reef facies of the Bonnetterre Dolomite. This model of ore genesis and deposition would require initial isotopic composition of the ore-forming fluids to be nearly identical to that of the dolostones. However, the isotopic data suggest that mineralization and dolomitization were genetically unrelated events.

Sulfide Minerals and Calcite

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the samples of galena are plotted against their corresponding $^{87}\text{Rb}/^{86}\text{Sr}$ ratios in a Rb-Sr isochron plot (Fig. 12). The data for a sample of galena (SL-29) from the barite district are also plotted on this diagram. Four of the five data points tend to indicate a linear array on the diagram. The slope of this line yields an age of about 375 m.y. with an intercept for the initial isotopic composition of 0.7110. The calculated age indicates that the mineralization occurred during the Devonian Period. By assigning the same age for all the samples, the initial ratio of the galena sample (SL-11), which plotted off the isochron, was calculated to be 0.7125. This apparent difference in the initial ratio among the sulfide minerals suggests that the isotopic composition of the fluids varied considerably during the mineralization period. As calcite has an extremely low Rb/Sr ratio, there cannot have been significant growth of radiogenic strontium since crystallization of the carbonate crystals. So, the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7128 and 0.7130 are their initial ratios.

A comparison between the initial strontium isotopic composition of the galena and that of the calcite shows that fluids from which calcite formed were more enriched in ^{87}Sr than those from which the galena formed. For the Magmont mine in the Viburnum trend, Hagni and Tranczynger (1977) proposed that calcite formed last among the principal minerals introduced into the host Bonneterre Dolomite. Thus it appears from the isotopic data that the isotopic composition of the mineralizing fluid changed during the period of ore-deposition with a time-dependent increase in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio from 0.7110 to 0.7130 in the mineralizing fluid.

C O N C L U S I O N S

The strontium isotopic data obtained from this investigation have been utilized either to respond to questions that remain largely unanswered or to provide additional lines of evidence to narrow the continuing debate over the origin of the Mississippi Valley-type sulfide deposits of southeastern Missouri and the Tri-State areas. These data have been used to address questions concerning sources of mineralizing fluids, mechanism of precipitation, and period of mineralization.

The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of barite, galena, and calcite from the ore deposits in southeastern Missouri range from 0.7099 to 0.7117, 0.7110 to 0.7125, and 0.7128 to 0.7130, respectively. These values are much higher than those of many magmatic minerals and rocks of mantle origin (Faure, 1978). Thus, the strontium in the mineralizing fluids cannot be derived from a magmatic source which originated in the mantle. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the ore minerals; however, do not answer the question of a magmatic hydrothermal source for the mineralizing fluids because many granitic igneous rocks of probable crustal origin are known to have initial strontium isotopic compositions similar to those observed for the ore minerals.

Fluid inclusion studies by Newhouse (1933) and Roedder (1967, 1977); lead isotopic studies by Brown and Snyder (1959), Eckelmann and Kulp (1959), Brown (1967), Doe and Delevaux (1972) and Sverjensky et al. (1979); and stable isotopic investigations by Ault and Kulp (1960), Brown (1967), Hall and Friedman (1969) and Sverjensky et al. (1979) provided critical evidence in support of crustal origin of the

mineralizing fluids; possibly they were brines chemically similar to those in many oilfield areas (Carpenter et al. 1974). The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, ranging from 0.7099 to 0.7130 for the ore minerals in these deposits are in agreement with the values of 0.7100 to 0.7330 obtained from oilfield brines (Chaudhuri, 1978). As the initial ratios of the ore minerals are significantly higher than those of the host rocks with present-day ratios between 0.7082 and 0.7089, Davis' (1977) suggestion of extracting significant quantities of metals from the host carbonate rocks is questionable.

Anderson (1975) cited cooling, dilution, high pH, and the addition of sulfur to the mineralizing solution as possible causes of precipitation of sulfides. He demonstrated that sulfide and lead ions cannot be transported together in the same solution unless the pH of the mineralizing solution is less than four. Lacking any concrete evidence for dissolution of the host concurrent with ore deposition, Anderson (1975) and Beales (1975) contended that the mixing of two fluids was the most probable cause of precipitation of the sulfide minerals in the Mississippi Valley-type deposits.

The Sr isotopic data of calcite and the cubic galena crystals from the Viburnum district are of major significance in the evaluation of the possible role of pH in the precipitation of ores. If the pH of the solutions was very low, as would be necessary to transport sulfide and metals together in the same solution, then the host carbonate rocks would have had to undergo considerable dissolution. The mineralizing solutions migrating through the rocks would tend to approach an isotopic composition similar to that of the host rocks.

The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the sulfide minerals and calcite range from 0.7110 to 0.7125 and from 0.7128 to 0.7130, respectively, which proves that the minerals were not in isotopic equilibrium with the host carbonate rocks which have ratios from 0.7082 to 0.7089. Moreover, no differences in the isotopic composition of Sr exist between the highly mineralized and the non-mineralized parts of the Bonnetterre Dolomite. The Sr isotopic data; therefore, rule out the possibility that the ore deposition resulted from reaction with the host rocks. Additionally, the results tend to suggest that the pH of the mineralizing solutions was not low enough (less than 4) to transport sulfide and lead ions together in the same solution. From the isotopic data it can be concluded further that most spaces in the host carbonate rocks probably developed prior to the ore deposition, probably during dolomitization of the carbonate rocks.

Although no difference exists in the Sr isotopic composition between the mineralized and the non-mineralized dolomite of the Bonnetterre Dolomite, Sverjensky and Wasserman (1978) noted a $\delta^{18}\text{O}$ enrichment of the mineralized dolomite (25 per mil) compared to that of the non-mineralized dolomite (21 per mil). The difference between the isotopic evidences can be resolved if $\delta^{18}\text{O}$ enrichment of the ore host took place at the very early stage of ore mineralization by a fluid which had an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio very similar to that of the host rock (0.7082 to 0.7089). This would then suggest not only a change in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the ore fluids during major sulfide mineralization, but also an increase in the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of sulfide minerals and calcite.

The initial ratios of the calcite and sulfide minerals from the Viburnum ore deposits are not identical. Thus the precipitation of these two phases from the same fluid is ruled out. The differences in the initial ratios among the sulfide minerals and calcite are indicative of an episodic precipitation history. Calcite has been considered a very late phase in the paragenetic sequence of the ore-mineral deposition (Hagni and Tranczynger, 1977), and the high initial ratios for the Viburnum calcite samples suggest that the mineralizing fluids became enriched in ^{87}Sr as the mineralization process continued.

Differences in the initial strontium isotopic composition also have been noted in the ore deposits of the barite district in southeast Missouri. Like the ore deposits of the barite district in the Viburnum area, barite and sulfide minerals were not in isotopic equilibrium with their host carbonate rocks of the Potosi Dolomite. The difference in the initial isotopic composition can be related to episodic precipitation of the ore minerals. As in Fig. 10, the data suggest a mixing of at least two fluids with distinctly different isotopic compositions and strontium contents prior to mineralization, accompanied by episodic changes in strontium isotopic compositions of the mineralizing fluids. The time-dependent variation in the strontium isotopic composition of the mineralizing fluids and their precipitates has parallel variations in the sulfur isotopic composition and lead isotopic composition of a single crystal of galena from the Southeast Missouri Lead District (Ault and Kulp, 1959; Eckelmann and Kulp, 1959).

The time of mineralization has been a major unknown factor in understanding the origin of these sulfide deposits. Previous estimates

of the age of mineralization have been based on structural and stratigraphic data. These field relationships have helped to set a limit on the maximum age of mineralization; however, a precise age cannot be established from the evidence of fault-ore relationships. Beales et al. (1974) attempted to date the mineralization event from the paleomagnetic data and suggested that the mineralization could have occurred shortly after the deposition of the host rocks.

The isotopic data in this paper are the first published accounts of an absolute age of the ore mineralization of any Mississippi Valley-type deposit. The Rb-Sr isochron age for three galena samples from the Viburnum Trend and one sample of galena from the barite-lead district of southeast Missouri is estimated to be about 375 m.y., a Devonian age for the mineralization. This age is in agreement with an age of 360 ± 3 m.y. ($\lambda = 1.42 \times 10^{-11}$) by Kish and Stein (1979) for the glauconite grains in the Bonneterre Dolomite which were probably reset by hot ore fluids.

Although the isotopic age for the ores in the southeast Missouri area can be construed as tentative for lack of good statistical control on the results, the age is contemporary with some igneous activities in this area. The Avon diatremes of mica periodotite, only a few miles from Mine La Motte and about 50 miles east of the Viburnum Trend, have been dated 390 ± 20 m.y. or Devonian, by Zartman et al. (1966).

The Sr isotopic data agree with the evolution of ore from sedimentary basins. A major problem for any basinal water theory lies in the difficulty of explaining a distal ore-fluid migration which maintained a temperature as high as 150° C at the site of deposition. The

likelihood of contemporaneity between the igneous activity and the ore mineralization in the Southeast Missouri District during the Devonian Period obviates the need for a distal migration of the ore fluids. The igneous source could have provided necessary heat to the mineralizing solutions and caused the fluids to move laterally and widely, resulting in mineralization over this district.

The attempt to establish a limit on the age of mineralization in the Tri-State District failed, because the Rb-Sr age of the samples of chert far exceeded the stratigraphic age of the host rocks. The data have been interpreted in terms of the mixing of at least two components with distinctly different strontium isotopic compositions and Rb/Sr ratios, generating an anomalous isochron.

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STRONTIUM ISOTOPES AS A TRACER FOR THE
ORIGIN OF MISSISSIPPI VALLEY-TYPE SULFIDE
DEPOSITS FROM THE SOUTHEAST MISSOURI
AND TRI-STATE DISTRICT OF MISSOURI

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A B S T R A C T

The Rb-Sr isotope method was used to study the Mississippi Valley-type deposits of the Southeast Missouri Lead District, the Southeast Missouri Barite District, and the Tri-State Lead-Zinc District. The data from this study were used to address questions concerning the sources of mineralizing fluids, mechanisms of precipitation, and the age of mineralization of these deposits.

Five samples of chert from the Picher field have present day $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.7180 and 0.7276. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of a sample of galena is 0.7112, of sphalerite 0.7135, and of dolomite 0.7095. When the Rb-Sr data from the samples of chert are plotted, a linear isochron indicates a 530 m.y. age and an initial ratio of 0.7121 results. Because the age assigned to the Keokuk Formation is Mississippian (310-345 m.y.), the age calculated from the Rb-Sr data is not consistent with that determined from other geologic data. The data are not sufficient to explain the process which generated the disparate ages. The data do indicate that the chert was not formed from the same fluids as the dolomite.

Samples of barite from the Southeast Missouri Barite District have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from 0.7099 to 0.7117, of host dolomite from 0.7082 to 0.7089, and of sulfide minerals from 0.7125 to 0.7135. The Rb-Sr data of the samples of barite are consistent with a mixing of two solutions at the site of deposition. An age of 380 m.y. was calculated from the Rb-Sr data of a single sample of galena.

The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios calculated for samples of galena, calcite, and host dolomite from the Viburnum Trend are 0.7110, 0.7129, and 0.7080, respectively. The Rb-Sr data for the samples of galena,

when plotted, yield a linear isochron representing a calculated age of about 375 m.y. A comparison of the isotopic data of the ore minerals with that of the dolomite host in mineralized and un-mineralized areas indicates that the mineralizing fluids did not react with the host Bonnetterre Dolomite. The isotopic data are consistent with a crustal origin for the mineralizing fluids.