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MINERALOGY AND PARAGENESIS OF THE CAVE-IN-ROCK FLUORSPAR DISTRICT HARDIN COUNTY, ILLINOIS

By

DAESUK HAN

A

THESIS

submitted to the faculty of the

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MASTER OF SCIENCE IN GEOLOGY

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Approved by

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ABSTRACT

The paragenesis of minerals occurring in the bedding-replacement fluorspar ores in the Crystal, Minerva No. 1 and Hill mines in the Cave-in-Rock district, Hardin County, Illinois, has been studied by underground, binocular, petrographic and ore microscopic examination. More than 300 hand specimens were collected from the mines, 100 thin sections were prepared and 36 polished surfaces were examined to prepare paragenetic diagrams for the Crystal and Minerva No. 1 mines.

The minerals determined in the fluorspar ores were: fluorite, sphalerite, galena, chalcopyrite, pyrite, marcasite, calcite, strontianite, witherite, barite, quartz, dolomite, oil and bitumen. Most of these minerals are present both in disseminated form and as crystals deposited in vugs, but calcite, strontianite, witherite and barite were observed to be deposited from the ore solutions only in cavities.

The paragenetic sequence of minerals formed in the disseminated ores has a general similarity to that of the minerals formed in vugs, particularly in the Crystal mine, but there are important differences between the two sequences. The latter sequence includes some minerals which are not present in the earlier sequence, but it is especially characterized by repetitive generations of mineral deposition. The repetitive nature is believed to be controlled by slight variations in the chemistry of the ore solutions during deposition.

The paragenesis in the Minerva mine No. 1 differs from that of the Crystal mine by the occurrence of strontianite and witherite,

by the number of generations and by the presence of important local, late corrosion. These differences in mineralogy and paragenesis are believed to have resulted from slight areal variations in the chemical nature of the ore solutions.

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Chapter I

INTRODUCTION

A. Purpose of Investigation

The principal purpose of this investigation was to determine the depositional sequence of the minerals occurring in the bedding-replacement deposits of three selected mines in the Cave-in-Rock fluorspar district, Hardin County, Illinois. All of the minerals found in those mines were studied and described.

B. Location and Accessibility

The Cave-in-Rock fluorspar district is located on the north-eastern margin of the Illinois-Kentucky fluorspar field, in Hardin County, Illinois. The district is bounded on the south and east by the Ohio River and on the northwest by the Peters Creek fault zone (Figure 1).

Three mines were examined for this investigation: 1) the Crystal mine, 2) the Minerva mine No. 1, both operated by the Minerva Oil Company, and 3) the Hill mine, which is operated by the Ozark-Mahoning Company. The Minerva mine No. 1 and the Hill mine are located about 5 miles north of the town of Cave in Rock, the former in the SW 1/4 of Sec. 24, T. 11 S., R. 9 E., and the latter in the E 1/2 of Sec. 23, T. 11 S., R. 9 E. The Crystal mine lies approximately 5 miles northwest of the town, in the S 1/2 of Sec. 23, T. 11 S., R. 9 E.

The mines are reached by dirt roads leading from Illinois State Highways 1 and 146 which traverse the district. The nearest

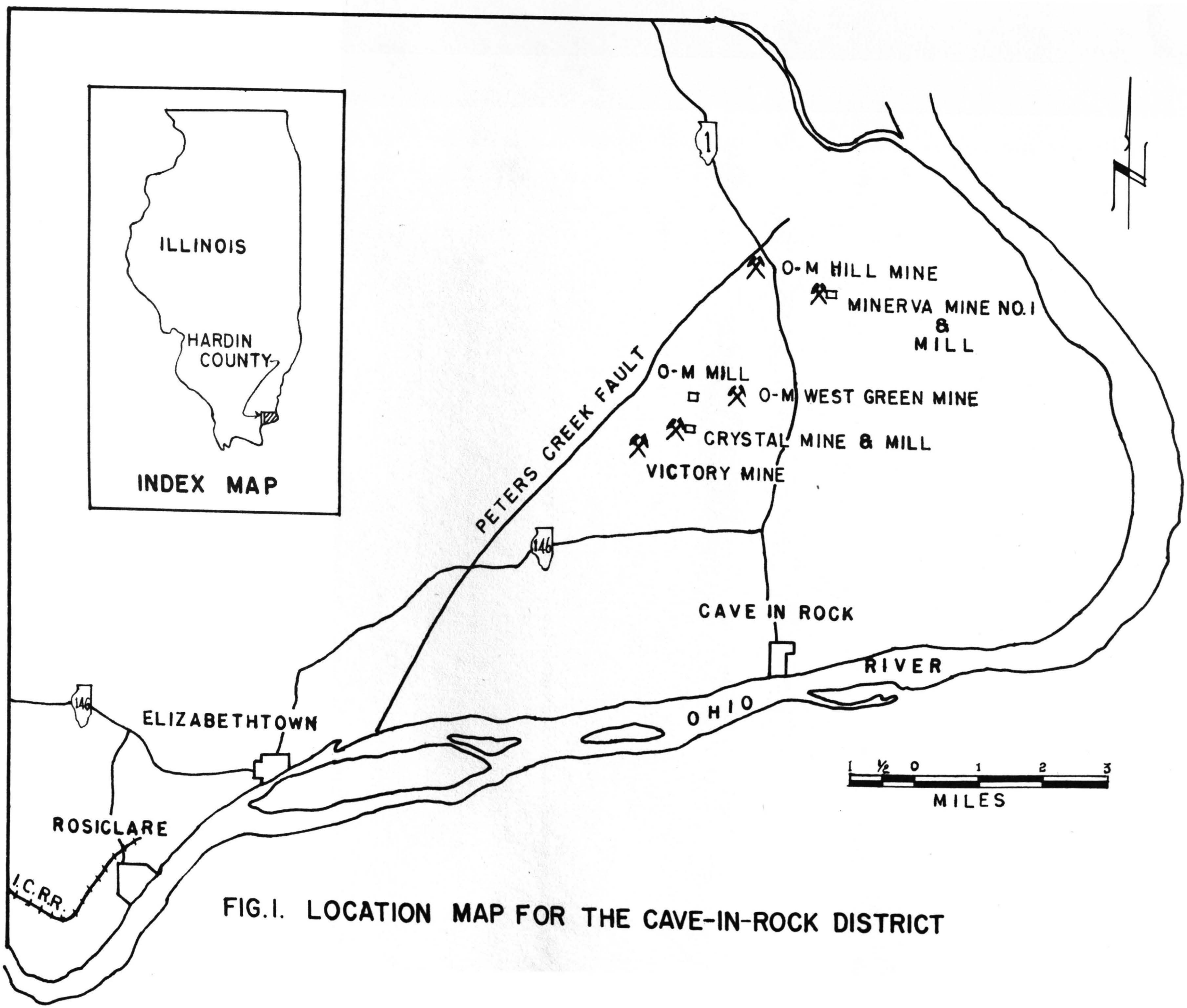

FIG.1. LOCATION MAP FOR THE CAVE-IN-ROCK DISTRICT

rail connection is available at Rosiclare, which is located about 15 miles southwest of the Crystal mine.

C. Field and Laboratory Work

A graduate field trip to the Crystal mine with Dr. Richard D. Hagni on April 2, 1965, brought to the writer's attention the need for the investigation of mineral paragenesis in selected mines in the fluorspar district. Subsequently, arrangements were made to study and collect from the Crystal, Minerva No. 1, and Hill mines. Several periods between June 1, 1965 and October 12, 1966 were utilized to examine those three mines and to collect over 300 specimens.

Laboratory work was performed mainly during the Autumn semester of 1966. All of the collected specimens were closely examined megascopically and with the aid of a binocular microscope. As an additional aid, 100 thin sections and 36 polished surfaces were prepared and examined. X-ray diffractometer and spectroscopic tests were utilized for uncertain mineral species. A paragenetic sequence was prepared for each specimen, and the individual sequences were interpreted and collected to prepare a composite paragenetic sequence for each of two mines, the Crystal mine and the Minerva mine No. 1. For the Hill mine, which received the least study, selected paragenetic relations were described but a diagram was not prepared.

D. Previous Work

The first report on the occurrence of fluorite in the southern

Illinois fluorspar district was published in 1819, but Bastin (1931, p. 55-65) was the first investigator to discuss in some detail the paragenesis of the ores in the bedding replacement deposits. He classified the minerals of the coarser non-banded ore into three groups, primary, secondary and miscellaneous. He discussed the relationships between the minerals but did not present a diagram to illustrate these paragenetic relationships. Based upon the relationships described in this report, a paragenetic diagram (Bastin, 1939, p. 113) was subsequently prepared. The paragenetic sequence given for the bedding replacement deposits was: fluorite, chalcopyrite, marcasite, galena and calcite.

Currier (1944, pp. 30-52) studied the bedding-replacement deposits in the Cave-in-Rock district and described the development of banded or coontail ore. He noted that the sulfide minerals, galena, sphalerite, chalcopyrite and marcasite, began depositing during the later stages of fluorite mineralization and believed that they were continuously deposited after the cessation of fluorite deposition.

Grawe and Nackowski (1949, p. 331) were the first to identify strontianite and witherite in the Cave-in-Rock district. They reported that strontianite was deposited prior to witherite, and that both minerals were deposited after fluorite, sphalerite, calcite and barite but before late fluorite, quartz and calcite.

Weller, Grogan and Tippie (1952, pp. 118-122) discussed the minerals occurring in the bedding-replacement deposits of the Cave-in-Rock district and noted that the mineral assemblage is similar to that of the Rosiclare district. They prepared a diagram of the general sequence of mineral deposition at the Davis-Deardorff mine in the Cave-in-Rock district. This sequence differed from that of Bastin by the addition of the minerals, sphalerite, quartz, barite and bitumen, the reverse order of deposition of marcasite and galena, and the recognition of two stages of deposition of fluorite, chalcopyrite, quartz and iron sulfide.

Freas (1961) studied the temperatures of mineral formation at the Victory and Deardorff mines. He recognized two generations of fluorite as well as two generations of sphalerite and quartz. He noted that early fluorite occurs commonly as the coarsely crystallized and lightly colored bands in coontail ore, whereas late fluorite, represented by purple or blue colors, occurs both in banded ore and in vugs.

Brecke (1962), in a paper on genesis of the Cave-in-Rock district ores, emphasized the multiplicity of fluorite depositional stages. He believed that the sphalerite replaced residual carbonates left by fluoritization of the impure bands of coontail ore.

Hall and Friedman (1963) discussed principally the composition of fluid inclusions in the minerals of the Cave-in-Rock district. To investigate the change in fluid composition through time, they prepared a paragenetic diagram for the cavity filling and vein forming minerals in the Oxford, Hill, and Deardorff mines. They recognized five stages of fluorite which were distinguished by color and paragenetic position.

Pinckney (1966) has found as many as seven stages of purple fluorite in his studies largely in the Hill-Leadford mine.

E. Historical Summary of Fluorspar Mining

In 1819, "fluo spar" or "fluat of lime" was discovered near Shawneetown, Illinois. The first discovery of lead ore seems to have been made in 1839 during the sinking of a well on the Anderson farm, about a mile southwest of Rosiclare, in southern Illinois.

In 1842, William Pell discovered fluorspar and galena on his farm located about one-half mile southwest of Rosiclare. He initiated the Pell mine, now part of the Rosiclare mine, which was the first mining operation in the southern Illinois fluorspar district. Only galena was recovered at that time and the associated fluorite was neglected.

About 1880 a decline in lead price and an increase in demand for fluorspar caused a transition from lead to fluorspar mining.

The first mining in the Cave-in-Rock district was initiated on Spar Mountain in 1903 by the Cleveland-Illinois Company. The district has been an important producer of fluorspar since 1918.

The flooding of the mines in the Rosiclare district in 1923 through 1924 stimulated the mining of the bedding-replacement deposits in the Cave-in-Rock district. Production from the latter area has steadily grown due to comparatively simple mining and milling methods and to the increase in demand for fluorspar in the steel, aluminum, ceramic and chemical industries.

In 1964, Illinois supplied 58% of the total domestic output of fluorspar to rank first among the fluorspar-producing states.

The larger portion of the southern Illinois fluorspar production comes from the mines in the Cave-in-Rock district. Most of those mines are operated by two mining companies, Minerva Oil and Ozark-Mahoning.

Three milling plants for fluorspar and zinc concentrate currently are operating in the Cave-in-Rock district (Figure 1). The Minerva Oil Company operates the Crystal mill and the Minerva No. 1 plant. The Ozark-Mahoning's heavy media plant is located near their West Green mine.

F. Acknowledgment

The author wishes to express his sincere appreciation to Dr. Richard D. Hagni, Associate Professor of Geology, for suggesting the study and for his guidance throughout the course of this research.

Sincere thanks are due Mr. Donald B. Saxby, Chief Geologist of the Minerva Oil Company, and Mr. B. L. Perry, Chief Geologist of the Ozark-Mahoning Company, for access to the mines, for accompanying the writer underground, and for the many courtesies extended during the writer's visits to the district.

Acknowledgments are due Dr. A. C. Spreng, who instructed the writer in the preparation of the macrophotographs, and Dr. S. K. Grant, who aided in the X-ray analysis.

Chapter II

GEOLOGY OF THE DISTRICT

A. General

The geologic formations exposed in the Cave-in-Rock district (Figure 2) are of Mississippian and Pennsylvanian age. They consist principally of limestones, sandstones, calcareous sandstones and shales. Some of the limestone members are shaly and sandy. The formations strike approximately N. 70° W. and dip to the northeast an average of 4°.

The southern part of the district is characterized by a gently rolling terrain ranging in elevation from 400 to 460 feet above sea level. The St. Louis Limestone of the Meramec Series outcrops in the terrain close to the Ohio River. It is the oldest formation known to outcrop in the district. The youngest surface formation is the Caseyville Sandstone and Conglomerate of Pennsylvanian age. It outcrops in the northeastern part of the district at an elevation of about 600 feet.

The igneous rocks in Hardin County have been subdivided by Currier (in Weller, 1920, p. 237) into: lamprophyre, mica-peridotite, and volcanic breccia (?). The first two rocks occur as dikes, while the last is known only from weathered boulders and drill core (Snyder and Gerdemann, 1965). All of the igneous rocks are dark gray to dark greenish gray in color where fresh, and contain brown and black mica, pyroxenes, olivine, apatite, magnetite, and titanite. They are extensively altered to carbonate, serpentine and chlorite. Many occurrences of these igneous rocks in Hardin County have been described by Weller and others (1952, pp. 71-73).

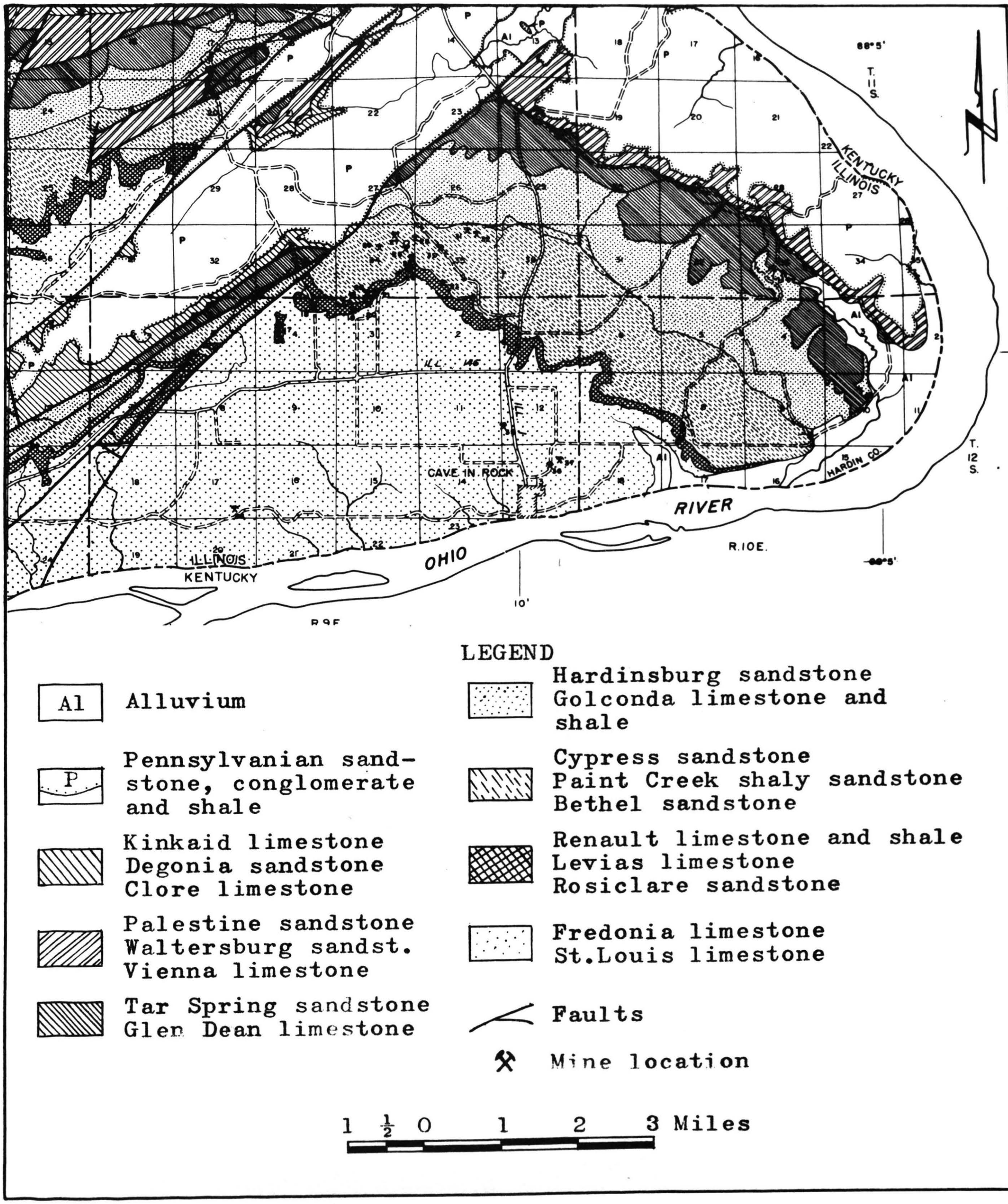

Fig. 2. Geologic map of the Cave-in-Rock district, Hardin County, Illinois (after J. M. Weller and R. M. Grogan, 1950). All of the formations are Mississipian except where indicated otherwise.

B. Stratigraphy

The columnar section of sedimentary formations in the Cave-in-Rock district, Hardin County, Illinois, modified from Mining Engineering (1958, no. 1, p. 65), is given in Figure 3. The portion of the stratigraphic column involved in this particular area is briefly described below.

1. Meramec Series

a. St. Louis Formation

Good outcrops of the St. Louis Formation occur in the Ohio River bluffs between the towns of Elizabethtown and Cave in Rock. The formation varies in color from pale blue or gray in fresh exposures. It is dominantly a fine- to very fine-grained limestone and it usually contains large amounts of lenticular or irregular nodules of chert which are arranged parallel to the bedding planes.

b. Ste. Genevieve Formation

The Ste. Genevieve Formation consists of three major members and one minor member. The three persistent members are the Fredonia Limestone, the Rosiclare Sandstone and the Levias Limestone. The minor member, which occurs within the Fredonia Limestone, is locally termed the "Sub-Rosiclare Sandstone" or the "Spar Mountain Sandstone" (Tippie, 1945, p. 1658).

(1) Fredonia Limestone

The Fredonia Limestone member is divided into the "upper" and the "lower" by the Sub-Rosiclare Sandstone. The lithologic characters of both parts differ considerably from bed to bed. They are highly fossiliferous, oolitic limestones. The

SYSTEM	SERIES	FORMATION	MEMBER	THICKNESS FEET
PEN.	POT.	CASEYVILLE		
MISSISSIPIAN	CHESTER	KINKAID		50 - 200
		DEGONIA		40 - 60
		CLORE		25 - 40
		PALESTINE		50 - 100
		MENARD		90 - 120
		WALTERSBURG		15 - 50
		VIENNA		20 - 60
		TAR SPRINGS		50 - 100
		GLEN DEAN		50 - 70
		HARDINSBURG		80 - 100
		GOLCONDA		100 - 150
		CYPRESS		80 - 150
		PAINT CREEK		0 - 60
		BETHEL		50 - 90
		RENAULT	DOWNEYS BLUFF	10 - 40
			SHETLERVILLE	30 - 50
	MERAMEC	STE. GENEVIEVE	LEVIAS	10 - 40
			ROSICLARE	20 - 30
			UPPER FREDONIA	50 - 90
			SUB-ROSICLARE	5 - 20
			LOWER FREDONIA	90 - 120
		ST. LOUIS		300+

FIG. 3. STRATIGRAPHIC SECTION FOR THE CAVE-IN-ROCK DISTRICT (MODIFIED FROM MINING ENGINEERING, 1958)

color varies from bluish gray to nearly white; it generally is lighter than that of the St. Louis Limestone.

The Sub-Rosiclare Sandstone is present 40 to 65 feet below the top of the Fredonia. It varies in composition from silty sandstone to sandy limestone.

(2) Rosiclare Sandstone

The Rosiclare Sandstone is composed dominantly of a fine-grained and grayish-green calcareous sandstone. The weathered or leached rock becomes a porous and rusty brown sandstone. A green shale layer varying in thickness from zero to 8 feet is common at the base of the sandstone. According to Tippie (1945, p. 1660), an unconformity exists locally between the Rosiclare Sandstone and the underlying Fredonia Limestone.

(3) Levias Limestone

Overlying the Rosiclare Sandstone is the youngest member of the Ste. Genevieve Formation, the Levias Limestone, formerly known as the "Lower Ohara Limestone" (Weller, 1920, p. 112). The member resembles the Fredonia Limestone, varying from light-gray, oolitic to darker, dense limestone.

2. Chester Series

a. Renault Formation

The Renault Formation, the lowest formation of the upper Mississippian, is divided into two parts, the Shetlerville Member and the Downeys Bluff.

(1) Shetlerville Member

The Shetlerville Member consists of interbedded limestone and shale. The limestone beds are gray and oolitic; the shales are greenish gray and calcareous. Both members locally are fossiliferous.

(2) Downeys Bluff

The Downeys Bluff is the upper member of the Renault Formation. It is gray or bluish gray to brown in color and it is crystalline to fine-grained. Small amounts of shale partings locally are present between the limestone layers. Oolitic or crinoidal limestone beds also are present.

b. Bethel Sandstone

The Bethel Sandstone varies in color from gray or nearly white in fresh exposures to brown in weathered exposures, and it is fine-grained and compact. Cross-bedding is common. The contact between the Bethel and Renault formations is unconformable.

c. Paint Creek Formation

The Paint Creek Formation consists of thinly interbedded layers of sandstone and shale. Sandstone is predominant locally.

d. Cypress Sandstone

The Cypress Sandstone is a massive and compact sandstone which is quite similar to the Bethel Sandstone. An unconformity is present between this formation and the underlying Paint Creek.

e. Golconda Formation

The Golconda Formation consists of successive beds of shale and limestone. The limestone beds are bluish to gray, and locally they contain abundant fossils. The shales are gray or dark gray to bluish, and locally fossiliferous.

f. Hardinsburg Sandstone

The Hardinsburg Sandstone is fine-grained and white to pale gray. The formation contains shale beds or shaly partings.

g. Glen Dean Sandstone

The Glen Dean Sandstone is composed of alternating beds of limestone and shale. The limestones of this formation are gray, crystalline and fossiliferous. The shales are calcareous and gray in color.

h. Tar Springs Sandstone

The Tar Springs Sandstone is tan to light gray in color and it generally is shaly. This formation forms the bedrock over part of the vicinity of the Minerva mine No. 1 (Nackowski, 1949, p. 20).

i. Vienna Limestone and Waltersburg Sandstone

According to Weller (1952), these two formations are poorly developed and are not known to outcrop in Hardin County.

j. Menard Limestone

The Menard Limestone is a formation which consists of a fine-grained limestone with shale beds.

C. Structure

Two features of regional structure are most striking in the Cave-in-Rock district, the Hicks Dome and northeast trending faulting. The Hicks Dome is a circular uplift of strata about 10 miles in diameter, in Hardin County, Illinois. From the center of the dome, which is located approximately 10 miles west of the mines examined for this study, the rocks dip outward 10° to 30° in all directions. Some writers believe that the domal structure was caused by deep-seated igneous activity in the region of the Illinois-Kentucky mining district (Brown, et al., 1954; Snyder and Gerdemann, 1965).

While the sedimentary rocks in the Cave-in-Rock district appear to have been relatively undisturbed structurally, the entire Illinois-Kentucky mining district is centered in the most complexly faulted area in the central part of the United States. Northwest of the Cave-in-Rock district the Peters Creek fault zone, which consists of several subparallel faults as shown in Figure 2, forms the southeast boundary of the Rock Creek graben. The graben block has been downthrown 1,000 feet or more. No profitable mineral deposits have been developed along the fault zone, but the bedding-replacement deposits of the Cave-in-Rock district are nearby and may be genetically related to the fault zone.

Chapter III

FLUORITE DEPOSITS

A. Introduction

Fluorite is produced in the United States from deposits in the following states: Illinois-Kentucky, Colorado, Montana, Nevada, New Mexico and Utah. The most important of these is the Illinois-Kentucky mining district where fluorite has been mined for nearly a century. The Illinois-Kentucky mining district may be subdivided into the Kentucky and southern Illinois districts. The latter, in turn, often is subdivided into the Cave-in-Rock and Rosiclare districts. The Cave-in-Rock district is the most important producer of fluorspar among the various district subdivisions.

The fluorite deposits of southern Illinois have been classified into two principal types, the so-called "bedding-replacement deposits" and the "vein deposits". The Cave-in-Rock district is characterized by the first type, and all of the mines examined for this investigation belong to that district. The bedding-replacement deposits locally are called "blanket deposits". The westerly neighboring Rosiclare district is characterized by vein deposits. Secondary residual deposits formed at the surface by weathering may be considered to constitute a third type from which a small amount of ores have been mined in the past but they are not being mined today.

The two primary types of ores exhibit nearly the same minerals, but the relative proportions of some minerals differ. For example, calcite and galena are more abundant in the vein deposits than in the bedding-replacement deposits.

The bedding-replacement deposits were nearly neglected during the early history of fluorspar mining in southern Illinois. Since about 1910, however, considerable attention has been directed toward their development, primarily because of the advantages involved in the mining of these deposits and because their large volumes helped meet the increase in demand for fluorspar.

The following discussion and subsequent sections of this thesis deal exclusively with the bedding-replacement type deposits of the Cave-in-Rock district.

B. Ore Horizons and Distribution

The replacement deposits occur in various favorable horizons of the thick Renault and Ste. Genevieve formations. Almost all of the ore currently being mined comes from three main stratigraphic horizons: 1) Bethel-Renault contact zone; 2) Rosiclare-Fredonia (upper) contact zone; and 3) Sub-Rosiclare horizon. The lithologic characters of these three contact zones are illustrated in Figure 4. Ores occur principally within the upper portion of the limestone members below these contact zones. Minor ore deposits occur in the upper part of the Levias Limestone, the basal portion of the Renault Limestone, and within the upper and lower Fredonia Limestones.

Figure 5 shows the areal distribution of ores mined in each of the three main ore-bearing horizons in the Cave-in-Rock district, southern Illinois. The main mineralized belt, as defined by Weller (1952, p. 108), is 4,000 to 5,000 feet wide and 5 miles long, and it lies at a distance of 1,800 to 4,600 feet southeast of the Peters Creek fault zone. Two of the mines studied, the Minerva's Crystal and No. 1 mines, are included in the main belt; they are representative of the Rosiclare and Bethel horizons, respectively. In the Ozark-Mahoning's Hill mine, which lies outside of the main belt, the ore occurs on both the Rosiclare and Sub-Rosiclare horizons.

The ore bodies typically are elongated and tabular or lenticular, usually lying parallel to the bedding of the host limestone. Based upon their structural relationships, the ore bodies either are rather symmetrical about a central fissure or they lie at one side of a minor fault (Figure 6). The southwestern portion of the ore bodies in the Crystal mine is typical of the first type. In this type the elongated ore body together with the overlying sedimentary formations exhibit an inclination from the periphery toward the center of the ore body approximately 15° to 30°. The nature of this structure is described by the local term "boat structure". Underground photographs of a "boat structure" are illustrated in Figures 7 and 8. The ore body of the A. L. Davis mine is a good example of the second type of structure shown in Figure 6.

The ore bodies vary in thickness from 3 to 30 feet, and in width from 30 to 900 feet. Lengths are commonly 200 to 1,500 feet, although lengths up to 4,000 feet have been mined.

C. Fabric

The fabric of the fluorspar deposits may vary somewhat from

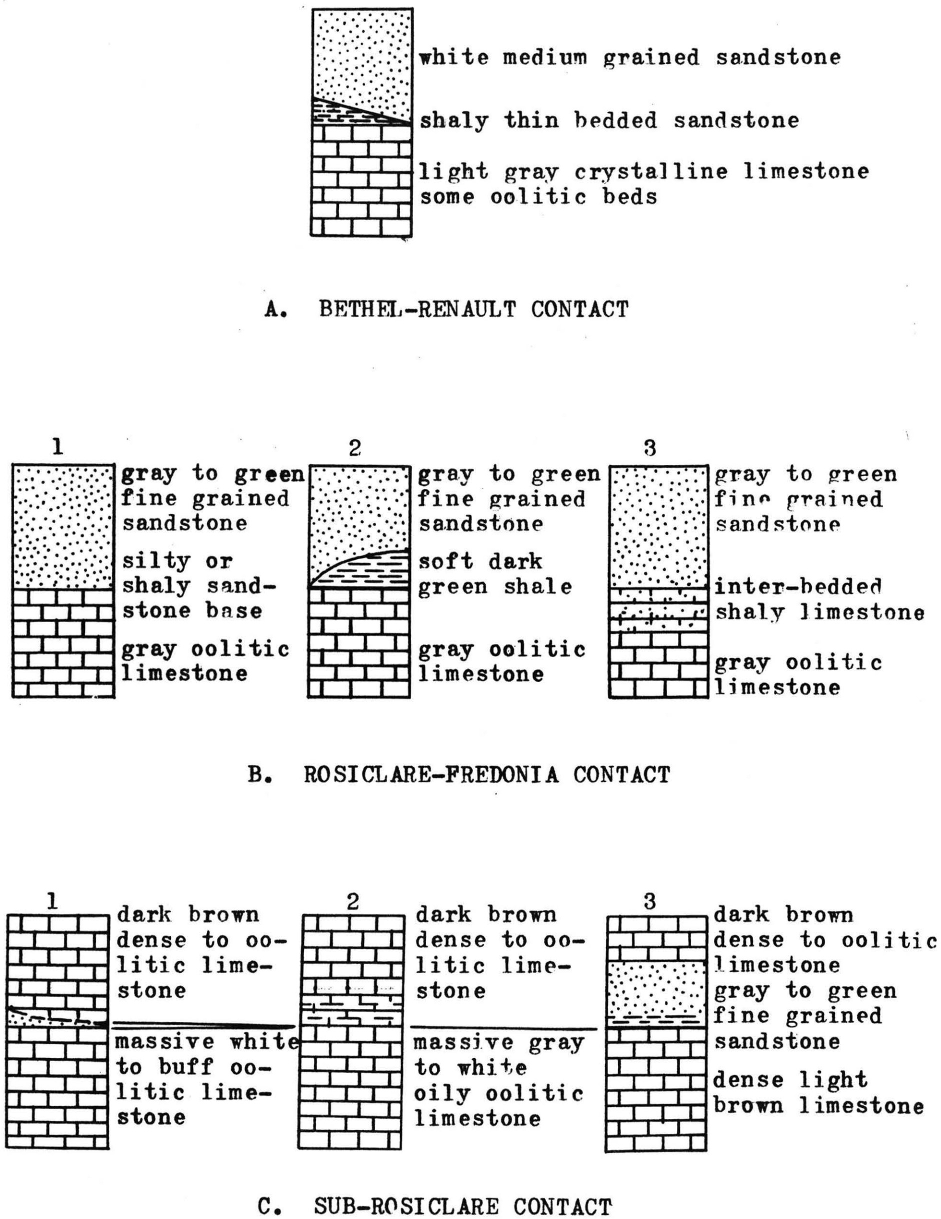

Fig. 4. Detail of contact lithology (after E. A. Brecke, 1962).

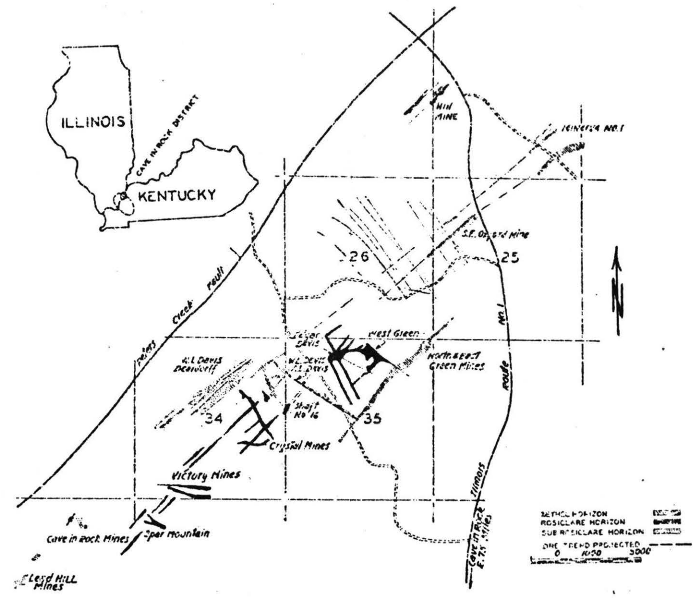

Fig. 5. Areal distribution of the three major ore horizons of the Cave-in-Rock district (from E. A. Brecke, 1962).

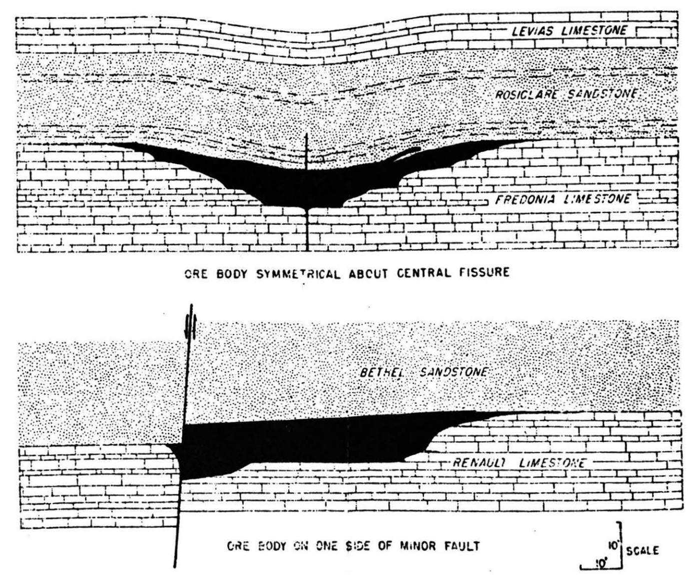

Fig. 6. Schematic cross-sections of the two general types of bedding-replacement deposits, southern Illinois (from R. M. Grogan, 1949).

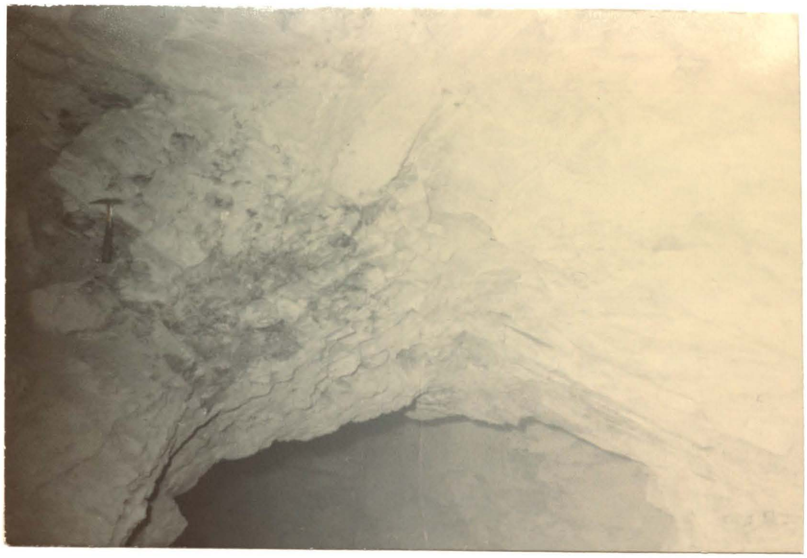

Fig. 7. Photograph looking along the shortest axis of a "canoe-shaped" ore body. Rosiclare-Fredonia contact zone, Crystal mine.

Fig. 8. Photograph looking along the longest axis of the ore body shown in Figure 7. Note the inclination and the thin fluorite bands (purple) developed along the bedding planes of the Rosiclare sandstone (grey) and along the fractures perpendicular to the bedding. Rosiclare horizon, Crystal mine.

place to place. The characteristic features, such as banding, vugs or cavities and comb structure, appear to be common throughout the mines in the Cave-in-Rock district.

Banding is perhaps the most noteworthy feature which may be said to characterize the bedding-replacement deposits. There are several types of banded ore, but the most common is that which locally is termed "coontail ore". It consists of alternating light- and dark-colored layers or bands. The light-colored bands are relatively pure fluorite, while the dark-colored, more impure bands may contain sphalerite, galena, carbonate and organic matter, in addition to fluorite. Coarsely crystalline, pure fluorite bands alternating with impure fluorite-galena bands are shown in Figure 9.

The layers or bands in coontail ore range in thickness commonly from a fraction of an inch to 2 inches, and they are parallel or subparallel to the bedding of the enclosing rock. Single bands locally may extend for a distance of several feet.

The alternating layers of fluorite in some coontail ore were observed locally to extend laterally more than 20 feet (Figure 10). The pure layers are mostly milky or creamy white in color, but some exhibit a purple tint. The impure bands are dark brown to gray with a purple tint. A typical specimen of coontail ore is shown in Figure 11. Microscopic examination of thin sections of coontail ore reveals that the darker layers consist of approximately 95% fluorite, and they often reveal stylolites (Figure 12).

Thin sections of some impure bands in coontail ore exhibit scattered finely crystalline fluorite cubes (Figure 13), which may

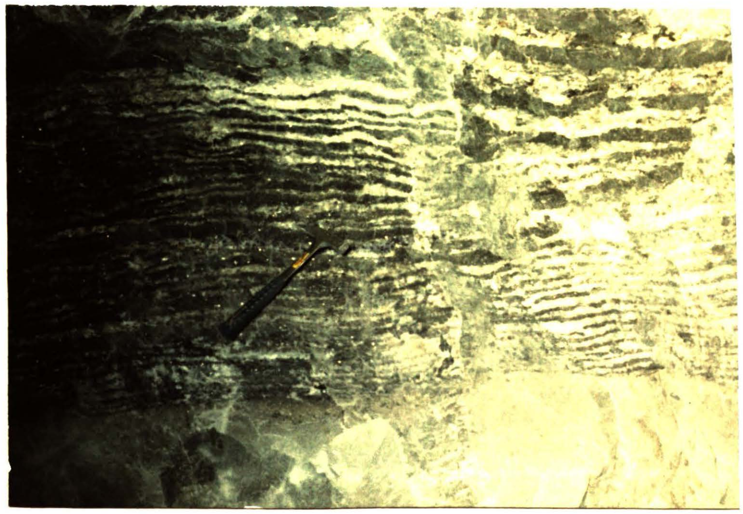

Fig. 9. Bands of fluorite (purplish white) alternating with those of galena-fluorite (bluish gray). Rosiclare horizon, Crystal mine.

Fig. 10. Alternating layers of light- and dark-colored fluorite ("coontail ore"). The banding, which occurs at the Rosiclare and Fredonia (upper) contact zone, is continuous for a lateral distance about 20 feet. Crystal mine.

Fig. 11. A typical "coontail ore" specimen. Note the tabular vugs (black) in the central portions of several pure layers (light yellow). Some vugs are crusted with thin layers of black bitumen. Same locality as Figure 10, Crystal mine.

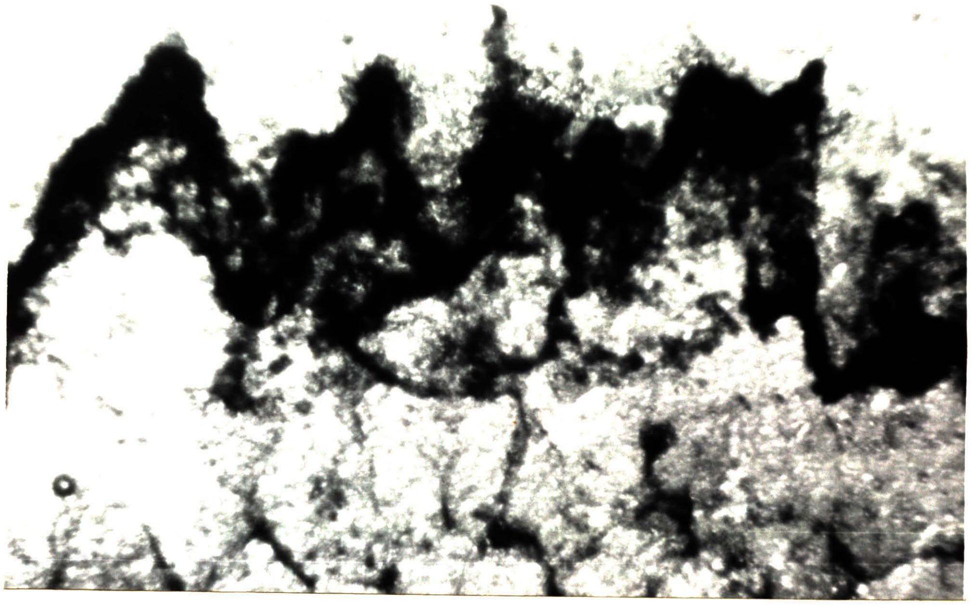

Fig. 12. Photomicrograph showing a stylolytic seam preserved in the relatively impure fluorite layers. Crystal mine. Plane polarized light. 50X.

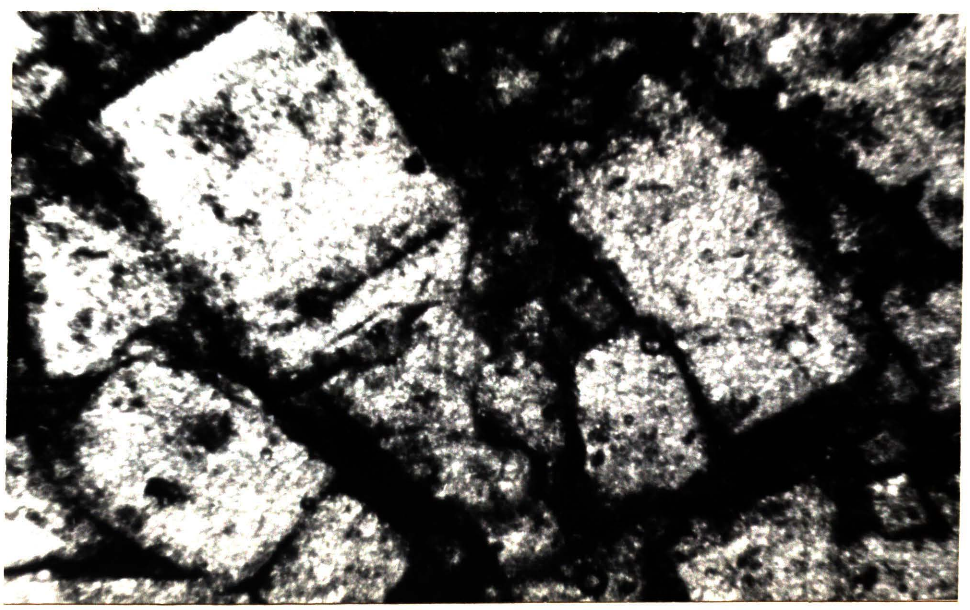

Fig. 13. Fluorite cubes in impure ore bands. The dark area consists of carbonaceous matter. The cubes contain tiny particles of unreplaced calcite. Minerva mine No. 1. Plane polarized light. 50X.

contain tiny remnants of calcite. Carbonates may occur in other banded ores, and thin sections prepared from the central portion of the fabric shown in Figure 14 exhibit scattered minute rhombohedral carbonates within fluorite (Figure 15). The carbonate rhombs may be dolomite, and Brecke (1962, p. 504) noted that carbonates in a similar occurrence are ferruginous dolomite.

Other types of banding locally are represented in the Cave-in-Rock district. Fluorite bands may intercalate with bands of other minerals, such as sphalerite, galena (Figure 16), barite and calcite.

Bastin (1931, p. 48) distinguished "V- and W-shaped" bandings from laterally extensive banding. In cross section, "V- and W-shaped" bandings contain one and two or three central, nearly vertical fractures, respectively. W-shaped banding, observed at a pillar near the working stope of the southwest ore body in the Minerva mine No. 1, consists of intercalated bands of sphalerite-fluorite and calcite with remnants of dissolved fluorite.

Some bands are wavy as shown in Figure 17. Some barite ore bands in the abandoned third ore body of the same mine have a wavy texture.

In contrast to the banded fabrics described above, some ore, termed "disseminated ore" is characterized by scattered grains of fluorite and other minerals, such as sphalerite, galena and chalcopyrite throughout the host rock. This ore is referred to by the miners as low-grade ore. Disseminated ore usually occurs at the outer margin of the deposits.

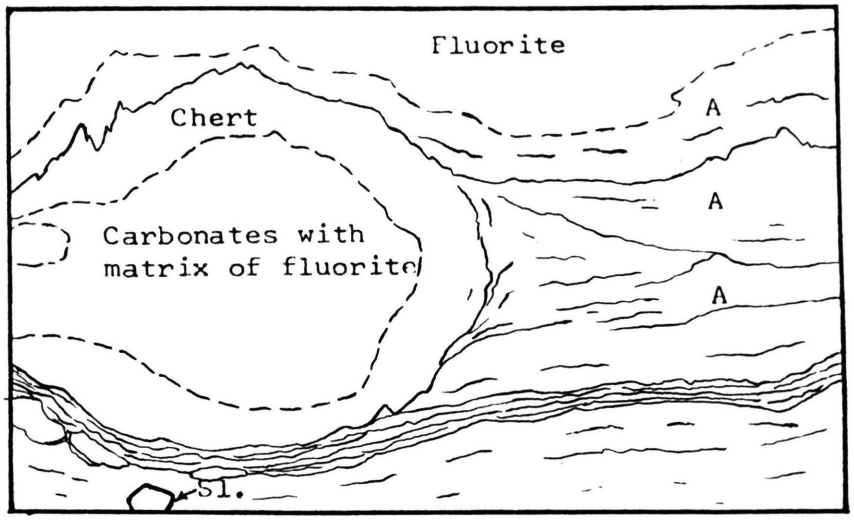

Fig. 14. Sketch showing impure part of a specimen from the Minerva mine No. 1. The area marked "A" consists of chert, carbonaceous matter and a small amount of fluorite. Note that the stylolytic and carbonaceous bands bend around the central carbonate-fluorite area. Bethel horizon. 6X.

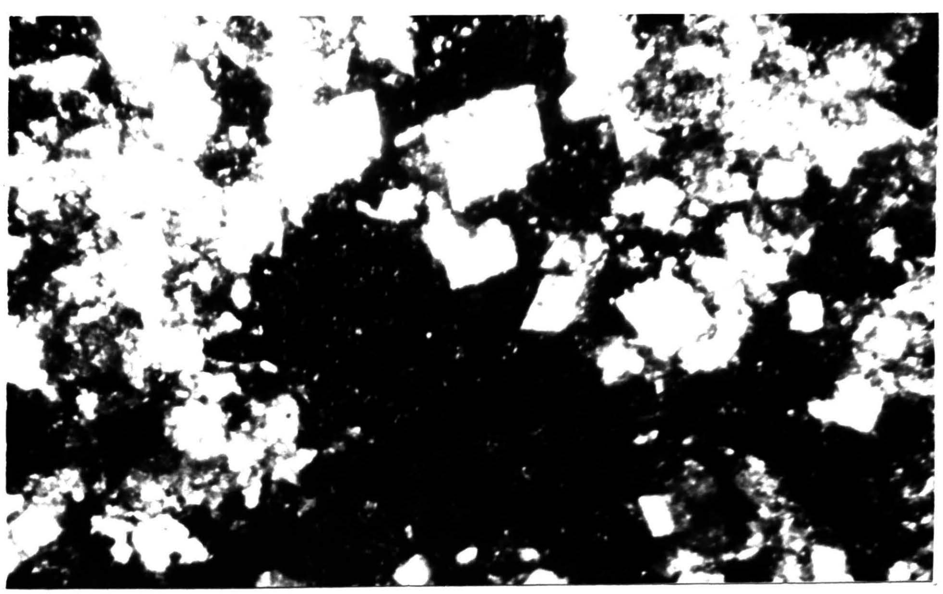

Fig. 15. Photomicrograph of dolomite (?) rhombs occurring within the central portion of the carbonate-fluorite area shown in Figure 14. The black area is fluorite. Crossed nicols. 50X.

Fig. 16. Thick irregular galena bands (dark blue gray) alternating with fluorite (yellowish white to purple). Note the narrow calcite vein (white, right of geologic pick) crossing the banding. Rosiclare horizon, Crystal mine.

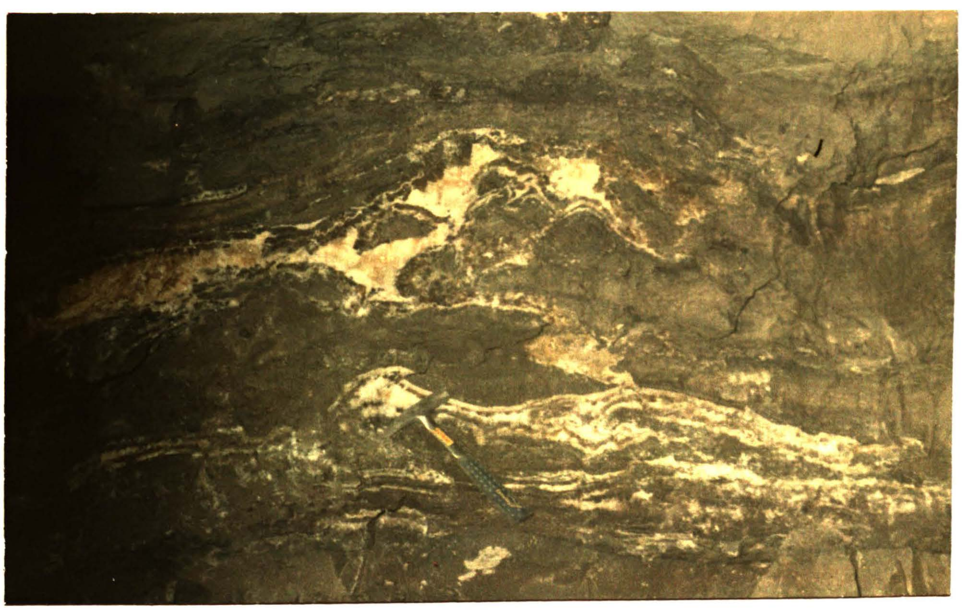

Fig. 17. Wavy bands of fluorite (purplish brown) and calcite (white). Sphalerite occurs associated with the fluorite. Bethel-Renault contact zone, Minerva mine No. 1.

Vugs or cavities frequently occur within the massive or coarse ore. Most vugs are elongate in shape, and their longer dimensions are nearly parallel to the bedding. Some vugs appear to be connected to each other (Figure 18). The vugs may be lined with well-formed crystals of fluorite, quartz, galena, sphalerite, calcite and barite.

Some pure layers of the ores show "comb structure" (Figure 19). Comb structure is a term applied to crusts of crystals that have grown inward from opposite walls of a fracture or fissure. Fluorite ores with comb structure tend to break along the vugs between the two opposing combs. Late crystals, such as calcite, tend to be deposited only on the bottom comb (Figure 20). Similar features, termed "snow on the roof" by Bastin (1931, p. 39), were thought by him to indicate gravitational control during the crystallization of calcite.

Fig. 18. Elongated, partly interconnected vugs within a massive fluorite. Rosiclare-Fredonia contact zone, Crystal mine.

Fig. 19. Specimen from the Crystal mine showing comb structure in the lowest thick band (see arrow mark).

Fig. 20. Vug surface of the bottom comb of the specimen shown in Figure 19. Note that tiny calcite crystals (yellowish white) coat the comb fluorite.

Chapter IV

MINERALOGY

A. Introduction

The minerals known to be present in the bedding-replacement deposits of the Cave-in-Rock district are fluorite, sphalerite, galena, chalcopyrite, pyrite, marcasite, calcie, witherite, strontianite, barite, quartz, dolomite, oil and bitumen. Although fluorite is the most valuable mineral in the district, sphalerite is of secondary economic importance in some deposits. More sphalerite is recovered from the Minerva mine No. 1 than from any other mine in the Cave-in-Rock district. Galena, which is locally abundant, rarely is recovered. The remainder of the minerals are present in smaller amounts and they constitute no present economic value. Secondary minerals known to occur in the Cave-in-Rock district are cerussite, smithsonite, anglesite, malachite and pyromorphite.

Fluorite is used in diverse industries. In the form of gravel or pellets it is used as a flux in the steel-making process. Finely ground fluorspar is consumed in the preparation of synthetic cryolite, a sodium aluminum fluoride mineral. This electrolyte is used in the aluminum industry to reduce aluminum from its oxide form. The chemical industry consumes fluorspar in the production of hydrofluoric acid, which is an important compound in the manufacture of refrigerants, pressurized gas for aerosol containers, resins for fluoroplastics, etc. Fluorspar is used in the ceramic industry in the manufacture of porcelain enamels, facings for bricks, etc.

Each of the minerals in the Cave-in-Rock district are discussed in this chapter in their general order of abundance or importance.

B. Description of Minerals

1. Fluorite (CaF_2)

Fluorite is one of the important halide minerals, along with halite (NaCl), sylvite (KCl), cryolite (Na_3AlF_6) and carnallite ($KMgCl_3 \cdot 6H_2O$). Fluorite is commercially called "fluorspar".

Fluorite is the most abundant mineral in the bedding-replacement deposits. It occurs mainly as banded, massive, and disseminated ore. The banded ore is composed of alternating layers of light-colored pure and dark-colored impure fluorite. The massive ore is shown in Figure 18. The disseminated ore is characterized by fine granular fluorite distributed through the host rock, often with other disseminated minerals such as sphalerite and galena.

Well-developed crystals occur as simple cubes in vugs or cavities where they range in size from microscopic dimensions up to about 13 cm. on a side. Cubes are the most common and their faces are more or less irregular or smooth and glassy. Such cubes often consist of a mosaic of numerous small crystals in nearly parallel aggregation, sometimes referred to as lineage structure (Buerger, 1932). Cubic crystals showing dodecahedral modifications were described by Currier (1944, p. 31), but they were not observed by the present writer. Cubic fluorite crystals averaging 6 mm. across and modified by the tetrahexahedron {310} (Figure 21) were rarely observed in the Crystal mine to be deposited on white quartz crystals in vugs. Fluorite cubes are remarkably cleavable along octahedral planes. Octahedral cleavage fragments commonly are sold in shops in the Cave-in-Rock district.

Fluorite from the district displays many strikingly beautiful colors. These include colorless or milky-white, pale or deep purple, lavender, yellow or amber, sky-blue and greenish-blue. The various shades of yellow and purple are the most common. While color zoning may occur in some massive ore, it is more common in crystals. Such zoning is parallel to the crystal faces and it may consist of two colors, commonly a yellow core enclosed by a purple shell, or it may consist of layers of various shades of one color as shown in Figure 22.

Inclusions frequently are present in fluorite crystals, where frequently they form bands parallel to the crystal faces of fluorite. Oil and bitumen were recognized in some fluid inclusions. Chalcopyrite, sphalerite, galena and quartz occur in some fluorite as solid inclusions. The cubic faces of some lilac fluorite are marked by small, dark purple spots around tiny chalcopyrite crystals which contribute locally to the coloration.

2. Sphalerite (ZnS)

Sphalerite was called "blende" by the early German miners who were disappointed to find it rather than galena. The term "sphalerite" from the Greek has the same meaning as "blende" derived from blenden (to deceive).

Sphalerite commonly occurs as fine or coarse grains in disseminated ore, and less commonly as crystals in vugs or cavities. Rarely it occurs in massive aggregates.

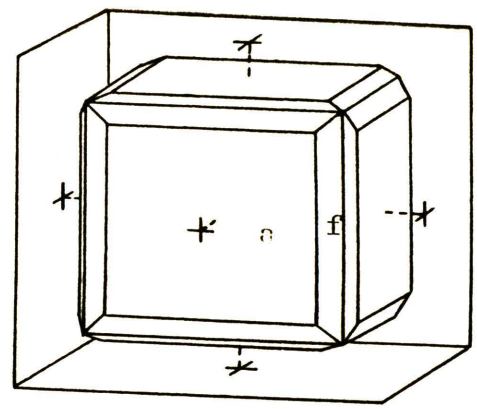

Fig. 21. An observed crystal form of fluorite, a cube a {100} with tetrahexahedron f {310}.

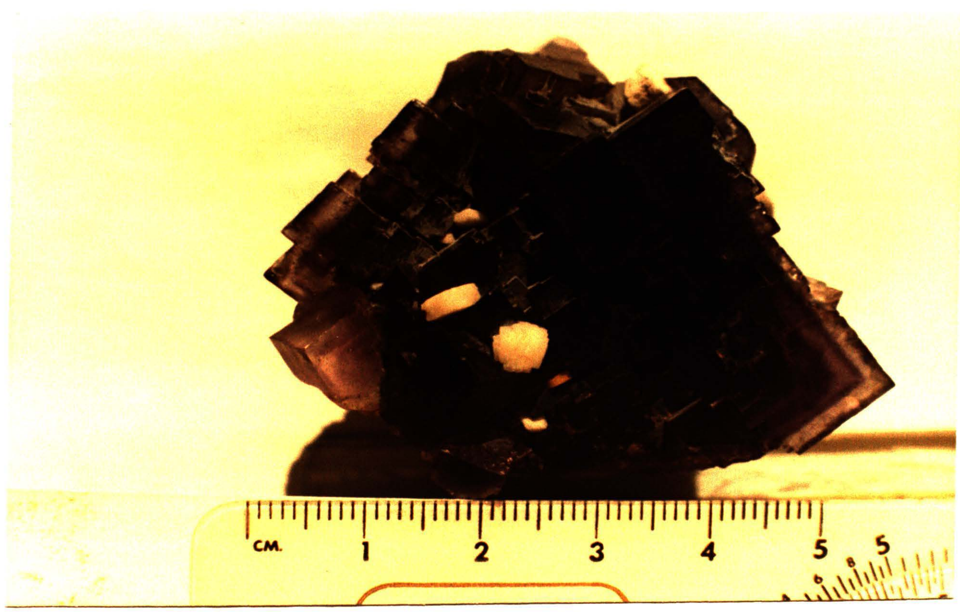

Fig. 22. Fluorite crystals showing color zoning. Barite (white) is superposed upon the fluorite. Crystal mine.

Sphalerite crystals generally are small in size, usually ranging from 2 to 6 mm. in diameter. The dominant crystal form is that of the tetrahedron with or without modifications by cubic or dodecahedral faces.

Most sphalerite varies in color from brown or brownish black to reddish or yellowish brown, but some is brownish green. Brownish black crystals are especially adamantine in luster (Figure 23). Darker-colored varieties of sphalerite are submetallic in luster, and they may have relatively higher iron contents.

Cadmium and germanium occur as trace elements in sphalerite from the Minerva mine No. 1. The Minerva's zinc concentrate contains as much as 1.0% cadmium and 0.03% germanium (Mining Engineering, 1958, no. 1, p. 67).

3. Galena (PbS)

While galena is the most abundant sulfide mineral in the vein type deposits (Currier in Weller, 1920, p. 253), it is locally abundant in the bedding-replacement deposits.

The mode of occurrence of galena is much like that of sphalerite. It commonly occurs in irregular or cubic forms in disseminated ore or in impure bands of coontail ore, and less commonly as well-formed crystals in vugs.

Galena cubes are restricted to disseminated ore, while cubo-octahedral galena occurs in vugs (Figure 24). All galena cubes deposited in vugs were observed by the writer to exhibit tiny octahedral truncations under the binocular microscope.

The galena crystals in both of the above types of occurrence range from 1 mm. to 2 cm. across.

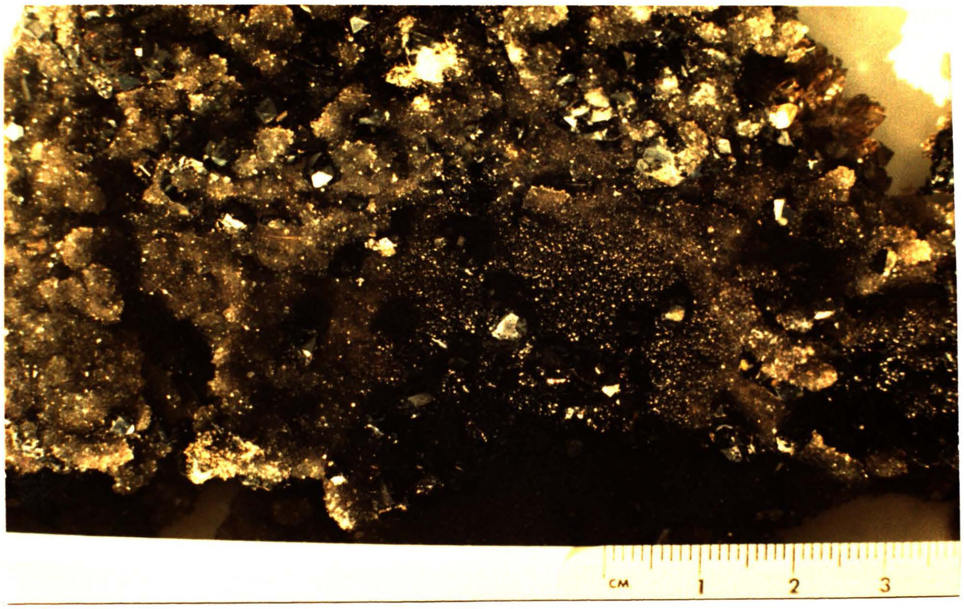

Fig. 23. Adamantine sphalerite (dark brown) deposited upon quartz (white). Viscous bitumen coats the minerals in the central and lower portions of the photograph. A later, coarser, brown variety of quartz is locally present (upper right). Hill mine.

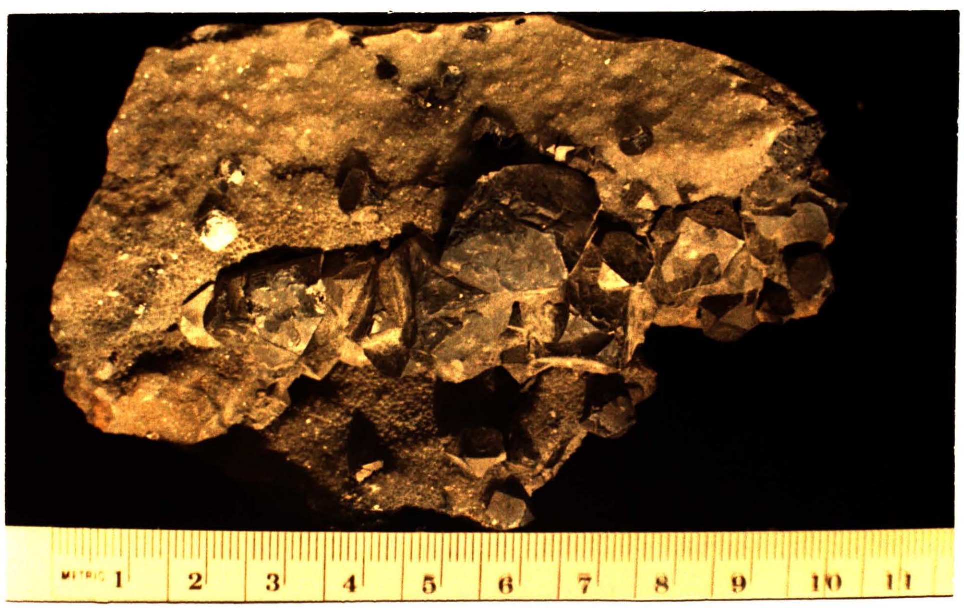

Fig. 24. Cubo-octahedral galena crystals deposited upon white quartz in a vug. Galena occurs between two combs of quartz (not shown in the photograph). Crystal mine.

4. Chalcopyrite ($CuFeS_2$)

Chalcopyrite was called "copper-pyrite" by Henkel in 1725 when he noticed the difference between this mineral and pyrite.

In the bedding-replacement deposits chalcopyrite occurs in small amounts but to a greater extent than do pyrite and marcasite. Chalcopyrite is widely distributed as inclusions within fluorite and calcite and as minute crystals deposited upon fluorite (Figure 25) and other minerals. Crystals within fluorite occur as acicular or nail-like forms, 1 to 4 mm. long. Chalcopyrite is associated with sphalerite and galena in disseminated ore.

Chalcopyrite crystals deposited upon other minerals generally are microscopic in size, but some are as large as 3 mm. in diameter. The common crystal form is the tetragonal disphenoid {112} either with or without the tetragonal dipyramid {011}. Some chalcopyrite crystals display slight iridescent colors due to tarnishing by surface alterations.

5. Pyrite (FeS_2)

The name pyrite originated from the Greek meaning "fire" and it was applied by Dioscorides and Pliny in the first century after Christ to those minerals which produced sparks when struck by a hammer.

Pyrite occurs as tiny crystals deposited upon fluorite (Figure 26) and upon strontianite, as inclusions within calcite and within strontianite, and as grains associated with sphalerite in impure bands of coontail ore.

Four kinds of pyrite crystal forms were observed by the writer. Two of these, the octahedron-pyritohedron and the cubo-pyritohedron,

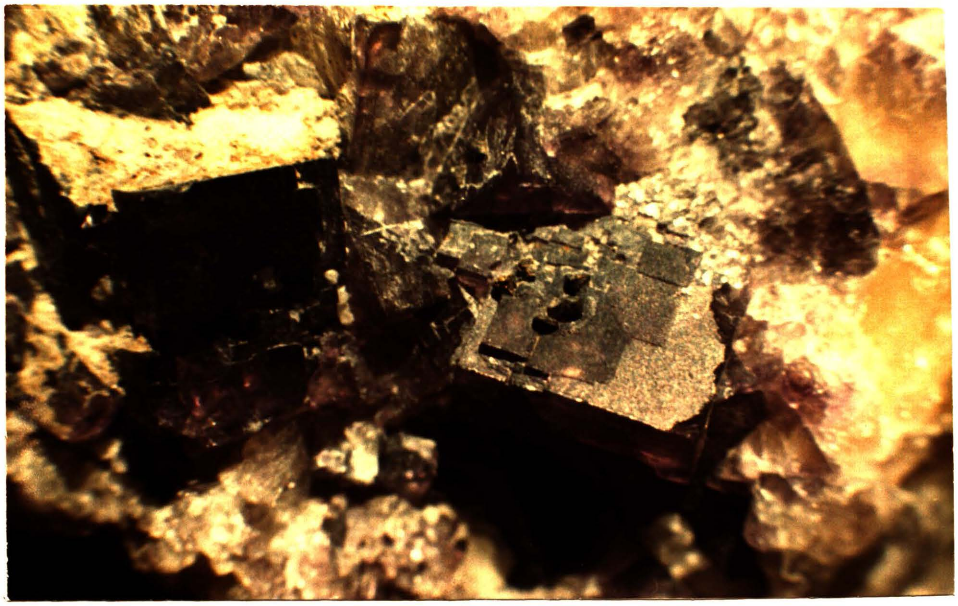

Fig. 25. Disphenoidal chalcopyrite crystals deposited upon purple fluorite. Crystal mine. 4X.

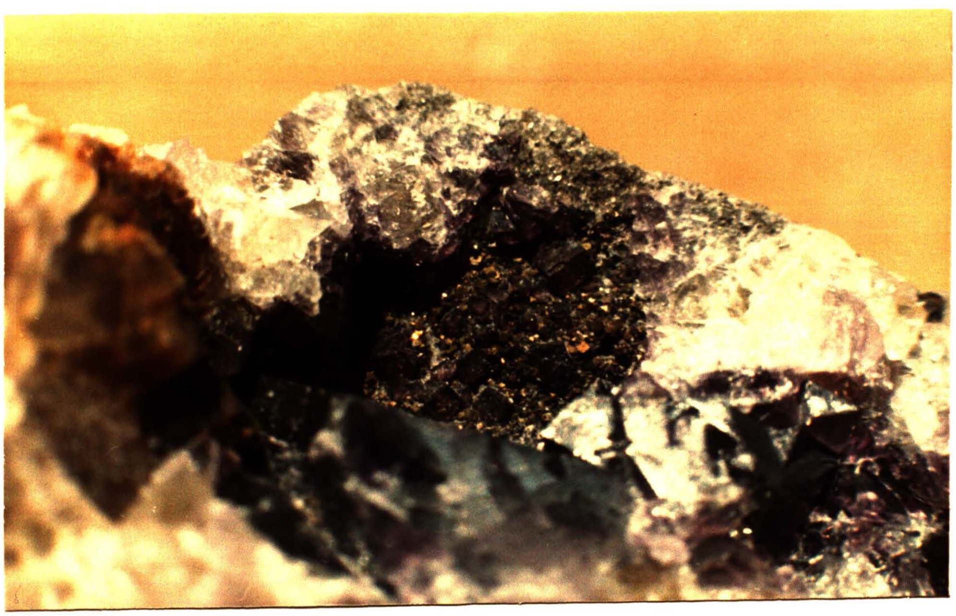

Fig. 26. Pyrite crystals deposited upon tiny purple fluorite. The pyrite cubes are modified by octahedral faces. Crystal mine. 4X.

are shown in Figure 27. The other two forms are cubes with and without octahedral faces.

All of the pyrite crystals are tiny in size, and none larger than 1/2 mm. in diameter were observed.

6. Marcasite (FeS_2)

In 1845, Hardinger recognized the difference in crystal system between marcasite and pyrite, and applied the old Moorish word "marcasite" to the orthorhombic form.

Marcasite is less common than pyrite in the bedding-replacement deposits. It occurs as long tabular crystals associated with fluorite, calcite and strontianite (Figure 28). The tiny crystals generally are larger than those of pyrite. Marcasite crystals twinned on {101} are common.

7. Calcite ($CaCO_3$)

Calcite occurs as well-formed crystals in vugs. Some calcite fills the spaces between the coarsely crystalline fluorite combs of banded ore. The most common calcite crystal form is that of a scalenohedron with or without modification by rhombohedral faces. Less common are hexagonal calcite prisms modified by rhombohedral faces. Twinned calcite is common (Figure 29). Figures 30 and 31 show so-called "dog-tooth spar" and scalenohedral calcite, respectively. One especially fine, 2 cm. long, calcite crystal collected from the Crystal mine is a combination of the negative rhombohedron $\{01\bar{1}2\}$ and the positive rhombohedron $\{16\cdot0\cdot\overline{16}\cdot1\}$.

Most crystals of calcite are white to yellowish in color. Their sizes generally range from 1 mm. to 4 cm. in length, but some are as long as 16 cm.

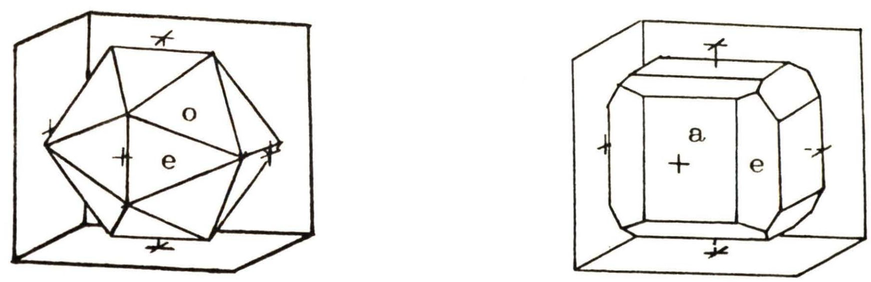

Fig. 27. Sketches of the crystal forms exhibited by pyrite. The left is octahedron o {111} and pyrithohedron e {210}. The right is cube and pyritohedron.

Fig. 28. Tabular marcasite crystals, often twinned on {101}. The yellow mineral is calcite. Minerva mine No. 1. 4X.

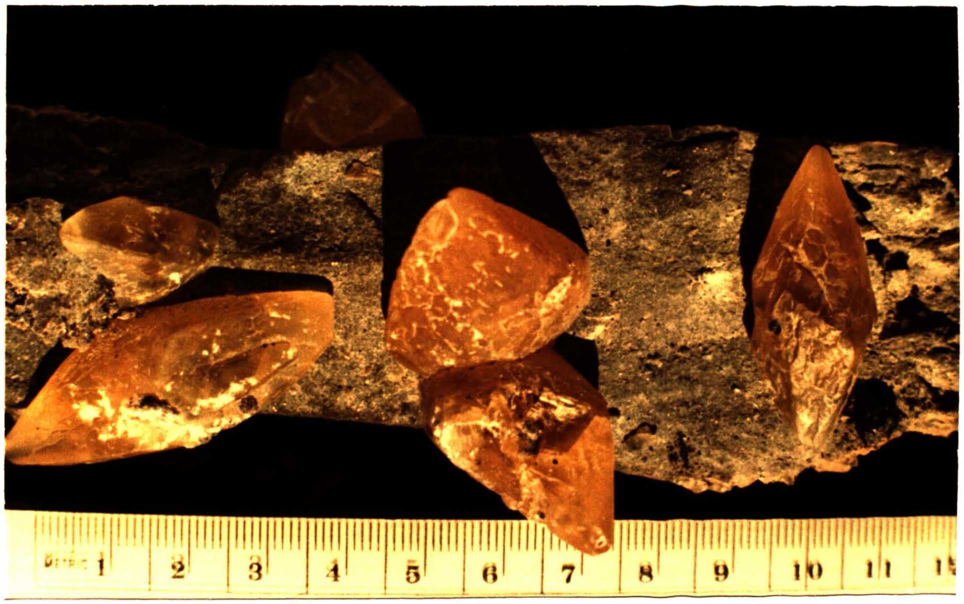

Fig. 29. Calcite twinned on $\{\bar{2}20\bar{1}\}$ (center of the photograph) and {0001} (right). Hill mine.

Fig. 30. Calcite, "dog-tooth spar", deposited upon cubes of fluorite. Hill mine.

Fig. 31. Calcite scalenohedron. Hill mine.

Calcite also occurs in nodular aggregates of small, elongated crystals as shown in Figure 32.

The globular carbonate shown in Figure 33 occurs at the Sub-Rosiclare horizon in the Hill mine, and is called aragonite by the miners. Hand specimens and thin sections reveal the carbonate to have a radially fibrous and concentrically zoned structure (Figure 34). The X-Ray pattern produced by this mineral shows that it is now calcite (see Table I). The mineral probably was aragonite originally, but subsequently it has inverted to calcite.

8. Witherite ($BaCO_3$)

Witherite was named after the mineralogist, Withering, who discovered the mineral in England in 1783.

In the southern Illinois fluorspar district, witherite was first identified by Grawe and Nackowski (1949). It has been found only in two mines, the Minerva mine No. 1 and the West Green mine.

Witherite occurs as white to yellowish white pseudohexagonal crystals which are repeatedly twinned on {110} to form columns (Figure 35). Such columns are terminated by nearly flat dipyramidal faces.

9. Strontianite ($SrCO_3$)

Strontianite was first found at Strontian on the west coast of Scotland in 1791 from which it derived its name.

In the Cave-in-Rock fluorspar district, strontianite is known to occur only in the Minerva mine No. 1. Strontianite generally occurs as columnar to fibrous aggregates exhibiting a radial structure.

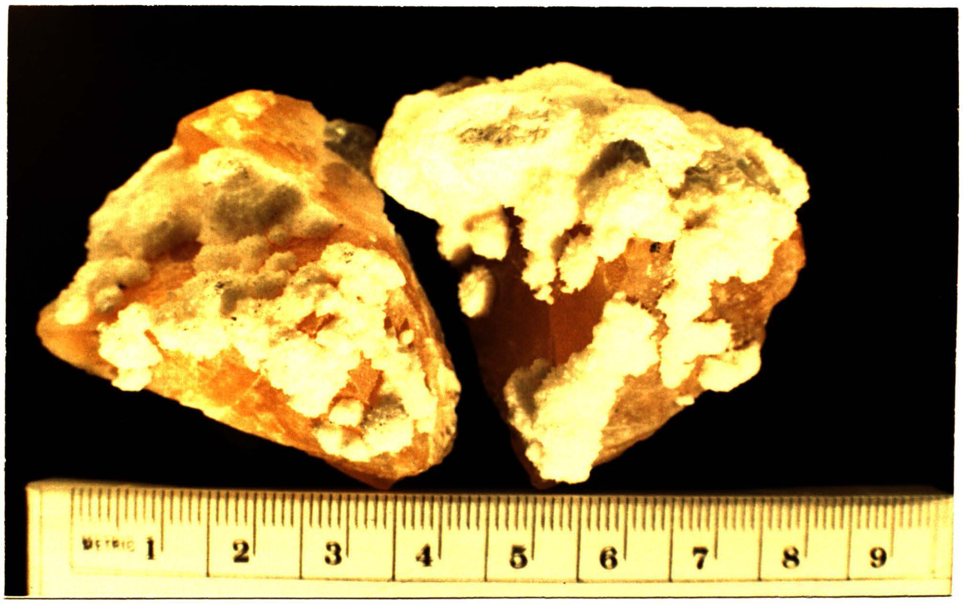

Fig. 32. Nodules of fine, elongated calcite on yellow fluorite. One tiny chalcopyrite crystal (brownish yellow) is deposited on the fluorite (right specimen). Minerva mine No. 1.

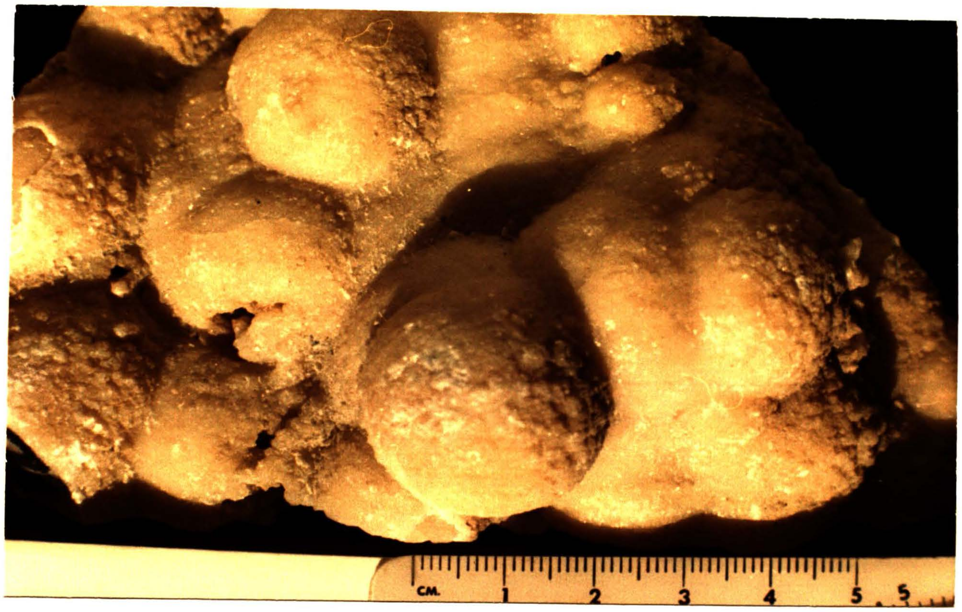

Fig. 33. Globular calcite. Hill mine.

Fig. 34. Photomicrograph showing radially fibrous structure of the calcite shown in Figure 33. Crossed nicols. 50X.

TABLE I

X-Ray Diffraction Pattern
for
the Globular Calcite Shown in Figure 37

Calcite		Calcite		Globular Calcite	
*Hanawalt, Rinn, and Frevel (1938)		*Swanson and Fuyat (1953)		Hill Mine Cave-in-Rock District	
d(A)	I	d(A)	I	d(A)	I(log)
3.87	8	3.86	12	3.85	11
3.05	100	3.035	100	3.037	100
----	---	2.845	3	2.849	9
2.50	20	2.495	14	2.495	18
2.28	24	2.285	18	2.281	27
2.09	20	2.095	18	2.094	26
1.92	32	1.927	5	-----	--
		1.913	17	1.912	36
1.87	24	1.875	17	1.877	32
----	--	1.626	4	1.626	7
1.60	16	1.604	8	1.600	13
----	--	1.587	2	1.587	9
----	--	1.525	5	1.521	13
1.51	12	1.518	4	1.517	14
1.478	5	1.510	3	1.509	12
----	--	1.473	2	1.470	6
1.442	8	1.440	5	1.441	14
1.428	5	1.422	3	1.419	14

*Standard X-ray diffraction powder patterns, N.B.S. Circular 539, vol. II, pp. 52-53.

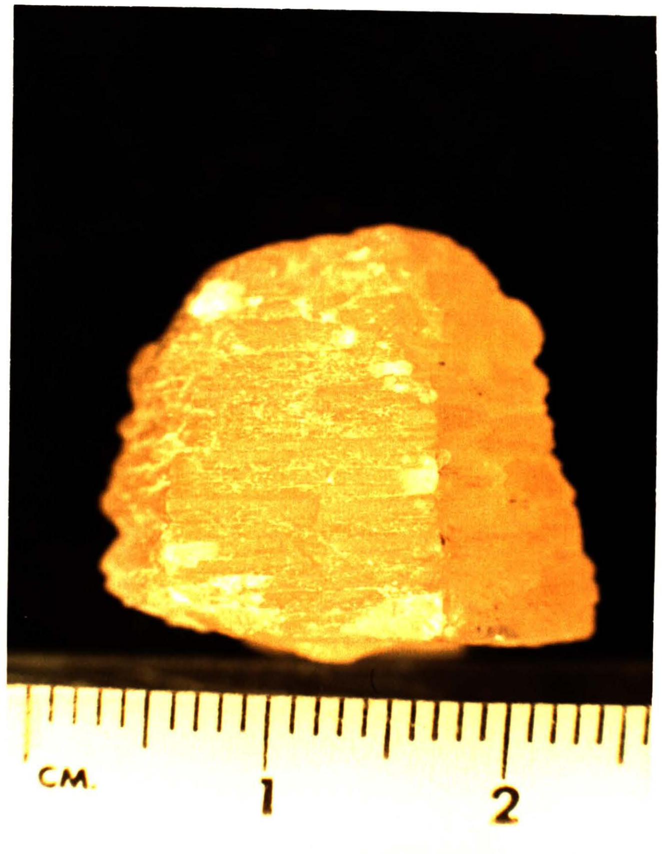

Fig. 35. A mosaic of twinned, pseudohexagonal crystals of witherite. Pale yellow tint is stronger in photograph than in actual specimen. Minerva mine No. 1.

Strontianite (Figure 36) generally is white to pinkish white in color, and exhibits a vitreous luster, but Grawe and Nackowski (1949) noted fibrous aggregates which were brown in color due to inclusions of oil. X-ray diffraction patterns obtained from the white and pinkish varieties of strontianite are similar (Table II).

10. Barite ($BaSO_4$)

Barite (Figure 37) varies in color from white to yellowish or bluish white. It occurs as well-formed crystals in vugs, and the crystals are tabular on {001} with {210}, or with {210} and {101}. Barite may occur as radiating groups of tabular crystals or as acicular to bladed aggregates in bands.

11. Quartz (SiO_2)

Quartz occurs as fine-grained crystals in disseminated ore, and as relatively coarser crystals in vugs. In disseminated ore, quartz often forms the cementing matrix and individual crystals may be included within other minerals.

Two types of quartz are present in vugs. One is white to colorless, and the other is brownish in color and larger in size. The former generally is an early vug lining (Figures 23 and 24), but it may also be deposited upon some of the other minerals. Some of these crystals are doubly terminated hexagonal prisms with two sets of rhombohedrons. White quartz crystals average 2 mm. in length. Brownish quartz crystals often include tiny globules of oil or bitumen, and their brown coloration apparently is due to those inclusions. The hexagonal prisms of brown quartz are horizontally striated, and some show inequal growth of their faces (Figure 38).

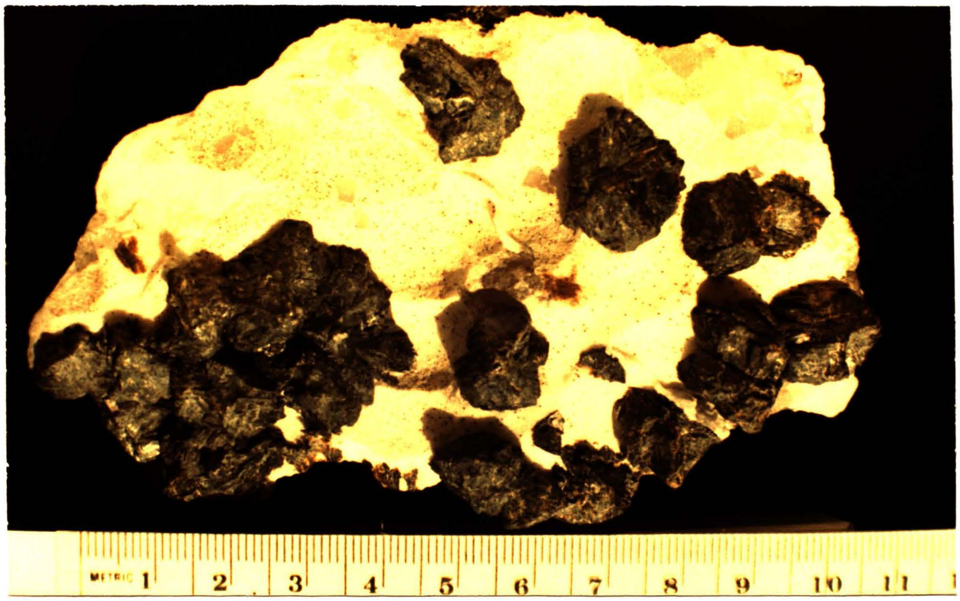

Fig. 36. Strontianite associating with fluorite (a few light crystals), sphalerite (brown) and pyrite (very tiny). The minerals have suffered subsequent corrosion. Minerva mine No. 1.

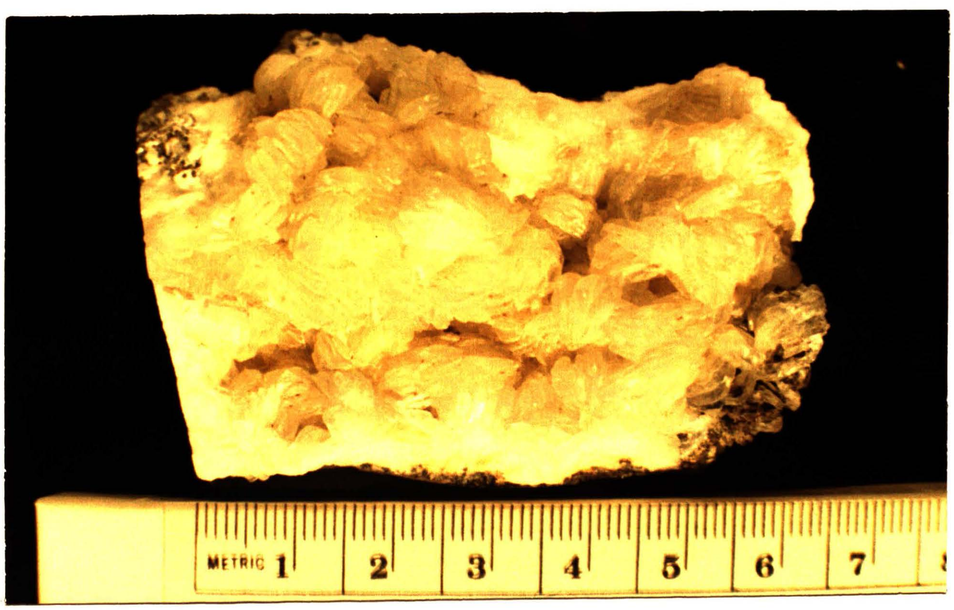

Fig. 37. Bluish barite crystals deposited upon white quartz. The crystals are tabular on {001} with modifications of {210} and {101}. The black stain (bottom right corner) is bitumen. Crystal mine.

TABLE II

X-Ray Diffraction Patterns
for
White and Pinkish Strontianite

Strontianite		White Strontianite		Pinkish Strontianite	
A. S. T. M. Index Card No. 5-0418		Minerva Mine No. 1		Minerva Mine No. 1	
Synthetically Prepared		Cave-in-Rock District		Cave-in-Rock District	
d(A)	I	d(A)	I(log)	d(A)	I(log)
4.367	14	4.374	14	4.353	12
4.207	6	4.201	10	4.208	9
3.535	100	3.538	100	3.534	100
3.450	70	3.453	79	3.446	54
3.014	22	3.013	25	3.008	18
2.859	5	-----	--	-----	--
2.838	20	2.838	35	2.836	28
2.596	12	2.592	25	2.596	17
2.554	23	2.558	45	2.556	37
2.481	34	2.476	48	2.473	43
2.458	40	2.457	73	2.455	59
2.4511	33	-----	--	-----	--
2.2646	5	2.2653	13	-----	--
2.1819	30	2.1819	30	2.1809	44
2.1035	7	2.0964	13	2.0941	15
2.0526	50	2.0512	70	2.0477	79
1.9860	26	1.9893	33	1.9811	37
1.9489	21	1.9489	33	1.9411	33
1.9053	35	1.9028	52	1.9005	30
1.8514	3	1.8396	7	1.8431	15
1.8253	31	1.8241	40	1.8180	23
1.8134	16	1.8139	40	1.8105	25

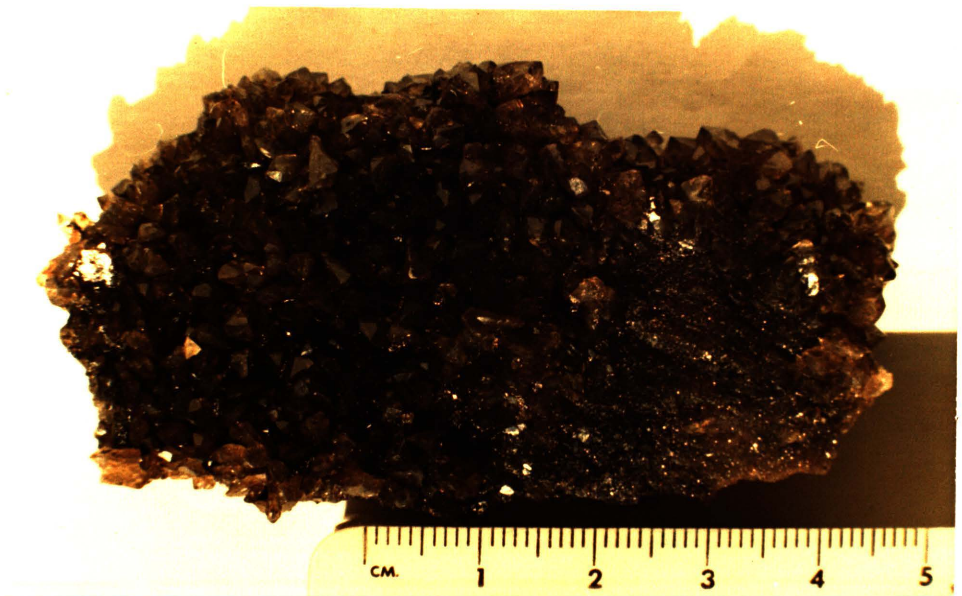

Fig. 38. Brown quartz. Hill mine.

12. Dolomite ($CaMg(CO_3)_2$)

Numerous tiny carbonate rhombs, 15 to 62 microns across, are found scattered through some of the disseminated ore or impure fluorite bands. Stain tests with alizarin red dye show that the carbonate is not calcite but rather it is another carbonate, probably dolomite. Brecke (1962, p. 505) indicated that tiny rhombs similar to these are dolomite.

Yellowish rhombohedrons of carbonate deposited in a vug upon corroded fluorite were noted in the Minerva mine No. 1 (Figure 39). Microscopic examination shows that the carbonate contains many small impurities. A stain test with alizarin red dye shows that it is not calcite. The pattern produced by X-ray analysis does not match that of dolomite and the writer was not able to match it to any other known pattern (Table III). The many inclusions which this mineral contains may have complicated the x-ray pattern.

13. Oil and Bitumen

Oil and bitumen appear to be of widespread occurrence in the bedding-replacement deposits of the Cave-in-Rock district. Oil occurs as tiny globules included within fluorite (Figure 40) and quartz. Air bubbles are present in some globules and when they are unbalanced the bubbles move in a manner similar to that of a hand level. The color of the oil inclusions ranges from yellowish to greenish brown.

Bitumen is a viscous or dry residue from oil. It occurs as small drops or thin layers coating other minerals. Masses of dark brown to black, viscous bitumen emitting a petroleum odor were noted in some vugs in the Hill mine, where it was deposited upon yellowish

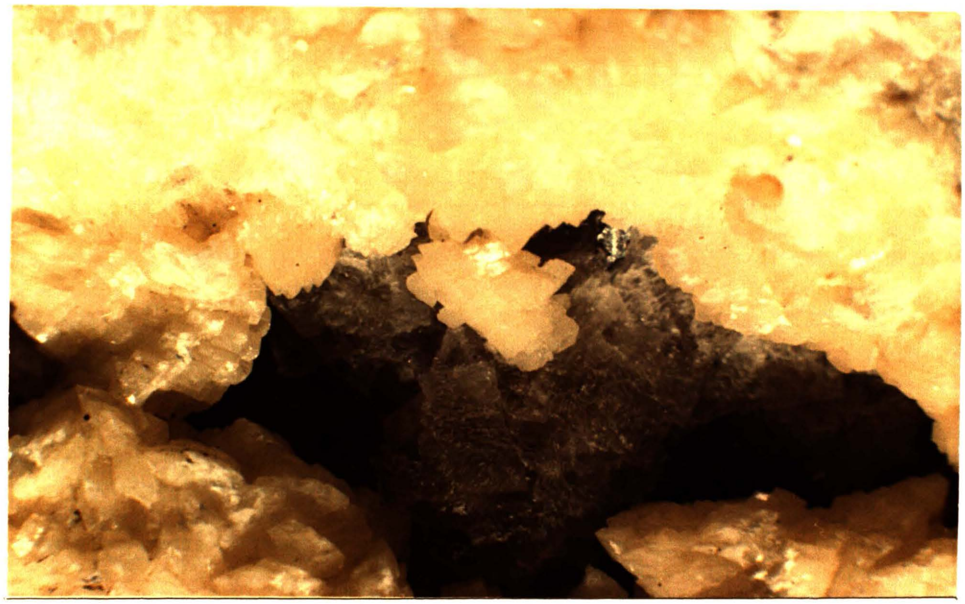

Fig. 39. Rhombohedral crystals of a carbonate deposited upon corroded surface of fluorite. Minerva mine No. 1. 3X.

TABLE III

X-Ray Diffraction Pattern
for
the Rhombohedral Carbonate Shown in Figure 39

d(A)	I
4.92	12
4.57	6
4.19	21
3.92	26
3.59	13
3.43	12
3.35	12
3.08	100
2.76	[illegible]7
2.53	35
2.44	19
2.22	17
2.18	12
2.12	24
2.04	9
2.00	8
1.98	9
1.94	21
1.90	32
1.86	11
1.72	10
1.69	7
1.63	6
1.63	15
1.61	10
1.59	9
1.54	19

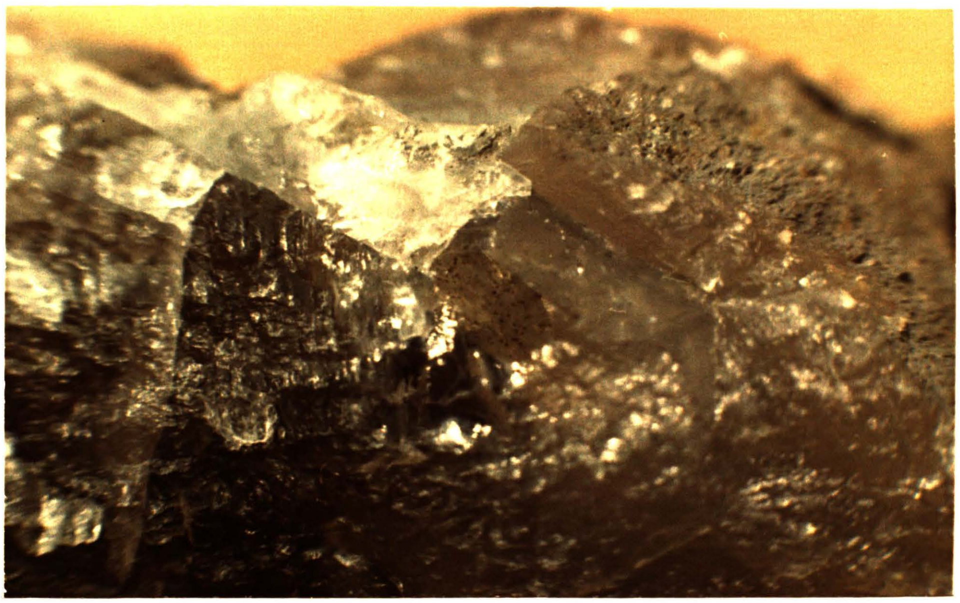

Fig. 40. Oil inclusions (brown spots) within fluorite. Crystal mine. 4X.

fluorite cubes (Figure 41) and upon quartz and sphalerite (Figure 23).

14. Chalcedony

Chalcedony occurs as spherulitic or banded aggregates in chert which has been partially replaced by fluorite (Figure 42).

15. Secondary Minerals

Currier (1944, p. 33) described the secondary minerals, cerussite and smithsonite:

> The carbonates of lead and of zinc have been observed in some of the deposits. The variety of smithsonite that is known, from its color and appearance, as "turkey-fat" has been found at Lead Hill as a coating on fluorspar crystals.

Weller, Grogan and Tippie (1952, p. 120) noted that:

> Smithsonite, cerussite and anglesite, and malachite are found in small quantities in the oxidized portions of near-surface deposits. They result from groundwater alteration of sphalerite, galena, and chalcopyrite, respectively.

Pyromorphite has been reported to occur in oxidized ore in the Patrick open-pit mine, about 3 miles west of the town of Cave in Rock (Grogan, 1946).

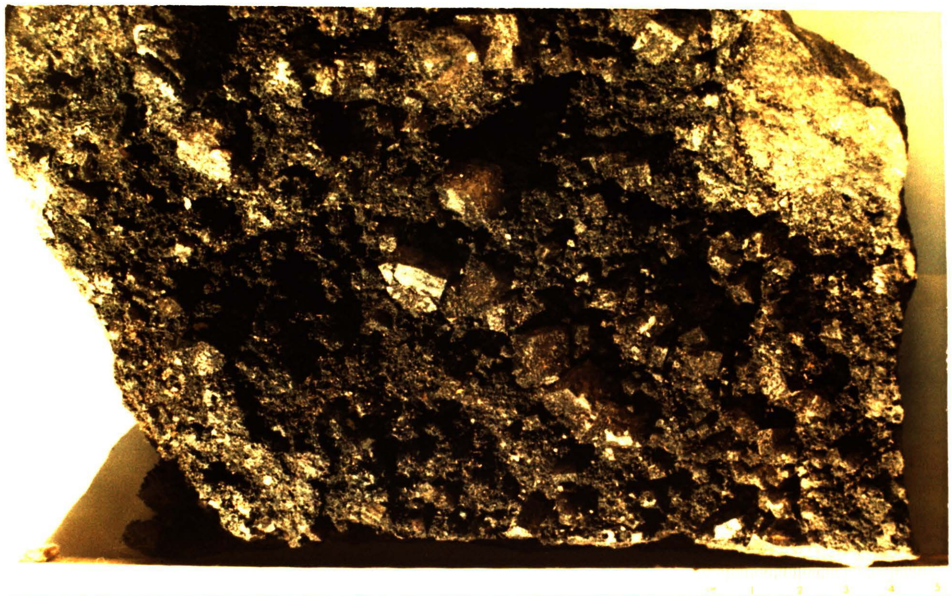

Fig. 41. Viscous bitumen coating fluorite. Hill mine.

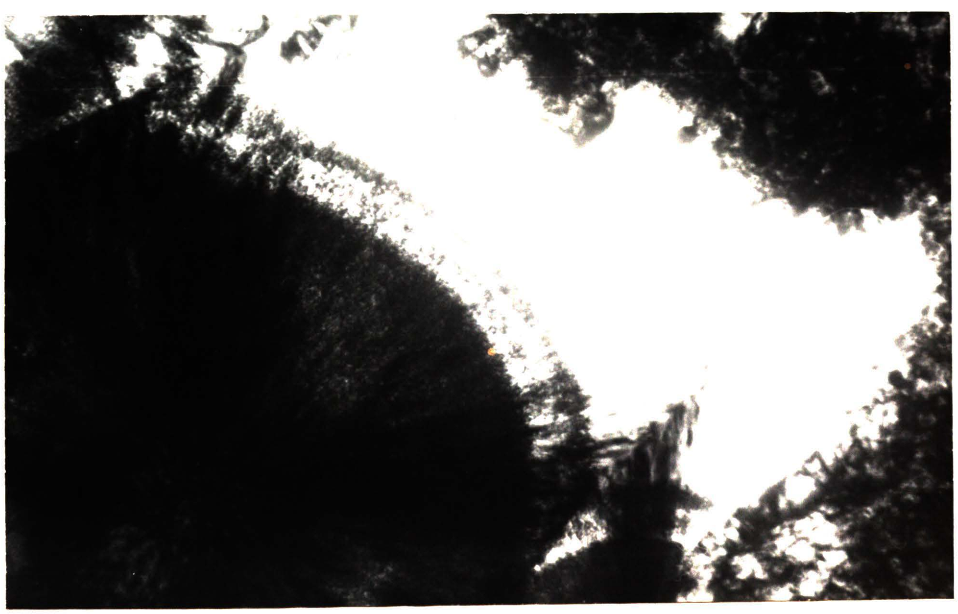

Fig. 42. Spherulitic chalcedony. Minerva mine No. 1. Crossed nicols. 50X.

Chapter V

PARAGENESIS

A. General

The deposition of minerals from ore-bearing solution takes place when the physical and chemical factors, such as temperature, pressure and composition become favorable to their precipitation. The deposition of any two ore minerals may be contemporaneous, successive or overlapping. The relative order of mineral deposition is known as the "paragenesis".

Historically, paragenetic determinations were done entirely by the examination of hand specimens prior to the use of microscope. The first microscopic examination of an ore for paragenetic purposes was that by Campbell and Knight (1906). Subsequent microscopic studies of various ores have produced a wealth of ore textures. The paragenetic interpretation of ore microtextures has been discussed by Bastin (1918 and 1950), Lindgren (1930), Bastin, et. al. (1931), Schwartz (1931 and 1951), Bandy (1954), Edwards (1954), and many others.

The present investigation of paragenesis in the Cave-in-Rock district began with careful examination of ore specimens with the naked eye and with the aid of the binocular microscope. Selected specimens were sawed to reveal additional mineral relationships. Both petrographic and reflecting microscopes were utilized to examine fine-grained mineral relationships. The specimens utilized for this investigation were selected from the Crystal, Minerva No. 1 and Hill mines.

B. Development of Banded Ores.

The development of banded or coontail ore has been the subject of much discussion because of its unusual texture. Coontail ore consists of alternating layers of coarse-pure and fine-impure fluorite. The impure fluorite bands may include a significant amount of other minerals, such as sphalerite and galena, forming sphalerite-fluorite or galena-fluorite banded ore. There are two general ideas on the development of such banding. The first has been advocated by Bastin (1931), who believes that the banding developed by rhythmic deposition during replacement by diffusion of the mineralizing solutions through a solid rock medium. Thus, both pure and impure bands are thought by Bastin to have developed by replacement.

Most writers, however, believe that while the impure, disseminated bands developed by replacement, the pure fluorite bands formed principally in open spaces developed by solution of the host rock limestone. Currier (1944, pp. 37-38), for instance, states that:

> ...active fluoriferous solutions from a feeding fissure proceeded along the purer limestone beds, progressively replacing the limestone. Hydrofluoric acid would easily and quickly react with the calcium carbonate of the limestone to form calcium fluoride,...The ratio between the amount of $CaCO_3$ dissolved and the CaF_2 formed would be completely stoichiometrical, and as the specific volume of CaF_2 is only about two-thirds the specific volume of $CaCO_3$ the fluorspar thus formed by the above reaction would have been of insufficient volume to fill completely the space that was occupied by the replaced calcite. In any solution cavity thus formed, additional fluorspar, existing as CaF_2 in the mineralizing solutions and picked up by these solutions because of reactions along the paths of travel, could be precipitated almost immediately, so that at no time would the open space be extensive.

Grogan (1949, p. 615) follows the thinking of Currier, and states that the volume reduction from stoichiometric replacement can theoretically amount to as much as 33 percent.

Weller, Grogan and Tippie (1952, p. 126) have stated well the second idea on the development of banded ore as follows:

> Although it seems obvious that the crystals comprising the coarse fluorspar layers grew into open spaces, no such spaces have been observed at the ends of coarse layers. It may be that the ore solutions continued to deposit fluorspar after they ceased to dissolve limestone, and thus filled with fluorspar the openings already made. The formation of the coarse fluorspar layers involved cavity filling and cannot be considered replacement in the strict volume-for-volume sense of the word, although the fine-grained layers apparently were formed in such a way.

Similarly, Brecke (1962, p. 317) views the formation of the low-grade or disseminated bands in the following manner:

> ...the solution advanced as a front of the mineralizing influence and replaced available calcium carbonate or converted it to calcium fluoride. The refractory materials such as dolomite and silica were taken into solution but were precipitated in a zone ahead of the front. Fluid petroleum was either flushed ahead of the front or displaced by growing fluorite crystals ...The zone zhead of the front, therefore, contained not only the impurities of the volume of host rock but also contained the impurities that occurred in volume replaced by fluorite and became a highly refractory zone. The zone of accumulated refractory material was eventually by-passed by the advancing mineralizing front leaving plate-like masses of low-grade spar that appear as bands in the cross section.

The present writer holds to the second theory, that the major portion of the pure layers of banded ore have formed by open space filling. The pure and highly crystalline nature of the fluorite-rich bands and the common presence of comb structure support such an interpretation. Thus, the well crystallized minerals occurring as the pure bands are placed with the vug-filling sequence in the paragenetic diagrams for the Crystal and Minerva No. 1 mines.

C. Paragenesis of the Crystal Mine

Fluorite ore in the Crystal mine occurs on the Rosiclare horizon. In the Crystal mine ore the following minerals and hydrocarbons were identified:

1) Dolomite (?)
2) Fluorite
3) Quartz
4) Chalcopyrite
5) Galena
6) Sphalerite
7) Marcasite
8) Pyrite
9) Calcite
10) Barite
11) Oil and Bitumen

The minerals occur both in disseminated form and in well-developed crystals deposited in open spaces. The minerals deposited in vugs generally appear to have formed after adjacent disseminated minerals and thus the former have been arbitrarily separated from and placed after the latter in the paragenetic diagram (Figure 43). The reader must bear in mind that while some proportion of those minerals which are disseminated may have formed by replacement at the same time at which their counterparts in the vugs were crystallizing, such time relationships are not recorded as ore textures and therefore they are not shown in the paragenetic diagram. Tiny veinlets of some minerals extending to or from their crystals in vugs across

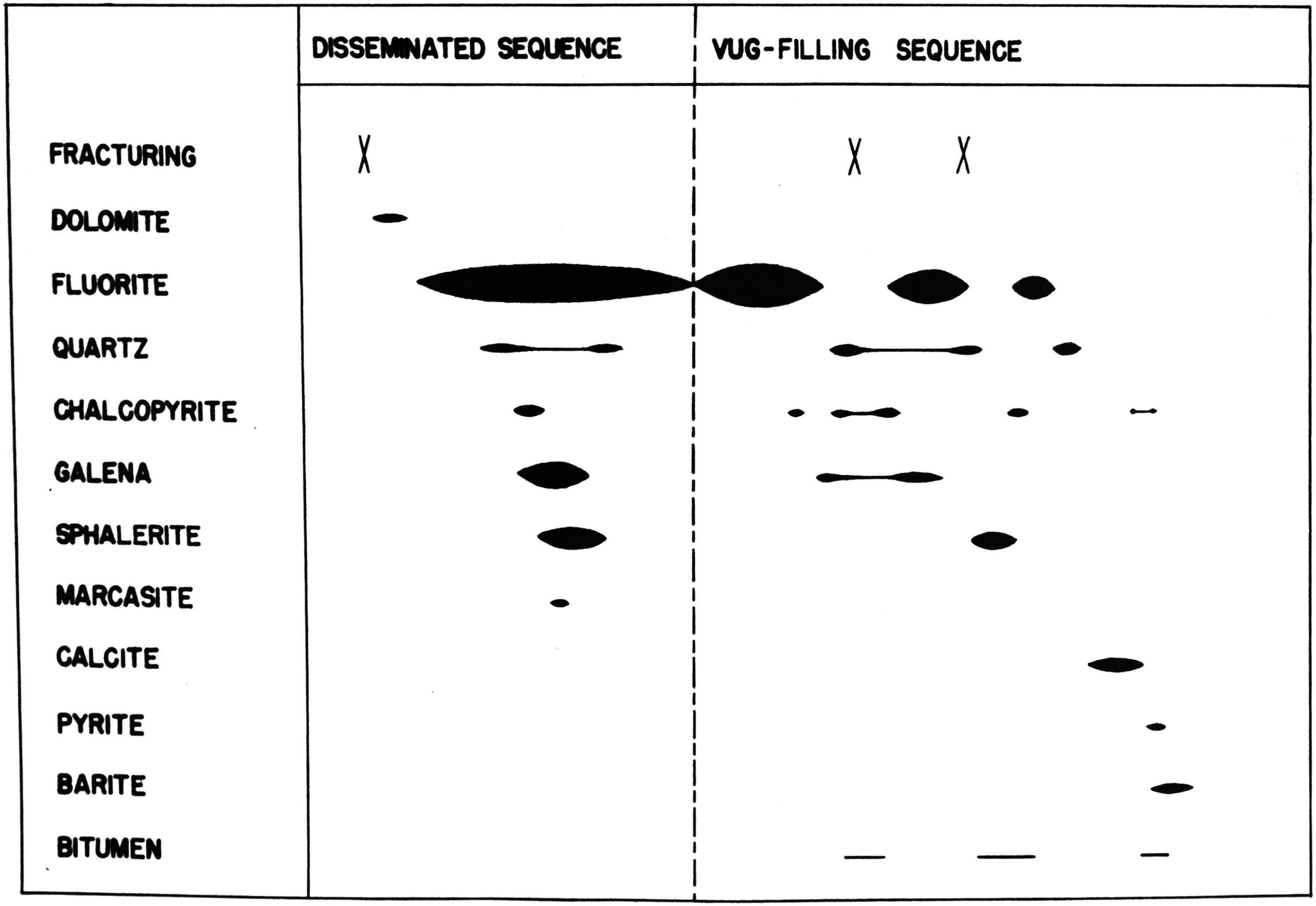

FIG. 43. PARAGENETIC DIAGRAM FOR THE CRYSTAL MINE

the disseminated ore show that most disseminated ore was consolidated before the vug sequence developed.

Each of the minerals listed are described below in the general paragenetic order.

1. Dolomite

A significant amount of carbonate was detected in thin sections prepared from impure bands of coontail ore or from disseminated ore where it occurs as rhombs 15 to 62 microns across. Some carbonate grains are as large as 1/2 mm. across (Figure 44). Alizarin red stain tests showed that the carbonate is not calcite, but probably is dolomite. Most of the dolomite occurs as idiomorphic rhombs, but some is less regular in shape. The writer believes that most of the dolomite has deposited from the mineralizing solutions, but some dolomite may have been an original constituent of the host rock limestones. Currier (1944, p. 31) noted a ferruginous carbonate or ankerite which he believed to be an original constituent of some of the limestone layers. Brecke (1962, p. 505) reported pearly, white, rhombic crystals of dolomite scattered in low-grade fluorspar which he believed to have formed from the ore solutions.

The disseminated dolomite rhombs are partly replaced by fluorite, sphalerite (Figure 45), quartz (Figure 46) and galena, and they may occur as inclusions in sphalerite (Figure 47) and quartz. These observations indicate that the dolomite was the first mineral to develop in the disseminated sequence.

2. Fluorite

Fluorite was the first mineral to be deposited in abundance.

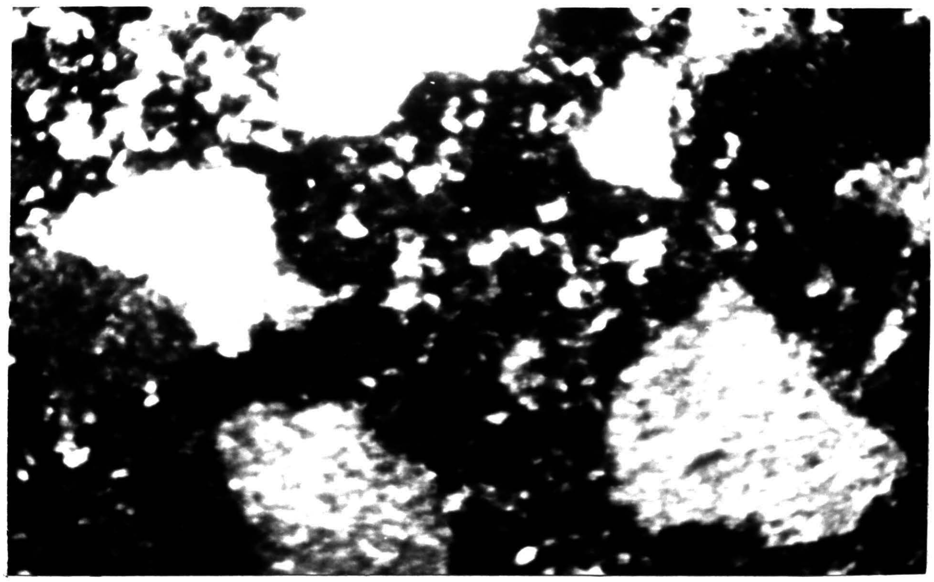

Fig. 44. An impure band of coontail ore consisting of fluorite (black), dolomite (light gray) and quartz (white, tiny grains). Crossed nicols. 50X.

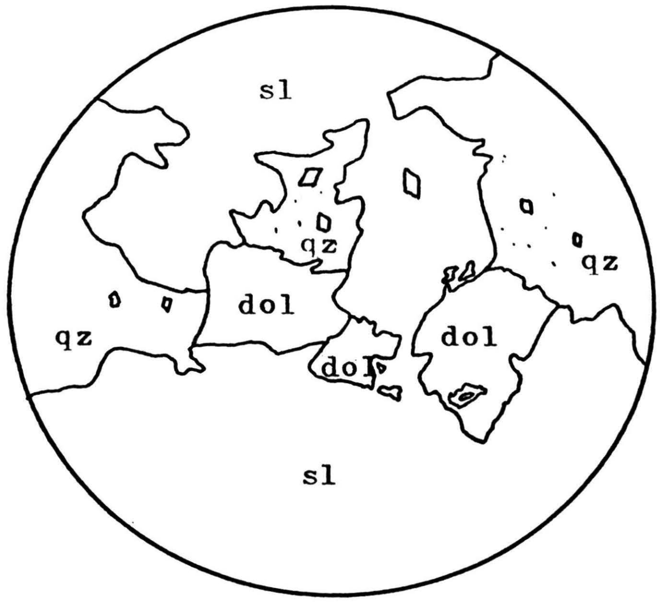

Fig. 45. Dolomite (dol) replaced by sphalerite (sl). Two dolomite grains to the right extinguish simultaneously, indicating that they originally were portions of the same rhomb. Note tiny rhombs of dolomite in sphalerite and quartz. 30X.

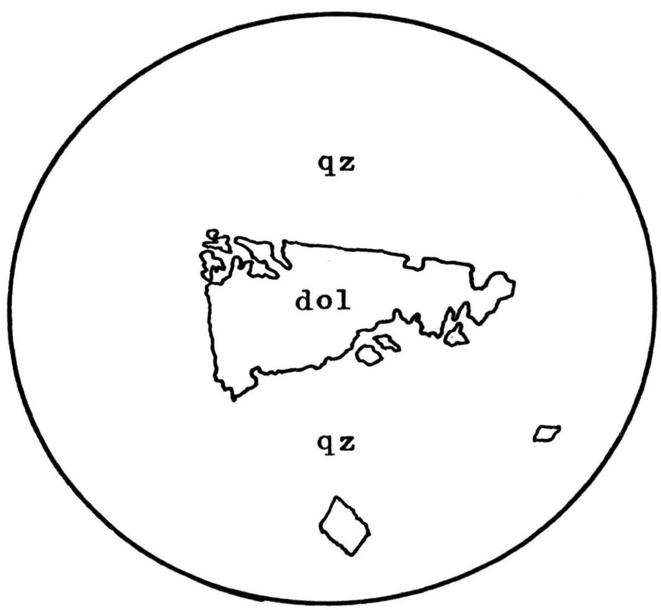

Fig. 46. Dolomite (dol) replaced by quartz (qz). All the remnants (center) extinguish uniformly. Note the general rhombic outline and several dolomite rhombs elsewhere in the quartz. 30X.

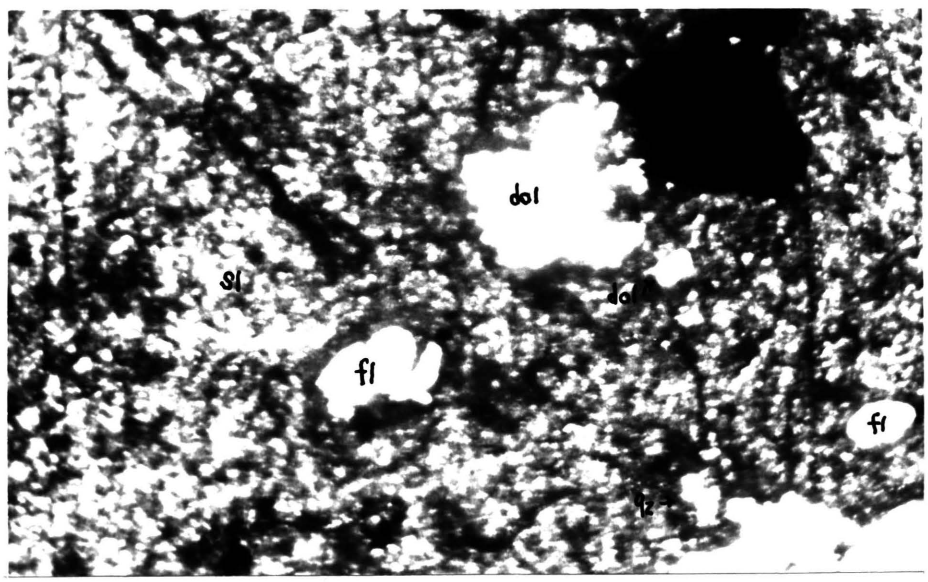

Fig. 47. Sphalerite (sl) with inclusions of galena (black), quartz (qz), fluorite (fl) and dolomite (dol) in an impure band of coon-tail ore. Plane polarized light. 50X.

Microscopic examination of disseminated ore reveals that part of the fluorite occurring in impure bands or disseminated ore exhibits cubic outlines but most is irregular. Such cubes average approximately 2 mm. Some irregular fluorite grains are included within sphalerite and galena crystals where they appear to be replacement remnants (Figures 47 and 48). Fluorite also has been replaced by quartz as shown in Figure 49. Thus, some fluorite has formed prior to those minerals.

The first fluorite to be deposited in open spaces consists of two occurrences, yellowish white to yellow fluorite in the pure bands of coontail or banded ore and yellow fluorite crystals deposited in vugs. The writer believes, as do Weller, Grogan and Tippie (1952, p. 126), that the pure layers or bands of banded ore formed primarily by open space filling, and that they were deposited at essentially the same time as well-crystallized yellow fluorite in adjacent vugs. Yellow fluorite comb structure also is developed in open spaces in green sandstone. Coarsely crystalline to massive fluorspar, called "acid spar", was deposited in cavities parallel to the bedding (Figure 50) primarily at the top and margin of the ore deposit.

Subsequent to the deposition of yellow fluorite, purple fluorite was deposited during at least two periods. The first generation of purple fluorite was deposited in fractures across yellow fluorite and it was deposited upon combs of yellow fluorite forming crystallographic overgrowths. Such specimens exhibit a thin layer of black bitumen which was deposited during a period between that of the earlier fluorite and that of subsequent purple

Fig. 48. Replacement remnants of fluorite (white) in galena (black). Plane polarized light. 50X.

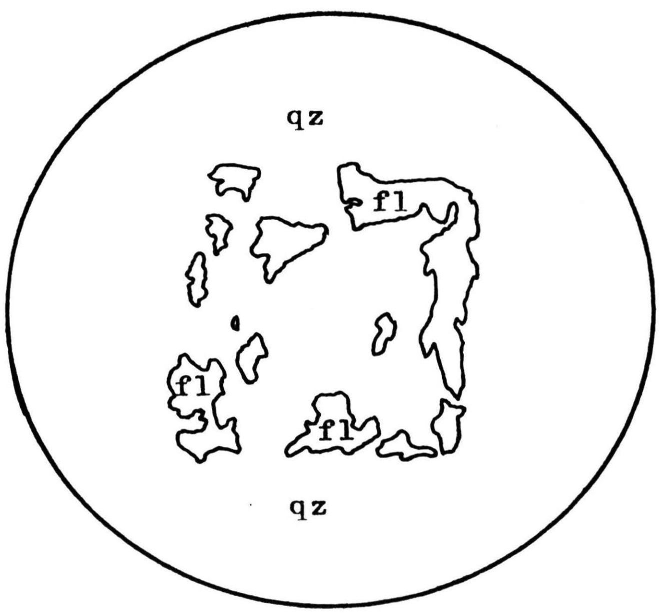

Fig. 49. Fluorite (fl) replaced by quartz (qz). The entire fluorite area has the general shape of an original fluorite cube. 30X.

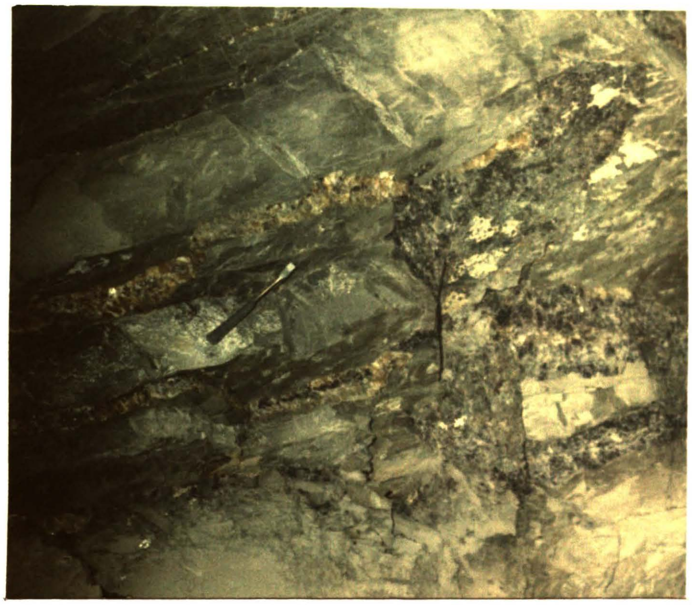

Fig. 50. Veins or bands of massive yellowish fluorite parallel to the bedding of sandstone. Note that purple fluorite is confined to the central portions of the yellowish bands. Rosiclare sandstone, Crystal mine.

fluorite.

The difference in color of the two generations of fluorite, the intervening deposition of bitumen and the occasional presence of tiny quartz crystals at the contact are evidence for a time separation of the two minerals. In those vugs in which yellow fluorite is not present, white quartz crystals often occur as the first lining mineral prior to the deposition of purple fluorite.

A later, less abundant, purple fluorite occurs as tiny cubes, 1 to 3 mm. on a side. It commonly is deposited upon quartz and galena (Figure 51), less commonly upon sphalerite. White quartz locally separates the deposition of early and late purple fluorites.

3. Quartz

Quartz appears five times in the paragenetic sequence. Quartz occurs as microscopic crystals in disseminated ores and in impure bands of coontail ore where they range from 25 microns to 0.4 mm. in length and from 25 microns to 0.2 mm. in diameter.

In those disseminated ores in which quartz is abundant, it forms a cementing matrix for galena, sphalerite and chalcopyrite, but some euhedral quartz crystals are included near the margins of the sulfide minerals (Figure 52). Part of the quartz apparently formed before the sulfide minerals and part formed later. Thus, quartz occurring in disseminated ore and impure bands of coontail ore has crystallized earlier than the sulfide minerals, galena, sphalerite, chalcopyrite and marcasite, but later than disseminated fluorite. Currier (1944, p. 39) believes that some quartz also may have formed before fluorite in impure layers.

Quartz deposited in vugs occurs as two types. The earlier

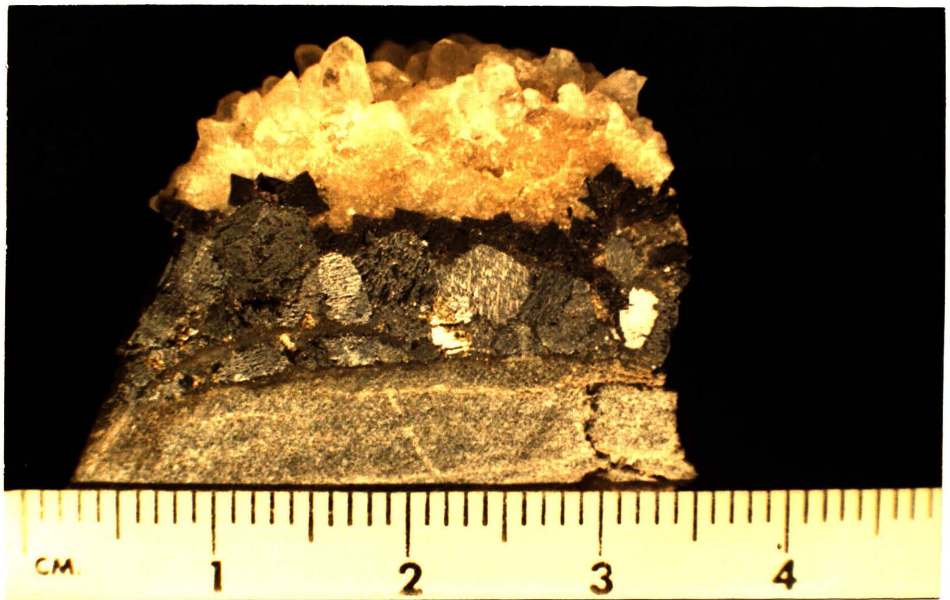

Fig. 51. Specimen showing crustification of calcite (yellowish white) on fluorite (dark purplish gray) on galena (medium gray). A thin band of white quartz first lines the vug, and some quartz locally is present between galena and purple fluorite. Small quantities of chalcopyrite (yellow) occur with the quartz, on quartz and within galena. The scalenohedral calcite is modified by the positive rhombohedron.

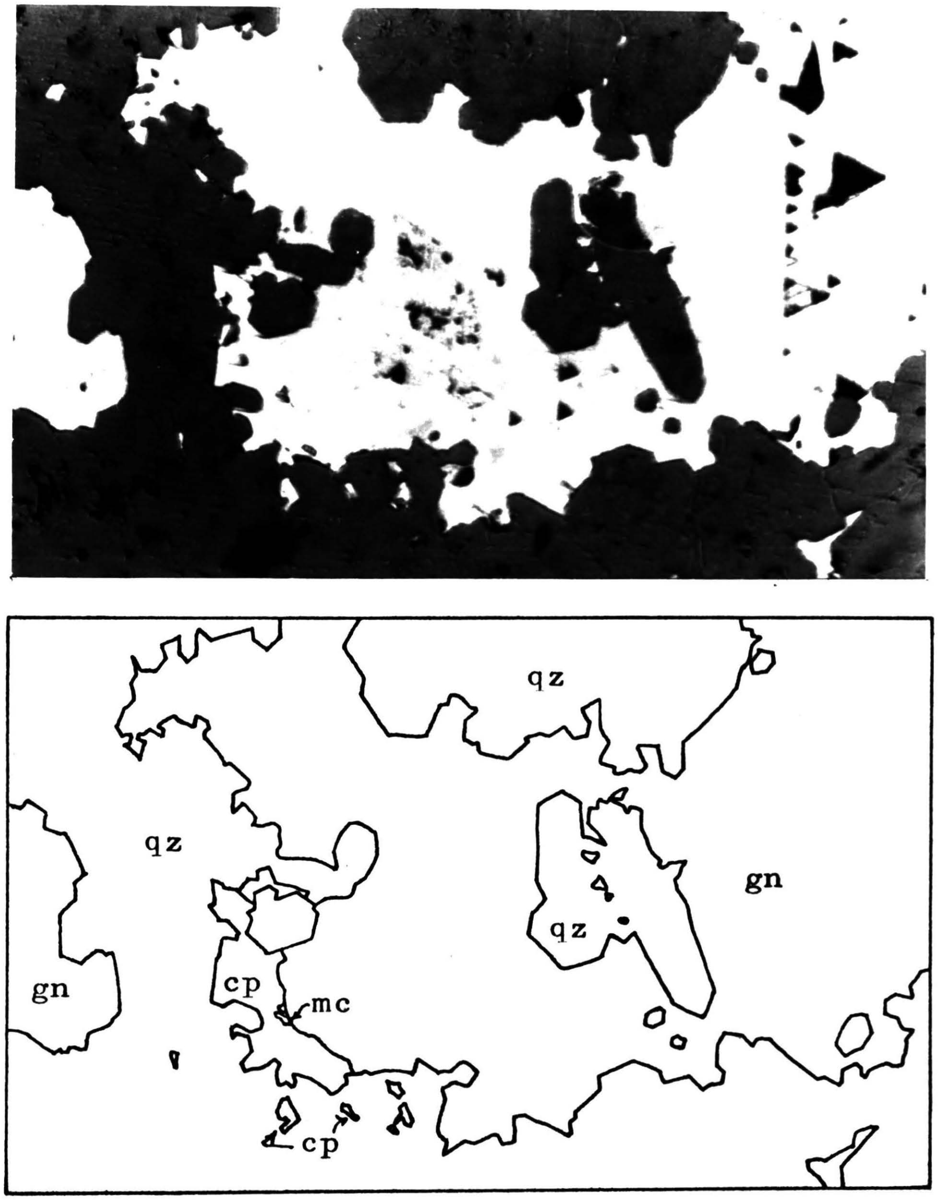

Fig. 52. Photomicrograph of polished surface showing euhedral quartz (qz) adjacent to and included by galena (gn) and chalcopyrite (cp). Marcasite (mc) occurs between the galena and chalcopyrite. 60X.

type is white, the later is a brownish color. The early white variety generally ranges from 1/2 to 1 mm. in diameter, although rare crystals up to 3 mm. were observed. It commonly forms an early vug lining (Figure 24), and it may coat unmineralized fragments of the host rock, often shaly sandstone. White quartz crystals may line both sides of fractures nearly perpendicular to banding, where they were deposited upon early purple fluorite. White to colorless quartz crystals deposited upon the cubic faces of early purple fluorite are shown in Figure 53, and such quartz may be relatively coarsely crystallized and doubly-terminated. Most white quartz was deposited before galena, but some crystals have continued to be deposited during and after the deposition of galena. Similar relationships were observed between quartz and sphalerite. White quartz generally was deposited as a first vug-lining mineral before sphalerite, but some was deposited after sphalerite.

The later brownish quartz deposited in vugs is relatively coarse, averaging approximately 3 mm. in diameter. Its pale to dark brownish color may be due primarily to inclusions of tiny globules of greenish to yellowish oil or brownish black bitumen. The prism faces of the quartz are horizontally striated. This late quartz may be deposited upon the early white quartz, cubo-octahedral galena, early yellow and purple fluorite and rarely on late purple fluorite as shown in Figure 54.

4. Chalcopyrite

Small amounts of chalcopyrite are of widespread occurrence in the Crystal mine. The mineral occurs in as many as seven

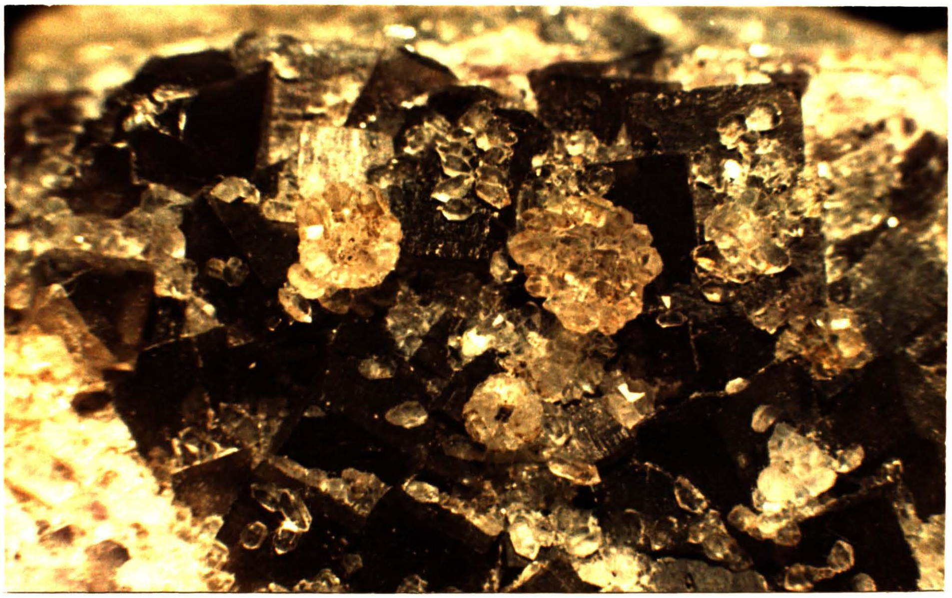

Fig. 53. Clear quartz deposited upon the cubic faces of early purple fluorite. The quartz prisms are terminated by two sets of rhombohedrons. Bitumen locally stains the quartz brown. Some quartz groups (central part) form "mosaic bowls". 3X.

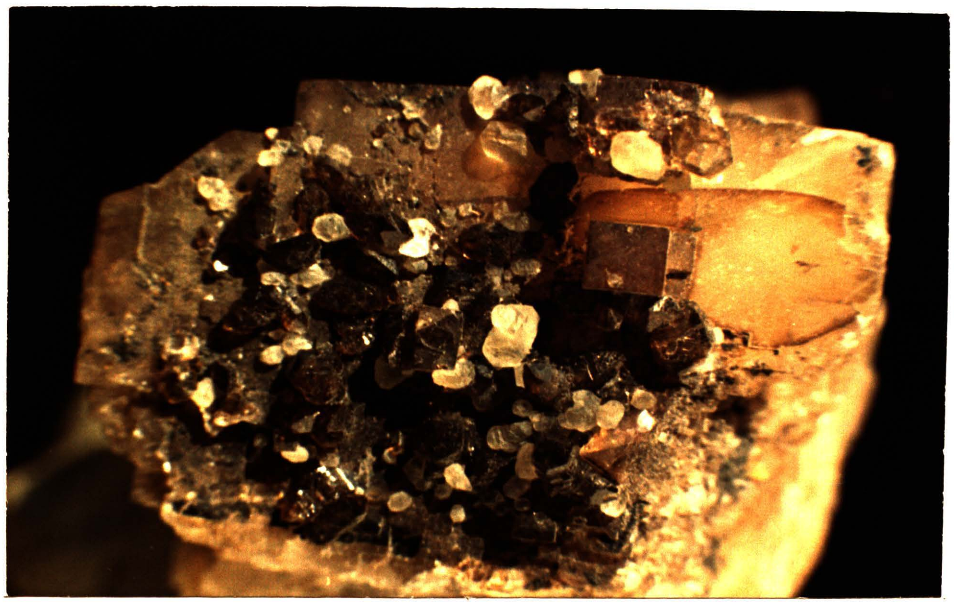

Fig. 54. Brownish, horizontally striated quartz deposited upon small late purple fluorite, which, in turn, is deposited upon yellow fluorite. Bitumen is deposited upon yellowish fluorite before purple fluorite. Calcite (white) is deposited upon both fluorites and on quartz. 3X.

paragenetic positions as irregular grains in disseminated ore, inclusions within yellowish fluorite and as crystals on other minerals in vugs.

In disseminated ore, chalcopyrite may contain inclusions of quartz and fluorite. Contiguous grains of chalcopyrite and galena most often show mutual boundaries, but rare euhedral chalcopyrite inclusions in galena suggest that chalcopyrite generally was earlier than galena (Figure 55). Although chalcopyrite was not observed to be contiguous to sphalerite in any of the polished surfaces prepared by the writer, its paragenetic position is known to be prior to that of sphalerite because of its relationship to galena.

Acicular or nail-like chalcopyrite crystals, 1 to 4 mm. long, frequently are included within yellowish fluorite. These crystals appear to be confined to certain planes of the fluorite where they were deposited during a cessation of fluorite deposition.

Chalcopyrite also may be deposited with white quartz which forms an early crust in many vugs. Another period or continuation of that period of chalcopyrite deposition is evidenced by chalcopyrite deposited upon the crust-forming quartz and before subsequent galena. That this period of chalcopyrite deposition continued during that of galena is shown by chalcopyrite inclusions within that galena.

Even later chalcopyrite occurs as well-formed, 1 to 3 mm., disphenoidal crystals deposited on sphalerite and other minerals (Figure 25), but earlier than late purple fluorite, brown quartz,

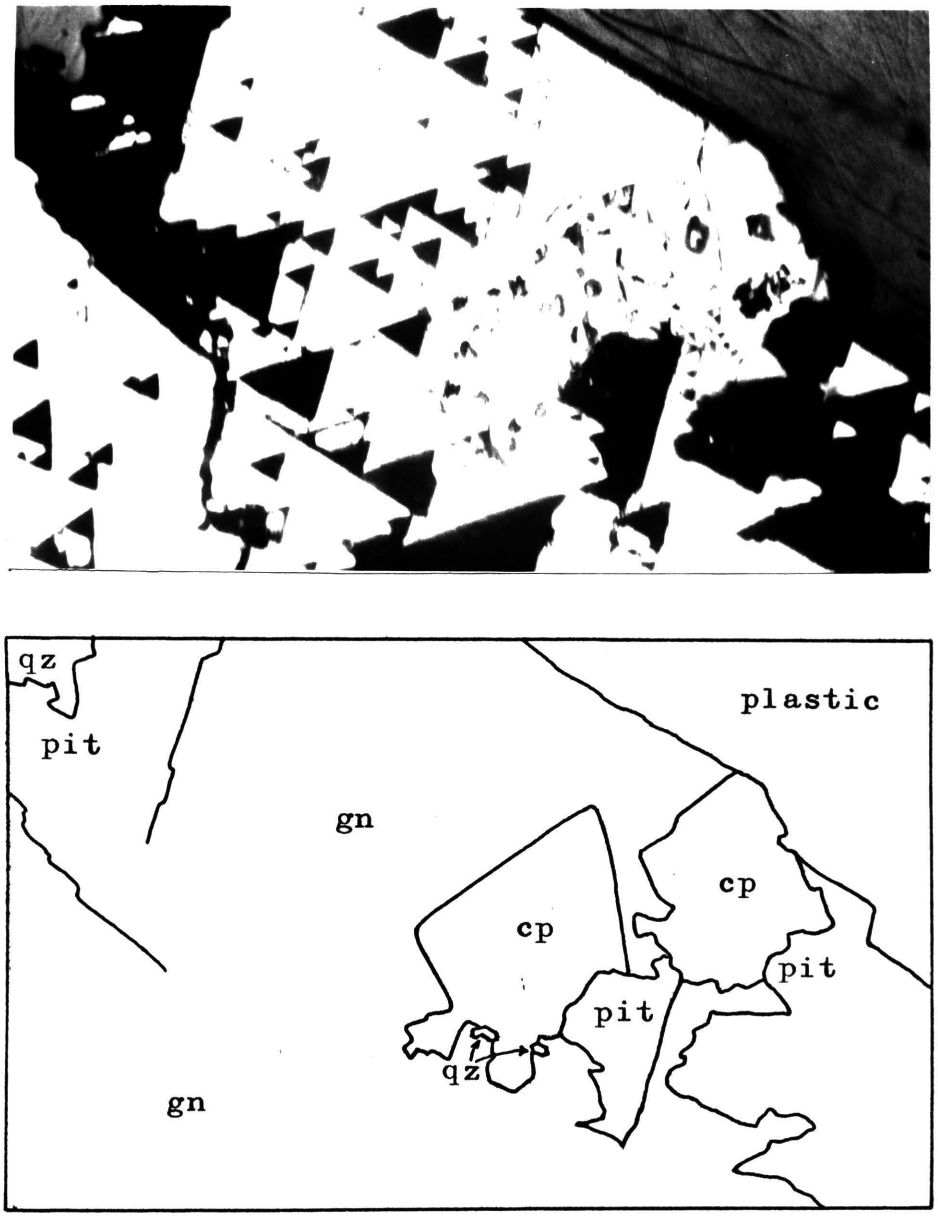

Fig. 55. Chalcopyrite (cp) included in and partly corroded by galena (gn) in disseminated ore. Tiny euhedral quartz (qz) locally is present. Reflected light. 60X.

calcite and barite. That this period of chalcopyrite deposition partly overlaps that of sphalerite is shown by the fact that some chalcopyrite crystals are partially included within sphalerite.

Chalcopyrite was deposited very late as fine-grained, 1/4 mm., crystals both within and on calcite. Similar crystals are deposited on earlier minerals.

5. Galena

Galena was deposited in at least three different generations. The earliest galena, that which occurs in disseminated ore and impure bands of coontail ore, contains inclusions of earlier dolomite, fluorite and quartz crystals. Its age relationship to sphalerite is more complex. Where the two minerals are contiguous they generally exhibit mutual boundaries. Some galena is euhedral against and earlier than sphalerite as shown in Figure 56. Least commonly, the reverse age relationships are shown, where the euhedral rotund shape of sphalerite impinges upon galena (Figure 57). Thus, the depositional periods of the two minerals overlapped, but most galena formed before sphalerite.

In vugs, galena was deposited in small amounts before the crystallization of the early white quartz as shown in the sketch (Figure 58), but galena was deposited in greater quantities after the deposition of the white quartz crust (Figures 24 and 59). All the galena crystals observed by the writer in vugs in the Crystal mine were cubes modified by the octahedron.

6. Sphalerite

Sphalerite occurs in two generations, in disseminated ore and impure bands of coontail ore, and as crystals in vugs. The

Fig. 56. Photomicrograph showing euhedral galena (black) crystallized before sphalerite (dark gray) in impure bands of coontail ore. Plane polarized light. 50X.

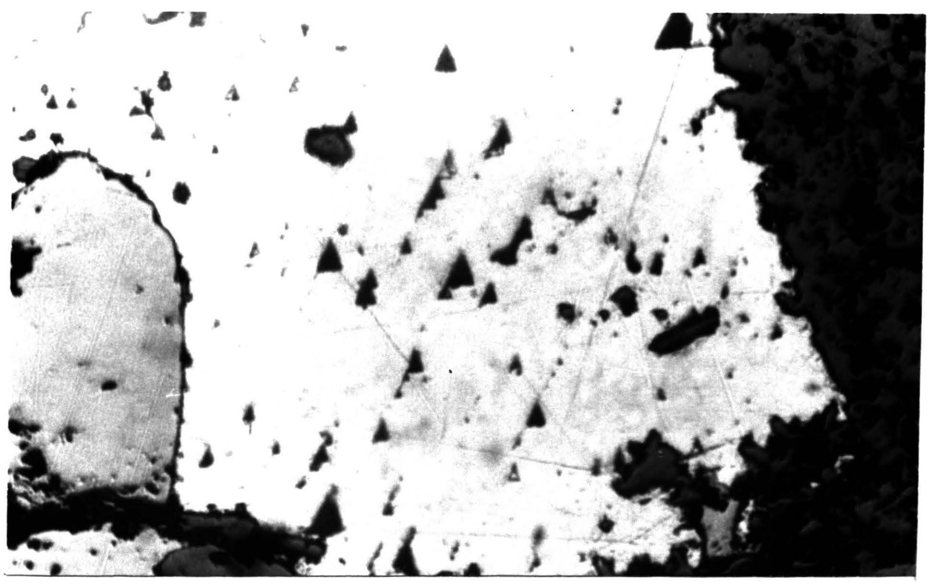

Fig. 57. Photomicrograph showing euhedral rotund sphalerite (medium gray) crystallized before galena (light gray) in disseminated ore. Reflected light. 60X.

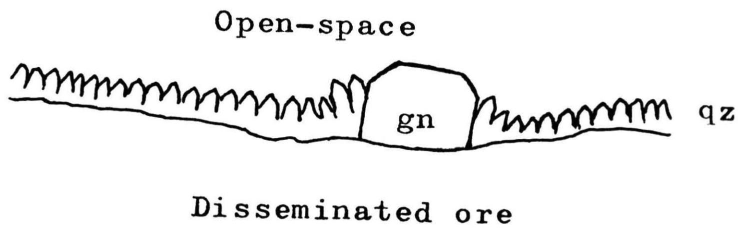

Fig. 58. Quartz crystals (qz) deposited beside and partly upon galena (gn) in a vug. 3X.

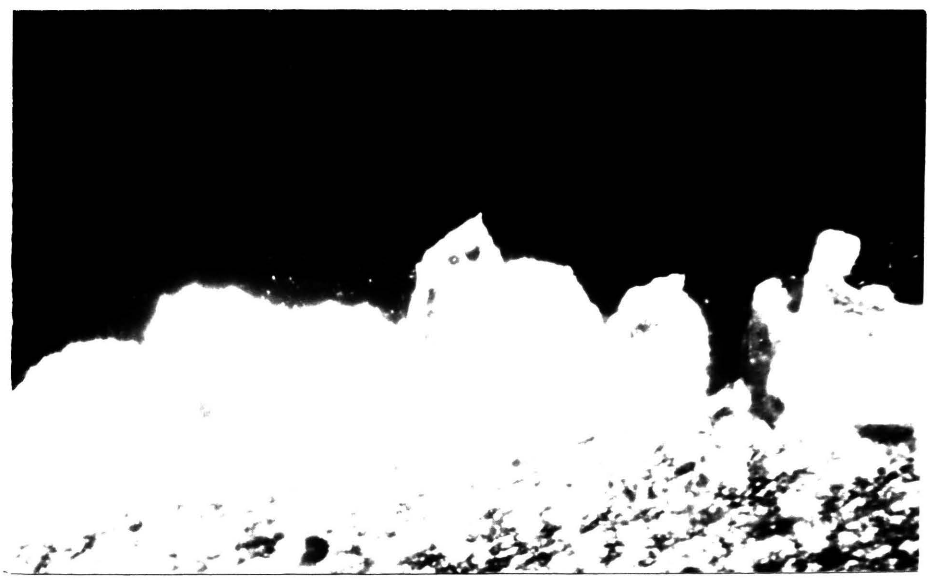

Fig. 59. Galena (black) deposited on white quartz in a vug. Crossed nicols. 50X.

first generation occurs as rudely euhedral crystals which may include the earlier formed minerals, dolomite, fluorite, galena and quartz (Figures 46 and 60).

Sphalerite also occurs as well-formed crystals in vugs. The tetrahedral crystals, with or without modification of cubic faces, were deposited on galena, white quartz and the early purple fluorite. The last age relationship also is shown by narrow sphalerite veinlets cutting early purple fluorite veinlets.

7. Marcasite and Pyrite

Marcasite and pyrite are the least abundant of the sulfide minerals. Each was observed to occur in one paragenetic position in the Crystal mine. Marcasite occurs in small amounts in disseminated ores where it generally is restricted to grains of chalcopyrite (Figure 52) and may have replaced that mineral.

Bastin (1931, p. 63) reported marcasite to be included within transparent fluorite in vugs as needle-like crystals, but Weller, et al. (1952, p. 120) believe those needles to be chalcopyrite. Marcasite was not observed to occur in any of the vug-fluorite studied by the writer.

Pyrite was observed to occur in one small vug in the Crystal mine. Tiny, 0.1 to 0.3 mm., pyrite cubes modified by octahedral faces were deposited upon small late purple fluorite (Figure 26). Weller, et al. (1952, p. 120) have observed small pyrite crystals encrusting fluorite and calcite in the Davis-Deardorff mine.

8. Calcite

Calcite is an abundant late mineral in the Crystal mine. The common crystal form is a scalenohedron with or without modification

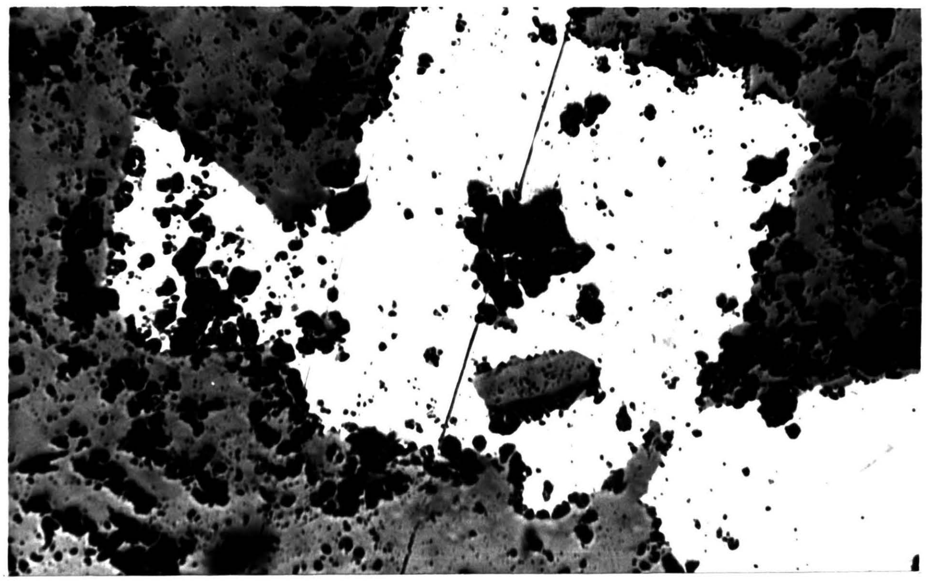

Fig. 60. Euhedral quartz crystal (dark gray) included by sphalerite (light gray) in disseminated ore. The black spots are pits. Reflected light. 60X.

by rhombohedral faces, shown respectively in Figures 51 and 61. It occurs less commonly as hexagonal prisms modified by rhombohedral faces (negative) and as rhombohedrons (combination of positive and negative rhombohedron). All forms of calcite were deposited after galena, white and brown quartz, all fluorite, sphalerite and chalcopyrite (Figures 54 and 61). Calcite commonly coats the early purple comb fluorite (Figure 21), and it was deposited after some bitumen (Figure 62). Calcite also occurs as narrow veinlets which traverse yellow fluorite (Figure 63) and early purple fluorite.

9. Barite

Barite was the last mineral observed by the writer to be deposited in vugs. It occurs as bluish to yellowish white, 1 to 8 mm., tabular crystals, which may be partly arranged in radiating groups. Barite was deposited after all of the other minerals, but rarely it is partly included in calcite. Barite crystals were observed to encrust early white quartz (Figure 35), to be deposited upon quartz and galena (Figure 64), and to include fragments of quartz (Figure 65).

10. Oil and Bitumen

Oil and bitumen probably were present rather continuously throughout the time of deposition of the ores (Hall and Friedman, 1963, p. 891), but they were especially prevalent in the Crystal mine at three periods indicated on the paragenetic diagram. The first was bitumen which was deposited upon yellowish fluorite, white quartz and galena. The second was that deposited upon both stages of purple fluorite, sphalerite and disphenoidal chalcopyrite. The last common stage of bitumen was deposited after calcite and

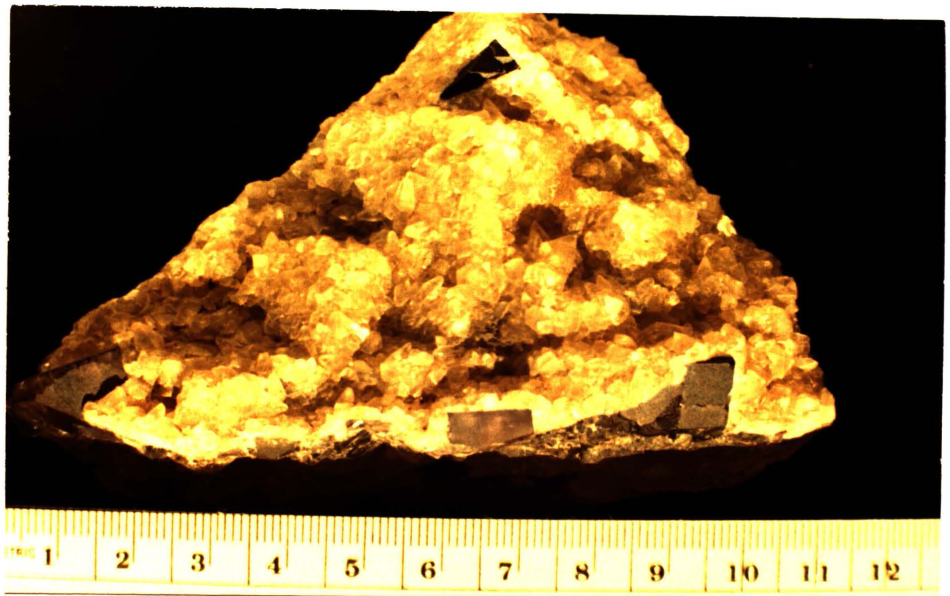

Fig. 61. Scalenohedral calcite deposited upon purple fluorite.

Fig. 62. Rhombohedral yellow calcite formed after bitumen (black) deposited upon greenish, fine-grained sandstone.

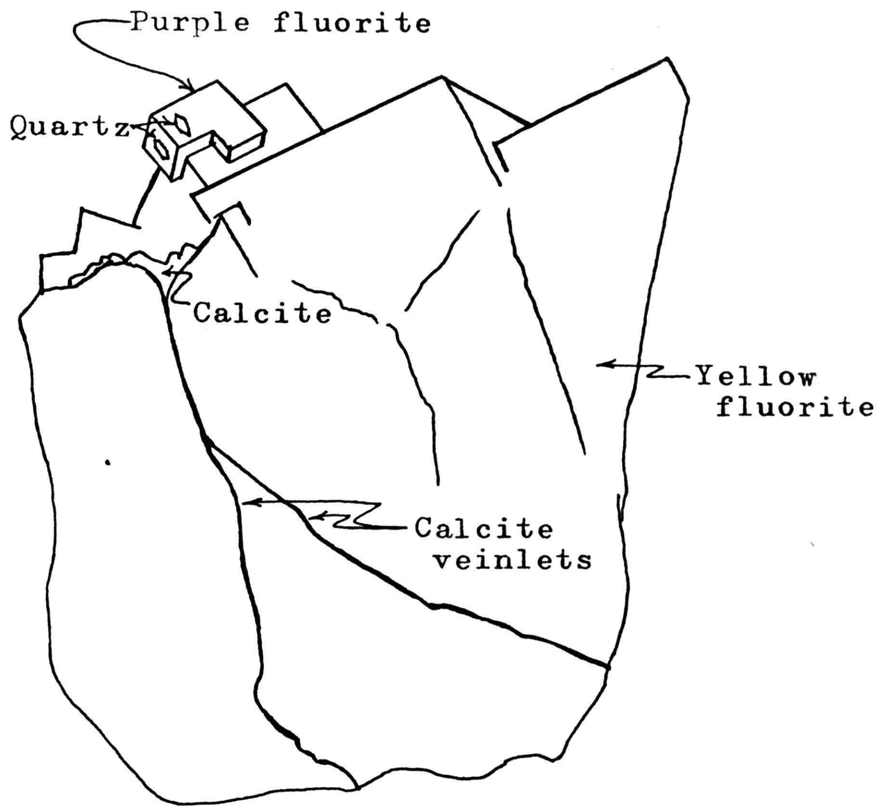

Fig. 63. Calcite veinlets transgressing yellow fluorite and connected with calcite crystals in a vug. Early purple fluorite has been deposited on yellow fluorite. Actual size.

Fig. 64. Barite crystals (yellowish white) deposited on quartz (white) and galena (dark gray). Note that part of the barite occurs in radiating groups. 3X.

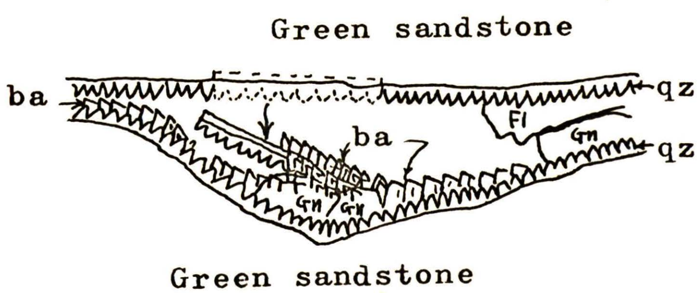

Fig. 65. Sketch showing a fragment of white vug quartz and host rock (dotted line) included in barite (ba). 2X.

before most barite.

11. Fracturing

Fracturing occurred during several periods. The most important fracturing was that which was prior to the introduction of ore-bearing solutions and which allowed those solutions access to the present sites of ore deposition. Such fracturing probably was connected with the uplift of the strata in southern Illinois.

Minor fracturing which occurred after the deposition of yellow fluorite is evidenced by the filling of fractures across yellow fluorite with early purple fluorite.

Subsequent minor fracturing occurred after early purple fluorite but before completion of sphalerite mineralization. This stage of fracturing is shown by veinlets of sphalerite which traverse veinlets of early purple fluorite and by veinlets of calcite which traverse yellow fluorite.

12. Summary of Paragenesis of Crystal Mine Ores

Most of the primary minerals in the Crystal mine were deposited during more than one period. Fluorite was deposited at least during four different periods, quartz during five, chalcopyrite during seven, galena during three and sphalerite during two. Dolomite, marcasite, calcite, pyrite and barite were deposited during one period.

The general order of formation of the minerals in disseminated ore was as follows: dolomite, fluorite, quartz, chalcopyrite, galena, sphalerite, marcasite and quartz. The order of deposition in open spaces was: yellowsih white to yellow fluorite, chalcopyrite, galena, early purple fluorite, white quartz, sphalerite, chalcopyrite, late purple fluorite, brown quartz, calcite with chalcopyrite, chalcopyrite and pyrite, and barite.

The two sequences of deposition, that of the disseminated minerals and that of the vug-filling minerals, exhibit both similarities and dissimilarities. They are similar in their general orders of deposition of fluorite, quartz, chalcopyrite, galena and sphalerite. Closer examination, however, reveals many dissimilarities between the two sequences. The most prominent of these are the occurrence of late calcite, pyrite and barite and the recurrence of additional generations of fluorite, quartz, chalcopyrite and galena in the vug-filling sequence which, except for two generations of quartz, are absent from the disseminated sequence. Other differences include the absence of marcasite in the vug-filling sequence, and the common simultaneous deposition of galena and sphalerite in the disseminated ores as contrasted to the consistent deposition of sphalerite after galena in the vug-filling ores.

D. Paragenesis of the Minerva Mine No. 1

Fluorspar in the Minerva mine No. 1 is mined on the Bethel horizon. Other horizons, such as the Levias, Rosiclare, and Sub-Rosiclare have been explored, but no production comes from those levels at the present time. Three ore bodies are developed on the Bethel horizon within the No. 1 mine.

The following minerals, periods of corrosion, and hydrocarbons were found to occur in the ore bodies in the No. 1 mine:

1) Dolomite
2) Fluorite
3) Quartz
4) Pyrite
5) Sphalerite
6) Chalcopyrite
7) Galena
8) Calcite
9) Barite
10) Strontianite
11) Corrosions
12) Marcasite
13) Witherite
14) Oil and Bitumen

Each of these minerals are discussed in the general paragenetic order listed above.

1. Dolomite

Dolomite occurs twice in the paragenetic sequence in the Minerva mine No. 1 as shown in the paragenetic diagram (Figure 66). It occurs as rhombohedral crystals in impure bands of coontail ore and in disseminated ore (Figure 15). Some dolomite grains may be partly included by fluorite and entirely within sphalerite (Figure 67). Small broken pieces of dolomite are included within fluorite, and cracks within some dolomite fragments are filled by purple fluorite (Figure 68).

Rhombs of yellowish dolomite (?) are deposited on etched surfaces of yellow fluorite and calcite (Figure 39). The identity

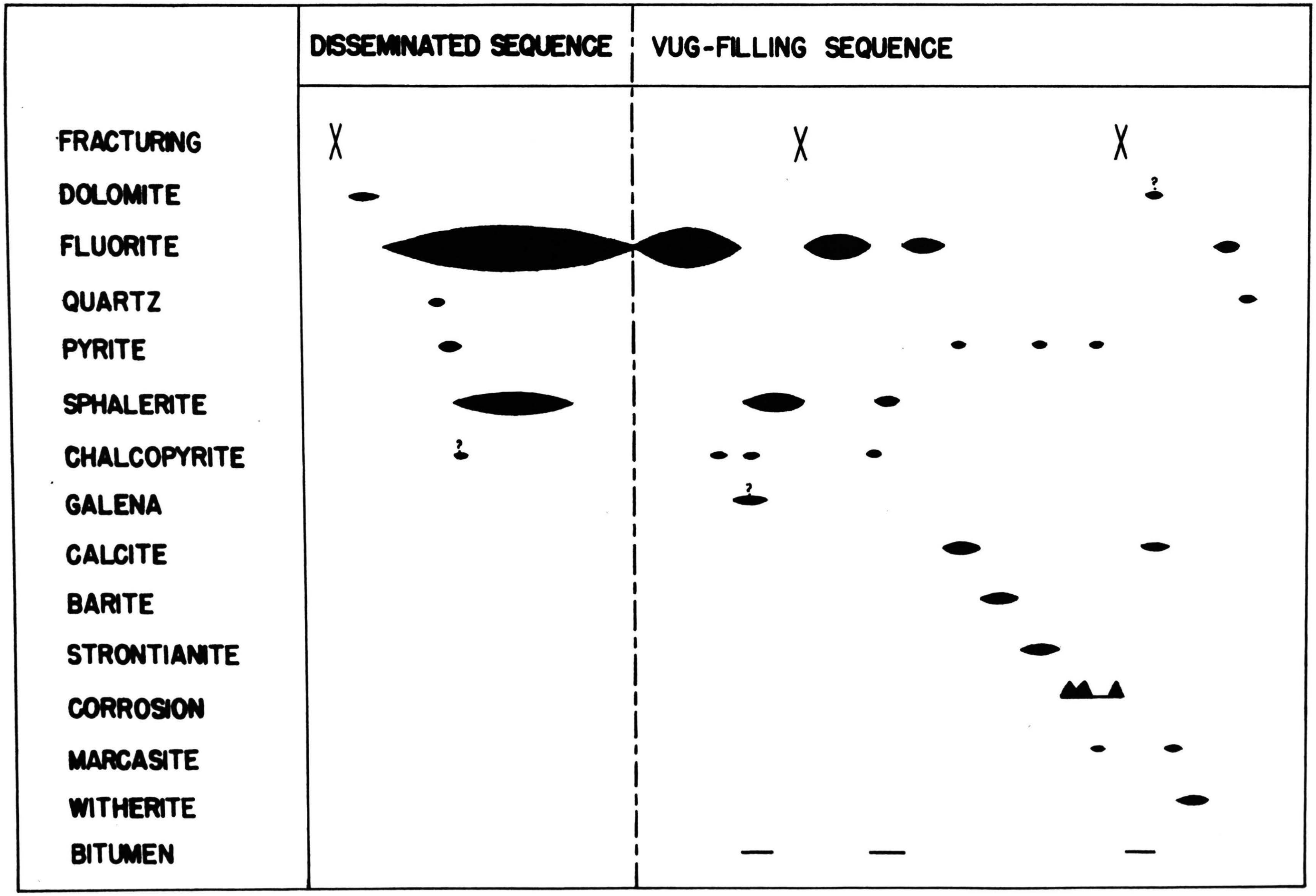

FIG. 66. PARAGENETIC DIAGRAM FOR THE MINERVA MINE NO. I

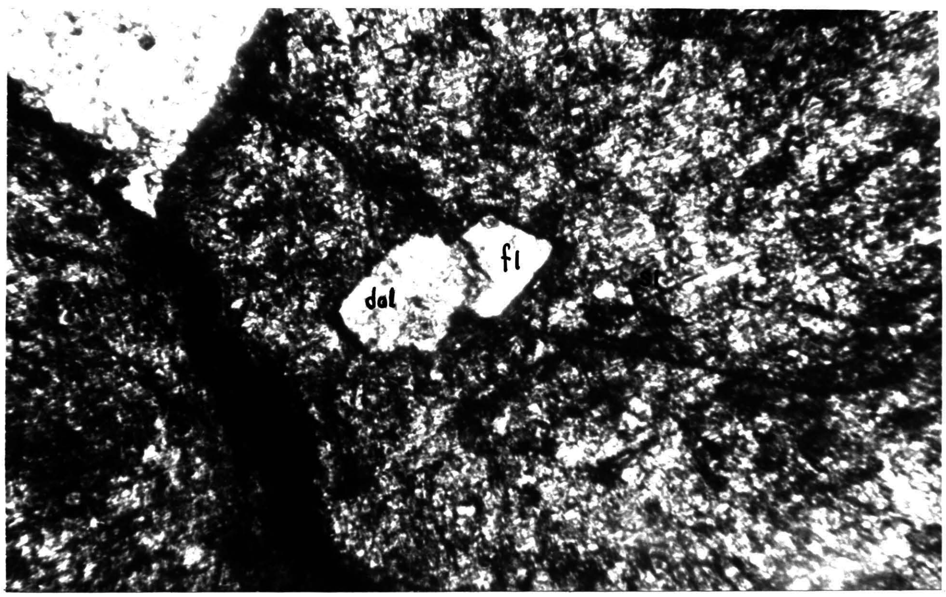

Fig. 67. Photomicrograph showing dolomite (dol) partly included by fluorite (fl) and entirely within sphalerite (sl). Plane polarized light. 200X.

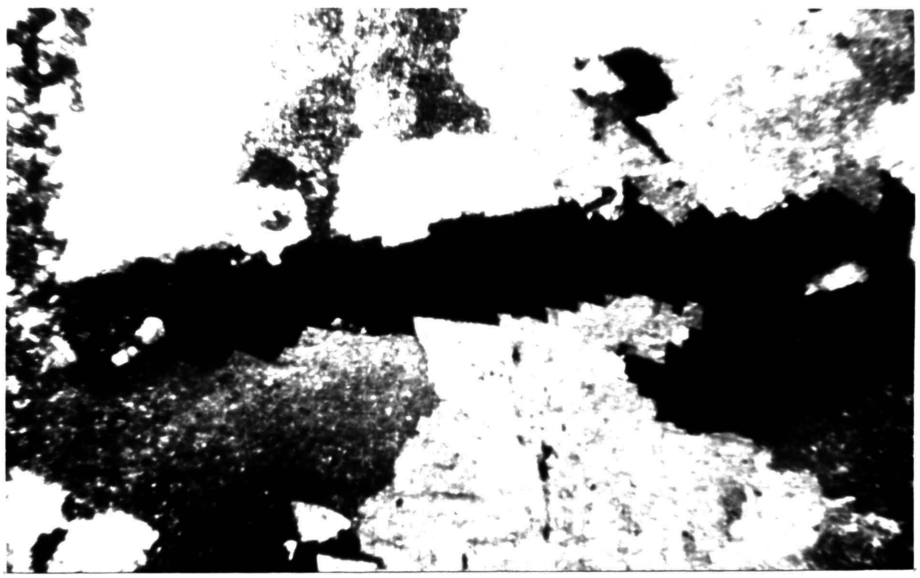

Fig. 68. Photomicrograph showing fragments of dolomite (light to medium gray) in fluorite (black). Crossed nicols. 50X.

of this dolomite is discussed in Chapter IV. Its paragenetic position is later than that of early calcite, but how much later could not be determined. Thus, its position on the paragenetic diagram is marked by a query.

2. Fluorite

Five generations of fluorite in the colors, yellowish white to yellow, purple and blue, occur in the Minerva mine No. 1. The first generation is that of tiny fluorite cubes which occur in the impure bands of coontail ore. They may be included by sphalerite and replaced by pyrite (Figure 69). Fluorite appears to have replaced some chert (Figure 70).

Yellow fluorite occurs as pure layers of banded ore and as crystals in vugs.

Purple fluorite occurs as veinlets traversing chert (Figure 71) and yellow fluorite (Figure 72), and as crystals deposited upon dark to reddish sphalerite. Some purple fluorite may occur as crystallographic overgrowth crusts deposited on yellow fluorite combs.

Blue fluorite occurs as small crystals deposited upon small yellow sphalerite crystals, which were, in turn, deposited on purple fluorite.

The last stage of fluorite deposition consists of tiny pale purple fluorite crystals, 1 to 3 mm. across, deposited on witherite. Such crystals also were described by Nackowski (1949, p. 35).

3. Quartz

Quartz occurs in very small quantities in some disseminated ore and impure bands of coontail ore. The relationship of the tiny

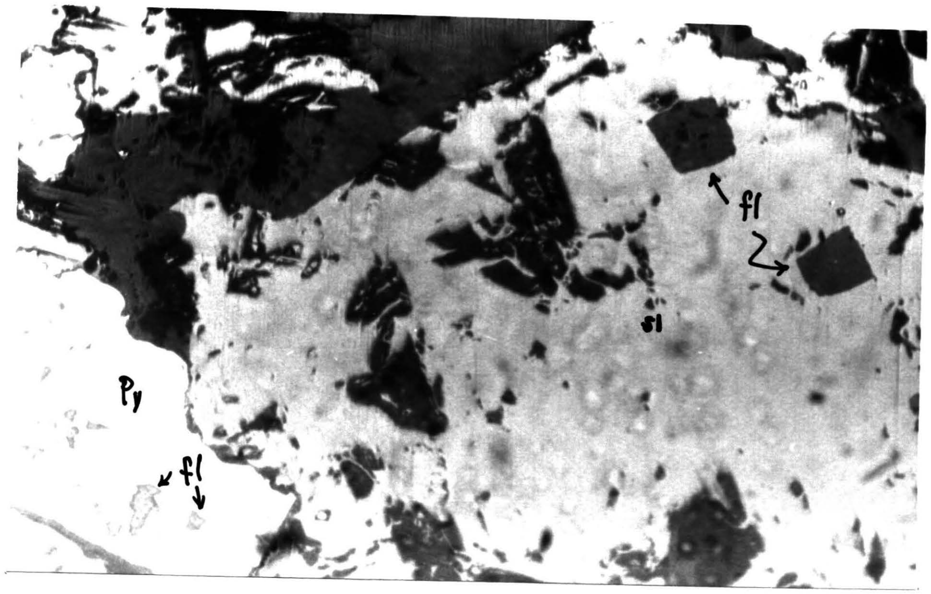

Fig. 69. Fluorite (fl) included in sphalerite (sl) and pyrite (py) in impure bands of coontail ore. Reflected light. 200X.

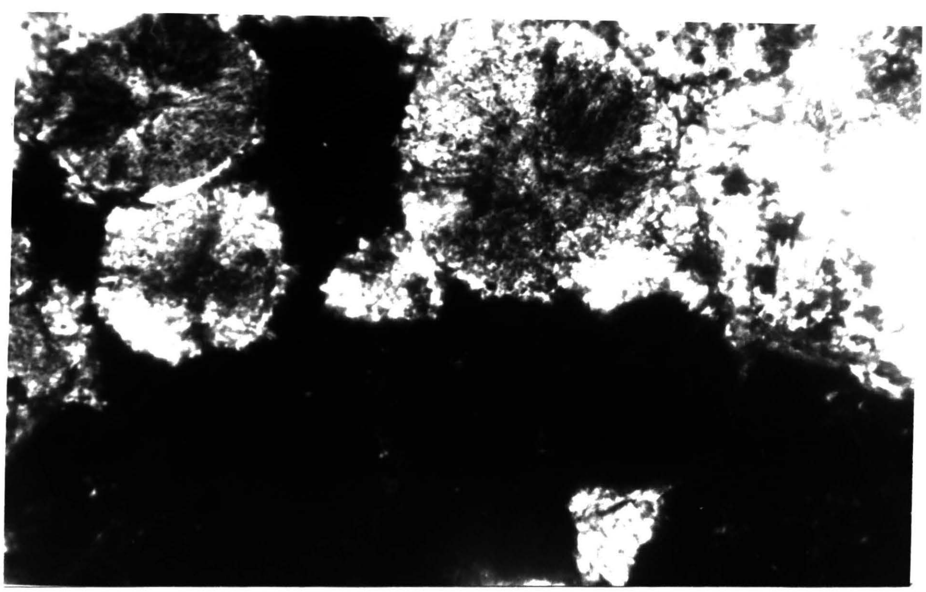

Fig. 70. Photomicrograph showing fluorite (black) replacing chert (white to gray). Crossed nicols. 200X.

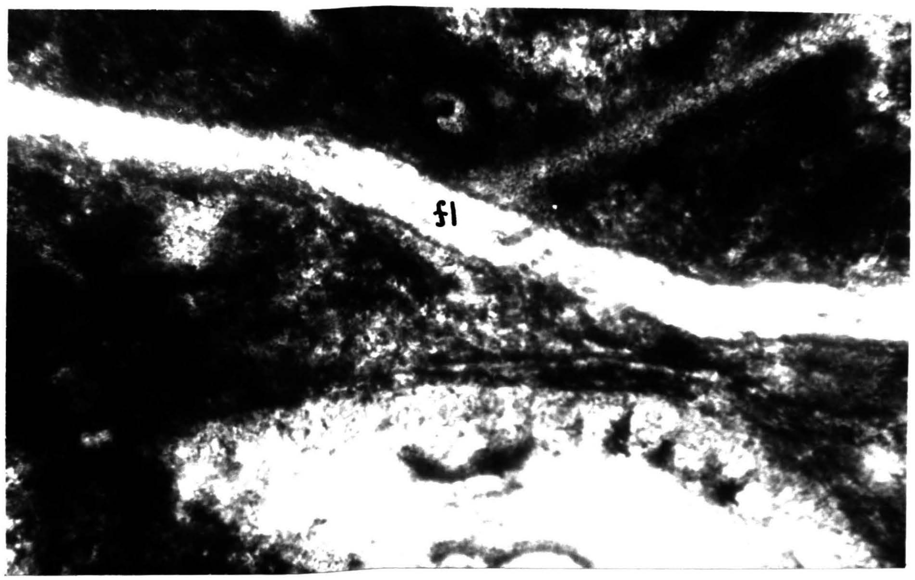

Fig. 71. Photomicrograph showing a veinlet of purple fluorite (fl) crossing chert (light gray to black). Plane polarized light. 200X.

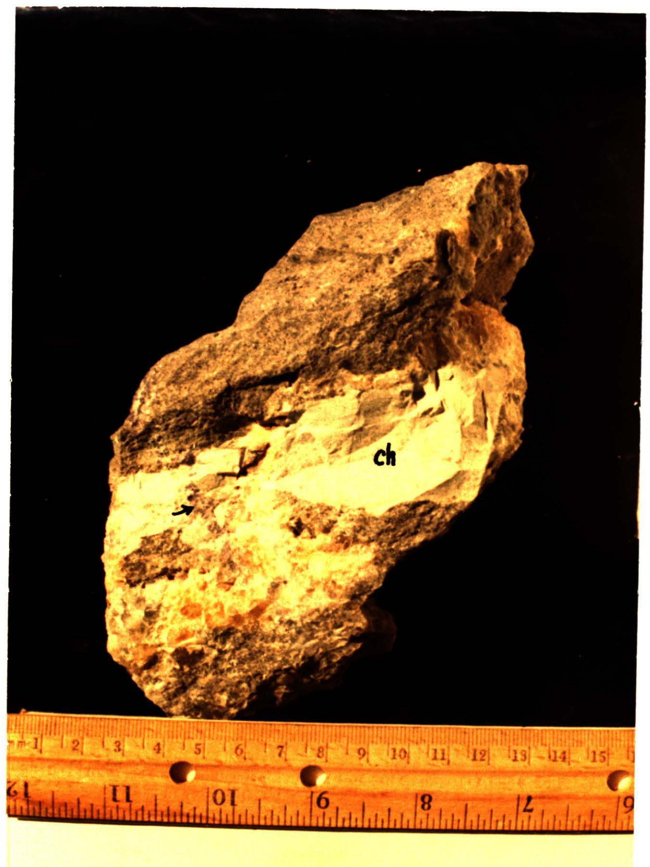

Fig. 72. Veinlet of purple fluorite (see arrow) cutting yellow fluorite, chert (ch) and disseminated ore (greenish gray).

quartz crystals to fluorite is not shown, but their occasional inclusions in disseminated sphalerite suggests that quartz formed before sphalerite. Quartz also shows its euhedral shapes against the margins of sphalerite grains.

Quartz crystals deposited in vugs were noted by Nackowski (1949, p. 37). They were deposited on fluorite, calcite, barite and witherite.

4. Pyrite

Pyrite occurs in small quantities four times in the paragenetic sequence. In impure bands of coontail ore, pyrite generally occurs as tiny cubes partly and entirely included within sphalerite, but some pyrite may have mutual boundaries with sphalerite. Thus, most of the disseminated pyrite has formed earlier than sphalerite, but its period of deposition may partly overlap that of sphalerite.

A second generation of pyrite occurs as tiny, 2 to 5 microns, crystals included within calcite crystals deposited in vugs. The calcite derives a grey color partly from the pyrite inclusions.

Third and fourth generations of pyrite are those of octahedrons modified by pyritohedrons deposited with strontianite (Figure 73) and upon corroded surfaces of strontianite (Figure 34).

5. Sphalerite

Sphalerite is much more abundant in the Minerva mine No. 1 than in the Crystal mine, and it occurs in three paragenetic positions. It occurs as anhedral to euhedral grains in disseminated ore and impure bands of coontail ore, as crystalline masses in vugs and as small yellowish crystals deposited on earlier sphalerite and fluorite.

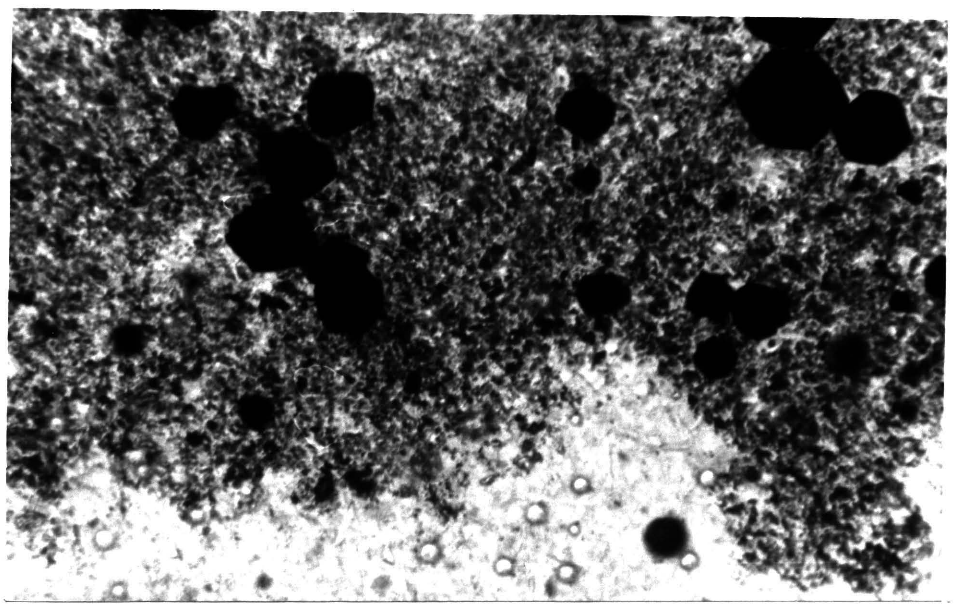

Fig. 73. Pyrite (black) occurring within strontianite (gray). Plane polarized light. 200X.

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In disseminated ore and impure bands of coontail ore, 1/2 to 3 mm. sphalerite crystals include and are later than dolomite, fluorite, quartz and pyrite (Figures 67 and 69).

Dark to reddish brown sphalerite is deposited in vugs on yellow fluorite.

Small quantities of yellowish brown, resinous sphalerite may be deposited locally upon the earlier dark variety of sphalerite and upon purple fluorite.

6. Chalcopyrite

Chalcopyrite occurs in small amounts four times in the paragenetic sequence. Minute grains of chalcopyrite rarely occur in impure bands of coontail ore, and no chalcopyrite grain was observed to be contiguous to pyrite and sphalerite. Thus, their paragenetic position is marked on Figure 66 by a query.

Small crystals, 1/4 to 1 mm. across, are included in and later deposited on yellow fluorite. Later, 1 mm. diameter crystals are included in or deposited on purple fluorite.

7. Galena

Galena was noted only in an ore body which is locally referred to as the third ore body and which was abandoned about 20 years ago. One thin, 2.5 cm. wide, band of galena was observed to occur near the top of a pillar, but its paragenetic relations to other minerals were indeterminate. Its position is approximated by comparison with its occurrence in the Crystal mine, but it is marked by a query in the paragenetic diagram.

8. Calcite

Calcite commonly occurs as scalenohedral crystals, and less commonly as rhombohedral ones. Two stages of calcite deposition were detected in the Minerva mine No. 1.

Early calcite occurs as crystals deposited on yellow, purple and blue fluorite, and as a filling of spaces between the two combs of some banded ores.

Late calcite occurs as 1/2 mm. to 5 cm. long, scalenohedral crystals deposited on the etched surfaces of fluorite (Figures 74 and 75), sphalerite, strontianite (Figure 76) and the early calcite. Calcite fills fractures in fluorite (Figure 77) and strontianite (Figure 78). It also fills corrosion cavities of fluorite in coontail ore (Figures 79, 80 and 81).

9. Barite

Barite occurs as white acicular aggregates in the Minerva mine No. 1, and replaces fluorite, calcite, limestone and impure fluorite bands. The specimen shown in Figure 82 is a good example of barite partially replacing pure fluorite and calcite bands. The upper comb of fluorite has been almost entirely replaced by barite. Microscopic examination reveals a very irregular boundary between barite and replaced fluorite (Figure 83). All of the earlier yellow, purple and blue fluorites may be replaced by barite.

10. Strontianite

Strontianite occurs as white to pinkish, fibrous to acicular aggregates with a radial structure. Strontianite was observed to include fluorite, sphalerite, early calcite and pyrite. Its relationship to barite is not certain in those specimens where the writer observed the two minerals to be contiguous, but Nackowski (1949, p. 37) reported that:

Fig. 74. Very tiny scalenohedral calcite crystals (white) deposited on corroded yellow fluorite cubes with local areas protected from corroding by prior deposition of bitumen (black). 4X.

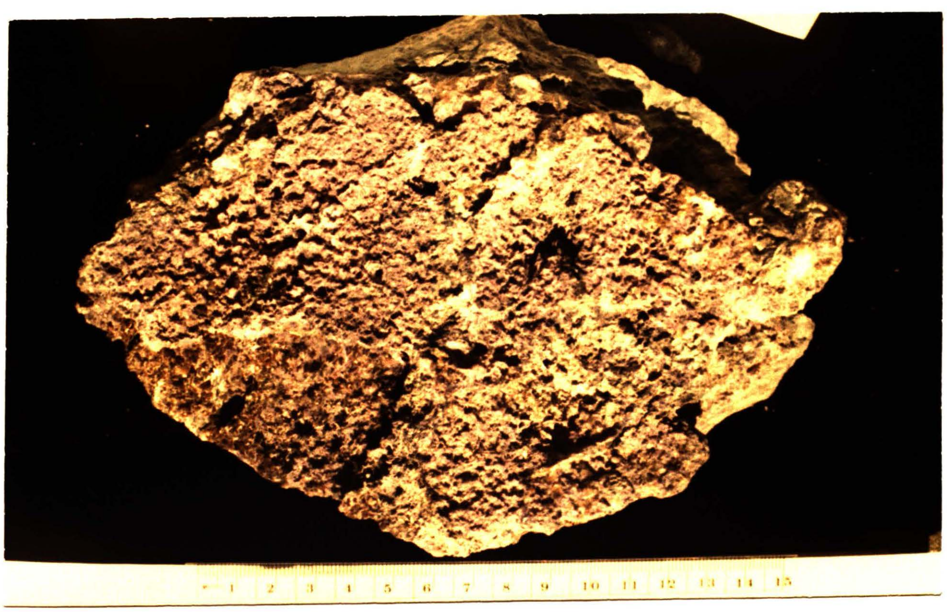

Fig. 75. Acicular and scalenohedral brown calcite (bottom left) occurring on corroded purple fluorite.

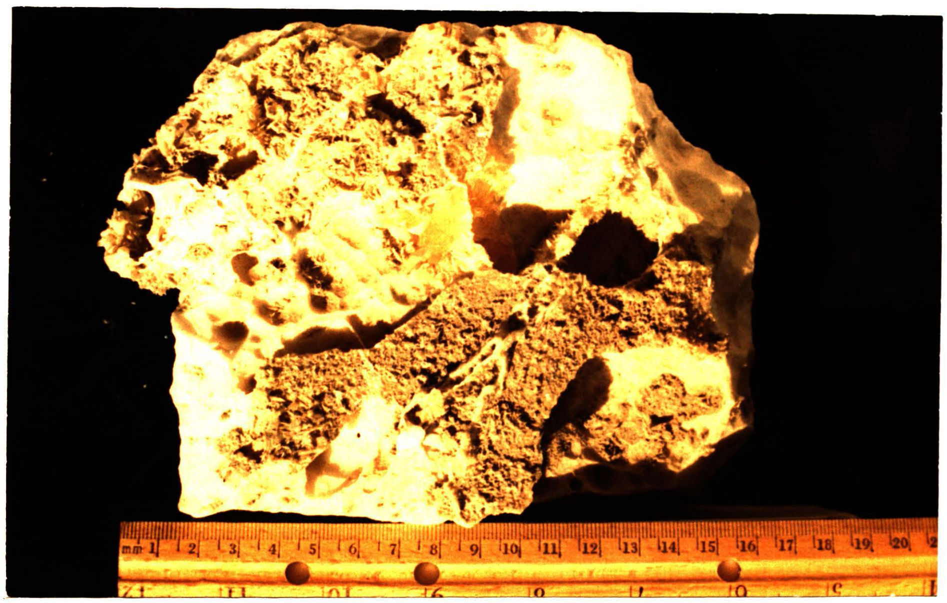

Fig. 76. Tiny scalenohedral calcite crystals (white to greenish gray) deposited on a box-work of strontianite (white) developed by corrosion. Note that the early calcite (yellow) also is corroded.

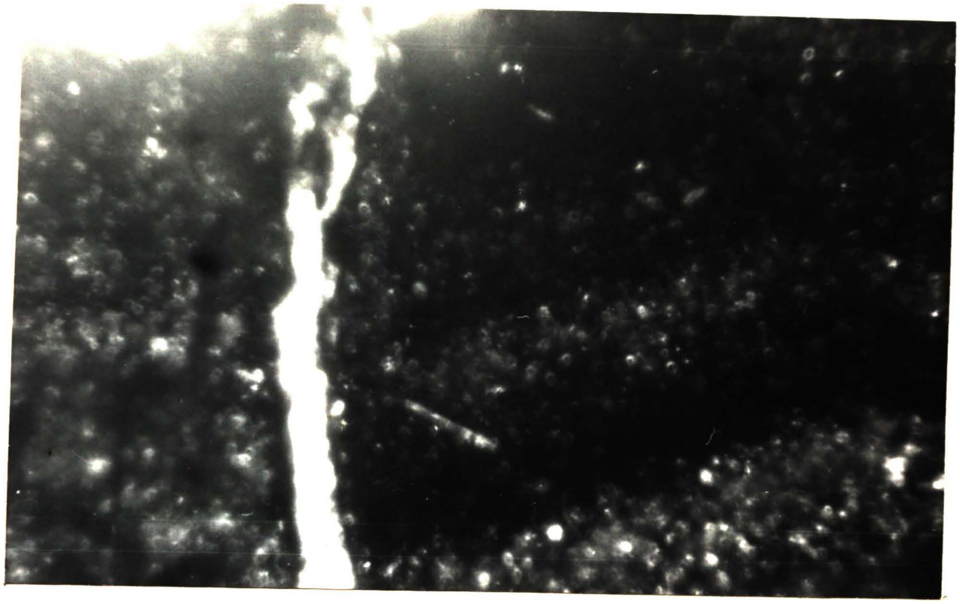

Fig. 77. Calcite (white) veinlet traversing fluorite (dark gray). Crossed nicols. 50X.

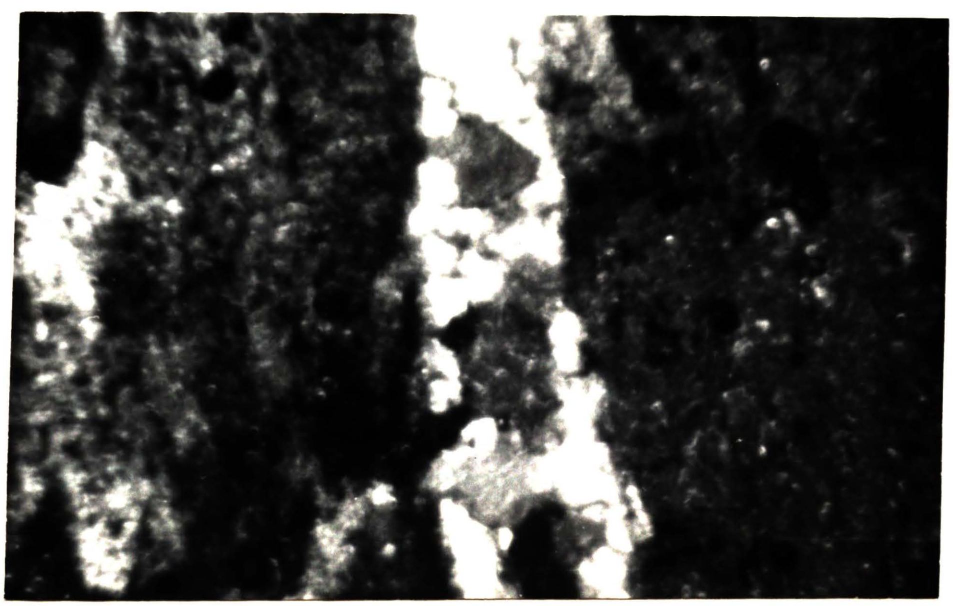

Fig. 78. Calcite (white) veinlet traversing strontianite (gray). Crossed nicols. 50X.

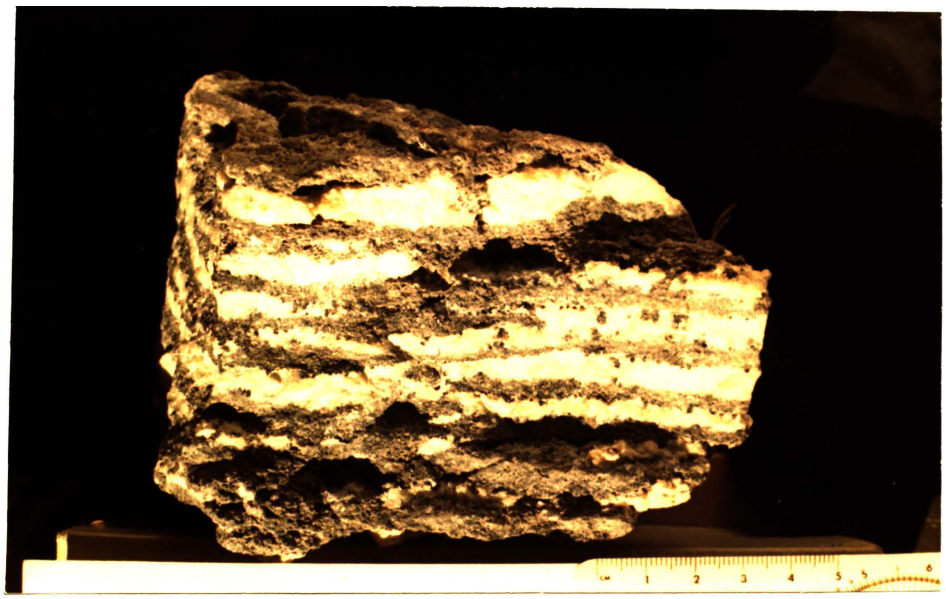

Fig. 79. Calcite (white) filling corrosion cavities of pure fluorite bands in coontail ore.

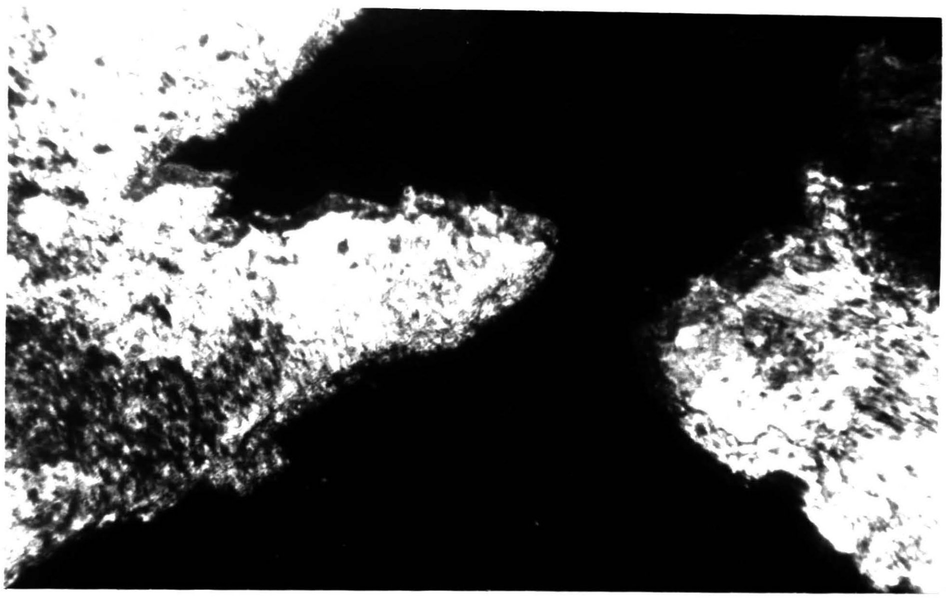

Fig. 80. Photomicrograph showing calcite (gray) filling corrosion cavities of fluorite (black) in coontail ore shown in Figure 79. Crossed nicols. 200X.

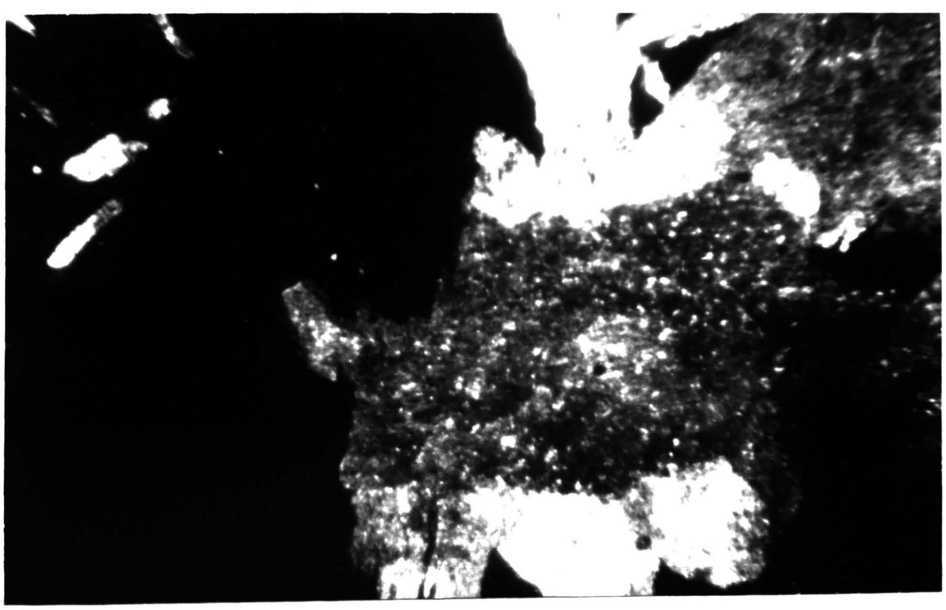

Fig. 81. Photomicrograph showing the same phenomenon as Figure 80. Crossed nicols. 200X.

Fig. 82. Banded ore consisting of (from top to bottom) barite, sphalerite-fluorite, barite, calcite, fluorite, barite, sphalerite-fluorite, barite, and fluorite with some calcite. Note the irregular replacement boundaries between barite and the other minerals and the replacement remnants of fluorite within some barite bands.

Fig. 83. Photomicrograph showing barite (white) replacing fluorite (black) in one of the barite bands shown in Figure 82. Crossed nicols. 50X.

Strontianite fills open spaces in masses of loosely aggregated barite needles. Strontianite has partly replaced barite needles, indicating that it was deposited after barite.

11. Corrosion

The minerals in some ore deposits exhibit periods of corrosion after their deposition. Such periods of corrosion have been neglected in the paragenetic studies of many deposits but they constitute an integral part of the time sequence. Corrosion in the Minerva mine No. 1 appears to have occurred principally after the deposition of strontianite and earlier minerals but before the deposition of late calcite and witherite which may occur upon the etched surfaces of fluorite (Figures 74, 75 and 84), sphalerite (Figure 34), early calcite (Figure 76) and strontianite (Figure 76). Two periods of corrosion are separated by pyrite and marcasite, which were deposited upon corroded surfaces of strontianite and subsequently corroded themselves. The weak corrosion after the deposition of pyrite (Figure 34) and marcasite (Figure 86) is evidenced by etch grooves which are continuous from strontianite through pyrite and marcasite.

12. Marcasite

Marcasite occurs in two paragenetic positions. The first generation of marcasite occurs deposited on corroded surfaces of strontianite and has been subsequently etched (Figure 86).

A later period of marcasite deposition is represented by tiny crystals included in late calcite.

13. Witherite

Witherite was observed only in the abandoned third ore body. It was deposited on late calcite (Figure 87) and on the

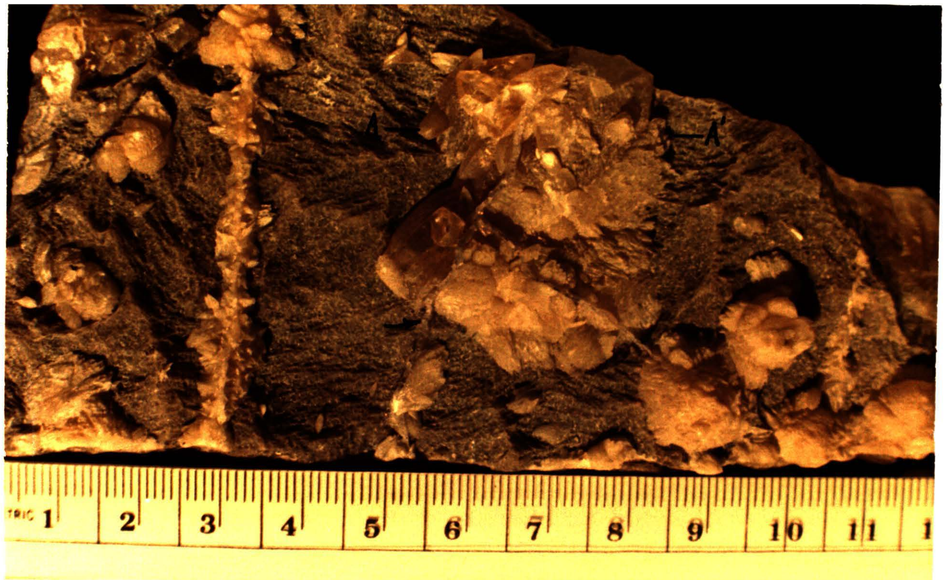

Fig. 84. Ragged, etched surface of an impure fluorite band (brown) upon which calcite (yellowish white) is deposited. Purple fluorite veinlets (see arrow) formed before corrosion often localize the sites of calcite deposition.

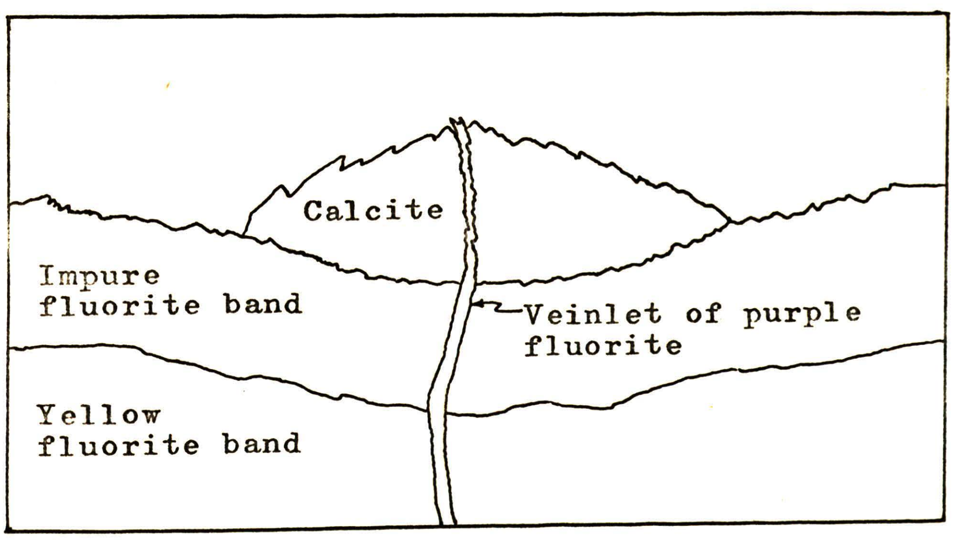

Fig. 85. Sketch showing the vertical section along the A-A' marked in Figure 84. 2X.

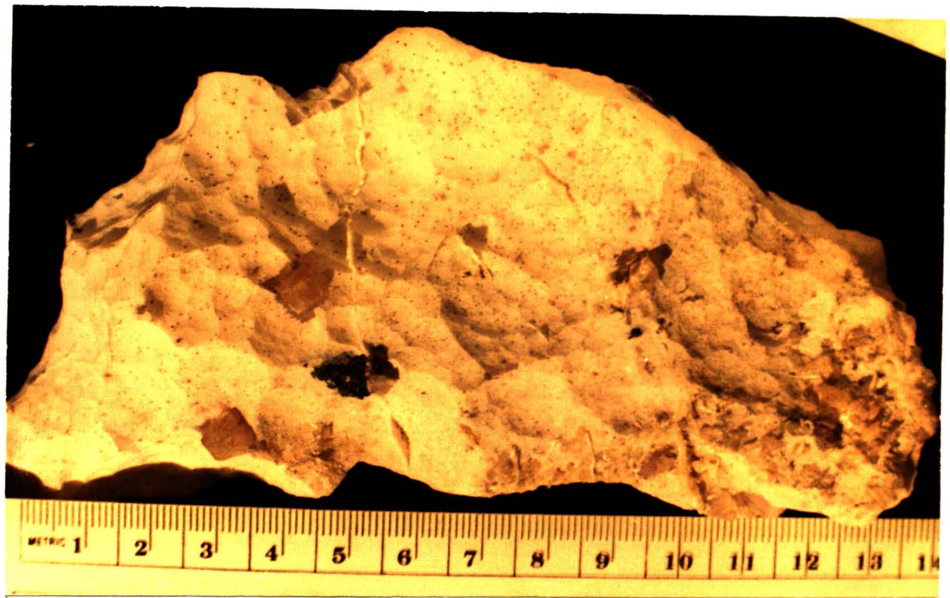

Fig. 86. Marcasite crystals (tiny black spots) deposited upon the ragged, corroded surface of strontianite. Note the effects of corrosion upon yellow fluorite, purple fluorite and dark brown sphalerite crystals.

Fig. 87. Pseudohexagonal twinned crystals of witherite (white) deposited on calcite (yellow) and previously etched fluorite (purple). 2.5X.

etched surface of fluorite (Figures 88 and 89). Witherite crystals often were deposited on the walls of box-work fluorite and calcite formed by corrosion.

14. Oil and Bitumen

Oil and bitumen are less abundant in the Minerva mine No. 1 than in the Crystal mine. While they may have been present throughout the entire period of mineralization, they were especially noted to be present during three periods. The first period was after yellow fluorite but before purple fluorite, the second after purple fluorite but before blue fluorite, and the last period was after corrosion but before witherite.

15. Fracturing

Several periods of fracturing occurred in the Minerva mine No. 1. The first of these was pre-mineral fracturing which provided access for the mineralizing solutions.

Minor fracturing which occurred during mineralization is shown by fractures in yellow fluorite (Figure 72) and impure bands of coontail ore (Figure 85) which were filled by purple fluorite.

Later minor fracturing is evidenced by fractures in corroded fluorite (Figure 77) and strontianite (Figure 78) which were filled with calcite.

16. Summary of Paragenesis of Minerva Mine No. 1 Ores

In the Minerva mine No. 1 fluorite was deposited at least during five different periods, chalcopyrite and pyrite during four, sphalerite during three, dolomite (?), quartz, calcite and marcasite during two periods. Barite, strontianite and witherite were deposited during one period.

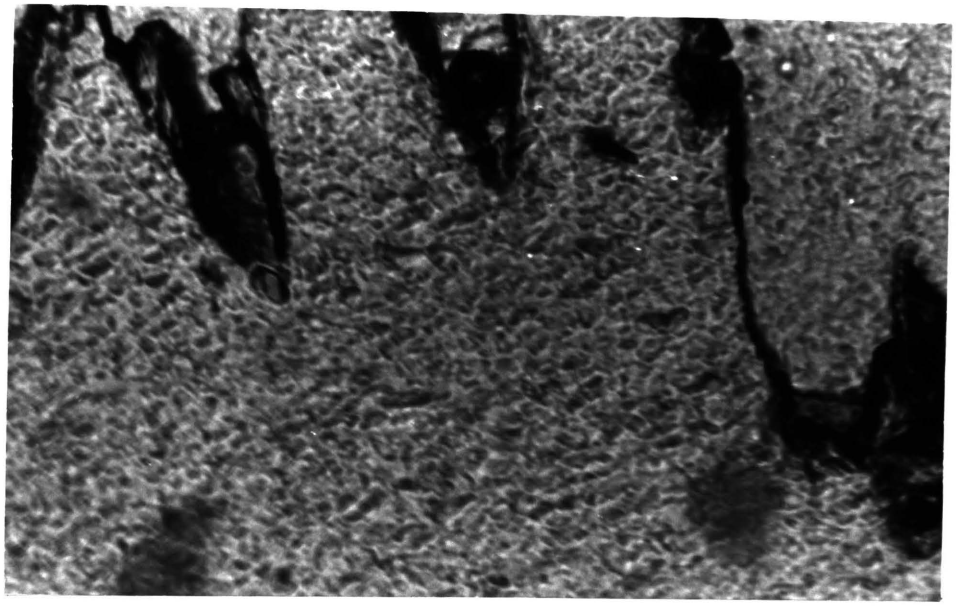

Fig. 88. Photomicrograph showing witherite (top) deposited on the etched surface of fluorite (below). Plane polarized light. 200X.

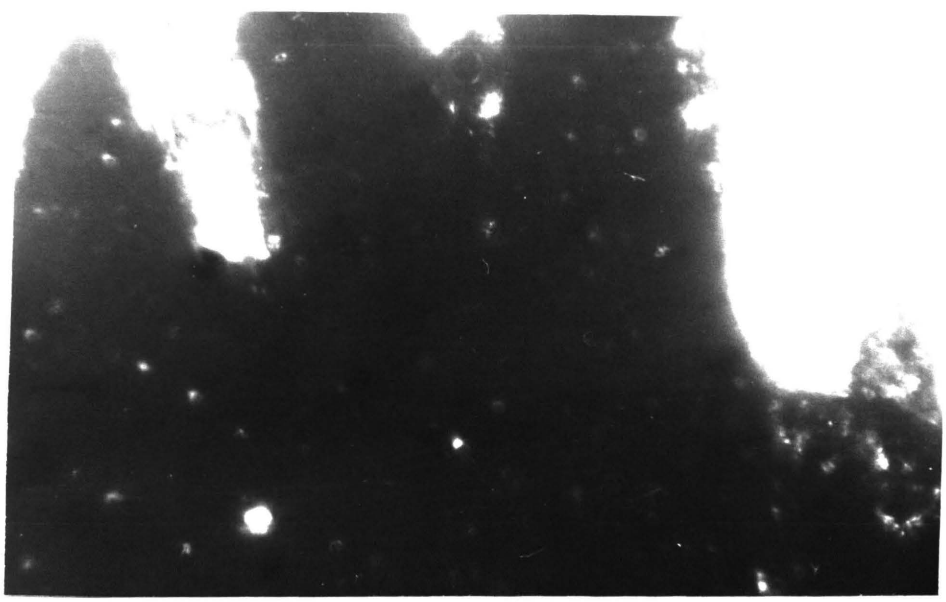

Fig. 89. Photomicrograph showing the same area as the above photograph but under crossed nicols. The white area is witherite, and the dark gray area is fluorite. 200X.

The general order of formation of the minerals in disseminated ore is: dolomite, fluorite, quartz, pyrite with chalcopyrite (?) and sphalerite. The order of deposition of the vug-filling minerals is: yellow fluorite, chalcopyrite, galena (?), sphalerite with chalcopyrite, purple fluorite, chalcopyrite, sphalerite, blue fluorite, calcite with pyrite, barite, strontianite with pyrite, corrosion, pyrite with marcasite, corrosion, calcite and dolomite (?), marcasite, witherite, pale purple fluorite and quartz. These two sequences, that of the disseminated ore and that of the vug-filling minerals are quite dissimilar. They contrast rather strongly in the minerals present, the sequence in which they were deposited and in the number of mineral generations present.

The general sequence of mineral deposition in the Minerva mine No. 1 is similar to that in the Crystal mine, but there are some differences in the minerals present, their abundance and the number of generations in which they appear. Witherite and strontianite are present in the Minerva mine No. 1, but they were not observed to occur in the Crystal mine. Quartz is much less abundant in the Minerva mine No. 1 than in the Crystal mine. Galena is less abundant and was not observed to occur in the disseminated sequence in the Minerva mine No. 1. The abundant minerals, fluorite, sphalerite and calcite appear in the ores of the Minerva mine No. 1 one more generation than they do in those of the Crystal mine. The less abundant minerals, however, appear more often in the Crystal mine ores, chalcopyrite and quartz in three additional generations, galena in two additional generations. Corrosion, which is so prominent toward the last stages of mineralization in the Minerva mine No. 1, appears to be lacking in the ores of the Crystal mine. Lastly, the differences between the disseminated and vug-filling sequences are greater in the Minerva mine No. 1 than between those sequences in the Crystal mine.

E. Paragenesis of the Hill Mine

Fluorspar occurs at two stratigraphic horizons in the Hill mine, the Sub-Rosiclare-lower Fredonia and the upper Fredonia-Rosiclare contact zones. A characteristic feature of the mine is that structurally it appears to have been developed along synclinal and collapsed zones of the overlying basal sandstone beds of the Rosiclare sandstone. Slump structures found in this mine are believed by Brecke (1962, p. 531) to have formed by a combination of host rock solution and stoping by penetration of fluorspar into the sandstone.

The mineralogy of the ores in the Hill mine is similar to those occurring in the Crystal mine.

The writer examined and described all the specimens collected from the Hill mine but the investigation was insufficient to prepare a paragenetic diagram and only some characteristic features of those specimens will be briefly described below.

Most of the fluorite in the Hill mine is pale to dark purple in color. Some specimens exhibit two stages of purple fluorite separated by bands of one or more of the minerals, chalcopyrite, sphalerite, galena and calcite deposited parallel to the cubic faces of the fluorite (Figure 90).

Other specimens exhibit three stages of purplish fluorite, a pale purple one and two dark purple varieties (Figure 91). White calcite with a yellowish tint was deposited after the pale purple fluorite, and a thin layer of calcite with sphalerite was deposited after the second fluorite. Brownish yellow calcite may form a crystallographic overgrowth enclosing the early white calcite.

As many as five stages of purple fluorite were noted in thin slices of specimens such as that shown in Figure 92. Various other minerals, especially sphalerite, but also galena and quartz, occur between fluorites of the various stages. Pinckney (1966) has found as many as seven stages of purple fluorite to occur in the Hill mine.

Some calcite scalenohedrons, 5 to 12 cm. long, are composed of two generations. The inner cores and outer zones of such crystals (Figure 93) can be distinguished by their different colors and by the fact that they tend to break along the contact between the two zones, and tiny pyrite crystals are confined to the inner cores of calcite crystals studied by the writer (Figure 94).

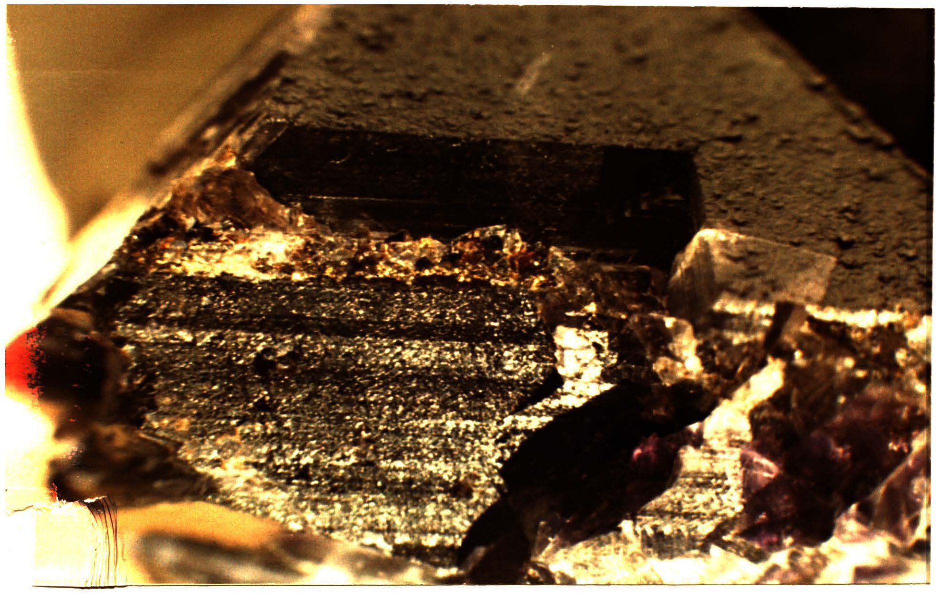

Fig. 90. Two stages of purple fluorite separated by the deposition of chalcopyrite (yellow) and sphalerite (yellowish brown). 4X.

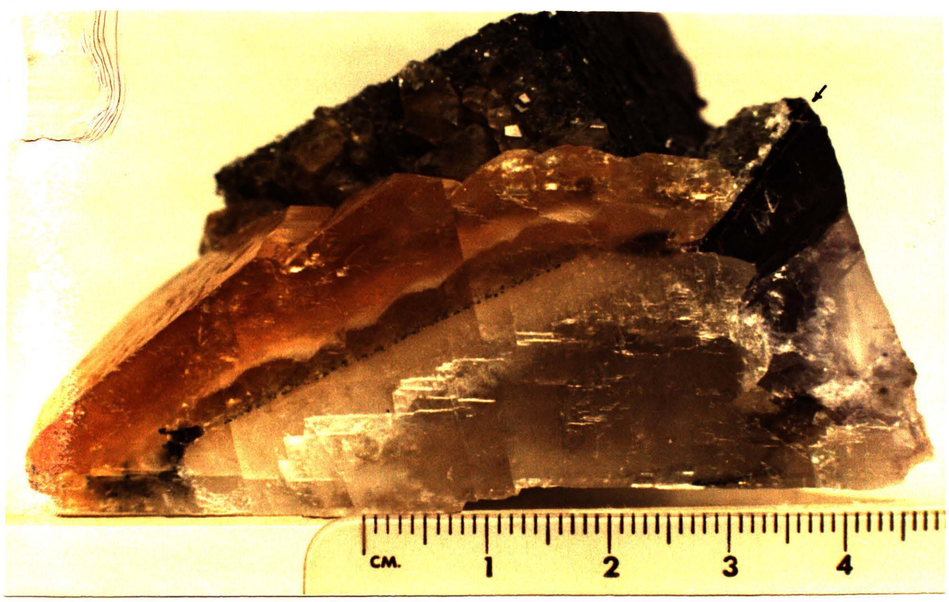

Fig. 91. Specimen showing three stages of purplish fluorite and two stages of calcite. A thin layer of white calcite (see arrow) occurs between the last two stages of dark purple fluorite. Numerous tiny chalcopyrite crystals are deposited on the surface of the early white calcite. Note the growth zoning of the brownish yellow calcite.

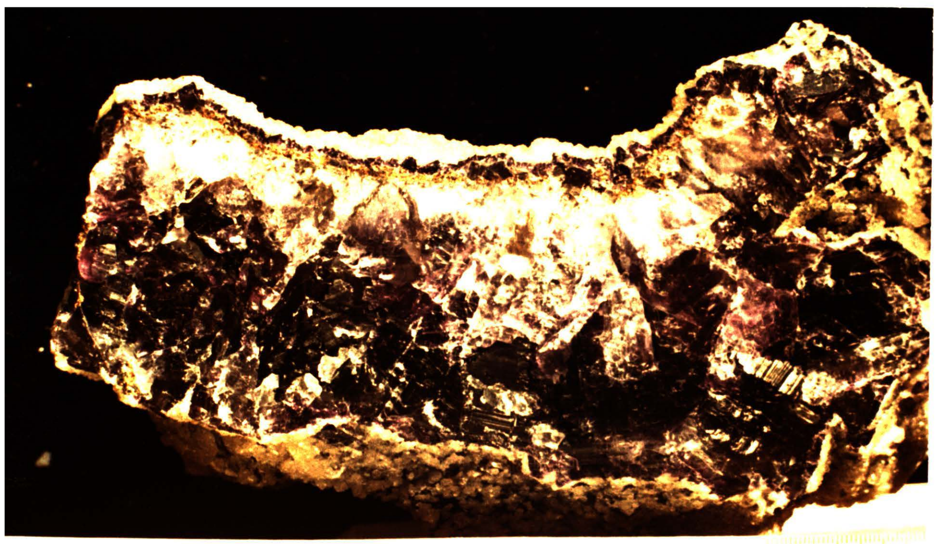

Fig. 92. Purple fluorite coated with calcite. Thin slices of this specimen reveal five stages of fluorite deposition separated by the deposition of sphalerite, galena and quartz. One band of sphalerite (yellow) may be seen toward the top of the specimen.

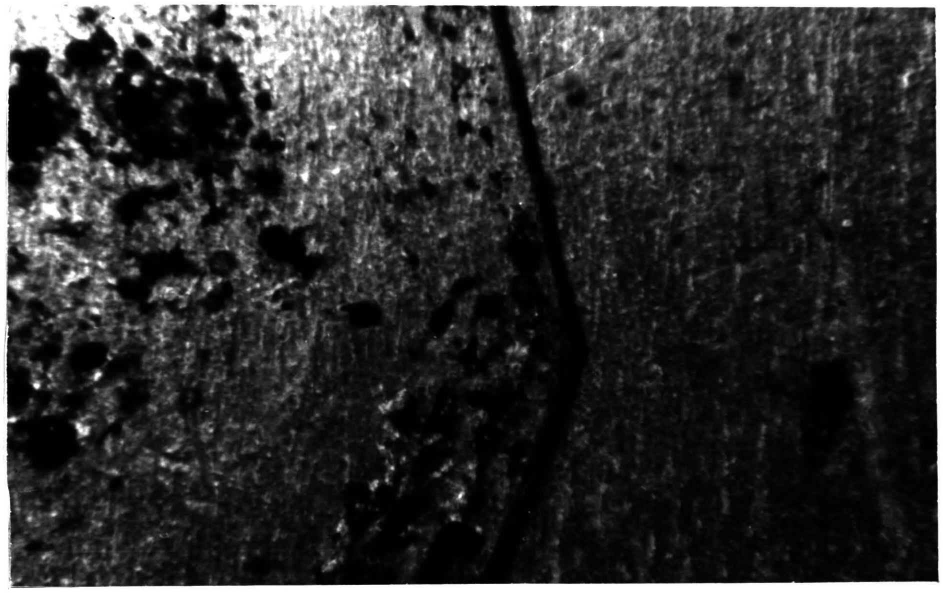

Fig. 93. Photomicrograph showing two stages of calcite deposition. The dark line is the crystal face (scalenohedral) which marks the boundary between the inner core calcite (left) and the outer zone (right). Crossed nicols. 50X.

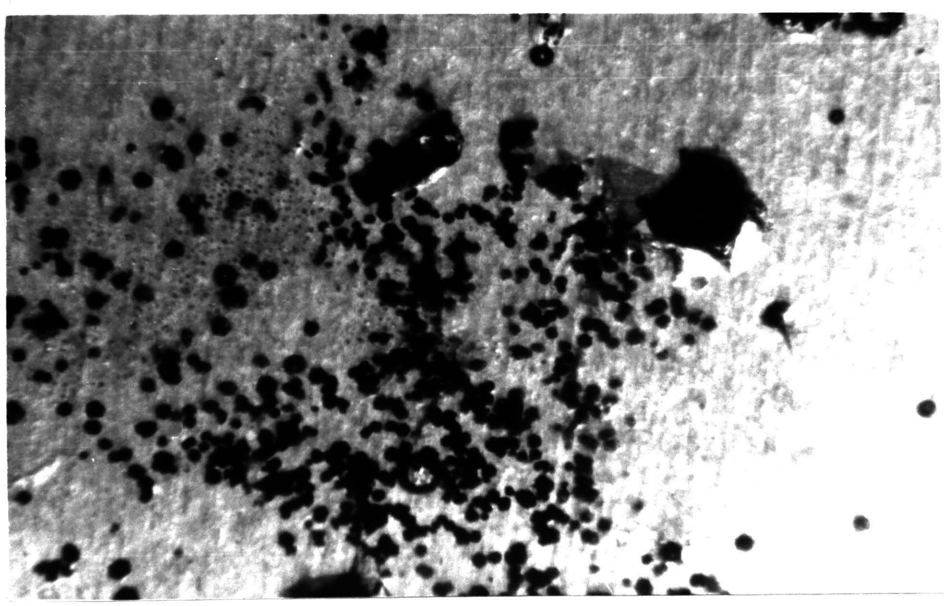

Fig. 94. Pyrite crystals (black) included within the inner core of calcite shown in Figure 93. Pyrite is absent from the outer zone of calcite. Plane polarized light. 50X.

Chapter VI

SUMMARY AND CONCLUSIONS

Underground observations, binocular examination of about 300 hand specimens, petrographic and ore microscopic study of about 100 thin sections and 36 polished surfaces have permitted the writer to determine the mineralogy and paragenesis of the fluorite ores in the Crystal and Minerva No. 1 mines, and to discuss some aspects of paragenesis of the ores in the Hill mine.

Thirteen minerals were found to occur in the two mines. Eight of these occur both in the disseminated form and as crystals deposited in cavities. Textural relationships observed in the disseminated ores and believed to be recorded here for the first time are: (1) euhedral dolomite, quartz, pyrite and galena included within sphalerite, (2) replacement remnants of fluorite within galena and pyrite, (3) euhedral quartz and chalcopyrite included within galena and (4) marcasite replacements of chalcopyrite. Relationships between minerals deposited in cavities believed to be recorded here for the first time are: (1) thin bitumen layer between yellow fluorite and early purple fluorite, (2) brown quartz deposited upon late purple fluorite and other minerals, (3) euhedral pyrite included within strontianite and calcite, (4) euhedral pyrite and marcasite deposited upon corroded strontianite and (5) euhedral marcasite included within late calcite.

The paragenetic sequence of minerals in the disseminated ores has a general similarity to the sequence of minerals deposited in vugs in the Crystal mine, but the sequence of vug-filling minerals differs from that of the disseminated minerals by the occurrence of late calcite, pyrite and barite and by the recurrence of additional generations of fluorite, chalcopyrite and galena. The differences between the paragenetic sequences of the disseminated and vug-filling minerals in the Minerva mine No. 1 are even more striking. They differ in the minerals present, the depositional sequence of those minerals and in the number of generations in which each mineral appears. The differences between the disseminated and cavity paragenetic sequences, together with textural evidence, suggest that most of the disseminated minerals formed before the deposition of minerals in vugs or cavities.

The most noteworthy feature of the paragenetic sequence in the ores of the mines examined for this investigation is that of the repetitive nature of the deposition of many of the minerals. Chalcopyrite has been deposited as many as seven times, fluorite and quartz five times, pyrite four times, galena and sphalerite three times and calcite, marcasite and dolomite(?) two times.

The writer interprets the paragenetic sequence to indicate that the nature of the solutions from which the minerals of the Cave-in-Rock fluorite ores were deposited changed gradually through time to provide the general paragenesis, but that local variations, particularly in pH, Eh and chemical concentrations, caused variations in the paragenesis from one mine to another. That the chemical conditions of the ore solutions often were near the boundary between deposition and non-deposition is shown by the repetitive nature of the deposition of many of the minerals.

Repetitive access of the ore solutions to some cavities may have been important in producing local repetitive mineral deposition.

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