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Mineral paragenesis and trace element distribution in the Tri-State zinc-lead district Missouri, Kansas, Oklahoma

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MINERAL PARAGENESIS AND TRACE ELEMENT DISTRIBUTION
IN THE TRI-STATE ZINC-LEAD DISTRICT
MISSOURI, KANSAS, OKLAHOMA

presented by Richard D. Hagni

a candidate for the degree of Doctor of Philosophy

and hereby certify that in their opinion it is worthy of acceptance.

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MINERAL PARAGENESIS AND TRACE ELEMENT DISTRIBUTION IN THE TRI-STATE ZINC-LEAD DISTRICT

MISSOURI, KANSAS, OKLAHOMA

An Abstract of A Dissertation
Presented to
the Faculty of the Graduate School
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In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

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by

Richard Davis Hagni

January 1962

MINERAL PARAGENESIS AND TRACE ELEMENT DISTRIBUTION IN THE TRI-STATE ZINC-LEAD DISTRICT

MISSOURI, KANSAS, OKLAHOMA

A review of the literature pertaining to the mineral paragenesis and trace element distribution in the Tri-State zinc-lead district of Missouri, Kansas, and Oklahoma revealed inconsistencies in observation and in interpretation and divergent hypotheses regarding the origin of the ores. In an attempt to reconcile the data collected by many investigators over nearly three-quarters of a century, the writer observed working faces in 37 mines, collected over 2,000 specimens for binocular examination and prepared and studied 110 polished surfaces and 60 thin sections of the ores and associated rocks utilizing mineralographic, petrographic, and x-ray techniques. This detailed study resulted in the determination of a general paragenetic sequence of the minerals in Tri-State ore involving 7 periods of mineralization, each characterized by its own mineral suite and sequence, and each separated from the next by a period of tectonic activity, a period of solution, a hiatus of deposition or by a return to the crystallization of earlier formed minerals. Local deviations from the general paragenetic sequence have been noted, but the recurrence of crystallization of several minerals has been found to be more frequent than previously believed. Chalcopyrite and pyrite were found to have been deposited during 8 intervals, sphalerite and marcasite during 6, and galena and quartz during 5. Fifty-one minerals have been described from Tri-State ores, three for the first time

in this thesis. Four mineral relationships previously believed to be absent in Tri-State ores have been observed and described. No significant variations in paragenetic sequence were detected either with respect to areal or stratigraphic distribution, contrary to the opinions of some who have worked in the district, but in accord with the results of previous studies of trace element distribution.

Previous trace element analyses have been made of rocks, ores, soil and vegetation in the Tri-State district. Since these analyses failed to reveal any significant variation in trace element distribution, the present investigation involved spectrographic analyses of the single minerals: dolomite, galena, and sphalerite, especially selected for their freedom from included impurities as revealed under a stereoscopic microscope. Of the many elements detected spectroscopically, only silver in galena and cadmium, gallium, germanium, and indium in sphalerite were considered worthy of detailed study. In galena, silver was found to vary from 0.2 to 1.6 p.p.m. In sphalerite, cadmium varied from 4,000 to 7,000 p.p.m., gallium from 15 to 480 p.p.m., germanium from 25 to 380 p.p.m. and indium from 10 to 30 p.p.m. While such variations are large, they are wholly unrelated to ereal, stratigraphic or paragenetic position, and substantiate the conclusion based on paragenetic studies that the ore-forming solutions in the Tri-State district were remarkably uniform and not significantly different from the ground water circulating in the district today. Indeed, the sulfide minerals which constitute the ores of the district are still being formed today.

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INTRODUCTION

PURPOSE OF INVESTIGATION

This investigation of paragenetic sequence and trace element distribution in the Tri-State zinc-lead district of Kansas, Missouri, and Oklahoma was suggested to the writer by Dr. O. R. Grawe, who pointed out the lack of agreement among previous investigators regarding the paragenetic sequence of the minerals comprising the ore. He believed that this disagreement might have been due to studies of too few specimens, which did not adequately represent the entire district, and that these were not always studied thoroughly, or that the paragenetic sequence might not be the same throughout the district. The writer undertook to resolve the diverse interpretations of paragenesis by combining extensive field work with both extensive and intensive microscopic investigation, to note local variations from the usual paragenetic sequence, and to correlate these variations with areal, stratigraphic and structural position. The trace element content of single minerals was investigated to ascertain if a correlation might exist between variations in trace element content and variations in paragenetic sequence and to determine what changes might have taken place in the character of the ore-forming solutions which would account for compositional and mineral variations and what bearing this might have on the origin of the ore.

METHOD OF INVESTIGATION

To obtain material for this study, during the summers of 1957 and 1958, the writer visited thirty-seven mines and worked more intensively in the Grace B, Jarrett, Lucky Jew, Big Elk, Netta, Netta White, St. Joe, Crawfish, Whitebird, Piokee and Kenoyer mines[1]. Specimens were collected for paragenetic studies and for spectrographic analysis. Each specimen was assigned a field number and data pertinent to the specimens such as the location and stratigraphic horizon and structural environment were recorded. The exact location of each specimen was recorded on a mine map scaled one inch to three hundred feet. Specimens for spectrographic analysis were carefully bagged to prevent contamination.

Paragenetic study

In the laboratory each specimen was first studied megascopically, and then with the aid of a stereoscopic microscope. The mineral sequence was recorded and all observable features were noted. If the relations were uncertain or concealed, the specimen was cut and polished to reveal the mineral relationships. Sixty thin sections and more than one hundred polished specimens were prepared by the writer. Each thin

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[1] Because of the large number of mines in the Tri-State district and the tendency to rename the mines, Figure 86, a map showing the locations and names currently used for mines in the Picher field and nearby area has been included in Appendix C, through the courtesy of the Eagle-Picher Company.

section and polished specimen was described individually and numerous photographs were taken to illustrate the features and relationship observed.

From the detailed study of the individual specimens a generalized paragenetic sequence was developed. Particular note was taken of variations from the usual sequence, and correlations were sought between these variations and other factors, such as: geographic distribution, stratigraphic position, and structure in the Picher field.

When it became apparent that such correlations were absent in the Picher field, the writer, upon Dr. O. R. Grawe's advice, expanded his studies beyond the Picher field to include other areas within the Tri-State district. For these studies the following collections were available for megascopic and microscopic study:

1) The University of Missouri, School of Mines and Metallurgy, Department of Geology Museum Collection, Rolla, Missouri.

2) The Schifferdecker Park Mineral Museum Collection, Joplin, Missouri.

3) The E. J. Palmer Collection, Webb City, Missouri.

4) The "Dana" Collection, University of Missouri, School of Mines and Metallurgy, Rolla, Missouri.

5) The E. T. McKnight Collection, University of Missouri, School of Mines and Metallurgy, Rolla, Missouri.

6) Dr. O. R. Grawe's personal collection, University of Missouri, School of Mines and Metallurgy, Rolla, Missouri.

7) The Mineragraphic Collection, University of Missouri, School of Mines and Metallurgy, Rolla, Missouri.

8) The Boodle Lane Collection, Galena, Kansas.

9) The Eagle-Picher Collection, Cardin, Oklahoma.

10) The W. A. Tarr Collection, University of Missouri, Columbia, Missouri.

The paragenetic sequence was observed in each specimen, and the sequence in each individual field within the Tri-State district was worked out. The types of correlation sought in the Picher field were now sought throughout the whole Tri-State district.

Trace element study

For spectrographic analysis, clean cleavage fragments of dolomite, galena and sphalerite were selected from coarsely crushed minerals. The elements Al, Cu, Fe, Mn, Na, Pb, Si, V and Zn were detected in dolomite; Ag, Al, Ca, Cr, Cu, Fe, Mg, Sb, Si, and Zn were detected in galena; Ag, Al, Ca, Cd, Cr, Cu, Fe, Ga, Ge, In, Mg, Mn, Pb, Si, and Ti were detected in sphalerite. The elements which showed significant variations in concentration and are believed to be present not as contaminant phases are: Cd, Ga, Ge, and In in sphalerite and Ag in galena.

The trace element content of Ag in galena and Cd, Ga, Ge, and In in sphalerite were plotted on overlays of Picher field maps to investigate areal zoning; and on vertical sections to investigate stratigraphic zoning. The Ge and Ga content of sphalerites of different ages was investigated to determine possible paragenetic relationships. Similarly, the trace element content of gray dolomite was compared with that of pink dolomite to determine if differences exist between the two varieties of this mineral.

ACKNOWLEDGMENTS

The writer wishes to express sincere appreciation and thanks to Dr. O. R. Grawe for suggesting the problem, his direction in the field and laboratory, and for critically editing the manuscript.

He wishes also to thank Drs. G. C. Amstutz, P. D. Proctor, A. C. Spreng of the Geology Department, Missouri School of Mines and Metallurgy; Dr. P. M. Bethke of the United States Geological Survey; Drs. W. D. Keller and A. G. Unklesbay, University of Missouri; Mr. D, C. Brockie, Dr. R. A. Chadwick, Mr. A. Kuklis, Mr. J. P. Lyden, and the late Mr. R. C. Lundin of the geological staff of the Eagle-Picher Company, for their helpful advice and suggestions. Mr. Lundin and Dr. Chadwick also frequently accompanied the writer in the mines.

Special thanks are due Miss M. E. Phillips of the Missouri Geological Survey for the spectrographic analyses of the galena samples; Mr. O. A. Rockwell, Vice-President and General Manager of the Eagle-Picher Company, for his cooperation in arranging for spectrographic analysis of the sphalerite samples by Mr. J. S. Bryson of the Research Department of the Eagle-Picher Company at Joplin, Missouri; Mr. D. R. Stark for drafting the plates.

The University of Missouri, at Columbia, the School of Mines and Metallurgy, at Rolla, the City of Joplin, Mr. E. J. Palmer, Dr. E. T. McKnight, Dr. O. R. Grawe, and Mr. Boodle Lane graciously permitted the writer to study their collections of Tri-State minerals.

Financial assistance from the Eagle-Picher Company during parts of the summers of 1957 and 1958 and a research fellowship from the University of Missouri, School of Mines and Metallurgy the summer of

1959 supported field and laboratory work for this thesis.

The writer is especially indebted to his wife, Mrs. Rachael Anne Hagni for her continued help, inspiration, and understanding.

CHAPTER II

GENERAL GEOLOGY OF THE TRI-STATE DISTRICT

LOCATION AND PRODUCTIVITY

The Tri-State zinc-lead district, in a broad sense, consists of an area of about 2000 square miles in southwest Missouri, northeast Oklahoma and southeast Kansas. Its longest axis from Springfield, Missouri to Miami, Oklahoma is about 300 miles.

Mining began in the Tri-State district near Joplin, Missouri, in 1848. During most of its history, and as late as 1949, this district was the world's greatest zinc producer and generally ranked third or fourth in world lead production. Up to and including 1945, the Tri-State district had produced 20,755,020 tons of zinc concentrates and 3,334,057 tons of lead concentrates, together valued at over one billion dollars[2]. Zinc concentrates averaged 58.67 per cent zinc and the lead concentrates averaged 78.46 per cent lead for the period 1907 to 1945.[3] From 1944 to 1948 the district produced an average of 132,552 tons of zinc and 25,224 tons of lead per year.[4]

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[2] A. J. Martin, "Summarized Statistics of production of Lead and Zinc in the Tri-State (Missouri-Kansas-Oklahoma) Mining District", U. S. Bur. Mines Inf. Circ. 7383, p. 3, 1946.

[3] Ibid., pp. 20-21.

[4] O. M. Bishop and R. L. Mentch, Chapters on Lead and on Zinc: "Mineral Facts and Problems", U. S. Bur. Mines Bull. 556, p. 434 and 983, 1956.

While mining began in the Joplin field, most of the production in recent years has come from the Picher field of Oklahoma and Kansas. Mining was curtailed in 1957 and at the present time, due to the depressed prices of zinc and lead, mining in the district is curtailed.

PHYSICAL GEOGRAPHY

Physiographically the Tri-State district occupies parts of the Springfield Plateau of the Ozark Plateaus province, and the Cherokee Lowland portion of the Osage Plains section of the Central Lowland province.[5] The former, mainly in Missouri, is hilly and its surface is underlain by Mississippian formations; the latter section, mostly in Oklahoma and Kansas, is flat and is underlain by Pennsylvanian formations. Altitudes in the district vary from about 780 to about 1200 feet above sea level. The surface is drained principally by the southward flowing Neohso and Spring Rivers.

STRATIGRAPHY

The youngest consolidated formations of the Tri-State district are of Pennsylvanian age. The ore deposits in these formations were not studied by the writer, and therefore the stratigraphy of the Pennsylvanian System is not considered here. These are underlain by Mississippian formations which like the Pennsylvanian are exposed in numerous places within the district. Older formations are not exposed,

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[5] N. M. Fenneman, Physiography of Eastern United States, McGraw-Hill, New York, 714 pp., 1938.

but have been encountered in deep drill holes. These are of Devonian, Ordovician, Cambrian, and Precambrian age. The oldest of these formations are granites which have been reached in deep drill holes at the following localities: 1) the Bird Dog mine in Oklahoma (SW¼, SE¼, SE¼, Sec. 13, T. 29 N., R. 22 E.) at 1245 feet,[6] 2) the John Beaver mine in Oklahoma (SW¼, SW¼, SE¼, Sec. 19, T. 29 N., R. 23 E.) at about 1775 feet,[7] 3) a deep water well at the city of Miami, Oklahoma (SE¼, SE¼, SW¼, Sec. 24, T. 28 N., R. 22 E.) at 1055 feet,[8] 4) a deep well at Carthage, Missouri (SW¼, SW¼, NE¼, Sec. 3, T. 28 N., R. 31 W.) at 1745 feet.[9] At the northwest margin of the district, granite was reached in a well at Columbus, Kansas (NE¼, NE¼, NW¼, Sec. 13, T. 33 S., R. 23 E.) at 1770 feet.[10] Although Weidman[11] believed the granite encountered in the Bird Dog well and that which outcrops at Spavinaw, Oklahoma about 40 miles south of the Tri-State district, to be intrusive, most geologists consider them to be Precambrian.[12]

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[6] Samuel Weidman, "The Miami-Picher Zinc-Lead District, Oklahoma," Okla. Geol. Survey Bull. 56, p. 26, 1932.

[7] H. A. Ireland, "Pre-Cambrian Surface in Northeastern Oklahoma and Parts of Adjacent States", Am. Assoc. Pet. Geol. Bull., vol. 39, p. 478, 1955.

[8] Ibid.

[9] H. G. Bain, C. R. Van Hise, and George I. Adams, "Preliminary Report on the Lead and Zinc Deposits of the Ozark Region", U. S. Geol. Survey, 22d Ann. Rept., pt. 2, p. 77, 1901.

[10] Weidman, op. cit., p. 6.

[11] Ibid., pp. 77-78.

[12] Ireland, op. cit., p. 482.

Paleozoic pre-Mississippian formations recognized by insoluble residue studies by the Missouri Geological Survey from cuttings from deep drill holes in or near the district include the following: Cambrian Lamotte Sandstone, Bonneterre Dolomite, and Eminence Dolomite; Ordovician Gunter Sandstone, Gasconade-Van Buren Dolomite, Roubidoux Sandstone, Jefferson City Dolomite, and Cotter Dolomite. Silurian formations are missing in the Tri-State district.[13] Devono-Mississippian (Chattanooga) Shale was reported to be present at depth in some parts of the district by Siebenthal.[14]

The Mississippian system consists of the Kinderhookian, Osagean, Meramecian and Chesterian Series. The top of the Mississippian System contains the Carterville Formation which belongs to the Chesterian Series. The principal ore bodies lie within the Meramecian and Osagean Series. These have been subdivided by Fowler and Lyden,[15] who have designated the subdivisions, which they commonly refer to as beds, by letters. C through J were assigned to successively lower subdivisions of the Meramecian Warsaw Formation; the letter I was not utilized; K through M were used for subdivisions of the Osagean Keokuk Formation which underlies the Warsaw. A prominent

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[13] Raymond C. Moore, et al., "The Kansas Rock Column", Kansas Geol. Survey Bull. 89, pp. 116-117, 1951.

[14] C. E. Siebenthal, "Mineral Resources of Northeastern Oklahoma", U. S. Geol. Survey Bull. 340, pp. 25-26, 1908.

[15] George M. Fowler, and Joseph P. Lyden, "The Ore Deposits of the Tri-State District", Am. Inst. Min. Met. Eng. Trans., vol. 102, p. 218, 1932.

oolite in the Keokuk Formation, the Short Creek oolite, is placed at the top of M bed by Lyden.[16] It is commonly used as a marker for surface and subsurface stratigraphic and structural studies. The presence of the Burlington Formation between the Keokuk and Grand Falls Formation is uncertain. Other investigators have not found the Burlington Formation in this area.[17] N through Q encompass the Grand Falls Formation of the Osagean Series.[18] R was assigned to the Reeds Spring Formation of the Osagean Series. The St. Joe Formation at the base of the Osagean Series was not assigned a letter. Only one mine, the Riverside mine, is known to have produced ore from this formation. The Kinderhookian Series, which includes the Northview Shale and the Compton Limestone occurs principally on the east margin of the district, but is not encountered in the mines.

A generalized stratigraphic column of the Carboniferous formations modified after Lyden[19] is given in Table I.

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[16] Joseph P. Lyden, "Aspects of Structure and Mineralization Used as Guides in the Development of the Picher Field", Am. Inst. Min. Met. Eng. Trans., vol. 187, p. 1253, 1950.

[17] Raymond C. Moore, George M. Fowler, and Joseph P. Lyden, in "Contributions to a Knowledge of the Lead and Zinc Deposits of the Mississippi Valley Region" edited by E. S. Bastin, Geol. Soc. America Spec. Paper 24, p. 9, 1939; L. M. Cline, "Osage Formations of Southern Ozark Region, Missouri, Arkansas, and Oklahoma", Am. Assoc. Pet. Geol. Bull. vol. 18, p. 1153, 1934; and L. R. Laudon, "Stratigraphy of Osage Subseries of Northeastern Oklahoma", Am. Assoc. Pet. Geol. Bull., vol. 23, p. 329, 1939.

[18] George M. Fowler, et al., "Chertification in the Tri-State Mining District", Am. Inst. Min. Met. Eng. Trans., vol. 115, p. 110, 1935.

[19] Lyden, loc. cit.

TABLE I

STRATIGRAPHIC COLUMN OF CARBONIFEROUS FORMATIONS IN THE TRI-STATE DISTRICT

System	Series	Formation	Bed	Thickness	Lithology	Importance as an Ore Horizon
Pennsylvanian	Desmoinesian Morrowan & Atokan	Several		0-300	Dark shale, sandstone	Minor importance
Mississippian	Chesterian	Carterville		0-100	Limestone conglomerate, shale and sandstone	Minor importance
	Meramecian	St. Louis (?)	B	0-20	Limestone	Unimportant
		Warsaw	C	0-32	Limestone and chert nodules	Unimportant
			D	18-22	"Cotton rock" and chert	Minor importance
			E	5-8	Limestone and chert nodules	Minor importance
			F	12-15	"Cotton rock" and chert	Unimportant
			G H	30-40	Thin bedded chert and limestone	Important
			J	0-40	Glauconitic, shaly limestone and chert	Unimportant
	Osagean	Keokuk	K	0-40	Limestone and chert nodules	Very important
			L	0-35	Chert	Unimportant
				2-5	Short Creek oolite Member	Most important
			M	0-70	Limestone and chert nodules	
		Grand Falls	N	20-30	Chert	Minor importance
			O	8-10	Thin bedded chert and limestone	Important
			P	0-10	Chert	Minor importance
			Q	0-10	Thin bedded chert and limestone	Minor importance
		Reeds Spring	R	50-100	Limestone and dark chert nodules	Important
		St. Joe		50	Limestone and chert nodules	Minor importance
	Kinderhookian	Northview		5-10	Shale	Unimportant
		Compton		5-10	Limestone	Unimportant

STRUCTURE

The Tri-State district is located on the northwest flank of the axis of the Ozark dome. The regional dip in the district is toward the northwest at fifteen to twenty feet per mile.

Structures of lesser magnitude in and near the Tri-State district are: the Horse Creek anticline, the Seneca fault, the Joplin anticline, the Lawton trough, and the Cow Creek anticline, as shown in Figure 1.

The Horse Creek anticline, fifteen miles south of the district, was described by Siebenthal[20] as an asymmetrical fold with a gentle northwest limb dipping two degrees and a steeper southeast limb dipping from five to eighteen degrees. The structure is observed about ten miles east of Tiff City, Missouri, from whence it trends due west to the Missouri-Oklahoma line and then west-southwest to the vicinity of Big Cabin, Oklahoma.

The Seneca fault or syncline, which crosses the Horse Creek anticline about fifteen miles south of the district, was described by Siebenthal[21] and by Weidman.[22] Siebenthal called the structure a double fault, but Weidman believed the structure to be a syncline with associated faulting. The structure extends from Seneca, Missouri,

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[20] C. E. Siebenthal, "Mineral Resources of Northeastern Oklahoma", U. S. Geol. Survey Bull. 340, p. 198, 1908.

[21] Ibid., p. 197.

[22] Samuel Weidman, "The Miami-Picher Zinc-Lead District, Oklahoma", Okla. Geol. Survey Bull. 56, pp. 35-36, 1932.

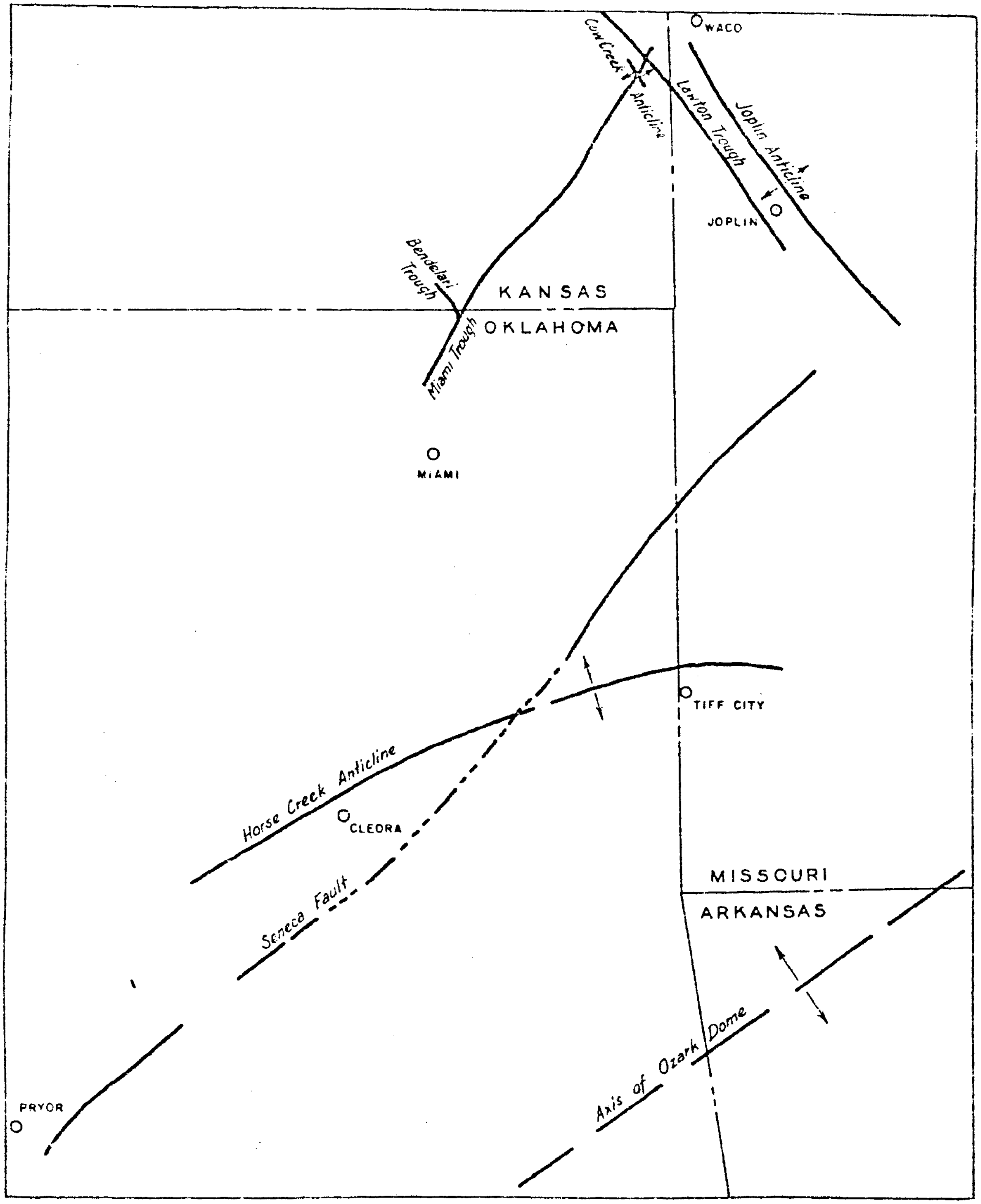

FIGURE I
MAJOR STRUCTURAL FEATURES OF THE TRI-STATE AREA

SCALE 0 5 10 MILES

southwestward to Coweta, Oklahoma. Displacement along this structure is reported to vary from 90 to 140 feet, causing Chester and Pennsylvanian rocks to be preserved within the structure.

Smith and Siebenthal[23] described the Joplin anticline and constructed a structure contour map of the Joplin field based on the top of the Short Creek Oolite. This fold enters the field from the southeast and trends toward Joplin, causing the Short Creek Oolite to rise 40 to 50 feet per mile. In the vicinity of Joplin the fold flattens out and loses its identity, but northwest of Joplin the anticline reappears.

The Lawton trough was shown by Pierce[24] on a structure contour map of the eastern portion of Cherokee County, Kansas. The structure is discontinuous, and trends nearly parallel to, and about three or four miles from, the Joplin anticline. The maximum difference in elevation of the base of the Cherokee Shale caused by the structure is about 120 feet.

The Cow Creek anticline, four miles west of the Joplin anticline, was described by Smith and Siebenthal.[25] It is observable as a rather sharp, northwest trending fold in the Cherokee Shale southwest of Cow Creek, near Lawton, Kansas.

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[23] W. S. Tangier Smith and C. E. Siebenthal, "Description of the Joplin District", in Geologic Atlas of the United States, U. S. Geol. Survey folio 148, p. 9, 1907.

[24] W. G. Pierce, "Contour Map of the Base of the Cherokee Shale in the Zinc and Lead District of Southeastern Kansas", Dept. of the Interior, Memorandum for the Press, 1935.

[25] Smith and Siebenthal, loc. cit.

In the Picher field the largest structures are the Miami and Bendelari troughs. These structures are known both from drilling and from their occurrence in some mines.[26] The trend of these structures is best illustrated on a tectonic map of the Picher field by Fowler.[27] The Miami structure trends northeast-north through the western portion of the Picher field and the Bendelari structure trends northwest from the Miami structure toward the northwest portion of the Picher field. The limbs of these structures appear as distinct faults in some mines, as shown in Figure 2, but occur as breccia zones in other mines, as illustrated in Figure 3. While Fowler[28] and Lyden[29] believed that these structures are a series of graben fault blocks or troughs, Weidman[30] thought that the Miami structure was a syncline with associated faulting, and Siebenthal[31] believed that this structure was formed by underground solution. Pierce[32] believed that all three processes were in

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[26] Fowler and Lyden, op. cit., p. 228.

[27] George M. Fowler, "Structural Deformation and Ore Deposits", Eng. Mining Jour., vol. 161, no. 6, pp. 184-185, 1960.

[28] George M. Fowler, "Structural Control of Ore Deposits in the Tri-State Zinc and Lead District", Eng. Mining Jour., vol. 139, no. 9, p. 46, 1938.

[29] Lyden, op. cit., p. 1254.

[30] Samuel Weidman, "The Miami-Picher Zinc-Lead District, Oklahoma", Okla. Geol. Survey Bull., 56, pp. 31-35, 1932.

[31] C. E. Siebenthal, "Sub-Shale of Picher Lead and Zinc District", U. S. Geol. Survey Circ. 17288, p. 4, 1927, cited by Samuel Weidman, "The Miami-Picher Zinc-Lead District, Oklahoma", Okla. Geol. Survey Bull. 56, p. 32, 1932.

[32] Pierce, op. cit., p. 2.

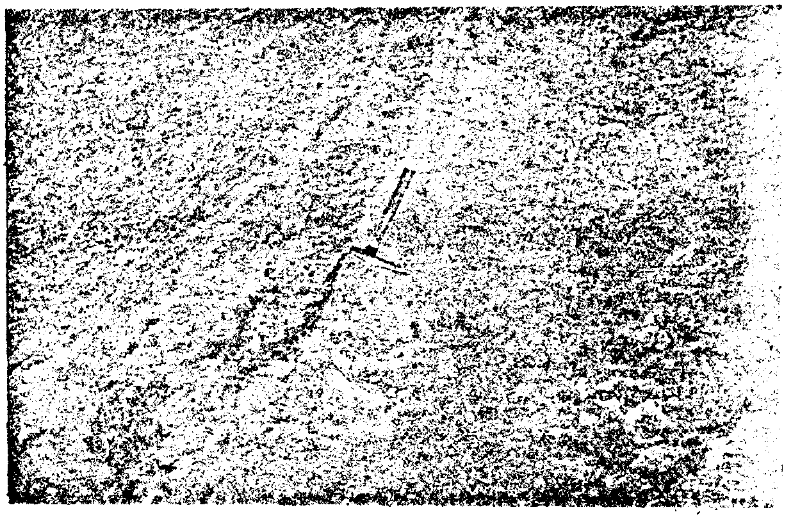

Figure 2. Faulted contact along the Miami trough between unmineralized Chester limestone (left) and mineralized M bed (right). A gouge zone about four inches wide occurs along the contact and beneath the pick. Blue Goose No. 1 mine.

Figure 3. Brecciated zone in G-H beds along the Miami trough. The limestone blocks (light gray) are cemented by jasperoid (dark gray). The lower left portion of the photograph is a pile of rubble resulting from mining. Anna Beaver mine.

evidence along the structures. Naething[33] thought that the Miami structure represented a pre-Chester erosion channel, controlled by pre-Chester faulting, which suffered post-Pennsylvanian faulting. According to Lyden, the Miami structure:

> . . . contains along its trend a series of elongated graben fault blocks, 500 ft to 1200 ft wide, and one half to three fourths of a mile long, that dropped vertically 100 ft to 250 ft.[34]

A fault of Precambrian age in the Precambrian basement rocks nearly coincident in trend with the Miami structure and with the west side upthrown about 600 feet has been inferred by Ireland[35] from studies of logs of deep drill holes in Kansas and adjoining states. Yet Jakosky, Dreyer and Wilson[36] concluded that the Miami trough is a relatively shallow structure which does not reach the basement, since the structure causes no discernible magnetic anomaly.

Various types of slump structures in the district formed by solution of limestone beds have been described. Smith and Siebenthal[37] described the occurrence of "circles" in the Joplin field and concluded

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[33] Foster S. Naething, "The Oklahoma-Kansas-Missouri Zinc-Lead Field", Eng. Mining Jour., vol. 122, no. 16, p. 605, 1926.

[34] Lyden, op. cit., p. 1253.

[35] H. A. Ireland, "Pre-Cambrian Surface in Northeastern Oklahoma and Parts of Adjacent States", Am. Assoc. Pet. Geol. Bull., vol. 39, p. 480, 1955.

[36] J. J. Jakosky, R. M. Dreyer, and C. H. Wilson, "Geophysical Investigations in the Tri-State Zinc and Lead Mining District", Kansas Geol. Survey Bull. 44, pp. 148-149, 1942.

[37] Smith and Siebenthal, op. cit., p. 11.

that the most satisfactory explanation for the origin of the "circles" was through the agency of underground solution. They described Gimlet circle in some detail. It had a diameter of between 400 and 600 feet and the center consisted of a broken shale mass which extended downward at least 60 feet. The outside chert wall exhibited brecciation in horizontal planes and the breccia was cemented by jasperoid.

Schmidt and Leonhard[38] described the circular deposit at Oronogo and ascribed its origin to underground solution of limestone. This circular structure exhibited a diameter of more than one mile and the brecciated central portion had slumped more than 70 feet.

Lyden[39] described slump structures which he attributed to settling and caving of the beds into solution-made openings in limestone.

The writer observed slump structures filled with shale in some mines in the Picher field. In some of these slumps the shale appears to be similar to the Cherokee Shale, but other slumps are filled with a mud. It is uncertain whether this material slumped from the overlying Pennsylvanian Shales. Similar structures filled with large limestone blocks and shaly calcareous material were observed by the writer in the Big Elk and other mines.

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[38] Adolf Schmidt, and Alexander Leonhard, "The Lead and Zinc Regions of Southwest Missouri", Mo. Geol. Survey Rept. for 1874, pp. 486-487 and 522, 1874.

[39] Joseph P. Lyden, "Aspects of Structure and Mineralization Used as Guides in the Development of the Picher Field", Am. Inst. Min. Met. Eng. Trans., vol. 187, pp. 1254-1255, 1950.

Pipe slumps have been described recently by Lyden.[40] They extend from O bed upward and some reach into the Cherokee Shale. They are cylindrical in shape, approximately 100 feet in diameter, about 300 feet in height, and they have dropped relative to the surrounding beds.

Folding or flexing of the beds in the Tri-State district has been long recognized. Smith and Siebenthal[41] detected folding as depicted on structure contour maps based on the top of M bed. More recently Fowler and Lyden,[42] McKnight,[43] Fowler,[44] and Lyden[45] have recognized flexing as illustrated by structure contour maps based on the tops of various beds. They believe that the flexing is related to regional deformation of the strata.

Vertical fracturing has been mapped in detail in the mines by Fowler and Lyden[46] and by other company geologists. These fractures are discontinuous vertically and horizontally and in places they are filled with pink dolomite. They are mapped from their exposures in the working faces and in the roof. The fractures are thought by Fowler

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[40] *Ibid*., p. 1255.

[41] Smith and Siebenthal, *op. cit*., p. 9.

[42] George M. Fowler, and Joseph P. Lyden, "The Ore Deposits of the Tri-State District", *Am. Inst. Min. Met. Eng. Trans*., vol. 102, p. 226-229, 1932.

[43] E. T. McKnight, *et al*., Maps Showing Structural Geology and Dolomitized Areas in Part of the Picher Zinc-Lead Field, U. S. Geol. Survey Tri-State Zinc-Lead Investigations Preliminary Maps 1-6, 1944.

[44] George M. Fowler, "Structural Control of Ore Deposits in the Tri-State Zinc and Lead District", *Eng. Mining Jour*., vol. 139, no. 9, p. 46, 1938.

[45] Lyden, *op. cit*., p. 1253-1254.

[46] Fowler and Lyden, *op. cit*., p. 226-229.

and Lyden to be related to the flexures and hence to regional deformation.

GENERAL FEATURES OF THE ORE BODIES

All of the ore deposits in the Tri-State district exhibit three outstanding features: 1) a close relationship to the surface of the earth, 2) a remarkable areal extent, and 3) no association with igneous rocks.

The most striking features of the ore deposits is their close relationship to the surface of the earth. All the ore deposits are less than 475 feet from the surface.

The deposits extend over a remarkably large area covering more than two thousand square miles along the flank of the Ozark dome.

The igneous rocks in the district are Precambrian in age. Crystalline Precambrian rocks are transected in drill holes in and near the district. Crystalline rocks outcrop in a Precambrian knob at Spavinaw, Oklahoma, forty miles south of the district.

The ore bodies of the Tri-State district may be divided into two groups of different character: 1) deposits localized in filled sink structures, and 2) deposits localized in fractured and brecciated Mississippian formations.

Ore deposits localized in filled sink structures

Ore deposits localized in filled sink structures possess roughly circular shapes, and hence they are called "circles". The "circles" occur where the Pennsylvanian strata are present, and have been mined principally in the northeastern fields of the district.

The relationship between the ore bodies and the sink structures was excellently exhibited at the Oronogo[47] and Gimlet "circles",[48] and at the Potter-Sim's Snapp mine[49] two miles northwest of Oronogo, Missouri. They have diameters of as much as 800 feet and reach depths over 80 feet. Commercial ore was generally confined to the bottoms and margins of the structures, but lesser amounts of sulfides were disseminated through the shale in some sinks.

Elsewhere in the Pennsylvanian shales, as reported by Buckley and Buehler,[50] sphalerite occurs as small disseminated crystals, as seams and veinlets, as nuclei of ironstone concretions, as the interior of septaria, and as centers of plant stems. Haworth[51] reported a commercial deposit of lead and zinc in Pennsylvanian strata at Pleasanton, Kansas. After summarizing numerous occurrences of sphalerite and galena in Leavenworth, Atchison, Douglas, Miami, Bourbon, Anderson, Osage, Coffee, and other counties in Kansas, he stated that:

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[47] Schmidt and Leonhard, op. cit., p. 484-487; Arthur Winslow, and James D. Robertson, "Lead and Zinc Deposits", Mo. Geol. Survey Rept., vol. 7, pp. 573-576, 1894.

[48] Smith and Siebenthal, op. cit., p. 11.

[49] Walter V. Searight, Guidebook, Field Trip, 2d Ann. Meeting, Assoc. Mo. Geol., Mo. Geol. Survey Rept. Inv. 20, pp. 11-13, 1955.

[50] E. R. Buckley and H. A. Buehler, "The Geology of the Granby Area", Mo. Geol. Survey Rept., vol. IV, 2d ser., pp. 81-82, 1905.

[51] Erasmus Haworth, "Special Report on Lead and Zinc", Kansas Geol. Survey Rept., vol. VIII, part I, pp. 69-70, 1904.

> It is probable that similar discoveries could be made in almost every township in the eastern fourth of the state. Apparently the shale beds contain vast quantities of these ores, and the limestone a small amount.[52]

Ore deposits localized in fractured and brecciated rock

Ore deposits located below the Pennsylvanian shales, are localized in fractured and brecciated Mississippian cherts and limestones. The general shapes of these ore bodies may be grouped into two types: 1) elongated ore bodies of chert breccias called "runs", which follow the bedding, but break through to other beds in places, and 2) partly broken chert bodies which follow the bedding and are referred to in the district as "sheet ground". These have large horizontal extent compared with their thickness. The runs are most common in M bed, but they also are common in some beds above M and in R bed (Reeds Spring) below M. These "runs" may be as much as two miles long, 150 feet wide, and 80 feet high, but "runs" of smaller dimensions are more common. The sheet deposits are confined to O, P, and Q beds. These are mined to a height of about ten to thirty feet, and generally have a lateral extent of 1000 feet or more.

The principal gangue minerals of the ore bodies in the "runs" and "sheet ground" are jasperiod and dolomite. Dolomite is more abundant in the center of the ore "runs" while jasperoid is more prevalent at the margins of the "runs".

The ore "runs" are related to flexing and fracturing of the beds.[53]

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[52] Ibid., p. 74.

[53] Joseph P. Lyden, "Aspects of Structure and Mineralization Used as Guides in the Development of the Picher Field", Am. Inst. Min. Met. Eng. Trans., vol. 187, pp. 1254, 1950.

The fracturing is best seen in the roof and working faces of the mines; the minor folds are best expressed by structure contour maps based on the bottoms of the various beds. The beds are generally most fractured on the flanks of the minor folds, and hence the ore "runs" generally follow the flanks of these folds. Yet, some ore "runs" apparently do not follow flexures or fractures, and some flexures and fractures cross the ore "runs" without any apparent control on the location of the ore.

GEOPHYSICAL PROSPECTING

No satisfactory geophysical method has yet been employed to consistently find ore in the Tri-State district. Geophysical and geochemical investigations in the district have been summarized by Hambleton, Lyden and Brockie;[54] the most detailed investigations were those of Jakosky, Dreyer and Wilson.[55]

Magnetic anomalies show no definite relationship to the ore deposits.[56] They probably are related to variations in magnetic properties of the Precambrian rocks rather than to variations in magnetic properties of the overlying sedimentary rocks.

Gravity meter surveys for the Eagle-Picher Company in 1939 and 1942 indicated that the Picher field ". . . is a terrace or bench that is subordinate to a basement structure, which lies to the southeast".[57] In local areas, Jakosky, Dreyer and Wilson[58] found that negative gravity anomalies were associated with fractured and cavernous areas, which in places have been mineralized and in other places have not. They found

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[54] William W. Hambleton, Joseph P. Lyden, and Douglas C. Brockie, "Geophysical Investigations in the Tri-State Zinc and Lead Mining District", Kansas Geol. Survey Bull. 137, pp. 357-375, 1959.

[55] J. J. Jakosky, R. M. Dreyer, and C. H. Wilson, "Geophysical Investigations in the Tri-State Zinc and Lead Mining District", Kansas Geol. Survey Bull. 44, p 151, 1942.

[56] Jakosky, Dreyer, and Wilson, op. cit., pp. 141-142.

[57] Hambleton, Lyden, and Brockie, op. cit., pp. 363.

[58] Jakosky, Dreyer, and Wilson, op. cit., pp. 142-143.

that gravity minima were also related to depressions in the limestone surface.

Geothermal surveys by Jakosky, Dreyer and Wilson[59] indicated that temperature minima were related to depressions in the limestone surface in a few places, but a consistent relationship between temperature variations and structural conditions or mineralized zones was not found.

Radioactive surveys conducted by Dreyer[60] have proved of no value in outlining ore deposits.

Resistivity surveys by Jakosky, Dreyer, and Wilson[61] have proved of value in locating water-saturated, brecciated and fractured areas, which may or may not contain ore. Resistivity anomalies also were related to the configuration of the limestone surface. Self-potential surveys by the same investigators[62] showed that high self-potential anomalies were associated with low resistivity and with gravity minima in one area, but in other areas there was no correlation between self-potential anomalies and structure or mineralization.

Radio surveys located fracture and fault zones which reach the earth's surface, but did not reveal those which do not reach the surface.[63]

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[59] Jakosky, Dreyer, and Wilson, op. cit. pp. 145-146.

[60] R. M. Dreyer, "Radioactive Surveys in the Kansas Part of the Tri-State Zinc and Lead Mining District, Cherokee County, Kansas", Kansas Geol. Survey Bull. 76, pp. 113-120, 1948.

[61] Jakosky, Dreyer, and Wilson, op. cit., pp. 144-145.

[62] Jakosky, Dreyer, and Wilson, op. cit., pp. 143-144.

[63] Hambleton, Lyden, and Brockie, op. cit., pp. 368-369.

Seismic refraction surveys were conducted by the Eagle-Picher Company in 1955 in an attempt to locate shale depressions and slump areas at the base of the Pennsylvanian shale.[64] Since slumping of shale is localized over areas of fracturing and solution thinning of the underlying Mississippian formations, these areas may contain ore. Three of the anomalies outlined by this method were drilled to determine their cause. One anomaly was caused by shale filling of an erosional depression and the other two anomalies were due to sandstone lenses in the Pennsylvanian shale.

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[64] _Ibid._, pp. 370-374.

PREVIOUS INVESTIGATIONS OF PARAGENESIS

The Tri-State district has been a subject of intensive geologic study because of its economic importance as one of the leading zinc-producing areas in the world, but studies of paragenetic sequence have usually been incidental to field investigations. Those investigators who dealt with paragenesis have differed in: 1) techniques of study, 2) areas investigated, and 3) interpretations of textures. As a result, various sequences of paragenesis have been proposed and this has lead to a confused state of paragenetic interpretation. With the hope of clarifying this confusion, the writer took up the present study.

PREVIOUS TRACE ELEMENT STUDIES

For a long time the existence of small amounts of minor elements in the Tri-State ores has been known and some have been produced commercially. The distribution of these trace elements in the district has been investigated to a slight extent by analyzing bulk rock samples, but no investigation has been published which deals with the areal and stratigraphic distribution of the trace elements in single minerals.

CHAPTER III

MINERALOGY

INTRODUCTION

The most important minerals of the Tri-State district are few in number and simple in composition. They are: quartz, dolomite, calcite, sphalerite, galena, chalcopyrite, pyrite and marcasite. In their simplicity they are like other ore deposits of the so-called Mississippi Valley type and are different from those of other types found throughout the world.

The Tri-State minerals are well crystallized, and the individual crystals commonly reach large sizes. Crystals of calcite two or more feet long have been recorded;[65] crystals of galena nearly one foot on edge are known,[66] and crystals of sphalerite over a foot across have been collected from the district.[67] For this reason, the Tri-State district has been one of the most outstanding localities in the world for the collection of beautifully crystallized mineral specimens.

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[65] H. G. Bain, C. R. Van Hise, and George I. Adams, "Preliminary Report on the Lead and Zinc Deposits of the Ozark Region", U. S. Geol. Survey, 22d Ann. Rept., pt. 2, p. 110, 1901; W. S. Tangier Smith and C. E. Siebenthal, Description of the Joplin District in Geologic Atlas of the United States, U. S. Geol. Survey folio 148, p. 13, 1907; Arthur Winslow and James D. Robertson, "Lead and Zinc Deposits", Mo. Geol. Survey Rept., vol. 7, p. 467, 1894; O. C. Farrington, "Crystal Forms of Calcite from Joplin, Missouri", Publications of the Field Columbian Museum, Geological Series, vol. I, no. 7, p. 234, 1900.

[66] Samuel Weidman, "The Miami-Picher Zinc-Lead District, Oklahoma", Okla. Geol. Survey Bull. 56, p. 54, 1932.

[67] Samuel Weidman, op. cit., p. 53.

Unlike many of the lead-zinc deposits of the western United States, the minerals of the Tri-State district are not intimately intergrown with each other, do not exhibit extensive replacement of one ore mineral by another, and commonly exhibit druses or encrusting structures. The minerals in the Tri-State district are relatively free from contamination by associated minerals. Much of the ore consists of crystals which were deposited on the surfaces of open spaces, one upon the other as is illustrated in Figures 4 and 5. Although the later minerals were deposited on slightly corroded surfaces of the older minerals, usually very little intergrowth has occurred. The uncontaminated nature of the minerals suggests that each has crystallized alone, rather than with other minerals.

The important minerals of the ore are ubiquitous. They occur in all of the mines, and the general sequence of mineral deposition has been the same throughout the district, although local repetitions and omissions of parts of the sequence occur.

The same minerals occur in both the host rocks and the ore deposits. The Mississippian host rocks consist principally of calcite, quartz, chalcedony, dolomite and glauconite, and the Pennsylvanian rocks are composed principally of quartz and clay minerals. The difference between rock and ore is the relative abundance of the sulfides: pyrite, marcasite, sphalerite, and galena. These may be present in amounts insufficient to constitute ore, or in amounts abundant enough to form ore deposits.

A list of the minerals found in the Tri-State ore deposits is

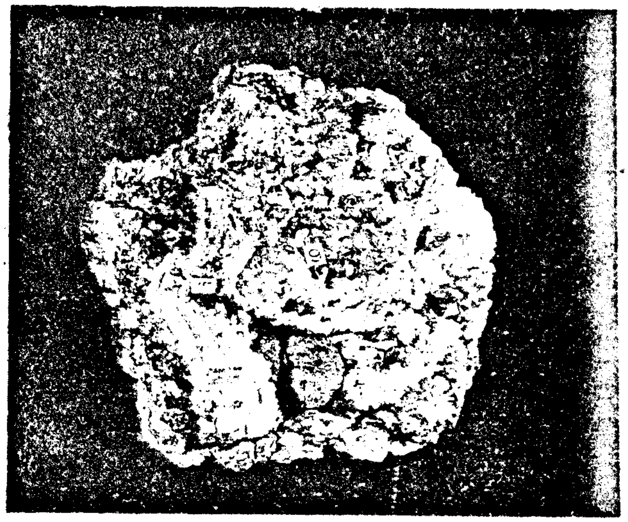

Figure 4. Vug lined with pink dolomite crystals (light gray to white) surmounted by sphalerite crystals (darker gray), typical of mineralization in open spaces. M bed, Lawyers-Chicago No. 2 mine.

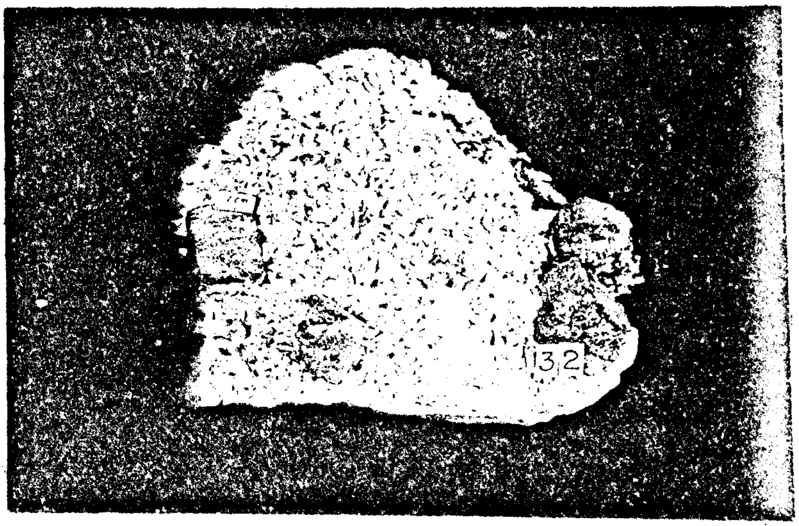

Figure 5. Galena crystals on pink dolomite crystals, typical of mineral deposition in vugs. G-H beds, Anna Beaver mine.

given in Table II. Here the minerals are divided into two groups, the major minerals and the minor minerals. In each they are arranged according to the Dana System.[68]

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[68] Charles Palache, Harry Berman, and Clifford Frondel, The System of Mineralogy, 7th Ed., vols. I and II, John Wiley and Sons, Inc., New York, 1944, 1951; Cornelius S. Hurlbut, Jr., Dana's Manual of Mineralogy, John Wiley and Sons, Inc., New York, p. 609, 1959.

TABLE II

MINERALS IN THE TRI-STATE ORES

Major Minerals

- Sulfides:
  - Galena
  - Sphalerite
  - Chalcopyrite
  - Pyrite
  - Marcasite
- Carbonates:
  - Calcite
  - Dolomite
- Silicates:
  - Quartz

Minor Minerals

- Native Elements:
  - Sulfur
- Sulfides:
  - Bornite
  - Wurtzite
  - Greenockite
  - Millerite
  - Covellite
- Sulfosalts:
  - Enargite
- Oxides:
  - Cuprite
  - Hematite
  - Pyrolusite
  - Limonite

Minor Minerals

- Carbonates:
  - Smithsonite
  - Aragonite
  - Cerussite
  - Hydrozincite
  - Aurichalcite
  - Malachite
  - Azurite
  - Leadhillite
- Sulfates:
  - Barite
  - Anglesite
  - Gypsum
  - Starkeyite
  - Chalcanthite
  - Melanterite
  - Epsomite
  - Goslarite
  - Linarite
  - Jarosite
  - Plumbojarosite
  - Aluminite
  - Copiapite
  - Caledonite
- Arsenates:
  - Picropharmacolite
  - Mimetite
- Phosphates:
  - Vivianite
  - Pyromorphite
  - Wavellite
- Silicates:
  - Hemimorphite
  - Allophane
  - Chrysocolla
  - Kaolinite
  - Glauconite

MINERAL DESCRIPTIONS

Major Minerals

Sulfides:

Galena PbS

Galena occurs as disseminated crystals in jasperoid and gray dolomite, as well-formed crystals deposited in vugs, as anhedral grains deposited contemporaneously with zinc sulfide in stalactites and as small crystals deposited upon nails.

Galena commonly is deposited in vugs upon pink dolomite and other minerals as is illustrated in Figure 5, page 31.

Galena occurs in crystals from microscopic sizes to nearly a foot in diameter.[69] The most common form of galena is the cube, often modified by the octahedron. Rarely is the octahedron the dominant form. Some galena occurs in hopper-like crystals in which the cube faces are inset in the center and the sides of the hopper are octahedral faces. The larger galena crystals commonly exhibit a mosaic structure, which has been discussed at length by Buerger.[70]

Rarely galena occurs in veins transgressing the bedding of limestone and chert as shown in Figures 6 and 7. Silicification is associated with one of these veins.

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[69] Samuel Weidman, op. cit., p. 54.

[70] M. J. Buerger, "The Significance of Block Structure in Crystals", Am. Mineralogist, vol. 7, pp. 177-191, 1932.

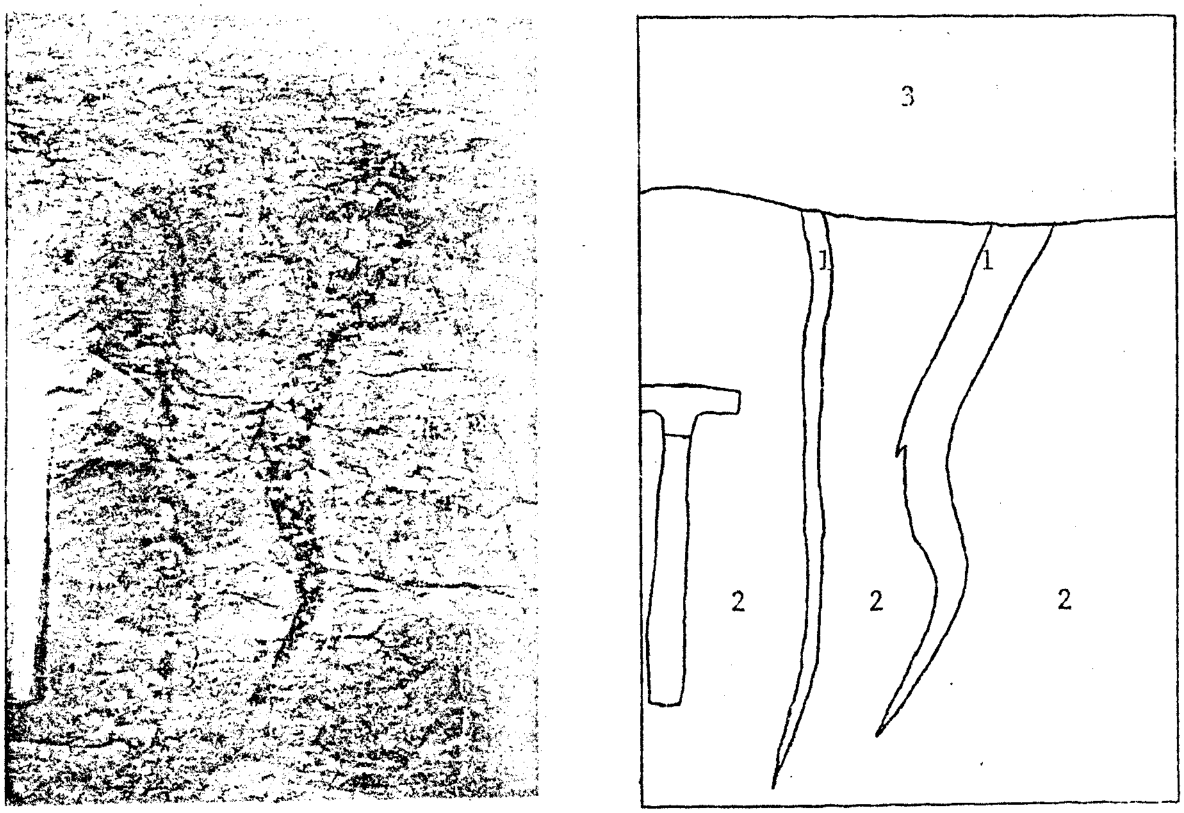
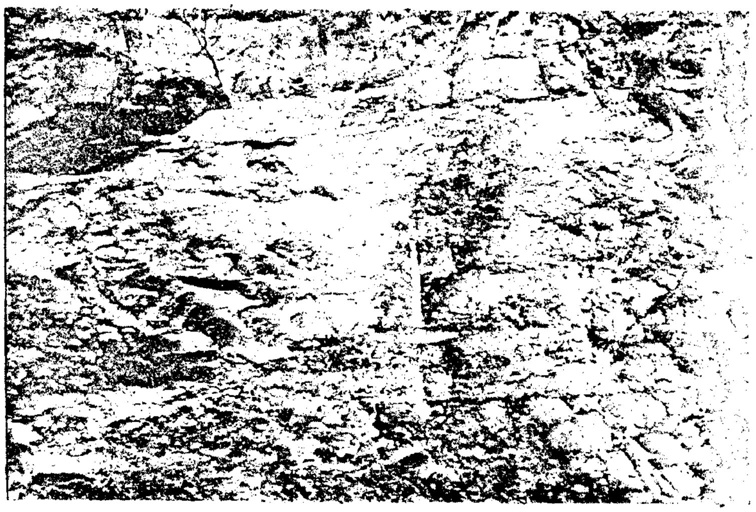


Figure 6. Galena (dark gray; 1) filling nearly vertical fractures in Chester limestone (medium gray; 2) beneath Pennsylvanian shale (lighter gray 3). The tongues of galena pinch out downward. Blue Goose No. 1 mine.



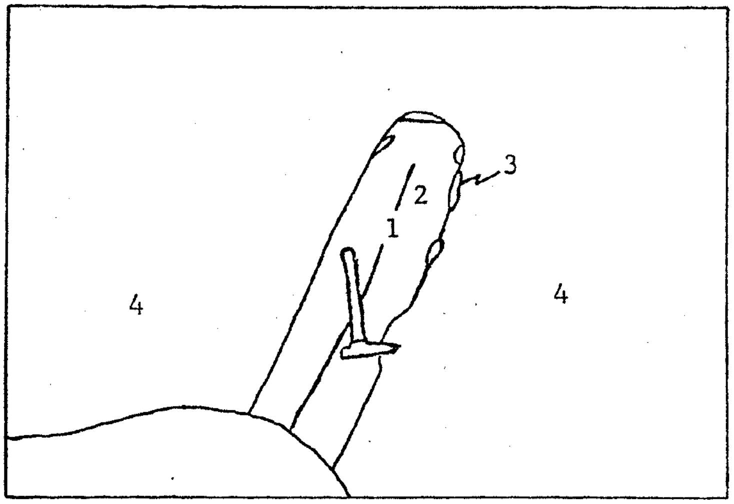


Figure 7. Alteration halo (center of photograph, dark grey; 2) around a very thin galena (light gray; 1) vein transgressing the bedding. The galena vein and alteration halo terminated upward. The rim of the halo is marked by discontinuous patches of calcite (white; 3). The alteration halo consists of chert mottled with jasperoid, whereas the surrounding country rock is chert (light gray; 4) mottled with limestone. E bed, Netta mine.

Galena disseminated in jasperoid was studied by the writer in polished specimens. Although under low magnification galena exhibits its cubic outline in a general way, under higher magnifications the contact of the galena with the jasperoid appears very irregular with the quartz grains of the surrounding jasperoid showing their own outlines against the galena. This is well illustrated by Figure 8, page 39.

Galena deposited in vugs rarely includes quartz. In such occurrences the quartz is euhedral and appears to be distributed discontinuously along a former crystal boundary of the galena. Very small pyrite grains occur in some of these quartz areas within galena crystals. Some galena crystals disseminated in jasperoid exhibit hopper shapes similar to the shapes of some galena crystals grown in silica gel by this writer.

The relationship between galena and sphalerite disseminated in jasperoid is variable even in the same polished specimen. Most commonly the rotund shape of sphalerite is exhibited against that of galena. Some boundaries are straight and parallel to the cleavage of the galena. More rarely sphalerite crystals contain inclusions of galena, especially when they are near larger galena crystals. Other boundaries between the two are wavy and suggestive of a mutual boundary texture.

Galena disseminated in jasperoid occasionally includes small grains of pyrite and marcasite. The iron sulfide generally shows its boundaries against the galena, and rarely do galena veins transect the marcasite.

Rarely galena occurs in zinc sulfide stalactites. This galena will be discussed under sphalerite.

That the deposition of galena was not confined to some past geologic time is proved by the occurrence of galena crystals, one-half to three-quarter centimeter on edge, deposited on nails. Specimens of this occurrence have been examined by the writer at the Joplin Mineral Museum. Close examination of the nails revealed that the galena cubes were deposited mainly after sphalerite, but considerable intergrowth of the two minerals also is present. Other instances of galena deposited on nails and tools have been noted by other investigators.[71]

Sphalerite - (Zn,Fe)S

Sphalerite occurs as yellowish brown, modified tetrahedral crystals in vugs; as light yellow crystals disseminated through jasperoid and dolomite, rarely through chert and silicified limestone; as small reddish brown crystals lining fractures; and rarely as stalactites.

In banded jasperoids the bending of the bands, both below and above the sphalerite crystals, has been observed in a few specimens, and it is pictured in Figure 9. This suggests that the jasperoid was not lithified at the time of sphalerite crystal growth.

In thin sections the grain size of the disseminated sphalerite crystals may be seen to range from about 0.040 mm. to about 3 mm.

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[71] H. G. Bain, C. R. Van Hise, and George I. Adams, "Preliminary Report on the Lead and Zinc Deposits of the Ozark Region", U. S. Geol. Survey, 22d Ann. Rept., pt. 2, pp. 158-159; Austin F. Rogers, pt. III in Erasmus Haworth, "Special Report on Lead and Zinc", Kansas Geol. Survey Rept., vol. VIII, pp. 467-490, 1904; E. R. Buckley and H. A. Buehler, "The Geology of the Granby Area", Mo. Geol. Survey Rept., vol. IV, 2d series, p. 84, 1905.

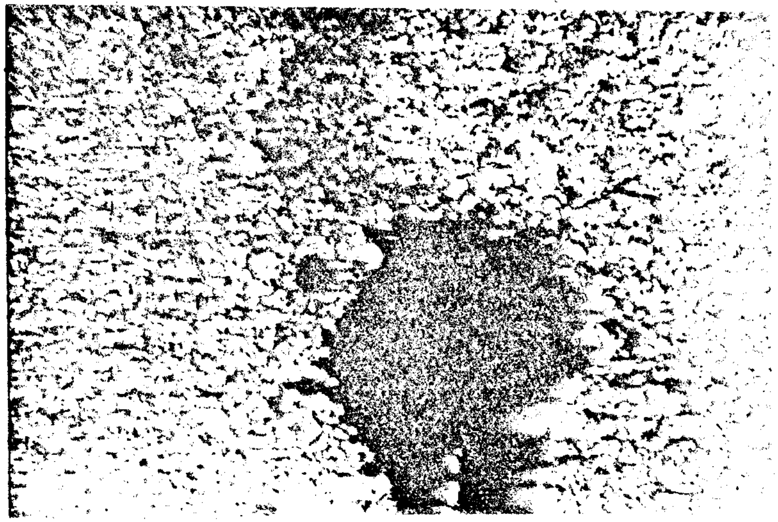

Figure 8. Galena (black) exhibiting a ragged boundary with jasperoid (gray, mottled). G-H bed, Tar Creek mine.

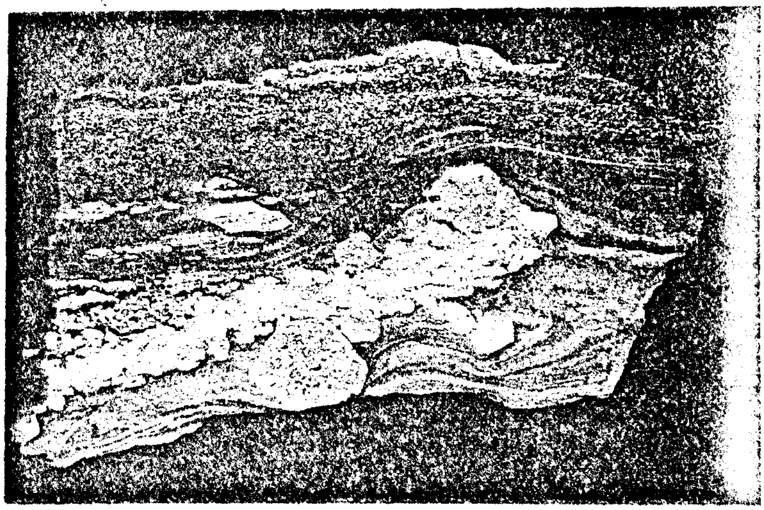

Figure 9. Geopetal fabric showing jasperoid bands (dark gray and light gray) warped over and under sphalerite crystals (white). The top broad jasperoid band contains fine disseminated sphalerite (white specks). A few chert fragments (light grey and white, banded) are present near the center of the specimen. M bed, Netta mine. One-half natural size.

Most sphalerite crystals are between 0.45 mm. and 0.75 mm. In some specimens two sizes of sphalerite crystals are present, smaller grains disseminated through the jasperoid and larger grains deposited at the edge of the jasperoid in vugs. Under lower magnifications, the individual sphalerite crystals generally exhibit rude, euhedral shapes, as illustrated by Figure 10, but at higher magnifications the sphalerite crystal boundaries generally are revealed to be quite irregular and characterized by quartz crystals of the jasperoid generally exhibiting their outlines against the ragged sphalerite boundaries, as shown in Figure 11. Occasionally sphalerite crystals include euhedral quartz crystals as shown in Figure 12, page 47. Not all sphalerite-quartz contacts are uneven, some sphalerite boundaries are quite straight, even under high magnifications.

Sphalerite generally exhibits its crystal outline against gray dolomite in thin sections of dolomitic jasperoids, but the reverse is also observed. Sphalerite disseminated in dolomitic jasperoid generally exhibits smoother boundaries against dolomite crystals, than it does against quartz.

In banded dolomitic jasperoid the more dolomitic bands frequently contain the greater percentage of disseminated sphalerite, but the sphalerite crystals are in the quartz portions of these bands and do not replace the dolomite. Very rarely dolomite crystals occur within sphalerite. Thin sections exhibiting the transition from jasperoid quartz to limestone, reveal that sphalerite occurs in the jasperoid quartz areas rather than in the limestone areas.

Figure 10. Euhedral sphalerite (black) in jasperoid (gray speckled). The smaller black, rounded grains are glauconite. K bed, Netta White mine. Ordinary light. 30X

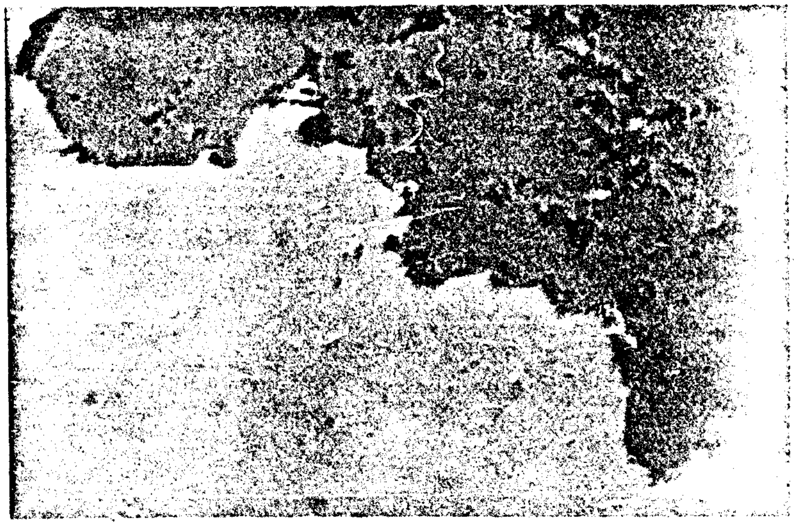

Figure 11. Euhedral quartz of the jasperoid (dark gray) crystallized adjacent to sphalerite (light gray). G-H beds, Piokee mine. 100X

Sphalerite disseminated in dense white chert has not been reported previously, but the writer observed this type of occurrence in the Piokee mine. The relationship between the sphalerite and chert, as observed in thin sections, is similar to the relationship between sphalerite and jasperoid.

Sphalerite not only is disseminated in jasperoid but it also is crystallized on the walls of vugs and fractures where it frequently is deposited as crystals on pink dolomite, as pictured in Figure 4, page 31. Generally these crystals are larger than the disseminated ones. The bases of these sphalerite crystals generally conform to the shape of the pink dolomite crystals while on their free surfaces the crystals exhibit their euhedral shapes. In some thin sections a thin coating of quartz about 0.03 mm. to 0.1 mm. thick was observed on the pink dolomite beneath the sphalerite crystals. This quartz conforms to the shape of the pink dolomite crystals, but exhibits nearly euhedral quartz shapes against the overlying sphalerite.

Rarely the dark brown sphalerite deposited in vugs is zoned. Such sphalerite usually has a more yellowish core while the rim is a darker yellowish brown. Usually the color zones are transitional, but in some crystals they are marked by the presence of chalcopyrite crystals which are deposited before the darker brown sphalerite is deposited. Although Smith and Siebenthal[72] stated that chalcopyrite

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[72] W. S. Tangier Smith and C. E. Siebenthal, Description of the Joplin District in Geologic Atlas of the United States, U. S. Geol. Survey folio 148, p. 13, 1907.

never occurs in sphalerite, the writer noted this occurrence in a number of polished sphalerite specimens. The chalcopyrite crystals are generally anhedral at the base, where they were deposited on the sphalerite, and euhedral at the top, where they grew out as pseudotetrahedrons into the open space of the vug. The darker sphalerite subsequently was deposited upon the lighter sphalerite and chalcopyrite.

Twinned sphalerite crystals were detected in some thin sections by variations in depth of color, offset of the color zones, and the multiple character of the twinning.

Zinc sulfide stalactites and stalagmites are quite rare in the Tri-State district, but they have been observed in specimens from the Firecracker, Combination, Zig Zag and Oswego mines near Joplin. The specimens examined by the writer in the Joplin Mineral Museum have botryoidal surfaces and do not possess hollow central tubes as do those in the Upper Mississippi Valley zinc-lead district,[73] however some of the stalactites examined by Siebenthal[74] did exhibit capillary tubes in the center. The largest of those examined by the writer is four inches long and one and one-quarter inches in diameter. A series of sections were cut perpendicular to the length of one stalactite and polished. Examination of these polished surfaces showed that the

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[73] Allen V. Heyl, Jr., et al., "The Geology of the Upper Mississippi Valley Zinc-Lead District", U. S. Geol. Survey Prof. Paper 309, p. 158, 1959.

[74] C. E. Siebenthal, "Origin of the Zinc and Lead Deposits of the Joplin Region - Missouri, Kansas, and Oklahoma", U. S. Geol. Survey Bull. 606, p. 260, 1915.

stalactitic material consisted of zinc sulfide and three to five per cent of galena. The zinc sulfide consists mostly of isotropic sphalerite, but some small scattered anisotropic needles, presumably wurtzite, are present, but x-ray analysis of the stalactitic material, as shown in Table III, did not confirm the presence of wurtzite, probably because it is present in an amount below the limit of detection. Preparation of the specimen for x-ray analysis might also have caused wurtzite to invert to sphalerite.

Galena was deposited with zinc sulfide in some stalactites and stalagmites. A study of the polished specimens showed that the center of this type of material is galena-free, but the remainder of the stalactite contains galena in elongated patches averaging about 0.15 mm. wide by 1.2 mm. long, which radiate outward. The percentage of galena varies progressively from about three per cent near the center of the stalactite to about five per cent toward the end of the specimen. The galena and sphalerite exhibit mutual boundaries against one another.

One polished specimen from the Missouri School of Mines ore microscopy collection is also quite certainly from stalactitic material. This specimen consists of isotropic zinc sulfide with marcasite intergrown with and coating the sphalerite. Galena is not present in this polished specimen.

Stalactitic zinc sulfide was studied in two thin sections. Concentric curved bands were observed which vary in color from dark brownish-yellow at the inner margin of each band to a pale yellow

TABLE III

X-RAY DIFFRACTION DATA FOR STALACTITIC ZINC SULFIDE

(I = relative intensity of diffraction line)
(d = interplanar spacings in Angstrom units)
(λ = 1.5405)

Sphalerite		Stalactitic Zinc Sulfide (Sphalerite)	
A.S.T.M. Index Card No. 5-0566		Firecracker mine	
Synthetically Prepared		Joplin, Missouri	
I	d	I	d
100	3.123	8	3.116
10	2.705	3	2.694
51	1.912	10	1.917
30	1.633	9	1.633
2	1.561	3	1.562
6	1.351	5	1.353
9	1.240	7	1.242
2	1.209	3	1.211
9	1.1034	7	1.106
5	1.0403	5	1.043
3	0.9557	4	0.958
5	0.9138	5	0.916
3	0.8543	4	0.857
2	0.0244	...	.....

at the outer margin of the band. The bands at the outer edge are narrower and more scalloped. Although the main portion of the stalactite is composed of isotropic zinc sulfide, needles of anisotropic zinc sulfide may be seen in the specimen under crossed nicols.

Recently Evans and McKnight[75] determined the small zinc sulfide crystals deposited upon the surface of sphalerite stalactites from the Zig Zag mine to be wurtzite. These also are intergrown with sphalerite,

Rarely repetitive crystallization of small sphalerite crystals was observed in specimens of late stalactitic marcasite deposited on calcite, as shown in Figure 13. The sphalerite crystals are concentrically arranged upon former growth surfaces of the stalactitic marcasite. They have flat bases but exhibit euhedral tops because they grew out into open space. Each coating of sphalerite crystals is covered by marcasite.

Sphalerite deposited on nails has been recorded in the literature.[76] The writer studied such a specimen at the Joplin

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[75] Howard T. Evans, Jr. and Edwin T. McKnight, "New Wurtzite Polytypes from Joplin, Missouri", Am. Mineralogist, vol. 44, p. 1215, 1959.

[76] H. G. Bain, C. R. Van Hise, and George I. Adams, "Preliminary Report on the Lead and Zinc Deposits of the Ozark Region", U. S. Geol. Survey, 22d Ann. Rept., pt. 2, pp. 158-159, 1901; E. R. Buckley and H. A. Buehler, "The Geology of the Granby Area", Mo. Geol. Survey Rept., vol. IV, 2d series, p. 84, 1905; Charles R. Keyes, "Diverse Origins and Diverse Times of Formation of the Lead and Zinc Deposits of the Mississippi Valley", Am. Inst. Min. Met. Eng. Trans., vol. 31, p. 611, 1901.

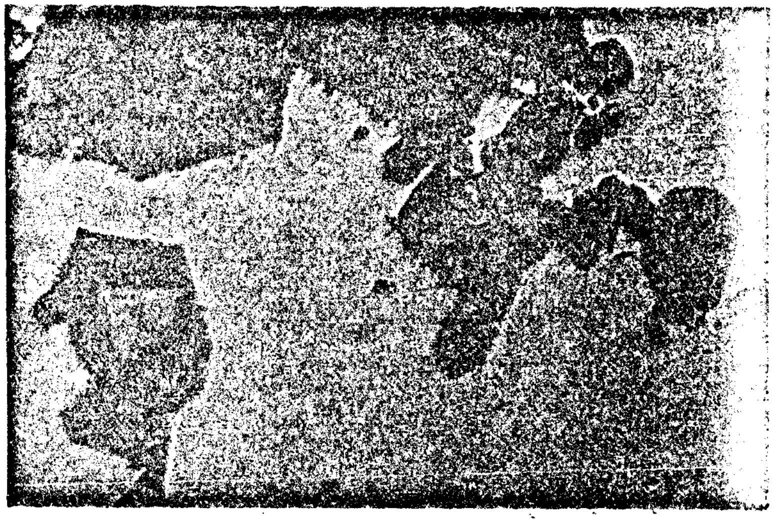

Figure 12. Quartz crystals (dark gray) included in sphalerite (light gray). G-H beds, Piokee mine. 100X.

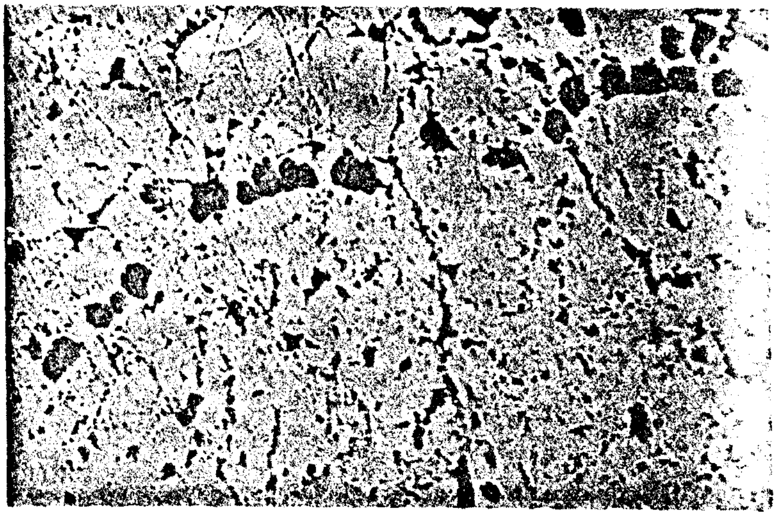

Figure 13. A band of small sphalerite crystals (medium gray) in stalactitic marcasite (light gray). A second band of smaller sphalerite crystals is shown in the upper left. Joplin. 100X.

Mineral Museum. The head of the nail of this specimen is coated by sphalerite crystals about one-half to three-quarters of a centimeter across.

White, earthy zinc sulfide was reported by Robertson[77] as occurring at Galena, Kansas. He believed this zinc sulfide to be an alteration product of normal sphalerite caused by the action of surface waters on that mineral.

Chalcopyrite - $CuFeS_2$

Chalcopyrite occurs in four ways in Joplin ores: most commonly as well-formed crystals deposited in vugs on pink dolomite and on sphalerite; less often as crystals in or under sphalerite; occasionally as crystals or grains disseminated in jasperoid and gray dolomite; and rarely as crystals on and in late calcite.

The chalcopyrite deposited in vugs on pink dolomite is well crystallized in simple, pseudotetrahedral, disphenoidal crystals. The crystal's bases normally take the shape of the underlying pink dolomite and show little or no intergrowth with the dolomite. The free ends of the chalcopyrite crystals are euhedral.

The direct association of chalcopyrite with sphalerite is more variable. Most often chalcopyrite crystals occur on sphalerite, but they generally do not form a complete coating over the sphalerite. Although Ridge[78] stated that none of the four main sulfides completely

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[77] James D. Robertson, "On a New Variety of Zinc Sulfide from Cherokee County, Kansas", Am. Jour. Sci., vol. 40, 3d ser., pp. 160-161, 1890.

[78] John Ridge, "The Genesis of the Tri-State Zinc and Lead Ores", Econ. Geology, vol. 31, p. 303, 1936.

cap one another, this writer has collected complete overgrowths of chalcopyrite on sphalerite from the Lawyers-Chicago mine. On some sphalerite crystals the chalcopyrite crystals are oriented, but are wholly unoriented on others. An examination of polished specimens show that these chalcopyrite crystals occasionally are inset in the underlying sphalerite.

More rarely chalcopyrite is included in sphalerite. In such occurrences the chalcopyrite usually is near the edge of the sphalerite crystals, having accompanied the last stages of the sphalerite deposition. More rarely the chalcopyrite is well within the sphalerite crystals. The included chalcopyrite crystals generally display irregular bases against the sphalerite surfaces on which they were deposited, but they exhibit euhedral tops because they grew out into open space. The chalcopyrite crystals became included in the sphalerite as it continued to be deposited. The color of this later sphalerite often is darker than that of the earlier sphalerite, thus forming color zones within the sphalerite crystal. The chalcopyrite crystals are symmetrically distributed along the zoned boundary, and they outline the sphalerite crystal as it was at the time of chalcopyrite deposition.

Very rarely chalcopyrite crystals occur beneath sphalerite crystals, having been deposited before the sphalerite. The euhedral triangular shapes of these chalcopyrite crystals project upward into the sphalerite and the boundary between the two generally is straight. Rarely small veinlets of sphalerite transect the margins of the chalcopyrite crystals, as is well illustrated by Figure 14.

The chalcopyrite crystals deposited on sphalerite generally are larger than those contained within sphalerite. Chalcopyrite crystals deposited before sphalerite are occasionally as much as four millimeters on edge. Those within the sphalerite average about 0.15 mm.

Chalcopyrite crystals of nearly euhedral triangular shape have been observed in some polished specimens of gray dolomite. When gray dolomite grades into pink dolomite the amount of chalcopyrite in the gray dolomite gradually increases toward the pink dolomite, yet the pink dolomite itself contains little chalcopyrite, although chalcopyrite crystals do occur upon the terminations of the pink dolomite crystals which line vugs.

The occurrence of massive chalcopyrite within jasperoid has been noted by Fowler.[79]

Chalcopyrite deposited in vugs frequently contains intimate intergrowths of cubic pyrite crystals and lath-shaped marcasite crystals, as revealed in polished surfaces and pictured in Figure 15.

Polished surfaces also have permitted detection of chalcopyrite within calcite crystals. This chalcopyrite occurs in various shapes: triangular, needle-shaped, and star-shaped. In these it is associated with marcasite and pyrite which were deposited on previous growth surfaces of the calcite crystals.

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[79] George M. Fowler, Oral Communication, 1959.

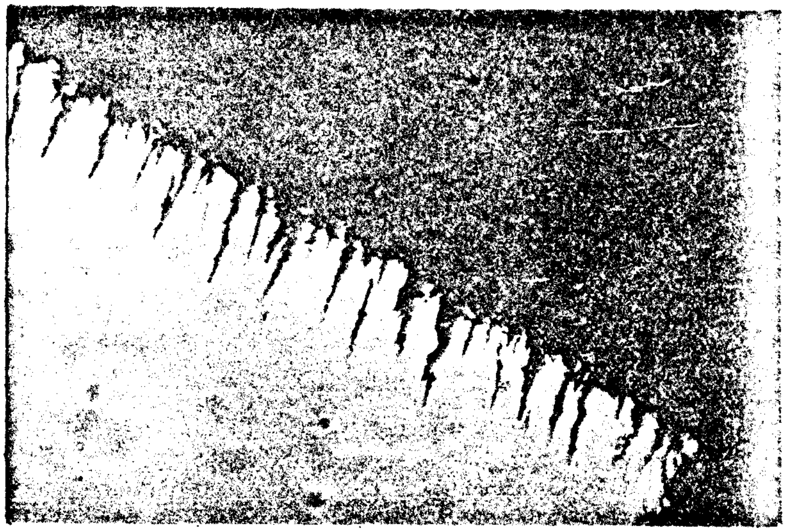

Figure 14. Sphalerite (dark gray) deposited upon and replacing chalcopyrite (light gray). Joplin. 475X, oil immersion.

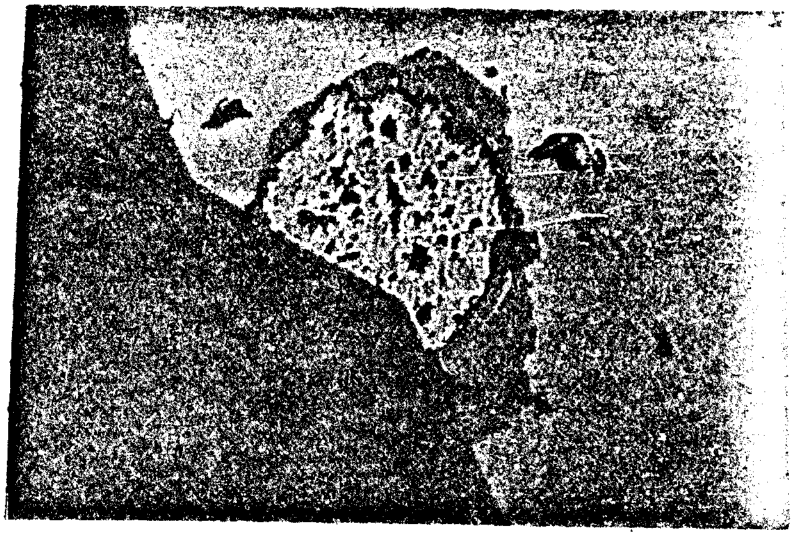

Figure 15. Bornite (medium gray) replacing chalcopyrite (light gray) and marcasite (very light gray) along a chalcopyrite-marcasite interface. Marcasite and chalcopyrite were deposited upon sphalerite (dark gray). Joplin. 475X, oil immersion.

Pyrite - FeS_2

Pyrite occurs as small crystals, pellets and anhedral grains disseminated in jasperoid, chert, grey dolomite and limestone, as small crystals intergrown with marcasite and chalcopyrite, as small crystals deposited in vugs on pink dolomite, sphalerite, galena, chalcopyrite and marcasite, and as small crystals included in calcite. Rarely pyrite occurs in larger masses as shown in Figure 16, page 53. Buckley and Buehler[80] reported bodies of pyrite of "considerable quantity" at a depth of from 250 to 350 feet in the Granby field. Fowler[81] noted a large mass of pyrite in the Southside mine, south of Joplin.

Pyrite commonly is finely disseminated in jasperoid, the size of the pyrite grains varying from 0.01 mm. to 3 mm. with most of the grains being between 0.02 mm. and 0.15 mm. The pyrite grains usually are cubic, but frequently they are irregular, with jasperoid quartz crystals showing euhedral boundaries against the pyrite as seen in polished surfaces and in thin sections. Less often the pyrite occurs intergrown with marcasite in nearly round grains. In a few polished surfaces, as shown in Figure 17, the writer has observed these pyrite spherules clustered together and forming a texture described by Rust[82] as framboidal. Magnified views of part of the

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[80] Buckley and Buehler, op. cit., p. 93.

[81] Fowler, loc. cit.

[82] George W. Rust, "Colloidal Primary Copper Ores at Cornwall Mines, Southeast Missouri", Jour. Geology, vol. 43, p. 407, 1935.

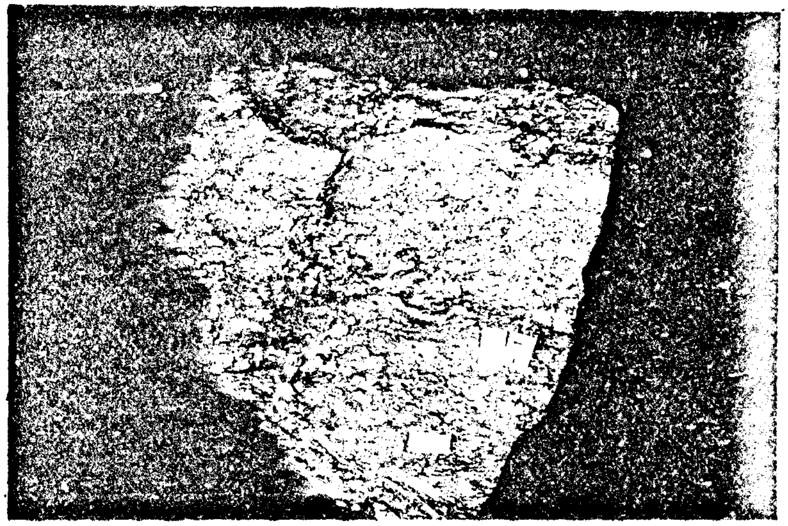

Figure 16. Massive pyrite (medium gray) in jasperoid (dark gray). Dolomite crystals (light gray) are scattered throughout the specimen. M bed, Lucky Jew Mine.

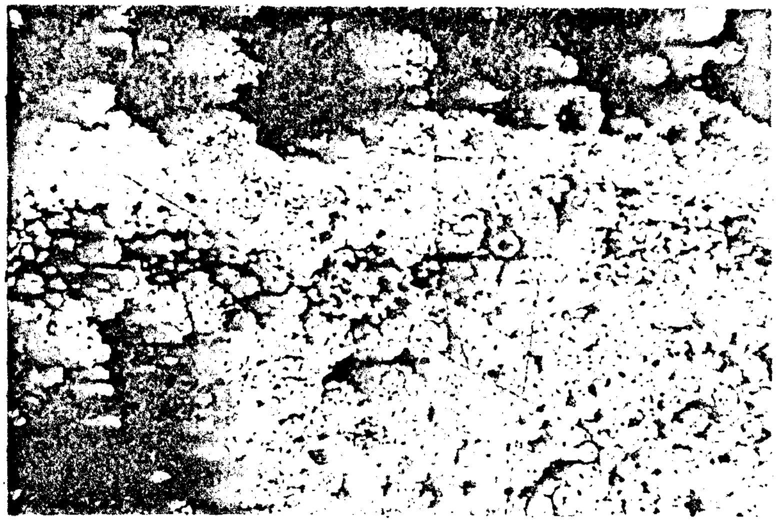

Figure 17. Rounded and framboidal pyrite and marcasite in jasperoid (dark gray and black). This texture is difficult to recognize in highly polished specimens. G-H beds, St. Joe mine. 50X.

field shown in Figure 17, are shown in Figures 20 and 21, page 57. These grains look similar to those described by other investigators who have proposed various mechanisms for their origin.

Schneiderhohn[83] believed that the pyrite spheres and other sulfide spheres found in the Mansfeld Kupferschiefer formed by the reaction of metal dissolved in sea water with sulfur produced by sulfur bacteria. Schouten[84] agreed with Schneiderhohn as to the origin of the pyrite spheres, but argued strongly that the spherical shapes of the other sulfides indicated that they had replaced spherical pyrite. Love[85] by dissolving pyrite spheres from the Scottish Lower Carboniferous oil shales in nitric acid revealed hitherto unknown microfossils, observable only under magnifications as high as 2500 times. He believed that these microfossils lived in the muds beneath still, foul waters and generated hydrogen sulfide which caused the crystallization of pyrite upon these organisms and in the surrounding sediments. Rust[86] described pyrite spheres from the Cornwall mines in Missouri, which he believed had formed from an

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[83] H. Schneiderhohn, "Erzfuhrung und Gefuge des Mansfelder Kupferschiefers", _Metall und Erz_, vol. XIV, pp. 144-145, 1926.

[84] C. Schouten, "The Role of Sulphur Bacteria in the Formation of the So-Called Sedimentary Copper Ores and Pyritic Ore Bodies", _Econ. Geology_, vol. 41, p. 529, 1946.

[85] Leonard Gregory Love, "Micro-Organisms and the Presence of Syngenetic Pyrite", _Geol. Soc. London Quart. Jour._, vol. 113, pp. 429-440, 1957.

[86] George W. Rust, _op. cit._, pp. 411-412.

Figure 18. Magnified view of part of the field shown in Figure 17, page 53. Specimen has been etched with $KMnO_4$ and H_2SO_4. Pyrite (gray) occurs in the interior and at the margins of the iron sulfide masses; marcasite (white) occurs in radiating crystals between the pyrite areas; the matrix is jasperoid (black). G-H beds, St. Joe mine. 100X.

Figure 19. More highly magnified view of the field shown in Figure 17, page 53, showing rounded to irregular central pyrite (medium gray), surrounded by radial marcasite crystals (light gray), which are, in turn, coated by more pyrite (medium gray). Jasperoid (dark gray) is shown at the margins of the photomicrograph. Etched with $KMnO_4$ and H_2SO_4. G-H beds, St. Joe mine. 400X.

inorganic gel.

Pyrite frequently occurs as very small grains disseminated in chert. These grains generally are irregular in shape, but some are euhedral, as shown in Figure 20, page 57. Rarely the crystals are zoned. When pyrite occurs in chert fragments cemented by jasperoid it is much less abundant in the chert than in the surrounding jasperoid. The pyrite grains in such chert fragments generally vary from 0.003 mm. to 0.3 mm., while those in the surrounding jasperoid are larger, varying from 0.01 mm. to 3 mm. Darker cherts usually contain more pyrite than light cherts and some dark cherts contain nearly as much pyrite as the jasperoid. Most white chert is nearly void of all sulfides.

The pyrite in some jasperoid, as seen in some hand specimens and in polished and thin sections, exhibits geopetal fabrics[87] in which bands of jasperoid are depressed beneath the pyrite grains.

In dolomitic jasperoid, the pyrite generally is confined to the jasperoid and quartz portions of the specimen, but occasionally a dolomite crystal contains small pyrite grains 0.003 mm. to 0.01 mm. across. Pyrite is especially abundant in dolomitic bands which also are rich in glauconite.

Pyrite is disseminated in limestone as shown in Figure 21.

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[87] Bruno Sander, translated by Eleanora Bliss Knopf, "Contributions to the Study of Depositional Fabrics", Am. Assoc. Pet. Geol. Tulsa, p. 2, 1951.

Figure 20. Euhedral pyrite (white) in chert. Dark areas are open spaces. M bed, Whitebird mine. 50X.

Figure 21. Rounded, irregular and subhedral grains of pyrite (white) in limestone. M bed, Kenoyer mine. 400X.

In some limestone the pyrite is most abundant in the shaly bands, and in others it is associated with stylolites.

Small, euhedral pyrite crystals commonly occur on pink dolomite, sphalerite, galena and chalcopyrite, which line the wall of vugs. These crystals are dominantly cubes, less commonly cubes modified by the pentagonal dodecahedron, pentagonal dodecahedrons, and rarely cubes modified by the octahedron. All of these forms or combination of forms have been observed in the same hand specimen. The crystals often are so small that a microscope is required to establish their presence. Rarely the pyrite crystals form nearly a complete coating over other minerals. Pyrite crystals generally are not intergrown with sphalerite or galena, but commonly are intergrown with chalcopyrite and marcasite. Rarely pyrite is associated with chalcopyrite crystals included within sphalerite crystals, but the writer has not observed pyrite alone within sphalerite crystals which were deposited in vugs.

Late pyrite crystals were deposited on late quartz and calcite crystals. It also is included along with marcasite in some calcite crystals, on which both minerals were deposited simultaneously and then covered by more calcite.

Stalactites of pyrite from Joplin, up to six inches long, were reported by Leonhard.[88]

Contrary to expectation, polished surfacesrevealed small pyrite

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[88] Alexander V. Leonhard, "Notes on the Mineralogy of Missouri", Trans. St. Louis Acad. Sci., vol. 4, p. 445, 1882.

crystals, about 0.01 mm. across, were included in hemimorphite formed by the alteration of sphalerite. Since the unreplaced remnants of sphalerite usually do not contain pyrite, the pyrite probably was formed at the same time as the hemimorphite. Some of the pyrite has been wholly or partially replaced by limonite which was formed more recently than the hemimorphite.

Marcasite - FeS_2

Marcasite occurs as crystals deposited in vugs on pink dolomite, sphalerite, galena and chalcopyrite; as crystals deposited on and in late calcite; as small grains disseminated in jasperoid, gray dolomite and chert; and as intergrowths with stalactitic sphalerite.

Marcasite most commonly occurs as small orthorhombic tabular crystals about 0.1 mm. long deposited in vugs on pink dolomite, sphalerite and chalcopyrite, but larger orthorhombic tabular and cockscomb-type crystals are common. Marcasite generally exhibits little to no intergrowth with pink dolomite and sphalerite, although rarely marcasite crystals are associated with chalcopyrite in or beneath sphalerite. Lath-shaped crystals of marcasite commonly are intergrown intimately with chalcopyrite. The presence of granular aggregates of marcasite crystals about 0.1 mm. long have been noted in some polished specimens of chalcopyrite. These aggregates tend to be spheres in which chalcopyrite forms the matrix for the marcasite grains.

Marcasite frequently occurs as crystals on galena in vugs, a somewhat favored site of crystallization being the edges of galena cubes. Marcasite usually exhibits little to no intergrowth with the underlying galena. Although Ridge[89] stated that none of the four main sulfides completely cap one another, the present writer has collected specimens of a complete overgrowth of marcasite on galena. Observation of polished surfaces has revealed quartz crystals occurring at or near the contact between galena and marcasite. Those which are on the boundary are encrusted with marcasite and exhibit euhedral outlines against this mineral.

Marcasite occurs with pyrite as disseminated grains in horizontal bands in jasperoid. In these pyrite bands, the marcasite grains usually have grown into open spaces formed by the breaking of the pyrite bands.

Intergrowths of fine-grained pyrite and marcasite, often associated with fine-grained sphalerite, are disseminated through jasperoid. In these intergrowths, as illustrated by Figures 18 and 19, page 55, the pyrite occurs as rounded pellets, averaging about 0.07 mm. in diameter, surrounded by marcasite crystals, averaging about 0.03 mm. long, which are intergrown with and radiate outward from the margins of the pyrite. The radial marcasite, in turn, is covered by more pyrite. This pyrite forms a coating about 0.01 mm. thick, and conforms to the shape of the underlying marcasite crystals, but in places right angles suggestive of the pyrite cube can be seen. The pyrite coating takes a better polish and etches to a lighter

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[89] John Ridge, "The Genesis of the Tri-State Zinc and Lead Ores", Econ. Geology, vol. 31, p. 303, 1936.

yellow-brown color than the earlier rounded pyrite. Each area of iron sulfide dissemination generally consists of many of these pyrite-marcasite groups.

Disseminated marcasite occurs in jasperoidal gray dolomite, but in such rock it occurs in the jasperoid portion.

Where marcasite is present in massive pyrite, part of it is intergrown with the pyrite and part is crystallized in vugs in the pyrite.

Some late calcite contains small crystals of marcasite about 0.15 mm. to 0.3 mm. long, arranged on previous growth surfaces of the calcite crystals. These marcasite crystals usually are uniformily distributed over the calcite crystal faces. But in some calcite crystals, observed in the Missouri School of Mines museum, marcasite is concentrated along the edges of the calcite, and in others it is concentrated along the center of the calcite faces. In some of this calcite, as shown in polished surfaces, the marcasite is intergrown with chalcopyrite.

Rarely stalactitic, botryoidal marcasite has been deposited upon late calcite. Microscopic examination of this marcasite as shown in Figure 13, page 47, revealed small sphalerite crystals which were repetitively deposited with the marcasite.

Siebenthal[90] described marcasite on stalactitic zinc sulfide in the Combination mine near Joplin. In one polished specimen of material of this type in the Missouri School of Mines ore microscopy

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[89] C. E. Siebenthal, "Origin of the Zinc and Lead Deposits of the Joplin Region - Missouri, Kansas, and Oklahoma", *U. S. Geol. Survey Bull.* 606, p. 260, 1915.

collection, this type of marcasite was observed to exhibit a zone of intergrowth with sphalerite and a little wurtzite as much as 1.5 mm. wide, near the margin of the stalactite.

Carbonates:

Calcite - $CaCO_3$

Calcite was deposited as a late mineral in many forms, as described by Farrington[91] and Rogers.[92] Of these the scalenohedron is the most common, but the rhombohedron is common in places. Abundant rhombohedral calcite was noted by Winslow and Robertson[93] at Aurora. The calcite of the Tri-State district generally is transparent, nearly colorless to amber in color and occurs in crystals which are as much as two feet long. This mineral is abundant especially along the fringes of the district, as in the Lucky Jew mine, where ore runs reach out into limy areas. Some mines contain caves lined with a continuous coating of calcite crystals. These caves frequently are lenticular in shape and generally are void of sulfide deposition.

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[91] O. C. Farrington, "Crystal Forms of Calcite from Joplin, Missouri", Publications of the Field Columbian Museum, Geological Series, vol. I, no. 7, pp. 232-241, 1900.

[92] Austin F. Rogers, pt. III in Erasmus Haworth, "Special Report on Lead and Zinc", Kansas Geol. Survey Rept., vol. VIII, pp. 467-490, 1904.

[93] Arthur Winslow and James D. Robertson, "lead and Zinc Deposits", Mo. Geol. Survey Rept., vol. 7, p. 457, 1894.

Calcite is a common cement for some of the breccias. Along with galena, sphalerite and other minerals, coarsely crystalline calcite partially to wholly fills the space between some breccia fragments of chert, jasperoid and gray dolomite.

Dolomite - $Ca(Mg,Fe,Mn)(CO_3)_2$

Three types of dolomite are present in the Tri-State district: 1) fine-grained, gray dolomite occurs in beds; 2) coarse-grained, gray dolomite generally in massive beds and as disseminated crystals in jasperoid; and 3) pink dolomite usually as crystals in vugs.

Fine-grained Gray Dolomite

Fine-grained gray dolomite usually is bedded, but also occurs as breccia fragments cemented by jasperoid and coarser-grained dolomite. It is part of the normal sedimentary section of the district. This dolomite usually consists of intergrown grains less than 0.05 mm. across, but in places the dolomite grains are embedded in a minor chert matrix, as is illustrated in Figure 22, page 64.

Coarse-grained Gray Dolomite

Coarse-grained, gray dolomite is intimately associated with the ore and perhaps constitutes the best ore guide in the district. Dolomite-rich areas usually form either the center or one wall of most ore runs, as is illustrated in Figure 23. It occurs in a variety of forms from massive beds to individual rhombohedral crystals, one-half to two millimeters on edge, disseminated in jasperoid. All thin sections of gray dolomite examined by the writer

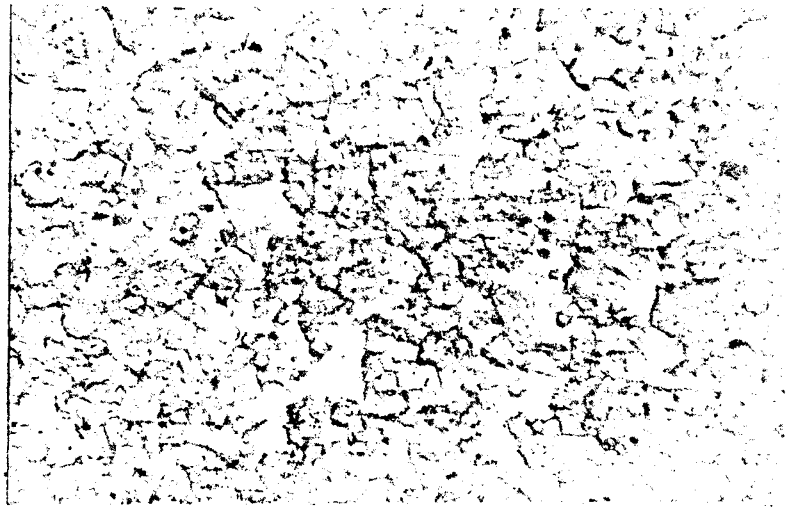

Figure 22. Fine-grained, gray dolomite (medium gray) in a chert matrix (light gray). Small black grains are pyrite. St. Joe Formation, Riverside mine dump. Ordinary light. 100X.

Figure 23. Dolomite (medium gray, speckled) wall typical of ore "runs". Note that the chert lens (white) in the center of the photograph is broken, but yet it is nearly in place and cemented by jasperoid (black). M bed, Whitebird mine.

contained some jasperoid quartz between the dolomite crystals. Rather rapid changes in the ratio of gray dolomite to jasperoid commonly produce pronounced horizontal banding, as is illustrated in Figures 24 and 25, page 66, and Figure 26, page 67. This is observable in many mines in the district. Gray dolomite, like jasperoid, frequently forms the matrix of ore-bearing chert breccias.

A study of thin sections of the gray dolomite reveals that individual crystals vary from 0.56 mm. to 2.0 mm. on edge; but most crystals are from 0.56 mm. to about 1 mm. on edge. The shape of the dolomite crystals varies from euhedral through subhedral to nearly anhedral. Usually the smaller the dolomite content of a dolomitic jasperoid, the greater is the tendency of the dolomite crystals to assume euhedral shapes and the smaller the crystals tend to be.

Although the dolomite crystals seem to show their crystal boundaries under low magnification, as shown in Figure 27, page 67, under higher magnification their boundaries appear more irregular, and frequently the surrounding jasperoid quartz crystals exhibit their own outlines against the margins of the dolomite rhombs. Some dolomite crystals include euhedral quartz crystals within their boundaries. Although larger crystals of gray dolomite may show undulating extinction, pink dolomite more commonly exhibits this property.

Irregularly shaped blocks of gray jasperoidal dolomite occurring in jasperoid and dolomitic jasperoid were observed by the writer in the Lucky Jew mine and are illustrated in Figures 28 and 29, page 68, and Figure 30, page 70. The bottom margins and sides

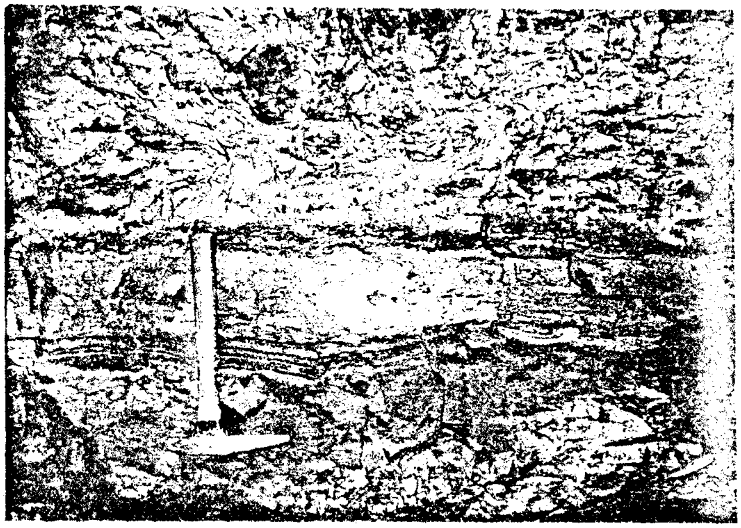

Figure 24. Brecciated chert nodules (light gray) in a jasperoid matrix (dark gray) is shown in the lower one-third of the photograph. This is overlain by well banded dolomite (medium gray) and dolomitic jasperoid (dark gray) grading upward into jasperoidal dolomite. This, in turn, is overlain by chert rubble cemented by jasperoid. K bed, Crawfish mine.

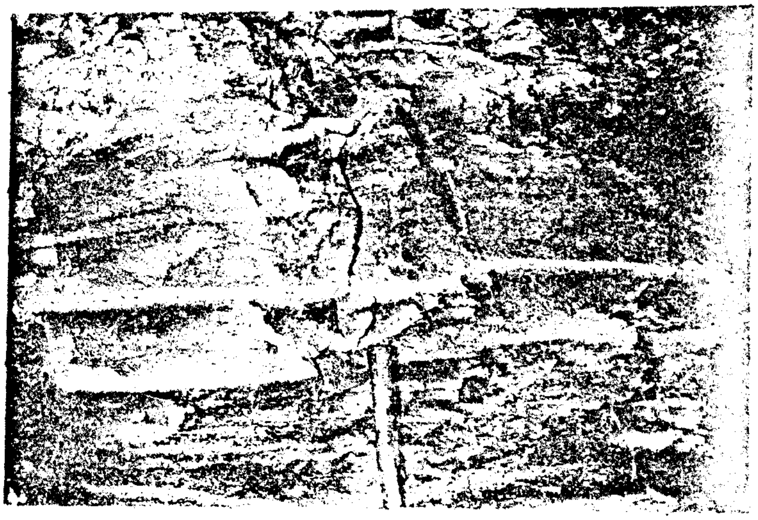

Figure 25. Interbanded jasperoidal gray dolomite (gray) and jasperoid (black) cut by vugs lined with pink dolomite crystals (white). M bed, Netta mine.

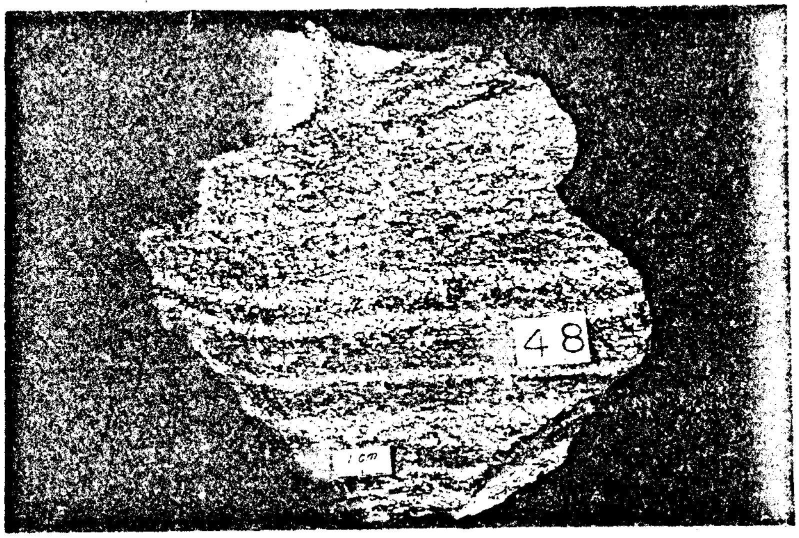

Figure 26. Typical horizontally banded, gray jasperoidal dolomite (light gray) and jasperoid (dark gray). G-H beds, Pickee mine.

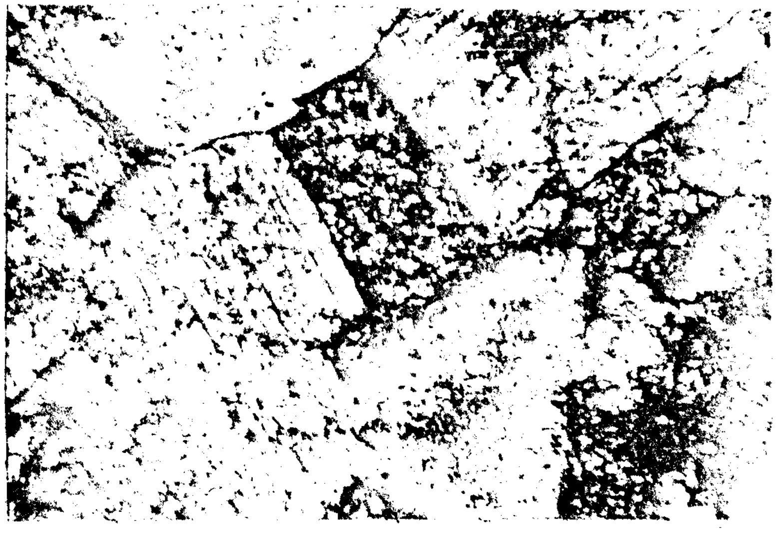

Figure 27. Coarse-grained, euhedral dolomite (light gray to white) in jasperoid (dark gray, speckled). M bed, Netta mine. Ordinary light. 50X.

Figure 28. Gray jasperoidal dolomite blocks (medium gray) with bottoms and sides fringed by pink dolomite (light gray) in a matrix of banded dolomitic jasperoid (dark gray). Jasperoid above blocks contains considerable sphalerite (speckled gray) whereas that beneath contains only a little sphalerite. M bed, Lucky Jew mine.

Figure 29. Chert breccia (white) above blocks of jasperoidal dolomite. M bed, Lucky Jew mine.

of these blocks were rimmed by pink dolomite, while the tops exhibited a marked concentration of sphalerite. A similar concentration of sphalerite was noted by the writer over some chert nodules and lenses in the Lucky Jew and other mines, as shown in Figure 31. Some of the banding of the surrounding dolomitic jasperoid bent both under and over these dolomite blocks, as is well illustrated in Figure 30.

Pink Dolomite

Pink dolomite occurs as saddle-shaped, rhombohedral crystals deposited in vugs on gray dolomite, jasperoid and chert; and as fracture fillings in gray dolomite, jasperoid and limestone. It most commonly occurs in runs near areas of gray dolomite. Very little pink dolomite is present in the sheet ground.

Pink dolomite is sharply defined against some gray dolomite, but it grades into other grey dolomite. It commonly forms veins in dolomitic jasperoid. In the Grace B mine some of these veins are fractured and offset, as is shown in Figure 32, page 71.

Some dolomites exhibit a fabric similar to that of a rock which is called "zebra rock" in some other mining districts.[94] In the Tri-State district this rock consists of gray dolomitic jasperoid cut by thin parallel bands of pink dolomite, which may contain considerable sphalerite. A hand specimen which is similar to this type of rock is pictured in Figure 33, page 71.

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[94] C. F. Park, Jr., "Dolomite and Jasperoid in the Metaline District, Northeastern Washington", Econ. Geology, vol. 33, p. 719, 1938.

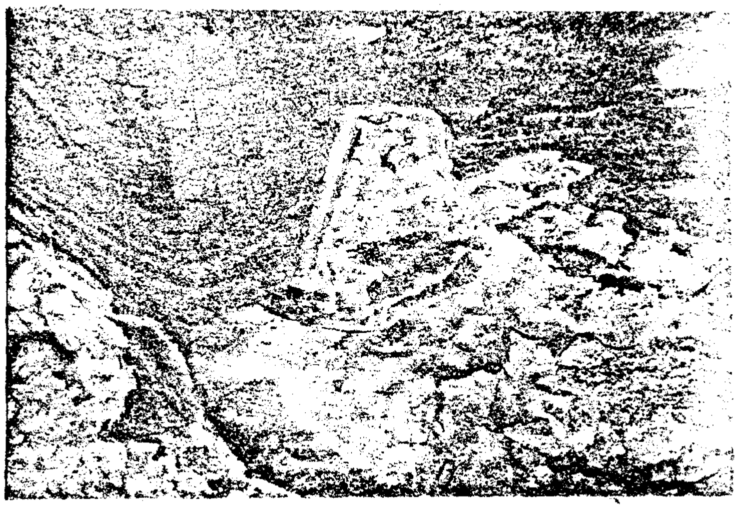

Figure 30. Blocks of gray jasperoidal dolomite (light gray) in banded dolomitic jasperoid (dark gray) which is sagged between the dolomite blocks. The light bands of gray at the margin of the blocks is pink dolomite. Calcite lined cavities are located in the lower left and lower right corners of photograph. M bed, Lucky Jew mine.

Figure 31. Sphalerite (medium gray) deposited upon the upper side of a chert nodule (light gray). Cementing matrix is jasperoid (dark gray). M bed, Kenoyer mine.

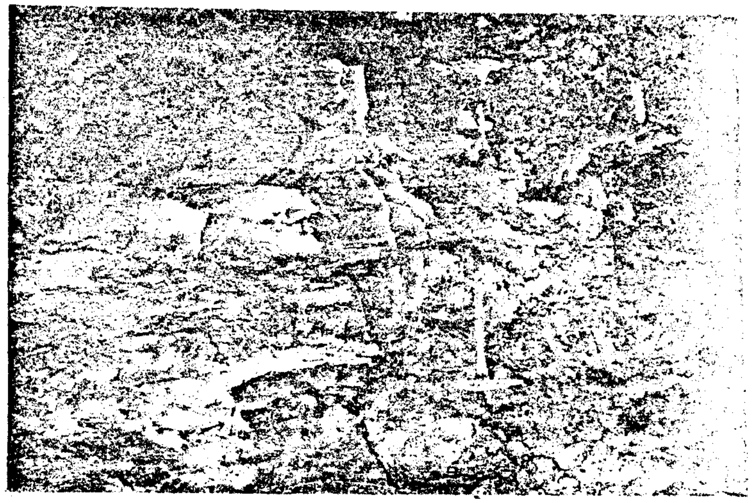

Figure 32. Pink dolomite (white) filling fractures and vugs cutting jasperoid (dark gray to black). M bed, Grace B mine.

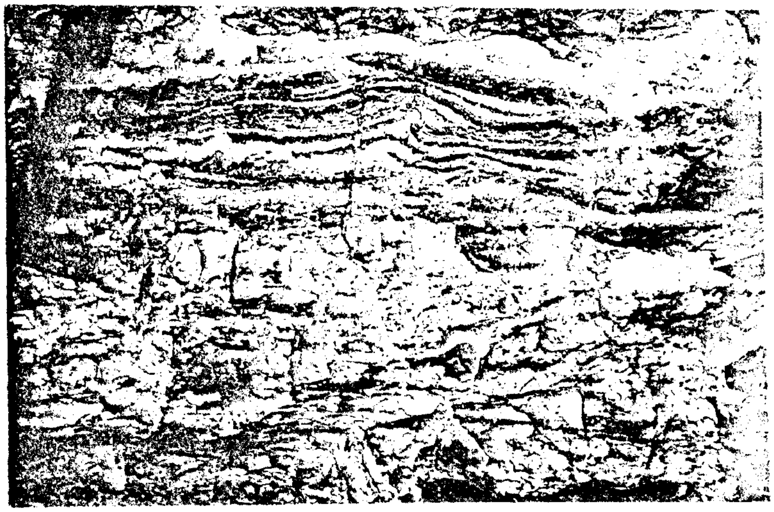

Figure 33. Interbanded pink dolomite (white) and jasperoid (dark gray) pierced by pink dolomite which also fills fractures in chert (white), as shown in the lower half of the photograph. M bed, Whitebird mine.

Pink dolomite is difficult to distinguish from gray dolomite under the microscope, but certain characteristics usually can be used to permit this distinction to be made. Pink dolomite crystals generally are about one to two millimeters across, while gray dolomite crystals generally are less than one millimeter. Pink dolomite usually is quite clear, while the gray dolomite frequently is cloudy. Pink crystals usually exhibit undulatory extinction, while the gray crystals tend to extinguish uniformly.

Pink dolomite usually grades into gray dolomite toward cavity walls and exhibits its own pink dolor and euhedral form in the other direction, where it has crystallized in an open space. Only rarely do areas of pink dolomite contain quartz, whereas this is very common in areas of gray dolomite.

Pink dolomite forms the major cementing material for broken blocks of gray dolomite and jasperoid in some places as is shown in Figure 34.

Silicates:

Quartz - SiO_2

Quartz is the most abundant gangue mineral of the Tri-State ore deposits. It appears in four forms: chert, jasperoid, quartz druse, and well-formed quartz crystals.

Chert

Chert occurs principally as: 1) massive beds up to thirty feet thick, exemplified by the L and N beds; 2) beds two to six inches thick like those in the G-H beds, shown in Figure 35, page 73 and in 36, page 75,

Figure 34. Pink dolomite (white) cementing and veining breccia blocks of jasperoidal dolomite (gray). M bed, Whitebird mine.

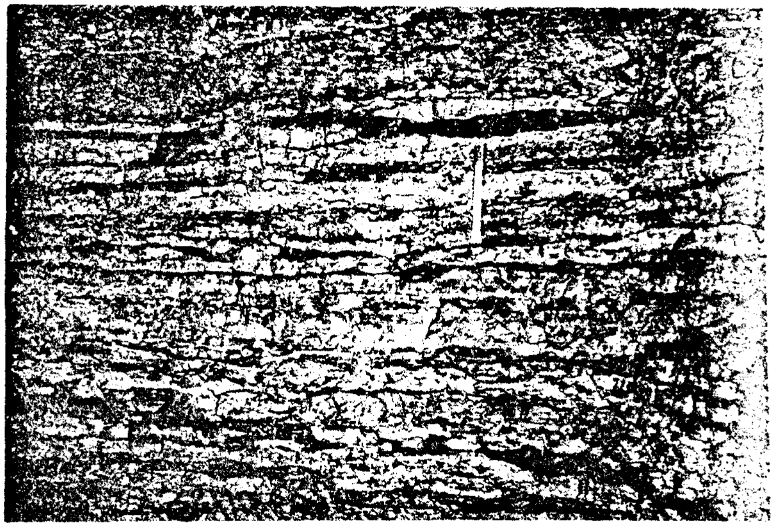

Figure 35. Horizontally banded chert (light gray) and jasperoid (black) typical of mineralized G-H beds. St. Joe mine.

and in the "sheet ground" of the O, P and Q beds, shown in Figure 37, page 75, and Figure 38, page 76; 3) nodules and lenses in zones parallel to the bedding, like those in the K and M beds, as shown in Figure 39, page 76.

The chert of the Mississippian formations varies in color from white through gray to blue-black. Grohskopf and McCracken[95] have summarized the characteristics of the cherts from insoluble residues of drill cuttings from Paleozoic formations in Missouri. The youngest Mississippian formation in the district, the Carterville Formation, is devoid of chert except that which occurs as pebbles at its base. The chert of the St. Louis Formation is white to light blue; that of the Warsaw Formation is gray and mottled to almost white; while that of the Keokuk Formation is smooth to rough, white, and dense to porous or tripolitic. The Grand Falls chert is generally smooth, tan to cream, and may be mottled. It is less fossiliferous than cherts from the Keokuk or Reeds Spring Formations. Chert from the Reeds Spring Formation is dense, smooth, subtranslucent, and exhibits a blue-black color and waxy luster. Fern Glen chert is smooth textured, light tan to white in color, and is subtranslucent and waxy in luster.

Much of the chert associated with the ore deposits in the Tri-State district obviously has been altered to soft dull, porous

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[95] John G. Grohskopf and Earl McCracken, "Insoluble Residues of some Paleozoic Formations of Missouri, Their Preparation, Characteristics and Application", Mo. Geol. Survey and Water Resources Rept. Inv. 10, pp. 18-22, 1949.

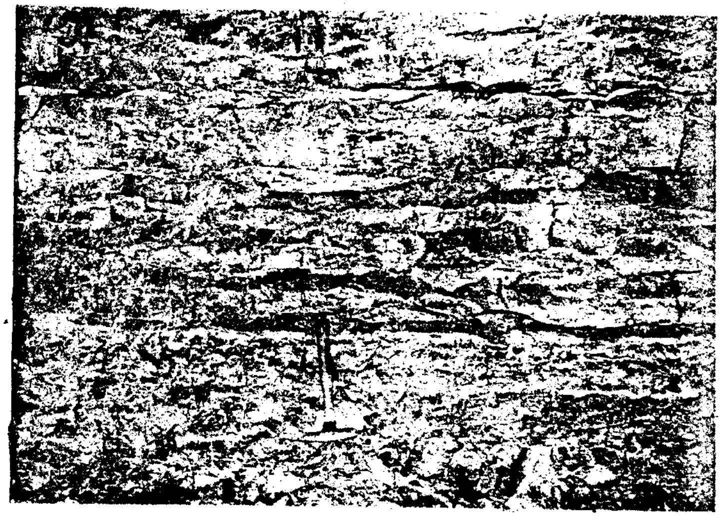

Figure 36. Unmineralized horizontally banded and nodular chert (light gray) in limestone (medium gray). A calcite vein (white) is shown near the top of the photograph. G-H beds, Piokee mine.

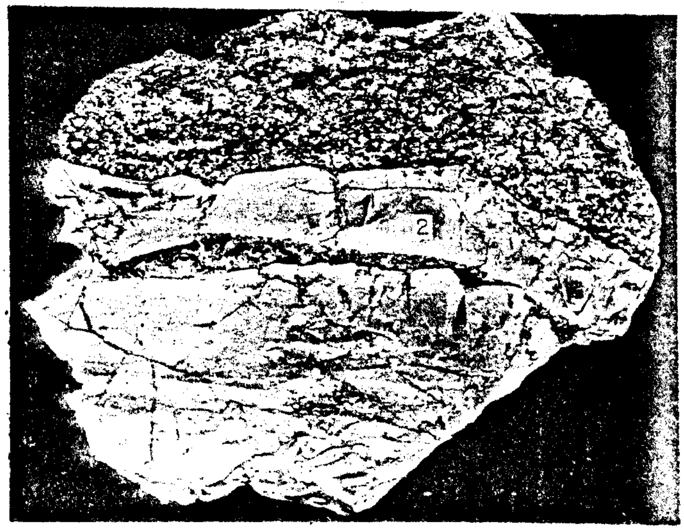

Figure 37. Thin chert lenses (white) separated by jasperoid (black) containing sphalerite (gray specks) typical of mineralized "sheet ground". Jasperoid also fills fractures in the chert. The vertical edge of the number plate is about one centimeter long. O bed, Blue Goose No. 1 mine.

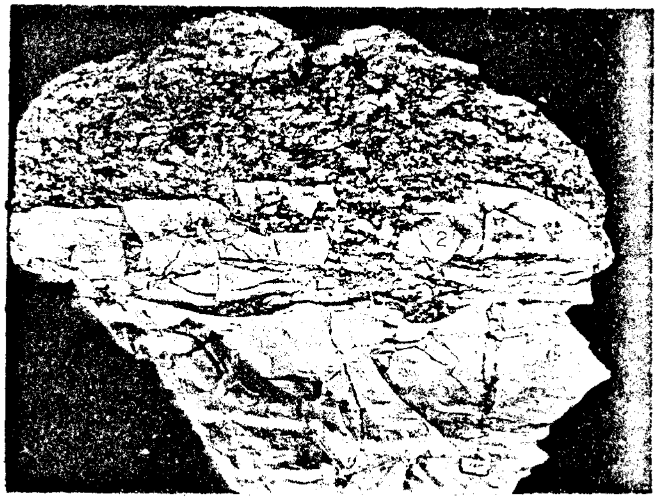

Figure 38. Reverse side of specimen shown in Figure 37, page 75, showing brecciation typical of that occurring in the "sheet ground beds". Blue Goose No. 1 mine.

Figure 39. Nodular and brecciated chert (white) typical of K bed, cemented by jasperoid (dark gray). Note the relatively undisturbed, horizontal chert lenses and nodules overlying the chert breccia. Crawfish mine.

and chalky, as illustrated in Figure 40. Such altered chert may occur in all of the Mississippian Formations. Some chert nodules and lenses exhibit lighter colored margins of this chalky type of chert. In some of these margins fossil fragments have been partly or wholly silicified while those in the interior of the chert nodule are calcareous.

Some of the chert exhibits alternating bands of lighter and darker color. These bands are nearly horizontal in chert beds and lenses, and are concentric in the nodules, conforming to the shape of the nodules. Rarely the banding conforms to the margins of chert breccia fragments, as shown in Figure 41. Some of the chert is mottled, as shown in Figure 42, page 80. It is commonly called "coach dog" chert, and it is not confined to a single formation. The mottling effect is due to the presence of irregular areas of limestone, darker chert or jasperoid in a matrix of lighter colored chert. In some places, as in the St. Joe mine, chert mottled with jasperoid grades horizontally into a similar looking chert in which the mottling is due to pods of limestone. This feature is shown in Figure 7, page 36.

The margins of some chert nodules and lenses contain calcareous material containing fossils. In some chert the fossils still are calcareous and effervesce freely, but in other chert they are partly or completely replaced by silica. This type of chert was called "cotton rock" by Fowler and Lyden,[96] but

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[96] George M. Fowler and Joseph P. Lyden, "The Ore Deposits of the Tri-State District", *Am. Inst. Min. Met. Eng. Trans.* vol. 115, p. 195, 1935.

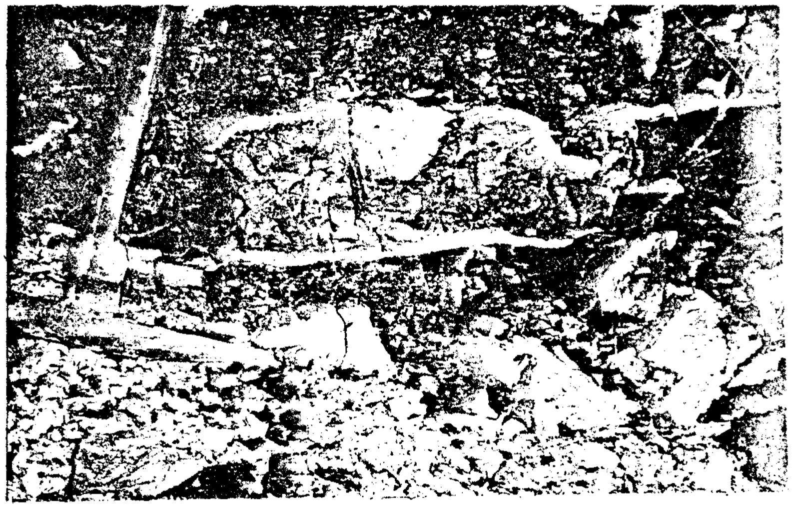

Figure 40. Tripolitic margin (white) of brecciated chert lens (medium gray). The broken portions of the lens are displaced only slightly. Cementing matrix is jasperoid (black). Lower portion of photograph depicts loose rock resulting from the mining operation. M bed, Whitebird mine.

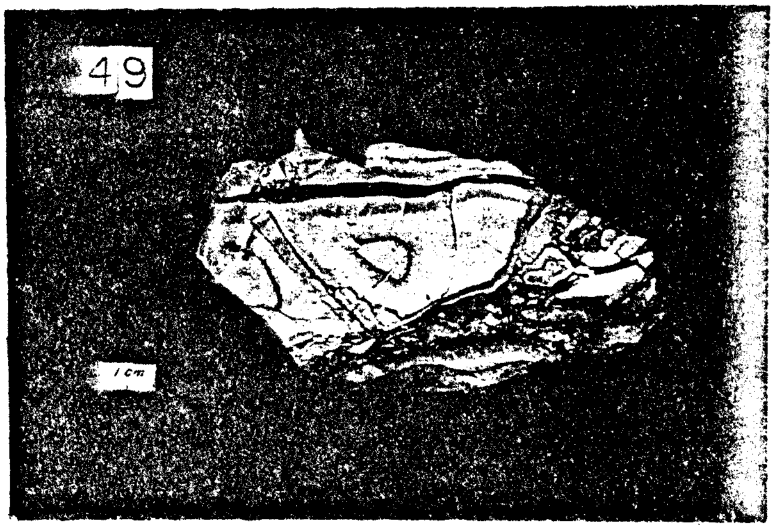

Figure 41. Color banding of fragments in a chert breccia developed after an early stage of brecciation. The cement is jasperoid (black). Picher field. Specimen donated by R. C. Lundin. Specific locality unknown.

Smith[97] pointed out that most geologists of the district have restricted the term to weathered chert.

Some chert bands exhibit top margins which are smooth, in contrast to their bottom margins which are more irregular, as is shown in Figure 43. Other bands do not exhibit this feature.

Brecciation is one of the most outstanding characteristics of the chert of the ore bodies, as is well illustrated in Figure 44, page 81 and in Figure 39, page 76. The breccia fragments are generally very angular, as shown in Figures 45 and 46, page 82, but occasionally are subangular to subrounded as shown in Figure 47, page 82, and Figure 48, page 83. Chert fragments of several different colors or textures may occur in the same specimen, as is shown in Figure 49, page 83. In some beds the breccia fragments form a mosaic and appear as though they could be placed back together again into a solid chert layer, as is well illustrated in Figure 23, page 64, in Figures 50 and 51, page 84, and in Figure 52, page 86. This is particularly characteristic of G-H beds, but occasionally occurs in K and M beds. In other beds the chert breccia is a rubble consisting of a heterogeneous mixture of fragments with no apparent relationship to one another. This is more characteristic of M bed, but it occurs in other beds. In some mines a horizontal band of chert fragments of one color or texture may occur between bands of chert fragments of other colors or textures.

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[97] W. S. Tangier Smith, in discussion of "Chertification in the Tri-State (Oklahoma-Kansas-Missouri) Mining District", by George M. Fowler, _et al_., _Am_. _Inst_. _Min_. _Met_. _Eng_. _Trans_., vol. 115, p. 195, 1935.

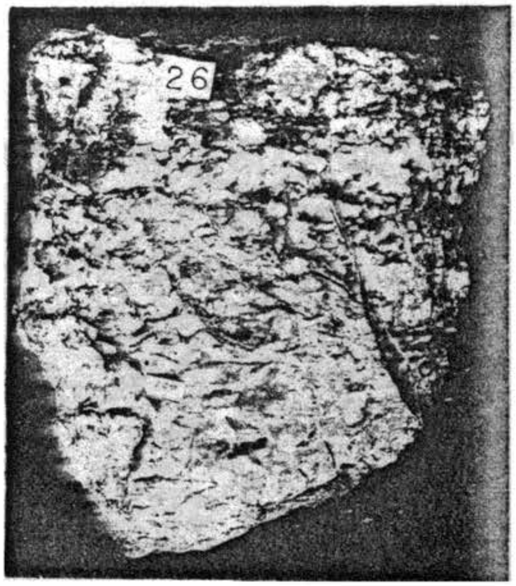

Figure 42. "Coach dog" chert. Chert (white) irregularly mottled by jasperoid (dark gray). G-H beds, Big Elk mine.

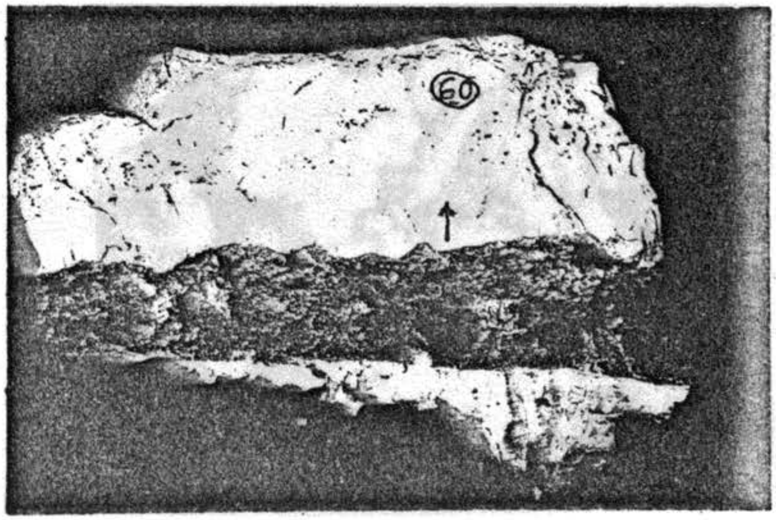

Figure 43. Interbanded chert (white) and jasperoid (black) typical of G-H beds. Note the smooth upper surface of the lower chert layer, in contrast to the wavy lower boundary of the upper chert layer. St. Joe mine. Three-quarters natural size.

Figure 44. Chert breccia (white) cemented by jasperoid (black) and gray dolomite (medium gray) typical of M bed. Webber mine.

Figure 45. Chert breccia (white) cemented by jasperoid (dark gray to black) typical of M bed. Note the swirling of the jasperoid bands beneath the large chert fragment at the left center portion of the photograph. Note the sutured boundary on the right side of the large chert fragment at the bottom center of the photograph and the angular fragments of jasperoid cemented by jasperoid near the number 3. The short black linear features are open vugs in the jasperoid. M bed, Lucky Jew mine.

Figure 46. Chert breccia (white) cemented by jasperoid (black) containing sphalerite (light gray). M bed, Lucky Jew mine.

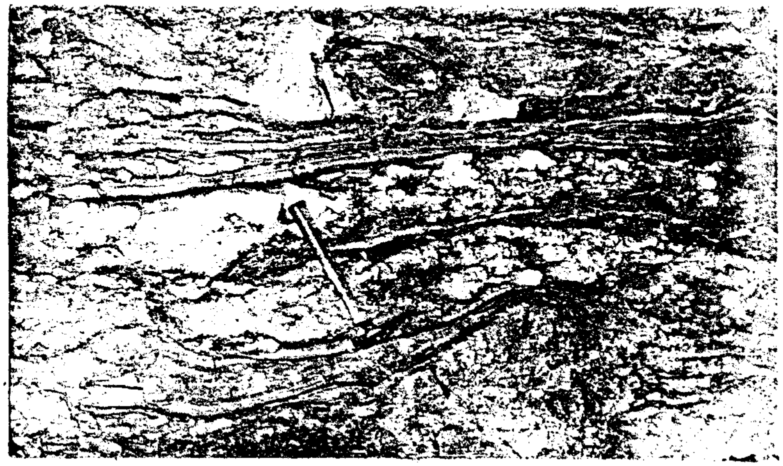

Figure 47. Subangular to subrounded chert fragments (white) overlain and underlain by unbroken banded shaly limestone and massive limestone. An intraformational chert conglomerate. M bed, Kenoyer mine.

Figure 48. Intraformational breccia of the Keokuk Formation. Subangular to subround chert fragments (white) cemented by limestone (gray). M bed, Webber mine.

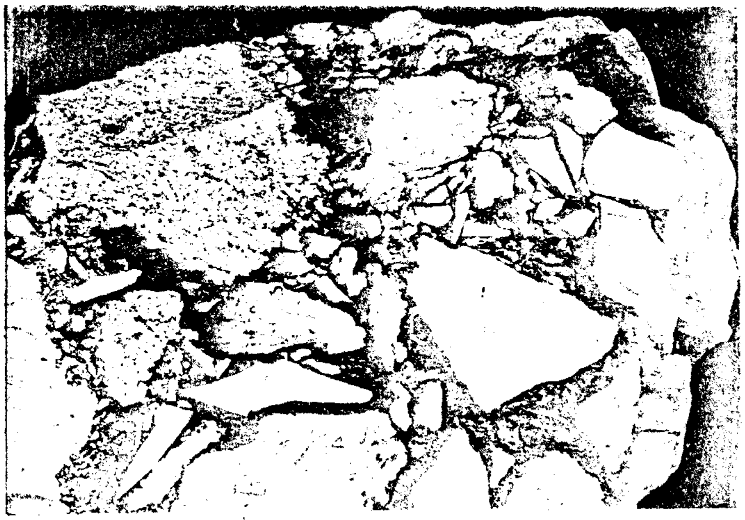

Figure 49. Chert breccia containing fragments which exhibit a variety of textures: massive white, banded light gray, and mottled. The mottled fragments consist of chert (light gray) and limestone (medium gray). The fragments are cemented by jasperoid (dark gray). M bed, Lucky Jew mine.

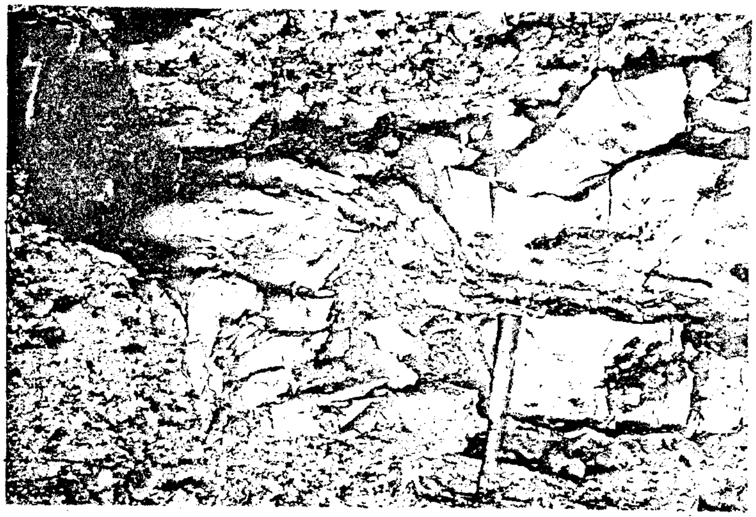

Figure 50. Mosaic chert breccia (white) in M bed, cemented by jasperoid (dark gray). Much of the breccia in the left portion of the photograph could be placed back together with the solid chert lens to the right. Note bands in jasperoid which bend over some chert fragments in the upper left portion of the photograph. Whitebird mine.

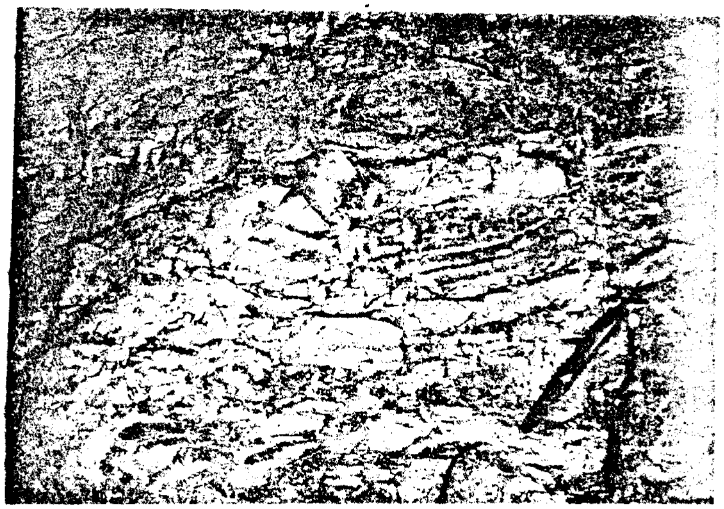

Figure 51. Mosaic breccia of banded chert (white and light gray) in G-H beds. Jasperoid (dark gray) cements the breccia. Netta mine.

Rarely bands of chert fragments are interbedded with horizontal bands of massive or lenticular, non-brecciated chert, as is well illustrated in Figure 39, page 76.

Although the breccia fragments usually are cemented by jasperoid or dolomite, some chert breccia fragments are embedded in younger chert or calcite. The chert breccia frequently is confined to the jasperoid cement where contacts between jasperoid and limestone can be observed in the mines, as is well illustrated in Figures 52, 53, and Figure 54, page 87.

In section 35, T. 28 N., R. 24 E., ten miles east of Miami, Oklahoma, the writer observed limestone and chert pebbles in the Carterville conglomerate. Some of the chert pebbles consist of chert fragments cemented by later chert. This chert is distinct from that of the ore deposits in that it occurs in a basal conglomerate above and away from the ore deposits.

The common Tri-State chert consists mainly of microcrystalline quartz, which occurs as interlocked grains of sizes from 0.003 mm. to 0.015 mm. as is illustrated in Figure 55, page 87. Small amounts of chalcedonic quartz occur as radial microfibrous aggregates and as microfibrous vug-fillings in the chert. The surface of one chert specimen from Joplin was studied by Folk and Weaver[98] with the electron microscope by the replica method. They found both microcrystalline quartz

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[98] Robert L. Folk and Charles Edward Weaver, "A study of the Texture and Composition of Chert", Am. Jour. Sci., vol. 250, pp. 498-510, 1952.

Figure 52. Sharp contact between massive limestone (lighter gray, on the left) and chert breccia (white) cemented by jasperoid (dark gray) typical of M bed. Blocks of limestone containing chert lenses, broken from the bedded limestone, are displaced to the right and surrounded by jasperoid. Lucky Jew mine.

Figure 53. Detailed view of cherty limestone blocks (light gray) which have slumped into jasperoid (black). M bed, Lucky Jew mine.

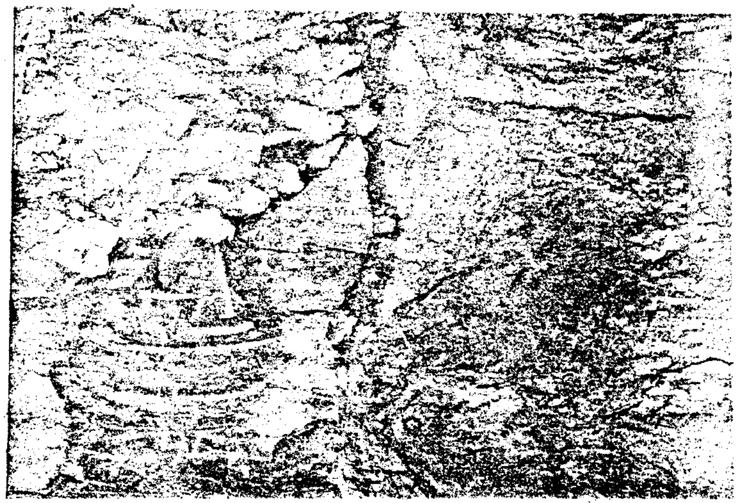

Figure 54. Sharp contact of massive limestone (light gray, on the right) with breccia. Breccia consists of chert fragments (white) and limestone blocks (light gray), cemented by jasperoid (dark gray). Jasperoid (lower left) exhibits banding. M bed, Lucky Jew mine.

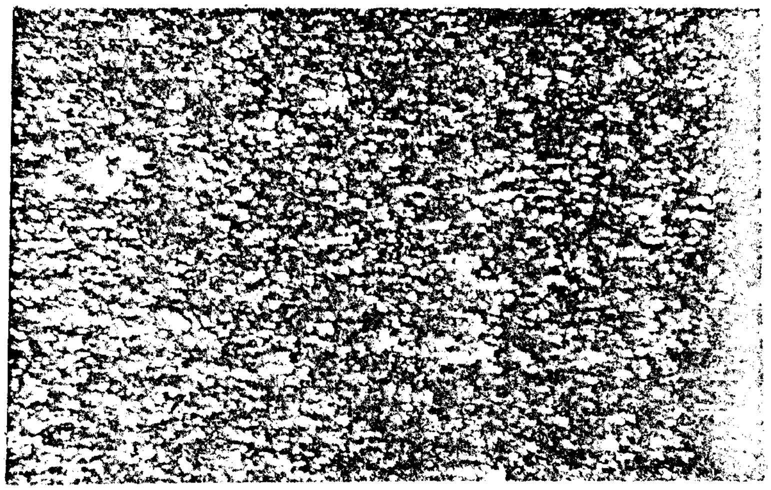

Figure 55. Typical chert as seen in thin section under crossed nicols. M bed, Whitebird mine. 100X.

consisting of distinct polyhedral grains containing very few cavities, and chalcedonic quartz which was massive and homogenous and contained many cavities.

Some Tri-State cherts contain small vugs and irregular fractures, averaging about 0.1 mm., which generally are filled with microcrystalline quartz and less often with chalcedonic quartz. The quartz filling of the vugs is generally of slightly larger grain size and it is cleaner than the microcrystalline quartz of the chert matrix. Some of the larger veinlets in vugs in the Tri-State chert exhibit encrusting structure, consisting of an early microfibrous chalcedonic quartz layer followed by a coating of quartz crystals up to about 0.12 mm. long. This same type of clear microcrystalline quartz also fills and replaces sponge spicules and other organic remains.

Other constituents of chert, recognizable with the aid of the microscope, are pyrite, glauconite, and calcite. Pyrite is a constant, but not abundant, constituent of the cherts, especially the darker cherts. It occurs as very small, usually anhedral grains, 0.003 mm. to 0.3 mm. in diameter. Glauconite occurs rarely in small rounded grains in some cherts, but it is much less abundant in chert than in jasperoid. Anhedral calcite is abundant in some cherts. Occasionally it outlines fossil ghosts, but usually there is little evidence to indicate whether the calcite was simply intermixed with the chert during sedimentation, or whether the areas of calcite represent unreplaced remnants of limestone. Agar[99] reported the

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[99] W. M. Agar in George M. Fowler, _et al_., "Chertification in the Tri-State Mining District", _Am_. _Inst_. _Min_. _Met_. _Eng_. _Trans_., vol. 115, p. 149, 1935.

occurrence of tourmaline grains in the Tri-State cherts. This must be quite rare for the writer has not seen tourmaline in any of the chert sections which he examined.

Jasperoid

The jasperoid differs from the chert of the Tri-State district in several respects. Jasperoid is more vitreous and more crystalline than chert. In many specimens small quartz crystals in jasperoid may be observed with the aid of the hand lens. Jasperoid is generally much darker than chert. Jasperoid has an uneven fracture while that of chert is smooth and sharp; jasperoid is less frequently brecciated than chert. Jasperoid commonly contains disseminated sphalerite, galena, marcasite, pyrite and glauconite; chert normally does not, although some chert contains very small grains of iron sulfide and more rarely contains disseminated sphalerite and glauconite. Jasperoid is closely associated with the sulfide mineralization whereas chert often occurs interbedded with limestone in barren areas between ore runs. In barren areas G-H beds as much as 30 feet thick consist of an alternation of chert and limestone, each about four to six inches thick, but in the mineralized areas the alternation is between chert and jasperoid.

One of the most noteworthy features of the jasperoid, exhibited principally where the jasperoid is interbedded with chert and to some extent where it fills the spaces between the chert fragments in breccias, is its characteristic banding, as is well illustrated in Figure 9, page 39, in Figures 24 and 25, page 66, in Figure 26, on page 67, in Figure 30, page 70, in Figure 33, page 71, in Figure 56 and 57, page 91, in Figures 58 and 59, page 92, and in Figure 60, page 93. With the aid of a hand lens the bands can be seen to differ in color, and in sulfide, glauconite and dolomite content. Usually the banding is horizontal, as shown in Figures 24 and 25, page 66, but rarely it is contorted and broken, as shown in Figures 58 and 59, page 92. The bands generally grade vertically into one another, but rarely the boundary between the bands is very sharp.

The banding has been observed to bend both under and over sulfides, chert fragments and rarely fossils, and some of these form geopetal fabrics.[100] Iron sulfide grains frequently exhibit this feature; chert fragments, sphalerite crystals and fossils exhibit it in some specimens, as shown in Figure 8, page 39.

Jasperoid commonly forms the matrix of the chert breccias. In some places little or no jasperoid cements the chert breccia, as shown in Figure 61, page 93, in places jasperoid fills most or all of the space between chert fragments, as shown in Figures 45, page 81, and 46, page 82, and in Figure 49, page 83, and in some places jasperoid forms the major fraction of the gangue and contains only a few floating chert breccia fragments. As indicated by this last instance, where the chert breccia fragments are completely

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[100] Bruno Sander, translated by Eleanora Bliss Knopf, "Contributions to the Study of Depositional Fabrics", Am. Assoc. Pet. Geol., Tulsa, p. 2, 1951.

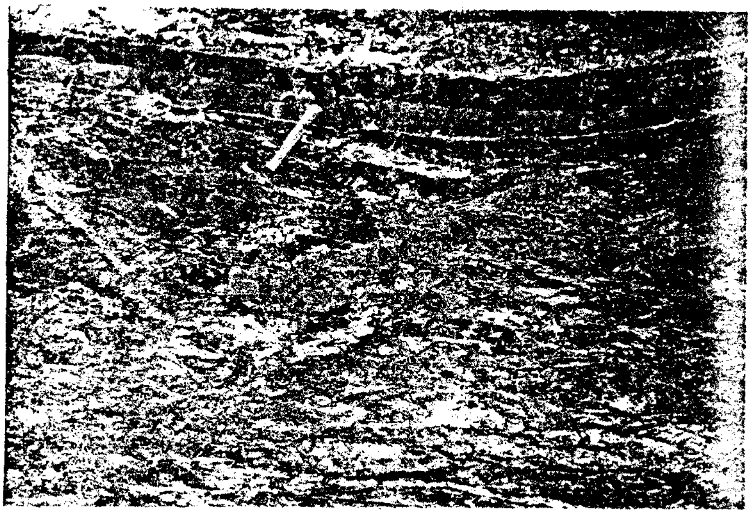

Figure 56. Well banded jasperoid (dark gray and black). The color variation is due to grain size and sphalerite content. A photomicrograph of this jasperoid is shown in Figure 60. The lower part of the banded jasperoid is covered by ore broken during mining. M bed, Webber mine.

Figure 57. Interbanded jasperoid (dark gray) and limestone (light gray). M bed, Lucky Jew mine.

Figure 58. Contorted and broken banded jasperoid. E bed, Tar Creek mine. One-half natural size.

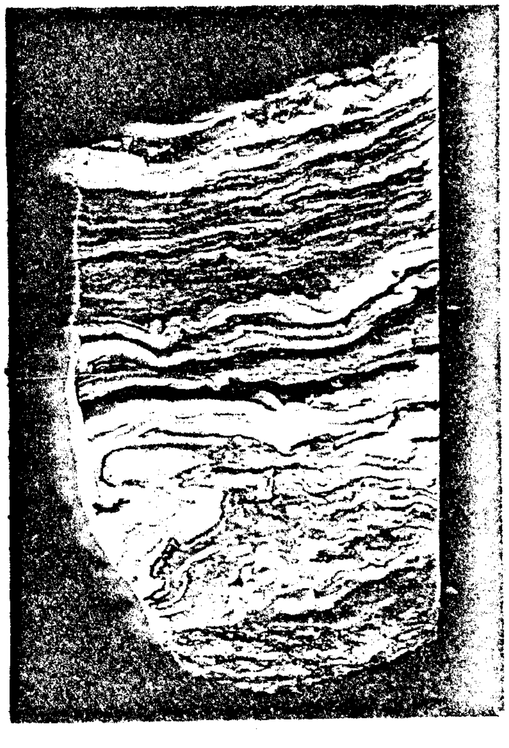

Figure 59. Contorted jasperoid bands. A few small scattered galena crystals (white specks) are present. E bed, Tar Creek mine. One-half natural size.

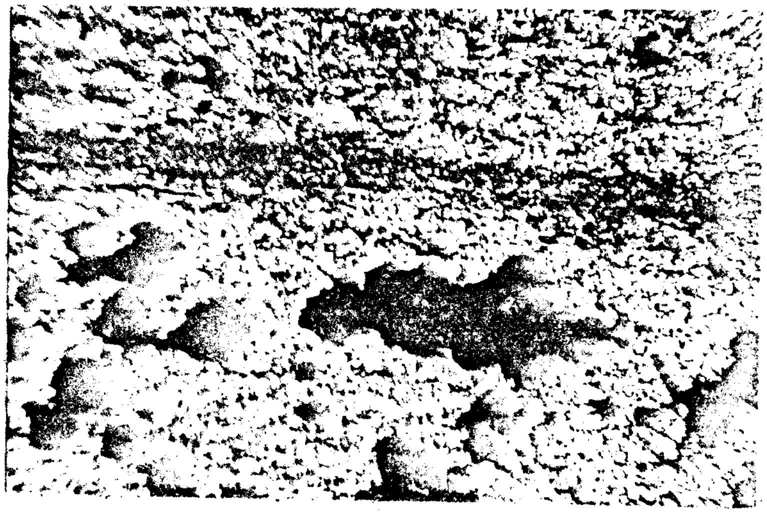

Figure 60. Two bands of jasperoid which differ from each other in quartz grain size, color, sphalerite content and sphalerite (large black crystals) grain size. This is a thin section of the jasperoid shown in Figure 56, page 91. M bed, Webber mine. Ordinary light. 30X.

Figure 61. Chert breccia (white) partially cemented by jasperoid (gray). From an outcrop of M bed about four miles southeast of Joplin.

separated from adjacent chert fragments, the jasperoid matrix must have been soft at the time of chert brecciation.

The boundary between chert and jasperoid generally is straight and sharp, yet some specimens show a sutured or irregular boundary, as shown in Figure 62, page 96, and rarely some chert breccia fragments exhibit a darker alteration rim next to jasperoid matrix. The alteration rims vary in thickness from about one to five millimeters, and appear gray to the naked eye in contrast to the white color of the unaltered chert. With the aid of a hand lens, the alteration rim may be seen to be a little more porous than the interior of the chert, and an occasional grain of pyrite and sphalerite may be detected. Thin sections reveal that this alteration rim differs from the unaltered chert in pyrite content, in grain size of the microcrystalline quartz and in general color. Anhedral grains of pyrite are relatively abundant in the alteration rim, particularly in the outer portions of the rim, and they may constitute as much as five per cent of the rim. The microcrystalline quartz of the alteration rim usually occurs in slightly larger grains than that of the unaltered chert. The alteration rim is darker than that of the unaltered chert, this darkening being due mainly to finely dispersed pyrite.

Occasional associates of the jasperoid are dark, semiconsolidated muds. Some of these muds contain glauconite, organic matter and disseminated sulfides, and grade horizontally and vertically into jasperoid. Smith and Siebenthal[101] found these muds to consist almost

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[101] W. S. Tangier Smith and C. E. Siebenthal, Description of the Joplin District in Geologic Atlas of the United States, U. S. Geol. Survey folio 148, p. 14, 1907.

entirely of microcrystalline quartz crystals which are similar to, but slightly larger than, those of the typical jasperoid. Other muds are more similar to the overlying Pennsylvanian shales, and these frequently are contorted and broken, as shown in Figure 63. The origin of the muds has been a subject of controversy: 1) Smith and Siebenthal[102] believed that they were formed by weathering of jasperoid; Jenny[103] and Stewart[104] believed that jasperoid forms by silicification of the muds; Lyden[105] held that while some had slumped from J bed or from the overlying Pennsylvanian shales, others had formed as residual material from the solution of limestone.

In thin sections jasperoid may be seen to consist mostly of microcrystalline quartz. The individual crystals are generally subhedral to anhedral and intimately interlocked with adjacent quartz crystals, as is shown in Figures 64 and 65, page 97. Where quartz crystals are enclosed in sphalerite or dolomite crystals, the quartz crystals are frequently euhedral, as is shown in Figure 12,

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[102] _Ibid_.

[103] Walter P. Jenny, "The Lead and Zinc Deposits of the Mississippi Valley", _Am_. _Inst_. _Min_. _Met_. _Eng_. _Trans_., vol. 22, pp. 195-196, 1893.

[104] Dan R. Stewart, Oral Communication, 1959.

[105] Joseph P. Lyden, "Aspects of Structure and Mineralization Used as Guides in the Development of the Picher field", _Am_. _Inst_. _Min_. _Eng_. _Trans_., vol. 187, pp. 1253 and 1255, 1950.

Figure 62. Gray chert mottled by white chert and overlain by jasperoid (black) containing abundant small crystals of sphalerite (gray specks). Note the irregular black jasperoid bands which contain no sphalerite and the irregular contact between the jasperoid and the chert. G-H beds, Piokee mine.

Figure 63. Limestone locally brecciated by squeezing. Blocks embedded in a shale matrix. Squeezed structure in M bed, Kenoyer mine.

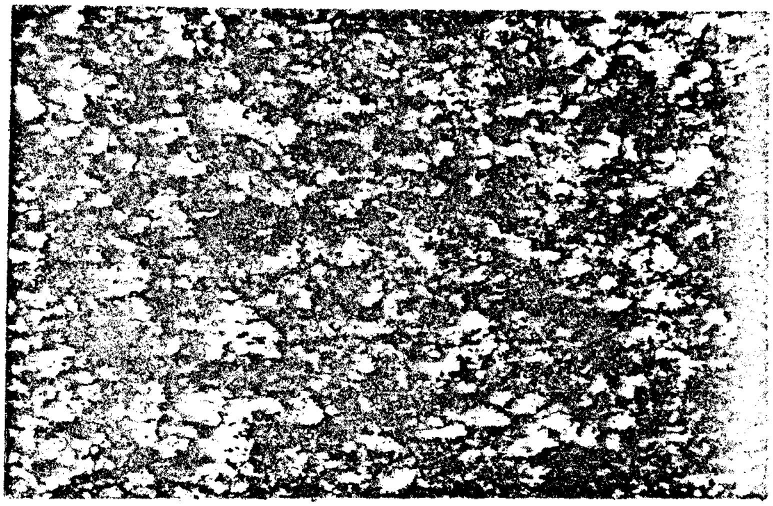

Figure 64. Typical jasperoid as seen in thin section under crossed nicols. K bed, Netta White mine. 100X.

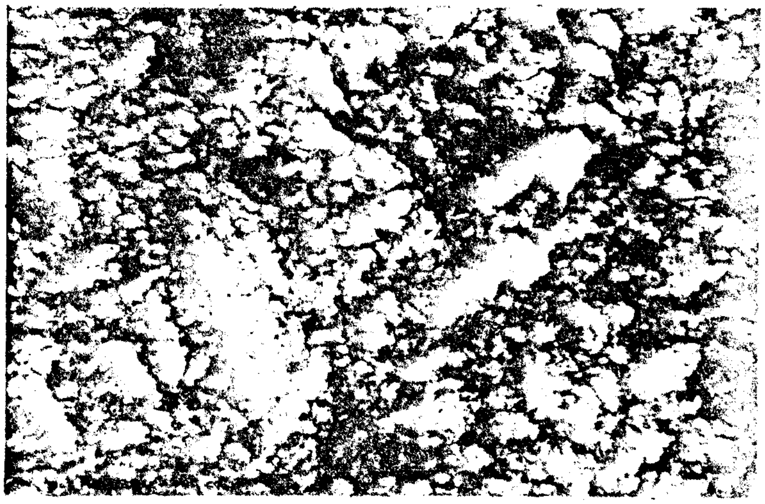

Figure 65. Elongated quartz crystals in a thin section of jasperoid under crossed nicols. Compare the coarser and more elongate character of the quartz grains with those in chert as shown in Figure 55, page 87. M bed, Netta White mine. 100X.

page 47. Although jasperoid and chert may be similar surficially, microscopically they are quite distinct. Compare Figures 64 and 65, page 97, with Figure 55, page 87. The grain size of the jasperoid varies from about 0.004 mm. to 0.140 mm; but most of the grains are about 0.014 mm. to 0.070 mm. across, whereas the grains in chert usually are less than 0.014 mm. across. The variation in the grain size of some jasperoids cause them to display a microtexture which is similar to that of a porphyritic rock, as is shown in Figure 65, page 97. Rarely larger quartz grains are present which apparently filled vugs in the jasperoid. The quartz crystals of the jasperoid tend to be elongate in shape and this is well illustrated in Figure 65, page 97, whereas those in chert normally are equant. Jasperoid normally contains sphalerite, galena, glauconite and dolomite, whereas chert usually does not contain these; it only contains a little iron sulfide and calcite.

Brown, opaque organic matter is present in most of the slides of jasperoid. It lends a brownish color to the jasperoid, but this color disapppears when the jasperoid is strongly heated. Differences in the amount of organic matter cause part of the banding in the jasperoid, but banding also is due to small differences in grain size and to variations in the amount of disseminated sphalerite, dolomite, calcite and glauconite. These minerals generally make up less than five per cent of the jasperoid, but glauconite and sphalerite may constitute 15 or 20 per cent of the rock, and the dolomite may comprise over 50 per cent.

Rarely very distinct horizontal bands in jasperoid, as shown in Figure 56, page 91, exhibit differences in the sphalerite on the upper side of the band as contrasted with the lower side. Thin sections of such a band in the Webber mine showed the lower side to contain about 13 to 17 per cent sphalerite with an average grain size of 0.28 mm., while the upper side contained less than two per cent sphalerite with an average grain size of less than 0.1 mm. Figure 60, page 93, is a photomicrograph of one of these thin sections. The size of the jasperoid quartz crystals also is different on each side of the contact. Those on the lower side are as large as 0.1 mm., while those on the upper side vary from 0.014 to 0.028 mm. in greatest dimension. In the Webber mine this horizontal contact is continuous for about twenty feet.

Straight to irregular and sutured contacts are observed in the jasperoid in some sections. Organic matter generally is concentrated along these contacts and occasionally they cut dolomite and less often glauconite grains, and they probably indicate some solution activity along them.

The transition from the jasperoid in the ore deposits to the limestone in unmineralized areas is generally gradational, and in places may consist of interbanded jasperoid and limestone, as shown in Figure 66 and in Figure 57, page 91. In many places a semi-consolidated "boulder zone", consisting of chert and limestone fragments only partly cemented by calcite, as shown in Figure 67, occurs between the jasperoid and undisturbed limestone.

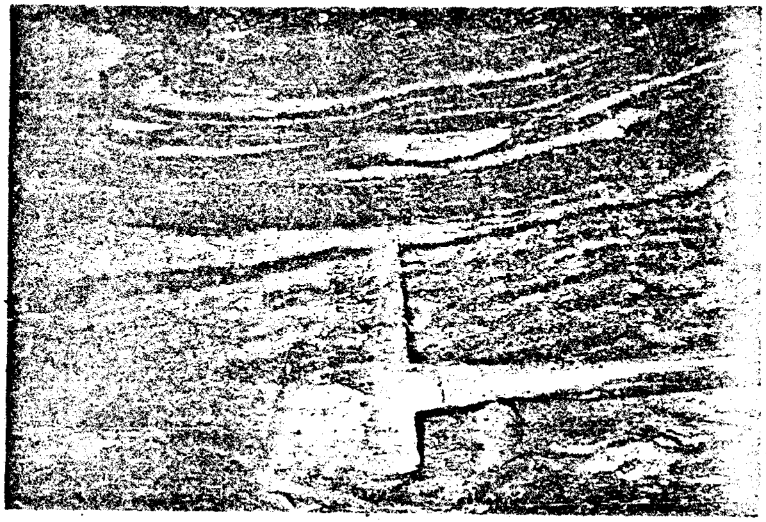

Figure 66. Interbanding of jasperoid (dark gray) and limestone (light gray) at a gradational contact between a breccia and massive limestone. M bed, Kenoyer mine.

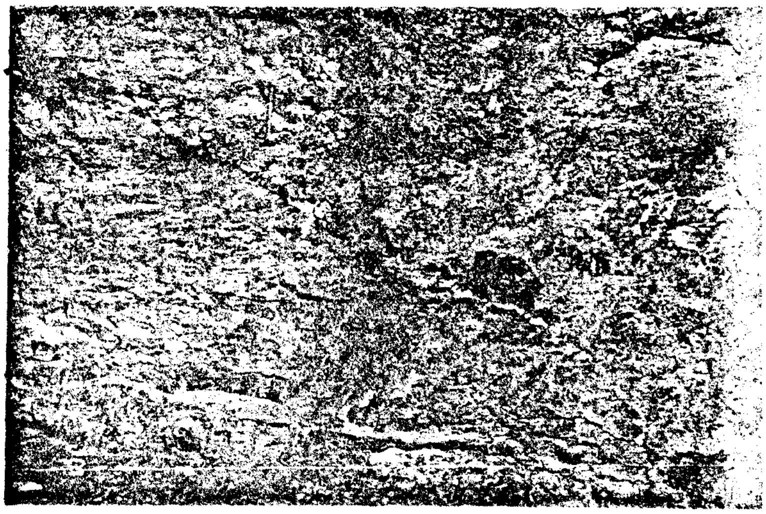

Figure 67. Sharp contact between relatively undisturbed limestone (lower left, dark gray) and a semiconsolidated breccia (upper right, lighter gray) consisting of limestone and chert fragments. To the right (off photograph) the breccia or "boulder zone" grades into a typical mineralized M bed breccia. "Full drift" Kenoyer mine.

In still other places the boundary is sharp and exhibits blocks of limestone which have slumped into the jasperoid, as shown in Figure 6, page 35, in Figure 53, page 86, and in Figure 54, page 87. The gradational transition from jasperoid to limestone was studied in some thin sections. These sections exhibit calcite and quartz mixtures in which the calcite is fine-grained and anhedral and the quartz crystals usually are euhedral. In one slide of mottled chert from margin of the alteration halo, shown in Figure 6, page 35, patches of limestone in the chert are seen to grade horizontally into patches of jasperoid.

In thin sections of dolomitic jasperoid, the rhomb-shaped dolomite crystals generally appear to be euhedral under lower magnifications. Under higher magnifications, some of the quartz crystals can be seen to show their outlines against the dolomite rhombs and also to be included within the individual dolomite rhombs. Thin sections of rocks with higher percentages of dolomite, which perhaps are best called jasperoidal dolomite, exhibit these same textural relationships between the dolomite rhombs and the quartz crystals.

Observation of thin sections show that jasperoid may contain breccia fragments which also consist of jasperoid quartz of essentially the same grain size as the enclosing jasperoid, but which frequently show a larger percentage of organic matter. The glauconite and sphalerite contents of the two jasperoids appear essentially the same in some fragments, but differ in other fragments.

The outlines of broken fossils rarely occur in jasperoid, and they are much less common in jasperoid than in chert.

Weidman[106] reported the presence of a small per cent of tourmaline in jasperoid, occurring as small prismatic crystals from 0.01 mm. to 0.03 mm. in diameter. The writer did not find tourmaline in any of the thin sections of jasperoid which he examined.

Quartz Druse

A fine quartz druse coats many of the vugs. It may be detected by its rough surface or with the aid of the binocular microscope. The quartz druse was deposited most commonly on chert and jasperoid. Rarely small quartz crystals may occur in galena, sphalerite, marcasite and other minerals deposited in the vugs.

Late Quartz

Late quartz crystals, which may be as large as a centimeter or two, were deposited on sulfides and other minerals in some vugs. This late quartz is not common and it is not present everywhere. It is more abundant in the sheet ground beds, and in the northeastern portion of the Picher field toward Baxter Springs and in fields toward the east.

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[106] Samuel Weidman, "Tourmaline in Jasperoid of the Miami-Picher Zinc-Lead District", (abstract), Geol. Soc. America Proc. 1933, pp. 117-118, 1934.

Minor Minerals

Native Elements:

Sulfur - S

Minute crystals of sulfur on cleavage surfaces of galena and on walls of cavities in sphalerite were noted by Rogers[107] who believed that this mineral had formed in an intermediate state during the oxidation of sulfides to carbonates. Ransome[108] observed small yellowish-green orthorhombic crystals of sulfur on chalcopyrite and sphalerite in a single specimen. The writer did not observe sulfur on any of his specimens.

Sulfides:

Bornite - Cu_5FeS_4

A pinkish brown, weakly anisotropic mineral was noted in some polished sections of iridescent chalcopyrite. The mineral exhibits a reflectivity of a little less than 30 percent, estimated by comparison with the reflectivities of adjacent sphalerite, chalcopyrite and marcasite, and a hardness slightly less than that of adjacent chalcopyrite. Dr. G. C. Amstutz suggested that the mineral might be bornite. Microchemical etch tests by the

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[107] Austin F. Rogers, pt. III in Erasmus Haworth, "Special Report on Lead and Zinc", Kansas Geol. Survey Rept., vol. VIII, pp. 449, 452, 1904; Austin F. Rogers, "Notes on Some Pseudomorphs, Petrifications and Alterations", Am. Phil. Soc. Proc. 49, p. 22, 1910.

[108] Alfred L. Ransome, "Enargite and Plumbojarosite at Picher, Oklahoma", Am. Mineralogist, vol. 20, p. 802, 1935.

writer tend to confirm the mineral as bornite: HNO_3 produced effervescence, $FeCl_3$ produced a faint orange stain, and HCl produced a negative reaction. The bornite forms an iridescent film on sphalerite and chalcopyrite and occurs as irregular patches and veinlets of bornite in chalcopyrite and marcasite. It most frequently occurs at the boundary between chalcopyrite and marcasite and has replaced those minerals, as shown in Figure 14, page 51.

Wurtzite - ZnS

Wurtzite crystals were described first by Rogers,[109] who identified them by goniometry. Recently Evans and McKnight,[110] using x-ray diffration, confirmed Rogers' determination. Utilizing crystals of wurtzite on zinc sulfide stalactites from the Zig Zag mine, near Joplin, they found this wurtzite to have three structures which they designate 10H, 8H and 6H. Their diffraction patterns contained lines belonging to sphalerite, indicating the presence of both forms of zinc sulfide.

Greenockite - CdS

Leonhard[111] reported small crystals of greenockite on sphalerite at Granby, but greenockite usually occurs as greenish to yellowish films on some sphalerite crystals and as thin coatings on hemimorphite, as may be seen on specimens in the Missouri School of Mines collection.

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[109] Rogers, op. cit. pp. 461-462.

[110] Howard T. Evans, Jr. and Edwin T. McKnight, "New Wurtzite Polytypes from Joplin, Missouri", Am. Mineralogist, vol. 44, pp. 1210-1218, 1959.

[111] Alexander V. Leonhard, "Notes on the Mineralogy of Missouri", Trans. St. Louis Acad. Sci., vol. 4, p. 444, 1882.

Millerite - NiS

Smith and Siebenthal[112] were the only investigators to report millerite from the Tri-State district. They included it among a list of minerals which were said to be found but rarely and in small amounts.

Covellite - CuS

The presence of covellite in the district was noted first by Rogers.[113] The writer observed it associated with bornite as he examined polished specimens of chalcopyrite. In these specimens the covellite occurs as irregular veinlets which grade into and occur within veinlets of bornite. It also occurs with bornite replacing both marcasite and chalcopyrite at their mutual grain boundaries, and a small amount of covellite has been noted in veinlets cutting hemimorphite.

Sulfosalts:

Enargite - Cu_3AsS_4

Enargite, first discovered in the Picher field by McKnight[114]

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[112] W. S. Tangier Smith, and C. E. Siebenthal, Description of the Joplin District in Geologic Atlas of the United States, U. S. Geol. Survey folio, 148, p. 12, 1907.

[113] Austin F. Rogers, pt. III, in Erasmus Haworth, "Special Report on Lead and Zinc", Kansas Geol. Survey Rept., vol. VIII, pp. 459-460, 1904.

[114] Edwin T. McKnight, "Occurrence of Enargite and Wulfenite in Ore Deposits of Northern Arkansas", Econ. Geology, vol. 30, p. 65, 1935.

malachite at the Big Coon mine, Galena, Kansas. This is the only mine in the district from which cuprite has been reported.

Hematite - Fe_2O_3

An alteration product of pyrite and marcasite in tallow clay from the Granby field was reported to be hematite by Buckley and Buehler.[117]

Pyrolusite - MnO_2

Small black spots in the tallow clay from the Granby field were thought to be pyrolusite by Buckley and Buehler.[118]

Limonite - $2Fe_2O_3 \cdot 3H_2O$

Limonite occurs in the ores of the Tri-State district wherever structure and erosion have brought them into the zone of oxidation. Excellent specimens of limonite pseudomorphic after pyrite and marcasite may be observed in the Missouri School of Mines collection. In some of these specimens limonite replacing and pseudomorphous after pyrite and marcasite is associated with hemimorphite. Limonite pseudomorphous after chalcopyrite was reported by Rogers[119]

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[117] E. R. Buckley and H. A. Buehler, "The Geology of the Granby Area", *Mo. Geol. Survey Rept.*, vol. IV, 2d series, p. 46, 1905.

[118] *Ibid.*

[119] Austin F. Rogers, "Notes on Some Pseudomorphs, Petrifactions and Alterations", *Am. Philo. Soc. Proc.* 49, p. 18, 1910.

from Granby.

Carbonates:

Smithsonite - $ZnCO_3$

Smithsonite commonly occurs in the oxidized ores as botryoidal masses. Excellent pseudomorphs of smithsonite and hemimorphite after calcite are in the Missouri School of Mines collection. They are as much as eight inches long and take the shape of the calcite scalenohedron. Their interiors usually are hollow, but some have calcite cores. The relationship between the smithsonite and hemimorphite in the pseudomorphs varies. Some pseudomorphs consist of a smooth layer of smithsonite coated either on the inside or outside or both by hemimorphite. Others consist of several smooth nearly parallel layers of smithsonite with hemimorphite between the layers. Some consist entirely of hemimorphite. A few pseudomorphs contain central spongy portions consisting of unreplaced calcite and small microscopic aggregates of hemimorphite.

Replacement of dolomite by smithsonite was described by Rogers[120] from Granby.

Aragonite - $CaCO_3$

Weidman[121] described calcite paramorphous after aragonite

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[120] Rogers, op. cit., p. 19.

[121] Samuel Weidman, "The Miami-Picher Zinc-Lead District, Oklahoma", Okla. Geol. Survey Bull. 56, pp. 58-60, 1932.

in cup-shaped forms, one to three inches in diameter, from the Golden Rod mine. That the mineral now is calcite was indicated by Meigen's test. He also observed the mineral in the Grace Walker, Beaver, Woodchuck and Ketta mines.

Similar cup-shaped forms, deposited upon sphalerite, were observed by this writer in the Lucky Bill mine. X-ray analysis as shown in Table IV showed this mineral to be calcite.

Buckley and Buehler[122] reported aragonite as an alteration product of boulders in the Pennsylvanian shale of the Granby field.

Cerussite - $PbCO_3$

Cerussite occurs in the oxidized ores of the fields to the east of the Picher field, where it forms prismatic crystals and massive coatings on galena and other minerals. Stalactites of cerussite and cerussite molds of galena crystals were noted by Buckley and Buehler[123] at Granby, and by the present writer in specimens in the Missouri School of Mines museum. Pseudomorphs of cerussite after calcite and galena from Granby were noted by Rogers.[124] A large body of cerussite at Spring City was reported by Schmidt and Leonhard.[125]

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[122] Buckley and Buehler, op. cit., p. 34.

[123] Buckley and Buehler, op. cit., p. 45-46.

[124] Austin F. Rogers, pt. III in Erasmus Haworth, "Special Report on Lead and Zinc", Kansas Geol. Survey Rept., vol. VIII, p. 492, 1904 Austin F. Rogers, "Notes on Some Pseudomorphs, Petrifications and Alterations", Am. Phil. Soc. Proc. 49, p. 19, 1910.

[125] Adolf Schmidt and Alexander Leonhard, "The Lead and Zinc Regions of Southwest Missouri", Mo. Geol. Survey Rept. for 1874, p. 456, 1874.

TABLE IV

X-RAY DIFFRACTION DATA FOR CUP-SHAPED CALCIUM CARBONATE FORMS

(I = relative intensity of diffraction line)
(d = interplanar spacings in Angstron units)

Calcite		Cup-Shaped Calcium Carbonate Forms	
A.S.T.M. Index Card No. 2-0649		Lucky Bill mine	
Synthetically Prepared		Cardin, Oklahoma	
$\lambda = 0.709$ A°		$\lambda = 1.5405$ A°	
I	d	I	d
60	3.84	3	3.86
100	3.02	10	3.04
60	2.49	6	2.50
70	2.28	7	2.29
70	2.09	7	2.10
90	1.92	9	1.92
80	1.87	8	1.88
40	1.62	4	1.63
50	1.60	5	1.61
60	1.52	1	1.52
40	1.47	1	1.48
50	1.44	5	1.44
40	1.42	5	1.42
10	1.36	4	1.36

TABLE IV (Continued)

I	d	I	d
40	1.33	4	1.34
30	1.29	4	1.30
20R	1.24	5	1.24
40	1.18	4	1.18
40	1.15	4	1.16
40	1.14	3	1.14
40	1.04	4	1.05
40	1.01	4	1.01
20R	0.984	2	0.988
30	0.964	4	0.966
10R	0.943	3	0.945
.....	....	1	0.893

Hydrozincite - $Zn_5(OH)_6(CO_3)_2$

Earthy hydrozincite was noted by Buckley and Buehler[126] at Granby. Material of this nature was observed by this writer at the Joplin Museum. Dr. O. R. Grawe observed and identified by x-ray analysis, hydrozincite in spring water issuing from Buttermilk Spring, southwest of Joplin.

Aurichalcite - $(Zn,Cu)_5(OH)_6(CO_3)_2$

Radial aggregates of monoclinic crystals of aurichalcite from Big Coon mine at Galena, Kansas, were described by Rogers,[127] He also reported bluish-green globular aggregates of aurichalcite from Granby. More recently, Keller[128] reported aurichalcite from the Shinn mine, Stark City, Missouri. Aurichalcite is a rare mineral in the Tri-State district.

Malachite - $Cu_2(OH)_2(CO_3)$

This writer observed a thin, drusy, green coating of malachite deposited over a covellite film on chalcopyrite and sphalerite in one specimen collected from the Lawyers-Chicago No. 2 mine. The

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[126] Buckley and Buehler, op. cit., p. 44.

[127] Austin F. Rogers, pt. III in Erasmus Haworth, "Special Report on Lead and Zinc", Kansas Geol. Survey Rept., vol. VIII, p. 493, 1904.

[128] W. D. Keller, "Aurichalcite in Missouri", Am. Mineralogist, vol. 25, p. 376, 1940.

mineral also was observed on chalcopyrite in a few museum specimens labeled Cardin, Oklahoma and Joplin, Missouri. Rogers[129] noted a similar occurrence and also reported malachite as an alteration of cuprite from the Big Coon mine, Galena, Kansas. Keller[130] noted malachite deposited on hemimorphite in the Shinn mine, Stark City, Missouri. Malachite is a rare mineral in the district.

Azurite - $Cu_3(OH)_2(CO_3)_2$

Azurite was noted in a single specimen by Rogers.[131] It is a rare mineral in the district.

Leadhillite - $Pb_4(SO_4)(CO_3)_2(OH)_2$

Leadhillite is a very rare mineral in the district. This writer observed transparent tabular crystals of leadhillite intergrown with cerussite on galena. It was reported by Pirsson and Wells[132] as deposited on and intergrown with cerussite at Granby.

Sulfates:

Barite - $BaSO_4$

Barite occurs as white to bluish orthorhombic tabular crystals up to about an inch in size. Barite is of very rare occurrence in

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[129] Rogers, loc. cit.

[130] Keller, loc. cit.

[131] Rogers, loc. cit.

[132] L. V. Pirsson and H. L. Wells, "On the Occurrence of Leadhillite in Missouri and its Chemical Composition", Am. Jour. Sci., vol. 48, 3d ser., pp. 219-226, 1894.

the Picher field, but it was noted in the Brewster, Grace Walker, and Dobson mines by Weidman.[133] Barite with a bluish tinge was rather common at Thom's Station and was occasionally found at Webb City.[134] Schmidt and Leonhard[135] reported barite from Joplin and from Seneca.

Anglesite - $PbSO_4$

Anglesite is not a common mineral in the Tri-State district. Small crystals were observed by Buckley and Buehler[136] on galena at Granby, by Rogers[137] near Galena, Kansas, and by Weidman[138] in some mines in the Picher field at a depth of about 300 feet.

Gypsum - $CaSO_4.2H_2O$

Small acicular crystals of gypsum, observable with a binocular microscope, occur on jasperoid and other minerals. Specimens from Dr. O. R. Grewe's personal collection exhibit selenite crystals, as much as one-quarter inch long, deposited on pyrite, marcasite,

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[133] Weidman, op. cit., p. 61.

[134] Ernest J. Palmer, Oral Communication, 1958.

[135] Schmidt and Leonhard, op. cit., p. 458.

[136] E. R. Buckley and H. A. Buehler, "The Geology of the Granby Area", Mo. Geol. Survey Rept., vol. IV, 2d ser., p. 45, 1905.

[137] Rogers, op. cit., p. 498

[138] Weidman, op. cit., p. 56.

galena and sphalerite. Rarely chert fragments exhibit thin coatings of gypsum, and some specimens from the sheet ground exhibit abundant earthy gypsum deposited around sphalerite crystals. Ransome[139] noted thin soft partial coatings on a single specimen of calcite, which he believed to be gypsum.

Starkeyite - $MgSO_4.4H_2O$

A white, powdery, bitter-tasting efflorescence formed on some of the writer's specimens of dolomitic jasperoid after removal from the Blue Goose No. 1 mine. X-ray analysis, as shown in Table V, optical examination, microchemical tests, and spectrographic analysis showed this mineral to be starkeyite, previously reported elsewhere in Missouri by Grawe.[140] Indicies of refraction were determined to be between 1.500 and 1.512. The mineral is intermixed with microcrystalline quartz.

Chalcanthite - $CuSO_4.5H_2O$

Small blue columnar crystals of chalcanthite, associated with sphalerite, pyrite and chalcopyrite were observed by Rogers[141] on a dump at the Irene mine, Empire City. It is a very rare mineral in the district.

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[139] Alfred L. Ransome, "Enargite and Plumbojarosite at Picher, Oklahoma", Am. Mineralogist, vol. 20, p. 801, 1935.

[140] Oliver R. Grawe, "Pyrites Deposits of Missouri", Mo. Geol. Survey and Water Resources, vol. 30, 2d ser., p. 209, 1945; Oliver R. Grawe, "Starkeyite, A correction": Am. Mineralogist, vol. 41, p. 662, 1956.

[141] Rogers, op. cit., p. 502.

TABLE V

X-RAY DIFFRACTION DATA FOR STARKEYITE

(I = relative intensity of diffraction line)
(d = interplanar spacings in Angstron units)

$MgSO_4.4H_2O$		Starkeyite	
A.S.T.M. Index Card No. 1-0341		Blue Goose No. 1 mine	
Effloresced		Cardin, Oklahoma	
$\lambda = 0.709$A°		$\lambda = 1.5405$A°	
I	d	I	d
40	6.9	4	6.91
60	5.5	10	5.49
28	4.71	2	4.80
100	4.48	10	4.50
60	3.96	8	4.00
8	3.60	1	3.62
32	3.40	5	3.41
40	3.21	2	3.26
100	2.95	8	2.97
40	2.75	1	2.77
28	2.56	3	2.57
24	2.46	1	2.47
24	2.41	2	2.42
24	2.35	2	2.36

TABLE V (Continued)

I	d	I	d
24	2.26	2	2.27
20	1.97	3	1.97
20	1.87	1	1.88
16	1.80	2	1.80
8	1.75	1	1.75
8	1.71	1	1.71
8	1.66	1	1.67
16	1.63	1	1.63
4	1.56	1	1.57
20	1.51	3	1.51
20	1.45	3	1.45
8	1.38	3	1.38
8	1.29	3	1.29
4	1.23	1	1.23
4	1.19	2	1.20

Melanterite - $FeSO_4.7H_2O$

Melanterite stalactites occur in some mines as a result of the oxidation of pyrite and marcasite since the mines were developed. They were described by Weidman.[142]

Epsomite - $MgSO_4.7H_2O$

Smith and Siebenthal[143] were the only investigators to report the occurrence of epsomite in the Tri-State district. It was said to form as a product of weathering and that it was not abundant.

Goslarite - $ZnSO_4.7H_2O$

Goslarite occurs as botryoidal and stalactitic coatings which have formed very recently on the walls of some mines. Its composition is variable due to partial replacement of zinc by iron and by copper. Varieties rich in iron and copper have been described by Wheeler[144] and by Rogers.[145]

Linarite - $PbCu(SO_4)(OH)_2$

A vitreous, azure blue mineral, believed by Rogers[146] to be linarite, was associated with caledonite, malachite, aurichalcite, and cerussite at the Big Coon mine, Galena, Kansas. This is the only mine in the district from which linarite has been reported.

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[142] Samuel Weidman, "The Miami-Picher Zinc-Lead District, Oklahoma", Okla. Geol. Survey Bull. 56, p. 57, 1932.

[143] W. S. Tangier Smith and C. E. Siebenthal, Description of the Joplin District in Geologic Atlas of the United States, U. S. Geol. Survey folio 148, p. 12, 1907.

[144] H. A. Wheeler, "Notes on Ferro-Goslarite, A New Variety of Zinc Sulphate", Am. Jour. Sci., vol. 41, 3d ser., p. 212, 1891.

[145] Rogers, op. cit., p. 501.

[146] Rogers, op. cit., p. 500.

Jarosite - $KFe_3(SO_4)_2(OH)_6$

Yellow, earthy jarosite was noted by the writer in one mine, the West Side mine, and identified by x-ray analysis as shown in Table VI. It occurs in cavities in jasperoid and probably is an oxidation product of iron sulfides.

Plumbojarosite - $PbFe_6(SO_4)_4(OH)_{12}$

Ransome[147] noted plumbojarosite in a single specimen from the Barr mine. It formed an earthy, brownish coating on galena.

Aluminite - $Al_2(SO_4)(OH)_4.7H_2O$

Wheeler[148] was the only investigator to record the occurrence of aluminite in the Tri-State district. He found it as a white incrustation on limestone at Joplin.

Copiapite - $(Fe,Mg)Fe_4(SO_4)_6(OH)_2.20H_2O$

Copiapite was noted by Rogers[149] as a yellow, crystalline, botryoidal or stalactitic incrustations on pyrite at Galena and at Cave Springs. He also noted that this yellow coating formed on melanterite upon exposure to air.

Caledonite - $Cu_2Pb_5(SO_4)_3(CO_3)(OH)_6$

Rogers[150] noted very small quantities of caledonite as a green

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[147] Ransome, op. cit., p. 803.

[148] H. A. Wheeler, "Recent Additions to the Mineralogy of Missouri", Trans. St. Louis Acad. Sci., vol. 7, p. 129, 1895.

[149] Austin F. Rogers, pt. III in Erasmus Haworth, "Special Report on Lead and Zinc", Kansas Geol. Survey Rept., vol. VIII, p. 502, 1904.

[150] Rogers, op. cit., p. 500.

TABLE VI

X-RAY DIFFRACTION DATA FOR JAROSITE

(I = relative intensity of diffraction line)
(d = interplanar spacings in Angstron units)

Jarosite		Jarosite	
A.S.T.M. Index Card No. 10-443		Webber mine	
Meadow Valley mine Pioche, Nevada		Treece, Kansas	
λ = 1.5418A°		λ = 1.5405A°	
I	d	I	d
30	5.94	4	6.04
20	5.74	4	5.78
40	5.09	5	5.12
10	3.65	2	3.68
60	3.11	9	3.13
100	3.08	10	3.10
10	2.97	2	2.98
20	2.870	2	2.882
30	2.547	3	2.564
50	2.292	7	2.298
50	1.978	8	1.988
20	1.941	1	1.948
10	1.913	.....	....
50	1.823	6	1.833
"several weak lines"		2	1.806
30	1.539	3	1.547
30	1.512	2	1.515
10	1.484	2	1.489

crystalline coating on partly altered galena at the Big Coon mine where it was associated with linarite, aurichalcite and cerussite. This is the only mine in the district from which caledonite has been reported.

Arsenates:

Picropharmacolite - $(Ca,Mg)_3(AsO_4)_2 \cdot 6H_2O$ (?)

Picropharmacolite was reported from Joplin by Genth,[151] who determined the mineral chemically. It occurred in radiating silky fibers which formed botryoidal incrustations, 2 to 15 mm. thick, on dolomite. Genth is the only investigator to have reported this mineral from the district.

Mimetite - $Pb_5(AsO_4,PO_4)_3Cl$

According to Wheeler[152] W. P. Jenny noted the occurrence of mimetite as a thin crystalline coating on galena near Seneca. This is the only recorded occurrence of this mineral in the district.

Phosphates:

Vivianite - $Fe_3(PO_4)_2 \cdot 8H_2O$

Wheeler[153] also credited Dr. Gustavus Hambach with the discovery

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[151] F. A. Genth, "Contributions to Mineralogy", Am. Jour. Sci., 3d series, vol. 40, p. 127, 1890.

[152] Wheeler, op. cit., p. 127.

[153] Wheeler, op. cit., p. 128.

of vivianite occurring as a blue, earthy powder at Joplin. This is the only recorded occurrence of this mineral in the district.

Pyromorphite - $Pb_5(PO_4,AsO_4)_3Cl$

Pyromorphite is a rare but well known mineral in the district. It occurs generally as small, greenish hexagonal prisms and finely crystalline, often enamel-like coatings on galena, cerussite, calcite, and other minerals. Rogers[154] reported botryoidal and stalactitic pyromorphite, and pyromorphite pseudomorphous after galena from Joplin and Granby.

Wavellite - $Al_3(OH)_3(PO_4)_2.5H_2O$

Wavellite in small, white radiating crystals were observed by Broadhead in Jasper County according to Wheeler.[155] This is the only recorded occurrence of this mineral in the district.

Silicates:

Hemimorphite - $Zn_4(Si_2O_7)(OH)_2.H_2O$

Hemimorphite generally occurs as colorless, white or yellowish crystals or botryoidal coatings on sphalerite, calcite and other minerals. Hemimorphite was the most common oxidized zinc mineral in the fields of the eastern part of the district, but only museum specimens were available to the writer. Excellent pseudomorphs of

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[154] Rogers, op. cit., p. 498; Austin F. Rogers, "Notes on Some Pseudomorphs, Petrifications and Alterations", Am. Philo. Soc. Proc. 49, p. 19, 1910.

[155] Wheeler, op. cit., p. 129.

hemimorphite and smithsonite after calcite are in the Missouri School of Mines museum collection. These already have been described with smithsonite.

Polished surfaces of some hemimorphite specimens exhibit unreplaced areas of sphalerite transected by abundant veins of hemimorphite and smithsonite, as shown in Figure 70, page 128.

Allophane - $Al_2SiO_5.nH_2O$

Light greenish-blue allophane was observed by Rogers[156] at the Irene mine, Empire, Kansas. He also observed thin incrustations of a hydrous aluminum silicate, which he believed to be allophane, at the Big Coon mine, Galena, Kansas.

Chrysocolla - $CuSiO_3.2H_2O$

Chrysocolla in thin bluish-green seams with other copper minerals was noted by Rogers[157] at the Big Coon mine, Galena. This is the only mine in the district from which chrysocolla has been reported.

Kaolinite - $Al_4(Si_4O_{10})(OH)_8$

Tarr and Keller[158] by x-ray analysis identified kaolinite

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[156] Austin F. Rogers, pt. III in Erasmus Haworth, "Special Report on Lead and Zinc", Kansas Geol. Survey Rept., vol. VIII, p. 497, 1904.

[157] Rogers, Ibid.

[158] W. A. Tarr and W. D. Keller, "Some Occurrence of Kaolinite Deposited from Solution", Am. Mineralogist, vol. 22, p. 933, 1937.

associated with sphalerite, galena, quartz and calcite in fractures in Pennsylvanian shale and in cavities and also as replacement of coarsely crystalline calcite at Oronogo. They believed the kaolinite to have been deposited from solution.

Glauconite - $K_2(Mg,Fe)_2Al_6(Si_4O_{10})_3(OH)_{12}$

Glauconite occurs as small, dark green granules and as lighter green irregular shaped grains in jasperoid and gray dolomite, particularly in J and K beds. It is often concentrated in certain bands in jasperoid, especially in the dolomitic bands. Less commonly glauconite occurs in chert.

The writer partially separated the glauconite from dolomite and jasperoid quartz by means of a Franz isodynamic separator and then completed the separation by hand picking in order to obtain a clean sample for petrographic examination and x-ray analysis. Under high magnification the glauconite granules were seen to be microcrystalline aggregates of crystals less than 0.003 mm. long. The individual crystals were too small to yield an interference figure, but occasionally elongated crystals exhibit very small extinction angles. The indicies of the glauconite were determined to be between 1.58 and 1.60.

The identity of this glauconite was confirmed by comparing its x-ray diffractograms with those published by Burst[159] as shown

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[159] J. F. Burst, "Mineral Heterogeneity in 'Glauconite' Pellets", Am. Mineralogist, vol. 43, pp. 486-487, 1958.

in Figures 68 and 69. The diffractograms of the Tri-State glauconite closely resemble those of the disordered glauconite studied by Burst. The basal diffraction peaks at 10 Å, 5 Å and 3.3 Å are subdued, asymmetric and exhibit broad bases.

Under the stereoscopic and ultropac microscopes the Joplin glauconite is seen to be of two types: a dark green ovoid to subspherical variety and a light green irregularly shaped variety. Occasionally dark green granules were seen to be enclosed within sphalerite crystals and other sulfides.

In thin sections the granules usually appear elliptical to round in shape, as illustrated by the darker glauconite in Figure 71, page 128. The granules vary in diameter from 0.014 mm. to 0.266 mm.; but most of the measurements were between 0.056 mm. and 0.144 mm. Some broken fragments of glauconite occur in most thin sections containing the mineral, and are illustrated in Figure 71, page 128.

Normally glauconite constitutes less than two per cent of the rock, rarely does it reach twenty per cent, but the per cent of glauconite varies from band to band in banded jasperoid. Dolomitic bands frequently contain more glauconite than non-dolomitic bands, and some of these bands are also sphalerite-rich. Dolomite seems to have excluded the glauconite granules from its boundaries during its crystallization, for glauconite tends to be concentrated at the boundary of some of the larger dolomite crystals.

Only rarely are glauconite granules in direct contact with dolomite crystals. When they are, they exhibit their rounded out-

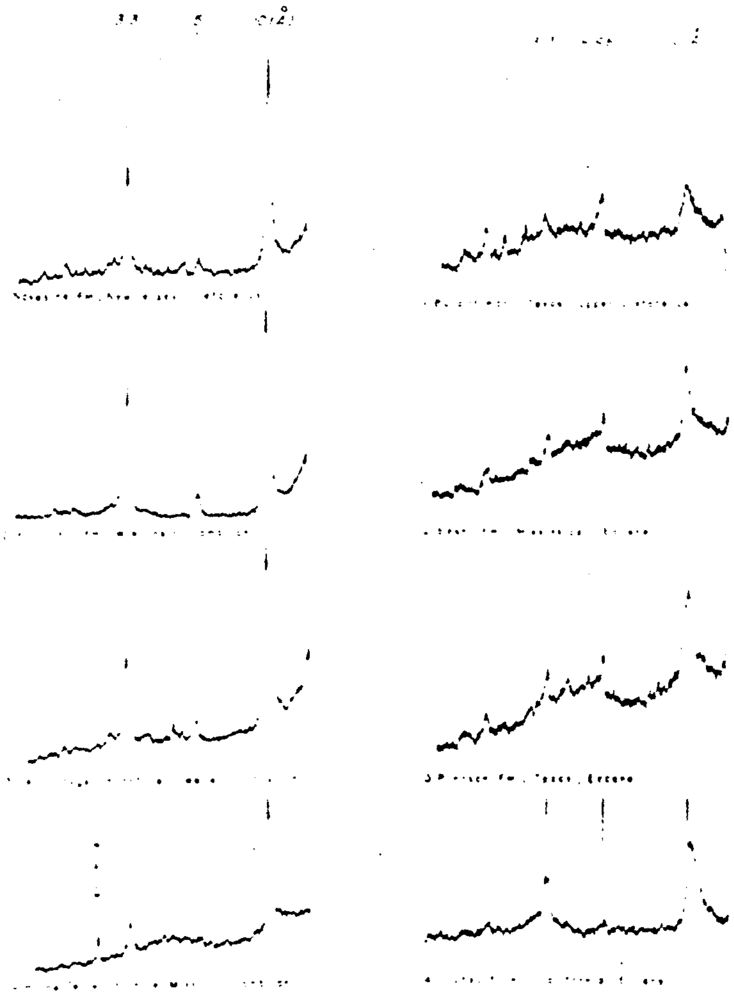

Figure 68. X-Ray diffractograms of well-ordered glauconites (left) and disordered glauconites (right). (From Burst, 1958).

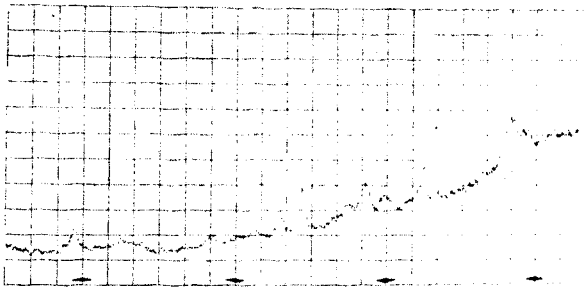

Figure 69. X-Ray diffractogram of Tri-State glauconite.

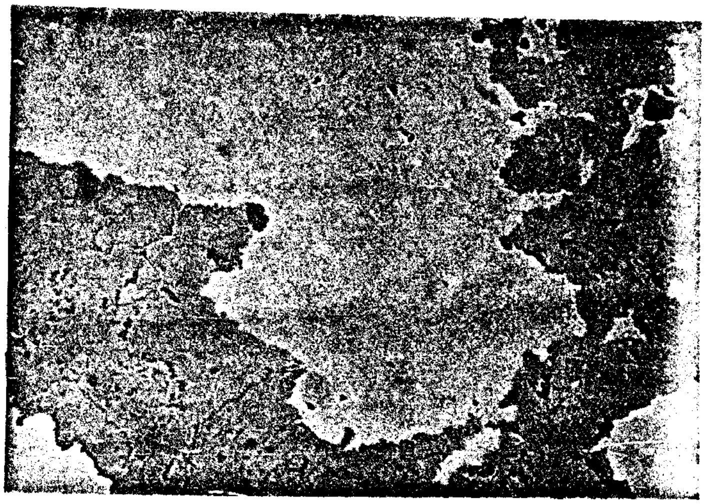

Figure 70. Smithsonite (dark gray, high relief) and hemimorphite (dark gray, low relief) replacing sphalerite (light gray). Granby. 100X.

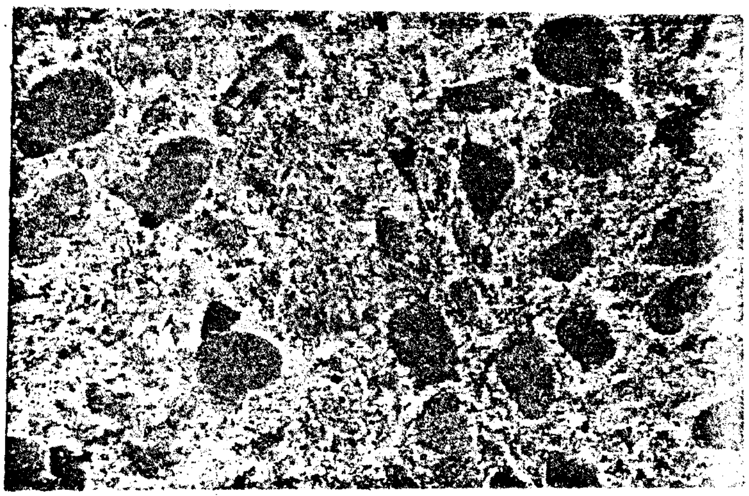

Figure 71. Glauconite granules and fragments (dark gray) in jasperoid. K bed, Netta White mine. Ordinary light. 100X.

lines against the dolomite. Only very rarely are glauconite granules included within dolomite crystals.

Rarely glauconite occurs in chert. In some thin sections, glauconite is seen to be somewhat concentrated in jasperoid along the edges of chert breccia fragments, but in other sections no such concentration is observed. Thin sections of chert breccia cemented by glauconitic jasperoid or gray dolomite generally show the chert to contain much less glauconite than the surrounding jasperoid or dolomite.

A few scattered glauconite granules were observed in thin sections of limestones. An occasional granule of glauconite may occur within fossils, such as within the central cavity of crinoid stems.

CHAPTER IV

PARAGENESIS

PREVIOUS INVESTIGATIONS

The first important discussion of mineral paragenesis in the Tri-State district was that of Schmidt and Leonhard,[160] in 1874. They considered five periods of mineral development in this area: 1) deposition of limestone and chert; 2) dolomitization, fracturing, and principal introduction of sulfide ore minerals; 3) solution of limestone and further deposition of sulfides; 4) deposition of calcite and jasperoid and continued deposition of sulfides; 5) oxidation of sulfides. When Schmidt and Leonhard studied these ores, mining had not begun at Galena, Kansas or at Picher, Oklahoma; therefore their work was confined to the Missouri portion of the Tri-State district. According to these investigators galena was deposited before sphalerite.

Jenny,[161] whose investigations of 1893 predate the discovery of the Picher field, was one of the few geologists who believed that all the ore minerals were deposited in a single sequence and that some of the minerals of this sequence were primary and others secondary. Jenny believed the paragenetic sequence of the primary minerals to be: dolomite, sphalerite, galena, pyrite, jasperoid and quartz crystals.

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[160] Adolf Schmidt and Alexander Leonhard, "The Lead and Zinc Regions of Southwest Missouri", Mo. Geol. Survey Rept. for 1874, pp. 412-414, 1874.

[161] Walter P. Jenny, "The Lead and Zinc-Deposits of the Mississippi Valley", Am. Inst. Min. Met. Eng. Trans., vol. 22, pp. 199-200, 1893.

He is the only investigator to consider the disseminated sulfides to be older than the jasperoid. He recognized the sequence of deposition of the secondary minerals to be variable and repetitious. The general order of crystallization deduced by Jenny was: pink dolomite, sphalerite, galena, pyrite, chalcopyrite, calcite, barite, and oxidized ores.

Winslow and Robertson[162] whose investigations of 1894 were confined to the Missouri portion of the Tri-State district, stated that the mineral paragenesis was not invariable, but that, in general, it was: dolomite, sphalerite, galena, barite, calcite, and pyrite. Their paragenetic sequence differs from that of Jenny in reversing the positions of calcite and barite and by placing pyrite after these minerals.

Rogers,[163] who collected specimens in the Galena, Kansas field, like Jenny recognized that the order of mineral deposition was variable, but that it usually was: dolomite, galena, sphalerite, chalcopyrite, marcasite, pyrite, calcite and barite, however he noted that some dolomite was formed even after some of the galena was corroded. Rogers considered the galena to be of two generations: the one deposited immediately after the early dolomite, and other, consisting of small octahedrons and cubo-octahedrons, deposited on sphalerite. Rogers' sequence differs from that of Jenny, and that of Winslow and Robertson

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[162] Arthur Winslow and James D. Robertson, "Lead and Zinc Deposits", <u>Mo</u>. <u>Geol</u>. <u>Survey</u> <u>Rept</u>., vol. 7, pp. 448-460, 1894.

[163] Austin F. Rogers, pt. III in Erasmus Haworth, "Special Report on Lead and Zinc", <u>Kansas</u> <u>Geol</u>. <u>Survey</u> <u>Rept</u>., vol. VIII, pp. 503-504, 1904.

in believing that most of the sphalerite was deposited after galena. Like Jenny, he concluded that barite crystallized after calcite and that both were preceded by pyrite.

Buckley and Buehler,[164] in their study of the Granby area, noted evidence for repetitive deposition of certain minerals. They stated that the sphalerite disseminated in dolomite constituted a second generation and formed later than the sphalerite disseminated in jasperoid; that hemimorphite formed both before pink dolomite and after pink dolomite; that some galena was disseminated in and contemporaneous with both gray dolomite and pink dolomite, and that very little galena had been deposited upon sphalerite.

Smith and Siebenthal[165] in their 1907 study of the Tri-State district, exclusive of the Picher field, found the order of mineral deposition in the cavities to be usually the same throughout the district: dolomite, chalcopyrite, galena, sphalerite, galena, chalcopyrite, marcasite, pyrite, calcite, barite and marcasite. Some deviations from this order were noted which they believed were caused by local occurrences of repetitive deposition of some minerals.

They noted that sphalerite and galena were deposited on chalcopyrite west of Joplin, that chalcopyrite did not occur within either sphalerite or galena, and that chalcopyrite was not deposited on galena. According to these geologists, galena usually formed before sphalerite,

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[164] E. R. Buckley and H. A. Buehler, "The Geology of the Granby Area", Mo. Geol. Survey Rept., vol. IV, 2d series, pp. 42-56, 1905.

[165] W. S. Tangier Smith and C. E. Siebenthal, Description of the Joplin District in Geologic Atlas of the United States, U. S. Geol. Survey folio 148, p. 13, 1907.

but in some places it formed after sphalerite. At Empire, Kansas they noted small sphalerite crystals in hemimorphite and associated with smithsonite and concluded that these crystals were either contemporaneous or later than the hemimorphite and smithsonite.

Marcasite was noted in the surface layer of one calcite specimen, and botryoidal marcasite was observed on some calcite crystals. It was their opinion that iron sulfide did not form before sphalerite and galena.

Unlike earlier investigators, Smith and Siebenthal recognized two generations of sphalerite, galena, chalcopyrite and marcasite. They also believed that disseminated sphalerite, dolomite and jasperoid formed at about the same time.

Snider[166] reported the sequence in Picher field to be: galena, sphalerite and pyrite, but while this sequence was clear in some places, in other places there was no apparent order of the deposition. Snider's partial sequence differs from that of Jenny, and agrees with that of Rogers, in placing sphalerite after galena.

In 1915, Siebenthal[167] described the deposition of galena, sphalerite and calcite on nails in the Joplin district showing that these minerals were deposited in very recent time after the mines had been opened.

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[166] L. C. Snider, "Preliminary Report on the Lead and Zinc of Oklahoma", Okla. Geol. Survey Bull. 9, p. 71, 1912.

[167] C. E. Siebenthal, "Origin of the Zinc and Lead Deposits of the Joplin Region - Missouri, Kansas, and Oklahoma", U. S. Geol. Survey Bull. 606, pp. 254-255, 1915.

Naething,[168] from a study of thin sections of ore specimens from the Picher field concluded that the order of deposition of primary minerals was: dolomite, chalcopyrite, galena, sphalerite, galena, chalcopyrite, marcasite, pyrite, calcite, barite and marcasite, a sequence exactly the same as that of Smith and Siebenthal.[169]

Fowler and Lyden[170] restudied the paragenesis of the Tri-State ores, particularly in the Picher field, and graphically indicated the following sequence of mineral deposition: limestone, dolomite and chert, jasperoid, galena and sphalerite, dolomite, calcite, quartz crystals, marcasite, pyrite and chalcopyrite, sphalerite. They indicated a partial contemporaneity for minerals adjacent to one another in the sequence. They noted that some jasperoid was deposited with sphalerite and galena. They differed from Winslow, Rogers, and Snider, in observing that the galena was almost always deposited on the sphalerite. They were the first to note that the quartz crystals, abundant near Baxter Springs, were deposited after calcite. They believed that the most recently formed, small, red sphalerite crystals resulted from solution and redeposition of the earlier sphalerite

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[168] Foster S. Naething, "Ores of the Joplin Region" (discussion), _Eng_. _Mining_ _Jour_., vol. 123, no. 14, p. 575, 1927.

[169] Smith and Siebenthal, _op_. _cit_., p. 13.

[170] George M. Fowler and Joseph P. Lyden, "The Ore Deposits of the Tri-State District", _Am_. _Inst_. _Min_. _Met_. _Eng_. _Trans_., vol. 102, pp. 234-235, 1932.

which they noted often is etched. They were the first to point out the late sphalerite and chalcopyrite deposited after calcite, and the first to show that galena was deposited contemporaneously with sphalerite, during the main period of deposition.

Although Weidman,[171] whose investigations also were conducted principally in the Picher field, did not discuss the paragenesis of the ores, he did note that galena followed sphalerite, that aragonite was deposited on sphalerite and calcite and alternated in deposition with calcite and ore minerals, and that marcasite was deposited on aragonite. He was the first to recognize the presence of aragonite in the mines.

Tarr[172] discussed the paragenesis of the Tri-State ores after a brief visit to the Picher field in 1932. He expressed the opinion that the sulfides were, in part, contemporaneous with the jasperoid, and that the period of crystallization of galena overlapped and followed that of sphalerite. He considered the chert to be contemporaneous with the limestone in which it occurs.

Fowler, Lyden, Gregory and Agar[173] differed with Tarr in believing the chert was of epigenetic origin and thus they placed it

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[171] Samuel Weidman, "The Miami-Picher Zinc-Lead District, Oklahoma", Okla. Geol. Survey Bull. 56, p. 53-68, 1932.

[172] W. A. Tarr, "The Miami-Picher Zinc-Lead District", Econ. Geology, vol. 28, p. 476, 1933.

[173] George M. Fowler, et al., "Chertification in the Tri-State Mining District", Am. Inst. Min. Met. Eng. Trans., vol. 115, pp. 106-163, 1935.

after limestone in the paragenetic sequence. Their conclusion was based on Fowler and Lyden's megascopic study of the minerals in the mines, Gregory's chemical analyses, and Agar's petrographic investigations. Among the arguments which they put forth in favor of an epigenetic origin were: 1) the association of chert with areas of structural disturbance, 2) gradations from chert to limestone, 3) cementation of chert breccias by later chert, and 4) the greater abundance of chert within the ore district than outside the district.

Ridge[174] studied specimens collected by Bastin, Svatik and himself in the Picher field and those in the Joplin Mineral museum. From these megascopic and mineralographic studies Ridge, in contrast to Fowler and Lyden, concluded: that the sulfides disseminated in jasperoid formed later than the jasperoid and partially replaced it, that sphalerite usually was deposited after galena, and that pyrite and enargite formed with calcite and after calcite during a second period of mineralization which was separated from the main period of mineralization by fracturing.

Bastin[175] restudied Ridge's specimens from the Picher field and found a large measure of similarity in all of the specimens. He agreed with Ridge[176] that the sulfides, galena, sphalerite, chalco-

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[174] John Ridge, "The Genesis of the Tri-State Zinc and Lead Ores", Econ. Geology, vol. 31, pp. 298-303, 1936.

[175] Edson S. Bastin and John D. Ridge, in "Contributions to a Knowledge of the Lead and Zinc Deposits of the Mississippi Valley Region", edited by Edson S. Bastin, Geol. Soc. America Spec. Paper 24, pp. 105-110, 1939.

[176] Ridge, loc. cit.

pyrite and marcasite were deposited together, but he did not indicate that the period of deposition for all four sulfides ended at the same time. He also agreed with Ridge that the sulfides had replaced jasperoid and dolomite.

More recently Stewart,[177] as a result of his experience in the mines of the district, expressed the opinion that:

> The paragenetic order of mineral deposition shows considerable variation, not only between the several districts, but within the individual districts themselves. Cyclic or recurrent sequences of mineralization further complicate detailed studies of paragenesis.

Lyden,[178] on the basis of further megascopic studies, revised the earlier paragenetic sequence of Fowler and Lyden[179] to bring out his belief in a greater amount of simultaneous and overlapping deposition. He considered gray dolomite, jasperoid, sphalerite, and galena to be deposited contemporaneously and noted that this interpretation disagreed with those of Bastin,[180] and Ridge.[181] Among the criteria cited to support his belief, was the occurrence of sphalerite in limestone only where the sphalerite is accompanied by jasperoid. He also believed that chalcopyrite, marcasite, and pyrite were deposited essentially contemporaneously with each other, but he also showed that the deposition of these sulfides also overlapped that of the above mentioned minerals.

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[177] Dan R. Stewart, "Some New Concepts Regarding the Age, Areal Distribution, and Mineral Assemblages of the Ore Producing Districts in the Central States Region", (Mimeographed), p. 38, 1948.

[178] Joseph P. Lyden, "Aspects of Structure and Mineralization Used as Guides in the Development of the Picher Field", Am. Inst. Min. Met. Eng. Trans., vol. 187, pp. 1258-1259, 1950.

[179] Fowler and Lyden, loc. cit.

[180] Bastin, loc. cit.

[181] Ridge, loc. cit.

Shortly after Lyden[182] published his paper, Bastin[183] reaffirmed his belief that sphalerite and galena were deposited after jasperoid and dolomite. Bastin noted that in thin section sphalerite exhibited ragged boundaries against the enclosing jasperoid.

Evans and McKnight[184] using x-ray diffraction, identified small crystals on the surface of sphalerite-galena stalactites as wurtzite of three structure types: 10H, 6H and 6H. A thin surface coating on the wurtzite crystals they believed to be sphalerite; and noted sphalerite within the wurtzite crystals as an intergrown or alternation phase.

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[182] Lyden, *loc. cit.*

[183] Edson S. Bastin, 'Paragenesis of the Tri-State Jasperoid", *Econ. Geology*, vol. 46, pp. 652-657, 1951.

[184] Howard T. Evans, Jr. and Edwin T. McKnight, "New Wurtzite Polytypes from Joplin, Missouri", *Am. Mineralogist*, vol. 44, pp. 1210-1218, 1959.

REASONS FOR PARAGENETIC STUDY

From the preceding review of the literature, the confused state of the paragenesis of the minerals of the Tri-State district is apparent. Jenny, and Winslow and Robertson held that sphalerite formed before galena. Rogers, Smith and Siebenthal, and Snider found galena to be formed before sphalerite. Fowler and Lyden, Ridge, and Lyden believed the two minerals to be contemporaneous. Smith and Siebenthal, Fowler and Lyden, and Lyden believed that the sulfides were formed contemporaneously with jasperoid and dolomite, but Ridge, and Bastin stated that the sulfides replace the jasperoid and dolomite. Winslow and Robertson indicated that jasperoid formed after sphalerite, galena, and dolomite. Jenny concluded that dolomite formed before sphalerite and galena, while jasperoid formed after these minerals. Buckley and Buehler believed the sphalerite disseminated in dolomite to be later than the sphalerite disseminated in jasperoid. Ridge was the first to include the early quartz druse in the paragenetic sequence. Marcasite, chalcopyrite and sphalerite deposited in and on late calcite were not recognized in the earlier studies of Jenny, and Winslow and Robertson. The recurrence of certain minerals has not been given due consideration.

The principal reasons for the variations in interpretation of the paragenetic sequence are:

1) Variation in techniques of study. Some workers, like

Fowler and Lyden[185] and Lyden,[186] based their conclusion on megascopic observations alone, while others, like Ridge[187] and Bastin,[188] have relied mostly upon microscopic investigations.

2) Concentration upon one particular field within the Tri-State district. Buckley and Buehler's[189] observations were confined to the Granby area; Rogers[190] collected most of his specimens near Galena, Kansas; and Ridge[191] studied specimens obtained principally from the Picher field. Bastin[192] simply restudied Ridge's specimens. Fowler and Lyden's[193] and Lyden's[194] observations were confined largely to the Picher field.

3) Different interpretations of the textural relationships between minerals. Fowler and Lyden[195] and Lyden[196] interpreted

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[185] Fowler and Lyden, loc. cit.

[186] Lyden, loc. cit.

[187] Ridge, loc. cit.

[188] Bastin, loc. cit.

[189] Buckley and Buehler, loc. cit.

[190] Austin F. Rogers, pt. III in Erasmus Haworth, "Special Report Lead and Zinc", Kansas Geol. Survey Rept., vol. VIII, pp. 447-538, 1904.

[191] Ridge, loc. cit.

[192] Bastin, loc. cit.

[193] Fowler and Lyden, loc. cit.

[194] Lyden, loc. cit.

[195] Fowler and Lyden, loc. cit.

[196] Lyden, loc. cit.

sphalerite and galena disseminated in jasperoid and dolomite as indicative of contemporaneous deposition, whereas Ridge[197] and Bastin[198] interpreted the same texture as one of replacement.

The present study of paragenesis has sought to resolve the above interpretations by combining extensive field work with both extensive and intensive microscopic investigation. Many specimens from many parts of the Tri-State district were collected and examined by mineralographic, stereoscopic and petrographic techniques.

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[197] Ridge, loc. cit.

[198] Bastin, loc. cit.

DISCUSSION OF PARAGENESIS

Although some geographic and stratigraphic variations in the paragenetic sequence of the minerals of the Tri-State district have been noted, a general sequence seems to be basic to the whole area. The variations appear to be caused by: 1) the omission of portions of the mineral sequence, 2) the recurrence of certain minerals, and 3) the reversal of the sequence of certain minerals.

This study has shown that the paragenesis may be discussed best by dividing the minerals into three groups: I) Bedded and Disseminated Minerals, II) Vug-filling Minerals, and III) Secondary Minerals.

Host Rock:

The host rock occupies the first position in the paragenetic sequence (Figure 72). The host rocks usually are limestones, however, locally shales and sandstones contain sulfides of economic importance. The limestones were deposited in warm, shallow, widespread Mississippian seas, favorable for the growth of organisms, especially crinoids, bryozoa and brachiopods. Following the deposition of the limestone, the area was uplifted and subjected to a long period of erosion, during which a karst topography developed upon the limestone surface.

This surface was then covered by a shallow sea in which Pennsylvanian shales were deposited on top of the eroded limestones in a near shore environment. Subsequent uplift followed or accompanied by solution of the limestone permitted slumping of the shale into

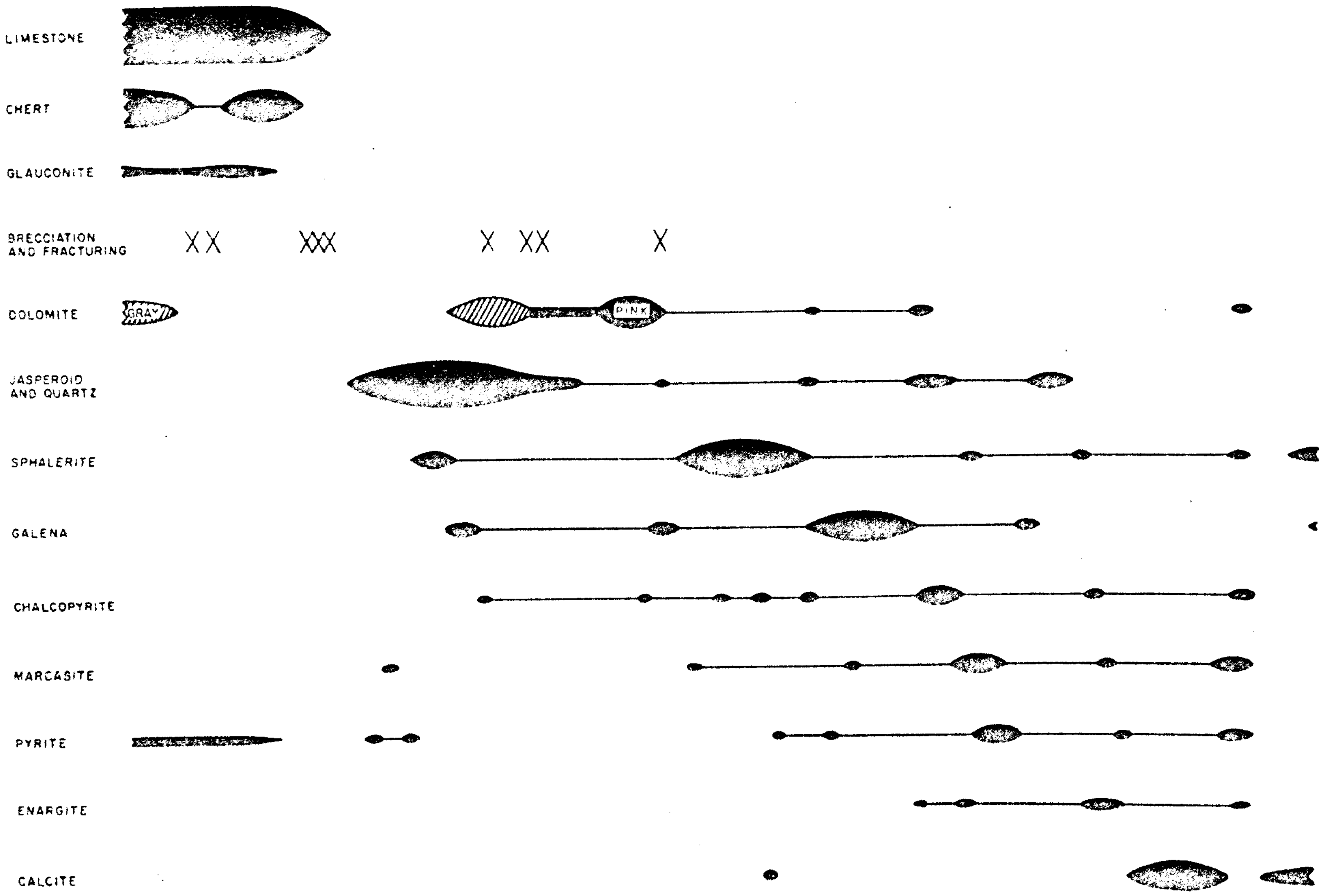

FIGURE 72

PARAGENETIC DIAGRAM

solution-made openings in the limestone.

I. Bedded and Disseminated Minerals:

The origin and paragenesis of the chert, jasperoid and dolomite of the bedded deposits in which sphalerite, galena, marcasite and pyrite are disseminated have been the subjects of controversy.

Chert

The origin and time of deposition of chert in the Mississippian limestone of the Tri-State district especially has been subject to argument. Hovey,[199] Haworth,[200] Schmidt and Leonhard,[201] Smith[202] and Tarr[203] held that the chert was syngenetic with the limestones. Buckley and Buehler[204] believed that part of the chert was formed as an original deposit with the limestone, but that part of the chert was con-

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[199] Edmund Otis Hovey, "A Study of the Cherts of Missouri", Appendix A of "Lead and Zinc Deposits" by Arthur Winslow and James D. Robertson, Mo. Geol. Survey, Rept., vol. VII, p. 733, 1894.

[200] Erasmus Haworth, "Special Report on Lead and Zinc", Kansas Geol. Survey Rept., vol. VIII, part I, p. 88, 1904.

[201] Adolf Schmidt and Alexander Leonhard, "The Lead and Zinc Regions of Southwest Missouri", Mo. Geol. Survey Rept. for 1874, p. 412, 1874.

[202] W. S. Tangier Smith, in discussion of "Chertification in the Tri-State (Oklahoma-Kansas-Missouri) Mining District", by George M. Fowler, et al., Am. Inst. Min. Met. Eng. Trans., vol. 115, p. 156, 1935.

[203] W. A. Tarr, "The Miami-Picher Zinc-Lead District", Econ. Geology, vol. 28, pp. 463-479, 1933.

[204] E. R. Buckley and H. A. Buehler, "The Geology of the Granby Area", Mo. Geol. Survey Rept., vol. IV, 2d series, p. 40, 1905.

tributed later by silica carried in ground waters. Dake[205] held that most of the cherts had formed as a product of weathering. Weidman,[206] Bastin,[207] Giles,[208] Fowler, Lyden, Gregory and Agar,[209] and Ridge[210] considered the chert to be an epigenetic replacement of limestone during the early phases of ore deposition from hydrothermal solutions. Folk and Weaver[211] on the basis of studies aided by the electron microscope, suggested that the microcrystalline quartz portions of the chert were due to the replacement of solid limestone or unconsolidated lime ooze by silica and that the chalcedonic quartz portions of the chert had formed by crystallization of silica in water-filled cavities and that some of the water was trapped in the chalcedony.

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[205] C. L. Dake, in discussion of "The Ore Deposits of the Tri-State District (Missouri-Kansas-Oklahoma)", by George M. Fowler and Joseph P. Lyden, Am. Inst. Min. Met. Eng. Trans., vol. 102, p. 242, 1932.

[206] Samuel Weidman, "The Miami-Picher Zinc-Lead District, Oklahoma", Okla. Geol. Survey Bull. 56, pp. 117-118, 1932.

[207] Edson S. Bastin, "Relations of Cherts to Stylolites at Carthage, Missouri", Jour. Geology, vol. 41, pp. 371-381, 1933.

[208] Albert W. Giles, "Boone Chert", Geol. Soc. America Bull., vol. 46, pp. 1815-1878, 1935.

[209] George M. Fowler, et al., "Chertification in the Tri-State Mining District", Am. Inst. Min. Met. Eng. Trans., vol. 115, pp. 106-163, 1935.

[210] John Ridge, "The Genesis of the Tri-State Zinc and Lead Ores", Econ. Geology, vol. 31, pp. 298-313, 1936.

[211] Robert L. Folk and Charles Edward Weaver, "A Study of the Texture and Composition of Chert", Am. Jour. Sci., vol. 250, pp. 506-509, 1952.

The present writer believes that most of the chert is formed as a primary sediment on the sea bottom. This is indicated by the occasional occurrence of subangular to subrounded reworked fragments of chert which occur within the limestone and are distributed along bedding planes to form intraformational chert conglomerates in some places. The horizontal bedded and nodular nature of the chert, the wide geographical distribution, the relative scarcity of chert in the pre-Mississippian formations of the district, and the occurrence of chert pebbles in the overlying Carterville Formation, support a primary origin for most of the chert. The presence of amino acids in the chert, detected by Barney,[212] indicates that the chert is not hydrothermal, since these acids are unstable at high temperatures.

The writer believes that the role of replacement by the chert has been overemphasized; that the amount of replacement has been only of minor importance. The observed replacement of carbonate fossils can be adequately explained by organisms falling into silica gel accumulating on the sea floor, and the local replacement of limestone or lime mud adjacent to chert nodules or lenses probably took place mainly during diagenesis. Some calcite-chert mixtures observed in thin sections can best be accounted for by contemporaneous deposition of chert and limestone, rather than by replacement of limestone by chert.

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[212] Emmet C. Barney, "Petrology of the Chert in the Boone Group and its Stratigraphic Relation in the Southwest Ozark Area", unpub. Masters Thesis Kansas Univ., 80 pp., 1959.

That two or more generations of chert are present is proved by the occurrence of chert fragments cemented by later chert. That two or more generations of chert were formed prior to Chester time is proved by this writer's discovery in the Chesterian Mayes conglomerate of chert pebbles which consist of chert breccia fragments cemented by a later darker chert.

Glauconite

Glauconite appears to have formed earlier than gray dolomite and sulfides disseminated in jasperoid and in dolomite, as it generally shows its rounded outlines against dolomite and disseminated sulfides. Glauconite granules may be observed within disseminated sphalerite in some specimens. Glauconite also formed earlier than jasperoid, since the glauconite granules generally exhibit their rounded outlines against the quartz crystals of the surrounding jasperoid.

Glauconite is much more abundant in jasperoid and gray dolomite than in chert. This probably indicates that the environment of deposition of chert was not especially favorable to the formation of glauconite.

Glauconite is a mineral which may yield information as to its environment of deposition. From its present-day environment of deposition and from the interpretation of its occurrence in solidified rocks, Cloud[213] concluded that glauconite is a product of marine diagenesis and that its formation is favored by reducing conditions, and

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[213] Preston E. Cloud, Jr., "Physical Limits of Glauconite Formation", Am. Assoc. Pet. Geol. Bull., vol. 39, pp. 490-491, 1955.

by slow or negative sedimentation. The close proximity of igneous or metamorphic rocks and a relatively shallow environment of deposition, lacking influx from important rivers were also considered favorable to the formation of glauconite. Grim[214] considered the presence of organic matter essential to the formation of glauconite. Galliher[215] found glauconite forming at the present time at depths from 30 to 300 feet in Monterey Bay, California. The lighter color and fragmentation of some of the glauconite in the Tri-State district probably indicates that part of the glauconite has suffered movement after its initial formation.[216]

Thus the glauconite probably formed on the sea bottom along with limestone and chert, and has reached its present position, by solution of the limestone and transportation by the solutions which gave rise to the jasperoid. Therefore its position in the paragenetic sequence accompanies that of limestone and chert and preceeds that of jasperoid, gray dolomite and sulfides.

Jasperoid

The nature and time of formation of jasperoid have been subjects

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[214] Ralph E. Grim, "The Depositional Environment of Red and Green Shales", Jour. Sed. Pet., vol. 21, p. 230, 1951.

[215] E. Wayne Galliher, "Glauconite Genesis", Geol. Soc. America Bull., vol. 46, p. 1353, 1935.

[216] Mitchell A. Light, "Evidence of Authigenic and Detrital Glauconite", Science, vol. 115, p. 74, 1952.

of great controversy. The writer believes that the jasperoid originated from epigenetic meteoric silica-bearing solutions which varied in nature through time and space. These variations included aqueous silica solution, colloidal silica solution and silica gel or mush. These solutions have both replaced favorable limestone beds and have filled open spaces providing cementation for chert, limestone and dolomite breccias. This conclusion is substantiated by: 1) the banded character of the jasperoid, 2) the high degree of contortion of some bands, 3) the support which it lent to the chert breccias, 4) the well crystallized form of dolomite and sulfides disseminated in the jasperoid, and 5) the occurrence of geopetal fabrics in jasperoid.

The writer further believes that the jasperoid is epigenetic. Evidence supporting this belief is: 1) the cementation of chert, limestone and dolomite breccias by jasperoid and the filling of fractures in the chert and in the limestone by jasperoid, 2) the sharp, nearly vertical contacts between limestone and jasperoid, 3) the abundance of sulfides in jasperoid, in contrast to the almost barren nature of chert and limestone, 4) the greatly brecciated nature of the chert, in contrast to the lesser brecciation of the jasperoid, 5) the areal and stratigraphic association of the jasperoid with the ore deposits, and 6) the unfossiliferous nature of the jasperoid. If the jasperoid were syngenetic it would seem likely that it would have formed breccias similar to those of the chert, that jasperoid breccias cemented by chert would occur, that chert would contain disseminated sulfides similar to those in the jasperoid, and that jasperoid would exhibit a wider and more continuous geographical distribution similar to that of the chert and limestone.

That the jasperoid formed after limestone is indicated by the fact that jasperoid fills fractures in limestone, cements blocks of limestone, and replaces limestone. These relationships are illustrated in Figures 6, 51, 52, 53, and 54. That jasperoid formed after chert is indicated by its common occurrence as fracture fillings in chert and as a matrix for chert breccias.

These relationships are best shown in Figures 42, 43, 44, 47, 48, 51, and 52. That jasperoid formed later than glauconite is proved by the cementation of broken fragments of glauconite by the jasperoid.

The writer believes that the jasperoid, the disseminated sulfides and gray dolomite were contemporaneous. While tiny quartz crystals of the jasperoid are included by the disseminated sulfides and by the gray dolomite, part of the jasperoidal quartz cements blocks of gray dolomite, cuts bands of dolomite, and forms a fine druse upon the surfaces of fractures which cut earlier jasperoid and disseminated sulfides. All of the jasperoid did not form at once but over a span of time. The recurrence of jasperoid shown by the occurrence of fragments of jasperoid and jasperoidal dolomite cemented by later jasperoid and jasperoidal dolomite.

In summary, the formation of jasperoid follows that of the formation and brecciation of chert, limestone, and glauconite. It was accompanied by the crystallization of gray dolomite and disseminated sulfides, but some of the jasperoidal quartz formed before these minerals and some formed after them.

Disseminated Sulfides

Sphalerite, galena, pyrite and marcasite commonly are disseminated through jasperoid and gray dolomite. According to Fowler[217] massive chalcopyrite sometimes occurs within jasperoid. Pyrite also commonly occurs disseminated through limestone and chert. The disseminated sulfides generally exhibit roughly euhedral shapes, but under high magnifications their boundaries can be seen to be quite irregular. Jasperoid quartz crystals generally can be seen to show their outlines against the sulfide grain boundaries and euhedral quartz crystals occur within some sulfide grains.

The time of deposition of the sulfides disseminated in jasperoid and gray dolomite has been a controversial subject. Bastin and Ridge believed that the sulfides had replaced jasperoid and gray dolomite and were emplaced contemporaneously with the sulfides deposited in vugs. Fowler and Lyden believed that jasperoid, gray dolomite and the disseminated sulfides were deposited essentially contemporaneously.

The writer holds that the disseminated sulfides crystallized in a jasperoid medium which was crystallizing at essentially the same time as the sulfides to form the jasperoid. The earliest formed

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[217] George M. Fowler, Oral Communication, 1959.

jasperoid quartz crystals were included in sphalerite which crystallized within the jasperoid medium. This quartz also prevented the sphalerite from forming smooth crystal boundaries. The last part of the jasperoid to crystallize formed a cement. This concept is supported by the following features: 1) the dissemination and banding of the sulfides in jasperoid is suggestive of crystallization in a gel, 2) the intimate textural relationship between the disseminated sulfides and the jasperoid indicates penecontemporaneous crystallization, 3) the pellet shape of some of the pyrite and marcasite is suggestive of oolite formation in a gel, 4) the occurrence of geopetal fabrics indicates that the silica medium was neither wholly fluid or completely rigid, and 5) certain previously proposed replacement textures are untenable.

Disseminated sulfides replacing jasperoid, would not yield the following observed relationships. Within single hand specimens jasperoid contains abundant sphalerite while adjacent or interbanded dolomite conteins little or no sphalerite. One would think that dolomite would be more readily replaceable than quartz. Thin sections of dolomitic jasperoid reveal that sphalerite occurs in the quartz portions, of the dolomite areas rather than in the dolomite itself. If the sphalerite replaced the dolomitic jasperoid, then it has selectively replaced jasperoid areas in preference to adjacent dolomite. This seems unreasonable.

Similar reasoning with respect to chert lends further support to the above conclusion. Sphalerite commonly occurs disseminated in jasperoid but rarely in chert. If the sphalerite had been emplaced after solidification of both chert and jasperoid, it would have had to selectively replace jasperoid in preference to chert. This seems unreasonable and therefore it is the writer's opinion that the disseminated sulfides were not introduced by replacement of jasperoid after it had solidified.

The paragenetic sequence of the sulfides disseminated in jasperoid is somewhat variable, but in general it is: pyrite, marcasite, pyrite, sphalerite, galena. Marcasite generally crystallizes after pyrite and frequently forms in small open spaces in massive pyrite and in broken bands of pyrite in jasperoid. It also exhibits considerable intergrowth with the pyrite. Crystallization of pyrite before and after marcasite is illustrated in Figures 19 and 20, pages 55 and 57. The sphalerite and galena disseminated in jasperoid frequently include small grains of pyrite and marcasite and hence they have formed after the iron sulfides. Rarely small galena veins cut disseminated pyrite and marcasite. Various textural relationships have been observed between the disseminated sphalerite and galena. Each may exhibit its outline against the other, but usually sphalerite shows its rotund outline against galena. Inclusions of galena in sphalerite have been noted. Disseminated sphalerite and galena formed at about the same time, but sphalerite usually preceded the galena.

The paragenetic relationships between gray dolomite crystals and sulfide crystals disseminated in jasperoid have been observed. The disseminated sulfides generally exhibit euhedral boundaries against dolomite, and some sulfide crystals are included within dolomite crystals, but in places gray dolomite shows its rhombic outline against sphalerite. The writer interprets these textural relationships to indicate that the sulfides generally formed in the jasperoid medium before gray dolomite, but occasionally sphalerite continued to be deposited after the gray dolomite had crystallized.

The presence of glauconite in the jasperoid is of unexpected interest. It is older than the jasperoid and must have been derived from the host rock. Glauconite exhibits its round to elliptical shape against gray dolomite and disseminated sulfides, and glauconite granules are included within these minerals. The association of glauconite with marine sediments would suggest its derivation from the host rock rather than being formed from the ore-forming solution.

To summarize, the writer believes that the sulfides disseminated in jasperoid formed in a jasperoid medium, and crystallized at about the same time as the crystallization of that medium, although some jasperoid quartz formed before the disseminated sulfides and some crystallized afterward. The paragenetic relation of the sulfides disseminated in jasperoid to each other is variable, but the general sequence is: pyrite, marcasite, pyrite, sphalerite, and galena. The formation of glauconite preceded the formation of disseminated sulfides and it must have been derived from the host rock. The crystallization of gray dolomite usually followed the crystallization of the disseminated sulfides but some sphalerite continued to crystallize after the gray dolomite. Crystallization of the silica gel to form jasperoid began early and ended after all the other minerals had formed.

Gray Dolomite

Two types of gray dolomite occur in the district; one a fine-grained and the other coarse grained. The bedded nature, wide horizontal extent and the presence of fine-grained dolomite fragments embedded in jasperoid and in coarse-grained gray dolomite, suggest that this fine-grained dolomite is of direct sedimentary or of diagenetic origin. This dolomite appears to be contemporaneous with the cherty limestones.

The coarse-grained gray dolomite often forms the matrix of chert breccias and therefore is clearly later than the brecciation of the chert.

The relationship of gray dolomite to jasperoid is not constant. In the mines this dolomite may be seen cutting jasperoid and jasperoid may be seen cutting dolomite, the latter relationship being more frequent. Most commonly dolomite is disseminated in or interbanded with jasperoid. In thin sections of this rock at low magnification, the dolomite rhombs appear to be essentially euhedral. Under higher magnification, however, the jasperoid quartz crystals can often be seen to show their outlines against the dolomite crystals and euhedral quartz crystals are included within some dolomite rhombs. Although some quartz crystallized before some gray dolomite the reverse also occurred and the writer believes that the dolomite and the jasperoid quartz crystallized contemporaneously.

Fracturing and Brecciation

The deposition of the jasperoid and gray dolomite was followed by fracturing and brecciation. The resulting breccia is quite different from chert breccia. The phenoclasts of the chert breccia are dense and sharp-edged whereas those of the dolomitic jasperoid are not so sharp and their contacts with the cement are not always distinct. The amount of fracturing and brecciation of jasperoid and gray dolomite is much less than that of the chert, and the vugs and fractures resulting from the brecciation frequently are lined with pink dolomite, sulfides and calcite.

All fracturing and brecciation did not occur at the same time. Early brecciation is evidenced by the occasional occurrence of phenoclasts which in themselves are composed of fragments of jasperoid cemented by later jasperoid. Less commonly gray jasperoidal dolomite blocks are cemented by dolomitic jasperoid. Later tectonic activity is evidenced by the fractured jasperoid and brecciated veins of pink dolomite.

II. Minerals Deposited in Vugs:

The sequence of mineral deposition in vugs has aroused less controversy than the disseminated bedded deposits. Many variations discussed below have not been noted previously or were not emphasized sufficiently.

Quartz

Many of the vugs initially were coated by a fine, gray to dark quartz druse. The quartz druse was deposited most commonly upon chert and jasperoid, rarely upon gray dolomite which generally grades directly into pink dolomite without this intervening quartz druse.

The quartz druse normally was deposited before pink dolomite, galena, sphalerite and marcasite, but rarely it occurs with or after these minerals. Rarely quartz druse is present on pink dolomite beneath sphalerite crystals; rarely it is present on sphalerite beneath galena. Quartz druse rarely is deposited on galena before marcasite or quartz crystals included within these two minerals. Small quartz crystals rarely occur within sphalerite deposited in vugs upon pink dolomite.

Late quartz crystals up to a centimeter or two in size cap the sulfides deposited during the main period of mineralization. This quartz generally is deposited on sphalerite without intergrowth and forms a complete coating over galena, sphalerite, chalcopyrite, marcasite, pyrite and other early minerals.

Quartz occurs or recurs several times in the paragenetic sequence. It appears as: 1) jasperoid, 2) quartz druse deposited upon chert, jasperoid, and on some gray dolomite, 3) quartz druse upon pink dolomite beneath sphalerite, 4) rare quartz crystals within sphalerite, 5) rare quartz druse on sphalerite beneath galena, 6) rare crystals within galena, upon galena beneath marcasite, and within marcasite, and 7) late quartz crystals deposited upon galena, sphalerite, chalcopyrite, marcasite, and pyrite.

Pink Dolomite

Pink dolomite is deposited in the vugs as saddle-shaped rhombohedral crystals on gray dolomite, jasperoid, chert fragments and quartz druse. In the mines it also may be observed as small fracture fillings parallel to and cutting the banding of gray dolomite, jasperoid, and limestone. In these places, pink dolomite is clearly later than jasperoid and its disseminated sulfides. In other places, pink dolomite grades into gray dolomite and seems to be contemporaneous with the gray dolomite.

Pink dolomite generally is free of quartz, but occasionally quartz druse occurs on pink dolomite. This is in distinct contrast to the gray dolomite, which generally contains considerable quartz intergrown with it.

Pink dolomite, in very minor amounts, reoccurs much later in the mineral sequence. The writer has observed a few crystals deposited on galena and on sphalerite. Very small dolomite crystals also were observed occurring within quartz druse deposited on sphalerite which, in turn, was older than galena. Ransome[218] reported pink dolomite on sphalerite in a single specimen. Rogers[219] observed pink dolomite on corroded galena; Buckley and Buehler[220] noted pink dolomite on hemimorphite.

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[218] Alfred L. Ransome, "Enargite and Plumbojarosite at Picher, Oklahoma", Am. Mineralogist, vol. 20, p. 803, 1935.

[219] Austin F. Rogers, pt. III in Erasmus Haworth, "Special Report on Lead and Zinc", Kansas Geol. Survey Rept., vol. VIII, p. 504, 1904.

[220] E. R. Buckley and H. A. Buehler, "The Geology of the Granby Area", Mo. Geol. Survey Rept., vol. IV, 2d series, p. 55, 1905.

Therefore, although pink dolomite was deposited mainly after gray dolomite, jasperoid, disseminated sulfides and quartz druse, it also crystallized in minor quantities both before and after its main period of deposition.

Sphalerite

Sphalerite is generally the first and most abundant sulfide to crystallize on pink dolomite in the vugs, but at Joplin and other camps to the east, galena seems more frequently to have been deposited before sphalerite. Since the sphalerite in the vugs is deposited on pink dolomite which fills fractures in jasperoid containing disseminated sphalerite, the sphalerite of the vugs is clearly later than the disseminated sphalerite.

Small, brown to reddish sphalerite crystals also occur on galena crystals which have formed on larger earlier lighter-brown sphalerite. These small sphalerite crystals are common in cavities in jasperoid and on chert breccia fragments. Rarely they occur on chalcopyrite, and rarely in and beneath heavy marcasite coatings deposited upon galena. Rarely small dark crystals of sphalerite occur on late quartz crystals and some of these sphalerite crystals are covered by calcite. More rarely sphalerite was deposited on calcite.

Stalactitic, botryoidal material consisting of zinc sulfide, galena, and marcasite has been observed in only a few mines.

Siebenthal[221] reported zinc sulfide stalactites deposited on marcasite and he[222] also observed botryoidal intergrowths of sphalerite and galena on chalcopyrite which in turn coated normal sphalerite on the wall of a vug. Stalactitic material studied by the present writer exhibits reticulated intergrowth of galena with the zinc sulfide, indicating contemporaneous deposition of these two minerals. Marcasite is intergrown with and deposited upon zinc sulfide at the margin of one stalactite. Evans and McKnight[223] proved the presence of small wurtzite crystals deposited upon the stalactites. Therefore the paragenetic sequence for the stalactitic material is: sphalerite and galena, wurtzite and marcasite. This stalactitic sequence is a late phase of the sulfide deposition and followed the main period of deposition of sphalerite, chalcopyrite and marcasite.

Sphalerite also has crystallized very recently on nails. This has been reported by others, but this writer studied a nail at the Joplin Mineral Museum, on the head of which crystals of both sphalerite and galena were deposited. The sphalerite begin to crystallize before the galena, but the two minerals exhibit considerable intergrowth. The occurrence of sulfides on nails shows that these sulfides still are

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[221] C. E. Siebenthal, "Origin of the Zinc and Lead Deposits of the Joplin Region - Missouri, Kansas, and Oklahoma", U. S. Geol. Survey Bull. 606, p. 260, 1951.

[222] *Ibid.*, p. 263.

[223] Howard T. Evans, Jr. and Edwin T. McKnight, "New Wurtzite Polytypes from Joplin, Missouri", Am. Mineralogist, vol. 44, pp. 1210-1218, 1959.

being formed from the local mine waters.

Sphalerite occurs and recurs many times in the paragenetic sequence. It appears: 1) as yellowish-brown crystals disseminated in jasperoid and gray dolomite, 2) as brownish crystals on pink dolomite in vugs, 3) as small reddish-brown crystals on galena, chalcopyrite and earlier sphalerite, 4) rarely crystals on late quartz crystals, but before late calcite, 5) more rarely as crystals on calcite, 6) as intergrowths with galena in stalactites, 7) as repetitive crystallization with marcasite in stalactites, and 8) as small crystals on nails.

Galena

In the Picher field galena normally is deposited on and intergrown with sphalerite. At Joplin and other fields to the east, galena frequently has crystallized before sphalerite.

Although Rogers[224] believed that octahedral galena is later than cubic galena, the present writer doubts this relationship.

A small amount of galena has been noted in stalactites of sphalerite. About three to five per cent of these stalactites is galena. The galena is intergrown with the zinc sulfide and in elongated patches which radiate outward from the center of the stalactitic material, but galena generally is absent from the core of these stalactites. Sphalerite first was deposited alone, and then contemporaneously with galena. These stalactites clearly are later than the principal period of

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[224] Rogers, _op_. _cit_., p. 452.

sphalerite, chalcopyrite and marcasite deposition.

The crystallization of small crystals of galena on nails and tools has been recorded in the literature.[225] A specimen of this sort is exhibited in the Joplin Mineral Museum. On this specimen galena was deposited after sphalerite, but the two minerals show considerable intergrowth. These crystals prove that galena is crystallizing from the groundwaters of the Joplin district at the present time.

From the above discussion one concludes that galena was deposited more than once: 1) as crystals disseminated in jasperoid and gray dolomite, 2) as crystals in vugs mostly after but also before the main period of sphalerite deposition, 3) as contemporaneous intergrowths with sphalerite in stalactitic material, and 4) most recently as small crystals on nails.

Chalcopyrite

The main period of deposition of chalcopyrite followed that of pink dolomite and sphalerite; chalcopyrite crystals commonly are found deposited upon these two minerals, but chalcopyrite also was deposited before and during as well as after sphalerite. Chalcopyrite crystals most commonly occur on sphalerite, and usually show little or no intergrowth with the sphalerite, more rarely chalcopyrite crystals

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[225] Bain, Van Hise, and Adams, loc. cit.; Buckley and Buehler, loc. cit.; Rogers, op. cit., p. 453.

are included in sphalerite, particularly near its margins. Two or more generations of chalcopyrite crystals are present within some sphalerite crystals. Chalcopyrite crystals covered by sphalerite are rare, but in such occurrences they exhibit euhedral outlines against the sphalerite. Rarely the later sphalerite occurs in small veinlets which replace chalcopyrite.

The paragenetic relationship between chalcopyrite and galena is difficult to determine because chalcopyrite generally grows on sphalerite rather than on adjacent galena. This suggests that sphalerite has acted as a seed crystal for the chalcopyrite or that the galena is younger than the chalcopyrite. Rarely chalcopyrite occurs beneath galena and a few crystals of chalcopyrite have been noted on galena, particularly in specimens from Joplin and other fields to the east. The writer believes that the main period of chalcopyrite deposition followed that of galena, but that chalcopyrite deposited upon sphalerite in preference to the galena.

Rarely chalcopyrite is deposited on late quartz, and occasionally it is coated by calcite. In some occurrences chalcopyrite is deposited on sphalerite which in turn is deposited on quartz. This is a late type of chalcopyrite but an even later type is the rare occurrence of chalcopyrite on calcite and filling fractures in calcite.

The above occurrences show that the chalcopyrite disseminated in jasperoid and gray dolomite was formed early in the mineralization process, but most of the chalcopyrite was crystallized after most of the sphalerite and galena, although some chalcopyrite was deposited before and during the main period of sphalerite deposition and some chalcopyrite was deposited after sphalerite but before galena. Minor chalcopyrite crystallization recurred after late quartz was deposited and again after calcite was deposited.

Pyrite and Marcasite

Pyrite occurs on both sphalerite and galena and shows little or no intergrowth with these minerals. It commonly is deposited on and intergrown with chalcopyrite and marcasite and it also is deposited on pink dolomite but exhibits no intergrowth with this mineral.

Marcasite generally forms small tabular crystals on pink dolomite, sphalerite and galena and generally exhibits little or no intergrowth with these minerals. Marcasite also occurs on galena and occasionally forms a complete coating over galena from which it may be separated by a discontinuous coating of a late drusy quartz.

Rarely marcasite was deposited after pyrite on chalcopyrite, all three having crystallized before the main period of galena deposition, but after the main period of sphalerite deposition.

Pyrite and marcasite were deposited mainly during and after chalcopyrite, but often the three minerals are intimately intergrown. Chalcopyrite was the first to complete its deposition. Usually pyrite continued to deposit after the deposition of marcasite had ceased, however the reverse sequence is common.

Marcasite and pyrite recur as small crystals on late quartz and in some instances were deposited before calcite.

Marcasite and pyrite also occur within calcite. They have been deposited on the surface of the calcite crystals, and they are concentrated along the edges of some calcite crystals. Continued calcite deposition enclosed these iron sulfide crystals. Marcasite occurs as small blades, which both lay flat on the calcite and also stand on end. It also occurs in stellate groups in some calcite specimens. Pyrite usually occurs in calcite as cubes. Marcasite is intergrown with the chalcopyrite in calcite and also occurs as free crystals in the calcite.

Small crystals of marcasite and pyrite also were deposited on calcite. Rarely, botryoidal, stalactitic marcasite was deposited on calcite.

In some stalactitic zinc sulfide, marcasite is intimately intergrown with and replaces the zinc sulfide of the outer portions of the stalactites. Stalactitic pyrite was reported by Leonhard,[226] associated with and probably deposited upon galena.

Marcasite and pyrite occur many times in the paragenetic sequence. Pyrite occurs as euhedral crystals and irregular shaped grains in limestone and chert and as euhedral crystals, round grains, and irregular to banded areas in jasperoid. Marcasite occurs in radial aggregates on the round grains of pyrite, and as grains on fracture surfaces which cut pyrite bands. Pyrite recurs on radial marcasite and rarely crystals of pyrite and marcasite are deposited with chalcopyrite on, with and after sphalerite, but before galena. Pyrite and marcasite crystals are commonly deposited with and on

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[226] Alexander V. Leonhard, "Notes on the Mineralogy of Missouri", Trans. St. Louis Acad. Sci., vol. 4, p. 445, 1882.

chalcopyrite which has been deposited on sphalerite. Pyrite and marcasite crystals rarely occur on late quartz beneath late calcite, and more commonly within and on late calcite. They also form stalactites upon calcite and earlier minerals. Marcasite occurs on and replaces stalactitic zinc sulfide.

Enargite

Enargite generally is later than quartz and earlier than calcite, however an occasional crystal has been noted beneath chalcopyrite and others have been observed to be intergrown with chalcopyrite of the main chalcopyrite period of deposition. Ransome[227] reported enargite deposited after calcite. Enargite apparently began to crystallize toward the end of the period of chalcopyrite deposition, and either continued to be deposited or recurred after the formation of late quartz crystals. Although enargite usually preceded calcite, some of the enargite was deposited after calcite.

Wurtzite

Wurtzite was detected in the Tri-State district first by Rogers.[228] Its presence was recently confirmed by the x-ray studies of Evans and McKnight.[229] The wurtzite crystals were deposited upon the surface

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[227] Alfred L. Ransome, "Enargite and Plumbojarosite at Picher, Oklahoma", Am. Mineralogist, vol. 20, p. 801, 1935.

[228] Austin F. Rogers, pt. III in Erasmus Haworth, "Special Report on Lead and Zinc", Kansas Geol. Survey Rept., vol. VIII, pp. 461-462, 1904.

[229] Howard T. Evans, Jr. and Edwin T. McKnight, "New Wurtzite Polytypes from Joplin, Missouri", Am. Mineralogist, vol. 44, pp. 1210-1218, 1959.

of stalactites containing sphalerite and galena and therefore are younger than the stalactitic sphalerite and galena, which were formed after the main periods of deposition of sphalerite, chalcopyrite and marcasite. The paragenetic relationship of wurtzite to late quartz and calcite is unknown since these minerals have not been observed associated with stalactitic sulfides.

The present writer observed anisotropic needles within the stalactites, which were believed to be wurtzite but the amount was too small to be detected by x-ray analysis, as shown in Table III.

Calcite

Calcite has been deposited after chert, jasperoid, gray dolomite, and after the main periods of deposition of sphalerite, galena, chalcopyrite, pyrite, marcasite and enargite. It exhibits little or no intergrowth with these minerals, and frequently it completely coats the earlier minerals. Yet, some calcite was deposited early, as shown by its rare occurrence within sphalerite crystals formed during the main period of sphalerite deposition.

Calcite crystallized during two or more periods rather than during one. Farrington[230] and Rogers,[231] described many types of calcite crystals, but did not discuss their paragenetic relationships. The deposition of small crystals of marcasite, pyrite and chalcopyrite

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[230] O. C. Farrington, "Crystal Forms of Calcite from Joplin, Missouri", Publications of the Field Columbian Museum, Geological Series, vol. I, no. 7, pp. 232-231, 1900.

[231] Rogers, op. cit., pp. 467-490.

upon former growth surfaces of calcite and the subsequent covering of these sulfides by calcite, indicates either coprecipitation of calcite and sulfides or deposition of calcite at two or more times. Scalenohedral calcite crystals on rhombhedral calcite crystals indicates some change in the character of the depositing solutions, but the nature of this change is unknown.

Calcite deposited before sphalerite and galena on a nail from a mine in the Joplin district was observed by the writer in the Joplin Museum. This indicates a very recent crystallization of calcite.

III. Secondary Minerals:

In the mines of the Picher field, where the writer conducted the major portion of his investigations the ores normally are not oxidized but secondary minerals have been observed by this writer on specimens in museum and private collections, and most of the secondary minerals have been described by previous investigators. Although the paragenetic relationships of the secondary minerals is variable, the writer has attempted to arrange these minerals according to their paragenetic positions.

Barite

The paragenetic relations between barite and calcite seem variable. The writer observed barite on calcite and marcasite which, in turn, was on calcite. Winslow and Robertson[232] noted calcite

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[232] Arthur Winslow and James D. Robertson, "Lead and Zinc Deposits", Mo. Geol. Survey Rept., vol. 7, p. 460, 1894.

on barite, and Rogers[233] reported both paragenetic relationships. Usually barite was the last of the two minerals to be deposited.

Aragonite

Weidman[234] observed cup-shaped forms of calcium carbonate which he believed originally were aragonite deposited upon calcite, sphalerite and chalcopyrite in the Golden Rod mine. He stated that " .... it occurs in more than one generation, as it alternates in deposition, not only with calcite, but also with the ore-minerals." Marcasite was deposited upon some aragonite cups.

Buckley and Buehler[235] reported aragonite on calcite boulders in the Pennsylvanian shales of the Granby field.

The writer studied cup-shaped calcium carbonate forms from the Lucky Bill mine of the Picher field by x-ray analysis, as shown in Table IV, page 119, and found them to be composed of calcite.

Smithsonite

The writer observed smithsonite on and replacing calcite crystals. Pseudomorphs of smithsonite after calcite exhibit interlayered smithsonite

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[233] Rogers, op. cit., p. 503.

[234] Samuel Weidman, "The Miami-Picher Zinc-Lead District, Oklahoma", Okla. Geol. Survey Bull. 56, pp. 58-60, 1932.

[235] E. R. Buckley and H. A. Buehler, "The Geology of the Granby Area", Mo. Geol. Survey Rept., vol. IV, 2d series, p. 34, 1905.

and hemimorphite.

Hemimorphite

Excellent pseudomorphs of hemimorphite and smithsonite after calcite are in the Missouri School of Mines museum. These show hemimorphite on smithsonite, or an interlayering of the two minerals.

Sphalerite

Earthy zinc sulfide on jasperoid and galena at Galena, Kansas, was noted by Robertson.[236] He believed that this zinc sulfide formed after the decomposition of normal sphalerite, Smithsonite and hemimorphite were not associated with this earthy zinc sulfide.

Small sphalerite crystals occurring in porous smithsonite were noted by Smith,[237] who believed that they had formed either during or after the formation of the smithsonite.

Bornite

Bornite is a rare secondary mineral in Joplin ores. It occurs as a thin film on sphalerite and chalcopyrite, and also as irregular patches and veinlets, principally along the grain boundaries between marcasite and chalcopyrite.

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[236] James D. Robertson, "On a New Variety of Zinc Sulfide from Cherokee County, Kansas", Am. Jour. Sci., vol. 40, 3d ser., pp. 160-161, 1890.

[237] W. S. Tangier Smith, "Secondary Character of Pebble and Ruby Jack of the Joplin District", Econ. Geology, vol. 30, p. 702, 1935.

Covellite

Covellite is a very minor secondary sulfide in Joplin ore. It generally is associated with bornite. It forms irregular veinlets which grade into veinlets of bornite, frequently associated with the grain boundaries between marcasite and chalcopyrite. Covellite intersects and replaces bornite and thus it is younger than bornite. Veinlets of covellite also have been observed by the writer to transgress smithsonite and hemimorphite and thus a period of sulfide formation followed one of oxidation.

Sulfur

Sulfur on covellite coating sphalerite and chalcopyrite was observed by Ransome[238] in a single specimen from the Barr mine, near Picher, Oklahoma. Secondary sulfur deposited upon chert, jasperoid, galena and sphalerite at Galena, Kansas, was reported by Rogers,[239] who believed that it formed before cerussite and anglesite.

Anglesite

Anglesite was observed on galena by several investigators: Buckley and Buehler[240] Rogers,[241] Weidman,[242] Leonhard,[243] and the present writer.

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[238] Ransome, op. cit., p. 802.

[239] Rogers, op. cit., pp. 449-450.

[240] Buckley and Buehler, op. cit., p. 45.

[241] Rogers, op. cit., p. 498.

[242] Weidman, op. cit., p. 56.

[243] Leonhard, op. cit., p. 442.

Cerussite

Rogers[244] observed cerussite pseudomorphic after calcite in specimens from Granby, Missouri. Cerussite molds of galena crystals were reported from Granby, Missouri, by Buckley and Buehler[245] The present writer also observed cerussite deposited on galena and on calcite in specimens in the Missouri School of Mines Museum.

Leadhillite

Pirsson and Wells[246] and Winslow and Robertson[247] reported leadhillite deposited upon cerussite, and Buckley and Buehler[248] noted leadhillite pseudomorphous after calcite. Leadhillite intergrown with cerussite deposited on galena was observed by the writer in specimens from Granby, Missouri.

Pyromorphite

Schmidt and Leonhard[249] observed pyromorphite on cerussite at Granby. Pyromorphite pseudomorphous after galena at Joplin and Granby was reported by Rogers[250] who noted that between the galena and pyromorphite cerussite occurred as an intermediate stage of alteration.

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[244] Rogers, op. cit., p. 492.

[245] Buckley and Buehler, op. cit., p. 45.

[246] L. V. Pirsson and H. L. Wells, "On the Occurrence of Leadhillite in Missouri and its Chemical Composition", Am. Jour. Sci., vol. 48, 3d ser., pp. 219-226, 1894.

[247] Winslow and Robertson, op. cit., p. 457.

[248] Buckley and Buehler, op. cit., p. 45.

[249] Adolf Schmidt and Alexander Leonhard, "The Lead and Zinc regions of Southwest Missouri", Mo. Geol. Survey Rept., for 1874, p. 390, 1874.

[250] Rogers, op. cit., p. 498; Austin F. Rogers, "Notes on Some Pseudomorphs, Petrifications and Alterations", Am. Philo. Soc. Proc. 49, p. 19, 1910.

The writer observed pyromorphite on calcite.

Gypsum

Various occurrences of gypsum have been observed by the writer in specimens in the Missouri School of Mines museum and in specimens from the personal collection of Dr. O. R. Grawe: 1) earthy gypsum on chert and sphalerite; 2) very small, acicular crystals of gypsum on jasperoid; 3) selenite crystals, up to one quarter inch long, deposited upon marcasite and pyrite which, in turn, had crystallized on galena and sphalerite; 4) gypsum crystals on calcite; and 5) gypsum cerussite which occurred on calcite.

Greenockite

Greenockite occurs as thin coatings on sphalerite, and on hemimorphite.

Aurichalcite

Aurichalcite at the Big Coon mine, Galena, Kansas, associated with cerussite, linarite, caledonite, malachite, chalcopyrite and sphalerite was observed by Rogers[251] but the paragenetic relationships to these minerals were not given. Keller[252] has reported aurichalcite on and mixed with hemimorphite from the Shinn mine, Stark City, Missouri.

Melanterite

Melanterite, deposited on the mine walls, was noted by Weidman[253] in the Picher field.

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[251] Austin F. Rogers, pt. III in Erasmus Haworth "Special Report on Lead and Zinc", Kansas Geol. Survey Rept., vol. VIII, p. 494, 1904.

[252] W. D. Keller, "Aurichalcite in Missouri", Am. Mineralogist, vol. 25, p. 494, 1904.

[253] Weidman, op. cit., p. 57.

Starkeyite

The present writer observed that starkeyite developed as an efflorescence on specimens of dolomitic jasperoid after they had been removed from the Blue Goose No. 1 mine.

Copiapite

Incrustations of copiapite on pyrite and melanterite were observed by Rogers[254] on the walls of a "cave in" at the Pilgrim mine at Cave Springs.

Cuprite

Cuprite altering to malachite was noted by Rogers[255] at the Big Coon mine, Galena, Kansas.

Malachite

Malachite as an alteration product of cuprite and as a thin coating on chalcopyrite and sphalerite was noted by Rogers[256] in specimens from the Big Coon mine, Galena, Kansas. Malachite deposited on hemimorphite at the Shinn mine, Stark City, Missouri, was reported by Keller.[257] The present writer observed a thin drusy coating of malachite on chalcopyrite and on a skin of covellite covering sphaleritein the Lawyers-Chicago No. 2 mine.

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[254] Rogers, op. cit., p. 502.

[255] Ibid., p. 466.

[256] Ibid., p. 466 and p. 493.

[257] Keller, loc. cit.

Hydrozincite

Schmidt and Leonhard[258] found hydrozincite on smithsonite which, in turn, was deposited on hemimorphite. That the mineral is forming at the present time is shown by the fact that it clouds water issuing from Buttermilk Spring, near Joplin.[259]

Goslarite

Goslarite was noticed by the writer deposited on the walls of the Big Elk, Southern and many other mines.

Limonite

The writer has observed limonite pseudomorphic after both pyrite and marcasite. Some of the limonite was on pyrite which has been deposited on calcite.

Jarosite

The writer found jarosite on jasperoid and quartz druse from the West Side mine, near Picher, Oklahoma.

Plumbojarosite

Plumbojarosite on galena from the Barr mine, New Picher, Oklahoma, was reported by Ransome.[260]

Hematite

Hematite as an alteration product of pyrite and marcasite was

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[258] Schmidt and Leonhard, op. cit., p. 394.

[259] Oliver R. Grawe, Oral Communication, 1960.

[260] Alfred L. Ransome, "Enargite and Plumbojarosite at Picher, Oklahoma", Am. Mineralogist, vol. 20, p. 803, 1935.

noted in a tallow clay at Granby, Missouri, by Buckley and Buehler.[261]

Pyrolusite

Pyrolusite as black spots in a tallow clay at Granby, Missouri, was reported by Buckley and Buehler.[262]

Chalcanthite

Chalcanthite, as an alteration product of chalcopyrite, was observed by Rogers[263] in specimens collected from a mine dump at the Irene mine, Empire City, Kansas.

Azurite

Rogers[264] noticed azurite in a single specimen, but he said nothing of its paragenetic relations with associated minerals.

Allophane

Rogers[265] reported allophane associated with sphalerite, chert and a soft clay-like material at the Big Coon mine, Galena, Kansas, but he did not discuss the paragenetic relationships of these minerals.

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[261] Buckley and Buehler, *op. cit.*, p. 46.

[262] *Ibid.*

[263] Rogers, *op. cit.*, p. 502.

[264] *Ibid*, p. 493.

[265] *Ibid*, p. 497.

Chrysocolla

Chrysocolla was reported by Rogers[266] as being associated with other copper minerals at the Big Coon mine, Galena, Kansas.

Caledonite

Caledonite was identified by Rogers[267] as a crystalline coating associated with linarite, aurichalcite, and cerussite at the Big Coon mine, Galena, Kansas, but did not report on its paragenetic relationship to these minerals.

Linarite

A lead, copper sulfate mineral was believed by Rogers[268] to be linarite, associated with cerussite, caledonite, malachite and aurichalcite at the Big Coon mine, Galena, Kansas. Its paragenetic relationship to the minerals was not mentioned.

Millerite

Smith and Siebenthal[269] reported the occurrence of millerite in the Tri-State district, but they did not discuss its paragenetic relationship to other minerals.

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[266] *Ibid.*

[267] *Ibid*, p. 500.

[268] *Ibid.*

[269] W. S. Tangier Smith and C. E. Smith, Description of the Joplin District in Geologic Atlas of the United States, *U. S. Geol. Survey folio* 148, p. 12, 1907.

Picropharmacolite

Picropharmacolite on dolomite at Joplin was reported by Genth.[270]

Wavellite

Wavellite deposited on chert was reported by Wheeler[271] to have been observed by Broadhead in Jasper County, Missouri.

Vivianite

Wheeler,[272] also reported that Dr. Gustavus Hambach had seen vivianite at Joplin. Its paragenetic relationship to other minerals is unknown.

Mimetite

Mimetite on galena was reported by Wheeler[273] to have been observed by Jenny near Seneca, Missouri.

Aluminite

Aluminite on limestone at Joplin was reported by Wheeler.[274]

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[270] F. A. Genth, "Contributions to Mineralogy", *Am. Jour. Sci.*, 3d series, vol. 40, p. 204, 1890.

[271] H. A. Wheeler, "Recent Additions to the Mineralogy of Missouri", *Trans. St. Louis Acad. Sci.*, vol. 7, p. 129, 1895.

[272] *Ibid.*, p. 128.

[273] *Ibid.*, p. 127.

[274] *Ibid.*, p. 129.

Kaolinite

Tarr and Keller[275] noted kaolinite deposited on calcite, sphalerite, galena and quartz at Oronogo, Missouri. They also noticed some replacement of calcite by kaolinite.

Epsomite

Smith and Siebenthal[276] reported epsomite as a weathering product, but they did not discuss its association with other minerals.

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[275] W. A. Tarr and W. D. Keller, "Some Occurrences of Kaolinite Deposited from Solution", *Am. Mineralogist*, vol. 22, p. 933, 1937.

[276] Smith and Siebenthal, *loc. cit.*

VARIATIONS IN PARAGENESIS, MINERAL ABUNDANCE AND BRECCIATION

As a result of a paragenetic study of the minerals in relation to their areal, stratigraphic and structural distribution, certain conclusions seem valid.

The character of brecciation is not everywhere the same. Some beds tend to form a mosaic breccia, in which the chert fragments appear capable of fitting back together. This type of brecciation is most characteristic of G-H beds. While mosaic type breccias may be observed in other beds, these more commonly are characterized by sporadic breccias in which the phenoclasts have no relationship to one another. M bed characteristically exhibits this type of brecciation. K bed shows both types of brecciation. The sheet ground beds O, P and Q generally are less brecciated than the others, but exhibit abundant nearly horizontal fracturing.

Brecciation had not taken place all at one time, but recurred several times. The main period of brecciation took place after lithification of the limestone and chert, and preceded the introduction of the jasperoid and gray dolomite. Brecciation recurred after some of the jasperoid and gray dolomite had been introduced. Breccia fragments of jasperoid and grey dolomite are cemented by these same minerals. Brecciation followed the formation of pink dolomite, for pink dolomite forms phenoclasts in the Grace B mine. Most recently fracturing accompanied by brecciation has produced fragments of all the above minerals and these fragments now are cemented locally by calcite.

Although a general paragenetic sequence is present throughout the district, this study has shown much more variation from the general sequence than was previously thought. Chalcopyrite and pyrite were deposited at eight different intervals, sphalerite and marcasite at least six, galena and quartz at least during five.

In the Picher field galena nearly always follows the main deposition of sphalerite. But at Joplin, Webb City, Granby and possibly other fields to the east of the Picher field galena commonly precedes the main deposition of sphalerite.

Late pyrite, that which crystallized after the main periods of deposition of pink dolomite, sphalerite, galena and chalcopyrite, appears to have been more abundant at Joplin than in the Picher field. The paragenetic relationship between this late pyrite and late marcasite is quite variable. The two minerals often are intergrown. In some places pyrite crystals are deposited on marcasite in other places marcasite is deposited on pyrite. The pyrite-marcasite paragenetic relationships were recorded for each specimen collected from the various beds and mines of the Picher field, but no suggestion of horizontal or vertical zoning of these minerals was found. Extension of the study over the rest of the Tri-State district yielded similar results.

The habits of small late euhedral pyrite crystals were noted. Cubes, cubes modified by the pyritohedren and pyritohedrons were observed, but no relation seems to exist between the habit of pyrite and its areal or stratigraphic distribution in the Picher field. An attempt to extend the study of the habit of pyrite throughout the Tri-State district was impossible because the exact areal and stratigraphic position of the available specimens were unknown.

Enargite is known from at least eleven mines in the Picher field, Its occurrence appears to be confined to K and M beds. The mineral appears to be most abundant in the north-central portion of the Picher field and it was not observed in specimens from the other fields in the Tri-State district.

Dolomite is rather abundant in the Picher field, at Granby and to the west of Joplin, but only a little dolomite was found in many mines east of Joplin such as those at Webb City and at Oronogo.[277] In some places, such as near Baxter Springs, dolomite is mainly fine-grained and bedded.

The quartz which was deposited as a coarse druse on sulfides is most abundant in the sheet ground beds to the northeast of the Picher field toward Baxter Springs.

Glauconite is most abundant in J bed. A little glauconite occurs in K and M beds in some places. The mineral rarely occurs in other beds.

Barite was very abundant at Thom's Station, and rather abundant at Webb City. Minor amounts have been observed at Joplin, Duenweg, Carterville, and Stark City. A little barite has been observed in some mines in the eastern part of the Picher field.

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[277] Ernest J. Palmer, Oral Communication, 1958.

Stalactitic zinc and lead sulfides have been observed at only a few places, namely at the Zig Zag, Oswego, Firecracker and Combination mines near Joplin, and at Oronogo.

Some of the secondary copper minerals, such as, chalcanthite, azurite, chrysocolla, caledonite and linarite have been observed only by Rogers at the Big Coon mine, Galena, Kansas.

REPETITIVE MINERALIZATION

A most significant result from this paragenetic study is the discovery of repetitive sequences of deposition of the sulfides. At least seven sequences can be distinguished. Each sequence is characterized by its own paragenesis, by its associated gangue minerals, by the presence or absence of certain minerals, and by its associated tectonic activity.

I. Mississippian Sedimentation

The earliest period of mineral deposition was that of Mississippian sedimentation. Syngenetic pyrite and possibly small amounts of other sulfides were deposited at this time along with limestone, chert, fine-grained bedded gray dolomite and glauconite. Diagenesis probably played an important part in the formation of some of these minerals.

II. Pennsylvanian Sedimentation

Pennsylvanian sedimentation followed the Mississippian. Syngenetic pyrite, marcasite, sphalerite and galena formed as disseminated crystals and masses at this time in shale, sandstone and limestone.

III. Disseminated Epigenetic Meteoric Mineralization

Following a period of major fracturing and brecciation of limestone and chert, major amounts of sulfides were deposited. These sulfides show the following paragenetic sequence: pyrite, marcasite, pyrite, sphalerite, galena, and chalcopyrite. Sphalerite and galena exhibit considerable overlap in paragenetic position. These disseminated sulfides were accompanied by the major introduction of jasperoid mush or gel and by the crystallization of most of the coarse-grained gray dolomite.

IV. Main Fracture-Filling and Vug-Filling Epigenetic Meteoric Mineralization

Following a later period of fracturing and solution which affected the previously formed jasperoid and gray dolomite as well as the limestone and chert, sulfides were deposited in fractures and vugs. These sulfides were deposited in the following general sequence: sphalerite, galena, chalcopyrite, marcasite, pyrite, and minor enargite. This sequence is characterized by overlap of adjacent minerals and by many local variations. The sulfides were preceded by the deposition of pink dolomite and the sequence is characterized by the deposition of only minor amounts of quartz and later pink dolomite.

V. Solution and Redeposition or Minor Sulfide Deposition

Following the deposition of late larger quartz crystals minor amounts of sulfides were deposited. These sulfides were deposited in the following paragenetic sequence: sphalerite, chalcopyrite, marcasite and pyrite. Most of the enargite was deposited during this period.

VI. Further Solution and Redeposition or Minor Sulfide Deposition

Accompanying and following the deposition of calcite minor amounts of marcasite and pyrite were deposited. These are followed by minor amounts of galena, sphalerite, chalcopyrite and rare enargite. Rarely pink dolomite was deposited at this time. Brecciation, solution and calcite deposition along limestone-jasperoid contacts preceded this sulfide deposition.

VII. Present-day Solution and Redeposition on Nails

Water entering the mines in recent times has deposited sulfides on nails and other metallic objects. In those cases noted by the writer the deposition of sphalerite was followed by that of galena. The deposition of the sulfides was preceded by that of calcite.

CHAPTER V

TRACE ELEMENT INVESTIGATIONS

PREVIOUS INVESTIGATIONS

The principal elements in the ores of the Tri-State district are: aluminum, calcium, carbon, copper, iron, lead, magnesium, oxygen, silicon, sulfur and zinc, but the presence of other elements has been known for more than half a century (see Table VII). Cadmium was chemically detected in sphalerite from the Joplin area in 1874 by Chauvenet.[278] Gallium was chemically detected in sphalerite from Joplin in 1880 by Cornwall,[279] and Urbain [280] in 1909 spectrographically revealed its presence in sphalerite from Webb City. McCutcheon[281] in 1915 chemically determined gallium and indium in smelter products from Tri-State ores. Two years later, Buchanan[282] found germanium in Joplin ore, and Waring[283] found thallium in zinc ore from the Webb

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[278] Adolf Schmidt and Alexander Leonhard, "The Lead and Zinc Regions of Southwest Missouri", Mo. Geol. Survey Rept. for 1874, p. 392, 1874.

[279] H. B. Cornwall, "Gallium in American Blendes", Am. Chem. Jour., vol. 2, pp. 44-45, 1880.

[280] G. Urbain, "Analyses Spectrographique des Blendes", Compt. Rend., vol. 149, p. 602-603, 1909.

[281] W. F. Hillebrand and J. A. Scherrer, "Recovery of Gallium from Spelter in the United States", Jour. Ind. Chem., vol. 8, p. 225, 1916.

[282] G. H. Buchanan, "The Occurrence of Germanium in Missouri and Wisconsin Blendes", Ind. Eng. Chem., vol. 9, pp. 661-663, 1917.

[283] W. George Waring, "The Zinc Ores of the Joplin District. Their Composition, Character, and Variation", Am. Inst. Min. Met. Eng. Trans., vol. 57, pp. 657-670, 1917.

TABLE VII

TRACE ELEMENTS FOUND IN TRI-STATE MINERALS

Author	*Date*	*Material*	*Elements*															
Schmidt and Leonard	1874	Sphalerite									Cd							
Cornwall	1880	Sphalerite														Ga		
Urbain	1909	Sphalerite														Ga		
Hillebrand and Scherrer	1916	Smelter products														Ga		
Buchanan	1917	Sphalerite															Ge	
Waring	1917	Flue Dust																
Papish and Stilson	1930	Sphalerite														Ga		
Claussen	1934	Sphalerite	Ag		As					Ca		Co		Cu	Fe			
		Galena	Ag							Ca			Cr	Cu	Fe			
Graton and Harcourt	1935	Sphalerite	Ag					Bi			Cd			Cu	Fe	Ga	Ge	
Stoiber	1940	Sphalerite									Cd	Co				Ga	Ge	
Frondel, Newhouse and Jarrell	1942	Galena	Ag	Al			Ba						Cr	Cu	Fe			
Jakosky, Dreyer and Wilson	1942	Rock and Soil	Ag	Al	As	Au	Ba	Bi	Bo		Cd	Co	Cr	Cu		Ga	Ge	Hg
Warren and Thompson	1945	Sphalerite	Ag								Cd			Cu	Fe	Ga	Ge	
Harbaugh	1950	Vegetation	Ag									Co		Cu				
Fowler	1950	Soil										Co				Ga		
Marshall and Joensuu	1961	Galena	Ag											Cu				
This Study	1962	Sphalerite	Ag	Al						Ca	Cd		Cr	Cu	Fe	Ga	Ge	
		Galena	Ag	Al						Ca			Cr	Cu	Fe			

TABLE VII (continued)

Author	Elements																				
Schmidt and Leonhard																					
Cornwall																					
Urbain																					
Hillebrand and Scherrer	In																				
Buchanan																					
Waring																	Tl				
Papish and Stilson																					
Claussen					Mg					Pb	Pd			Sn							
		Ir			Mg				Ni	Pb		Sb		Sn						Zn	
Graton and Harcourt	In					Mn				Pb											
Stoiber						Mn			Ni												
Frondel, Newhouse and Jarrell					Mg								Si								
Jakosky, Dreyer and Wilson	In		K	Li	Mg	Mn	Mo	Na	Ni	Pb		Sb		Sn	St	Ti		V	W	Zn	Zr
Warren and Thompson										Pb											
Harbaugh									Ni	Pb				Sn						Zn	
Fowler									Ni	Pb				Sn							
Marshall and Joensuu												Sb									
This Study	In				Mg	Mn				Pb			Si			Ti					
					Mg							Sb	Si	Sn				V		Zn	

City-Carterville fields. In 1930, Papish and Stilson[284] confirmed the presence of gallium in sphalerite from Joplin, Webb City and Baxter Springs.

In 1934, Claussen[285] found: Ag, As, Ca, Co, Cu, Fe, Mg, Pb, Pd, and Sn in sphalerite; and Ag, Ca, Cr, Cu, Fe, Ir, Mg, Ni, Pb, Sb, Sn, and Zn in galena. In the same year Newhouse[286] by chemical and spectrographic means, detected the presence of vanadium in these minerals.

In 1935, Graton and Harcourt[287] using spectrographic means detected: Ag, Bi, Cd, Cu, Fe, Ga, Ge, In, Mn and Pb in six sphalerite specimens from the Tri-State district.

In 1940, Stoiber[288] spectrographically analyzed seventy-five sphalerite specimens, nine of which were from the Tri-State district. He detected Cd, Co, Ga, Ge, Mn and Ni in the Tri-State specimens. He concluded that gallium and germanium are concentrated in sphalerite

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[284] Jacob Papish and Chester B. Stilson, "Gallium IV. Occurrence of Gallium in Zinc Minerals", Am. Mineralogist, vol. 15, pp. 521-527, 1930.

[285] Gerard E. Claussen, "Spectroscopic Analysis of Certain Galenas, Sphalerites, and Pyrites", Am. Mineralogist, vol. 19, pp. 221-224, 1934.

[286] W. H. Newhouse, "The Source of Vanadium, Molybdenum, Tungsten, and Chromium in Oxidized Lead Deposits", Am. Mineralogist, vol. 19, pp. 209-220, 1934.

[287] L. C. Graton and G. A. Harcourt, "Spectrographic Evidence on Origin of Ores of Mississippi Valley Type", Econ. Geology, vol. 30, p. 803, 1935.

[288] Richard E. Stoiber, "Minor Elements in Sphalerite", Econ. Geology, vol. 35, pp. 501-519, 1940.

of low temperature deposits, and that indium and cadmium are concentrated in intermediate and high temperature deposits.

In 1942, Frondel, Newhouse, and Jarrell[289] using spectrographic means detected Ag, Al, Ba, Cr, Cu, Fe, Mg, and Si; and they believed that silver and silicon were relatively concentrated in the octahedral face-loci of galena crystals from Joplin and other districts. They also believed that Al, Ba, Ca, Cr, Cu, Fe, Mg and Sr exhibited significant quantitative variations within the galena crystals, but they believed that these variations were unrelated to faces of the galena crystals.

In 1942, Jakosky, Dreyer and Wilson[290] spectrographically analyzed soil and bulk rock samples from the Tri-State district to determine the relationship between trace element distribution and the location of ore deposits. They found no correlation between the two.

In 1945, Warren and Thompson[291] spectrographically analyzed 164 sphalerite samples, two of which were from Joplin. They found Ag, Cd, Cu, Ga, Ge, Fe, and Pb in the Joplin samples. One specimen was ruby blende, which contained more Ga, Ge, and Pb, and less Fe

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[289] C. Frondel, W. H. Newhouse, and R. F. Jarrell, "Special Distribution of Minor Elements in Single-Crystals", *Am. Mineralogist*, vol. 27, pp. 726-745, 1942.

[290] J. J. Jakosky, R. M. Dryer, and C. H. Wilson, "Geophysical Investigations in the Tri-State Zinc and Lead Mining District", *Kansas Geol. Survey Bull.* 44, 151 pp., 1942.

[291] H. V. Warren and R. M. Thompson, "Sphalerites from Western Canada", *Econ. Geology*, vol. 40, pp. 309-335, 1945.

and Ag than the normal yellow-brown sphalerite. Their results regarding the relative concentrations of minor elements associated with this type of deposit agreed with those of Stoiber.

In 1950, Harbaugh[292] spectrographically and chemically analyzed vegetation to determine if the trace element content of twigs, leaves, grasses and herbaceous plants could be used as a prospecting tool in the Tri-State district. He found only the zinc content to be areally related to the ore bodies. Ag, Co, Cu, Ni, Pb and Sn showed negligible correlation with the areas of sulfide ore.

In 1950, Fowler[293] reported that the use of the elements Co, Ga, Ni, Pb and Sn gave the most reliable results in the search for ore bodies. As a consequence of these studies one small ore body was discovered.

In 1961, Marshall and Joensuu[294] spectrographically studied the relationship between the concentrations of Ag, Cu and Sb and the crystal habit of 31 galena samples, 16 of which were from the Picher field in northeastern Oklahoma. Only antimony varied with crystal habit, and the lowest concentrations occurred in octahedral crystals.

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[292] John W. Harbaugh, "Biochemical Investigations in the Tri-State District", Econ. Geology, vol. 45, pp. 548-567, 1950.

[293] George M. Fowler, "Geochemical Prospecting in the Mississippi Valley (abstract), Min. Cong. Jour., vol. 36, p. 69, 1950.

[294] Royal R. Marshall and Oiva Joensuu, "Crystal Habit and Trace Element Content of Some Galenas", Econ. Geology, vol. 56, pp. 758-771, 1961.

ZONING

Horizontal and vertical zoning of ore deposits is a well established fact in districts such as Butte, Montana, and Cornwall, England. More recently this fact has been reported from many other districts, as exemplified by the work of Riley,[295] Graf and Kerr,[296] and Austin.[297] In most of this work the distribution of trace elements has been based upon the analysis of rock and ore samples. But recently, Bradbury[298] investigated the variations of trace element content in single minerals, particularly in sphalerite, galena and pyrite over the Wisconsin-Illinois zinc-lead district. He found little to indicate the existence of zoning in that district.

In the Tri-State district various types of zoning have been

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[295] L. B. Riley, "Ore Body Zoning", Econ. Geology, vol. 31, pp. 170-184, 1936.

[296] Donald L. Graf and Paul F. Kerr, "Trace Element Studies, Santa Rita, New Mexico", Geol. Soc. America Bull., vol. 61, pp. 1023-1052, 1950.

[297] Carl F. Austin, "Geochemical Exploration", unpub. Doctoral Thesis Univ. of Utah, 90 pp., 1959.

[298] James C. Bradbury, "Mineralogy and the Question of Zoning, Northwest Illinois Zinc-Lead District" (abstract), Mining Eng., vol. 11, no. 12, p. 1231, 1959.

suggested. Some investigators, for instance, Buckley and Buehler,[299] Siebenthal,[300] Fowler and Lyden,[301] and Weidman[302] have noted that, in general, galena was more abundant in the upper beds and that sphalerite was more abundant in the lower beds. This relationship, however, is only a broad generalization, and it should be kept in mind that many exceptions occur. For instance, ore runs in the Reeds Spring, one of the lower ore-bearing beds, contain relatively abundant galena. The cause of this type of zoning lies partly in the fact that galena is more resistant to weathering than sphalerite and hence it is relatively concentrated in the surface residuum. Therefore the upper workings of some of the earlier mines to the east of the Picher field contained more lead near the "grass roots".

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[299] E. R. Buckley and H. A. Buehler, "The Geology of the Granby Area", *Mo. Geol. Survey Rept.*, vol. IV, 2d series, p. 85, 1905.

[300] C. E. Siebenthal, "Origin of the Zinc and Lead Deposits of the Joplin Region - Missouri, Kansas, and Oklahoma", *U. S. Geol. Survey Bull.* 606, p. 229, 1915.

[301] George M. Fowler and Joseph P. Lyden, "The Ore Deposits of the Tri-State District", *Am. Inst. Min. Met. Eng. Trans.*, vol. 102, p. 235, 1932.

[302] Samuel Weidman, "The Miami-Picher Zinc-Lead District, Oklahoma", *Okla. Geol. Survey Bull.* 56, p. 71, 1932.

Horizontal zoning of the ores has been suggested frequently by some geologists and mining engineers, who have pointed out that higher lead-zinc ratios occur at the margins of the runs than in the center of the ore deposit. The writer has seen this relationship in some K bed ore runs. Although this may be true for some runs, the reverse relationship has also been noted in some runs in K bed. In most runs in the various beds, no apparent uniform horizontal distribution of galena and sphalerite exists.

The greater abundance of galena in the upper portions of single runs in the district also has been suggested. At best this relationship can be considered only a very general one. The writer has noted that the galena-rich portions are frequently found in the upper portions of a working face, but thin galena-rich seams generally may be found throughout the vertical range of an ore run.

A fourth type of zoning in the district is one which occurs on a small scale. It was described first by Siebenthal.[303] The writer noted the relationship especially in the sheet ground, but also in some K bed runs. Within a vertical distance of about six inches, as shown in Figure 73, the rock changes gradually from jasperoid containing little or no sphalerite at the base, to jasperoid containing abundant sphalerite, then to sphalerite, and finally to sphalerite and galena at the top. Where open space is present above the sequence, galena crystals occasionally occur on the surface of the opening.

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[303] Siebenthal, op. cit., pp. 235-236.

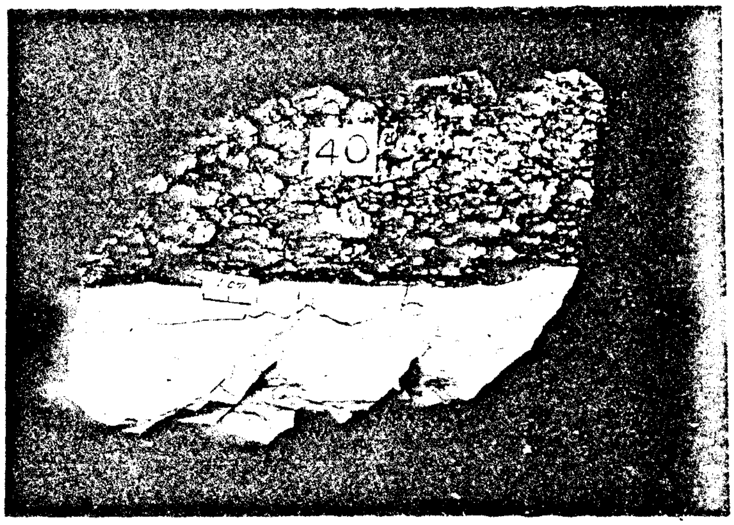

Figure 73. Mineralized "sheet ground". Sphalerite (gray specks and areas) content of the jasperoid (black) increases upward. Top portion of the specimen consists entirely of sphalerite. Lower portion of the specimen is chert (white). 0 bed, Blue Goose No. 1 mine.

Weidman[304] reported a fifth type of zoning, the presence of higher lead-zinc ratios associated with the Miami trough. This conclusion was based upon the relative abundance of lead and zinc concentrates from 34 mines in the Picher field. Such an analysis is impractical today because of the common practice of mixing ores from various mines. Weidman made his study when it was common practice to "hit the lead runs" when lead prices were up or when times were hard. Therefore Weidman's conclusions should be interpreted with caution.

Weidman,[305] Fowler[306] and Lyden[307] emphasized that the ore runs are associated with areas of structural deformation in which greater quantities of silica occurs than in the surrounding undeformed areas. A similar type of zoning over greater distances has been suggested by Giles,[308] who, after a measurement of 88 stratigraphic sections,

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[304] Weidman, op. cit., p. 76.

[305] Weidman, op. cit., p. 87.

[306] George M. Fowler, "Structural Control of Ore Deposits in the Tri-State Zinc and Lead District", Eng. Mining Jour., vol. 139, no. 9, pp. 46-51, 1938.

[307] Joseph P. Lyden, "Aspects of Structure and Mineralization Used as Guides in the Development of the Picher Field", Am. Inst. Min. Met. Eng. Trans., vol. 187, pp. 1251-1259, 1950.

[308] Albert W. Giles, "Boone Chert", Geol. Soc. America Bull., vol. 46, pp. 1632-1834, 1935.

concluded that the amount of chert in the Boone formation decreased eastward into Arkansas from the Tri-State district, and that it also decreased upward in the Boone formation.

Zoning of a sort, was sought in the district by Stoiber,[309] who attempted to determine the directions of flow of the mineralizing solutions by a study of asymmetrical crystal growths and arrangements in vugs. For 159 localities, he recorded preferred growth on the stoss sides of crystals, overgrowths of later crystals on the stoss sides of earlier ones, and irregular distributions of crystals within the vugs. The determinations showed much variation, but he believed that, in general, the solutions had originated from the Miami trough and flowed to the north and to the south from that structure. The vertical component of flow usually was determined to be downward, which he interpreted to be due to gravity settling from the solution filling the vugs.

The most recent study of zoning in the Tri-State district is that of Lyden,[310] who used zoning as a guide to mining in the Picher field. The close association of the gray dolomite to the ore bodies

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[309] Richard E. Stoiber, "Movement of Mineralizing Solutions in the Picher Field, Oklahoma-Kansas", Econ. Geology, vol. 41, p. 800-812, 1946.

[310] Lyden, op. cit., p. 1256.

of some mines was noted by Smith and Siebenthal[311] and mapped by McKnight and others.[312] More recently Lyden pointed out that the pillars or one wall of most ore runs are rich in dolomite (Figure 22, page 64); the outer wall of the runs contain principally jasperoid (Figure 74); while away from the main ore runs the predominant rock is limestone, as revealed in pull drifts (Figure 66, page 100; and in Figure 75) and in drill holes. The richest zinc-lead ores occur between the dolomite and jasperoid areas. McKnight[313] observed: (1) that the centers of the dolomite cores commonly contain Cherokee shale introduced by cave filling, (2) that chalcopyrite and enargite are confined almost entirely to the zone of overlap of dolomite and jasperoid, (3) that the galena zone overlaps that of sphalerite but tends to extend farther toward the unaltered limestone, and (4) that a barren boulder zone containing marcasite and abundant calcite occurs at the inner margin of the unaltered limestone.

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[311] W. S. Tangier Smith and C. E. Siebenthal, Description of the Joplin District in Geologic Atlas of the United States, *U. S. Geol. Survey folio* 148, p. 13, 1907.

[312] Edwin T. McKnight, *et al.*, Maps Showing Structural Geology and Dolomitized Areas in Part of the Picher Zinc-Lead Field, U. S. Geol. Survey Tri-State Zinc-Lead Investigations Preliminary Maps 1-6, 1944.

[313] Edwin T. McKnight, "Zoning of Ore Deposits in the Tri-State District" (abstract), *Wash. Acad. Sci. Jour.*, vol. 32, p. 282, 1942.

Figure 74. Jasperoid wall typical of ore "runs" showing jasperoid (black) and chert (white). M bed, Whitebird mine.

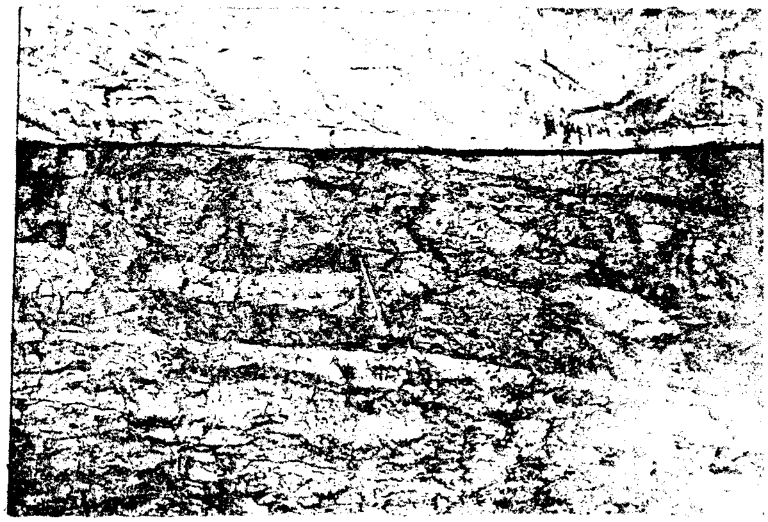

Figure 75. Chert nodules and lenses (white) in limestone (medium gray). G-H beds, Piokee mine.

PURPOSE OF INVESTIGATION

Previous investigators found very little correlation between trace element distribution and the presence of ore. Since their analyses were those of soils, vegetation and bulk rock samples, the present writer investigated the areal, stratigraphic, and structural distribution of certain trace elements in single minerals: sphalerite and galena.

PROCEDURE

Samples for spectrographic analyses were selected under a binocular and a mineralographic microscope to obtain material free of contaminant phases. Clean cleavage fragments were ground to minus 100 mesh with an agate mortar and pestle to provide samples weighing at least fifty milligrams. The powder was finely ground but not screened.

Galena

The spectrographic analyses of galena were made by Mabel E. Phillips of the Missouri Geological Survey, using a Baird-Atomic Inc. 3-Meter Grating Spectrograph, which has a concave eagle mounted grating ruled 15,000 lines per inch. The instrument has a dispersion of 5.5 Å per mm. in the first order.

A cup, 4 mm. deep and 1½ mm. in diameter, in the lower positive electrode was filled level with pulverized sample. High purity grade electrodes were used which showed no traces of silver in "blank" runs. The samples were arced for one minute in a 10 to 11 ampere current at 30 to 45 volts across a 2 mm. gap. The slit width was 25 microns.

The arc spectra were recorded on Eastman Kodak Spectrum Analysis Number One plates. A Jarrell-Ash Comparator Microphotometer was used to record spectral line densities.

In preliminary analyses of galena Ag, Al, Ca, Cr, Cu, Fe, Mg, Sb, Si and Zn were detected. Since Ag was found in all samples and exhibited a tendency to vary in concentration, and was believed not to be present in contaminant phases, it was selected for further study.

A lead line at 3262.353 Å was compared with the silver line at 3280.683 Å. The densities of these lines and the background adjacent to each line were determined with a Jarrell-Ash Comparator Microphotometer. For each analysis the reciprocals were obtained for the above recordings and they were converted to intensity values using the characteristic or emulsion curve, which was prepared by the use of a step sector. The background intensities were subtracted from the intensity of the silver and lead lines and the ratio $I_{Ag}-I_{B_{Ag}}/I_{Pb}-I_{B_{Pb}}$ was calculated. The amount of silver in per cent was determined from a previously prepared working curve, which was obtained by analyzing samples prepared by adding known amounts of silver oxide to fixed weights of Tri-State galena known to be low in silver.

The development procedure was held rigidly constant. The photographic plates were all developed in Eastman D-19 developer for a period of four minutes at 70° Fahrenheit under continuous mechanical agitation in a tray type container. After a thirty minute rinsing in water, they were placed in rapid liquid fixer for ten minutes, and then washed in running water for thirty minutes. The use of an internal standard minimizes deviations from constant development procedure.

The effects of reversal or self-absorption are negligible when the line used as an internal standard has an intensity less than 10% of the intensity of the strongest line involving the ground state of the atom. The intensity of the Pb 3262.353 internal standard line used in this investigation was much less than the most sensitive and strongest lead line, Pb 4057.820. The intensity of the Pb 4057.820 line is 2000 and the intensity of the Pb 3262.353 line averages about 20.[314]

For best results the element to be determined and the internal standard should have similar ionization potentials. Trace element

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[314] George Russell Harrison, Massachusetts Institute of Technology Wavelength Tables, John Wiley and Sons, Inc., New York, 429 pp., 1939.

silver and the internal standard lead utilized in this investigation have ionization potentials which are very similar. The ionization potential of silver is 7.54 volts and that of lead is 7.38 volts. If sufficient voltage is used the differences in ionization potential become less important.

Each sample was run at least three times to insure reproducibility and minimize possible sources of error.

Sphalerite

The sphalerite samples were spectrographically analyzed by the complete volatilization method in contrast to the galena samples which were analyzed by the use of an internal standard. Clean cleavage fragments of sphalerite were ground by the writer to minus 100 mesh to provide samples of more than 50 milligrams and these were sent to Mr. J. S. Bryson at the research department of the Eagle-Picher Company at Joplin, Missouri, who made the spectrographic analyses.

Fifty milligrams of the sample powder was mixed with fifty milligrams of spectrographically pure graphite powder in a clean agate mortar. Duplicate samples of forty milligrams each of the mix were placed into crater type anodes of highest purity graphite. The cathode, 1.5 inch by 1/8 inch, was highest purity graphite.

The sample was completely volatilized in a 10 ampere d.c. arc at 300 volts across a 3 millimeter gap. Eastman SA no. 1 film was exposed to 8% of the total light. The spectrum range used was from 2300 Å to 4500 Å.

The film was processed under standarized conditions, and the Ge 2651.2 Å, Ga 2943.6 Å, Cd 3261.1 Å and Pb 2833.1 Å lines were measured photometrically and compared directly with standarized materials.

Standards of ten different concentrations were prepared for the elements Ag, Al, Ca, Cr, Cu, Fe, In, Mg, Mn, Si and Ti. Selected lines for these elements were assigned values from one through ten. A value of one was assigned to a line which was barely visible and a value of ten to a wide and very dense line. A concentration-density chart was constructed which was based upon known concentrations of those elements. The selected lines for those elements in the sphalerite samples were assigned values from one to ten and the concentrations of those elements were read from the chart. The lines selected for those elements were: Ag 3281.7 Å, Al 3082.2 Å, Ca 3933.7 Å, Cr 4254.3 Å, Cu 3247.5 Å, Fe 3020.6 Å, In 3256.1 Å, Mg 2852.1 Å, Mn 2794.8 Å, Si 2881.6 Å, and Ti 3372.8 Å.

MODE OF OCCURRENCE

Trace elements may occur in minerals due to solid solution, as adsorbed elements, as constituents of separate solid mineral phases, and as constituents of fluid inclusions. Since care was taken to select material which exhibit only one phase under the microscope, the trace elements of interest in this study probably occur mainly in solid solution.

Although the consideration of ionic radii and the 15% rule of Goldschmidt[315] have allowed predictions as to the likelihood of solid solutions of certain trace elements in oxide and silicate minerals, the same has not always held true for the sulfide minerals. This discrepancy probably is due largely to the fact that the bonding in the sulfides, in contrast to that of the oxides and silicates, is mostly of a covalent nature.[316] Goldschmidt[317] suggested that tetrahedral covalent radii be used in studying the mode of occurrence of guest elements in the sphalerite structure. If the tetrahedral oovelent radii as given by Pauling[318] may be used, then it is possible to

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[315] V. M. Goldschmidt, Geochemistry, Oxford Univ. Press, London, 730 pp., 1954.

[316] Linus Pauling, The Nature of the Chemical Bond, 3d Ed., Cornell Univ. Press, Ithica, N. Y., 1960, p. 442.

[317] Goldschmidt, op. cit., p. 267.

[318] Pauling, op. cit., p. 246.

evaluate the likelihood of the presence of an element as a diadochic solid solution in the sulfide minerals.

The principal trace elements studied in this work were: germanium, gallium, cadmium and indium in sphalerite; and silver in galena. No independent minerals of these elements were observed megascopically or in polished surfaces of samples submitted for spectrographic analysis.

Ag, Al, Ca, Cr, Cu, Fe, Mg, Mn, Pb, Si, and Ti also were detected in sphalerite, but were not used for zoning studies due to their presence as contaminants. In galena: Al, Ca, Cr, Cu, Fe, Mg, Sb, Si, Sn, V and Zn were detected in preliminary runs, but were either considered present as contaminants or present in too few samples to be of value in a study of zoning.

Silver

Silver is present in all galenas, but in the Tri-State galenas, the amount of silver is very small, measured in parts per million. The silver content of galena has been variously ascribed to mechanical mixtures of silver-bearing minerals, such as, argentite, tetrahedrite, and matildite ($AgBiS_2$); or to a solid solution of silver in galena. Because galenes rich in silver are also often rich in bismuth, matildite in particular has been thought to hold the silver detected in galena. Since bismuth was not detected in Tri-State galena samples, and since silver-bearing minerals were not detected in polished sections of Tri-State galenas, silver does not occur as a mechanical mixture of some silver-bearing mineral in galena.

Goldschmidt[319] believed that silver is captured in galena between the four nearest sulfur atoms. This is suggested by the fact that the distance between the center of each tetrahedral interstice and the center of each sulfur atom is 2.57 Å, and that the interionic distance between silver and sulfur, corrected for tetrahedral coordination and polarization of the ions, is 2.43 Å, which is close to the value 2.57.

Therefore it would seem that silver may occur in galena either as a diadochic solid solution with lead, or as an interstitial solid solution in the tetrahedral interstices between four adjacent sulfur atoms, or in both positions.

Germanium

Germanium is found in the rare minerals argyrodite ($4Ag_2S.GeS_2$), germanite ($Cu_3(Fe,Ge)S_4$) and ultrabasite ($28(Pb,Fe)S.11(Ag,Cu)_2S.3GeS_2$ Sb_2S_3), according to Rankama and Sahama.[320] No germanium-bearing minerals were noted in polished surfaces of the Tri-State sphalerite examined by the present writer. Warren and Thompson[321] stated that

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[319] Goldschmidt, op. cit., p. 408.

[320] Kalvero Rankama and Th. G. Sahama, Geochemistry, Univ. of Chicago Press, Chicago, p. 734, 1949.

[321] H. V. Warren and R. M. Thompson, "Sphalerites from Western Canada", Econ. Geology, vol. 40, p. 322, 1945.

germanium may be present in sphalerite either as GeS or as an atomic dispersion of Ge. Because the tetrahedral covalent radii of germanium (1.22) and zinc (1.31) are less than seven per cent of one another, and because the amount of germanium in Tri-State sphalerite is less than 0.04 per cent, thus causing little strain in the sphalerite structure, the writer believes that germanium is present in sphalerite as a diadochic solid solution with zinc.

Cadmium

Cadmium may occur as the independent mineral greenockite (CdS). Tri-State sphalerite from upper strata may possess a visible coating of greenockite, but for this investigation clean cleavage fragments from the center of sphalerite crystals were selected for spectrographic analysis and greenockite was not observed megascopically or microscopically in specimens submitted for analysis. Since the difference in size of the tetrahedral covalent radii of cadmium (1.48) and zinc (1.31) is less than 13 per cent of the latter, and the amount of cadmium in Tri-State sphalerite is about one-half of one per cent, cadmium most likely occurs as an diadochic solid solution with zinc in sphalerite.

Gallium

Gallium was believed to be present in sphalerite as GaAs by Goldschmidt and Peters[322] due to their similar crystal structure and

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[322] V. M. Goldschmidt and Cl. Peters, "Zur Geochemie des Galliums", Nachr. Wiss. Gottingen, Math.-Physik. Klasse, III; Iv, p. 165, 1931.

face-centered tetragonal structure type and because the atomic diameter of indium exceeds the allowable 15 per cent. They noted that InSb has the same crystal structure, but that the atomic diameter exceeds 15 per cent. They suggest therefore that InSb may form only a very limited solid solution with sphalerite. Erametsa[328] noted that In^{3+} ions (0.92 kX) are similar to Zn^{2+} ions (0.83) in size and he suggested therefore that indium is captured in the sphalerite structure. If the tetrahedral covalent radii of indium (1.44) and zinc (1.31) are considered, it is seen that the difference between the two is less than ten per cent of the latter and also since the amount of indium in Tri-State sphalerite is only about 0.003 per cent, it is suggestive that indium may occur in sphalerite as a diadochic solid solution with zinc.

DISCUSSION OF RESULTS

Mineral Analyses

Preliminary analyses of galena detected the elements Ag, Al, Ca, Cr, Cu, Fe, Mg, Sb, Si and Zn. Of these elements Ag was found in all samples, exhibited a tendency to vary in concentration, and was believed not to be present in contaminant phases. Therefore Ag was selected for further study; these data are given in Table VIII.

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[328] Olavi Erämetsä, "Über die Verbreitung des Indiums in finnischen Mineralen und über seine Trennung von anderen Metallen", *Ann. Acad. Sci. Fennicae*, ser. A, vol. 51, no. 1, 1938, cited in Kalervo Rankama and Th. G. Sahama, *Geochemistry*, Univ. Chicago Press, Chicago, p. 725, 1949.

TABLE VIII

SPECTROGRAPHIC ANALYSES OF GALENA

Analysis No.	Sample No.	Location	Bed	Ag (p.p.m.)
1	278	Black Eagle mine	K	1.01
2	20	Big John mine	K	1.40
3	272	Tar Creek mine	E	1.52
4	275	Tar Creek mine	E	0.60
5	64	Grace B mine	M	1.18
6	9a	Gordon No. 3 mine	M	0.44
7	308	Royal mine	M	0.23
8	11	New York mine	R	0.75
9	307[1]	Grace Walker mine	K	1.28
10	42	Grace Walker mine	R	0.63
11	23	New York mine	R	0.51
12	306	Royal mine	M	0.54
13	1	Jay Bird mine	O	0.71
14	315a	Blue Goose No. 1 mine	G-H	0.89
15	315	Blue Goose No. 2 mine	M	0.67
16	315	Blue Goose No. 2 mine	N	1.37
17	315	Blue Goose No. 1 mine	O	0.43
18	10[1]	Anna Beaver mine	G-H	0.76
19	11[1]	New York mine	M	0.61
20	154	Kenoyer mine	M	0.57
21	60	St. Joe mine	G-H	0.35
22.	170	Netta mine	G-H	0.46
23	51	Netta mine	M	1.38
24	137	Whitebird mine	M	0.45
25	121	Crawfish mine	K	0.30
26	13a	John Beaver mine	O	0.83
27	10[2]	Netta White mine	K	1.38
28	174	Blue Goose No. 1 mine	O	0.53
29	179	Black Eagle mine	G-H	0.50
30	20[1]	Piokee mine	G-H	0.82
31	64	Grace B mine (duplicate of No. 5)	M	0.91
32	11[1]	New York mine (duplicate of No. 8)	R	1.14
33	308	Royal mine (duplicate of No.7)	M	0.51
34	154	Kenoyer mine	M	0.60
35	154	Kenoyer mine	M	1.37
36	60	St. Joe mine	G-H	0.40
37	60	St. Joe mine	G-H	0.56

TABLE VIII (continued)

Analysis No.	Sample No.	Location	Bed	Ag (p.p.m.)
38	60	St. Joe mine	G-H	0.28
39	309	Dump southeast of Picher field		0.59
40	204	Grace B mine	M	1.38
41	205	Grace B. mine	M	0.55
42	322	Sunflower mine	M	0.79
43	117	Hunt mine	M	1.41
44	45.15	Commonwealth mine	G-H	0.27
45	45.29	Lucky Jew mine	M	1.32
46	45.82	Oronogo mine		0.55
47	45.33	Miami, Okla.		0.58
48	45.41	Carterville, Mo.		0.68
49	45.108	Aurora, Mo.		1.20
50	96.24	Webb City, Mo.		1.33
51	1975	Granby, Mo.		1.00
52	180	Duenweg, Mo.		1.29
53	180	Duenweg, Mo.		0.97

The sphalerite samples were analyzed for Ag, Al, Ca, Cd, Cr, Cu, Fe, Ga, Ge, In, Mg, Mn, Pb, Si and Ti. Of these elements Ge, Ga, Cd and In were not present in contaminant phases. The spectrographic analyses for these four elements are given in Table IX. The spectrographic analyses for the remaining elements are given in Tables XI, XII and XIII in Appendix A.

Pink and gray dolomite were separated from five specimens and compared by qualitative spectrographic analysis to examine the relationship between trace element content and color of dolomite. No significant differences were detected between the pink and gray dolomite of each sample, except those differences believed due to contamination. The spectrographic analyses for dolomite are given in Table XIV, Appendix B.

Range of Trace Element Content

The range of trace element content in galena and sphalerite is given in Table X.

Accuracy

The average difference in determinations for duplicate samples is about 0.2 p.p.m. for silver in galena, 2.5 p.p.m. for germanium in sphalerite, 60 p.p.m. for gallium in sphalerite, 2000 p.p.m. for cadmium in sphalerite, and 5 p.p.m. for indium in sphalerite. The small range of values and the high analytical error in determinations of cadmium and indium makes the use of these elements of doubtful value in distribution studies.

TABLE IX

SPECTROGRAPHIC ANALYSES OF SPHALERITE

Analysis No.	Sample No.	Location	Bed	P.P.M.			
				Ge	Ga	Cd	In
182	62	Netta mine	M	36	200	5000	<10
183	16	Lucky Bill mine	M	30	200	5000	<10
184	277	Black Eagle mine	K	200	400	5000	<10
185	20	Big John mine	E	33	22	5000	<10
186	32	Lucky Jew mine	M	94	140	5000	<10
187	2	Jay Bird mine	O	37	15	5000	<10
188	92	Kenoyer mine	M	95	350	5000	<10
189	8_1	Lawyers Chicago No. 2 mine	M	52	130	5000	<10
190	63	Grace B mine	M	100	200	6000	<10
191	176	Hum-Bah-Wa-Tah mine	O	100	150	4000	<10
192	7_0	Webber mine	M	130	30	4000	<10
193	315	Blue Goose No. 1 mine	G-M	54	400	6000	<10
194	315	Blue Goose No. 2 mine	M	120	170	5000	<10
195	315	Blue Goose No. 2 mine	M	66	280	6000	<10
196	148	Blue Goose No. 1 mine	Ch.	40	260	6000	<10
197	307	Grace Walker mine	K	35	220	6000	<10
198	305	Royal mine	M	80	140	6000	<10
199	27	New York mine	R	60	62	6000	<10
200	269	Tar Creek mine	E	150	320	6000	<10
201	121	Crawfish mine	K	100	70	4000	<10
202	137	Whitebird mine	M	60	200	5000	<10
203	13b	Cardin Townsite mine	M	38	130	6000	<10
204	10_1	Anna Beaver mine	G-M	120	400	6000	20
205	214	Jarrett mine	M	44	30	5000	<10
206	298	Barr mine	M	30	170	5000	<10
207	8	Gordon No. 3 mine	M	30	36	6000	<10
208	276	Tar Creek mine	E	250	480	6000	<10

TABLE IX (continued)

Analysis No.	Sample No.	Location	Bed	p.p.m.			
				Ge	Ga	Cd	In
209	18_0	Piokee mine	G-H	330	200	5000	<10
210	59	St. Joe mine	M	25	62	5000	<10
211	9_1	Lawyers Chicago No. 2 mine	M	50	380	5000	<10
212	159	Kenoyer mine	M	120	36	5000	<10
213	215	Jarrett mine	M	75	310	7000	20
214	216	Jarrett mine	M	40	150	6000	<10
215	63	Grace B mine	M	110	180	7000	<10
216	174	Hum-Bah-Wa-Tah mine	O	35	200	6000	<10
217	175	Hum-Bah-Wa-Tah mine	O	35	150	7000	<10
218	298	Barr mine (duplicate of No. 206)	M	35	250	7000	10
219	9_1	Lawyers Chicago No. 2 mine (duplicate of No. 211)	M	50	430	6000	<10
220	280	Black Eagle mine	G-H	200	170	7000	<10
221	13a	John Beaver mine	O	60	75	7000	<10
222	10_2	Netta White mine	K	90	320	5000	30
223	243	Grace B mine	M	43	17	7000	<10
224	170	Netta mine	G-H	320	320	6000	<10
225	11_2	Kenoyer mine	M	28	150	6000	<10

TABLE X

RANGE OF TRACE ELEMENT CONTENT IN ORE MINERALS FROM THE PICHER FIELD

Element	Mineral	Ranges of Trace Element Content	
		Minimum	Maximum
Silver	Galena	0.2 p.p.m.	1.6 p.p.m.
Germanium	Sphalerite	25 p.p.m.	380 p.p.m.
Gallium	Sphalerite	15 p.p.m.	480 p.p.m.
Cadmium	Sphalerite	4000 p.p.m.	7000 p.p.m.
Indium	Sphalerite	10 p.p.m.	30 p.p.m.

Areal Distribution

The areal variations in the concentrations of silver in galena and Ge, Ga, Cd, and In in sphalerite were sought by plotting the concentrations on overlaysof a mine map of the Picher field. Circles were used for values obtained from galena and sphalerite taken from M bed or from lower beds. Solid dots were used for values obtained from specimens from the upper beds, as shown in Figures 76, 77, 78, and 79. This study showed that the trace elements in the galena and sphalerite of the Picher field do not exhibit pronounced areal zoning. Cadmium in sphalerite and silver in galena are slightly more abundant toward the edge of the Picher field. Germanium and gallium are somewhat more abundant in sphalerite at the northwestern edge of the Picher field, but these trends are not marked.

Vertical Distribution

The stratigraphic variations in the concentrations of silver, germanium, gallium, cadmium and indium were studied by plotting these values according to stratigraphic zone, as shown in Figures 80, 81, 82, and 83.

The variation in concentrations of these elements within each bed is large, and nearly as great as that between beds, although slightly higher values were obtained from the upper beds than from those from the lower beds.

The variation between duplicate determinations and the wide

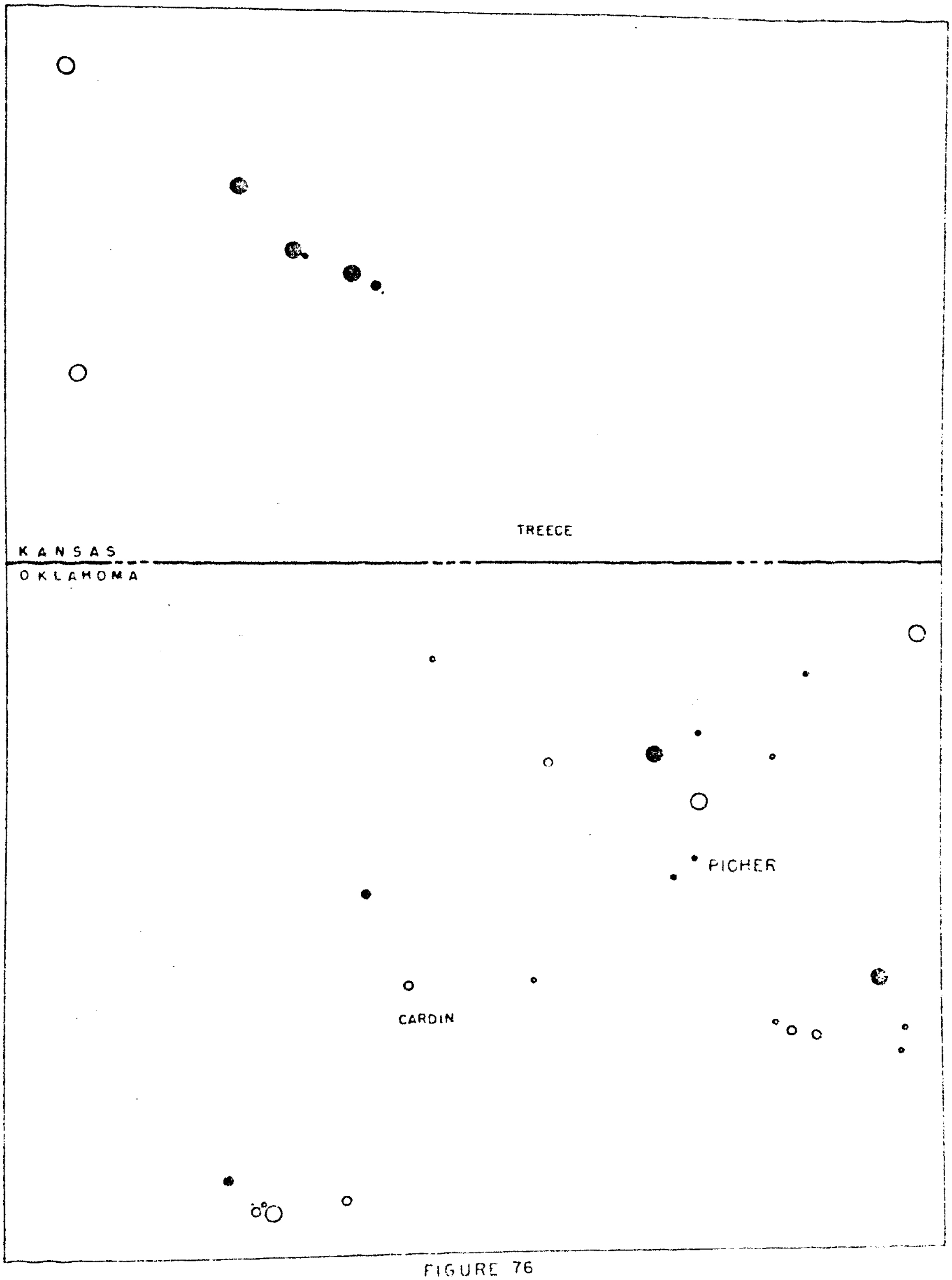

FIGURE 76

AREAL DISTRIBUTION OF SILVER IN GALENA

ABOVE M BED		M. BED AND BELOW
●	MORE THAN 1.0 PPM	○
●	0.6 TO 1.0 PPM	○
●	LESS THAN 0.6 PPM	○

SCALE 0 1/4 1/2 3/4 1
MILES

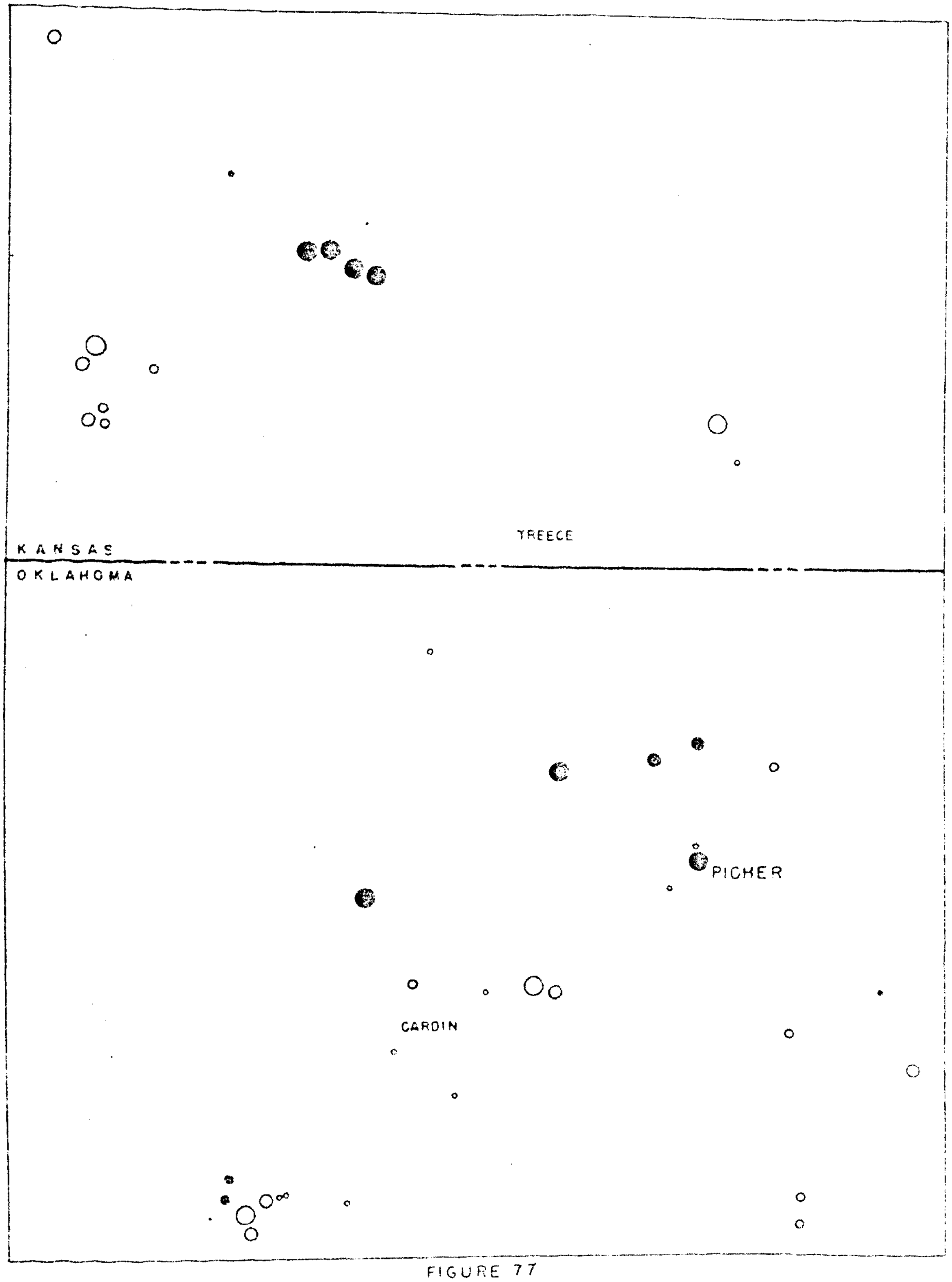

FIGURE 77

AREAL DISTRIBUTION OF GERMANIUM IN SPHALERITE

ABOVE M BED		M BED AND BELOW
●	100 TO 360 P P M	○
●	70 TO 100 P P M	○
●	40 TO 70 P P M	○
•	25 TO 40 P P M	○

SCALE 0 1/4 1/2 3/4 1
MILES

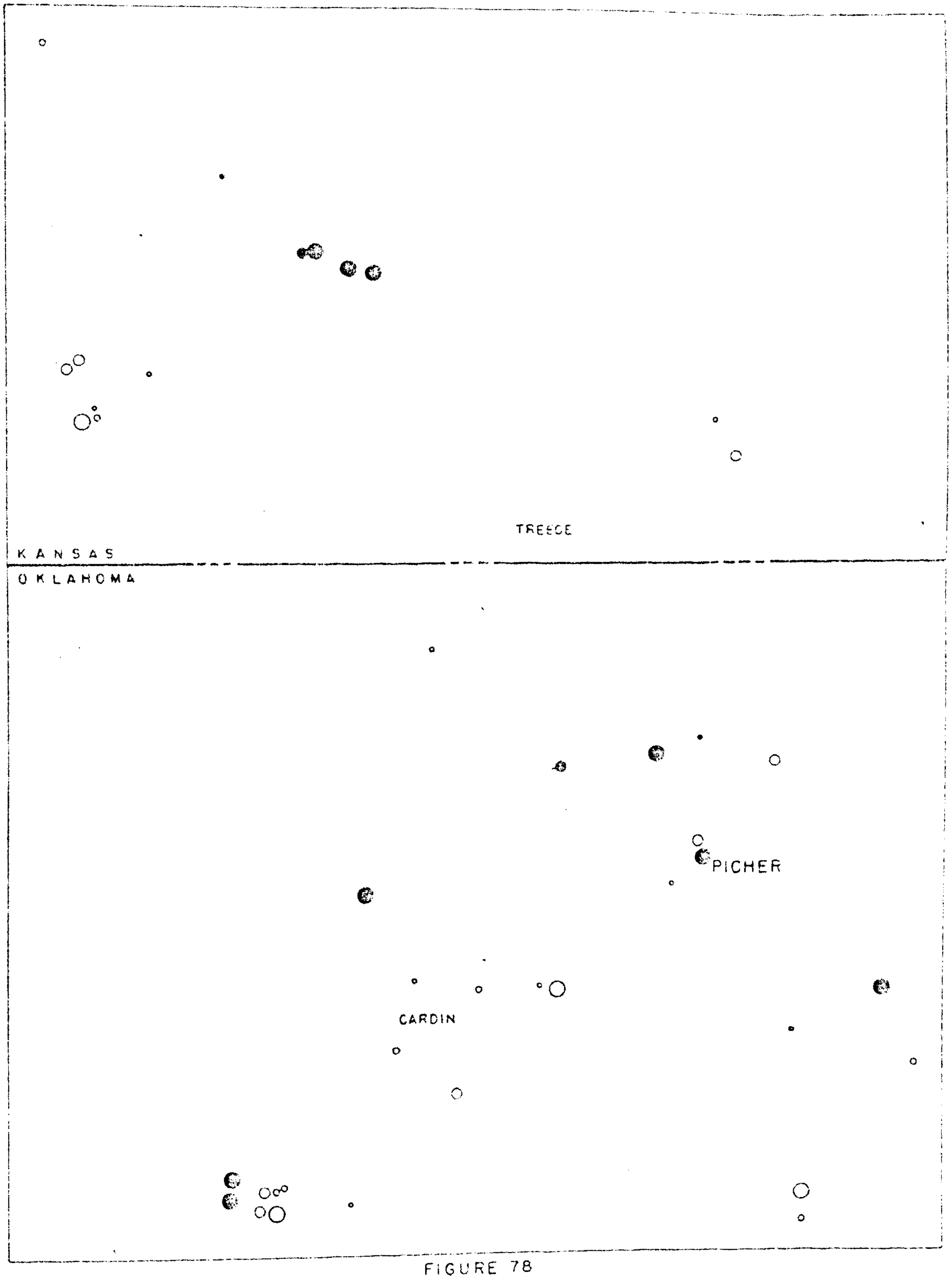

FIGURE 78

AREAL DISTRIBUTION OF GALLIUM IN SPHALERITE

ABOVE M BED		M BED AND BELOW
⬤	200 TO 480 P.P.M.	◯
●	150 TO 200 P.P.M.	○
•	75 TO 150 P.P.M.	◦
·	15 TO 75 P.P.M.	∘

SCALE 0 ¼ ½ ¾ 1
MILES

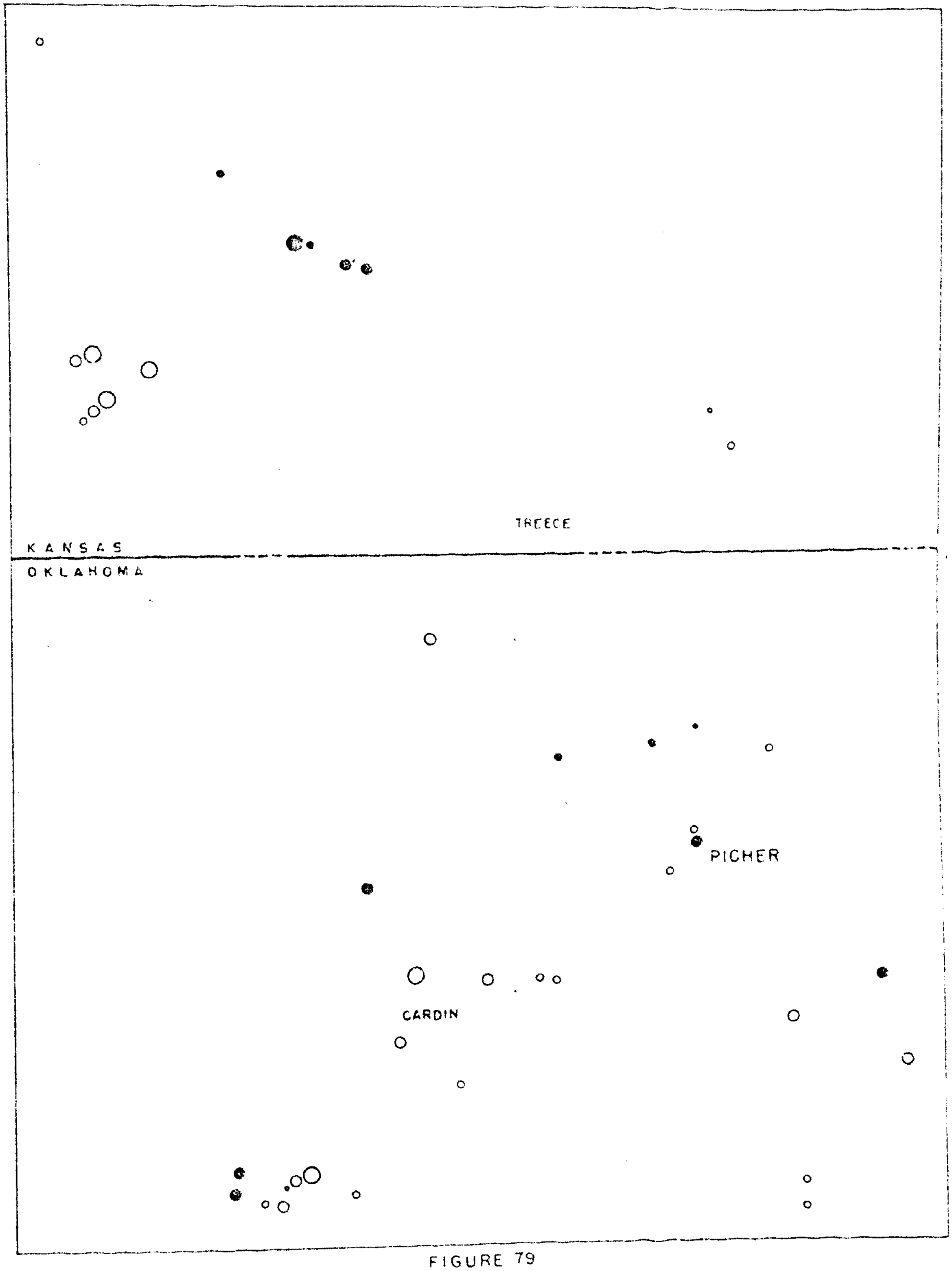

FIGURE 79

AREAL DISTRIBUTION OF CADMIUM IN SPHALERITE

ABOVE M BED		M BED AND BELOW
●	7000 P.P.M.	○
●	6000 P.P.M.	○
●	5000 P.P.M.	○
•	4000 P.P.M.	◦

SCALE 0 ¼ ½ ¾ 1 MILES

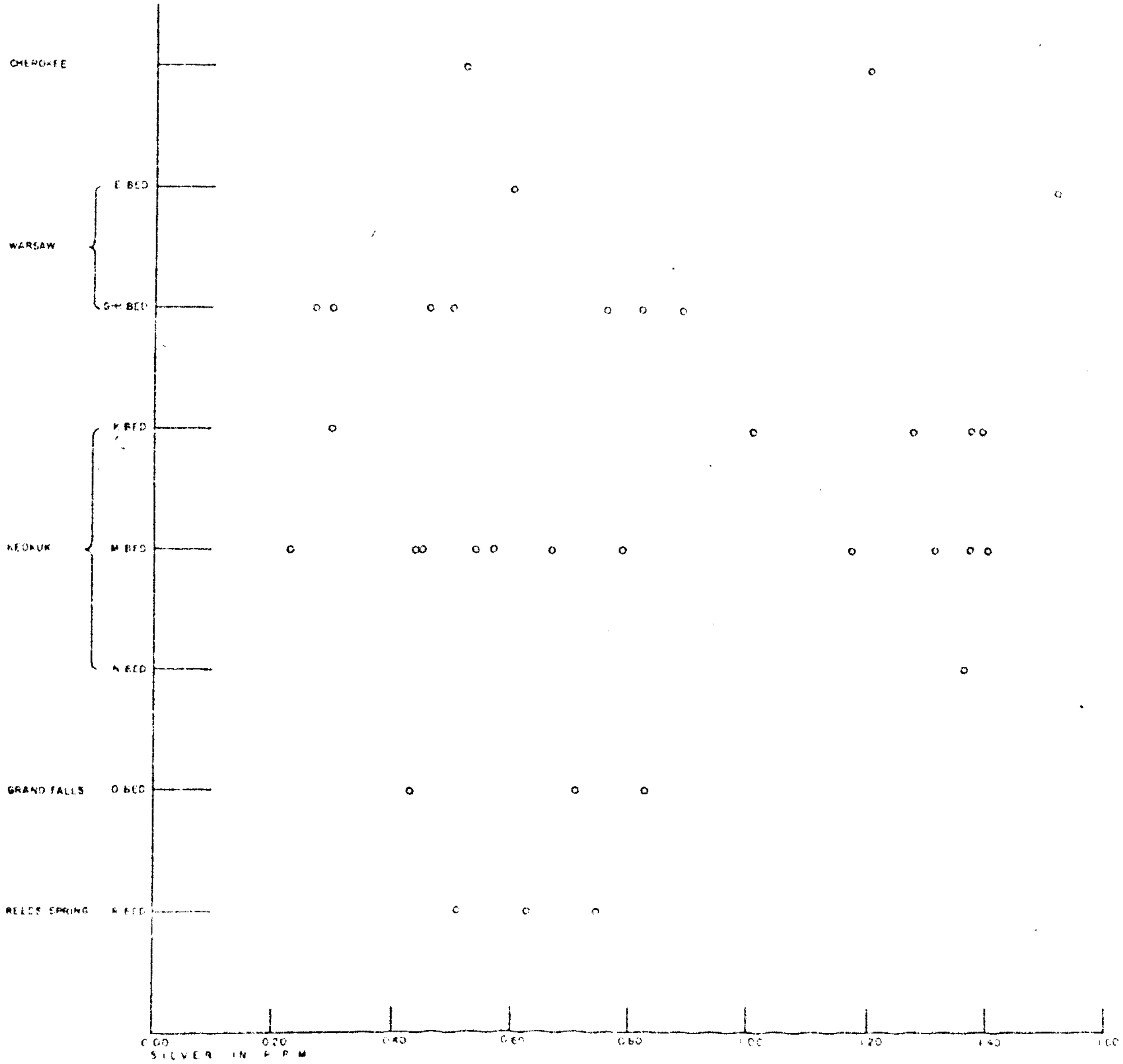

FIGURE 80
STRATIGRAPHIC DISTRIBUTION OF SILVER IN GALENA

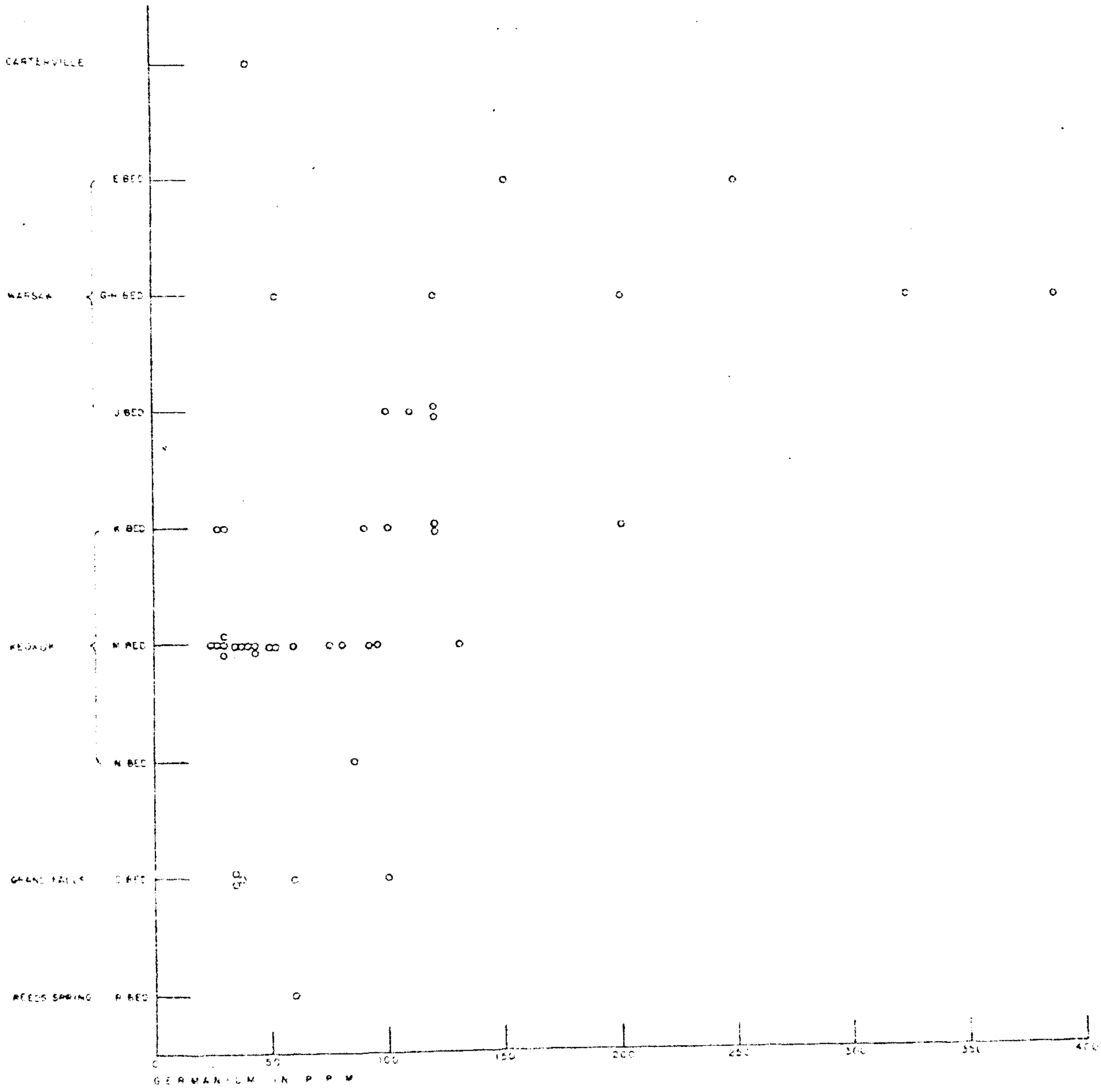

FIGURE 84

STRATIGRAPHIC DISTRIBUTION OF GERMANIUM IN SPHALERITE

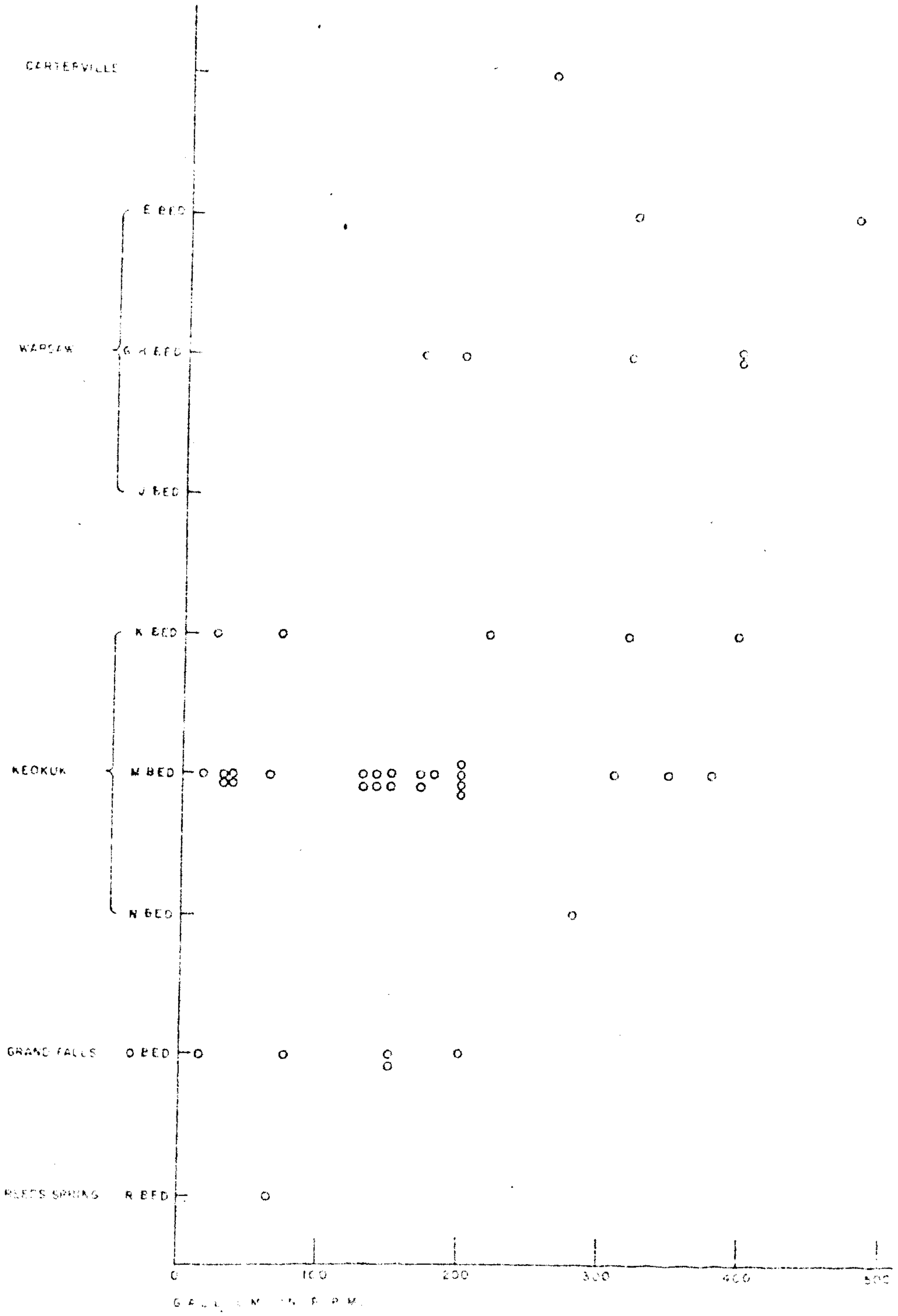

FIGURE 82

STRATIGRAPHIC DISTRIBUTION OF GALLIUM IN SPHALERITE

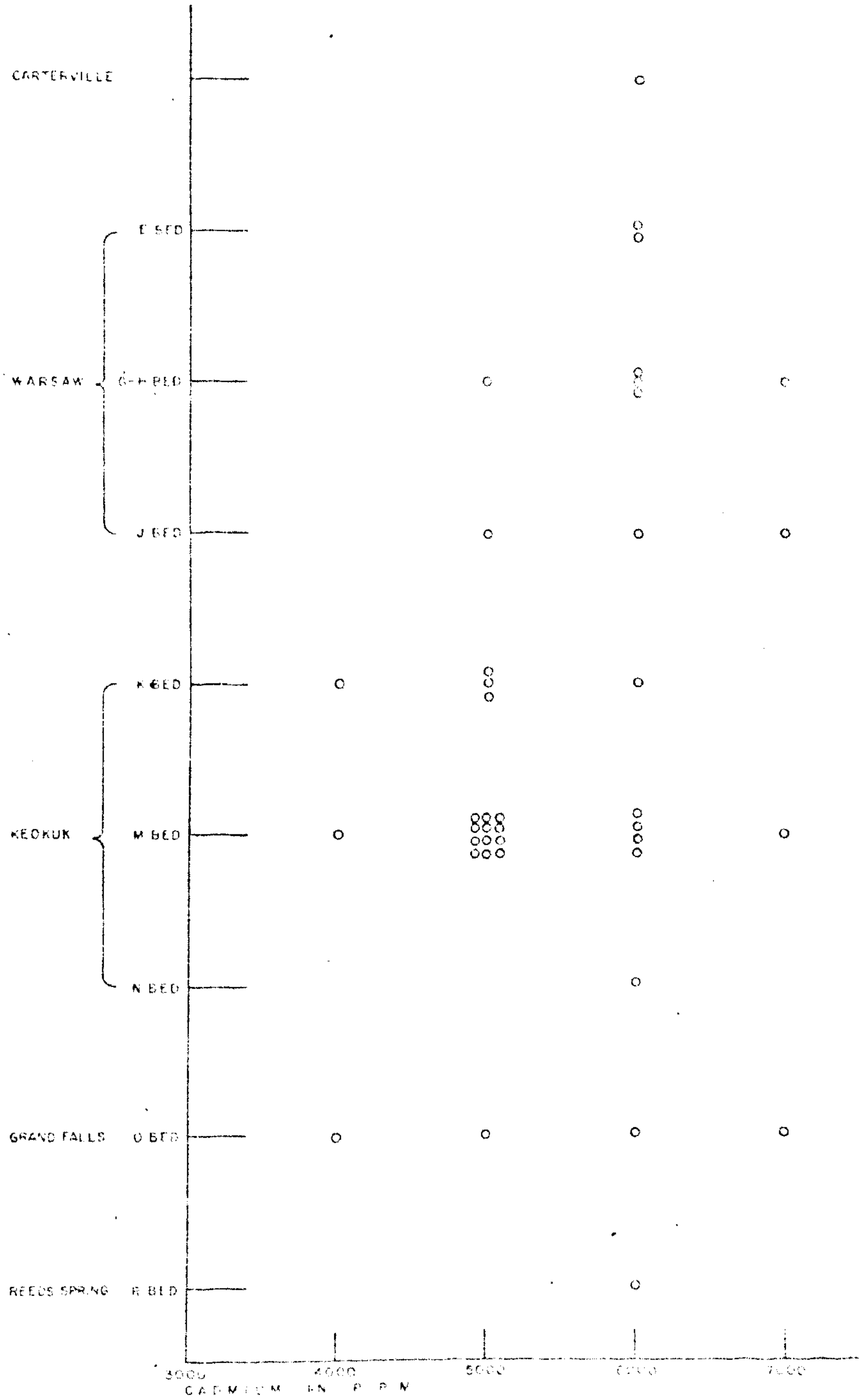

FIGURE 83

STRATIGRAPHIC DISTRIBUTION OF CADMIUM IN SPHALERITE spread of determinations for any given bed preclude any generalization regarding stratigraphic control of trace elements.

Relationship to Paragenesis

A study of trace element distribution with regard to paragenetic position of sphalerite was undertaken. The germanium content and gallium content of early yellowish-brown sphalerite, later brown sphalerite and late red sphalerite are shown in Figures 84 and 85. The range of values for sphalerite of each color is great and no correlation seems to exist between trace element content and paragenetic position of the sphalerite.

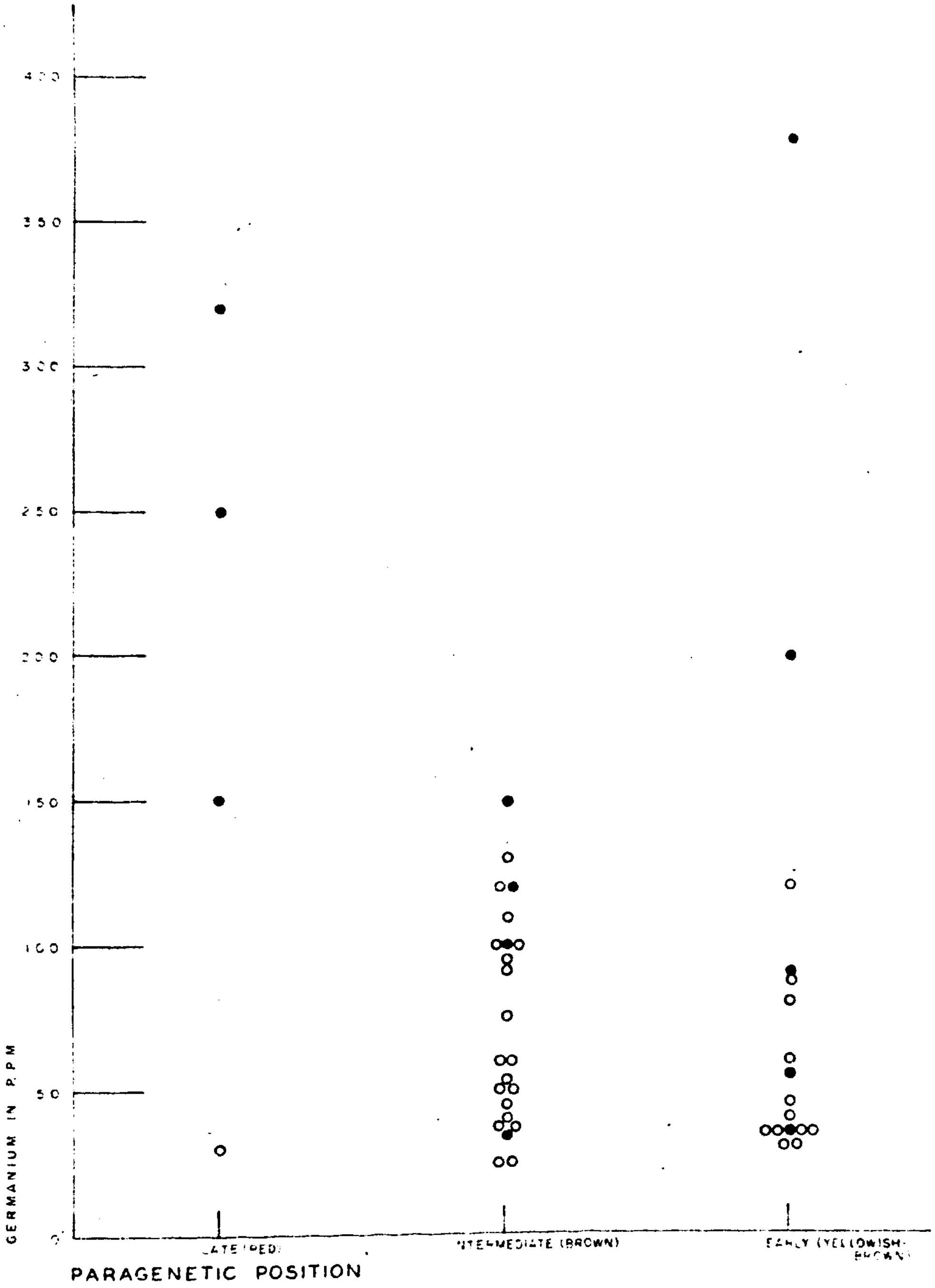

FIGURE 84
PARAGENETIC DISTRIBUTION OF GERMANIUM IN SPHALERITE

○ M BED AND BELOW ● ABOVE M BED

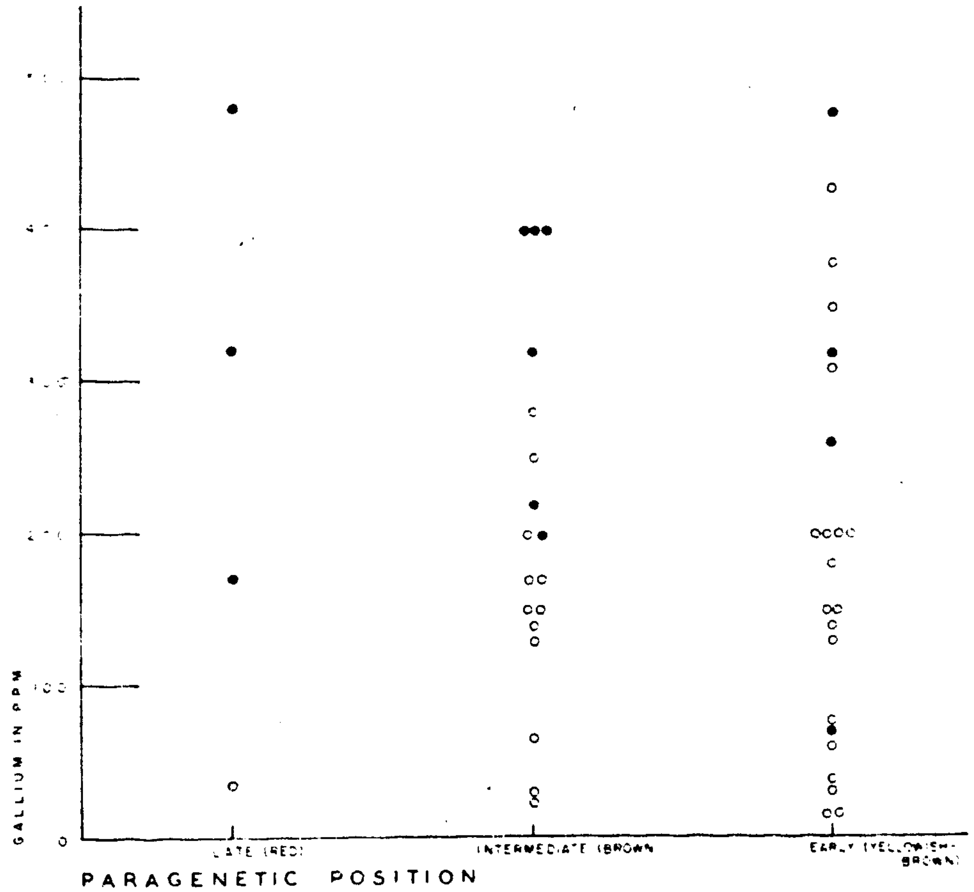

FIGURE 85

PARAGENETIC DISTRIBUTION OF GALLIUM IN SPHALERITE

○ M BED AND BELOW ● ABOVE M BED

CHAPTER VI

CONCLUSIONS

Underground observations in 37 mines, binocular examination of over 2000 hand specimens, petrographic and mineralographic study of 60 thin sections and 110 polished surfaces and spectrographic determinations of the trace element content of 53 carefully selected galena and 44 sphalerite samples have permitted the writer to acquire a detailed knowledge of the mineralogy of Tri-State ore, to determine the paragenesis of its minerals, the distribution of its trace elements and to offer some ideas regarding its genesis.

MINERALOGY

Fifty-one minerals are known to occur in Tri-State ores. Three of these minerals, bornite, jarosite and starkeyite are listed here for the first time. The presence of glauconite, covellite and organic matter about which there had been some doubt in Joplin ores were confirmed during the course of this study.

The textural relationships between the various minerals have been studied in detail and some relationships are recorded here for the first time: 1) pyrite spheres coated by radial marcasite and pyrite, 2) geopetal fabrics of pyrite and sphalerite in banded jasperoid, 3) intimate intergrowths of pyrite and marcasite with chalcopyrite, 4) sphalerite veining chalcopyrite, 5) repetitive deposition of sphalerite in stalactitic marcasite, 6) bornite and covellite veining chalcopyrite and marcasite.

Mineral relationships previously believed to be lacking in Tri-State ores but observed and described by the writer are: 1) complete coatings of marcasite over galena, 2) chalcopyrite over sphalerite, 3) pyrite over chalcopyrite, and 4) chalcopyrite inclusions in sphalerite.

Mosaic breccias and intraformational breccias underlain and overlain in some places by undisturbed horizontal beds are illustrated and described. Alteration of chert nodules and fragments, and two ages of color banding in some cherts were also illustrated and described. Some chert pebbles in the Carterville conglomerate were discovered to exhibit breccia fragments cemented by chert. Other textural relationships between Tri-State minerals as seen underground, in hand specimens, and under the microscope have been abundantly illustrated.

PARAGENESIS

As a result of this detailed study of interrelationships of the minerals in Tri-State ore, their general paragenetic sequence has been worked out and presented in Figure 72. Local deviations from this general sequence have been noted and recurrence of crystallization of many of the minerals was found to be more frequent than previously believed. Chalcopyrite and pyrite have been found to have been deposited at 8 different intervals, sphalerite and marcasite at least during 6, galena and quartz at least during 5.

Although earlier geologists noted the tendency of galena to crystallize before sphalerite in the eastern part of the Tri-State district and the reverse to be true in the Picher field, a strong tendency toward a systematic variation of paragenetic sequence with either geographic or stratigraphic position is lacking. The abundance of certain minerals, like well crystallized quartz and enargite, and the paucity of other minerals, like dolomite, in some areas appear to be local variants without great genetic significance.

The writer has discovered at least 7 cycles of repetitive mineralization in the Tri-State district. Each is characterized by its own paragenetic sequence. These cycles are marked by their own mineral suites and are separated from one another either by an intervening period of tectonic activity or solution, by a hiatus in deposition, or simply by the recurrent crystallization of earlier formed minerals. These seven cycles are:

1. Mississippian Sedimentation.
2. Pennsylvanian Sedimentation.
3. Disseminated epigenetic meteoric mineralization.
4. Main fracture-filling and vug-filling epigenetic meteoric mineralization.
5. Solution and redeposition or minor sulfide deposition.
6. Further solution and redeposition or minor sulfide deposition.
7. Present-day solution and redeposition of sulfides.

In a further attempt to discover some variation in mineralization in the Tri-State district either in regard to space or to time, the trace element content of the principal ore minerals, galena and sphalerite was studied. Of the 27 trace elements known to be present in these minerals, only silver in galena, and cadmium, gallium, germanium and indium in sphalerite were found to be persistent enough and in sufficient quantity to permit a study of variance. In galena the quantity of Ag varies from .2 to 1.6 p.p.m.; in sphalerite Cd varies from 4000 to 7000 p.p.m., Ga varies from 15 to 480 p.p.m., Ge varies from 25 to 380 p.p.m., and In varies from 10 to 30 p.p.m. Plots of the abundance of these trace elements with respect to areal, stratigraphic and paragenetic position failed to reveal any striking trend in the variation of these constituents.

THE CHARACTER OF THE ORE-FORMING SOLUTIONS

The mineralogy of the Tri-State district permits certain inferences to be drawn in regard to the genesis of the ore. The close association and intergrowth of certain mineral pairs, such as, calcite and marcasite, pyrite and marcasite, and sphalerite and wurtzite would seem to indicate that the pH of the ore solutions, while variable, never was far from 7. The numerous recurrences of the common minerals in the paragenetic sequence suggests that the character of the ore solutions, as defined by pH, Eh and concentration, fluctuated but never was far removed from an average value. The presence of organic matter and the presence of the sulfides themselves, suggest that the Eh of the solutions was negative.

The variation in paragenetic sequence and trace element content of galena and sphalerite throughout the Tri-State district indicates that the nature of the ore-forming solutions varied not only through time but also from place to place throughout the district. The lack of definite zoning indicates that the character of the ore-forming solutions was nearly the same throughout the district.

The numerous recurrences of the major minerals in the paragenetic sequence and the non-uniform variations in the trace element content of sphalerite and galena would be expected in ores formed from downward-moving, cold meteoric waters, but would be less likely to result from an upward-moving, cooling, hydrothermal solution.

The writer concludes that the ores were formed from ore-bearing solutions which were nearly the same throughout the district and not very different from the ground water of the area as it exists today, for the period of sulfide deposition still is going on at the present time.

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APPENDIX A

TABLE XI

SPECTROGRAPHIC ANALYSES OF SPHALERITE

Analysis No.	Sample No.	Location	Bed	p.p.m.				
				Si	Al	Ti	Mn	Cr
182	62	Netta mine	M	400	5	<10	<0.5	<3
183	16	Lucky Bill mine	M	400	5	<10	<0.5	<3
184	277	Black Eagle mine	K	500	10	<10	<0.5	<3
185	20	Big John mine	K	30000	100	<10	1	10
186	32	Lucky Jew mine	M	500	10	<10	<0.5	<3
187	2	Jay Bird mine	O	300	5	<10	<0.5	<3
188	9_2	Kenoyer mine	M	1000	5	<10	<0.5	<3
189	8_1	Lawyers Chicago No. 2 mine	M	500	5	<10	<0.5	<3
190	63	Grace B mine	M	300	5	<10	<0.5	<3
191	176	Nee-Bah-Wa-Tah mine	O	2000	20	<10	<0.5	<3
192	7_0	Webber mine	M	100	10	<10	<0.5	<3
193	315	Blue Goose No. 1 mine	G-H	2000	10	<10	<0.5	<3
194	315	Blue Goose No. 2 mine	M	50	20	<10	<0.5	<3
195	315	Blue Goose No. 2 mine	M	5000	20	<10	<0.5	<3
196	148	Blue Goose No. 1 mine	Ch.	3000	20	<10	<0.5	<3
197	307	Grace Walker mine	K	5000	30	<10	<0.5	<3
198	305	Royal mine	M	30000	100	80	5	<3
199	27	New York mine	R	3000	10	<10	1	<3
200	269	Tar Creek mine	E	10000	20	<10	<0.5	<3
201	121	Crawfish mine	K	5000	20	<10	<0.5	<3
202	137	Whitebird mine	M	300	10	20	<0.5	<3
203	13b	Cardin Townsite mine	M	5000	70	<10	<0.5	<3
204	10_1	Anna Beaver mine	G-H	5000	20	<10	1	<3
205	214	Jarrett mine	M	30000	100	30	<0.5	<3
206	298	Barr mine	M	3000	20	<10	0.5	<3
207	8	Gordon No. 3 mine	M	5000	50	<10	5	<3
208	276	Tar Creek mine	E	30000	50	<10	<0.5	<3

TABLE XI (continued)

Analysis No.	Sample No.	Location	Bed	p.p.m.				
				Si	Al	Ti	Mn	Cr
209	18_0	Pickee mine	G-H	30000	50	<10	1	<3
210	59	St. Joe mine	M	2000	50	<10	<0.5	<3
211	9_1	Lawyers Chicago No. 2 mine	M	1000	10	<10	<0.5	<3
212	159	Kenoyer mine	M	500	10	<10	<0.5	<3
213	215	Jarrett mine	M	5000	30	<10	1	<3
214	216	Jarrett mine	M	500	20	<10	0.5	<3
215	63	Grace B mine	M	500	10	<10	0.5	<3
216	174	Hum-Bah-Wa-Tah mine	O	30000	100	30	0.5	<3
217	175	Hum-Bah-Wa-Tah mine	O	10000	40	<10	0.5	<3
218	298	Barr mine (duplicate of No. 206)	M	3000	20	<10	1	<3
219	9_1	Lawyers Chicago No. 2 mine (duplicate of No. 211)	M	1000	10	<10	0.5	<3
220	280	Black Eagle mine	G-H	10000	50	20	0.5	<3
221	13a	John Beaver mine	O	30000	40	10	1	<3
222	10_2	Netta White mine	M	100	10	<10	<0.5	<3
223	243	Grace B mine	M	10000	200	<10	1	<3
224	170	Netta mine	G-H	10000	30	<10	<0.5	<3
225	11_2	Kenoyer mine	M	10000	50	10	<0.5	<3

TABLE XII

SPECTROGRAPHIC ANALYSES OF SPHALERITE

Analysis No.	Sample No.	Location	Bed	p.p.m. Fe	p.p.m. Cu	p.p.m. Pb	p.p.m. Ag
182	62	Netta mine	M	200	100	30	50
183	16	Lucky Bill mine	M	200	200	20	10
184	277	Black Eagle mine	M	200	200	20	10
185	20	Big John mine	K	200	80	20	10
186	32	Lucky Jew mine	M	100	100	20	30
187	2	Jay Bird mine	O	500	80	10	10
188	9_2	Kenoyer mine	M	500	200	10	1
189	8_1	Lawyers Chicago No. 2 mine	M	500	100	10	80
190	63	Grace B mine	M	500	100	20	2
191	176	Hum-Bah-Wa-Tah mine	O	100	100	400	1
192	7_o	Webber mine	M	1000	100	10	1
193	315	Blue Goose No. 1 mine	G-H	1000	400	10	2
194	315	Blue Goose No. 2 mine	M	1000	400	10	1
195	315	Blue Goose No. 2 mine	M	1000	400	20	5
196	148	Blue Goose No. 1 mine	Ch.	1000	400	10	2
197	307	Grace Walker mine	K	100	100	10	10
198	305	Royal mine	M	500	100	100	5
199	27	New York mine	R	500	100	10	5
200	269	Tar Creek mine	K	500	200	1000	2
201	121	Crawfish mine	K	500	100	10	2
202	137	Whitebird mine	M	1000	100	<10	1
203	13b	Cardin Townsite mine	M	1000	100	<10	1
204	10_1	Anna Beaver mine	G-H	1000	400	40	2
205	214	Jarrett mine	M	1000	80	<10	1
206	298	Barr mine	M	1000	100	<10	1
207	8	Gordon No. 3 mine	M	1000	80	10	2
208	276	Tar Creek mine	K	1000	400	60	2

TABLE XII (continued)

Analysis No.	Sample No.	Location	Bed	p.p.m. Fe	p.p.m. Cu	p.p.m. Pb	p.p.m. Ag
209	16_0	Pickee mine	G-R	1000	400	40	20
210	59	St. Joe mine	M	700	80	<10	0.5
211	9_1	Lawyers Chicago No. 2 mine	M	1000	200	30	2
212	159	Kenoyer mine	M	1000	100	20	2
213	215	Jarrett mine	M	1000	200	30	5
214	216	Jarrett mine	M	1000	200	20	5
215	63	Grace B mine	M	1000	200	20	5
216	174	Hum-Bah-Wa-Tah mine	O	1000	200	200	1
217	175	Hum-Bah-Wa-Tah mine	O	700	100	10	1
218	298	Barr mine (duplicate of No. 206)	M	700	200	10	1
219	9_1	Lawyers Chicago No. 2 mine (duplicate of No. 211)	M	700	200	30	0.5
220	280	Black Eagle mine	G-R	700	200	20	1
221	13a	John Beaver mine	O	1000	100	200	0.5
222	10_2	Netta White mine	K	1000	400	10	0.5
223	243	Grace B mine	M	3000	100	10	1
224	170	Netta mine	G-R	1000	400	400	10
225	11_2	Kenoyer mine	M	1000	100	<10	0.5

TABLE XIII

SPECTROGRAPHIC ANALYSES OF SPHALERITE

Analysis No.	Sample No.	Location	Bed	p.p.m. Ca	p.p.m. Mg
182	62	Netta mine	M	100	40
183	16	Lucky Bill mine	M	100	40
184	277	Black Eagle mine	K	100	40
185	20	Big John mine	K	300	200
186	32	Lucky Jew mine	M	100	30
187	2	Jay Bird mine	O	100	10
188	9_2	Kenoyer mine	M	100	20
189	8_1	Lawyers Chicago No. 2 mine	M	100	50
190	63	Grace B mine	M	100	30
191	176	Hum-Bah-Wa-Tah mine	O	100	30
192	7_0	Webber mine	M	200	10
193	315	Blue Goose No. 1 mine	G-H	200	10
194	315	Blue Goose No. 2 mine	M	200	10
195	315	Blue Goose No. 2 mine	N	200	30
196	148	Blue Goose No. 1 mine	Ch.	1000	30
197	307	Grace Walker mine	K	300	50
198	305	Royal mine	M	30000	100
199	27	New York mine	R	1000	100
200	269	Tar Creek mine	E	400	30
201	121	Crawfish mine	K	300	40
202	137	Whitebird mine	M	100	20
203	13b	Cardin Townsite mine	M	300	70
204	10_1	Anna Beaver mine	G-H	5000	200
205	214	Jarrett mine	M	600	70
206	298	Barr mine	M	600	70
207	8	Gordon No. 3 mine	M	50000	700
203	276	Tar Creek mine	E	400	40

TABLE XIII (continued)

Analysis No.	Sample No.	Location	Bed	p.p.m.	
				Ca	Mg
209	18_o	Piokee mine	G-H	400	40
210	59	St. Joe mine	M	1000	40
211	9_1	Lawyers Chicago No. 2 mine	M	400	70
212	159	Kenoyer mine	M	600	70
213	215	Jarrett mine	M	400	20
214	216	Jarrett mine	M	300	20
215	63	Grace B. mine	M	200	7
216	174	Hum-Bah-Wa-Tah mine	O	600	40
217	175	Hum-Bah-Wa-Tah mine	O	300	10
218	298	Barr mine (duplicate of No. 206)	M	10000	100
219	9_1	Lawyers Chicago No. 2 mine (duplicate of No. 211)	M	300	70
220	280	Black Eagle mine	G-H	1000	50
221	13a	John Beaver mine	O	400	30
222	10_2	Netta White mine	K	200	5
223	243	Grace B mine	M	10000	200
224	170	Netta mine	G-H	400	10
225	11_2	Kenoyer mine	M	600	50

APPENDIX B

TABLE XIV

SPECTROGRAPHIC ANALYSES OF GRAY AND PINK DOLOMITE

pres. - present	f. tr. - faint trace
low - minor constituent	b.v. - barely visible
tr. - trace	n.d. - not detected

Element	Gray Dolo.	Pink Dolo.	Gray Dolo.	Pink Dolo.	Gray Dolo.	Pink Dolo.	Gray Dolo.	Pink Dolo.	Gray Dolo.	Pink Dolo.	Dolomite	% Oxide
	Big John mine		Grace B mine		Whitebird mine		Royal mine		Grace Walker mine		U. S. Bur. Std. No. 88	
Si	pres.	tr.	pres.	tr.	pres.	tr.	pres.	low	pres.	tr.	low	0.31
Al	low	b.v.	low	b.v.	low	b.v.	low	tr.	low	b.v.	tr.	0.67
Fe	low	low	low	low	low	low	low	low	low	low	tr.	0.084
Ti	b.v.	n.d.	tr.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.005
Mn	low	low	low	low	low	low	low	low	low	low	tr.	0.006
Na	b.v.	b.v.	tr.	b.v.	b.v.	b.v.	f.tr.	n.d.	b.v.	n.d.	b.v.	0.08
K	n.d.	n.d.	b.v.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.03
Cu	b.v.	f.tr.	f.tr.	f.tr.	b.v.	b.v.	tr.	tr.	b.v.	b.v.	tr.	
Zn	n.d.	n.d.	n.d.	n.d.	b.v.	b.v.	n.d.	n.d.	b.v.	n.d.	n.d.	
Pb	b.v.	f.tr.	b.v.	f.tr.	b.v.	b.v.	b.v.	f.tr.	f.tr.	b.v.	tr.	
V	b.v.	b.v.	f.tr.	n.d.	b.v.	b.v.	b.v.	b.v.	n.d.	n.d.	n.d.	
Ag	n.d.	n.d.	b.v.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	b.v.	
Ni	n.d.	n.d.	b.v.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	

Elements not detected in any of the five samples were: As, Ba, Bi, Co, Cr, Ge, Sb, Sn, Sr, Ta, W, Zr.

VITA

Richard Davis Hagni was born April 29, 1931 at Howell, Michigan. After being graduated from Howell High School in 1949, he entered Hope College, Holland, Michigan, but transferred to Michigan State University in 1951. He received his Bachelor of Science degree in geology from Michigan State University in 1953, and his Master of Science degree in geology from this same institution in 1954.

He was employed by the Jones and Laughlin Steel Corporation for geological investigations in northern Wisconsin, but in November 1954 he was drafted into the United States Army. After receiving an honorable discharge from the army in 1956 he joined the faculty of the Missouri School of Mines and Metallurgy, Rolla, Missouri, as part-time instructor in geology in order to continue graduate study leading to the degree of Doctor of Philosophy.

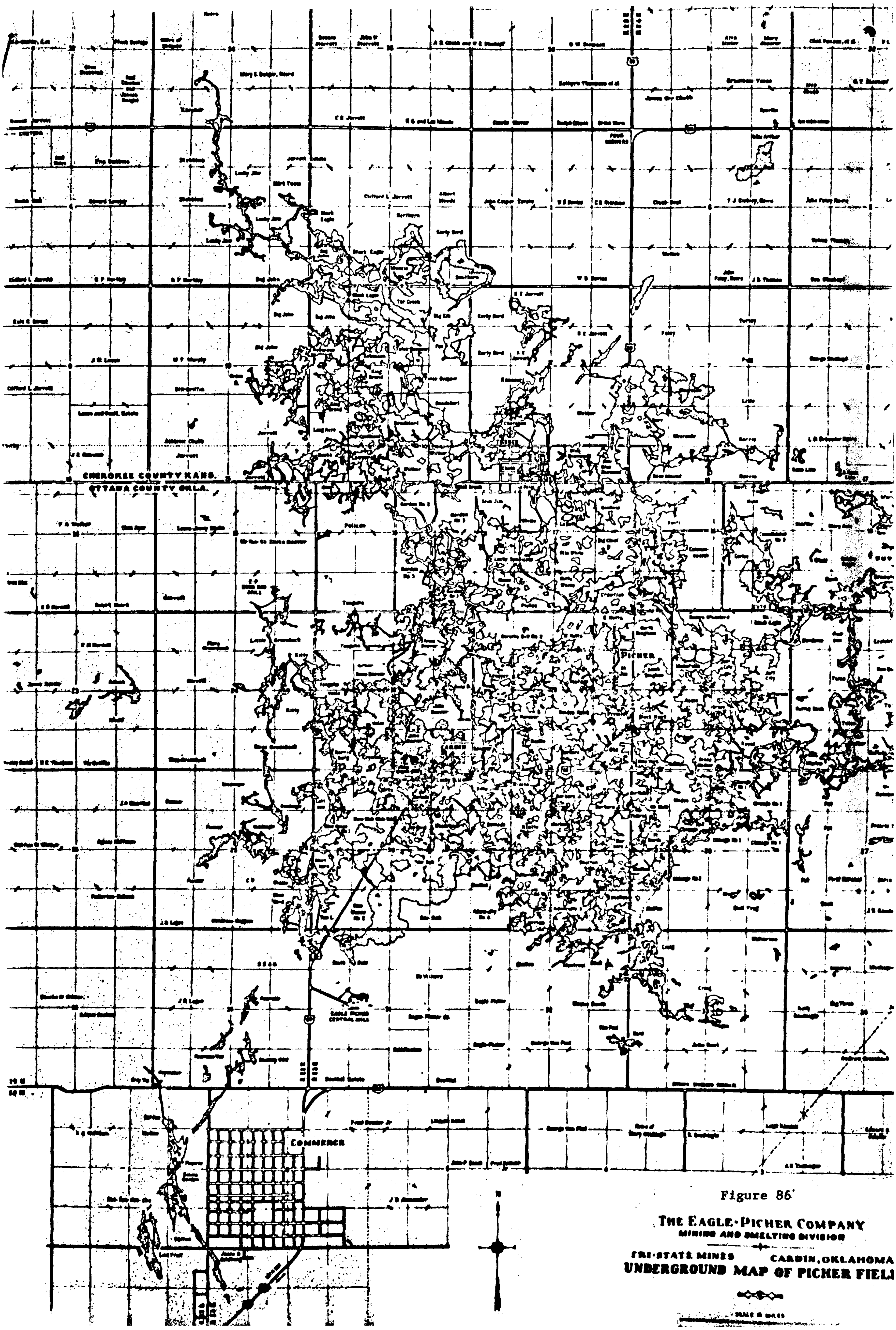
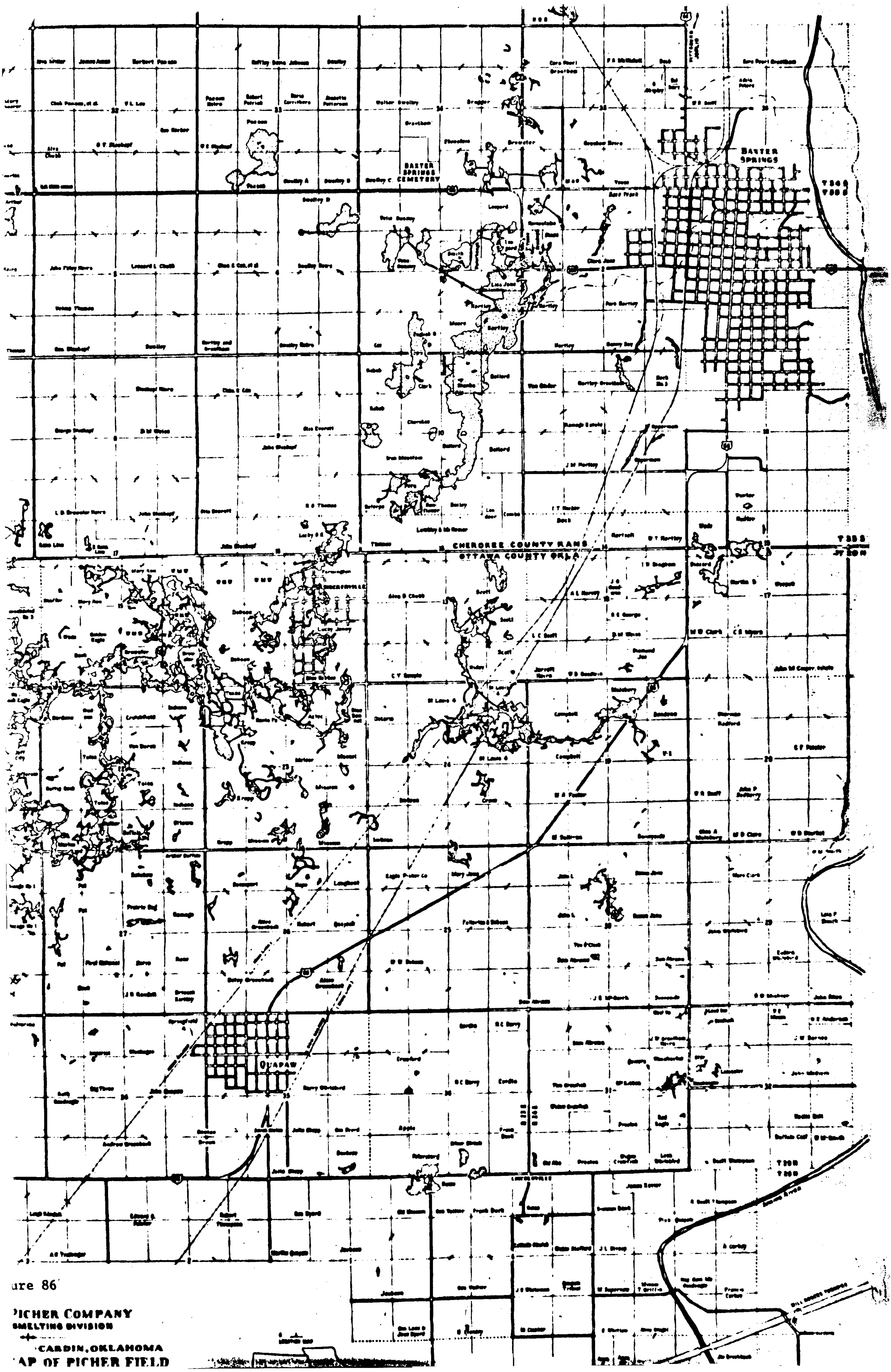
CHEROKEE COUNTY KANS.
OTTAWA COUNTY OKLA.
PICHER
CARDIN
COMMERCE
THE EAGLE-PICHER COMPANY
MINING AND SMELTING DIVISION
TRI-STATE MINES
CARDIN, OKLAHOMA
UNDERGROUND MAP OF PICHER FIEL

Figure 86


BAXTER SPRINGS
BAXTER SPRINGS CEMETERY
CHEROKEE COUNTY KANS
OTTAWA COUNTY OKLA
QUAPAW
ICHER COMPANY
SMELTING DIVISION
CARDIN, OKLAHOMA
AP OF PICHER FIELD

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